Theory of Rotational Excitations in Solid Ortho-Hydrogen*⁾

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A theoretical study is made on the rotational excitations in solid fcc ortho-hydrogen below T_λ. The effective Hamiltonian which is quadratic in the rotational excitation operators of each molecule is set up by the method analogous to the Holstein-Primakoff theory of spin waves. The dispersion relation and the energy spectrum of the rotational excitation mode are obtained by the perturbational calculation. The expectation value of the angular momentum of each molecule generally vanishes in each energy eigenstate and the excited states can approximately be described in terms of quasi-particles for librational excitation which may be called librons. At 0°K libron has a minimum excitation energy of about $10k_B$ and band width of about $5k_B$. The thermodynamic quantities such as free energy are numerically calculated using the state density, and the phase transition is estimated to be of first order and $T_\lambda \simeq 4.2°K$.

§ 1. Introduction

Solid hydrogen has a specific-heat anomaly at high ortho-hydrogen concentrations ($\geq 60\%$).[1] Corresponding to this anomaly there is a change in the shape of the nuclear magnetic resonance absorption.[2] It has been pointed out that this anomaly may be associated with a rotational order-disorder transition of ortho-molecules.[3] The rotational constant of H_2 is 86°K, and is sufficiently higher than the melting temperature 13°K, so that the rotational state of ortho-hydrogen in the solid may always be considered to be in the subspace $J=1$. In this subspace Nakamura[4] has shown that the electric quadrupole-quadrupole interaction between ortho-molecules is the most important contribution to the energy of ordering. Thus, the ordered orientation of molecules in solid ortho-hydrogen would be in the lowest state of the quadrupole-quadrupole interaction between the molecules.

For a face-centered cubic structure (fcc) this lowest state was obtained classically by Nagai and Nakamura[5] (N-N model), generalizing Luttinger and Tisza's method. For a hexagonal close-packed structure (hcp) Danielian[6] proposed an ordered configuration of molecules using the Hartree approximation under the assumption that the quantization axis of angular momentum of each

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molecule is parallel to the hexagonal axis. Although the energy of the ground state obtained by Danielian is somewhat lower than that of the configuration assumed in the previous works,[7] the assumption of the parallel quantization axis can hardly be justified. On the other hand, Felsteiner[8] has shown by extending Nagai and Nakamura's classical calculation that the energy of the lowest state is lower in fcc than hcp, confirming the ordered orientations of molecules in fcc proposed by the previous authors. This result suggests that molecules in pure solid ortho-hydrogen at 0°K will prefer to form fcc rather than hcp. Experimental observations of infrared absorption spectrum[9] and X-ray photographs[10] seem to support the above suggestion.

According to such classical calculation for the lowest state in fcc, there are four distinct sublattices in each of which the quadrupoles are aligned along a different body diagonal of the cubic unit cell. Quantum-mechanically the classical lowest state can be interpreted as the ground state of the Hartree approximation in which each sublattice has its own quantization axis (Z-axis) of the angular momentum along the different body diagonal of the cubic unit cell and each molecule in the sublattice is in the state $J_z = 0$.

In this paper we discuss low-lying rotational excited states in fcc taking the above state as a first approximation for the lowest ordered state. Here, we are primarily concerned with the rotational states, so that we consider the model in which the center of gravity of each molecule is held fixed at the rigid fcc lattice point. The present problem is similar to the spin-wave theory of anti-ferromagnetism, because the lattice has a sublattice structure and the ground state in the Hartree approximation is the ordered state but not the exact ground state of the system. An important difference is that the approximate ground state is here described by $J_z = 0$ instead of $J_z = \pm J$ as in the usual spin wave theory.

In § 2 we derive the effective Hamiltonian H_{eff} for discussing such low-lying excited states corresponding to the Holstein-Primakoff theory of spin waves. Although one might be able to diagonalize H_{eff} by extending the Bogoliubov transformation as in the case of the spin wave theory, it seems rather complex because of the presence of the four sublattices. Therefore, as a first step toward the complete solution we obtain in § 3 the excited states using a perturbation theory. Then, the excited state is analogous to a rotational exciton state obtained by Van Kranendonk in solid para-hydrogen.[11] We calculate dispersion relation and state density of the excitation modes.

After discussing in § 4 the nature of the excited states thus obtained, in § 5 we calculate thermodynamic quantities based on these excited states. The last section § 6 is devoted to discussion. In the Appendix we show that the ground state obtained by Danielian in hcp not only has a higher energy than that recently obtained by Miyagi and Nakamura[12] but also is unstable for excitations, so that the Danielian model cannot be considered to be valid.

§ 2. The effective Hamiltonian for low-lying rotational excited states

The quadrupole interaction energy between the two ortho-hydrogens labelled as i and j with quadrupole moment μ_Q can be written in the subspace $J=1$ as

$$V_{ij} = (8/25)\,(3e^2\mu_Q^2/4r^5)f_{ij}\,, \tag{2·1}$$

$$f_{ij} = (3J_{zi}^2 - 2)(3J_{zi}^2 - 2)$$
$$- \{(J_{zi}J_{+i} + J_{+i}J_{zi})(J_{zj}J_{-j} + J_{-j}J_{zi}) + \text{c.c.}\}$$
$$+ \frac{1}{4}(J_{+i}^2 J_{-j}^2 + \text{c.c.})\,, \tag{2·2}$$

where the x, y, and z axes are so chosen that the z-axis is parallel to the line connecting the two molecules separated by a distance r.

The Hamiltonian of the system is given by

$$H = \sum_{\langle i,j \rangle} f_{ij}\,, \tag{2·3}$$

where $\sum_{\langle i,j \rangle}$ denotes the summation over all pairs of nearest neighbor molecules and we use $(8/25)\,(3\,e^2\mu_Q^2/4r^5)$ as a unit of energy. This approximation is fairly good because the ground state energy per molecule in this approximation is $4.12\,k_B$ whereas that of the N-N model is $4.65\,k_B$.[12] The kinetic energy being a constant of motion in the subspace $J=1$, we can neglect it in the H. To get the effective Hamiltonian H_{eff} for the N-N model we rewrite the components of angular momentum operators of each molecule in Eq. (2·2) in terms of the angular momentum operators of molecules whose components are written in their respective sublattice coordinate systems.

We introduce the following three coordinate systems:

1) The crystal coordinate system whose axes are parallel to the cubic axes of the crystal.

2) The sublattice coordinate system in which Z-axis is parallel to the quantization axis of the sublattice. The N-N model is composed of four sublattices in each of which the quantization axis is along the different body diagonal of the cubic unit cell.

3) The bond coordinate system in which z-axis is parallel to the line connecting the nearest neighbor molecules (i) and (j) which belong to the sublattice (α) and (β), respectively. The quantity f_{ij} given by (2·2) is written in terms of the components of angular momentum operators defined in the bond coordinate system. In the N-N model we have twelve different bond coordinate systems.

