Spin diffusion in an inhomogeneous internal field (non equidistant energy spectrum)

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Abstract

The theory of NQR spin diffusion is extended to the case of spin lattice relaxation and spin diffusion in an inhomogeneous field. Two coupled equations describing the mutual relaxation and the spin diffusion of the nuclear magnetization and dipolar energy were obtained by using the method of nonequilibrium state operator. The equations were solved for short and long times approximation corresponding to the direct and diffusion relaxation regimes.
Introduction

Studies of the NMR [1, 2, 3] and NQR of nuclei have demonstrated that spin diffusion plays an important role in the relaxation of nuclei in the presence of 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, 2, 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, first, 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 and, second, most of them deal with the process of a spin diffusion in homogeneous magnetic fields [4, 5].

In many samples spin systems consist of nuclei with \( I > 1/2 \) and they 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 the NMR-case, the NQR energy spectrum is 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.

Besides, the spin diffusion processes no longer exactly conserve nuclear quadrupole energy in an inhomogeneous field [6] because the quadrupole interaction energy is not identical for neighboring nuclear spins. In order for the spin diffusion process to take place, the nuclear quadrupole energy difference must be taken up by another thermodynamic reservoir, for example, by the dipole-dipole energy one.

Recently the theories for spin diffusion of the nuclear dipolar order via PI’s [8, 9] in NMR and NQR [10] and spin diffusion in an inhomogeneous field [11] have been developed. It was shown that thermodynamics reservoir of the dipolar order plays an important role in the spin lattice relaxation and spin diffusion in an inhomogeneous feild. Nuclear dipolar order is characterized by a state with nuclear spins oriented along an internal local field generated by the dipole-dipole interactions (DDI) and can be described by a dipolar temperature [12, 13, 14, 15]. Here we consider the phenomena of spin lattice relaxation and spin diffusion.
for both the nuclear quadrupole and dipolar energies of the nuclear spins due to their DDI in solids containing PI’s in an inhomogeneous field.

**Theory**

1. **Hamiltonian**

The evolution of the spin system consisting of nuclear spins with $I > 1/2$ and PI spins may be described by a solution of the equation for density matrix $\rho(t)$ (in units of $\hbar = 1$)

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

with the Hamiltonian

$$H(t) = H_Q + H_{dd} + H_{PI} + H_P + H_{br}(t).$$  \hspace{1cm} (2)

Here $H_Q$ represents the interaction of the $I$-spin system with the EFG; $H_{dd}$ and $H_{PI}$ are the Hamiltonians of the dipole-dipole interaction between nuclear spins and nuclear and PI spins, respectively; $H_P$ describes the impurity spin system; $H_{br}(t) = \sum_{q=-2}^{2} E^{(-q)}(t) A^q$ the spin-lattice interaction Hamiltonian, describes spin-lattice relaxation caused by the torsional vibrations (Bayer mechanism) [16], where $A^q$ is a bilinear function of the spin operators and $E^{(-q)}(t)$ is a random function of time [14].

Using the projection operators $e_{\mu}^{mn} \text{ and } \varepsilon_{mn}^{ij}$ defined by their matrix elements

$$\langle m' | e_{\mu}^{mn} | n' \rangle = \delta_{m'm} \delta_{n'n} \text{ and } \langle \nu' | \varepsilon_{\nu\sigma}^{\mu} | \sigma' \rangle = \delta_{\nu'\nu} \delta_{\sigma'\sigma}$$

and introducing a projection density operators, $e_{mn}(\vec{r})$, for the nuclear spins $I$, and $\varepsilon_{mn}(\vec{r})$ for PI spins

$$e_{mn}(\vec{r}) = \sum_{\mu} \delta(\vec{r} - \vec{r}_{\mu}) e_{\mu}^{mn}; \varepsilon_{mn}(\vec{r}) = \sum_{j} \delta(\vec{r} - \vec{r}_j) \varepsilon_{mn}^{ij}$$  \hspace{1cm} (3)

the density of the Hamiltonians $H_Q$, $H_{dd}$, and $H_{PI}$ can be written down in the following form:

$$H_Q(\vec{r}) = (2I + 1)^{-1} \sum_{mn} \omega_{mn}^{0} e_{mn}(\vec{r}),$$  \hspace{1cm} (4)

