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Orientation dependences of quadrupolar spin–lattice relaxation rates of spin-3/2 nuclei subject to a random two-site exchange in a high magnetic field: a theoretical study

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Abstract. Orientational dependences of the quadrupole spin–lattice relaxation rates are calculated for a system of spin-3/2 nuclei in a single crystal subject to a random two-site exchange in a high magnetic field. A technique with which the transition probabilities per unit time w_1 ($\Delta m = 1$) and w_2 ($\Delta m = 2$) can be measured with approximately equal accuracies is proposed. The possibility of extracting the elements of the fluctuating electric-field-gradient tensor in a crystal-fixed coordinate system together with the exchange rate from the orientational dependences of the spin–lattice relaxation rates w_1 and w_2 is discussed. Two examples—a thermal exchange between two equilibrium sites in a temperature-independent double-potential well and an exchange between two sites above and below an order–disorder phase transition—are briefly discussed.

1. Introduction

Quadrupole-perturbed NMR is often used to investigate the structure and dynamics of crystalline solids. An atom with a quadrupole nucleus of spin I ($I \geq 1$) exhibits in a high magnetic field a quadrupole-perturbed NMR spectra consisting of $2I$ lines. The quadrupolar shifts of the NMR frequencies from the Larmor frequency depend on the electric-field-gradient (EFG) tensor at the site of the nucleus multiplied by the electric quadrupole moment eQ of the nucleus and on the orientation of the external magnetic field in the principal-axis coordinate system of the EFG tensor. The EFG tensor V is a second-rank tensor composed of the second derivatives $\partial^2 V / \partial x_i \partial x_j$ of the electrostatic potential V with respect to the coordinates. From the orientation dependences of the quadrupolar shifts of the NMR frequencies one can calculate the elements of the EFG tensor multiplied by eQ in a coordinate system fixed to the crystal [1]. One can further calculate the principal values for and the principal directions of the EFG tensor.

The principal values for and the principal directions of the EFG tensor may be related to the crystal structure and to the electrical environment of the observed atom. Nuclei of crystallographically inequivalent atoms have in general different principal values for the EFG tensors. Nuclei of crystallographically equivalent atoms occupying positions which are related by a symmetry operation have the same principal values for the EFG tensors but they differ in the orientations of the principal axes. The structure of the EFG tensor also reflects the point symmetry of the crystal at the site of the nucleus.

Any motion which modulates the EFG tensor V causes a change in the quadrupole-perturbed NMR spectra. When the characteristic time τ_c of the motion is short compared with the inverse value ω_L^{-1} of the Larmor frequency ω_L then the quadrupolar shifts of the

NMR frequencies are determined by the time-averaged EFG tensor $\langle V \rangle$. When τ_c becomes longer than ω_L^{-1} only a partial averaging of the EFG tensor is observed, whereas at very long values for τ_c no averaging of the EFG tensor is observed at all [2, 3].

Measurements of the spin-lattice relaxation rates are also often used to study the dynamics of atomic and molecular motions in solids. The spin-lattice relaxation rates of a system of quadrupole nuclei in solids are usually dominated by the fluctuations of the EFG tensors. These quadrupolar spin-lattice relaxation rates are usually measured as functions of temperature, in order to determine some details of the process which modulates the EFG tensor.

The orientation dependences of the quadrupolar spin-lattice relaxation rates which may be used to determine the elements of the time-dependent part of the EFG tensor in a crystal-fixed coordinate system have not been analysed in general. Hughes and Spencer [4] have studied the orientation dependence of the nuclear-quadrupole spin-lattice relaxation time in crystals for the case of equidistant energy levels.

The data obtained from the orientation dependences of the quadrupolar spin-lattice relaxation rates are of particular importance in molecular solids in which the molecules or some parts of the molecules undergo some thermally activated motion. In such a case the part of the molecule which undergoes motion and the parameters of the motion, as for example the directions and magnitudes of the displacements and the time-scale of the motion, can be determined from the quadrupolar spin-lattice relaxation data.

The next possible application of the orientation dependence of the quadrupolar spin-lattice relaxation rates is the study of the order-disorder phase transitions in solids. Also, in this case, the fluctuating part of the EFG tensor—which is obtained from the orientation dependences of the quadrupolar spin-lattice relaxation—may be related to the magnitudes and directions of the atomic displacements from their positions in the fully ordered phases.

