Investigation of the conditions of multiquantum NMR echo formation in magnet materials

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The optimal conditions for formation of multiphoton NMR echos from quadrupole nuclei in magnet materials were studied. The values of the optimal amplitudes and width of the first and second rf pulses were found theoretically. The theoretical values are in good agreement with the experimental values.

INTRODUCTION

In Refs. 1 and 2 it is shown that in the case of NMR of quadrupole nuclei with spin $I = 3/2$ the unequal spacing of the lines in the energy spectrum results in the appearance of a two-pulse spin echo at the time $t = 4\tau$ (τ is the time interval between the pulses). In contrast to the echo at $t = 2\tau$, the echo at the time 4τ is formed only when the carrier frequency of the excitation pulses is equal to the frequency corresponding to the spectroscopic transition $\pm 1/2 \leftrightarrow \mp 1/2$ and determined only by the magnetic hyperfine interactions (HFI). It was also shown that for the fixed parameters of the excitation pulses the amplitude of the echo at 4τ depends on the magnitude of the quadrupole splitting of the NMR spectrum. All experiments in Refs. 1 and 2 were performed on polycrystalline ferromagnetic materials. In order to study in greater detail the conditions under which the echo at 4τ is formed and observed we performed additional calculations and experiments on ^{53}Cr ($I = 3/2$) nuclei in a $CdCr_2Se_4$ single crystal in an external saturating magnetic field of 0.66 T at 77 K.

EXPERIMENT

The $CdCr_2Se_4$ sample took the form of a triangular wafer whose surface was perpendicular to the crystallographic axis $\langle 111 \rangle$. The crystal was rotated around this axis in a magnetic field. The wafer was 2 mm thick and its edge was 6 mm long.

In the structure of the spinel $CdCr_2Se_4$ the Cr atoms occupy the trigonally distorted B positions. A unit cell contains four types of Cr^{3+} B ions, differing by the orientations of the symmetry axes of the type $\langle 111 \rangle$. For this reason, when the crystal is rotated around the $\langle 111 \rangle$ axis, in the general case, four branches of resonance lines corresponding to the four quadrupole triplets are observed.

The conditions under which the 4τ echo are formed were investigated on the central line (the spectroscopic transition $\pm 1/2 \leftrightarrow \mp 1/2$) of one of the triplets. The rotation angle φ was measured from the $\langle 110 \rangle$ direction in the range from 0° up to 60° with a step of 1°. The angle θ between the direction of electronic magnetization **M** and the corresponding local-symmetry axis ranged from 35° up to 90°; this made it possible to change the quadrupole splitting of the NMR spectrum $4\nu_q$ from the minimum value (tens of kHz), corresponding to the magic angle $\theta = \theta_m$ ($\cos\,\theta_m = 3^{-1/2}$) and determined by the second-order shift, up to the maximum value of 1.8 MHz at $\theta = 35°$ and 90°. The accuracy with which **M** was aligned along $\langle 110 \rangle$, the direction from which φ is measured, was monitored according to the NMR spectra $V_{2\tau}(\nu)$ with an error of at most 10′. The dependence of the optimal conditions of excitation (rf pulse widths t_1 and t_2 and the amplitude of the rf field ν_1 expressed in frequency units) of the 4τ echo on the magnitude of the quadrupole splitting $4\nu_q$ was investigated experimentally.

In Refs. 1 and 2 it was shown that a smaller pulse width should correspond to larger quadrupole splitting. The experiment showed that when the magnitude of the quadrupole splitting $4\nu_q$ is changed, both the amplitude of the rf field ν_1 and the rf pulse width t_1 and t_2 must be changed in order to obtain the maximum echo signal at 4τ. As the splitting increases the amplitude of the rf field must be increased and the pulse widths must be decreased, and in addition the width of the first pulse t_1 must be greater than the width of the second pulse t_2. The minimum amplitude of the rf field and the maximum width of the pulses were observed for $\varphi \approx 22°$. Irrespective of the magnitude of $4\nu_q$, the areas of the pulses $\nu_1 t_1$ and $\nu_1 t_2$ as well as their ratio remained constant; in addition, $\nu_1 t_1/\nu_1 t_2 = 1.6$–$1.9$. In order to obtain the maximum echo signal at 4τ the width of the first rf pulse must be equal to $\sim 1/4\nu_q$. In addition, the ratio of the amplitudes of the rf pulses for different quadrupole splittings was found to be close to the ratio of the quadrupole splittings themselves (Fig. 1).

