Nuclear magnetic resonance detection of the nuclear spins near paramagnetic impurities in solids

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Abstract
It was shown that on applying two radio-frequency fields, both of the same amplitude, one rotating at the frequency ω^I for nuclei inside the diffusion barrier and one rotating at the frequency ω^S for nuclei outside the diffusion barrier, the Hartmann–Hahn condition will be reached, which results in conservation of Zeeman energy in the spin-diffusion process and destruction of the spin-diffusion barrier. This technique can be used to detect the nuclear magnetic resonance signal from the nuclei located near paramagnetic impurities.

1. Introduction

The concept of spin diffusion, as a means of transporting nuclear spin energy, was introduced by Bloembergen [1] in order to explain the unexpected fast nuclear magnetic relaxation in solids containing paramagnetic impurities (PI). Such relaxation originates from the magnetic dipole–dipole interaction of PI with neighbouring 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 in the vicinity of the PI region is very large, the Larmor frequencies of nuclei located near the PI differ appreciably from those in the bulk of the sample. This results in two effects [2, 4]: (i) the nuclei from the region near to the PI do not contribute to the signal produced by the other nuclei in a measurement; and (ii) in this region, it is no longer possible for the spin-diffusion process to 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 which the diffusion is strongly quenched. The size of such a region can be defined as the distance from a PI at which the local magnetic field of the PI is of the order of the local dipolar field produced by nuclear spins. For NMR it is of the order of $\sim 10^{-7}$ cm [2, 4, 5]. The NMR signal of the nuclei from the vanishing-diffusion region is very difficult to detect [6], because the number of nuclei inside the diffusion barrier area is smaller than that in the bulk of the

sample. For the NMR case the fraction of these nuclei is of the order of $\sim 10^{-2}$–10^{-4}. At the same time, the spectrum of the nuclei from the vanishing-diffusion region is extremely sensitive to 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 NMR point of view we have two nuclear species: inside the diffusion barrier and outside the diffusion barrier with different resonance frequencies. In the present paper we consider the possibility of destroying the diffusion barrier and detecting the impurity-shifted signal from spins located inside of the diffusion barrier by using the double-nuclear-resonance technique [7], applying two radio-frequency fields, both of the same amplitude (H_1) but oscillating at different frequencies. The Hartmann–Hahn condition [7] will be reached, which results in conservation of Zeeman energy in the process of spin diffusion between the nuclear spins inside and outside the diffusion barrier and destruction of the spin-diffusion barrier.

2. Theory

Let us assume that any given nucleus is influenced by one PI, so the sample can be divided up into N_P subsystems with characteristic size $R = \sqrt[3]{3V/(4\pi N_P)}$ (N_P and V are the number of PI and the volume of the sample, respectively), each of which include only one PI surrounded by nuclear spins. Furthermore, let us divide the subsystems into three regions [8,9]: (A) $0 < r < r_n$, where r_n is the distance from the PI to the nearest nucleus; (B) $r_n < r < \delta$, where δ is the radius of the diffusion barrier; and (C) $\delta < r < R$. Region A does not contain any nuclei at all, and the majority of the nuclei are in region C. Nuclei from region B located at equal distances from the PI have the same resonance frequency. The typical atomic constant (the distance between nuclei) in solids is of the order of $l \sim (2\text{–}4) \times 10^{-8}$ cm and the nuclear spins nearest to the PI are at about the same distance. If the distribution of the atoms in solids is regular, then we can estimate the number of layers in region B, N_S, consisting of nuclei with the same resonance frequency, $(\delta - r_n)/l \sim 2$–5, and the fraction of the nuclei in each layer, $N_S/N_I \sim 10^{-2}$–10^{-5}, where N_I is number of nuclei located in region C. Below, we shall only consider the nuclei from one layer of region B inside the diffusion barrier and label them as S-spins. We shall label nuclear spins from region C as I-spins.

