

Rotating-frame nuclear spin-lattice relaxation due to the motion-induced time variation of quadrupolar and dipolar interactions in crystals

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Starting from Hebel and Slichter's single-spin-temperature theory, the comprehensive perturbation formalism developed recently for the calculation of $T_{1\rho}$ due to the motion-induced time dependence of nuclear dipole interactions in both high and low rotating fields is extended to include quadrupolar effects in crystals. The total relaxation rate $T_{1\rho}^{-1}$ is written in terms of dipolar and quadrupolar "lattice correlation functions" associated with the internal motions, and "spin correlation functions" governed by processes of internal equilibration of the Zeeman, dipolar, and quadrupolar Hamiltonians of the spin system. While the lattice correlation functions are found to determine the high-field $T_{1\rho}$ minima in the motionally-narrowed regions, low field $T_{1\rho}$ minima occurring at temperatures between the weak- and strong-collision regions are found to be strongly influenced by the processes accounted for by the spin correlation functions. In the limiting case of strong collisions (so-called Slichter-Ailion region) the results of Rowland and Fradin are confirmed. The applicability of the present method to interpret rotating-frame relaxation studies of defect migration in cubic crystals such as, e.g., self- or impurity diffusion via randomly migrating point defects, or dislocation dynamics during plastic deformation, is discussed.

I. INTRODUCTION

In cubic crystals the interaction between the electric quadrupole moments of the nuclei due to their nonspherical charge distributions ($I \geq 1$) and electric field gradients (EFG's) is determined by lattice imperfections.¹ While static quadrupolar effects associated, e.g., with point defects or dislocations, are usually analyzed in terms of width, shape, and intensity of the NMR absorption signal,^{2,3} effects originating from implicitly *time-dependent* quadrupolar interactions due, e.g., to lattice vibrations,⁴ the thermally activated self-diffusion of free⁴⁻⁶ or bound⁷ vacancies, or the long-range migration of dislocations during plastic deformation,⁸ are studied through the related spin-lattice relaxation rates T_1^{-1} in the laboratory frame,⁴⁻⁶ or, if the internal motions are rather slow, $T_{1\rho}^{-1}$ in the rotating frame.^{7,8}

The fundamental difference between dynamic quadrupolar and dipolar effects associated with lattice imperfections on the nuclear magnetic relaxation processes is easily understood, e.g., in the case of randomly migrating vacancies. While their dipolar effects are only "seen" *indirectly* in that they induce relative motions of nuclear magnetic moments, quadrupolar effects allow a closer and more direct "look" at vacancies since they represent local distortions of the cubic symmetry of the crystal, hence creating electric field gradients which interact *directly* with the nuclear quadrupole moments. Therefore, quadrupolar spin-lattice relaxation effects are sensitive to the atomic concentration of field gradients. In the case of randomly migrating

vacancies this allows one to determine both the sum *and* the difference of formation and migration energies, E_V^F and E_V^M , from measurements of the temperature dependence of the relaxation rates.⁵ This is in contrast to the dipolar relaxation properties which are influenced by varying defect concentrations only in that the nuclei jump more or less frequently, but the total dipolar energy of the crystal remains unchanged, and the relaxation rates as a function of temperature are governed by the activation energy, $E_V^F + E_V^M$, alone. Also, the temperature or field ranges in which the dipolar and the quadrupolar relaxation contributions, respectively, are dominant are usually well separated from each other owing to the different natures of the underlying relaxation mechanisms.

If, as is usual in cubic crystals, the quadrupolar interactions are relatively weak and of the same order of magnitude as the dipolar interactions among the spins, static quadrupolar effects may be observed, e.g., via the additional broadening of the central absorption line, combined with the decrease of its peak intensity.^{2,3,9} Then, except in the case where the occupation differences between individual energy levels may be characterized by a *Zeeman spin temperature*, the relaxation of longitudinal magnetization in the laboratory frame is no longer simply exponential with a single time constant T_1 .

Similarly, in the rotating frame a single relaxation time $T_{1\rho}$ may be defined only if during the relaxation the spin system may be ascribed a *single* spin temperature. If the amplitude H_1 of the rotating field is comparable to the local

field $H_{L\rho}$ in the rotating frame ($H_1 < H_{L\rho}$), a *common* spin temperature between the Zeeman, dipolar, and quadrupolar thermal reservoirs may often be established, while, for $H_1 \gg H_{L\rho}$, the *single* spin temperature has to be of the Zeeman type as in the laboratory frame. As illustrated in the rest of this article, in both situations the single-spin-temperature theory of Hebel and Slichter¹⁰⁻¹² may be applied to predict the relaxation properties associated with simultaneously time-dependent dipolar and quadrupolar interactions.

A first comprehensive discussion of the combined dipolar and quadrupolar effects on $T_{1\rho}$ governed by diffusion was presented by Rowland and Fradin.¹³ In the so-called Slichter-Ailion ("strong-collision") region¹⁴ their relation for $T_{1\rho}$, originally derived for the simultaneous diffusion of host and impurity atoms in aluminum, may be written as follows¹³:

$$\frac{1}{T_{1\rho}} = \frac{1}{H_1^2 + H_{d\rho}^2 + H_{q\rho}^2} \left(H_{d\rho}^2 \frac{1-p}{\tau_c^d} + H_{q\rho}^2 \frac{1-q}{\tau_c^q} \right), \quad (1.1)$$

where $H_{d\rho}$ and $H_{q\rho}$ denote the dipolar and quadrupolar contributions to the local field in the rotating frame. τ_c^d symbolizes the mean time between consecutive changes of the dipolar energy between a pair of nuclei (in the case of uncorrelated self-diffusion $\tau_c^d = \frac{1}{2}\tau$, where τ denotes the mean time of stay of a nucleus at a given lattice site), while τ_c^q is the correlation time associated with the time variation of the quadrupolar Hamiltonian. The parameters p and q are related to the microscopic features of the mechanisms causing internal motions.^{13,14}

The main assumption underlying Eq. (1.1) is that in the presence of the rf field \vec{H}_1 strong enough to saturate the NMR absorption a *common spin temperature* is established among the Zeeman, dipolar, and quadrupolar thermal reservoirs in the rotating frame between consecutive changes of both the dipolar and quadrupolar interactions. This requires $\tau_c^d, \tau_c^q \gg T_m$, where, qualitatively, T_m is a time constant associated with the processes of thermal mixing. (For $H_1 \approx H_{d\rho} \approx H_{q\rho}$, the "mixing time" T_m is approximately equal to the spin phase coherence time in a "rigid lattice," T_2^{RL}).^{13,14}

In the motionally-narrowed (weak-collision) region of the rotating frame, Rowland and Fradin¹³ used a Bloembergen-Purcell-Pound type of theory for the calculation of $T_{1\rho}^{-1}$, extending arguments of Abragam.⁹ The assumptions underlying their approximate treatment of this region are not quite clear, however (see Sec. IIB of Ref. 13).

In the present paper the basic problem of dipolar and quadrupolar rotating-frame spin-lattice relaxation is reconsidered. After the discussion of the basic Hamiltonians involved (see Sec. II), Hebel and Slichter's theory will be used to derive an expression for $T_{1\rho}$ valid in the entire temperature region (see Sec. III). In the absence of quadrupolar interactions the present theory becomes identical with the comprehensive perturbation formalism presented recently by Wolf and Jung.¹⁵ Therefore, as in Ref. 15, "strong" and "weak" collisions are included as special cases in a more general relation for $T_{1\rho}$ (see Sec. IV), which, as discussed in Sec. V, is also valid in the intermediate regions, where the low-field dipolar and quadrupolar $T_{1\rho}$ minima occur, respectively.

II. BASIC HAMILTONIANS AND DEFINITIONS

The laboratory-frame Hamiltonian of a system of N identical interacting nuclear spins with quantum number I and gyromagnetic ratio γ in a constant magnetic field $\vec{H}_0 = H_0 \hat{z}$ and an alternating field $\vec{H}_1 = H_1(\hat{x} \cos \omega t + \hat{y} \sin \omega t)$ is given by (in units of \hbar)

$$\mathcal{H}_{\text{lab}} = \omega_0 \sum_j I_{jz} + \omega_1 \cos \omega t \sum_j I_{jx} + \omega_1 \sin \omega t \sum_j I_{jy} + \mathcal{H}_d(t) + \mathcal{H}_q(t), \quad (2.1)$$

where $\omega_0 = \gamma H_0$ and $\omega_1 = \gamma H_1$ denote the Larmor precession frequencies associated with the fields \vec{H}_0 and \vec{H}_1 , respectively.

