Spin Diffusion in Pure Multiple-Pulse NQR

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We present a detailed theoretical and experimental NQR multiple-pulse spin-locking study of spin-lattice relaxation and spin diffusion processes in the presence of paramagnetic impurities in solids. The obtained diffusion equation was obtained allows to find the time dependence of the magnetization in the effective field. The spin lattice relaxation times were calculated, both for direct and diffusion regimes, as functions of the correlation time and multiple-pulse parameters. Measurements of relaxation times in rotating frame allow to determine the diffusion coefficient and the radius of the diffusion barrier in γ-irradiated polycrystalline samples of $NaClO_3$.

Key words: NQR; Paramagnetic Impurities; Spin Diffusion.

1. Introduction

In the present paper both spin lattice relaxation and spin diffusion processes in γ-irradiated polycrystalline samples of $NaClO_3$ were studied by multiple-pulse spin-locking technique. The analysis of the nuclear magnetization decays for various concentrations of PI allows to distinguish between the direct relaxation regime and the diffusion relaxation regime and to determine coefficients of spin-diffusion for the NQR-case.

2. Theory

2.1. System Hamiltonian

The evolution of the spin system, consisting of nuclear spins $I > 1/2$ and Paramamagnetic Impurity (PI) spins $1/2$, influenced by the external multiple-pulse r. f. magnetic field acting only on nuclear spins, may be described by a solution of the equation for the density matrix $\rho(t)$ (in units of $\hbar = 1$)

$$i\frac{\mathrm{d}\rho(t)}{\mathrm{d}t} = [\mathcal{H}(t), \rho(t)] \tag{1}$$

with the Hamiltonian

$$\mathcal{H}(t) = \mathcal{H}_\mathrm{Q} + \mathcal{H}_\mathrm{dd} + \mathcal{H}_\mathrm{PI} + \mathcal{H}_\mathrm{P} + \mathcal{H}_\mathrm{br}(t) + \mathcal{H}_\mathrm{r.f.}(t)\,. \tag{2}$$

Here $\mathcal{H}_\mathrm{Q}$ is the interaction of the I-spin system with the EFG; $\mathcal{H}_\mathrm{dd}$ and $\mathcal{H}_\mathrm{PI}$ are the Hamiltonians of the dipole-dipole interaction of nuclear spins and nuclear with PI spins, respectively; $\mathcal{H}_\mathrm{P}$ describes the impurity spin system; $\mathcal{H}_\mathrm{br}(t) = \sum_{q=-2}^{2} E^{(-q)}(t)\, A^q$, the spin-lattice interaction Hamiltonian, describes the spin-lattice relaxation caused by torsional vibrations (Bayer mechanism) [1], where A^q is a bilinear function of the spin operators and $E^{(-q)}(t)$ is a random function of time [2]. $\mathcal{H}_\mathrm{r.f.}(t)$ gives the action of the r. f. field on the nuclear spin system.

Using the projection operators e^{μ}_{mn} and ε^{j}_{mn} defined by their matrix elements $\langle m^{'} | e^{\mu}_{mn} | n^{'} \rangle = \delta_{m^{\prime}m}\delta_{n^{\prime}n}$ and $\langle \nu^{'} | \varepsilon^{\mu}_{\nu\sigma} | \sigma^{'} \rangle = \delta_{\nu^{\prime}\nu}\delta_{\sigma^{\prime}\sigma}$, $|m\rangle$ and $|\nu\rangle$ are eigenvectors of the operators $\mathcal{H}_\mathrm{Q}$ and $\mathcal{H}_\mathrm{P}$, respectively. Introducing a projection density operators, $e_{mn}(\boldsymbol{r})$, for the nuclear spins I, and $\varepsilon_{mn}(\boldsymbol{r})$ for PI spins,

$$\begin{aligned} e_{mn}(\boldsymbol{r}) &= \sum_{\mu} \delta\left(\boldsymbol{r} - \boldsymbol{r}_\mu\right) e^{\mu}_{mn}; \\ \varepsilon_{mn}(\boldsymbol{r}) &= \sum_{j} \delta\left(\boldsymbol{r} - \boldsymbol{r}_j\right) \varepsilon^{j}_{mn} \end{aligned} \tag{3}$$

the density of the Hamiltonians $\mathcal{H}_\mathrm{Q}$, $\mathcal{H}_\mathrm{dd}$, and $\mathcal{H}_\mathrm{PI}$ can be written in the form

$$\mathcal{H}_\mathrm{Q}(\boldsymbol{r}) = (2I+1)^{-1} \sum_{mn} \omega^{0}_{mn} e_{mm}(\boldsymbol{r})\,, \tag{4}$$