The fluctuating part of the EFG tensor, which is obtained from the orientation dependences of the quadrupolar spin-lattice relaxation rates, thus represents the complement of the time-averaged EFG tensor which is obtained from the orientation dependences of the quadrupolar-perturbed NMR frequencies. Both can be used to elucidate motions in crystalline solids. Since we find a theoretical analysis of the orientation dependences of the quadrupolar spin-lattice relaxation rates quite general we decided to publish it separately. The applications of the proposed technique to some actual materials, especially to the hydrogen-bonded ferroelectrics and antiferroelectrics, will be published elsewhere.

In this paper we first propose a technique with which the transition probabilities per unit time between the quadrupole energy levels w_1 ($\Delta m = 1$) and w_2 ($\Delta m = 2$) can be measured. Next we analyse the orientation dependences of the spin-lattice relaxation rates of a system of spin-3/2 nuclei, with non-equidistant energy levels in a high magnetic field, for the case of a random two-site exchange. We show in which way the orientation dependences of the nuclear-quadrupole spin-lattice relaxation rates are related to the fluctuating part of the time-dependent EFG tensor, which generally allows us to discriminate between various dynamical processes which may occur in crystals. In particular we analyse two examples of the two-site exchange: a thermal exchange between two equilibrium sites in a temperature-independent double-potential well, and an exchange between two sites above and below an order-disorder phase transition.

2. Measurements of the spin-lattice relaxation rates

The quadrupole spin-lattice relaxation of a system of spin-3/2 nuclei in a high magnetic

field has already been treated by Andrew and Tunstall [5]. They studied the spin-lattice relaxation for two initial conditions:

- (i) when the sample is initially in thermal equilibrium in zero magnetic field and then an external magnetic field is suddenly applied; and
- (ii) when a given NMR transition is initially saturated by a strong radio-frequency magnetic field.

Here we analyse a third case in which the sample is first in thermal equilibrium in a high magnetic field and then a short exciting θ -pulse is applied to the sample, followed by a detection 90° pulse after a time τ (figure 1). Both pulses are applied at the frequency of the central $-1/2$ to $1/2$ transition. The $-1/2$ to $1/2$ transition frequency is not shifted from the Larmor frequency in the first-order perturbation theory. It is therefore only weakly dependent on the orientation of the sample in an external magnetic field and is thus easy to observe.

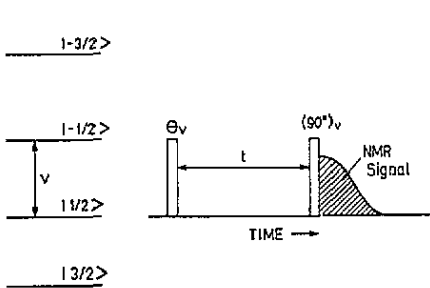


Figure 1. Pulse sequence for the measurement of w_1 and w_2 .

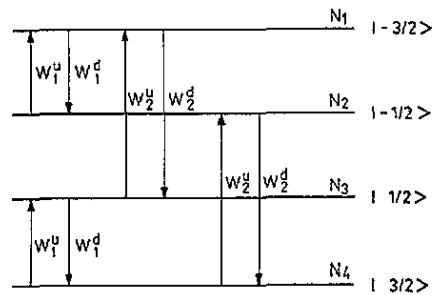


Figure 2. Population of the energy levels and the transition probabilities per unit time between the energy levels of a system of quadrupole spin-3/2 nuclei in a high magnetic field.

The quadrupolar spin-lattice relaxation of a system of spin-3/2 nuclei in a high magnetic field depends on two pairs w_1^u and w_1^d and w_2^u and w_2^d of the transition probabilities per unit time. This situation is shown in figure 2. The rate equations governing the populations of the quadrupole-perturbed Zeeman energy levels read

$$\begin{aligned}
 (d/dt)N_1 &= -(w_1^d + w_2^d)N_1 + w_1^u N_2 + w_2^u N_3 \\
 (d/dt)N_2 &= -(w_1^u + w_2^d)N_2 + w_1^d N_1 + w_2^u N_4 \\
 (d/dt)N_3 &= -(w_1^d + w_1^u)N_3 + w_1^u N_4 + w_2^d N_1 \\
 (d/dt)N_4 &= -(w_1^u + w_2^u)N_4 + w_1^d N_3 + w_2^d N_2.
 \end{aligned}
 \tag{1}$$

The four transition probabilities per unit time w_1^u , w_1^d , w_2^u and w_2^d are not independent. After a long time a Boltzmann distribution is established over the four energy levels with populations

$$N_1 = \frac{1}{4}N(1 - 3\delta) \quad N_2 = \frac{1}{4}N(1 - \delta) \quad N_3 = \frac{1}{4}N(1 + \delta) \quad N_4 = \frac{1}{4}N(1 + 3\delta).$$

