Fractional quadrupole spin echo in the NMR of magnetically ordered materials

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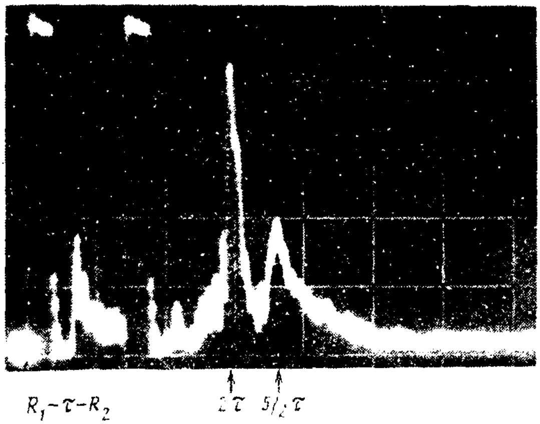
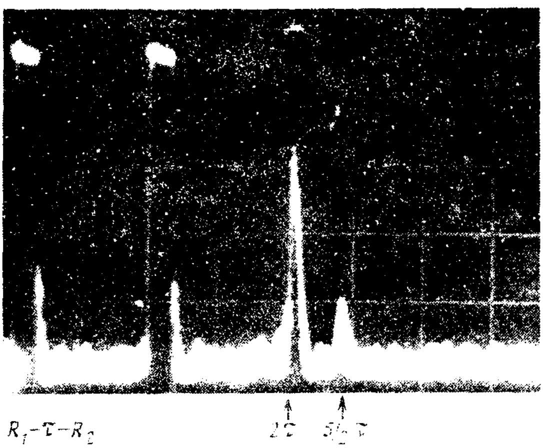
An additional spin echo signal from quadrupole nuclei with $I = 3/2$ (^{53}Cr nuclei in $CdCr_2Se_4$) produced at the time $t = 5/2\tau$ has been detected. The frequency dependence of the fractional echo amplitude is found to reflect only the quadrupole structure of the NMR spectrum.

In addition to the induction of the fundamental echo signal at the time 2τ, additional echo signals, which occur at a time which is a multiple of τ: 3τ, 4τ, etc. (τ is a time interval between rf pulses), can be induced in nuclear spin systems with $I \geqslant 1$ (Refs. 1–3). It was shown in Ref. 4 that in the case of quadrupole nuclei with $I = 3/2$ the frequency dependence of the echo amplitude at 4τ reflects only the magnetic hyperfine interactions of nuclei, while the spectrum of the fundamental echo at 2τ is determined by the quadrupole and magnetic hyperfine interactions. We present here the results of an experimental study of a fractional echo signal from the nuclei with $I = 3/2$, which is detected at the time $t = 5/2\tau$. The fractional echo signals were previously predicted and studied in diamagnetic crystals only for the nuclei with $I = 5/2$ and $7/2$ (Refs. 1 and 5).

At the time $t = 5/2\tau$ (Fig. 1) a spin echo was detected in ^{53}Cr nuclei ($I = 3/2$) in a magnetic semiconductor $CdCr_2Se_4$ at $T = 4.2$ K and $T = 77$ K. The echo signals



a



b

FIG. 1. Oscilloscope traces of an ordinary echo signal, $V_{2\tau}$, and an additional echo, $V_{5/2\tau}$, in $CdCr_2Se_4$ at 4.2 K. $t_1 = 2$ μs, $t_2 = 1$ μs, and $U_{rf} = 1800$ V. (a) Echo signals from nuclei in the domains (rf quadrupole satellite) $\tau = 14$ μs; (b) echo signals from nuclei in the domain wall. $\nu = 42.1$ MHz, $\tau = 20$ μs. The scale of the abscissa is 10 μs/div.

