

THEORY OF NUCLEAR SPIN-LATTICE RELAXATION IN SOLID ORTHOHYDROGEN

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An expression is obtained for the time of longitudinal nuclear spin-lattice relaxation in terms of the spectral intensities of correlation functions. The libron subsystem plays the role of the lattice. The correlation functions of the libron subsystem are calculated in the random phase approximation.

1. INTRODUCTION

Great interest has recently been evinced [2-4] for investigations of the nature of elementary excitations in solid orthohydrogen below the phase transition point [1]. Apart from its own physical importance, this system is also interesting from the point of view of the general many-body theory in that it is another model in which a phase transition is possible [5-9].

Calculations show [2-4] that definite collective excitations exist below the transition point. These excitations, which are known as librions, are due to the intermolecular quadrupole-quadrupole interaction. These quasiparticles are "rotational waves" in the sense that they propagate like a wave and are associated with the excitation of rotational degrees of freedom. However, since the average value of the angular momentum of each hydrogen molecule vanishes in the low-temperature region, one should speak rather of librational motion and not rotation. In other words, the quadrupole-quadrupole interaction slows down the rotation of the molecules to a slight extent, doing this in such a way that the total angular momentum of each molecule remains the same (i. e., $J = 1$) but the z component of the angular momentum varies.

No direct experimental confirmation of the existence of librions has yet been made [10, 11]. It is therefore important to make further theoretical and experimental investigations of processes in solid hydrogen such as spin-lattice relaxation [12-15], nuclear magnetic resonance [16], infrared absorption [17], etc.

In the present paper we shall study the longitudinal relaxation of the subsystem of nuclear spins resulting from its interaction with the libron subsystem, which is treated in the random phase approximation.

In studying this problem, Homma [13] treated the libron subsystem in an approximation analogous to the Gol'shtein-Primakov method in the theory of spin waves. The order of magnitude of the relaxation time obtained by Homma is confirmed qualitatively by the experimental results [15]. Previously, nuclear spin-lattice relaxation was considered by Moriya and Motizuki [12] and Harris and Hunt [14] for temperatures above the phase transition. A number of investigations into spin-lattice relaxation have been made by Sung [18-20] for dilute solids solutions of hydrogen and hydrogen and deuterium.

Following Moriya and Motizuki [12], we assume the following relaxation mechanisms: 1) intramolecular dipole-dipole interaction and I - J coupling modulated by the intermolecular quadrupole-quadrupole interaction; 2) intermolecular dipole-dipole interaction modulated by the lattice vibrations. However, the second mechanism makes a small contribution compared with the first [13], and we shall therefore restrict ourselves to the first relaxation mechanism. In the low-temperature phase, one can say that relaxation occurs as a result of inelastic scattering of librions by nuclear spins. The main contribution is made by

Joint Institute of Nuclear Research, Dubna. Translated from *Teoreticheskaya i Matematicheskaya Fizika*, Vol. 4, No. 3, pp. 383-393, September, 1970. Original article submitted January 30, 1970.

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Raman processes and direct processes are forbidden since the energy gap in the libron spectrum is of the order of 10°K, which is much greater than the distance between the nuclear Zeeman levels.

In Section 2, we calculate the correlation functions for the libron subsystem in the random phase approximation. Equations are obtained for the ordering parameter. In Section 3, we obtain an expression for the time of longitudinal nuclear spin-lattice relaxation in terms of the spectral intensities of the correlation functions of the lattice. In Section 4, the time of longitudinal spin-lattice relaxation is calculated for temperatures below the phase transition point.

2. CORRELATION FUNCTIONS FOR THE LIBRON SUBSYSTEM

We shall consider an orthohydrogen crystal below the phase transition point. The Hamiltonian of a system of orthohydrogen molecules in the rotational state $J = 1$ and coupled by the quadrupole-quadrupole interaction can be written in the form [4]

$$\mathcal{H} = \sum_{ij} \sum_{m,n} \gamma_{ij}^{mn} O_i^m O_j^n, \quad m, n = 0, \pm 1, \pm 2. \quad (1)$$

Here, γ_{ij}^{mm} are coupling constants [4], and the operators O_i^m are related to the operators $J_i^{Z, \pm}$ in the subspace $J = 1$ as follows ($J^\pm = J^X \pm iJ^Y$):

$$\begin{aligned} O_i^0 &= 3(J_i^z)^2 - 2, \\ O_i^{\pm 1} &= J_i^z J_i^\pm + J_i^\pm J_i^z, \\ O_i^{\pm 2} &= (J_i^\pm)^2. \end{aligned} \quad (1a)$$

The Hamiltonian (1) is written down in a system of coordinates (henceforth known as the sublattice system) in which the z_i axis of each molecule i is directed along the symmetry axis of the molecule i . It has been found [21-24] that the molecular lattice of solid hydrogen below the phase transition point consists of four simple cubic sublattices. For each sublattice, the quantization axes are aligned along the different diagonals of the cubic unit cell of the face-centered cubic lattice.

