Multiple structure of spin echoes in inhomogeneously broadened systems with a quadrupole interaction

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The multiple structure of echo signals in inhomogeneously broadened quadrupole spin systems with $I = 3/2$ has been studied experimentally and theoretically. If there is a correlation between the magnetic inhomogeneous broadening and the quadrupole inhomogeneous broadening, some additional echo signals can appear. The times at which they appear are determined exclusively by the time interval between the pulses and by the correlation parameter. They do not depend on the lengths of the rf pulses.

INTRODUCTION

The multiple structure of two-pulse echo signals in inhomogeneously broadened spin systems has been the subject of many studies.[1-11]

It was shown in Refs. 1–4 that a multiple echo structure arises for spin systems with $I = 1/2$ if the height of the long rf pulses does not exceed the inhomogeneous linewidth of the nuclear magnetic resonance. The multiple echo structure in such spin systems consists of a set of additional peaks which are shifted in time from the main echo signal (which is observed at the time 2τ, where τ is the time interval between the pulses) by amounts which are determined by the lengths of the exciting rf pulses, t_i $(i = 1,2)$.

An echo signal with multiple structure was observed in Refs. 5 and 6 in spin systems with a quadrupole interaction $(I > 1/2)$ and an energy spectrum with variable spacing. In this case, as in the case of spin systems with $I = 1/2$, the additional echo signals are detected near the main echo signal at 2τ. Their shifts from the position $t = 2\tau$ are determined exclusively by the lengths of the rf pulses, t_i.

In contrast with the multiple echo structure which has been described, in quadrupole spin systems with $I = 3/2$ one observes some additional echo signals, whose temporal positions do not depend on the lengths of the rf pulses and are determined exclusively by the time interval τ between these pulses.[7-10] It was shown theoretically in Refs. 8 and 11 that additional echo signals of this sort can form only at times which are integer multiples of τ.

The appearance of additional echo signals for quadrupole nuclei with $I > 3/2$, both at times which are integer multiples of τ and at times $t \neq n\tau$, is well known.[12,13]

We have recently observed a so-called fractional echo in spin systems with $I = 3/2$. This echo forms at a time $\approx (5/2)\tau$ and behaves in a manner completely different from that of the echoes at 2τ and 4τ (Ref. 14). Our detailed study of the formation of this echo has shown that the additional fractional echo at $\approx (5/2)\tau$ is not the only one possible in quadrupole spin systems with $I = 3/2$.

In the present paper we are reporting an experimental and theoretical study of these additional echo signals in quadrupole spin systems with $I = 3/2$.

EXPERIMENTAL RESULTS

The experiments were carried out at 4.2 and 77 K on a pulsed NMR spectrometer with amplitude detection of the signal. The test samples were single crystals and polycrystalline samples of the ferromagnetic chalcogenide spinels $CdCr_2Se_4$, $HgCr_2Se_4$, and $CuCr_2Se_4$, with the natural abundance of the magnetic isotope ^{53}Cr. Figure 1 shows oscilloscope traces of the signals of the two-pulse responses of the ^{53}Cr nuclei. On these curves we can clearly see the multiple structure of the echo signals. In addition to the main echo signals at 2τ and 4τ, we observe echo signals at times of approximately $(4/3)\tau$, $(3/2)\tau$, $(5/3)\tau$, $(5/2)\tau$, $(7/2)\tau$, $(9/2)\tau$, 5τ, and 6τ. All the additional echo signals are observed under experimental conditions typical of the detection of the echo signal at 4τ. With allowance for the gain, the amplitude of the rf pulses in frequency units was chosen comparable to the magnitude of the quadrupole splitting of the 2τ NMR spectra (Fig. 2). The length of the first rf pulse, t_1, was greater than that of the second, t_2 (Ref. 8).

