Multiquantum effects in NMR of ^{55}Mn in an $Mn_{1+\delta}$ system

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Multiple ^{55}Mn NMR spin-echo signals formed at instants $n\tau$ that are multiples of the time interval τ ($n = 2, 3, 4, 5, 6$) between the excitation pulses are investigated. It is shown that NMR spectra from echo signals with $n = 2, 3, 4$, and 5 contain five, four, three, and two peaks, respectively, and carry information on the quadrupole splitting, whereas for $n = 6$ the spectrum shows only magnetic hyperfine interaction. Different dependences of the multiple echo signal amplitudes on τ and on the broadening of the energy levels of the nuclear system are found. All the results are attributed to a manifestation of multiquantum effects in NMR of magnetically ordered systems.

INTRODUCTION

The action of two radio-frequency (rf) pulses, separated by a time interval τ, on a system of spins with quadrupole splitting is known to produce several echo signals in the energy spectrum.[1–4] It is shown in Refs. 3 and 4 that in the case of half-integer nuclear spin ($S = 3/2$) the NMR spectrum determined from the amplitude of the spin echo produced at the instant 4τ on the rf-pulse carrier frequency ν is independent of the quadrupole splitting and is indicative only of anisotropy of the hyperfine interaction. This effect is attributed in Refs. 3 and 4 to excitation of multiquantum transitions in the spin system. We report here an experimental study of the NMR spectrum of ^{55}Mn ($S = 5/2$) obtained from echo signals produced at instants $n\tau$ ($n = 2, 3, 4, 5, 6$). We determine the dependence of the amplitudes of both the primary ($n = 2$) and the secondary ($n > 2$) echo signals on τ and on the degree of nuclear-system energy-level broadening. Our calculations show that the behavior observed is due to a multiquantum mechanism that forms the supplementary echo signals.

The samples investigated were of $Mn_{1+\delta}Sb$, known as a variable-composition NiAs phase in which variation of the Mn concentration, within the homogeneity range ($0.04 \leqslant \delta \leqslant 0.22$) causes appreciable changes of the crystal-lattice parameters and of the magnetic, electric, and other physical properties.[5,6] A unique feature of the most stoichiometric composition of this system ($\delta = 0.04$, i.e., a 51 at. % Mn + 49 at. % Sb alloy) is the presence, in the NMR spectrum of ^{55}Mn, of a well resolved quadrupole structure due to the structure peculiarities of the domain wall of this magnet.[7,8] In particular, the magnetization vector in the entire region of the wall is perpendicular to the electric-field gradient (EFG), so that the spectral-transition frequencies are independent of the relative orientation of the magnetization vector and the EFG; this affords the rather rare opportunity of observing a resolved quadrupole structure in the NMR spectrum of a multidomain polycrystalline ferromagnet.[4,9] Another unique feature of the investigated system is the relatively low anisotropy of the hyperfine interaction, simplifying thereby the interpretation of the NMR spectrum and permitting observation of a number of new effects due to multiquantum transitions.

EXPERIMENT

Polycrystalline $Mn_{1+\delta}Sb$ samples were obtained by high-temperature solid-phase reaction of the component elements, followed by prolonged annealing.[10] The ^{55}Mn NMR spin-echo signals were recorded at $T = 77$ K with a spin-echo spectrometer having a pass band on the order of 1.5 MHz. For the sample with $\delta = 0.04$ we observed both a primary ($n = 2$) and a number of secondary ($n > 2$) echo signals; simultaneous appearance of signals with $n = 3, 4, 5$, and 6 was possible only at relatively short exciting-pulse durations (t_1 and t_2), and the amplitude of the first rf pulse (0.5 Oe) was two or three times larger than that of the second (see Fig. 1). When the system was excited by longer pulses the intensities of the secondary echo signals with $n = 5$ and 6 decreased somewhat (Figs. 1a, b). It should be noted that, in contrast to the results of Ref. 4, the formation, in our system, of echo signals at the instants 3τ and 5τ was not connected with the excitation-cycle repetition frequency, and occurred following a single application of the pulses. It was also noted that the intensity of the echo-signals formed at the instants 3τ and 5τ decreased substantially with increase of the Mn concentration in the compound (i.e., with increase of δ and hence on the local distortions in the crystal lattice near the so-called extra Mn atoms),[5,6,10,11] whereas the signals with $n = 2$ and 4 were not changed as noticeably (Figs. 1c, d).

