Destruction of the Spin Diffusion Barrier near Paramagnetic Impurities in Pure NQR

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The double resonance process between nuclei inside and outside the spin diffusion barrier is considered. By applying two radiofrequency fields, both of the same amplitude, one rotating at the frequency ω^S for nuclei inside of the diffusion barrier and one rotating at the frequency ω^I for nuclei outside of the diffusion barrier, the Hartmann-Hahn condition will be reached, which results in conservation of the quadrupole energy in the spin diffusion process and destruction of the spin diffusion barrier. This technique can be used to detect NQR signals from nuclei near paramagnetic impurities.

Key words: Paramagnetic Impurity; Spin Diffusion; Double Resonance.

1. Introduction

The concept of transporting nuclear spin energy by means of spin diffusion has been introduced by Bloembergen [1] in order to explain the unexpected fast nuclear magnetic relaxation in solids containing paramagnetic impurities (PI). Such a type of relaxation originates from the magnetic dipole-dipole interaction of PI's with neighboring nuclei, which leads to the local spin-lattice relaxation rate being inversely proportional to the sixth power of the distance from the PI. Thus, near the PI the equilibrium with the lattice is reached at a faster rate [1 - 3]. So, 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 spins.

Since the local magnetic field near the PI region is very large, the Larmor frequencies of nuclei located near the PI differ appreciable from those in the bulk of the sample. This results in two effects [2, 4, 5]: i) the nuclei near the PI do not contribute to the signal produced by the other nuclei and ii) in this region the spin diffusion process can no longer occur since the total Zeeman energy of the spins is not conserved by the flip-flop transitions. So, near each PI there is a region inside of which the diffusion is strongly quenched. The size of such regions can be estimated by computing the distance from the PI at which the magnetic field of the PI equals the local dipolar field. For NQR it is of the order of $\sim 10^{-7}$ cm [6 - 8]. The NMR signal of the nuclei from the diffusion-vanishing region is very difficult to detect [9] because the number of nuclei inside of the diffusion barrier area is smaller than in the bulk of the sample. For the NQR case the fraction of these nuclei is of the order of $\sim 10^{-3} - 10^{-5}$. At the same time, the spectrum of the nuclei in the diffusion vanishing region is extremely sensitive to the nuclear position and therefore can be a useful tool for determining the geometric and electronic structure.

The situation is very similar to the case of spins in low abundance ("rare" spins). From the magnetic resonance point of view we have two nuclear species, S (inside of the diffusion barrier) and I (outside of the diffusion barrier), with different resonance frequencies ω^S and ω^I. In the present paper we consider the possibility of destroying the diffusion barrier and detecting the impurity-shifted signal from spins S by using the double nuclear resonance technique [10], applying two radiofrequency fields, both of the same amplitude H_1, but oscillating at different frequencies. The Hartmann-Hahn condition [10] will be reached,

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which results in conservation of the quadrupole energy under the spin diffusion process and destruction of the spin diffusion barrier.

2. Theory

Let the spin system consists of nuclear quadrupole spins located in an inhomogeneous electric crystal field and coupled to PI spins, each equal to $1/2$, by dipole-dipole interaction. Irradiation by two radiofrequency fields, acting on nuclear spins inside and outside of the diffusion barrier, 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

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

Here $\mathcal{H}_{\mathrm{Q}}$ represents the interaction of the quadrupole spin system with the electric field gradient (EFG); $\mathcal{H}_{\mathrm{dd}}$ is the Hamiltonians of the dipole-dipole interaction between nuclear spins, and $\mathcal{H}_{\mathrm{PI}}$ is the Hamiltonian of the dipole-dipole interaction between nuclear spins and PI spins. $\mathcal{H}_{\mathrm{P}}$ describes the impurity spin system; $\mathcal{H}_{\mathrm{L}}(t) = \sum_{q=-2}^{2} E^{(-q)}(t) A^{q}$, the spin-lattice interaction Hamiltonian, describes the spin-lattice relaxation caused by the torsional vibrations (Bayer mechanism) [11], where A^{q} is a bilinear function of the spin operators and $E^{(-q)}(t)$ is a random function of time [12]. $\mathcal{H}_{\mathrm{r.f.}}(t) = \mathcal{H}^{I}_{\mathrm{r.f.}}(t) + \mathcal{H}^{S}_{\mathrm{r.f.}}(t)$ gives the action of the r. f. fields, both on the I- and S-spin system, with its own resonance frequencies.

Let us assume that any given nucleus is influenced by one PI, so the sample can be divided into N_{P} subsystems with a characteristic size of $R = \sqrt[3]{3V/4\pi N_{\mathrm{P}}}$ (N_{P} and V are the number of PI's and the volume of the sample, respectively), each of which including only one PI surrounded by nuclear spins. Furthermore, let us divide the subsystem into three region [13, 14]: A) $0 < r < r_n$, r_n being the distance from the PI to the nearest nucleus; B) $r_n < r < \delta$, δ being the radius of the diffusion barrier; and C) $\delta < r < R$. The region A is empty and most of the nuclei are in the region C. Nuclei from the region B, located at equal distances from the PI, have the same resonance frequency. The typical distance between nuclei in solids is of the order of $l \sim (2-4) \times 10^{-8}$ cm. If the distribution of the atoms in solids is regular, then we can estimate the number of layers in the region B consisting of nuclei with the same resonance frequency, $\sim (\delta - r_n)/l \sim 2-5$, and the fraction of the nuclei in each layer having the same resonance frequency $N_{\mathrm{B}}/N_{\mathrm{C}} \sim 10^{-2} - 10^{-5}$, where N_{C} is number of nuclei located in the region C and N_{B} is number of nuclei located in one layer of the region B.

