Multiquantum effects in NMR of $CdCr_2Se_4$

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The manifestation of multiquantum effects in nuclear magnetic resonance (NMR) of magnetically ordered substances is investigated with $CdCr_2Se_4$ as the example. It is shown that in nuclear spin systems with half-integer spin ($I = 3/2$) the nonequivalence of the energy spectrum leads to the appearance of a secondary two-pulse echo signal at the instant of time 4τ. The NMR spectrum recorded with the aid of this secondary echo signal reflects only the magnetic hyperfine interactions of resonant nuclei.

INTRODUCTION

In pulsed nuclear magnetic resonance (NMR) of magnetically ordered substances the NMR spectra are usually recorded by using the Hahn two-pulse sequence.[1] The distinctive features of the echo formation in this case were investigated in sufficient detail by analyzing the Bloch equations.[2–4] In particular, it was shown in a number of papers that besides the primary echo signal produced at the instant 2τ (τ is the time interval between the pulses), additional secondary pulses can appear at the instants 3τ, 4τ, etc.[5–8] The experimental investigation of the properties of these additional echo signals was limited mainly to a study of the conditions for their formation and to measurement of the relaxation times.[5–7] It was noted in some reports that the NMR spectra recorded with the aid of the secondary echo signals are identical with the NMR signal of the primary echo signal at the instant 2τ (Refs. 5 and 7).

We have recently shown[9] that in the case of NMR of quadrupole nuclei with half-integer spin there can appear at the instant 4τ an additional echo signal with unusual properties: The NMR spectrum recorded with the aid of the echo at the instant 4τ shows the spread of the resonant NMR frequencies that are due only to magnetic hyperfine interactions (HFI) and are independent of the quadrupole interactions of the nuclei, whereas the spectrum of the usual echo at the instant 2τ is determined by quadrupole and magnetic HFI interactions. This property of the echo at the instant 4τ increases significantly the resolving power of the NMR echo when quadrupole nuclei in magnetically ordered substances are investigated.

We report here new experimental and theoretical results on the echo produced at the instant 4τ in ^{53}Cr nuclei ($I = 3/2$) in the magnetic semiconductor $CdCr_2Se_4$. These results corroborate the mechanism proposed in Ref. 9 whereby the secondary echo signal is produced via multiquantum effects.

EXPERIMENTAL RESULTS

The experiments were performed at $T = 4.2$ K in a pulsed automatic-recording NMR spectrometer. The samples were single crystals of the magnetic semiconductor $CdCr_2Se_4$. The NMR spectra of the ^{53}Cr nuclei were recorded in a zero external magnetic field. They represent the echo-signal amplitudes at the instants 2τ ($V_{2\tau}(\nu)$) and 4τ ($V_{4\tau}(\nu)$) vs the carrier frequency ν of the exciting pulses. The radio-frequency (rf) pulses were produced by a high-frequency pulse generator excited by video pulses of adjustable amplitude, and depended linearly on the video pulse amplitudes U_v. The NMR spectra of the ^{53}Cr nuclei in domains were recorded by a procedure proposed in Ref. 10.

Primary echo signal $V_{2\tau}(\nu)$

The conditions under which the echo $V_{2\tau}$ is formed in $CdCr_2Se_4$ are close to the Hahn conditions.[1] Figures 1a and 1b show the NMR spectra of ^{53}Cr in $CdCr_2Se_4$, recorded with the aid of $V_{2\tau}$. Since the Cr atoms occupy in the spinel structure of $CdCr_2Se_4$ trigonally distorted octahedral positions, a contribution to the NMR frequency is made not only by the isotropic HFI but also by the isotropic magnetic and electric quadrupole HFI. In this case, the form of the NMR spectrum of ^{53}Cr depends on the angle between the magnetization **M** and directions of type [111], which are the principal axes of the magnetic and quadrupole HFI tensors. It is shown in Ref. 10 that action of two rf pulses on $CdCr_2Se_4$ leads to simultaneous excitation of the nuclei in the domains and in the domain walls, as a result of which the $V_{2\tau}(\nu)$ spectrum recorded in standard fashion (with the entire echo signal integrated) is a superposition of the spectra from the intradomain nuclei, which have a discrete fine structure, and of the continuum from the intrawall nuclei (Fig. 1a). The intradomain NMR spectrum of ^{53}Cr shown in Fig. 1b reflects the presence in $CdCr_2Se_4$ of domains of three different types, in which the orientation of the magnetization **M** coincides with the crystallographic directions [100], [110] and [111] (Ref. 10). Lines a_0 and a_+ correspond to **M** directed along [111] axes, lines b_-, b_0, and b_+ to **M** directed along [110] axes, and line c_2 is located at the isotropic-HFI frequency 44.08 MHz and corresponds to **M** directed along [100].[10]