We now go over to the Fourier representation for the operators O_i^m :

$$\mathcal{H} = \sum_{\mathbf{k}} \sum_{\alpha\beta} \sum_{m,n} \gamma_{\alpha\beta}^{mn}(\mathbf{k}) O_\alpha^m(\mathbf{k}) O_\beta^n(-\mathbf{k}), \quad (2)$$

where

$$\begin{aligned} \gamma_{\alpha\beta}^{mn}(\mathbf{k}) &= \sum_{\mathbf{R}(\alpha) - \mathbf{R}(\beta)} \exp\{i\mathbf{k} \cdot (\mathbf{R}(\alpha) - \mathbf{R}(\beta))\} \gamma_{\alpha\beta}^{mn}(\mathbf{R}(\alpha) - \mathbf{R}(\beta)), \\ O_\alpha^m(\mathbf{k}) &= \frac{1}{\sqrt{N}} \sum_{\mathbf{R}(\alpha)} O^m(\mathbf{R}(\alpha)) \exp(-i\mathbf{k} \cdot \mathbf{R}(\alpha)). \end{aligned}$$

Here, α and β are the subscripts of the sublattices, $\alpha, \beta = 1, 2, 3, 4$, and N is the number of unit cells in the crystal. We note that the set of operators $\{O_i^m, J_i^{Z, \pm}\}$ forms an algebra (see Table 1). It is therefore convenient to introduce the following notation:

$$\begin{aligned} [O_i^m, O_j^n] &= K_{mn}(J_i) \delta_{ij}, \\ [J_i^m, O_j^n] &= L_{mn}(O_i) \delta_{ij}, \end{aligned} \quad (3)$$

where $K_{mn}(J_i)$ and $L_{mn}(O_i)$ are certain functions of the operators $J_i^{Z, \pm}$ and O_i^m , respectively, whose specific form depends on the values of the subscripts m and n .

The equations of motion are

$$i \frac{dO_\alpha^m(\mathbf{k})}{dt} = \frac{1}{\sqrt{N}} \sum_{\mathbf{q}, \beta} \sum_{m', n'} \gamma_{\alpha\beta}^{m'n'}(\mathbf{q}) \{K_{mm'}(J_\alpha(\mathbf{k} + \mathbf{q})) O_\beta^{n'}(-\mathbf{q}) + O_\beta^{n'}(-\mathbf{q}) K_{mm'}(J_\alpha(\mathbf{k} + \mathbf{q}))\}, \quad (4)$$

$$i \frac{dJ_\alpha^m(\mathbf{k})}{dt} = \frac{1}{\sqrt{N}} \sum_{\mathbf{q}, \beta} \sum_{m', n'} \gamma_{\alpha\beta}^{m'n'}(\mathbf{q}) \{L_{mm'}(O_\alpha(\mathbf{k} + \mathbf{q})) O_\beta^{n'}(-\mathbf{q}) + O_\beta^{n'}(-\mathbf{q}) L_{mm'}(O_\alpha(\mathbf{k} + \mathbf{q}))\}. \quad (5)$$

We linearize these equations, using the random phase approximation:

$$K_{mm'}(J_\alpha(\mathbf{k} + \mathbf{q})) O_\beta^{n'}(-\mathbf{q}) \approx K_{mm'}(J_\alpha(\mathbf{k} + \mathbf{q})) \langle O_\beta^{n'}(-\mathbf{q}) \rangle + \langle K_{mm'}(J_\alpha(\mathbf{k} + \mathbf{q})) \rangle O_\beta^{n'}(-\mathbf{q}), \quad (6)$$

$$L_{mm'}(O_\alpha(\mathbf{k} + \mathbf{q})) O_\beta^{n'}(-\mathbf{q}) \approx L_{mm'}(O_\alpha(\mathbf{k} + \mathbf{q})) \langle O_\beta^{n'}(-\mathbf{q}) \rangle + \langle L_{mm'}(O_\alpha(\mathbf{k} + \mathbf{q})) \rangle O_\beta^{n'}(-\mathbf{q}). \quad (7)$$

TABLE 1

A \ B	O ⁰	O ⁺¹	O ⁻¹	O ⁺²	O ⁻²	J ⁺	J ⁻	J ^z
O ⁰	0	3J ⁺	-3J ⁻	0	0	3O ⁺¹	-3O ⁻¹	0
O ⁺¹	-3J ⁺	0	2J ^z	0	-2J ⁻	2O ⁺²	2O ⁰	-O ⁺¹
O ⁻¹	3J ⁻	-2J ^z	0	2J ⁺	0	-2O ⁰	-2O ⁻²	O ⁻¹
O ⁺²	0	0	-2J ⁺	0	4J ^z	0	2O ⁺¹	-2O ⁺²
O ⁻²	0	2J ⁻	0	-4J ^z	0	-2O ⁻¹	0	2O ⁻²
J ⁺	-3O ⁺¹	-2O ⁺²	2O ⁰	0	2O ⁻¹	0	2J ^z	-J ⁺
J ⁻	3O ⁻¹	-2O ⁰	2O ⁻²	-2O ⁺¹	0	-2J ^z	0	J ⁻
J ^z	0	O ⁺¹	-O ⁻¹	2O ⁺²	-2O ⁻²	J ⁺	-J ⁻	0

Taking into account the results of calculations in the molecular field approximation, we also assume (see [3, 5])

$$\langle O_\beta^n(\mathbf{k}) \rangle = 0, \quad n \neq 0; \quad \langle J_\beta^n(\mathbf{k}) \rangle = 0. \quad (8)$$