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$$\mathcal{H}_{\mathrm{dd}}(\boldsymbol{r}) = \int \mathrm{d}\boldsymbol{r}' \sum_{mnm'n'} G_{mn}^{m'n'}(\boldsymbol{r}-\boldsymbol{r}') \cdot e_{mn}(\boldsymbol{r})\, e_{m'n'}(\boldsymbol{r}'), \tag{5}$$

$$\mathcal{H}_{\mathrm{PI}}(\boldsymbol{r}) = \int \mathrm{d}\boldsymbol{r}' \sum_{mnm'n'} F_{mn}^{m'n'}(\boldsymbol{r}-\boldsymbol{r}') \cdot e_{mn}(\boldsymbol{r})\, \varepsilon_{m'n'}(\boldsymbol{r}'), \tag{6}$$

where $\omega_{mn}^0 = \lambda_m - \lambda_n$, λ_m is the eigenvalue of the operator $\mathcal{H}_{\mathrm{Q}}$; $G_{mn}^{m'n'}$ and $F_{mn}^{m'n'}$ are matrix elements of the dipole-dipole Hamiltonians $\mathcal{H}_{\mathrm{dd}}$ and $\mathcal{H}_{\mathrm{PI}}$ in $\mathcal{H}_{\mathrm{Q}}$-representation [3].

$$\mathcal{H}_{\mathrm{br}}(t) = \sum_q \sum_{mn} E^{(-q)}(t)\, A_{mn}^q \int \mathrm{d}\boldsymbol{r}\, e_{mn}(\boldsymbol{r}), \tag{7}$$

$$\mathcal{H}_{\mathrm{r.f.}}(t) = \omega_1(t) \cos(\omega t + \phi) \sum_{mn} (\boldsymbol{a} \cdot \boldsymbol{I})_{mn} \cdot \int \mathrm{d}\boldsymbol{r}\, e_{mn}(\boldsymbol{r}), \tag{8}$$

where ω is the applied frequency, $\omega_1(t) = \vartheta_0 \delta(t)$ and $\phi = 0$ for the preparatory pulse, and $\omega_1(t) = \vartheta \sum_{k=0}^{\infty} \delta[t - (k + \frac{1}{2})\, t_{\mathrm{c}}]$ and $\phi = \pi/2$ for the remaining pulses, $\vartheta = \gamma H_1 t_w$, H_1 and t_w are the amplitude and pulse duration of the r. f. pulses ; t_{c} is the period of the multiple-pulse sequence; $\boldsymbol{a}$ is a unit vector directed along the r. f. field, and γ is the gyromagnetic ratio of the nuclear spins.

The action of a periodic radiofrequency pulse field on a nuclear spin system consists of a preparatory (first) pulse taking the spin system out of equilibrium and a multiple-pulse sequence which leads to fast oscillating terms in the Hamiltonian. It can be shown in a way analogous to that used in [3] that by using the unitary transformation, these fast oscillating terms can be removed. In this case the sum $\mathcal{H}_{\mathrm{Q}} + \mathcal{H}_{\mathrm{r.f}}$ in (2) can be replaced by the operator $\boldsymbol{\omega}_{\mathrm{e}} \boldsymbol{S}$ ($\boldsymbol{S}$ is the effective spin operator) if $\boldsymbol{\omega}_{\mathrm{e}} = \omega_{\mathrm{e}} \boldsymbol{a}$ is defined as

$$\cos(\omega_{\mathrm{e}} t_{\mathrm{c}}/2) = \cos(\vartheta/2) \cos(\Delta t_{\mathrm{c}}/2) \tag{9}$$

and

$$a_1 = \sin(\vartheta/2) / \sin(\omega_{\mathrm{e}} t_{\mathrm{c}}/2)\,;\, a_2 = 0; \quad a_3 = \cos(\vartheta/2) \sin(\Delta t_{\mathrm{c}}/2) / \sin(\omega_{\mathrm{e}} t_{\mathrm{c}}/2)\,. \tag{10}$$

Here Δ is the off set. After the unitary transformation, the Hamiltonian of the spin system can be presented as

$$\mathcal{H}(t) = \int \mathrm{d}\boldsymbol{r} \mathcal{H}(\boldsymbol{r}, \omega_{\mathrm{e}}, t) \tag{11}$$

where

$$\mathcal{H}(\boldsymbol{r}, \omega_{\mathrm{e}}, t) = \omega_{\mathrm{e}}(\boldsymbol{a}\boldsymbol{S}) + \mathcal{H}_{\mathrm{d}}(\boldsymbol{r}) + \mathcal{H}_{\mathrm{PI}}(\boldsymbol{r}, \omega_{\mathrm{e}}, t) + \mathcal{H}_{\mathrm{IL}}(\boldsymbol{r}, \omega_{\mathrm{e}}, t), \tag{12}$$

$$\mathcal{H}_{\mathrm{d}}(\boldsymbol{r}) = \sum_{l=-2}^{2} \int \mathrm{d}\boldsymbol{r}' \sum_{mnm'n'} g_{mn}^{m'n'}(\boldsymbol{r}-\boldsymbol{r}') \cdot K_{mn}^l(\boldsymbol{r})\, K_{m'n'}^{-l}(\boldsymbol{r}'), \tag{13}$$

