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Nuclear Magnetic Relaxation Induced by Random Reorientations of Molecules in Crystals

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General formulas for the correlation function and spectral density function of a random molecular quantity are obtained for molecules executing anisotropic reorientations in crystals. The spin-lattice relaxation times T_1 and $T_{1\rho}$ (along the constant and rotating magnetic fields) are calculated for the spins of the nuclei in molecules moving in a crystalline potential field of point symmetry. Experimental data on T_1 and $T_{1\rho}$ for protons in a monocrystal of NH_4Cl in the temperature range 125–300°K are given as an example, and agree with the theory.

ONE of the effective methods of studying the motions of groups of coordinated atoms (ions, molecules or their fragments) in condensed media is the study, in a broad temperature range, of the spin-lattice relaxation times T_1 and $T_{1\rho}$ of the nuclear magnetization along the constant (H_0) and rotating (H_1) magnetic fields. The foundations of the theory of nuclear magnetic relaxation due to random modulations of the dipole interactions by the motions of the nuclear spins were laid by Bloembergen, Purcell and Pound[1,2]. According to this theory, the relaxation times are determined by the spectral density $J_m(\omega)$ of a certain molecular[1)] quantity depending on the nature of the random process. Different forms of the diffusional motion have been investigated in some detail. The least studied are reorientational motions in solids. For particular models, such a problem was solved in[3,4], while the results of solving a more general problem in[5] differed almost not at all from the results for a model of the diffusional motion with a distribution of probabilities of individual rotations that was continuous over the angles. In crystals, because of the symmetry properties of both the molecules and their environment at low temperatures, the most probable rotational motions are random rotations through definite finite angles. Therefore, in studying these motions, it is necessary to take into account both the symmetry of the molecule itself and the local symmetry of the crystal field at the site of the molecule[6]; the magnitude of the angle of rotation depends on these symmetries.

1. THE CORRELATION FUNCTIONS AND SPECTRAL DENSITY

We shall assume that, because of the interaction with the field of the environment, a molecule in the crystal occupies a finite number of equilibrium rotational positions (orientations). In the equilibrium orientations, it executes rotational oscillations (other degrees of freedom are not considered here). For such a molecule, there is a certain probability of changing the orientation by rotations which form a finite point symmetry group of pure rotations, isomorphous to the symmetry group of the Hamiltonian of the molecule situated in the crystal lattice.

In a stationary state, the conditional probability $P(g_0)$ of finding the molecule in the initial orientation g_0 is given by the δ-function

$$P(g_0) = \delta(g - g_0), \tag{1}$$

where g is the solid-angle coordinate. We shall assume first that the motion of the molecule occurs about rotation axes belonging to only one class. Then, for a Markov process of random changes of orientation of the molecule, the conditional probability P(g, N) of an arbitrary orientation g after N separate reorientations from the initial position g_0 can be expressed in the form of a sum of products of the probabilities $p_j(g_1)$ of single reorientations g_1 from the previous positions g_j multiplied by the probabilities $P(g_j, N-1)$ of the latter, i.e.,

$$P(g,N) = \sum_j p_j(g_1) P(g_j, N-1). \tag{2}$$

The summation over j in (2) is performed over all the axes of the class, the number σ of which is determined by the order of the class of the finite point symmetry group of the pure rotations of the molecule[7]. By means of the group operation $\hat{T}_j(g_1)$ for a rotation, we can connect the probabilities $P(g_j, N-1)$ and $P(g, N-1)$ by the relation

$$P(g_j, N-1) = \hat{T}_j(g_1^{-1}) P(g, N-1), \tag{3}$$

which enables us to rewrite (2) in the form

$$P(g,N) = \sum_j p_j(g_1) \hat{T}_j(g_1^{-1}) P(g, N-1). \tag{4}$$

The functions P(g, N) and P(g, N − 1) depend on the orientation g occupied by the molecule in the crystal, and can be represented in the form of a series expansion in the eigenfunctions of the operator of the energy of the rotational states of the molecule[8]. The splitting of the rotational energy levels of the molecule in the crystal is determined by the symmetry properties of the Hamiltonian of the molecule, including its interaction with the environment; to each eigenvalue of the Hamiltonian there corresponds an irreducible representation Γ^α of the crystallographic point groups, and the eigenfunctions $\Psi^\alpha_\beta(g)$ of the Hamiltonian, which form the bases for the inequivalent representations Γ^α[9] (β labels the function in the basis) transform according to this irreducible representation. Below, we shall assume that the quantum-mechanical problem is solved, and the function Ψ known. We write the expansion of P(g, N) in Ψ:

[1)] By the term "molecule" here and in the following, we mean a group of atoms (including a molecule) with rotational degrees of freedom.

$$P(g,N)=\sum_{\alpha,\beta,\nu} C^{\alpha}_{\beta,\nu}(N)\,\Psi^{\alpha}_{\beta\nu}(g). \tag{5}$$

The summation in (5) includes both a summation over equivalent representations (which we have not indicated) and a summation over the different bases of label (weight) ν; the label β of a function in the basis is determined by the form, which is the same for all the bases, of the matrix of the transformations. Of course, the functions Ψ satisfy the usual normalization conditions. The group operation $\hat{T}_j$ applied to the functions Ψ gives

$$\hat{T}_j(g_1^{-1})\,\Psi_{\beta\nu}{}^{\alpha}(g)=\sum_{s}\Gamma^{\alpha}_{js\beta}(g_1^{-1})\,\Psi_{s\nu}{}^{\alpha}(g), \tag{6}$$

where $\Gamma^{\alpha}_{js\beta}$ is the transformation matrix.

The solution of Eq. (2) with the initial condition (1) can now be written in the form

$$P(g,N)=\sum_{\alpha\beta\nu}\Psi_{\beta\nu}{}^{\alpha *}(g_0)\,[A_{\beta}{}^{\alpha}(g_1^{-1})]^{N}\,\Psi_{\beta\nu}{}^{\alpha}(g), \tag{7}$$

where A is the averaged transformation effected by an element of our class in one operation:

$$A_{\beta}{}^{\alpha}(g_1)=\sum_{j}p_j(g_1)\,\Gamma^{\alpha}_{j\beta\beta}(g_1). \tag{8}$$

If we now assume that the number N of arbitrary reorientations of the molecule in time t obeys the Poisson distribution

$$w(N,t)=\frac{1}{N!}\left(\frac{t}{\tau}\right)^{N}e^{-t/\tau}, \tag{9}$$

where τ is the average time between two consecutive reorientations, then the unconditional probability $W(g, g_0, t)$ that the molecule will go over from the orientation g_0 at the initial moment to the orientation g at time t can be written as follows:

$$W(g,g_0,t)=\frac{1}{\sigma}\sum_{N=0}^{\infty}w(N,t)P(g,N)$$
$$=\frac{1}{\sigma}\sum_{\alpha\beta\nu}\Psi_{\beta\nu}{}^{\alpha *}(g_0)\,\Psi_{\beta\nu}{}^{\alpha}(g)\exp\left\{-[1-A_{\beta}{}^{\alpha}(g_1^{-1})]\frac{t}{\tau}\right\}. \tag{10}$$

The factor $1/\sigma$ determines the probability of the initial orientation g_0.

We have obtained the expression (10) under the condition that all reorientations of the molecule occur about axes of one class, e.g., the i-th class. However, it can be generalized without difficulty to the arbitrary case. We note that only the quantities A^{α}_{β}, τ and, of course, σ depend on the class index i. Therefore, introducing the class-effectiveness factor q_i and summing (10) over all i with weight q_i, we find the required expression

$$W(g,g_0,t)=\sum_{\alpha\beta\nu}\Psi_{\beta\nu}{}^{\alpha *}(g_0)\,\Psi_{\beta\nu}{}^{\alpha}(g)\sum_{i}\frac{q_i}{\sigma_i}\exp\left\{-[1-A_{i\beta}{}^{\alpha}(g_1^{-1})]\frac{t}{\tau_i}\right\}. \tag{11}$$

