Spin diffusion in nuclear quadrupole resonance

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The nonequilibrium Zubarev density-matrix method is used in a derivation of the transport equations describing spin diffusion processes in the case of quadrupole resonance of nuclei of spin 3/2. Nonequilibrium states of the reservoir of dipole-dipole interactions and diffusion of energy in this reservoir are allowed for. Expressions are obtained for the diffusion coefficients and relaxation times. It is shown that electrical diffusion barriers play an important role in the diffusion of spin in nuclear quadrupole resonance, the diffusion of the dipole-dipole interaction energy is not impeded by barriers, and the spin-lattice relaxation time of the dipole-dipole reservoir energy is approximately 100–1000 times shorter than the relaxation time of the quadrupole energy.

1. Investigations of the nuclear magnetic resonance and dynamic polarization of nuclei have demonstrated that spin diffusion plays an important role in the relaxation of nuclei in the presence of paramagnetic impurities.[1] This process transfers the Zeeman energy of individual nuclei to paramagnetic impurities which undergo fast spin-lattice relaxation. Relaxation equations allowing for the diffusion of spin under magnetic resonance conditions are derived in[2] by the nonequilibrium Zubarev density matrix (statistical operator) method.

Spin diffusion processes should also occur under nuclear quadrupole (NQR) conditions, except that, in this case, the quadrupole energy of individual nuclei diffuses. The present paper gives a theoretical analysis of this situation in the case of quadrupole resonance of nuclei of spin 3/2. Once again, the nonequilibrium density matrix method is used for the derivation of the appropriate equations. The diffusion coefficient has been calculated in[3] for NQR of I = 1 spins. The NQR spectra of different spins differ very considerably and, consequently, the effective parts of the operators describing the dipole-dipole interaction and the interaction with the alternating field are also different from one spin to another. Consequently, the spin diffusion under NQR conditions must be considered separately for each type of spin.

However, the principal difference between our results and those obtained by Buishvili and Volgina[3] or the investigations of spin diffusion under magnetic resonance conditions is an allowance for the diffusion of the energy in the reservoir of dipole-dipole interactions or, briefly, in the dipole-dipole reservoir (DDR). It is well known that the DDR plays an important role in the dynamics of spin systems of solids. The nonequilibrium DDR energy occurs in the transport equations alongside the nonequilibrium energy which governs the spin spectrum. Therefore, it is necessary to allow for the spin diffusion of both energies, especially as the DDR diffusion coefficient is considerably greater.

The spin diffusion processes are due to the magnetic dipole-dipole interactions $\mathscr{H}_{dd}$ of nuclei. In order to develop the necessary theory, we must consider the relationship between $\mathscr{H}_{dd}$ and the interaction of nuclei with the lattice $\mathscr{H}_{IL}$: If the interaction $\mathscr{H}_{dd}$ is much greater than $\mathscr{H}_{IL}$, it is necessary to consider separately an independent system in the form of a dipole-dipole reservoir.[4] The transport equations describing the NQR spin system in a homogeneous sample depend strongly on whether a DDR is present[5,6] or not[7]. These considerations also apply to the derivation of the transport equations for inhomogeneous systems.

2. We shall consider a system of nuclei of spin 3/2 with a quadrupole moment Q immersed in an axially symmetric field in a molecular crystal. The quadrupole energy levels are then given by the operator

$$\mathscr{H}_Q = {}^1/_2\hbar\omega_Q \sum_k [p^k_{33} + p^k_{\bar3\bar3} - p^k_{11} - p^k_{\bar1\bar1}], \tag{1}$$

where ω_Q is the quadrupole resonance frequency, p^k_{mn} are the projective operators defined in[7]. The nuclei interact with one another via magnetic dipole-dipole interactions H_{dd} of which the most important is the part H_d which is adiabatic relative to the operator H_Q and is described by (see[7])

$$\begin{gathered}
\mathscr{H}_d=\hbar\sum_{i\neq j}\sum_{\alpha=-2}^{2}\mathscr{P}_{ij}^{-\alpha}f_{ij}^{\alpha},\\
f^0_{ij}=I^i_zI^j_z-(p^i_{1\bar1}p^j_{\bar11}+p^i_{\bar11}p^j_{1\bar1})-{}^3/_4(p^i_{31}p^j_{13}+p^i_{\bar1\bar3}p^j_{\bar3\bar1}+p^i_{\bar3\bar1}p^j_{\bar1\bar3}+p^i_{13}p^j_{31}),\\
f^1_{ij}=2(I^i_zp^j_{1\bar1}+I^j_zp^i_{1\bar1}),\quad f^2_{ij}=3(p^i_{31}p^j_{\bar1\bar3}+p^i_{\bar1\bar3}p^j_{31})+4p^i_{1\bar1}p^j_{1\bar1},\quad p_{\bar m\bar n}=p_{-m,-n},\\
f_{ij}{}^{-\alpha}=f_{ij}{}^{\alpha+},\quad \mathscr{P}_{ij}{}^{\pm2}=-{}^3/_4\hbar\gamma^2r_{ij}{}^{-3}\sin^2\theta_{ij}\exp(\pm i\cdot2\varphi_{ij}),\\
\mathscr{P}_{ij}{}^{\pm1}=-{}^3/_2\hbar\gamma^2r_{ij}{}^{-3}\sin\theta_{ij}\cos\theta_{ij}\exp(\pm i\varphi_{ij}),\quad \mathscr{P}_{ij}{}^{0}=\hbar\gamma^2r_{ij}{}^{-3}(1-3\cos^2\theta_{ij}),
\end{gathered}\tag{2}$$