$$\mathcal{H}_{\mathrm{PI}}(\boldsymbol{r}, \omega_{\mathrm{e}}, t) = \sum_{l=-1}^{1} \int \mathrm{d}\boldsymbol{r}' \sum_{mnm'n'} f_{mn}^{m'n'}(\boldsymbol{r}-\boldsymbol{r}') \cdot e^{-il\omega_{\mathrm{e}} t} \chi_l(t)\, K_{mn}^l(\boldsymbol{r})\, \varepsilon_{m'n'}(\boldsymbol{r}'), \tag{14}$$

$$\mathcal{H}_{\mathrm{IL}}(\boldsymbol{r}, \omega_{\mathrm{e}}, t) = \sum_{l=-1}^{1} \sum_q \sum_{mn} E^{(-q)} A_{mn}^q(\boldsymbol{r}-\boldsymbol{r}') \cdot e^{-il\omega_{\mathrm{e}} t} e^{-i\omega_{mn}} \chi_l(t)\, K_{mn}^l(\boldsymbol{r}), \tag{15}$$

$$\chi_l(t) = \sum_{n=-\infty}^{\infty} \chi_l^n e^{-i\omega_n t}; \omega_n = \frac{2\pi n}{t_{\mathrm{c}}}, \tag{16}$$

$$\chi_l^n = \frac{(-1)^n \sin(l\omega_{\mathrm{e}} t_{\mathrm{c}}/2)}{2\pi n + l\omega_{\mathrm{e}} t_{\mathrm{c}}}, \tag{17}$$

$$g_{mn}^{m'n'} = G_{mn}^{m'n'} \left[(\delta_{mn} + \delta_{m\bar{n}})(\delta_{m'n'} + \delta_{m'\bar{n}'}) + (\delta_{mn'} + \delta_{m\bar{n}'})(\delta_{m'n} + \delta_{m'\bar{n}}) \right], \tag{18}$$

$$f_{mn}^{m'n'} = F_{mn}^{m'n'} (\delta_{mn} + \delta_{m\bar{n}})(\delta_{m'n'} + \delta_{m'\bar{n}'}) \tag{19}$$

The expression of the operator $K_{mn}^l(\boldsymbol{r})$ is rather complicated, and we restrict ourselves to putting down only the commutation law: $[(\boldsymbol{a}\boldsymbol{S}), K_{mn}^l(\boldsymbol{r})] = lK_{mn}^l(\boldsymbol{r})$.

2.2. *Spin Diffusion Equation*

To obtain the evolution equation we will use the method of non-equilibrium state operator [4] which has been originally applied to the spin diffusion in NMR [5]. The diffusion equation can be obtained by

$$\frac{\partial \beta_{\mathrm{e}}(\boldsymbol{r},t)}{\partial t} = \left(D\Delta - T_{1\rho}^{-1}(\boldsymbol{r})\right)\left(\beta_{\mathrm{e}}(\boldsymbol{r},t) - \beta_{\mathrm{L}}\right) \tag{20}$$

with the boundary condition

$$\nabla \beta_{\mathrm{e}}(r,t)\,|_{r=b} = 0, \tag{21}$$

where b is the radius of the diffusion barrier [6], within which the spin diffusion process is quenched. Here it is worthwhile to mention that for the NQR-case distortions of the crystal field (as a result of the inclusion of the PI) should be also taken into account. It results in additional electrical diffusion barriers [7] of order $\sim r_0(Ze^2Q\zeta/\gamma\hbar^2)^{1/4}$, here r_0 is the distance between neighboring nuclei, ζ the Sternheimer antishielding factor [8], and the distortion of the electric field was assumed to be equivalent to the presence of a charge Ze [7]. The first term on the right side of (20) describes the spin the diffusion process with diffusion coefficient

$$\begin{aligned} D = \int \mathrm{d}\boldsymbol{r}' \sum_{l=-1}^{1} l^2 \left(\boldsymbol{r}-\boldsymbol{r}'\right)^2 \sum_{mnm'n'} g_{mn}^{m'n'}\left(\boldsymbol{r}-\boldsymbol{r}'\right) \\ \cdot \sum_{pqp'q'} g_{pq}^{p'q'}\left(\boldsymbol{r}-\boldsymbol{r}'\right) \\ \cdot \left\langle K_{mn}^{l}(\boldsymbol{r}) K_{p'q'}^{-l}(\boldsymbol{r}) K_{m'n'}^{l}(\boldsymbol{r}') K_{pq}^{-l}(\boldsymbol{r}')\right\rangle / \mathrm{Tr}(\boldsymbol{a}\cdot\boldsymbol{S})^2, \end{aligned} \tag{22}$$

and the second term gives the variation of $\beta_{\mathrm{e}}(\boldsymbol{r},t)$ due to the direct relaxation to PI with relaxation time $T_{\mathrm{PI}}(\boldsymbol{r})$, and to the lattice with $T_{1\mathrm{L}}(\boldsymbol{r})$:

$$T_{1\rho}^{-1}(\boldsymbol{r}) = T_{1\mathrm{PI}}^{-1}(\boldsymbol{r}) + T_{1\mathrm{L}}^{-1}(\boldsymbol{r}), \tag{23}$$