Notice must be taken of the asymmetry in the intensities of the intradomain spectral lines. Thus, no low-frequency quadrupole satellite is observed in domains with $\mathbf{M}\|[111]$. In addition, the intensity ratio of lines a_0 and a_+ (high-frequency quadrupole satellite) differ strongly from the theoretical 4:3 (Ref. 11). The observed singularities of the NMR spectrum in domains with $\mathbf{M}\|[111]$ point, in our opinion, to a local spread of the direction of the magnetization relative the axes of type [111], or to a spread of the principal axis of the magnetic or quadrupole HFI relative to **M**. This can be explained qualitatively by the following reasoning.

The frequency of the NMR transition $m \leftrightarrow m-1$ of a quadrupole nucleus, assuming the magnetic and quadrupole HFI tensor to be axisymmetric and having the same directions as the principal axes, is given by[12]

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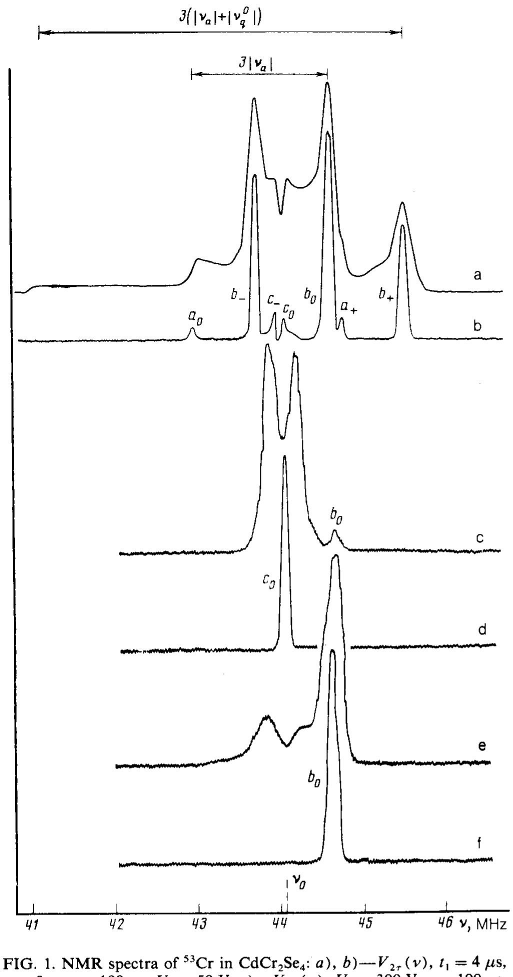

FIG. 1. NMR spectra of ^{53}Cr in $CdCr_2Se_4$: *a*), *b*)—$V_{2\tau}(\nu)$, $t_1 = 4$ μs, $t_2 = 8$ μs $\tau = 100$ μs, $U_v = 50$ V; c)—$V_{4\tau}(\nu)$, $U_v = 300$ V, $\tau = 100$ μs; d)—$V_{4\tau}(\nu)$, $U_v = 150$ V, $\tau = 70$ μs e), f)—$V_{4\tau}(\nu)$, $U_v = 1350$ V, $\tau = 100$ μs.

$$\nu_{m,m-1}=\nu_0+[\nu_a+\nu_q^0(m-{}^1/_2)](3\cos^2\theta-1), \qquad (1)$$

where ν_0 and ν_a are respectively the isotropic and anisotropic magnetic-HFI constants, ν_q^0 the quadrupole-interaction constant for $I = 3/2$ and equal to $e^2qQ/4h$, θ the angle between the magnetization **M** and the direction of the principal axis of the HFI tensor, $m = 1/2$ for the $(1/2\leftrightarrow -1/2)$ transition, and $m = -1/2, 3/2$ for the $(\pm 3/2\leftrightarrow \pm 1/2)$ transitions. If a magnetically ordered crystal exhibits a spread in the angle θ, the result is a broadening of the spectral transition, which can be estimated, as follows from (1), from the equation

$$\Delta\nu_{m,m-1}=[\overline{(\nu_{m,m-1}(\theta)-\bar{\nu}_{m,m-1}(\theta))^2}]^{1/2}$$
$$=3|\nu_a+\nu_q^0(m-{}^1/_2)|[\overline{\sin^2(2\theta_0+\delta\theta)\sin^2(\delta\theta)}]^{1/2}. \qquad (2)$$

Here θ_0 is the angle characterizing the most probable direction of **M** relative to the principal axis of the HFI tensor, $\delta\theta = \theta - \theta_0$, and the superior bar denotes averaging over random spread of θ.