where r_{ij}, θ_{ij}, and φ_{ij} are the spherical coordinates of the radius vector joining nuclei i and j, and γ is the gyromagnetic ratio. The operator describing the interaction between the nuclei and an alternating magnetic field $2H_1\cos\omega t$ perpendicular to the crystal-field axis is

$$\mathscr{H}_t' = -\frac{\sqrt{3}}{2}\hbar\omega_1\sum_k[(p^k_{31}+p^k_{\bar3\bar1})e^{-\omega t}+(p^k_{13}+p^k_{\bar1\bar3})e^{i\omega t}], \tag{3}$$

where $\omega_1 = \gamma H_1$. The operator (3) consists only of the terms which describe the resonance transitions between the spin energy levels.[7]

The spin-lattice relaxation of nuclei in a magnetic crystal is governed by the interaction of these nuclei with torsional vibrations (Bayer mechanism):[7]

$$\mathscr{H}_{IL}{}^{B}={}^1/_4\hbar\omega_Q\sum_k\sum_{\alpha=-2}^{2}F_k{}^{-\alpha}Q_k{}^{\alpha}, \tag{4}$$

$$\begin{array}{lll}
Q^0=3I_z{}^2-I(I+1), & F_k{}^0=-2\xi_k{}^2, & \xi_k=\theta_k-\langle\theta_k\rangle_L,\\
Q^{\pm1}=I_\pm I_z+I_zI_\pm, & F_k{}^{\pm1}=\xi_k, & \xi_k{}^2=\theta_k{}^2-\langle\theta_k{}^2\rangle_L,\\
Q^{\pm2}=(I_x\pm iI_y)^2=(I_\pm)^2, & F_k{}^{\pm2}={}^1/_2\xi_k{}^2, & \\
 & \langle A\rangle_L=\mathrm{Tr}(Ae^{-\beta\mathscr{H}_L})/\mathrm{Tr}\,e^{-\beta\mathscr{H}_L}, &
\end{array}$$

where θ_k is the angle made by the instantaneous direction of the axis of a molecule k and its equilibrium orientation $\langle\theta_k\rangle_L$, H_L is the Hamiltonian of the lattice which is regarded as a thermostat kept at a temperature $1/k_B\beta$.

In the case when a crystal contains magnetic impurities, the relaxation of nuclear spins may also give rise to a magnetic dipole interaction with these impurities

$$\mathscr{H}_{IL}^{M}=\hbar\sum_{j,n}\sum_{\alpha,\beta}\Phi_{jn}^{\alpha\beta}I_\alpha^jS_\beta{}^\eta,\qquad \Phi_{jn}^{\alpha\beta}=\Phi^{\alpha\beta}(\mathbf{r}_{jn}), \tag{5}$$

where S^n is the operator of the spin of a magnetic impurity. Impurities unavoidably cause distortions of the lattice and, consequently, they shift the NQR frequency. In the first approximation, these shifts are given by the operator

$$\mathscr{H}_E = \frac{1}{2}\hbar\sum_{j,n}\Omega(\mathbf{r}_{jn})\,[p^j_{33}+p^j_{\bar{3}\bar{3}}-p^j_{11}-p^j_{\bar{1}\bar{1}}], \tag{6}$$

where $\Omega(\mathbf{r}_{jn})$ is the shift of the NQR frequency of a nucleus j because of the distortion of the crystal field by an ion at a site n. The change in the rate of the Bayer relaxation near a magnetic ion can be ignored compared with the magnetic relaxation rate.

