PHYSICAL REVIEW B VOLUME 15, NUMBER 11 1 JUNE 1977

Semiclassical analysis of spin-lattice relaxation of a tetrahedrally coordinated four-spin-1/2 system

J. Peternelj*
Department of Physics, The University of Alberta, Edmonton, Canada

M. M. Pintar
Department of Physics, The University of Waterloo, Waterloo, Ontario, Canada

(Received 26 July 1976)

A semiclassical calculation of the proton spin-lattice relaxation of a tetrahedrally coordinated four-spin-1/2 group is presented. In this calculation, the nuclear spins are treated quantum mechanically, while the random reorientations are treated classically. The relaxation mechanism considered is the thermally activated reorientation of the spin group simultaneously about its twofold and threefold symmetry axes. The reorientation rates around the twofold and threefold axes are assumed to be different. On this basis, the temperature dependence of the relaxation is calculated, and it is shown that double extrema in the T_1 temperature dependence can occur semiclassically as well as by tunneling.

INTRODUCTION

A number of experiments on proton spin relaxation of solids with one NH_4 group per unit cell[1,2] at temperatures above 50 K have shown two minima in T_1 and $T_{1\rho}$, the spin-lattice relaxation times in the laboratory and rotating frames, respectively. It is known that in weakly hindered lattices, tunneling of the NH_4 ion can be an important mechanism for spin relaxation, particularly at low temperatures. In such cases, two minima may also appear in the temperature dependence of the relaxation time, although usually the lower-temperature minimum appears below 50 K.[3] We investigated whether or not the occurrence of two minima in the temperature dependence of relaxation times in solids where the NH_4^+ ion is strongly hindered can be explained using the semiclassical model of Bloembergen, Purcell, and Pound.[4] For this purpose it was assumed that the NH_4 tetrahedron reorients around all (three) twofold (C_2) or fourfold (C_4) and all (four) threefold (C_3) symmetry axes. The corresponding rates of reorientation are denoted by ν_2, ν_4, and ν_3, respectively. The ν_2 and ν_3 reorientations are assumed to take place by rotational jumps preserving the orientational symmetry of the NH_4 ion, while the ν_4 reorientation represents jumps by ±90° around the C_2 axis.

The NH_4 ion reorienting about a single C_2 axis and a single C_3 axis was studied some time ago by Genin and O'Reilly.[5] These authors, however, only calculated the spin-lattice relaxation time in the limit in which the reorientation about the C_3 axis is fast compared to the reorientation about the C_2 axis. Their result, using their notation, is $1/T_1 = \frac{1}{3}(1/T_1)_2 + (1/T_1)_3$. Recently,[6] we solved the above limit exactly, and showed that the correct result is $1/T_1 = \frac{1}{2}(1/T_1)_2 + (1/T_1)_3$.

In 1972 Kodama[7] studied the spin-lattice relaxation in ammonium chloride. He studied the NH_4 ion reorienting about a single C_2 axis or about a single C_3 axis, assuming that the two motions are totally uncorrelated. For this reason he also obtained the incorrect Genin and O'Reilly result.

A year later Mandema and Trappeniers (MT)[8] reconsidered and improved Kodama's treatment of the proton spin-lattice relaxation in NH_4Cl. They discussed two models. In their model (*a*), only stepwise reorientations by ±90° about the C_2 axes, and by ±120° about the C_3 axes are allowed. In their model (*b*), reorientations to all possible (24) orientations of the NH_4 ion are permitted directly.

What is still missing is the exact solution of the single C_2-C_3 pair model, and its generalization, in which reorientations preserving the orientational symmetry of the NH_4 ion about all C_2 axes and all C_3 axes are allowed. For the sake of completeness (and simplicity), we also reproduce the MT results for model (*a*). We have assumed, using their notation, that $\nu = \nu' = 2\nu_4$, and $q = q' = 2\nu_3$.

It has long been known, that for more than two spins in a molecule, it is necessary to include the correlations between different single-pair interactions in the relaxation theory of such spin groups.[9] In general, the effect of the so-called cross correlations is to cause a nonexponential magnetization recovery. It has also been shown,[10] that for systems described initially by a spin temperature, the effect of cross correlations always retards the relaxation. Furthermore, it was established that these effects are more pronounced in the case of anisotropic reorientations in solids. However, experimentally the only material found so far, in which the deviations from the single exponential recovery were significant, is CH_3CN and a solid solution of CH_3CN in CD_3CN.[9] The effect of cross correlations on the proton spin-lattice relaxation of the NH_4 ion reorienting randomly about its symmetry axes was treated recently by MT.[8,11] They found that the observed nonexponential decay of T_1 in NH_4Cl at low temperatures cannot be explained by cross-correlation effects. We have observed the nonexponential behavior of nuclear magnetization also in several other ammonium salts, such as NH_4SnCl_3 and $(NH_4)_2SnCl_6$. However, on the basis of the existing theory (on cross correlations), cross correlations cannot be responsible for the observed nonexponential behavior of the proton spin-lattice relaxation in these solids.

Because they cannot affect in any way the structure of the multiple minima in the temperature dependence of the proton spin-lattice relaxation, the possible effect of cross correlations is ignored completely in the present calculation. Furthermore, only polycrystalline samples are considered. The possibility that in this case anisotropy of T_1 may cause nonexponential decay is discussed briefly in Appendix C.

The detailed analysis of the experimental results[12] showed that the theoretical results compare well with the measured experimental relaxation times in strongly hindered solids, such as NH_4VO_3.[1] The discrepancies between theory and experiment are large in weakly hindered lattices, such as NH_4SnCl_3. In these solids, it is believed that the tunneling mechanism plays an important role in the relaxation.

I. FORMULATION OF THE PROBLEM

In the semiclassical approximation, where the lattice is treated classically and the spins quantum mechanically, the spin-lattice relaxation time T_1 due to the spin-spin dipolar interactions is given by[13]

$$\frac{1}{T_1} = \tfrac{9}{8}(\gamma^2\hbar)^2 \sum_i (1-\delta_{ij})[J_{ij}^{(1)}(\omega_0) + J_{ij}^{(2)}(2\omega_0)] . \qquad (1)$$

In this equation the summation runs over all spins, δ_{ij} is the Kronecker delta, and ω_0 is the Larmor frequency. The spectral densities are defined as

$$J_{ij}^{(k)}(\omega) = 2\int_0^\infty \cos\omega\tau\, G_{ij}^{(k)}(\tau)\, d\tau , \qquad (2)$$

where

$$G_{ij}^{(k)}(\tau) = \langle F_{ij}^{-k}(t+\tau)F_{ij}^{k}(t) - (F_{ij}^{-k})(F_{ij}^{k}) \rangle , \qquad (3)$$

is the so-called classical correlation function.[13] The symbol $\langle\ \rangle$ represents the ensemble average over the lattice coordinates. The motion of the lattice coordinates is assumed to represent a stationary random process. Also

$$F_{ij}^{\pm 1} \equiv \mp (1/r_0^3)(\tfrac{8}{15}\pi)^{1/2} Y_2^{\pm 1}(\theta_{ij}, \phi_{ij}) , \qquad (4a)$$

$$F_{ij}^{\pm 2} \equiv (1/r_0^3)(\tfrac{32}{15}\pi)^{1/2} Y_2^{\pm 2}(\theta_{ij}, \phi_{ij}) . \qquad (4b)$$

The normalized spherical harmonics $Y_k^m(\theta, \phi)$ are given by

$$Y_2^0(\theta, \phi) = -(\tfrac{5}{16}\pi)^{1/2}(1 - 3\cos^2\theta) , \qquad (5a)$$

$$Y_2^{\pm 1}(\theta, \phi) = \mp (\tfrac{15}{8}\pi)^{1/2} \cos\theta \sin\theta\, e^{\pm i\phi} , \qquad (5b)$$

$$Y_2^{\pm 2}(\theta, \phi) = (\tfrac{15}{32}\pi)^{1/2} \sin^2\theta\, e^{\pm i2\phi} . \qquad (5c)$$

In the above equation r_0 is the spin-spin separation (it is implicitly assumed that all distances are equal), and θ and ϕ are the polar angles defining the orientation of the spin-spin vector with respect to the direction of the magnetic field.