Below, we shall consider the nuclear spins from one layer of the region B and label them as S-spins. Nuclear spins from the region C will be labeled as I-spins.

The quadrupole Hamiltonian, $\mathcal{H}_{\mathrm{Q}}(\boldsymbol{r})$ can also be divided into two parts: $\mathcal{H}_{\mathrm{Q}}(\boldsymbol{r}) = \mathcal{H}^{S}_{\mathrm{Q}}(\boldsymbol{r}) + \mathcal{H}^{I}_{\mathrm{Q}}(\boldsymbol{r})$. $\mathcal{H}^{S}_{\mathrm{Q}}(\boldsymbol{r}) = \sum_{n=1}^{n_S} \mathcal{H}^{n}_{\mathrm{Q}}(\boldsymbol{r}) + \mathcal{H}_{\mathrm{PS}}$ represents the interaction of the quadrupole spins S with the EFG and with the PI, which leads to the resonance frequency of the S-spins being shifted. $\mathcal{H}^{I}_{\mathrm{Q}}(\boldsymbol{r})$ describes the interaction of the I-spins with the EFG outside the diffusion barrier (in the region C). Similarly, the nuclear dipole-dipole interaction Hamiltonian can be divided into three parts: $\mathcal{H}_{\mathrm{dd}} = \mathcal{H}_{\mathrm{II}} + \mathcal{H}_{\mathrm{SS}} + \mathcal{H}_{\mathrm{IS}}$, where $\mathcal{H}_{\mathrm{II}}$ and $\mathcal{H}_{\mathrm{SS}}$ describe the dipole-dipole interaction inside and outside of the diffusion barrier (in the regions B and C), respectively, and $\mathcal{H}_{\mathrm{IS}}$ represents the dipolar interaction between the I- and S-spins.

Using the projection operators $e^{\mu,j}_{mn}$ and $\varepsilon^{j}_{\nu\sigma}$ defined by their matrix elements $\langle m' | e^{\mu}_{mn} | n' \rangle = \delta_{m'm}\delta_{n'n}$ and $\langle \nu' | \varepsilon^{\mu}_{\nu\sigma} | \sigma' \rangle = \delta_{\nu'\nu}\delta_{\sigma'\sigma}$, the index j connecting with j-th PI, and introducing projection density operators, $e_{mn}(\boldsymbol{r})$, for the nuclear spins S and I, and $\varepsilon_{\nu\sigma}(\boldsymbol{r})$ for PI spins [15],

$$e_{mn}(\boldsymbol{r}_k) = \sum_{\mu=1}^{N_k} \delta\left(\boldsymbol{r}_k - \boldsymbol{r}_\mu\right) e^{\mu}_{mn}, \tag{3}$$

where $k = S, I$; $\varepsilon_{\nu\sigma}(\boldsymbol{r}) = \sum_{j=1}^{N_{\mathrm{P}}} \delta\left(\boldsymbol{r} - \boldsymbol{r}_j\right) \varepsilon^{j}_{\nu\sigma}$,

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

$$\mathcal{H}_{\mathrm{Q}}(\boldsymbol{r}) = (2I+1)^{-1} \sum_{j=1}^{N_{\mathrm{P}}} \sum_{k=S,I} \sum_{mn} \omega^{k}_{mn} e^{k,j}_{mm}(\boldsymbol{r}), \tag{4}$$

$$\mathcal{H}_{kk'}(\boldsymbol{r}) = \sum_{j=1}^{N_\mathrm{P}} \int \mathrm{d}\boldsymbol{r}' \sum_{mnm'n'} G_{mn}^{m'n'}\left(\boldsymbol{r}-\boldsymbol{r}'\right) e_{mn}^{k,j}(\boldsymbol{r}) \cdot e_{m'n'}^{k',j}\left(\boldsymbol{r}'\right), \text{ with } k,k' = I,S, \quad (5)$$

$$\mathcal{H}_{\mathrm{P}k}(\boldsymbol{r}) = \sum_{j=1}^{N_\mathrm{P}} \int \mathrm{d}\boldsymbol{r}' \sum_{mn\nu\sigma} F_{mn}^{\nu\sigma}(\boldsymbol{r}-\boldsymbol{r}') e_{mn}^{k,j}(\boldsymbol{r}) \varepsilon_{\nu\sigma}(\boldsymbol{r}'), \quad (6)$$

$$\mathcal{H}_\mathrm{L}(t) = \sum_{j=1}^{N_\mathrm{P}} \sum_{k=S,I} \sum_{q} \sum_{mn} E^{(-q)}(t) A_{mn}^{q} \int \mathrm{d}\boldsymbol{r} e_{mn}^{k,j}(\boldsymbol{r}), \quad (7)$$

where $\omega_{mn}^{k} = \lambda_m^k - \lambda_n^k$, $k = S,I$; λ_m^k, $\left|m^k\right\rangle$, and $\left|n^k\right\rangle$ are the eigenvalues and the eigenvectors of the operator $\mathcal{H}_\mathrm{Q}$ for $k = I$, and $\mathcal{H}_\mathrm{Q} + \langle\mathcal{H}_\mathrm{PS}\rangle$ for $k = S$. $|\nu\rangle$ and $|\sigma\rangle$ are the eigenvectors of the operator $\mathcal{H}_\mathrm{P}$; $G_{mn}^{m'n'}$ and $F_{mn}^{m'n'}$ are the matrix elements of the dipole-dipole Hamiltonians $\mathcal{H}_\mathrm{dd}$ and $\mathcal{H}_\mathrm{PI}$ in $\mathcal{H}_\mathrm{Q}$-representation [15].