We denote the components of angular momentum operators in these three coordinate systems by the components of the column vector $\boldsymbol{J}_c$, $\boldsymbol{J}_s^{(\alpha)}$, and $\boldsymbol{J}_b^{(l)}$ respectively; where subscript c, s, and b mean crystal, sublattice and bond,

Table I.

$$S^{(\mathrm{I})}=\begin{pmatrix} 0 & \sqrt{\dfrac{2}{3}} & \dfrac{1}{\sqrt{3}} \\[2mm] -\dfrac{1}{\sqrt{2}} & -\dfrac{1}{\sqrt{6}} & \dfrac{1}{\sqrt{3}} \\[2mm] \dfrac{1}{\sqrt{2}} & -\dfrac{1}{\sqrt{6}} & \dfrac{1}{\sqrt{3}} \end{pmatrix} \qquad S^{(\mathrm{II})}=\begin{pmatrix} 0 & \sqrt{\dfrac{2}{3}} & -\dfrac{1}{\sqrt{3}} \\[2mm] \dfrac{1}{\sqrt{2}} & \dfrac{1}{\sqrt{6}} & \dfrac{1}{\sqrt{3}} \\[2mm] \dfrac{1}{\sqrt{2}} & \dfrac{-1}{\sqrt{6}} & -\dfrac{1}{\sqrt{3}} \end{pmatrix}$$

$$S^{(\mathrm{III})}=\begin{pmatrix} \dfrac{1}{\sqrt{2}} & \dfrac{1}{\sqrt{6}} & \dfrac{1}{\sqrt{3}} \\[2mm] \dfrac{1}{\sqrt{2}} & -\dfrac{1}{\sqrt{6}} & -\dfrac{1}{\sqrt{3}} \\[2mm] 0 & \sqrt{\dfrac{2}{3}} & -\dfrac{1}{\sqrt{3}} \end{pmatrix} \qquad S^{(\mathrm{IV})}=\begin{pmatrix} \dfrac{1}{\sqrt{2}} & -\dfrac{1}{\sqrt{6}} & -\dfrac{1}{\sqrt{3}} \\[2mm] 0 & \sqrt{\dfrac{2}{3}} & -\dfrac{1}{\sqrt{3}} \\[2mm] \dfrac{1}{\sqrt{2}} & \dfrac{1}{\sqrt{6}} & \dfrac{1}{\sqrt{3}} \end{pmatrix}$$

Table II.

$$B^{(1)}=\begin{pmatrix} -1 & 0 & 0 \\[2mm] 0 & -\dfrac{1}{\sqrt{2}} & \dfrac{1}{\sqrt{2}} \\[2mm] 0 & \dfrac{1}{\sqrt{2}} & \dfrac{1}{\sqrt{2}} \end{pmatrix} \qquad B^{(2)}=\begin{pmatrix} -1 & 0 & 0 \\[2mm] 0 & \dfrac{1}{\sqrt{2}} & \dfrac{1}{\sqrt{2}} \\[2mm] 0 & \dfrac{1}{\sqrt{2}} & -\dfrac{1}{\sqrt{2}} \end{pmatrix}$$

$$B^{(3)}=\begin{pmatrix} 0 & 0 & -1 \\[2mm] -\dfrac{1}{\sqrt{2}} & \dfrac{1}{\sqrt{2}} & 0 \\[2mm] \dfrac{1}{\sqrt{2}} & \dfrac{1}{\sqrt{2}} & 0 \end{pmatrix} \qquad B^{(4)}=\begin{pmatrix} 0 & 0 & -1 \\[2mm] \dfrac{1}{\sqrt{2}} & \dfrac{1}{\sqrt{2}} & 0 \\[2mm] \dfrac{1}{\sqrt{2}} & -\dfrac{1}{\sqrt{2}} & 0 \end{pmatrix}$$

$$B^{(5)}=\begin{pmatrix} 0 & -1 & 0 \\[2mm] \dfrac{1}{\sqrt{2}} & 0 & -\dfrac{1}{\sqrt{2}} \\[2mm] \dfrac{1}{\sqrt{2}} & 0 & \dfrac{1}{\sqrt{2}} \end{pmatrix} \qquad B^{(6)}=\begin{pmatrix} 0 & -1 & 0 \\[2mm] \dfrac{1}{\sqrt{2}} & 0 & \dfrac{1}{\sqrt{2}} \\[2mm] -\dfrac{1}{\sqrt{2}} & 0 & \dfrac{1}{\sqrt{2}} \end{pmatrix}$$

$$B^{(7)}=\begin{pmatrix} -1 & 0 & 0 \\[2mm] 0 & \dfrac{1}{\sqrt{2}} & -\dfrac{1}{\sqrt{2}} \\[2mm] 0 & -\dfrac{1}{\sqrt{2}} & -\dfrac{1}{\sqrt{2}} \end{pmatrix} \qquad B^{(8)}=\begin{pmatrix} -1 & 0 & 0 \\[2mm] 0 & -\dfrac{1}{\sqrt{2}} & -\dfrac{1}{\sqrt{2}} \\[2mm] 0 & -\dfrac{1}{\sqrt{2}} & \dfrac{1}{\sqrt{2}} \end{pmatrix}$$

$$B^{(9)}=\begin{pmatrix} 0 & 0 & -1 \\[2mm] \dfrac{1}{\sqrt{2}} & -\dfrac{1}{\sqrt{2}} & 0 \\[2mm] -\dfrac{1}{\sqrt{2}} & -\dfrac{1}{\sqrt{2}} & 0 \end{pmatrix} \qquad B^{(10)}=\begin{pmatrix} 0 & 0 & -1 \\[2mm] -\dfrac{1}{\sqrt{2}} & -\dfrac{1}{\sqrt{2}} & 0 \\[2mm] -\dfrac{1}{\sqrt{2}} & \dfrac{1}{\sqrt{2}} & 0 \end{pmatrix}$$

$$B^{(11)}=\begin{pmatrix} 0 & -1 & 0 \\[2mm] -\dfrac{1}{\sqrt{2}} & 0 & \dfrac{1}{\sqrt{2}} \\[2mm] -\dfrac{1}{\sqrt{2}} & 0 & -\dfrac{1}{\sqrt{2}} \end{pmatrix} \qquad B^{(12)}=\begin{pmatrix} 0 & -1 & 0 \\[2mm] -\dfrac{1}{\sqrt{2}} & 0 & -\dfrac{1}{\sqrt{2}} \\[2mm] \dfrac{1}{\sqrt{2}} & 0 & -\dfrac{1}{\sqrt{2}} \end{pmatrix}$$

Table III.

l	1	2	3	4	5	6	7	8	9	10	11	12
i	I	I	I	I	I	I	III	III	II	II	II	II
j	II	II	III	III	IV	IV	IV	IV	IV	IV	III	III

superscript (α) is the label of sublattice, and (l) represents one of the different twelve bond systems.

The transformation equations between these vectors $\boldsymbol{J}_{\mathrm{c}}$, $\boldsymbol{J}_{\mathrm{s}}^{(\alpha)}$ and $\boldsymbol{J}_{\mathrm{b}}^{(l)}$ are

$$\boldsymbol{J}_{\mathrm{b}}^{(l)} = \boldsymbol{B}^{(l)} \boldsymbol{J}_{\mathrm{c}} ,$$

$$\boldsymbol{J}_{\mathrm{c}} = \boldsymbol{S}^{(\alpha)} \boldsymbol{J}_{\mathrm{s}}^{(\alpha)} ,$$

hence

$$\boldsymbol{J}_{\mathrm{b}}^{(l)} = \boldsymbol{B}^{(l)} \boldsymbol{S}^{(\alpha)} \boldsymbol{J}_{\mathrm{s}}^{(\alpha)} . \tag{2.4}$$

We tabulate the transformation matrices $\boldsymbol{S}^{(\alpha)}$ and $\boldsymbol{B}^{(l)}$ appropriate to the N-N model in Tables I and II, and give in Table III the combination of the sublattice (α) and (β) connected by the bond (l).

