Multiple echos and multiquantum effects in the NMR of magnetically ordered substances

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An additional spin-echo signal involving ^{53} Cr nuclei ($I = 3/2$) has been discovered in the magnetic semiconductor $CdCr_2Se_4$. This new echo reflects only the magnetic hyperfine interactions and is caused by multiquantum effects.

The application of two rf pulses to the nuclear spin system of a magnetically ordered substance may induce, in addition to the main spin-echo signal, some additional signals[1] having the same spectrum as that of the main signal. In the present letter we report the first experimental results revealing an additional spin-echo signal with a spectrum different from that of the main signal.

The additional spin-echo signal (Fig. 1) is observed at ^{53}Cr nuclei in polycrystalline $CdCr_2Se_4$ in the temperature range 4.2–77 K; it appears at a time $t = 4\tau$ after the end of the first rf pulse (τ is the time interval between the first and second pulses). The relation between the lengths of the pulses that form the echo signal at 4τ is quite different from the relation for the ordinary echo at 2τ. For observation of the additional echo at 4τ, the length of the first pulse, t_1, must exceed that of the second pulse, t_2. For equal amplitudes of the rf pulses, the ratio of pulse lengths which is the optimum ratio from the standpoint of the height of the echo at 4τ is $t_1/t_2 \cong 2$. That the NMR spectra, plotted as the amplitudes of the echo signals at 2τ and 4τ versus the carrier frequency of the exciting pulses, are quite different can be seen from Fig. 2. Analysis of the spectra with the help of the values found for the hyperfine interaction constants in a study of the angular dependence of the NMR spectra of a $CdCr_2Se_4$ single crystal in a saturating magnetic field[2,3] showed that while the spectrum of the ordinary echo signal at 2τ is determined by the nuclear quadrupole and magnetic hyperfine interactions, the spectrum of the echo signal at 4τ is determined only by the magnetic isotropic and anisotropic hyperfine interactions. The experimental facts—the time at which the echo appears, its frequency position, and the ratio of pulse lengths—cannot be explained by the mechanisms which have previously been proposed for the formation of secondary echo signals.[1] As we show below, the way in which the echo

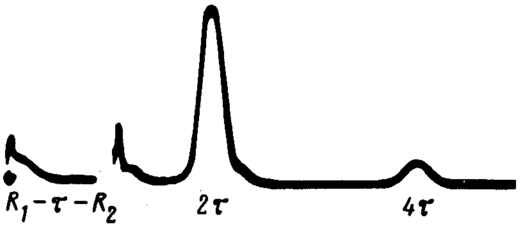

FIG. 1. Oscilloscope trace of the signals representing the ordinary echo at 2τ and the additional echo at 4τ (4.2 K, $\tau = 40$ μs).

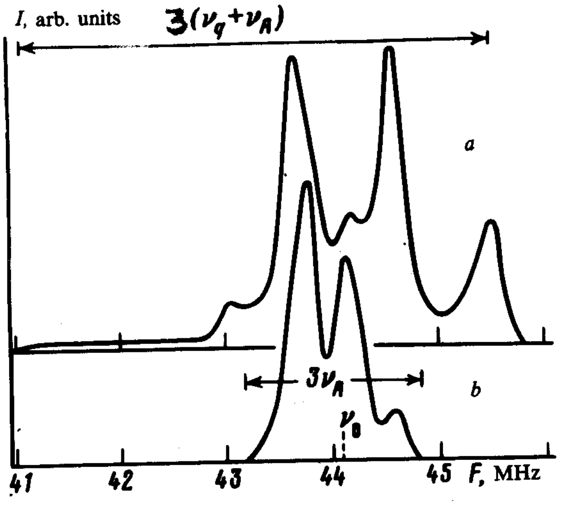

FIG. 2. The NMR spectra of ^{53}Cr nuclei at $T = 4.2$ K in CdCr$_2$Se$_4$ found through the use of (a) the echo at 2τ and (b) the echo at 4τ. ν_0—Isotropic component of the hyperfine field; ν_A and $\nu_q = e^2qQ/4h$—constants of the magnetic anisotropic interaction and quadrupole interaction.

signal appears at 4τ and the spectrum of this signal can be explained in terms of multiquantum effects.

The Hamiltonian ($\hbar = 1$) of a quadrupole nucleus with a spin $I = 3/2$ is

$$\mathscr{H}_0 = -\omega_0 I_z + \omega_q (I_z^2 - 5/4). \tag{1}$$

Here ω_0 is the resonant frequency of the nucleus, which is determined in magnetically ordered substances by the hyperfine field at the nucleus; the second term is the secular part of the Hamiltonian of the quadrupole interaction of the nucleus ($\omega_q \ll \omega_0$); $2\omega_q = (e^2qQ/4\hbar)(3\cos^2\theta - 1 + \eta \sin^2\theta \cos 2\varphi)$, where $e^2qQ/4\hbar$ is the quadrupole coupling constant; η is the asymmetry parameter of the tensor of the electric field gradient; and the angles θ and φ specify the orientation of the hyperfine field with respect to the principal axes of the tensor of the electric field gradient.