where

$$T_{1\mathrm{PI}}^{-1}(\boldsymbol{r}) = r^{-6}B(\boldsymbol{r}), \tag{24}$$

$$\begin{aligned} B(\boldsymbol{r}) = \omega_{\mathrm{e}}^2 \sum_{l=-1}^{1} l^2 \sum_{mn}\sum_{pq} P_{mn}^{pq}(\boldsymbol{r}) \\ \cdot \left\langle K_{mn}^{l}(\boldsymbol{r})\, K_{pq}^{-l}(\boldsymbol{r},t)\right\rangle / \mathrm{Tr}(\boldsymbol{a}\cdot\boldsymbol{S})^2, \end{aligned} \tag{25}$$

$$\begin{aligned} P_{mn}^{pq}(\boldsymbol{r}) = \int \mathrm{d}\boldsymbol{r}' \sum_{m'n'}\sum_{p'q'} f_{mn}^{m'n'}\left(\boldsymbol{r}-\boldsymbol{r}'\right) \\ \cdot f_{pq}^{p'q'}\left(\boldsymbol{r}-\boldsymbol{r}'\right) W_{m'n'}^{p'q'}\left(\boldsymbol{r}', l\omega_{\mathrm{e}}, t_{\mathrm{c}}\right), \end{aligned} \tag{26}$$

$$\begin{aligned} W_{m'n'}^{p'q'}\left(\boldsymbol{r}', l\omega_{\mathrm{e}}, t_{\mathrm{c}}\right) = \mathrm{Re}\sum_{n} \chi_l^n \chi_{-l}^n \\ \cdot J_{m'n'}^{p'q'}\left(\boldsymbol{r}', l\omega_{\mathrm{e}} - 2\pi n/t_{\mathrm{c}}\right). \end{aligned} \tag{27}$$

Here $J_{m'n'}^{p'q'}\left(\boldsymbol{r}',\omega\right)$ is spectral density of the impurity's spins correlation function

$$J_{m'n'}^{p'q'}\left(\boldsymbol{r}',\omega\right) = \int_{-\infty}^{\infty} \mathrm{d}\tau\, g_{m'n'}^{p'q'}\left(\boldsymbol{r}',\tau\right) e^{-i\omega\tau} \tag{28}$$

and $g_{m'n'}^{p'q'}\left(\boldsymbol{r}',\tau\right)$is the correlator of the impurity's spins thermal motion

$$g_{m'n'}^{p'q'}\left(\boldsymbol{r}',\tau\right) = \left\langle \varepsilon_{m'n'}\left(\boldsymbol{r}',t\right) \varepsilon_{p'q'}\left(\boldsymbol{r}',t-\tau\right) \right\rangle. \tag{29}$$

The spin lattice relaxation time $T_{1\mathrm{L}}^{-1}(\boldsymbol{r})$ determines the relaxation process due to the thermal modulation of the EFG:

$$\begin{aligned} T_{1\mathrm{L}}^{-1}(\boldsymbol{r}) = \sum_{l=-1}^{1} l^2 \sum_{mnm'n'}\sum_{\nu\nu'} \psi_{\nu\nu'}\left(\omega_{mn} - l\omega_{\mathrm{e}}\right) \\ \cdot A_{mn}^{\nu} A_{m'n'}^{\nu'} \left\langle K_{mn}^{l}(\boldsymbol{r}) K_{m'n'}^{-l}(\boldsymbol{r},t)\right\rangle / \mathrm{Tr}(\boldsymbol{a}\cdot\boldsymbol{S})^2. \end{aligned} \tag{30}$$

The dependence of $T_{1\mathrm{L}}^{-1}(\boldsymbol{r})$ on the pulse sequence parameters and the lattice motion characteristics is given by the function

$$\begin{aligned} \psi_{\nu\nu'}\left(\omega_{mn} - l\omega_{\mathrm{e}}\right) = \sum_{k} J_{\nu\nu'}\left(\omega_{mn} - \frac{2k\pi}{t_{\mathrm{c}}} - l\omega_{\mathrm{e}}\right) \\ \cdot A_{mn}^{q} A_{m'n'}^{q'} \chi_l^k \chi_{-l}^k, \end{aligned} \tag{31}$$

where

$$J_{\nu\nu'}(\omega) = \int_{-\infty}^{\infty} \mathrm{d}\tau\, g_{\nu\nu'}(\tau) \tag{32}$$

is the spectral density of the lattice thermal motion and

$$g_{\nu\nu'}(\tau) = \left\langle E^{(-\nu)}(t)\, E^{(-\nu')}(t-\tau)\right\rangle \tag{33}$$

is the correlator of the lattice motion.