Here

$$\delta = \hbar\omega_L/2kT
 \tag{2}$$

is assumed to be much smaller than one and N is the number of observed nuclei in the sample. A Boltzmann distribution is established over the four energy levels if $w_1^u/w_1^d = 1 - 2\delta$ and $w_2^u/w_2^d = 1 - 4\delta$. We may thus write

$$w_1^u = w_1(1 - \delta) \quad w_1^d = w_1(1 + \delta) \quad w_2^u = w_2(1 - 2\delta) \quad w_2^d = w_2(1 + 2\delta). \quad (3)$$

Here the transition probabilities per unit time w_1 and w_2 correspond to an infinite temperature when $\delta = 0$. Further we define three population differences: $X = N_2 - N_1$, $Y = N_3 - N_2$ and $Z = N_4 - N_3$ (cf [5]). The time derivatives of X , Y and Z are obtained from expressions (1) as

$$\begin{aligned} dX/dt &= N\delta w_1 - (2w_1 + w_2)X + w_2Z \\ dY/dt &= -N\delta(w_1 - 2w_2) - 2w_2Y + (w_1 - w_2)(X + Z) \\ dZ/dt &= N\delta w_1 - (2w_1 + w_2)Z + w_2X. \end{aligned} \quad (4)$$

The solutions for expressions (4) are:

$$\begin{aligned} X(t) &= \frac{1}{2}\delta N + \frac{1}{2}(X(0) - Z(0)) \exp(-2w_1t - 2w_2t) + \frac{1}{2}(X(0) + Z(0) - \delta N) \exp(-2w_1t) \\ Y(t) &= \frac{1}{2}\delta N + \frac{1}{2}(\delta N - X(0) - Z(0)) \exp(-2w_1t) + \frac{1}{2}(2Y(0) + X(0) + Z(0) - \delta N) \exp(-2w_2t) \\ Z(t) &= \frac{1}{2}\delta N - \frac{1}{2}(X(0) - Z(0)) \exp(-2w_1t - 2w_2t) + \frac{1}{2}(X(0) + Z(0) - \delta N) \exp(-2w_1t). \end{aligned} \quad (5)$$

The NMR signal following a 90° pulse applied at the $-1/2$ to $1/2$ transition frequency is proportional to Y . The initial values $X(0)$, $Y(0)$ and $Z(0)$ are the ones obtained immediately after the exciting θ -pulse. The populations of the four quadrupole-perturbed Zeeman energy levels are immediately after the θ -pulse equal to: $N_1 = \frac{1}{4}N(1 - 3\delta)$, $N_2 = \frac{1}{4}N(1 - \delta \cos \theta)$, $N_3 = \frac{1}{4}N(1 + \delta \cos \theta)$, $N_4 = \frac{1}{4}N(1 + 3\delta)$ and thus the initial values $X(0)$, $Y(0)$ and $Z(0)$ read: $X(0) = \frac{1}{4}N\delta(3 - \cos \theta)$, $Y(0) = \frac{1}{2}N\delta \cos \theta$ and $Z(0) = \frac{1}{4}N\delta(3 - \cos \theta)$. With these initial conditions we obtain:

$$Y(t) = \frac{1}{2}N\delta - \frac{1}{4}N\delta(1 - \cos \theta)[\exp(-2w_1t) + \exp(-2w_2t)]. \quad (6)$$

The dependence of the NMR signal on the time t between the exciting θ -pulse and the detection 90° pulse is thus double-exponential with relaxation rates $2w_1$ and $2w_2$. The weight factors of the two exponential terms are equal. Thus from the t -dependence of the NMR signal the two transition probabilities per unit time w_1 and w_2 can easily be calculated.

For the initial conditions of the results in [5] our calculations agree with those published.

It should be noted that our results are valid only when the three transition frequencies $\nu_{-3/2 \text{ to } -1/2}$, $\nu_{-1/2 \text{ to } 1/2}$ and $\nu_{1/2 \text{ to } 3/2}$ are well separated. However this is the most common situation in quadrupole-perturbed NMR and only at some special orientations of the external magnetic field do some of the transition frequencies overlap.

