Determination of Longitudinal Relaxation Times for Magnetic Resonance of Atomic Nuclei in an Intense High-Frequency Magnetic Field

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Two methods for determining the longitudinal relaxation time T_1 are treated. The methods are based on the use of the inversion of the dispersion signals observed in an intense high-frequency magnetic field during a change in the constant field and on the change in the time interval which precedes the inversion point. In order to verify the methods, an evaluation of the effect of the intermediate region which connects the resonance region and the region of free relaxation was carried out. Relationships are obtained which allow the determination of the longitudinal relaxation time. In order to confirm the methods experimentally, the dependence of the longitudinal relaxation time on the concentration of paramagnetic ions was measured in aqueous solutions of cupric sulfate and ferric nitrate.

1. INTRODUCTION

IN the present work methods are explained for the determination of the longitudinal relaxation time T_1 in the case of magnetic resonance of atomic nuclei in an intense high-frequency magnetic field accompanied by periodic modulation of the constant magnetic field. By an intense high-frequency magnetic field is meant a field under the application of which the magnetization vector **M** undergoes a strong perturbation and becomes inverted.

The theory of magnetic resonance for the case of an intense high-frequency magnetic field is given in reference 1, where it is shown that if the conditions

$$\Delta t \ll T_1, \quad T_2 \ll T_1, \quad T_2 \ll T \tag{1}$$

(where Δt is the duration of the signals being observed, T_1 and T_2 are the longitudinal and transverse relaxation times, respectively, and T is the period of the modulation) are fulfilled, then the complete process of passage through resonance under modulation may be divided into two regions: the region of resonance, in which the magnetization vector **M** undergoes a strong perturbation and becomes inverted, and the region of free relaxation of the magnetization vector **M** to its statistical magnitude $\mathbf{M}_0$.

Let us introduce the dimensionless parameters

$$\nu = \frac{1}{\omega_m T_1}, \quad \mu = \frac{1}{\omega_m T_2}, \quad k = \frac{H_m}{H_1}, \tag{2}$$

and the dimensionless time

$$x = \omega_m t, \tag{3}$$

where ω_m is the frequency of the modulating magnetic field, H_m is the amplitude of the modulating magnetic field and H_1 is half the amplitude of the high-frequency magnetic field.

As is shown in reference 1, a change in the longitudinal component of the magnetization $M_z(x)$ in the region of resonance is characterized by a magnitude of the coefficient of inversion R, defined as the ratio of the maximum magnitude of the longitudinal component of magnetization at the time of leaving the region of resonance $[M_z(x_2)]$ to the maximum magnitude of the longitudinal component of magnetization at the beginning of the resonance region $[M_z(x_1)]$

$$R = \frac{M_z(x_2)}{M_z(x_1)} \tag{4}$$

The magnitude of the coefficient of inversion R depends on the parameter k, that is, on the ratio of the amplitudes of the modulating and the high-frequency fields, and may take on values lying between the limits[2]

$$-1 \leqslant R \leqslant 0. \tag{5}$$

The absolute value of the coefficient of inversion increases with decreasing k. In the region of free relaxation the longitudinal component on the magnetization $M_z(x)$ satisfies the relationship

[1] S. D. Gvozdover and A. A. Magazanik, J. Exper. Theoret. Phys. USSR **20**, 705 (1950).

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

$$M_z(x) = M_0 - [M_0 - M_z(x_2)]\, e^{-\nu (x-x_2)}, \qquad (6)$$

where $M_z(x_2)$ is the magnitude of M_z on leaving the region of resonance ($x > x_2$).

The magnitude of the dispersion signal u observed during resonance is proportional to the value of the longitudinal component of the magnetization M_z at entrance into the region of resonance [1].

On sinusoidal modulation of the magnetic field, resonance regions occur twice during each modulation period. If the signals are observed on the screen of an oscilloscope, then, with an elliptical sweep pattern synchronized with the modulating magnetic field, two signals separated from each other appear on the screen. If we change the spacing between signals, changing the constant magnetic field, then the amplitudes of the second signal become unique probes, with the aid of which we may obtain the curve of the variation of M_z in the region of free relaxation.

