

7 Spin-Lattice Relaxation

The recovery of the population ratio N_i/N_j of the Zeeman levels i and j from an off-equilibrium state to the Boltzmann equilibrium $N_i/N_j = \exp[(m_i - m_j)h\gamma B_0/k_B T]$ is known as nuclear magnetic spin-lattice relaxation and is described by the so-called longitudinal relaxation time T_1 . A consideration of one transition is sufficient for spin-1/2 nuclei, whereas several transitions occur and interact for quadrupolar nuclei. Single-exponential behavior of the relaxation cannot be expected. The selective excitation and observation of one transition is possible for quadrupolar nuclei in a single crystal. But it was shown in Sect. 2 that a pure selective excitation for powder material is impossible. This problem becomes more pronounced in the case of MAS. Even the accurate adjustment of the magic angle can be important for relaxation measurements, analogous to the case in STMAS (see Sect. 6), since the excitation during a long pulse sequence reaches the whole spectrum and the satellite population differences can be transferred to the central transition by cross-relaxation. The satellite frequencies vary for each microscopic part of the sample during the rotor period and cross the frequency of the central transition.

Measurements of the longitudinal relaxation time, T_1 , of signals from powder material with strong quadrupole coupling cannot be performed by inversion recovery or by a $\pi/2 - \tau - \pi/2$ pulse group, since non-selective π - or $\pi/2$ -pulses are unrealizable. Accumulation of the central transition signal after a single selective $\pi/2$ -pulse with a varying repetition delay, τ_{rep} , gives a very rough estimate of $T_1 \approx \tau_{\text{rep}}$ (63%). The latter corresponds to the repetition delay for which the signal amplitude amounts to the $(1 - 1/e)$ -fold intensity of its maximum value for infinite delay. A relatively well-defined determination of T_1 for the central transition in static powder spectra can be performed by the saturation of all transitions by means of a long decoupling pulse sequence and the observation of the recovery of the signal after increasing time τ by means of a selective $\pi/4$ -pulse. The band width of the saturation pulse sequence, consisting of phase-shifted pulses slightly shorter than selective π -pulses, e. g. SPINAL-64 [1], should cover the spectral range of the static central transition spectrum. The two crucial points are that the duration of the saturation sequence must be longer than the expected T_1 and the repetition delay must be at least 50 times longer than the pulsing time for safety reasons (transmitter and probe). RF pulsing and sample rotation must not be synchronized in the case of MAS. An increase of the sample temperature by RF irradiation should be avoided, since the quadrupole interaction is temperature dependent.

For recent presentations of the general theory of spin-lattice relaxation, we refer to Goldman [2] and Redfield [3]. Recent reviews concerning the spin-lattice relaxation of quadrupolar nuclei have been given by Yesinowski [4-6] and Werbelow [7, 8] and for spin-3/2 nuclei by Wimperis [9]. The main field of application of the theory of spin-lattice relaxation is nuclear magnetic relaxometry. One of the reviews in this field was given by Kuhn *et al.* [10] concerning ^7Li relaxometry of potential battery materials.

The discussion of relaxation effects of half-integer quadrupolar nuclei in solids was begun in a pioneering study by Pound [11]. He discussed the transitions $\Delta m = \pm 1$ and $\Delta m = \pm 2$ for spin-3/2 nuclei and found that "the thermal equilibrium of the spin system with the lattice is brought about by the electric quadrupole interaction" and that "the satellite line is relatively less saturated than the central line" [11]. The next three subsections are a modified version of our previous review [12] and include studies up to 1992.

