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The Orientation Dependence of Spin–Lattice Relaxation Times in Single Crystals

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The orientation dependence of T_1^{-1} and $T_{1\rho}^{-1}$ for single crystals is discussed in terms of the second moment tensor formalism applied to dipolar solids. It is shown that for long correlation times, T_1^{-1} is a linear function of the maximum possible second moment reduction that may be caused by the motion responsible for the relaxation. Similarly, $T_{1\rho}^{-1}$ in the vicinity of the $T_{1\rho}^{-1}$ maximum is proportional to the same second moment reduction. For short correlation times the symmetry restrictions on the orientation dependence of T_1^{-1} are discussed and are found to differ from the restrictions on the second moment tensor for some crystal symmetries. The nonexponentiality of the relaxation for polycrystalline samples, resulting from anisotropy of the relaxation rates for single crystals is discussed.

Nuclear magnetic relaxation caused by the modulation of magnetic dipole–dipole interactions by motions in solids has been discussed by numerous authors, and a recent monograph by Wolf (*1*) covers much of the theory developed so far. In an earlier paper (*2*) one of us introduced a convenient procedure for the calculation of relaxation rates for such processes. In that paper expressions were given for relaxation rates in terms of second moment tensors. These expressions reduce considerably the computational effort otherwise required in a calculation of relaxation rates for single crystals as a function of their orientation relative to the external magnetic field. In the present paper this procedure is investigated further; in particular we discuss the restrictions imposed by crystal symmetry on the orientational dependence of the spin–lattice relaxation rate, T_1^{-1}, and find that these restrictions are sometimes different from those imposed on second moment tensors (*3*).

MATHEMATICS

For the convenience of the reader some of the mathematics of Ref. (*2*) is repeated here. The high field, laboratory frame, spin–lattice relaxation rate may be written

$$T_1^{-1} = \tfrac{2}{3}K^{(1)}\frac{\tau}{1+\omega_0^2\tau^2} + \tfrac{8}{3}K^{(2)}\frac{\tau}{1+4\omega_0^2\tau^2}. \qquad [1]$$

Similarly, the rotating frame Zeeman relaxation rate may be written

$$T_{1\rho}^{-1} = K^{(0)}\frac{\tau}{1+4\omega_1^2\tau^2} + \tfrac{5}{3}K^{(1)}\frac{\tau}{1+\omega_0^2\tau^2} + \tfrac{2}{3}K^{(2)}\frac{\tau}{1+4\omega_0^2\tau^2}. \qquad [2]$$

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The orientational dependence of the relaxation constants $K^{(0)}$, $K^{(1)}$, and $K^{(2)}$ can be expressed in terms of tensor quantities $\mathbf{S}^{(m)}$ by the relation

$$K^{(m)} = \tilde{\mathbf{q}}\mathbf{S}^{(m)}\mathbf{q}. \qquad [3]$$

The five components of the vector $\mathbf{q}$ are given in Table 1 in terms of the unit vector $\tilde{\mathbf{h}} = (h_1, h_2, h_3)$ along the static magnetic field vector $\mathbf{B}_0$. The simple vectors $\mathbf{q}$ carry all the orientation dependence of the relaxation constants; this is the essence of the procedure of Ref. (*2*)—tedious calculation of lattice sums do not have to be carried out for each crystal orientation. It is sufficient to calculate such sums for each of the (orientation independent) components of the tensors $\mathbf{S}^{(m)}$. For the subsequent discussion of symmetry properties the components of $\mathbf{h}$, and hence also $\mathbf{q}$ and $\mathbf{S}^{(m)}$, are defined in an orthonormal coordinate system $\mathbf{i}$, $\mathbf{j}$, and $\mathbf{k}$ with $\mathbf{i}$ parallel to the crystallographic axis $\mathbf{a}$, $\mathbf{k}$ parallel to the reciprocal axis $\mathbf{c}^*$, and $\mathbf{j} = \mathbf{k} \times \mathbf{i}$.

