# Nuclear Magnetic Relaxation Induced by the Dynamics of Lattice Defects in Solids ($I=3/2$, $I=2$, and $I=5/2$)

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Results are presented for the relaxation of the nuclear magnetization via quadrupolar interactions caused by the dynamics of point-like lattice defects in cubic solids. For systems with nuclear spins $I=3/2$, several aspects of the lineshape function of the absorption signal are considered. The treatment includes the transition to the rigid lattice case, the presence of additional static quadrupolar interactions as well as the dynamic shift of the absorption, and saturation effects. For spins $I=2$, expressions are given in detail for the parameters governing the relaxation of the longitudinal and the transverse magnetization. For the $I=5/2$ case, numerical results are presented for the same quantities accounting for complete and incomplete excitation of the spin system.

## 1. Introduction

In solids, the nuclear spin relaxation of nuclei with spin number $I \geqq 1$ is often found to be dominated by the interaction of the electric nuclear quadrupole moment $Q$ with electrical field gradients (EFG) $V_{ik}$ present at the positions of the nuclei [1, 2]. In ideal crystals these interactions vanish for nuclei at sites of perfect cubic symmetry. In real cubic crystals, however, the perfect symmetry can be destroyed by lattice defects, e.g. vacancies, impurities, and dislocations [2, 3]. The motion of these lattice imperfections then causes fluctuations of the EFGs which may give rise to strong nuclear spin relaxation effects. In the pioneering theoretical and experimental work of Cohen and Reif [2, 4, 5] this was demonstrated for the case of lattice vacancies. In recent years this method has been extended to the investigation of the diffusion of both hetero- and homovalent impurities [6—10], to the movement of dislocations [11, 12] and to the study of the localized motion of "off center" ions [13] in ionic crystals. By a slight modification of the method, the diffusion of lattice ions has also been measured [14]. In metals, quadrupolar relaxation effects have been used to monitor the diffusion of impurities [15—17] and the motion of dislocations [18].

The theory of nuclear spin relaxation caused by dynamic quadrupolar interactions has been considered for various experimental conditions and spin systems with different nuclear spin numbers $I$, see e.g. [1, 2, 5, 15, 19—24]. However, most of the information obtained so far on the dynamics of lattice defects has been deduced from experiments on nuclei with spin $I=3/2$. In this class there is a large number of important nuclei such as the chlorine and bromine isotopes and many metals, e.g. $^7$Li, $^{23}$Na, $^{63}$Cu, and $^{87}$Rb.

For the relaxation of the longitudinal magnetization via quadrupole interactions there is an important distinction to be made. In solids, a common temperature of the spin system may evolve as a consequence of the so-called "flip-flop" processes caused by dipolar interactions of the nuclei [21, 25]. However, for cubic crystals containing defects and in crystals of non-cubic symmetry, quadrupolar interactions give rise to unequal spacings of energy levels and thus can prevent the development of a common spin-temperature.

For $I=3/2$, the behaviour of the longitudinal magnetization $M_z(t)$ in the absence of a common spin-temperature during a pulse experiment was first considered by Cohen and Reif [2] and later by Kondo and Yamashita [26] using the classical concept of population numbers of energy states. The double exponential form of $M_z(t)$ obtained by these authors was later confirmed by Hubbard [27] in a quantum mechanical density matrix treatment. For $I=3/2$ and full excitation of the central and satellite transitions he obtained after a "$\theta$-degree

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pulse"

$$M_z(t) - M_z^{\mathrm{T}} = M_z^{\mathrm{T}}(\cos\theta - 1) \cdot [c_1 \exp(-a_1 t) + c_2 \exp(-a_2 t)] \quad (1)$$

with $c_1 = \frac{4}{5}$, $c_2 = \frac{1}{5}$ and

$$a_1 = \tfrac{1}{6}(eQ/\hbar)^2 J_2(2\omega_0), \quad a_2 = \tfrac{1}{6}(eQ/\hbar)^2 J_1(\omega_0), \quad (2)$$

where $M_z^{\mathrm{T}}$ is the thermal equilibrium value of $M_z$. If the EFGs at the $n_{\mathrm{q}}$ quadrupole nuclei are caused by $n_{\mathrm{d}}$ statistically independent defects distributed in the lattice, the spectral density functions $J_j(\omega)$ $(j = 0, 1, 2)$ are given by

$$J_j(\omega) = \frac{2}{n_{\mathrm{q}}} \int_0^\infty \sum_{n=1}^{n_{\mathrm{q}}} \sum_{l=1}^{n_{\mathrm{d}}} \cdot \langle V_{ln}^{(-j)}(t'+t)\, V_{ln}^{(+j)}(t')\rangle_{t'} \cos\omega t \,\mathrm{d}t, \quad (3)$$

where the brackets denote the corresponding time average and the EFG functions $V^{(\pm j)}$ are defined by [2]

$$V^{(0)} = V_{zz}, \quad V^{(\pm 1)} = V_{xz} \pm \mathrm{i} V_{yz}, \quad V^{(\pm 2)} = \tfrac{1}{2}(V_{xx} - V_{yy}) \pm \mathrm{i} V_{xy}. \quad (4)$$

If the satellite component of the absorption is strongly broadened for larger quadrupole interactions, only the central line can be excited in a pulse experiment. In this case, where there is incomplete excitation of the spin system, the pre-exponential factors in (1) are changed to $c_1 = c_2 = \frac{1}{2}$ [7].