For domains with $\mathbf{M}\|[111]$ and $\theta_0 = 0$ we obtain from (2)

$$\Delta\nu_{m,m-1}=3\sqrt{3}|\nu_a+\nu_q^0(m-{}^1/_2)|\overline{\delta\theta^2}.$$

It follows therefore, since ν_a of $CdCr_2Se_4$ is negative,[13] that the widths $\Delta\nu_l$ and $\Delta\nu_h$ of the low- and high-frequency quadrupole satellites and $\Delta\nu_c$ of the central line meet the condition

$$\Delta\nu_l < \Delta\nu_c < \Delta\nu_h.$$

Thus, as a result of the local spread of the magnetization or of the principal axis of the HFI tensor, the most broadened is the low-frequency line of the quadrupole triplet of domains with $\mathbf{M}\|[111]$. For domains with $\mathbf{M}\|[110]$ and angle $\theta_0 = 90°$, according to (1) and (2), the scatter with respect to the angle θ would make the high-frequency quadrupole satellite less intense than the low-frequency one, as is indeed observed in experiment. Note that our estimates show that the observed asymmetry of the spectral-line intensities can be accounted for in the range $(\delta\theta^2)^{1/2}\sim 2-3°$.

Attention is called to the secondary line near the line c_0 due to the domains with $\mathbf{M}\|[100]$ (Fig. 1b). For these domains we have $3\cos^2\theta - 1 = 0$ and hence there should be no quadrupole splitting of the line. If, however, the electric-field gradient at the ^{53}Cr nucleus has a nonzero asymmetry parameter, a quadrupole splitting determined by the asymmetry parameter should be observed in this case. It can therefore be suggested that the secondary line c_- is a low-frequency quadrupole satellite. The absence of a high-frequency quadrupole satellite c_+ in this case and the intensity asymmetry of the lines c_-, c_0, and c_+ are attributed, in analogy with the spectral lines (a_-, a_0, a_+) and (b_-, b_0, b_+), to the scatter of the directions of **M** relative to the orientation of the electric field gradient. This assumption is confirmed by results of using an echo at the instant 4τ, which will be discussed below.

Secondary echo signal $V_{4\tau}(\nu)$

The conditions for formation of a secondary signal echo at the instant 4τ (Fig. 2) differ substantially from those for formation of the usual echo at the instant 2τ. First, it is necessary that, at equal amplitudes, the duration t_1 of the first pulse exceed the duration t_2 of the second. Second, the amplitudes of the rf pulses that form the echo signal at the instant 4τ must exceed the amplitudes needed to form the echo at the instant 2τ. A substantial difference is observed also in the NMR spectra of both the principal echo signal $[V_{2\tau}(\nu)]$ and the secondary one $[V_{4\tau}(\nu)]$.

Figures 1c–1f show the NMR spectra of ^{53}Cr recorded with the aid of the echo at the instant 4τ. It can be seen that the frequency range of the $V_{4\tau}(\nu)$ spectra is much narrower than that of the $V_{2\tau}(\nu)$ spectra and is located in the range of the frequencies determined by the anisotropic mangetic HFI.

An interesting fact is that the rf-pulse amplitude needed to form the echo signal at the instant 4τ depends on the deviation of the rf-pulse carrier frequency on the frequency ν_0 of the isotropic magnetic HFI in the NMR spectrum. As the deviation increases (i.e., with increase of the quadrupole

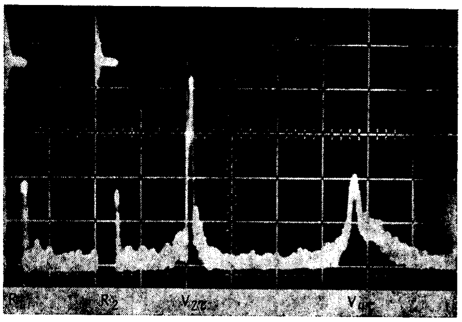

FIG. 2. Oscillograms of the signals $V_{2\tau}$ of the primary echo and $V_{4\tau}$ of the secondary in $CdCr_2Se_4$; $U_v = 1350$ V, $\tau = 40$ ms $\nu_{rf} = 44.65$ MHz. The horizontal scale is 20 μs/div.

splitting in the NMR spectrum), it is necessary to increase the amplitude to the rf pulses needed to form the echo signal $V_{4\tau}$.