A. Dipolar Hamiltonian

The total nuclear dipole Hamiltonian \mathcal{H}_d of the crystal may be written as follows:

$$\begin{aligned} \mathcal{H}_d &= \frac{1}{2} \sum_i \sum_j (\mathcal{H}_d)_{ij} \\ &= \frac{1}{2} \sum_i \sum_j \sum_{p=-2}^{+2} A_{ij}^{(p)} F_{ij}^{(p)}, \end{aligned} \quad (2.2)$$

where the quantum-mechanical operators are given by (in the notation of Abragam⁹)

$$A_{ij}^{(0)} = \frac{2}{3} \alpha_d [-I_{iz} I_{jz} + \frac{1}{4} (I_i^+ I_j^- + I_i^- I_j^+)], \quad (2.3a)$$

$$A_{ij}^{(1)} = \alpha_d (I_{iz} I_j^+ + I_i^+ I_{jz}), \quad (2.3b)$$

$$A_{ij}^{(2)} = \frac{1}{2} \alpha_d (I_i^+ I_j^+), \quad (2.3c)$$

with

$$\alpha_d = -\frac{3}{2} \gamma^2 \hbar \quad (2.4a)$$

and

$$A_{ij}^{(-p)} = A_{ij}^{(p)+}, \quad A_{ij}^{(p)} = A_{ji}^{(p)}. \quad (2.4b)$$

Through their spherical coordinates ϑ_{ij} , φ_{ij} , and r_{ij} with respect to the "magnetic" coordinate system (with $\hat{z} \parallel \vec{H}_0$), the classical geometrical "lattice" functions $F_{ij}^{(p)}$ are implicitly time dependent if the nuclei move relative to each other. They are given by⁹

$$F_{ij}^{(0)} = r_{ij}^{-3} (1 - 3 \cos^2 \vartheta_{ij}), \quad (2.5a)$$

$$F_{ij}^{(1)} = r_{ij}^{-3} \sin \vartheta_{ij} \cos \vartheta_{ij} e^{-i \varphi_{ij}}, \quad (2.5b)$$

$$F_{ij}^{(2)} = r_{ij}^{-3} \sin^2 \vartheta_{ij} e^{-2i \varphi_{ij}}, \quad (2.5c)$$

and

$$F_{ij}^{(-p)} = F_{ij}^{(p)*}, \quad F_{ij}^{(p)} = F_{ji}^{(p)}. \quad (2.6)$$

B. Quadrupolar Hamiltonian in cubic crystals

The tensor coupling between the nonspherical charge distribution inside a nucleus n (with spin quantum number $I \geq 1$) and its noncubic surroundings may be written as the product of the Cartesian quadrupole tensor $Q_{\alpha\beta}$ and the EFG tensor operator at the center \vec{r}_n of the nucleus (for details see Refs. 6, 16, and 17):

$$(\mathcal{H}_q)_n = \sum_{\alpha=1}^3 \sum_{\beta=1}^3 (Q_{\alpha\beta})_n \left(\frac{\partial^2 \tilde{V}}{\partial x_\alpha \partial x_\beta} \right)_{\vec{r}_n}, \quad (2.7)$$

where \tilde{V} denotes the operator of the electric potential. In bulk matter, \tilde{V} may be replaced by its expectation value. Then, if the source of the electric field gradients is a given spatial distribution of ν_{\max} different types of lattice defects such as, e.g., different kinds of dislocations or point defects), with atomic concentrations $c_d^\nu = N_d^\nu / N$ ($\nu = 1, \dots, \nu_{\max}$), the EFG at the center of some nucleus n becomes

$$(V_{\alpha\beta})_{\vec{r}_n} = \left(\frac{\partial^2 \tilde{V}}{\partial x_\alpha \partial x_\beta} \right)_{\vec{r}_n} = \sum_{\nu=1}^{\nu_{\max}} \sum_{l_\nu=1}^{N_d^\nu} (V_{\alpha\beta}^{l_\nu})_{\vec{r}_n}, \quad (2.8)$$

where $(V_{\alpha\beta}^{l_\nu})_{\vec{r}_n}$ denotes the $\alpha\beta$ component of the EFG tensor at the center of atom n induced by defect l_ν ($= 1$ to N_d^ν) of type ν . With Eq. (2.8) the quadrupolar interaction Hamiltonian of the system of N spins with their *rigid* surroundings may be rewritten as follows:

$$\begin{aligned} \mathcal{H}_q &= \sum_{n=1}^N (\mathcal{H}_q)_n \\ &= \sum_{n=1}^N \sum_{\nu=1}^{\nu_{\max}} \sum_{l_\nu=1}^{N_d^\nu} \sum_{\alpha=1}^3 \sum_{\beta=1}^3 (Q_{\alpha\beta})_n (V_{\alpha\beta}^{l_\nu})_{\vec{r}_n}. \end{aligned} \quad (2.9)$$

The nuclear charges precess very rapidly about the nuclear spin direction. Therefore, in the principal-axes coordinate system of the tensor ellipsoid of $(Q_{\alpha\beta})_n$ (with its z axis parallel to \vec{I}_n ,

the direction of the nuclear spin) the five independent components of the traceless symmetric quadrupole tensor may be expressed in terms of a single number, the quadrupole *moment* eQ_n of nucleus n , and we have in this coordinate system⁶

$$\begin{aligned} (Q_{\alpha\beta})_n &= [eQ_n / 6I_n(2I_n - 1)] \\ &\times \left[\frac{3}{2} (I_{n\alpha} I_{n\beta} + I_{n\beta} I_{n\alpha}) - \delta_{\alpha\beta} I_n(I_n + 1) \right]. \end{aligned} \quad (2.10)$$

Similarly, the traceless symmetric EFG tensor associated with a given defect of type ν has five independent components, three determining the spatial orientation of the principal-axes system X, Y, Z of the tensor ellipsoid of $(V_{\alpha\beta}^{l_\nu})_{\vec{r}_n}$ (unambiguously defined by the condition $|V_{zz}^{l_\nu}| \geq |V_{xx}^{l_\nu}|$ and the following two⁶:

$$eQ_{l_\nu n} = (V_{zz}^{l_\nu})_{\vec{r}_n}, \quad (2.11)$$

called the "magnitude" of the EFG, and

$$\eta_{l_\nu n} = [(V_{xx}^{l_\nu})_{\vec{r}_n} - (V_{yy}^{l_\nu})_{\vec{r}_n}] / (V_{zz}^{l_\nu})_{\vec{r}_n}, \quad (2.12)$$

referred to as the "asymmetry parameter." For field gradients which are axially symmetric with respect to the axis of greatest field gradient (Z axis), $\eta_{l_\nu n} = 0$ at any nuclear site \vec{r}_n .

Let the orientation of the principal-axes system associated with a field gradient l_ν of type ν (X, Y, Z system) and the principal-axes system of the tensor $(Q_{\alpha\beta})_n$ (x, y, z system) be characterized by the three Euler angles $\theta_{l_\nu n}$, $\phi_{l_\nu n}$, and $\psi_{l_\nu n}$, the latter being arbitrary for symmetric field gradients, since only the relative orientations of the z and Z axes are physically relevant.

If a strong constant external field \vec{H}_0 is applied at angles θ and ϕ relative to the main crystal axes, the nuclear spins are quantized along the direction of \vec{H}_0 , which coincides with the z axis of the quadrupole-tensor ellipsoid, and the angles $\theta_{l_\nu n}$ and $\phi_{l_\nu n}$ characterize the orientation of the symmetry axis of the EFG tensor with respect to this "magnetic" coordinate system. Then, in order to exploit the relaxation properties of \mathcal{H}_q more clearly, Eq. (2.9) is rewritten in a way similar to the dipolar Hamiltonian (2.2)^{6,16}:

$$\mathcal{H}_q = \sum_{n=1}^N \sum_{\nu=1}^{\nu_{\max}} \sum_{l_\nu=1}^{N_d^\nu} \sum_{q=-2}^{+2} Q_n^{(q)} V_{l_\nu n}^{(-q)}, \quad (2.13)$$

with

$$Q_n^{(0)} = \alpha_q (3I_{nz}^2 - I^2), \quad (2.14a)$$

$$Q_n^{(\pm 1)} = \alpha_q (I_{nz} I_n^\pm + I_n^\pm I_{nz}), \quad (2.14b)$$

$$Q_n^{(\pm 2)} = \alpha_q (I_n^\pm)^2, \quad (2.14c)$$

and, for *symmetric* field gradients,

$$V_{l\nu n}^{(0)} = \frac{1}{2}eq_{l\nu n}(3\cos^2\theta_{l\nu n}-1), \quad (2.15a)$$

$$V_{l\nu n}^{(\pm 1)} = \frac{3}{2}eq_{l\nu n}\sin\theta_{l\nu n}\cos\theta_{l\nu n}e^{\pm i\phi_{l\nu n}}, \quad (2.15b)$$

$$V_{l\nu n}^{(\pm 2)} = \frac{3}{4}eq_{l\nu n}\sin^2\theta_{l\nu n}e^{\pm 2i\phi_{l\nu n}}. \quad (2.15c)$$

In writing Eqs. (2.13)–(2.15), it was assumed that all nuclei have the same magnetic dipolar and electric quadrupolar moments, with

$$\alpha_q = eQ/4I(2I-1). \quad (2.16)$$

The meaning of the individual q terms in Eq. (2.13) is obvious: While the term for $q=0$ is secular [it commutes with the Zeeman Hamiltonian in Eq. (2.1)], the terms for $q=\pm 1, \pm 2$ cause spin-lattice relaxation if \mathcal{H}_q varies with time, i.e., if a spin n and some defect l_ν change their relative positions in the crystal lattice so that $q_{l\nu n}$, $\theta_{l\nu n}$, and $\phi_{l\nu n}$ and therefore $V_{l\nu n}^{(q)}$ in Eq. (2.13), become functions of time.