Obviously, the q_i must satisfy the normalization condition

$$\sum_{i}q_i=1. \tag{12}$$

By means of the expression (11), we can calculate the correlation function K(t) and the spectral density $J(\omega)$ of the stationary random molecular quantity $F(t) \equiv F[g(t)]$, using the following definitions[2]:

$$K(t)=\iint F^{*}(g)F(g_0)W(g,g_0,t)\,dg\,dg_0, \tag{13}$$

$$J(\omega)=\int_{-\infty}^{\infty}\operatorname{Re}K(t)\,e^{-i\omega t}\,dt. \tag{14}$$

Taking into account that, in crystals, the basis functions $\Psi^{\alpha}_{\beta\nu}$ are taken, for example, to be linear combinations of normalized spherical harmonics $Y^{m}_{\nu}(\theta, \varphi)$[10] and that the function F(g) can be expanded in a series in the same functions:

$$\Psi_{\beta\nu}{}^{\alpha}(g)=i^{\nu}\sum_{m=-\nu}^{\nu}\psi_{\beta\nu}{}^{\alpha m}\,Y_{\nu}{}^{m}(\vartheta,\varphi), \tag{15}$$

$$F(g)=\sum_{\nu,m}f_{\nu}{}^{m}\,Y_{\nu}{}^{m}(\vartheta,\varphi), \tag{16}$$

and using (11), we see that the expression (14) takes the form

$$J(\omega)=2\sum_{\alpha\beta\nu}\left|\sum_{m}f_{\nu}{}^{m}\psi_{\beta\nu}{}^{\alpha m}\right|^{2}$$
$$\times\sum_{i}\frac{q_i}{\sigma_i}\,\frac{\tau_i/[1-\operatorname{Re}A_{i\beta}{}^{\alpha}(g_1)]}{1+\{\omega\tau_i/[1-\operatorname{Re}A_{i\beta}{}^{\alpha}(g_1)]\}^{2}}. \tag{17}$$

2. NUCLEAR MAGNETIC RELAXATION

The following expressions have been obtained in[1,2,11] for the magnetic relaxation times T_1 and $T_{1\rho}$ of identical nuclei with spin $I = 1/2$ in the laboratory and rotating coordinate frames, the relaxation being caused by modulations of the dipole-dipole interactions by the random motions of the relaxing spins:

$$T_1^{-1}={}^{9}/_{8}\gamma^{4}\hbar^{2}{\sum_{k}}'\{J_1(\omega_0)+J_2(2\omega_0)\}_{jk}, \tag{18}$$

$$T_{1\rho}^{-1}={}^{9}/_{8}\gamma^{4}\hbar^{2}{\sum_{k}}'\{{}^{1}/_{4}J_0(\omega_1)+{}^{2}/_{5}J_1(\omega_0)+{}^{1}/_{4}J_2(2\omega_0)\}_{jk}, \tag{19}$$

where γ is the gyromagnetic ratio of the nucleus, and ω_0 and ω_1 are the resonance frequencies of the spins in the constant and alternating magnetic fields, H_0 and H_1. The sum in (18) and (19) is taken over all interacting spins k not equal to j. The spectral densities $J_1(\omega_0)$, $J_2(2\omega_0)$ and $J_0(2\omega_1)$ are calculated starting from a concrete model for the random process. Here, we consider the case when the spin-1/2 nuclei are in molecules executing thermal reorientational motions in crystals. Therefore, the spectral densities, calculated on the basis of (17), of the dipole-dipole interaction are equal to

$$J_m(\omega)=2|f_2{}^{m}(b)|^{2}\sum_{\alpha\beta}\left|\sum_{n=-2}^{2}T_2{}^{mn}(\Omega)\,\psi_{\beta 2}{}^{\alpha n}\right|^{2}$$
$$\times\sum_{i}\frac{q_i}{\sigma_i}\,\frac{\tau_i/[1-\operatorname{Re}A_{i\beta}{}^{\alpha}(g_1)]}{1+\{\omega\tau_i/[1-\operatorname{Re}A_{i\beta}{}^{\alpha}(g_1)]\}^{2}}, \tag{20}$$