The spectrum of Fig. 1c was obtained for rf-pulse amplitudes optimal for the formation of echo signals near ν_0, and consists of three lines: two intense ones symmetric about the minimum that coincides with isotropic magnetic HFI frequency, and one at the frequency 44.65 MHz, which coincides with the b_0 line of the central $(1/2 \to -1/2)$ transition for $\mathbf{M} \| [110]$ in the echo spectrum at the instant 2τ. As the amplitude of the rf pulses increases, the intensity of the echo signal at the b_0-line frequency increases monotonically. The spectrum on Fig. 1e was obtained under conditions when the optimal echo signal was produced at this frequency at the instant 4τ. It must be noted that an echo signal at this frequency is a superposition of two components having different relaxation times T_2^* (Fig. 2) and reflecting the simultaneous excitation of the intradomain and intrawall nuclei. Separation of the intradomain component of the spectrum yields a single line (Fig. 1f) of the same frequency as the line b_0 in the echo signal spectrum at the instant 2τ (Fig. 1b). Note that the spectra c–f of Fig. 1 were recorded at short rf-pulse durations ($t_1 = 2\,\mu$s and $t_2 = 1.1\,\mu$s), which are optimal for echo-signal frequencies in the frequency-scattering range determined by the anisotropic magnetic HFI. With increase of the pulse durations ($t_1 = 8\,\mu$s, $t_2 = 5\,\mu$s) and at relatively small rf-pulse amplitudes, the echo signal is formed only at the frequency ν_0 of the anisotropic HFI, while the echo spectrum at the instant 4τ (Fig. 1d) is a single narrow line that coincides with the line c_0 of the intradomain spectrum $V_{2\tau}(\nu)$.

Analysis of the spectra of Fig. 1 using HFI constants obtained in investigations of the angular dependence of the NMR spectra of $CdCr_2Se_4$ in a saturating magnetic field[13] shows that the spectrum of the usual echo signal at the instant 2τ is determined by nuclear quadrupole and magnetic HFI, and the spectrum of the echo signal at the instant 4τ reflects only the magnetic isotropic (Fig. 1d) and anisotropic (Figs. 1c–f) HFI in the domains and domain walls.

Note also the difference observed between the echo-signal shapes at the instant 4τ in different sections of the intrawall NMR spectrum (Figs. 3a–c). The multicomponent form of the echo signal (Fig. 3b) appears only near ν_0 corresponding to isotropic magnetic HFI and to a "dip" in the intrawall NMR spectrum at the instant 4τ (Fig. 2c). When the rf pulse frequency deviates from ν_0, the echo signal becomes symmetric.

To conclude this section, we point out that with increase of the rf-pulse repetition frequency there appears, besides the echos at the instants 2τ and 4τ, also an echo at the instant 3τ. All the experimental results cited above were obtained at the lowest possible rf-pulse repetition frequencies (including a one-shot pulse), when there is no echo at the instant 3τ.

DISCUSSION OF EXPERIMENTAL RESULTS

We begin with an analysis of the response of a system of quadrupole nuclei with spin $I = 3/2$ to the action of a two-pulse sequence $R_1 - \tau - R_2 - t$, where R_1 and R_2 are operators that describe the evolution of a nuclear spin system acted upon by rf pulses.

The Hamiltonian ($h = 1$) of a quadrupole nucleus with $I = 3/2$ is given by[14]

$$\mathcal{H}_0 = -\nu I_z + {}^1/_3 \nu_q [3I_z^2 - I(I+1)]. \quad (3)$$

Here ν is the resonance frequency of the nucleus, determined in a magnetically ordered substance by the hyperfine magnetic field at the nucleus, while the second term of (3) is the secular part of the quadrupole-interaction Hamiltonian of the nucleus ($\nu_q \ll \nu$)

$$2\nu_q = \nu_q^0 (3\cos^2\theta - 1 + \eta \sin^2\theta \cos 2\varphi), \quad (4)$$

where η is the asymmetry parameter of the electric field gradient (EFG) tensor at the nucleus, while θ and φ are angles that determine the orientation of the hyperfine field relative to the principal axes of the EFG tensor.