The total Hamiltonian of the system can be divided into the main part $\mathscr{H}_0$ and a small perturbation V_t as follows

$$\mathscr{H}_0=\widetilde{\mathscr{H}}_Q+\mathscr{H}_d+\mathscr{H}_L,\quad V_t=\mathscr{H}_t'+\mathscr{H}_{IL},$$
$$\widetilde{\mathscr{H}}_Q=\mathscr{H}_Q+\mathscr{H}_E+\mathscr{H}_M,\quad \mathscr{H}_M=\langle\mathscr{H}_{IL}{}^M\rangle_L,$$
$$\mathscr{H}_{IL}=\mathscr{H}_{IL}{}^{B}+\mathscr{H}_{IL}{}^M-\langle\mathscr{H}_{IL}{}^M\rangle_L.$$

The operators $\mathscr{H}_E$ and $\mathscr{H}_M$ give rise to the shifts

$$\Omega_j=\sum_n\Omega(\mathbf{r}_{jn}),\quad \omega_j=\sum_n\Phi^{00}(\mathbf{r}_{jn})\langle S_z{}^n\rangle_L$$

of the energy levels which depend on the distances from the magnetic impurities. At moderate impurity concentrations these shifts exceed the NQR line width only for a small number of spins near an impurity. For this reason we shall allow for the shifts Ω_j and ω_j only in those expressions which do not contain the NQR frequency ω_Q.

For this form of the operator $\mathscr{H}_0$ the parameters which describe a nonequilibrium state of a homogeneous system will be selected in the form of the operators $\mathscr{H}_Q$, $\mathscr{H}_d$, and $\mathscr{H}_L$.[6] The presence of magnetic impurities in the system gives rise to a spatial inhomogeneity and a nonequilibrium state should be described by the densities of the operators $\widetilde{\mathscr{H}}_Q$ and $\mathscr{H}_d$:

$$\widetilde{\mathscr{H}}_Q(\mathbf{r})=\frac{1}{6}\hbar\sum_j(\omega_Q+\Omega_j)Q_j{}^0\delta(\mathbf{r}-\mathbf{r}_j)+\hbar\sum_j\omega_jI_j{}^z\delta(\mathbf{r}-\mathbf{r}_j),$$
$$\mathscr{H}_d(\mathbf{r})=\hbar\sum_{i\neq j}\sum_{\alpha=-2}^{2}\mathscr{P}_{ij}^{-\alpha}f_{ij}{}^\alpha\delta(\mathbf{r}-\mathbf{r}_j). \tag{7}$$

In this case, the entropy operator is of the form

$$\mathscr{S}(t,0)=\Phi(t)+\beta\mathscr{H}_L+\int d^3r[\beta_Q(\mathbf{r},t)\widetilde{\mathscr{H}}_Q(\mathbf{r})+\beta_d(\mathbf{r},t)\mathscr{H}_d(\mathbf{r})], \tag{8}$$

where $\beta_Q(\mathbf{r}, t)$ and $\beta_d(\mathbf{r}, t)$ are the parameters conjugate to $\widetilde{\mathscr{H}}_Q(\mathbf{r})$ and $\mathscr{H}_d(\mathbf{r})$ in the nonequilibrium thermodynamic sense,[8] and $\Phi(t)$ is the Massieu-Planck potential.

3. Applying the Zubarev method,[8] we obtain a nonequilibrium statistical operator corresponding to the entropy operator of Eq. (8) and then we apply the same Zubarev operator in the derivation of the transport equations of the nonequilibrium averages $\langle\mathscr{H}_{Q,\,d}(\mathbf{r})\rangle^t$ of the operators (7). Such calculations yield equations of the type

$$\frac{\partial}{\partial t}\langle\mathscr{H}_p(\mathbf{r})\rangle^t=\sum_q\Big\{\sum_{\mu,\nu}\frac{\partial}{\partial x_\mu}D^{\mu\nu}_{pq}\frac{\partial}{\partial x_\nu}\langle\mathscr{H}_q(\mathbf{r})\rangle^t$$
$$-W_{pq}\langle\mathscr{H}_q(\mathbf{r})\rangle^t-[R^{-1}_{pq}+T^{-1}_{pq}][\langle\mathscr{H}_q(\mathbf{r})\rangle^t-\langle\mathscr{H}_q(\mathbf{r})\rangle^0]\Big\}, \tag{9}$$

where $\langle A\rangle^0$ is the equilibrium average of the operator A, $D^{\mu\nu}_{pq}$ are the diffusion coefficients, and p, q = Q, d. The system (9) represents diffusion-type equations which describe local changes in the quadrupole energy and in the energy of the dipole-dipole interactions due to the application of an alternating field, relaxation processes, and transport phenomena.

The relaxation times T_{pq} due to the Bayer mechanism and the probabilities of transitions W_{pq} under the influence of an alternating magnetic field are calculated in[6]. The quantities $R_{pq} = R_{pq}(\mathbf{r})$ are the relaxation times due to the interaction with impurities:

$$R^{-1}_{QQ}=\frac{54\hbar^2\omega_Q{}^2\langle S_z{}^2\rangle N}{\langle\mathscr{H}_Q{}^2\rangle}\frac{\tau_e}{1+\tau_e{}^2\omega_Q{}^2}\sum_n|\Phi^{10}(r-r_n)|^2,$$
$$R^{-1}_{dd}=R^{-1}_{QQ}\frac{\Delta_2}{\omega_Q{}^2}\frac{\langle\mathscr{H}_Q{}^2\rangle}{\langle\mathscr{H}_d{}^2\rangle},$$

where Δ_2 is the second moment of the NQR line, and τ_e is the correlation time of the z component of the spin of a magnetic impurity.

