

transition.

We shall conclude by estimating the intensity of sound at which these phenomena can be expected. If  $\omega = 10^{10}$  sec $^{-1}$  and  $\tau_{ph} = 10^{-9}$  sec, we find that

$$w = \left( \frac{e_0 \tau_{ph}}{\hbar} \right) \frac{6}{\pi^2 Z} \frac{m_e M_{at} \omega s}{\hbar \tau_{ph}} \sim \left( \frac{e_0 \tau_{ph}}{\hbar} \right) \frac{6A}{\pi^2 Z} \text{ erg/cm}^2.$$

Here,  $A$  is the atomic weight. The appearance of the Planck constant in the above expressions is due to the selection of the units employed in the present paper.

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Translated by A. Tybulewicz

## Relaxation of nuclear magnetization under many-pulse NMR experimental conditions

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(Submitted 9 June 1978)

Zh. Eksp. Teor. Fiz. 75, 1837–1846 (November 1978)

An investigation was made of the behavior of nuclear magnetization subjected to a pulse sequence  $90^\circ - \tau - (\varphi_x - 2\tau)^N$  under off-resonance conditions. Establishment of quasiequilibrium regimes in the spin system was investigated. The effects of many-spin resonance absorption of the energy of an external agency were detected. The concept of an effective field  $\omega_e$ , of magnitude and direction governed by the parameters of the exciting pulses and detuning  $\Delta$ , was introduced. The measured resonance values of  $\varphi_x$  and  $\Delta\tau$  were in good agreement with those calculated in the effective field framework. The experimental results were compared with the conclusions of a thermodynamic theory of narrowing of NMR lines of a solid, given in the following paper in the present issue.

PACS numbers: 76.60.Es

Investigations of NMR in a rotating coordinate system in the presence of a continuously acting pulsed hf magnetic field are used widely to study solids. Experiments of this kind have frequently improved the sensitivity of the NMR method<sup>1</sup> and have given information on relatively slow molecular motion in matter,<sup>2</sup> as well as NMR spectra of solids with much enhanced resolution.<sup>3,4</sup>

A pulse variant of such experiments, called the spin-locking method, has been proposed recently.<sup>5</sup> This method is of great practical importance because it can be used to measure the spin-lattice relaxation time  $T_1$ , in a rotating coordinate system much faster and more conveniently than by the traditional method with a continuously acting hf field.<sup>2,6</sup> Moreover, pulse spin locking is the simplest many-pulse experiment which can be used as a satisfactory model in theoretical analyses of the behavior of nuclear magnetization under the action of pulse sequences. It is pointed out in Refs. 7 and 8 that some of the phenomena observed under pulse spin-locking conditions cannot be explained by the theory of the

average Hamiltonian<sup>9</sup> usually employed in dealing with such experiments. A different approach has been developed<sup>8</sup> for the spin dynamics of many-pulse NMR experiments: it is based on the determination of quasiequilibrium states of the spin system and allowance for many-spin processes of the absorption of energy of an external agency. This approach gives a satisfactory agreement with the results of experimental investigations<sup>5,7</sup> employing pulse spin locking in the specific case when the exact resonance conditions are satisfied. In the present paper, which is a continuation of Ref. 7, we shall consider the processes of establishing quasiequilibrium states and relaxation of a spin system with the dipole coupling in the case of pulse spin locking in the more general off-resonance case.

### 1. EXPERIMENTAL METHOD

Our measurements were carried out using a many-pulse NMR spectrometer<sup>10</sup> tuned to the resonance fre-

quency of the  $^{19}\text{F}$  nuclei, which was 57.0 MHz. A study was made of the behavior of the component  $M_x$  of the nuclear magnetization in a rotating coordinate system under the action of a pulse sequence of the  $90^\circ - \tau - (\varphi_x - 2\tau)^N$  type ( $\varphi_x$  denotes that an rf pulse rotates the magnetization about the  $x$  axis of the coordinate system by an angle  $\varphi$ ). A polarizing field  $H_0$  was shifted from the resonance value by an amount corresponding to the frequency detuning  $\Delta$ . A single-crystal  $\text{CaF}_2$  sample with transverse dimensions of the order of 6 mm was used. All the measurements were carried out when this sample was oriented close to the  $H_0 \parallel [111]$  direction (to within  $\sim 5^\circ$ ) at room temperature. Under these conditions the spin-lattice relaxation time was about 5 sec. The pulsed rotating magnetic field applied was  $H_1 \approx 35$  Oe. The resonance value of  $H_0$  was taken to be the field corresponding to vanishing at times  $\gg T_2$  ( $T_2 \approx 35 \mu\text{sec}$ ) of the  $M_x$  component of the nuclear magnetization of the sample during the  $(\varphi_x - 2\tau)^N$  pulse sequence.<sup>11</sup> The inhomogeneity of the field  $H_0$  in the interior of the sample corresponded to a line width of  $\sim 50$  Hz and the inhomogeneity of the field  $H_1$  was  $\sim 2\%$ .

