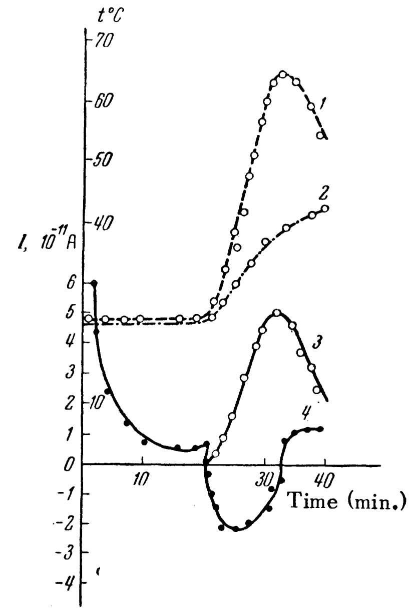


FIG. 4. The dependence of current and various electrode temperatures on time for the dielectric SVT. *1*-- temperature on the "hot" electrode, *2*--temperature of the "cold" electrode, *3*--the difference in temperature of the electrodes, *4*--current through the sample.

and then the specimen is heated, the current changes its sign. Specially prepared samples showed that the reverse current can be determined by the rapidity of change of the temperature difference of the electrodes. The corresponding curves are in Fig. 4. One can think that with a change of temperature gradient in the sample with time, a reverse thermal diffusion current arises, determined by the recombination of space charge. In view of the small direct current conductivity, this reverse current can exceed the direct current, and the total current changes sign.

---

[1] G. I. Skanavi and A. I. Demeshina, J. Exptl. Theoret. Phys. (U.S.S.R.) 19, 3 (1949).

[2] G. I. Skanavi, Elektrichestvo 8, 15 (1947); J. Exptl. Theoret. Phys. (U.S.S.R.) 17, 399 (1947).

Translated by L. A. D'asaro
219

---

SOVIET PHYSICS JETP VOLUME 3, NUMBER 6 JANUARY, 1957

# The Shape of the Dispersion Signal in Nuclear Magnetic Resonance with Strong High-Frequency Magnetic Fields

N. M. IEVSKAIA
*Moscow State University*
(Submitted to JETP editor April 18, 1955)
J. Exptl. Theoret. Phys. (U.S.S.R.) 30, 1040-1046 (June, 1956)

Approximate solutions are given for the system of equations which describe the behavior of the components of the magnetization vector in a strong high-frequency magnetic field for intermediate relaxation times; both symmetrical and asymmetrical sinusoidal modulation are considered. The approximation is investigated and the limits of its applicability indicated. The solution is used to derive expressions for the longitudinal and transverse relaxation times. The theoretical conclusions are found to be in agreement with the results of experimental studies.

---

## INTRODUCTION

THE shapes of the dispersion and absorption signals in nuclear magnetic resonance depend on the relaxation times (longitudinal and transverse), which are characteristics of the internal fields, and on the external conditions (the strength of the high-frequency magnetic field, the amplitude, frequency and wave-shape of the modulating magnetic field, etc.). Although numerous analyses of the signal shape have been given in the literature[1-10] there are still many experimentally encountered cases which have not been considered.

The present paper is concerned with the signal shape when a "strong" high-frequency magnetic field is applied; sinusoidal modulation of the longitudinal magnetic field is assumed. We shall be interested in the intermediate relaxation-time case, i.e., the case in which the period of the modulating field $T_m$ is comparable to the relaxation times (the longitudinal relaxation time is designated by $T_1$ and the transverse relaxation time by $T_2$). By "strong" high-frequency magnetic field, as is customary[1,5,10,11], is meant a field such that the vector **M**, which describes the nuclear magnetization, is highly perturbed or turned over at resonance. The case of intermediate relaxation times is of interest since it is frequently encountered in practice.

