

# Magic echo in a heteronuclear spin system

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An investigation has been made of the magic echo of a signal due to various off-diagonal terms of the density matrix corresponding to the interactions between spins in the heteronuclear spin system of LiF. The same object was used in a study of the magic echo of free induction signals of the  $^7\text{Li}$  and  $^{19}\text{F}$  nuclei. The random phase approximation was found to be unsuitable for the description of the evolution of the off-diagonal terms of the density matrix in the heteronuclear case.

Schneider and Schmiedel<sup>1</sup> proposed in 1969 a pulse sequence for observing the magic echo of a free induction signal. Waugh *et al.*<sup>2,3</sup> investigated experimentally in detail the magic echo of a free induction signal of the nuclear magnetic moments of  $^{19}\text{F}$  in  $\text{CaF}_2$ . These experiments<sup>2,3</sup> demonstrated the possibility of a reversible evolution of the transverse component of the magnetization in a macroscopic system and, consequently, the unsuitability of the random phase approximation for the description of such evolution.<sup>4</sup> The discovery and study of a dipole magic echo, due to reversibility in the evolution of off-diagonal terms of the density matrix corresponding to two-particle operators of the dipole-dipole interactions in a system of nuclear spins, were reported in Refs. 5 and 6. These experiments<sup>5,6</sup> were carried out, like those of Refs. 2 and 3, on the spin system of the  $^{19}\text{F}$  nuclei in  $\text{CaF}_2$ . A single crystal of  $\text{CaF}_2$  can be regarded as a system with one type of nuclear spins (homonuclear system). Stochastization seems to be much more likely in systems with two or more types of nuclear spin (heteronuclear systems) than in homonuclear systems. Fundamental progress made in stochastic dynamics (see, for example, Refs. 7 and 8) has considerably advanced theoretical analysis of the problems of stochastization in spin systems.<sup>9</sup> However, a comprehensive theoretical solution of the problem of stochastization in arbitrary macroscopic systems is hardly possible without the introduction of additional assumptions of a phenomenological nature. It therefore seems to us essential to obtain new experimental data on reversibility and irreversibility in the evolution of macro systems. Spin systems provide an exceptionally convenient if not unique model for this purpose.

It is known<sup>7,8</sup> that even a transition from one set of initial conditions to another can make the motion of a system stochastic. It is not clear *a priori* what change can be expected as a result of a change in the type of the investigated system. We carried out several experiments on the validity of the random phase approximation for the description of the evolution of off-diagonal terms in the density matrix of heteronuclear spin systems. Measurements were carried out on the spin system of the  $^7\text{Li}$  and  $^{19}\text{F}$  nuclei in an LiF single crystal at a working frequency of  $\omega_0/2\pi = 22.5$  MHz applied at room temperature. The spin-lattice relaxation times  $T_{1z}$  obtained in the  $H_0 \parallel [110]$  orientation were 1.2 and 1.6 sec for  $^{19}\text{F}$  and  $^7\text{Li}$ , respectively. The spin-spin relaxation times deduced from the decay of the free induction signal for the  $H_0 \parallel [111]$ ,  $H_0 \parallel [110]$ , and  $H_0 \parallel [100]$  orientations were

approximately 18, 14, and 7  $\mu\text{sec}$  in the case of  $^{19}\text{F}$ , and 52, 35, and 23  $\mu\text{sec}$  for  $^7\text{Li}$ .

When the spin system of LiF was subjected to sequences of rf pulses in resonance with the spins of  $^7\text{Li}$  and  $^{19}\text{F}$ , we observed and investigated a dipole magic echo due to various off-diagonal terms of the density matrix and also a magic echo of the free induction signals of the  $^7\text{Li}$  and  $^{19}\text{F}$  nuclei.

The dipole magic echo signals were obtained using pulse sequences 1 and 2 (Fig. 1). We shall now consider the evolution of a heteronuclear system when the pulse sequence 1 is applied. The Hamiltonian of the spin system considered in the laboratory coordinates is

$$\mathcal{H} = \omega_{0I}I_z + \omega_{0S}S_z + \mathcal{H}'_{d_I} + \mathcal{H}'_{d_{IS}} + \mathcal{H}'_{d_S} + \mathcal{H}''_{d_I} + \mathcal{H}''_{d_{IS}} + \mathcal{H}''_{d_S}. \quad (1)$$

