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# Spin diffusion and nuclear spin-lattice relaxation in irradiated solids: a multiple-pulse NQR study

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## Abstract

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 relaxation function of the nuclear spin system at the beginning of the relaxation process is given by  $\exp\left(-\frac{t}{T_{1\rho}}\right)^\alpha$ , where  $T_{1\rho}$  is spin-lattice relaxation time in rotating frame and  $\alpha = d/6$ ,  $d$  is the sample dimensionality. Then the relaxation proceeds asymptotically to an exponential function of time, which was attributed to the spin-diffusion regime. Using the experimental data obtained from the analysis of those two relaxation regimes in  $\gamma$ -irradiated powdered  $\text{NaClO}_3$ , spin diffusion coefficient has been determined and the radius of the diffusion barrier has been estimated. © 1999 Elsevier Science B.V. All rights reserved.

**Keywords:** NQR; Relaxation; Spin diffusion; Paramagnetic impurities

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## 1. Introduction

The concept of spin diffusion, as a mean of transporting nuclear spin energy, has been introduced by Bloembergen [1] in order to explain the nuclear magnetic relaxation in solids containing paramagnetic impurities (PI). Such type of relaxation originates from the magnetic dipole–dipole interaction of PI with neighboring nuclei, which is inversely proportional to the sixth power of the distance. Thus, near the PI the equilibrium with the lattice is reached at a faster rate [1–3]. The nuclear magnetization during the relaxation process is spatially inhomogeneous over a sample volume, and this induces a spatial diffusion of the nuclear spin energy by, for

example, flip-flop transitions due to the dipole–dipole interactions between nuclear spin.

However, till now most studies of the nuclear spin diffusion were related to systems with nuclear spin  $I = 1/2$ , described by the Hamiltonian, whose main term includes just linear functions of spin operators and, correspondingly, forms equidistant energy spectra. However, in many systems nuclei interact with their environment through the electric quadrupole moment  $Q$ , and these interactions are strong enough to observe magnetic resonance of nuclei in the absence of an external magnetic field (pure NQR-case). Unlike NMR-case, the NQR energy spectrum is always non-equidistant and, in many cases, degenerated. These circumstances lead to certain difficulties in obtaining a diffusion equation and a calculation of a diffusion coefficient. Only the cases of nuclear

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spins  $I = 1$  and  $I = 3/2$ , located in axially symmetric electric field gradient (EFG), have been theoretically analyzed [4,5]. Furthermore, at high temperature a magnetic relaxation mechanism is not effective and may be masked by the NQR spin-lattice relaxation caused by thermal modulation of the EFG (Bayer mechanism) [6]. At low concentration of PI, the Bayer mechanism of relaxation dominates. At higher PI content, the relaxation process should become more complicated. If the r.f. excitation is homogeneous over the sample (no gradient of the magnetization), just after the excitation the diffusion should not occur while the direct interaction of nuclear spins with PI plays an important role. Following the analogy with the NMR-case, such a regime may be called as diffusion-vanishing regime [7,8]. At this stage the time dependence of the nuclear magnetization is expected to be non-exponential [7] and then proceeds asymptotically to an exponential function of time, to the so-called diffusion-limited relaxation regime [8].

In the present paper both spin lattice relaxation and spin diffusion processes in  $\gamma$ -irradiated polycrystalline samples of  $\text{NaClO}_3$  were studied by multiple-pulse spin-locking technique. The analysis of the nuclear magnetization decays for various concentrations of PI allows us to distinguish between the diffusion-vanishing and the diffusion-limited regimes and to determine coefficients of spin-diffusion for the NQR-case.

## 2. Theory

The evolution of the spin system consists of nuclear spins  $I > 1/2$  and PI spins equal to  $1/2$  and 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 density matrix  $\rho(t)$  (in units of  $\hbar = 1$ )

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

with the Hamiltonian

$$\mathcal{H}(t) = \mathcal{H}_Q + \mathcal{H}_{dd} + \mathcal{H}_{PI} + \mathcal{H}_P + \mathcal{H}_{br}(t) + \mathcal{H}_{r.f.}(t). \quad (2)$$

Here  $\mathcal{H}_Q$  represents the interaction of the  $I$ -spin system with the EFG;  $\mathcal{H}_{dd}$  and  $\mathcal{H}_{PI}$  are the Hamiltonians of the dipole–dipole interaction between nuclear spins and nuclear and PI spins, respectively;  $\mathcal{H}_P$  describes the impurity spin system;  $\mathcal{H}_{br}(t) = \sum_{q=-2}^2 E^{(-q)}(t) A^q$  the spin-lattice interaction Hamiltonian, describes spin-lattice relaxation caused by the torsional vibrations (Bayer mechanism) [6], where  $A^q$  is a bilinear function of the spin operators and  $E^{(-q)}(t)$  is a random function of time [9].  $\mathcal{H}_{r.f.}(t)$  gives the action of r.f. field on the nuclear spin system.