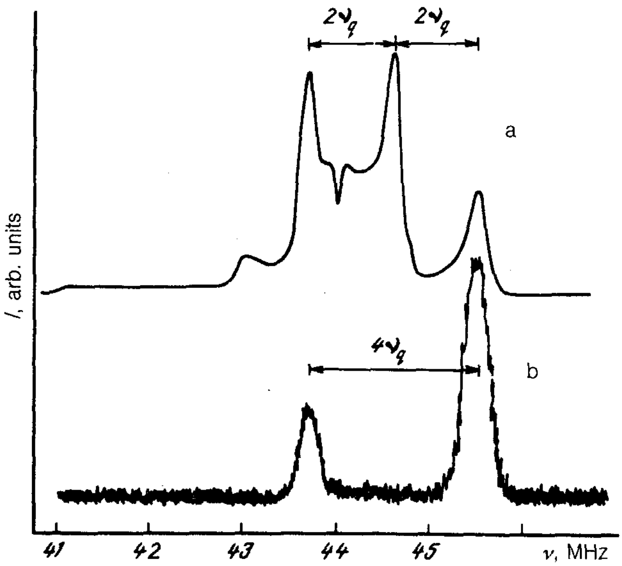


FIG. 2. NMR spectra of ^{53}Cr in $CdCr_2Se_4$. (a) $V_{2\tau}(\nu)$. $t_1 = 4$ μs, $t_2 = 8$ μs, $\tau = 100$ μs, $U_{rf} = 50$ V; (b) intradomain spectrum $V_{5/2\tau}(\nu)$. $t_1 = 2$ μs, $t_2 = 1$ μs, $\tau = 60$ μs, $U_{rf} = 1800$ V. U_{rf} is the amplitude of the rf pulses.

were detected from nuclei in the domains and from nuclei in the domain walls. The echo from nuclei in the domains (Fig. 1a) was detected at frequencies corresponding to the quadrupole lines (the spectroscopic transitions $\pm 3/2 \leftrightarrow 1/2$) in the NMR spectrum $V_{2\tau}(\nu)$ (Fig. 2a).[6] The echo signal at $5/2\tau$ inside the domain wall was measured within the limits of the whole NMR spectrum $V_{2\tau}(\nu)$. To detect a fractional echo, the length of the first rf pulse, t_1, must be greater than the length of the second pulse, t_2. For the given pulse length the amplitudes of the rf pulses must be greater than the amplitudes of the rf pulses necessary to produce a maximum echo signal at 2τ. As the quadrupole splitting of the NMR spectrum increases, the fractional echo reaches a maximum at large amplitudes of the rf pulses. In contrast with the $V_{2\tau}$ and $V_{4\tau}$ signals, the $V_{5/2\tau}$ echo signal is detected only in the case of short pauses between the exciting rf pulses. With an increase in τ, the fractional echo broadens sharply and decays in a time T_2^* which characterizes an inhomogeneous broadening of the NMR spectrum. In $CdCr_2Se_4$ the echo at $5/2\tau$ can be detected only at $\tau \leqslant 60$ μs. Figure 2b shows the NMR spectrum $V_{5/2\tau}(\nu)$ for $CdCr_2Se_4$, which was measured with the help of the echo at $5/2\tau$. Analysis of the NMR spectra $V_{5/2\tau}(\nu)$ and $V_{2\tau}(\nu)$ with the help of the values found for the hyperfine interaction constants[7] shows that while the spectrum of the echo signal at 2τ is determined by the quadrupole and magnetic hyperfine interactions, the echo at $5/2\tau$ represents only the quadrupole structure of the NMR spectrum.

The observable peculiarities of the formation and behavior of the fractional echo from the nuclei with $I = 3/2$ can be explained qualitatively in the following way. The time t_e at which the spin echo from the quadrupole nucleus with $I > 1$ is detected is given by[1,6]

$$t_e = \tau[1 + \frac{\nu_q(m' + m'') - \Delta}{(2m + 1)\nu_q - \Delta}(m' - m'')],\qquad (1)$$

where ν_q is the quadrupole interaction constant of the nucleus, $\Delta = \nu_{rf} - \nu_0$, ν_{rf} is the modulated frequency of the rf pulses, ν_0 is the Larmor frequency of the nucleus which is determined in magnetically ordered materials by a hyperfine magnetic field,[8] and m, m', and m'' are the quantum numbers which characterize the projection of the nuclear spin along the direction of the hyperfine field.