3. Calculation of w_1 and w_2

We shall calculate w_1 and w_2 in the approximation of infinite temperature. In this approximation we are dealing with the Hamiltonian H

$$H = H_Z + H_Q(t) = H_Z + \langle H_Q \rangle + \delta H_Q(t) \quad (7)$$

in which $H_Z = -\hbar\omega_L I_z$ is the Zeeman part and $H_Q(t) = \langle H_Q \rangle + \delta H_Q(t)$ is the time-dependent quadrupolar part which can be treated as a perturbation. In a coordinate system in which the z axis is chosen as the quantization axis, $H_Q(t)$ reads as

$$H_Q(t) = (eQ/12)[V_0(t)(3I_z^2 - I(I+1)) + V_{+1}(t)(I_z I_- + I_- I_z) + V_{-1}(t)(I_z I_+ + I_+ I_z) + V_{+2}(t)I_-^2 + V_{-2}(t)I_+^2]. \quad (8)$$

Here $V_0(t) = V_{zz}(t)$, $V_{\pm 1}(t) = V_{xz}(t) \pm iV_{yz}(t)$ and $V_{\pm 2}(t) = \frac{1}{2}[V_{xx}(t) - V_{yy}(t)] \pm iV_{xy}(t)$ are the combinations of the elements of the time-dependent EFG tensor which we write as $V_l(t) = \langle V_l \rangle + \delta V_l(t)$; $l = 0, \pm 1, \pm 2$. The two parts $\langle H_Q \rangle$ and $\delta H_Q(t)$ of the Hamiltonian are obtained by dividing expression (8) into time-averaged and fluctuating parts.

The transition probabilities per unit time w_1 and w_2 are now calculated under the assumption that a lattice motion (two-stage exchange) modulates the EFG tensor V , which results in the time-dependent part $\delta H_Q(t)$ of the Hamiltonian. This is in fact the approximation of infinite temperature since in this approximation the populations of the four energy levels approach the value $\frac{1}{4}N$ after a long time. The transition probability per unit time w_{kl} between the k th and the l th energy levels, which is a consequence of the fluctuating part of $\delta H_Q(t)$ of the Hamiltonian is given as [2]

$$w_{kl} = \frac{1}{\hbar^2} \int_0^\infty \langle (\delta H_Q(0))_{kl} (\delta H_Q(-t))_{lk} \exp(i\omega_{kl}t) + (\delta H_Q(0))_{lk} (\delta H_Q(-t))_{kl} \exp(-i\omega_{kl}t) \rangle dt. \quad (9)$$

Here $\langle \dots \rangle$ represents an ensemble average. By inserting $\delta H_Q(t)$ in the form of (8) into expression (9) we obtain the two transition probabilities per unit time, w_1 and w_2 as

$$w_1 = \frac{\pi^2}{3} \left(\frac{eQ}{\hbar} \right)^2 \int_0^\infty \langle \delta V_{-1}(0) \delta V_{+1}(-t) \exp(i\omega_L t) + \delta V_{+1}(0) \delta V_{-1}(-t) \exp(-i\omega_L t) \rangle dt \quad (10a)$$

$$w_2 = \frac{\pi^2}{3} \left(\frac{eQ}{\hbar} \right)^2 \int_0^\infty \langle \delta V_{-2}(0) \delta V_{+2}(-t) \exp(2i\omega_L t) + \delta V_{+2}(0) \delta V_{-2}(-t) \exp(-2i\omega_L t) \rangle dt. \quad (10b)$$

For a random exchange between two states A and B, which are not necessarily equivalent, the autocorrelation function $\langle \delta V_l(0) \delta V_l(-t) \rangle$ reads [6] as

$$\langle \delta V_l(0) \delta V_l(-t) \rangle = P_A P_B |V_l^A - V_l^B|^2 \exp(-Wt). \quad (11)$$

Here P_A and P_B are the probabilities of finding the system in the states A and B, respectively, V_l^A and V_l^B are the l th combinations of the EFG tensor elements ($l = 0, \pm 1, \pm 2$) corresponding to the states A and B and $W = w_{AB} + w_{BA}$ is the sum of the transition probability per unit time from the state A to the state B (w_{AB}) and of the transition probability per unit time from the state B to the state A (w_{BA}). From expressions (10) and (11) we obtain

$$\begin{aligned} w_1 &= \frac{2}{3} \pi^2 P_A P_B (U_{xz}^2 + U_{yz}^2) F(\omega_L, W) \\ w_2 &= \frac{2}{3} \pi^2 P_A P_B \left[\frac{1}{4} (U_{xx} - U_{yy})^2 + U_{xy}^2 \right] F(2\omega_L, W). \end{aligned} \quad (12)$$

Here

$$U_{ij} = (eQ/h)(V_{ij}^A - V_{ij}^B) \quad (13)$$

and

$$F(X, W) = W^{-1}/(1 + X^2W^{-2}). \quad (14)$$

The transition probabilities per unit time are now expressed in terms of the elements of the difference of the two EFG tensors $V^A - V^B$ in a coordinate system in which the z axis points in the direction of the external magnetic field.

