

INTERFERENCE EFFECT IN NUCLEAR MAGNETIC RELAXATION IN LIQUID $^{10}\text{BF}_3$. VII

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Owing to the interference between the dipole-dipole interaction and the anisotropy of electronic screening, a non-exponential time dependence of the magnetization for fluorine nuclei in liquid $^{10}\text{BF}_3$ appears. In the paper we present a theory of the interference effect in spin-lattice and spin-spin relaxation for liquid $^{10}\text{BF}_3$ as well as experimental evidence of this effect. It was shown that time dependence of the longitudinal component of magnetization in temperatures 163 K and 182 K may be expressed as a linear combination of four exponential functions with different amplitudes and time constants. From the fit of the theoretical results to the experimental data the value of the anisotropy of the electronic screening $|\Delta\sigma_F| = 300 \pm 70$ ppm follows.

1. Introduction

In the papers I–VI the interference effect in nuclear magnetic relaxation for different types of spin systems in liquid was considered. In particular it was shown that nonexponential relaxation may appear owing to interference between the dipolar interaction and anisotropy of the electronic screening. Here we consider the interference effect in spin-lattice and spin-spin relaxation in liquid $^{10}\text{BF}_3$ for fluorine nuclei. The intramolecular dipole-dipole interaction between nuclei of the fluorine $G^d(t)$, anisotropy of the electronic screening $G^\sigma(t)$, and spin-rotation interaction $G^r(t)$ were taken into account. The time-dependent spin Hamiltonian may be presented as the sum

$$G(t) = G^d(t) + G^\sigma(t) + G^r(t). \quad (1)$$

In further considerations of the system we neglect the influence of ^{10}B nuclei on the fluorine relaxation process because the gyromagnetic ratio for ^{10}B is much smaller than that for

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fluorine nuclei and because the scalar coupling constant $J_{10\text{BF}}$ is negligible small (Bacon, Gillespie, Quail 1963). The presented theory of relaxation is based on the semiclassical theory of density matrix (Redfield 1957), assuming isotropic rotational diffusion of molecules in liquid $^{10}\text{BF}_3$. The numerical calculations were made as described elsewhere (Blicharski, Nosel 1970) using the digital computer "Odra" 1204. The experimental time dependence of the longitudinal component of nuclear magnetization for nuclei ^{19}F in $^{10}\text{BF}_3$ was measured in temperatures 163 K, 182 K, 197.5 K, and 217 K.

2. Spin-lattice relaxation

We consider the system of three fluorine nuclei of spin $I_i = \frac{1}{2}$ in $^{10}\text{BF}_3$ molecule which belongs to D_{3h} point group symmetry. The calculations were performed in the representation

$$|I_{12}I_3Im\rangle = \sum_{\substack{m_1, m_2, \\ m_3}} |m_1 m_2 m_3\rangle (I_1 I_2 m_1 m_2 | I_{12} m_{12}) (I_{12} I_3 m_{12} m_3 | Im) \quad (2)$$

where

$$I_{12} = I_1 + I_2, \quad I = I_{12} + I_3, \quad m_{12} = m_1 + m_2, \quad m = m_{12} + m_3 \quad (3)$$

as in paper IV. The correlation functions of the spherical harmonics (which we need to know to calculate the correlation matrix $P_{\alpha\beta\alpha'\beta'}(\tau) = \langle G_{\alpha\beta}(t)G_{\alpha'\beta'}^\dagger(t-\tau) \rangle$) may be expressed in terms of Legendre's polynomial of the second order $P_2(\cos \beta)$. It is assumed that for fluorine nuclei the tensor of the electronic screening has axial symmetry and principal axis Z_i is parallel to the C_2 symmetry axis of the molecule.

The angles β between the internuclear directions r_{ij} are equal to $0, \pm\frac{1}{3}\pi, \pm\frac{2}{3}\pi$, the angles β between the symmetry axes Z_i of the screening tensor for different nuclei are $0, \pm\frac{2}{3}\pi, \pm\frac{4}{3}\pi$, and the angles between different directions r_{ij} and Z_i are $\pm\frac{1}{6}\pi, \pm\frac{1}{2}\pi$.