Associating two kinds of boson annihilation operators x_i and x_{-i} to each molecule (here, the i-th molecule), we can write in the subspace $J=1$ that

$$J_{\mathrm{z}i} = x_i{}^+ x_i - x_{-i}^+ x_{-i} ,$$

$$J_{+i} = \sqrt{2} (1 - x_{-i}^+ x_{-i}) (x_i{}^+ + x_{-i}) (1 - x_i{}^+ x_i), \tag{2.5}$$

$$J_{-i} = J_{+i}^+ .$$

The state $J_{\mathrm{z}i} = 0$ is represented by $|00\rangle$ or the vacuum state of the boson field, whereas the states $J_{\mathrm{z}i} = \pm 1$ correspond to $|10\rangle \equiv x_i{}^+|00\rangle$, and $|01\rangle \equiv x_{-i}^+|00\rangle$, respectively. The feature of our operator is that the matrix element $\langle n'm'|J|nm\rangle$ calculated by using Eq. (2.5) for $|nm\rangle = |10\rangle$, $|00\rangle$ or $|01\rangle$ not only coincides with the exact matrix elements of $\boldsymbol{J}$ between the corresponding states but also is non-zero only when $|n'm'\rangle$ is $|10\rangle$, $|00\rangle$ or $|01\rangle$. This shows the fact that the operator given by Eq. (2.5) leaves the space spanned by $|10\rangle$, $|00\rangle$ and $|01\rangle$ invariant.

If the Hartree approximation such that $J_{\mathrm{z}i} = 0$ for all i in the ground state is a good one, we may say that bosons are not very much excited at low temperatures. We, then, linearize the right-hand side of J_+ and J_- given by Eq. (2.5) as

$$J_{+i} = \sqrt{2} (x_i{}^+ + x_{-i}),$$

$$J_{-i} = \sqrt{2} (x_i + x_{-i}^+). \tag{2.6}$$

This approximation is fairly good so long as we consider one elementary excitation because both sides of Eq. (2.6) give the same matrix elements between

the excited states (i.e., $Y_1^{\pm 1}(\Omega_i)$ or $|01\rangle$, $|10\rangle$) and the vacuum state (i.e. $Y_1^0(\Omega_i)$ or $|00\rangle$).

Substituting Eq. (2·6) and $J_{zi}=x_i^+x_i-x_{-i}^+x_{-i}$ into each component of the angular momentum operator $J_s^{(\alpha)}$ and using Eq. (2·4), (2·3) and Table III, we get H_{eff} in terms of the boson operator. In this procedure we make rearrangement in each term in order to set the creation operators to the left of the annihilation operators and neglect terms higher than the quadratic, because it is supposed that the number of bosons is small in the low temperature region:

$$H_{\text{eff}}= - (76/3)N+19\sum_{\alpha, i}\sum_{\nu=\pm 1} (x_{\nu\alpha}^+(i)\, x_{\nu\alpha}(i))$$

$$+\sum_{\alpha, \beta}\sum_{\langle i, j\rangle}[\,\{f_l\!\begin{pmatrix}\alpha\\\beta\end{pmatrix}(x_\alpha(i)-x_{-\alpha}^+(i))\,(x_\beta(j)-x_{-\beta}^+(j))+\text{c.c.}\} \qquad (2\cdot 7)$$

$$+\,\{g_l\begin{pmatrix}\alpha\\\beta\end{pmatrix}(x_\alpha(i)-x_{-\alpha}^+(i))\,(x_\beta^+(j)-x_{-\beta}(j))+\text{c.c.}\}\,],$$

where $\alpha(\beta)$ represents each sublattice and $i(j)$ represents a lattice point of sublattice $\alpha(\beta)$. Each sublattice contains N molecules so that the system is

Table IV. $f_l\binom{\alpha}{\beta}$, $g_l\binom{\alpha}{\beta}$

α	β	l	$f\times 144$	$g\times 144$
I	II	1	$56+ 6\sqrt{3}\, i$	$40+10\sqrt{3}\, i$
	"	2	$56+ 6\sqrt{3}\, i$	$40-10\sqrt{3}\, i$
	III	3	$-19-31\sqrt{3}\, i$	$15-25\sqrt{3}\, i$
	"	4	$-19-31\sqrt{3}\, i$	$-35-15\sqrt{3}\, i$
	IV	5	$-37+25\sqrt{3}\, i$	$-35+15\sqrt{3}\, i$
	"	6	$-37+25\sqrt{3}\, i$	$- 5+25\sqrt{3}\, i$
II	I	1	$56+ 6\sqrt{3}\, i$	$40-10\sqrt{3}\, i$
	"	2	$56+ 6\sqrt{3}\, i$	$40+10\sqrt{3}\, i$
	III	11	$-56- 6\sqrt{3}\, i$	$5+25\sqrt{3}\, i$
	"	12	$-56- 6\sqrt{3}\, i$	$35+15\sqrt{3}\, i$
	IV	9	$-56- 6\sqrt{3}\, i$	$5-25\sqrt{3}\, i$
	"	10	$-56- 6\sqrt{3}\, i$	$35-15\sqrt{3}\, i$
III	I	3	$-19-31\sqrt{3}\, i$	$15+25\sqrt{3}\, i$
	"	4	$-19-31\sqrt{3}\, i$	$-35+15\sqrt{3}\, i$
	II	11	$-56- 6\sqrt{3}\, i$	$5-25\sqrt{3}\, i$
	"	12	$-56- 6\sqrt{3}\, i$	$35-15\sqrt{3}\, i$
	IV	7	$-56- 6\sqrt{3}\, i$	$5+25\sqrt{3}\, i$
	"	8	$-56- 6\sqrt{3}\, i$	$35+15\sqrt{3}\, i$
IV	I	5	$-37+25\sqrt{3}\, i$	$-35-15\sqrt{3}\, i$
	"	6	$-37+25\sqrt{3}\, i$	$- 5-25\sqrt{3}\, i$
	II	9	$-56- 6\sqrt{3}\, i$	$5+25\sqrt{3}\, i$
	"	10	$-56- 6\sqrt{3}\, i$	$35+15\sqrt{3}\, i$
	III	7	$-56- 6\sqrt{3}\, i$	$5-25\sqrt{3}\, i$
	"	8	$-56- 6\sqrt{3}\, i$	$35-15\sqrt{3}\, i$

composed of $4N$ molecules. The coefficients $f_i\binom{\alpha}{\beta}$ and $g_i\binom{\alpha}{\beta}$ are constants which depend on α and β and the vector $\boldsymbol{r}_i$ connecting the nearest neighbor lattice points (α, i) and (β, j). We give these coefficients in Table IV.

The first and second terms on the right-hand side in Eq. (2·7) represent respectively the ground state energy and excitation energy in the Hartree approximation. The last term represents the effect of correlations. Since in the first approximation (Hartree approximation) the system is in the vacuum state of the boson field, the linear term of $H_{\rm eff}$ in the boson operator identically vanishes as it should.