C. Complete Hamiltonian in the rotating frame

With \mathcal{H}_d and \mathcal{H}_q given by Eqs. (2.2) and (2.13), respectively, the laboratory-frame Hamiltonian (2.1) may be transformed into the rotating reference frame to yield

$$\mathcal{H}_\rho = \Delta I_z + \omega_l I_x + \mathcal{H}_d^{(0)}(t) + \mathcal{H}_q^{(0)}(t), \quad (2.17)$$

with the abbreviations

$$I_\pm = \sum_j I_{j\pm}, \quad I_x = \sum_j I_{jx}, \quad \Delta = \omega_0 - \omega. \quad (2.18)$$

In writing Eq. (2.17) the nonsecular terms of \mathcal{H}_d and \mathcal{H}_q have been dropped in the usual fashion, thus restricting the following analysis to temperatures far below the dipolar or quadrupolar T_1 minimum.

To ensure the success of a perturbation treatment even in rather low relaxation fields ($H_1 \lesssim H_{d\rho}$, $H_{q\rho}$), the Hamiltonian (2.17) is rearranged by adding and subtracting the rigid-lattice dipolar and quadrupolar Hamiltonians, $\mathcal{H}_d^{(0)RL}$ and $\mathcal{H}_q^{(0)RL}$. Then, in analogy to the procedure described in Ref. 15 (henceforth referred to as paper I), we write

$$\mathcal{H}_\rho = \mathcal{H}_{0\rho} + \mathcal{H}_{1\rho}(t) \quad (2.19)$$

and consider

$$\mathcal{H}_{1\rho}(t) = \mathcal{H}_d^{(0)}(t) - \mathcal{H}_d^{(0)RL} + \mathcal{H}_q^{(0)}(t) - \mathcal{H}_q^{(0)RL} \quad (2.20)$$

as a small perturbation on the time-independent Hamiltonian

$$\mathcal{H}_{0\rho} = \Delta I_z + \omega_l I_x + \mathcal{H}_d^{(0)RL} + \mathcal{H}_q^{(0)RL} \quad (2.21)$$

of the spin system isolated from the “lattice bath” causing the motions. The deeper reason for including the rigid-lattice Hamiltonians in the unperturbed Hamiltonian (2.21) lies in the fact that

even without internal motions these terms are inherent to the isolated *spin* system. Therefore, as indicated by Eq. (2.20), only the *difference* between the rigid lattice and the actual dipolar and quadrupolar Hamiltonian in the presence of “lattice” motions should be considered as the perturbation.

III. EFFECT OF TIME-DEPENDENT NUCLEAR DIPOLE AND QUADRUPOLE INTERACTIONS ON SPIN-LATTICE RELAXATION IN THE ROTATING FRAME

A. Bloch-Wangsness-Redfield theory and the assumption of a common spin temperature

In Abragam's formulation⁹ of the Bloch-Wangsness-Redfield theory (see, e.g., Refs. 11 and 18) the expectation value $\langle \mathcal{H}_{0\rho} \rangle$ of the energy of the spin system varies with time according to

$$\frac{d\langle \mathcal{H}_{0\rho} \rangle}{dt} = \int_0^\infty dt' \text{Tr} \{ \langle [\tilde{\mathcal{H}}_{1\rho}(t'), \mathcal{H}_{0\rho}] \times [\mathcal{H}_{1\rho}, \sigma^*(t') - \sigma_L] \rangle \}, \quad (3.1)$$

where the brackets $\langle \rangle$ symbolize an average over a thermal-equilibrium ensemble, and the interaction representation of $\mathcal{H}_{1\rho}(t)$ was defined by

$$\tilde{\mathcal{H}}_{1\rho}(t) = e^{i\mathcal{H}_{0\rho}t} \mathcal{H}_{1\rho}(t) e^{-i\mathcal{H}_{0\rho}t}. \quad (3.2)$$

As illustrated in I, the characterization of the spin density matrix σ^* in Eq. (3.1) by a *single* spin temperature θ_s allows to reduce Eq. (3.1) to the simple exponential-type relaxation equation¹⁹

$$\frac{d}{dt} \left(\frac{1}{\theta_s} \right) = - \frac{1}{T_{1\rho}} \left(\frac{1}{\theta_s} - \frac{1}{\theta_L} \right), \quad (3.3)$$

where θ_L denotes the “lattice” temperature, and the spin-lattice relaxation rate $T_{1\rho}^{-1}$ is governed by the following expression:

$$\frac{1}{T_{1\rho}} = \frac{1}{\text{Tr}(\mathcal{H}_{0\rho}^2)} \int_0^\infty dt' \text{Tr} \{ \langle [\mathcal{H}_{0\rho}, \tilde{\mathcal{H}}_{1\rho}(t')] [\mathcal{H}_{1\rho}, \mathcal{H}_{0\rho}] \rangle \}. \quad (3.4)$$

Equation (3.4) may alternately be derived from the well-known Hebel-Slichter equation¹⁰⁻¹² by determining the usual “lattice”-induced transition probabilities W_{mn} between the eigenstates $|m\rangle$ and $|n\rangle$ of $\mathcal{H}_{0\rho}$ in terms of a first-order perturbation expansion.²⁰

In addition to the assumption of a single spin temperature, the main restriction underlying Eq. (3.4) is that the *correlation* time τ_c of $\mathcal{H}_{1\rho}(t)$ must be short compared to T_1 and T_2 ($\tau_c \ll T_1, T_2$).¹⁸ Contrary to common belief, in a crystal lattice this does *not* imply that τ , the mean time between consecutive jumps of an *atom*, must be small compared to T_1 and T_2 . The reason is obvious: The dipolar and quadrupolar interaction Ham-

iltonian of a spin surrounded by other nuclei or by defects undergoes many fluctuations before each spin or defect has moved just once; therefore, in a crystal lattice $\tau_c \ll \tau$. Hence Eq. (3.4) holds even if $\tau > T_1, T_2$, and both weak and strong collisions should be included properly. The situation is different, of course, if, as often in molecular liquids, the relaxation of a *single pair* of nuclear spins (coupled, e.g., via their intramolecular interaction) is observed, and, therefore, $\tau_c \approx \tau$ in that case.

B. Dipolar, quadrupolar, and mixed relaxation contributions

Inserting Eq. (2.20) and using the explicit forms of $\mathcal{H}_d^{(0)}$ and $\mathcal{H}_q^{(0)}$, the form (3.2) becomes

$$\begin{aligned} \tilde{\mathcal{H}}_{1\rho}(t) = & \frac{1}{2} \sum_i \sum_j [F_{ij}^{(0)}(t) - F_{ij}^{(0)\text{RL}}] \tilde{A}_{ij}^{(0)}(t) \\ & + \sum_{n=1}^N \sum_{l=1}^{N_d} [V_{in}^{(0)}(t) - V_{in}^{(0)\text{RL}}] \tilde{Q}_n^{(0)\text{RL}}(t), \end{aligned} \quad (3.5)$$

where, for the sake of simplicity of our notation, only one type of field gradient was assumed to contribute to relaxation ($\nu_{\max}=1$); hence, N_d^v may be replaced by N_d . In analogy to (3.2) the interaction representations of the spin-operator terms

$A_{ij}^{(0)}$ and $Q_n^{(0)}$ were defined as follows:

$$\tilde{A}_{ij}^{(0)}(t) = e^{i\mathcal{H}_{0\rho}t} A_{ij}^{(0)} e^{-i\mathcal{H}_{0\rho}t}, \quad (3.6)$$

$$\tilde{Q}_n^{(0)}(t) = e^{i\mathcal{H}_{0\rho}t} Q_n^{(0)} e^{-i\mathcal{H}_{0\rho}t}. \quad (3.7)$$

Substituting Eqs. (3.5) and (2.21) into Eq. (3.4), and defining the "lattice correlation functions"

$$K_{ij}^d(t) = \langle [F_{ij}^{(0)}(t' + t) - F_{ij}^{(0)\text{RL}}] [F_{ij}^{(0)}(t') - F_{ij}^{(0)\text{RL}}] \rangle_{t'}, \quad (3.8a)$$

$$K_{in}^q(t) = \langle [V_{in}^{(0)}(t' + t) - V_{in}^{(0)\text{RL}}] [V_{in}^{(0)}(t') - V_{in}^{(0)\text{RL}}] \rangle_{t'}, \quad (3.8b)$$

$$K_{iji}^{dq}(t) = \langle [F_{ij}^{(0)}(t' + t) - F_{ij}^{(0)\text{RL}}] [V_{ij}^{(0)}(t') - V_{ij}^{(0)\text{RL}}] \rangle_{t'}, \quad (3.8c)$$

$$K_{iji}^{qd}(t) = \langle [V_{ij}^{(0)}(t' + t) - V_{ij}^{(0)\text{RL}}] [F_{ij}^{(0)}(t') - F_{ij}^{(0)\text{RL}}] \rangle_{t'}, \quad (3.8d)$$

the total relaxation rate $T_{1\rho}^{-1}$ is found to consist of four partial relaxation rates, according to

$$\frac{1}{T_{1\rho}} = \left(\frac{1}{T_{1\rho}} \right)_d + \left(\frac{1}{T_{1\rho}} \right)_q + \left(\frac{1}{T_{1\rho}} \right)_{dq} + \left(\frac{1}{T_{1\rho}} \right)_{qd}. \quad (3.9)$$