After appropriate calculations we obtained the system of the differential equations describing the relaxation processes in liquid $^{10}\text{BF}_3$. In the extreme narrowing case $\omega_0\tau_c \ll 1$ one gets:

$$\frac{dx_i(t)}{dt} = \frac{9}{20T_0} \sum_j a_{ij}(\varepsilon)x_j(t), \quad (i, j = 1, \dots, 6), \quad (4)$$

$$\left. \begin{aligned} T_0 &= d^{-2}\tau_c^{-1}, \\ \varepsilon &= \omega_0\Delta\sigma_F d^{-1}, \end{aligned} \right\} \quad (5)$$

where d is the dipolar constant, τ_c correlation time for molecular reorientations, ω_0 is the angular frequency of Larmor precession, and matrix elements $a_{ij}(\varepsilon)$ are expressed in terms of the secular elements of the relaxation matrix $R_{\alpha\alpha'\beta\beta'}$. The values $x_i(t)$ are the linear combinations of diagonal elements of the density matrix $\tilde{\sigma}_{\alpha\alpha'}(t) = \sigma_{\alpha\alpha'}(t) - \sigma_{\alpha\alpha'}^T$,

where $\sigma_{\alpha\alpha}^T$ are the matrix elements at thermal equilibrium in temperature T

$$\begin{aligned}x_1(t) &= \tilde{\sigma}_{11}, \\x_2(t) &= \tilde{\sigma}_{22}, \\x_3(t) &= \frac{1}{\sqrt{2}}(\tilde{\sigma}_{33} + \tilde{\sigma}_{44}), \\x_4(t) &= \frac{1}{\sqrt{2}}(\tilde{\sigma}_{66} + \tilde{\sigma}_{77}), \\x_5(t) &= \tilde{\sigma}_{55}, \\x_6(t) &= \tilde{\sigma}_{88}.\end{aligned}\tag{6}$$

The coefficients $a_{ij}(\varepsilon)$ are

$$a_{ij}(\varepsilon) = a_{ji}(\varepsilon),\tag{7}$$

$$a_{ij}(\varepsilon) = a_{7-j,7-i}(-\varepsilon),\tag{8}$$

$$\eta = \frac{2^0}{9} T_0,\tag{9}$$

$$a_{11}(\varepsilon) = \eta R_{1111} = -\left(\frac{2^3}{4} - \frac{5}{3}\varepsilon + \frac{4}{9}\varepsilon^2 + 5\beta_0\right),$$

$$a_{22}(\varepsilon) = \eta R_{2222} = -\left(\frac{2^3}{4} + \frac{5}{3}\varepsilon + \frac{2}{3}\varepsilon^2 + \frac{3^5}{3}\beta_0\right),$$

$$a_{33}(\varepsilon) = \eta(R_{3333} + R_{3344}) = -\left(\frac{1^5}{4} - \frac{1}{3}\varepsilon + \frac{17}{27}\varepsilon^2 + \frac{5}{3}\beta_0\right),$$

$$a_{12}(\varepsilon) = \eta R_{1122} = 1 - \frac{2}{3}\varepsilon + \frac{1}{9}\varepsilon^2 + 5\beta_0,$$

$$a_{13}(\varepsilon) = \eta \sqrt{2} R_{1133} = \sqrt{2} \left(\frac{3}{8} - \frac{1}{2}\varepsilon + \frac{1}{6}\varepsilon^2\right),$$

$$a_{14}(\varepsilon) = \eta \sqrt{2} R_{1166} = \frac{3}{2} \sqrt{2},$$

$$a_{15}(\varepsilon) = \eta R_{1155} = 1,$$

$$a_{16}(\varepsilon) = \eta R_{1188} = 0,$$

$$a_{23}(\varepsilon) = \eta \sqrt{2} R_{2233} = \sqrt{2} \left(\frac{3}{4} + \frac{2}{3}\varepsilon + \frac{4}{27}\varepsilon^2\right),$$