7.1 Basic Considerations of the Quadrupolar Spin-Lattice Relaxation

Spin-lattice relaxation, described by a characteristic time constant T_1 , is an irreversible energy transfer from a nuclear-spin system to a "lattice" (an energy reservoir), in which the non-equilibrium magnetization approaches its thermodynamic equilibrium value. The "lattice" can be any system with a much larger heat capacity than that of the nuclear-spin system. The large heat capacity of the "lattice" ensures that the lattice temperature can be assumed to be constant during the relaxation process. Furthermore, it is assumed that dissipative processes within the lattice destroy any coherences caused by contact with the spin system within a characteristic time τ_c , the correlation time of the lattice. In insulating solids, the physical nature of the "lattice" can be described by ordinary lattice vibrations (phonons), or by two-level systems (disorder modes) for amorphous solids and temperatures below $T = 100$ K. Adsorbed atoms or molecules in crystals or porous materials can also represent the "lattice" if they have a large heat capacity. For example, in hydrated zeolites most of the heat capacity stems from adsorbed water molecules.

For spin-lattice relaxation of quadrupole nuclei in solids, the static part of the quadrupole interaction, which causes a shift of the Zeeman levels, is most often large enough to inhibit the spin exchange between different transitions. Thus, a spin temperature will not be established as fast as for the case of a vanishing quadrupole coupling, and the time-dependence of the magnetization build-up is different for each transition. This is inconsistent with the BPP theory [13] of relaxation, in which the spin-temperature concept is invoked. If the static quadrupole interaction prohibits spin-flipping, the degree of freedom for the population numbers of the $2I + 1$ levels is $2I$ since the total number of spins is a constant. Assuming exponential decays, $2I$ eigenvalues (T_1) are to be expected for the decay of the magnetization of a single transition. For crude estimates of the spin-lattice relaxation the effect of the static quadrupole interaction, which suppresses spin-flipping, may be discarded. However, for more detailed studies the above-mentioned effects have to be considered.

The total Hamiltonian for the description of the spin-lattice relaxation is

$$\mathcal{H} = \mathcal{H}_L + \mathcal{H}_Q(t) + \mathcal{H}_R, \quad (7.01)$$

where \mathcal{H}_L and \mathcal{H}_R represent the time-independent Hamiltonians for the spin-system (Larmor) and the lattice (Reservoir), respectively. $\mathcal{H}_Q(t)$ denotes the time-dependent coupling between the spin system and the energy reservoir. For the eigenfunctions of the combined system, \mathcal{H} , we use the product functions $|m, r\rangle = |m\rangle|r\rangle$, where

$$\mathcal{H}_L|m\rangle = E_m|m\rangle, \quad \mathcal{H}_R|r\rangle = E_r|r\rangle. \quad (7.02)$$

By separating the time-independent part of \mathcal{H} , $\mathcal{H}_0 = \mathcal{H}_L + \mathcal{H}_R$, we use the interaction representation with $\mathcal{H}_{R,i} = \mathcal{H}_R$, $\mathcal{H}_{L,i} = \mathcal{H}_L$, and

$$\mathcal{H}_{Q,i}(t) = \exp\left\{-\frac{i}{\hbar}(\mathcal{H}_L + \mathcal{H}_R)t\right\} \mathcal{H}_Q(t) \exp\left\{\frac{i}{\hbar}(\mathcal{H}_L + \mathcal{H}_R)t\right\}. \quad (7.03)$$

Then, for small changes in the population of the levels $|m, r\rangle$, $|m', r'\rangle$, one may apply Dirac's first-order time-dependent perturbation theory to obtain for the transition probability, P , given the transition $|m, r\rangle \rightarrow |m', r'\rangle$,

$$\langle m', r' | P | m, r \rangle = \frac{1}{\hbar^2} \left| \int_0^t \langle m', r' | \mathcal{H}_{Q,i}(t') | m, r \rangle dt' \right|^2. \quad (7.04)$$

The transition rate,

$$\langle m', r' | W | m, r \rangle \equiv W_{mr, m'r'} = \frac{\partial \langle m' r' | P | m r \rangle}{\partial t}, \quad (7.05)$$

is the rate at which the photon necessary to accomplish the spin-flip in the nuclear spin-system is absorbed (emitted) by the lattice. If \mathcal{H}_Q is time-independent, and the lattice states are close enough, we have

$$\langle m' | W | m \rangle = \frac{2\pi}{\hbar} |\langle m' | \mathcal{H}_Q | m \rangle|^2 \rho(E), \quad (7.06)$$

where $\rho(E)$ represents the energy density of the considered processes in the lattice. More generally, it follows from Eq. (7.04) that

$$W_{mr, m'r'} = \frac{1}{\hbar^2} \times \int_0^t [\langle m' r' | \mathcal{H}_{Q,i}(t) | m r \rangle \langle m' r' | \mathcal{H}_{Q,i}(t') | m r \rangle + \langle m r | \mathcal{H}_{Q,i}(t) | m' r' \rangle \langle m r | \mathcal{H}_{Q,i}(t') | m' r' \rangle] dt'. \quad (7.07)$$