The tensors $\mathbf{S}^{(m)}$ are related to the second moment tensor $\mathbf{S}$ defined by

$$M_2 = \tilde{\mathbf{q}}\mathbf{S}\mathbf{q} \qquad [4]$$

where M_2 is the second moment. In fact it was shown in (*2*) that

$$\mathbf{S}^{(0)} = \mathbf{S}_{\text{rigid}} - \mathbf{S}_{\text{motion}} \qquad [5]$$

where $\mathbf{S}_{\text{rigid}}$ is the second moment tensor in the absence of nuclear motions and $\mathbf{S}_{\text{motion}}$ the same quantity averaged over the motions responsible for the spin–lattice relaxation. Thus

$$K^{(0)} = \Delta M_2 = M_{2\ \text{rigid}} - M_{2\ \text{motion}} \qquad [6]$$

where $M_{2\,\text{rigid}}$ and $M_{2\,\text{motion}}$ are the second moments without or with motional averaging, respectively.

The tensors $\mathbf{S}^{(1)}$ and $\mathbf{S}^{(2)}$ appearing in the expression for the spin–lattice relaxation rates $T_{1\rho}^{-1}$ and T_1^{-1} can be calculated from $\mathbf{S}^{(0)}$ as demonstrated in Ref. (*2*). Unfortunately, a number of sign errors appear in the relations between $\mathbf{S}^{(0)}$, $\mathbf{S}^{(1)}$ and $\mathbf{S}^{(2)}$

TABLE 1

COMPONENTS OF THE VECTOR $\mathbf{q}$ IN TERMS OF THE COMPONENTS h_i OF A UNIT VECTOR ALONG THE STATIC MAGNETIC FIELD

i	q_i
1	$\frac{\sqrt{5}}{2}(1 - 3h_3^2)$
2	$\frac{\sqrt{15}}{2}(h_1^2 - h_2^2)$
3	$\sqrt{15}h_1h_2$
4	$\sqrt{15}h_1h_3$
5	$\sqrt{15}h_2h_3$

TABLE 2

THE RELAXATION TENSORS $\mathbf{S}^{(1)}$ AND $\mathbf{S}^{(2)}$ EXPRESSED IN TERMS OF THE TENSOR $\mathbf{S}^{(0)}$

$S_{11}^{(1)} = \frac{1}{6}(3S_{44}^{(0)} + 3S_{55}^{(0)})$	$S_{11}^{(2)} = \frac{1}{6}(3S_{22}^{(0)} + 3S_{33}^{(0)})$
$S_{12}^{(1)} = \frac{1}{6}(2dS_{44}^{(0)} - 2dS_{55}^{(0)})$	$S_{12}^{(2)} = \frac{1}{6}(-3S_{12}^{(0)} - 2dS_{44}^{(0)} + 2dS_{55}^{(0)})$
$S_{13}^{(1)} = \frac{1}{6}(2dS_{45}^{(0)})$	$S_{13}^{(2)} = \frac{1}{6}(-3S_{13}^{(0)} - 2dS_{45}^{(0)})$
$S_{14}^{(1)} = \frac{1}{6}(-3S_{14}^{(0)} - dS_{24}^{(0)} - dS_{35}^{(0)})$	$S_{14}^{(2)} = \frac{1}{6}(dS_{24}^{(0)} + dS_{35}^{(0)})$
$S_{15}^{(1)} = \frac{1}{6}(-3S_{15}^{(0)} + dS_{25}^{(0)} - dS_{34}^{(0)})$	$S_{15}^{(2)} = \frac{1}{6}(-dS_{25}^{(0)} + dS_{34}^{(0)})$
$S_{22}^{(1)} = \frac{1}{6}(4S_{33}^{(0)} + S_{44}^{(0)} + S_{55}^{(0)})$	$S_{22}^{(2)} = \frac{1}{6}(3S_{11}^{(0)} - S_{33}^{(0)} + 2S_{44}^{(0)} + 2S_{55}^{(0)})$
$S_{23}^{(1)} = \frac{1}{6}(-4S_{23}^{(0)})$	$S_{23}^{(2)} = \frac{1}{6}(S_{23}^{(0)})$
$S_{24}^{(1)} = \frac{1}{6}(-dS_{14}^{(0)} - S_{24}^{(0)} + 3S_{35}^{(0)})$	$S_{24}^{(2)} = \frac{1}{6}(dS_{14}^{(0)} - 2S_{24}^{(0)} - 3S_{35}^{(0)})$
$S_{25}^{(1)} = \frac{1}{6}(dS_{15}^{(0)} - S_{25}^{(0)} - 3S_{34}^{(0)})$	$S_{25}^{(2)} = \frac{1}{6}(-dS_{15}^{(0)} - 2S_{25}^{(0)} + 3S_{34}^{(0)})$
$S_{33}^{(1)} = \frac{1}{6}(4S_{22}^{(0)} + S_{44}^{(0)} + S_{55}^{(0)})$	$S_{33}^{(2)} = \frac{1}{6}(3S_{11}^{(0)} - S_{22}^{(0)} + 2S_{44}^{(0)} + 2S_{55}^{(0)})$
$S_{34}^{(1)} = \frac{1}{6}(-dS_{15}^{(0)} - 3S_{25}^{(0)} - S_{34}^{(0)})$	$S_{34}^{(2)} = \frac{1}{6}(dS_{15}^{(0)} + 3S_{25}^{(0)} - 2S_{34}^{(0)})$
$S_{35}^{(1)} = \frac{1}{6}(-dS_{14}^{(0)} + 3S_{24}^{(0)} - S_{35}^{(0)})$	$S_{35}^{(2)} = \frac{1}{6}(dS_{14}^{(0)} - 3S_{24}^{(0)} - 2S_{35}^{(0)})$
$S_{44}^{(1)} = \frac{1}{6}(3S_{11}^{(0)} + dS_{12}^{(0)} + S_{22}^{(0)} + S_{33}^{(0)} + S_{55}^{(0)})$	$S_{44}^{(2)} = \frac{1}{6}(-dS_{12}^{(0)} + 2S_{22}^{(0)} + 2S_{33}^{(0)} + 2S_{55}^{(0)})$
$S_{45}^{(1)} = \frac{1}{6}\,(2dS_{13}^{(0)} - S_{45}^{(0)})$	$S_{45}^{(2)} = \frac{1}{6}(-2dS_{13}^{(0)} - 2S_{45}^{(0)})$
$S_{55}^{(1)} = \frac{1}{6}(3S_{11}^{(0)} - dS_{12}^{(0)} + S_{22}^{(0)} + S_{33}^{(0)} + S_{44}^{(0)})$	$S_{55}^{(2)} = \frac{1}{6}(dS_{12}^{(0)} + 2S_{22}^{(0)} + 2S_{33}^{(0)} + 2S_{44}^{(0)})$