Here

$$\left(\frac{1}{T_{1\rho}} \right)_d = \frac{1}{\text{Tr}(\mathcal{H}_{0\rho}^2)} \frac{1}{2} \sum_i \sum_j \int_0^\infty K_{ij}^d(t') \text{Tr} \{ [\mathcal{H}_{0\rho}, \tilde{A}_{ij}^{(0)}(t')] [A_{ij}^{(0)}, \mathcal{H}_{0\rho}] \} dt' \quad (3.10)$$

is formally identical with the dipolar spin-lattice relaxation rate obtained in I, with a slightly different meaning of $\mathcal{H}_{0\rho}$, however. The quadrupolar relaxation rate is given by

$$\left(\frac{1}{T_{1\rho}} \right)_q = \frac{1}{\text{Tr}(\mathcal{H}_{0\rho}^2)} \sum_i \sum_n \int_0^\infty K_{in}^q(t') \text{Tr} \{ [\mathcal{H}_{0\rho}, \tilde{Q}_n^{(0)}(t')] [Q_n^{(0)}, \mathcal{H}_{0\rho}] \} dt', \quad (3.11)$$

while the mixed rates have the following forms:

$$\left(\frac{1}{T_{1\rho}} \right)_{dq} = \frac{1}{\text{Tr}(\mathcal{H}_{0\rho}^2)} \frac{1}{2} \sum_i \sum_j \sum_l \int_0^\infty K_{iji}^{dq}(t') \text{Tr} \{ [\mathcal{H}_{0\rho}, \tilde{A}_{ij}^{(0)}(t')] [Q_j^{(0)}, \mathcal{H}_{0\rho}] \} dt', \quad (3.12)$$

$$\left(\frac{1}{T_{1\rho}} \right)_{qd} = \frac{1}{\text{Tr}(\mathcal{H}_{0\rho}^2)} \frac{1}{2} \sum_i \sum_j \sum_l \int_0^\infty K_{iji}^{qd}(t') \text{Tr} \{ [\mathcal{H}_{0\rho}, \tilde{Q}_j^{(0)}(t')] [A_{ij}^{(0)}, \mathcal{H}_{0\rho}] \} dt'. \quad (3.13)$$

In writing Eqs. (3.10)–(3.13), higher than pair correlation functions have been neglected (see also I), thus reducing quadruple to double sums. By their very nature, the mixed relaxation rates (3.12) and (3.13) involve correlations between the motions of two nuclear spins and some arbitrary defect (see Fig. 1).

Using the equations of motion of $\tilde{A}_{ij}^{(0)}(t)$ and $\tilde{Q}_n^{(0)}(t)$ [see Eqs. (3.6) and (3.7)]

$$\frac{d}{dt} \tilde{A}_{ij}^{(0)}(t) = i [\mathcal{H}_{0\rho}, \tilde{A}_{ij}^{(0)}(t)], \quad (3.14)$$

$$\frac{d}{dt} \tilde{Q}_n^{(0)}(t) = i [\mathcal{H}_{0\rho}, \tilde{Q}_n^{(0)}(t)], \quad (3.15)$$

the commutators in Eqs. (3.10)–(3.13) may be rewritten, and the resulting expressions may be integrated by parts. Applying this procedure twice and noting the invariance of traces under cyclic permutation of

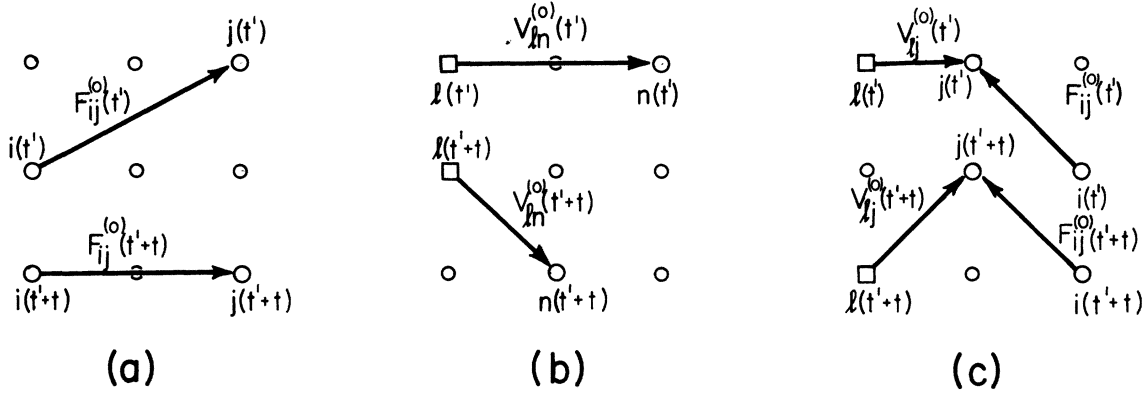


FIG. 1. Schematic illustration of the types of correlation functions defined by Eqs. (3.8a)–(3.8d). Solid circles symbolize nuclear spins, squares represent field gradients (e.g., vacancies). Both are assumed to move in a plane crystal lattice from their sites at time t' to their sites at a later time $t'+t$. Figures (a) and (b) show the terms governing the pair correlation functions (3.8a) and (3.8b), while figure (c) illustrates the character of the correlation functions (3.8c) and (3.8d) involving both dipolar and quadrupolar interactions.

the operators involved, after a few steps Eqs. (3.10)–(3.13) become (see also paper I)

$$\left(\frac{1}{T_{1\rho}}\right)_d = \frac{1}{\text{Tr}(\mathcal{H}_{0\rho}^2)} \frac{1}{2} \sum_i \sum_j \left[-\left(\frac{dg_{ij}^d(t)}{dt}\right)_{t=0} \text{Tr}[(A_{ij}^{(0)})^2] - \int_0^\infty \frac{d^2 g_{ij}^d(t)}{dt^2} \text{Tr}[\tilde{A}_{ij}^{(0)}(t) A_{ij}^{(0)}] dt \right], \quad (3.16)$$

$$\left(\frac{1}{T_{1\rho}}\right)_q = \frac{1}{\text{Tr}(\mathcal{H}_{0\rho}^2)} \sum_i \sum_n \left[-\left(\frac{dg_{in}^q(t)}{dt}\right)_{t=0} \text{Tr}[(Q_n^{(0)})^2] - \int_0^\infty \frac{d^2 g_{in}^q(t)}{dt^2} \text{Tr}[\tilde{Q}_n^{(0)}(t) Q_n^{(0)}] dt \right], \quad (3.17)$$

$$\left(\frac{1}{T_{1\rho}}\right)_{dq} = \frac{1}{\text{Tr}(\mathcal{H}_{0\rho}^2)} \frac{1}{2} \sum_i \sum_j \sum_l \left[-\left(\frac{dg_{ijl}^{dq}(t)}{dt}\right)_{t=0} \text{Tr}(A_{ij}^{(0)} Q_l^{(0)}) - \int_0^\infty \frac{d^2 g_{ijl}^{dq}(t)}{dt^2} \text{Tr}[\tilde{A}_{ij}^{(0)}(t) Q_l^{(0)}] dt \right], \quad (3.18)$$

$$\left(\frac{1}{T_{1\rho}}\right)_{qd} = \frac{1}{\text{Tr}(\mathcal{H}_{0\rho}^2)} \frac{1}{2} \sum_i \sum_j \sum_l \left[-\left(\frac{dg_{ijl}^{qd}(t)}{dt}\right)_{t=0} \text{Tr}(Q_j^{(0)} A_{il}^{(0)}) - \int_0^\infty \frac{d^2 g_{ijl}^{qd}(t)}{dt^2} \text{Tr}[\tilde{Q}_j^{(0)}(t) A_{il}^{(0)}] dt \right]. \quad (3.19)$$

As shown in I, the time-independent rigid-lattice contributions to the correlation functions (3.8) do not effect the relaxation process and may therefore be dropped, thus defining the new correlation functions

$$\begin{aligned} g_{ij}^d(t) &= \langle F_{ij}^{(0)}(t'+t) F_{ij}^{(0)}(t') \rangle_{t'}; \\ g_{in}^q(t) &= \langle V_{in}^{(0)}(t'+t) V_{in}^{(0)}(t') \rangle_{t'}; \\ g_{ijl}^{dq}(t) &= \langle F_{ij}^{(0)}(t'+t) V_{lj}^{(0)}(t') \rangle_{t'}; \\ g_{ijl}^{qd}(t) &= \langle V_{ij}^{(0)}(t'+t) F_{lj}^{(0)}(t') \rangle_{t'}. \end{aligned} \quad (3.20)$$

In deriving Eqs. (3.16)–(3.19) the disappearance of the above correlation functions and their first time derivatives for $t \rightarrow \infty$ has been postulated.

