NUCLEAR MAGNETIC RELAXATION IN SOLID HYDROGEN

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Formerly we[1] showed that the nuclear spin-lattice relaxation time T_1 is not due to Waller's process but to the following mechanisms:

1) Intramolecular dipole-dipole interaction.
2) Spin-orbit coupling.
3) Diffusion near the melting point.

Moriya-Motizuki[2] calculated the relaxation time T_1 by the same ideas. In the present paper we dealt with this problem by the different way of calculating. The result agreed with experimental values.

§1. Introduction

Solid hydrogen has many interesting problems, for example, the rotational transition[3][4] at 1.6° K (in the case of 75% ortho-concentration), the anomalous specific heat[3][5] (especially λ-type anomaly at the transition temperature), the ortho-para conversion[6] and the nuclear magnetic resonance[7].

Many authors[7] studied the nuclear magnetic relaxation both experimentally and theoretically. In particular, Sugawara investigated the temperature dependence and the ortho-concentration of nuclear spin-lattice relaxation time T_1 and he got the value $10^{-1}\sim10^{-3}$ sec. It is very short time in comparison with that of Waller's theory[8] ($10^{16}\sim10^{17}$ sec in the region of solid hydrogen). He observed also the line shape above the transition point and the magnitude of the line width was larger than the expected values given by the intermolecular dipole-dipole interaction. He found the reason that even above the transition point there is the local ordering and the side peak of the line width affects the magnitude of the line width. Rollin-Watson[7] showed experimentally that the magnitude of the line width is almost constantly 5.5 gauss in the region 1.5~9° K. But 3.5 gauss is the expected value from the intermolecular dipole-dipole interaction and this interaction will change it according to temperatures.

The present work will show that the nuclear spin-lattice relaxation time T_1 is due to the intramolecular dipole-dipole interaction in the region between the transition point and the below melting point as we showed before.[1] We shall deal them by some different way of calculating from the one before[1] and Moriya-Motizuki's work[2].

§2. Intramolecular Dipole-Dipole Interaction

We assume an uniform distribution of the ortho-molecules although the distribution will be actually random, and also assume the free rotation of the ortho-molecules.

The interactions between the spin system and the rotational system are the intramolecular dipole-dipole interaction and the spin-orbit interaction. The Hamiltonian is

$$\mathscr{H}'(\mathbf{I},\mathbf{J})=\sum_k \mathscr{H}'_k$$

$$=\sum_k\Big[a\Big\{3(\mathbf{I}_k\cdot\mathbf{J}_k)^2+\frac{3}{2}\mathbf{I}_k\cdot\mathbf{J}_k-I(I+1)J(J+1)\Big\}+c\mathbf{I}_k\cdot\mathbf{J}_k\Big], \tag{1}$$

where

$$a=\frac{\gamma^2\hbar^2}{5d^3}.$$

$\mathbf{I}_k$ is the nuclear spin the k-th proton, $\mathbf{J}_k$ the rotational angular momentum, a and c respectively the magnetic dipole-dipole interaction between the two protons in the molecule and the spin-orbit interaction, d the distance between the two protons in the molecule, γ the magneto-mechanical ratio in a proton.

Our consideration is only for the ortho-molecules. The rotational degeneracy temperature of hydrogen molecule is 86° K, and is sufficiently higher than the temperature of solid hydrogen. Therefore, the rotational state of ortho-molecule is almost in $J=I=1$.

We may rewrite Eq. (1) as

$$\mathscr{H}'_k=\sum_{\alpha=-2}^{2}\mathscr{H}'_{k\alpha}$$

$$=\sum_{\alpha=-2}^{2}\Phi_k^{\alpha}\{k\}_{-\alpha}+\sum_{\alpha=-1}^{1}\Psi_k^{\alpha}[k]_{-\alpha}, \tag{2}$$