When the Hamiltonian of the system also contains the radio frequency (rf) interaction term, one can formulate the spin-lattice relaxation time in the rotating frame.[14] At exact resonance, that is, when the frequency of the oscillating field ω is equal to the Larmor frequency ω_0 of the nuclear spins, $T_{1\rho}$ is given by

$$\frac{1}{T_{1\rho}} = \tfrac{9}{8}(\gamma^2\hbar)^2 \sum_i (1-\delta_{ij})[\tfrac{1}{4} J_{ij}^{(0)}(2\omega_1) + \tfrac{5}{2} J_{ij}^{(1)}(\omega_0) + \tfrac{1}{4} J_{ij}^{(2)}(2\omega_0)] , \qquad (6)$$

where $\omega_1 = \gamma H_1$ and H_1 is the amplitude of the rf field. $J_{ij}^{(0)}(\omega)$ and $G_{ij}^{(0)}(\tau)$ are defined by Eqs. (2) and (3). The function of lattice coordinates F_{ij}^0 is

$$F_{ij}^0 \equiv -(\tfrac{16}{5}\pi)^{1/2}(1/r_0^3) Y_2^0(\theta_{ij}, \phi_{ij}) . \qquad (4c)$$

II. CALCULATION OF THE SPIN-LATTICE RELAXATION TIME IN THE LABORATORY FRAME AND OF THE SPIN-LATTICE RELAXATION TIME IN THE ROTATING FRAME FOR THE NH_4 ION REORIENTING RANDOMLY ABOUT TWOFOLD AND THREEFOLD AXES

In the following, the time dependence of the probabilities $p_i(t)$ that a proton-proton vector of the NH_4 ion is in the ith position ($i = 1, 2, \ldots, 6$) is considered. The rate equation for p_i for reorientation of the NH_4 ion about all the twofold and threefold symmetry axes, see Fig. 1 (only one axis of each type is labeled in Fig. 1), are derived in the following. We consider three models of reorientation:

Model A (Genin and O'Reilly): NH_4 ion is allowed to reorient at any given time, about a single (fixed) C_2 axis and a single (fixed) C_3 axis. For a powder, the final expressions for T_1 and $T_{1\rho}$ are independent of how we choose the C_2-C_3 pair. The rates of interchange of proton-proton vectors upon reorientation about the twofold and threefold axes

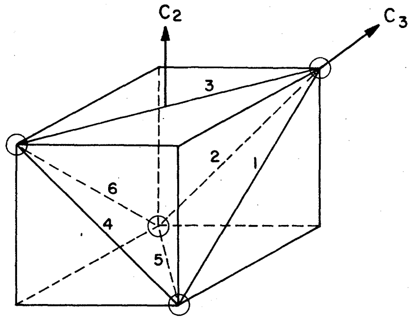

FIG. 1. Geometry of the NH_4 tetrahedron with the C_2 and C_3 symmetry axes.

are denoted by ν_2 and ν_3, respectively.

Model B: NH_4 ion is allowed to reorient at any given time about all (three) C_2 axes and all (four) C_3 axes, with the corresponding rates denoted by ν_2 and ν_3, respectively. As in the model A, the reorientations take place by rotational jumps which preserve the orientational symmetry of the NH_4 ion in the lattice.

Model C: is the same as B, except that the reorientations about the C_2 axes take place by ± 90° jumps. The corresponding rate of reorientation is denoted by ν_4.

In all these cases, the time dependence of the probabilities $p_i(t)$ is governed by a set of coupled differential equations, which can be written in the form

$$\frac{dp_i}{dt} = \sum_{j=1} H_{ij} p_j \, , \tag{7}$$

where the matrices H, for the various models are given by

$$H_A = \begin{bmatrix} -\nu_3 - \nu_2 & \frac{1}{2}\nu_3 & \frac{1}{2}\nu_3 & 0 & 0 & \nu_2 \\ \frac{1}{2}\nu_3 & -\nu_3 - \nu_2 & \frac{1}{2}\nu_3 & \nu_2 & 0 & 0 \\ \frac{1}{2}\nu_3 & \frac{1}{2}\nu_3 & -\nu_3 & 0 & 0 & 0 \\ 0 & \nu_2 & 0 & -\nu_3 - \nu_2 & \frac{1}{2}\nu_3 & \frac{1}{2}\nu_3 \\ 0 & 0 & 0 & \frac{1}{2}\nu_3 & -\nu_3 & \frac{1}{2}\nu_3 \\ \nu_2 & 0 & 0 & \frac{1}{2}\nu_3 & \frac{1}{2}\nu_3 & -\nu_3 - \nu_2 \end{bmatrix} , \tag{8a}$$

$$H_B = \begin{bmatrix} -4\nu_3 - 2\nu_2 & \nu_3 & \nu_3 & \nu_3 & \nu_3 & 2\nu_2 \\ \nu_3 & -4\nu_3 - 2\nu_2 & \nu_3 & 2\nu_2 & \nu_3 & \nu_3 \\ \nu_3 & \nu_3 & -4\nu_3 - 2\nu_2 & \nu_3 & 2\nu_2 & \nu_3 \\ \nu_3 & 2\nu_2 & \nu_3 & -4\nu_3 - 2\nu_2 & \nu_3 & \nu_3 \\ \nu_3 & \nu_3 & 2\nu_2 & \nu_3 & -4\nu_3 - 2\nu_2 & \nu_3 \\ 2\nu_2 & \nu_3 & \nu_3 & \nu_3 & \nu_3 & -4\nu_3 - 2\nu_2 \end{bmatrix} , \tag{8b}$$

and

$$H_C = \begin{bmatrix} -4\nu_3 - 3\nu_4 & \nu_3 + \frac{1}{2}\nu_4 & \nu_3 + \frac{1}{2}\nu_4 & \nu_3 + \frac{1}{2}\nu_4 & \nu_3 + \frac{1}{2}\nu_4 & \nu_4 \\ \nu_3 + \frac{1}{2}\nu_4 & -4\nu_3 - 3\nu_4 & \nu_3 + \frac{1}{2}\nu_4 & \nu_4 & \nu_3 + \frac{1}{2}\nu_4 & \nu_3 + \frac{1}{2}\nu_4 \\ \nu_3 + \frac{1}{2}\nu_4 & \nu_3 + \frac{1}{2}\nu_4 & -4\nu_3 - 3\nu_4 & \nu_3 + \frac{1}{2}\nu_4 & \nu_4 & \nu_3 + \frac{1}{2}\nu_4 \\ \nu_3 + \frac{1}{2}\nu_4 & \nu_4 & \nu_3 + \frac{1}{2}\nu_4 & -4\nu_3 - 3\nu_4 & \nu_3 + \frac{1}{2}\nu_4 & \nu_3 + \frac{1}{2}\nu_4 \\ \nu_3 + \frac{1}{2}\nu_4 & \nu_3 + \frac{1}{2}\nu_4 & \nu_4 & \nu_3 + \frac{1}{2}\nu_4 & -4\nu_3 - 3\nu_4 & \nu_3 + \frac{1}{2}\nu_4 \\ \nu_4 & \nu_3 + \frac{1}{2}\nu_4 & \nu_3 + \frac{1}{2}\nu_4 & \nu_3 + \frac{1}{2}\nu_4 & \nu_3 + \frac{1}{2}\nu_4 & -4\nu_3 - 3\nu_4 \end{bmatrix} . \tag{8c}$$