Here,  $\mathcal{H}'_{d_I} + \mathcal{H}'_{d_{IS}} + \mathcal{H}'_{d_S}$  and  $\mathcal{H}''_{d_I} + \mathcal{H}''_{d_{IS}} + \mathcal{H}''_{d_S}$  are, respectively, the secular and nonsecular parts of the dipole-dipole interaction, where

$$\mathcal{H}'_{d_I} = \sum_{i < j} a_{ij} [I_{zi}I_{zj} - 1/4(I_{+i}I_{-j} + I_{-i}I_{+j})],$$

$$\mathcal{H}'_{d_{IS}} = \sum_{k,l} b_{kl} I_{zk}S_{zl}, \quad (2)$$

$$\mathcal{H}'_{d_S} = \sum_{m < n} c_{mn} [S_{zm}S_{zn} - 1/4(S_{+m}S_{-n} + S_{-m}S_{+n})].$$

Adiabatic demagnetization in a rotating coordinate sys-

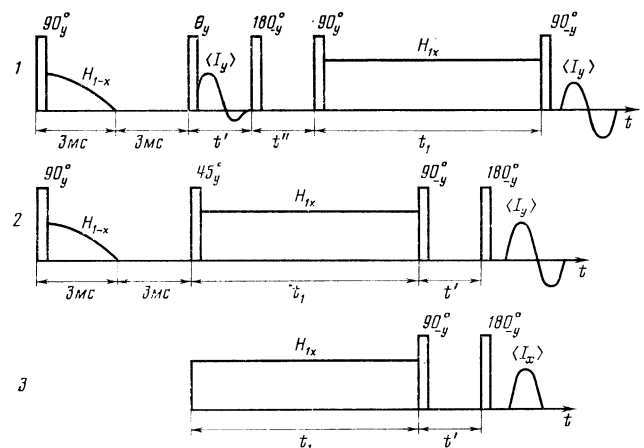


FIG. 1. Investigated pulse sequences.

tem rapidly cools the reservoir of the secular part of the dipole-dipole interactions, and the density matrix of this spin system before the arrival of a  $\theta$  pulse can be described by

$$\sigma = 1 - \beta (\mathcal{H}'_{d_I} + \mathcal{H}'_{d_{IS}} + \mathcal{H}'_{d_S}). \quad (3)$$

Equation (3) is derived on the assumption that the secular interactions in systems with two types of spin represent the only energy reservoir.<sup>10</sup>

The action of a  $\theta$  pulse transforms the density matrix of Eq. (3) as follows:

$$\begin{aligned} \sigma' &= \exp(-i\theta I_y) \sigma \exp(i\theta I_y) \\ &= 1 - \beta \left[ \frac{1}{2} (3 \cos^2 \theta - 1) \mathcal{H}'_{d_I} + \frac{3}{8} P_I \sin^2 \theta \right. \\ &\quad \left. + \frac{3}{4} Q_I \sin \theta \cos \theta + Q_{IS} \sin \theta + \mathcal{H}'_{d_{IS}} \cos \theta + \mathcal{H}'_{d_S} \right], \\ P_I &= \mathcal{H}_{d_I}^{(2)} + \mathcal{H}_{d_I}^{(-2)}, \quad \mathcal{H}_{d_I}^{(2)} = \mathcal{H}_{d_I}^{(-2)*} = \sum_{i < j} a_{ij} I_{+i} I_{+j}, \\ Q_I &= \mathcal{H}_{d_I}^{(1)} + \mathcal{H}_{d_I}^{(-1)}, \quad \mathcal{H}_{d_I}^{(1)} = \mathcal{H}_{d_I}^{(-1)*} = \sum_{i < j} a_{ij} I_{zi} I_{+j}, \\ Q_{IS} &= \frac{1}{2} (Q_{IS}^+ + Q_{IS}^-), \quad Q_{IS}^\pm = \sum_{k,l} b_{kl} I_{\pm k} S_z. \end{aligned} \quad (4)$$

In a two-frequency rotating coordinate system, which is represented by means of the operator

$$U_1 = \exp[i(\omega_0 I_z + \omega_0 S_z)t],$$

the evolution of the spin system in the absence of an rf field is described by the Hamiltonian

$$\mathcal{H}_R = \mathcal{H}'_{d_I} + \mathcal{H}'_{d_{IS}} + \mathcal{H}'_{d_S}. \quad (5)$$