For cases where a common spin-temperature is established Andrew and Tunstall [21] derived a single exponential form of $M_z(t)$ for arbitrary spins with

$$a = \frac{2I+3}{40 I^2 (2I-1)} \cdot (eQ/\hbar)^2 [J_1(\omega_0) + 4 J_2(2\omega_0)]. \quad (5)$$

For $I = 3/2$ Wikner et al. [28] showed that (1) and (5) can be obtained as limiting cases of a slightly more general treatment which explicitly accounts for the "flip-flop" term in the dipolar Hamiltonian.

The time dependence of the transverse magnetization for $I = 3/2$ is given [27] by

$$M_{xy}(t) = M_z^{\mathrm{T}} \sin\theta \cdot [d_1 \exp(-b_1 t) + d_2 \exp(-b_2 t)] \quad (6)$$

with $d_1 = \frac{3}{5}$, $d_2 = \frac{2}{5}$ and

$$b_1 = \tfrac{1}{12}(eQ/\hbar)^2 [\tfrac{3}{2} J_0(0) + J_1(\omega_0)], \quad (7\mathrm{a})$$

$$b_2 = \tfrac{1}{12}(eQ/\hbar)^2 [J_1(\omega_0) + J_2(2\omega_0)]. \quad (7\mathrm{b})$$

Fourier transformation of $M_{xy}(t)$ gives the lineshape function $g_{\mathrm{q}}(\omega)$ of the nuclear absorption signal measured in an cw experiment under the condition of very small RF fields. In Sect. 2, $g_{\mathrm{q}}(\omega)$ for $I = 3/2$ will be derived in a manner more appropriate for the cw broad-line experiments previously reported [5–10] which uses Redfield's density matrix formalism and includes a treatment of saturation effects. The case of the rigid lattice will be considered as well as the presence of additional dipolar and static quadrupolar interactions together with the dynamic shift of the absorption.

No full treatment seems to have been given in the literature for spin numbers $I \geqq 2$ and cases in which the spin-temperature concept does not apply. However, provided the quadrupolar perturbations are small compared to the Zeeman interaction, as will be assumed throughout this paper, the following general remarks can be made.

i) For both complete and incomplete excitation of the spin system and correlation times $\tau$ not short compared to the Larmor period, $M_z(t)$ [21, 27] as well as $M_{xy}(t)$ [27] for integer spins are given by a sum of $I$ exponential terms, while for non-integer spins the relaxation is characterized by $I + \frac{1}{2}$ exponentials.

ii) In the limit of extreme narrowing, i.e. $\omega_0 \tau \ll 1$, the longitudinal as well as the transverse magnetization are single exponential for the case of complete excitation and possess equal rate constants [27]:

$$a = b = \tfrac{1}{8}(eQ/\hbar)^2 \cdot [(2I+3)/I^2(2I-1)]\, J_1(0). \quad (8)$$

The restriction to small quadrupolar interactions means that changes in the transition frequencies are assumed to be small compared to the unperturbed frequencies $\omega_0$ and $2\omega_0$, respectively. This condition ensures that the actual transition probabilities are adequately described by the $J_j(j\omega_0)$ and that quadrupole effects of first order are operative. In Sect. 3, results will be presented for the longitudinal and transverse magnetization of spin systems with $I = 2$ and $I = 5/2$ derived under the assumption that there exists no spin-temperature.

While the $I=2$ case is of less importance, nuclei with spin $I=5/2$ form a large class of quadrupole nuclei including isotopes such as $^{27}$Al, $^{121}$Sb, $^{127}$I, and the important, though low abundant, $^{17}$O.

## 2. The Lineshape Function $g_q(\omega)$ for $I=3/2$

Under conditions of linear response, the quadrupolar lineshape function $g_q(\omega)$ and transverse magnetization $M_{x,y}(t)$, Eq. (6), are Fourier-transforms of each other. In cw-spectroscopy, however, the effect of the RF-field $B_1 = 2B_{10}(\cos\omega t, 0, 0)$ must be considered. The total Hamiltonian $\mathscr{H}$ of the system in addition to the Zeeman Hamiltonian $\mathscr{H}_0$ and the time dependent quadrupolar perturbation $\mathscr{H}_1(t)$ then contains a term $\mathscr{H}_{\mathrm{RF}}$ resulting from the radiation field. To calculate $g_q(\omega)$ use was made of the general relation between the lineshape function $g(\omega)$ of an absorption signal and the RF susceptibility component $\chi''(\omega)$ in quadrature with $B_1$:

$$\begin{aligned}\chi''(\omega) &= \frac{\gamma\hbar i N}{4B_{10}}\left[\langle I_+\rangle e^{-i\omega t} - \langle I_-\rangle e^{i\omega t}\right] \\ &= \tfrac{1}{2}\pi\chi_0\omega_0 g(\omega)\,, \end{aligned} \tag{9}$$

where $\chi_0$ is the static susceptibility, $N = n_q/V$ is the number of spins per unit volume and $\gamma$ the magnetogyric ratio. The brackets indicate expectation values of the corresponding spin operators. In the density matrix formalism these are given by