$$H_{dd}(\vec{r}) = \int d\vec{r}' \sum_{mm'n'n'} g_{mm'n'n'}^{m'n'}(\vec{r} - \vec{r}') e_{mn}(\vec{r}) e_{m'n'}(\vec{r}')$$  \hspace{1cm} (5)

$$H_{PI}(\vec{r}) = \int d\vec{r}' \sum_{mm'n'n'} f_{mm'n'n'}^{m'n'}(\vec{r} - \vec{r}') e_{mn}(\vec{r}) \varepsilon_{m'n'}(\vec{r}')$$  \hspace{1cm} (6)
\[ \mathcal{H}_{br} (t) = \sum_q \sum_{mn} E^{(-q)} (t) A^0_{mn} \int d\vec{r} e_{mn} (\vec{r}) \] (7)

where \( \omega^0_{mn} = \lambda_m - \lambda_n, \lambda_m, |m\rangle \), and \( |n\rangle \) are the eigenvalues and eigenvectors of the operator \( \mathcal{H}_Q \). \( |\nu\rangle \) and \( |\sigma\rangle \) are eigenvectors of the operator \( \mathcal{H}_P \); matrix elements \( g^{m'n'}_{mn} (\vec{r} - \vec{r}') \) and \( f^{m'n'}_{mn} (\vec{r} - \vec{r}') \) can be presented as

\[ g^{m'n'}_{mn} (\vec{r} - \vec{r}') = G^{m'n'}_{mn} (\vec{r} - \vec{r}') \left[ (\delta_{mn} + \delta_{pq}) (\delta_{m\bar{n}} + \delta_{p\bar{q}}) + (\delta_{mq} + \delta_{pn}) (\delta_{m\bar{q}} + \delta_{p\bar{n}}) \right] \] (8)

with \( \bar{n} = n \) and

\[ f^{m'n'}_{mn} (\vec{r} - \vec{r}') = F^{m'n'}_{mn} (\vec{r} - \vec{r}') (\delta_{mn} + \delta_{pq}) (\delta_{m\bar{n}} + \delta_{p\bar{q}}), \] (9)

\( G^{m'n'}_{mn} \) and \( F^{m'n'}_{mn} \) are matrix elements of the dipole-dipole Hamiltonians \( \mathcal{H}_{dd} \) and \( \mathcal{H}_{PI} \) in \( \mathcal{H}_Q \)-representation \[17\].

2. Diffusion equations

To obtain the equation describing the spin diffusion and spin lattice relaxation of both the quadrupole and dipolar orders we will use the method of nonequilibrium state operator \[18\], which has been applied to obtain the diffusion equation in cases of the Zeeman order spin diffusion \[19\] and dipolar order \[8\] spin diffusion.

Using the commutation rules between the components of the projection operators (3) \( [e_{mn} (\vec{r}), e_{m'n'} (\vec{r}')] = \delta (\vec{r} - \vec{r}') (\delta_{nm'} e_{mn} (\vec{r}) - \delta_{n'm} e_{m'n} (\vec{r})) \) and \( [e_{mn} (\vec{r}), e_{m'n'} (\vec{r}')] = 0 \), we can obtain the following equations in the form of localized laws of conservation of the spin energy densities

\[ \frac{\partial e_{mn} (\vec{r})}{\partial t} + \text{div} \left( \vec{j}_{mn} (\vec{r}) \right) = K_{mn} (\vec{r}) + L_{mn} (\vec{r}), \] (10)

\[ \frac{\partial \mathcal{H}_{dd} (\vec{r})}{\partial t} + \text{div} \left( \vec{j}_{dd} (\vec{r}) \right) + \sum_{mn} \vec{j}_{mn} (\vec{r}) \frac{\partial \omega^0_{mn} (\vec{r})}{\partial \vec{r}} = K_{dP} (\vec{r}) + L_{dP} (\vec{r}), \] (11)

\[ \frac{\partial \mathcal{H}_P}{\partial t} = - \int d\vec{r} \left\{ (2I + 1)^{-1} \frac{\partial}{\partial \vec{r}} \left[ \sum_{mn} \beta_{mn} (\vec{r}) \omega^0_{mn} (\vec{r}) e_{mn} (\vec{r}) \right] + \frac{\partial \mathcal{H}_{dd} (\vec{r})}{\partial t} \right\}. \] (12)