It is usually assumed that the ensemble average, $\overline{\langle m' r' | \mathcal{H}_{Q,i}(t) | m r \rangle \langle m' r' | \mathcal{H}_{Q,i}(t') | m r \rangle}$, vanishes for $|t - t'| \rightarrow \infty$. This means that the involved transitions become phase-incoherent after the time difference, $\tau_c = t - t'$. In addition, the correlations are assumed to be stationary, i.e., in the ensemble average the products of the matrix elements in Eq. (7.07) are a function of the time difference, $t - t'$, only. For $\mathcal{H}_Q(t)$ we consider the time-dependent quadrupole Hamiltonian, and especially the fact that in the ensemble average, the matrix elements of $\mathcal{H}_{Q,i}$ vanish, $\overline{\langle m' r' | \mathcal{H}_{Q,i}(t) | m r \rangle} = 0$, or the mean value is considered to be part of the static quadrupole interaction. $\mathcal{H}_{Q,i}$ follows from Eq. (1.60), as

$$\mathcal{H}_{Q,i}(t) = \frac{eQ}{2I(2I-1)} \sum_{m=-2}^{+2} (-1)^m T_m^{(2)} V_{-m,i}^{(2)} \exp(iq\omega_c t), \quad (7.08)$$

where

$$V_{-m,i}^{(2)}(t) = \exp\left\{-\frac{i}{\hbar}(\mathcal{H}_R)t\right\} V_{-m}^{(2)}(t) \exp\left\{\frac{i}{\hbar}(\mathcal{H}_R)t\right\} \quad (7.09)$$

are the operators for the components of the electric field gradient. The index m (see Eqs. (7.08) and (7.09)) is not identical with the magnetic quantum number m which is used in the following equations. Eqs. (7.07) and (7.08) show that the spin-dependent part of the quadrupole Hamiltonian restricts the transitions in the spin-system according to the matrix elements

$$\langle m' | T_0^{(2)} | m \rangle = \frac{3m^2 - I(I+1)}{\sqrt{6}} \delta_{m'm} , \quad (7.10)$$

$$\langle m' | T_{\pm 1}^{(2)} | m \rangle = \mp(2m \pm 1) W_m^{\pm} \delta_{m', m \pm 1} , \quad (7.11)$$

$$\langle m' | T_{\pm 2}^{(2)} | m \rangle = 2 W_{m \pm 1}^{\pm} W_m^{\pm} \delta_{m', m \pm 2} , \quad (7.12)$$

where (cf. Eq. (1.34))

$$W_m^\pm = \frac{1}{2} \sqrt{(I \mp m)(I \pm m + 1)}. \quad (7.13)$$

Since we are calculating the transition rates, $m' \neq m$, one is left with single- and double-quantum transitions. The matrix elements $\langle m' | T_{0,\pm 1,\pm 2}^{(2)} | m \rangle$, Eqs. (7.10)–(7.12), are introduced into Eq. (7.07), and with the above-mentioned assumption one can write

$$W_{mr,m'r'}^\pm = \frac{2}{\hbar^2} \left[\frac{eQ}{2I(2I-1)} \right]^2 \times \left[(2m \pm 1)^2 (W_m^\pm)^2 \tilde{W}_1(r, r') \delta_{m'm \pm 1} + (2W_m^\pm)^2 (W_{m \pm 1}^\pm)^2 \tilde{W}_2(r, r') \delta_{m'm \pm 2} \right] \quad (7.14)$$

with

$$\tilde{W}_n(r, r') = \int_{-\infty}^{+\infty} \exp\{i[\pm n\omega_L + (E_r - E_{r'})/\hbar]\tau\} \times \text{Re} \left[\langle r' | V_{\pm 2}^{(2)}(t) | r \rangle \langle r | V_{\mp 2}^{(2)}(t - \tau) | r' \rangle \right] d\tau. \quad (7.15)$$