We see from Eq. (1) that in the case of a nucleus with $I = 3/2$ the echo occurs at the time $t_e = 5/2\tau$ only if the modulated frequency of the rf pulses coincides with the frequency of the quadrupole satellites of the NMR spectrum ($\Delta = \pm 2\nu_q$). If $\Delta = +2\nu_q$, we would then have $m = -3/2$, $m'' = -3/2$, $m' = 1/2$ and if $\Delta = -2\nu_q$, we would have $m = 1/2$, $m' = 3/2$, and $m'' = -1/2$. The echo amplitude at $5/2\tau$ is determined by the following matrix element of the operator of the density matrix $\rho(\tau + t)$ which describes the evolution of the nuclear spin system

$$\langle \frac{1}{2} | R_2 | \frac{3}{2} \rangle \langle \frac{3}{2} | R_1 I_z R_1^{-1} | -\frac{1}{2} \rangle \langle -\frac{1}{2} | R_2 | \frac{3}{2} \rangle .\qquad (2)$$

Here R_1 and R_2 are the operators which describe the effect of the rf pulses of length t_i ($i = 1, 2$), $R_i = \exp(i, \mathscr{H}_1 t_i)$,

$$\mathscr{H}_1 = -\Delta I_z + \nu_q I_z^2 - \nu_1 I_x ,\qquad (3)$$

and ν_1 is the amplitude of the rf field at the nucleus.

If $\nu_1 \gg \nu_q$, the operators R_i function as operators which perform rotation of the nuclear spin around the effective field of the nucleus in a rotating coordinate system. In this case $R_1 I_z R_1^{-1} = \alpha I_x + \beta I_y + \gamma I_z$ and therefore $\langle 3/2 | R_1 I_z R_1^{-1} | -1/2 \rangle = 0$. If, on the other hand, $\nu_1 \ll \nu_q$, the operators R_i have virtually no effect on the nuclear spin system ($[\mathscr{H}_1 I_z] \approx 0$) and $V_{5/2\tau}$ again will be zero. One would expect, therefore, that the amplitude of the fractional echo is nonvanishing only when $\nu_1 \approx \nu_q$. With an increase in the quadrupole splitting of the NMR spectrum, i.e., with an increase in ν_q, the maximum echo signal can be reached by increasing the amplitude of the rf pulses, striving to satisfy the condition $\nu_1 \approx \nu_q$.

In actual magnetically ordered materials the isochromatic curves of nuclei will have, because of the scatter of electric and magnetic hyperfine interactions, different ν_q and ν_0 (inhomogeneous broadening).[8] We denote in terms of $\bar{\nu}_q$ and $\bar{\Delta}$ the mean values of the quadrupole hyperfine interaction constant and the frequency deviation $\bar{\Delta} = \nu_{rf} - \bar{\nu}_0$ and we represent in terms of $\delta\nu_q^j$ and $\delta\Delta^j$ the deviations of ν_q^j and Δ^j from these mean values (the index j specifies different isochromatic curves). For $\bar{\Delta} = \pm 2\bar{\nu}_q$ and corresponding m, m', and m'' we can then write from (1)

$$t_e = \frac{5}{2}\tau + \Delta t^j\qquad (4)$$

for any jth isochromatic curve, where

$$\Delta t^{j} \approx \tau \frac{\delta\Delta^{j} + \delta\nu_q^{j}}{\bar{\nu}_q} . \qquad (5)$$

It follows from (4) and (5) that the displacement of the echo maximum from $t = 5/2\tau$ on the jth isochromatic curve decreases with decreasing τ. With an increase in τ, various isochromatic curves will "gather" at different times, which manifests itself effectively in the broadening of the echo signal and in a decrease of its amplitude. Since the scatter $\Sigma_j |\delta\Delta^{j} + \delta\nu_q^{j}| \sim (T_2^*)^{-1}$, we see from (4) and (5) that the amplitude of the echo at $5/2\tau$, in contrast with the amplitude of the echo at 2τ, decreases with increasing τ in a time T_2^*. Using a similar line of reasoning, we find that if $\bar{\Delta} = \pm 2\nu_q + \xi$ $(\xi \sim 1/T_2^*)$, the maximum of the echo will shift from the point $t_e = 5/2\tau$ either down the time scale ($\xi < 0$) or up the scale ($\xi > 0$)—a situation which has also been observed experimentally.

This study has thus enabled us to explain all the observable basic features of the formation of a fractional echo from the quadrupole nucleus with $I = 3/2$.

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