The additional echo signals decayed much more rapidly than the main echo signals at 2τ and 4τ. They were essentially not observed for $\tau \gtrsim 30\,\mu s$. The number of observed additional echo signals depended on the carrier frequency of the rf pulses. Figure 2 shows a schematic diagram of this dependence. In contrast with $CdCr_2Se_4$ and $HgCr_2Se_4$, in the $CuCr_2Se_4$ case we observe only three echo signals: at 2τ, 3τ, and 4τ (Fig. 3). The experimental results show that the temporal positions of the additional echo signals do not depend on the lengths of the rf pulses, being determined solely by the time interval τ between pulses. All the additional echo signals are also observed during a one-time application of rf pulses.

DISCUSSION OF EXPERIMENTAL RESULTS

We begin our discussion of the experimental results with the two-pulse response of the quadrupole nuclei with $I = 3/2$ to a two-pulse sequence $R_1 - \tau - R_2 - t$, where the operators R_1 and R_2 describe the effect of the pulses on the nuclear spin system.

The Hamiltonian $(\hbar = 1)$ of the quadrupole nucleus with $I = 3/2$ is[15]

$$H = -\nu I_z + \nu_q (I_z^2 - {}^5/_4). \tag{1}$$

Here ν is the resonant frequency of the nucleus, which is determined in a magnetically ordered substance by the magnetic field at the nucleus due to the magnetic hyperfine interaction. If the gradient of the electric field is an axisymmetric tensor, ν_q is[15]

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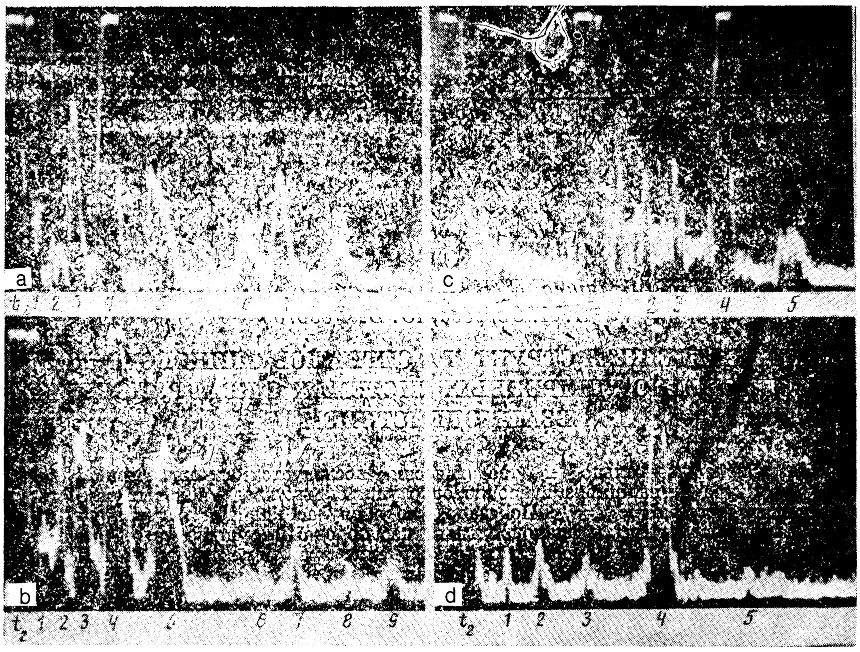

FIG. 1. Oscilloscope traces of echo signals in $HgCr_2Se_4$ at $T = 4.2$ K. The amplitude of the rf pulses is $U = 600$ V; $t_1 = 1.5$ μs; $t_2 = 1$ μs. The horizontal scale is 10 μs/div. The echo signals: 1—$4/3\tau$; 2—$3/2\tau$; 3—$5/3\tau$; 4—2τ; 5—$5/2\tau$; 6—$7/2\tau$; 7—4τ; 8—$9/2\tau$; 9—5τ. a) $\nu_{rf} = 43.26$ MHz; b) $\nu_{rf} = 43.02$ MHz; c) $\nu_{rf} = 43.26$ MHz; d) $\nu_{rf} = 43.33$ MHz. Only the second rf pulse is shown in parts a, b, and d.