Let us consider the spin system consisting of $I = 1/2$ nuclear spins located in an external high magnetic field and coupled to PI spins by dipole–dipole interaction (DDI). The evolution of the spin system irradiated by two radio-frequency fields acting on nuclear spins inside (located in a layer of region B) and outside (located in region C) the diffusion barrier, may be described by a solution of the equation for the density matrix $\rho(t)$ (in units of $\hbar = 1$):

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

with the Hamiltonian

$$\mathcal{H}(t) = \mathcal{H}_Z + \mathcal{H}_{dd} + \mathcal{H}_{PI} + \mathcal{H}_P + \mathcal{H}_{rf}(t). \tag{2}$$

The Hamiltonian $\mathcal{H}_Z$ can be separated into a sum of two parts: $\mathcal{H}_Z = \mathcal{H}_Z^S + \mathcal{H}_Z^I$, where $\mathcal{H}_Z^S = \sum_{\mu=1}^{N_S} \gamma \vec{H}_0 S_\mu^Z + \mathcal{H}_{PS}$ represents the interaction of the nuclear spins S with the magnetic field $\vec{H}_0 \parallel Z$-axis and with the PI, which leads to the resonance frequency of the S-spins being shifted by the impurity. γ is the gyromagnetic ratio of the nuclear spins. $\mathcal{H}_Z^I$ describes the interaction of the I-spins with $\vec{H}_0$ outside the diffusion barrier (in region C). Similarly the nuclear DDI Hamiltonian $\mathcal{H}_{dd}$ can be divided into three parts: $\mathcal{H}_{dd} = \mathcal{H}_{II} + \mathcal{H}_{SS} + \mathcal{H}_{IS}$, where $\mathcal{H}_{II}$ and $\mathcal{H}_{SS}$ describe DDI inside and outside of the diffusion barrier (in any one layer of

region B and in region C), respectively, and $\mathcal{H}_{IS}$ represents the DDI between I- and S-spins. $\mathcal{H}_{PI}$ is the Hamiltonian of the DDI between nuclear I-spins and PI spins. $\mathcal{H}_P$ describes the impurity spin system. $\mathcal{H}_{rf}(t) = \mathcal{H}_{rf}^I(t) + \mathcal{H}_{rf}^S(t)$ gives the action of the rf fields, on both the I- and S-spin systems, with its own resonance frequencies, ω^I and ω^S, respectively.

The first rf field, which acts on the I-spin system:

$$\mathcal{H}_{rf}^I(t) = \omega_1(t) \cos(\omega^I t + \phi^I) \sum_{\mu=1}^{N_I} I_\mu^x \tag{3}$$

consists of two parts, the first of them, with $\omega_1(t) = (\pi/2)\delta(t)$ and $\phi = 0$ for the preparatory pulse, directed along the Y-axis and the second one, with constant $\omega_1 = \gamma H_1$ and $\phi = \pi/2$ for all times immediately after the first pulse, directed along the X-axis. This technique is used to achieve two main goals: first, to bring the magnetization of the I-spin system to the spin-locking state with a very low spin temperature [7]; and second, to decrease the spin-diffusion relaxation time by at least twice the decrease of the spin-diffusion constant in the rotating frame [10–13]. The second rf field which acts only on S-spins:

$$\mathcal{H}_{rf}^S(t) = \omega_1(t) \cos(\omega^S t) \sum_{\mu_S=1}^{N_S} I_{\mu_S}^x \tag{4}$$

(where ω^S is the applied frequency) is equal to the impurity-shift resonance frequency, $\omega_1(t) = \vartheta \sum_{k=0}^{\infty} \delta[t - (k + \frac{1}{2})t_c]$, where $\vartheta = \gamma H_1 t_w$. H_1 and t_w are the amplitude and pulse duration of the rf pulses; t_c is the period of the multiple-pulse sequence. This multiple-pulse sequence is used for thermal mixing between S- and I-spin systems.

The spin system is situated in an external magnetic field coupled with the nuclear spins and produces an interaction that is assumed to be very large in comparison to the DDI for region C. For this case, the non-secular terms of the Hamiltonians, $\mathcal{H}_{dd}$ and $\mathcal{H}_{PI}$ (those terms that do not commute with $\mathcal{H}_Z$), may be neglected. The procedure of separation of the truncated Hamiltonians $\mathcal{H}_{dd}^{sec}$ and $\mathcal{H}_{PI}^{sec}$ can be carried out by using the unitary transformation $\rho(t) = P^+(t)\tilde{\rho}(t)P(t)$ with

$$P(t) = \prod_{k=S,I} \exp\left\{ it(2I+1)^{-1}\omega^k \sum_{\mu_k=1}^{N_k} I_{\mu_k}^z \right\}. \tag{5}$$