4. Orientation dependences of w_1 and w_2

Let a , b and c be the axes of an orthogonal coordinate system fixed to a crystal. In the case of an orthorhombic crystal the axes a , b and c may be the crystallographic axes. Let us further assume that the external magnetic field lies in the a - b plane and forms an angle Φ with the a axis (figure 3). Then the transition probabilities per unit time, w_1 and w_2 , as functions of Φ read as

$$\begin{aligned} w_1(\Phi) &= \frac{2}{3}\pi^2 P_A P_B F(\omega_L, W)(C_0^1 + C_2^1 \cos 2\Phi + S_2^1 \sin 2\Phi + C_4^1 \cos 4\Phi + S_4^1 \sin 4\Phi) \\ w_2(\Phi) &= \frac{2}{3}\pi^2 P_A P_B F(2\omega_L, W)(C_0^2 + C_2^2 \cos 2\Phi + S_2^2 \sin 2\Phi + C_4^2 \cos 4\Phi + S_4^2 \sin 4\Phi). \end{aligned} \quad (15)$$

Here

$$\begin{aligned} C_0^1 &= \frac{1}{2}(U_{ab}^2 + U_{ac}^2 + U_{bc}^2) + \frac{1}{8}(U_{aa} - U_{bb})^2 & C_2^1 &= \frac{1}{2}(U_{ac}^2 - U_{bc}^2) & S_2^1 &= U_{ac}U_{bc} \\ C_4^1 &= \frac{1}{2}U_{ab}^2 - \frac{1}{8}(U_{aa} - U_{bb})^2 & S_4^1 &= -\frac{1}{2}U_{ab}(U_{aa} - U_{bb}) \end{aligned} \quad (16)$$

and

$$\begin{aligned} C_0^2 &= \frac{1}{32}[18U_{cc}^2 + (U_{aa} - U_{bb})^2 + 4U_{ab}^2 + 16(U_{ac}^2 + U_{bc}^2)] \\ C_2^2 &= \frac{1}{8}[3U_{cc}(U_{aa} - U_{bb}) - 4(U_{ac}^2 - U_{bc}^2)] & S_2^2 &= \frac{3}{4}U_{cc}U_{ab} - U_{ac}U_{bc} \\ C_4^2 &= \frac{1}{32}[(U_{aa} - U_{bb})^2 - 4U_{ab}^2] & S_4^2 &= \frac{1}{8}U_{ab}(U_{aa} - U_{bb}). \end{aligned} \quad (17)$$

The Fourier coefficients C_r^q and S_r^q which are expressed in terms of the elements of the tensor U can not be directly calculated from the experimental data. Measurements give the Φ -dependences of w_1 and w_2 which give—when expanded in the Fourier series—the Fourier coefficients A_r^q and B_r^q

$$\begin{aligned} w_1(\Phi) &= A_0^1 + A_2^1 \cos 2\Phi + B_2^1 \sin 2\Phi + A_4^1 \cos 4\Phi + B_4^1 \sin 4\Phi \\ w_2(\Phi) &= A_0^2 + A_2^2 \cos 2\Phi + B_2^2 \sin 2\Phi + A_4^2 \cos 4\Phi + B_4^2 \sin 4\Phi. \end{aligned} \quad (18)$$

The Fourier coefficients A_r^q and B_r^q are related to C_r^q and S_r^q by $A_r^q = K_q C_r^q$ and $B_r^q = K_q S_r^q$, where

$$K_q = \frac{2}{3}\pi^2 P_A P_B F(q\omega_L, W). \quad (19)$$

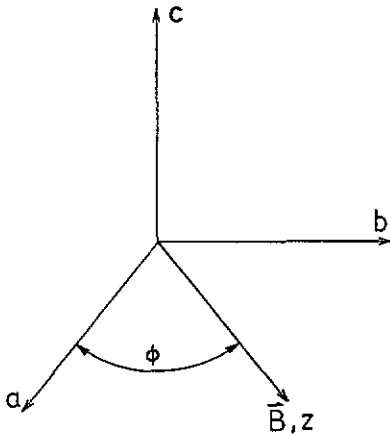


Figure 3. The direction (z) of the external magnetic field B in a crystal-fixed coordinate system a, b, c .