In preparation for the analysis of the signal shape, which follows, we introduce the dimensionless parameters:

$$\nu = \frac{1}{\omega_m T_1}, \quad \mu = \frac{1}{\omega_m T_2}, \quad k = \frac{H_m}{H_1}, \tag{1}$$

$$\varkappa = \frac{H_c}{H_m}, \quad \lambda = \frac{\omega_m H_m}{|\gamma| H_1^2}$$

and the dimensionless time $x = \omega_m t$ ($t$ is the time; $\omega_m$ is the angular frequency of the modulating field; $H_m$ is the amplitude of the modulating magnetic field; $H_1$ is the amplitude of the high-frequency magnetic field and $H_c$ is a fixed quantity which is superimposed on the resonance value of the dc magnetic field $H_0$.

A general expression for the dispersion signal $u$ in a strong high-frequency field ($\lambda < 1$) has been given in Refs. 1 and 10. The solution is given as a series expansion in terms of the parameter $\lambda$. When the longitudinal magnetic field is sinusoidally modulated, the zeroth approximation has the form

$$u^0(x) = u^0(x_0)\frac{G(x_0)}{G(x)} \tag{2}$$

$$\times \exp\{\nu(x_0 - x) + (\mu - \nu)[H(x_0) - H(x)]\}$$

$$+ M_0 \int_{x_0}^{x} \frac{\nu k(\varkappa + \sin\eta)}{G(x)G(\eta)}$$

$$\times \exp\{\nu(\eta - x) + (\mu - \nu)[H(\eta) - H(x)]\}\, d\eta,$$

where $x_0$ is the initial time and $M_0$ is the constant component of the magnetization vector

$$G(x) = [1 + k^2(\varkappa + \sin x)^2]^{1/2},$$

$$H(\eta) - H(x) = \int_x^{\eta} [G(\xi)]^{-2}\, d\xi.$$

In the symmetrical modulation case ($\varkappa = 0$), the shape of the dispersion signal is given by the expression[10]

$$u^{(0)}(x) = u^{(0)}(x_0)\frac{g(x_0)}{g(x)}\exp\{f(x_0) - f(x)\} \tag{3}$$

$$+ M_0 \int_{x_0}^{x} \frac{\nu k \sin\eta}{g(x)g(\eta)} \exp\{f(\eta) - f(x)\}\, d\eta,$$

where

$$f(x) = \nu x + \frac{\mu - \nu}{\sqrt{1 + k^2}} \operatorname{arc\,tg}(\sqrt{1 + k^2}\,\operatorname{tg} x),$$

$$g(x) = [1 + k^2 \sin^2 x]^{1/2}.$$

Examination of Eqs. (2) and (3) shows that in the steady-state ($x_0 \to -\infty$) the form of the dispersion signal is determined by the second term in Eqs. (2) and (3). It has been shown in Ref. 10 that in the first approximation the steady-state value of $u^{(1)}$ is zero. Hence, if the parameter $\lambda$ is small, the shape of the dispersion signal $u$ is given by the zeroth approximation, Eqs. (2) and (3) (to second order terms in $\lambda$). In the following the zero symbol will be omitted in the quantity $u^{(0)}(x)$.

## 1. SYMMETRICAL MODULATION

We shall consider the form of the steady-state dispersion signal $u_{st}(x)$ for symmetrical modulation ($\varkappa = 0$), i.e., the case in which the longitudinal magnetic field $H_z$ is of the form $H_z = H_0 + H_m \sin x$. From Eq. (3) we have

$$u_{st}(x) = \frac{M_0}{g(x)} e^{-f(x)} \int_{-\infty}^{x} \frac{\nu k \sin\eta}{g(\eta)} e^{f(\eta)} d\eta. \tag{4}$$

The analysis of this signal is difficult because the integral which appears in Eq. (4) cannot be expressed in terms of tabulated functions.

Under certain conditions, Eq. (4) can be simplified considerably. We introduce the notation

$$C_\tau = \int_{-\infty}^{x_\tau} \frac{\nu k \sin\eta}{g(\eta)} e^{f(\eta)} d\eta, \tag{5}$$

$$J(x, x_\tau) = \int_x^{x_\tau} \frac{\nu k \sin\eta}{g(\eta)} e^{f(\eta)} d\eta.$$

Then

$$u_{st}(x) = [M_0/g(x)]\, e^{-f(x)} [C_\tau + J(x, x_\tau)]; \tag{6}$$

$$C_\tau = \frac{u_{st}(x_\tau)}{M_0} g(x_\tau) e^{f(x_\tau)}. \tag{7}$$

The quantity $x_T$ is the time corresponding to the onset of resonance, i.e., $u(x_T) = 0.5\,u(x_m)$ where $x_m$ is the time at which the signal reaches its maximum value. It has been shown in Ref. 10 that $x_T < 0$.