The dependence of the amplitude of the echo at 4τ on the magnitude of the quadrupole splitting with fixed parameters of the exciting pulses ($\nu_1 t_1$ and $\nu_1 t_2$) was also investigated. For a fixed quadrupole splitting the optimal conditions $\nu_1 t_1$ and $\nu_1 t_2$ were found in order to achieve the maximum echo at 4τ, after which the value of $4\nu_q$ was changed by rotating the crystal, i.e., the dependence of $V_{4\tau}$ on the ratio ν_1/ν_q was measured. One can see from Fig. 2 that under the optimal conditions for large quadrupole splitting (large amplitudes of the rf field and short widths) as the magic angle is approached the amplitude of the echo decreases. In addition, the farther away from the magic angle that optimal tuning is performed the more efficiently the echo at 4τ is suppressed at angles $\theta \simeq \theta_m$. Figure 2 also shows the dependence of $V_{4\tau}$ on ν_1/ν_q with optimal tuning near the magic angle (small amplitudes of the rf field and large pulse widths). Increasing the quadrupole splitting results in more rapid suppression of the echo signal.

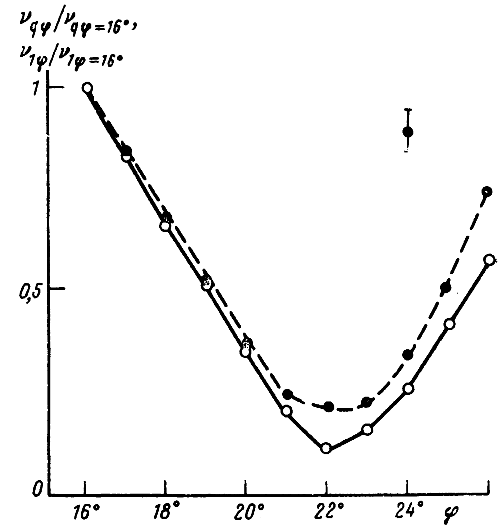

FIG. 1. The ratios of the quadrupole splittings $\nu_{q\varphi}/\nu_{q\varphi=16°}$ (○) and the ratios of the rf amplitudes $\nu_{1\varphi}/\nu_{1\varphi=16°}$ (●) corresponding to the optimal conditions of excitation of an echo at 4τ for each value of the angle φ.

DISCUSSION

It is shown in Ref. 1 that the amplitude of the echo at 4τ is determined by the expression

$$V_{4\tau}\sim\langle {}^3/_2|R_1 I_z R_1^{-1}|-{}^3/_2\rangle\langle -{}^1/_2|R_2|{}^3/_2\rangle \times\langle -{}^3/_2|R_2^{-1}|{}^1/_2\rangle\exp(2\pi i\Delta(4\tau-t)), \tag{1}$$

where

$$R_j^{\pm}=\exp(\pm 2\pi i t_j[-\Delta I_z+\mathcal{H}_q-\nu_1 I_x]). \tag{2}$$

Here Δ is the deviation of the carrier frequency of the rf pulses from the resonance frequency ν_0 of the isochromatic curve; I_x and I_z are the operators of the x and z components of the spin, respectively; $\mathcal{H}_q$ is the quadrupole interaction Hamiltonian of the nucleus, and taking into account the second-order shift we can represent it in the form[3]

$$\mathcal{H}_q=\nu_{q0}(3\cos^2\theta-1)(I_z^2-{}^1/_3 I(I+1)) -\frac{\nu_{q0}^2}{2\nu_0}[\sin^2 2\theta(8I_z^3-4I_zI^2+I_z)-\sin^4\theta(2I_z^3-2I_zI^2+I_z)], \tag{3}$$