$$\{k\}_0=3I_{kz}^2-I(I+1),\qquad \Phi_k^0=\frac{a}{2}[3J_{kz}^2-J(J+1)],$$

$$\{k\}_{\pm1}=I_{kz}I_{k\pm}+I_{k\pm}I_{kz},\qquad \Phi_k^{\pm1}=\frac{3a}{4}[J_{kz}J_{k\pm}+J_{k\pm}J_{kz}], \tag{2a}$$

$$\{k\}_{\pm2}=I_{k\pm}^2,\qquad \Phi_k^{\pm2}=\frac{3a}{4}J_{k\pm}^2,$$

$$[k]_0=I_{kz},\qquad \Psi_k^0=cJ_{kz}, \tag{2b}$$

$$[k]_{\pm1}=I_{k\pm},\qquad \Psi_k^{\pm1}=\frac{c}{2}J_{k\pm}.$$

Here we take the z-axis in the direction of the static magnetic field. The rotational system is a heat bath (on account of very large specific heat) and the energy dissipate to the rotational system through Eq. (1).

§ 3. The Hamiltonian of the Rotational System

Nakamura[9] found the intermolecular interactions in solid hydrogen by the analysis of the anomalous specific heat above the transition point.

Let us confine our consideration to the interactions between two nearest neighbouring molecules, the rotational orientation-dependent part of the intermolecular interaction is

$$\mathscr{H}_r = \sum_i \mathscr{H}_r(i) + \sum_{i>j} \mathscr{H}_r(r_{ij}), \tag{3}$$

$$\mathscr{H}_r(i) = -\left(4\lambda_0\lambda_2 V e^{-r_0/\rho} - \frac{2Q}{5r_0^6} + \frac{4R}{15r_0^6}\right)\sum_k (3J_{zi}^2 - 2)_k, \tag{3a}$$

$$\begin{aligned}\mathscr{H}_r(r) &= \left(\frac{8}{25}\frac{3e^2\mu_Q^2}{4r^5} + 4\lambda_2^2 V e^{-r/\rho} - \frac{2R}{25r^6}\right)(3J_{zi}^2-2)(3J_{zj}^2-2)\\ &-\left(\frac{8}{25}\frac{3e^2\mu_Q^2}{4r^5} - \frac{1}{25}\frac{2R}{r^6}\right)\{(J_{zi}J_{+i}+J_{+i}J_{zi})(J_{zj}J_{-j}+J_{-j}J_{zj})+(J_{zi}J_{-i}+J_{-i}J_{zi})(J_{zj}J_{+j}+J_{+j}J_{zj})\}\\ &+\frac{2}{25}\left(\frac{3e^2\mu_Q^2}{4r^5} - \frac{R}{2r^6}\right)(J_{+i}J_{+i}J_{-j}J_{-j} + J_{-i}J_{-i}J_{+j}J_{+j}),\end{aligned} \tag{3b}$$

where r_0 is the distance between two neighbouring molecules. In Eqs. (3a) and (3b) the terms of $4\lambda_0\lambda_2 V e^{-r_0/\rho}$ and $4\lambda_2^2 V e^{-r_0/\rho}$ represent the valence forces, r_0^{-6} and r^{-6} the van der Waals forces, and r^{-5} the quadrupole-quadrupole interactions. The index k in Eq. (3a) runs over all the nearest neighbours irrespectively of para- or ortho-molecule, and $(3J_{zi}^2-2)_k$ means that the quantization axis is along the line connecting i and j molecules. But the indices i and j in Eq. (3b) run over all the pairs of ortho-molecules neighbouring each other.

The numerical values in Eqs. (3a) and (3b) are as follows:

$$\begin{aligned}&4\lambda_0\lambda_2 V e^{-r_0/\rho} = 1.43\times10^{-16}\,\text{erg},\\ &4\lambda_2^2 V e^{-r_0/\rho} = 0.14\times10^{-16}\,\text{erg},\\ &\frac{Q}{r_0^6} = 2.72\times10^{-16}\,\text{erg},\\ &\frac{R}{r_0^6} = 0.77\times10^{-16}\,\text{erg},\\ &\frac{3e^2\mu_Q^2}{4r_0^5} = 2.82\times10^{-16}\,\text{erg},\\ &\mu_Q = 0.11\times10^{-16}\,\text{cm}^2,\\ &r_0 = 3.75\times10^{-8}\,\text{cm}.\end{aligned}$$

Therefore we shall find that the quadrupole-quadrupole interaction is exclusively responsible for the quenching of the rotational states.