Using (6)-(8), we transform Eqs. (4) and (5) to the form

$$i \frac{dO_\alpha^{\pm 1}(\mathbf{k})}{dt} \approx \mp \frac{19\Gamma}{2} J_\alpha^\mp(\mathbf{k}) \langle O^0 \rangle, \quad (9)$$

$$i \frac{dJ_\alpha^\pm(\mathbf{k})}{dt} = \mp \frac{19\Gamma}{2} \langle O^0 \rangle \left\{ O_\alpha^\mp(\mathbf{k}) + \frac{8}{19\Gamma} \sum_{\beta, n} \gamma_{\alpha\beta}^{\pm 1, n}(\mathbf{k}) O_\beta^n(\mathbf{k}) \right\}, \quad (10)$$

where we have introduced the notation

$$-\frac{19}{12} \Gamma = \sum_{\beta} \gamma_{\alpha\beta}^{00}(0).$$

We have restricted ourselves to the nearest-neighbor approximation [4] (allowance for the next-nearest neighbors [25] does not lead to significant changes).

From (9) and (10) we deduce the equation

$$\frac{d^2 J_\alpha^\pm(\mathbf{k})}{dt^2} = - \left(\frac{19\Gamma \langle O^0 \rangle}{2} \right)^2 \left\{ J_\alpha^\mp(\mathbf{k}) + \frac{8}{19\Gamma} \sum_{\beta} (\pm \gamma_{\alpha\beta}^{\pm 1, -1}(\mathbf{k}) J_\beta^-(\mathbf{k}) \mp \gamma_{\alpha\beta}^{\pm 1, +1}(\mathbf{k}) J_\beta^+(\mathbf{k})) \right\}. \quad (11)$$

We introduce the notation (see also [4])

$$\begin{aligned} f_{\alpha\beta}(\mathbf{k}) &= \frac{4}{19\Gamma} \gamma_{\alpha\beta}^{\pm 1, -1}(\mathbf{k}), \quad f_{\alpha\beta}^*(\mathbf{k}) = \frac{4}{19\Gamma} \gamma_{\alpha\beta}^{\pm 1, +1}(\mathbf{k}), \\ g_{\alpha\beta}(\mathbf{k}) &= \frac{4}{19\Gamma} \gamma_{\alpha\beta}^{\pm 1, +1}(\mathbf{k}), \quad g_{\alpha\beta}^*(\mathbf{k}) = \frac{4}{19\Gamma} \gamma_{\alpha\beta}^{\pm 1, -1}(\mathbf{k}), \\ \bar{C}(\mathbf{k}) &= \begin{bmatrix} J_1^-(\mathbf{k}) \\ \vdots \\ J_4^-(\mathbf{k}) \\ J_1^+(\mathbf{k}) \\ \vdots \\ J_4^+(\mathbf{k}) \end{bmatrix} = \begin{bmatrix} c_1(\mathbf{k}) \\ \vdots \\ c_4(\mathbf{k}) \end{bmatrix}, \quad \bar{F}(\mathbf{k}) = \begin{bmatrix} \bar{f}(\mathbf{k}) & -\bar{g}(\mathbf{k}) \\ \vdots & \vdots \\ -\bar{g}^*(\mathbf{k}) & \bar{f}^*(\mathbf{k}) \end{bmatrix}, \end{aligned} \quad (12)$$

and also

$$\bar{M}(\mathbf{k}) = \left(\frac{19\Gamma}{2} \langle O^0 \rangle \right)^2 [1 + 2\bar{F}(\mathbf{k})] \quad (13)$$

(here, the bar denotes matrix quantities).

In order to calculate the correlation functions, we shall use the method of Green's functions [26].

We introduce the Green's function

$$\bar{G}(E, \mathbf{k}) = \langle\langle \bar{C}(\mathbf{k}) | \bar{C}^+(\mathbf{k}) \rangle\rangle_E,$$

which satisfies the equation

$$E^2 \bar{G}(E, \mathbf{k}) = \frac{i}{2\pi} \{ E \langle [\bar{C}(\mathbf{k}), \bar{C}^+(\mathbf{k})] \rangle + \langle [[\bar{C}(\mathbf{k}), \mathcal{H}] \bar{C}^+(\mathbf{k})] \rangle + \bar{M}(\mathbf{k}) G(\mathbf{k}, E) \}. \quad (14)$$

Further, we introduce the diagonalizing matrix $\bar{V}(\mathbf{k}); \bar{V}^{-1}(\mathbf{k}) = \bar{V}^+(\mathbf{k})$,

$$\bar{V}^+(\mathbf{k}) \bar{M}(\mathbf{k}) \bar{V}(\mathbf{k}) = \left(\frac{19\Gamma}{2} \langle O^0 \rangle\right)^2 [1 + 2\bar{V}^+(\mathbf{k}) \bar{F}(\mathbf{k}) \bar{V}(\mathbf{k})] = \left(\frac{19\Gamma}{2} \langle O^0 \rangle\right)^2 [1 + 2\bar{\Phi}(\mathbf{k})] = \bar{\omega}^2(\mathbf{k}). \quad (15)$$