At the instant of the action of the rf pulse, the operator R_i ($i = 1, 2$) is of the form

$$R_i = \exp(i2\pi \mathcal{H}_i t_i), \quad (5)$$

where t_i is the time of action of the ith pulse,

$$\mathcal{H}_i = -\Delta I_z + \nu_q I_z^2 - \nu_1 I_x, \quad (6)$$

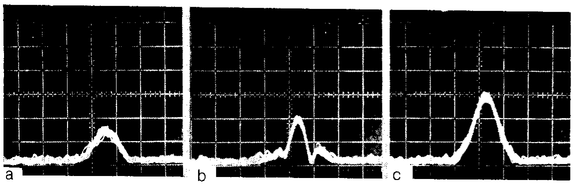

FIG. 3. Oscillograms of echo signals in different sections of the intrawall spectrum $V_{4\tau}(\nu)$ for $\tau = 20\,\mu$s: a) $\nu_{rf} = 43.8$ MHz, b) $\nu_{rf} = 44.04$ MHz, c) $\nu_{rf} = 44.2$ MHz. Horizontal scale—5 μs/div.

$\Delta = \nu - \nu_{rf}$, ν_{rf} is the carrier frequency, and ν_1 is the effective amplitude (in frequency units) of the rf pulse. Note that in NMR of magnetically ordered substances we have $\nu_1 = \xi \nu_1'$, where ν_1' is the true rf-pulse amplitude and ξ is the gain.[1] Expressing R_i in the form (5), we assume for simplicity that the two rf pulses have equal amplitudes and are aligned with the x axis in a reference frame that rotates at an angular frequency $(2\pi\nu_{rf})$.

The response of a nuclear spin system with Hamiltonian (3) to the action of a two-pulse sequence was first calculated by Solomon[15]:

$$v(t+\tau) = \operatorname{Im} \sum_{m,m',m''} [I(I+1) - m(m+1)]^{1/2} \langle m|R_2|m'\rangle \times \langle m'|R_1\rho(0)R_1^{-1}|m''\rangle \langle m''|R_2^{-1}|m+1\rangle \times \exp\{i2\pi[(t-\tau)[(2m+1)\nu_q - \Delta] + \tau[\Delta + \nu_q(m'+m'')](m'-m'')]\}. \quad (7)$$

Here m and $|m\rangle$ are the eigenvalues and eigenfunctions of the operator I_z ($I_z|m\rangle = m|m\rangle$), and $\rho(0)$ is the operator of the nuclear-spin-system density matrix at zero time.

In a real magnetically ordered substance, in view of the possible spread of ν_q (inhomogeneous quadrupole broadening) and of ν (inhomogeneous magnetic broadening), the experimentally recorded NMR signal is described by the expression

$$V(t,\tau) = \int_{-\infty}^{\infty}\int f(\nu)\,\Phi(\nu_q)\,v(t,\tau)\,d\nu\,d\nu_q, \quad (8)$$

where $v(t,\tau)$ is defined by Eq. (7), while $f(\nu)$ and $\Phi(\nu_q)$ are disribution functions that describe respectively the inhomogeneous magnetic and quadrupole broadenings:

$$\int_{-\infty}^{\infty} f(\nu)\,d\nu = 1, \qquad \int_{-\infty}^{\infty} \Phi(\nu_q)\,d\nu_q = 1.$$

It follows from (7) that an echo will be observed in the response of the nuclear spin system at an instant of time t at which the argument of the exponential (7) vanishes, i.e., if t is given by

$$t = \tau(1+\alpha), \quad (9)$$

where

$$\alpha = \frac{\nu_q(m'+m'') - \Delta}{(2m+1)\nu_q - \Delta}(m'-m''). \quad (10)$$

Table I lists the values of α for different admissible values of m, m' and m''. It is seen from the table that α is independent of ν_q and Δ at certain values of m, m', and m'', and is equal to one or three. Consequently, for any isochromat (nuclear group having approximately equal ν and ν_q within the limits of homogeneous broadening), the density matrix will always contain elements that lead to the appearance of an echo at the instants 2τ and 4τ. Besides these values of α, the table includes α that depend on ν_q and Δ, and cause in the general case, in view of the scatter of ν_q and Δ, the echo to appear at different times for different isochromats. If the magnetic inhomogeneity is small and $\Delta_{max} \ll \bar{\nu}_q$ (Δ_{max} is the maximum possible detuning, and $\bar{\nu}_q$ is the mean value of ν_q), contributions to the echo at the instant 2τ will be made also by those terms of Table I for which $\Delta m = m' - m'' = \pm 2$. If, on the contrary, the magnetic inhomogeneity is so high ($\Delta_{max} \gg \bar{\nu}_q$), that the triplet structure of the NMR spectrum is not resolved at all, it follows from Table I that an echo can appear at the instant 3τ. Since, however, contributions to this echo are made only by terms with $\Delta m = m' - m'' = \pm 2$, it can be shown that the echo amplitude at the instant 3τ will be zero, and consequently only the echo at the instant 2τ should appear for an unresolved quadrupole structure of the NMR spectrum.