The first r.f. field which acts on the I-spin system,

$$\mathcal{H}_{\mathrm{r.f.}}^{I}(t) = \omega_1(t)\cos\left(\omega^I t + \phi^I\right) \cdot \sum_{j=1}^{N_\mathrm{P}} \sum_{mn} (\boldsymbol{a}\cdot\boldsymbol{I})_{mn} \int_{\delta}^{R} \mathrm{d}\boldsymbol{r} e_{mn}^{I,j}(\boldsymbol{r}), \quad (8)$$

consists of two parts, the first of them, with $\omega_1(t) = \pi\delta(t)/2$ and $\phi = 0$ for the preparatory pulse, and the second with constant $\omega_1 = \gamma H_1$ and $\phi = \pi/2$ for all the times immediately after the first pulse. $\boldsymbol{a}$ is a unit vector directed along the $r.f.$ field, and γ is the gyromagnetic ratio of the nuclear spins. This technique is used for two goals: first, to bring the magnetization of the I-spin system to the spin locking state with a very low spin temperature [10], and second, to decrease the spin diffusion relaxation time by at least twice the decrease of the spin diffusion constant in the rotating frame [18 - 18]. The second r.f. field acts only on S-spins:

$$\mathcal{H}_{r.f.}^{S}(t) = \omega_1(t)\cos\left(\omega^S t\right) \cdot \sum_{j=1}^{N_\mathrm{P}} \sum_{mn} (\boldsymbol{a}\cdot\boldsymbol{I})_{mn} \int_{r_n}^{\delta} \mathrm{d}\boldsymbol{r} e_{mn}^{S,j}(\boldsymbol{r}), \quad (9)$$

where the applied frequency ω^S equals the impurity-shift resonance frequency, $\omega_1(t) = \vartheta\sum_{k=0}^{\infty}\delta[t - \left(k+\frac{1}{2}\right)t_c]$, and $\vartheta = \gamma H_1 t_w$. H_1 and t_w are an amplitude and the pulse duration of the r.f. pulses; t_c is the period of the multiple-pulse sequence which is used for thermal mixing between the S- and I-spin systems. In (7 - 9) it is assumed that the torsional vibrations and the radiofrequency field are homogeneously distributed over the sample.

The spin system is situated in an 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 the region C. For this case, the nonsecular terms of the Hamiltonians, $\mathcal{H}_\mathrm{dd}$ and $\mathcal{H}_\mathrm{PI}$ (those terms that do not commute with the $\mathcal{H}_\mathrm{Q} = \int \mathrm{d}\boldsymbol{r}\mathcal{H}_\mathrm{Q}(\boldsymbol{r})$), may be neglected. The procedure of the separation of the truncated Hamiltonians $\mathcal{H}_\mathrm{dd}^\mathrm{sec}$ and $\mathcal{H}_\mathrm{PI}^\mathrm{sec}$ can be carried out by using the unitary transformation $\rho(t) = P^+(t)\tilde{\rho}(t)P(t)$ with

$$P(t) = \mathit{\Pi}_{k=S,I}\exp\{it(2I+1)^{-1} \cdot \sum_{j=1}^{N_\mathrm{P}} \int \mathrm{d}\boldsymbol{r} \sum_{mn} \omega_{mn}^{k} e_{mn}^{k,j}(\boldsymbol{r})\}, \quad (10)$$

where $\omega_{mn} = \omega^I$ and ω^S from (8,9), if ω^I and ω^S are close to the resonance frequency ω_{mn}^S or ω_{mn}^I; and $\omega_{mn} = \omega_{mn}^k$ with $k = S,I$ otherwise. After the transformation we obtain

$$i\frac{\mathrm{d}\tilde{\rho}(t)}{\mathrm{d}t} = \left[\tilde{\mathcal{H}}(t), \tilde{\rho}(t)\right] \quad (11)$$

with

$$\tilde{\mathcal{H}}(t) = \sum_{j=1}^{N_\mathrm{P}} \sum_{k=I,S} \mathcal{H}_k^j + \mathcal{H}_\mathrm{dd}^\mathrm{sec} + \mathcal{H}_\mathrm{PI}^\mathrm{sec} + \mathcal{H}_\mathrm{P} + \tilde{\mathcal{H}}_\mathrm{L}(t). \quad (12)$$

Here

$$\mathcal{H}_I^j = \omega_1^I \int_\delta^R \mathrm{d}\boldsymbol{r}\left(\boldsymbol{a}\cdot\boldsymbol{I}^j(\boldsymbol{r})\right), \quad (13)$$

$$\mathcal{H}_S^j = \omega_1^S(t) \int_{r_n}^{\delta} \mathrm{d}\boldsymbol{r}\left(\boldsymbol{a}\cdot\boldsymbol{S}^j(\boldsymbol{r})\right), \quad (14)$$

$$\boldsymbol{I}^j(\boldsymbol{r}) = \sum_{\mu=1}^{N_I} \delta\left(\boldsymbol{r}-\boldsymbol{r}_\mu\right)\boldsymbol{I}_\mu^j, \quad (15)$$

$$\boldsymbol{S}^j(\boldsymbol{r}) = \sum_{\mu=1}^{N_S} \delta\left(\boldsymbol{r} - \boldsymbol{r}_\mu\right) \boldsymbol{I}_\mu^j, \tag{16}$$

where $\boldsymbol{I}_\mu$ are effective spin operators [15].