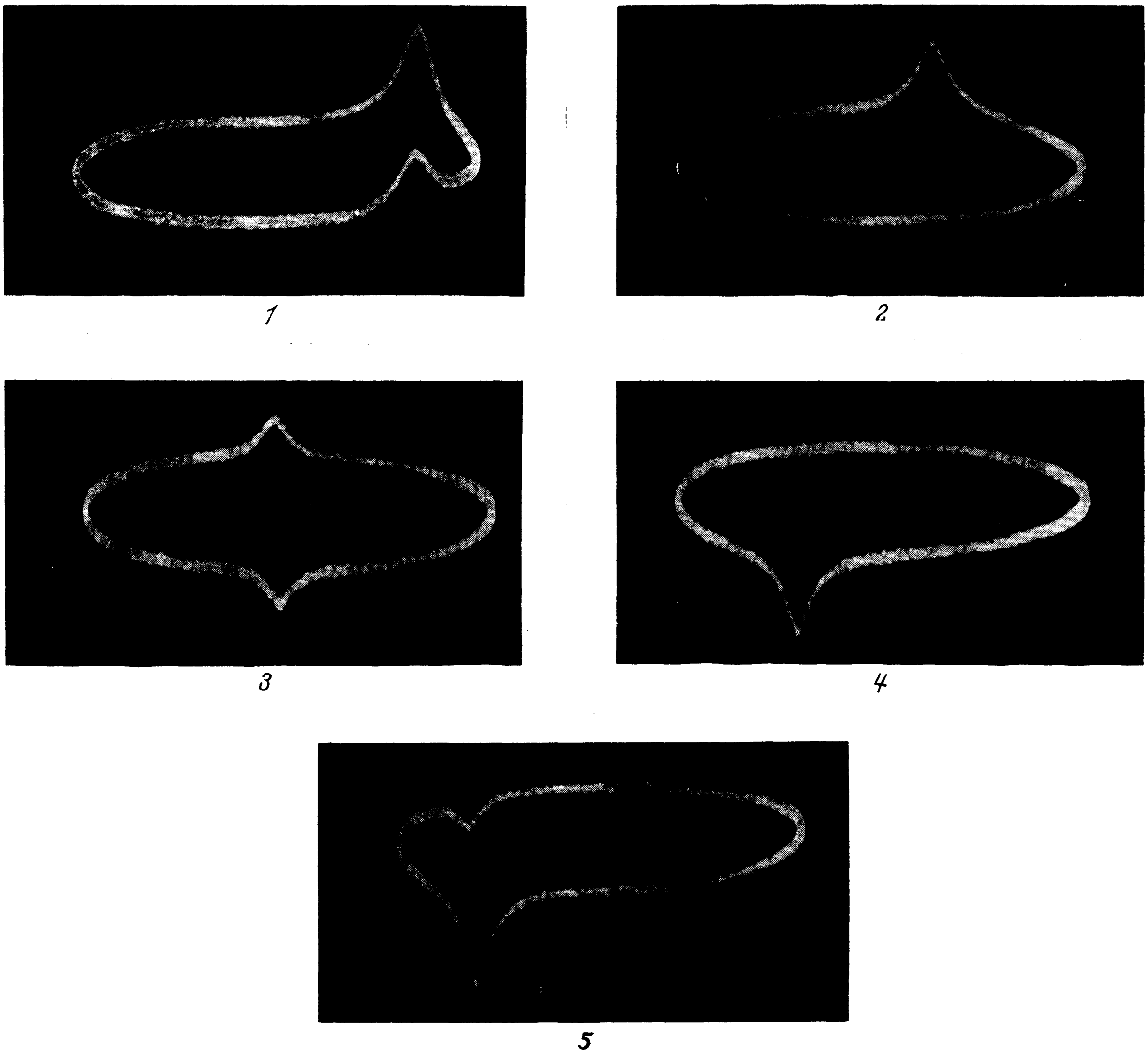

FIG. 1. Change in magnitude and sense of the dispersion signals during a gradual change in the constant magnetic field. The oscillograms were obtained with a 0.01 *M* solution of $Fe(NO_3)_3$ under the conditions: modulation frequency 50 cps, amplitude of the modulating magnetic field 19 oersteds, half amplitude of the high-frequency magnetic field 1 oersted.

In Fig. 1 are shown typical oscillograms, illustrating the change of magnitude and sense of the dispersion signals on change of the constant magnetic field. Oscillograms *2* and *4* (Fig. 1) correspond to the case in which the second probing resonance field occurs just at the instant when M_z passes through zero during free relaxation to its statistical magnitude. At this instant, called the instant of inversion, the probing signal is not observed.