Inserting W_m^\pm from Eq. (7.13) and given that

$$W_n(r, r') = \frac{e^2 Q^2}{4I\hbar^2} \tilde{W}_n(r, r'), \quad (7.16)$$

it follows that

$$W_{mr,m'r'} = \frac{(2m \pm 1)^2 (I \mp m)(I \pm m + 1)}{2I(2I-1)^2} W_1(r, r') \delta_{m'm \pm 1} + \frac{(I \mp m)(I \pm m + 1)(I \mp m - 1)(I \pm m + 2)}{2I(2I-1)^2} W_2(r, r') \delta_{m'm \pm 2}. \quad (7.17)$$

The definitions of W_1 and W_2 , as given by Eq. (7.10), differ from some of those in the literature. Eq. (7.10) corresponds to those used by Yosida and Moriya [14], Andrew and Tunstall [15], and Hughes and Reed [16]. It is also common [17, 18] to extract the spin-quantum number I from the definition of $W_{1,2}$, resulting in a change of I to I^2 in the numerators of Eq. (7.17). The integral in Eq. (7.15) represents a spectral density; the real part, $\text{Re}[\]$, is the correlation function of the processes in the lattice. In order to find the total transition rate corresponding to a single- or double-quantum process in the spin system, $W_{1,2}(r, r')$ has to be multiplied by the density of the states and summed over r, r' .

So far, we have only been concerned with the expressions for transitions in the spin system and the lattice. In order to describe the time-dependence of the magnetization one can start with the master equation of the population numbers, N_m , the average number of spins populating the Zeeman level, m ,

$$\frac{dN_m}{dt} = \sum_{n=-I}^I W_{nm} (N_n - N_{n0}) - (N_m - N_{m0}) \sum_{n=-I}^I W_{nm}, \quad (7.18)$$

where N_{m0} is the thermal equilibrium population of level E_m . W_{nm} follows from Eq. (7.14) and denotes the transition rate $n \rightarrow m$ in the spin system for all possible transitions in the lattice. Eq. (7.11) is a system of coupled linear differential equations. The general solution is of the form

$$N_m(t) - N_{m0} = \sum_{k=-I}^{I-1} C_k(t=0) \exp\{-\lambda_k t\}. \quad (7.19)$$

By introducing the differences in the population numbers, $n_m = N_m - N_{m+1}$ and $n_{m0} = N_{m0} - N_{m0+1}$, one can write

$$n_m(t) - n_{m0} = \sum_{k=-I}^{I-1} c_k(t=0) \exp\{-\lambda_k t\}. \quad (7.20)$$

Since the total number of spins is a constant, the system has only $2I$ non-vanishing eigenvalues, λ_k . The initial conditions are given by the excitation, e. g., a $\pi/2$ -pulse at the carrier frequency, ω_L (Larmor frequency), will yield $N_n(t=0) = -N_{-n}(t=0)$. As a result of special initial conditions, some of the constants c_k will vanish. The solution of the eigenvalue problem for $I > 3/2$ is not simple since higher-order equations have to be solved for every ratio of W_2/W_1 . In addition, the constants c_k have to be determined using the initial conditions and the eigenvectors for every W_2/W_1 . These procedures can easily be accomplished using computers, making any further discussion unnecessary. For the case of a classical lattice and nonselective excitation of the central transition we will give approximations for the T_1 minimum.

The excitation of the spin system affects the relaxation behavior: The initial conditions influence the constant, c_k , in Eq. (7.20). Thus, only the eigenvalues, λ_k , for which the c_k does not vanish are important for the relaxation process. This may cause a change in the multi-exponential character for the measured T_1 .