Here, $\bar{\omega}^2(\mathbf{k})$ is a diagonal matrix with the elements

$$\omega_\mu^2(\mathbf{k}) = \left(\frac{19\Gamma}{2} \langle O^0 \rangle\right)^2 \varepsilon_\mu^2(\mathbf{k}), \quad \mu = 1, 2, \dots, 8;$$

where $\varepsilon_\mu^2(\mathbf{k})$ are the eigenvalues of the matrix $[1 + 2\bar{\Phi}(\mathbf{k})]$; $\omega_\mu(\mathbf{k})$ are the libron frequencies, which, like the matrix $\bar{V}(\mathbf{k})$, must be found numerically. Estimates show [2-4] that for $\mathbf{k} = 0$ and $T = 0^\circ\text{K}$ the energy gap in the libron spectrum is of order 10°K and that the width of the libron band is of order $4-5^\circ\text{K}$. One can now readily obtain equations for the Green's functions of the operators $J^\pm(\mathbf{k})$. As an example, we give one of the equations:

$$\langle\langle J_\alpha^+(\mathbf{k}) | J_\alpha^-(\mathbf{k}) \rangle\rangle_E = \frac{i}{2\pi} \sum_\lambda |V_{\alpha\lambda}(\mathbf{k})|^2 \frac{\omega_\lambda^2(\mathbf{k})}{E^2 - \omega_\lambda^2(\mathbf{k})}.$$

Making the standard calculations [26], we obtain expressions for the spectral intensities of the correlation functions, which we denote by

$$I_{J_\alpha^+(\mathbf{k}) J_\alpha^-(\mathbf{k})}(\omega) = I_{J^+ J^-}(\omega, \mathbf{k}, \alpha).$$

We have

$$I_{J^+ J^+}(\omega, \mathbf{k}, \alpha) = \frac{2}{19\Gamma} \sum_\lambda (V_{\alpha\lambda}^*(\mathbf{k}))^2 \omega_\lambda(\mathbf{k}) \left\{ \frac{\delta(\omega - \omega_\lambda(\mathbf{k}))}{e^{\beta\omega} - 1} - \frac{\delta(\omega + \omega_\lambda(\mathbf{k}))}{e^{\beta\omega} - 1} \right\}, \quad (16)$$

$$I_{J^+ J^-}(\omega, \mathbf{k}, \alpha) = \frac{2}{19\Gamma} \sum_\lambda |V_{\alpha\lambda}(\mathbf{k})|^2 \omega_\lambda(\mathbf{k}) \left\{ \frac{\delta(\omega - \omega_\lambda(\mathbf{k}))}{e^{\beta\omega} - 1} - \frac{\delta(\omega + \omega_\lambda(\mathbf{k}))}{e^{\beta\omega} - 1} \right\}. \quad (17)$$

These spectral intensities will be needed later to calculate the relaxation time.

We shall also obtain an equation for the so-called "ordering parameter" $\langle O^0 \rangle$. To this end, we use the relations $J^- J^+ + J^+ J^- = 2(|J|^2 - (J^Z)^2)$ and (1a).

The following equation holds:

$$\frac{2}{4N} \sum_{\alpha, \mathbf{k}} \int_{-\infty}^{\infty} I_{J^+ J^-}(\omega, \mathbf{k}, \alpha) d\omega = \frac{2}{3} (4 - \langle O^0 \rangle).$$

Using (17), we obtain

$$\langle O^0 \rangle = 4 - \frac{3}{2} \langle O^0 \rangle \frac{1}{N_0} \sum_{\lambda, \mathbf{k}} \varepsilon_\lambda(\mathbf{k}) \text{cth} \beta \frac{19\Gamma}{4} \langle O^0 \rangle \varepsilon_\lambda(\mathbf{k}), \quad (18)$$

where $N_0 = 4N$ is the number of orthohydrogen molecules in the crystal. Our result corresponds to the analogous equation of [3] but differs from the corresponding equation of Raich and Eters [4]. This difference is evidently due to the fact that Raich and Eters did not use the operators J^Z, \pm to investigate the libron subsystem but certain other operators whose correlation functions were calculated on the basis of Wallace's statistical method (see [4]).

Setting $\omega_\mu(\mathbf{k}) = 1$ in Eq. (18), we obtain the well-known results of molecular field theory [5]. The results of [3, 4] and the present paper are evidently similar, since in all these investigations the expression for $\langle O^0 \rangle$ calculated at $T = 0^\circ\text{K}$ differs by only a few percent from the results obtained in the molecular field approximation.

3. DERIVATION OF AN EXPRESSION FOR THE RECIPROCAL TIME OF LONGITUDINAL NUCLEAR SPIN-LATTICE RELAXATION

Bearing in mind the relaxation mechanism discussed in Section 1, we write the Hamiltonian of an orthohydrogen molecule in an external static magnetic field H_0 as follows [12]:

$$\mathcal{H} = \mathcal{H}_s + V, \quad V = \mathcal{H}_{sd} + \mathcal{H}_{t.s.} \quad (19)$$