2. THE EFFECT OF THE INTERMEDIATE REGION CONNECTING THE RESONANCE REGION AND THE REGION OF FREE RELAXATION

The idea that $M_z(x)$ completes, for each period of the modulation, a closed cycle consisting of two exponential sections obeying Eq.(6) and two resonance regions joining them and obeying Eq. (4) is, of course, an approximation. Actually, during the approach to the resonance region and during the leaving of it, an intermediate region exists, in which the behavior of $M_z(x)$ is more complicated. As a consequence of the presence of the transitional intermediate field, the values of $M_z(x)$ at points x_1 and x_2 are somewhat diminished in comparison with what they would have been if M_z had merely conformed to an exponential growth up to the instant x_1. Let us evaluate the error which arises in such an approximate treatment. We shall designate by $M_z(x)$ the values which M_z actually has at points x_1 and x_2 and by $M_z'(x)$ the values which it would have had if resonance conditions had occurred instantaneously:

$$M_z(x_1) = M_z'(x_1) - \Omega_1(x_1, k, \omega_m, \mu, \nu), \qquad (7)$$
$$|M_z(x_2)| = |M_z'(x_2)| - |\Omega_2(x_2, k, \omega_m, \mu, \nu)|.$$

The functions Ω_1 and Ω_2 characterize a decrease in the magnitude of the signal as a result of the beginning of the action of the resonance conditions. For the coefficient of inversion R, we obtain, on taking account of Eq. (7), the expression

$$|R| = \left|\frac{M_z(x_2)}{M_z(x_1)}\right| \qquad (8)$$
$$= |R'|\left[1 + \frac{\Omega_1}{M_z'(x_1)} - \left|\frac{\Omega_2}{M_z'(x_2)}\right|\right],$$

where $R' = M_z'(x_2)/M_z'(x_1)$.

Under the conditions

$$\frac{\Omega_1}{M_z'(x_1)} \ll 1, \qquad \left|\frac{\Omega_2}{M_z'(x_2)}\right| \ll 1 \qquad (9)$$

it follows from Eq. (8) that

$$R = R'.$$

In the intermediate region Eq. (6) takes the form

$$M_z(x) = M_0' - [M_0' - M_z(x_2)] \qquad (10)$$
$$\times e^{-\nu(x-x_2)} + (|\Omega_2| - \Omega),$$

where $M_0' = M_0 - |\Omega_2|$ and $\Omega \leq \Omega_1$ characterize the decrease in the signal at an arbitrary point x.

Equation (10) is analogous to Eq. (6) with changed coefficients. If

$$\frac{\Omega_1}{M_0} \ll 1, \qquad \left|\frac{\Omega_2}{M_0}\right| \ll 1, \qquad (11)$$

then Eqs. (10) and (6) coincide.

Conditions (9) and (11) allow us to estimate the error which arises on the employment of Eqs. (4) and (6), not taking into account the intermediate region. For example, under the conditions

$$\nu = 0.1, \quad \mu = 1, \quad k = 10, \quad \omega_m = 314,$$

an estimate of the values of $M_z(x)$ and $M_z'(x)$ gives

$$\frac{\Omega_1(x_1)}{M_0} < 0.02, \qquad \frac{\Omega_1(x_1)}{M_z'(x_1)} < 0.2, \qquad (12)$$
$$\left|\frac{\Omega_2(x_2)}{M_0}\right| < 0.02, \qquad \left|\frac{\Omega_2(x_2)}{M_z'(x_2)}\right| < 0.2.$$

Noting that the difference $(\Omega_1 - |\Omega_2|)$ occurs in Eqs. (8) and (10), we see that an error of less than 5-10% is introduced by the use of Eqs. (4) and (6).

3. DETERMINATION OF T_1 BY THE INVERSION METHOD

Let us introduce the width of the signal into the expressions given in reference 1 for the magnitude of the dispersion signals arising during a closed cycle of the modulation.