Consequently, the operator

$$Q = \frac{3}{4} Q_I \sin \theta \cos \theta + Q_{IS} \sin \theta$$

in the density matrix (4) is described by

$$Q(t) = D_1^{-1} Q D_1, \quad D_1 = \exp[i(\mathcal{H}'_{d_I} + \mathcal{H}'_{d_{IS}} + \mathcal{H}'_{d_S})t]. \quad (6)$$

It follows from Ref. 11 that the  $\theta$  pulse induces a signal due to  $Q(t)$ :

$$\langle I_y \rangle = -\beta \text{Tr} \{ I_y Q(t) \}. \quad (7)$$

The application of a  $180^\circ_y$  pulse alters the sign of the operator  $\mathcal{H}'_{d_{IS}}$  in the arguments of the exponential functions in Eq. (6) and, consequently, in Eq. (7), as well as the sign of the operator  $Q_{IS}$  in the expression for  $Q(t)$ . Consequently, after the  $180^\circ_y$  pulse in the sequence 1, we obtain

$$\begin{aligned} Q(t' + t'') &= D_1^{-1}(t'') D_2^{-1}(t') Q D_2(t') D_1(t''), \\ D_2(t') &= \exp[i(\mathcal{H}'_{d_I} - \mathcal{H}'_{d_{IS}} + \mathcal{H}'_{d_S})t'], \\ Q_I &= \frac{3}{4} Q_I \sin \theta \cos \theta - Q_{IS} \sin \theta. \end{aligned} \quad (8)$$

It is clear from the system (8) that the application of the  $180^\circ$  pulse to a heteronuclear system can influence considerably the rate of disappearance of the dipole signal by reducing the contribution of the cross stem  $\mathcal{H}'_{d_{IS}}$  to this disappearance (similarly, a series of  $180^\circ$  pulses results in heteronuclear decoupling in observations of a free induction signal under high-resolution NMR conditions<sup>12</sup>).

In our experiments we applied a resonance rf field of

amplitude  $H_1 = \omega_1 \gamma^{-1} = 18.7 \text{ G}$  for a time  $t_1$ ; this was done for all the sequences employed in the present study. In an inclined two-frequency rotating system with the transformation parameter

$$U_2 = \exp(i/2 t \pi I_y) \exp[i(\omega_0 I_z + \omega_0 S_z)t]$$

the Hamiltonian in the presence of a field in resonance with the  $I$  spins becomes

$$\mathcal{H}_{TR} = \omega_1 I_z - \frac{1}{2} \mathcal{H}'_{d_I} + \frac{3}{8} P_I - Q_{IS} + \mathcal{H}'_{d_S}. \quad (9)$$

If this inclined coordinate system is adopted when the rf field is applied and a rotating two-frequency system is used in the absence of the rf field, then the evolution of the operator  $Q$  after the pulse sequence 1 (Fig. 1) can be described by the expression

$$\begin{aligned} Q(t' + t'' + t_1 + t) &= A_1^{-1} Q_1 A_1, \\ A_1 &= D_2(t') D_1(t'') C(t_1) D_1(t), \quad C(t_1) = \exp(i \mathcal{H}_{TR} t_1). \end{aligned} \quad (10)$$

In writing down Eq. (10) we allowed for the fact that the transformations corresponding to a  $90^\circ$  pulse and to the transition from a two-frequency rotating coordinate system to an inclined two-frequency rotating system balance one another. It should be stressed that a change in the sign of the operators  $\mathcal{H}'_{d_I}$  and  $\mathcal{H}'_{d_{IS}}$  in  $A_1$  occurs for reasons which are fundamentally different from the physical point of view.

Applying the Feynman formula,<sup>13</sup> we shall rewrite  $A_1$  in the form

$$A_1 = B(t') \exp[i \mathcal{H}'_{d_{IS}}(t'' - t')] B(t'') C(t_1) \exp(i \mathcal{H}'_{d_{IS}} t_1) B(t), \quad (11)$$

$$B(t)$$

$$= T \exp \left[ i \int_0^t \exp(-i \mathcal{H}'_{d_{IS}} \tau) (\mathcal{H}'_{d_I} + \mathcal{H}'_{d_S}) \exp(i \mathcal{H}'_{d_{IS}} \tau) d\tau \right], \quad (12)$$