Here, $\mathcal{H}_z = -aI^z - bJ^z$ is the Zeeman Hamiltonian; $\mathbf{I} = \mathbf{I}^{(1)} + \mathbf{I}^{(2)}$ is the operator of the total nuclear spin of the orthohydrogen molecule; $\mathcal{H}_{I,J} = -c \cdot \mathbf{I} \cdot \mathbf{J}$ is the Hamiltonian of the $\mathbf{I} \cdot \mathbf{J}$ interaction;

$$\mathcal{H}_{int} = -5d \left\{ 3 \frac{\mathbf{I}^{(1)} \cdot \mathbf{r}}{r} \cdot \frac{\mathbf{I}^{(2)} \cdot \mathbf{r}}{r} - \mathbf{I}^{(1)} \cdot \mathbf{I}^{(2)} \right\} \quad (20)$$

is the Hamiltonian of the intramolecular dipole-dipole interaction of the nuclear spins of the protons in the molecule; and r is the distance between them. We use the notation

$$a = 2\mu_n H_0, \quad b = \frac{\mu_n J}{J} H_0, \\ c = 2\mu_n H', \quad d = \frac{4}{5} \mu_n^2 \langle r^{-3} \rangle$$

(the determination and numerical values of these quantities are discussed in [12]).

The Hamiltonian (19) determines the profile of the nuclear magnetic resonance line in solid hydrogen and leads to relaxation processes. It can be conveniently represented in the form

$$V = -d \cdot \mathbf{J}^2 \mathbf{I}^2 - \left(c - \frac{3}{2} d \right) \mathbf{I} \cdot \mathbf{J} + 3d (\mathbf{I} \cdot \mathbf{J})^2. \quad (21)$$

Using the nonequilibrium statistical operator method of Zubarev [28], one can show [27] that the probabilities of transitions between states with different $\mathbf{I}^z = m$ can be represented in the form of spectral intensities of the correlation functions of the lattice operators alone. We shall assume that the state of the spin system is characterized by the spin temperature β_S . Then the time of longitudinal spin-lattice relaxation is determined as follows:

$$\frac{d\beta_S}{dt} = \frac{\beta - \beta_S}{T_1}, \\ \frac{1}{T_1} = \frac{1}{2} \frac{\sum_{m, m_1} (m - m_1)^2 W_{m \rightarrow m_1}}{\sum_m m^2}, \quad (22)$$

where $-1 \leq m$ and $m_1 \leq 1$ and $W_{m \rightarrow m_1}$ are the transition probabilities expressed in terms of the spectral intensities. Using the method of [27], we represent the expression (22) in the form

$$\frac{1}{T_1} = \frac{2\pi}{N} \sum_{\mathbf{R}(\alpha)} \left\{ \frac{9}{8} d^2 \langle O^{-1}(\mathbf{R}(\alpha)) | O^1(\mathbf{R}(\alpha)) \rangle_a + \frac{9}{2} d^2 \langle O^{-2}(\mathbf{R}(\alpha)) | O^{+2}(\mathbf{R}(\alpha)) \rangle_{2a} + \frac{c^2}{2} \langle J^-(\mathbf{R}(\alpha)) | J^+(\mathbf{R}(\alpha)) \rangle_a \right\}. \quad (23)$$

Here, $\langle \dots | \dots \rangle_a$ is the time Fourier transform of the corresponding correlation function taken at the point $\omega = a$. Since a is very small compared with the libron energies, we shall henceforth assume that it vanishes.

The expression (23) is written down in a coordinate system related to the external magnetic field. We note that it can be reduced to the expression used in [12]. In order to calculate the relaxation time below the phase transition point, we write the relation (24) in the sublattice coordinate system

$$\frac{1}{T_1} = \frac{2\pi}{N} \sum_{\mathbf{R}(\alpha)} \left\{ \frac{9}{2} d^2 \sum_{m, n=-2}^2 \left[R_{n, m}^{+2, -2} \langle O^m(\mathbf{R}(\alpha)) | O^n(\mathbf{R}(\alpha)) \rangle_{2a} \right. \right. \\ \left. \left. + \frac{1}{4} R_{n, m}^{+1, -1} \langle O^m(\mathbf{R}(\alpha)) | O^n(\mathbf{R}(\alpha)) \rangle_a \right] + \frac{c^2}{2} \sum_{m, n=-1}^1 T_{n, m}^{+1, -1} \langle J^m(\mathbf{R}(\alpha)) | J^n(\mathbf{R}(\alpha)) \rangle_a \right\}. \quad (24)$$

Here, we have introduced the notation

$$R_{nm}^{n'm'}(\alpha) = \frac{A_n A_m}{A_{n'} A_{m'}} D_{nn'}^{2^*}(\varphi_\alpha, \theta_\alpha, 0) D_{mm'}^{2^*}(\varphi_\alpha, \theta_\alpha, 0), \\ m, n = \pm 2, \pm 1, 0, \\ A_0 = -\frac{1}{5} \left(\frac{5}{4\pi} \right)^{1/2}, \quad A_{\pm 1} = \pm \frac{1}{10} \left(\frac{15}{2\pi} \right)^{1/2}, \quad A_{\pm 2} = -\frac{1}{10} \left(\frac{15}{2\pi} \right)^{1/2}; \\ T_{nm}^{n'm'}(\alpha) = \frac{B_n B_m}{B_{n'} B_{m'}} D_{nn'}^{1^*}(\varphi_\alpha, \theta_\alpha, 0) D_{mm'}^{1^*}(\varphi_\alpha, \theta_\alpha, 0), \\ m, n = \pm 1, 0,$$

$$B_0 = \left(\frac{3}{4\pi}\right)^{1/2}, \quad B_{\pm 1} = \mp \left(\frac{3}{4\pi}\right)^{1/2} \frac{1}{\sqrt{2}},$$

where θ_α and φ_α are the axial and azimuthal angles of the quantization axis in the sublattice α .