We use the designations

$$m(x) = M_z(x)/M_0'; \qquad (13)$$

$$m(x_{1,1}) = m_{11}, \qquad m(x_{2,1}) = m_{21}$$
$$m(x_{1,2}) = m_{12}, \qquad m(x_{2,2}) = m_{22}, \qquad (14)$$

where the first index denotes the instant of entering and leaving the resonance region, and the second indicates the number of the resonance region. If the resonance region is sufficiently narrow, then the instants of time at which M_z attains its extreme values are near the instants of time for which $u_x/u_{max} = 1/2$. Consequently, we shall take the distance between the points of half amplitude of the dispersion signal $u(x)$ as the width of the signal Δ. We denote by η the interval of time between signals from maximum to maximum. With these designations,

$$x_{12} - x_{21} = \eta - \Delta,$$
$$x_{11} - x_{22} = 2\pi - \eta - \Delta. \tag{15}$$

Then, from Eqs. (8), (10), (13) and (15), neglecting the terms (12), we obtain

$$m_{11} = \frac{1 - Re^{-\nu(2\pi-2\Delta)} - (1-R)e^{-\nu(2\pi-\eta-\Delta)}}{1 - R^2 e^{-\nu(2\pi-2\Delta)}}, \tag{16}$$

$$m_{12} = \frac{1 - Re^{-\nu(2\pi-2\Delta)} - (1-R)e^{-\nu(\eta-\Delta)}}{1 - R^2 e^{-\nu(2\pi-2\Delta)}},$$

where m_{11} determines the amplitude of the upper signal and m_{12} the amplitude of the lower signal.

As follows from Eq. (16), the magnitude of the signal depends on the distance η between signals and on the width of the signal Δ. Moreover, the magnitude of the signals depends on the coefficient of inversion R and on the ratio of the longitudinal relaxation time T_1 to the modulation period T.

Expressions for the magnitude of the signals have also been obtained in reference 3. However, the relations introduced in this work are written on the supposition that $R = 1$, and no account is taken in them of the width of the signal. This, as follows from Eq. (16), results in a rough approximation. In those cases where the inversion of the signals arising gives a sufficiently great portion of the exponential [for which it is necessary to use a modulation frequency such that T/T_1 will be greater than unity and at the same time will fulfill condition (1)], it is possible to use it for the determination of the longitudinal relaxation time T_1. An indication of the possibility of employing such a method was given in reference 1.

Both formulas (16), corresponding to the upper and lower signals, can be put into the form

$$m = P - |Q| e^{-\nu y}, \tag{17}$$

where
$$P = \frac{1 - Re^{-\nu(2\pi-2\Delta)}}{1 - R^2 e^{-\nu(2\pi-2\Delta)}}, \tag{18}$$

$$Q = -\frac{1 - R}{1 - R^2 e^{-\nu(2\pi-2\Delta)}},$$

and y corresponds to the time elapsed from the end of the preceding signal to the beginning of the following one, which is equal to

$$y = x_{11} - x_{22} = 2\pi - \eta - \Delta \text{ for the upper signal,} \tag{19}$$
$$y = x_{12} - x_{21} = \eta - \Delta \text{ for the lower signal, respectively.}$$

As has already been stated above, the amplitude of the signal u arising is proportional to m, that is,

$$u = Nm = N[P - |Q| e^{-\nu y}], \tag{20}$$

where N is a coefficient which is constant for a given substance and definite experimental conditions. In order to determine T_1 it is necessary, according to (20), to know P and Q, which, in their turn, are functions of T_1, and also R, the magnitude of which is unknown.

We consider two neighboring signals (either two upper or two lower)

$$u_i = N[P - |Q| e^{-\nu y_i}],$$
$$u_{i+1} = N[P - |Q| e^{-\nu y_{i+1}}]. \tag{21}$$

Taking the difference of their amplitudes and then taking its logarithm, we obtain

$$\ln(u_{i+1} - u_i) = \ln N|Q| - \nu y_i + \ln[1 - e^{-\nu(y_{i+1}-y_i)}]. \tag{22}$$

Under the condition that $\nu(y_{i+1} - y_i) < 0.1$, we may take

$$e^{-\nu(y_{i+1}-y_i)} = 1 - \nu(y_{i+1} - y_i). \tag{23}$$

Putting (23) into (22) and introducing the symbols:

$$\alpha_i = \ln(u_{i+1} - u_i) - \ln(y_{i+1} - y_i), \tag{24}$$
$$\beta = \ln N|Q|\nu,$$

we obtain

$$\alpha_i = \beta - \nu y. \tag{25}$$

Equation (25) is the equation of a straight line,

[3] L. E. Drain, Proc. Phys. Soc. (London) A62, 301 (1949).

the ordinates and the abscissas of which are determined by experiment; it is necessary to find the slope of the straight line.