We now ascertain the values of $\nu$, $\mu$ and $k$ in Eq. (6) for which $J(x, x_T)$ can be neglected as compared with the quantity $C_T$. Analysis of Eq. (5) indicates that in the region from $-|x_T|$ to $|x_T|$, the quantity $J(x, x_T)$ assumes its maximum values at $x = 0$ and $x = |x_T|$. We are concerned with the intermediate relaxation time case, i.e, the case in which $T_m T_1$ varies within the limits 0.1 to 10 (as has been pointed out in Refs. 3 and 12, $T_2 < T_1$ and the quantity $T_m/T_2$ can vary over wider limits). To estimate the relative magnitudes of the quantities $C_T$ and $J(x, x_T)$, the values of $J(0, -|x_T|)$, $J(|x_T|, -|x_T|)$ and $C_T$ were computed by numerical integration, using the following values for the parameters: $\nu$ from 0.001 to 5, $\mu$ from $\mu = \nu$ to 20 for $k$ equal to 10 and 20 and $x_T$ equal to 0.2 and 0.1, respectively. The results are presented graphically in Fig. 1 which shows the different regions of the dependence of $\mu$ on $\nu$. The curves which bound the regions $k = 10$ and $k = 20$ are plotted using the conditions:

$$J(0, -|x_\tau|) = 0.1C_\tau,$$
$$J(|x_\tau|, -|x_\tau|) = 0.1C_\tau.$$

The following condition is satisfied within these regions:

$$-J(x, -|x_\tau|) < 0.1C_\tau.$$

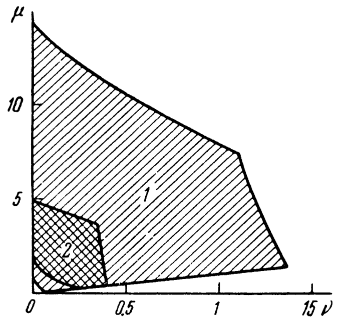


FIG. 1. Limits of applicability of the approximate solutions for two values of the quantity $k$. Regions 1 and 2 correspond to $k = 20$ and $k = 10$, respectively.

Thus for a specified value of $k$, if for a given value of the quantity $\nu$, the value of $\mu$ lies within the region indicated, then the quantity $J(x, x_T)$ in Eq. (16) can be neglected (for a signal width of $2|x_T|$ and 10 percent accuracy). Then we obtain the following expression for $u_{st}$ from Eqs. (6) and (7):

$$u_{st}(x) = u_{st}(x_\tau)\frac{g(x_\tau)}{g(x)}\exp\{f(x_\tau) - f(x)\}. \quad (8)$$

this expression is valid in the resonance region.

Comparing Eqs. (8) and (3), we see that the steady state and transient solutions have the same form; hence, for rapid passage through resonance, the form of the dispersion signal remains fixed, although its magnitude varies with time.

The rate at which the signal builds up can be used to determine the longitudinal relaxation time $T_1$ in those cases for which the build-up time is large compared with the modulation period. From Eqs. (3) and (8) it follows that

$$u(x) = \frac{C_0}{g(x)}e^{-f(x)} + u_{st}(x), \quad (9)$$

$$C_0 = u(x_0)\,g(x_0)e^{f(x_0)}.$$

After a time 2m (i.e., after $n$ modulation periods) the magnitude of the signal will be

$$u(x + 2\pi n) \quad (10)$$
$$= \frac{C_0}{g(x)}\exp\{-f(x) - 2\pi n\nu\} + u_{st}(x).$$