4. CALCULATION OF THE TIME OF SPIN-LATTICE RELAXATION BELOW THE PHASE TRANSITION POINT

The spectral intensities of the correlation functions occurring in Eq. (24) can only be calculated with difficulty on the basis of the random phase approximation developed in Section 2. The difficulties that arise are of the same nature as those in the calculation of a correlation function of the "density-density" type in the Heisenberg model. We first write the expression (24) in the form

$$\frac{1}{T_1} = \frac{2\pi}{N} \sum_{\mathbf{k}, \alpha} \left\{ \frac{9d^2}{2} \sum_{m, n = \pm 2, 0} \left[R_{m, n}^{+2, -2}(\alpha) + \frac{1}{4} R_{m, n}^{+1, -1}(\alpha) \right] \right. \\ \left. \times \langle O_\alpha^n(\mathbf{k}) | O_\alpha^m(-\mathbf{k}) \rangle_{\omega=0} + T_{00}^{+1, -1} \frac{c^2}{2} \langle J_\alpha^z(\mathbf{k}) | J_\alpha^z(-\mathbf{k}) \rangle_{\omega=0} \right\}. \quad (25)$$

All the spectral intensities with $m, n = \pm 1$ have been omitted since they are not responsible for Raman processes. In order to calculate the spectral intensities that occur in this expression, we adopt an approximation of the following type. Consider, for example, $\langle O_\alpha^{-2}(\mathbf{k}) | O_\alpha^{+2}(-\mathbf{k}) \rangle_{\omega=0}$

$$\frac{1}{N} \sum_{\mathbf{k}} \int_{-\infty}^{\infty} \langle O_\alpha^{-2}(\mathbf{k}) O_\alpha^{+2}(-\mathbf{k}, t) \rangle dt \\ = \frac{1}{N^2} \sum_{\mathbf{k}} \sum_{\mathbf{q}, \mathbf{q}_1} \int_{-\infty}^{\infty} \langle J_\alpha^-(\mathbf{k}-\mathbf{q}) J_\alpha^-(\mathbf{q}) J_\alpha^+(-\mathbf{k}-\mathbf{q}_1, t) J_\alpha^+(\mathbf{q}_1, t) \rangle dt \\ \approx \frac{2}{N^2} \sum_{\mathbf{k}, \mathbf{q}} \int_{-\infty}^{\infty} d\omega I_{J^+J^-}(-\omega, \mathbf{k}-\mathbf{q}, \alpha) I_{J^+J^-}(\omega, \mathbf{q}, \alpha), \quad (26)$$

i. e., we shall ignore the fourfold correlators of the operators J^\pm which cannot be expressed in terms of binary correlators. As an example, we shall also calculate $\langle O_\alpha^0(\mathbf{k}) O_\alpha^0(-\mathbf{k}) \rangle_{\omega=0}$:

$$\frac{1}{N} \sum_{\mathbf{k}} \int_{-\infty}^{\infty} \langle O_\alpha^0(\mathbf{k}) O_\alpha^0(-\mathbf{k}, t) \rangle dt \approx \frac{9}{N^2} \sum_{\mathbf{k}, \mathbf{q}} \left\{ \int_{-\infty}^{\infty} d\omega I_{J^+J^-}(-\omega, \mathbf{k}-\mathbf{q}, \alpha) \right. \\ \left. \times I_{J^+J^-}(\omega, \mathbf{q}, \alpha) + \int_{-\infty}^{\infty} d\omega I_{J^+J^-}(-\omega, \mathbf{k}-\mathbf{q}, \alpha) I_{J^+J^+}(\omega, \mathbf{q}, \alpha) \right\}. \quad (27)$$

All the correlation functions occurring in the expression (25) can be represented in the form of fourfold correlators of the operators J^\pm and estimated in accordance with their type by (26) and (27).

As an example, we give one expression for the convolution of spectral intensities:

$$\sum_{\mathbf{k}, \mathbf{q}} \int_{-\infty}^{\infty} I_{J^+J^-}(-\omega, \mathbf{k}-\mathbf{q}, \alpha) I_{J^+J^-}(\omega, \mathbf{q}, \alpha) d\omega = \frac{4}{(19T)^2} \sum_{\mathbf{k}, \mathbf{q}} \sum_{\lambda, \lambda'} |V_{\alpha\lambda}(\mathbf{k}-\mathbf{q})|^2 |V_{\alpha\lambda'}(\mathbf{q})|^2 \\ \times \frac{[e^{i\omega\lambda'(\mathbf{q})} + e^{i\omega\lambda(\mathbf{k}-\mathbf{q})}] \omega_\lambda(\mathbf{k}-\mathbf{q}) \omega_{\lambda'}(\mathbf{q})}{(e^{i\omega\lambda(\mathbf{k}-\mathbf{q})} - 1)(e^{i\omega\lambda'(\mathbf{q})} - 1)} \delta(\omega_\lambda(\mathbf{k}-\mathbf{q}) - \omega_{\lambda'}(\mathbf{q})). \quad (28)$$

We introduce the notation $\mathbf{k}-\mathbf{q} = \mathbf{k}; \mathbf{q} = \mathbf{k}_1; z = -19T/2 \langle O^0 \rangle$. We make the substitution

$$\frac{1}{N} \sum_{\mathbf{k}} \rightarrow \frac{\Omega}{(2\pi)^3} \int_{\Omega^*} d^3\mathbf{k},$$

where Ω^* is the volume of the first Brillouin zone and Ω is the volume of the unit cell.