$$a_{24}(\varepsilon) = \eta \sqrt{2} R_{2266} = \sqrt{2} \left(\frac{9}{8} + \frac{1}{2}\varepsilon + \frac{1}{18}\varepsilon^2\right),$$

$$a_{25}(\varepsilon) = \eta R_{2255} = \frac{4}{27}\varepsilon^2 + \frac{2^0}{3}\beta_0,$$

$$a_{34}(\varepsilon) = \eta(R_{3366} + R_{4466}) = \frac{7}{27}\varepsilon^2 + \frac{5}{3}\beta_0,\tag{10}$$

$$\beta_0 = \left(\frac{1}{T_1}\right)_{\text{SR}} / \left(\frac{3}{2T_0}\right),\tag{11}$$

where $(1/T_1)_{SR}$ is the spin-rotational contribution to the fluorine relaxation rate. The initial conditions for the values $x_i(t)$ are determined after $\pi/2$ pulse which gives the initial nuclear longitudinal magnetization $M_z(0) = 0$.

$$x(0) = -\frac{\hbar\omega_0}{16kT} \delta, \quad (12)$$

$$\delta = (3, 1, \sqrt{2}, -\sqrt{2}, -1, -3). \quad (13)$$

The expectation value of the longitudinal nuclear magnetization can be expressed as

$$M_z(t) - M_0 = \frac{1}{2} N\gamma\hbar\delta \cdot x(t), \quad (14)$$

where N is the number of molecules per unit volume. The solution of the equations (4) (Blicharski, Nosel 1970) may be presented in the form

$$x_i(t) = \sum_{j=1}^6 d_{ij} e^{-\frac{9}{20T_0} \tilde{\lambda}_j t}, \quad (15)$$

whence

$$M_z(t) - M_0 = (M_z(0) - M_0) \sum_{i=1}^6 c_i e^{-\frac{\tilde{\lambda}_i t}{T_1}}, \quad (16)$$

$$\sum_{i=1}^6 c_i = \sum_{i=1}^6 c_i \lambda_i = 1, \quad (17)$$

$$\frac{1}{T_1} = \left(\frac{1}{T_1}\right)_d \left(2 + \frac{4}{45} \varepsilon^2 + \beta_0\right). \quad (18)$$

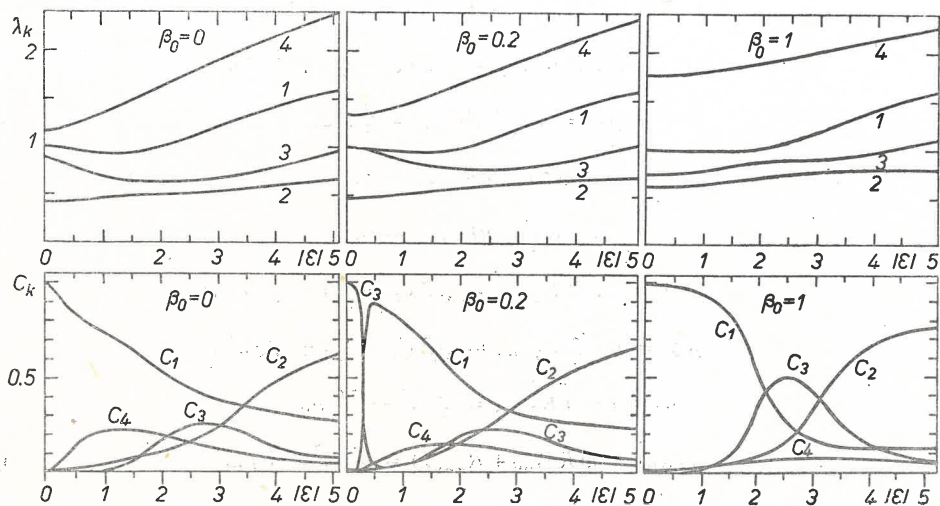


Fig. 1. Calculated values of λ_k and c_k as a function ε for $\beta_0 = 0, 0.2, 1$ for longitudinal magnetization in liquid $^{10}\text{BF}_6$.