The last equation is result of the energy conservation law. In Eqs (10) \( \vec{j}_{mn} (\vec{r}) \) is the flux of operator \( e_{mn} (\vec{r}) \).
\[
\vec{J}_{mm} (\vec{r}) = -\frac{i}{2} \int d\vec{r} \sum_k (\vec{r} - \vec{r}') G_{mk}^{km} (\vec{r} - \vec{r}') \{ e_{mk} (\vec{r}) e_{km} (\vec{r}) - e_{mk} (\vec{r}') e_{km} (\vec{r}') \} \\
- e_{km} (\vec{r}') e_{mk} (\vec{r}) + e_{km} (\vec{r}) e_{mk} (\vec{r}') \}
\]

(13)

\[
K_{mm} (\vec{r}) = i [H_{PI}, e_{mm} (\vec{r})] \text{ and } L_{mm} (\vec{r}) = i [H_{br}, e_{mm} (\vec{r})] \text{ in Eq. (10) are the change of the nuclear quadrupolar energy density due to the interaction with the PI and caused by the torsional vibrations (Bayer mechanism), respectively. In Eq.(11), } \vec{J}_{dd} (\vec{r}) \text{ is the operator of the flux of nuclear dipolar energy,}
\]

\[
\vec{J}_{dd} (\vec{r}) = -2i \sum_{mnpq} \sum_{m'n'p'} \int d\vec{r}'' \int d\vec{r}'' (r'' - r) G_{mnpq}^{mn} (r'' - r) e_{mn} (r'') e_{m'n'} (\vec{r}') \\
\quad \sum_{m'n'qp'} \left[ G_{m'n'qp'} (r' - r) e_{pp'} (\vec{r}) - G_{m'n'p'p} (r' - r) e_{p'q} (\vec{r}) \right],
\]

(14)

\[
K_{ddP} (\vec{r}) = i [H_{PI}, H_{dd} (\vec{r})] \text{ and } L_{ddP} (\vec{r}) = i [H_{br}, H_{dd} (\vec{r})] \text{ in Eq. (11) are the change of the nuclear dipolar energy density due to the interaction with the PI and caused by the torsional vibrations (Bayer mechanism), respectively. Note, that in the case with a homogenous magnetic field, } \frac{\partial \omega_0^{mn} (\vec{r})}{\partial \vec{r}}, \text{ from the system equations (10) and (11) we have two separate equations: Eq. (10) leads to the localized law of conservation of the quadrupolar energy densities [20] and Eq. (11) leads to conservation law of the dipolar energy [10].}
\]

In the high temperature approximation we can write the density matrix in the following form [18]

\[
\sigma = \left\{ 1 - \int_0^1 d\lambda [\mathcal{B} (t + i\lambda) - \langle \mathcal{B} (t + i\lambda) \rangle] \right\} \sigma_{eq},
\]

(15)

where the thermodynamic average \(\langle ... \rangle\) corresponds to an average with the quasi-equilibrium operator \(\sigma_{eq}=e^{-A}/Te^{-A}\), and

\[
A = \int d\vec{r} \left[ (2I + 1)^{-1} \sum_{mn} \beta_{mn} (\vec{r}) \omega_0^{mn} (\vec{r}) e_{mn} (\vec{r}) + \beta_d (\vec{r}) H_{dd} (\vec{r}) \right] - \beta_p H_{PI},
\]

(16)
\begin{equation}
B(t + i\lambda) = e^{-\lambda A} \int_{-\infty}^{0} dt e^{\epsilon t} \int d\vec{r} (2I + 1)^{-1} \sum_{mn} \{ \omega_{mn}^{0} (\vec{r}) \vec{j}_{mn} (\vec{r}, t) \nabla \beta_{mn} (\vec{r}, t) + \vec{j}_{mn} (\vec{r}, t) \times \\
\times [\beta_{mn} (\vec{r}, t) - \beta_{d} (\vec{r}, t)] \frac{\partial \omega_{mn}^{0} (\vec{r})}{\partial \vec{r}} + \vec{j}_{d} (\vec{r}, t) \nabla \beta_{d} (\vec{r}, t) \\
+ [\beta_{mn} (\vec{r}, t) - \beta L] K_{ZS} (\vec{r}, t) + [\beta_{d} (\vec{r}, t) - \beta L] K_{D} (\vec{r}, t) \} e^{\lambda A}. \quad (17)
\end{equation}