After the transformation we obtain

$$i\frac{d\tilde{\rho}(t)}{dt} = [\tilde{\mathcal{H}}_\rho, \tilde{\rho}(t)] \tag{6}$$

with the effective Hamiltonian in the rotating frame

$$\tilde{\mathcal{H}}_\rho = \sum_{k=I,S} \left(\mathcal{H}_k^j + \mathcal{H}_{dd,k}^{sec} + \mathcal{H}_{Pk}^{sec} \right) + \mathcal{H}_{IS}^{sec} + \mathcal{H}_P \tag{7}$$

where

$$\mathcal{H}_I^j = \omega_1^I \sum_{\mu_I}^{N_I} I_{\mu_I}^x \qquad \mathcal{H}_S^j = \omega_1^S(t) \sum_{\mu_S}^{N_S} I_{\mu_S}^x. \tag{8}$$

$\mathcal{H}_{dd,k}^{sec}$ is the secular part of the nuclear DDI Hamiltonian. In the 'heteronuclear' $\mathcal{H}_{IS}^{sec}$ and impurity–nuclear DDI Hamiltonians we retain only the secular relative Z-axis term which gives the dominant contribution to the relaxation process:

$$\mathcal{H}_{IS}^{sec} = \frac{1}{2} \sum_{\mu_k \neq \eta_S} a_{\mu_k \eta_k} I_{\mu_I}^z I_{\eta_S}^z \tag{9}$$

where $a_{\mu_k \eta_k} = \gamma_I^2 r_{\mu_k \eta_k}^{-3}(1 - 3\cos^2\theta_{\mu_k \eta_k})$ (here $r_{\mu_k \eta_k}$ and $\theta_{\mu_k \eta_k}$ are the spherical coordinates of the vector $\vec{r}_{\mu_k \eta_k}$ connecting the μth and ηth nuclei in a coordinate system with the Z-axis along the direction of the external magnetic field $\vec{H}_0$), and

$$\mathcal{H}_{kP}^{\rm sec} = \tfrac{1}{2}\sum_{\mu_k \neq j} b_{\mu_k j} I_{\mu_k}^z L_j^z. \tag{10}$$

In this equation, $b_{\mu_k} = \gamma_I \gamma_P r_{\mu_k j}^{-3}(1 - 3\cos^2\theta_{\mu_k j})$, where γ_P is the gyromagnetic ratio of the PI, and $r_{\mu_k j}$ is the distance between μth nuclear and jth PI spins.

Thermal mixing between the two spin systems I and S occurs when mutual flip-flop processes, induced by dipole–dipole interaction, can take place with conservation of the total energy. The conditions for such energy-conserving processes are realized at the crossover between two frequencies ω_1^I and ω_1^S when rf pulses with amplitude H_1 and frequency ω^S are applied. The Hartmann–Hahn condition [7] will be reached: $\omega_1^I = \gamma_I H_1 = \gamma_S H_1 = \omega_1^S$. We note that $\gamma_I = \gamma_S$.

In the case of $\omega_1^k \approx \omega_P^{\rm loc} \gg \omega_{PI} \gg \omega_{\rm dd}^{\rm loc}$ (here $\omega_g^{\rm loc} \sim ||\mathcal{H}_g||$ is the norm of the operator $\mathcal{H}_g$ and $g \equiv P, PI, {\rm dd}$) which holds, for example, if $\gamma_I \ll \gamma_p$, it is convenient to expand the secular parts of the Hamiltonians $\mathcal{H}_{\rm dd}^{\rm sec}$, $\mathcal{H}_{IS}^{\rm sec}$, and $\mathcal{H}_{Pk}$ as follows:

$$\mathcal{H}_{kk'}^{\rm sec} = \sum_{i=-2}^{2} \mathcal{H}_{kk'}^i \tag{11}$$

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

$$\mathcal{H}_{kk}^0 = -\tfrac{1}{2}\sum_{\mu_k \neq \eta_k} a_{\mu_k \eta_k}\left[I_{\mu_k}^x I_{\eta_k}^x - \tfrac{1}{4}(I_{\mu_k}^+ I_{\eta_k}^- + I_{\mu_k}^- I_{\eta_k}^+)\right] \tag{12}$$

and $\mathcal{H}_{kk}^i$ with $i \neq 0$ are the non-secular terms relative to $\mathcal{H}_k$ ($[\mathcal{H}_k, \mathcal{H}_{kk}^i] \neq 0$):

$$\mathcal{H}_{kk}^{\pm 2} = \sum_{\mu_k \neq \eta_k} a_{\mu_k \eta_k} I_{\mu_k}^{\pm} I_{\eta_k}^{\pm}. \tag{13}$$