Using the projection operators  $e_{mn}^\mu$  and  $\varepsilon_{mn}^j$  defined by their matrix elements  $\langle m' | e_{mn}^\mu | n' \rangle = \delta_{m'm} \delta_{n'n}$  and  $\langle \nu' | \varepsilon_{mn}^\mu | \sigma' \rangle = \delta_{\nu'\nu} \delta_{\sigma'\sigma}$  and introducing a projection density operators,  $e_{mn}(\vec{r})$ , for the nuclear spins  $I$ , and  $\varepsilon_{mn}(\vec{r})$  for PI spins

$$e_{mn}(\vec{r}) = \sum_{\mu} \delta(\vec{r} - \vec{r}_{\mu}) e_{mn}^{\mu};$$

$$\varepsilon_{mn}(\vec{r}) = \sum_j \delta(\vec{r} - \vec{r}_j) \varepsilon_{mn}^j \quad (3)$$

the density of the Hamiltonians  $\mathcal{H}_Q$ ,  $\mathcal{H}_{dd}$ , and  $\mathcal{H}_{PI}$  can be written down in the following form:

$$\mathcal{H}_Q(\vec{r}) = (2I + 1)^{-1} \sum_{mn} \omega_{mn}^0 e_{mn}(\vec{r}), \quad (4)$$

$$\mathcal{H}_{dd}(\vec{r}) = \int d\vec{r}' \sum_{mm'n'} G_{mn}^{m'n'}(\vec{r} - \vec{r}') e_{mn}(\vec{r}) \times e_{m'n'}(\vec{r}'), \quad (5)$$

$$\mathcal{H}_{PI}(\vec{r}) = \int d\vec{r}' \sum_{mm'n'} F_{mn}^{m'n'}(\vec{r} - \vec{r}') \times e_{mn}(\vec{r}) \varepsilon_{m'n'}(\vec{r}'), \quad (6)$$

where  $\omega_{mn}^0 = \lambda_m - \lambda_n$ ,  $\lambda_m$ ,  $|m\rangle$ , and  $|n\rangle$  are the eigenvalues and eigenvectors of the operator  $\mathcal{H}_Q$ .  $|\nu\rangle$  and  $|\sigma\rangle$  are eigenvectors of the operator  $\mathcal{H}_P$ ;  $G_{mn}^{m'n'}$  and  $F_{mn}^{m'n'}$  are matrix elements of the dipole–dipole Hamiltonians  $\mathcal{H}_{dd}$  and  $\mathcal{H}_{PI}$  in  $\mathcal{H}_Q$ -representation [10].

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

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

where  $\omega$  is applied frequency,  $\omega_1(t) = \vartheta_0 \delta(t)$  and  $\phi = 0$  for the preparatory pulse and  $\omega_1(t) = \vartheta \sum_{k=0}^{\infty} \delta[t - (k + (1/2)) t_c]$  and  $\phi = \pi/2$  for the remaining pulses,  $\vartheta = \gamma H_1 t_w$ ,  $H_1$  and  $t_w$  are an amplitude and pulse duration of the r.f. pulses;  $t_c$  is the period of the multiple-pulse sequence;  $\vec{a}$  is a unit vector directed along the r.f. field,  $\gamma$  is gyromagnetic ratio of the nuclear spins. In the Eqs. (7) and (8) it is assumed that the torsional vibrations and radiofrequency field are homogeneously distributed over the sample.

The spin system is situated in an inner EFG coupled with the nuclear quadrupole moment to produce an interaction that is assumed to be very large in comparison to the dipole–dipole interaction. For this case, the nonsecular terms of the Hamiltonians,  $\mathcal{H}_{dd}$  and  $\mathcal{H}_{PI}$  (those terms that do not commute with the  $\mathcal{H}_Q = \int d\vec{r} \mathcal{H}_Q(\vec{r})$ ) may be neglected. The procedure of the separation of the truncated Hamiltonians  $\mathcal{H}_{dd}^{\text{sec}}$  and  $\mathcal{H}_{PI}$  can be carried out by using the unitary transformation  $\rho(t) = P^\dagger(t) \tilde{\rho}(t) P(t)$  with

$$P(t) = \exp \left\{ it(2I + 1)^{-1} \int d\vec{r} \sum_{mn} \omega_{mn} e_{mn}(\vec{r}) \right\}, \quad (9)$$

where  $\omega_{mn} = \omega$  from Eq. (8) if  $\omega$  is close to resonance frequency  $\omega_{mn}^0$  and  $\omega_{mn} = \omega_{mn}^0$  otherwise. After the transformation we obtain

$$i \frac{d\tilde{\rho}(t)}{dt} = [\tilde{\mathcal{H}}(t), \tilde{\rho}(t)], \quad (10)$$

with

$$\begin{aligned} \tilde{\mathcal{H}}(t) = & \omega_1(t) \int d\vec{r} (\vec{e} \cdot \vec{S}(\vec{r})) + \mathcal{H}_d^{\text{sec}} + \mathcal{H}_{PI}^{\text{sec}} + \mathcal{H}_P \\ & + \tilde{\mathcal{H}}_{br}(t), \end{aligned} \quad (11)$$

here  $\vec{e}$  is the unit vector of the effective field  $\vec{\omega}_e$  [10],

$$\vec{S}(\vec{r}) = \sum_{\mu} \delta(\vec{r} - \vec{r}_{\mu}) \vec{S}_{\mu}, \quad (12)$$

where  $\vec{S}_{\mu}$  is the effective spin operator [10].

In the case of  $\omega_e \approx \omega_p^{\text{loc}} \gg \omega_{PI} \gg \omega_d^{\text{loc}}$  (here  $\omega_g^{\text{loc}} \sim \|\mathcal{H}_g\|$ , norm of the operator  $\mathcal{H}_g$  and  $g \equiv P, PI, dd$ ) which takes place, for example, if  $\gamma_1 \ll \gamma_p$ , the

secular parts of the Hamiltonians  $\mathcal{H}_d^{\text{sec}}$  and  $\mathcal{H}_{PI}$  take the forms

$$\mathcal{H}_{dd}^{\text{sec}} = \mathcal{H}_{dd}^0 + \sum_{k=-2, k \neq 0}^2 \mathcal{H}_{dd}^k \quad (13)$$

where  $\mathcal{H}_{dd}^0$  is the term which commutes with the operator  $\int d\vec{r} (\vec{e} \cdot \vec{S}(\vec{r}))$ :

$$\mathcal{H}_{dd}^0 = \sum_{l=-1}^1 \sum_{\mu\eta} \sum_{mnm'n'} g_{mn}^{m'n'}(\mu\eta) K_{mn}^{-l\mu} K_{m'n'}^{-l\eta} \quad (14)$$

and

$$\mathcal{H}_{PI} = \sum_{l=-1}^1 \sum_{\mu j} \sum_{mnm'n'} f_{mn}^{m'n'}(\mu\eta) K_{mn}^{-l\mu} \mathcal{E}_{m'n'}^j \quad (15)$$