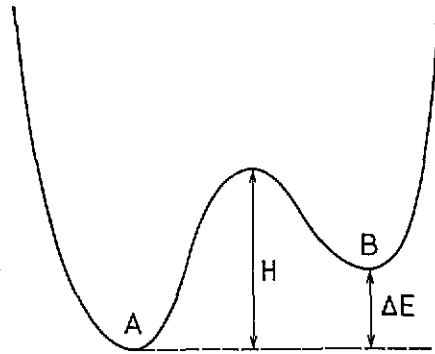


Figure 4. Schematic picture of a double-potential well.

As can be seen from expressions (16) and (17) $S_4^1 = -4S_4^2$ and $C_4^1 = -4C_4^2$. Thus $|B_4^1| > 4|B_4^2|$ and $|A_4^1| > 4|A_4^2|$. These last inequalities, which can be used to distinguish between w_1 and w_2 , follow from the fact that $F(2\omega_L, W) < F(\omega_L, W)$.

Expressions (16) contain two pairs of equations with two unknowns. The solutions of these are

$$\begin{aligned}
 U_{ab} &= \pm \sqrt{C_4^1 + \sqrt{(C_4^1)^2 + (S_4^1)^2}} = \pm \sqrt{\left(A_4^1 + \sqrt{(A_4^1)^2 + (B_4^1)^2}\right) / K_1} \\
 U_{aa} - U_{bb} &= -2S_4^1 / U_{ab} = \mp 2B_4^1 / \sqrt{\left(A_4^1 + \sqrt{(A_4^1)^2 + (B_4^1)^2}\right) K_1} \\
 U_{ac} &= \pm \sqrt{C_2^1 + \sqrt{(C_2^1)^2 + (S_2^1)^2}} = \pm \sqrt{\left(A_2^1 + \sqrt{(A_2^1)^2 + (B_2^1)^2}\right) / K_1} \\
 U_{bc} &= S_2^1 / U_{ac} = \pm B_2^1 / \sqrt{\left(A_2^1 + \sqrt{(A_2^1)^2 + (B_2^1)^2}\right) K_1}.
 \end{aligned}
 \tag{20}$$

From the Fourier coefficients A_r^q and B_r^q , which can be determined from the experimental data, one can thus calculate absolute values for $\sqrt{K_1}U_{ab}$, $\sqrt{K_1}(U_{aa} - U_{bb})$, $\sqrt{K_1}U_{ac}$, and $\sqrt{K_1}U_{bc}$ plus the relative signs of U_{ab} and $U_{aa} - U_{bb}$, and of U_{ac} and U_{bc} .

When the external magnetic field B is in the $a-c$ plane or in the $b-c$ plane the corresponding Fourier coefficients C_r^q and S_r^q of the Fourier expansions of w_1 and w_2 can be expressed in terms of the elements of the tensor U by cyclic permutations of indices in expressions (16) and (17).

The angular dependences of w_1 and w_2 when B is, say, in the $a-c$ plane give similarly, as above, absolute values for $\sqrt{K_1}U_{ac}$, $\sqrt{K_1}(U_{aa} - U_{cc})$, $\sqrt{K_1}U_{ab}$ and $\sqrt{K_1}U_{bc}$ plus the relative signs of U_{ac} and $U_{aa} - U_{cc}$ and of U_{ab} and U_{bc} . These data together with the data from the spin-lattice relaxation measurements when B is in the $a-b$ plane are in principle sufficient to calculate the tensor U_R , $U_R = \pm \sqrt{K_1}U = \pm \sqrt{K_1}(eQ/h)(V^A - V^B)$. The proper sign + or - and the scaling factor $\sqrt{K_1}$ can not be determined from the orientation dependences of the

spin-lattice relaxation rates. The factor K_1 , $K_1 = \frac{2}{3}\pi^2 P_A P_B W / (W^2 + \omega_L^2)$, depends on the occupation probabilities P_A and $P_B = 1 - P_A$ and on the exchange rate W , $W = w_{AB} + w_{BA}$, between the states A and B.

When the tensors V^A and V^B are known the tensor $\pm\sqrt{K_1}(V^A - V^B)$ determined from the orientation dependences of the spin-lattice relaxation rates can be used to see whether the fluctuations of the EFG tensor are indeed the dominant relaxation mechanism. If this is the case K_1 can be calculated and if the occupation probabilities P_A and P_B are known, say from the temperature dependence of the time-averaged EFG tensor $\langle V \rangle = P_A V^A + P_B V^B$, the exchange rate W can be calculated.