§ 4. Relaxation Time

Our consideration is for the temperature region above the transition point and below about 10° K (above 10° K diffusion occurs), and we assume an uniform distribution and the free rotation of the ortho-molecules as stated above.

The expression of the relaxation time T_1 is given by Kubo-Tomita's theory[10]. The unperturbed Hamiltonian $\mathscr{H}_0$ is

$$\mathscr{H}_0 = \mathscr{H}_F + \mathscr{H}_r, \tag{4}$$

$$\mathscr{H}_F = -\gamma\hbar H_z \sum_k I_{kz} = -\hbar\omega_z \sum_k I_{kz}, \tag{4a}$$

where H_z is the static magnetic field. Nuclear spin system is affected by the $\mathscr{H}_r$

through $\mathscr{H}'$. We transform $\mathscr{H}'$:

$$\mathscr{H}'(t) = \exp\,(it\,\mathscr{H}_0/\hbar)\,\mathscr{H}'\exp\,(-it\,\mathscr{H}_0/\hbar)$$

$$= \sum_{\alpha=-2}^{2} \exp(i\alpha\omega_z t)\,\mathscr{H}'_\alpha(t), \tag{5}$$

$$\mathscr{H}'_\alpha(t) = \exp\,(it\,\mathscr{H}_r/\hbar)\,\mathscr{H}'_\alpha\exp\,(-it\,\mathscr{H}_r/\hbar), \tag{5a}$$

$$\mathscr{H}'_\alpha = \sum_k \mathscr{H}'_{k\alpha}.$$

The relaxation time T_1 is

$$\frac{1}{T_1} = \frac{1}{2\hbar^2}\sum_{\alpha=-2}^{2}\int_{-\infty}^{\infty}\alpha^2\hbar^2\omega_z^2\frac{\langle\mathscr{H}'_{-\alpha}(t)\,\mathscr{H}'_\alpha(0)\rangle}{\langle\mathscr{H}_F^2\rangle}\exp\,(i\alpha\omega_z t)dt, \tag{6}$$

where $\langle\ \rangle$ means the statistical average:

$$\langle\mathscr{H}'_{-\alpha}(t)\,\mathscr{H}'_\alpha(0)\rangle = \frac{Tre^{-\beta\mathscr{H}_0}\mathscr{H}'_{-\alpha}(t)\,\mathscr{H}'_\alpha(0)}{Tre^{-\beta\mathscr{H}_0}}, \tag{6a}$$

$$\langle\mathscr{H}_F^2\rangle = \hbar^2\omega_2^z\,\frac{Tre^{-\beta\mathscr{H}_0}\sum_k I_{kz}}{Tre^{-\beta\mathscr{H}_0}}, \tag{6b}$$

$$\beta = \frac{1}{kT}.$$

The temperature range of our consideration is high, therefore we can put $e^{-\beta\mathscr{H}_0} = 1$.

Now we shall calculate Eqs. (6a) and (6b), and expand Eq. (5a) as a power series of t, and we may get

$$\mathscr{H}'_{-\alpha}(t) = \mathscr{H}'_{-\alpha}(0) + t\dot{\mathscr{H}}'_{-\alpha}(0) + \frac{t^2}{2}\ddot{\mathscr{H}}'_{-\alpha}(0) + \cdots, \tag{7}$$

then

$$\langle\mathscr{H}'_{-\alpha}(t)\,\mathscr{H}'_\alpha(0)\rangle = \langle\mathscr{H}'_{-\alpha}(0)\,\mathscr{H}'_\alpha(0)\rangle + t\langle\dot{\mathscr{H}}'_{-\alpha}(0)\,\mathscr{H}'_\alpha(0)\rangle$$

$$+\frac{t^2}{2}\langle\ddot{\mathscr{H}}'_{-\alpha}(0)\,\mathscr{H}'_\alpha(0)\rangle + \cdots. \tag{8}$$