A general expression for the response of a nuclear spin system with Hamiltonian (1) to a two-pulse sequence $R_1 - \tau - R_2 - t$ was first derived by Solomon[4]

$$V(t+\tau) = \operatorname{Im} \sum_{m,m',m''} \sqrt{I(I+1) - m(m+1)} < m | R_2 | m' > < m' | R_1 \rho(0) R_1^{-1} | m'' >$$

$$\times < m'' | R_2^{-1} | m+1 > \exp i \{ (t-\tau)[(2m+1)\omega_q - \Delta]$$

$$+ \tau [\Delta(m' - m'') + \omega_q (m''^2 - m'^2)] \}. \tag{2}$$

The operators R_1 and R_2 describe the evolution of the nuclear spin system during its bombardment by rf pulses of length $t_i\,(i = 1,2), R_i = \exp(i\mathscr{H}_1 t_i)$; $\mathscr{H}_1 = -\Delta I_z + \omega_q I_z^2 - \omega_1 I_x$, where $\Delta = \omega_0 - \omega$; ω is the carrier frequency; ω_1 is the amplitude of the rf pulse; 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 density-matrix operator of the nuclear spin system at the time 0. It follows from (2) that the echos will be observed at the times t given by

$$t-\tau=\tau\,\frac{\omega_q(m'^2-m''^2)+\Delta(m''-m')}{(2m+1)\omega_q-\Delta}\,. \tag{3}$$

The echo that arises at the time 2τ after the end of the first pulse (the Solomon echo) has been studied previously. It can be seen from (3), however, that at $\Delta \ll \omega_q$ there is yet another type of nuclear echo, which appears at the time 4τ. The echo at 4τ is described by the next term in (2):

$$4\,\mathrm{Im}\,\langle -1/2\,|R_2|\,3/2\rangle\langle 3/2\,|R_1\rho(0)R_1^{-1}|-3/2\rangle\langle -3/2\,|R_2^{-1}|\,1/2\rangle \exp[i(4\tau-t)\Delta]\,. \tag{4}$$

It can be seen from (4) that the formation of the echo at 4τ results from only the scatter in the values of the hyperfine fields at the nuclei; it does not depend on the quadrupole frequency ω_q. The echo at 4τ has a nonzero amplitude only if a nonvanishing matrix element $\langle 3/2|R_1\rho(0)R_1^{-1}|-3/2\rangle$ appears in the density matrix after the application of the first pulse. Since $\rho(0)\sim I_z$, the first rf pulse would have to excite the three-quantum transition $\pm 3/2 \leftrightarrow \mp 3/2$, thereby "coupling" these states, in order to make this matrix element nonvanishing. A calculation using the known eigenfunctions and eigenvalues of the Hamiltonian[5] $\mathscr{H}_1$ under the conditions $\Delta=0$ and $\omega_1 \ll \omega_q$ leads to the following expression for the amplitude of the echo signal at 4τ:

$$V(4\tau)=9/8\,(\omega_1/\omega_q)^2\sin^2(\omega_1 t_2)\sin[(3\omega_1^3/2\omega_q^2)t_1]\,. \tag{5}$$

It follows from (5) that the first rf pulse must have the following parameters if the three-quantum transition is to be excited:

$$(3\omega_1^3/2\,\omega_q^2)t_1=(n+1/2)\,\pi,\quad (n=0,1,2,\ldots)\,. \tag{6}$$

The amplitude of the echo reaches a maximum at $\omega_1 t_2=(k+1/2)\pi, (k=0,1,2,\ldots)$. With $n=k=0$ we find a relation between the lengths of the first pulse (t_1) and the second pulse (t_2):

$$(t_2/t_1)=3/2\,(\omega_1/\omega_q)^2. \tag{7}$$

Since $\omega_1 \ll \omega_q$, we see from (7) that t_1 must be greater than t_2 if an echo is to form at 4τ, in agreement with experiment.

It has thus been shown both experimentally and theoretically that in nuclear spin systems with $I=3/2$ the formation of the new echo at 4τ is caused by three-quantum transitions $\pm 3/2 \leftrightarrow \mp 3/2$, whose frequency does not depend on the strength of the quadrupole interaction. For this reason, the echo at 4τ appears only if the frequency of the applied pulse is equal to the frequency determined by the magnetic hyperfine interaction, and the spectrum of the echo at 4τ will reflect only the anisotropy of the magnetic hyperfine interaction.

The possibility of using the echo at 4τ to distinguish between effects caused by magnetic and quadrupole hyperfine interactions will significantly increase the amount of information that can be obtained by the NMR method in studies of magnetically ordered crystals.

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Observation in $TmFeO_3$ of direct electronic transitions inside the principal multiplet of a rare-earth ion

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The far-IR absorption spectra of $TmFeO_3$ measured at $T = 4.2$–300 K and $\nu = 100$–1000 GHz have revealed five magnetic-resonance lines. Two of these lines are associated with the antiferromagnetic resonance of the Fe subsystem and the other three lines are associated with the electronic transitions between the lower singlets of the principal multiplet of the Tm^{3+} ion.

In the crystals of rare-earth orthoferrites $RFeO_3$, the principal multiplet of the rare-earth R^{3+} ion splits in a crystal field either into doublets (the Kramers ions) or into singlets (the non-Kramers ions).[1] The electronic transitions inside the Kramers