Here the operators  $K_{mn}^{l\mu}$  obey the following commutator rules [10]

$$\left[ \int d\vec{r} (\vec{e} \cdot \vec{S}(\vec{r})), K_{mn}^{-l\mu} \right] = l K_{mn}^{-l\mu} \quad (16)$$

and [10]

$$\begin{aligned} g_{mn}^{m'n'}(\mu\eta) = & G_{mn}^{m'n'}(\mu\eta) [(\delta_{mn} + \delta_{m\bar{n}})(\delta_{m'n'} + \delta_{m'\bar{n}}) \\ & + (\delta_{mn'} + \delta_{m\bar{n}'})(\delta_{nm'} + \delta_{n\bar{m}})] \end{aligned} \quad (17)$$

$$f_{mn}^{m'n'}(\mu\eta) = F_{mn}^{m'n'}(\mu\eta)(\delta_{mn} + \delta_{m\bar{n}}), \quad \bar{n} = -n. \quad (18)$$

To obtain the evolution equation we will use the method of non-equilibrium state operator [11] which has been originally applied to the spin diffusion in NMR [12]. Using the unitary transformation

$$U(t) = \exp \left\{ -i \int_0^t dt' [\omega_e - \omega_1(t')] (\vec{a} \cdot \vec{S}) \right\}, \quad (19)$$

we will consider the case, that the nuclear spins are in the effective field  $\vec{\omega}_e = \vec{a} \arccos[\cos(\vartheta/2)\cos(\Delta t_c)]$  where  $\Delta$  is the resonance offset, and we obtain the Hamiltonian in the new representation

$$\begin{aligned} \tilde{\mathcal{H}}(t, \omega_e) = & \mathcal{H}_e(\vec{r}, \omega_e) + \mathcal{H}_{dd}^0 + \mathcal{H}_{PI}(t, \omega_e) + \mathcal{H}_P \\ & + \tilde{\mathcal{H}}_{br}(t, \omega_e), \end{aligned} \quad (20)$$

where

$$\mathcal{H}_e(\vec{r}, \omega_e) = \omega_e \int d\vec{r} (\vec{a} \cdot \vec{S}(\vec{r})) \quad (21)$$

$$\begin{aligned} \mathcal{H}_{PI}(t, \omega_e) = & \sum_{l=-1}^1 \sum_{\mu j} \sum_{mnm'n'} f_{mn}^{m'n'}(\mu\eta) e^{-il\omega_e t} \chi_l(t) \\ & \times K_{mn}^{l\mu} \mathcal{E}_{m'n'}^j \end{aligned} \quad (22)$$

$$\begin{aligned} \tilde{\mathcal{H}}_{br}(t, \omega_e) = & \sum_{l=-1}^1 \sum_q \sum_{mn} E^{(-q)}(t) A_{mn}^q e^{-il\omega_e t} \\ & \times e^{-i\omega_{mn}t} \chi_l(t) \sum_{\mu} K_{mn}^{l\mu} \end{aligned} \quad (23)$$

$$\chi_l(t) = \sum_{n=-\infty}^{\infty} \frac{(-1)^n \sin(l\omega_e t_c/2)}{2\pi n + l\omega_e t_c}. \quad (24)$$

According to the structure of the system, we will choose  $\mathcal{H}_e(\vec{r}, \omega_e)$  and  $\mathcal{H}_p$  as a local integral of motion operators, other terms in Eq. (20) may be considered as a small perturbations. Following Zubarev [11], we assume that the quasi-equilibrium state is established in spin system, and the density matrix can be written as

$$\begin{aligned} \rho = Z^{-1} \exp \left\{ - \int d\vec{r} \beta_e(\vec{r}) \mathcal{H}_e(\vec{r}) - \beta_{\mu} \mathcal{H}_p \right. \\ \left. + \int_{-\infty}^0 dt e^{\epsilon t} \left[ \int d\vec{r} \beta_e(\vec{r}) \frac{\partial \mathcal{H}_e(\vec{r})}{\partial t} + \beta_p \frac{\partial \mathcal{H}_p}{\partial t} \right] \right\}, \end{aligned} \quad (25)$$

where  $Z = \text{Tr} \exp\{\dots\}$ , and  $\beta_e(\vec{r})$  is the local inverse spin temperature, conjugate to  $\mathcal{H}_e(\vec{r})$ . In Eq. (25) all operators are taken in the Heisenberg representation and after the integration is performed, we set  $\epsilon = 0$  [11]. If the heat capacity of PI reservoir,  $-\delta/\delta\beta_p \langle \mathcal{H}_p \rangle$  is large in comparison with the nuclear spin heat capacities and the PI's spin lattice relaxation time is very short, a case which is experimentally implemented, it is reasonable to consider only the relaxation process with constant inverse spin temperature of PI,  $\beta_p$ , equal to that of the lattice:  $\beta_p = \beta_L$ . Therefore, the PI reservoir is in the thermal equilibrium with the lattice and  $\beta_p$  is independent of the position. The time dependence of the slowly varying thermodynamics quantities in the in-

tegral of Eq. (23) were neglected in comparison with the rapidly varying correlators [12].