The operators $\mathcal{H}_{IS}^{\rm sec}$ and $\mathcal{H}_{Pk}$ consist only of terms that are non-secular relative to $\mathcal{H}_I$ or $\mathcal{H}_S$:

$$\mathcal{H}_{IS}^{\rm sec} = \sum_{\mu_k \neq \eta_S} a_{\mu_I \eta_S}(I_{\mu_I}^+ + I_{\mu I}^-)(I_{\mu_S}^+ + I_{\mu_S}^-) \tag{14}$$

$$\mathcal{H}_{kP}^{\rm sec} = \tfrac{1}{2}\sum_{\mu_k \neq j} b_{\mu_k j}(I_{\mu_k}^+ + I_{\mu_k}^-)L_j^z \tag{15}$$

where $I_{\mu_k}^{\pm} = I_{\mu_k}^z \pm iI_{\mu_k}^y$.

To obtain the evolution equation for the spin system, we will use the method of non-equilibrium state operators [14] which was originally applied to the spin diffusion in NMR [15]. Introducing the nuclear spin-density operator

$$\vec{I}(\vec{r}_k) = \sum_{\mu_k=1}^{N_k} \delta(\vec{r} - \vec{r}_\mu)\vec{I}_{\mu_k} \tag{16}$$

the densities of the operator $\mathcal{H}_k^j$ can written in the following form:

$$\mathcal{H}(\vec{r}_k) = \omega_1^k \sum_{\mu_k=1}^{N_k} \delta(\vec{r}_k - \vec{r}_{\mu_k})I_{\mu_k}^x. \tag{17}$$

In the following, we consider the times when the rf pulse with frequency ω^S is applied. In view of the structure of the system, we will choose $\mathcal{H}(\vec{r}_k)$ (with $k = I, S$) and $\mathcal{H}_P$ as the local integral-of-motion operators; the other terms in equation (7) may be considered as

small perturbations. Following Zubarev [14], we assume that the quasi-equilibrium state is established in the spin system, and the density matrix can be written as

$$\rho = Z^{-1} \exp \left\{ - \sum_{k=I,S} \int_{r_1^k}^{r_2^k} \mathrm{d}\vec{r}\, \beta(\vec{r}_k) \mathcal{H}(\vec{r}_k) - \beta_P \mathcal{H}_P \right.$$
$$\left. + \int_{-\infty}^{0} \mathrm{d}t\, \mathrm{e}^{\epsilon t} \left[\sum_{k=I,S} \int_{r_1^k}^{r_2^k} \mathrm{d}\vec{r}\, \beta(\vec{r}_k) \frac{\partial \mathcal{H}(\vec{r}_k)}{\partial t} + \beta_P \frac{\partial \mathcal{H}_P}{\partial t} \right] \right\} \tag{18}$$

where $Z = \mathrm{Tr}\exp\{\cdots\}$, and $\beta_k^j(\vec{r})$ is the local inverse spin temperature, conjugate to $\mathcal{H}_k^j(\vec{r})$, $r_1^k = \delta$ and $r_2^k = R$ for $k = I$, and $r_1^k = ml + r_n$ and $r_2^k = (m+1)l + r_n$ for $k = S$, where $m = 0$–5 is the layer number in region B, containing nuclei with the same resonance frequency, beginning from the layer nearest to the PI. In equation (18) all operators are taken in the Heisenberg representation and, after the integration is performed, we set $\epsilon = 0$ [14]. If the heat capacity of the PI reservoir, $-(\delta/\delta\beta_P)\langle\mathcal{H}_P\rangle$, is large in comparison with the nuclear spin heat capacities and the PI spin–lattice relaxation time is very short, a case which is experimentally implementable, it is reasonable to consider only the relaxation process with the constant inverse spin temperature of the PI, β_P, equal to that of the lattice: $\beta_P = \beta_L$. Therefore, the PI reservoir is in thermal equilibrium with the lattice and β_P is independent of the position. The time dependences of the slowly varying thermodynamic quantities in the integral of equation (18) were neglected in comparison with the rapidly varying corrections [15].