Using the method of least squares[4] for the determination of $\nu = 1/\omega_m T_1$, we obtain

$$T_1 = \frac{1}{\omega_m} \frac{n \sum_{i=1}^{n} (y_i)^2 - \left(\sum_{i=1}^{n} y_i\right)^2}{\sum_{i=1}^{n} \alpha_i \sum_{i=1}^{n} y_i - n \sum_{i=1}^{n} \alpha_i y_i}. \quad (26)$$

It is assumed that in Eq. (26) we have n points; consequently, in accordance with (24), $n + 1$ signals.

In a practical application of this method to oscillograms such as those introduced in Fig. 1, the position, width and amplitude of the signals are measured. The amplitudes of the signals u are measured during a superposition on the oscillogram-with-signal of the oscillogram ellipse without signals, taken when the longitudinal magnetic field H_z does not reach the resonance value. Knowing the modulation frequency ω_m and taking into consideration that the sweep of the oscillogram, as also of the modulation field, is sinusoidal, we may determine y.

An experimental verification of the methods showed that repeated determinations of T_1 for one and the same sample according to Eq. (26), under conditions where the values of u and y were of an exactitude of 5-10%, give an error in the determination of T_1 of the order of 10-20%.

4. DETERMINATION OF T_1 BY THE METHOD OF THE INVERSION POINT

An expression for the coefficient of inversion R can be obtained from Eq. (16). At the inversion point $m_{12} = 0$ and

$$R = \frac{1 - e^{\nu(\eta_0 - \Delta)}}{1 - e^{-\nu(2\pi - \eta_0 - \Delta)}}, \quad (27)$$

whence $\eta_0 - \Delta$, the distance from the end of the upper signal to the inversion point of the lower signal,is equal to

$$\eta_0 - \Delta = \frac{1}{\nu} \ln\left(\frac{1 - R}{1 - Re^{-\nu(2\pi - 2\Delta)}}\right). \quad (28)$$

The inversion point of the upper signal is located at the same distance from the lower signal (see oscillograms *2* and *4* of Fig. 1). The dependence of $\frac{\eta_0 - \Delta}{2\pi} = \frac{\tau_0 - \delta}{T}$ on R and $\nu\, 2\pi = \frac{T}{T_1}$ is given in Fig. 2 (τ_0 and δ have the dimension of time and are equal, respectively, to $\frac{\eta_0}{\omega_m}$ and $\frac{\Delta}{\omega_m}$). As follows from Fig. 2, the distance to the inversion point depends, for constant modulation period, on the value of the longitudinal relaxation time T_1 and on the magnitude of the coefficient of inversion. It follows from Eq. (27) that if T_1 is found and the values of η_0 and Δ are known—the magnitudes being determined experimentally, then we may find the coefficient of inversion R, and, conversely, if the magnitude of R is known, then T_1 may be determined from Eq. (27). The absolute value of the coefficient of inversion R, as is shown in reference 2, must increase with dedreasing $k = H_m/H_1$. If the values of T and T_1 are constant, then, as follows from Fig. 2, the distance to the point of inversion must increase on increase in $|R|$.

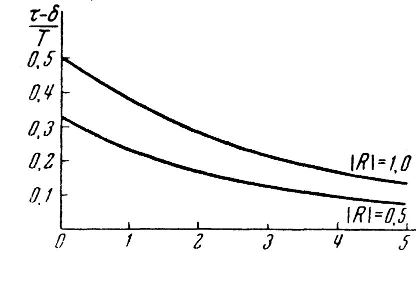

FIG. 2. Dependence of the position of the inversion point on the ratio of the modulation period to the longitudinal relaxation time (T/T_1) for $|R| = 1$ and $|R| = 0.5$.

In order to explain the behavior of R in its dependence on k, the dependence of the distance to the inversion point η_0 on the magnitude of the ratio V_{L1}/I_m, proportional to $1/k$, was taken (V_{L1} is the amplitude of the voltage at the generator coil, proportional to H_1, I_m is the current through the modulation coils, proportional to H_m[5]). The dependence of η_0 and $\eta_0 - \Delta$ on V_{L1}/I_m, taken in a 0.064 M solution of $CuSO_4$, is represented in Fig. 3. Experiment shows that for an increase in H_1, with constant H_m and ω_m, beginning from a certain value of H_1 (in Fig. 3, for $V_{L1}/I_m > 40$), $\eta_0 - \Delta$ is of constant magnitude, to within an accuracy of a few percent.