## 2. EXPERIMENTAL RESULTS

In general, the decay of magnetization can generally be divided into three regions of variation of  $M_x$ , labeled as I, II, and III in Fig. 1b. Region I represents a short transient process lasting a period several times greater than the time  $T_2$ ; in regions II and III the signal may be represented by a sum of two exponential functions with very different time constants. For certain values of  $\varphi_x$  and  $\Delta\tau$  we can expect either regions I and II (Fig. 1a) or I and III (Fig. 1c) to be observed. In the cases shown in Fig. 1 the signal is recorded at the end of each interval between two pulses.

Under quasisteady conditions the variation of the magnetization in the interval between pulses at times corresponding to regions II and III is bell-shaped for the detuning corresponding to  $|\Delta\tau| < 2\pi$  and the relative

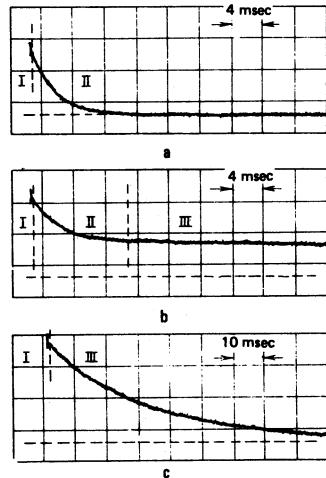


FIG. 1. Decay oscillosograms of the nuclear magnetization  $M_x$  obtained for various values of  $\varphi_x$  and  $\Delta\tau$  ( $\tau=6.6 \mu\text{sec}$ ): a)  $\varphi_x = 72^\circ$ ,  $\Delta\tau = 0.91 \text{ rad}$ ; b)  $\varphi_x = 72^\circ$ ,  $\Delta\tau = 0.84 \text{ rad}$ ; c)  $\varphi_x = 72^\circ$ ,  $\Delta\tau = 1.09 \text{ rad}$ . The horizontal dashed lines represent zero value.

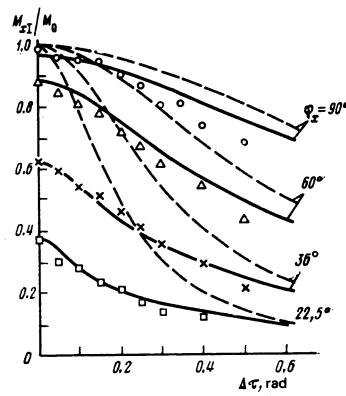


FIG. 2. Dependences of  $M_{x1}/M_0$  on  $\Delta\tau$  (for  $\tau=10 \mu\text{sec}$ ): ○)  $\varphi_x = 90^\circ$ ; △)  $\varphi_x = 60^\circ$ ; ×)  $\varphi_x = 36^\circ$ ; □)  $\varphi_x = 22.5^\circ$ . The dashed lines correspond to Eq. (9) and the continuous one to Eq. (10) with the values of  $\varphi_x$  given alongside each curve.

height of the "bell" increases on increase of  $|\Delta\tau|$ . For greater detuning this variation of the magnetization is close to a segment of a sinusoid containing more than one period. In all cases, the value of  $M_x$  varies with the period  $2\tau$  and its maximum lies in the middle of the interval between the pulses.

The first quasisteady value, i.e., the value assumed by  $M_x$  at the end of region I and denoted by  $M_{x1}$ , decreases on reduction of the detuning to a value corresponding to  $|\Delta\tau| = \pi/2$ . Figure 2 shows the experimental values of the ratio  $M_{x1}/M_0$  measured for different values of  $\Delta\tau$ ;  $M_0$  is the value of  $M_x$  immediately after the first  $90^\circ$  pulse. The true value of  $M_0$  can be found by extrapolation of the observed signal to the pulse bearing in mind the known form of the decay curve of the free induction in  $\text{CaF}_2$  (Ref. 12). In the determination of  $M_{x1}$  the magnetization is measured at midpoints of the intervals between the pulses. It should be noted that for  $|\Delta\tau| = \pi/2$  the magnetization at the end of region I vanishes irrespective of the value of  $\varphi_x$  and this is true also for  $\varphi_x = 180^\circ$  irrespective of  $\Delta\tau$ .