The formal solution of the Eqs. (7) can be written in terms of the eigenvalues of the matrices H as[15]

$$p_i(t) = \sum_{j=1}^{6} C_{ij} e^{\lambda_j t} \, . \tag{9}$$

If we introduce the correlation times, corresponding to the above models,

$$1/\tau_{CI} = \tfrac{3}{2}\nu_3 \, , \tag{10.1a}$$

$$1/\tau_{C\,\mathrm{II}} = \tfrac{3}{2}\nu_3 + 2\nu_2 \,, \tag{10.2a}$$

$$\frac{1}{\tau_{C\,\mathrm{III}}} = \tfrac{1}{2}\{(\tfrac{3}{2}\nu_3 + 2\nu_2) - [(\tfrac{3}{2}\nu_3)^2 + (2\nu_2)^2 - 2\nu_2\nu_3]^{1/2}\} \,, \tag{10.3a}$$

$$\frac{1}{\tau_{C\,\mathrm{IV}}} = \tfrac{1}{2}\{(\tfrac{3}{2}\nu_3 + 2\nu_2) + [(\tfrac{3}{2}\nu_3)^2 + (2\nu_2)^2 - 2\nu_2\nu_3]^{1/2}\} \,, \tag{10.4a}$$

$$1/\tau_{C\,\mathrm{I}} = 4\nu_3 + 4\nu_2 \,, \tag{10.1b}$$

$$1/\tau_{C\,\mathrm{II}} = 6\nu_3 \,, \tag{10.2b}$$

$$1/\tau_{C\,\mathrm{I}} = 4\nu_3 + 4\nu_4 \,, \tag{10.1c}$$

$$1/\tau_{C\,\mathrm{II}} = 6\nu_3 + 3\nu_4 \,, \tag{10.2c}$$

and impose the initial and asymptotic conditions

$$p_r(t=0) = \delta_{r,s} \,,$$

$$p_r(t\to\infty) = \tfrac{1}{6} \,,$$

then the solutions (9) for the models A, B, and C can be written as

$$p_{r,s}(\tau) = \frac{1}{6}\Big(6\delta_{r,s}\, e^{-\tau/\tau_{C\,\mathrm{IV}}} + 1 - e^{-\tau/\tau_{C\,\mathrm{IV}}} + \sum_{\alpha=\mathrm{I}}^{\mathrm{III}} C^{(\alpha)}_{r,s}\,(e^{-\tau/\tau_{C\alpha}} - e^{-\tau/\tau_{C\,\mathrm{IV}}})\Big) \,, \tag{11a}$$

and

$$p_{r,s}(\tau) = \tfrac{1}{6}[\,6\delta_{r,s}\, e^{-\tau/\tau_{C\,\mathrm{II}}} + 1 - e^{-\tau/\tau_{C\,\mathrm{II}}} + 3(\delta_{r,s} - \delta_{r,\tilde{s}})(e^{-\tau/\tau_{C\,\mathrm{I}}} - e^{-\tau/\tau_{C\,\mathrm{II}}})] \,. \tag{11b,c}$$

The correlation times are given by Eqs. (10). The matrices $C^{(\alpha)}_{r,s}$ are given in Appendix A. In the above expressions the symbols r, s, $\tilde{s}$ run from 1 to 6, $\delta_{r,s}$ is the Kronecker delta, and $\tilde{s}$ denotes the position of the proton-proton vector, which can be reached from the position s by a C_2 jump (for example if $s=1$, then $\tilde{s}=6$ as can be seen from Fig. 1). The p_i's Eq. (9), have in Eqs. (11) two subscripts (r, s). The subscript r is equivalent to the former i, and s characterizes the choice of the initial conditions. $p_{r,s}(\tau)$ is the so-called conditional probability. The probability that a proton-proton vector is in a position s at the time $\tau=0$ and in the position r at a later time τ is

$$W_{r,s}(\tau) = \tfrac{1}{6}\, p_{r,s}(\tau) \,. \tag{12}$$

Since $\langle F^k_{ij}\rangle = 0$, the correlation functions $G^{(k)}_{ij}(\tau)$ defined by (3) are simply

$$G^{(k)}_{ij}(\tau) = \langle F^{-k}_{ij}(\tau) F^{k}_{ij}(0)\rangle \,. \tag{13}$$

The polar angles (θ_{ij}, ϕ_{ij}) determine the orientation of the NH_4^+ ion with respect to the coordinate system (x, y, z) which is oriented so that the externally applied magnetic field H_0 is parallel to the z axis. It is convenient to choose a second coordinate system (x', y', z'), such that its z' axis is parallel to the one of the symmetry axes of the NH_4 ion. The spherical harmonics with the polar angles (θ_{ij}, ϕ_{ij}) in the unprimed system are transformed into the spherical harmonics in the primed system by

$$Y_2^m(\theta_{ij}, \phi_{ij}) = \sum_{m'} D^{(2)*}_{m,m'}(\alpha\beta\gamma)\, Y_2^{m'}(\theta'_{ij}, \phi'_{ij}) \,, \tag{14}$$

where $D^{(2)}_{m,m'}(\alpha\beta\gamma)$ are the elements of the rotation matrix,[16] and $(\alpha\beta\gamma)$ are the Euler angles determining the relative orientation of the coordinate systems (x, y, z) and (x', y', z'). Using the above equation and Eqs. (4), the expression (13) for the correlation function becomes, apart from the constant multiplicative factor,

$$G^{(k)}_{ij}(\tau) \propto \sum_{m',m''} D^{(2)*}_{-k,m'}(\alpha\beta\gamma) D^{(2)*}_{k,m''}(\alpha\beta\gamma) \times \langle Y_2^{m'}(\theta'_{ij}(\tau), \phi'_{ij}(\tau))\, Y_2^{m''}(\theta'_{ij}(0)\phi'_{ij}(0))\rangle \,, \tag{15}$$

where the ensemble average is given by

$$\langle Y_2^{m'}(\theta'_{ij}(\tau), \phi'_{ij}(\tau))\, Y_2^{m''}(\theta'_{ij}(0), \phi'_{ij}(0))\rangle = \sum_{r,s} W_{r,s}(\tau)\, Y_2^{m'}(\theta'^{(r)}_{ij}, \phi'^{(r)}_{ij})\, Y^{m''}(\theta'^{(s)}_{ij}, \phi'^{(s)}_{ij}) \,. \tag{16}$$