$$\langle I_\pm\rangle = \mathrm{Tr}(\varrho I_\pm)\,. \tag{10}$$

Within the Redfield density matrix formalism [20, 29, 30] the time dependence of the individual matrix elements $\varrho_{\alpha\alpha'}$ is governed by

$$\begin{aligned}\frac{\mathrm{d}\varrho_{\alpha\alpha'}}{\mathrm{d}t} &= \frac{i}{\hbar}\left[\varrho, \mathscr{H}_0 + \mathscr{H}_{\mathrm{RF}}\right]_{\alpha\alpha'} \\ &\quad + \sum_{\beta\beta'}{}' R_{\alpha\alpha'\beta\beta'}(\varrho_{\beta\beta'} - \varrho^T_{\beta\beta'})\,, \end{aligned} \tag{11}$$

where the indices $\alpha$, etc., label the eigenfunctions of $\mathscr{H}_0$ and where the elements $R_{\alpha\alpha'\beta\beta'}$ of the complex relaxations matrix $R$ [30, 31] are determined by the relevant spectral densities of the EFG functions $V^{(\pm j)}(t)$. The prime at the summation indicates that only those terms satisfying the energy condition $E_\alpha - E_{\alpha'} = E_\beta - E_{\beta'}$ should be retained. This system of inhomogenous linear differential equations can be solved for the experimental conditions of slow passage and weak RF-fields by seeking a steady state solution, $\overset{\circ}{\varrho}_{\alpha\alpha'} = 0$, and assuming that the actual populations of energy levels maintain their thermal equilibrium values during passage, i.e. $\varrho_{\alpha\alpha} = \varrho^T_{\alpha\alpha}$. Using the high-temperature approximation for the $\varrho^T_{\alpha\alpha'}$, $\chi_0 = 5N\gamma^2\hbar^2/4kT$ and taking the real and imaginary part of $R$ into account, then from (9) and (10) the following result is deduced for the normalized quadrupolar lineshape function $g_q(\omega)$ for $I=3/2$:

$$\begin{aligned} g_q(\omega) &= \frac{3}{5}g_q^s(\omega) + \frac{2}{5}g_q^c(\omega) \\ &= \frac{1}{\pi}\left[\frac{3}{5}\,\frac{b_1}{b_1^2 + (\omega-\omega_0+\Omega^s)^2}\right. \\ &\qquad \left. + \frac{2}{5}\,\frac{b_2}{b_2^2+(\omega-\omega_0+\Omega^c)^2}\right]. \end{aligned} \tag{12}$$

Equation (12) corresponds to a superposition of two Lorentzians; the half-widths $b_1$ and $b_2$ of the satellite and the central line, respectively, are given by (7). The imaginary part of the relaxation matrix causes shifts $\Omega^{c,s}$ of the absorption signals [30, 31], which in the present case are given by

$$\begin{aligned} \Omega^c &= \tfrac{1}{6}(eQ/\hbar)^2[k_2(2\omega_0) - k_1(\omega_0)] \quad \text{and} \\ \Omega^s &= \tfrac{1}{6}(eQ/\hbar)^2 k_1(\omega_0)\,, \end{aligned} \tag{13}$$

where the $k_j(\omega)$ are sine-transforms analogous to (3). In such cases as considered below, these shifts are predicted to be quite sizable and may contain valuable information especially in cases where the concentration of lattice defects is temperature dependent, see (14) below. However, there does not appear to be any experimental verification of this effect in the NMR literature.

To discuss (12), explicit expressions for the spectral densities $J_j(\omega)$ are needed and it will be assumed that the time dependence of the quadrupolar interaction is caused by the diffusion of lattice defects bearing an excess charge relative to the perfect lattice, e.g. vacancies, interstitial ions and heterovalent impurities. Assuming exponential correlation functions, a calculation in a simplified point charge model [2] yields for the spectral densities

$$J_j(j\omega_0) = C_j N_d \frac{\tau}{1 + j^2\omega_0^2\tau^2} \tag{14}$$

with

$$\tfrac{3}{2}C_0 = C_1 = C_2 = (16\pi/5)(\beta z e)^2 d^{-3}.$$

$N_d = n_d/V$ is the number of lattice defects per volume, $\tau$ the correlation time of electric field gradient fluctuations, and $d$ the shortest distance between the site of a point defect and the position of the nucleus being measured. $\beta$ accounts for modifications of the field gradients due to lattice polarization and due to antishielding effects. $ze$ is the excess charge of the lattice defect relative to the perfect lattice. In cases often encountered in ionic crystals, the experiments are performed on halogen ions with quadrupolar nuclei. Usually these are practically immobile and then the anion sublattice can be regarded as a fixed array of EFG probes through which the defects diffuse. Hence, $\tau$ is solely determined by the mean jump frequency $\nu$ of the atomic defects. The relation between $\tau$ and $\nu$ has already been considered [9, 10, 32] using the „encounter model'' of Eisenstadt and Redfield [33, 34] extended to account for correlation effects due to impurity diffusion. If the excess charges move on the cation sublattice of an NaCl-type crystal then $N_d = 4 x_d a_0^{-2}$ and for the experiments performed on the anion nuclei $d = \frac{1}{2} a_0$ holds, where $a_0$ is the lattice constant and $x_d$ the mole fraction of defects. Other experimental situations may be of interest as well, e.g. that of the diffusion of quadrupole sensitive lattice ions which are being measured relative to immobile lattice defects [10]. This method can be used to investigate the diffusion of lattice anions or cations [14]. At sufficiently high doping levels, impurity diffusion may also be followed by performing NMR experiments on the nuclei of the impurity itself [17], but the considerations given here can easily be reformulated to apply to such other cases as well.