where θ is the angle between the local symmetry axis and the direction of electronic magnetization $\mathbf{M}$, ν_{q0} is the quadrupole splitting constant ($\nu_{q0}=e^2qQ/4h$), and

$$\nu_q=\nu_{q0}(3\cos^2\theta-1).$$

Using Eq. (1) we performed numerical calculations of the dependence of the amplitude of the echo at 4τ on the areas of the excitation pulses for fixed amplitudes of the rf field. We found that the optimal widths of the excitation pulses, corresponding to maximum $V_{4\tau}$, depended on ν_1 and fell into the range $2\pi\nu_1 t_1=(1\text{–}1.3)\pi$ and $2\pi\nu_1 t_2=(0.5\text{–}0.65)\pi$. The ratio of the area of the first pulse to that of the second pulse was equal to ≈ 2 and did not depend on the value of ν_1. Thus for $\nu_1=1.75\nu_q$ the maximum amplitude of the echo at 4τ was obtained with areas of the first and second pulses equal to 1.2π and 0.6π, respectively (Fig. 3).

The results of the numerical calculation of the dependence of the amplitude ν_1 of the 4τ echo on the magnitude of the rf field with fixed areas of the exciting pulses ($2\pi\nu_1 t_1=1.2\pi$ and $2\pi\nu_1 t_2=0.6\pi$) are presented in Fig. 4. In the calculations we set $\Delta=0$ and in the Hamiltonian (3) we included only the term describing the quadrupole splitting in first order of the perturbation theory. We found that the position of the maximum of $V_{4\tau}$ depended on the areas of the exciting pulses and was reached at $\nu_1=(1.5\text{–}2)\nu_q$. The best agreement between theory and experiment was ob-

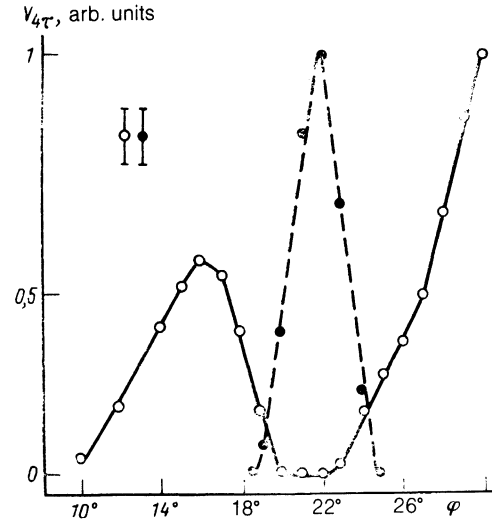

FIG. 2. The dependence of the amplitude of the echo at 4τ on the angle φ for optimal conditions of excitation: $\varphi=30°$ (○) and $\varphi=22°$ (●); $\theta\simeq\theta_m$. For $\varphi=30°$ the central lines of the two triplets are excited simultaneously.

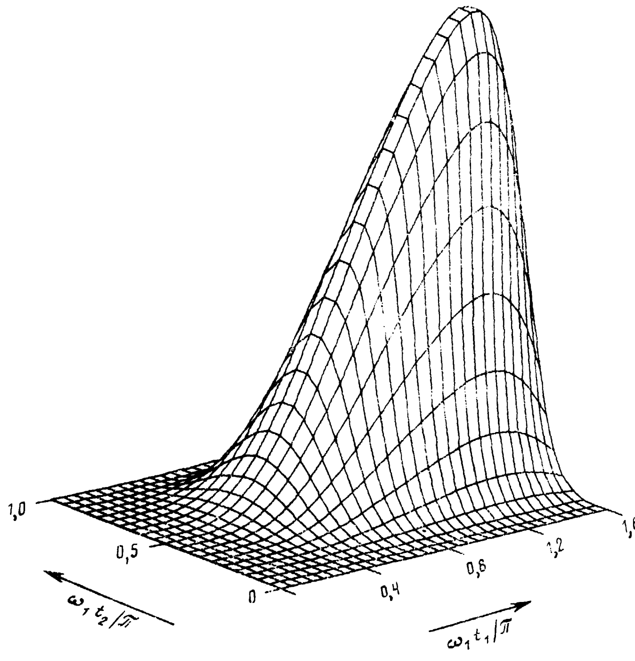

FIG. 3. The computed dependence of the amplitude of the 4τ echo on the areas of the rf pulses. Here $\omega_1=2\pi\nu_1$.