C. Interaction representation and doubly-rotating frame

The main problem in evaluating Eqs. (3.16)–(3.19) is the determination of the explicit time dependence of the traces under the integrals. Defining operators F and G by

$$F = \mathcal{H}_d^{(0)\text{RL}} + \mathcal{H}_q^{(0)\text{RL}}, \quad G = \Delta I_z + \omega_1 I_x, \quad (3.21)$$

and noting that, due to the term $\omega_1 I_x$, F and G do

not commute, $\mathcal{H}_{0\rho}$ may be replaced by $F+G$, and the interaction representation (3.6) becomes

$$\tilde{A}_{ij}^{(0)}(t) = e^{iFt} e^{i[F,G]t/2} e^{iGt} A_{ij}^{(0)} e^{-iGt} e^{-i[F,G]t/2} e^{-iFt}, \quad (3.22)$$

where F and G were assumed to commute with $[F, G]$, and a procedure for the evaluation of exponential operators described by Slichter¹¹ has been applied. The transformation of $A_{ij}^{(0)}$ involving the operator G in Eq. (3.22) may be interpreted as a transformation into the doubly-rotating frame (also see I) with its z' axis defined by the direction of the effective field

$$\begin{aligned} \vec{H}_{\text{eff}} &= \left(H_0 - \frac{\omega}{\gamma} \right) \hat{z} + \frac{\omega_1}{\gamma} \hat{x} \\ &= \frac{\omega_{\text{eff}}}{\gamma} \hat{z}' = \frac{(\Delta^2 + \omega_1^2)^{1/2}}{\gamma} \hat{z}'. \end{aligned} \quad (3.23)$$

Hence

$$e^{iGt} A_{ij}^{(0)} e^{-iGt} = \sum_{p=-2}^{+2} a^{(p)} e^{i\omega^{(p)}t} A_{ij}^{(p)'}, \quad (3.24)$$

where the prime symbolizes the representation

of $A_{ij}^{(p)}$ in the doubly-rotating frame. Denoting the angle between the z direction (parallel to \tilde{H}_0) and the z' axis (parallel to \tilde{H}_{eff}) by ϑ , the geometrical factors $a^{(p)}$ become^{15,21}

$$\begin{aligned} a^{(0)} &= \frac{1}{2}(1 - 3 \cos^2 \vartheta); \\ a^{(\pm 1)} &\simeq -\frac{1}{2} \sin \vartheta \cos \vartheta; \\ a^{(\pm 2)} &= -\frac{1}{2} \sin^2 \vartheta, \end{aligned} \quad (3.25)$$

while the frequencies $\omega^{(p)}$ are given by $\omega^{(p)} = p\omega_{\text{eff}}$. At $t = 0$ Eqs. (3.24) and (3.22) yield

$$\tilde{A}_{ij}^{(0)}(0) = A_{ij}^{(0)} = \sum_{p=-2}^{+2} a^{(p)} A_{ij}^{(p)'}. \quad (3.26)$$

In complete analogy to the above discussion, the

quadrupolar operators may be transformed into the doubly-rotating frame, according to

$$e^{iGt} Q_n^{(0)} e^{-iGt} = \sum_{p=-2}^{+2} b^{(p)} e^{i\omega^{(p)}t} Q_n^{(p)'}, \quad (3.27)$$

where, with the definitions (2.14),

$$\begin{aligned} b^{(0)} &= \frac{1}{2}(3 \cos^2 \vartheta - 1); \\ b^{(\pm 1)} &= -\frac{3}{2} \sin \vartheta \cos \vartheta; \\ b^{(\pm 2)} &= \frac{3}{4} \sin^2 \vartheta. \end{aligned} \quad (3.28)$$

Substituting Eqs. (3.22), (3.24), (3.26), and (3.27) into the partial relaxation rates (3.16)–(3.19), we obtain

$$\left(\frac{1}{T_{1\rho}}\right)_d = \frac{1}{\text{Tr}(\mathcal{H}_{0\rho}^2)} \frac{1}{2} \sum_i \sum_j \left[-\left(\frac{dg_{ij}^d}{dt}\right)_{t=0} \text{Tr}[(A_{ij}^{(0)})^2] - \sum_p \sum_r a^{(p)} a^{(r)} \int_0^\infty \frac{d^2 g_{ij}^d}{dt^2} \text{Tr}[A_{ij}^{(p)'}(t) A_{ij}^{(r)'}] e^{i\omega^{(p)}t} dt \right], \quad (3.29)$$

$$\left(\frac{1}{T_{1\rho}}\right)_q = \frac{1}{\text{Tr}(\mathcal{H}_{0\rho}^2)} \sum_i \sum_n \left[-\left(\frac{dg_{in}^q}{dt}\right)_{t=0} \text{Tr}[(Q_n^{(0)})^2] - \sum_p \sum_r b^{(p)} b^{(r)} \int_0^\infty \frac{d^2 g_{in}^q}{dt^2} \text{Tr}[Q_n^{(p)'}(t) Q_n^{(r)'}] e^{i\omega^{(p)}t} dt \right], \quad (3.30)$$

$$\begin{aligned} \left(\frac{1}{T_{1\rho}}\right)_{dq} &= \frac{1}{\text{Tr}(\mathcal{H}_{0\rho}^2)} \frac{1}{2} \sum_i \sum_j \sum_l \left[-\left(\frac{dg_{ijl}^{dq}}{dt}\right)_{t=0} \text{Tr}(A_{ij}^{(0)} Q_j^{(0)}) \right. \\ &\quad \left. - \sum_p \sum_r a^{(p)} b^{(r)} \int_0^\infty \frac{d^2 g_{ijl}^{dq}}{dt^2} \text{Tr}[A_{ij}^{(p)'}(t) Q_j^{(r)'}] e^{i\omega^{(p)}t} dt \right], \end{aligned} \quad (3.31)$$

$$\begin{aligned} \left(\frac{1}{T_{1\rho}}\right)_{qd} &= \frac{1}{\text{Tr}(\mathcal{H}_{0\rho}^2)} \frac{1}{2} \sum_i \sum_j \sum_l \left[-\left(\frac{dg_{ijl}^{qd}}{dt}\right)_{t=0} \text{Tr}(Q_j^{(0)} A_{ij}^{(0)}) \right. \\ &\quad \left. - \sum_p \sum_r b^{(p)} a^{(r)} \int_0^\infty \frac{d^2 g_{ijl}^{qd}}{dt^2} \text{Tr}[Q_j^{(p)'}(t) A_{ij}^{(r)'}] e^{i\omega^{(p)}t} dt \right], \end{aligned} \quad (3.32)$$

where the operators $A_{ij}^{(p)'}(t)$ and $Q_n^{(p)'}(t)$ in the doubly-rotating frame were defined as follows [see Eqs. (3.22) and (3.24)]:

$$A_{ij}^{(p)'}(t) = e^{iFt} e^{i[F,G]t/2} A_{ij}^{(p)'} e^{-i[F,G]t/2} e^{-iFt}, \quad (3.33a)$$

$$Q_n^{(p)'}(t) = e^{iFt} e^{i[F,G]t/2} Q_n^{(p)'} e^{-i[F,G]t/2} e^{-iFt}. \quad (3.33b)$$

D. Spin dynamics and spin correlation functions

As discussed in I, the time-dependent “*spin correlation functions*” under the integrals in Eqs. (3.29)–(3.32) are closely related to motion-independent processes allowing the establishment of internal equilibrium inside the spin system in the rotating frame. Qualitatively, such processes may be represented by the establishment of a dipolar, quadrupolar, and Zeeman spin temperature, respectively, as well as the thermal mixing

between them during the establishment of a *common* spin temperature in the rotating frame. In spite of the fact that the analysis of the processes described by these correlation functions associated with the spin system is very difficult, it seems reasonable to *assume* that some kind of internal equilibrium is achieved while the spin correlation functions decay to zero. Therefore, using the independence of the trace operation of representation, on phenomenological grounds the following general forms of the spin correlation functions are *assumed*:

$$\text{Tr}[A_{ij}^{(p)}(t) A_{ij}^{(r)}] = \text{Tr}(A_{ij}^{(p)} A_{ij}^{(r)}) k_d^{(p,r)}(t), \quad (3.34)$$

$$\text{Tr}[Q_n^{(p)}(t) Q_n^{(r)}] = \text{Tr}(Q_n^{(p)} Q_n^{(r)}) k_q^{(p,r)}(t), \quad (3.35)$$

$$\text{Tr}[A_{ij}^{(p)}(t) Q_j^{(r)}] = \text{Tr}(A_{ij}^{(p)} Q_j^{(r)}) k_{dq}^{(p,r)}(t), \quad (3.36)$$

$$\text{Tr}[Q_j^{(p)}(t) A_{ij}^{(r)}] = \text{Tr}(Q_j^{(p)} A_{ij}^{(r)}) k_{qd}^{(p,r)}(t). \quad (3.37)$$

Owing to the qualitatively different effects eventually arising from secular and nonsecular terms

in the dipolar and quadrupolar Hamiltonian, in writing Eqs. (3.34)–(3.37) qualitatively different decay properties for different combinations of p and r have been taken into account in the “reduced” dipolar, quadrupolar, and mixed spin correlation functions $k^{(p,r)}(t)$.