The numerical solution of this problem was performed by the method described in paper IV. The calculated values of the amplitudes $c_i(\varepsilon)$, β_0 and eigenvalues $\lambda_i(\varepsilon, \beta_0)$ as a function of ε for several values of β_0 are shown in Fig. 1. According to the numerical results presented in Fig. 2, the longitudinal magnetization is equal to the linear combination of four exponential functions. It is a characteristic feature of the interference effect that for a given value of ε there occurs the maximum deviation from single exponential decay. In Fig. 2 the time

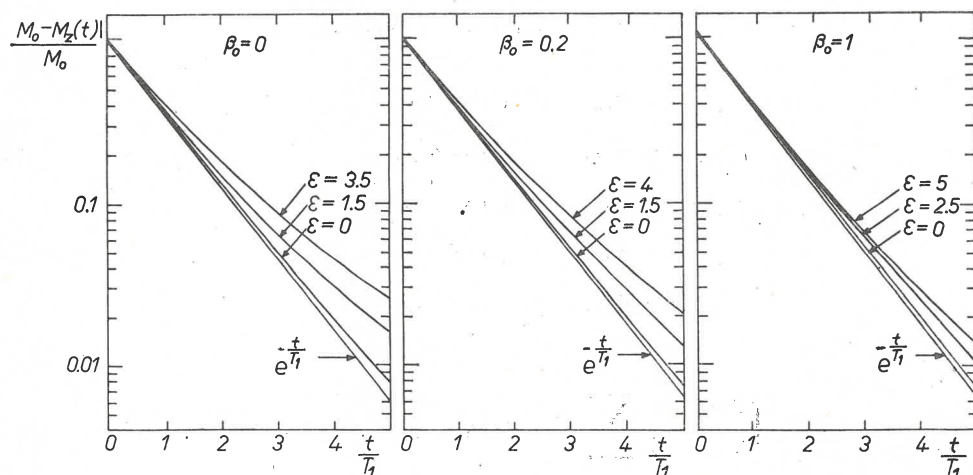


Fig. 2. Time dependence of longitudinal nuclear magnetization in liquid $^{10}\text{BF}_3$ for different ε and β_0 values

dependence of $(M_0 - M_z(t))/M_0$ for different values of ε and β_0 are shown e.g. for $\varepsilon = 3.5$, 4, 5 and $\beta_0 = 0, 0.2, 1$ respectively. For the mentioned values ε the deviations of the nuclear magnetization from single exponential decays are maximal ones. The relative deviation of the magnetization for $\varepsilon = 3.5$, $\beta_0 = 0$ from its value for $\varepsilon = 0$, $\beta_0 = 0$ in the time $t = 4T_1$ is equal to 60 per cent.

3. Spin-spin relaxation

In the "coupled" representation $|I_{12}I_3Im\rangle$ we have the following non-vanishing elements of the operators $I_{\pm} = I_x \pm iI_y$

$$\begin{aligned} (I_+)_{12} &= (I_+)_{58} = \sqrt{3}, \\ (I_+)_{36} &= (I_+)_{47} = -1, \\ (I_+)_{25} &= 2, \\ (I_-)_{\alpha\beta} &= (I_+)_{\beta\alpha}, \end{aligned} \quad (19)$$

and the expectation value of the corresponding component of magnetization $M_-(t) = M_x(t) - iM_y(t)$ in the interaction representation is

$$M_-^*(t) = N\gamma\hbar[\sqrt{3}(\tilde{\sigma}_{12}^*(t) + \tilde{\sigma}_{58}^*(t)) + 2\tilde{\sigma}_{25}^*(t) - (\tilde{\sigma}_{36}^*(t) + \tilde{\sigma}_{47}^*(t))]. \quad (20)$$