The values of $b_1$ and $b_2$ are presented in Fig. 1 as a function of $\omega_0 \tau$, (14), for a defect concentration of $x_d = 1 \cdot 10^{-3}$ and evaluated for the case corresponding to the diffusion of an excess charge on the cation sublattice in AgBr with $^{81}$Br as the measuring nucleus. The two half-widths depend quite differently on $\omega_0 \tau$. The width, $b_2$, of the central line exhibits a $(1/T_1)$-like behaviour with a maximum at $\omega_0 \tau = 0.813$ but the satellite width $b_1$ displays a $(1/T_2)$-like narrowing with decreasing $\omega_0 \tau$. For the case where $\omega_0 \tau > 1$, $b_1 \gg b_2$ and therefore only the central line will be observed due to broadening of the satellites. For the case of the rigid lattice, $\omega_0 \tau \to \infty$, the Redfield density matrix formalism is no longer valid [20, 30]. In this limit the satellite half-width $\Delta\omega_q^{so}$ can be deduced from consideration of a static random defect configuration and for defect concentrations $x_d \ll 0.1$ a line of Lorentzian shape is predicted [2] with

$$\Delta\omega_q^{so} = \frac{32}{9\sqrt{3}} \pi^2 \frac{2m-1}{2I(2I-1)} \frac{\beta e^2 Q}{\hbar} d^{-3} x_d \quad (15)$$

for the transition $m \to m-1$ $(-I \leqq m \leqq I)$. The interpolation between $\Delta\omega_q^{so}$ and $b_1$ is achieved by means of an expression of the form

$$\Delta\omega_q^{s} = \Delta\omega_q^{s*} + \frac{2}{\pi} \Delta\omega_q^{so} \arctan\left(\frac{b_1}{\Delta\omega_q^{so}} \frac{\pi}{2}\right) \quad (16)$$

with $\Delta\omega_q^{s*} = 0$ and the value of $b_1$ and $\Delta\omega_q^{so}$ derived from (7) and (15), respectively; for $\Delta\omega_q^{s*}$ see below.

The experimental half-widths $\Delta\omega^{\alpha}$ $(\alpha = c, s)$ may also contain contributions from the dipolar interactions of the nuclear moments. The dipolar lineshape function $g_d(\omega)$ can usually be observed in the pure crystals, whereas in the doped samples both interactions contribute to the signal. According to the statistical theory of spectral lineshapes [35], the overall lineshape, $g(\omega)$, then corresponds to the convolution, $\otimes$, of $g_d$ and $g_q$ $(I = 3/2)$:

$$\begin{aligned} g(\omega) &= g_q(\omega) \otimes g_d(\omega) \\ &= \tfrac{3}{5} g^s(\omega) + \tfrac{2}{5} g^c(\omega) . \end{aligned} \quad (17)$$

The calculation of the dipolar lineshape in solids is a difficult task and often more empirical schemes have been adopted in its description [20]. If $g_d$ can be approximated by a Lorentian, then the width $\Delta\omega^{\alpha}$ of $g^{\alpha}(\omega)$, shown in Fig. 1, simply is

$$\Delta\omega^{\alpha} = \Delta\omega_q^{\alpha} + \Delta\omega_d \quad (18)$$

with $\Delta\omega_q^c = b_2$ and $\Delta\omega_q^s$ given by (16). In cases where this assumption is not justified, in principle numerical deconvolution methods can be used to determine $g_q^{\alpha}(\omega)$ from $g^{\alpha}(\omega)$ and $g_d(\omega)$. The conclusion therefore is that for this model with independently moving excess charges the central line exhibits lifetime broadening while for the satellite line a motional narrowing phenomenon familiar from dipolar interactions is predicted.

As a consequence of this model the signal intensity measured for $\omega_0 \tau \ll 1$ should be 2.5 times greater than that measured for $\omega_0 \tau \gg 1$ because in the high temperature regime $\Delta\omega^c = \Delta\omega^s$. The expected increase in intensity is not observed, however, for $\omega_0 \tau \ll 1$ in experiments on $^{81}$Br in polycrystalline AgBr [6] and other cubic ionic crystals doped with impurity ions [6—10]. This is attributed to the presence of additional, EFGs producing lattice defects which has not been accounted for in the