7.2 Spin-Phonon Coupling in Crystals

Relaxation due to a fluctuating EFG caused by lattice phonons involves processes by which the photons, necessary for nuclear spin-flips, are emitted/absorbed by the lattice. The effectiveness of such processes depends on the spin-lattice coupling and the lattice properties, and both have to be expressed in quantum mechanical terms. Van Kranendonk [19] presented the first theoretical approach for these processes. In a later paper, Van Kranendonk and Walker [20] introduced a new mechanism, and reviewed the previous literature; see also Abragam [21]. The electric field gradients in Eq. (7.14) are usually expanded in terms of the components of the mechanical strain tensor, ε_k . Symbolically one may write, $V = V_0 + V_k \varepsilon_k + \varepsilon_k V_{kl} \varepsilon_l + \dots$. The strains, ε_k , are derivatives of the displacements of the nuclei with respect to the coordinates, which can be calculated from the quantized displacement operators given by the lattice Hamiltonian. The components of the EFG in the basis of the strain tensor components depend on the actual lattice structure. However, it is usually assumed that these components are comparable to the magnitude of the static electric field gradient, a rather crude estimate. The lattice Hamiltonian, which depends on the actual structure as well, is approximated by its harmonic and anharmonic parts. The static part of the quadrupole interaction is neglected. Nevertheless, with the mentioned assumptions and Debye's model of the phonon density, it is possible to find the field and temperature dependence for several terms, and to estimate their magnitudes using Eq. (7.06). Since the energies for the two possible nuclear spin-flips, $\hbar\omega_L$ or $2\hbar\omega_L$, are very small quantities compared with the lattice, the density of phonons can be approximately regarded as being constant over an energy range of $2\hbar\omega_L$; hence, $W_1 \approx W_2$. The first term of the expanded EFG is the constant (static) term. The second term is proportional to ε_k , and thus involves only one phonon. In this direct process, the lattice absorbs (emits) the photon necessary for the nuclear spin-flip. One finds for the relaxation rate [19], $W_{m,m+1} \approx W_{m,m+2} \approx 1/T_1$, for the *direct process*

$$\frac{1}{T_1} = C_1 \omega_L^2 T, \quad (7.21)$$

where C_1 is a constant and T is the absolute temperature. Although the probability for multi-phonon processes in the lattice decreases rapidly with the number of involved phonons, it has been shown [19] that the direct process can be neglected compared with the two-phonon process (*Raman process*), the third term in the expansion for V , where the photon necessary for the nuclear spin-flip is absorbed (emitted) by a two-phonon process in the lattice. The conservation of energy yields $n\hbar\omega_L = \hbar\omega_1 + \hbar\omega_2$. The relaxation rate for the *Raman process* becomes

$$\frac{1}{T_1} \approx C_2 \frac{T^2}{\theta_D}, \quad (7.22)$$

where θ_D is the Debye temperature of the lattice and C_2 is a constant. At lower temperatures the dependence is more complicated, and we have for the *low-temperature Raman process*

$$\frac{1}{T_1} \approx C'_2 \frac{T^7}{\theta_D^6}, \quad (7.23)$$

where C'_2 is a constant.

Lattice vibrations in a crystal are always more or less anharmonic (a necessity for heat conductivity). Van Kranendonk and Walker[20] showed that for anharmonic crystals, another process called the anharmonic Raman process can be very important. Phonons are created (or absorbed) by inelastic scattering of two phonons. This process shows the same temperature dependence as given by Eqs. (7.22) and (7.23).

It should be mentioned that the spin-lattice relaxation times, T_1 , as given by Eqs. (7.21 - 7.23) are crude estimates; the temperature and field dependence are the main features of the above equations. Relaxation due to spin-phonon coupling has often been found to be too weak to account for experimentally measured relaxation rates, especially at moderate and higher temperatures. This is probably due to the lack of knowledge of the actual fluctuations of the EFG in the crystal. Also, other, more effective relaxation mechanisms like moving ions/defects, reorientation of polar groups or adsorbed species, and relaxation due to paramagnetic impurities, often mask the relaxation induced by the spin-phonon coupling.