$$2\nu_q = C(3\cos^2\theta - 1), \tag{2}$$

where θ is the angle between the electron magnetization **M** and the principal axis of the field-gradient tensor, and C is the quadrupole coupling constant of the nucleus.[15]

The response of a nuclear spin system with an interaction Hamiltonian (1) to a two-pulse sequence ($R_1 - \tau - R_2 - t$) was first found by Solomon:[16]

$$V(\tau,t) \propto \sum_{m,m',m''} [I(I+1) - m(m+1)]^{1/2} \times \langle m|R_2|m'\rangle \langle m'|R_1 I_z R_1^{-1}|m''\rangle \times \langle m''|R_2^{-1}|m+1\rangle \exp\{2\pi i[(t-\tau)[(2m+1)\nu_q - \Delta] + \tau[\Delta + \nu_q(m'+m'')](m'-m'')]\}. \tag{3}$$

Here $\Delta = \nu - \nu_{rf}$, and ν_{rf} is the carrier frequency of the rf pulses.

Because of the spread in the values of ν (the inhomogeneous magnetic broadening) and in the values of ν_q (the inhomogeneous quadrupole broadening) in a real substance, the signal found experimentally is given by

$$F(\tau,t) = \int d\nu \int d\nu_q V(\tau,t)\Phi(\nu,\nu_q), \tag{4}$$

where the function $\Phi(\nu,\nu_q)$ describes the inhomogeneous quadrupole broadening and the inhomogeneous magnetic broadening.

If the characteristics of the rf pulses are such that the conditions $\nu_1 \gg \sigma_\nu, \sigma_q$ hold, where ν_1 is the amplitude of the rf field in the pulses, and σ_ν and σ_q characterize the magnetic and quadrupole broadening of the NMR line, then the factor

$$\langle m|R_2|m'\rangle \langle m'|R_1 I_z R_1^{-1}|m''\rangle \langle m''|R_2^{-1}|m+1\rangle$$

can be taken through the integral sign when (3) is substituted into (4).

We write the quantities ν and ν_q in (3) in the form

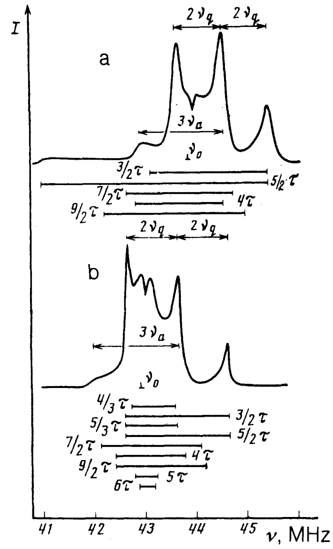

FIG. 2. NMR spectra of ^{53}Cr in (a) $CdCr_2Se_4$ and (b) $HgCr_2Se_4$ at $T = 4.2$ K. The amplitude of the rf pulses is $U = 50$ V; $t_1 = 5$ μs; $t_2 = 10$ μs. a—$2\nu_q = 0.90$ MHz, $\nu_A = 0.56$ MHz; b—$2\nu_q = 0.99$ MHz, $\nu_A = 0.63$ MHz. Shown below the spectra are the frequency intervals in which the additional echo signals are observed.