Since most experimental results are available for powder samples, we have to perform the powder average over the Euler angles α, β, and γ. This is achieved by using the orthogonality condition[16]

$$\frac{1}{8\pi^2}\int_0^{2\pi}\int_0^{\pi}\int_0^{2\pi} D^{(2)*}_{k,m''}(\alpha\beta\gamma) D^{(2)*}_{-k,m'} \times (\alpha\beta\gamma)\, d\alpha \,\sin\beta\, d\beta\, d\gamma = \tfrac{1}{5}(-1)^{-k-m'}\,\delta_{m''\,-m'} \,, \tag{17}$$

which yields

$$\langle G^{(k)}_{ij}(\tau)\rangle_{\mathrm{av}} \propto \frac{1}{5}\sum_{m}(-1)^{-k-m}\sum_{r,s} W_{r,s}(\tau)\, Y_2^{m}(\theta'^{(r)}_{ij}\, \phi'^{(r)}_{ij}) \times Y_2^{-m}(\theta'^{(s)}_{ij}, \phi'^{(s)}_{ij}) \,. \tag{18}$$

The polar angles $(\theta'^{(r)}_{ij}, \phi'^{(r)}_{ij})$ are easily determined, once the ion-fixed coordinate system (x', y', z') is chosen. Then, using the expressions (11) and (12), one can calculate $\langle G^{(k)}_{ij}(\tau)\rangle_{\mathrm{av}}$. Finally, using Eqs. (1), (2), and (6), one obtains the following expressions for T_1 and $T_{1\rho}$

$$\frac{1}{T_1}=\tfrac{9}{40}K\sum_{\alpha=\mathrm{I}}^{\mathrm{IV}} D_1(\omega_0,\tau_{C\alpha}), \tag{19a}$$

$$1/T_1=\tfrac{9}{40}KD_1(\omega_0,\tau_{C\,\mathrm{II}})+\tfrac{27}{40}KD_1(\omega_0,\tau_{C\,\mathrm{I}}), \tag{19b,c}$$

$$\frac{1}{T_{1\rho}}=\tfrac{9}{40}K\sum_{\alpha=\mathrm{I}}^{\mathrm{IV}} D_{1\rho}(\omega_0,\omega_1,\tau_{C\alpha}), \tag{20a}$$

$$1/T_{1\rho}=\tfrac{9}{40}KD_{1\rho}(\omega_0,\omega_1,\tau_{C\,\mathrm{II}})+\tfrac{27}{40}KD_{1\rho}(\omega_0,\omega_1,\tau_{C\,\mathrm{I}}), \tag{20b,c}$$

where the correlation times $\tau_{C\alpha}$, corresponding to the various models are given by Eqs. (10). We have introduced the notation $K=(\gamma^2\hbar/r_0^3)^2$. In addition

$$D_1(\omega_0,\tau_C)\equiv\frac{\tau_C}{1+\omega_0^2\tau_C^2}+\frac{4\tau_C}{1+4\omega_0^2\tau_C^2},$$

$$D_{1\rho}(\omega_0,\omega_1,\tau_C)\equiv\frac{3}{2}\,\frac{\tau_C}{1+4\omega_1^2\tau_C^2}+\frac{5}{2}\,\frac{\tau_C}{1+\omega_0^2\tau_C^2}+\frac{\tau_C}{1+4\omega_0^2\tau_C^2}.$$

The result (19c) is identical with the MT model A[8] if we set, using their notation, $\nu=\nu'=2\nu_4$ and $q=q'=2\nu_3$.

III. DISCUSSION AND CONCLUSIONS

In the following analysis some special applications of formulas (19) and (20) are considered.

(i) Pure C_3 reorientation $\nu_2=\nu_4=0$, $\nu_3\neq 0$.

$$1/T_1=\tfrac{27}{40}KD_1(\omega_0,\tau_{C3}), \tag{21a}$$

$$1/T_1=\tfrac{9}{40}KD_1(\omega_0,\tau_{C3}^{\mathrm{II}})+\tfrac{27}{40}KD_1(\omega_0,\tau_{C3}^{\mathrm{I}}), \tag{21b,c}$$

$$1/T_{1\rho}=\tfrac{27}{40}KD_{1\rho}(\omega_0,\omega_1,\tau_{C3}), \tag{22a}$$

$$1/T_{1\rho}=\tfrac{9}{40}KD_{1\rho}(\omega_0,\omega_1,\tau_{C3}^{\mathrm{II}})+\tfrac{27}{40}KD_{1\rho}(\omega_0,\omega_1,\tau_{C3}^{\mathrm{I}}). \tag{22b,c}$$

The correlation times are defined as

$$\tau_{C3}\equiv(\tfrac{3}{2}\nu_3)^{-1},\quad \tau_{C3}^{\mathrm{I}}\equiv(4\nu_3)^{-1},\quad \tau_{C3}^{\mathrm{II}}\equiv(6\nu_3)^{-1}.$$

(ii) Pure C_2 reorientation $\nu_3=0, \nu_2\neq 0, \nu_4\neq 0$.

$$1/T_1=\tfrac{9}{20}KD_1(\omega_0,\tau_{C2}), \tag{23a}$$

$$1/T_1=\tfrac{27}{40}KD_1(\omega_0,\tau_{C2}^{B}), \tag{23b}$$

$$1/T_1=\tfrac{9}{40}KD_1(\omega_0,\tau_{C4}^{\mathrm{II}})+\tfrac{27}{40}KD_1(\omega_0,\tau_{C4}^{\mathrm{I}}), \tag{23c}$$

$$1/T_{1\rho}=\tfrac{9}{20}KD_{1\rho}(\omega_0,\omega_1,\tau_{C2}), \tag{24a}$$

$$1/T_{1\rho}=\tfrac{27}{40}KD_{1\rho}(\omega_0,\omega_1,\tau_{C2}^{B}), \tag{24b}$$

$$1/T_{1\rho}=\tfrac{9}{40}KD_{1\rho}(\omega_0,\omega_1,\tau_{C4}^{\mathrm{II}})+\tfrac{27}{40}KD_{1\rho}(\omega_0,\omega_1,\tau_{C4}^{\mathrm{I}}), \tag{24c}$$

with the corresponding correlation times given by

$$\tau_{C2}\equiv(2\nu_2)^{-1},\quad \tau_{C2}^{B}\equiv(4\nu_2)^{-1},$$
$$\tau_{C4}^{\mathrm{I}}\equiv(4\nu_4)^{-1},\quad \tau_{C4}^{\mathrm{II}}\equiv(3\nu_4)^{-1}.$$

(iii) C_2 reorientation with concomitant rapid C_3 reorientation $\nu_2/\nu_3\ll 1$, $\nu_4/\nu_3\ll 1$.

$$1/T_1\cong\tfrac{27}{40}KD_1(\omega_0,\tau_{C3})+\tfrac{1}{2}\times\tfrac{9}{20}KD_1(\omega_0,\tfrac{3}{2}\tau_{C2}), \tag{25a}$$

$$1/T_1\cong\tfrac{9}{40}KD_1(\omega_0,\tau_{C3}^{\mathrm{II}})+\tfrac{27}{40}KD_1(\omega_0,\tau_{C3}^{\mathrm{I}}), \tag{25b,c}$$

$$1/T_{1\rho}\cong\tfrac{27}{40}KD_{1\rho}(\omega_0,\omega_1,\tau_{C3})+\tfrac{1}{2}\times\tfrac{9}{20}KD_{1\rho}(\omega_0,\omega_1,\tfrac{3}{2}\tau_{C2}), \tag{26a}$$

$$1/T_{1\rho}\cong\tfrac{9}{40}KD_{1\rho}(\omega_0,\omega_1,\tau_{C3}^{\mathrm{II}})+\tfrac{27}{40}KD_{1\rho}(\omega_0,\omega_1,\tau_{C3}^{\mathrm{I}}). \tag{26b,c}$$