7.3 Spin Relaxation in Amorphous Materials

In addition to regular phonons, disorder modes, assumed to be two-level systems (TLS) are present in amorphous materials. In this case, the electric field gradient, V , is expanded not only in terms of the strain tensor elements, ε_k , but also in terms of the disorder modes. Since the latter is a two-level system, it can be described by a pseudospin σ [22]. The EFG is then given by the symbolic sum, $V = V_0 + V_k \varepsilon_k + \varepsilon_k V_{kl} \varepsilon_l + V_i \sigma_i + \varepsilon_k V_{ki} \sigma_i + \varepsilon_k V_{ki} \sigma_i + \dots$. The first, static term does not contribute to the relaxation. The second term is the *direct process*, and as already mentioned is usually not important for the relaxation. The third term leads to Raman processes involving two phonons, and does not fit the experimental results of an almost linear temperature dependence of the relaxation rate for $T < 100$ K. Reinecke and Ngai [23] suggested a Raman process involving two disorder modes, $\sigma_i V_{ij} \sigma_j$. Starting from Eq. (7.06) and the spin-temperature approximation they estimated the relaxation rate, $1/T_1 \sim W_2$, as

$$\frac{1}{T_1} \approx \frac{2\pi}{\hbar^2} T_m^2 \int_0^{E_m} |V|^2 \rho(E)^2 \left[1 + \cosh \frac{E}{k_B T} \right]^{-1} dE, \quad (7.24)$$

where T_m corresponds to one of the matrix elements in Eq. (7.10), V is the matrix element of the EFG, $\rho(E)$ is the density of disorder modes, and E is the energy splitting of the disorder modes. The maximum energy splitting in the material is E_m . We have $E_m \gg k_B T$ for $T \lesssim 100$ K. Then, by assuming an almost constant energy density of the disorder modes, $\rho(E) = \rho_0 E^\eta$, where $\eta < 1$ is found experimentally at low temperatures, and also assuming that the derivative of the EFG with respect to the strains is independent of the energy E , they find for the *Raman process involving two disorder modes*

$$\frac{1}{T_1} \approx T^{1+\eta}. \quad (7.25)$$

Szeftel and Alloul [24] proposed the process, $\varepsilon_k V_{ki} \sigma_i$, involving a phonon and a disorder mode, but as they pointed out later [25], this process led to the wrong temperature dependence. In the latter paper they found that the Raman process, $\varepsilon_k V_{ki} \sigma_i$, yields vanishing matrix elements, contradicting the suggestion of Reinecke and Ngai [23]. The process represented by the term $V_i \sigma_i$, which involves only one TLS, and which was discarded by Szeftel and Alloul [24], was later reintroduced by the same authors [25]. Assuming $W_1 \approx W_2$, it follows from Eq. (7.17), by summing over the lattice, that

$$\frac{1}{T_1} \approx \frac{1}{10} \frac{e^2 Q^2}{\hbar^2} \int_{-\infty}^{+\infty} V_i^2 \langle \sigma_i(t) \sigma_i(0) \rangle \exp\{-i\omega_L t\} dt, \quad (7.26)$$

where

$$\langle \sigma_i(t) \sigma_i(0) \rangle \equiv \text{tr}_r \left[\exp \left\{ \frac{i}{\hbar} \mathcal{H}_R t \right\} \sigma_i(t) \exp \left\{ -\frac{i}{\hbar} \mathcal{H}_R t \right\} \sigma_i \rho_R(0) \right] \quad (7.27)$$

includes the sum over all lattice states $|r\rangle$ with the equilibrium distribution

$$\rho_R(0) = \frac{\exp \left\{ -\frac{\mathcal{H}_R}{k_B} \right\}}{\text{tr}_r \left[\exp \left\{ -\frac{\mathcal{H}_R}{k_B} \right\} \right]}. \quad (7.28)$$