If p ≠ q, the quantities R^{-1}_{pq} are proportional to the first moment of the NQR line, as always found in problems of this type, and they can be ignored compared with the diagonal terms. In considering spin diffusion, it is usual to employ the reciprocal relaxation times R^{-1}_{pp} averaged over the angles:

$$R^{-1}_{pp}=\sum_n C_p|r-r_n|^{-6},$$

$$C_Q=\frac{27}{5}\frac{S(S+1)(\gamma_e\gamma\hbar)^2\tau_e}{1+\omega_Q{}^2\tau_e{}^2},\quad C_d=\frac{\Delta_2}{\omega_d{}^2}C_Q, \tag{10}$$

$$\omega_d{}^2=\omega_Q{}^2\mathrm{Tr}\mathscr{H}_d{}^2/\mathrm{Tr}\mathscr{H}_Q{}^2=(918/5)\gamma^4\hbar^2\sum_k r_{jk}^{-6}.$$

4. The diffusion coefficients in Eq. (9) are

$$D^{\mu\nu}_{pq}(\mathbf{r})=(\mathrm{Sp}\mathscr{H}_p{}^2)^{-1}\int d^3r'\int_{-\infty}^{0}dt_1e^{\epsilon t_1}\langle J_p{}^\mu(\mathbf{r})J_q{}^\nu(\mathbf{r}',t)\rangle, \tag{11}$$

$$J_Q(\mathbf{r})=-\frac{i\hbar\omega_Q}{12}\sum_{i\neq j}\sum_{\alpha=-2}^{2}\mathscr{P}_{ij}^{-\alpha}[Q_i{}^0,f_{ij}{}^\alpha)\delta(\mathbf{r}-\mathbf{r}_j),$$
$$J_d(\mathbf{r})=-\frac{i\hbar}{4}\sum_{i\neq j,\,k\neq l}\sum_{\alpha,\beta=-2}^{2}\mathscr{P}_{ij}^{-\alpha}\mathscr{P}_{kl}^{-\beta}f_{ij}{}^\alpha f_{kl}{}^\beta\delta(\mathbf{r}-\mathbf{r}_j), \tag{12}$$

where $J_{Q,\,d}(\mathbf{r})$ are the fluxes of the operators $\mathscr{H}_Q(\mathbf{r})$ and $\mathscr{H}_d(\mathbf{r})$.

The diffusion coefficients can be calculated if we know the spin correlation functions of the type

$$\langle f_{ij}{}^\alpha f_{kl}{}^\beta(t)\rangle,\ \langle f_{ij}{}^\alpha f_{kl}{}^\beta f_{mn}{}^\gamma(t)f_{uv}{}^\delta(t)\rangle,\ldots, \tag{13}$$

where the time dependence is governed by "bordering" with the operator $\mathscr{H}_d+\mathscr{H}_E+\mathscr{H}_M$. The functions (13) are the Fourier transforms of the cross-relaxation curves, which are usually approximated in the form[9]

$$\langle f^\alpha_{ij}f^\beta_{kl}(t)\rangle\approx\langle f^\alpha_{ij}f^\beta_{kl}\rangle g^{\alpha\beta}_{ijkl}(t),$$
$$\langle f^\alpha_{ij}f^\beta_{kl}f^\gamma_{mn}(t)f^\delta_{uv}(t)\rangle\approx\langle f^\alpha_{ij}f^\beta_{kl}f^\gamma_{mn}f^\delta_{uv}\rangle g^{\alpha\beta\gamma\delta}_{ijklmnuv}(t), \tag{14}$$

where the time dependence is entirely due to the factor g(t). In this approximation the only nonvanishing diffusion coefficients are $D^{\mu\nu}_{pq}=D^{\mu\nu}_p\delta_{p,q}$, which are diagonal with respect to the indices p and q.

In calculations of g(t) the bordering by the operators $\mathscr{H}_d$, $\mathscr{H}_E$, and $\mathscr{H}_M$ is performed independently because they commute. Then,

$$\exp(i\mathscr{H}_Mt\hbar^{-1})I_k{}^\alpha\exp(-i\mathscr{H}_Mt\hbar^{-1})=\exp(i\alpha\omega_kt)I_k{}^\alpha,$$
$$\exp(it\mathscr{H}_E\hbar^{-1})p_{mn}{}^k\exp(-it\mathscr{H}_E\hbar^{-1})=\exp\{i\,\mathrm{sign}(m-n)\Omega_kt\}p_{mn}{}^k,$$

and the result of bordering with the operator $\mathscr{H}_d$ is usually interpolated by Gaussian curves of the type $\exp\{-\omega_d^2t^2/2\}$.