The diffusion equation (20) describes the spin diffusion and the spin lattice relaxation via PI caused by torsional motion in the spin system with a multiple-level nonequidistant energy spectrum. Equation (20) has the same form as for the case of NMR [6] and differs from the latter only by the kinetic coefficients. Immediately after a disturbance of the nuclear spin system, there is no gradient of β_e, and diffusion is not of importance [9]. To describe the relaxation, we may use (20) without the first term, this is the so called direct relaxation regime [10]. Further, usually the spin-lattice relaxation in NQR in the absence of the PI is caused by thermal modulation of the electric field gradient (EFG) [1]. This relaxation mechanism is very effective, and it is reasonable to suppose that at low PI concentrations the influence of the PI should not be taken into account, which is implementing when $T_{1\mathrm{PI}}^{-1}(\boldsymbol{r}) \ll T_{1\mathrm{L}}^{-1}(\boldsymbol{r})$, and the character of the relaxation regime remains the same. In this case, the term which determines the direct relaxation via PI, can be neglected and the relaxation process can be described exponentially with the relaxations time $T_{1\mathrm{L}}^{-1} = \int \mathrm{d}\boldsymbol{r} T_{1\mathrm{L}}^{-1}(\boldsymbol{r})$. In the case of the exponential time dependence of the correlator

$$g_{\nu\nu'}(\tau) = \delta_{\nu\nu'} \left\langle E^{(\nu)2}(0) \right\rangle e^{-|t|/\tau_\nu}, \tag{34}$$

the function $\psi_\nu(\omega_{mn} - l\omega_\mathrm{e})$ is

$$\begin{aligned} \psi_\nu(\omega_{mn} - l\omega_\mathrm{e}) &= \tau_\nu \left\langle E^{(\nu)2}(0) \right\rangle \\ &\cdot \Bigg\{ \frac{1}{1+\tau_\nu^2\omega_{mn}^2} + \frac{2\omega_{mn}\tau_\nu^2 \sin\left(l\omega_\mathrm{e}t_\mathrm{c}/2\right)}{t_\mathrm{c}\left(1+\tau_\nu^2\omega_{mn}^2\right)^2} \\ &\quad - \tau_\nu t_\mathrm{c}[1-\cos\left(l\omega_\mathrm{e}t_\mathrm{c}/2\right)] \\ &\qquad \cdot \left[\left(1-\tau_\nu^2\omega_{mn}^2\right) \sinh\left(\frac{t_\mathrm{c}}{\tau_\nu}\right) + 2\omega_{mn}\tau_\nu \right. \\ &\qquad\qquad \left. \cdot \sin\left(\omega_{mn}t_\mathrm{c} - l\omega_\mathrm{e}t_\mathrm{c}/2\right) \right] \\ &\qquad \cdot \left[\left(1+\tau_\nu^2\omega_{mn}^2\right)^2 \left[\cosh\left(\frac{t_\mathrm{c}}{\tau_\nu}\right) \right.\right. \\ &\qquad\qquad \left.\left. - \cos\left(\omega_{mn}t_\mathrm{c} - l\omega_\mathrm{e}t_\mathrm{c}/2\right)\right]\right]^{-1} \Bigg\}, \end{aligned} \tag{35}$$

which gives the dependence of the relaxation time $T_{1\mathrm{L}}^{-1}$ on the correlation time τ_ν and the pulse sequence parameters t_c and ϑ.

In the presence of high PI concentration, at the beginning of the relaxation process (20) has the solution

$$\begin{aligned} \beta_\mathrm{e}(\boldsymbol{r},t) &= \beta_\mathrm{e}(\boldsymbol{r},\infty) \\ &+ [\beta_\mathrm{e}(\boldsymbol{r},0) - \beta_\mathrm{e}(\boldsymbol{r},0)] \exp\left(-\frac{t}{T_{1\rho}(\boldsymbol{r})}\right), \end{aligned} \tag{36}$$

where $\beta_\mathrm{e}(\boldsymbol{r},\infty)$ is the equilibrium local inverse temperature. Assuming that all local inverse temperatures are equal at the initial moment and in the equilibrium state, the value to be average is $R(\boldsymbol{r},t) = \left[\beta_\mathrm{e}(\boldsymbol{r},t) - \beta_\mathrm{e}(\boldsymbol{r},\infty)\right] / \left[\beta_\mathrm{e}(\boldsymbol{r},0) - \beta_\mathrm{e}(\boldsymbol{r},0)\right]$,the normalized local relaxation function. In the limit as the number of PI, $N_\mathrm{P} \to \infty$, a volume of sample, $V_\mathrm{L} \to \infty$, and $N_\mathrm{P}/V_\mathrm{L} = C_\mathrm{P}$, the PI concentration, we have [9, 11]

$$R(t) = \exp\left[-\frac{t}{T_{1\mathrm{L}}} - \left(\frac{t}{T_{1\mathrm{PI}}}\right)^\alpha\right], \tag{37}$$

where $\alpha = d/6$, d is the dimensionality of the sample, $T_{1\mathrm{L}}$ is the spin lattice relaxation time in the absence of PI, and

$$T_{1\mathrm{PI}}^{-1} = B \left[\frac{2\pi^{d/2}\Gamma\left(1-d/6\right)C_P}{\mathrm{d}\Gamma\left(d/2\right)}\right]^{6/d}. \tag{38}$$