Equation (28) can then be rewritten in the form

$$- \frac{2}{19T} \langle O^0 \rangle \frac{\Omega^2}{(2\pi)^6} \int_{\Omega^*} d^3\mathbf{k} d^3\mathbf{k}_1 \sum_{\lambda\lambda'} |V_{\alpha\lambda}(\mathbf{k})|^2 |V_{\alpha\lambda'}(\mathbf{k}_1)|^2 F_{\lambda\lambda'}(\mathbf{k}, \mathbf{k}_1), \quad (29)$$

where

$$F_{\lambda\lambda'}(\mathbf{k}, \mathbf{k}_1) = \frac{(e^{\beta z \varepsilon_\lambda(\mathbf{k})} + e^{\beta z \varepsilon_{\lambda'}(\mathbf{k}_1)}) \varepsilon_\lambda(\mathbf{k}) \varepsilon_{\lambda'}(\mathbf{k}_1)}{(e^{\beta z \varepsilon_\lambda(\mathbf{k})} - 1)(e^{\beta z \varepsilon_{\lambda'}(\mathbf{k}_1)} - 1)} \delta[\varepsilon_\lambda(\mathbf{k}) - \varepsilon_{\lambda'}(\mathbf{k}_1)]. \quad (30)$$

Calculating the spectral intensities of the type (26) and (27) that occur in the relation (25) and writing the corresponding convolutions in accordance with (29), we represent the expression (25) in the form

$$\frac{1}{T_1} = \frac{18\pi d^2}{19\Gamma} |\langle O^0 \rangle| \frac{\Omega^2}{(2\pi)^6} \sum_{\lambda, \lambda'} \int_{\Omega^*} d^3\mathbf{k} d^3\mathbf{k}_1 G_{\lambda\lambda'}(\mathbf{k}, \mathbf{k}_1) F_{\lambda\lambda'}(\mathbf{k}, \mathbf{k}_1). \quad (31)$$

The quantity $G_{\lambda\lambda'}(\mathbf{k}, \mathbf{k}_1)$ depends on the elements of the matrices \bar{R} and \bar{V} (see the Appendix) and, hence, on the lattice structure. In order to separate explicitly the temperature factor, we shall assume that the dependence of $G_{\lambda\lambda'}(\mathbf{k}, \mathbf{k}_1)$ on \mathbf{k} and \mathbf{k}_1 can be neglected. Introducing the spectrum densities (see also [13])

$$g_{\lambda}(\varepsilon) = \frac{\Omega}{(2\pi)^3} \int_{\varepsilon_{\lambda}(\mathbf{k})=\varepsilon} \frac{dS}{|\nabla_{\mathbf{k}}\varepsilon_{\lambda}(\mathbf{k})|},$$

we obtain finally

$$\frac{1}{T_1} = \frac{18\pi d^2}{19\Gamma} |\langle O^0 \rangle| \sum_{\lambda\lambda'} G_{\lambda\lambda'} F_{\lambda\lambda'}(\beta), \quad (32)$$

where

$$F_{\lambda\lambda'}(\beta) = 2 \int_{\varepsilon_{\min}}^{\varepsilon_{\max}} \frac{d\varepsilon e^{\beta z\varepsilon}}{(e^{\beta z\varepsilon} - 1)^2} \varepsilon^2 g_{\lambda}(\varepsilon) g_{\lambda'}(\varepsilon),$$

($\varepsilon_{\max} - \varepsilon_{\min}$) is the width of the band of libron waves and $G_{\lambda\lambda'}$ is a factor connected with the lattice structure.

5. DISCUSSION

Thus, we have obtained expressions for the reciprocal time of longitudinal nuclear spin-lattice relaxation in solid orthohydrogen in terms of the spectral intensities. These are very convenient for studying relaxation problems. The calculated relation for the relaxation time (31) enables one to consider this process in a wider range of temperatures than was possible in [13]. Estimates of the order of magnitude of the relaxation time agree with Homma's result [13]. Our results are based on a number of simplifying assumptions, such as, for example, (26) and (27), and they are therefore of a qualitative nature.

In a later paper, we intend to give the results of some numerical calculations and estimates.

Finally, we should like to point out that our results obtained in Section 2 give a very convenient and fairly simple method for treating the libron subsystem on the basis of the random phase approximation.

We should like to thank D. N. Zubarev and N. M. Plakida for assisting in the investigation. We are grateful to B. V. Vasil'ev and V. B. Priezhev for discussions.