Substituting Eq. (14) into Eq. (11), we obtain

$$D_Q^{\mu\nu}(\mathbf{r})={}^9/_8\sum_j(x^\mu-x_j^\mu)(x^\nu-x_j^\nu)\,[{}^1/_4|\mathscr{P}_{ij}^0|^2F(\omega_r-\omega_j+\Omega_r-\Omega_j)$$
$$+16|\mathscr{P}_{ij}^2|^2F(\omega_r+\omega_j+\Omega_r-\Omega_j)], \tag{15}$$

where F is a function of the profile of the cross-relaxation curve:

$$F(x)=(2\pi\omega_d^2)^{-1/2}\exp\{-x^2/2\omega_d^2\}.$$

We shall assume that the concentration of magnetic impurities is sufficiently low so that each nucleus effectively interacts with just one impurity. We shall consider one paramagnetic ion located at the origin of the coordinates. Then, the vector r in Eq. (15) is measured from this ion. The presence of the functions F in the diffusion coefficients gives rise to diffusion barriers. At large distances from a defect the arguments of these functions are small compared with ω_d and D(r) is independent of r. Near defects the frequency shifts are large and D(r) decreases rapidly on approach to a defect. A measure of the changes in D(r) near an impurity is provided by the radius of a diffusion barrier and δ is that distance from an impurity at which the shift of the NQR levels induced by the impurity is equal to the nuclear dipole-dipole width of the NQR line. In solving the diffusion equations the concept of a diffusion barrier and its radius is used in the case of Gaussian approximation of the function g(t) so that we can assume approximately that

$$D_p^{\mu\nu}(\mathbf{r})=\begin{cases}\text{const}=D_p^{\mu\nu}, & r>\delta,\\ 0 & , \ r<\delta.\end{cases} \tag{16}$$

In contrast to the diffusion of spin in the nuclear resonance of the nuclei of spin I = 1/2, there may be several diffusion barriers to the diffusion of spins of the nuclei with I > 1/2. The additional barriers appear because the I > 1/2 nuclei have electric quadrupole moments, (so that, they interact with the crystal field of the lattice) and because of special features of the NQR spectrum.

We shall consider separately the magnetic and electric shifts of the NQR frequency. In the magnetic case ($\Omega_j = 0$) Eq. (15) includes $F(\omega_r + \omega_j)$ and $F(\omega_r - \omega_j)$. When the neighboring nuclei distributed radially around a magnetic ion at distances equal to the lattice constant a from one another, we have

$$\omega_j\mp\omega_{j+1}=3\hbar\gamma_e\gamma\langle S_z\rangle\left[\frac{1}{r_j^3}\mp\frac{1}{|r_j+a|^3}\right]\approx\frac{3\hbar\gamma_e\gamma\langle S_z\rangle}{r_j^3}\left[1\mp\left(1-\frac{a}{r_j}\right)\right].$$

Since the ratio a/r_j is small, the frequency difference corresponds to a diffusion barrier radius δ_M which is smaller than the radius corresponding to the frequency sum. This means that the terms proportional to $F(\omega_r + \omega_j)$ correspond to a diffusion flux of energy excitations closer to a paramagnetic ion, i.e., they correspond to a faster relaxation. In view of this, we can drop the term $F(\omega_r + \omega_j)$. The radius of a diffusion barrier for the frequency difference and sum is found by equating $\omega_j \mp \omega_{j+1}$ to $\omega_d \sim 6\gamma^2 ha^{-3}$:

$$\delta_M^-\approx a\left[\frac{\gamma_e}{\gamma}\langle S_z\rangle\right]^{1/4},\quad \delta_M^+\approx a\left[\frac{\gamma_e}{\gamma}\langle S_z\rangle\right]^{1/3}. \tag{17}$$

This expression includes the effective average value S_z. If $\tau_e\omega_d \gg 1$, which means that during the time needed for the reorientation of a nuclear spin because of the dipole-dipole interaction with the neighboring nuclei an electron spin does not change its orientation, we find that $\langle S_z\rangle \sim 1$. In the opposite case, we find that $\langle S_z\rangle \sim h\gamma H_0/k_BT \ll 1$, where H_0 is the terrestrial field.

The radius of an electric diffusion barrier can be estimated if we know the distortion of the crystal field resulting from the introduction of a paramagnetic impurity into the lattice. We shall assume that this distortion of the field is equivalent to the presence of a charge Ze; then

$$\Omega_j-\Omega_{j+1}=\frac{3Ze^2Q\gamma_Q a}{r_j^3},\quad \delta_E\approx a\left[\frac{Ze^2Q\gamma_Q}{\gamma^2\hbar^2}\right]^{1/4}, \tag{18}$$

where γ_Q is the antiscreening parameter.[10]

In solving the diffusion equations it is convenient to assume that the diffusion coefficient $D_p^{\mu\nu} = D_p\delta_{\mu\nu}$ is isotropic, which is strictly true only if the distribution of the quadrupole nuclei has the cubic symmetry. If, moreover, the expression for $D_p^{\mu\nu}$ is simplified by retaining only those terms which correspond to the minimum diffusion barrier, it is found that, in the case of a magnetic diffusion barrier,

$$D_Q\approx{}^3/_4F(0)\gamma^2\hbar^2{\sum_j}' r_{ij}^{-4}, \tag{19}$$

where the summation is carried out over the nearest-neighbor nuclei j.