From Eqs. (9) and (10) we have

$$\nu = \frac{1}{2\pi n}\ln\left[\frac{u(x) - u_{st}(x)}{u(x + 2\pi n) - u_{st}(x)}\right]. \quad (11)$$

If $\nu \to 0$ then from Eqs. (5) and (6) $u_{st}(x) \to 0$ and

$$\nu = \frac{1}{2\pi n}\ln\left[\frac{u(x)}{u(x + 2\pi n)}\right]. \quad (12)$$

To make practical use of this scheme, the screen of the oscilloscope can be photographed with exposure times equal to 3-5 modulation periods. Using Eqs. (11) and (12) the value of $T_1$ can be determined from the ratio of the amplitudes of several pulses which appear in sequence on the photograph.

In Ref. 10 a detailed analysis of the shape of the dispersion signal in the transient state was given for symmetrical modulation with $\nu \to 0$. It has been indicated above that the conditions for which Eq. (8) is valid are such as to make the transient and steady state solutions identical. Under these conditions an analysis of Eq. (8), similar to that which was carried out in Ref. 10, indicates that the dispersion signal is bell-shaped and asymmetrical. We now introduce the following notation: $x_m$ is the time which corresponds to $u(x_m) = u_{max}$; $x_a$ and $x_b$ indicate the instants at which $u(x) = 0.5\, u_{max}$ ($x_a < x_m$, $x_b > x_m$). For $\nu < \mu$ we have

$$\frac{1}{k} = 0{,}144\Delta\left[1+\sqrt{1-3{,}74\frac{\varepsilon^2}{\Delta^2}}\right]; \quad (13)$$

$$\frac{1}{k} = 0{,}289\Delta\left[1-0{,}935\frac{\varepsilon^2}{\Delta^2}\right] \quad \text{for } \frac{\varepsilon}{\Delta}<0.2; \quad (14)$$

$$x_m^2 = 0{,}461\frac{\Delta}{k}\left[1-\frac{3{,}464}{\Delta k}\right], \quad (15)$$

$$|x_m| = 0{,}353\varepsilon\left[1-\frac{3{,}115}{k^2}\right];$$

$$\mu = -{}^1/_2 k^2 \sin 2x_m, \quad (16)$$

where $\Delta = x_a + x_b$ is the half-width of the signal and $\epsilon = (|x_a| - |x_m|) - (x_b + |x_m|)$ is a measure of the signal asymmetry.

As in Ref. 10, using Eqs. (13)-(16), it is possible to determine the transverse relaxation time $T_2$ from a knowledge of the half-width and asymmetry of the signal; also, if the strength of the modulating field $H_m$ is known, the amplitude of the high-frequency magnetic field $H_1$ can be found. We may note that this method can be used only when the high-frequency magnetic field $H_1$ is sufficiently homogeneous over the region of the sample; if there are any homogeneities, $\Delta$ and $\epsilon$ become average values determined by the different environmental conditions in the various parts of the sample.

## 2. ASYMMETRICAL MODULATION

Experimentally it is necessary to vary the time interval between the signal pulses which occur as the magnetic field is modulated[5,11]. Under these conditions the magnitude of the dc magnetic field differs from the resonance value, i.e., $H_z$ is of the form

$$H_z = H_0 + H_m(\varkappa + \sin x), \quad (17)$$

in which $\varkappa$ can have either sign depending on the sign of $H_c$.

For asymmetrical modulation the shape of the dispersion signal is given by Eq. (2). We are interested only in the steady-state solution. In order to find this solution it is necessary to compute the integral $I = H(\eta) - H(x)$ [cf. Eq. (2)].

Using certain approximations it is possible to find $I$. It follows from Eq. (17) that the magnitude of the displacement term $H_c$ must be smaller than the modulation amplitude $H_m$. Since it is always true that $\varkappa \leq 1$ we may make the substitution $\varkappa = \sin\psi$. It also follows from Eq. (17) that the resonance conditions obtain when $x_{res} \cong -\psi$. We divide $I$ into two integrals $I = I_1 + I_2$, where

$$I_1 = \int\limits_{x}^{x-\Delta} [G(\xi)]^{-2}\,d\xi; \quad I_2 = \int\limits_{x-\Delta}^{\eta} [G(\xi)]^{-2}d\xi. \quad (18)$$

If the half-width of the signal $\Delta$ is small, then $I_1$ can be computed by expanding $\sin x$ in a series about the resonance value.

$$I_1 = \frac{1}{p}\operatorname{arctg}[p(\xi+\psi)]\,\Big|_x^{x-\Delta}, \quad (19)$$

where $p = k\cos\psi$.