By using Eqs. (10) - (16), and taking into account that for single crystal sample of cubic symmetry, the diffusion coefficients, both for quadrupolar and dipolar energies, which in the general case of noncubic symmetry is a symmetrical tensor of second rank \[5\], reduces to a scalar quantity. By introduction the quantities \[\beta_{mn} (\vec{r}, t) - \beta L = \xi_{mn} (\vec{r}, t)\] and \[\beta_{d} (\vec{r}, t) - \beta L = \zeta (\vec{r}, t)\], the diffusion equations can be obtained

\begin{equation}
\frac{\partial \xi_{mn} (\vec{r}, t)}{\partial t} = \frac{1}{\omega_{mn}^{0} (\vec{r})} \nabla \{ D_{mn} (\vec{r}) \{ \omega_{mn}^{0} (\vec{r}) \nabla \xi_{mn} (\vec{r}, t) + (\xi_{mn} (\vec{r}, t) - \zeta (\vec{r}, t)) \nabla \omega_{mn}^{0} (\vec{r}) \} \} - \\
- W_{mn} (\vec{r}) \xi (\vec{r}, t), \quad (18)
\end{equation}

\begin{equation}
\frac{\partial \zeta (\vec{r}, t)}{\partial t} = \sum_{mn} \frac{D_{mn} (\vec{r}) \nabla \omega_{mn}^{0} (\vec{r})}{M_{mn}} \{ \omega_{mn}^{0} (\vec{r}) \nabla \xi_{mn} (\vec{r}, t) + (\xi_{mn} (\vec{r}, t) - \zeta (\vec{r}, t)) \nabla \omega_{mn}^{0} (\vec{r}) \} + \\
\nabla (D_{d} (\vec{r}) \nabla \zeta (\vec{r}, t)) - W_{d} (\vec{r}) \zeta (\vec{r}, t). \quad (19)
\end{equation}

where \(M_{mn} = \int d\vec{r} G^{2} (\vec{r} - \vec{r}') \langle e_{mn}^{2} (\vec{r}') \rangle\).

The first term in the square brackets of the right side of Eq. (18) describes the time dependence of the \(\xi_{mn} (\vec{r}, t)\) due to the spin diffusion with a diffusion coefficient of

\begin{equation}
D_{mn} (\vec{r}) = \int_{0}^{1} d\lambda \int_{-\infty}^{\infty} dt e^{\epsilon t} \langle \vec{j}_{mn} (\vec{r}, \lambda, t) \vec{j}_{mn} (\vec{r}) \rangle / Tr (e_{mn}^{2} (\vec{r})) \ . \quad (20)
\end{equation}

The second term gives the variation of \(\beta_{mn} (\vec{r}, t)\) due to interaction with the dipolar reservoir in the inhomogeneous field. The last term in the right side of Eq. (18) gives the relaxation of \(\xi_{mn} (\vec{r}, t)\) toward the inverse lattice temperature with density of the transition probability per unit time, \(W_{mn} (\vec{r})\), which for a cubic crystal is given by \((K_{mn} (\vec{r}) + L_{mn} (\vec{r}))\), where

\begin{equation}
W_{mn} (\vec{r}) = \int_{0}^{1} d\lambda \int_{-\infty}^{\infty} dt e^{\epsilon t} \langle (K_{mn} (\vec{r}, \lambda, t) + L_{mn} (\vec{r}, \lambda, t)) (K_{mn} (\vec{r}) + L_{mn} (\vec{r})) \rangle / Tr (e_{mn} (\vec{r})) \ . \quad (21)
\end{equation}
The first term in the curly brackets of right side of Eq. (19) describes the time variation of the dipolar energy due to the spin diffusion with diffusion coefficient

\[ D_d (\vec{r}) = \int_0^1 d\lambda \int_{-\infty}^{\infty} dt e^{t \lambda} \left\langle \sum_{n} \int \vec{j}_d (\vec{r}, \lambda, t) \vec{j}_d (\vec{r}) \right\rangle / Tr (\mathcal{H}_d \mathcal{H}_d (\vec{r})) . \]  