Note. $d = 3^{1/2}$

in Ref. (*3*). Therefore a corrected version of the relevant relations, expressing $\mathbf{S}^{(1)}$ and $\mathbf{S}^{(2)}$ in terms of $\mathbf{S}^{(0)}$ are given here in Table 2. The corrected relations imply that

$$\tfrac{1}{2}\mathbf{S}^{(0)} + \mathbf{S}^{(1)} + \mathbf{S}^{(2)} = \tfrac{1}{2}\mathbf{I}\,\mathrm{Tr}\,\mathbf{S}^{(0)} \qquad [7]$$

where $\mathbf{I}$ is a 5×5 identity matrix. As shown in (*2*), the trace Tr $\mathbf{S}^{(0)}$ is equal to the reduction of the second moment for a powder by motional averaging.

T_1^{-1} FOR LONG CORRELATION TIMES

At low temperatures for which $\omega_0\tau \gg 1$, [1] reduces to

$$T_1^{-1} = \frac{2}{3\omega_0^2\tau}(K^{(1)} + K^{(2)}). \qquad [8]$$

Combining [8] with [3] and [7] then gives

$$T_1^{-1} = \frac{1}{3\omega_0^2\tau}(5\ \mathrm{Tr}\,\mathbf{S}^{(0)} - \tilde{\mathbf{q}}\mathbf{S}^{(0)}\mathbf{q}). \qquad [9]$$

The orientation dependence of T_1^{-1} is contained in the second term in the bracket, $\tilde{\mathbf{q}}\mathbf{S}^{(0)}\mathbf{q}$, which is simply the difference between the second moments of rigid lattice and motionally averaged spectra, whereas the trace in the orientation independent term is the corresponding difference for a powder. Thus, apart from a constant offset, the spin–lattice relaxation rate T_1^{-1} at low temperatures, varies essentially in the same way with crystal orientation as the orientation dependence of the second moment reduction produced by the molecular motion responsible for the relaxation.

T_1^{-1} FOR SHORT CORRELATION TIMES

At high temperatures where $\omega_0\tau \ll 1$ [1] reduces to

$$T_1^{-1} = \frac{2\tau}{3}(K^{(1)} + 4K^{(2)}) = \frac{2\tau}{3}\tilde{\mathbf{q}}\mathbf{R}\mathbf{q} \qquad [10]$$

where

$$\mathbf{R} = \mathbf{S}^{(1)} + 4\mathbf{S}^{(2)}. \qquad [11]$$

Clearly, also in this case T_1^{-1} may be expressed in terms of the second moment reduction tensor components, S_{ij}^0. However, the relation is not as simple as in the long correlation time limit.