$$\begin{aligned} C(t_1) &= T \exp \left\{ i \left[ -\frac{1}{2} \mathcal{H}'_{d_I} t_1 + \mathcal{H}'_{d_S} t_1 \right. \right. \\ &\quad \left. \left. + \int_0^{t_1} \left[ \frac{3}{8} \mathcal{H}'_{d_I} \exp(i 2 \omega_I \tau) + \frac{3}{8} \mathcal{H}'_{d_I} \right] \right. \right. \\ &\quad \left. \left. \times \exp(-i 2 \omega_I \tau) - \frac{1}{2} Q_{IS}^+ \exp(i \omega_I \tau) \right. \right. \\ &\quad \left. \left. - \frac{1}{2} Q_{IS}^- \exp(-i \omega_I \tau) \right] d\tau \right\} \exp(i \omega_I I_z t_1). \end{aligned} \quad (13)$$

The quantity  $T$  in Eqs. (12) and (13) is the Dyson time-ordering operator.

If we follow Ref. 14 and separate in  $C(t_1)$  the main part of the contribution to the dipole apparatus responsible for the slow variation of  $Q_1$  as a function of  $t_1$ , we find from Eq. (13) that

$$\begin{aligned} C'(t_1) &= \exp \left\{ i \left[ -\frac{1}{2} \mathcal{H}'_{d_I} + \mathcal{H}'_{d_S} \right. \right. \\ &\quad \left. \left. + \left( \frac{3}{8} \right)^2 \frac{[\mathcal{H}'_{d_I} \mathcal{H}'_{d_I} \mathcal{H}'_{d_I}]}{2 \omega_I} + \frac{[Q_{IS}^+ Q_{IS}^-]}{4 \omega_I} \right] \right\} \cdot t_1 \exp(i \omega_I I_z t_1). \end{aligned} \quad (14)$$

It is clear from Eqs. (10)–(14) that when the conditions  $t' + t'' - t_1/2 + t = 0$  and  $t'' - t' + t = 0$  are satisfied, a magic echo signal may appear, corresponding to the

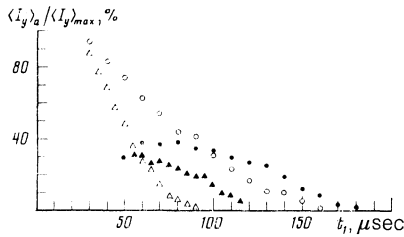


FIG. 2. Dependence on  $t_1$  of the amplitude of the dipole magic echo signal of  ${}^7\text{Li}$  observed on application of the pulse sequence 1 in the [111] orientation ( $\circ$  and  $\bullet$ ) and in the [110] orientation ( $\Delta$  and  $\blacktriangle$ ). The absence of a  $180^\circ$  pulse corresponds to  $\circ$  and  $\Delta$ .

operator  $Q_1(t)$  after a  $\theta$  pulse. If instead of a  $180^\circ_{-y}$  pulse we use a  $180^\circ_{-x}$  pulse, then the sign in front of  $Q_{IS}$  in the expression for  $Q$  is not affected. In this case the echo corresponds to a signal actually observed after a  $\theta$  pulse.

In agreement with Eqs. (10)–(14), application of the pulse sequence 1 in the case when  $\theta = 45^\circ$  produced a dipole magic echo (the relationships  $t' = t'' - t_1/2 = 0$  and  $t' = t''$  were satisfied in our measurements). Figures 2 and 3 show the dependences of the echo amplitude on  $t_1$  in the case when the spins  $I$  are the magnetic moments of the  ${}^7\text{Li}$  and  ${}^{19}\text{F}$  nuclei. Disappearance of the echo signal as  $t_1$  increased occurred both because of partial compensation of the dipole-dipole interaction when the pulse sequence 1 was used and because of gradients of the magnetic fields. The contributions of the operators  $\mathcal{H}'_{d_1}$ ,  $\mathcal{H}'_{d_{IS}}$ , and  $\mathcal{H}'_{d_S}$  to the decay of the observed signals could be characterized most conveniently by the second moments of the NMR lines of the  ${}^7\text{Li}$  and  ${}^{19}\text{F}$  nuclei.<sup>11</sup> The values of the moments  ${}^{\text{F}}M_{2(\text{F-F})}$ ,  ${}^{\text{Li}}M_{2(\text{Li-Li})}$ , and  ${}^{\text{F}}M_{2(\text{F-Li})}$  were determined for various orientations in Ref. 15. One could readily find also the values of  ${}^{\text{Li}}M_{2(\text{F-Li})}$ . Table I gives the calculated moments. It is clear from Fig. 2 that in the  $H_0 \parallel [110]$  orientation characterized by a large moment  ${}^{\text{Li}}M_{2(\text{F-Li})}$  the echo signal was much weaker for the same value of  $t_1$  than in the  $H_0 \parallel [111]$  case.