The most pronouncedly dependent on n are the forms of the NMR spectra. Thus, Fig. 2 shows plots of the amplitudes I of the primary and secondary echo signals on the rf-pulse carrier frequency. It is seen that the NMR spectrum obtained with the primary echo signal for the sample with $\delta = 0.04$ consists of five well-resolved quadrupole-splitting peaks (Figs. 2a), spaced 2 MHz apart; this spectrum agrees well with the results by others.[7,11] The NMR spectrum of the same sample for the 3τ echo signal contains four peaks shifted in frequency by $\Delta\nu/2$ from the maxima in the $I(2\tau)$ spectrum (see Figs. 2a, b), i.e., the $I(3\tau)$ spectrum carries information on the quadrupole spectrum, although it does differ from the $I(2\tau)$ spectrum. The $I(4\tau)$ and $I(5\tau)$ spectra, similarly, contain respectively two and three peaks, and the peak positions in the $I(4\tau)$ and $I(5\tau)$ spectra coincide respectively with those of $I(2\tau)$ and $I(3\tau)$ (see Fig. 2). All the NMR spectra obtained with echo signals having $n = 2, 3, 4$, and 5 contain thus respectively 5, 4, 3, and 2 peaks spaced $\Delta\nu$ apart. A different frequency dependence is observed for the $I(6\tau)$ spectrum (its intensity was too low to be shown in Fig. 2). This spectrum constitutes one broad maximum at the central-transition frequency $\nu \approx 257$ MHz, with a width on the order of 0.8–1.0 MHz. All the NMR spectra shown in

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Fig. 2 were plotted at an exciting-pulse amplitude ratio $A_1/A_2 = 2$ to 3, and a duration ratio t_1/t_2 with $t_1 = 0.4$–$1.2\ \mu s$.

A unique feature of the echo signals in systems with quadrupole splitting in the NMR spectrum is an oscillatory dependence of the echo amplitude on the time spacing τ of the exciting pulses; the period τ_n of the oscillations depends on the echo number n and on the quadrupole splitting $\Delta\nu$ (Refs. 1 and 2). The aforementioned modulations of the envelopes of the echo signals with different n were observed by us also in the investigated $Mn_{1+\delta}Sb$ systems. It was noted, however, that when δ is increased the depths of the $n = 2$ and 4 echo signal oscillations decrease, and the oscillations vanish completely for the composition with 54 at. % Mn ($\delta = 0.17$), in which case the profiles of the NMR spectra also change substantially.[12] Whereas a pronounced quadrupole structure is observed for compositions with $\delta \leqslant 0.06$ (see Fig. 2a), for $\delta = 0.17$ the $I(2\tau)$ and $I(4\tau)$ spectra are already broad lines without indication of quadrupole splitting (Figs. 3a, b); here, as noted above, no echo signals with $n = 3$ and 5 are observed.

It can thus be concluded from the experimental data that the results of the present investigation differ from the data of Refs. 2–4. It follows from general considerations first set forth in Refs. 3 and 4 that the secondary echo signals are produced in the $Mn_{1+\delta}Sb$ system via a multiquantum mechanism, but it is obviously necessary to consider these effects separately for the case for the spin $S = 5/2$.