Applying the commutation rules  $[e_{mn}(\vec{r}), \mathcal{E}_{m'n'}(\vec{r})] = 0$ , the transport equations in the form of localized laws of conservation of the spin energy densities can be obtained

$$\frac{\partial \mathcal{H}_e(\vec{r})}{\partial t} + \text{div} \vec{j}_e(\vec{r}) = K_e(\vec{r}) + L_e(\vec{r}), \quad (26)$$

$$\begin{aligned} \frac{\partial \mathcal{H}_p}{\partial t} = & - \int d\vec{r} \frac{\partial \mathcal{H}_e(\vec{r})}{\partial t} \\ = & - \int d\vec{r} (K_e(\vec{r}) + L_e(\vec{r})), \end{aligned} \quad (27)$$

where

$$\begin{aligned} K_e(\vec{r}) = & -i [\mathcal{H}_e(\vec{r}), \mathcal{H}_{np}^{\text{sec}}(t, \omega_e)] \\ = & -i \omega_e \int d\vec{r}' \sum_l l \sum_{mnm'n'} f_{mn}^{m'n'}(\vec{r} - \vec{r}') \\ & \times e^{-il\omega_e t} \chi_l(t) K_{mn}^{-l}(\vec{r}) \mathcal{E}_{m'n'}^j(\vec{r}') \quad (28) \\ L_e(\vec{r}) = & -i [\mathcal{H}_e(\vec{r}), \tilde{\mathcal{H}}_{SL}(t, \omega_e)] \\ = & -i \omega_e \sum_{q,l} l E^{(-q)}(t) \sum_{mn} A_{mn}^q e^{i\omega_{mn}t} K_{mn}^l(\vec{r}). \end{aligned} \quad (29)$$

Here  $K_{mn}^l(\vec{r}) = \sum_{\mu} \delta(\vec{r} - \vec{r}_{\mu}) K_{mn}^{-l\mu}$ . Eq. (27) is the result of the energy conservation law. In Eq. (26)  $\vec{j}_e(\vec{r})$  is the operator of the flux of the density quadrupole energy

$$\begin{aligned} \vec{j}_e(\vec{r}) = & - \frac{i\omega_e}{2} \int d\vec{r}' (\vec{r} - \vec{r}') \sum_l l \\ & \times \sum_{mnm'n'} g_{mn}^{m'n'}(\vec{r} - \vec{r}') \\ & \times [K_{mn}^l(\vec{r}) K_{m'n'}^{-l}(\vec{r}') - K_{mn}^{-l}(\vec{r}') K_{m'n'}^l(\vec{r})]. \end{aligned} \quad (30)$$

At high temperatures we can obtain the density matrix in the form [11]

$$\rho = \left\{ 1 - \int_0^1 d\lambda [\mathcal{B}(i\lambda) - \langle \mathcal{B}(i\lambda) \rangle_{eq}] \right\} \rho_{eq} \quad (31)$$

where the thermodynamic average  $\langle \dots \rangle$  corresponds to an average with the quasi-equilibrium operator  $\rho_{eq} = e^{-\mathcal{H}} / \text{Tr} e^{-\mathcal{H}}$ , where

$$\mathcal{H} = \int d\vec{r} \beta_e(\vec{r}) \mathcal{H}_e(\vec{r}) + \beta_p \mathcal{H}_c, \quad (32)$$

$$\begin{aligned} \mathcal{B}(t + i\lambda) = & \int_{-\infty}^0 dt e^{\epsilon t} \int d\vec{r} \left\{ \nabla \beta_e(\vec{r}, t) \right. \\ & \times \left[ e^{-\lambda \mathcal{H}} \vec{j}_e(\vec{r}, t) e^{\lambda \mathcal{H}} \right] \\ & + \left[ \beta_e(\vec{r}, t) - \beta_L \right] \times e^{-\lambda \mathcal{H}} \\ & \left. \times \left[ K_e(\vec{r}, t) + L_e(\vec{r}, t) \right] e^{\lambda \mathcal{H}} \right\}. \quad (33) \end{aligned}$$

Let us make some remarks before we obtain the equation describing the spin diffusion and spin lattice relaxation of the dipolar order in solids containing PI. In the general case of non-cubic symmetry, the diffusion process is strongly anisotropic and the diffusion coefficient,  $D$ , is a symmetrical tensor of a second rank [13]. Usually for polycrystalline samples the anisotropy of  $D$  cannot be determined experimentally. Since we confine ourselves to polycrystalline systems, we will further neglect such an anisotropy and consider  $D$  as a scalar. By using Eqs. (26), (29)–(33) and taking into account that for such a case  $\langle \mathcal{B}(t + i\lambda) \rangle_{eq} = 0$  (if it is not equal to zero, the suitable choice of quantities  $\tilde{\mathcal{B}} \equiv \mathcal{B} - \langle \mathcal{B} \rangle_{eq}$  leads to the same result) the diffusion equation can be obtained

$$\frac{\partial \beta_e(\vec{r}, t)}{\partial t} = (D\Delta - T_{1\rho}^{-1}(\vec{r}))(\beta_e(\vec{r}, t) - \beta_L), \quad (34)$$

with the boundary condition

$$\nabla \beta_e(r, t)|_{r=b} = 0, \quad (35)$$

where  $b$  is the radius of the diffusion barrier [13], 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 inculcation of the PI) should be also taken into account. It results in additional electrical diffusion barriers [5] of order  $\sim r_0(Ze^2 Q \zeta / \gamma \hbar^2)^{1/4}$ , here  $r_0$

is distance between neighboring nuclei,  $\zeta$  is the Sternheimer antishielding factor [14] and the distortion of the electric field was assumed to be equivalent to the presence of a charge  $Ze$  [5]. The first term on the right side of Eq. (34) describes the spin diffusion process with diffusion coefficient