In the case of an electric diffusion barrier, we have

$$D_Q\sim{}^{15}/_8F(0)\gamma^2\hbar^2\sum_j r_{ij}^{-4}. \tag{20}$$

Equation (20) is also valid in the case of a magnetic barrier if the relaxation radius b (this point is discussed later) is greater than δ and the role of a barrier in the diffusion process is unimportant. In this case, we may assume that $D_Q(\mathbf{r})$ is constant for all values of r.

The diffusion coefficient D_d is given by expressions more cumbersome than Eq. (15). It follows from the special features of the quadrupole spectrum of nuclei and from the properties of the functions f_{ij}^α in Eq. (2) that the general expression for the coefficient D_d includes terms proportional to F(0). They correspond to nonbarrier diffusion and the fastest relaxation processes. Retaining only these terms and assuming that the diffusion coefficient is isotropic, we obtain

$$\begin{gathered}D_d^{\mu\nu}(r)={}^{20}/_3F(0)\,\omega_d^{-2}\delta_{\mu\nu}\sum_{j\neq k}r_{ji}^2W_{ijk},\\ W_{ijk}=5|(ijk)|^2+5|(ikj)|^2+5|(kij)|^2\\ +(kij)(kji)+(jki)(ikj)+(jki)(kij),\\ (kij)\equiv\mathscr{P}_{ki}^1\mathscr{P}_{ij}^{-1}-\mathscr{P}_{ij}^1\mathscr{P}_{ki}^{-1}.\end{gathered} \tag{21}$$

Hence, it follows that $D_d^{\mu\nu}$ is independent of r.

Assuming that the diffusion coefficient is isotropic and using Eq. (2) as well as the transition probability W_{pq},[6] we find that the transport equations (9) can be represented in the form

$$\frac{\partial}{\partial t}\langle\mathscr{H}_Q(\mathbf{r})\rangle^t=D_Q\Delta\langle\mathscr{H}_Q(\mathbf{r})\rangle^t-W\left[\langle\mathscr{H}_Q(\mathbf{r})\rangle^t+\frac{\omega_Q(\omega-\omega_Q)}{\omega_d^2}\langle\mathscr{H}_d(\mathbf{r})\rangle^t\right]$$
$$-\left[\frac{1}{T_{QQ}}+\frac{C_Q}{r^6}\right][\langle\mathscr{H}_Q(\mathbf{r})\rangle^t-\langle\mathscr{H}_Q(\mathbf{r})\rangle^0], \tag{22}$$

$$\frac{\partial}{\partial t}\langle\mathscr{H}_d(\mathbf{r})\rangle^t=D_d\Delta\langle\mathscr{H}_d(\mathbf{r})\rangle^t-W\frac{\omega-\omega_Q}{\omega_Q}$$
$$\times\left[\langle\mathscr{H}_Q(\mathbf{r})\rangle^t+\frac{\omega_Q(\omega-\omega_Q)}{\omega_d^2}\langle\mathscr{H}_d(\mathbf{r})\rangle^t\right]$$
$$-\left[\frac{1}{T_{dd}}+\frac{C_d}{r^6}\right][\langle\mathscr{H}_d(\mathbf{r})\rangle^t-\langle\mathscr{H}_d(\mathbf{r})\rangle^0], \tag{23}$$

where $W = \pi\omega_1^2G(\omega - \omega_Q)$ and G is a function of the NQR line profile.

5. In analyzing the physical consequences of the

transport equations (9), we shall follow the work of Khutsishvili.[1] We shall assume that each nucleus interacts only with one magnetic ion and that a sample can be represented in the form of N_m spheres of radius R, each of which surrounds one magnetic ion. The radius R is given by the condition $(4\pi/3)R^3N_m^0 = 1$, where N_m^0 is the number of impurities per unit volume.

It is convenient to begin with the case when there is no alternating field (W = 0) and relaxation occurs only in magnetic impurities ($T_{pp}^{-1} = 0$). The solution of Eq. (23) can be used to find the quadrupole energy flux $U_Q(R)$ across a sphere of radius R:[1]

$$\frac{\partial U_Q(R)}{\partial t}=-\frac{1}{T_{QD}}[U_Q(R)-U_Q{}^0(R)],$$
$$\frac{1}{T_{QD}}=4\pi N_m{}^0D_QF_Q,\quad F_Q=\begin{cases}0.7b_Q, & b_Q>\delta\\ {}^1/_3(b_Q/\delta)^3b_Q, & b_Q<\delta\end{cases} \qquad (24)$$

where $b_Q = (C_Q/D_Q)^{1/4}$ is the relaxation radius defined so that if $r < b_Q$ the rate of direct magnetic relaxation exceeds the rate of diffusion of the spin energy and $U_Q^0(R)$ is the average value of the quadrupole energy of all the nuclei in a sphere whose radius is R under equilibrium conditions.[1] Multiplying Eq. (24) by N_m we can find the change in the quadrupole energy of the whole sample as a result of relaxation at impurities.