(22)

The second term gives the variation of \( \beta_d (\vec{r}, t) \) due to the interaction with the quadrupole reservoir in an inhomogeneous field. The last term in the right side of Eq. (19) gives the relaxation with the density of the transition probability per unit time, \( W_d (\vec{r}) \), which for a cubic crystal is given by

\[ W_d (\vec{r}) = \int_0^1 d\lambda \int_{-\infty}^{\infty} dt e^{t \lambda} \langle [K_{dP} (\vec{r}, \lambda, t) + L_{dP} (\vec{r}, \lambda, t)] [K_{dP} (\vec{r}) + L_{dP} (\vec{r})] \rangle / Tr (\mathcal{H}_d \mathcal{H}_d (\vec{r})) \]  

(23)

The boundary conditions can be introduced by defining a sphere with radius \( l \) about each PI, called the spin diffusion barrier radius. Inside this sphere the spin diffusion process goes to zero:

\[ \nabla \beta_{mn} (\vec{r}, t) |_{|\vec{r}|=l} = 0 \quad \text{and} \quad \nabla \beta_d (\vec{r}, t) |_{|\vec{r}|=l_d} = 0 . \]  

(24)

To obtain the radius of spin diffusion barrier, let us emphasize that \( D_{mn} (\vec{r}) \) and \( D_d (\vec{r}) \) are a function of the distance \( \vec{r} \) from the nearest PI. In the Gaussian limiting case the stochastic theory of magnetic resonance [21] the dimensional dependence of the diffusion coefficients \( D_{mn} (\vec{r}) \) and \( D_d (\vec{r}) \) can be expressed by the following function [19]

\[ D_{mn} (\vec{r}), D_d (\vec{r}) \sim \exp \left[ - \left( \frac{\nabla \omega_{mn}^0 (\vec{r}) \vec{r}}{\omega_d} \right)^2 \right] . \]  

(25)

Using Eq. (26) the diffusion barrier radius [1, 2, 22, 23, 25] for the spin diffusion of quadrupole energy can be found by solving the equation,

\[ \frac{3 \gamma_S}{l^3} \left\langle S_z \right\rangle \left[ \frac{q e \mu}{\langle S_z \rangle \gamma_S} |\vec{r}_0| + 1 \pm \left( 1 - \frac{|\vec{r}_0|}{l} \right) \right] = 6 \gamma_I / |\vec{r}_0|^3, \]  

(26)

where the first term in square brackets in Eq. (26) describes a distortions of the crystal field as a result of the inclusion of the PI. In Eq.(26) \( r_0 \) is distance between neighboring nuclei, \( \mu \) is the Sternheimer antishielding factor [24]. It was assumed that the distortion of the electric field is equivalent to the presence of a charge \( q \) [25].

The examination of the functional dependence (25) for the dipolar diffusion coefficient results that the main term for \( D_d (\vec{r}) \) does not include any dimensional dependence. Thus
the radius of the diffusion barrier for dipolar energy is \( l_d = |\vec{r}_0| \), which corresponds to non-barrier diffusion and to the fastest relaxation of the dipolar energy.

In the case of a homogeneous magnetic field, \( \nabla \omega^0_{mn} (\vec{r}) = 0 \), equations (20) and (21) give the results obtain earlier for the spin diffusion of the quadrupole \[5\] and of the dipolar energies \[8\]. From Eqs. (20) and (21) we get that the dissipation of the density quadrupolar and dipolar energies are driven by: i) the exchange between them; ii) spin diffusion process; and iii) direct relaxation to the PI.