where $f_2^0(b) = b^{-3}(16\pi/5)^{1/2}$, $f_2^1(b) = b^{-3}(8\pi/15)^{1/2}$, $f_2^2(b) = b^{-3}(32\pi/15)^{1/2}$[2], and b is the distance between the interacting spins j and k. In addition, in expression (20), the orientation of the crystal in the constant magnetic field H_0 is taken into account by the angle Ω, defined by the Euler angles, and the coefficients $T_2^{mn}(\Omega)$ are generalized spherical functions[12]. Averaging (20) over all orientations Ω, we obtain for a polycrystal

$$J_m(\omega)=\frac{2}{5}|f_2{}^{m}(b)|^{2}\sum_{\alpha\beta i}\frac{q_i}{\sigma_i}\,\frac{\tau_i/[1-\operatorname{Re}A_{i\beta}{}^{\alpha}(g_1)]}{1+\{\omega\tau_i/[1-\operatorname{Re}A_{i\beta}{}^{\alpha}(g_1)]\}^{2}}. \tag{21}$$

3. PROTON RELAXATION IN AMMONIUM CHLORIDE

Below 184.3°C, the unit cell of NH_4Cl has a body-centered cubic structure of the CsI type[13]. At tem-

Values of the coefficients $Q^{\alpha}_{m\Gamma}$ occurring in the formulas (22) and (23)

Direction of H_0	$Q_{m\Gamma^\alpha}$					
	$Q_{1\Gamma'_4}$	$Q_{2\Gamma'_4}$	$Q_{0\Gamma'_4}$	$Q_{1\Gamma'_{23}}$	$Q_{2\Gamma'_{23}}$	$Q_{0\Gamma'_{23}}$
$H_0 \parallel [001]$	1	$1/2$	0	0	$1/2$	1
$H_0 \parallel [110]$	$1/2$	$5/8$	$3/4$	$1/2$	$3/8$	$1/4$
$H_0 \parallel [111]$	$1/3$	$2/3$	1	$2/3$	$1/3$	0
Polycrystal	$3/5$	$3/5$	$3/5$	$2/5$	$2/5$	$2/5$

peratures $T_\lambda = -30.5°$ C, an order-disorder phase transition, associated with the possible orientations of the ammonium ions, occurs. In the ordered (below T_λ) and disordered (above T_λ) phases, there are 12 and 24 orientations of the NH_4^+ ion in the unit cell of NH_4Cl; between these, the ammonium ion can execute reorientations with angular rotations which form the tetrahedral and octahedral finite pure-rotation point symmetry groups.

By making use of basis functions transforming according to the irreducible representations Γ'_{23}, Γ'_4 and Γ_3, Γ_5 of the tetrahedral and octahedral groups respectively, and the matrices of these representations,[10] and assuming that the relaxation is caused by the intra-ionic dipole-dipole interaction of the four protons, we can find expressions for the proton relaxation times from the formulas (18)—(20) for arbitrary alignment of the constant field relative to the NH_4Cl unit cell. For the ordered phase, these calculations lead to the following results:

$$T_{1\rho}^{-1} = \frac{3\pi}{10}\frac{\gamma^4\hbar^2}{b^6}\Big\{3q_{C_2}\Big[\frac{5}{2}Q_{1\Gamma_{4'}}\frac{\tau_{C_2}}{1+(^3/_4\omega_0\tau_{C_2})^2} + Q_{2\Gamma_{4'}}\frac{\tau_{C_2}}{1+(^3/_2\omega_0\tau_{C_2})^2} + \frac{3}{2}Q_{0\Gamma_{4'}}\frac{\tau_{C_2}}{1+(^3/_2\omega_1\tau_{C_2})^2}\Big] + 2q_{C_3}\Big[\frac{5}{2}Q_{1\Gamma_{23'}}\frac{\tau_{C_3}}{1+(^2/_3\omega_0\tau_{C_3})^2} + Q_{2\Gamma_{23'}}\frac{\tau_{C_3}}{1+(^4/_3\omega_0\tau_{C_3})^2} + \frac{3}{2}Q_{0\Gamma_{23'}}\frac{\tau_{C_3}}{1+(^4/_3\omega_1\tau_{C_3})^2}\Big]\Big\}, \tag{22}$$