We define the rotation wave variables $X_\alpha{}^+(\boldsymbol{k})$ and $X_{-\alpha}^+(\boldsymbol{k})$ of the α-th sublattice ($\alpha=$I, II, III, IV) by

$$X_\alpha{}^+(\boldsymbol{k}) = N^{-1/2} \sum_{j \in S(\alpha)} \exp(-i\boldsymbol{k}\cdot\boldsymbol{R}_j)\, x_\alpha{}^+(j),$$
$$X_{-\alpha}^+(\boldsymbol{k}) = N^{-1/2} \sum_{j \in S(\alpha)} \exp(-i\boldsymbol{k}\cdot\boldsymbol{R}_j)\, x_{-\alpha}^+(j) . \tag{2·8}$$

Here $\boldsymbol{R}_j$ is the position vector of the j-th molecule, $S(\alpha)$ is the set of N molecules belonging to the α-th sublattice so that the summation is taken over all the molecules of the α-th sublattice.

Thus, $H_{\rm eff}$ can be written as

$$H_{\rm eff} = -(76/3)N + \sum_{\boldsymbol{k}} H(\boldsymbol{k}), \tag{2·9}$$

$$
\begin{aligned}
H(\boldsymbol{k}) = {} & 19 \sum_{\alpha,\nu} X_{-\nu}^+(\boldsymbol{k}) X_{\nu\alpha}(\boldsymbol{k}) + \sum_{\alpha,\beta}\Big[\big\{ F_k\binom{\alpha}{\beta} \big(X_\alpha(\boldsymbol{k}) X_\beta(-\boldsymbol{k}) \\
& + X_{-\alpha}^+(\boldsymbol{k}) X_{-\beta}^+(-\boldsymbol{k}) - X_{-\alpha}^+(\boldsymbol{k}) X_\beta(\boldsymbol{k}) - X_\alpha(\boldsymbol{k}) X_{-\beta}^+(\boldsymbol{k})\big) + {\rm c.c.}\big\} \\
& + \big\{ G_k\binom{\alpha}{\beta} \big(X_\alpha(\boldsymbol{k}) X_\beta{}^+(\boldsymbol{k}) + X_{-\alpha}^+(\boldsymbol{k}) X_{-\beta}(\boldsymbol{k}) - X_\alpha(\boldsymbol{k}) X_{-\beta}(-\boldsymbol{k}) \\
& - X_{-\alpha}^+(\boldsymbol{k}) X_\beta{}^+(-\boldsymbol{k})\big) + {\rm c.c.}\big\}\Big],
\end{aligned}
\tag{2·10}
$$

$$F_k\binom{\alpha}{\beta} = \gamma_i(\boldsymbol{k}) f_i\binom{\alpha}{\beta}, \quad G_k\binom{\alpha}{\beta} = \gamma_i(\boldsymbol{k}) g_i\binom{\alpha}{\beta},$$
$$\gamma_i(\boldsymbol{k}) = 2\cos\boldsymbol{k}\cdot\boldsymbol{r}_i . \tag{2·11}$$

If we could diagonalize this Hamiltonian, the correlation effect and the spectrum of the excitation energy would be obtained analytically. This diagonalization, however, is difficult because it accompanies the unitary transformation of eight variables.

Therefore, treating the off-diagonal terms in Eq. (2·10) as a perturbation, we numerically calculate the dispersion relation and the energy spectrum of the excitation mode by the first order perturbation and the correlation energy in the ground energy by the second order perturbation.

§ 3. The dispersion relation and state density
of the rotational excitation modes

————*The correlation effect*————

We first calculate the correlation energy in the ground state by the second-order perturbation calculation.

The second-order correlation ΔE_2 is given dy

$$\Delta E_2 = -\sum_n \frac{\langle 0|H'|n\rangle\langle n|H'|0\rangle}{E_n - E_0}, \qquad (3\cdot1)$$

where $|0\rangle$ represents the ground state, $|n\rangle$ the excited state and H' is the off-diagonal terms of H_{eff} in Eq. (2·9). Only the double creation terms such as $X_\alpha^+(\boldsymbol{k})X_{-\beta}^+(\boldsymbol{k})$ contribute to the perturbation given by Eq. (3·1).

Thus we get

$$\Delta E_2 = -\sum_k \sum_{\alpha,\beta} \frac{1}{38}\left[|F_k\left(\begin{matrix}\alpha\\\beta\end{matrix}\right)|^2 \times 2 + |G_k\left(\begin{matrix}\alpha\\\beta\end{matrix}\right)|^2 \times 2\right]$$

$$= -0.62N$$

$$= -0.1\, k_B/\text{molecule}$$

The ground energy of the N-N model in the Hartree approximation is given by a constant term in Eq. (2·7). Denoting it by E_0, we find

$$\Delta E_2/E_0 = \frac{1}{41}.$$

This fact means that the correlation effect on the ground energy is rather small.

We, next, calculate the dispersion relation and state density of the rotational excitation modes. If we make one molecule in the crystal excite from $|00\rangle$ to $|10\rangle$ or $|01\rangle$, this excitation can be passed on from one site to the other by the transfer type term such as $x_\alpha^+(i)x_{-\beta}(j)$ of the off-diagonal terms in Eq. (2·7). The degeneracy of excited states in the Hartree approximation can be lifted by the first order perturbation taking this process into account.

The dispersion relation and state density of such rotational excitation modes are obtained by seeking the roots of the secular equation whose matrix element is such as $\langle X_{\nu'\alpha'}(\boldsymbol{k})|H(\boldsymbol{k})|X_{\nu\alpha}^+(\boldsymbol{k})\rangle \equiv h_{\nu\alpha}^{\nu'\alpha'}(\boldsymbol{k})$, where the ket means the vacuum state in boson field. There are some symmetry relations in $h_{\nu\alpha}^{\nu'\alpha'}(\boldsymbol{k})$.

i) $\quad h_{\nu\alpha}^{\nu'\alpha'}(\boldsymbol{k}) = h_{\nu'\alpha'}^{\nu\alpha*}(\boldsymbol{k}),$ $\qquad\qquad\qquad$ (3·2)

ii) $\quad h_{\nu\alpha}^{\nu'\alpha'}(\boldsymbol{k}) = h_{-\nu\alpha}^{-\nu'\alpha'*}(\boldsymbol{k}),$ $\qquad\qquad\qquad$ (3·3)

iii) $\quad h_{\nu\alpha}^{\nu'\alpha}(\boldsymbol{k}) = 0.$ $\qquad\qquad\qquad\qquad\qquad$ (3·4)

We give the explicit form of $h_{\nu\alpha}^{\nu'\alpha'}(\boldsymbol{k})$ in Table V.

Figures 1a) and 1b) show the dispersion curves for the (1, 1, 1) and (0, 0, 1)

Table V. $h_{\nu\alpha}^{\nu'\alpha'}(k)$.