We shall integrate Eq. (22) over the volume of a sphere of radius R. The integral of the terms

$$D_Q\Delta\langle\mathscr{H}_Q(\mathbf{r})\rangle^t-\frac{C_Q}{r^6}[\langle\mathscr{H}_Q(\mathbf{r})\rangle^t-\langle\mathscr{H}_Q(\mathbf{r})\rangle^0]$$

is equal to the right-hand side of Eq. (24). The subsequent summation over all the spheres yields the following transport equation for the quadrupole energy of the whole system:

$$\frac{\partial}{\partial t}\langle\mathscr{H}_Q\rangle^t=-W\left[\langle\mathscr{H}_Q\rangle^t+\frac{\omega_Q(\omega-\omega_Q)}{\omega_d^2}\langle\mathscr{H}_d\rangle^t\right]-\frac{1}{T_Q}[\langle\mathscr{H}_Q\rangle^t-\langle\mathscr{H}_Q\rangle^0],$$
$$T_Q{}^{-1}=T_{QQ}{}^{-1}+T_{QD}{}^{-1}. \qquad (25)$$

A similar procedure reduces Eq. (23) to

$$\frac{\partial}{\partial t}\langle\mathscr{H}_d\rangle^t=-W\frac{\omega-\omega_Q}{\omega_Q}\left[\langle\mathscr{H}_Q\rangle^t+\frac{\omega_Q(\omega-\omega_Q)}{\omega_d^2}\langle\mathscr{H}_d\rangle^t\right]-\frac{1}{T_d}[\langle\mathscr{H}_d\rangle^t-\langle\mathscr{H}_d\rangle^0], \qquad (26)$$
$$T_d{}^{-1}=T_{dd}{}^{-1}+T_{dD}{}^{-1},\quad T_{dD}{}^{-1}=4\pi N_mD_dF_d,$$
$$F_d=0.7b_d\equiv0{,}7\,(C_d/D_d)^{1/4}.$$

It should be noted that, in contrast to the quadrupole energy relaxation, the dipole-dipole reservoir (DDR) relaxation always includes the case corresponding to a small-radius diffusion barrier. This is due to the presence in D_d of the principal terms corresponding to nonbarrier diffusion. The terms omitted from the coefficient D_d in the $b_d > \delta$ case contribute to the relaxation time to the same extent as the nonbarrier terms. Otherwise ($b_d < \delta$) their contribution is $(b_d/\delta)^3$ times smaller than the contribution of the nonbarrier terms.

6. We shall now estimate the nuclear spin-lattice relaxation times associated with the impurity mechanism. We shall consider low temperatures (liquid nitrogen or lower) at which the Bayer relaxation times (rising exponentially with decreasing temperature) cease to contribute significantly to the nuclear relaxation rate. In these estimates we shall retain only the nearest neighbors in all the lattice sums and assume that the number of these neighbors is six. Then,

$$\omega_d\sim33\gamma^2\hbar/a^3,\quad D_d=576F(0)a^2(\gamma^2\hbar/a^3)^2,$$
$$D_Q=\frac{3}{40}F(0)a^2\left(\frac{\gamma^2\hbar}{a^3}\right)^2\xi,\quad \xi=\begin{cases}1, & \delta_M>\delta_E,\ b_Q\\ 25, & \delta_E>\delta_M \text{ or } b_Q>\delta_{E,M}.\end{cases}$$

We shall use the following typical values of the parameters which occur in the expressions for the relaxation times:

$$\gamma/2\pi=10^4\text{ Hz/G},\quad Q=10^{-25}\text{ cm}^2,\quad \gamma_Q=10,\quad \omega_Q/2\pi=3\times10^7\text{ Hz},$$
$$Z=1,\quad S={}^3/_2,\quad \gamma_e=2\beta,\quad N_m=10^{17},\quad a=4\times10^{-8}\text{ cm},$$

where β is the Bohr magneton. For these values of the parameters we obtain

$$D_Q\approx\xi\cdot10^{-13}\text{ cm}^2/\text{sec},\quad D_d\approx7\cdot10^{-11}\text{ cm}^2/\text{sec},$$
$$\omega_d\sim5\cdot10^4\text{ rad/sec},\quad \delta_E\sim7a=2{,}8\cdot10^{-7}\text{ cm}.$$

The correlation times of the components of electron spin vary strongly from ion to ion and they also depend on the temperature and concentration.[1] At liquid nitrogen temperatures and for concentrations $N_m^0 = 10^{17}$ cm^{-3} the impurity spin correlation time is governed by the spin-lattice relaxation processes; in estimates we may assume that $\tau_e \sim 5\times10^{-7}$ sec. In this case, we have $\omega_d\tau_e \ll 1$ and a magnetic barrier is unimportant. The relaxation radii are found to be smaller than δ_E: $b_Q \approx 1.7\times10^{-7}$ cm, $b_d \approx 7\times10^{-8}$ cm. The relaxation times are: $T_{QD} \sim 30$ sec, $T_{dD} \sim 0.25$ sec.