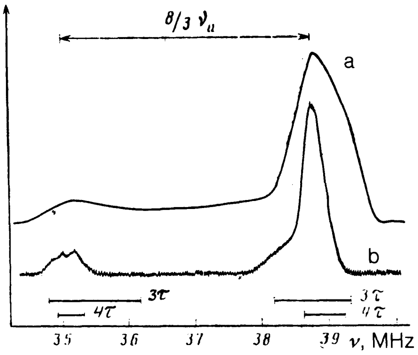

FIG. 3. NMR spectra of ^{53}Cr in $CuCr_2Se_4$ at $T = 4.2$ K. The amplitude of the rf pulses is $U = 30$ V; $t_1 = 3$ μs; $t_2 = 6$ μs. a—$\tau = 40$ μs; b—$\tau = 1500$ μs.

$$\nu=\nu_0+\delta\nu, \quad \nu_q=\nu_q^{(0)}+\delta\nu_q,$$

where the frequency ν_0 corresponds to the center of the spectroscopic transition ($\pm 1/2 \leftrightarrow \mp 1/2$); $\delta\nu$ is the deviation of the resonant frequency of the nucleus from ν_0 as a result of the inhomogeneous magnetic broadening; the frequencies $\nu_0 \pm 2\nu_q^{(0)}$ correspond to the centers of the quadrupole satellite lines (the transitions $\pm 3/2 \leftrightarrow \pm 1/2$); and $\delta\nu_q$ is the deviation from $\nu_q^{(0)}$ due to the inhomogeneous quadrupole broadening. Using the new notation ν and ν_q, when we substitute expression (3) into (4) we can also take the exponential factors containing ν_0 and $\nu_q^{(0)}$ through the integral sign. It is not difficult to see that these factors determine either an oscillatory τ dependence of the echo amplitude or a modulated shape of the echo signal.[7,8] The expression which remains within the integral in (4) determines the number of echo signals and the times at which they are formed.

To pursue the evaluation of the integral in (4), we need to specify the function $\Phi(\nu,\nu_q)$. It is customary to assume that the inhomogeneous magnetic broadening and the inhomogeneous quadrupole broadening are independent and to assume that the averaging over $\delta\nu$ and $\delta\nu_q$ in expression (4) can be carried out separately. In this case, as was shown in Refs. 7 and 11, some additional echo signals—signals in addition to the main echo signal—can appear at the times 3τ and 4τ.

The model of independent (uncorrelated) magnetic and quadrupole broadenings presupposes that these two types of inhomogeneous broadening are caused by distinct and independent physical mechanisms. Actually, it is not difficult to see that these two types of broadening may in general be correlated. This dependence can be demonstrated most simply in the example of inhomogeneous broadening stemming from a spread in the directions of the electron magnetization **M** with respect to the principal axes of the tensors of the magnetic hyperfine interaction and of the electric field gradient. For the axisymmetric tensor of the magnetic hyperfine interaction, the expression for ν is[15]

$$\nu=\nu_0+\nu_a(3\cos^2\theta-1), \tag{5}$$

where ν_0 is the isotropic component of the hyperfine interaction, and ν_a is the anisotropic constant of the magnetic hyperfine interaction. The value of ν_q is given by (2). It follows from (2) and (5) that, if there is a spread in the values of the angle θ in a crystal as a result of a spread in the directions of the electron magnetization **M** about the local symmetry axis, then we have

$$\begin{aligned} \delta\nu &\approx 3\nu_a \sin 2\theta_0\cdot\delta\theta, \\ \delta\nu_q &\approx {}^3/_2 C \sin 2\theta_0\cdot\delta\theta, \end{aligned} \tag{6}$$

where θ_0 is the most probable value of the angle θ, and $\delta\theta=\theta-\theta_0$. It thus follows from (6) that in the case of an inhomogeneous broadening resulting from a spread in the direction of the electron magnetization **M** about the principal symmetry axis of the immediate surroundings of the resonating nuclei the ratio $\delta\nu_q/\delta\nu$ will be directly proportional to the ratio of the quadrupole and hyperfine magnetic interaction constants.