We confine ourselves hereafter to the echo at the instant 4τ. This echo is described, as follows from (7) and from Table I, by the expression

TABLE I. Values of α in Eq. (10).

m''	m' = $3/2$	$1/2$	$-1/2$	$-3/2$
		$m = 1/2$		
$3/2$	0	-1	$2(\Delta - \nu_q)/(2\nu_q - \Delta)$	$3\Delta/(2\nu_q - \Delta)$
$1/2$	1	0	$\Delta/(2\nu_q - \Delta)$	$2(\nu_q + \Delta)/(2\nu_q - \Delta)$
$-1/2$	$2(\nu_q - \Delta)/(2\nu_q - \Delta)$	$-\Delta/(2\nu_q - \Delta)$	0	$(2\nu_q + \Delta)/(2\nu_q - \Delta)$
$-3/2$	$-3\Delta/(2\nu_q - \Delta)$	$-2(\nu_q + \Delta)/(2\nu_q - \Delta)$	$-(2\nu_q + \Delta)/(2\nu_q - \Delta)$	0
		$m = -1/2$		
$3/2$	0	$(2\nu_q - \Delta)/\Delta$	$2(\nu_q - \Delta)/\Delta$	-3
$1/2$	$(\Delta - 2\nu_q)/\Delta$	0	-1	$-2(\nu_q + \Delta)/\Delta$
$-1/2$	$2(\Delta - \nu_q)/\Delta$	1	0	$-2(\nu_q + \Delta)/\Delta$
$-3/2$	3	$2(\nu_q + \Delta)/\Delta$	$(2\nu_q + \Delta)/\Delta$	0
		$m = -3/2$		
$3/2$	0	$(2\nu_q - \Delta)/(2\nu_q + \Delta)$	$2(\nu_q - \Delta)/(2\nu_q + \Delta)$	$-3\Delta/(2\nu_q + \Delta)$
$1/2$	$(\Delta - 2\nu_q)/(2\nu_q + \Delta)$	0	$-\Delta/(2\nu_q + \Delta)$	$-2(\nu_q + \Delta)/(2\nu_q + \Delta)$
$-1/2$	$2(\Delta - \nu_q)/(2\nu_q + \Delta)$	$\Delta/(2\nu_q + \Delta)$	0	-1
$-3/2$	$3\Delta/(2\nu_q + \Delta)$	$2(\nu_q + \Delta)/(2\nu_q + \Delta)$	1	0

TABLE II. Eigenvalues and eigenfunctions of the Hamiltonian $\mathscr{H}_1(6)$ $(\Delta = 0)$.

Eigenvalues $(h = 1)$	Eigenfunctions
$E_1 = -\frac{\nu_1}{2} + \frac{\sqrt{3}\nu_1}{2}\sin(2\beta_+)$	$\lvert\Psi_1\rangle = \frac{1}{\sqrt{2}}\{-\cos\beta_+\lvert 3/2\rangle - \sin\beta_+\lvert 1/2\rangle + \sin\beta_+\lvert -1/2\rangle + \cos\beta_+\lvert -3/2\rangle\}$
$E_2 = -\frac{\nu_1}{2} - \frac{\sqrt{3}\nu_1}{2}\sin(2\beta_+)$	$\lvert\Psi_2\rangle = \frac{1}{\sqrt{2}}\{-\sin\beta_+\lvert 3/2\rangle + \cos\beta_+\lvert 1/2\rangle - \cos\beta_+\lvert -1/2\rangle + \sin\beta_+\lvert -3/2\rangle\}$
$E_3 = \frac{\nu_1}{2} + \frac{\sqrt{3}\nu_1}{2}\sin(2\beta_-)$	$\lvert\Psi_3\rangle = \frac{1}{\sqrt{2}}\{\cos\beta_-\lvert 3/2\rangle + \sin\beta_-\lvert 1/2\rangle + \sin\beta_-\lvert -1/2\rangle + \cos\beta_-\lvert -3/2\rangle\}$
$E_4 = \frac{\nu_1}{2} - \frac{\sqrt{3}\nu_1}{2}\sin(2\beta_-)$	$\lvert\Psi_4\rangle = \frac{1}{\sqrt{2}}\{\sin\beta_-\lvert 3/2\rangle - \cos\beta_-\lvert 1/2\rangle - \cos\beta_-\lvert -1/2\rangle + \sin\beta_-\lvert -3/2\rangle\}$