$$\begin{aligned} D = & \int d\vec{r}' \sum_{l=-1}^1 l^2 (\vec{r} - \vec{r}')^2 \sum_{mm'n'} g_{mn}^{m'n'}(\vec{r} - \vec{r}') \\ & \times \sum_{pp'q'} g_{pq}^{p'q'}(\vec{r} - \vec{r}') \times \text{Tr} [K_{mn}^l(\vec{r}) K_{p'q'}^{-l}(\vec{r}) \\ & \times K_{m'n'}^l(\vec{r}') K_{pq}^{-l}(\vec{r}')] / \text{Tr}(\vec{a} \cdot \vec{S})^2 \quad (36) \end{aligned}$$

and the second term gives the variation of  $\beta_e(\vec{r}, t)$  due to the direct relaxation to PI with relaxation time  $T_{PI}(\vec{r})$ , and to the lattice, with  $T_L(\vec{r})$ :

$$T_{1\rho}^{-1}(\vec{r}) = T_{1nc}^{-1}(\vec{r}) + T_{1L}^{-1}(\vec{r}) \quad (37)$$

where

$$T_{1PI}^{-1}(\vec{r}) = r^{-6} B(\vec{r}) \quad (38)$$

$$\begin{aligned} B(\vec{r}) = & \int dt \int d\vec{r}' \sum_{l=-1}^1 l^2 \sum_{mm'n'} \sum_{pp'q'} f_{mn}^{m'n'}(\vec{r} - \vec{r}') \\ & \times f_{pq}^{p'q'}(\vec{r} - \vec{r}') \langle p_{m'n'}(\vec{r}') p_{p'q'}(\vec{r}', t) \rangle \\ & \times \text{Tr} [K_{mn}^l(\vec{r}) K_{p'q'}^{-l}(\vec{r}, t)] / \text{Tr}(\vec{a} \cdot \vec{S})^2 \quad (39) \end{aligned}$$

$$\begin{aligned} T_{1L}^{-1}(\vec{r}) = & \int dt \int d\vec{r}' \sum_{l=-1}^1 l^2 \sum_{qq'} \langle E^{(-q)} E^{(-q')}(t) \rangle \\ & \times A_{mn}^q A_{m'n'}^{q'} \chi_l(t) \chi_{-l}(t) \\ & \times \text{Tr} [K_{mn}^l(\vec{r}) K_{m'n'}^{-l}(\vec{r}, t)]. \quad (40) \end{aligned}$$

The diffusion equation (Eq. (34)) describes the spin diffusion and the spin lattice relaxation via PI caused by torsional motion in the spin system with a multiple-level non-equidistant energy spectrum. Eq. (34) has the same form as for the case of NMR [2] and differs from the latter only by the kinetic coefficients. Immediately after a disturbance of the nuclear spin system, there is no gradient of  $\beta_e$ , and diffusion is not of importance [7]. To describe the relaxation we may use Eq. (34) without the first term, this is the so-called diffusion vanishing regime [8]. Further, usually the spin-lattice relaxation in NQR in the

absence of the PI is caused by thermal modulation of the EFG [6]. 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  $T_{1\text{PI}}^{-1}(\vec{r}) \ll T_{1L}^{-1}(\vec{r})$ , 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  $T_{1L}^{-1} = \int d\vec{r} T_{1L}^{-1}(\vec{r})$ . In the presence of high PI concentration, at the beginning of the relaxation process, Eq. (34) has the solution

$$\beta_e(\vec{r}, t) = \beta_e(\vec{r}, \infty) + [\beta_e(\vec{r}, 0) - \beta_e(\vec{r}, \infty)] \times \exp\left(-\frac{t}{T_{1\rho}(\vec{r})}\right). \quad (41)$$

where  $\beta_e(\vec{r}, \infty)$  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  $R(\vec{r}, t) = \frac{\beta_e(\vec{r}, t) - \beta_e(\vec{r}, \infty)}{\beta_e(\vec{r}, 0) - \beta_e(\vec{r}, \infty)}$ , the normalized local relaxation function. In the limit as the number of PI,  $N_p \rightarrow \infty$ , a volume of sample,  $V_L \rightarrow \infty$ , and  $N_p/V_L = C_p$ , the PI concentration, we have [7,15]

$$R(t) = \exp\left[-\frac{t}{T_{1L}} - \left(\frac{t}{T_{1\text{PI}}}\right)^\alpha\right] \quad (42)$$

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

$$T_{1\text{PI}}^{-1} = B \left[ \frac{2\pi^{d/2}\Gamma(1-d/6)C_p}{d\Gamma(d/2)} \right]^{6/d}. \quad (43)$$

Here  $B = \langle B(\vec{r}) \rangle_{\theta_{\mu\eta}, \phi_{\mu\eta}}$  is an average over the spherical coordinates of the vector  $\vec{r}_{\mu\eta}$ , concerning the  $\mu$ -th nuclear spin and  $\eta$ -th PI spin,  $\Gamma(x)$  is the Gamma function.

As the result of diffusion-vanishing relaxation regime the local inverse temperature  $\beta_e(\vec{r}, t)$  becomes spatially distributed over the sample. In this case we consider also the first term in Eq. (34). To solve this equation and determine the time depen-

dence we introduce the eigenfunctions  $\varphi_n(\vec{r})$  of the operator  $D\Delta - T_{1\rho}^{-1}(\vec{r})$  [16]. Assuming the spherical symmetry approximation, the general solution of the Eq. (24) can be written as an expansion in terms of the ortogonal functions  $\varphi_n(\vec{r})$  in the following form

$$\beta_e(r, t) = \exp\left(-\frac{t}{T_{1L}(\vec{r})}\right) \times \int dr' \sum_n \exp(-k_n^2 Dt) \varphi_n(r) \tilde{\varphi}_n^*(r'), \quad (44)$$