In Regions II–III in the range  $45^\circ \leq \varphi_x \leq 90^\circ$  it is found that variation of the detuning causes the total magnetization decay time to vary nonmonotonically. For some values of  $\Delta\tau$ , equal to  $(\Delta\tau)_r$ , a strong reduction in the decay time of  $M_x$  to zero is observed when  $\varphi_x$  is fixed (Fig. 1a). These effects are also observed in the range  $90^\circ \leq \varphi_x \leq 135^\circ$  except that now  $M_{xII}$  (second quasisteady

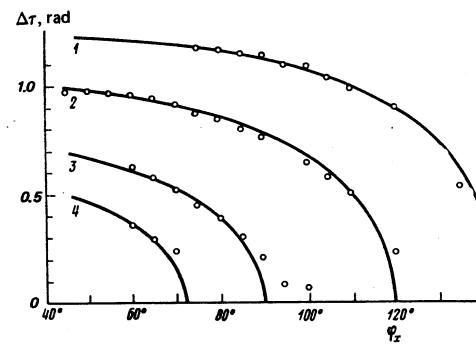


FIG. 3. Dependences of the resonance values  $\Delta\tau = (\Delta\tau)_r$  on  $\varphi_x$  for  $\tau=8.9 \mu\text{sec}$ . The continuous curves represent calculations based on: 1) Eq. (16); 2) Eq. (13); 3) Eq. (14); 4) Eq. (15).

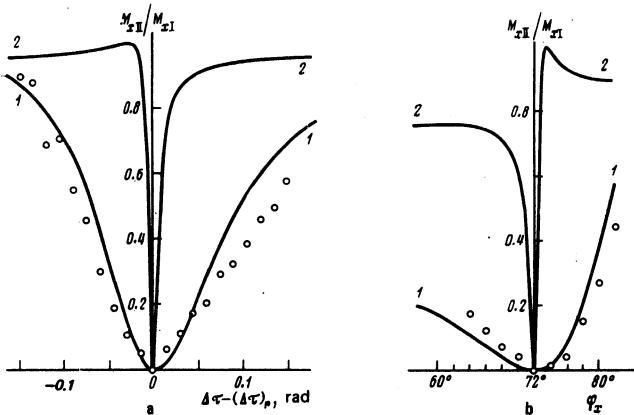


FIG. 4. Changes in  $M_{xII}/M_{xI}$  on deviation from the three-spin resonance conditions: a) deviation governed by the detuning; b) deviation governed by the change in  $\varphi_x$ . The continuous curves are based on Eq. (17): 1) for the resonance value  $\varphi_x = 72^\circ$ ; 2) for the resonance value  $\varphi_x = 90^\circ$ .

value which  $M_x$  reaches at the end of region II does not vanish but reaches its minimum value at the point  $\Delta\tau = (\Delta\tau)_r$ . These effects are not observed in the ranges  $\varphi_x \leq 45^\circ$  and  $\varphi_x \geq 135^\circ$ . The circles in Fig. 3 are the experimental values of  $(\Delta\tau)_r$ , determined for various  $\varphi_x$ . It is clear from Fig. 3 that these values of  $(\Delta\tau)_r$  are distributed in groups (denoted by 1–4 in Fig. 3) and each of them has its own dependence on  $\varphi_x$ . It should be noted that the value of  $(\Delta\tau)_r$  is independent of the orientation of a crystal.

In the case of small deviations of  $(\Delta\tau)_r$ , which can be introduced by altering  $\Delta$  or  $\varphi_x$ , the decay of  $M_x$  in regions II and III can be described by a sum of two exponential functions (Fig. 1b). Figure 4 gives the experimental values of the ratio of two quasisteady magnetizations  $M_{xII}/M_{xI}$  in the vicinity of a point taken from group 2 (in Fig. 3) and characterized by the coordinates  $\varphi_x = 72^\circ$  and  $\Delta\tau = 0.91$  rad. In case a (Fig. 4) the detuning is varied, whereas in case b, the angle  $\varphi_x$  is varied.