Here $B = \langle B(\boldsymbol{r})\rangle_{\theta_{\mu\eta},\phi_{\mu\eta}}$ is an average over the spherical coordinates of the vector $\boldsymbol{r}_{\mu\eta}$, concerning the μ-th nuclear spin and η-th PI spin, and $\Gamma(x)$ is the Gamma function. The dependence of $T_{1\mathrm{PI}}^{-1}(\boldsymbol{r})$ on the pulse sequence parameters and the lattice motion characteristics is given by the function $W_{m'n'}^{p'q'}\left(\boldsymbol{r}', l\omega_\mathrm{e}, t_\mathrm{c}\right)$ in (27). To calculate the spectral density $J_{m'n'}^{p'q'}(\boldsymbol{r}',\omega)$ of the correlation function of the impurity spins, the correlator function $g_{m'n'}^{p'q'}(\boldsymbol{r}',\tau) = \left\langle \varepsilon_{m'n'}(\boldsymbol{r}',t)\varepsilon_{p'q'}(\boldsymbol{r}',t-\tau)\right\rangle$ is needed. We assume that in the high temperature approximation this correlation is exponential with a correlation time τ_c. This leads to

$$\begin{aligned} T_{1\mathrm{PI}} &\sim \tau_\nu \left\langle E^{(\nu)2}(0)\right\rangle \left\{1 - \frac{\tau_\nu}{t_\mathrm{c}}\left[1-\cos\left(l\omega_\mathrm{e}t_\mathrm{c}/2\right)\right]\right. \\ &\qquad \left. \cdot \frac{\sinh\left(t_\mathrm{c}/\tau_\nu\right)}{\left[\cosh\left(\frac{t_\mathrm{c}}{\tau_\nu}\right) - \cos\left(l\omega_\mathrm{e}t_\mathrm{c}/2\right)\right]}\right\}^{-1}. \end{aligned} \tag{39}$$

As the result of direct relaxation regime the local inverse temperature $\beta_\mathrm{e}(\boldsymbol{r},t)$ becomes spatially distributed over the sample. In this case we consider also the first term in the (20). To solve this equation and determine the time dependence we introduce the eigenfunctions $\varphi_n(\boldsymbol{r})$ of the operator $D\Delta - T_{1\rho}^{-1}(\boldsymbol{r})$ [12]. Assuming the spherical symmetry approximation, the general solution of (20) can be written as an expansion in terms of the ortogonal functions $\varphi_n(\boldsymbol{r})$ in the form

$$\beta_e(r,t) = \exp\left(-\frac{t}{T_{1L}(\boldsymbol{r})}\right) \tag{40}$$

$$\cdot \int \mathrm{d}r' \sum_n \exp\left(-k_n^2 Dt\right) \varphi_n(r)\, \tilde{\varphi}_n^\star(r'),$$

where the functions $\varphi_n(r)$ satisfy the equation

$$\Delta\varphi_n(r) - \left(T_{1PI}(r)/D\right)\varphi_n(r) = -k_n^2\varphi_n(r) \tag{41}$$

with the boundary condition

$$\nabla\varphi_n(r)\,|_{r=b} = 0. \tag{42}$$

Equation (41) is well know in the theory of scattering for the low energy limit [13]. It has an asymptotic solution $\varphi_n(r) \sim \sin(k_n r + \delta_n)/r$ for $r \gg b$, where $\delta_n \sim k_n\xi$ is the phase shift and ξ is the scattering length [13]. Taking into account the spherical symmetry (after the averaging over a polycrystalline sample) and using the boundary condition (42) we obtain [13]

$$\xi = \left(\frac{B}{D}\right)^{1/4} \frac{\Gamma(3/4)}{2\Gamma(5/4)}. \tag{43}$$

Using the last result, for the long time approximation, $t \gg b^2/D$, we obtain the normalized relaxation function for the diffusion-limited regime

$$R(t) = \exp\left(-\frac{t}{T_{1L}} - \frac{t}{T_{1D}}\right), \tag{44}$$

where

$$T_{1D} = \left[2\pi C_P D^{3/4} B^{1/4} \frac{\Gamma(3/4)}{\Gamma(5/4)}\right]^{-1}. \tag{45}$$

Under an assumption analogous to those in the case of the direct relation regime we obtain the dependence of T_{1D} on the pulse sequence parameters and correlation time

$$T_{1D} \sim \Big\{\tau_\nu \left\langle E^{(\nu)2}(0)\right\rangle \{1 - \frac{\tau_\nu}{t_c}\left[1 - \cos\left(l\omega_e t_c/2\right)\right] \tag{46}$$

$$\cdot \frac{\sinh\left(t_c/\tau_\nu\right)}{\left[\cosh\left(t_c/\tau_\nu\right) - \cos\left(l\omega_e t_c/2\right)\right]}\Big\}^{-1/4}.$$