	+I	+II	+III
+II	$40A^+$ $+i\,10\sqrt{3}\,A^-$		
−II	$-56A^+$ $-i\,6\sqrt{3}\,A^+$		
+III	$-20B^+ + 15B^-$ $-i\,(20B^+ - 5B^-)\sqrt{3}$	$20C^+ - 15C^-$ $+i\,(20C^+ + 5C^-)\sqrt{3}$	
−III	$19B^+$ $+i\,31\sqrt{3}\,B^+$	$56C^+$ $+i\,6\sqrt{3}\,C^+$	
+IV	$-20C^+ - 15C^-$ $+i(20C^+ - 5C^-)\sqrt{3}$	$20B^+ - 15B^-$ $-i(20B^+ + 5B^-)\sqrt{3}$	$20A^+ - 15A^+$ $+i(20A^+ + 5A^-)\sqrt{3}$
−IV	$37C^+$ $-i\,25\sqrt{3}\,C^+$	$56B^+$ $+i\,6\sqrt{3}\,B^+$	$56A^+$ $+i6\sqrt{3}\,A^+$

$$A^+ = 4\cos\frac{a}{\sqrt{2}}k_y\,\cos\frac{a}{\sqrt{2}}k_z, \qquad A^- = -\sin\frac{a}{\sqrt{2}}k_y\,\sin\frac{a}{\sqrt{2}}k_z$$

$$B^+ = 4\cos\frac{a}{\sqrt{2}}k_x\,\cos\frac{a}{\sqrt{2}}k_y, \qquad B^- = -4\sin\frac{a}{\sqrt{2}}k_x\,\sin\frac{a}{\sqrt{2}}k_y$$

$$C^+ = 4\cos\frac{a}{\sqrt{2}}k_x\,\cos\frac{a}{\sqrt{2}}k_z, \qquad C^- = -4\sin\frac{a}{\sqrt{2}}k_x\,\sin\frac{a}{\sqrt{2}}k_z$$
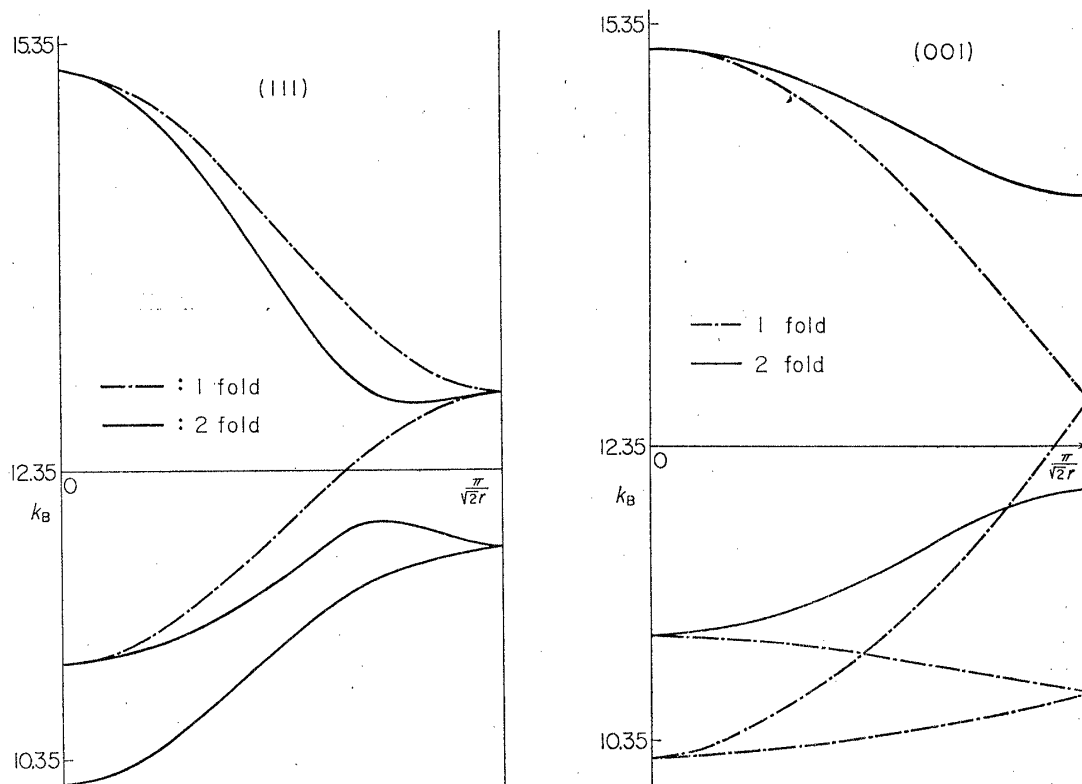
Figs. 1a) and 1b). The dispersion relation of libron along (111) and (001) directions in k-space. Unit of energy is the Boltzmann constant.
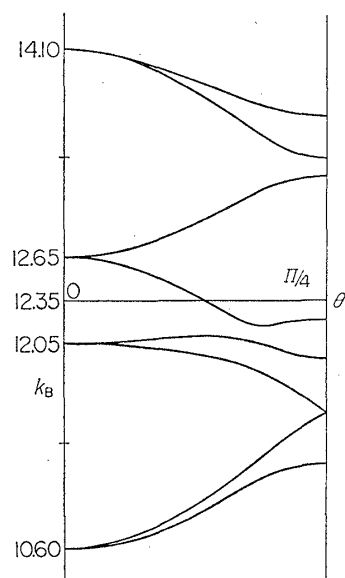
Fig. 1c). The libron energy versus θ. $k_x=0$ and $k_z=k$ $\times\cos\theta$ and $k_y=k\sin\theta$

$$k=\frac{\pi}{\sqrt{2}\,a}$$

Fig. 2. The state density of librons obtained by the root sampling method.

directions obtained by using a computer. From Fig. 1 it is obvious that the correlation effect is important for the excited states because the band width of the excitation spectrum amounts to about $5\,k_B$. (The excitation energy in Hartree approximation is $12.35\,k_B$ which is the coefficient of the diagonal term $\sum_{\alpha,\nu} X^+_{\nu\alpha}(k)\,X_{\nu\alpha}(k)$ in Eq. (2·10).) There is an energy gap of order $10\,k_B$ between the ground state and the excited states even at $k=0$ where k_B is the Boltzmann constant. This fact is in contrast to the case of ferromagnetic magnon where an energy gap is zero at $k=0$ so long as we treat the Hamiltonian including only exchange interaction. This is to be expected, since the potential energy varies under the uniform rotation of molecules so that our Hamiltonian has an anisotropy.

Figure 2 shows the state density of the excitation modes obtained by the root sampling method from the dispersion relation calculated for 1000 different k-values.

§ 4. The nature of the rotational excitations

Moriya and Mochizuki[13] suggested in the discussion of nuclear magnetic relaxation in solid hydrogen that the state of solid H_2 at very low temperatures may be described by ‘rotation wave’ picture.[*] The excited states derived in the preceding section certainly correspond to the ‘rotation wave’ in the sense that the excitation has a wave-like character and the excitation is of rotational degrees of freedom of molecules. However, the term ‘rotation wave’ is somewhat misleading since the expectation value of the angular momentum of each

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[*] Frenkel[14] had pointed out that the rotational part of the classical heat motion in dipolar crystals can be described as a superposition of "rotation-oscillation" waves, which are quite analogous to the optical waves in the case of an ionic crystal lattice.
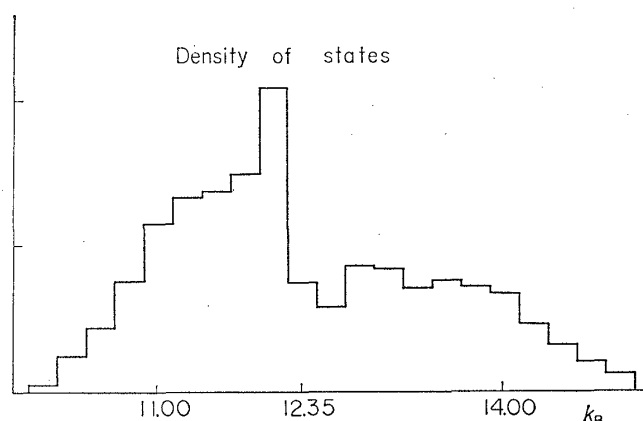
molecule generally vanishes not only in the ground state but in the excited states as shown below.