Szeftel and Alloul [25] evaluated the correlation function $\langle \sigma_i(t) \sigma_i(0) \rangle$ under the assumption that \mathcal{H}_R includes the harmonic lattice and a coupling between the two-level systems. They concluded that the relaxation rate should have the form

$$\frac{1}{T_1} \approx \nu_Q \tau_z \left(\cosh \frac{E}{2k_B T} \right)^{-2}, \quad (7.29)$$

where τ_z is the correlation time of the disorder modes and E is its energy. After averaging over different TLS energies, E , they found basically the same temperature dependence as given by Eq. (7.25). Both approaches seem to describe the spin-lattice relaxation. The temperature dependence, the independence on the Larmor frequency and the magnitude of the relaxation rate are thus all explained.

7.4 Activated Processes

Moving electric charges and dipolar moments causes fluctuations of the electric field gradient. In this case E_r and $E_{r'}$ are assumed to be infinitely close and the V in Eq. (7.14) can be considered as a classical component of the EFG tensor. We assume the following correlation function:

$$\overline{V_{\pm m}(t) V_{\mp m}(t - \tau)} = V_0^2 \exp\{-\tau/\tau_c\}, \quad (7.30)$$

where V_0 is the maximum EFG at the nuclear site (which might include antishielding effects) and τ_c is the correlation time of the motion. Then, the transition rates W_1 and W_2 from Eq. (7.17) can be calculated as

$$W_{m,m'} = \frac{(2m \pm 1)^2 (I \mp m)(I \pm m + 1)}{2I(2I - 1)^2} \frac{e^2 Q^2 V_0^2}{2I \hbar^2} \frac{\tau_c}{1 + (\omega_L \tau_c)^2} \delta_{m,m \pm 1}. \quad (7.31)$$

An often-used assumption about the temperature dependence of the correlation function is the Arrhenius equation,

$$\tau_c = \tau_0 \exp \frac{E_A}{RT}, \quad (7.32)$$

where E_A is the Arrhenius activation energy, $R = N_A k_B$ the gas constant, N_A the Avogadro constant and T the absolute temperature. With Eqs. (7.30) and (7.31) and the knowledge of the initial conditions, the master equation, Eq. (7.20), can be solved, and the magnetization recovery, T_1 , E_A and τ_0 can be determined.

It has been shown [18] that for powders the selective excitation and detection of the central transition gives a nearly single-exponential relaxation; hence, the minimum T_1 can be estimated by choosing the dominating eigenvalue in the master equation. For selective saturation and detection of the central transition one finds [18]

$$T_{1 \min} = k_1(I) \frac{\hbar \omega_L}{e^2 Q^2 V_0^2} = k_2(I) \frac{\nu_Q}{\nu_Q^2}, \quad (7.33)$$

where $k_1(I) = 3/2, 10/3, 21/4,$ and $36/5$ and $k_2(I) = 6, 4000/27, 1029,$ and $20736/5$ for $I = 3/2, 5/2, 7/2,$ and $9/2,$ respectively.

7.5 References

- [1] B.M. Fung, A.K. Khitrin, K. Ermolaev, An Improved Broadband Decoupling Sequence for Liquid Crystals and Solids, *J. Magn. Reson.* 142 (2000) 97-101.
- [2] M. Goldman, Formal Theory of Spin-lattice Relaxation, *J. Magn. Reson.* 149 (2001) 160-187.
- [3] A.G. Redfield, Relaxation Theory: Density Matrix Formulation, in: D.M. Grant, R.K. Harris (Eds.) *Encyclopedia of Nuclear Magnetic Resonance*, John Wiley & Sons, Chichester, 1996, pp. 4085-4092.
- [4] J.P. Yesinowski, Quadrupolar NMR of Semiconductors, in: R.E. Wasylshen, S.E. Ashbrook, S. Wimperis (Eds.) *NMR of Quadrupolar Nuclei in Solid Materials*, Wiley, Chichester, 2012, pp. 417-438.
- [5] J.P. Yesinowski, Quadrupolar NMR of Semiconductors, in: *eMagRes*, John Wiley & Sons, Ltd, 2007.
- [6] J.P. Yesinowski, Magnetization-recovery Experiments for Static and MAS-NMR of $I=3/2$ Nuclei, *J. Magn. Reson.* 180 (2006) 147-161.