On the other hand,

$$\dot{\mathscr{H}}'_{-\alpha}(0) = -\frac{i}{\hbar}[\mathscr{H}'_{-\alpha}(0), \mathscr{H}_r]$$

$$\simeq -\frac{i}{\hbar}[\mathscr{H}'_{-\alpha}(0), \mathscr{H}_r], \tag{9}$$

because $\mathscr{H}_F \ll \mathscr{H}_r$ then $\mathscr{H} \simeq \mathscr{H}_r$.
Similarly

$$\ddot{\mathscr{H}}'_{-\alpha}(0) \simeq -\frac{i}{\hbar}[\dot{\mathscr{H}}'_{-\alpha}(t), \mathscr{H}_r]$$

$$\simeq -\frac{1}{\hbar^2}[[\mathscr{H}'_{-\alpha}(0), \mathscr{H}_r], \mathscr{H}_r]. \tag{10}$$

We then get

$$\langle \mathscr{H}'_{-\alpha}(t)\,\mathscr{H}'_{\alpha}(0)\rangle \simeq \langle \mathscr{H}'_{-\alpha}(0)\,\mathscr{H}'_{\alpha}(0)\rangle\Big(1-\frac{it}{\hbar}\frac{\langle[\mathscr{H}'_{-\alpha}(0),\,\mathscr{H}_r]\,\mathscr{H}'_{\alpha}(0)\rangle}{\langle \mathscr{H}'_{-\alpha}(0)\,\mathscr{H}'_{\alpha}(0)\rangle}$$

$$-\frac{t^2}{2\hbar^2}\frac{\langle[[\mathscr{H}'_{-\alpha}(0),\,\mathscr{H}_r],\,\mathscr{H}_r]\,\mathscr{H}'_{\alpha}(0)\rangle}{\langle \mathscr{H}'_{-\alpha}(0)\,\mathscr{H}'_{\alpha}(0)\rangle}+\cdots\Big) \tag{11}$$

$$\simeq \langle \mathscr{H}'_{-\alpha}(0)\,\mathscr{H}'_{\alpha}(0)\rangle \exp\Big\{-\frac{it}{\hbar}\frac{\langle[\mathscr{H}'_{-\alpha}(0),\,\mathscr{H}_r]\,\mathscr{H}'_{\alpha}(0)\rangle}{\langle \mathscr{H}'_{-\alpha}(0)\,\mathscr{H}'_{\alpha}(0)\rangle}$$

$$-\frac{t^2}{2\hbar^2}\Big(\frac{\langle[[\mathscr{H}'_{-\alpha}(0),\,\mathscr{H}_r],\,\mathscr{H}_r]\,\mathscr{H}'_{\alpha}(0)\rangle}{\langle \mathscr{H}'_{-\alpha}(0)\,\mathscr{H}'_{\alpha}(0)\rangle}-\frac{\langle[\mathscr{H}'_{-\alpha}(0),\,\mathscr{H}_r]\,\mathscr{H}'_{\alpha}(0)\rangle^2}{\langle \mathscr{H}'_{-\alpha}(0)\,\mathscr{H}'_{\alpha}(0)\rangle^2}\Big)\Big\}. \tag{12}$$

therefore

$$\frac{1}{T_1}=\frac{1}{2\hbar^2}\frac{(\hbar\omega_z)^2}{\langle\mathscr{H}^2_F\rangle}\sum_{\alpha=-2}^{2}\alpha^2\langle \mathscr{H}'_{-\alpha}(0)\,\mathscr{H}'_{\alpha}(0)\rangle\int_{-\infty}^{\infty}\exp\Big\{it\Big(\alpha\omega_z-\frac{\langle[\mathscr{H}'_{-\alpha}(0),\,\mathscr{H}_r]\mathscr{H}'_{\alpha}(0)\rangle}{\hbar\langle \mathscr{H}'_{-\alpha}(0)\,\mathscr{H}'_{\alpha}(0)\rangle}\Big)$$