$$T_1^{-1} = \frac{3\pi}{10}\frac{\gamma^4\hbar^2}{b^6}\Big\{3q_{C_2}\Big[Q_{1\Gamma_{4'}}\frac{\tau_{C_2}}{1+(^3/_4\omega_0\tau_{C_2})^2} + 4Q_{2\Gamma_{4'}}\frac{\tau_{C_2}}{1+(^3/_2\omega_0\tau_{C_2})^2}\Big] + 2q_{C_3}\Big[Q_{1\Gamma_{23'}}\frac{\tau_{C_3}}{1+(^2/_3\omega_0\tau_{C_3})^2} + 4Q_{2\Gamma_{23'}}\frac{\tau_{C_3}}{1+(^4/_3\omega_0\tau_{C_3})^2}\Big]\Big\}, \tag{23}$$

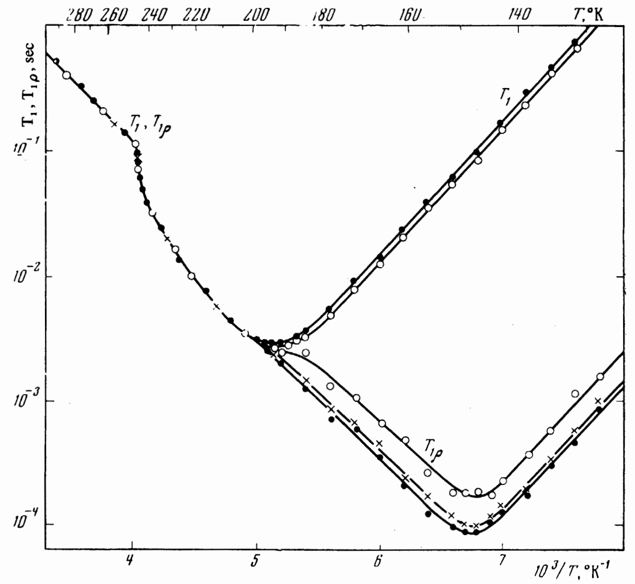
where $b = 1.038 \times (8/3)^{1/2}$ Å[14], and the indices C_2 and C_3 label the tetrahedral classes of the second-order and combined third-order physical rotation axes of the NH_4^+ ion. The coefficients $Q^{\alpha}_{m\Gamma}$ are functions of the orientation of the crystal in the constant magnetic field and are given in the table for H_0 parallel to the second-, third- and fourth-order axes of the NH_4Cl cube, and also for the polycrystal.

For the disordered phase of NH_4Cl, a branch for which $\omega_1\tau_i$ and $\omega_0\tau_i$ are much less than 1 (the case of rapid motion of the NH_4^+ ion) is observed experimentally. We assume, therefore, that it is adequate to confine ourselves to this approximation only:

$$T_{1\rho}^{-1} = T_1^{-1} = \frac{3\pi}{10}\frac{\gamma^4\hbar^2}{b^6}\Big(9q_{C_2}\tau_{C_2} + 2q_{C_3}\tau_{C_3} + \frac{9}{2}q_{C_4}\tau_{C_4} + 9q_{C_4^2}\tau_{C_4^2}\Big), \tag{24}$$

where C_2, C_3, C_4 and C_4^2 are indices of the cubic classes of the physical rotation axes of the NH_4^+ ion.

Experimental investigations of the proton spin-lattice relaxation times T_1 and $T_{1\rho}$ were carried out on a monocrystalline sample of ammonium chloride using a coherent-pulse NMR instrument at frequency 14 MHz with $H_1 = 32.6$ Oe[15] in the temperature range from 125°K to room temperature. The direction of the constant magnetic field H_0 was chosen along the three principal axes, [001], [110] and [111], of the crystal. The experimental data, plotted in the Figure by light and shaded circles and crosses, correspond to the above field directions.[2)] The experimental results in the temperature range from room temperature down to ~196°K confirm the conclusions, which follow from formulas (22)—(24) for $\omega_1\tau_i$, $\omega_0\tau_i \ll 1$, that the relaxation times along the constant and rotating magnetic fields are equal and independent of the orientation of the crystal in the constant magnetic field.