According to the result of the preceding section the creation operator of the excitation of the γ-th excitation mode with wave vector $\boldsymbol{k}$ can be written as

$$B^+(\boldsymbol{k}, \gamma) = \sum_{\nu, \alpha} C_{\gamma;\nu\alpha}(\boldsymbol{k}) X_{\nu\alpha}^+(\boldsymbol{k}), \qquad (4\cdot1)$$

where $C_{\gamma;\nu\alpha}(\boldsymbol{k})$ is the element of the unitary matrix which approximately diagonalizes $H(\boldsymbol{k})$.[*] Using Eqs. (2·8) and (2·5) we find for the molecule i belonging to the sublattice α that

$$\langle B(\boldsymbol{k}, \gamma)|J_{zi}|B^+(\boldsymbol{k}, \gamma)\rangle = |C_{\gamma,+\alpha}(\boldsymbol{k})|^2 - |C_{\gamma;-\alpha}(\boldsymbol{k})|^2,$$

$$\langle B(\boldsymbol{k}, \gamma)|J_{xi}|B^+(\boldsymbol{k}, \gamma)\rangle = \langle B(\boldsymbol{k}, \gamma)|J_{yi}|B^+(\boldsymbol{k}, \gamma)\rangle = 0. \qquad (4\cdot2)$$

By virtue of the relation (3·3) the matrix $\{h_{\nu\alpha}^{\nu'\alpha'}(\boldsymbol{k})\}$ can be expressed in the form

$$\bar{H}(\boldsymbol{k}) = \begin{pmatrix} A & B \\ B^* & A^* \end{pmatrix}, \qquad (4\cdot3)$$

where $A = A^\dagger$ and $B = \widetilde{B}$ are 4×4 matrices. The superscript $*$, $\dagger$, and $\sim$ denote complex conjugate, Hermitian conjugate, and transpose, respectively. Let $\begin{pmatrix} \boldsymbol{u} \\ \boldsymbol{v} \end{pmatrix}$ be the γ-th eigenvector of the above matrix belonging to the eigenvalue λ, where

$$\boldsymbol{u} = \begin{pmatrix} C_{\gamma;1}(\boldsymbol{k}) \\ C_{\gamma;2}(\boldsymbol{k}) \\ C_{\gamma;3}(\boldsymbol{k}) \\ C_{\gamma;4}(\boldsymbol{k}) \end{pmatrix}, \qquad \boldsymbol{v} = \begin{pmatrix} C_{\gamma;-1}(\boldsymbol{k}) \\ C_{\gamma;-2}(\boldsymbol{k}) \\ C_{\gamma;-3}(\boldsymbol{k}) \\ C_{\gamma;-4}(\boldsymbol{k}) \end{pmatrix}. \qquad (4\cdot4)$$

Then, we have the equations

$$A\boldsymbol{u} + B\boldsymbol{v} = \lambda\boldsymbol{u}, \qquad (4\cdot5)$$

$$B^*\boldsymbol{u} + A^*\boldsymbol{v} = \lambda\boldsymbol{v}. \qquad (4\cdot5')$$

From the definition we find that except for $|k_x| = |k_y| = |k_z| = (1/a)(\pi/\sqrt{2})$,

$$\text{Det } B \neq 0 \quad \text{in general.} \qquad (4\cdot6)$$

Then, from (4·5) we get

$$\boldsymbol{v} = B^{-1}(\lambda - A)\boldsymbol{u}. \qquad (4\cdot7)$$

Substituting this in (4·5') we obtain

$$\boldsymbol{u} = B^{*-1}(\lambda - A^*)B^{-1}(\lambda - A)\boldsymbol{u}. \qquad (4\cdot8)$$

---

[*] $C_{\gamma;\nu\alpha}$ is the element of the unitary matrix which diagonalizes the operator obtained from $H(\boldsymbol{k})$ by deleting the terms corresponding to double creation and double annihilation of bosons.

Similarly we obtain

$$v^* = B^{*-1}(\lambda - A^*)B^{-1}(\lambda - A)v^* . \tag{4·8'}$$

Equations (4·8) and (4·8') shows that both u and v^* are eigenvectors belonging to the eigenvalue 1 of the same matrix.

As shown in Fig. 1c), λ is generally a non-degenerate eigenvalue of $\bar{H}(k)$. Therefore, u and v^* are the non-degenerate eigenvector of $B^{*-1}(\lambda - A^*)B^{-1}(\lambda - A)$, so that

$$v^* = cu , \tag{4·9}$$

where c is a constant. Substituting (4·9) in (4·5) and (4·5') we get

$$Au + c^*Bu^* = \lambda u , \tag{4·10}$$

$$Bu^* + cAu = c\lambda u , \tag{4·10'}$$

from which

$$(|c|^2 - 1)Bu^* = 0 . \tag{4·11}$$

By virtue of (4·6), we have $|c| = 1$. Using (4·11), from (4·2) we find that

$$\langle B(k, \gamma) |J| B^+(k, \gamma) \rangle = 0 . \tag{4·12}$$

Thus each molecule librates rather than rotates. For the sake of simplicity and clarity of terminology, henceforth we call the elementary quantum of excitation obtained in the previous section 'libron' in association with libration. Then $B^+(k, \gamma)$ is a libron creation operator. As shown in Fig. 1 the minimum excitation energy of libron is about $10\,k_B$ and is rather higher than the energy corresponding to the observed order-disorder transition temperature T_λ, which is less than $4°K_B$. This indicates that librons can hardly be thermally excited in pure ortho-H_2 solid well below T_λ.

On the other hand, the order-disorder transition temperature may be considered to be the temperature where the number of librons is of the order of the number of molecules. We see in the next section whether these situations can be reconciled.

§ 5. Evaluation of thermodynamic quantities

In this section, we numerically calculate the thermodynamic quantities such as free energy F_{rot}, entropy S_{rot}, and specific heat C_{rot} as a function of T and estimate T_λ by using the state density of Fig. 2. Subscript "rot" means that these quantities arise from the effect of the rotational degree of freedom of each molecule.

We must be careful when we use the state density of Fig. 2 because it is applicable only when the number of librons is much smaller than the number of molecules in the system. We note that above T_λ no long-range orientational

order exists, so that there must be no excitation energy due to long-range order for rotational excitations. Therefore, as a simplest approximation for the temperature effect on the excitation energy one may assume that the excitation energy $\varepsilon_\alpha(T)$ of the α-th libron at temperature T as

$$\varepsilon_\alpha(T) = \varepsilon_\alpha^0 x(T), \qquad (5\cdot1)$$

where ε_α^0 is the α-th excitation energy at 0°K and $x(T)$ is an order parameter defined by

$$x(T) = 1 - \frac{n(T)}{4N}, \qquad (5\cdot2)$$

where $4N$ is the total number of molecules in the system and $n(T)$ is an average number of molecules which are in excited states at temperature T.