In region I of the magnetization decay the variation of  $M_x$  is in the form of damped oscillations falling to  $M_{xI}$  (Fig. 5) and the period of these oscillations depends both on  $\Delta\tau$  and  $\varphi_x$ . For the values of  $\Delta\tau$  and  $\varphi_x$  corresponding to the points in Fig. 3 it is found that the ratio of the oscillation period to the duration of the interval between the pulses is close to the ratio of two integers. For group 1 this ratio is 5:2, for group 2 it is 3:1, for group 3 it is 4:1, and for group 4 it is 5:1. By way of example, Fig. 5 shows an oscillogram of the decay of  $M_x$  in region I for values of  $\Delta\tau$  and  $\varphi_x$  corresponding to a point from group 2 (Fig. 3). It is clear from Fig. 5 that one oscil-

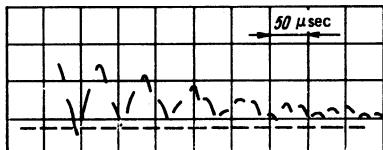


FIG. 5. Oscillogram of the initial decay of  $M_x$  in a three-spin resonance process. The discontinuities of the signal correspond to the positions of the exciting pulses.

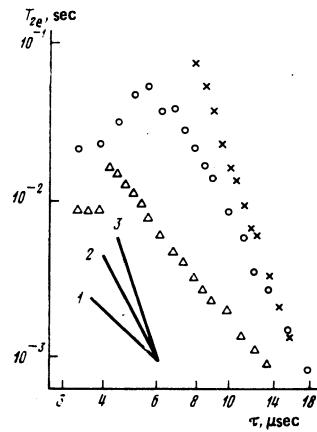


FIG. 6. Dependences of  $T_{2e}$  on  $\tau$  under resonance conditions:  $\triangle$ )  $R_3$ ;  $\circ$ )  $R_4$ ;  $\times$ )  $R_{5/2}$ . The continuous curves correspond to the dependence  $T_{2e} \propto \tau^{-k}$ : 1)  $k = 2$ ; 2)  $k = 4$ ; 3)  $k = 6$ .

lation period corresponds to three intervals between the pulses. For brevity, we shall denote the groups of points in Fig. 3 by  $R_{5/2}$ ,  $R_3$ ,  $R_4$ , and  $R_5$ .

Measurements of the decay time constant  $T_{2e}$  in region II as a function of  $\tau$  indicated that, in a certain range of values of  $\tau$ , the groups of points  $R_{5/2}$ ,  $R_3$ , and  $R_4$  obey  $T_{2e} \propto \tau^{-k}$  with different values of  $k$  for each group. Experimental values of  $T_{2e}$  are given in Fig. 6. The values of  $T_{2e}$  and  $\tau$  are plotted on logarithmic scales. The exponents are  $k \approx 6$  for  $R_{5/2}$ ,  $k \approx 4$  for  $R_4$ , and  $k \approx 2.5$  for  $R_3$ . The deviations from these dependences occur for  $R_3$  at  $\tau \leq 4.5 \mu\text{sec}$  and for  $R_4$  at  $\tau \leq 7.5 \mu\text{sec}$ . We checked whether this was associated with the finite pulse duration in a control experiment in which the field  $H_1$  in a pulse was increased to 60 Oe (and the pulse duration was reduced correspondingly) to satisfy the conditions  $R_4$ . No significant changes in the observed dependence of  $T_{2e}$  on  $\tau$  were observed. We were unable to determine the time constant  $T_{2e}$  for  $R_5$  because the decay of  $M_x$  was not purely exponential but was similar to that shown in Fig. 1b.

Determination of the dependence of  $T_{2e}$  on  $\varphi_x$  ( $\varphi_x < \pi/2$ ) revealed that, as in the on-resonance case,<sup>5,7</sup> there was an increase in the decay time of  $M_x$  on reduction of  $\varphi_x$ . Figure 7 shows the experimental values of  $T_{2e}$  corresponding to the condition  $R_3$ .

### 3. DISCUSSION OF EXPERIMENTAL RESULTS

Our own experimental data and also those obtained in on-resonance spin locking<sup>5,7</sup> show that after a time long-

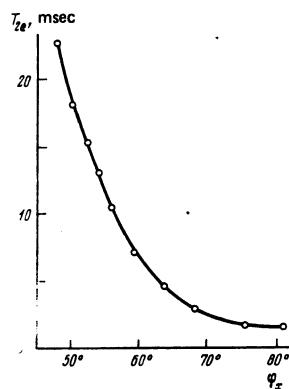


FIG. 7. Dependence of  $T_{2e}$  on  $\varphi_x$  for a three-spin resonance process ( $\tau = 6.6 \mu\text{sec}$ ).