In the considered spin-system one finds fifteen transitions with $\Delta m = +1$ between the eigenstates of the Zeeman Hamiltonian G_0 and in consequence one gets the system of fifteen differential equations. However, the transversal magnetization may be expressed as the sum of five exponential functions. Introducing the following values

$$\begin{aligned}
 y_1^*(t) &= \tilde{\sigma}_{12}^*, & y_8^*(t) &= \tilde{\sigma}_{36}^*, \\
 y_2^*(t) &= \tilde{\sigma}_{13}^*, & y_9^*(t) &= \frac{1}{\sqrt{2}}(\tilde{\sigma}_{37}^* + \tilde{\sigma}_{46}^*), \\
 y_3^*(t) &= \tilde{\sigma}_{14}^*, & y_{10}^*(t) &= \tilde{\sigma}_{45}^*, \\
 y_4^*(t) &= \tilde{\sigma}_{25}^*, & y_{11}^*(t) &= \tilde{\sigma}_{47}^*, \\
 y_5^*(t) &= \tilde{\sigma}_{26}^*, & y_{12}^*(t) &= \tilde{\sigma}_{58}^*, \\
 y_6^*(t) &= \tilde{\sigma}_{27}^*, & y_{13}^*(t) &= \tilde{\sigma}_{68}^*, \\
 y_7^*(t) &= \tilde{\sigma}_{35}^*, & y_{14}^*(t) &= \tilde{\sigma}_{78}^*,
 \end{aligned} \tag{21}$$

we obtain

$$\frac{dy_j^*(t)}{dt} = \frac{1}{T_0} \sum_j a'_{ij}(\varepsilon) y_j^*(t), \quad (i, j = 1, \dots, 14), \tag{22}$$

where the initial condition after $\pi/2$ pulse is given by

$$\mathbf{y}^*(0) = -\frac{\hbar\omega_0}{16kT} \boldsymbol{\delta}', \tag{23}$$

$$\boldsymbol{\delta} = (\sqrt{3}, 0, 0, 2, 0, 0, 0, -1, 0, 0, -1, \sqrt{3}, 0, 0). \tag{24}$$

The transversal magnetization may be expressed by $\mathbf{y}^*(t)$ in the form

$$M_{\perp}^*(t) = N\gamma\hbar\boldsymbol{\delta}' \cdot \mathbf{y}^*(t). \tag{25}$$

Finally, after solution of the Eqs (22), the amplitude of the transversal magnetization $M_{\perp}(t) = |M_{\perp}^*(t)|$ may be presented by the following expression

$$M_{\perp}(t) = M_{\perp}(0) \sum_{i=1}^{14} c'_i e^{-\lambda'_i \frac{t}{T_2}}, \tag{26}$$

$$\sum_{i=1}^{14} c'_i = \sum_{i=1}^{14} c'_i \lambda'_i = 1, \tag{27}$$

$$\frac{1}{T_2} = \left(\frac{1}{T_2} \right)_d \left(2 + \frac{14}{135} \varepsilon^2 + \beta_0 \right). \tag{28}$$

The diagrams in Fig. 3, show numerical results for the coefficients $c'_i(\varepsilon, \beta_0)$, $\lambda'_i(\varepsilon, \beta_0)$ as a function ε for a different value of the parameters β_0 . In Fig. 4 is presented the time