In the case of $\omega_1^k \approx \omega_{\mathrm{P}}^{\mathrm{loc}} \gg \omega_{\mathrm{PI}} \gg \omega_d^{\mathrm{loc}}$ (here $\omega_g^{\mathrm{loc}} \sim \|\mathcal{H}_g\|$, the magnitude of the operator $\mathcal{H}_g$, and $g \equiv \mathrm{P}, \mathrm{P}I, \mathrm{d}d$), which takes place, for example, if $\gamma_I \ll \gamma_{\mathrm{P}}$, the secular parts of the Hamiltonians $\mathcal{H}_{\mathrm{dd}}^{\mathrm{sec}}$ and $\mathcal{H}_{\mathrm{PI}}$ have the forms

$$\mathcal{H}_{kk'}^{\mathrm{sec}} = \sum_{i=-2}^{2} \mathcal{H}_{kk'}^{i}, \tag{17}$$

where $\mathcal{H}_{kk'}^0$ is the term which commutes with the operator $\mathcal{H}_k^j$:

$$\mathcal{H}_{kk'}^0 = \sum_{l=-1}^{1} \sum_{\mu\eta} \sum_{mnm'n'} g_{mn}^{m'n'}(\mu\eta) T_{mn}^{lk}(\mu) T_{m'n'}^{-lk'}(\eta), \tag{18}$$

and $\mathcal{H}_{kk'}^i$ with $i \neq 0$, is the non-secular term relative to $\mathcal{H}_k^j : \left[\mathcal{H}_k^j, \mathcal{H}_{kk'}^i\right] \neq 0$,

$$\mathcal{H}_{\mathrm{P}k} = \sum_{l=-1}^{1} \sum_{\mu j} \sum_{mnm'n'} f_{mn}^{m'n'}(\mu\eta) T_{mn}^{lk}(\mu) \varepsilon_{m'n'}^{j}. \tag{19}$$

Here the operators $T_{mn}^{lk}(\mu)$ obey the commutator rules [15]

$$\left[\mathcal{H}_k^j, T_{mn}^{lk}(\mu)\right] = \delta_{j\mu} l \omega_1^k T_{mn}^{lk}(\mu), \tag{20}$$

and [15]

$$g_{mn}^{m'n'}(\mu\eta) = G_{mn}^{m'n'}(\mu\eta)[(\delta_{mn} + \delta_{m\bar{n}})(\delta_{m'n'} + \delta_{m'\bar{n}'}) + (\delta_{mn'} + \delta_{m\bar{n}'})(\delta_{nm'} + \delta_{n\bar{m}'})], \tag{21}$$

$$f_{mn}^{m'n'}(\mu\eta) = F_{mn}^{m'n'}(\mu\eta)(\delta_{mn} + \delta_{m\bar{n}}), \bar{n} = -n. \tag{22}$$

To obtain the evolution equation for the spin system, we will consider the time when the r.f. pulse with frequency ω^S is applied, and use the method of non-equilibrium state operator [19], which has originally been applied to the spin diffusion in NMR [20].

According to the structure of the system, we will choose $\mathcal{H}_I(\boldsymbol{r})$, $\mathcal{H}_S(\boldsymbol{r})$ and $\mathcal{H}_{\mathrm{P}}$ as local integral of motion operators, other terms in (12) may be considered as small perturbations. Following Zubarev [19], we assume that the quasi-equilibrium state is established in the spin system, and the density operator can be written as

$$\rho = Z^{-1} \exp\{-\sum_{j=1}^{N_{\mathrm{P}}} \sum_{k=I,S} \int_{r_1^k}^{r_2^k} \mathrm{d}\boldsymbol{r} \beta_k^j(\boldsymbol{r}) \mathcal{H}_k^j(\boldsymbol{r}) - \beta_{\mathrm{P}} \mathcal{H}_{\mathrm{P}} + \int_{-\infty}^{0} \mathrm{d}t e^{\epsilon t} [\sum_{j=1}^{N_{\mathrm{P}}} \sum_{k=I,S} \int_{r_1^k}^{r_2^k} \mathrm{d}\boldsymbol{r} \beta_k^j(\boldsymbol{r}) \frac{\partial \mathcal{H}_k^j(\boldsymbol{r})}{\partial t} + \beta_{\mathrm{P}} \frac{\partial \mathcal{H}_{\mathrm{P}}}{\partial t}]\}, \tag{23}$$

where $Z = Tr \exp\{...\}$, and $\beta_k^j(\boldsymbol{r})$ is the local inverse spin temperature, conjugate to $\mathcal{H}_k^j(\boldsymbol{r})$, $r_1^k = \delta$ and $r_2^k = R$ for $k = I$ and $r_1^k = ql + r_n$ and $r_2^k = (q+1)l + r_n$ for $k = S$, where $q = 0 - 5$ is the layer number in the region B beginning from the layer nearest to the PI. In (23) all operators are taken in the Heisenberg representation, and after the integration is performed, we set $\epsilon = 0$ [19]. If the heat capacity of the PI reservoir, $-\delta/\delta\beta_{\mathrm{P}}\langle\mathcal{H}_{\mathrm{P}}\rangle$, 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 th PI, β_{P}, equal to that of the lattice: $\beta_{\mathrm{P}} = \beta_{\mathrm{L}}$. Therefore, the PI reservoir is in thermal equilibrium with the lattice, and β_{P} is independent of the position. The time dependence of the slowly-varying thermodynamic quantities in the integral of (23) was neglected in comparison with the rapidly-varying correlators [20].