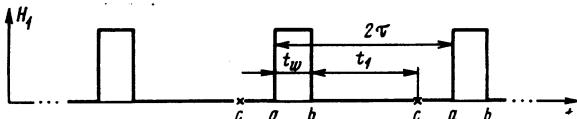


FIG. 8. Schematic representation of a part of a pulse sequence used in the present study. The crosses are the points at which the signal is observed.

er than the spin-lattice relaxation time  $T_2$  the magnetization of a solid may have a different direction than the field  $H_0$ . This is evidence of a difference between the populations of the energy levels of spins in some effective field which has a different direction from that of  $H_0$ . Clearly, the magnitude and direction of the effective field are governed by the effects of a pulse sequence and of detuning on the spin system. We shall introduce an effective field  $\omega_e$  defined as follows. In a time  $2\tau$  between two observation points the effective field rotates the magnetization (in a rotating coordinate system) in the same way as the pulse and detuning fields acting during the same period. We shall allow simultaneously for the finite duration of the pulses ( $t_w$ ) and we shall do this by representing rotation during a pulse by rotation about the direction of the combined pulse and detuning field. Figure 8 shows schematically a fragment of the adopted pulse sequence. In the time interval  $ca$  the detuning field rotates the magnetization vector  $M$  through an angle  $\varphi_1 = \Delta(2\tau - t_1 - t_w)$  about the  $z$  axis of the rotating coordinate system. The corresponding rotational transformation will be denoted by  $A_1$ . In the time interval  $ab$ , equal to the pulse duration  $t_w$ , the rotation is through an angle  $\varphi_2 = [\varphi_x^2 + (\Delta t_w)^2]^{1/2}$  about the axis lying in the  $xy$  plane of the coordinate system making an angle with the  $x$  axis such that the cosine of this angle is  $C_x = \varphi_x / \varphi_2$ . This rotation will be described by the transformation  $A_2$ . Finally, in the time interval  $bc$ , equal to  $t_1$ , the magnetization is rotated through an angle  $\varphi_3 = \Delta t_1$  about the  $z$  axis. The corresponding transformation is denoted by  $A_3$ . The product of these transformations  $A_e = A_3 A_2 A_1$  describes the rotation of  $M$  about the direction of the field  $\omega_e$  in a time  $2\tau$  through an angle  $2\omega_e\tau$ . The effective field  $\omega_e$  and the direction cosines in the rotating coordinate system are given by

$$\cos 2\omega_e\tau = \frac{1}{2} [ (2 \cos \varphi_2 - C_x^2 \cos \varphi_2 + C_x^2) \times \cos(\varphi_1 + \varphi_3) - 2C_x \sin \varphi_2 \sin(\varphi_1 + \varphi_3) + C_x^2 (\cos \varphi_2 - 1) ], \quad (1)$$

$$n_x = \frac{C_x \sin \varphi_2 (\cos \varphi_1 + \cos \varphi_3) - C_x C_x (1 - \cos \varphi_2) (\sin \varphi_1 + \sin \varphi_3)}{2 \sin 2\omega_e\tau}, \quad (2)$$

$$n_y = \frac{C_x \sin \varphi_2 (\sin \varphi_1 - \sin \varphi_3) + C_x C_x (1 - \cos \varphi_2) (\cos \varphi_1 - \cos \varphi_3)}{2 \sin 2\omega_e\tau}, \quad (3)$$

$$n_z = \frac{(2 \cos \varphi_2 - C_x^2 \cos \varphi_1 + 1) \sin(\varphi_1 + \varphi_3) + 2C_x \cos(\varphi_1 + \varphi_3)}{2 \sin 2\omega_e\tau}. \quad (4)$$

Here,  $C_x = \Delta t_w / \varphi_2$ . An analysis of Eqs. (1)–(4) shows that for  $t_w / 2\tau \approx 0.05, \dots, 0.15$  and  $\Delta\tau \leq 1$  in our experiments, the deviations of  $\omega_e$ ,  $n_x$ ,  $n_y$ , and  $n_z$  from the values corresponding to the ideal case of infinitesimally short pulses does not exceed 1–2%. Hence, we can ignore the finite pulse duration in the determination of  $\omega_e$ . The formulas (1)–(4) then simplify to

$$\cos 2\omega_e\tau = (\cos \varphi_2 + 1) \cos^2 \Delta\tau - 1, \quad (5)$$

$$n_x = [\sin \varphi_2 \cos \Delta\tau \cos \Delta(t_1 - \tau)] / \sin 2\omega_e\tau, \quad (6)$$

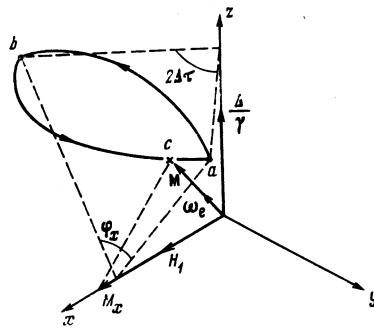


FIG. 9. Motion of the nuclear magnetization vector  $M$  under steady-state conditions. The cross is the point of observation of the signal.

$$n_x = [\sin \varphi_2 \cos \Delta\tau \sin \Delta(t_1 - \tau)] / \sin 2\omega_e\tau, \quad (7)$$

$$n_z = \sin 2\Delta\tau \cos(\varphi_2/2) / \sin 2\omega_e\tau. \quad (8)$$

Expressions similar to Eqs. (5)–(8) are obtained also in Ref. 13.