Note. Here $\tan 2\beta_+ = \sqrt{3}/(2p+1)$, $\tan 2\beta_- = \sqrt{3}/(2p-1)$, $p = \nu_q/\nu_1$.

$$v_{4\tau} = \mathrm{Im}\,\{\langle 3/2|R_1\rho(0)R_1^{-1}|-3/2\rangle \exp[i2\pi\Delta(4\tau-t)] \times[2\langle -1/2|R_2|3/2\rangle\langle -3/2|R_2^{-1}|1/2\rangle + \sqrt{3}\langle 1/2|R_2|3/2\rangle\langle -3/2|R_2^{-1}|3/2\rangle \exp[i4\pi\nu_q(t-\tau)] + \sqrt{3}\langle -3/2|R_2|3/2\rangle\langle -3/2|R_2^{-1}|-1/2\rangle \exp[i4\pi\nu_q(t-\tau)]]\}. \quad (11)$$

This equation leads to two important consequences. First, echo formation at the instant 4τ is due only to the spread of the hyperfine fields at the nuclei. All that depends on the quadrupole interaction ν_q is the amplitude of this echo. Second, the echo at the instant 4τ has a nonzero amplitude only if the action of the first pulse leads to the appearance in the density matrix of a nonzero matrix element

$$\langle 3/2|R_1\rho(0)R_1^{-1}|-3/2\rangle. \quad (12)$$

At the zeroth instant of time the density matrix of the nuclear spin system is $\rho(0) \propto I_z$. Consequently, if the matrix element (12) is not to vanish, it is necessary that the first rf pulse transform the nuclear spin system into a coherent state whose wave function would be a superposition of the states $|3/2\rangle$ and $|-3/2\rangle$. Since the states $|3/2\rangle$ and $|-3/2\rangle$ are separated in energy by $3h\nu$, the pulse that "connects" the states $|3/2\rangle$ and $|-3/2\rangle$, is called the pulse that excites the three-quantum transition.[16] The probability of such a three-quantum transition is a maximum when $\Delta = 0$ (Ref. 16). We put henceforth $\Delta = 0$ when calculating the matrix elements in (11). The eigenfunctions and eigenvalues of the Hamiltonian (6) take in this case the forms listed in Table II. The final expression for $V_{4\tau}$ is quite unwieldy. We present therefore the expression obtained for $V_{4\tau}$ by expanding the exact solution in powers of the small parameter (ν_1/ν_q):

$$V_{4\tau} = {}^9/_8(\nu_1/\nu_q)\sin[(3\nu_1^3/8\nu_q^2)2\pi t_1] \times\{(\nu_1/\nu_q)\sin^2(2\pi\nu_1 t_2) - \sin[4\pi\nu_q(t-\tau)] \times\sin[(3\nu_1^3/8\nu_q^2)2\pi t_2]\}G(t-4\tau). \quad (13)$$

Here $G(t-4\tau)$ is the form of the echo at the instant 4τ, due only to the spread of the hyperfine fields at the nuclei. We assume for simplicity that the spread of ν_q in (13) is small. The subsequent use of (13) is justified by the fact that $\nu_1 \gg \nu_q$ the operators R_i behave as operators for the rotation of the nuclear spin around the x axis in a rotating coordinate frame, so that the matrix element (12) is zero for strong rf fields and small quadrupole splittings. At small ν_q it is therefore necessary to use large rf pulse amplitudes, whereas at large ν_q large amplitudes are needed to obtain the maximum possible amplitude of the echo at the instant of time 4τ. Note that the term $\sin[4\pi\nu_q(t-\tau)]$ in (13) describes the modulation of the echo amplitude at the instant 4τ as a function of τ (Ref. 17).

It follows from (13) that the three-quantum transition $(3/2 \leftrightarrow -3/2)$ is optimally excited for the following parameters of the first pulse:

$$\frac{6}{8}\frac{\nu_1^3}{\nu_q^2}t_1 = \left(n + \frac{1}{2}\right), \quad n = 0, 1, 2, \ldots . \quad (14)$$

A similar condition was obtained earlier in an analysis of multiquantum effects in NMR of diamagnetic solids by the formalism of fictitious spin operators.[18,19]

Expression (13) explains qualitatively all observed features of the echo at the instant 4τ and of its spectrum in $CdCr_2Se_4$. Indeed, for the echo (13) to be a maximum at the instant 4τ it is necessary that the parameters of the first pulse meet the condition (14), and that the parameters of the second pulse meet the condition

$$2\nu_1 t_2 = (k + 1/2), \quad k = 0, 1, 2, \ldots . \quad (15)$$

Putting $k = n = 0$ in (14) and (15), we obtain the following relation between the durations t_1 and t_2 of the first and second pulses:

$$t_2/t_1 = {}^3/_8(\nu_1/\nu_q)^2. \quad (16)$$

Since excitation of the three-quantum transition $(3/2 \leftrightarrow -3/2)$ is effective when $\nu_1 < \nu_q$, we find from (16) that the echo at the instant 4τ is extremely sensitive to the durations of the exciting rf pulses, and is produced when $t_1 > t_2$, as was indeed observed in experiment.