Appendix

The exact expression for $G_{\lambda\lambda'}(\mathbf{k}, \mathbf{k}_1)$ has the form

$$\begin{aligned} G_{\lambda\lambda'}(\mathbf{k}, \mathbf{k}_1) = & \sum_{\alpha} \left\{ 2 \left[R_{+2, -2}^{+2, -2}(\alpha) + \frac{1}{4} R_{+2, +2}^{+1, -1}(\alpha) \right] (V_{\alpha\lambda}^{*2}(\mathbf{k}) V_{\alpha\lambda'}^{*2}(\mathbf{k}_1)) \right. \\ & + V_{\alpha\lambda}^2(\mathbf{k}) V_{\alpha\lambda'}^2(\mathbf{k}_1) + 9 \left[R_{0, 0}^{+2, -2}(\alpha) + \frac{1}{4} R_{0, 0}^{+1, -1}(\alpha) \right] (V_{\alpha\lambda}^{*2}(\mathbf{k}) V_{\alpha\lambda'}^2(\mathbf{k}_1)) \\ & + \left[2R_{+2, -2}^{+2, -2}(\alpha) + 2R_{-2, +2}^{+2, -2}(\alpha) + 9R_{0, 0}^{+2, -2}(\alpha) + \frac{1}{2} R_{+2, -2}^{+1, -1}(\alpha) \right. \\ & \left. + \frac{1}{2} R_{-2, +2}^{+1, -1}(\alpha) + \frac{9}{4} R_{0, 0}^{+1, -1}(\alpha) \right] (|V_{\alpha\lambda}(\mathbf{k})|^2 |V_{\alpha\lambda'}(\mathbf{k}_1)|^2) \\ & \left. - 6 \left[R_{+2, 0}^{+2, -2}(\alpha) + R_{0, +2}^{+2, -2}(\alpha) + \frac{1}{4} R_{+2, 0}^{+1, -1}(\alpha) + \frac{1}{4} R_{0, +2}^{+1, -1}(\alpha) \right] (V_{\alpha\lambda}^{*2}(\mathbf{k}) |V_{\alpha\lambda'}(\mathbf{k}_1)|^2 + V_{\alpha\lambda}^2(\mathbf{k}) |V_{\alpha\lambda'}(\mathbf{k}_1)|^2) \right\}. \end{aligned}$$

We have used the readily verifiable properties of the matrices \bar{R} .

LITERATURE CITED

1. T. Nakamura, *Progr. Theor. Phys.*, **14**, 135 (1955).
2. S. Homma, K. Okada, and H. Matsuda, *Progr. Theor. Phys.*, **38**, 767 (1967).

3. T. Matsubara and H. Ueyama, *Progr. Theor. Phys.*, 38, 784 (1967).
4. J. C. Raich and R. D. Ethers, *Phys. Rev.*, 168, 425 (1968).
5. J. C. Raich and R. D. Ethers, *Phys. Rev.*, 155, 457 (1967).
6. J. C. Raich and R. D. Ethers, *J. Phys. Chem. Solids*, 29, 1561 (1968).
7. K. Walasek, Preprint P4-4182 [in Russian], JINR, Dubna (1968).
8. A. B. Harris, *Solid St. Commun.*, 6, 149 (1968).
9. R. A. Tahir-Kheli, *Solid St. Commun.*, 6, 579 (1968).
10. W. N. Hardy, I. F. Silvera, and I. P. McTague, *Phys. Rev. Lett.*, 22, 297 (1969).
11. S. Homma and H. Matsuda, *Progr. Theor. Phys.*, 40, 1191 (1968).
12. T. Moriya and K. Motizuki, *Progr. Theor. Phys.*, 18, 183 (1957).
13. S. Homma, *Progr. Theor. Phys.*, 40, 1 (1968).
14. A. B. Harris and E. Hunt, *Phys. Rev. Lett.*, 16, 845 (1966).
15. M. J. Smith, D. White, and I. R. Gaines, *J. Chem. Phys.*, 49, 3317 (1968).
16. L. I. Amstutz, H. Meyer, S. M. Myers, and D. C. Rorer, *Phys. Rev.*, 181, 589 (1969).
17. J. Van Kranendonk and G. Karl, *Rev. Mod. Phys.*, 40, 531 (1968).
18. C. C. Sung, *Phys. Rev.*, 167, 271 (1968).
19. C. C. Sung, *Phys. Rev.*, 177, 435 (1969).
20. C. C. Sung, *Solid St. Commun.*, 6, 93 (1968).
21. J. C. Raich and H. M. James, *Phys. Rev. Lett.*, 16, 173 (1966).
22. H. M. James and J. C. Raich, *Phys. Rev.*, 162, 649 (1967).
23. O. Nagai and T. Nakamura, *Progr. Theor. Phys.*, 24, 432 (1960).
24. J. Felsteiner, *Phys. Rev. Lett.*, 15, 1025 (1965).
25. A. J. Berlinsky, A. B. Harris, and C. F. Coll., *Solid St. Commun.*, 7, 1491 (1969).
26. S. V. Tyablikov, *Methods of Quantum Theory of Magnetism*, Plenum Press, New York (1967).
27. K. Walasek and A. L. Kuzemsky, Preprint E4-4862, JINR, Dubna (1970).
28. D. N. Zubarev, *Dokl. Akad. Nauk SSSR*, 140, 92 (1961), *Teor. i Matem. Fiz.*, 1, 137 (1969).