At helium temperatures we find that $\tau_e \sim 10^{-4}$ sec or longer. In this case, the radius of a magnetic diffusion barrier is $\delta_M \sim 2\times10^{-7}$ cm $< \delta_E$ and the relaxation radii are $b_Q \sim 4.5\times10^{-8}$ cm, $b_d \sim 1.8\times10^{-8}$ cm. The relaxation times are $T_{QD} \sim 6\times10^3$ sec and $T_{dD} \sim 1$ sec.

At higher impurity concentrations the correlation time τ_e is governed by the spin-spin interactions of impurities: $\tau_e = 1/\sqrt{M_2}$, where M_2 is the second moment associated with these interactions. If $N_m^0 = 10^{19}$ cm^{-3}, we find that, for example, $\tau_e \sim 3\times10^{-7}$ sec. In this case, we find that $T_{QD} \sim 0.2$ sec and $T_{dD} \sim 1.5\times10^{-3}$ sec.

We find that, in all cases, $T_{QD} \gg T_{dD}$. This is due to the fact that, under the conditions considered here, the diffusion of the quadrupole energy is hindered by a barrier ($b_Q < \delta$), whereas the dipole-dipole energy diffuses unhindered by any barriers. If we vary the type of magnetic impurities and their concentration, we can alter the relaxation time within a range wider than that given by the above estimates.

In NQR processes a typical relaxation time representing the interaction between the electron quadrupole moment and thermal vibrations of the lattice amounts to several tenths of a second at liquid nitrogen temperatures and several tens of seconds at helium temperatures. Our estimates show that at high impurity concentrations ($N_m^0 \sim 10^{19}$ cm^{-3}) the relaxation via paramagnetic impurities begins to compete with the relaxation via the lattice vibrations even at liquid nitrogen temperature, at lower impurity concentrations this begins at helium temperatures. The range in which the spin diffusion in NQR is important is shifted toward low temperatures compared with the magnetic resonance of spins 1/2. This is due to the unavoidable competition of stronger relaxation mechanisms in NQR.

The occurrence, under these conditions, of shorter dipole-dipole reservoir (DDR) relaxation times should influence the saturation effects. In the case of saturation slightly away from resonance ($\omega \neq \omega_Q$) the transport equations (25) and (26) for $\langle\mathscr{H}_Q\rangle^t$ and $\langle\mathscr{H}_d\rangle^t$ are combined into a single system so that the line profile under saturation depends not only on T_Q but also on T_d ($\ll T_Q$).[6]

7. Equations (25) and (26) are formally identical with a system of the transport equations for homogeneous media.[6] However, in the present case, the relaxation time includes a contribution of the diffusion of spins toward magnetic impurities. An analysis of the solutions of equations such as (25) or (26) is given in[6].

If the nuclear dipole-dipole interactions are not stronger than the spin-lattice interactions, we cannot introduce the DDR concept. In this case, we can use the Zubarev method to derive a system of transport equations for the operators $p_{mn}(\mathbf{r}) = \sum_k p_{mn}^k \delta(\mathbf{r} - \mathbf{r}_k)$ which is of the following form for the assumptions made above:

$$\frac{\partial}{\partial t}\langle p_{mn}(\mathbf{r})\rangle^t = \sum_{rs}\sum_{\mu\nu} \frac{\partial}{\partial x^\mu} D^{\mu\nu}_{mn,rs} \frac{\partial}{\partial x^\nu}\langle p_{rs}(\mathbf{r})\rangle^t$$

$$+\frac{1}{i\hbar}\langle [p_{mn}(\mathbf{r}), \tilde{\mathcal{H}}_Q + \mathcal{H}_t'] \rangle^t - \sum_{rs} \frac{\langle p_{rs}(\mathbf{r})\rangle^t - \langle p_{rs}(\mathbf{r})\rangle^0}{T_{mn,\,rs}}.$$

Apart from the relaxation mechanism involving magnetic impurities, which we have considered above, an inhomogeneous relaxation may take place in the presence of electric charges and other lattice defects. If the direct spin-lattice relaxation time of the nuclei located near defects is considerably shorter than those of the nuclei far from defects, we may find that such "electric" defects govern the relaxation of the sample as a whole because of the spin diffusion processes.

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