$$-\frac{t^2}{2\hbar^2}\Big(\frac{\langle[[\mathscr{H}'_{-\alpha}(0),\,\mathscr{H}_r],\,\mathscr{H}_r]\,\mathscr{H}'_{\alpha}(0)\rangle}{\langle \mathscr{H}'_{-\alpha}(0)\,\mathscr{H}'_{\alpha}(0)\rangle}-\frac{\langle[\mathscr{H}'_{-\alpha}(0),\,\mathscr{H}_r]\,\mathscr{H}'_{\alpha}(0)\rangle^2}{\langle \mathscr{H}'_{-\alpha}(0)\,\mathscr{H}'_{\alpha}(0)\rangle^2}\Big)\Big\}dt$$

$$=\frac{1}{\hbar}\sqrt{\frac{\pi}{2}}\frac{(\hbar\omega_z)^2}{\langle\mathscr{H}^2_F\rangle}\sum_{\alpha=-2}^{2}\alpha^2\frac{\langle \mathscr{H}'_{-\alpha}(0)\,\mathscr{H}'_{\alpha}(0)\rangle}{\Big\{\frac{\langle[[\mathscr{H}'_{-\alpha}(0),\,\mathscr{H}_r],\,\mathscr{H}_r]\mathscr{H}'_{\alpha}(0)\rangle}{\langle \mathscr{H}'_{-\alpha}(0)\,\mathscr{H}'_{\alpha}(0)\rangle}-\Big(\frac{\langle[\mathscr{H}'_{-\alpha}(0),\,\mathscr{H}_r]\,\mathscr{H}'_{\alpha}(0)\rangle}{\langle \mathscr{H}'_{-\alpha}(0)\,\mathscr{H}'_{\alpha}(0)\rangle}\Big)^2\Big\}^{1/2}}$$

$$\times\exp\left\{-\frac{1}{2}\frac{\Big(\alpha\hbar\omega_z-\frac{\langle[\mathscr{H}'_{-\alpha}(0),\,\mathscr{H}_r]\,\mathscr{H}'_{\alpha}(0)\rangle}{\langle \mathscr{H}'_{-\alpha}(0)\,\mathscr{H}'_{\alpha}(0)\rangle}\Big)^2}{\frac{\langle[[\mathscr{H}'_{-\alpha}(0),\,\mathscr{H}_r],\,\mathscr{H}_r]\mathscr{H}'_{\alpha}(0)\rangle}{\langle \mathscr{H}'_{-\alpha}(0)\,\mathscr{H}'_{\alpha}(0)\rangle}-\Big(\frac{\langle[\mathscr{H}'_{-\alpha}(0),\,\mathscr{H}_r]\,\mathscr{H}'_{\alpha}(0)\rangle}{\langle \mathscr{H}'_{-\alpha}(0)\,\mathscr{H}'_{\alpha}(0)\rangle}\Big)^2}\right\}. \tag{13}$$

§5. Calculation of the Relaxation Time

We shall now calculate the relaxation time represented by Eq. (13). In the considered high temperature region, the anomalous specific heat per molecule, C_V, is

$$C_V=\frac{d\langle E\rangle}{dT}=\frac{d}{dT}\frac{Tr e^{-\beta\mathscr{H}_0}\mathscr{H}_r}{Tr e^{-\beta\mathscr{H}_0}}$$

$$=\frac{1}{kT^2}\Big\{\frac{Tr e^{-\beta\mathscr{H}_0}\mathscr{H}_r^2}{Tr e^{-\beta\mathscr{H}_0}}-\Big(\frac{Tr e^{-\beta\mathscr{H}_0}\mathscr{H}_r}{Tr e^{-\beta\mathscr{H}_0}}\Big)^2\Big\}$$

$$=\frac{1}{kT^2}(\langle\mathscr{H}_r^2\rangle-\langle\mathscr{H}_r\rangle^2), \tag{14}$$

where $\langle E\rangle$ is the internal energy, T the absolute temperature, k Boltzmann constant. According to Nakamura's analysis[9] we may get

$$\Gamma\equiv\frac{C_V T^2}{k}\simeq 1.1\,c+15.7\,c^2, \tag{15}$$

where c is the ortho-concentration. Then we have

$$\langle\mathscr{H}_r^2\rangle-\langle\mathscr{H}_r\rangle^2=C_V kT^2=k^2\Gamma. \tag{16}$$