(iv) C_3 reorientation with concomitant rapid C_2 reorientation $\nu_2/\nu_3\gg 1$, $\nu_4/\nu_3\gg 1$.

$$1/T_1\cong\tfrac{9}{20}KD_1(\omega_0,\tau_{C2})+\tfrac{9}{40}KD_1(\omega_0,\tau_{C3})+\tfrac{9}{40}KD_1(\omega_0,\tfrac{3}{2}\tau_{C3}), \tag{27a}$$

$$1/T_1\cong\tfrac{9}{40}KD_1(\omega_0,\tau_{C3}^{\mathrm{II}})+\tfrac{27}{40}KD_1(\omega_0,\tau_{C2}^{B}), \tag{27b}$$

$$1/T_1\cong\tfrac{9}{40}KD_1(\omega_0,\tau_{C4}^{\mathrm{II}})+\tfrac{27}{40}KD_1(\omega_0,\tau_{C4}^{\mathrm{I}}), \tag{27c}$$

$$1/T_{1\rho}\cong\tfrac{9}{20}KD_{1\rho}(\omega_0,\omega_1,\tau_{C2})+\tfrac{9}{40}KD_{1\rho}(\omega_0,\omega_1,\tau_{C3})+\tfrac{9}{40}KD_{1\rho}(\omega_0,\omega_1,\tfrac{3}{2}\tau_{C3}), \tag{28a}$$

$$1/T_{1\rho}\cong\tfrac{9}{40}KD_{1\rho}(\omega_0,\omega_1,\tau_{C3}^{\mathrm{II}})+\tfrac{27}{40}KD_{1\rho}(\omega_0,\omega_1,\tau_{C2}^{B}), \tag{28b}$$

$$1/T_{1\rho}\cong\tfrac{9}{40}KD_{1\rho}(\omega_0,\omega_1,\tau_{C4}^{\mathrm{II}})+\tfrac{27}{40}KD_{1\rho}(\omega_0,\omega_1,\tau_{C4}^{\mathrm{I}}). \tag{28c}$$

For a thermally activated process, the reorientation rates ν_i $(i=2,3,4)$ are assumed to obey the Arrhenius equation

$$(\nu_i)^{-1}=\tau_{0i}\,e^{E_{ai}/kT}, \tag{29}$$

where E_{ai} is usually referred to as the activation energy. By inspection of the approximate results given in the Eqs. (21)–(28), we can conclude that the expressions (19a), (19b), (20a), and (20b) will give two minima in the temperature dependence of the proton spin-lattice relaxation time. For the model B, to give two minima, the condition $E_{a2}<E_{a3}$ has to be satisfied as well. In this case, it follows from Eqs. (27b) and (28b) that the ratio of the high-temperature minimum $(T_1)_{\min}^{\mathrm{HT}}$, and the low temperature minimum $(T_1)_{\min}^{\mathrm{LT}}$ is given by

$$(T_1)_{\min}^{\mathrm{HT}}/(T_1)_{\min}^{\mathrm{LT}}\cong 3, \tag{30b}$$

and similarly for $T_{1\rho}$. Therefore, model B will yield two minima in the temperature dependence of the proton spin-lattice relaxation, provided that the reorientation about the C_2 axes is hindered less than the reorientation about the C_3 axes. Two examples of T_1 and $T_{1\rho}$ temperature dependence for the model B are shown in Fig. 2. On all graphs, $\log T_1$ and $\log T_{1\rho}$ are plotted versus the inverse temperature $1000/T$, and the relaxation times are given in units of 10^{-3} sec. The upper graph in Fig. 2 represents the situation when $E_{a2} > E_{a3}$. Only one minimum in the temperature dependence of T_1 and $T_{1\rho}$ exists. The only indication of the existence of two modes of reorientation of the NH_4 ion in this case is a slight variation of the slope on the high-temperature side of the T_1 and $T_{1\rho}$ graph. The lower graph in Fig. 2 is characteristic for $E_{a3} > E_{a2}$. Two minima in the temperature dependence of T_1 and $T_{1\rho}$ are observed. The high-temperature and the low-temperature slopes of this graph are determined by the values E_{a3} and E_{a2}, respectively. The parameters E_{ai} and τ_{0i} were chosen such as to display most clearly the double minimum structure of the temperature dependence of T_1 and $T_{1\rho}$.

On the other hand, the model A displays two well-separated minima in the temperature dependence of the spin-lattice relaxation, when $E_{a2} > E_{a3}$ as well as if $E_{a3} > E_{a2}$. Figure 3 shows the situation when $E_{a3} > E_{a2}$. Here the high-temperature minimum is due to the C_3 reorientation with the concomitant rapid C_2 reorientation, and the low-temperature minimum is due to the C_2 reorientation. For the ratio of the high- and low-temperature minima we now have

$$(T_1)_{\min}^{\mathrm{HT}}/(T_1)_{\min}^{\mathrm{LT}} \cong 1, \tag{31a}$$

and the same for $T_{1\rho}$. If the condition is $E_{a2} > E_{a3}$, Fig. 4, we again obtain two minima in the T_1 and $T_{1\rho}$ temperature dependence. In this case, however, the high-temperature minimum is due to the C_2 reorientation with concomitant rapid C_3 reorientation of the NH_4 ion. It follows from Eqs. (25a) and (26a), that

$$(T_1)_{\min}^{\mathrm{HT}}/(T_1)_{\min}^{\mathrm{LT}} \cong 3 \tag{32a}$$

and the same holds for $T_{1\rho}$. The parameters E_{ai} and τ_{0i} for model A, were chosen such as to fit the theoretical curves to the experimental results obtained for NH_4VO_3.[1] As already mentioned, the model C yields one minimum only in all situations and typical graph for this case is given in Fig. 5.

Apart from demonstrating the occurrence of double minima in the temperature dependence of the spin-lattice relaxation, this analysis yields also the following interesting result. Comparing Eqs. (25a) and (27b) and (26a) and (28b), we can see that both models, A and B, will give an almost identical temperature dependence of the spin-lattice relaxation, provided $E_{a2} > E_{a3}$ for model A and $E_{a3} > E_{a2}$ for model B. In both models, the low-temperature minimum is given by