When the  $180^\circ_{-y}$  pulse was excluded from the pulse sequence 1, we observed a signal from the operator  $Q$  which for small values of  $t_1$  was greater than the signal from  $Q_1$  obtained using the  $180^\circ_{-y}$  pulse. As  $t_1$  increased the contribution of the operator  $Q_{IS} \sin\theta$  to the signal practically disappeared ( $Q_{IS}$  did not commute with  $\mathcal{H}'_{d_S}$  and the sign of  $\mathcal{H}'_{d_S}$  in the pulse sequence 1 remained constant), and the amplitude of the echo obtained using the  $180^\circ_{-y}$  pulse became greater than in the absence of the  $180^\circ_{-y}$  pulse (Figs. 2 and 3) because of the change in the sign of  $\mathcal{H}'_{d_{IS}}$ , in the

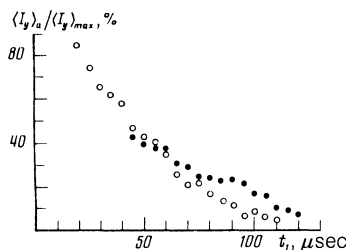


FIG. 3. Dependence on  $t_1$  of the amplitude of the dipole magic echo signal of  ${}^{19}\text{F}$  observed on application of the pulse sequence 1 in the [111] orientation. The absence of a  $180^\circ$  pulse is indicated by  $\circ$ .

TABLE I.

LiF	[100]	[110]	[111]
${}^{\text{Li}}M_{2(\text{Li-Li})}, \text{G}^2$	0.942	1.345	1.479
${}^{\text{F}}M_{2(\text{F-F})}, \text{G}^2$	6.473	9.236	10.16
${}^{\text{Li}}M_{2(\text{F-Li})}, \text{G}^2$	5.191	1.487	0.257
${}^{\text{F}}M_{2(\text{F-Li})}, \text{G}^2$	25.90	7.434	1.278

arguments of the exponential functions. When the  $180^\circ_x$  pulse was used instead of  $180^\circ_{-y}$ , then at low values of  $t_1$  the echo signal increased because the sign of  $Q_{IS}$  changed from negative to positive, and we were unable to study experimentally the disappearance of the contribution made to the signal by the operator  $Q_{IS} \sin\theta$ .

The pulse sequence 2 serves the same purposes as the pulse sequence 1. The evolution of the operator  $Q(\theta = 45^\circ)$  in the density matrix is described as follows when the pulse sequence 2 is applied:

$$Q(t_1 + t' + t) = A_2^{-1} Q A_2, \quad (15)$$

$$A_2 = \exp[i(-\omega_I I_z - 1/2 \mathcal{H}'_{d_1} + \mathcal{H}'_{d_S} - Q_{IS} + 3/8 P_1) t_1] D_2(t') D_1(t) \\ = C(t_1) \exp(-i\omega_I I_z t_1) B(t') \exp[i\mathcal{H}'_{d_{IS}}(t-t')] B(t).$$

The signal observed for  $t' + t - t_1/2 = 0$  and  $t' - t = 0$  after the pulse sequence 2 was a dipole magic echo corresponding to the signal of the operator  $Q$  after a  $45^\circ$  pulse in the absence of the rf field. The amplitude of the dipole magic echo as a function of the duration of application of the field  $t_1$  is shown in Fig. 4 for the case when the spins  $I$  were the magnetic moments of the  ${}^7\text{Li}$  nuclei. Since in the sequence 2 a  $45^\circ$  pulse was used instead of a  $135^\circ$  pulse, the right-hand of Eq. (15) contained  $Q$  and not  $Q_1$ . Consequently, the dipole magic echo signal obtained for small values of  $t_1$  on application of the pulse sequence 2 was much greater than when the pulse sequence 1 was applied in the  $H_0 \parallel [111]$  orientation. For the same reason and also because the number of pulses was smaller, the time for disappearance of the dipole magic echo signal after the pulse sequence 2 was somewhat longer than the time after the pulse sequence 1.