Comparing Eqs. (3.6), (3.7), (3.22), and (3.24) with Eqs. (3.34)–(3.37), we readily find that, independent of any of the above approximations,

$$k_d^{(p,r)}(0) = k_q^{(p,r)}(0) = k_{dq}^{(p,r)}(0) = k_{qd}^{(p,r)}(0) = 1. \quad (3.38)$$

As discussed above, for long times the spin correlation functions are assumed to decay to zero. Hence, we postulate that

$$k_d^{(p,r)}(\infty) = k_q^{(p,r)}(\infty) = k_{dq}^{(p,r)}(\infty) = k_{qd}^{(p,r)}(\infty) = 0. \quad (3.39)$$

E. Evaluation of the traces involved

Most of the dipolar traces in Eq. (3.34) have been calculated in I, and the remaining traces involving dipolar and quadrupolar spin operators are given by

$$\text{Tr}[(Q_n^{(0)})^2] = \frac{1}{5} \alpha_q^2 I(I+1)(2I+3)(2I-1)(2I+1)^N, \quad (3.40a)$$

$$\text{Tr}[(Q_n^{(\pm 1)})^2] = \text{Tr}[(Q_n^{(\mp 1)})^2] = 0, \quad (3.40b)$$

$$\text{Tr}(Q_n^{(\pm 1)} Q_n^{(\mp 1)}) = \frac{2}{15} \alpha_q^2 I(I+1)(2I+3)(2I-1)(2I+1)^N, \quad (3.40c)$$

$$\text{Tr}(Q_n^{(\pm 2)} Q_n^{(\mp 2)}) = \frac{2}{15} \alpha_q^2 I(I+1)(2I+3)(2I-1)(2I+1)^N, \quad (3.40d)$$

$$\text{Tr}(Q_n^{(0)} Q_n^{(\pm 1)}) = \text{Tr}(Q_n^{(0)} Q_n^{(\pm 2)}) = 0, \quad (3.40e)$$

$$\text{Tr}(A_{ij}^{(\pm 1)} A_{ij}^{(\mp 1)}) = \gamma^4 \hbar^2 I^2 (I+1)^2 (2I+1)^N, \quad (3.40f)$$

and all the mixed traces vanish, i.e.,

$$\text{Tr}(A_{ij}^{(p)} Q_j^{(r)}) = 0 \quad (p, r = 0, \pm 1, \pm 2). \quad (3.40g)$$

Using these results, the trace involving the unperturbed Hamiltonian is readily evaluated:

$$\text{Tr}(\mathcal{H}_{0\rho}^2) = \frac{1}{3} N \gamma^2 I(I+1)(2I+1)^N (\Delta^2 + \omega_1^2 + \gamma^2 H_{L\rho}^2). \quad (3.41)$$

The total local field, introduced by the relation

$$H_{L\rho}^2 = H_{d\rho}^2 + H_{q\rho}^2, \quad (3.42)$$

is determined by a dipolar contribution

$$H_{d\rho}^2 = \frac{\text{Tr}[(\mathcal{H}_d^{(0)})^2]}{\gamma^2 \text{Tr}(I_z^2)} = \frac{1}{4} \gamma^2 \hbar^2 I(I+1) \sum_j |F_{ij}^{(0)}|^2 \quad (3.43)$$

and a quadrupolar term. In the general case of ν_{\max} different types of defects

$$H_{q\rho}^2 = \frac{\text{Tr}[(\mathcal{H}_q^{(0)})^2]}{\gamma^2 \text{Tr}(I_z^2)} = \frac{3}{80} \frac{e^2 Q^2 (2I+3)}{\gamma^2 I^2 (2I-1)} \frac{1}{N} \sum_{j=1}^N \left(\sum_{v=1}^{\nu_{\max}} \sum_{\nu=1}^{N_d^v} V_{i\nu j}^{(0)} \right)^2. \quad (3.44)$$

For given concentrations and geometrical arrangements of lattice defects, an *average* EFG \bar{q} at the center of a “representative” nucleus j may be defined by¹³

$$e\bar{q}^2 = e \left\langle \left(\sum_{v=1}^{\nu_{\max}} \sum_{\nu=1}^{N_d^v} q_{i\nu k} (3 \cos^2 \theta_{i\nu k} - 1)^2 \right) \right\rangle_k, \quad (3.45)$$

where the explicit form (2.15a) of $V_{i\nu j}^{(0)}$ has been inserted into Eq. (3.44), and the angular brackets symbolize an average over all nuclei k . With Eq. (3.45) the quadrupolar local field (3.44) may be simplified as follows:

$$H_{q\rho}^2 = \frac{3}{320} \frac{e^4 Q^2 (2I+3)}{I^2 (2I-1) \gamma^2} \bar{q}^2. \quad (3.46)$$

F. Dipolar and quadrupolar relaxation rates

Substituting the spin correlation functions (3.34)–(3.37) into Eqs. (3.29)–(3.32) and using the traces listed above and in I, we readily see that the mixed relaxation rates (3.31) and (3.32) vanish, i.e.,

$$\left(\frac{1}{T_{1\rho}} \right)_{q,d} = \left(\frac{1}{T_{1\rho}} \right)_{d,q} = 0. \quad (3.47)$$

This result might also have been predicted intuitively by assuming that the *quadrupolar* interaction between some spin j and some field gradient l [see Fig. 1(c)] is independent of the time variation of the *dipolar* interaction between spin j and some other spin, thus assuming that at all times the mixed “lattice” correlation functions $K_{iji}(t)$ are negligible compared to the dipolar and quadrupolar pair correlation functions $K_{ijl}^d(t)$ and $K_{ln}^q(t)$ defined by Eqs. (3.8).

Therefore, the total relaxation rate

$$\frac{1}{T_{1\rho}} = \left(\frac{1}{T_{1\rho}} \right)_d + \left(\frac{1}{T_{1\rho}} \right)_q \quad (3.48)$$

contains the dipolar and quadrupolar contributions. For arbitrary distance $h = (\omega_0 - \omega)/\gamma$ of the field \vec{H}_0 off resonance they become

$$\begin{aligned} \left(\frac{1}{T_{1\rho}} \right)_d = \frac{1}{4} \frac{\gamma^2 \hbar^2 I(I+1)}{h^2 + H_1^2 + H_{d\rho}^2 + H_{q\rho}^2} & \left[- \left(\frac{dG^d(t)}{dt} \right)_{t=0} - \frac{1}{4} (1 - 3 \cos^2 \vartheta)^2 \int_0^\infty \frac{d^2 G^d(t)}{dt^2} k_d^{(0,0)}(t) dt \right. \\ & - \frac{3}{4} \sin^4 \vartheta \operatorname{Re} \int_0^\infty \frac{d^2 G^d(t)}{dt^2} k_d^{(2,-2)}(t) e^{2i\omega_{\text{eff}} t} dt \\ & \left. - 3 \sin^2 \vartheta \cos^2 \vartheta \operatorname{Re} \int_0^\infty \frac{d^2 G^d(t)}{dt^2} k_d^{(1,-1)}(t) e^{i\omega_{\text{eff}} t} dt \right], \end{aligned} \quad (3.49)$$

$$\begin{aligned} \left(\frac{1}{T_{1\rho}} \right)_q = \frac{3}{80} \frac{2I+3}{\gamma^2 I^2 (2I-1)} \frac{e^2 Q^2}{h^2 + H_1^2 + H_{d\rho}^2 + H_{q\rho}^2} & \left[- \left(\frac{dG^q(t)}{dt} \right)_{t=0} - \frac{1}{4} (1 - 3 \cos^2 \vartheta)^2 \int_0^\infty \frac{d^2 G^q(t)}{dt^2} k_q^{(0,0)}(t) dt \right. \\ & - \frac{3}{4} \sin^4 \vartheta \operatorname{Re} \int_0^\infty \frac{d^2 G^q(t)}{dt^2} k_q^{(2,-2)}(t) e^{2i\omega_{\text{eff}} t} dt \\ & \left. - 3 \sin^2 \vartheta \cos^2 \vartheta \operatorname{Re} \int_0^\infty \frac{d^2 G^q(t)}{dt^2} k_q^{(1,-1)}(t) e^{i\omega_{\text{eff}} t} dt \right]. \end{aligned} \quad (3.50)$$

Here the complete dipolar and quadrupolar lattice correlation functions $G^d(t)$ and $G^q(t)$ were defined by

$$G^d(t) = \frac{1}{N} \sum_i \sum_j g_{ij}^d(t) \quad (3.51)$$

and, in the general case of ν_{max} different types of lattice defects,

$$G^q(t) = \frac{1}{N} \sum_{j=1}^N \sum_{\nu=1}^{\nu_{\text{max}}} \sum_{l\nu=1}^{N_{\nu}^l} g_{l\nu j}^q(t), \quad (3.52)$$

where $g_{ij}^d(t)$ and $g_{l\nu j}^q(t)$ are given by Eqs. (3.20). In deriving Eqs. (3.49) and (3.50) it was assumed that

$$k_d^{(\rho,-\rho)}(t) = k_d^{(-\rho,\rho)}(t); \quad k_q^{(\rho,-\rho)}(t) = k_q^{(-\rho,\rho)}(t). \quad (3.53)$$

It is interesting to note that in spite of the disappearance of the mixed relaxation rates [see Eq. (3.47)] the dipolar and quadrupolar partial relaxation rates (3.49) and (3.50) may be coupled in as many as three physically different ways:

- (i) via the total local field (3.42) containing dipolar and quadrupolar terms;
- (ii) via the dipolar and quadrupolar spin corre-

lation functions $k_d^{(\rho,-\rho)}(t)$ and $k_q^{(\rho,-\rho)}(t)$, which account for processes of internal equilibration of the different parts of the spin energy reservoir;

(iii) via the "lattice" correlation functions $G^d(t)$ and $G^q(t)$ which are coupled if the motion of some defect is correlated with the motion of magnetic moments, such as, e.g., the diffusion of impurity atoms carrying nuclear magnetic moments, or the motion of dislocations, which involves jumps of spins in their surroundings.

IV. STRONG VERSUS WEAK COLLISIONS (REF. 22)

As illustrated in this section, the relative quickness of the decays of "lattice" and "spin correlation functions" in Eqs. (3.49) and (3.50) determines whether we are dealing with "strong" or "weak" collisions (see also I).