In Ref. (*3*) the restrictions on the second moment tensor imposed by crystal symmetry were tabulated. Combining these restrictions with the definition of the tensor **R**, the symmetry restrictions on **R** can easily be derived. The result is reported in Table 3 along with the symmetry restrictions on the second moment tensor. For orthorombic, trigonal, cubic, and some tetragonal crystals the symmetry restrictions are different for the **R** and the **S** tensors. As an example, it is clear from Table 2 that the spin–lattice relaxation rate T_1^{-1} is independent of crystal orientation for cubic crystals when $\omega_0\tau \ll 1$, whereas the second moment for spectra of such crystals is anisotropic, characterized by two independent tensor components.

ROTATING FRAME $T_{1\rho}^{-1}$

For the common case $\omega_1 \ll \omega_0$, the second and third term in [2] may be neglected in the vicinity of the $T_{1\rho}^{-1}$ maximum and [2] reduces to

$$T_{1\rho}^{-1} = K^{(0)} \frac{\tau}{1 + 4\omega_1^2\tau^2} \qquad [12]$$

or, using [3]

$$T_{1\rho}^{-1} = \tilde{\mathbf{q}}\mathbf{S}^{(0)}\mathbf{q} \frac{\tau}{1 + 4\omega_1^2\tau^2}. \qquad [13]$$

Thus the rate $T_{1\rho}^{-1}$ is proportional to the second moment reduction $M_{2\,\mathrm{rigid}} - M_{2\,\mathrm{motion}}$ caused by the motion responsible for the relaxation. It is also clear from a comparison of [9] and [13] that $T_{1\rho}^{-1}$ in general will show a larger relative variation with crystal orientation than the laboratory frame T_1^{-1} (at least for long correlation times, the

TABLE 3

SYMMETRY RESTRICTIONS ON THE TENSORS $\mathbf{S}^{(i)}$ AND $\mathbf{R}$($S_{jk}^{(i)} = S_{kj}^{(i)}$ AND $R_{jk} = R_{kj}$)

Crystal class	Laue symmetry	Nonzero, unique elements	
		S	**R**
Triclinic	$\bar{1}$	All 15	All 15
Monoclinic[a]	$2/m$	$S_{11}S_{12}S_{14}S_{22}S_{24}S_{33}S_{35}S_{44}S_{55}$	$R_{11}R_{12}R_{14}R_{22}R_{24}R_{33}R_{35}R_{44}R_{55}$
Orthorhombic	mmm	$S_{11}S_{12}S_{22}S_{33}S_{44}S_{55}$	$R_{11}R_{12}R_{22} = R_{33}R_{44}R_{55}$
Tetragonal	$4/m$	$S_{11}S_{22}S_{23}S_{33}S_{44} = S_{55}$	$R_{11}R_{22}R_{33}R_{44} = R_{55}$
	$4/mmm$	$S_{11}S_{22}S_{33}S_{44} = S_{55}$	
Trigonal[b]	$\bar{3}$	$S_{11}S_{22} = S_{33}S_{44} = S_{55}S_{24} = -S_{35}S_{34} = S_{25}$	$R_{11}R_{22} = R_{33}R_{44} = R_{55}$
	$\bar{3}m$	$S_{11}S_{22} = S_{33}S_{44} = S_{55}S_{34} = S_{25}$	
Hexagonal	$6/mmm$	$S_{11}S_{22} = S_{33}S_{44} = S_{55}$	$R_{11}R_{22} = R_{33}R_{44} = R_{55}$
Cubic	$m3m$	$S_{11} = S_{22}S_{33} = S_{44} = S_{55}$	$R_{11} = R_{22} = R_{33} = R_{44} = R_{55}$

[a] The symmetry axis is **b**.

[b] The symmetry axis is **c** in the corresponding hexagonal cell.

regime of validity of Eq. [9]); the laboratory frame relaxation rate T_1^{-1} is dominated by the orientation independent part proportional to Tr **S**. Very large orientation dependencies have in fact been observed for $T_{1\rho}^{-1}$ in some crystals. One example is provided by pyromellitic acid dihydrate for which the proton $T_{1\rho}^{-1}$ varies by more than one order of magnitude (*4*).