The ratio K_2/K_1 , $K_2/K_1 = (W^2 + \omega_L^2)/(W^2 + 4\omega_L^2)$, can be obtained by comparing the Fourier coefficients A_r^1 and B_r^1 to the Fourier coefficients A_r^2 and B_r^2 . The Fourier coefficients A_r^2 can be for example expressed as $A_r^2 = (K_2/K_1)(K_1 C_r^2)$ and the factors $K_1 C_r^2$ can be calculated from the elements of the tensor $\pm\sqrt{K_1}U$. The ratio K_2/K_1 is, in the case of a fast exchange ($W \gg \omega_L$), equal to one whereas it is, in the case of a slow exchange ($W \ll \omega_L$), equal to $\frac{1}{4}$. In the transition region when W is close to ω_L the ratio K_2/K_1 can be used to determine the exchange rate W , and if P_A and P_B are known also, to determine the tensor $U = (eQ/h)(V^A - V^B)$.

In any case a tensor proportional to $V^A - V^B$ and the ratio K_2/K_1 can be determined from the orientation dependences of the spin-lattice relaxation rates when the spin-lattice relaxation rates are dominated by the fluctuations of the EFG tensor. The ratio K_2/K_1 tells us whether the exchange rate W is fast or slow compared with the Larmor frequency ω_L . The tensor $\pm\sqrt{K_1}(V^A - V^B)$ can, together with the time-averaged EFG tensor $\langle V \rangle$, $\langle V \rangle = P_A V^A + P_B V^B$, be used to study the motions in solids and to discriminate between different exchange mechanisms.

5. Application to some typical examples

5.1. Motion in a temperature-independent double-potential well

We first assume that the time dependence of the EFG tensor is the consequence of a thermal motion between two equilibrium sites in a double-potential well. The potential well is shown in figure 4. The energy separation ΔE of the sites A and B, as well as the barrier height H are assumed to be temperature independent. The barrier height H is also assumed to be much higher than kT so that the transition probabilities per unit time w_{AB} and w_{BA} are functions of temperature, given by the Arrhenius-type expressions

$$w_{AB} = w_0 \exp(-H/kT) \quad w_{BA} = w_0 \exp(-(H - \Delta E)/kT). \quad (21)$$

The occupation probabilities P_A and P_B are given by the Boltzmann distribution as

$$P_A = 1/(1 + \exp(-\Delta E/kT)) \quad P_B = \exp(-\Delta E/kT)/(1 + \exp(-\Delta E/kT)). \quad (22)$$

As a result of the measurements of the orientation dependences of the quadrupole-perturbed NMR frequencies and quadrupole spin-lattice relaxation rates, we wish to determine the parameters ΔE and H of the double-potential well, the EFG tensors V^A and V^B multiplied by eQ/h , and the transition probabilities per unit time w_{AB} and w_{BA} .

In the limit of fast exchange when $W = w_{AB} + w_{BA} \gg \omega_L$ the quadrupole-perturbed NMR frequencies depend on the time-averaged EFG tensor $\langle V \rangle$, $\langle V \rangle = P_A V^A + P_B V^B$. The

tensor $(eQ/h)\langle V \rangle$ can be determined from the orientation dependences of the quadrupole-perturbed NMR frequencies by the method of Volkoff [1].

If the double-potential well is asymmetric ($\Delta E \neq 0$) then from the temperature dependence of the tensor $(eQ/h)\langle V \rangle$ the tensors $(eQ/h)V^A$ and $(eQ/h)V^B$ and the energy separation $\Delta E = E_B - E_A$ can be determined.

On the other hand, from the orientation dependences of the spin-lattice relaxation rates the tensor $U_R = \pm\sqrt{K_1}(eQ/h)(V^A - V^B)$ can be determined. Thus $K_1 = \frac{2}{3}\pi^2 P_A P_B w^{-1}$ and the exchange rate W can be calculated. From the temperature dependence of W

$$W = w_0 \exp(-H/kT)(1 + \exp(\Delta E/kT)) \quad (23)$$

one can further calculate the barrier height H and the constant w_0 .

If the double-potential well is symmetric ($\Delta E = 0$) the time-averaged EFG tensor $\langle V \rangle$, $\langle V \rangle = \frac{1}{2}(V^A + V^B)$, does not depend on temperature and the tensors $(eQ/h)V^A$ and $(eQ/h)V^B$ can not be determined, as before. They can, for example, be obtained by cooling the sample to a low temperature, at which the exchange between the sites A and B is slow on the NMR time scale. In this case two sets of quadrupole-perturbed NMR lines are observed corresponding to the states A and B. Another possibility is that the principal values for, or some symmetry properties of the EFG tensors V^A and V^B in the studied compounds, are known from the experimental studies of some closely related compounds. Then K_1 is adjusted in such a way that the principal values for or some symmetry properties of the tensors $(eQ/h)V^{A,B} = \langle V \rangle \bullet U_R/\sqrt{K_1}$ match the expected ones. The exchange rate W and the barrier height H are further determined in the same way as before.