So we may obtain the expression describes the exponential time dependence of $\beta_e(t)$ with the relaxation time

$$T_{1\rho} = \frac{T_{1L}T_{1D}}{T_{1L} + T_{1D}}. \tag{47}$$

3. Experimental

PI in polycrystalline samples of $NaClO_3$ were induced by γ-irradiation (by the courtesy of Dr. I. Zilberman, Nuclear Research Center of the Negev) with doses of 0.2, 1, 3, 5, 10, 20, and 50 Mrad. The origin of PI and their concentration dependence on doses were studied by room temperature EPR spectroscopy using a Bruker EM 220 digital X-band EPR spectrometer (ν = 9.4 GHz). The ^{35}Cl NQR spectra and the spin-lattice relaxation times in rotating frame $T_{1\rho}$ have been measured at 77 K with a Tecmag Libra pulse NMR spectrometer. The spectra have been obtained using Fourier transformation of the Hahn echo signals. Spin-lattice relaxation times in rotating frame $T_{1\rho}$ have been measured using the $\pi/2$-τ-[$\pi/2$-τ-...- τ-$\pi/2$-]$_n$ multiple-pulse sequence. The length of the $\pi/2$ pulse was 7.5 µs.

4. Results and Discussion

The initial, non-irradiated, sample of $NaClO_3$ powder was found to be EPR silent and did not contain paramagnetic impurities. Following γ-irradiation results in removing an electron from the electron shell and thus induces an increasing number of PI which are clearly detected and identified by EPR. The amount of γ-induced PI increases linearly with the dose for both low and high dose region (Fig. 1) and varies within the range of $10^{16} \div 10^{18}$ spin/cm^3.

The NQR frequency and line width in non-irradiated sample at 77 K were found to be 30.632450 MHz and 1.2 kHz, respectively. Figure 2 displays dependencies of the line shift $\delta\nu$ and the line width HHFW on the dose of irradiation. The line width shows linear dependence on the irradiation within the whole range of doses. The line broadening is mostly caused by the distribution of EFG, as were established in NQR studies of mixed and defected crystals [8, 14]. On the other hand, a large amount of PI may also produce a static broadening because of the dipole-dipole interaction between unpaired magnetic moments of the impurities and magnetic moments of

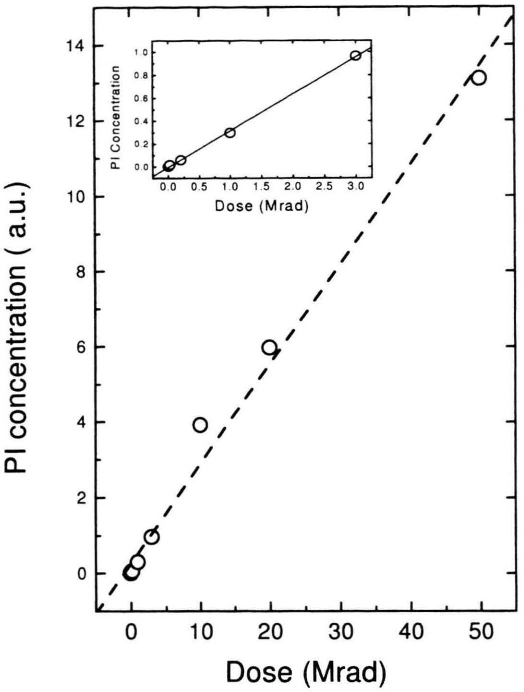

Fig. 1. Dependence of the total amount of induced paramagnetic impurities in γ-irradiated polycrystalline $NaClO_3$ on the irradiation dose.

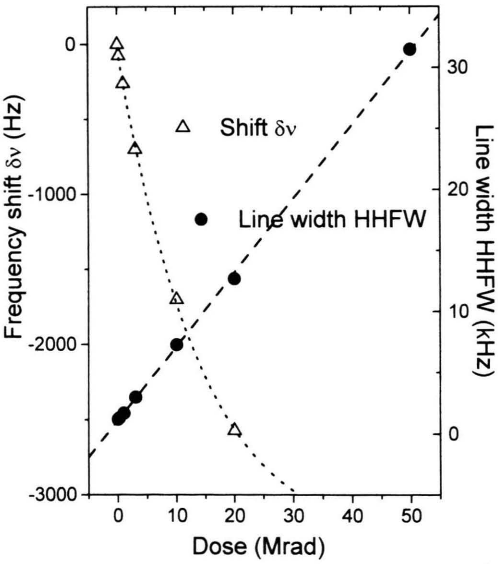

Fig. 2. Dependencies of ^{35}Cl NQR line width (right axis) and line shift from the initial frequency $\nu = 30.632450$ MHz (left axis) on the irradiation dose for polycrystalline $NaClO_3$ at 77 K.