Applying the commutation rules $[I^x(\vec{r}_k), I^y(\vec{r}_{k'})] = \mathrm{i}\delta(\vec{r}_k - \vec{r}_{k'})I^z(\vec{r}_k)$, the transport equations, in the form of localized laws of conservation of the spin energy densities, can be obtained:

$$\frac{\partial \mathcal{H}(\vec{r}_k)}{\partial t} + \mathrm{div}\, \vec{j}(\vec{r}_k) = K(\vec{r}_k) + F(\vec{r}_k) \tag{19}$$

$$\frac{\partial \mathcal{H}_P}{\partial t} = - \sum_{k=I,S} \int_{r_1^k}^{r_2^k} \mathrm{d}\vec{r}\, \frac{\partial \mathcal{H}(\vec{r}_k)}{\partial t} \tag{20}$$

where

$$K(\vec{r}_k) = -\mathrm{i}[\mathcal{H}(\vec{r}_k), \mathcal{H}_{Pk}^{\mathrm{sec}}(t)] = \mathrm{i}\frac{\omega_1^k}{2} \int_V \mathrm{d}\vec{r}_L\, b(\vec{r}_k - \vec{r}_L) I^y(\vec{r}_k) L^z(\vec{r}_L) \tag{21}$$

$$F(\vec{r}_k) = -\mathrm{i}[\mathcal{H}(\vec{r}_k), \mathcal{H}_{IS}^{\mathrm{sec}}(t)] = \mathrm{i}\omega_1^k \int_{r_1^{k'}}^{r_2^{k'}} \mathrm{d}\vec{r}_{k'}\, a(\vec{r}_k - \vec{r}_{k'}) I^y(\vec{r}_k) I^z(\vec{r}_{k'}). \tag{22}$$

Equation (20) is the result of the energy conservation law. In equation (19), $\vec{j}_k(\vec{r})$ is the operator for the flux of the density of the nuclear spin energy:

$$\vec{j}(\vec{r}_k) = \frac{\mathrm{i}\omega_1^k}{4} \int_{r_1^k}^{r_2^k} \mathrm{d}\vec{r}_k'\, (\vec{r}_k - \vec{r}_k') a(\vec{r}_k - \vec{r}_k') [I^+(\vec{r}_k) I^-(\vec{r}_k') - I^-(\vec{r}_k) I^+(\vec{r}_k')]. \tag{23}$$

At high temperatures we can obtain the density matrix in the form [14]

$$\rho = \left\{ 1 - \int_0^1 \mathrm{d}\lambda\, [\mathcal{B}(\mathrm{i}\lambda) - \langle \mathcal{B}(\mathrm{i}\lambda) \rangle_{\mathrm{eq}}] \right\} \rho_{\mathrm{eq}} \tag{24}$$

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

$$\mathcal{A} = \sum_{k=I,S} \int_{r_1^k}^{r_2^k} \mathrm{d}\vec{r}_k\, \beta(\vec{r}_k) \mathcal{H}(\vec{r}_k) + \beta_P \mathcal{H}_P \tag{25}$$

$$\mathcal{B}(t + \mathrm{i}\lambda) = \int_{-\infty}^{0} \mathrm{d}t\, \mathrm{e}^{\epsilon t} \sum_{k=I,S} \int_{r_1^k}^{r_2^k} \mathrm{d}\vec{r}\, \{\nabla \beta(\vec{r}_k, t)[\mathrm{e}^{-\lambda \mathcal{A}} \vec{j}(\vec{r}_k, t)\mathrm{e}^{\lambda \mathcal{A}}]$$

$$+ [\beta(\vec{r}_k, t) - \beta_L]\mathrm{e}^{-\lambda \mathcal{A}}[K(\vec{r}_k, t) + F(\vec{r}_k, t)]\mathrm{e}^{\lambda \mathcal{A}}\}. \tag{26}$$