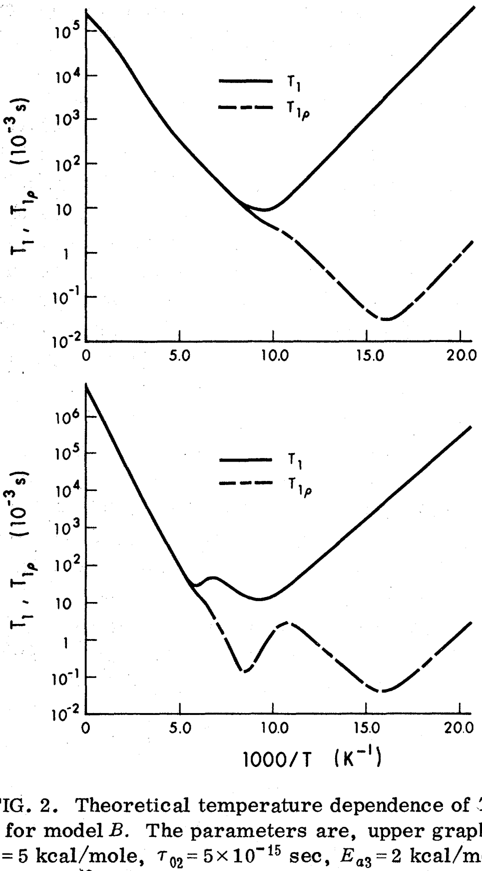

FIG. 2. Theoretical temperature dependence of T_1 $T_{1\rho}$ for model B. The parameters are, upper graph: $E_{a2} = 5$ kcal/mole, $\tau_{02} = 5\times10^{-15}$ sec, $E_{a3} = 2$ kcal/mole, $\tau_{03} = 8\times10^{-13}$ sec. Lower graph: $E_{a2} = 2$ kcal/mole, $\tau_{02} = 8\times10^{-13}$ sec, $E_{a3} = 5$ kcal/mole, $\tau_{03} = 5\times10^{-15}$ sec, $H_0 = 10$ kG, $H_1 = 10$ G.

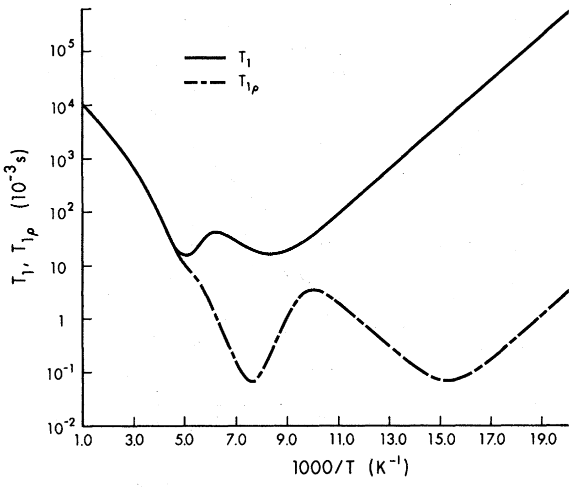

FIG. 3. Theoretical temperature dependence of T_1 and $T_{1\rho}$ for model A. The parameters are $E_{a2} = 1.9$ kcal/mole, $\tau_{02} = 8\times10^{-13}$ sec, $E_{a3} = 5.1$ kcal/mole, $\tau_{03} = 5\times10^{-15}$ sec, $H_0 = 9.9$ kG, $H_1 = 10.6$ G.

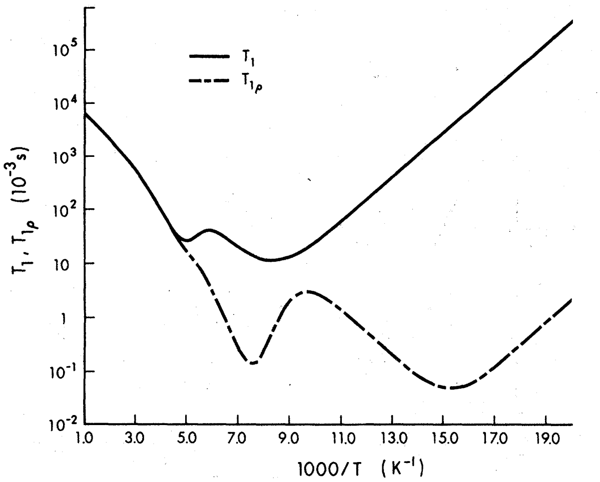

FIG. 4. Theoretical temperature dependence of T_1 and $T_{1\rho}$ for model *A*. The parameters are $E_{a2}=5.1$ kcal/mole, $\tau_{02}=5\times10^{-15}$ sec, $E_{a3}=1.9$ kcal/mole, $\tau_{03}=8\times10^{-13}$ sec, $H_0=9.9$ kG, $H_1=10.6$ G.

$$1/(T_1)^{\mathrm{LT}}_{\min}=\tfrac{27}{40}KD_{1\,\max}\,, \tag{33a,b}$$

$$1/(T_{1\rho})^{\mathrm{LT}}_{\min}=\tfrac{27}{40}KD_{1\rho\,\max}\,, \tag{34a,b}$$

and also the ratio of the high-temperature minimum and the low-temperature minimum is 3 in both cases. The only notable difference between the two models is on the high-temperature side of the high-temperature minimum, as can be seen from Figs. 2–4. However, experimentally this difference would be hard to detect, because at higher temperatures other mechanisms become important in relaxing the spin system and the reorientational contribution is difficult to establish accurately.

Another way to discriminate between models *A* and *B* apart from studying single crystals (see Appendix B) is to consider the proton absorption spectrum in the vicinity of the low-temperature minimum. In model *A* the absorption spectrum is motionally narrowed because of the rapid reorientation of the NH_4 ion about a single C_3 axis, while in model *B*, the motional narrowing is due to the rapid reorientation about all C_2 axes. The line shapes for both cases and for polycrystalline samples are given in Refs. 12 and 17. They are distinctly different. It should be noted also that the calculated second moments of the motionally narrowed spectra are the same for both models. If we write

$$M_2=M_2'+\Delta^2\,,$$

where Δ^2 is the interionic broadening and M_2' is the intraionic contribution, then

$$M_2'=\tfrac{27}{80}\gamma^2\hbar^2/r_0^6\,. \tag{35a,b}$$

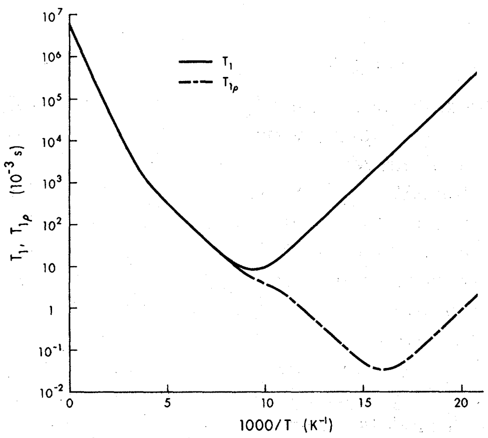

FIG. 5. Theoretical temperature dependence of T_1 and $T_{1\rho}$ for model *C*. The parameters are $E_{a3}=2$ kcal/mole, $\tau_{03}=8\times10^{-13}$ sec, $E_{a4}=5$ kcal/mole, $\tau_{04}=5\times10^{-15}$ sec, $H_0=10$ kG, $H_1=10$ G.

As illustrated by models *A*, *B*, and *C* it can be expected in general that double minima will occur in the temperature dependence of the spin-lattice relaxation, and also that many different types of reorientation will yield similar or sometimes almost identical temperature dependences of the proton spin-lattice relaxation. For example, one can see without detailed calculation, that $1C_2+1C_3$ with the condition $E_{a2}>E_{a3}$, $4C_3+3C_2$ with the condition $E_{a3}>E_{a2}$, and $3C_2+1C_3$ with the condition $E_{a2}>E_{a3}$, all give almost identical temperature dependence of the spin-lattice relaxation. It might seem that models *B* and *C* represent the most natural choices for the reorientation of the NH_4 ion, and that all other possibilities can be discarded. However, the experimental results on proton spin-lattice relaxation and proton magnetic resonance absorption in NH_4VO_3,[1, 12] for example, show that model *A* describes more correctly the motion of the NH_4 ion in this solid.