It follows from Eq. (27) that for constant ν (that is, for constant ω_m and T_1) the magnitude of $\eta_0 - \Delta$ can be constant only for constant R. As k decreases, $|R|$ must increase accordingly, but it is

[4] K. P. Iakolev, *Mathematical Treatment of Experimental Results*, GITTL, 1950.

[5] S. D. Gvozdover and N. M. Ievskaia, J. Exper. Theoret. Phys. USSR **25**, 435 (1953).

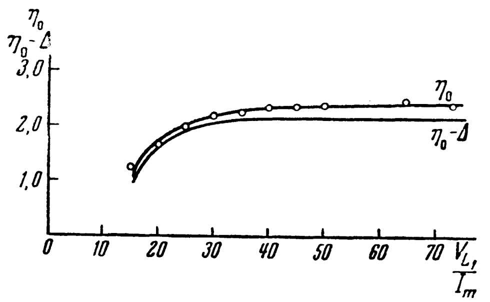

FIG. 3. Dependence of the distance to the inversion point η_0 and $(\eta_0-\Delta)$ on the ratio of the high-frequency voltage at the generator coil to the modulation current. This ratio is proportional to $1/k$.

practically unchanged; consequently, $|R|$ is near unity, and the following method may be proposed for the evaluation of T_1.

We introduce the notation

$$z_1 = \nu(2\pi - \eta_0 - \Delta), \quad z_2 = \nu(\eta_0 - \Delta). \quad (29)$$

Then Eq. (27) takes the form

$$R = \frac{1-e^{z_2}}{1-e^{-z_1}}. \quad (30)$$

If the ratio

$$\frac{z_2}{z_1} = \frac{\eta_0-\Delta}{2\pi-\eta_0-\Delta}, \quad (31)$$

which is determined experimentally, is known, then, knowing a magnitude, for example, of z_2, which fulfills Eq. (30) for a given R, and with the assigned z_2/z_1, we can determine T_1 from Eq. (29). For the purpose of such an evaluation,

TABLE I

z_2	$\left(\frac{z_2}{z_1}\right)_{R=-1}$	$\left(\frac{z_2}{z_1}\right)_{R=-0.9}$	z_2	$\left(\frac{z_2}{z_1}\right)_{R=-1}$	$\left(\frac{z_2}{z_1}\right)_{R=-0.9}$
0.01	1.00	0.91	0.36	0.64	0.55
0.02	0.98	0.87	0.37	0.62	0.54
0.03	0.97	0.86	0.38	0.61	0.53
0.04	0.96	0.85	0.39	0.60	0.52
0.05	0.95	0.84	0.40	0.59	0.50
0.06	0.94	0.84	0.41	0.58	0.49
0.07	0.93	0.83	0.42	0.57	0.48
0.08	0.92	0.83	0.43	0.56	0.47
0.09	0.91	0.82	0.44	0.55	0.46
0.10	0.90	0.81	0.45	0.54	0.45
0.11	0.89	0.80	0.46	0.52	0.44
0.12	0.88	0.79	0.47	0.51	0.43
0.13	0.87	0.78	0.48	0.50	0.42
0.14	0.86	0.77	0.49	0.49	0.40
0.15	0.85	0.76	0.50	0.48	0.39
0.16	0.84	0.75	0.51	0.47	0.38
0.17	0.83	0.74	0.52	0.45	0.37
0.18	0.82	0.73	0.53	0.44	0.35
0.19	0.81	0.72	0.54	0.43	0.34
0.20	0.80	0.71	0.55	0.42	0.33
0.21	0.79	0.70	0.56	0.40	0.31
0.22	0.78	0.69	0.57	0.39	0.30
0.23	0.77	0.68	0.58	0.38	0.28
0.24	0.76	0.67	0.59	0.36	0.26
0.25	0.75	0.66	0.60	0.35	0.24
0.26	0.74	0.65	0.61	0.33	0.22
0.27	0.73	0.64	0.62	0.32	0.20
0.28	0.72	0.63	0.63	0.30	0.17
0.29	0.71	0.62	0.64	0.28	0.12
0.30	0.70	0.61	0.65	0.26	
0.31	0.69	0.60	0.66	0.24	
0.32	0.68	0.59	0.67	0.22	
0.33	0.67	0.58	0.68	0.19	
0.34	0.66	0.57	0.69	0.14	
0.35	0.65	0.56			