Let us make some remarks before we obtain the equation describing the spin diffusion and spin–lattice relaxation of the nuclear spin system 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 second rank [9]. However, in the case of a polycrystalline sample or cubic symmetry, D reduces to a scalar quantity. We now confine our consideration to a system with a polycrystalline sample or cubic symmetry. By using equations (19) and (24)–(26) and taking into account that for such a case $\langle \mathcal{B}(t + \mathrm{i}\lambda)\rangle_{\mathrm{eq}} = 0$ (if it is not equal to zero, a suitable choice of the quantities $\tilde{\mathcal{B}} \equiv \mathcal{B} - \langle \mathcal{B}\rangle_{\mathrm{eq}}$ leads to the same result), the diffusion equation can be obtained:

$$\frac{\partial \beta(\vec{r}_k, t)}{\partial t} = (D_k \Delta_k - T_{1\rho}^{-1}(\vec{r}_k))(\beta(\vec{r}_k, t) - \beta_L)$$

$$- \int \mathrm{d}\vec{r}_{k'}\, T_{IS}^{-1}(\vec{r}_k - \vec{r}_{k'})(\omega_1^k \beta(\vec{r}_k, t) - \omega_1^{k'} \beta(\vec{r}_{k'}, t)) \tag{27}$$

with the boundary condition

$$\nabla \beta(r_k, t)|_{r_k = b_k} = 0 \qquad \text{where } b_k = \begin{cases} r_n + ml & \text{for } k = S \\ \delta & \text{for } k = I. \end{cases} \tag{28}$$

The first term on the right-hand side of equation (27) describes the spin-diffusion process with the diffusion coefficient

$$D_k = \tfrac{1}{4} \int_{r_1^k}^{r_2^k} \mathrm{d}\vec{r}_k'\, (\vec{r}_k - \vec{r}_k')^2 a^2(\vec{r}_k - \vec{r}_k') \int_0^{\infty} \mathrm{d}\tau\, G(\vec{r}_k, \vec{r}_k', \tau). \tag{29}$$

Here $G(\vec{r}_k, \vec{r}_k', \tau) = \langle I^+(\vec{r}_k)I^-(\vec{r}_k)\rangle_{\mathrm{eq}}$ is the correlation function of the nuclear spins. The second term gives the variation of $\beta_k(\vec{r}, t)$ due to the direct relaxation to the PI with relaxation time $T_{1\rho}(\vec{r}_k)$:

$$T_{1\rho}^{-1}(\vec{r}_k) = \int_V \mathrm{d}\vec{r}_j\, b^2(\vec{r}_k - \vec{r}_j) \int_0^{\infty} \mathrm{d}\tau\, g_{kj}(\tau) \cos \omega_1^k \tau / \mathrm{Tr}[\mathcal{H}(\vec{r}_k)]^2 \tag{30}$$

with the correlation function of the nuclear and PI spins $g_{kj}(\tau) = \langle I^y(\vec{r}_k, 0)I^y(\vec{r}_k, \tau)\rangle_{\mathrm{eq}} \langle I^z(\vec{r}_j, 0)I^z(\vec{r}_j, \tau)\rangle_{\mathrm{eq}}$. The last term in equation (27) represents the thermal mixing between I- and S-spin systems with the local relaxation time

$$T_{IS}^{-1}(\vec{r}_k - \vec{r}_{k'}) = \omega_1^k a^2(\vec{r}_k - \vec{r}_{k'}) \int_0^{\infty} \mathrm{d}\tau\, g_{kk'}(\tau) \cos(\omega_1^k - \omega_1^{k'})\tau / \mathrm{Tr}[\mathcal{H}(\vec{r}_k)]^2 \tag{31}$$

where $g_{kk'}(\tau) = \langle I^y(\vec{r}_k, 0)I^y(\vec{r}_k, \tau)I^z(\vec{r}_{k'}, 0)I^z(\vec{r}_{k'}, \tau)\rangle_{\mathrm{eq}}$.

3. Results and discussion

By means of equations (27) and (28) the spin dynamics, with both spin temperatures ($\beta(\vec{r}_I, t)$ and $\beta(\vec{r}_S, t)$) time dependent, can be described.

First, let us determine the dependence of the relaxation time of the thermal mixing, $T_{IS}^{-1}(\vec{r}_k - \vec{r}_{k'})$, on the amplitudes of the rf fields, H_1^I and H_1^S. Using the simplest approximation for $g_{kk'}(\tau)$ [7]:

$$g_{kk'}(\tau) = g_{kk'}(0) \exp\left[-\left(\frac{\tau}{2\sigma}\right)^2\right] \tag{32}$$

after performing the integration over τ, we obtain

$$T_{IS}^{-1}(\vec{r}_k - \vec{r}_{k'}) \sim \exp\left[-\frac{\gamma^2(H_1^k - H_1^{k'})^2\tau^2}{2}\right] \qquad \text{with } k, k' = I \text{ or } S. \quad (33)$$

So, the process of mixing of nuclear spins located near PI and in the bulk of the sample is a very sharp function of the difference between the amplitudes of the rf fields acting on the I- and S-spin systems, $H_1^k - H_1^{k'}$. The double-resonance process takes place when this difference is close to zero: $H_1^I \approx H_1^S$.