DISCUSSION OF RESULTS

The ^{55}Mn nucleus with spin $S = 5/2$ is described by a spin Hamiltonian

$$H = -\nu_Z S_z + {}^1/_4 \nu_q [S_z^2 - {}^{35}/_{12}], \qquad (1)$$

where ν_Z is the Zeeman-splitting frequency, and $\nu_q = \frac{3}{20} \cdot e^2 qQ/\hbar$ is the quadrupole interaction constant that relates the nuclear quadrupole moment Q with the EFG q.[1,13,14] It follows from Refs. 3, 4, and 13 that the two-pulse echo signal is proportional to $I(t)$:

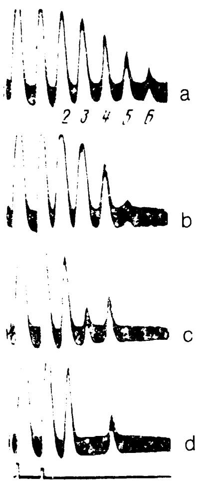

FIG. 1. Spin-echo-signal oscillograms for ^{55}Mn NMR in the $Mn_{1+\delta}Sb$ system at $T = 77$ K at δ values 0.04 (a, b), 0.08 (c), and 0.17 (d). Excitation conditions: pulse durations $t_1 = 0.4$ and $t_2 = 0.62\ \mu s$ (a) and $t_1 = 1.2\ \mu s$ and $t_2 = 1.5\ \mu s$ (b, c, d). The echo-signal appearance times (the values of n) are labeled 2, 3, ..., 6. Lower trace—signal from detector recording the exciting-pulse time position and amplitude.

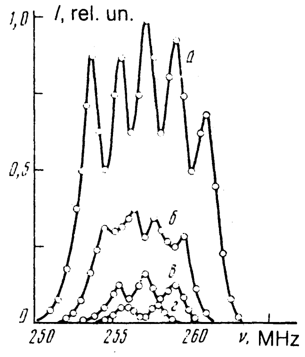

FIG. 2. Echo-signal amplitude I for sample with $\delta = 0.04$ at $T = 77$ K vs the excitation frequency ν and the echo time position—$n = 2$ (a), 3 (b), 4 (c), and 5 (d).

$$I(t) = \sum_{m,m',m''} [{}^{35}/_4 - m(m+1)]^{1/2} \langle m|R_2|m'\rangle \times \langle m'|R_1 \rho(0) R_1^{-1}|m''\rangle \times \langle m''|R_2^{-1}|m+1\rangle \exp\{i[{}^1/_4\nu_q(2m+1) - (\nu_Z - \nu)](t-\tau) + i\tau[(\nu_Z - \nu)(m'-m'') + {}^1/_4(m''^2 - m'^2)]\}, \qquad (2)$$

where m, m', and m'' are the nuclear-spin components in the direction of the constant (in our case, hyperfine) magnetic field, R_1 and R_2 are the operators of the action of the first and second pulses on the spin system, and $\rho(0)$ is the equilibrium density matrix of the system.

Assuming that the main factor in the inhomogeneous broadening in an ensemble of manganese nuclei is the scatter of the Zeeman frequencies ν_Z, whereas the quadrupole-splitting frequency ν_q remains the same for all nuclei, and following Refs. 1, 4, 13, and 14, we can conclude that echo signals should be observed at the instants 2τ, 3τ, 4τ, 5τ, and 6τ, i.e., the sum (2) contains terms corresponding to the response of the spin system due to the phasing of the orthochromats at $t = n\tau$ ($n = 2$, 3, 4, 5, 6). The echo signal formed at the instant $t = 2\tau$ should have a maximum amplitude at rf-pulse carrier frequencies

$$\nu_1^{(1)} = \nu_Z - \nu_q, \quad \nu_2^{(1)} = \nu_Z - {}^1/_2\nu_q, \quad \nu_3^{(1)} = \nu_Z, \quad \nu_4^{(1)} = \nu_Z + {}^1/_2\nu_q, \quad \nu_5^{(1)} = \nu_Z + \nu_q.$$

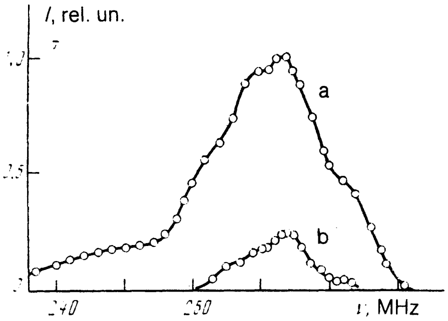

FIG. 3. Echo-signal amplitude I for sample with $\delta = 0.17$ at $T = 77$ K vs the excitation frequency ν and the values $n = 2$ (a) and 4 (b).