Applying the commutation rules $\left[e_{mn}^{k,j}(\boldsymbol{r}), \varepsilon_{m'n'}^{j}(\boldsymbol{r}')\right] = 0$ and (20), the transport equations in the form of localized laws of conservation of the spin energy densities can be obtained:

$$\frac{\partial \mathcal{H}_k^j(\boldsymbol{r})}{\partial t} + \mathrm{div} \boldsymbol{j}_k^j(\boldsymbol{r}) = K_k^j(\boldsymbol{r}) + L_k^j(\boldsymbol{r}) + F_k^j(\boldsymbol{r}), \tag{24}$$

$$\frac{\partial \mathcal{H}_p}{\partial t} = -\sum_{j=1}^{N_p} \sum_{k=I,S} \int_{r_1^k}^{r_2^k} \mathrm{d}\boldsymbol{r} \frac{\partial \mathcal{H}_k^j(\boldsymbol{r})}{\partial t}, \tag{25}$$

where

$$K_k^j(\boldsymbol{r}) = -i[\mathcal{H}_k^j(\boldsymbol{r}), \mathcal{H}_{\mathrm{P}k}^{\mathrm{sec}}(t)]$$
$$= -i\omega_1^k \int_{r_1^k}^{r_2^k} \mathrm{d}\boldsymbol{r}' \sum_l l \sum_{mn\nu\sigma} f_{mn}^{\nu\sigma}(\boldsymbol{r}-\boldsymbol{r}')$$
$$\cdot\, e^{-il\omega_1^k t} T_{mn}^{lk}(\boldsymbol{r})\, \varepsilon_{\nu\sigma}^j(\boldsymbol{r}'), \quad (26)$$

$$L_k^j(\boldsymbol{r}) = -i[\mathcal{H}_k^j(\boldsymbol{r}), \tilde{\mathcal{H}}_{\mathrm{L}}(t)] \quad (27)$$
$$= -i\omega_1^k \sum_{q,l} l E^{(-q)}(t) \sum_{mn} A_{mn}^q e^{i\omega_{mn}t} T_{mn}^{lk}(\boldsymbol{r}),$$

$$F_k(\boldsymbol{r}) = -i[\mathcal{H}_k(\boldsymbol{r}), \mathcal{H}_{\mathrm{IS}}^{\mathrm{sec}}(t)]$$
$$= -i\omega_1^k \int_{r_1^k}^{r_2^k} \mathrm{d}\boldsymbol{r}' \sum_l l \sum_{mn\nu\sigma} f_{mn}^{m'n'}(\boldsymbol{r}-\boldsymbol{r}')$$
$$\cdot\, e^{-il\omega_1^{kt}} e^{-il\omega_1^{k't}} T_{mn}^{lk}(\boldsymbol{r}) T_{m'n'}^{lk'}(\boldsymbol{r}'). \quad (28)$$

Here $T_{mn}^{lk}(\boldsymbol{r}) = \sum_\mu \delta(\boldsymbol{r}-\boldsymbol{r}_\mu) T_{mn}^{lk}(\mu)$. Equation (25) is the result of the energy conservation law. In (24) $\boldsymbol{j}_k(\boldsymbol{r})$ is the operator of the flux of the density quadrupole energy

$$\boldsymbol{j}_k(\boldsymbol{r}) = -\frac{i\omega_1^k}{2} \int \mathrm{d}\boldsymbol{r}'(\boldsymbol{r}-\boldsymbol{r}') \sum_l l \sum_{mnm'n'} g_{mn}^{m'n'}(\boldsymbol{r}-\boldsymbol{r}')$$
$$\cdot \left[T_{mn}^{lk}(\boldsymbol{r}) T_{m'n'}^{-lk}(\boldsymbol{r}') - T_{mn}^{lk}(\boldsymbol{r}') T_{m'n'}^{-lk}(\boldsymbol{r})\right]. \quad (29)$$

At high temperatures we can obtain the density matrix in the form [19]

$$\rho = \left\{1 - \int_0^1 \mathrm{d}\lambda \left[\mathcal{B}(i\lambda) - \langle\mathcal{B}(i\lambda)\rangle_{eq}\right]\right\} \rho_{eq}, \quad (30)$$

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

$$\mathcal{A} = \sum_{k=I,S} \int_{r_1^k}^{r_2^k} \mathrm{d}\boldsymbol{r}\beta_k(\boldsymbol{r}) \mathcal{H}_k(\boldsymbol{r}) + \beta_p \mathcal{H}_c, \quad (31)$$

$$\mathcal{B}(t+i\lambda) = \int_{-\infty}^0 \mathrm{d}t e^{\epsilon t} \sum_{k=I,S} \int_{r_1^k}^{r_2^k} \mathrm{d}\boldsymbol{r} \quad (32)$$
$$\cdot \left\{ \nabla\beta_k(\boldsymbol{r},t) \left[e^{-\lambda\mathcal{A}} \boldsymbol{j}_k(\boldsymbol{r},t) e^{\lambda\mathcal{A}}\right]\right.$$
$$+ \left[\beta_k(\boldsymbol{r},t) - \beta_{\mathrm{L}}\right] e^{-\lambda\mathcal{A}}$$
$$\left.\cdot \left[K_k(\boldsymbol{r},t) + L_k(\boldsymbol{r},t) + F_k(\boldsymbol{r},t)\right] e^{\lambda\mathcal{A}}\right\}.$$