The motion of the magnetization observed at one point in the interval between the pulses can be regarded as the precession in an effective field of frequency  $\omega_e$ . In region I (Fig. 1) the magnetization component perpendicular to  $\omega_e$  disappears. Next, in the regions II and III the component of the magnetization parallel to  $\omega_e$  is damped out. Figure 9 illustrates the nature of the motion of the vector  $M$  in the quasisteady conditions corresponding to regions II and III. It follows from the quasisteady condition that in the interval between the pulses the rotation of the magnetization about the  $z$  axis of the selected system due to the detuning ( $bca$  in Fig. 9) is compensated completely by the rotation about the  $x$  axis of the same system due to the action of a pulse (arc  $ab$ ). The closed curve  $abca$  is the hodograph of the magnetization vector  $M$ . In this simplified approach, we obtain

$$M_{x1}/M_0 = n_x^2. \quad (9)$$

The curves corresponding to Eq. (9), shown dashed in Fig. 2, do not agree with the experimental results. This is because we have ignored establishment of a general spin temperature of the dipole and Zeeman (in the field  $\omega_e$ ) energy reservoirs. This effect has been considered earlier in the on-resonance case.<sup>8</sup> This factor is allowed for in Ref. 13 and the following expression is observed for the point of observation located in the middle of the interval between the pulses:

$$M_{x1}/M_0 = n_x^2 / [1 + A(\omega_{loc}/\omega_e)^2]. \quad (10)$$

Here,

$$A = \frac{(3n_z^2 - 1)^2}{4} + 6n_z^2(1 - n_z^2) \frac{\sin^2(\theta/2)}{(\theta/2)^2} + \frac{3}{4}(1 - n_z^2)^2 \frac{\sin^2 \theta}{\theta^2},$$

where  $\omega_{loc}/\gamma$  is the local field at a nucleus;  $\theta = 2\omega_e\tau$ ;  $\gamma$  is the gyromagnetic ratio.

The continuous curves in Fig. 2 correspond to Eq. (10) for  $\omega_{loc}/\gamma = 1.0$  Oe. This value is selected to give the best agreement between Eq. (10) and the experimental data. The deviation from the theoretical value  $\omega_{loc}/\gamma = 0.87$  Oe in the case of  $\text{CaF}_2$  with the  $H_0 \parallel [111]$  orientation<sup>14</sup> can be explained by inaccurate orientation of the

crystal. The discrepancies between the experimental points and the theoretical curve corresponding to  $\varphi_x = 90^\circ$  (Fig. 2) can be explained by the too fast decay of the component of the magnetization parallel to  $\omega_e$  in region I for  $\varphi_x \approx 90^\circ$ , which results in an additional reduction in  $M_{xII}$  at the moment of observation.

The frequency of oscillations of  $M_x$  in region I is governed directly by the effective field  $\omega_e$ . The fact that the oscillation period and the interval between the pulses  $\Delta\tau = (\Delta\tau)_0$  are related by simple expressions (Sec. 2) means that both  $\omega_e$  and the frequency of the external agency are related by similar expressions, namely:

$$m\omega_e = n\pi/\tau, \quad (11)$$

where we can have  $m=3, 4$ , and  $5$  for  $n=1$  and for  $m=5, n=2$ . Since the effect involves acceleration of the magnetization decay, we may assume that resonance absorption of the energy of the external agency by the spin system occurs at  $\Delta\tau = (\Delta\tau)_0$ , and this is accompanied by the acceleration of equalization of the populations of the Zeeman levels in the field  $\omega_e$ . Since  $n < m$ , it follows that  $\omega_e < \pi/\tau$  and, consequently, the resonance absorption can occur only in a system of several spins coupled by the dipole-dipole interaction. Thus, the values of  $m$  and  $n$  indicate that the first harmonic of the external agency excites transitions in a system of three, four, or five spins, whereas the second harmonic excites them in a system of five spins. Equation (5) readily yields an expression relating  $\Delta\tau$  and  $\varphi_x$  if the resonance condition (11) is satisfied:

$$\cos^2 \Delta\tau (\cos \varphi_x + 1) - 1 = \cos(2n\pi/m). \quad (12)$$

For  $m=3$  and  $n=1$ , Eq. (12) becomes

$$2 \cos^2 \Delta\tau (\cos \varphi_x + 1) = 1; \quad (13)$$

for  $m=4$  and  $n=1$ ,

$$\cos^2 \Delta\tau (\cos \varphi_x + 1) = 1; \quad (14)$$

for  $m=5$  and  $n=1$ ,

$$4 \cos^2 \Delta\tau (\cos \varphi_x + 1) = \sqrt{5} + 3; \quad (15)$$

for  $m=5$  and  $n=2$ ,

$$4 \cos^2 \Delta\tau (\cos \varphi_x + 1) = 3 - \sqrt{5}. \quad (16)$$

Curve 1 in Fig. 3 corresponds to Eq. (16), curve 2 to Eq. (13), curve 3 to Eq. (14), and curve 4 to Eq. (15). The good agreement with the experimental values confirms the correctness of Eqs. (5) and (11) and, consequently, the selection of the effective field and resonance conditions. The discrepancy between the experimental data and theoretical curves at low values of  $\Delta\tau$  can be attributed to the inhomogeneity of the field  $H_1$ . It is interesting to note that Eqs. (13)-(16) can also be obtained for other values of  $m$  and  $n$ . For example, for  $m=3$  and  $n=2$  the equation relating the resonance values of  $\varphi_x$  and  $\Delta\tau$  is identical with Eq. (13) and for  $m=5$  and  $n=3$  it is identical with Eq. (16). However, the observed frequencies of oscillations in region I support the values of  $m$  and  $n$  selected above.

The behavior of the spin system near resonance points is considered in Ref. 13. The saturation theory<sup>15</sup> is used

to obtain an expression representing steady states in the case of small deviations from resonance:

$$M_{xII}/M_{xI} = [1 + A_0^2 (\omega_{loc}/\delta\omega_e)^2]^{-1}. \quad (17)$$

Here,  $A_0 = (3n_e^2 - 1)/2$  and  $\delta\omega_e$  is the deviation of  $\omega_e$  from the resonance value. The continuous curves in Fig. 4 correspond to Eq. (17) with  $c \omega_{loc}/\gamma = 0.87$  Oe. The experimental points are obtained on deviation from conditions for a three-spin resonance process. The nature of changes in the experimental values is generally in agreement with the theoretical predictions, although there are discrepancies which are attributed in Ref. 13 to the influence of other resonances and to the nonideal nature of the pulses. The shape of curve 2 in Fig. 4b explains why  $M_{xII} \neq 0$  at the resonance points corresponding to  $\varphi_x \approx 90^\circ$ . Undoubtedly, this is explained by inhomogeneity of the field  $H_1$  in a pulse, i.e., by the inability to establish the same value of  $\varphi_x$  throughout the volume of a sample.

As in the on-resonance case,<sup>5,7</sup> it is found that in the presence of detuning the magnetization decay time increases steeply on reduction in  $\varphi_x$  ( $\varphi_x \leq 90^\circ$ ). Figure 7 illustrates this feature in the case of a three-spin resonance process. It should be noted that this is generally in conflict with the theory of the average Hamiltonian, according to which the reduction in  $\varphi_x$  increases the duration of a cycle<sup>9</sup> and this accelerates the decay.

#### 4. CONCLUSIONS

Our experiments give information on the behavior of a spin system under spin-locking conditions and they show that many-spin resonances make a very important contribution to the relaxation. Clearly, in developing a theory explaining the behavior of magnetization for an arbitrary detuning and arbitrary angles of rotation of the pulses we have to allow for the influence of all or at least the nearest possible many-spin resonances.

The authors are grateful to B. N. Provotorov, É. B. Fel'dman, and Yu. N. Ivanov for valuable discussions.