5.2. An order-disorder phase transition

Next we assume that the two-stage exchange is associated with an order-disorder phase transition. Above the transition temperature T_i some objects (atoms, groups or molecules) move between two equivalent equilibrium sites whereas below T_i the two sites become inequivalent and their populations can be expressed in terms of an order parameter S . For one half of the objects the occupation probabilities P'_A and P'_B are below T_i given as $P'_A = \frac{1}{2}(1 + S)$ and $P'_B = \frac{1}{2}(1 - S)$. For the other half of the objects the occupation probabilities P''_A and P''_B are below T_i given as $P''_A = P'_B$ and $P''_B = P'_A$. The ratio of the transition probabilities w_{AB}/w_{BA} is in the former case equal to $(1 - S)/(1 + S)$, whereas in the latter case it is equal to $(1 + S)/(1 - S)$. The exchange rates $W = w_{AB} + w_{BA}$ are in both cases equal.

Above T_i the time-averaged EFG tensor $\langle V \rangle$, $\langle V \rangle = \frac{1}{2}(V^A + V^B)$, is temperature independent whereas below T_i two time-averaged EFG tensors $\langle V \rangle_A$ and $\langle V \rangle_B$

$$\begin{aligned} \langle V \rangle_A &= P'_A V^A + P'_B V^B = \frac{1}{2}(V^A + V^B) + (S/2)(V^A - V^B) \\ \langle V \rangle_B &= P''_A V^A + P''_B V^B = \frac{1}{2}(V^A + V^B) - (S/2)(V^A - V^B) \end{aligned} \quad (24)$$

are observed for the case of a fast exchange. Far below T_i the time-averaged EFG tensor $\langle V \rangle_A$ is approaching V^A and $\langle V \rangle_B$ is approaching V^B . Thus the tensors $(eQ/h)V^A$ and $(eQ/h)V^B$ can be determined from the orientation dependences of the quadrupole-perturbed NMR frequencies far below T_i . When these two tensors are known the parameter K_1 , $K_1 = \frac{1}{6}\pi^2(1 - S^2)F(\omega_L, W)$, can be calculated, and if the order parameter S is known also the exchange rate W can be calculated. The order parameter S can in fact be determined from the splitting of the quadrupole-perturbed NMR lines which overlap above T_i and split below T_i . The order parameter S can also be determined from the temperature dependence of some other physical quantities—for example, spontaneous polarization in ferroelectrics—which depend on S .

6. Conclusions

Spin-lattice relaxation of a system of spin-3/2 nuclei with non-equidistant energy levels, which are subject to a random exchange between two states A and B has been studied. It is shown that if the spin system is excited by a radiofrequency pulse at the frequency of the $-1/2$ to $1/2$ transition then the NMR signal measured after a 90° pulse is applied at the same frequency, at a time t after the exciting pulse, depends double-exponentially on t . The relaxation rates are $2w_1$ and $2w_2$ where w_1 and w_2 are the transition probabilities per unit time between the quadrupole-perturbed energy levels corresponding to $\Delta m = 1$ and $\Delta m = 2$, respectively. If the spin system is in a thermal equilibrium with the crystal lattice before the exciting pulse is applied then the two exponential terms have the same weight factors. Thus from the t dependence of the NMR signal the two transition probabilities per unit time w_1 and w_2 can be determined with approximately equal accuracies.

The transition probabilities per unit time w_1 and w_2 are expressed in terms of the elements of the tensor $U = eQ/h(V^A - V^B)$, occupation probabilities P_A and P_B , and the exchange rate W , $W = w_{AB} + w_{BA}$. Here V^A and V^B are the EFG tensors corresponding to the states A and B which are in general inequivalent.

It is shown that from the orientation dependences of w_1 and w_2 a tensor U_R , $U_R = \pm\sqrt{K_1}[(eQ/h)V^A - (eQ/h)V^B]$ can be calculated. Here $K_1 = \frac{2}{3}\pi^2 P_A P_B W / (W^2 + \omega_L^2)$. The temperature dependence of the tensor U_R , together with the temperature dependence of the time-averaged EFG tensor $\langle V \rangle$ multiplied by (eQ/h) , which is obtained from the orientation dependences of the quadrupole-perturbed NMR frequencies, can be used to find the parameters of the two-state exchange and to discriminate between different exchange mechanisms.

Two examples—a two-state exchange in a temperature-independent double-potential well and a two-state exchange associated with an order-disorder phase transition—have been briefly discussed.

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