Figure 5 reproduces an oscillogram of the signal obtained after the pulse sequence 2 for  $t_1 = 200 \mu\text{sec}$ . In the case of a homonuclear system if nonsecular terms are ignored in an inclined rotating coordinate system, the evolution of the operator  $Q_1$  in the pulse sequence 2 is described by the expression

$$Q_1(t_1 + t) = A_3^{-1} Q_1 A_3, \quad A_3 = \exp(i\omega_I I_z t_1) \exp[i\mathcal{H}'_{d_1}(t-t_1/2)]. \quad (16)$$

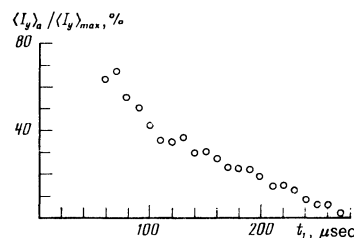


FIG. 4. Dependence of the amplitude of the dipole magic echo signal of  ${}^7\text{Li}$  on  $t_1$ , after the pulse sequence 2 applied in the [111] orientation.

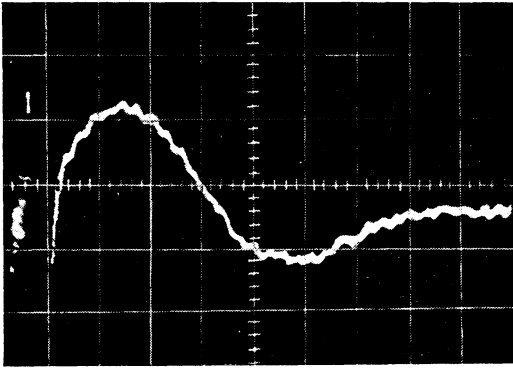


FIG. 5. Oscillogram of the dipole magic echo signal of  ${}^7\text{Li}$  after the pulse sequence 2 applied in the  $[111]$  orientation when  $t_1 = 200 \mu\text{sec}$ . The horizontal scale is  $20 \mu\text{sec}/\text{div}$ .

In contrast to the signal after a  $\theta$  pulse in the absence of the rf field, when the time in the arguments of the exponential functions can only be positive, the value of  $t - t_1/2$  in Eq. (16) changes its sign depending on  $t$ . Consequently, if  $t - t_1/2 < 0$ , the signal observed by amplitude detection should be a mirror image, relative to the point  $t - t_1/2 = 0$ , of the signal for  $t - t_1/2 > 0$  if the nonsecular terms and the inhomogeneities of the fields are ignored. In the heteronuclear case the signal of the dipole magic echo can also be described approximately by expressions of the type given by Eq. (16), which accounts for the nature of the signal shown in Fig. 5 and obtained as a result of lock-in detection.

We observed the signal due to the magic free induction echo by applying the pulse sequence 3 (Fig. 1) to the spin system. In the case of an inclined two-frequency rotating coordinate system the density matrix at the moment of application of an rf field can be described by

$$\sigma = 1 - \beta_1 \omega_1 I_x. \quad (17)$$

Using the same coordinate system during the action of the rf field and going over to a two-frequency rotating coordinate system after a  $90^\circ$  pulse, we find that the evolution of the operator  $I_x$  in Eq. (17) can be described as follows:

$$I_x(t_1 + t' + t) = A_2^{-1} I_x A_2. \quad (18)$$

Figure 6 shows the  $t_1$  dependences of the amplitude of the magic free induction signal observed for  $t' + t - t_1/2 = 0$  and  $t' - t = 0$  in accordance with Eq. (18), plotted for the case when the role of the spins  $I$  is played by the magnetic

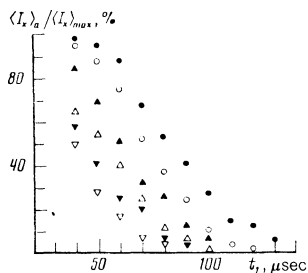


FIG. 6. Dependence, on  $t_1$ , of the amplitude of the magic echo of the free induction signal of the  ${}^{19}\text{F}$  nuclei after the pulse sequence 3 applied in the  $[111]$  ( $\circ$  and  $\bullet$ ),  $[110]$  ( $\Delta$  and  $\blacktriangle$ ), and  $[100]$  ( $\nabla$  and  $\blacktriangledown$ ) orientations. The absence of a  $180^\circ$  pulse is indicated by  $\circ$ ,  $\Delta$ , and  $\nabla$ .