From Reif-Purcell's theory[7] we can consider that

$$\langle \mathscr{H}'_{-\alpha}(0)\, \mathscr{H}'_{\alpha}(0) \rangle \simeq (\hbar\omega_p)^2 = (2\pi\hbar a)^2 \simeq 1.46\times 10^{-43}\,\mathrm{erg}^2, \tag{17}$$

and considering high temperature ($\omega\hbar_z \ll kT$)

$$\langle \mathscr{H}^2_{\Gamma} \rangle \simeq (\hbar\omega_z)^2 \Big(\frac{1}{3} \sum_{Iz=-1}^{1} I_z^2 \Big) = \frac{2}{3} (\hbar\omega_z)^2. \tag{18}$$

Now we may approximately rewrite Eq. (13), considering $\alpha\hbar\omega_z \ll \langle \mathscr{H}_r \rangle$,

$$\frac{1}{T_1} \simeq \frac{1}{\hbar} \sqrt{\frac{\pi}{2}} \frac{(\hbar\omega_z)^2}{\langle \mathscr{H}^2_{\Gamma} \rangle} \sum_{\alpha=-2}^{2} \alpha^2 \frac{\langle \mathscr{H}'_{-\alpha}(0) \mathscr{H}'_{\alpha}(0) \rangle}{(\langle \mathscr{H}^2_r \rangle - \langle \mathscr{H}_r \rangle^2)^{1/2}} \exp\Big\{ -\frac{1}{2} \frac{\langle \mathscr{H}_r \rangle^2}{\langle \mathscr{H}^2_r \rangle - \langle \mathscr{H}_r \rangle^2} \Big\}. \tag{19}$$

Substituting Eqs. (16), (17) and (18) into Eq. (19), and taking $\langle \mathscr{H}_r \rangle^2 \simeq (2.82\times 10^{-16})^2\,\mathrm{erg}^2$, we have

$$T_1 = 5.30\times 10^{-2} \sqrt{\Gamma}\, \exp\frac{2.09}{\Gamma} \tag{20}$$

where

$$\Gamma \equiv \frac{C_V T^2}{k} \simeq 1.1\,c + 15.7\,c^2.$$

Then we get

$$T_1 \simeq 0.2\,\mathrm{sec} \qquad (\text{for } c = 0.74,\ 3 < T < 9^\circ\,\mathrm{K}), \tag{21}$$

and we shall also show the curves for T_1 versus T.

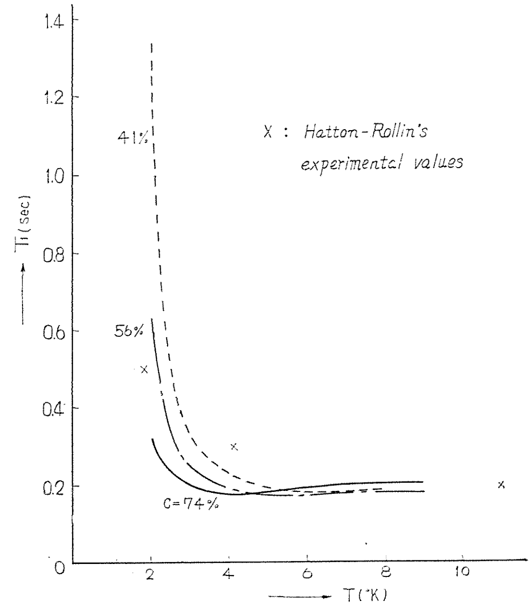

FIG. 1. Curves for T_1 versus T.

The theoretical values agreed with the experimental values given by Hatton-Rollin[7].

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