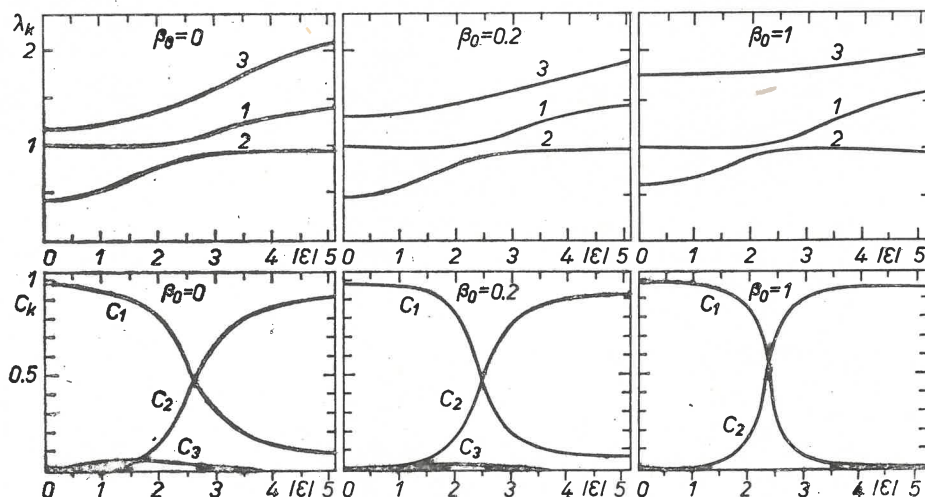


Fig. 3. Calculated values of λ'_k and c'_k as a function ϵ for $\beta_0 = 0, 0.2, 1$ for transversal magnetization in liquid $^{10}\text{BF}_3$

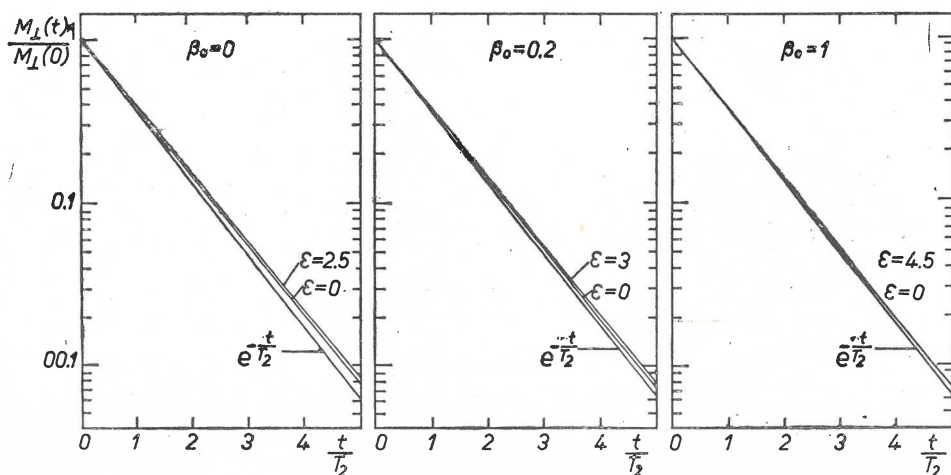


Fig. 4. Time dependence of transversal nuclear magnetization in liquid $^{10}\text{BF}_3$ for different ϵ and β_0 values

dependence of the $M_{\perp}(t)$ in the case of maximal deviation from the single exponential decay for $\epsilon = 2.5, 3, 4.5$ and $\beta_0 = 0, 0.2, 1$ respectively. One may note that the predicted deviations are very small. For example, the relative deviation from single exponential decay after the time $t = 4T_2$ for $\epsilon = 2.5$ and $\beta_0 = 0$ is equal to 3.5 per cent.

4. Experimental

Boron trifluoride has the following characteristic constants (Kirk, Othmer): melting point 145.9 K, boiling point 172.7 K, critical temperature 260.75 K, critical pressure 49.2 atm. The sample was prepared using $^{10}\text{BF}_3$ where ^{10}B was enriched to 90 per cent.