Substituting $I_1$ and $I_2$ in Eq. (2), dividing the integral $\int\limits_{-\infty}^{x}$ into two parts as in the symmetrical case and keeping only the part which is of importance in the resonance region, we get

$$u_{st}(x) = u_{st}(x_\tau)\,\frac{G(x_\tau)}{G(x)}\,\exp\{F(x_\tau) - F(x)\}, \quad (20)$$

where

$$F(x) = \nu x + \frac{\mu-\nu}{p}\operatorname{arctg}[p(x+\psi)].$$

Comparing Eqs. (8) and (20), we see that the more exact symmetrical-modulation solution (8) will have the same form as (20) when $\tan x \cong x$, $\sqrt{1+k^2} \cong k$, i.e., for sufficiently large values of $k$ and small values of $x$. In the asymmetrical-modulation case the role of the parameter $k$ is played by the quantity $p$.

Using the analysis developed in Ref. 10 we can now examine Eq. (20); when $\nu < \mu$ (the notation is the same as that used in the symmetric-modulation case) we have:

$$1/p = 0{,}144\Delta\,[1+\sqrt{1-3{,}74(\varepsilon^2/\Delta^2)}]; \quad (21)$$

$$1/p = 0.289\Delta\,[1-0.935\varepsilon^2/\Delta^2] \quad (22)$$

$$\text{for } \varepsilon/\Delta < 0{,}2;$$

$$(x_m+\psi)^2 = 0{,}461\frac{\Delta}{p}\,[1-3{,}464/\Delta p], \quad (23)$$

$$|x_m+\psi| = 0{,}353\varepsilon;$$

$$\mu = -p^2(x_m+\psi). \quad (24)$$

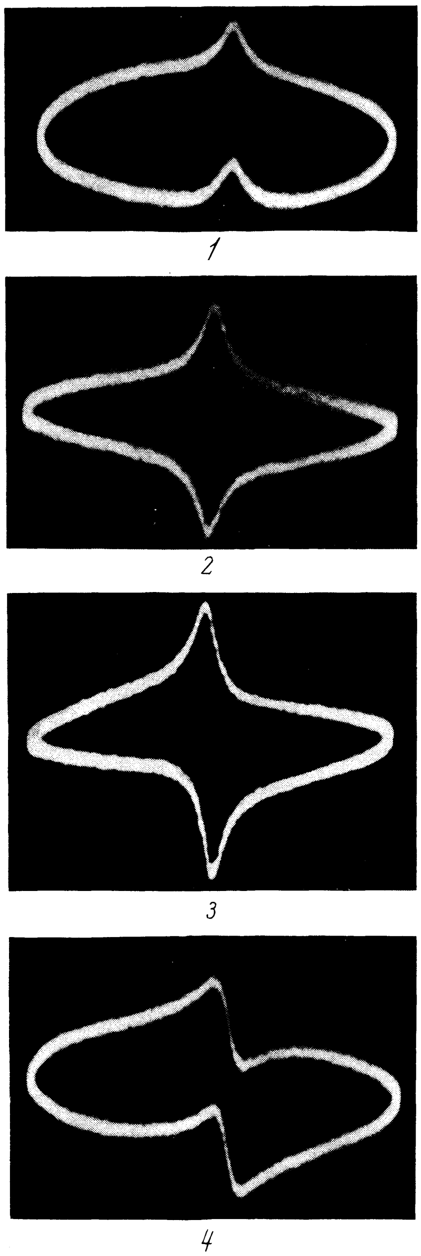


FIG. 2. The change in the shape of the dispersion signal as the quantities $\nu$ and $\mu$ are varied. These pictures were obtained with water solutions as follows: *1* – 0.001 molar $CuSO_4$, *2* -- 0.02 molar $Fe(NO_3)_3$, *3* – molar $CuSO_4$, *4* -- 2 molar $Fe(NO_3)_3$; $f_m = 50$ cps, $H_m = 19$ gauss, $H_1 = 1$ gauss. The values of $\nu$ and $\mu$ are, respectively: *1* -- 0.0035 and 6.9; *2* -- 0.57 and 10; *3* -- 3.7 and 17; *4* -- 59 and 78.