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's. In the general case of non-cubic symmetry, the diffusion process is strongly anisotropic and the diffusion coefficient, D, is a symmetrical tensor of second rank [14]. However, in the case of a polycrystalline sample, D reduces to a scalar quantity. We confine ourselves to a polycrystalline sample. By using (30 - 32) and taking into account that for such a case $\langle\mathcal{B}(t+i\lambda)\rangle_{\mathrm{eq}} = 0$ (if it is not equal to zero, the suitable choice of quantities $\tilde{\mathcal{B}} \equiv \mathcal{B} - \langle\mathcal{B}\rangle_{\mathrm{eq}}$ leads to the same result), one can obtain the diffusion equation

$$\frac{\partial\beta_k(\boldsymbol{r},t)}{\partial t} = \left(D_k \Delta_k - T_{1k\rho}^{-1}(\boldsymbol{r})\right)(\beta_k(\boldsymbol{r},t) - \beta_L)$$
$$- T_{kk'}^{-1}(\beta_k(\boldsymbol{r},t) - \beta_{k'}(\boldsymbol{r},t)) \quad (33)$$

with the boundary condition

$$\nabla\beta_k(r,t)\,|_{r_k=b_k} = 0, \quad (34)$$

where $b_k = r_n + ql$ for $k = S$ and $b_k = \delta$ for $k = I$.

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. This results in additional electrical diffusion barriers [7] of the order $\sim r_n\left(Ze^2Q\zeta/\gamma\hbar^2\right)^{1/4}$, where ζ, the Sternheimer antishielding factor [21], 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 (33) describes the spin diffusion process with the diffusion coefficient

$$D_k = \left(\omega_1^k\right)^2 \int_{r_1^k}^{r_2^k} \mathrm{d}\boldsymbol{r}' \sum_{l=-1}^{1} l^2(\boldsymbol{r}-\boldsymbol{r}')^2 \quad (35)$$
$$\cdot \sum_{mnm'n'} g_{mn}^{m'n'}(\boldsymbol{r}-\boldsymbol{r}') \sum_{pqp'q'} g_{pq}^{p'q'}(\boldsymbol{r}-\boldsymbol{r}')$$
$$\cdot\, \mathrm{Tr}\left[T_{mn}^{lk}(\boldsymbol{r}) T_{p'q'}^{-lk}(\boldsymbol{r}') T_{m'n'}^{lk}(\boldsymbol{r}') T_{pq}^{-lk}(\boldsymbol{r}')\right] / \mathrm{Tr}(\mathcal{H}_k(\boldsymbol{r}))^2,$$

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

$$T_{1k\rho}^{-1}(\boldsymbol{r}) = T_{1k\mathrm{P}}^{-1}(\boldsymbol{r}) + T_{1k\mathrm{L}}^{-1}(\boldsymbol{r}), \tag{36}$$

where

$$T_{1k\mathrm{P}}^{-1}(\boldsymbol{r}) = r^{-6} B_k(\boldsymbol{r}), \tag{37}$$

$$B_k(\boldsymbol{r}) = \left(\omega_1^k\right)^2 \int \mathrm{d}\,t \int_{r_1^k}^{r_2^k} \mathrm{d}\,\boldsymbol{r}' \sum_{l=-1}^{1} l^2 \sum_{mnm'n'} \sum_{pqp'q'}$$

$$f_{mn}^{m'n'}(\boldsymbol{r}-\boldsymbol{r}') f_{pq}^{p'q'}(\boldsymbol{r}-\boldsymbol{r}') \left\langle T_{m'n'}(\boldsymbol{r}') T_{p'q'}^{-lk}(\boldsymbol{r}', t)\right\rangle$$

$$\cdot \operatorname{Tr}\left[T_{mn}^{lk}(\boldsymbol{r}) T_{pq}^{-lk}(\boldsymbol{r}, t)\right] / \operatorname{Tr}(\mathcal{H}_k(\boldsymbol{r}))^2, \tag{38}$$

$$T_{1k\mathrm{L}}^{-1}(\boldsymbol{r}) = \int \mathrm{d}\,t \int_{r_1^k}^{r_2^k} \mathrm{d}\,\boldsymbol{r}' \sum_{l=-1}^{1} l^2 \sum_{qq'} \left\langle E^{(-q)} E^{(-q')}(t)\right\rangle$$

$$\cdot A_{mn}^{q} A_{m'n'}^{q'} \operatorname{Tr}\left[T_{mn}^{lk}(\boldsymbol{r}) T_{m'n'}^{-lk}(\boldsymbol{r}', t)\right], \tag{39}$$

$$T_{kk'}^{-1}(\boldsymbol{r}) = \int \mathrm{d}\,t \int_{r_1^k}^{r_2^k} \mathrm{d}\,\boldsymbol{r}' \sum_{l=-1}^{1} l^2$$

$$\cdot \sum_{mnm'n'} f_{mn}^{m'n'}(\boldsymbol{r}-\boldsymbol{r}') \sum_{pqp'q'} f_{pq}^{p'q'}(\boldsymbol{r}-\boldsymbol{r}')$$

$$\cdot \operatorname{Tr}\left[e^{-il\omega_1^k t} e^{-il\omega_1^{k'} t} T_{mn}^{lk}(\boldsymbol{r}) T_{m'n'}^{-lk'}(\boldsymbol{r}')\right]. \tag{40}$$

The diffusion equation (33) describes the spin diffusion and the spin lattice relaxation via the PI caused by torsional motion in the spin system with a multiple-level nonequidistant energy spectrum.