In other words, the NMR spectrum obtained with the primary echo spin should consist of five lines, as is indeed observed in experiment (see Fig. 2a). The frequencies of these lines coincide with those of the single-quantum transitions with $\Delta m = 1$ in a system of ^{55}Mn non-equidistant levels specified by the Hamiltonian (1). It follows similarly from Eq. (2) that the echo signal produced at the instant 3τ should have a maximum amplitude when the rf-pulse frequency coincides with one of the following four:

$$\nu_1^{(2)}=\nu_Z-{}^3/_4\nu_q,\quad \nu_2^{(2)}=\nu_Z-{}^1/_4\nu_q,$$

$$\nu_3^{(2)}=\nu_Z+{}^1/_4\nu_q,\quad \nu_4^{(2)}=\nu_Z+{}^3/_4\nu_q.$$

Participating in the echo formation are in this case spin transitions with $\Delta m = 2$ having frequencies $\nu_i^{(2)}$ ($i = 1, 2, 3, 4$) and due to simultaneous absorption or emisison of two rf-field quanta.

The signal of the second secondary echo ($n = 4$) should reach a maximum at pulse-carrier frequencies

$$\nu_1^{(3)}=\nu_Z-{}^1/_2\nu_q,\quad \nu_2^{(3)}=\nu_Z,\quad \nu_3^{(3)}=\nu_Z+{}^1/_2\nu_q.$$

The NMR spectrum obtained from this echo signal should consist of three lines connected with spin transitions $\Delta m = 3$ induced by three-quantum processes. Analogously, the NMR spectrum from the echo signal produced at the instant $t = 5\tau$ should consist of two lines:

$$\nu_1^{(4)}=\nu_Z-{}^1/_4\nu_q,\quad \nu_2^{(4)}=\nu_Z+{}^1/_4\nu_q.$$

It is formed by contributions from four-quantum processes with selection rule $\Delta m = 4$.

Finally, the last echo ($n = 6$) should be observed at the frequency $\nu = \nu_Z$, and is due to a five-quantum transition between the outermost spin levels of the manganese nucleus ($\Delta m = 5$), i.e., the NMR spectrum obtained at $t = 6\tau$ is free of quadrupole splittings, whereas the spectra of all the remaining signals involve the quantity ν_q equal to double the splitting of the corresponding single-quantum or multiquantum NMR lines.

Comparing the results of the analysis of Eq. (2) with the experimental data, we can conclude that the multiquantum mechanism of formation of multiple echo signals explains fully the experimentally observed picture of the distribution of the intensities in the NMR spectra obtained from the echo signals formed at the instants $n\tau$.

Let us consider the dependence of the echo-signal amplitudes $I(n\tau)$ on the time shift τ and on the degree of broadening of the spin-system energy levels. As shown in Ref. 1, modulation of the envelope of the multiple echo signals is due to the presence of quadrupole interactions in the nuclear spin system. The dependence of the echo amplitude on τ, for signals produced at the instants 2τ, 4τ, and 6τ, takes respectively the form

$$I(2\tau)=c_0^{(1)}+F_1(\nu_q\tau),\quad I(4\tau)=c_0^{(3)}+F_3(\nu_q\tau),$$
$$I(6\tau)=c_0^{(5)}+F_5(\nu_q\tau), \tag{3}$$

where $c_0^{(1)}$, $c_0^{(3)}$ and $c_0^{(5)}$ are constants independent of τ. The analogous relations for echo signals produced at the instants 3τ and 5τ are

$$I(3\tau)=F_2(\nu_q\tau),\quad I(5\tau)=F_4(\nu_q\tau), \tag{4}$$

i.e., they do not contain a constant term; $F_1, \ldots, F_5$ in (3) and (4) are harmonic functions of the argument $\nu_q\tau$, given explicitly by Eqs. (35)–(39) of Ref. 1. Since there is no constant term in $I(3\tau)$ and $I(5\tau)$, the envelope modulation depths of the echo signals with $n = 3$ or 5 will be larger than for the echo with $n = 2$, 4, or 6; this agrees well with experiment.