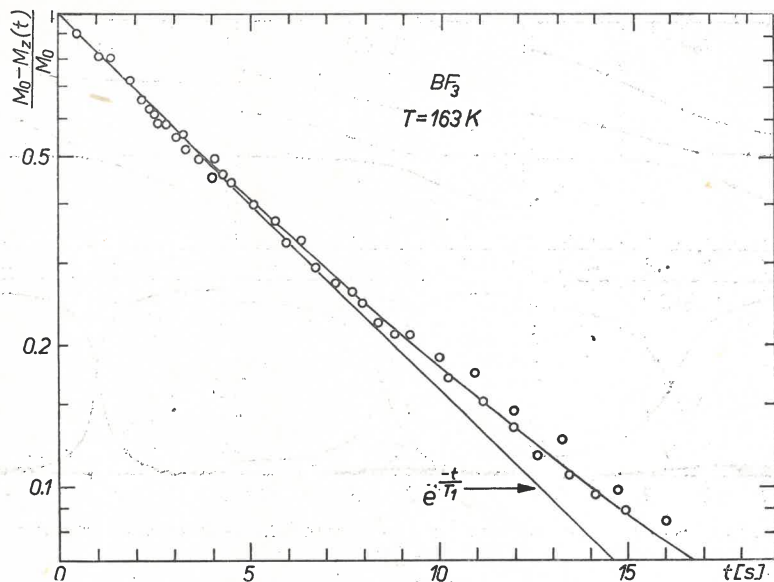


Fig. 5. Experimental time dependence of longitudinal magnetization for fluorine nuclei in liquid $^{10}\text{BF}_3$ in temperature 163 K, where $T_1 = 5.8$ s

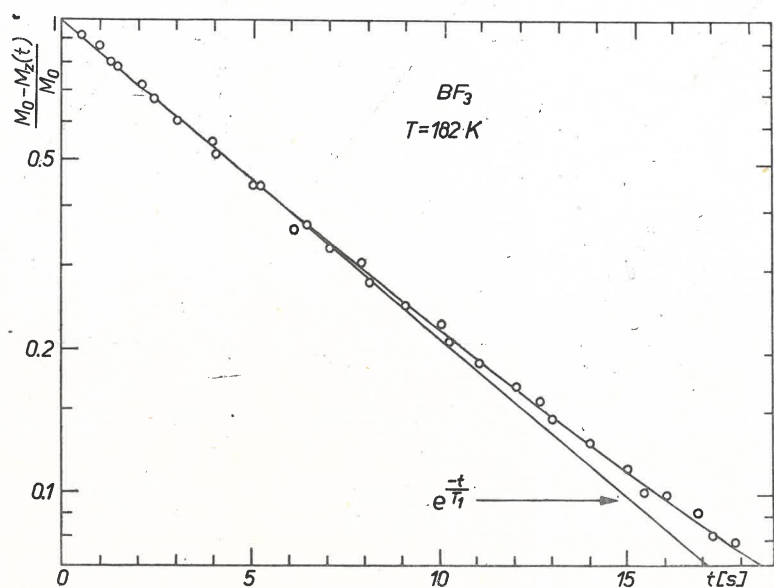


Fig. 6. Experimental time dependence of longitudinal magnetization for fluorine nuclei in liquid $^{10}\text{BF}_3$ in temperature 182 K, where $T_1 = 6.5$ s

The oxygen was removed by freeze-pump-thaw technique (below 10^{-3} mmHg). The method given by Hennel and Hryniewicz (1958) was used for time dependence of the longitudinal magnetization, and T_1 measurements at 28 MHz. The temperature

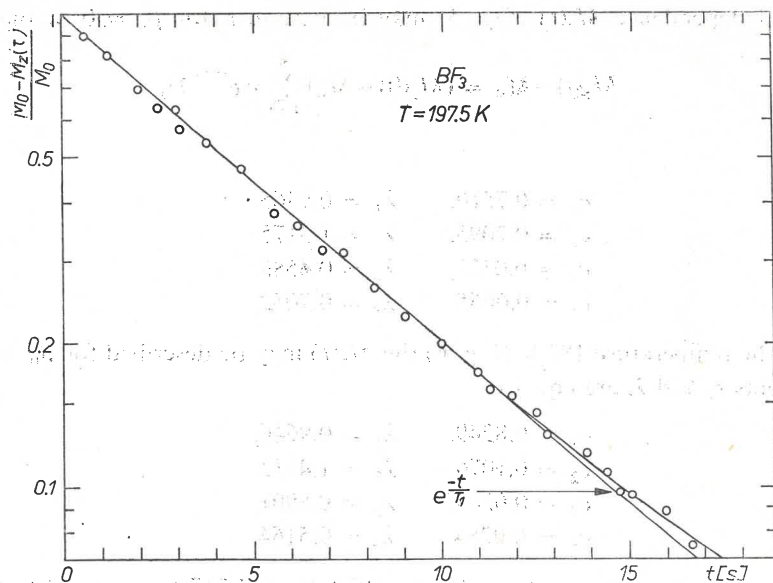


Fig. 7. Experimental time dependence of longitudinal magnetization for fluorine nuclei in liquid $^{10}\text{BF}_3$ in temperature 197.5 K, where $T_1 = 6.7$ s