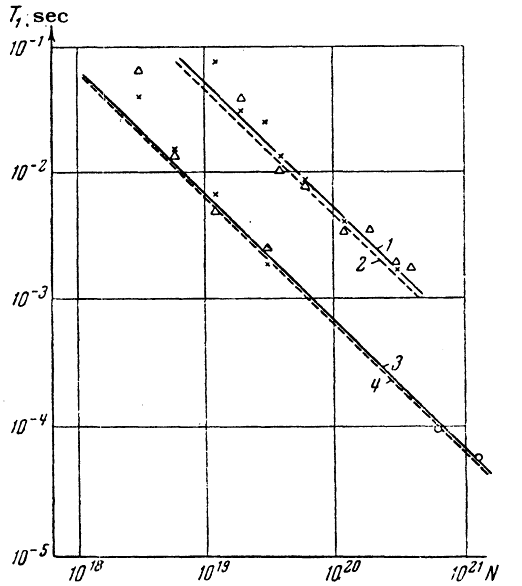

FIG. 4. Dependence of the longitudinal relaxation time T_1 on the concentration of paramagnetic ions N for water solutions of $CuSO_4$ and $Fe(NO_3)_3$. The following symbols are used in the figure: Δ for measurements by the method of inversion, $\times$ for measurements by the method of the inversion point, O for measurements by the form of the signal: *1* is T_1 for Cu^{++} ions, *2* is T_1 for the same ions according to reference 8, *3* is T_1 for Fe^{+++} ions, *4* is T_1 for the same ions according to reference 8.

tables of values of z_2 satisfying Eq. (30) for $R = -1$ and $R = -0.9$ have been composed (Table I). We may analogously draw up a similar table satisfying any chosen R.

An anlaysis of expression (30) shows that an evaluation of T_1 for $R = -1$ gives the minimum possible value

$$(T_1)_{R=-1} < (T_1)_R, \tag{32}$$

and that for $z_2/z_1 < 0.4$ $(T_1)_{R=-1}$ differs from $(T_1)_{R=-0.9}$ by not more than 12%. A determination of $(T_1)_{R=-1}$ under the conditions that η_0 and Δ are determined only with an accuracy of up to 5% gives a maximum error of 10%. Thus, if conditions are created under which the distance to the inversion point remains practically unchanged, then a determination of T_1 from Eqs. (30), (29) and the Table will give an error of not more than 20%.

The method proposed is quite simple and permits a rapid determination of the longitudinal relaxation time T_1 with an accuracy not less than the accuracy given by other methods. An essential advantage of the method, as of every method employing periodic modulation of the constant magnetic field, is the possibility of working in an unstabilized magnetic field, which possibility considerably simplifies the setup for the measurement of the longitudinal relaxation time.

5. EXPERIMENTAL VERIFICATION OF THE METHODS

As a test, in a special arrangement[5], of the methods described, values of the longitudinal relaxation time T_1 were measured for water solutions of various concentrations of cupric sulfate, $CuSO_4$, and ferric nitrate, $Fe(NO_3)_3$.

The obtained dependence of T_1 on the concentration of paramagnetic ions Cu^{++} and Fe^{+++} in the solution is given in Fig. 4 (curves *1* and *3*). The values of T_1 for 2*M* and 1*M* solutions of ferric nitrate were determined with the aid of the solution for the form of the signal in an intense high-frequency magnetic field in the case of short relaxation times[6]. From Fig. 4 it is clear that the dependence of T_1 on the concentration of paramagnetic ions is represented by a straight line making an angle of 45° with the axis of abscissa; whence it follows that the magnitude of the longitudinal relaxation time T_1 is inversely proportional to the concentration of paramagnetic ions. The deviation from the law of inverse proportionality for small concentrations may be explained by inaccuracy in the preparation of the solutions. As a consequence of the fact that the solutions were prepared by means of successive dilutions, the percentage content of Cu^{++} and Fe^{+++} ions at small concentrations was somewhat reduced as a result of hydrolysis, and this led to the apparent increase in T_1.

A comparison of the results of the measurement of T_1 by the method of inversion and by the method of the inversion point shows that the values of T_1 coincide within the limits of the error of the measurement and, moreover, coincide, within the limits of the error, with the results given in the literature[7,8] (see Fig. 4, curves *2* and *4*). This confirms the correctness of the methods we have treated.

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[7] N. Bloembergen, E. M. Purcell and R. V. Pound, Phys. Rev. 73, 679 (1948).

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

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