Librons obey Bose statistics, so that

$$n(T) = \sum_\alpha (\exp(\beta\varepsilon_\alpha(T)) - 1)^{-1}. \qquad (5\cdot3)$$

We use Eqs. (5·1) and (5·3) in (5·2), then

$$x = 1 - \frac{1}{4N} \sum_\alpha (\exp(\varepsilon_\alpha^0/k_B T^*) - 1)^{-1}, \qquad (5\cdot4)$$

where

$$T = xT^*. \qquad (5\cdot5)$$

Thus we can calculate numerically the order parameter x and " true temperature T " as a function of "reduced temperature T^*" on the basis of Eq. (5·4) and state density given by Fig. 2.

We give in Figs. 3 and 4 the relation of " x versus T^{*-1} " and " T versus T^* ". The thermodynamic quantities such as $F_{\rm rot}$ which are calculated as a
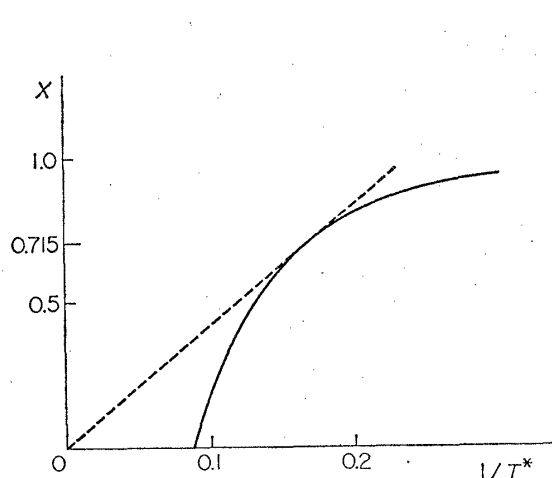

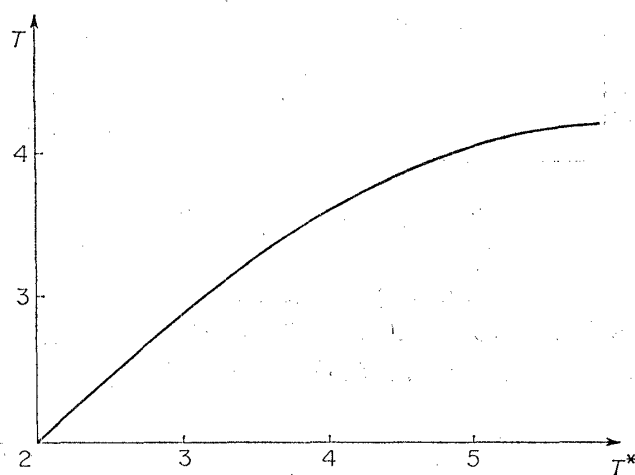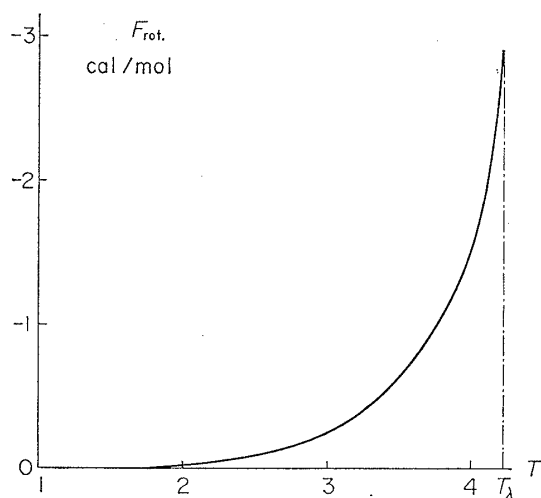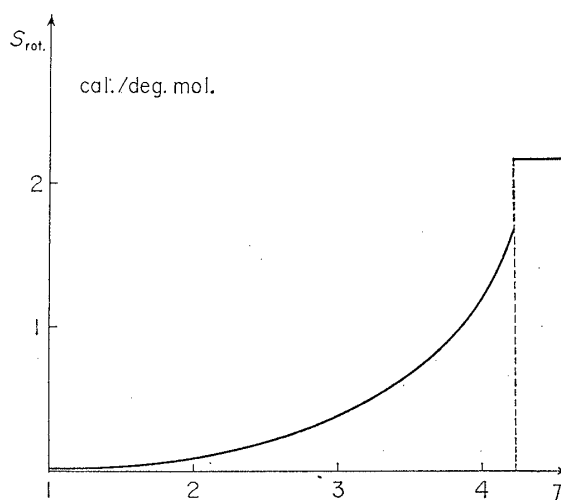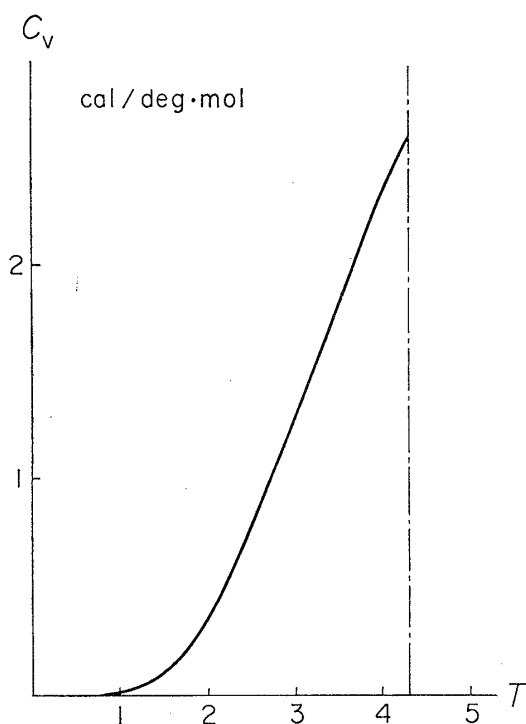Fig. 3. The relation between the order parameter x and reduced tempeature T^*.

Fig. 4. The relation between the true temperature T and reduced temperature T^*.

Fig. 5. Free energy F_{rot} below T_λ.

Fig. 6. Entropy S_{rot} below T_λ.

Fig. 7. Specific heat C_v below T_λ.

function of T^* by using the partition function $Z_{\text{rot}} = \prod_\alpha (1 - \exp(-\varepsilon_\alpha^0/k_B T^*))^{-1}$ are transformed to the function of T by using Eq. (5·5). We give these quantities in Figs. 5–7 as a function of T.

In Fig. 3 the gradient of the line which connects the origin and the point on the curve represents T. This fact indicates that the maximum gradient, that is, the tangent drawn from the origin is T_λ. We find that

$$T_\lambda = x_\lambda T_\lambda^* = 4.2°\text{K} \qquad (5·6)$$

So long as one neglects the short-range order effect, the phase transition is found to be of the first order from Fig. 3, hence the entropy gap is estimated as

$$\Delta S = R \ln 3 - S(T_\lambda)$$
$$= 2.1 \text{ Joule/Mol.} \qquad (5·7)$$

From the experiment by Ahlers and Orttung[1] the entropy gap at $T_\lambda = 1.6°\text{K}$ is found to be about 1.6 Joule/Mol at 73.1% ortho-hydrogen. This fact indicates that our estimate (5·7) is a fairly good one.