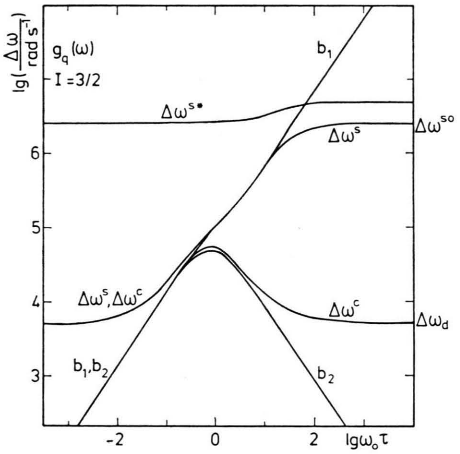

Fig. 1. Half-width of the satellite and the central line for $I = 3/2$ as a function of lg $\omega_0 \tau$ for spectral density functions of the Debye-type (see (14)). In the case of pure quadrupolar interactions the widths are given by $b_1$ and $b_2$, Eqs. (7), in the validity range of the density matrix formalism. For the rigid lattice case, $\omega_0 \tau \rightarrow \infty$, the quadrupolar satellite width is given by $\Delta\omega_q{}^{s0}$ (see (15)). The resultant satellite half-width $\Delta\omega_q{}^s$ is obtained from Eqs. (16) and (18), accounting for the presence of dipolar linewidth contributions. $\Delta\omega^{s*}$ is the satellite width for the case of additional quadrupolar interactions, $\Delta\omega_q{}^{s*}$, due to immobile lattice defects. The resultant half-width of the central line is obtained from Eqs. (7b) and (18). The input data $a_0 = 0.577$ nm, $z = 1$, $\beta = 50$, $Q = 28 \cdot 10^{-30}$ m² and $\Delta\omega_d = 5 \cdot 10^3$ rad s⁻¹ were chosen to model the behaviour of the absorption of $^{81}$Br in AgBr at 16 MHz for the diffusion of bivalent impurity ions, $x_d = 10^{-3}$, in the cation sublattice.

above model, e.g. dislocations and crystallite surfaces. Supporting evidence for the existence of these additional quadrupolar interactions is supplied by the fact that in pure polycrystalline AgBr [2] and even in single crystals of alkali bromides [36, 37] the satellite line is already broadened beyond detection. Because defects of this kind are practically immobile, the linewidth contribution, $\Delta\omega_q^{s*}$, they give rise to does not average out at the positions of the static measuring nuclei and, hence, determines the satellite linewidth after the narrowing of the contribution from the mobile defects. Equation (16) accounts for these static quadrupolar interactions in a simple manner. Notably for the crystallite surfaces, the magnitude of $\Delta\omega_q^{s*}$ is difficult to determine for polycrystalline samples. Therefore in Fig. 1, $\Delta\omega_q^{s*}$ was chosen to be equal to the contribution made by the mobile defects in the case of the rigid lattice: $\Delta\omega_q^{s*} = \Delta\omega_q^{s0}$. Figure 1 shows the satellite width for this case, $\Delta\omega^{s*}$, and explains why the satellite line in polycrystalline material usually does not contribute to the observed signals of quadrupole sensitive nuclei throughout the solid phase.

Notwithstanding the limits imposed by the use of the simple point charge model, these approximate calculations clearly demonstrate the possibility of observing linewidth maxima for the absorptions of quadrupole-sensitive nuclei in simple cubic ionic crystals caused by the diffusion of lattice defects. In a quantitative comparison, the calculated value at the maximum of $\Delta\omega_q^c = 4.8 \cdot 10^4$ rad s⁻¹ agrees quite well with results obtained from linewidth maxima caused by the diffusion of several bivalent cations in AgBr [6, 10]. Depending on the nature of the impurity, $\Delta\omega_q^c(^{81}\mathrm{Br})$ was found to take values between $5.3 \cdot 10^4$ ($\mathrm{Cd}^{2+}$) and $25 \cdot 10^4$ rad s⁻¹ ($\mathrm{Mn}^{2+}$), $x_d = 10^{-3}$.

The value of $\beta = (1 - \gamma_\infty)\,\beta^s = 50$ used in the numerical calculation originally was deduced from the relaxation effect caused by cation vacancies in AgBr [2]. In a recent theoretical calculation of the Sternheimer antishielding factor $\gamma_\infty = -85.5$ was obtained for Br⁻ crystal ions [38]. In the continuum approximation $\beta^s = (2\,\varepsilon + 3)/5\,\varepsilon$ holds [2]. The value of $\beta \approx 40$ obtained in this approximation is in fair agreement with experiment. However, the results quoted above indicate the need for more detailed models accounting for the chemical nature of the EFG-producing defect.

In carrying out cw broad-line experiments, a knowledge of the limitations of (12) is indispensable. To derive an expression for $g_q(\omega)$ not subject to the restricting condition of vanishingly small RF-fields, the assumption must be dropped that the diagonal elements maintain their equilibrium values during passage through the absorption. The additional differential equations of the $\varrho_{\alpha\alpha}$ are easily obtained from (11). These equations together with those for the $\varrho_{\alpha\alpha'}$, $\alpha \neq \alpha'$, form a system of ten equations sufficient to determine the required steady state solution for $g_q(\omega)$. Neglecting the dynamic shift of the absorption, the calculation yields the following result correct to second order in $\omega_1$:

$$g_q(\omega) = \frac{1}{\pi}\left[\frac{3}{5}\,\frac{b_1}{b_1^2 + 3\,\dfrac{b_1}{a_2}\,\omega_1^2 + (\omega - \omega_0)^2} + \frac{2}{5}\,\frac{b_2}{b_2^2 + 4\,\dfrac{b_2^2}{a_1 a_2}\,\omega_1^2 + (\omega - \omega_0)^2}\right], \tag{19}$$

where $\omega_1 = \gamma B_{10}$. Under the condition $\omega_1^2 \ll a_1 a_2$, which corresponds to negligible saturation, (19) reduces to (12) as expected. For the central transition this condition corresponds to $\omega_1 < 0.3 \Delta \omega_q^c$, which can be easily satisfied in the experiments.