A. Spin-lattice relaxation in the strong-collision (Slichter-Ailion) region

If both dipolar and quadrupolar spin correlation functions decay *before* the "lattice" correlation functions change considerably, those terms in Eqs. (3.49) and (3.50) involving $G^d(t)$ and $G^q(t)$ may be considered as constants under the integrals. Thus, Eq. (3.49) reveals

$$\begin{aligned} \left(\frac{1}{T_{1\rho}} \right)_d = \frac{1}{4} \frac{\gamma^2 \hbar^2 I(I+1)}{h^2 + H_1^2 + H_{d\rho}^2 + H_{q\rho}^2} & \left[- \left(\frac{dG^d(t)}{dt} \right)_{t=0} \right. \\ & - \left(\frac{d^2 G^d(t)}{dt^2} \right)_{t=0} \left(\frac{1}{4} (1 - 3 \cos^2 \vartheta)^2 \int_0^\infty k_d^{(0,0)}(t) dt + \frac{3}{4} \sin^4 \vartheta \operatorname{Re} \int_0^\infty k_d^{(2,-2)}(t) e^{2i\omega_{\text{eff}} t} dt \right. \\ & \left. \left. + 3 \sin^2 \vartheta \cos^2 \vartheta \operatorname{Re} \int_0^\infty k_d^{(1,-1)}(t) e^{i\omega_{\text{eff}} t} dt \right) \right]. \end{aligned} \quad (4.1)$$

Similarly, the quadrupolar spin-lattice relaxation rate (3.50) becomes

$$\begin{aligned}
\left(\frac{1}{T_{1\rho}}\right)_q = & \frac{3}{80} \frac{2I+3}{\gamma^2 I^2 (2I-1)} \frac{e^2 Q^2}{h^2 + H_1^2 + H_{d\rho}^2 + H_{q\rho}^2} \left[- \left(\frac{dG^q(t)}{dt} \right)_{t=0} \right. \\
& - \left(\frac{d^2 G^q(t)}{dt^2} \right)_{t=0} \left(\frac{1}{4} (1 - 3 \cos^2 \vartheta)^2 \int_0^\infty k_q^{(0,0)}(t) dt \right. \\
& + \frac{3}{4} \sin^4 \vartheta \operatorname{Re} \int_0^\infty k_q^{(2,-2)}(t) e^{i\omega_{\text{eff}} t} dt \\
& \left. \left. + 3 \sin^2 \vartheta \cos^2 \vartheta \operatorname{Re} \int_0^\infty k_q^{(1,-1)}(t) e^{i\omega_{\text{eff}} t} dt \right) \right]. \quad (4.2)
\end{aligned}$$

According to Eqs. (4.1) and (4.2), the strong-collision relaxation rates are affected by the spectral densities of the spin correlation functions $k^{(p,-p)}(t)$ for $p=1$ and $p=2$ as well as the integral decay properties of $k^{(0,0)}(t)$. Owing to the smallness of the motion-dependent prefactors $(d^2 G/dt^2)_{t=0}$ multiplying the related integrals, and the postulated rapidness of the decays of the spin correlation functions, i.e., the shortness of the "mixing" constants defined somewhat arbitrarily by the relations

$$\begin{aligned}
\int_0^\infty k_d^{(p,-p)}(t) dt &= T_d^{(p)}, \\
\int_0^\infty k_q^{(p,-p)}(t) dt &= T_q^{(p)}, \quad (4.3)
\end{aligned}$$

the first term on the right-hand side of Eqs. (4.1) and (4.2), respectively, dominates over all terms involving spin correlation functions. Therefore, introducing the local fields defined by Eqs. (3.43) and (3.44) and using the definitions (3.51) and (3.52), the partial relaxation rates (4.1) and (4.2) simplify as follows:

$$\left(\frac{1}{T_{1\rho}}\right)_d = \frac{H_{d\rho}^2}{h^2 + H_1^2 + H_{d\rho}^2 + H_{q\rho}^2} \frac{1}{G^d(0)} \left(- \frac{dG^d(t)}{dt} \right)_{t=0}, \quad (4.4)$$

$$\left(\frac{1}{T_{1\rho}}\right)_q = \frac{H_{q\rho}^2}{h^2 + H_1^2 + H_{d\rho}^2 + H_{q\rho}^2} \frac{1}{G^q(0)} \left(- \frac{dG^q(t)}{dt} \right)_{t=0}. \quad (4.5)$$

To illustrate the relation of these results with the usual forms of relaxation rates in the strong-collision region, the first time derivatives entering Eqs. (4.4) and (4.5) are approximated by (see also I)

$$\left(- \frac{dG^d(t)}{dt} \right)_{t=0} = - \frac{G^d(0) - G^d(\tau_c^d)}{\tau_c^d} \quad (4.6)$$

and

$$\left(- \frac{dG^q(t)}{dt} \right)_{t=0} = - \frac{G^q(0) - G^q(\tau_c^q)}{\tau_c^q}, \quad (4.7)$$

where the mean times τ_c^d and τ_c^q between successive changes of the dipolar interaction of the spin pair $i-j$ and the quadrupolar interaction of some spin i with a defect l_ν of type ν , respectively, were assumed to be independent of the particular pair considered. If this is not true, i.e., if

$$\tau_c^d = \tau_c^d(i, j), \quad \tau_c^q = \tau_c^q(j, l_\nu), \quad (4.8)$$

as, e.g., for dipolar spin-lattice relaxation associated with a point-defect mechanism of self-diffusion in crystals,²³⁻²⁵ in a more general way we have to write (see also I)

$$\left(- \frac{dG^d(t)}{dt} \right)_{t=0} = - \frac{1}{N} \sum_i \sum_j \frac{g_{ij}^d(0) - g_{ij}^d(\tau_c^d(i, j))}{\tau_c^d(i, j)} \quad (4.9)$$

and

$$\begin{aligned}
\left(- \frac{dG^q(t)}{dt} \right)_{t=0} &= - \frac{1}{N} \sum_j \sum_\nu \sum_{l_\nu} \frac{g_{j l_\nu}^q(0) - g_{j l_\nu}^q(\tau_c^q(l_\nu, j))}{\tau_c^q(l_\nu, j)}. \quad (4.10)
\end{aligned}$$

Inserting Eqs. (4.9) and (4.10) into (4.4) and (4.5), denoting the dipolar energy of a spin pair $i-j$ before a collision by $E_d^b(i, j)$ and by $E_d^a(i, j)$ after a collision, and defining similar quantities for the quadrupolar energy contributions, we obtain

$$\begin{aligned}
\left(\frac{1}{T_{1\rho}}\right)_d &= \frac{H_{d\rho}^2}{h^2 + H_1^2 + H_{d\rho}^2 + H_{q\rho}^2} \frac{1}{\bar{E}_d^b} \\
&\times \frac{1}{N} \sum_i \sum_j \frac{E_d^b(i, j) - E_d^a(i, j)}{\tau_c^d(i, j)} \quad (4.11)
\end{aligned}$$

and

$$\begin{aligned}
\left(\frac{1}{T_{1\rho}}\right)_q &= \frac{H_{q\rho}^2}{h^2 + H_1^2 + H_{d\rho}^2 + H_{q\rho}^2} \frac{1}{\bar{E}_q^b} \\
&\times \frac{1}{N} \sum_j \sum_\nu \sum_{l_\nu} \frac{E_q^b(l_\nu, j) - E_q^a(l_\nu, j)}{\tau_c^q(l_\nu, j)}, \quad (4.12)
\end{aligned}$$

where \bar{E}_d^b and \bar{E}_q^b , proportional to $G^d(0)$ and $G^q(0)$, respectively, symbolize the average dipolar and quadrupolar energy per spin *before* a collision.

If different spins or field gradients move *randomly*,²⁵ the simpler relations (4.6) and (4.7) may be inserted into Eqs. (3.48), (4.4), and (4.5), yielding

$$\frac{1}{T_{1\rho}} = \frac{H_{d\rho}^2}{h^2 + H_1^2 + H_{d\rho}^2 + H_{q\rho}^2} \frac{1-p}{\tau_c^d} + \frac{H_{q\rho}^2}{h^2 + H_1^2 + H_{d\rho}^2 + H_{q\rho}^2} \frac{1-q}{\tau_c^q} \quad (4.13)$$

with

$$p = \bar{E}_d^a / \bar{E}_d^b, \quad q = \bar{E}_q^a / \bar{E}_q^b, \quad (4.14)$$

where \bar{E}_d^a and \bar{E}_q^a denote the average dipolar and quadrupolar energies per spin *after* a collision.

If the field \bar{H}_0 is applied at exact resonance ($h=0$), Eq. (4.13) becomes identical with Eq. (1.1) derived by Rowland and Fradin¹³ from a modified Slichter-Ailion¹⁴ approach. Consequently, their result holds only for uncorrelated motions of nuclear spins relative to each other and with respect to electric field gradients.