Introducing the parameter $\xi=2\delta\nu_q/\delta\nu$, and working from expression (3), we find

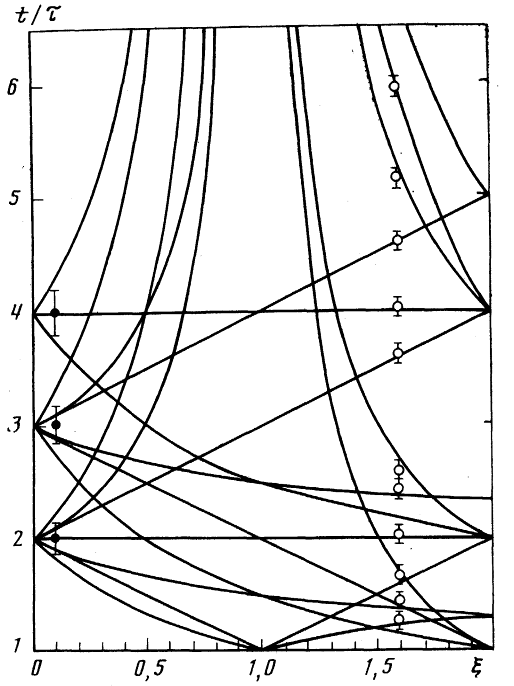

FIG. 4. Calculated times at which the echo signals form versus the parameter ξ for the case in which the magnetic and quadrupole broadenings are correlated. ●—Experimental data on $CuCr_2Se_4$; ○—experimental data on $CdCr_2Se_4$ and $HgCr_2Se_4$.

$$V(\tau,t)\propto\exp\{\delta\nu[t(\xi(m+{}^1/_2)-1) +\tau(1+m'-m''+{}^1/_2\xi(m'^2-m''^2-(2m+1)))]\}. \tag{7}$$

The argument of the exponential function in (7) vanishes when τ, t, and the parameter ξ satisfy a completely definite relation, regardless of the value of $\delta\nu$. In other words, it vanishes at the same time for all isochromates of an inhomogeneously broadened spectral line. Consequently, the time at which an echo is formed can be found without regard to the nature of the functions characterizing the inhomogeneous magnetic broadening and the inhomogeneous quadrupole broadening. Figure 4 shows calculations of the times at which the echo signals are formed, as a function of the parameter ξ. It follows from Fig. 4 that the number of additional echo signals which are possible increases significantly—particularly at times greater than 4τ—when the magnetic inhomogeneous broadening is correlated with the quadrupole inhomogeneous broadening.

These theoretical results explain all the basic features observed in the formation of the multiple echo structure in chalcogenide spinels. The additional fractional echo signals which are observed experimentally for $t>4\tau$ in $CdCr_2Se_4$ and $HgCr_2Se_4$ indicate that the inhomogeneous magnetic broadening and the inhomogeneous quadrupole broadening are not independent in these substances. For $CdCr_2Se_4$ and $HgCr_2Se_4$, the ratio of the constants is $C/\nu_a=1.60\pm0.02$. The times at which the echo signals are observed to form experimentally agree well with those calculated, within the error due to the lengths of the echo signals (Fig. 4). The additional echo signals at the times 1.15τ and 2.15τ could not be resolved experimentally. The absence of the fractional echo signals in $CuCr_2Se_4$ indicates that the parameter ξ is much less than unity in this substance. Indeed, we know from experimental data obtained by the FMR method and by magnetic measurements that the magnetic crystallographic anisotropy constants K_1 and K_2 are negative, that they are 10^4 J/cm^3 in order of magnitude, and that the easy-magnetization axis of $CuCr_2Se_4$ runs along a $\langle 111 \rangle$ direction.[17] From the NMR spectrum in Fig. 3 we find $\nu_a \approx 1.42$ MHz. Using the value[18] $C \approx 140$ kHz for the spectral line at the frequency $\nu = 38.8$ MHz, we find $\xi \approx 0.1$. At values $\xi \ll 1$, according to Fig. 4, we should observe only the echoes at 2τ, 3τ, and 4τ-again, in agreement with experiment.

In summary, the multiple structure observed in the echo signals in these chalcogenide spinels of chromium occurs because the inhomogeneous magnetic broadening and the inhomogeneous quadrupole broadening in these substances are correlated with each other.