## 3. Longitudinal and Transverse Relaxation for $I = 2$ and $I = 5/2$

The case of nuclear spin $I = 2$ represents the simplest example of nonexponential behaviour of the nuclear magnetization for systems with integer spin numbers. In this respect a comparison with the results for the $I = 3/2$ is of interest despite the fact that there are no stable nuclei with $I = 2$. However, unstable nuclei with this spin can be produced by the neutron activation method as has been done in $^7$Li and alloys of $^7$Li [16, 39] and where, using polarized neutrons and nuclear radiation detection, the relaxation of the longitudinal magnetization of the $\beta$-active $^8$Li could be detected.

To compute the components of the nuclear magnetization, one may continue from (10). The relevant matrix elements $\varrho_{\alpha\alpha'}(t)$ then can be evaluated by use of (11), with $\mathscr{H}_{\mathrm{RF}} = 0$, which provides a system of differential equations for the $\varrho_{\alpha\alpha'}$. Following these lines, the double exponential form of (1) is obtained for $M_z(t)$. Since there is no central transition for $I = 2$, only the case of complete excitation of the spin system is to be considered, leading to the following results for the parameters in (1):

$$c_{1,2} = \frac{1}{2} \pm \frac{3}{20} \frac{A - B}{\Delta} \mp \frac{2}{5} \frac{C}{\Delta} \tag{20}$$

and

$$a_{1,2} = \frac{A + B}{2} \pm \Delta \tag{21}$$

with

$$\Delta = \sqrt{\left(\frac{A - B}{2}\right)^2 + C^2}. \tag{22}$$

The quantities $A$, $B$ and $C$ depend on the spectral densities and are given by

$$\begin{aligned} A &= A_q^2 (36 J_1 + 24 J_2), \\ B &= A_q^2 (42 J_1 + 72 J_2), \\ C &= 36\, A_q^2 J_1 \end{aligned} \tag{23}$$

with

$$A_q = \frac{e Q}{4 I (2 I - 1) \hbar} \quad \text{and}$$

$$J_j = J_j(j \omega_0), \quad j = 0, 1, 2.$$

This result is in agreement with that given in [39] where, however, a different density matrix formalism was used in the derivation. In Fig. 2, the parameters characterizing the time dependence of $M_z(t)$ are shown as a function of $\omega_0 \tau$ using Debye spectral densities, (14). As can be seen, the longitudinal magnetization effectively exhibits a simple single exponential behaviour for all values of $\omega_0 \tau$.

For the transverse magnetization, the double exponential form of (6) applies to the $I = 2$ case too, thus again fulfilling i) from Sect. 1 concerning the number of exponentials needed to describe the relaxation. The following results are deduced for the four parameters in (6):

$$d_{1,2} = \frac{1}{2} \mp \frac{A - B}{20 \Delta} \mp \frac{2}{5} \sqrt{\frac{3}{2}} \frac{C}{\Delta} \tag{24}$$

and

$$b_{1,2} = \frac{A + B}{2} \pm \Delta \tag{25}$$

with $\Delta$ given by (22). However, for $M_{xy}(t)$ the quantities $A$, $B$ and $C$ are defined by

$$\begin{aligned} A &= \tfrac{1}{2} A_q^2 (81 J_0 + 78 J_1 + 60 J_2), \\ B &= \tfrac{1}{2} A_q^2 (\ 9 J_0 + 66 J_1 + 84 J_2), \\ C &= 6\sqrt{6}\, A_q^2 (J_1 + 2 J_2). \end{aligned} \tag{26}$$

The dependence of the parameters relevant to $M_{xy}(t)$ on $\omega_0 \tau$ is also presented in Figure 2.

As can be easily shown, in the case of extreme narrowing $M_z(t)$ as well as $M_{xy}(t)$ are single exponential, see Fig. 2, and the value of $a_2 = b_2$ is given by (8). It is of interest to note that the transition to the single exponential form is related to the fact that the preexponential factors are functions of the spectral densities which causes one of the preexponential factors ($c_1$, $d_1$) to vanish in this limit. In contrast, for $I = 3/2$ the $c_{1,2}$ and $d_{1,2}$ are constants and the simple exponential behaviour occurs because $a_1 = a_2$ and $b_1 = b_2$ for $\omega_0 \tau \ll 1$. As a further distinction, it should be mentioned that no lifetime broadening is exhibited by the absorption signal because both $b_1$ and $b_2$, (25), increase in pro-