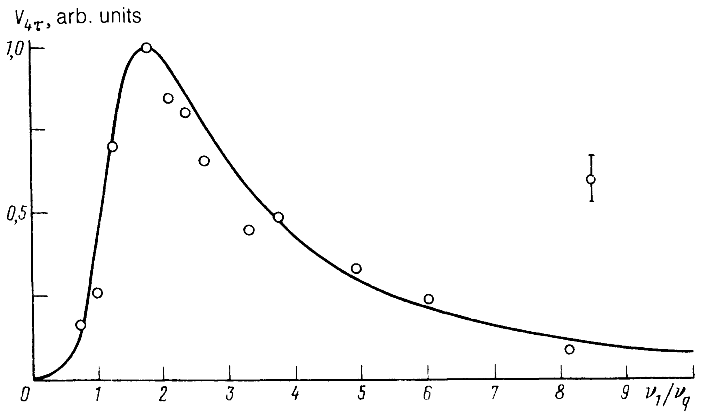

FIG. 4. The dependence of the amplitude of the 4τ echo on the ratio ν_1/ν_q for fixed areas of the first and second pulses, equal to 1.2π and 0.6π, respectively. O—experiment.

served with areas of the first and second pulses equal to 1.2π and 0.6π, respectively (Fig. 4).

Thus optimum excitation of the echo at 4τ corresponds to an rf amplitude $\nu_1 = 1.75 \pm 0.25\nu_q$ (Fig. 4), and for the width of the first pulse we obtain $t_1 = 1.2/2 \cdot 1.75\nu_q \sim 1/4\nu_q$, which corresponds to the experimental conditions under which the echo at 4τ is observed.

Similar calculations were performed for the case $\theta = \theta_m$. In this case, as follows from the expression (3), there is no quadrupole splitting in first order of the perturbation theory and the splitting due to the second-order shift is observed. The unequal spacing of the lines in the energy spectrum in this case also results in the appearance of a three-photon echo at 4τ with maximum amplitude at the frequency of the spectroscopic transition $\pm 1/2 \leftrightarrow \mp 1/2$. The computed dependence of $V_{4\tau}$ on ν_1 is analogous to the dependence shown in Fig. 4, with the difference that the maximum of $V_{4\tau}$ is achieved for rf amplitudes approximately equal to one-fourth the spacing between the extreme lines in the spectrum, owing to the second-order quadrupole shift. The theoretical results explain well the characteristics of formation of the echo at 4τ with $\theta = \theta_m$ ($\varphi \simeq 22°$).

The good agreement obtained between the experimental and theoretical results for the optimal conditions of formation of an echo at 4τ can be used to estimate the magnitude of the effective (taking into account the gain) rf field acting on quadrupole nuclei in magnetically ordered materials.

CONCLUSIONS

Thus our experimental and theoretical investigations of the conditions under which a multiphoton echo is formed at 4τ on ^{53}Cr ($I = 3/2$) nuclei in a single crystal have shown that in order to observe the echo at the time 4τ the area $\nu_1 t_1$ of the first pulse must be 1.5–2 times larger than the area $\nu_1 t_2$ of the second pulse. Our calculations showed that the maximum amplitude of the echo at 4τ is observed when $2\pi\nu_1 t_1 = 1.2\pi$ and $2\pi\nu_1 t_2 = 0.6\pi$.

In order for the optimal echo to form at 4τ with a fixed quadrupole splitting the width of the first rf pulse must be equal to $\sim 1/4\nu_q$ while the rf amplitude satisfies $\nu_1 = 1.75 \pm 0.25\nu_q$.

The appearance of an echo at 4τ with $\theta = \theta_m$ is governed by the second-order quadrupole shift.

The results obtained in this work make it possible to increase significantly the accuracy with which the resonance frequency of a nucleus and the magnitude of the quadrupole splitting are determined and they open up new possibilities for measuring the gain of the rf field on quadrupole nuclei in magnets.

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