It has been noted already that knowledge of the detailed structure of the proton absorption spectrum[17] is important for distinguishing different modes of reorientation. In addition, the angular dependence of the proton spin-lattice relaxation in single crystals can also be used to distinguish those types of reorientation of the NH_4 ion, which cannot be distinguished on the basis of the data from polycrystalline samples. For this purpose, we derive in Appendix B the orientational dependence of T_1 and $T_{1\rho}$ in single crystals for models *B* and *C*. Model *A* will be discussed in detail in Ref. 12.

ACKNOWLEDGMENT

The authors are grateful to R. S. Hallsworth for his help with the computer work.

APPENDIX A

The constants $C_{r,s}^{(\alpha)}$ are determined from the equations

$$\sum_{j=1}^{6} (H_{ij} - \Lambda_\alpha \delta_{ij}) C_{j,s}^{(\alpha)} = 0 \tag{A1}$$

and

$$\Lambda_{\mathrm{IV}}(6\delta_{r,s} - 1) = 6H_{r,s} + \sum_{\alpha=\mathrm{I}}^{\mathrm{III}} (\Lambda_{\mathrm{IV}} - \Lambda_\alpha) C_{r,s}^{(\alpha)} , \tag{A2}$$

where $\Lambda_\alpha \equiv -1/\tau_{C\alpha}$, with $\tau_{C\alpha}$ given by the Eqs. (10.1a)–(10.4a) and $H_{r,s}$ given by the Eq. (8a). The result is

$$C_{r,s}^{(\mathrm{I})} = \begin{bmatrix} 2 & -1 & -1 & -1 & -1 & 2 \\ -1 & 2 & -1 & 2 & -1 & -1 \\ -1 & -1 & 2 & -1 & 2 & -1 \\ -1 & 2 & -1 & 2 & -1 & -1 \\ -1 & -1 & 2 & -1 & 2 & -1 \\ 2 & -1 & -1 & -1 & -1 & 2 \end{bmatrix} , \tag{A3}$$

$$C_{r,s}^{(\mathrm{II})} = \begin{bmatrix} -A & -B & 0 & B & 0 & A \\ A & B & 0 & -B & 0 & -A \\ 0 & 0 & 0 & 0 & 0 & 0 \\ -A & -B & 0 & B & 0 & A \\ 0 & 0 & 0 & 0 & 0 & 0 \\ A & B & 0 & -B & 0 & -A \end{bmatrix} , \tag{A4}$$

$$C_{r,s}^{(\mathrm{III})} = \begin{bmatrix} -C & -C & -D & C & D & C \\ -C & -C & -D & C & D & C \\ -D & -D & -E & D & E & D \\ C & C & D & -C & -D & -C \\ D & D & E & -D & -E & -D \\ C & C & D & -C & -D & -C \end{bmatrix} , \tag{A5}$$

with the following definitions

$$\xi \equiv \nu_2/\nu_3, \quad a \equiv +\left[\left(\tfrac{3}{4}\right)^2 + \xi^2 - \tfrac{1}{2}\xi \right]^{1/2}, \quad X\pm \equiv \tfrac{3}{4} + a \pm \xi ,$$

$$A \equiv \frac{-3X_-^2}{(2X_- + X_+)(\frac{3}{4} + \xi - a)} - \frac{\frac{3}{4} + 3\xi - 3a}{\frac{3}{4} + \xi - a} ,$$

$$B \equiv \frac{-3X_-^2}{(2X_- + X_+)(\frac{3}{4} + \xi - a)} + \frac{\frac{3}{2}}{\frac{3}{4} + \xi - a} ,$$

$$C \equiv -\frac{3}{2}\,\frac{X_-^2}{a(2X_- + X_+)} , \quad D \equiv -\frac{3}{2}\,\frac{X_+ X_-}{a(2X_- + X_+)} ,$$

$$E \equiv -\frac{3}{2}\,\frac{X_+^2}{a(2X_- + X_+)} .$$

APPENDIX B

To obtain the expressions for T_1 and $T_{1\rho}$ in a single crystal the correlation functions $G_{ij}^{(k)}(\tau)$, given by Eqs. (15) and (16), have to be calculated. The result for models B and C is

$$\frac{1}{T_1} = \tfrac{9}{8} K \sum_{k=1}^{2} (-1)^k k^2 [A_k j(k\omega_0, \tau_{C\mathrm{II}}) + B_k j(k\omega_0, \tau_{C\mathrm{I}})] \tag{B1}$$

and

$$\begin{aligned} 1/T_{1\rho} = \tfrac{9}{8} K \{ &\tfrac{3}{2}[A_0 j(2\omega_1, \tau_{C\mathrm{II}}) + B_0 j(2\omega_1, \tau_{C\mathrm{I}})] \\ &- \tfrac{5}{2}[A_1 j(\omega_0, \tau_{C\mathrm{II}}) + B_1 j(\omega_0, \tau_{C\mathrm{I}})] \\ &+ [A_2 j(2\omega_0, \tau_{C\mathrm{II}}) + B_2 j(2\omega_0, \tau_{C\mathrm{I}})] \} , \end{aligned} \tag{B2}$$

where the correlation times $\tau_{C\mathrm{I}}$ and $\tau_{C\mathrm{II}}$ are given by Eqs. (10.1b), (10.2b), (10.1c) and (10.2c)

$$j(\omega_0, \tau_C) \equiv \tau_C/(1 + \omega_0^2 \tau_C^2) ,$$

and the angular functions A_k and B_k are defined by

$$\begin{aligned} A_k(\alpha\beta\gamma) = \tfrac{1}{2} D_{-k,0}^{(2)*}(\alpha\beta\gamma) D_{k,0}^{(2)*}(\alpha\beta\gamma) + \tfrac{1}{4}\{ &[D_{-k,2}^{(2)*}(\alpha\beta\gamma) D_{k,2}^{(2)*}(\alpha\beta\gamma) + D_{-k,-2}^{(2)*}(\alpha\beta\gamma) D_{k,-2}^{(2)*}(\alpha\beta\gamma)] \\ &+ [D_{-k,2}^{(2)*}(\alpha\beta\gamma) D_{k,-2}^{(2)*}(\alpha\beta\gamma) + D_{-k,-2}^{(2)*}(\alpha\beta\gamma) D_{k,2}^{(2)*}(\alpha\beta\gamma)] \} , \end{aligned} \tag{B3a}$$

$$\begin{aligned} B_k(\alpha\beta\gamma) = \tfrac{1}{2} \{ &[D_{-k,2}^{(2)*}(\alpha\beta\gamma) D_{k,-2}^{(2)*}(\alpha\beta\gamma) + D_{-k,-2}^{(2)*}(\alpha\beta\gamma) D_{k,2}^{(2)*}(\alpha\beta\gamma)] \\ &- [D_{-k,2}^{(2)*}(\alpha\beta\gamma) D_{k,2}^{(2)*}(\alpha\beta\gamma) + D_{-k,-2}^{(2)*}(\alpha\beta\gamma) D_{k,-2}^{(2)*}(\alpha\beta\gamma)] \} \\ &- [D_{-k,1}^{(2)*}(\alpha\beta\gamma) D_{k,-1}^{(2)*}(\alpha\beta\gamma) + D_{-k,-1}^{(2)*}(\alpha\beta\gamma) D_{k,1}^{(2)*}(\alpha\beta\gamma)] , \end{aligned} \tag{B4a}$$

where $k = 0, 1, 2$. The powder averages of functions A_k and B_k are obtained by using Eq. (17):

$$\langle A_k(\alpha\beta\gamma) \rangle_{\mathrm{av}} = \tfrac{1}{5}(-1)^k , \quad \langle B_k(\alpha\beta\gamma) \rangle_{\mathrm{av}} = \tfrac{3}{5}(-1)^k .$$

Inserting these expressions into Eqs. (B1) and (B2) we recover the results for powder given by Eqs. (19b,c) and (20b,c).