2. Direct relaxation regime

Exact solutions of Eqs. (20) and (21) are extremely difficult, even for simple a model situations. That is why we consider evolution of the spin system in time by using the next considerations. Immediately after a disturbance of the nuclear spin system, the gradients of \( \xi_{mn} (\vec{r}, t) \) and \( \zeta (\vec{r}, t) \) are sufficiently small and diffusion cannot be of importance at the start of the relaxation process \[22\], this is the so called diffusion vanishing regime \[22\]. To describe the relaxation at that time interval we can use Eqs.(20) and (21) by putting all inverse temperature gradient-terms equal zero, \( \nabla \xi_{mn} (\vec{r}, t) = 0 \) and \( \nabla \zeta (\vec{r}, t) = 0 \). We also accept the approximation that at distances larger then the radius of the diffusion barrier the diffusion coefficient is independent of \( \vec{r} \) \[4\]. Under these approximations Eqs. (20) and (21) come to

\[
\frac{\partial \xi_{mn} (\vec{r}, t)}{\partial t} = \frac{D_{mn} (\vec{r}) \Delta \omega^0_{mn} (\vec{r})}{\omega^0_{mn} (\vec{r})} \{[(\xi_{mn} (\vec{r}, t) - \zeta (\vec{r}, t))] - W_{mn} (\vec{r}) \xi (\vec{r}, t) \}, \tag{27}
\]

\[
\frac{\partial \zeta (\vec{r}, t)}{\partial t} = \sum_{mn} \frac{D_{mn} (\vec{r})}{} \frac{\nabla \omega^0_{mn} (\vec{r})^2}{M_{mm}} [\xi_{mn} (\vec{r}, t) - \zeta (\vec{r}, t)] - W_d (\vec{r}) \zeta (\vec{r}, t) \]. \tag{28}
\]

The evolutions of the \( \xi_{mn} (\vec{r}, t) \) and \( \zeta (\vec{r}, t) \) toward their steady-state values is a linear combination of \((2I+1)\) exponents with \( N = (2I+1) \) relaxation times \( \tau_N (\vec{r}) \). These relaxation times \( \tau_N (\vec{r}) \) are the function of the position \( \vec{r} \). In order to obtain the experimentally observed signals, the solutions of Eq. (27) and (28), must be averaged over the sample. For this averaging procedure one needs the knowledge the field distribution.

As a result of the diffusion vanishing relaxation regime the local inverse temperatures, \( \xi_{mn} (\vec{r}, t) \) and \( \zeta (\vec{r}, t) \), become spatially distributed over the sample with a distribution which is not the equilibrium one. In this case we have to take into account also the gradient-terms
, $\nabla \xi_{mn}(\vec{r}, t)$ and $\nabla \zeta(\vec{r}, t)$ in Eqs.(20) and (21). In the next section we will consider the influence of the spin diffusion process.

3. Diffusion relaxation regime

Assuming that at distances larger than the radius of the diffusion barrier the diffusion coefficient is independent of $\vec{r}$ [4]. Multiplying Eq. (20) by $\gamma \omega_{mn}^0(\vec{r}) \langle e_{mm}(\vec{r}) \rangle$ and Eq.(21) by $\sum_m M_{mm}$ and by integrating Eqs. (29) and (30) over space variable $\vec{r}$, we obtain the equations describe the evolution of the experimentally observed values, the quantity that connects with the $Z$ component of the total nuclear magnetization ($M_z(t) - M_z(0) = \sum_{mn} E_{mn}(t)$), $E_{mn}(t)$

$$\frac{\partial E_{mn}(t)}{\partial t} = - \frac{\gamma}{\sum_m M_{mm}} D_{mn} \int d\vec{r} E_d(\vec{r}, t) \nabla \omega_{mn}^0(\vec{r}) \xi_{mn} \langle e_{mm}(\vec{r}, t) \rangle$$

and the total dipolar energy, $E_d(t)$

$$\frac{\partial E_d(\vec{r}, t)}{\partial t} = - \sum_m D_{mn} \int d\vec{r} E_{mn}(\vec{r}, t) \Delta \omega_{mn}^0(\vec{r}) - \int d\vec{r} W_d(\vec{r}) E_d(\vec{r}, t),$$

where $E_{mn}(t) = \int d\vec{r} E_{mn}(\vec{r}, t)$, $E_{mn}(\vec{r}, t) = \gamma \omega_{mn}^0(\vec{r}) \xi_{mn} \langle e_{mm}(\vec{r}, t) \rangle$, $E_d(t) = \int d\vec{r} E_d(\vec{r}, t)$, and $E_d(\vec{r}, t) = \sum_m M_{mm} \zeta(\vec{r}, t)$.