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

$$\Delta\varphi_n(r) - (T_{1\text{PI}}/D)\varphi_n(r) = -k_n^2\varphi_n(r) \quad (45)$$

with the boundary condition

$$\nabla\varphi_n(r)|_{r=b} = 0 \quad (46)$$

Eq. (45) is well know in the theory of scattering for the low energy limit [17]. It has an asymptotic solution  $\varphi_n(r) \sim \sin(k_n r + \delta_n)/r$  for  $r \gg b$ , where  $\delta_n \sim k_n \xi$ , the phase shift and  $\xi$  is the scattering length [17]. Taking into account the spherical symmetry (after the averaging over a polycrystalline sample) and using the boundary condition (46) we obtain [17]

$$\xi = \left(\frac{B}{D}\right)^{1/4} \frac{\Gamma(3/4)}{2\Gamma(5/4)}. \quad (47)$$

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

$$R(t) = \exp\left(-\frac{t}{T_{1L}} - \frac{t}{T_{1D}}\right), \quad (48)$$

where

$$T_{1D} = \left[2\pi C_p D^{3/4} B^{1/4} \frac{\Gamma(3/4)}{\Gamma(5/4)}\right]^{-1}. \quad (49)$$

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

$$T_{1\rho} = \frac{T_{1L}T_{1D}}{T_{1L} + T_{1D}}. \quad (50)$$

### 3. Experimental

PI in polycrystalline samples of  $\text{NaClO}_3$  were induced by  $\gamma$ -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 Bruker EM 220 digital X-band EPR spectrometer ( $\nu = 9.4$  GHz). Digital processing (numerical integration, filtering etc.) and simulation of EPR spectra were done using Bruker WIN-EPR and SimFonia Software. The  $^{35}\text{Cl}$  NQR spectra, the spin-lattice relaxation times in both laboratory and rotating frames,  $T_1$  and  $T_{1\rho}$ , respectively, as well as the spin-spin relaxation time  $T_2$  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 accumulated with the 16-phase cycled sequence [18], which allows to eliminate instrumental distortions of the line shape.  $T_1$  has been measured using  $\pi - \tau - \pi/2$  inversion recovery sequence.  $T_2$  has been measured using  $\pi/2 - \tau - \pi$  Hahn echo sequence. Spin-lattice relaxation times in rotating frame  $T_{1\rho}$  have been measured using  $\pi/2 - \tau - [\pi/2 - \tau - \dots - \tau - \pi/2 - ]_n$  multiple-pulse sequence. The length of the  $\pi/2$  pulse was 7.5  $\mu\text{s}$ .

### 4. Results and discussion

#### 4.1. EPR monitoring of paramagnetic impurities

The initial, non-irradiated, sample of  $\text{NaClO}_3$  powder was found to be EPR silent and did not contain paramagnetic impurities. Consequent  $\gamma$ -irradiation results in removing an electron from the electron shell and thus induces increasing number of PI which are clearly detected by EPR. The simulation and spectral decomposition of the polycrystalline EPR lineshapes allowed to identify all  $\gamma$ -induced PI. Three types of paramagnetic fragments were identified: anisotropic  $\text{O}_3^-$ -center (ozonide) [19,20],  $\text{ClO}_2$  radicals, and isotropic Cl-like centers [21,22]. At doses below 3 Mrad just  $\text{O}_3^-$  and Cl-like centers (in ratio 3:1) were observed. Above 3 Mrad  $\text{ClO}_2$  radicals appear and their relative concentration increases reaching 25% of the total amount of PI at

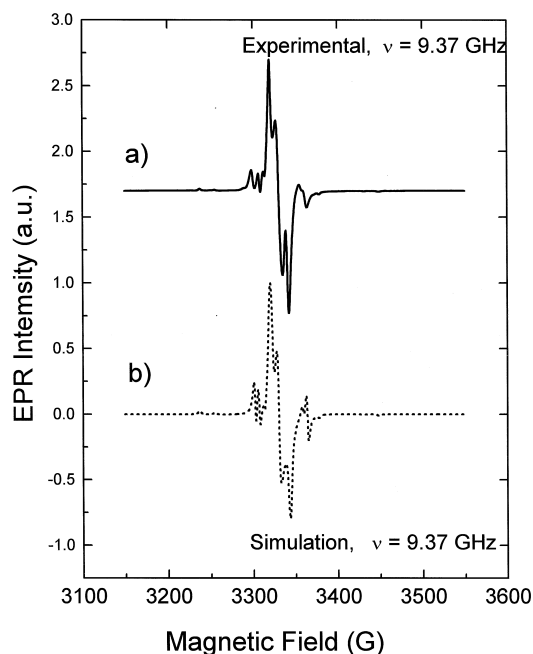


Fig. 1. X-band EPR spectra of  $\gamma$ -irradiated polycrystalline  $\text{NaClO}_3$  sample at room temperature: (a) experimental spectrum of 50 Mrad irradiated sample; (b) spectrum simulated as the composition of Cl-like,  $\text{O}_3^-$  and  $\text{ClO}_2^-$  radicals in the ratio of 1:5:1.3.