RELAXATION IN POLYCRYSTALLINE SAMPLES

For polycrystalline samples, spin diffusion between crystallites is generally very slow compared to spin diffusion inside the crystallites and therefore the spin–lattice relaxation inside a crystallite proceeds essentially independently of the relaxation in neighboring crystallites. If the relaxation time is dependent on orientation, this then leads to a nonexponential magnetization recovery in a spin–lattice relaxation time measurement for a polycrystalline sample even if the magnetization recovery for each crystallite is exponential. As has been pointed out by Wolf (*5*), the proper way of calculating the spin–lattice relaxation behavior for a polycrystalline sample is to average the magnetization recovery rather than the spin–lattice relaxation rate over the orientations of the crystals. Barton and Sholl (*6*) have discussed the magnetization recovery for powders of some cubic crystals and have examined the deviation of the recovery from exponentiality. For most of the cases discussed by these authors the

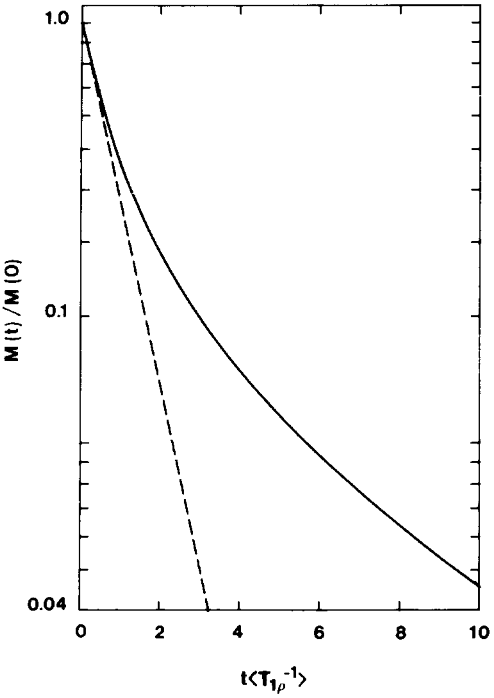

FIG. 1. Calculated decay of the normalized spin-locked magnetization, $M(t)/M(0)$, in polycrystalline pyromellitic acid dihydrate. The solid curve has been obtained by a proper averaging of exponential decay curves for pseudorandomly oriented crystallites. The dashed line represents a hypothetic exponential decay with an average relaxation rate, $\langle T_{1\rho}^{-1}\rangle$.

deviation is relatively small. For crystals of lower symmetry, and in particular for $T_{1\rho}$, the anisotropy of the relaxation rate may be considerably larger than for the cases treated by Barton and Sholl.

A proper averaging of the magnetization recovery curves over random orientations of the crystallites in a powder is easily carried out using the second moment tensor formalism. As an example we have performed such calculations for the decay of the spin-locked magnetization in the rotating frame for pyromellitic acid dihydrate which, as stated above, has a very large anisotropy in $T_{1\rho}^{-1}$: the ratio between the highest and lowest relaxation rate at a given temperature is about 35. The calculation of the average decay curve was carried out in two steps. First $\mathbf{S}^{(0)}$ was calculated using the relaxation model of Ref. (*4*). Then, using this tensor, relaxation curves were generated and averaged for about 1600 evenly distributed directions of the static magnetic field. The resulting average decay curve is shown in Fig. 1. For comparison we also show the exponential decay corresponding to $\langle T_{1\rho}^{-1}\rangle$, the average of the relaxation rate over the same distribution of magnetic field directions. As can be seen, the two graphs diverge quite rapidly from each other; already after $2\langle T_{1\rho}^{-1}\rangle^{-1}$ the properly calculated magnetization is twice the magnetization calculated from $\langle T_{1\rho}^{-1}\rangle$. It is clear that the exponential decay curve is a very poor representation of the actual magnetization decay in this case.

REFERENCES

1. D. Wolf, "Spin Temperature and Nuclear-Spin Relaxation in Matter," Oxford Univ. Press, London, 1979.

2. R. Sjöblom, *J. Magn. Reson.* **22**, 425 (1975).

3. R. Sjöblom, *J. Magn. Reson.* **22**, 411 (1975).

4. W. Schajor, U. Haeberlen, and J. Tegenfeldt, *J. Magn. Reson.* **49**, 233 (1982).

5. D. Wolf, *J. Magn. Reson.* **17**, 1 (1975).

6. W. A. Barton and C. A. Sholl, *J. Phys. C* **9**, 4315 (1976).