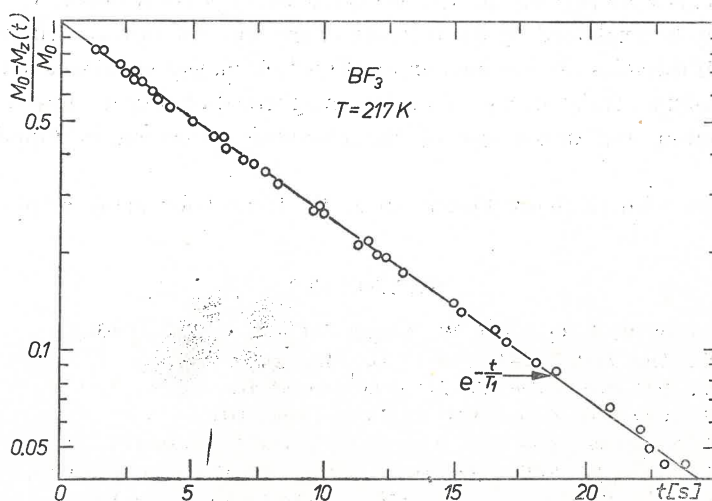


Fig. 8. Experimental time dependence of longitudinal magnetization for fluorine nuclei in liquid $^{10}\text{BF}_3$ in temperature 217 K, where $T_1 = 7.5$ s

stability was of the order 0.1 K. The accuracy of T_1 measurements was below 10 per cent. The time dependence of longitudinal magnetization in temperatures 163 K, 182 K, 197.5 K and 217 K was measured (Figs 5, 6, 7, 8). By fitting by the least squares method (using the computer) the theoretical results to the experimental ones one can find that $\varepsilon = 0.9 \pm 0.2$ whence $|\Delta\sigma_F| = 300 \pm 70$ ppm. In the temperature 163 K, $T_1 = 5.8$ s and the

experimental dependence $M_z(t)$ (Fig. 5) may be described for $\beta_0 = 0$ in the form

$$M_z(t) - M_0 = (M_z(0) - M_0) \sum_{i=1}^4 c_i e^{-\lambda_i \frac{t}{T_1}}, \quad (29)$$

where

$$\begin{aligned} c_1 &= 0.7510, & \lambda_1 &= 0.9365, \\ c_2 &= 0.2095, & \lambda_2 &= 1.3175, \\ c_3 &= 0.0322, & \lambda_3 &= 0.4583, \\ c_4 &= 0.0065, & \lambda_4 &= 0.7052, \end{aligned} \quad (30)$$

whereas in the temperature 182 K (Fig. 6) the $M_z(t)$ may be described for $\beta_0 = 0.2$ where the coefficients c_i and λ_i are equal to

$$\begin{aligned} c_1 &= 0.8249, & \lambda_1 &= 0.9646, \\ c_2 &= 0.1076, & \lambda_2 &= 1.4332, \\ c_3 &= 0.0383, & \lambda_3 &= 0.8901, \\ c_4 &= 0.0284, & \lambda_4 &= 0.5164. \end{aligned} \quad (31)$$

The relaxation times in temperatures 182 K, 197.5 K, and 217 K are equal to 6.5 s, 6.7 s, and 7.5 s respectively. One can see from Figs 7 and 8 that in temperatures 197.5 K and 217 K the relaxation has an exponential character in the time from 0 up to $3T_1$ where the measurements were performed. The observed effect is conformable to the presented theory and may be explained by the increase of the spin-rotation contribution in higher temperatures. If the spin-rotation interaction (Figs 5, 6) plays a small role in the relaxation process, a non-exponential decay of nuclear magnetization due to interference dipole-dipole interaction and anisotropy of the electronic screening in liquid $^{10}\text{BF}_3$ can be registered.

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