Using the formulas given in Ref. 16, the expressions (B3a) and (B4a) can be rewritten in the following form:

$$A_k(\alpha\beta\gamma)=\tfrac{2}{5}\pi\, Y^{-k}_{+2}(\beta,0)Y^{k}_{+2}(\beta,0)+\frac{1}{4}\left(\frac{4!}{(2+k)!(2-k)!}\right)(\tfrac{1}{2}\sin\beta)^4 \times\left\{(-1)^k\left[\left(\frac{1+\cos\beta}{\sin\beta}\right)^{2k}+\left(\frac{1-\cos\beta}{\sin\beta}\right)^{2k}\right]+2\cos 4\gamma\right\}, \tag{B3b}$$

and

$$B_k(\alpha\beta\gamma)=\left(\frac{4!}{(2+k)!(2-k)!}\right)(\tfrac{1}{2}\sin\beta)^2\left((-1)^k\left\{\left(\frac{1+\cos\beta}{\sin\beta}\right)^{2k}[\tfrac{1}{2}(\tfrac{1}{2}\sin\beta)^2+\tfrac{1}{4}(k-2\cos\beta)^2] + \left(\frac{1-\cos\beta}{\sin\beta}\right)^{2k}[\tfrac{1}{2}(\tfrac{1}{2}\sin\beta)^2+\tfrac{1}{4}(k+2\cos\beta)^2]\right\}-(\tfrac{1}{2}\sin\beta)^2\cos 4\gamma\right). \tag{B4b}$$

In the above calculation the coordinate system (x,y,z) is oriented with its z axis parallel to the direction of the external magnetic field $\vec{H}_0$. The z' axis of the ion-fixed coordinate system (x',y',z') is parallel to one of the C_2 symmetry axes. The Euler angles $(\alpha\beta\gamma)$, determining the relative orientation of the coordinate systems (x,y,z) and (x',y',z'), are chosen using the convention in Ref. 16. That is, the Euler angles α and β are identical to the polar coordinates ϕ,θ of the z' axis with respect to the coordinate system (x,y,z).

APPENDIX C

If expressions (B3b) and (B4b) are inserted into Eq. (B1) the result is

$$\frac{1}{T_1}=\tfrac{9}{8}K\left[\left(f\frac{\tau_{CII}}{1+\omega_0^2\tau_{CII}^2}+(1-f)\frac{\tau_{CII}}{1+4\omega_0^2\tau_{CII}^2}\right)+\left((1-2f)\frac{\tau_{CI}}{1+\omega_0^2\tau_{CI}^2}+2(1+f)\frac{\tau_{CI}}{1+4\omega_0^2\tau_{CI}^2}\right)\right], \tag{C1}$$

where

$$f\equiv\sin^2\beta-\tfrac{7}{8}\sin^4\beta-\tfrac{1}{8}\sin^4\beta\cos 4\gamma .$$

In a polycrystalline sample, the observed magnetization is the average over the Euler angles (α,β,γ). That is,

$$\langle M_0(t)\rangle=M_0(1-\langle e^{-R(\beta,\gamma)t}\rangle),$$

where we have assumed that the thermal equilibrium magnetization M_0 is $M_0(t=0)=0$; and $R(\beta,\gamma)\equiv 1/T_1(\beta,\gamma)$. The average in the above expression is given by

$$\langle e^{-R(\beta,\gamma)t}\rangle=\frac{1}{4\pi}\int_0^{\pi}\int_0^{2\pi}e^{-R(\beta,\gamma)t}\sin\beta\, d\beta\, d\gamma . \tag{C2}$$

Equation (C2) can be written in the form[18]

$$\langle e^{-Rt}\rangle=\exp\left(-\langle R\rangle t+\sum_{n=2}^{\infty}(-1)^n\frac{t^n}{n!}M_n\right), \tag{C3}$$

where M_n are called semi-invariants or cumulants and are given by

$$M_n=\sum_{\{n_i\}}(-1)^{\Sigma_i n_i-1}\left(\sum_i n_i-1\right)!\prod_i\left[\frac{1}{n_i!}\left(\frac{\langle R^i\rangle}{i!}\right)^{n_i}\right]. \tag{C4}$$

The average $\langle R^i\rangle$ is defined by

$$\langle R^i\rangle=\frac{1}{4\pi}\int_0^{\pi}\int_0^{2\pi}R^i\sin\beta\, d\beta\, d\gamma .$$

The sum in (C4) runs over the integers n_i, satisfying the condition $\sum_i i n_i=n$. The first four cumulants are

$$M_1=\langle R\rangle,\quad M_2=\langle R^2\rangle-\langle R\rangle^2,$$
$$M_3=\langle R^3\rangle-3\langle R^2\rangle\langle R\rangle+2\langle R\rangle^3,$$
$$M_4=\langle R^4\rangle-4\langle R^3\rangle\langle R\rangle-3\langle R^2\rangle^2+12\langle R^2\rangle\langle R\rangle^2-6\langle R\rangle^4 .$$

We calculated the expression

$$\exp(-\langle R\rangle t+\tfrac{1}{2}M_2t^2-\tfrac{1}{6}M_3t^3)\cong\langle\exp(-Rt)\rangle$$

for the graphs in Fig. 2 and for the values of t ranging from 0 to $3/\langle R\rangle$. The effect of averaging for the upper graph of Fig. 2 is such that

$$\Delta\equiv\frac{\langle\exp(-Rt)\rangle}{\exp(-\langle R\rangle t)}-1>0,$$

and is increasing with the increasing inverse temperature. However, the value of Δ is so small ($\Delta\leqslant 10^{-3}$), that it cannot give rise to any observable nonexponentiality in the time evolution of the magnetization.

For the lower graph on Fig. 2, Δ is initially increasing with the inverse temperature, from $\Delta\cong 0$, at $\beta=4$ to $\Delta=2\times10^{-2}$ at $\beta=6$ and $t=3/\langle R\rangle$ ($\beta=6$ is roughly the position of the high-temperature T_1 minimum on this graph). In the region between the two minima, Δ is at first decreasing and reaches the value 6×10^{-5} at $\beta=8$ and for $t=3/\langle R\rangle$, and then starts increasing, so that at $\beta=12$ and $t=3/\langle R\rangle$, $\Delta=5\times 10^{-2}$. For the values of $t=2/\langle R\rangle$, the deviations from the simple exponential decay are even smaller. Therefore, also in this case, the averaging over the Euler angles does not give rise to any appreciable effect in the decay of the magnetization.

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*Supported by the National Research Council.

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