the highest dose of 50 Mrad (Fig. 1a). The following EPR parameters were found from the spectral simulation (Fig. 1b):

$$\text{O}_3^- \text{ - centers: } g_x = 2.0040 \pm 0.0005,$$

$$g_y = 2.0178 \pm 0.0005, \quad g_z = 2.0113 \pm 0.0005,$$

$$\text{Cl - like center: } g_{\text{iso}} = 2.0096 \pm 0.0005,$$

$$A_{\text{iso}}(^{35}\text{Cl}) = 2.06 \pm 0.01 \text{ mT},$$

$$A_{\text{iso}}(^{35}\text{Cl}) = 1.72 \pm 0.01 \text{ mT},$$

$$\text{ClO}_2^- \text{ - centers: } g_x = 2.0039 \pm 0.0005,$$

$$g_y = 2.018 \pm 0.001, \quad g_z = 2.013 \pm 0.001,$$

$$A_x(^{35}\text{Cl}) = 7.05 \pm 0.01 \text{ mT},$$

$$A_y(^{35}\text{Cl}) = 1.1 \pm 0.1 \text{ mT},$$

$$A_z(^{35}\text{Cl}) = 1.4 \pm 0.1 \text{ mT},$$

$$A_x(^{37}\text{Cl}) = 5.87 \pm 0.01 \text{ mT},$$

$$A_y(^{37}\text{Cl}) = 0.9 \pm 0.1 \text{ mT},$$

$$A_z(^{37}\text{Cl}) = 1.2 \pm 0.1 \text{ mT}. \quad (51)$$



The amount of  $\gamma$ -induced PI increases linearly with the dose for both low and high dose region (Fig. 2) and varies within the range of  $10^{16} \div 10^{18}$  spin/cm<sup>3</sup>. The isothermal behavior of radiation induced PI shows a long term stability of the total amount of those impurities. The number of PI slightly increases during several days after the irradiation, then decreases and remains unchanged for about 6 months. This fact is important for producing long time NQR measurements using the same samples. After 6 months the number of PI begins to decrease slowly.

#### 4.2. NQR spectra

NQR frequency and line width in non-irradiated sample at 77 K were found to be 30.632450 MHz and 1.2 kHz, respectively. NQR spectra are shown in Fig. 3. Fig. 4 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 was established in NQR studies of mixed and defected crystals [14,23]. On the other hand, a

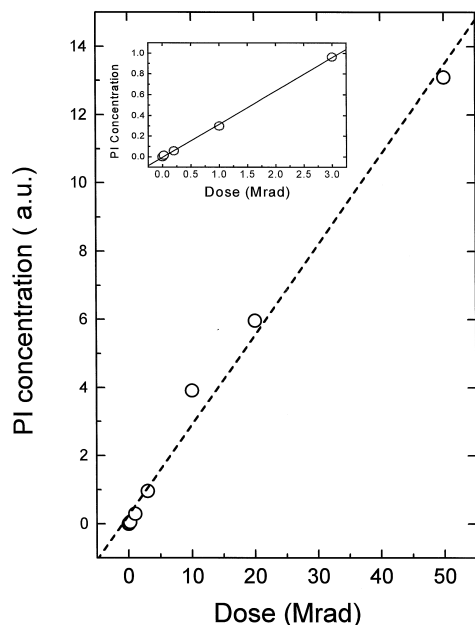


Fig. 2. Dependence of the total amount of induced paramagnetic impurities in  $\gamma$ -irradiated polycrystalline  $\text{NaClO}_3$  on the irradiation dose.

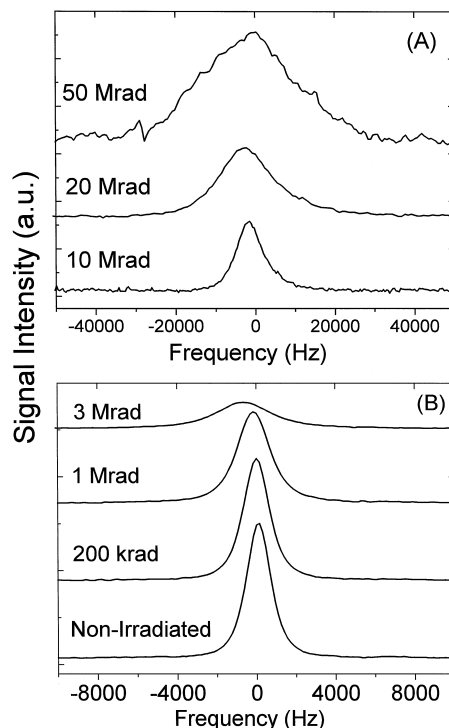


Fig. 3. Evolution of the  $^{35}\text{Cl}$  NQR spectrum of polycrystalline  $\text{NaClO}_3$  with increase of the irradiation dose. Zero frequency shift corresponds to  $\nu = 30.632450$  MHz;  $T = 77$  K.

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 the resonant nuclei [14]. The changes of resonance frequency result from distortions of the EFG. We note that, at least for small doses, our results are in qualitative agreement with the literature data on  $\text{NaClO}_3$  [24], where linear dependencies of  $\delta\nu$  and HHFW on the dose of irradiation for doses  $\leq 5$  Mrad were reported.

#### 4.3. NQR relaxation in rotating frame

Spin-lattice relaxation time in the rotating frame  $T_{1\rho}$  shows no visible changes for the irradiation doses up to 3 Mrad. The typical magnetization decays are shown in Fig. 5. Decays for both non- and low dose-irradiated samples are long and well described by the single exponential function (Fig. 5a). Thus, we conclude that up to 3 Mrad the relaxation

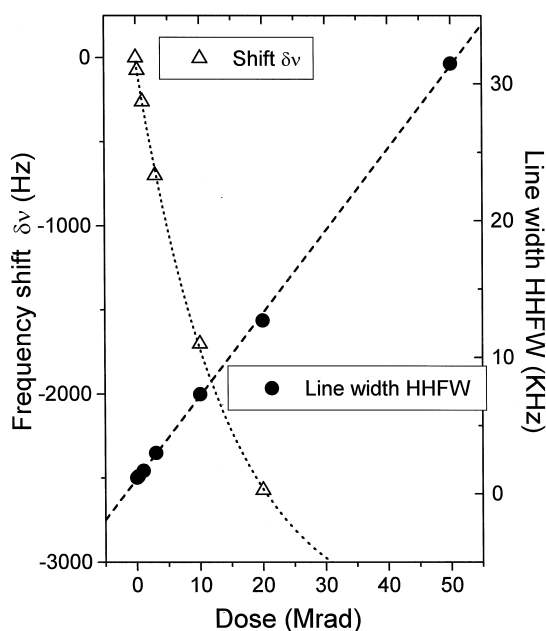


Fig. 4. Dependencies of  $^{35}\text{Cl}$  NQR line width (right axis) and line shift from the initial frequency  $\nu = 30.632450$  MHz (left axis) on the irradiation dose for polycrystalline  $\text{NaClO}_3$  at  $T = 77$  K.