B. Spin-lattice relaxation in the weak-collision (motionally-narrowed) region

If both lattice correlation functions $G^d(t)$ and $G^q(t)$ decay before the spin correlation functions change considerably, $k_d^{(p,-p)}(t)$ and $k_q^{(p,-p)}(t)$ in Eqs. (3.49) and (3.50) may be replaced by their initial values governed by Eq. (3.38). Then, integrating by parts, for arbitrary distance off resonance we obtain

$$\left(\frac{1}{T_{1\rho}}\right)_d = \frac{3}{8} \frac{\gamma^4 \hbar^2 I(I+1) H_{\text{eff}}^2}{h^2 + H_1^2 + H_{d\rho}^2 + H_{q\rho}^2} \times [\sin^4 \vartheta \mathcal{J}_d^{(0)}(2\omega_{\text{eff}}) + \sin^2 \vartheta \cos^2 \vartheta \mathcal{J}_d^{(0)}(\omega_{\text{eff}})] \quad (4.15)$$

and

$$\left(\frac{1}{T_{1\rho}}\right)_q = \frac{9}{160} \frac{(2I+3)e^2 Q^2}{I^2(2I-1)} \frac{H_{\text{eff}}^2}{h^2 + H_1^2 + H_{d\rho}^2 + H_{q\rho}^2} \times [\sin^4 \vartheta \mathcal{J}_q^{(0)}(2\omega_{\text{eff}}) + \sin^2 \vartheta \cos^2 \vartheta \mathcal{J}_q^{(0)}(\omega_{\text{eff}})], \quad (4.16)$$

where the dipolar and quadrupolar spectral density functions were defined by

$$\mathcal{J}_d^{(0)}(\omega) = \int_{-\infty}^{+\infty} G^d(t) e^{i\omega t} dt, \quad (4.17)$$

$$\mathcal{J}_q^{(0)}(\omega) = \int_{-\infty}^{+\infty} G^q(t) e^{i\omega t} dt. \quad (4.18)$$

According to Eqs. (4.15) and (4.16), in three different ways dipolar and quadrupolar relaxation

rates are affected by the off-resonance field $h = (\omega_0 - \omega)/\gamma$: (i) via the effective field determined by $H_{\text{eff}}^2 = H_1^2 + h^2$ [see Eq. (3.23)]; (ii) via the spectral density functions at the frequencies $\omega_{\text{eff}} = \gamma H_{\text{eff}}$ and $2\omega_{\text{eff}}$, respectively, and; (iii) via the angle ϑ , decreasing from $\frac{1}{2}\pi$ (at exact resonance) towards zero for increasing distance off resonance, in accordance with its definition by $\cos \vartheta = h/H_{\text{eff}}$. At *exact resonance* ($h=0$, $\vartheta = \frac{1}{2}\pi$) Eqs. (4.15) and (4.16) become

$$\left(\frac{1}{T_{1\rho}}\right)_d = \frac{3}{8} \gamma^4 \hbar^2 I(I+1) \frac{H_1^2}{H_1^2 + H_{d\rho}^2 + H_{q\rho}^2} \mathcal{J}_d^{(0)}(2\omega_1), \quad (4.19)$$

$$\left(\frac{1}{T_{1\rho}}\right)_q = \frac{9}{160} \frac{(2I+3)e^2 Q^2}{I^2(2I-1)} \frac{H_1^2}{H_1^2 + H_{d\rho}^2 + H_{q\rho}^2} \mathcal{J}_q^{(0)}(2\omega_1). \quad (4.20)$$

Similar to the relaxation rates in the strong-collision region (see Sec. IV A), via the local field the dipolar and quadrupolar relaxation contributions are coupled. With increasing amplitude of \bar{H}_1 this coupling becomes less effective, and in the high-field limit ($H_1^2 \gg H_{L\rho}^2$) the individual rates are completely decoupled, according to

$$\frac{1}{T_{1\rho}} = \frac{3}{8} \gamma^4 \hbar^2 I(I+1) \mathcal{J}_d^{(0)}(2\omega_1) + \frac{9}{160} \frac{(2I+3)e^2 Q^2}{I^2(2I-1)} \mathcal{J}_q^{(0)}(2\omega_1). \quad (4.21)$$

For a given set of correlation functions $G^q(t)$ and $G^d(t)$, Eqs. (4.15)–(4.21) predict a dipolar and a quadrupolar $T_{1\rho}$ minimum as a function of the correlation times τ_c^d and τ_c^q of a spin-spin or a defect-spin *pair*, respectively. If the underlying microscopic mechanisms causing internal motions are thermally activated, such as, e.g., for self- or impurity diffusion,^{4,5,13} the shape and width of these minima may be investigated as a function of temperature. If the quadrupolar relaxation effects are due to the stress-induced motion of dislocations during plastic deformation,⁸ the related $(T_{1\rho})_q$ minimum is studied in terms of the rate at which the crystal is deformed. According to Eqs. (4.15) and (4.16) the shape and width of these minima should not only depend upon the microscopic mechanisms of motion, but also on the distance off resonance characterized by the angle ϑ and the quantity h . For $\vartheta \neq \frac{1}{2}\pi$ the appropriate spectral density functions both at frequency ω_{eff} and $2\omega_{\text{eff}}$ contribute to the relaxation process.

In analogy to the dipolar results of I, on the weak-collision side of the low-field dipolar and quadrupolar $T_{1\rho}$ minimum Eqs. (4.15), (4.16), (4.19), and (4.20) predict a field (H_1) dependence of $(T_{1\rho})_d$ and $(T_{1\rho})_q$. Since, so far, there is no

experimental evidence for such an effect, the applicability of the above results under low-field weak-collision conditions is not quite clear. Two of the reasons for the possible failure of the present theory in this region might be the following:

(i) If τ_c^d and τ_c^q are shorter than the inverse dipolar or quadrupolar linewidth contributions $(\Delta\omega_d^{\text{RL}})^{-1}$ and $(\Delta\omega_q^{\text{RL}})^{-1}$ in a rigid lattice, in a *low* H_1 field ($H_1 \approx H_{d\rho}, H_{q\rho}$) the assumption of a *single* (common) spin temperature might break down due to the speed of the motions. In a *high* H_1 field the spins are preferentially aligned along \vec{H}_1 and the single-spin-temperature theory should nevertheless hold owing to the establishment of a *Zeeman* spin temperature in the rotating frame. Thermal mixing is then irrelevant due to the small heat capacities of the dipolar and quadrupolar thermal reservoirs.

(ii) By its very nature the entire spin-temperature concept is meaningful only if the establishment of any type of spin temperature is a fast process compared to spin-lattice relaxation. For $H_1 \lesssim H_{d\rho}, H_{q\rho}$, at the dipolar and quadrupolar minimum $(T_{1\rho})_d$ and $(T_{1\rho})_q$ are very short and of the same order of magnitude as $(\Delta\omega_d^{\text{RL}})^{-1}$ and $(\Delta\omega_q^{\text{RL}})^{-1}$, respectively. Since, on the other hand, in low fields, $(\Delta\omega_d^{\text{RL}})^{-1}$ and $(\Delta\omega_q^{\text{RL}})^{-1}$ represent rough measures for the time required for the establishment of dipolar and quadrupolar spin temperatures as well as their thermal mixing, in the questionable low-field weak-collision region the entire spin-temperature concept becomes questionable.

C. Combined dipolar and quadrupolar weak- and strong-collision effects

During the discussion of Secs. IV A and IV B, dipolar and quadrupolar contributions to $T_{1\rho}$ were assumed to be both simultaneously of a strong- or weak-collision type. In reality, however, owing to the different physical natures of dipolar and quadrupolar relaxation effects, on a τ_c^d or a τ_c^q scale the related $T_{1\rho}$ minima are often well separated.

Thus, dipolar and quadrupolar effects associated with randomly migrating vacancies give rise to two $T_{1\rho}$ minima as a function of temperature: (i) the quadrupolar minimum^{4,5,26} appearing at temperatures for which $\omega_1\tau_v \approx 1$, where τ_v denotes the mean time between successive jumps of a *vacancy*, and (ii) the dipolar minimum^{15,20,23} occurring at temperatures for which $\omega_1\tau \approx 1$, where τ symbolizes the mean time between successive jumps of an *atom*. Noting that $\tau_v/\tau = c_v$, the thermally created concentration of vacant lattice sites, the quadrupolar $T_{1\rho}$ minimum due to the random jumps of *vacancies*, if found at all, appears at

much lower temperatures than the dipolar minimum associated with the correlated jumps of *atoms*.²³

Therefore, in reality any combination of the dipolar and quadrupolar weak- and strong-collision relaxation rates derived in Secs. IV A and IV B may be encountered. However, if the dipolar and the quadrupolar minimum are well separated, experiments may often be confined to regions where one of the two relaxation contributions dominates over the other, thus simplifying their interpretation considerably in that only one type of "lattice" correlation functions has to be known.

V. SPIN-LATTICE RELAXATION IN THE INTERMEDIATE REGIONS

In the regions where the dipolar and quadrupolar $T_{1\rho}$ minima appear, the related "lattice" and "spin correlation functions" decay about equally fast, and the evaluation of Eqs. (3.49) and (3.50) is complicated by our lack of understanding of the internal equilibration processes governing the *spin* correlation functions.

Qualitatively, however, it is clear that according to Eqs. (3.49) and (3.50) low-field $T_{1\rho}$ minima are determined by both atomic or defect motions in the crystal *and* by certain internal processes inside the spin system itself. These properties are in contrast to high-field $T_{1\rho}$ minima in the weak-collision region or the relaxation behavior in the strong-collision region (see Sec. IV), which are both governed exclusively by *motions* in the crystal.

It is therefore concluded that in order to use the nuclear spin system as a probe for the study of microscopic mechanisms causing the motions of atoms or molecules, point defects, dislocations, etc., the relaxation properties (such as the shape and width of dipolar and quadrupolar $T_{1\rho}$ minimum, anisotropies of the relaxation times with respect to the crystallographic orientation of the constant external magnetic field \vec{H}_0 , etc.) should be investigated in field and temperature regions where they are governed by internal motions alone. This suggests experiments to be carried out in the weak- or strong-collision region for the dipolar or quadrupolar relaxation contributions, thus avoiding the difficulties in extracting information on internal motions from low-field $T_{1\rho}$ minima.

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