CONCLUSION

This analysis of the multiple echo structure for the particular case of chalcogenide spinels of chromium shows that the appearance of additional echo signals, including some at $t > 4\tau$, in nuclear spin systems with $I = 3/2$ is a consequence of the correlation between the quadrupole broadening and the magnetic broadening of the MNR spectral lines. We have suggested one possible mechanism for a correlation of these two types of broadening. According to this suggestion, the correlation would stem from a spread in the direction of the electron magnetization about the local symmetry axis. The relationship which we have found between the number of additional echo signals and the parameter describing the correlation between the inhomogeneous magnetic broadening and the inhomogeneous quadrupole broadening opens up some new opportunities for studying the actual structure of magnetically ordered substances by means of NMR.

[1] R. W. N. Kinnear, S. J. Campbell, and D. H. Chaplin, Phys. Lett. A **76**, 311 (1980).

[2] D. K. Fowler, D. C. Creagh, R. W. N. Kinnear, and G. V. H. Wilson, Phys. Status Solidi (a) **92**, 545 (1985).

[3] M. Kunitomo and T. Hashi, Phys. Lett. A **81A**, 299 (1981).

[4] A. L. Bloom, Phys. Rev. **98**, 1105 (1955).

[5] A. E. Reĭngardt, V. I. Tsifrinovich, O. V. Novoselov, and V. K. Mal'tsev, Fiz. Tverd. Tela (Leningrad) **25**, 3183 (1983) [Sov. Phys. Solid State **25**, 1823 (1983)].

[6] R. H. Dean and R. I. Urwin, J. Phys. C **3**, 1747 (1970).

[7] H. Abe, H. Yasuoka, and A. Hirai, J. Phys. Soc. Jpn. **21**, 77 (1966).

[8] G. N. Abelyashev, V. N. Berzhanskiĭ, N. A. Sergeev, and Yu. V. Fedotov, Zh. Eksp. Teor. Fiz. **94**(1), 227 (1988) [Sov. Phys. JETP **67**(1), 127 (1988)].

[9] M. I. Kurkin and V. V. Serikov, Fiz. Tverd. Tela (Leningrad) **16**, 1177 (1974) [Sov. Phys. Solid State **16**, 755 (1974)].

[10] G. I. Mamniashvili and V. P. Chekmarev, Fiz. Tverd. Tela (Leningrad) **22**, 2984 (1980) [Sov. Phys. Solid State **22**, 1742 (1980)].

[11] V. I. Tsifrinovich, Zh. Eksp. Teor. Fiz. **94**(7), 208 (1988) [Sov. Phys. JETP **67**(1), 1413 (1988)].

[12] V. S. Grechishkin, *Nuclear Quadrupole Interactions in Solids*, Nauka, Moscow, 1973, Chap. 10.

[13] G. K. Shoep, H. J. Valk, G. A. M. Frijters *et al.*, Physica **77**, 449 (1974).

[14] G. N. Abelyashev, V. N. Berzhanskiĭ, N. A. Sergeev, and Yu. V. Fedotov, Pis'ma Zh. Eksp. Teor. Fiz. **48**, 619 (1988) [JETP Lett. **48**, 670 (1988)].

[15] A. Abragam, *The Principles of Nuclear Magnetism*, Oxford Univ., London, 1961 (Russ. transl., IIL, Moscow, 1963, Chap. 7).

[16] I. Solomon, Phys. Rev. **110**, 61 (1958).

[17] I. Nakatani, H. Hose, and K. Masumoto, J. Phys. Chem. Solids **39**, 743 (1978).

[18] A. A. Babitsina, S. M. Ryabchenko, and Yu. V. Fedotov, Fiz. Tverd. Tela (Leningrad) **25**, 2520 (1983) [Sov. Phys. Solid State **25**, 1449 (1983)].

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