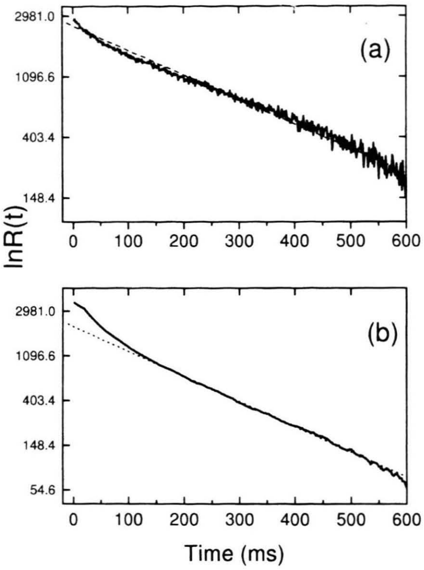

Fig. 3. Logarithmic plot of the magnetization decay vs time for irradiation doses (a) 1 Mrad and (b) 20 Mrad.

the resonant nuclei [8]. The changes of the resonance frequency $\delta\nu$ result from distortions of the electric field gradient (EFG). We note that, at least for small doses, our results are in qualitative agreement with the literature data on $NaClO_3$ [15], where linear dependencies of $\delta\nu$ and HHFW on the dose of irradiation for doses ≤ 5 Mrad were reported.

The Spin-lattice relaxation time in the rotating frame $T_{1\rho}$ shows no visible changes for the irradiation doses up to 3 Mrad. Magnetization decays for both non- and low dose-irradiated samples are long and well described by a single exponential function (Fig. 3a). Thus we conclude that up to 3 Mrad the relaxation is mostly caused by the thermal fluctuations of the electric field gradient [1]. Fitting the magnetization decay of the non-irradiated sample with the expression $R(t) = \exp(-t/T_{1L})$, we found $T_{1L} = 298$ ms. For higher doses of irradiation, the magnetization decay becomes shorter and comprises two different regimes (Figure 3). This fact shows that the irradiation yields additional (to the quadrupole contribution) mechanisms of relaxation. According to the above theory, the initial part of the decay has been attributed to the simultaneous contributions of quadrupole relaxation and direct relaxation via paramagnetic impurities and has been fitted with (37), where the T_{1L} value was taken from the measurement on the non-irradiated sample and $\alpha = 0.5$ in accord with the spacial dimension of the sample $d = 3$. The logarithmic fit of the magnetization vs. time plot for the dose 20 Mrad (Fig. 3b) clearly shows that

Table 1. Dependence of the contributions to the spin-lattice relaxation in rotating frame on the content of paramagnetic centers. The accuracy of relaxation time calculations is within 12%.

Dose (Mrad)	C_P (spin/cm^3)	$T_{1L}(ms)$ (ms)	T_{1PI} (ms)	T_{1D} (ms)	α	D (cm^2/sec)
0	—	298	—	—	1	—
10	$1.02 \cdot 10^{18}$	298	168	467	0.5	$3.29 \cdot 10^{-13}$
20	$1.56 \cdot 10^{18}$	298	94	448	0.5	$2.16 \cdot 10^{-13}$
50	$3.42 \cdot 10^{18}$	298	46	345	0.5	$1.45 \cdot 10^{-13}$

at times longer than 120 ms the relaxation regime is changed to the diffusion-limited one characterized by the single exponential function of time. Similar results were found for samples irradiated by 10 Mrad and 50 Mrad. It is not surprising that this time is independent on the dose, because it needs a certain characteristic time of establishing of the gradient of local inverse temperature. The diffusion-limited part of the decay was attributed to the simultaneous contributions of quadrupole relaxation and relaxation via paramagnetic impurities due to the spin diffusion and fitted with the (44). The values of T_{1PI}, T_{1D} and α are given in the Table 1. One can see that the irradiation doses above 10 Mrad reduce both T_{1PI} and T_{1D}. Reduced values of T_{1PI} with increased PI concentration properly reflect the influence of PI to the spin-lattice relaxation. The dependence of the relaxation time T_{1D} on the PI concentration is close to inverse proportionality $T_{1D}^{-1} \sim C_P$ in accordance with the (45). This is in a good qualitative agreement with the above theory. Using the experimental results, from the analysis of those two regimes we can calculate the diffusion coefficient D

$$D = \left(\frac{T_{1PI}}{T_{1D}^4}\right)^{1/3} \left(\frac{\pi \Gamma(1/2)}{6\Gamma(3/2)}\right)^{2/3} \left(\frac{\Gamma(5/4)}{\Gamma(3/4)}\right)^{4/3} C_P^{-2/3} \tag{48}$$

for the γ-irradiated polycrystalline samples of $NaClO_3$. The obtained diffusion coefficient D is of the order of 10^{-13} cm^2/sec (Table 1), which is close to the case of Zeeman energy spin diffusion for inorganic solids [6, 16]. Taking into account that the direct relaxation regime should be valid until the time [9] $t \sim B^{1/2}D^{-3/2}$, for $t \sim 120$ ms we can estimate the diffusion barrier radius $b \sim 10^{-7}$ cm, which coincides with the result obtained for $I = 3/2$ [7].

In summary, we obtained a strong experimental evidence that a spin diffusion process takes place in solids containing paramagnetic impurities in the case of pure nuclear quadrupole resonance. In $NaClO_3$ powder, high doses of γ-irradiation produce enough paramagnetic impurities to create an inhomogeneous distribution of local inverse spin temperatures, which allowed to distinguish clearly between the direct relaxation and diffusion-limited relaxation regimes. Measurements of relaxation times in a rotating frame allow to determine the spin diffusion coefficient, which was found to be of the same order as for NMR in inorganic solids.

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