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

$$\beta_I C_I H_1^2 + \beta_S C_S H_S^2 = \beta_{\mathrm{f}}(C_I H_1^2 + C_S H_S^2) \quad (34)$$

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. $C_{I,S} = \frac{1}{3} N_{I,S} I(I + 1)\gamma_I^2$ is the Curie constant. Under the condition $\omega_1^I = \gamma_I H_1 = \gamma_S H_1 = \omega_1^S$, the change of the ratio $\beta_{\mathrm{f}}/\beta_I$ is $\beta_{\mathrm{f}}/\beta_I = [N_I + (\beta_S/\beta_I)N_S]/N$, where $N = N_I + N_S$. Assuming that the S-spin system is very hot, $\beta_S \approx 0$, we have $\beta_I/\beta_{\mathrm{f}} \approx N_I/N \approx 1/(1 + \xi)$, where $\xi = N_S/N_I = [(ml + r_n)^3 - r_n^3]/(R^3 - \delta^3) \ll 1$ for the m-layer.

For instance, we find that for CaF_2 doped with Mn^{2+} [13] with impurity concentration $C_P = 3.1 \times 10^{18}$ cm^{-3} and the average impurity separation $R = 42.5$ Å, where for F nuclei form a simple cubic structure with the lattice constant $l = 2.725$ Å and $\delta = 1.3 \times 10^{-7}$ cm, the number of layers in region B is $\delta/l \sim 4$ and $\xi \sim 0.07$. So, in this case four layers in region B can be extracted and, using the rf irradiation [16] with four different resonance frequencies ω^S, the NMR signals of the nuclei from each layer can be detected; also the observed decrease of β_I can be reproduced using ten thermal mixing contacts.

More detailed consideration shows that immediately after a disturbance of the nuclear spin system, there is no gradient of $\beta(\vec{r}_k)$, and diffusion is not of importance [4]. To describe the relaxation we may use equations (27) without the diffusion term; this is the so-called vanishing-diffusion regime [12]. Furthermore, the S-spins relax most effectively with the PI, with the result that the S-spins are located very close to the PI which leads to them having a very short local relaxation time, $T_{1\rho}(\vec{r}_S)$. So, after the short time, $T_{1\rho}(\vec{r}_S) \ll T_{1\rho}(\vec{r}_I)$, T_{IS}, the S-spin system reaches the equilibrium state and only the spin temperature $\beta(\vec{r}_I)$ of the I-spin system is changed during the relaxation processes, as described by the following equation:

$$\frac{\partial \beta(\vec{r}_I, t)}{\partial t} = (D_I \Delta_I - T_{1\rho}^{-1}(\vec{r}_I) - T_{IS}^{-1}(\vec{r}_I))(\beta(\vec{r}_I, t) - \beta_L) \quad (35)$$

where $T_{IS}^{-1}(\vec{r}_I) = \int_{r_n}^{\delta} d\vec{r}_S\, T_{IS}^{-1}(\vec{r}_I - \vec{r}_S)$, $\beta(\vec{r}_S) = \beta_L$, and $\omega_1^I = \omega_1^S$.

In the presence of a high PI concentration, at the beginning of the relaxation process equation (35) for the I-spin system has the solutions

$$\beta(\vec{r}_I, t) = \beta(\vec{r}_I, \infty) + [\beta(\vec{r}_I, 0) - \beta(\vec{r}_I, \infty)] \exp\left(-\frac{t}{T_{1e}(\vec{r}_I)}\right) \quad (36)$$

where $T_{1e}^{-1}(\vec{r}_I) = T_{1\rho}^{-1}(\vec{r}_I) + T_{IS}^{-1}(\vec{r}_I)$ and $\beta(\vec{r}_I, \infty)$ 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 averaged is

$$R(\vec{r}_I, t) = \frac{\beta(\vec{r}_I, t) - \beta(\vec{r}_I, \infty)}{\beta(\vec{r}_I, 0) - \beta(\vec{r}_I, \infty)} \quad (37)$$