If stoichiometry is disturbed, the Mn concentration in the compound is increased, and local distributions appear in the lattice, a scatter appears in the quadrupole-splitting frequencies ν_q. To obtain in this case a final expression describing the echo signal, expressions (3) and (4) must be averaged over ν_q. If the scatter of ν_q is large enough and "smears out" the quadrupole structure in the NMR spectra, averaging leads to vanishing of the integrals containing $F_i(\nu_q\tau)$ ($i = 1, 2, 3, 4, 5$); this causes in turn the echo signals at the instants $t = 3\tau$ and 5τ to vanish and suppresses the oscillations on the plots of the τ-dependence of the amplitudes of the echo signals produced at the instants $t = 2\tau$, 4τ, and 6τ. These results agree fully with the experimentally established laws described in the preceding section.

CONCLUSION

Our results show that five echo signals are produced in the NMR spectrum of an $Mn_{1+\delta}Sb$ compound with spin $S = 5/2$ and with a well pronounced quadrupole splitting; secondary echo signals with $n > 2$ are formed in this case via a multiquantum mechanism of spin-system excitation. In constrast to the results of Refs. 3 and 4, we have shown that echo signals with $n = 3$, 4 and 5 contain information on the quadrupole splitting, and only the echo with $n = 6$, due to a transition with selection rules $\Delta m = 5$, is similar to the echo signal with $n = 4$ for nuclei with 3/2 spin. In other words, the NMR spectrum obtained from the dependence of the echo amplitude $I(6\tau)$ on the excitation frequency is independent of the quadrupole splitting and is determined only by the magnetic isotropic and anisotropic hyperfine interactions. Obviously, a similar property will be possessed by echo signals with $n = 3$ if $S = 1$, with $n = 8$ if $S = 7/2$, etc. It has been established that as the local distortions of the crystal and magnetic structures increase the amplitudes of the secondary echo signals with $n = 3$ and 5 decreases abruptly; this can also be explained in the context of the multiquantum mechanism of formation of secondary echo signals. Similarly explained are the oscillations of the echo-signal amplitudes and their dependences on the time delay between the exciting pulses and on the degree of local distortion in the lattice.

Special attention should be paid to the conditions for multiquantum-transition excitation, i.e., to the choice of the optimal pulse durations and powers. We know that the maximum intensities of the echo signals from nuclei in domain walls are reached when the turning angles of the exciting rf pulses are unequal; in this case, depending on the number of quanta participating in the transitions, the optimal conditions for focusing the nuclear isochromats are different.[3,4] The conditions used in the present paper for excitation of multiquantum transitions agree in the main with those recommended in Ref. 4. In particular, the isochromat magnetization rotation angle $\varphi_1 = \omega_1^{(1)}t_1$, in the first pulse was two–three times larger than the angle $\varphi_2 = \omega_1^{(2)}t_2$ in the second pulse (here $\omega_1^{(1),(2)}$ are the rf-pulse amplitudes, in frequency units, in the first and second pulses).

It should be noted that the dependences of the amplitudes of the primary and secondary echo-signal amplitudes on the excitation conditions is nonmonotonic and strongly oscillating.[3,4,14] For nonmagnetic systems this dependence was investigated theoretically in detail for an echo with $n = 2$ in Ref. 14, but a direct comparison of the results of this reference, as well as of the recommendations contained in Refs. 3 and 4, with the NMR data for magnetically ordered systems leads only to an approximate qualitative correspondence. An actual calculation of the amplitudes of the primary and secondary echo signals as functions of the excitation conditions in multidomain ferromagnets requires a consistent account of the inhomogeneity, inherent in these systems, of the rf-field gain, i.e., requires averaging with allowance for the distribution of the nuclei over the gains.[15,16]

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