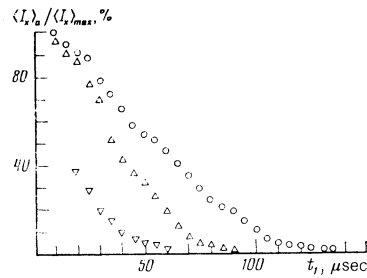


FIG. 7. Dependence, on  $t_1$ , of the amplitude of the magic echo of the free induction signal of the  ${}^7\text{Li}$  nuclei when a  $180^\circ$  pulse was excluded from the pulse sequence 3 in the  $[111]$  ( $\circ$ ),  $[110]$  ( $\Delta$ ), and  $[100]$  ( $\nabla$ ) orientations.

moments of the  ${}^{19}\text{F}$  nuclei. For comparison, Fig. 6 includes also the  $t_1$  dependences of the magic echo amplitude observed when a  $180^\circ_{-y}$  pulse is excluded from the sequence 3. The results of measurements of the magic free induction echo signal of  ${}^7\text{Li}$  (in the absence of a  $180^\circ$  pulse) are shown in Fig. 7. It is clear from Figs. 7, 2, and 4 that in the case of the experiments on the  ${}^7\text{Li}$  nuclei the free evolution time of the system ( $t_1/2$ ), corresponding to the decay of the echo by the factor  $e$ , is slightly longer than  $T_2$  for the corresponding orientations. However, in this case again the proposed pulse sequences (even in the absence of a  $180^\circ$  pulse) make it possible to record the echo signals after such free evolution time that the free induction or dipole signals themselves are no longer observable. This circumstance allows us to speak of the observation of the magic echo for the  ${}^7\text{Li}$  nuclei, although under experimental conditions these nuclei produce effects much weaker than the  ${}^{19}\text{F}$  nuclei.

The magic echo decays more strongly in the  $H_0 \parallel [100]$  orientation, when the value of  $M_{2(\text{F-Li})}$  is largest (Table I). In our opinion, in this case the main contribution to the decay of the signal comes from the operator  $Q_{IS}$  in  $A_2$ . An increase in the rf field intensity can reduce the contribution of the nonsecular operators to the decay of the signals of the dipole magic echo and of the magic echo of free induction. Unfortunately, we are at present unable to increase the value of  $H_1$ .

More effective compensation of the contribution of the operator  $\mathcal{H}$  to decay of the echo signals can be achieved by a series of  $180^\circ$  pulses with respect to the spins  $I$  and  $S$ , instead of one  $180^\circ$  pulse, and the  $180^\circ$  pulses for the spins  $S$  should be applied throughout the evolution time of the system. For an alternating field intensity of  $H_1 = \omega_1 \gamma^{-1} = 18.7 \text{ G}$  the nonsecular operators in  $\mathcal{H}_{TR}$  result in a fairly rapid disappearance of the echo signals. Consequently, when a series of  $180^\circ$  pulses is used, the intervals between the pulses become comparable with the pulse durations. For this reason we used only one  $180^\circ$  pulse in the observation of the magic echo in LiF.

The operators responsible for the echo signals reported in Refs. 2, 3, 5, and 6 do not correspond to analogous operators in the Hamiltonian of the system. In other words, these operators do not correspond to energy. In the heteronuclear case we observed echo signals due to operators which were also absent from the Hamiltonian. These operators can be attributed nominally to systems that do not have energy and are consequently not thermodynamic. The reversibility of the time evolution of such systems clearly does not contra-

dict the laws of thermodynamics. We can describe our measurements without invoking the hypothesis of chaos. This means that the random phase approximation is unsuitable for the description of the evolution of the off-diagonal terms in the density matrix of heteronuclear systems, exactly as in the homonuclear case. As pointed out in Ref. 4, we cannot exclude the possibility that limitations imposed by the random phase approximation are associated in a natural manner with the general concept of temperature and they apply to more trivial thermodynamic systems. It would therefore be extremely interesting to observe analogs of the magic echo in systems of nonspin nature. In particular, one should consider the question of the photon magic echo. Such an expansion of the range of investigations of reversibility and irreversibility relationships in the evolution of macroscopic systems can provide new interesting data for the solution of important problems in statistical physics.

The practical value of the dipole magic echo and the magic echo of a free induction signal in heteronuclear systems is due to the fact that, as in the homonuclear case, the profile and amplitude of the echo signals carry extensive information on the interactions in the spin system.

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