§ 6. Discussion

We have studied the rotational excitations of pure solid fcc ortho-hydrogen on the rigid lattice and nearest neighbor quadrupole-quadrupole interaction

model, the Hamiltonian of which is given by H in (2·3). First we have set up the effective Hamiltonian H_{eff} which is considered to be a good approximation at sufficiently low temperatures. Then using the first-order perturbation calculation we have approximately diagonalized H_{eff} and obtained the dispersion relation and state density of the excitation mode. One may as well apply the first-order perturbation directly to H; one can easily show that the result is identical with ours. The reason why we have bipassed through H_{eff} is that in principle it can be diagonalized by extending the Bogoliubov transformation and it seems to be convenient to improve the approximation in analogy with the spin wave theory. Since the correction coming from the second-order perturbation is found small the result of the first-order calculation will be significant. We have discussed the nature of the quasi-particle called libron thus obtained. However, we have not calculated the life time of libron, so that the question whether libron can truly be a good quasi-particle is still an open problem. According to our calculation at 0°K libron has a minimum excitation energy of about $10 k_{\text{B}}$, so that it can hardly be thermally excited sufficiently below T_λ. Simple self-consistent calculation in § 5 shows that when one increases the temperature until just below T_λ which is estimated to be about 4.2°K then librons become cooperatively excited. Although our simple estimate of such a temperature effect seems to agree with experiment qualitatively further refinements of the theory would be necessary.

On the other hand, at present there is no available experimental data on the solid H_2 with high ortho-molecule concentration, say above 85% at very low temperatures to compare quantitatively with our theory. Further investigations of the excitation in solid H_2 at very low temperatures are to be hoped both theoretically and experimentally.

Appendix

——*Instability of the Danielian model*——

Danielian[6] showed that in hcp-lattice if one takes the quantization axis of the angular momentum of each molecule (Z-axis) parallel to the c-axis of the crystal and assumes that each molecule is either in the state $J_z = 0$ (state A) or $J_z = \pm 1$ (state B), the configuration shown in Fig. 8 has the lowest energy of the nearest neighbor quadrupole-quadrupole interaction.

In the above Hartree approximation the interaction energy of nearest neighbor pairs is tabulated in Table VI. This table indicates that the total interaction energy between neighboring layers vanishes either in the configuration (a) or (b) of Fig. 9. Therefore, the energy of the ground state is the sum of energies
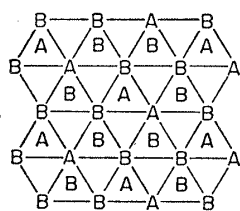
Fig. 8. The ground-state superlattice structure of $A(J_z=0)$ and $B(J_z=\pm1)$ ortho-hydrogen molecules on a hcp lattice proposed by Danielian.[6] The letters A or B at the centers of the triangles represent two other triangular layers: one above and the other beneath the triangular layer shown. Each one of the three layers has an identical configurational pattern.

Fig. 9. The two possible ground-state tetrahedral configurations of A and B molecules.

Fig. 11. The ground state energy per molecule (broken line) and the energy of an excited molecule (solid line). The energy of single molecular excitation is the difference of the two energies. This excitation energy can be $-13/24$ due to the correlation effect, showing the instability of the Denielian model.
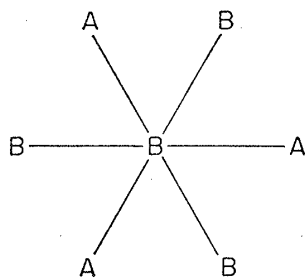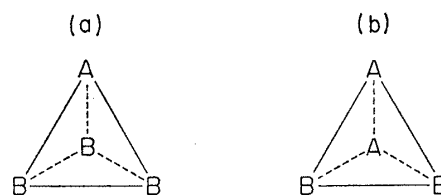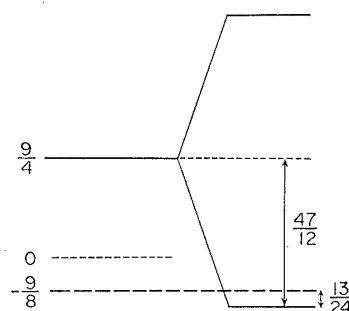

Fig. 10. The ground-state coplanar pattern with B-molecule at the center.

Table VI. The interaction energy of nearest neighbor pairs in the unit $(8/25)\,(3e^2\mu_Q{}^2/4r^5)$

	in the same layer	between neighboring layers
A–A	3/2	$-13/18$
A–B	$-3/4$	13/36
B–B	3/8	$-13/72$

of the coplanar patterns in Fig. 10. The energy per pattern or per molecule is $-9/8$ independently of the configuration of neighboring layers. If a central molecule is excited from B to A then the energy changes from $-9/8$ to $9/4$. This single excitation can migrate from site to site. The transfer energy per bond is calculated from (2·3) and (2·2) to be 3/4 in the same layer, and 5/12 between layers. Since there are 3 transferable bonds in the same layer and 4 transferable bonds between layers for the excitation. Therefore, the band width of excitation amounts to

$$2\left(\frac{3}{4}\times3+\frac{5}{12}\times4\right)=\frac{47}{6}\,.$$

As shown in Fig. 11, the lower band edge is lower than the ground state energy per molecule. This shows that the Danielian model is unstable for excitations.

References

1) R. W. Hill and B. W. A. Ricketson, Phil. Mag. **45** (1954), 277.
   G. Ahlers and W. H. Orttung, Phys. Rev. **133** (1964), A1642.
2) J. Hatton and B. V. Rollin, Proc. Roy. Soc. **A199** (1949), 222.
   F. Reif and E. M. Purcell, Phys. Rev. **91** (1953), 631.
   G. W. Smith and R. M. Housley, Phys. Rev. **117** (1960), 732.
3) K. Tomita, Proc. Phys. Soc. **A68** (1955) 213.
4) T. Nakamura, Prog. Theor. Phys. **14** (1955), 135.
5) O. Nagai and T. Nakamura, Prog. Theor. Phys. **24** (1960), 432; Prog. Theor. Phys. **30** (1963), 412.
6) A. Danielian, Phys. Rev. **138** (1965), A282.
7) G. M. Bell and W. M. Fairbairn, Mol. Phys. **4** (1961), 481; Mol. Phys. **5** (1962), 605; **8** (1964), 497.
8) J. Felsteiner, Phys. Rev. Letters **15** (1965), 1025.
9) M. Clouter and H. P. Gush, Phys. Rev. Letters **15** (1965), 200.
10) R. L. Mills and A. F. Schuch, Phys. Rev. Letters **15** (1965), 722.
    R. L. Mills, A. F. Schuch, and D. A. Depatie, Phys. Rev. Letters **17** (1966), 1131.
11) J. Van Kranendonk, Physica **25** (1959) 1080.
12) H. Miyagi and T. Nakamura, Prog. Theor. Phys. **37** (1967), 641.
13) T. Moriya and K. Motizuki, Prog. Theor. Phys. **18** (1957), 183.
14) J. Frenkel, *Kinetic Theory of Liquids* (Oxford University Press, London, 1946) p.84.