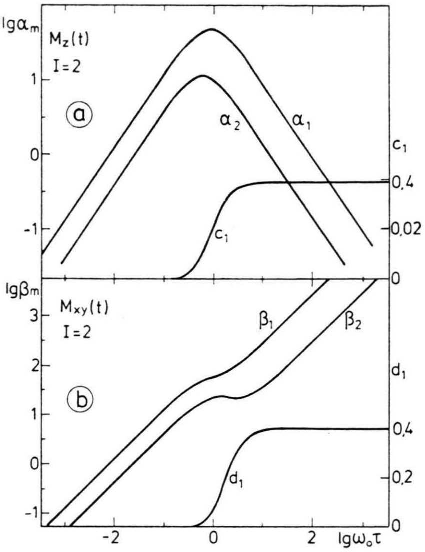

Fig. 2. Parameters governing the relaxation of (a) the longitudinal and (b) the transverse magnetization of spins $I=2$, Eqs. (1) and (6), as a function of lg $\omega_0\tau$. Debye spectral densities, Eq. (14), were used in the computation of the $c_m$, $\alpha_m=a_m\omega_0/(A_q{}^2C_1)$, $d_m$, and $\beta_m=b_m\omega_0/(A_q{}^2C_1)$, $m=1, 2$.

portion with $J_0(0)$ for $\omega_0\tau \gg 1$. In this limit the preexponentials are given by $d_1=\frac{2}{5}$ and $d_2=\frac{2}{5}$. As expected, these values agree with the weights of the individual components of the absorption in the case of the rigid lattice which are proportional to $I(I+1)-m(m-1)$ for the transition $m \rightarrow m-1$ [2, 3].

In addition to the case $I=3/2$, nuclei with spin $I=5/2$ are an important group of quadrupole nuclei. Its members $^{127}$I and $^{17}$O form two large classes of inorganic compounds and, hence, extend considerably the range of systems suitable for investigations into the dynamics of lattice defects by a large number of cubic iodides [40] and oxides. Therefore the behaviour of the longitudinal and transverse relaxation of a spin system with $I=5/2$ is of some interest.

Performing the calculations as indicated above, $M_z(t)$ and $M_{xy}(t)$ are found to be given by a sum of three exponentials:

$$M_z(t)-M_z^{\mathrm{T}}=M_z^{\mathrm{T}}(\cos\theta-1) \cdot \sum_{m=1}^{3} c_m \exp(-a_m t)\,, \tag{27}$$

$$M_{xy}(t)=M_z^{\mathrm{T}}\sin\theta\sum_{m=1}^{3} d_m \exp(-b_m t)\,. \tag{28}$$

The $a_m$ and $b_m$ are the eigenvalues of the $3\times 3$ relaxation matrix of $M_z$ or $M_{xy}$, respectively:

$$R_z=A_q^2\begin{pmatrix}-80J_1-40J_2 & 80J_1 & 40J_2\\ 80J_1 & -112J_1-72J_2 & 32J_1-72J_2\\ 40J_2 & 32J_1-72J_2 & -32J_1-112J_2\end{pmatrix}, \tag{29}$$

$$R_{xy}=A_q^2\begin{pmatrix}-72J_0-96J_1-56J_2 & 16\sqrt{10}\,J_1 & 48\sqrt{5}\,J_2\\ 16\sqrt{10}\,J_1 & -18J_0-72J_1-20J_2 & 0\\ 24\sqrt{5}\,J_2 & 0 & -32J_1-112J_2\end{pmatrix}. \tag{30}$$

It has not been possible to find simple analytical expressions for these exponents which are each roots of a cubic equation. Therefore graphical solutions will be given of all the quantities involved in (27) and (28). In addition to the case of full excitation of the spin system, for the longitudinal relaxation also the case will be considered in which only the central transition is excited in the pulse experiment.

$M_z(t)$ only depends on the spectral densities $J_1(\omega_0)$ and $J_2(2\omega_0)$ and consequently, for arbitrary forms of spectral densities, the parameters

$$\Gamma_m=a_m/(A_q^2J_1(\omega_0))$$

can be expressed as functions of $x=J_2(2\omega_0)/J_1(\omega_0)$ as shown in Figure 3a. When dealing with Debye spectral densities, (14), then a more convenient variable to use is $\omega_0\tau$ and the $\alpha_m=a_m/(A_q^2C_1\omega_0^{-1})$ are presented in Figure 3b. Figure 3c shows the corresponding $c_m$ for the case of full excitation of the spin system. From the definition of the $J_j(\mathrm{j}\,\omega_0)$ in (14) the $\omega_0\tau$ scale corresponds to an interval of $0.25 \leqq J_2(2\omega_0)/J_1(\omega_0) \leqq 1.00$ on the $x$-scale. In agreement with (8), for very short correlation times the decay of $M_z$ is single exponential with $a_3=64A_q^2J_1(\omega_0)$. The significant result of the calculations shown in Fig. 3b, c is that $\alpha_1, \alpha_2 > \alpha_3$ and $c_1+c_2 < 7\cdot 10^{-2}$ which implies that the time dependence of the longitudinal magnetization is in effect a single exponential for all values of $\omega_0\tau$, i.e. $M_z(t) \simeq c_3\exp(-a_3t)$. As can be shown, this result