3. Results and Discussion

By means of (33) and (34) the spin dynamics with both time dependent spin temperatures, $\beta_I(\boldsymbol{r}, t)$ and $\beta_S(\boldsymbol{r}, t)$, can be described.

The thermal mixing between I- and S- spin systems is determined by the last term in (33) with the relaxation time $T_{kk'}^{-1}(\boldsymbol{r})$. The expression for the I-S relaxation time can be represent as

$$T_{kk'}^{-1}(\boldsymbol{r}) = \frac{1}{r^6} \sum_{l=-1}^{1} \int \mathrm{d}\,t \Gamma_{kk'}^{l}(t) l^2 \cos\left[l(\omega_1^k - \omega_1^{k'})t\right], \tag{41}$$

where

$$\Gamma_{kk'}^{l}(t) = \int_{r_1^k}^{r_2^k} \mathrm{d}\,\boldsymbol{r}' \sum_{mnm'n'} f_{mn}^{m'n'}(\boldsymbol{r}-\boldsymbol{r}') \tag{42}$$

$$\cdot \sum_{pqp'q'} f_{pq}^{p'q'}(\boldsymbol{r}-\boldsymbol{r}') \operatorname{Tr}\left[T_{mn}^{lk}(\boldsymbol{r}) T_{m'n'}^{-lk'}(\boldsymbol{r}')\right].$$

Using the simplest approximation for $\Gamma_{kk'}^{l}(t)$ [10]

$$\Gamma_{kk'}^{l}(t) = \Gamma_{kk'}^{l}(0) \exp\left[-\left(\frac{t}{2\tau}\right)^2\right] \tag{43}$$

after performing the integration over τ we obtain

$$T_{kk'}^{-1}(\boldsymbol{r}) \sim \exp\left[-\gamma^2\left(H_1^k - H_1^{k'}\right)^2 \tau^2/2\right]. \tag{44}$$

So, the mixing process between the nuclear spins located near the PI and in the bulk of the sample is a very sharp function of the diference between the amplitude of r.f. fields acting on the I- and S- spin systems, $H_1^k - H_1^{k'}$. The double resonance process takes place when this diference is close to zero. In this case the nuclei located near the PI strongly connect with the nuclei in the bulk of the sample.

Now, let us estimate the effect in the simplest case when during the thermal mixing the nuclear spin system is isolated ($t_w \leq T_{kk'} \ll T_{1k\rho}$) and energy is conserved:

$$\beta_I C_I H_I^2 + \beta_S C_S H_S^2 = \beta_f \left(C_I H_I^2 + C_S H_S^2\right), \tag{45}$$

where β_I and β_S are the initial inverse spin temperatures of the I- and S-spin systems, and β_f is the final one, after thermal mixing. $C_{I,S} = N_{I,S} I(I+1)\gamma_I^2/3$ is the Curie constant. Under the condition $\omega_1^I = \gamma_I H_I = \gamma_S H_S = \omega_1^S$ there is $\beta_f/\beta_I = N_I + \beta_S \beta_I^{-1} N_S/N$, where $N = N_I + N_S$. Assuming that S-spin system is very hot, $\beta_S \approx 0$, we have $\beta_I/\beta_f \approx N_I/N \approx 1/1+\xi$, where $\xi = N_S/N_I = \left[(r_n + ql)^3 - r_n^3\right]/[R^3 - \delta^3] \ll 1$ for the q-layer.

For instance, we find that for a γ-irradiated polycrystalline sample of $\mathrm{NaClO_3}$ [8] with the impurity concentration $C_\mathrm{P} \sim 10^{18}\mathrm{cm}^{-3}$ (the average impurity separation $R \sim 6 \times 10^{-7}$cm), $r_n \sim 4 \times 10^{-8}$cm, and the diffusion barrier $\delta \sim 10^{-7}$cm, the number of layers in the region B is $\frac{\delta}{r_n} \sim 3$ and $\xi \approx 0.08$. So, in this case three layers in the region B can be extracted and, using the multiple-contact thermal mixing sequence [22] with three different resonance frequencies ω^S, the NQR signals of the nuclei from each layer can be detected.

A more detailed consideration shows that immediately after the disturbance of the nuclear spin system there is no gradient of β_k, and diffusion is not of importance [4]. To describe the relaxation we may use (33) without the diffusion term, this is the so called diffusion vanishing regime [17]. Further, usually the spin-lattice relaxation in NQR in the absence of PI's is caused by thermal modulation of the EFG [11]. 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 $T_{1k\mathrm{P}}^{-1}(\boldsymbol{r}) \ll T_{1k\mathrm{L}}^{-1}(\boldsymbol{r})$, and the character of the relaxation regime remains the same. In this case, the term which determines the direct relaxation via the PI can be neglected and the relaxation process can be described exponentially with the relaxations time $T_{1k\mathrm{L}}^{-1} = \int \mathrm{d}\,\boldsymbol{r}\, T_{1kL}^{-1}(\boldsymbol{r})$. Furthermore, the S-spins relax most effectively because they are located very close to the PI. This leads to a very short local relaxation time of them, $T_{1S\rho}(\boldsymbol{r})$. So, after the short time, $T_{1S\rho}(\boldsymbol{r}) \ll T_{1I\rho}(\boldsymbol{r})$, $T_{kk'}$, the S-spin system reaches the equilibrium state at the faster rate, and only the spin temperature $\beta_I(\boldsymbol{r})$ of the I-spin system is changed during the relaxation processes, which is described by the solution of (33):