To obtain the solution of the Eqs. (29) and (30) and to calculate the relation times, both for the nuclear magnetization and for the dipolar energy, we need to know the internal distribution function of the field, $\omega_{mn}^0(\vec{r})$. As it follows from Eqs. (29) and (30) that for a special distribution of the internal field, $\Delta \omega_{mn}^0(\vec{r}) = 0$, the diffusion equations gives two uncoupled equations:

$$\frac{\partial E_{mn}(t)}{\partial t} = - \int d\vec{r} W_{mn}(\vec{r}) E_{mn}(\vec{r}, t),$$

and

$$\frac{\partial E_d(t)}{\partial t} = - \int d\vec{r} W_d(\vec{r}) E_d(\vec{r}, t).$$

Solving Eqs. (31) and (32), we obtain the normalized relaxation functions

$$R_{mn}(t) = \frac{E_{mn}(t) - E_{mn}(\infty)}{E_{mn}(0) - E_{mn}(\infty)} = e^{-t/T_{mn}},$$

(33)
and

$$R_d(t) = \frac{E_d(t) - E_d(\infty)}{E_d(0) - E_d(\infty)} = e^{-t/T_{1d}},$$

(34)

where $T_{1mn} = \frac{0.12}{C_pD_{m/F}^3}$ and $T_{1d} = \frac{0.12}{C_pD_d^3/F}$, $C_p$ is the concentration of the PI and $F$ is the angular average of the coupling dipolar constant of the DDI between the nuclear and PI. It follows from the solutions (33) and (34) that at a long time after the excitation of the spin system, the nuclear magnetization describes by the sum of exponents $M_z \simeq \sum_{mn} a_{mn} e^{-t/T_{1mn}}$, while the dipolar energy decreases to equilibrium exponentially.

**Results and discussion**

We will compare the results obtained here with the relaxation processes of the nuclear magnetization \cite{7} and the dipolar energy \cite{6} in the mixed state conventional superconducting vanadium ($I = 7/2$). In the type II superconductors, an applied magnetic field $\vec{H}_0$, in the range between the lower and upper critical field, $H_{c1} < H_0 < H_{c2}$, penetrates into the bulk sample in the form of vortices, each with a quantum flux of $\Phi_0 = \frac{\hbar}{2e}$, which form a two-dimensional structure in the plane perpendicular to $\vec{H}_0$ [?]. The distribution of the internal vortex field can be obtained by solving the Landau-Ginzburg equation, which gives

$$H(\rho) = \frac{\phi_0}{2\pi\lambda^2} \ln \frac{\rho}{\lambda} \text{ for } r < \lambda$$

(35)

where $\lambda$ is the London penetration length and $\rho$ is the distance from the core of vortex in the cylindrical coordinate, $r^2 = \rho^2 + z^2$. Using experimental data \cite{6,7}, we obtain the spin relaxation time for the nuclear magnetization, $T_1 = 43 \text{ sec}$ and the spin relaxation time for the dipolar energy, $T_{1d} = 93 \text{ msec}$. As a consequence, the dipolar energy decreases to the equilibrium state with an anomalously short time as compare to the relaxation time of the nuclear magnetization, $\frac{T_1}{T_{1d}} = 442$. Theoretical estimation of the ratio of the relaxation time, using Eqs. (33) and (34), results $\frac{T_1}{T_{1d}} = \left( \frac{l}{r_0} \right)^3$. Taking into account that the distance between neighboring vanadium nuclei $r_0 = 2.63 \times 10^{-8} \text{ cm}$ and the radius $l = 1.96 \times 10^{-7} \text{ cm}$, for the ratio $\frac{T_1}{T_{1d}} = 413$, which is in a good agreement with the result obtained from experimental data.

**Conclusions**

In conclusion, we obtained coupled equations describing mutual relaxation and spin diffusion of the quadrupole energy and dipolar energy by using the method of nonequilibrium
state operator \[18\]. The equations were solved at a short and long times approximations corresponding to the direct and diffusion relaxation regimes. We showed that at the beginning of relaxation process, the direct relaxation regime is preferred. The relaxation regime changes both for the nuclear quadrupolar and the dipolar energies, to the diffusion one.

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