- [7] L.G. Werbelow, Relaxation Theory for Quadrupolar Nuclei, in: D.M. Grant, R.K. Harris (Eds.) Encyclopedia of Nuclear Magnetic Resonance, John Wiley & Sons, Chichester, 1996, pp. 4092-4101.
- [8] L.G. Werbelow, Relaxation Theory for Quadrupolar Nuclei, in: eMagRes, John Wiley & Sons, Ltd, 2007.
- [9] S. Wimperis, Relaxation of Quadrupolar Nuclei Measured via Multiple Quantum Filtration, in: D.M. Grant, R.K. Harris (Eds.) Encyclopedia of Nuclear Magnetic Resonance, John Wiley & Sons, Chichester, 1996, pp. 4078-4084.
- [10] A. Kuhn, M. Kunze, P. Sreeraj, H.D. Wiemhofer, V. Thangadurai, M. Wilkening, P. Heitjans, NMR Relaxometry as a Versatile Tool to Study Li Ion Dynamics in Potential Battery Materials, Solid State Nucl. Magn. Reson. 42 (2012) 2-8.
- [11] R.V. Pound, Nuclear Electric Quadrupole Interactions in Crystals, Phys. Rev. 79 (1950) 685-702.
- [12] D. Freude, J. Haase, Quadrupole Effects in Solid-State NMR, NMR Basic Principles and Progress 29 (1993) 1-90.
- [13] C.P. Slichter, Principles of Magnetic Resonance, Springer Verlag, Berlin, Heidelberg, New York, London, Paris, Tokyo, Hong Kong, 1990.
- [14] K. Yosida, T. Moriya, The Effects of Covalency on the NMR in Ionic Crystals, J. Phys. Soc. Japan 11 (1956) 33-49.
- [15] E.R. Andrew, D.P. Tunstall, Spin-lattice Relaxation in Imperfect Cubic Crystals and in Non-cubic Crystals, Proc. Phys. Soc. 78 (1961) 1-11.
- [16] D.G. Hughes, K. Reed, Orientation Dependence of the ^{23}Na Nuclear Quadrupole Spin-lattice Relaxation in Sodium Nitrate, J. Phys. C.: Solid State Phys. 4 (1971) 2945-2961.
- [17] J. Haase, H. Pfeifer, W. Oehme, J. Klinowski, Longitudinal NMR Relaxation of ^{27}Al in Zeolites, Chem. Phys. Lett. 150 (1988) 189-193.
- [18] J. Haase, K.D. Park, K. Guo, H.K.C. Timken, E. Oldfield, NMR Spectroscopic Study of Spin-lattice Relaxation of Quadrupolar Nuclei in Zeolites, J. Phys. Chem. 95 (1991) 6996-7002.
- [19] J. Van Kranendonk, Theory of Quadrupolar Nuclear Spin-Lattice Relaxation, Physica 20 (1954) 781-800.
- [20] J. Van Kranendonk, M.B. Walker, Theory of Spin-lattice Relaxation in Anharmonic Crystals, Can. J. Phys. 46 (1968) 2441-2461.
- [21] A. Abragam, Principles of Nuclear Magnetism (paperback reprint 1989), Oxford University Press, Oxford, 1961.
- [22] K. Blum, Density Matrix Theory and Applications, Plenum Press, New York, 1981.
- [23] T.L. Reinecke, K.L. Ngai, Low-temperature Nuclear-spin-lattice Relaxation in Glasses, Phys. Rev. B 12 (1975) 3476-3478.
- [24] J. Szeftel, H. Alloul, Nuclear Spin-Lattice Relaxation Associated with Low-Energy Excitations in Glasses, Phys. Rev. Lett. 34 (1975) 657-660.
- [25] J. Szeftel, H. Alloul, Nuclear Spin Lattice Relaxation in the Amorphous State: towards an understanding, J. Non-Cryst. Solids 29 (1978) 253-281.