As already noted, an echo is produced at the instant of time 4τ when the frequency of the pulsed excitation coincides with the frequency of the magnetic HFI of the nuclei in a magnetically ordered crystal. Consequently, by recording the echo at the instant 4τ, we can write down for various excitation frequencies only the frequency spectrum of the magnetic HFI of the nuclei that are at resonance in the magnet. The NMR spectrum of nuclei located inside a domain wall should in this case assume a two-component form, for when the resonance frequency ν is measured, the nuclei for which $\nu_q < \nu_1$ will produce no echo at the instant 4τ, a fact effectively manifested by a dip in the NMR spectrum (Fig. 1c). The dip of the spectrum of the nuclei in the domain walls should occur at the frequency of the cyclotron magnetic HFI, for in this case $\nu_q = 0$. It was assumed in the description of the experimental results that the additional line c_- near ν_0 is a quadrupole satellite. From the analysis presented in the present section it follows unequivocally that the fact that the line c_0 was observed in the echo spectrum at the instant 4τ (Fig. 1) confirms this assumption and indicates that the local symmetry of the surrounding of the ^{53}Cr nucleus is lower than 3.

Expression (13) explains also the observed multicomponent form of the echo at the instant 4τ near ν_0 (Fig. 3b). Indeed, when the rf pulse frequency is varied in either direction away from the dip (Fig. 1c) an increase of ν_q takes place and the term $\sin [4\pi\nu_q (t-\tau)]$ of (13) comes into play at the position of the echo maximum. The form of the echo can then become quite complicated, as shown by experiment (Fig. 3b). With further increase of ν, the period of the oscillations of the term $\sin [4\pi\nu_q (t-\tau)]$ in (13) becomes much shorter than the width of the echo so that the shape of the echo at the instant 4τ again becomes symmetric (Figs. 3a and 3b).

CONCLUSION

Investigation of the NMR of ^{53}Cr in $CdCr_2Se_4$ has shown that beside the principal echo signal $V_{4\tau}$ there is produced under certain conditions a secondary echo signal $V_{4\tau}$. The NMR spectra recorded both for $V_{2\tau}$ and $V_{2\tau}$ are superpositions of intradomain and intrawall spectra. The intradomain spectrum $V_{2\tau}(\nu)$ has a fine structure due to the anisotropic magnetic and electric HFI. The intensity distribution of the lines in the NMR spectrum differ from the theoretical one because of the spread of the angles between the magnetization and the principal axis of the HFI tensor.

The conditions for the formation of the secondary echo $V_{4\tau}$ differ from those for the principal echo $V_{2\tau}$. It is necessary that the duration t_1 of the first pulse exceed the duration t_2 of the second. In addition, the amplitude of the rf pulses that form the $V_{4\tau}$ echo signal depend on the quadrupole splitting of the NMR spectrum. When the quadrupole splitting increases it is necessary to increase the rf pulse amplitude in order to form the $V_{4\tau}$ echo signal. The $V_{4\tau}(\nu)$ spectra, in contrast to the $V_{2\tau}(\nu)$ spectra, reflect only the anisotropic magnetic HFI in the domains and in the domain walls. The intrawall spectrum has two components with a "dip" at the frequency of the isotropic magnetic HFI. All the peculiarities of the excitation of the $V_{2\tau}(\nu)$ echo and of its spectra are explained by the theory expounded in this article and are the consequence of multiquantum effects that are manifested by the onset, after the first pulse, of a coherent superposition state that binds together energy levels separated by $3h\nu$.

We note in conclusion that the use of multiquantum effects in NMR of magnetically ordered substances uncovers, besides the here-demonstrated possibility of separating the magnetic and electric HFI, a number of new possibilities from the viewpoint of developing microwave-spectroscopy research into magnets, as well as from the viewpoint of obtaining new information on the magnetic and electric HFI, and also on the relaxation processes in magnetically ordered substances.

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