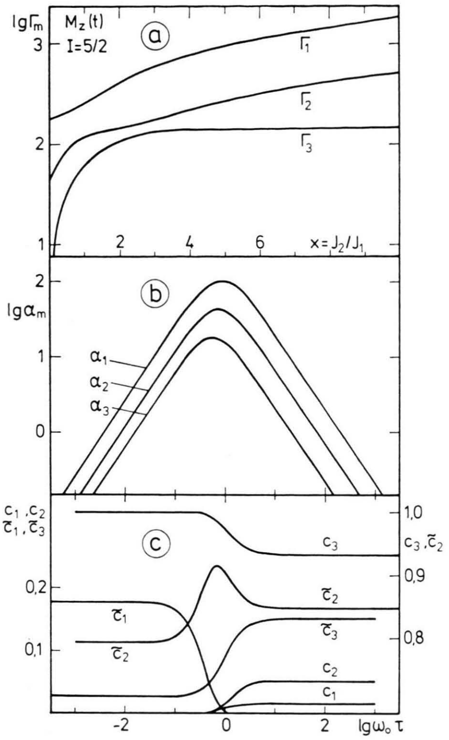

Fig. 3. Parameters governing the relaxation of the longitudinal magnetization of spins $I=5/2$ (see (27)). (a) Width parameter $\Gamma_m = a_m/(A_q{}^2 J_1(\omega_0))$ as a function of
$$x = J_2(2\,\omega_0)/J_1(\omega_0)$$
for arbitrary forms of spectral densities, $m = 1, 2, 3$. (b) Parameters $\alpha_m = a_m\,\omega_0/(A_q{}^2 C_1)$ as a function of lg $\omega_0\,\tau$. (c) Preexponential factors $c_m$ and $\tilde{c}_m$ as a function of lg $\omega_0\,\tau$ for the case of complete and incomplete excitation of the spin system, respectively. Debye spectral densities, Eq. (14), were used in the computation of the $c_m$, $\tilde{c}_m$, and $\alpha_m$, $m = 1, 2, 3$.

is not restricted to the special form of (14) chosen for the spectral densities as long as $0.125 \leq x \leq 2$ for all $\omega_0\,\tau$. The results presented in Figs. 3a—3c apply whenever quadrupolar interactions render the spacings of energy levels, i.e. the transition frequencies, sufficiently unequal to suppress the evolution of a common spin-temperature, yet leave the satellites excitable and observable in a pulse experiment. For larger quadrupolar interactions as may be encountered in imperfect cubic solids and in noncubic crystals, the satellites can become very broad and only the central transition may be excitable. The latter situation appears to be commonly found for $^{127}$I even in carefully prepared cubic single crystals [36, 37]. This causes changes in the preexponential factors of (27). The preexponentials, $\tilde{c}_m$, corresponding to this case are also shown in Figure 3c. As can be seen, for correlation times $\tau$ not short compared to the Larmor period $M_z(t)$ is closely approximated by a sum of two exponentials. But because $\tilde{c}_2 > 0.79$, the decay of $M_z$ is dominated by the exponent $a_2$. It is worth mentioning that there is no simple exponential behaviour in the limit of extreme narrowing under these conditions of incomplete excitation.

The transverse magnetization depends on the spectral densities $J_0$, $J_1$ and $J_2$. Therefore, in Fig. 4 the parameters $d_m$ and $b_m$ which govern the relaxation of $M_{xy}$ are given as functions of $\omega_0\,\tau$. The behaviour for $\omega_0\,\tau \ll 1$ is found to be that predicted by (8) with $d_1 = d_2 = 0$. For correlation times $\tau$ not short compared to $\omega_0^{-1}$, $M_{xy}(t)$ is composed of three exponentials of comparable weight. Which, for very long $\tau$, become identical to those corresponding to the case of the rigid lattice, $d_1 = \frac{10}{35}$, $d_2 = \frac{16}{35}$, and $d_3 = \frac{9}{35}$. In view of the relation of $M_{xy}(t)$ to the lineshape function $g_q(\omega)$ each exponential term can be assigned to the central ($m = 3$) and two satellite transitions. Figure 4 shows that lifetime broadening behaviour is exhibited for $m = 3$ and that for $m = 1, 2$ motional narrowing is observed in an analogous fashion to the $I = 3/2$ case. The linewidth transition to the rigid lattice can be easily treated following the lines indicated in Sect. 2 using (15) and (16) and taking proper account of further EFGs producing lattice imperfections.

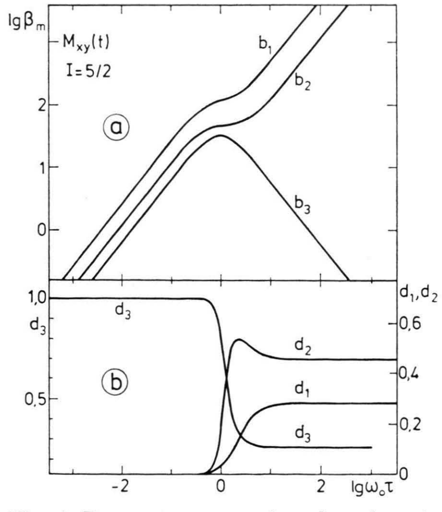

Fig. 4. Parameters governing the relaxation of the transverse magnetization of spins $I=5/2$, Eq. (28), as a function of lg $\omega_0\,\tau$. Debye spectral densities, Eq. (14), were used in the computation of (a) the $d_m$ and (b) the
$$\beta_m = b_m\,\omega_0/(A_q{}^2 C_1),\ m = 1, 2, 3.$$

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