Temperature dependence of T_1 and $T_{1\rho}$ of protons in a monocrystal of NH_4Cl ($\gamma H_0/2\pi = 14$ MHz, $H_1 = 32.6$ Oe): ○–$H_0 \parallel$ [001], ×–$H_0 \parallel$ [110], ●–$H_0 \parallel$ [111].

The presence of anisotropy of T_1 and $T_{1\rho}$ makes it possible to determine the parameters q_i uniquely. For the ordered phase, the curves $T_1 = T_1(T°K)$ and $T_{1\rho} = T_{1\rho}(T°K)$ pass through the corresponding minima and, below 196°K, indicate anisotropy of the relaxation rates. For this phase, it turns out to be simpler to determine the q_i by comparing the formula (22) with the minimum values of $T_{1\rho}$ with the directions of the constant field along the third- and fourth-order axes of the NH_4Cl cube. Then

$$q_{C_2} = 0.288, \quad q_{C_3} = 0.201 \tag{25}$$

and, if we take (12) into account,

$$q_E = 0.511,$$

where E denotes the identical rotation. The minima of the other four curves in the Figure can be used as controls. If we assume that $\tau_{C_2} = \tau_{C_3} = \tau$ and take (25) into account, the minimum values of T_1 and $T_{1\rho}$, calculated

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[2)] For convenience in reading the graphs, the curve of T_1 for $H_0 \parallel [110]$ is not given.

from formulas (22) and (23), and the conditions for the minimum are

$$T_{1\rho}^{\min}[110] = 101(100)\,\mu\,\text{sec}, \quad \omega_1\tau = 0.678 \quad (147.5^\circ\,\text{K}),$$

$$T_1^{\min}[001] = 2.81(2.78)\,\mu\,\text{sec}, \quad \omega_0\tau = 0.889 \quad (192^\circ\,\text{K}),$$

$$T_1^{\min}[110] = 2.96(2.85)\,\mu\,\text{sec}, \quad \omega_0\tau = 0.836 \quad (193^\circ\,\text{K}),$$

$$T_1^{\min}[111] = 3.01(2.88)\,\mu\,\text{sec}, \quad \omega_0\tau = 0.818 \quad (193.5^\circ\,\text{K}),$$

where, for comparison, we have given in the brackets the corresponding experimental minimum values of T_1 and $T_{1\rho}$ and their temperatures.

A comparison of the calculated and experimental ratios of T_1 for $\omega_0\tau \gg 1$, and of $T_{1\rho}$ for $\omega_0\tau$, $\omega_1\tau \gg 1$, for directions of the constant magnetic field along the principal crystallographic axes, i.e., the ratios

$$T_1\,[001] : T_1[110] : T_1[111] = \begin{cases} 1{:}1{,}09{:}1{,}13 & \text{(theory)} \\ 1{:}1.12{:}1{,}17 & \text{(experiment)} \end{cases}$$

$$T_{1\rho}\,[001] : T_{1\rho}[110] : T_{1\rho}[111] = \begin{cases} 1{:}0{,}66{:}0{,}59 & \text{(theory)} \\ 1{:}0{,}63{:}0{,}54 & \text{(experiment)} \end{cases}$$

is further evidence of the satisfactory agreement of the theory with experiment.

Thus, the data on the proton relaxation in the particular case of an NH_4Cl crystal in the temperature range from 125°K to room temperature indicate a rotational reorientational mechanism of the motion of the NH_4^+ ion, and this mechanism can be described with a sufficient degree of accuracy by the theory developed in Secs. 1 and 2, which takes into account the symmetry group of the Hamiltonian of the molecule in the crystal field. The fact, which follows from (25), that reorientations about the second-order axes are preferred to those about the thrid-order axes of the NH_4^+ tetrahedron agrees with calculations of the potential barriers[14].

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