Equations (21)-(24) can be used to determine the transverse relaxation time $T_2$ and the amplitude of the high-frequency magnetic field $H_1$ when the signal pulse does not fall at the center of the oscilloscope pattern. Comparing Eqs. (21)-(24) with Eqs. (13)-(16), we see that the expressions are identical up to terms of the order of $k^{-2}$.

An estimate of the limits of applicability of Eqs. (21)-(24) shows that these expressions are accurate to within 10 per cent for values up to $\varkappa = 0.65$ ($k = 20$) and up to $\varkappa = 0.5$ ($k = 10$).

It is still necessary to verify that the expressions given above for symmetric modulation Eqs. (13)-(16) and asymmetrical modulations Eqs. (21)-(24) are being used in cases for which the experimental values of $\mu$ and $\nu$ lie within the limits of the regions shown in Fig. 11. We may note that in asymmetrical modulation the parameter $p$ should be used instead of $k$ in Fig. 1 and the regions $\mu(\nu)$ should be compressed as $\varkappa$ is increased.

## EXPERIMENTAL RESULTS

The theoretical results obtained in Secs. 1 and 2 were checked with an electrically compensated crossed-coil setup. Proton resonances were studied in all cases. The experiments were performed in distilled water, aqueous solutions of varying concentrations of $CuSO_4$ and of $Fe(NO_3)_3$, paraffin, glycerin and various types of synthetic rubber.

It has been shown above that the form and magnitude of the dispersion signal for a strong high-frequency magnetic field are determined by the values of the quantities $T_1$, $T_2$, $H_1$, $H_m$, $\omega_m$ and $H_c$. If for a given value of $k$, the values of $\nu$ and $\mu$ lie within the regions shown in Fig. 1, then the signal is bell-shaped and is given by Eqs. (8) and (20). On the other hand, if the value of $\nu$ corresponding to this value of $k$ is outside the region, then the effect of the quantity $J(x, x_T)$ becomes important and the curve is distorted.

The oscilloscope photographs shown in Fig. 2 illustrate the change which takes place in the dispersion signal when $\nu$ and $\mu$ are increased. These photographs were made with aqueous $CuSO_4$ solutions and $Fe(NO_3)_3$ solutions under the following conditions: $f_m = 50$ cps, $H_m = 19$ gauss and $H_1 = 1$ gauss. The corresponding values of $\nu$ and $\mu$ are given for each photograph. The theoretical predictions regarding the dependence of the signal-shape on $\nu$ and $\mu$ are borne out in these photographs.

To verify the functional dependence of the half-width $\Delta$ on $k$, given in Eqs. (14) and (22), we found the experimental dependence of this quantity

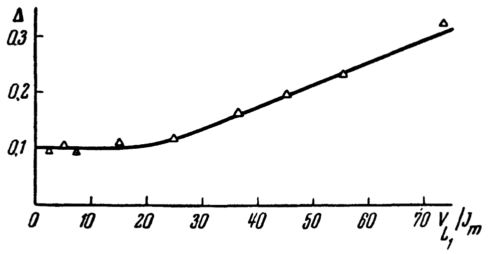


FIG. 3. The signal half-width Δ as a function of the ratio of the high-frequency voltage in the driving coil to the modulation current; this ratio is proportional to $1/k$.