$$\beta_I(\boldsymbol{r},t) = \beta_I(\boldsymbol{r},\infty) + [\beta_I(\boldsymbol{r},0) - \beta_I(\boldsymbol{r},\infty)] \cdot \exp\big(-t/T_{1I\rho}(\boldsymbol{r})\big), \tag{46}$$

where $\beta_I(\boldsymbol{r},\infty)$ is the equilibrium local inverse temperature. Assuming that all local inverse temperatures are equal initially and in equilibrium, the average is $R(\boldsymbol{r},t) = \left[\beta_I(\boldsymbol{r},t) - \beta_I(\boldsymbol{r},\infty)\right] / \left[\beta_I(\boldsymbol{r},0) - \beta_I(\boldsymbol{r},\infty)\right]$, the normalized local relaxation function. In the limit as the number of nuclei and PI, $N_S \to \infty$ and $N_P \to \infty$, a volume of sample, $V \to \infty$, and $N_P/\,V_L = C_P$, the PI concentration and $N_S/\,V_L = C_S$, the S-spin concentration , we have [4, 23]

$$R(t) = \exp\Big[-\big(t/T_{1\mathrm{IL}}\big) - \big(t/T_{1\mathrm{IP}}\big)^{\alpha}\Big], \tag{47}$$

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

$$T_{1\mathrm{IP}}^{-1} = \left[\frac{2\pi^{d/2}\Gamma\left(1-d/6\right)}{d\Gamma\left(d/2\right)}\right]^{6/d}\left(AC_S^{6/d} + BC_P^{6/d}\right). \tag{48}$$

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

If the influence of the PI inside the diffusion barrier is close to homogeneous, then the diffusion barrier is going to the value r_n. In this case, from the NMR point of view the I- and S-spin systems are fully equivalent, and in order to described the evolution of the nuclear spin system only one equation is enough instead of two evolution equations (33).

As the result of a diffusion-vanishing relaxation regime the local inverse temperature $\beta_I(\boldsymbol{r},t)$ becomes spatially distributed over the sample. In this case we consider also the first term in (33). To solve this equation and determine the time dependence we introduce the eigenfunctions $\varphi_n(\boldsymbol{r})$ of the operator $D_I\Delta_I - T_{1I\rho}^{-1}(\boldsymbol{r})$ [24]. Assuming the spherical symmetry approximation, the general solution of (33) can be written as an expansion in terms of the ortogonal functions $\varphi_n(\boldsymbol{r})$ in the form

$$\beta_I(r,t) = \exp\big(-t/T_{1\mathrm{IL}}(\boldsymbol{r})\big) \cdot \int \mathrm{d}\,r' \sum_n \exp\left(-k_n^2 D_I t\right)\varphi_n(r)\,\tilde{\varphi}_n^*(r'), \tag{49}$$

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

$$\Delta_I\varphi_n(r) - \left(T_{1IP}(r)/D_I\right)\varphi_n(r) = -\xi_n^2\varphi_n(r) \tag{50}$$

with the boundary condition

$$\nabla_I\varphi_n(r)\,|_{r=r_n+ql} = 0. \tag{51}$$

Equation (50) is well known in the theory of scattering for the low energy limit [25]. It has an asymptotic solution $\varphi_n(r) \sim \sin(\xi_n r + \zeta_n)/r$ for $r >> r_n$, where $\zeta_n \sim \xi_n\lambda$ is the phase shift and λ is the scattering length [25]. Taking into account the spherical symmetry (after the averaging over a polycrystalline sample) and using the boundary condition (51) we obtain [25]

$$\xi = \left(\frac{A+B}{D_I}\right)^{1/4}\frac{\Gamma(3/4)}{2\Gamma(5/4)}. \tag{52}$$

Using the last result, for the long time approximation , $t \gg (r_n + ql)^2 / D_I$, we obtain the normalized relaxation function for the diffusion-limited regime

$$R(t) = \exp\left(- \frac{t}{T_{1\mathrm{IL}}} - \frac{t}{T_{1\mathrm{ID}}} \right), \tag{53}$$

where

$$T_{1\mathrm{ID}} = \left[2\pi C 2 P D_I^{3/4} (A + B)^{1/4} \frac{\Gamma(3/4)}{\Gamma(5/4)} \right]^{-1} \tag{54}$$

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

$$T_{1\mathrm{I}\rho} = \frac{T_{1\mathrm{IL}} T_{1\mathrm{ID}}}{T_{1\mathrm{IL}} + T_{1\mathrm{ID}}}. \tag{55}$$

4. Conclusion

In conclusion, we obtained an evolution equation describing the double resonance phenomenon between nuclei inside and outside the spin diffusion barrier. By applying two radiofrequency fields with the same amplitude, one rotating at the frequency ω^I for nuclei inside of the diffusion barrier and one rotating at the frequency ω^S for nuclei outside of the diffusion barrier, the Hartmann-Hahn condition will be reached, which results in conservation of quadrupole energy in the spin diffusion process and destruction of the spin diffusion barrier. This technique can be used to detect the NQR signal from nuclei near the PI. Measurements of the NQR signal allow the determination of the geometric and electronic structure of the sample.

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