which is the normalized local relaxation function. In the limit as the number of nuclei $N_S \to \infty$ and number of PI $N_P \to \infty$, and the volume of the sample $V \to \infty$, and also for $N_P/V_L = C_P$, the PI concentration, and $N_S/V_L = C_S$, the S-spin concentration, we have [4, 17]

$$R(t) = \exp\left[-\left(\frac{t}{T_{1e}}\right)^{\alpha}\right] \tag{38}$$

where $\alpha = d/6$, (d is the dimensionality of the sample), and

$$T_{1e}^{-1} = T_{1\rho}^{-1} + T_{IS}^{-1} \tag{39}$$

$$T_{1\rho}^{-1} = B\left[\frac{2\pi^{d/2}\Gamma(1-d/6)C_P}{d\Gamma(d/2)}\right]^{6/d} \tag{40}$$

$$T_{IS}^{-1} = A\left[\frac{2\pi^{d/2}\Gamma(1-d/6)C_S}{d\Gamma(d/2)}\right]^{6/d}. \tag{41}$$

Here $A = \langle a(\vec{r})\rangle_{\theta_{\mu\eta},\phi_{\mu\eta}}$ and $B = \langle b(\vec{r})\rangle_{\theta_{\mu j},\phi_{\mu j}}$ are averages over the spherical coordinates of the vector $\vec{r}_{\mu\eta}$ connecting the μth and ηth nuclear spins and that connecting the μth and jth PI spins, respectively. $\Gamma(x)$ is the gamma function.

As the result of being in the vanishing-diffusion relaxation regime, the local inverse temperature, $\beta(\vec{r}_I, t)$, becomes spatially distributed over the sample. But for the multiple-contact method of thermal mixing, this process will cease in the case where $t_c \leqslant T_{1\text{dif}}$, the spin–lattice relaxation time of the diffusion part of the relaxation process. If $t_c \geqslant T_{1\text{dif}}$, then from the NMR point of view the I- and S-spin systems are fully equivalent and the radius of the spin-diffusion barrier becomes equal to r_n. In this case we consider also the first term in equation (35). To solve this equation and determine the time dependence, we introduce the eigenfunctions $\varphi_n(\vec{r})$ of the operator $D\Delta - T_{1e}^{-1}(\vec{r})$ [18]. Assuming the spherical symmetry approximation to apply, the general solution of equation (35) can be written as an expansion in terms of the orthogonal functions $\varphi_n(\vec{r})$ in the following form:

$$\beta(r_I, t) = \int dr' \sum_n \exp(-m_n^2 Dt)\varphi_n(r)\tilde{\varphi}_n^*(r') \tag{42}$$

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

$$\Delta\varphi_n(r) - (T_{1e}(r)/D)\varphi_n(r) = -q_n^2\varphi_n(r) \tag{43}$$

with the boundary condition

$$\nabla\varphi_n(r)|_{r=r_n+ml} = 0. \tag{44}$$

Equation (43) is well known in the theory of scattering for the low-energy limit [19]. It has an asymptotic solution $\varphi_n(r) \sim \sin(q_n r + \varsigma_n)/r$ for $r \gg r_n$, where $\varsigma_n \sim q_n\varkappa$ is the phase shift and $\varkappa$ is the scattering length [19]. Taking into account the spherical symmetry (after averaging over a polycrystalline sample) and using the boundary condition (44), we obtain [19]

$$\xi = \left(\frac{A+B}{D}\right)^{1/4}\frac{\Gamma(3/4)}{2\Gamma(5/4)}. \tag{45}$$

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

$$R(t) = \exp\left(-\frac{t}{T_{1\text{dif}}}\right) \tag{46}$$

where

$$T_{1\text{dif}} = \left[2\pi C_P D^{3/4}(A+B)^{1/4}\frac{\Gamma(3/4)}{\Gamma(5/4)}\right]^{-1}. \tag{47}$$

In conclusion, we have obtained an evolution equation describing the phenomenon of double resonance between nuclei inside and outside the spin-diffusion barrier. On applying two radio-frequency fields, of the same amplitude, one rotating at the frequency ω^I for nuclei inside the diffusion barrier and one rotating at the frequency ω^S for nuclei outside the diffusion barrier, the Hartmann–Hahn condition will be reached, which results in conservation of Zeeman energy under the spin-diffusion process and destruction of the spin-diffusion barrier. This technique can be used to detect the NMR signal from the nuclei near the PI, which will be useful in the determination of crystal structure.

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