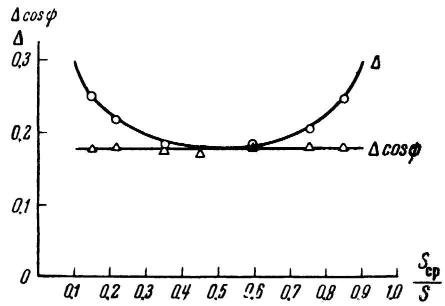


FIG. 4. The signal half-width Δ as a function of position on the oscilloscope pattern.

$[S_{rel}/S = 1/2(1+\varkappa)]$.

on the ratio $V_{L1}/J_m$, which is proportional to $1/k$ ($V_{L1}$ is the amplitude of the voltage in the driving coil and is proportional to $H_1$. $J_m$ is the current in the modulating coil and is proportional to $H_m$ [13] ). This dependence is shown in Fig. 3 which was obtained using a 0.064 molar solution of $CuSO_4$ with $\nu = 0.26$, $\mu = 7.1$ and $\epsilon/\Delta < 0.2$.

The strong-field case ($\lambda < 1$), which is the subject of this paper, is realized experimentally when $V_{L1}/J_m > 30$. It is apparent from Fig. 3 that for $V_{L1}/J_m < 25$ the half-width Δ increases in proportion to $V_{L1}J_m$; this is in agreement with the theoretical prediction. The region $V_{L1}/J_m < 10$, in which the quantity Δ remains constant, corresponds to the weak-field case ($\lambda > 1$); here, the width of the signal, as is well known[3,4,14], is determined by the transverse relaxation time $T_2$ and the modulation rate is independent of the strength of the high-frequency magnetic field $H_1$.

An experimental investigation was also undertaken to determine the dependence of the half-width Δ on the position of the signal on the oscilloscope pattern in the asymmetrical-modulation case.

A typical curve is shown in Fig. 4 which was obtained using a 0.064 molar solution of $CuSO_4$ with $f_m = 50$ cps, $H_m = 19$ gauss and $H_1 = 1$ gauss. It is evident from this figure that the quantity $\Delta \cos\psi$ remains constant to within 5 percent; thus, within experimental errors, the changes in the signal-width owing to variation in position on the oscilloscope pattern are given correctly by Eq. (22).

In conclusion, the author wishes to thank Professor S. D. Gvozdover for valuable advice in the course of this work and also E. G. Pozniakii, A.V. Luk'ianov and T. M. Cherkasov for undertaking the numerical integrations.

---

[1] F. Bloch, Phys. Rev. **70**, 460 (1946).

[2] K. V. Vladimirskii, Dokl. Akad. Nauk SSSR **58**, 1625 (1947).

[3] N. Bloembergen, *Nuclear Magnetic Relaxation*, The Hague, 1948.

[4] B.A.Jacobsohn and R. K. Wangsness, Phys. Rev. **73**, 942 (1948).

[5] S. D. Gvozdover and A. A. Magazanik, J. Exptl. Theoret. Phys. (U.S.S.R.) **20**, 705 (1950).

[6] E. E. Salpeter, Proc. Phys. Soc. (London) **63A**, 337 (1950).

[7] M. R. Gabillard, Compt. Rend. **232**, 1477 (1951).

[8] M. R. Gabillard, Compt. Rend. **232**, 1551 (1951).

[9] S. D. Gvozdover and N. M. Pomerantsev, Vestn. Moscow State Univ. **6**, 85 (1953).

[10] S. D. Gvozdover and N. M. Pomerantsev, Vestn. Moscow State Univ. **9**, 79 (1953).

[11] S. D. Gvozdover and N. M. Ievskaia, J. Exptl. Theoret. Phys. (U.S.S.R.) **29**, 637 (1955); Soviet Phys. JETP **2**, 486 (1956).

[12] R. K. Wangsness and F. Bloch, Phys. Rev. **89**, 728 (1953).

[13] S. D. Gvozdover and N. M. Ievskaia, J. Exptl. Theoret. Phys. (U.S.S.R.) **25**, 435 (1953).

[14] S. D. Gvozdover and N. M. Ievskaia, J. Exptl. Theoret. Phys. (U.S.S.R.) **29**, 227 (1955); Soviet Phys. JETP **2**, 90 (1956).

Translated by H. Lashinsky
218