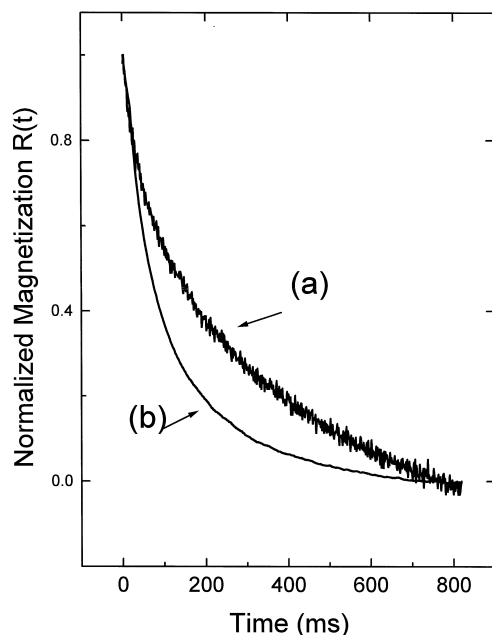


Fig. 5. Magnetization decay in polycrystalline  $\text{NaClO}_3$  for irradiation doses (a) 1 Mrad and (b) 20 Mrad.

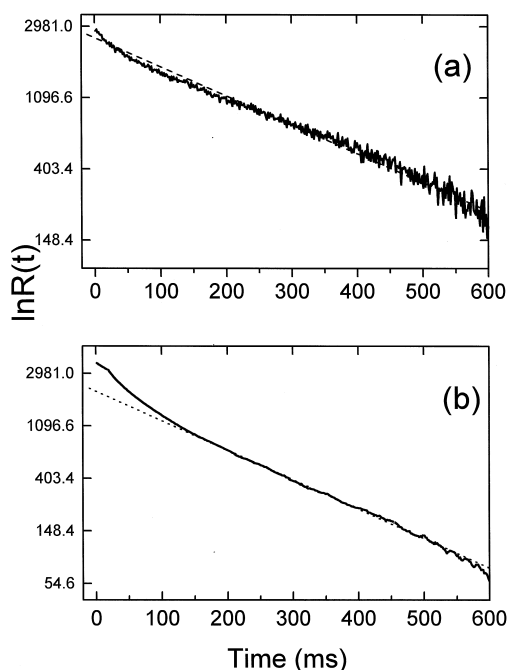


Fig. 6. Logarithmic plot of the magnetization decay vs. time for irradiation doses (a) 1 Mrad and (b) 20 Mrad.

is mostly caused by the thermal fluctuations of the EFG [6]. Fitting the magnetization decay of 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 (Fig. 5b) and comprises two different regimes (Fig. 6). 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 in the diffusion-vanishing regime and has been fitted with Eq. (42), where  $T_{1L}$  value was taken from the measurement on non-irradiated sample and  $\alpha = 0.5$  in accordance with the spacial dimension of the sample  $d = 3$ . Logarithmic fit of the magnetization vs. time plot for the dose 20 Mrad (Fig. 6) clearly shows that 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

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 <sup>3</sup> )	$T_{1L}$ (ms)	$T_{1PI}$ (ms)	$T_{1D}$ (ms)	$\alpha$	$D$ (cm <sup>2</sup> /sec)
0	—	298	—	—	1	—
10	$1.02 \times 10^{18}$	298	168	467	0.5	$3.29 \times 10^{-13}$
20	$1.56 \times 10^{18}$	298	94	448	0.5	$2.16 \times 10^{-13}$
50	$3.42 \times 10^{18}$	298	46	345	0.5	$1.45 \times 10^{-13}$

not surprising that this time is independent of the dose, because it is a certain characteristic time of establishing 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 Eq. (48). The values of  $T_{1PI}$ ,  $T_{1D}$  and  $\alpha$  are given in 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 closed to inverse proportionality  $T_{1D}^{-1} \sim C_p$  in accordance with Eq. (49). This is in good qualitative agreement with the above theory. Using the experimental results, from the analysis of those two regimes we can calculate the diffusion coefficient  $D$  for the  $\gamma$ -irradiated polycrystalline samples of NaClO<sub>3</sub> (Table 1). The obtained diffusion coefficient  $D$  is of the order of  $10^{-13}$  cm<sup>2</sup>/s, which is close to the case of Zeeman energy spin diffusion for inorganic solids [13,25]. Taking into account that diffusion-vanishing relaxation regime should be valid until time  $t \sim B^{1/2}D^{-3/2}$  [7], for  $t \sim 120$  ms we can estimate the diffusion barrier radius  $b \sim 10^{-7}$  cm, which coincides with the result obtained for  $I = 3/2$  [5].

## 5. Conclusion

In conclusion, we obtained strong experimental evidence that spin diffusion process takes place in solids containing paramagnetic impurities in the case of pure nuclear quadrupole resonance. In NaClO<sub>3</sub> powder, high doses of  $\gamma$ -irradiation produce the amount of paramagnetic impurities enough to create

inhomogeneous distribution of local inverse spin temperatures, which allowed to distinguish clearly between the diffusion-vanishing and diffusion-limited relaxation regimes. Measurements of relaxation times in rotating frame allowed the determination of the diffusion coefficient, which was found to be of the same order as for NMR in inorganic solids.

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