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Translated by A. Tybulewicz

# Thermodynamic theory of narrowing of NMR spectral lines in solids

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(Submitted 9 June 1978)

Zh. Eksp. Teor. Fiz. **75**, 1847–1861 (November 1978)

A new solution is proposed for the problem of narrowing of the many-pulse NMR spectra in solids. The dynamics of the spin system is investigated when the sample is acted upon by the pulse sequence  $90^\circ_y - \tau - (\varphi_x - 2\tau -)^N$  when the field goes off resonance by an amount  $\Delta$  ( $\varphi_x$  denotes a pulse that rotates the spin through an angle  $\varphi$  around the  $x$  axis;  $2\tau$  is the distance between pulses). It is shown that when the system is acted upon by pulses and by detuning in a time  $t > > \tau$ , the spins precess around an effective field  $\omega_{\text{eff}}$  whose magnitude and direction are determined by the parameters  $\varphi$  and  $\Delta\tau$ . In addition, the spins absorb the quanta of the dipole-dipole interaction modulated by the RF field and by the detuning; the magnitudes of these quanta depend only on the pulse repetition frequency. Within short times  $\sim T_2$  ( $T_2 \sim \|H_d\|^{-1} \sim \omega_{\text{loc}}$ ) the system reaches a quasiequilibrium state [M. Goldman, Spin Temperature and Nuclear Magnetic Resonance in Solids, Oxford U. Press, 1970, Chap. 6] corresponding to thermal mixing of the Zeeman and dipole-dipole interaction reservoirs. The type of the quasiequilibrium depends on the ratio of  $\omega_{\text{eff}}$  to the local field  $\omega_{\text{loc}}$ . The quantum absorption process takes place in times  $t > > T_2$  and at  $\omega_{\text{eff}} > > \omega_{\text{loc}}$  it is connected with transfer of part of the energy into the dipole-dipole reservoir. This energy transfer does not take place under resonance conditions, i.e., when  $n\omega_{\text{eff}} = m\pi/\tau$  ( $n$  and  $m$  are integers). The resonance conditions correspond to the experimentally observed [L. N. Erofeev et al., Sov. Phys. JETP **48**, 925, (1978)] minima in the magnetization-damping times when  $\varphi$  and  $\Delta\tau$  are varied. The variations of the magnetization damping times are calculated for different types of resonances (for different  $n$  and  $m$ ). The kinetics of the damping of the magnetization near the resonances is investigated. The results differ substantially from those obtained by the average-Hamiltonian method (U. Haeberlen and J. S. Waugh, Phys. Rev. **175**, 453, 1968), and explain a number of experiments [W.-K. Rhim et al., Phys. Rev. Lett. **37**, 1764 (1976); L. N. Erofeev and B. A. Shumm, JETP Lett. **27**, 149 (1978); L. N. Erofeev et al., Sov. Phys. JETP **48**, 925 (1978)] that contradict this theory.

PACS numbers: 76.60. – k.

## 1. INTRODUCTION

A number of experimental methods have been recently developed by which to improve considerably the resolution of the lines in nuclear magnetic resonance (NMR) spectra of solids.<sup>1–7</sup> Methods most widely used are many-pulse methods<sup>4–7</sup> of line narrowing, which make it possible in practice to narrow down the NMR spectral lines of solids from several kilohertz to several dozen hertz.<sup>8</sup> In view of the great increase of the resolution of the many-pulse method, it becomes important to develop a theory of line narrowing. The hitherto known theory of many-pulse experiments starts from the premise that the pulse sequence causes the dipole-dipole interaction or part of it to become dependent on the time and average out over the cycle time  $\tau_c$ . In addition to the time  $\tau_c$ , which characterizes the motion of the nuclear spins under the influence of the pulses, the many-pulse problem involves one other time  $T_2$ , which characterizes the motion of the spins in the local field. If the dipole-dipole interaction is averaged over the time of the cycle, the influence of the local fields on the motion of the spins is neglected. This, of course, is

fully justified in the case of one or several cycles at  $\tau_c \ll T_2$ . However, the damping of the magnetization in many-pulse experiments takes place over time  $t \gg T_2$ , i.e., over hundreds or thousands of pulse cycles. Therefore the influence of the local fields on the spin dynamics becomes substantial and the abbreviated description of the system is permissible only in the case of averaging over a time interval  $T_2 \gg \tau_c$ .

It must also be noted that in the average-Hamiltonian theory one does not follow the evolution of the density matrix in time. To the contrary, it is customary to make with respect to the density matrix an additional assumption<sup>9</sup> which in many cases is not justified.<sup>10–12</sup>

On the other hand, there is deep analogy between the behavior of a spin system in fields produced by pulse sequences, on the one hand, and in continuous external RF fields, on the other. This can be particularly clearly traced using as an example the pulse sequence  $90^\circ_y - \tau - (\varphi_x - 2\tau -)^N$  as  $\varphi \rightarrow 0$  and  $\tau \rightarrow 0$ .<sup>10</sup> This circumstance makes it possible to construct for many-pulse line narrowing a theory that is similar to a considerable degree to the theory of continuous “locking” of the spin