PHYSICAL REVIEW VOLUME 158, NUMBER 2 10 JUNE 1967

Orientational Ordering in Solid Hydrogen

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(Received 27 January 1967)

A model for solid orthohydrogen in the temperature range of the observed second-order transition is considered. The lattice structure is taken to be hexagonal close packed and the quadrupole-quadrupole interaction energy is minimized with respect to parameters defining a self-consistent set of one-particle rotational wave functions, with $J=1$. Values of the ground-state energy are deduced when, respectively, (i) all lattice sites are equivalent, and (ii) superlattice ordering occurs in planes perpendicular to an axis of threefold symmetry of the crystal. In the latter case, a zeroth-order statistical treatment of the free energy is given using an orthogonal set of rotational wave functions, approximately consistent with the ground-state wave functions. It is found that a second-order transition occurs at 2.9°K and that the change in entropy per orthohydrogen molecule over the transition range is $\mathbf{k}\ln 3$, in accordance with experiment.

I. INTRODUCTION

THE cooperative phenomenon observed in the temperature range 1–3°K in specific-heat measurements[1,2] and in nuclear-magnetic-resonance experiments[3–5] with solid hydrogen having a high concentration of orthohydrogen has been the subject of various theoretical investigations[6–8]; the previous papers by the present authors (Ref. 7) will be referred to as I, II, and III. Because the cooperative behavior of the molecules in the crystal is due to the orthocomponent, it is convenient to start with a theoretical analysis of a system composed of pure orthohydrogen. The dilution problem (i.e., the effect of the paracomponent) can be investigated after a realistic model has been obtained for solid orthohydrogen.[9]

It has been pointed out[10,11] that previous theoretical analyses using a fixed axis of quantization are not necessarily self-consistent in the sense that the axially symmetric field assumed at all lattice sites might not always be identical with the field calculated by summing over the interactions between pairs of molecules for an orientationally ordered distribution. Raich and James[10] have reported a method for obtaining a self-consistent internal field by minimizing the configurational free energy (for fixed temperature) with respect to the rotational molecular wave functions in the crystal. The wave function for a molecule on a particular lattice site is expanded in terms of a complete set of orthonormal solutions of the time-independent Schrödinger equation which contains the self-consistent single-particle potential (the internal field). The coefficients in the expansion (truncated, in practice) of the wave function are used as discrete variables for the minimization of the free energy.

For complete generality, these coefficients should be independent for each lattice site, but to define a solvable problem one must stipulate relations between the coefficients for different subsets of lattice sites. In other words, a possible superlattice ordering must be proposed and the possibility of transitions from the disordered high-temperature state into such an ordered state can then be investigated. This is restrictive in the sense that all possible superlattices should be considered to obtain a final result.

The analysis of the present paper is similar in that it produces a self-consistent set of wave functions and in that each possible superlattice ordering should be considered separately. However, we may decide whether any particular self-consistent superlattice ordering is likely to produce a second-order transition by evaluating the configurational energy in the completely ordered state and by requiring that this latter state has a symmetry which permits a second-order transition.

Firstly, we determine the form of the configurational energy due to the quadrupole-quadrupole interaction between nearest-neighbor molecules in the crystal, under the restriction that all molecules are in the $J=1$ state, but all lattice sites are allowed to be inequivalent. The axis of quantization is arbitrary for each lattice

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[1] R. W. Hill and B. W. A. Ricketson, Phil. Mag. **45**, 277 (1954).

[2] G. Ahlers and W. H. Orttung, Phys. Rev. **133**, A1642 (1964).

[3] F. Reif and E. M. Purcell, Phys. Rev. **91**, 631 (1953).

[4] G. W. Smith and R. M. Housley, Phys. Rev. **117**, 732 (1960).

[5] S. A. Dickson and H. Meyer, Phys. Rev. **138**, A1293 (1965).

[6] K. Tomita, Proc. Phys. Soc. (London) **A68**, 214 (1955).

[7] G. M. Bell and W. M. Fairbairn, Mol. Phys. **4**, 481 (1961); **5**, 605 (1962); **8**, 497 (1964). Referred to as I, II, and III, respectively, in the text.

[8] A. Danielian, Phys. Rev. **138**, A282 (1965).

[9] The change in lattice structure from hcp to fcc which has been found in measurements of the infrared absorption spectrum [M. Clouter and H. P. Gush, Phys. Rev. Letters **15**, 200 (1965)] and in x-ray diffraction studies [R. L. Mills and A. F. Schuch, Phys. Rev. Letters **15**, 722 (1965)] of solid hydrogen occurs at a lower temperature than the cooperative ordering transition which is discussed in this paper, and should therefore be discussed separately.

[10] J. C. Raich and H. M. James, Phys. Rev. Letters **16**, 173 (1966).

[11] G. M. Bell and W. M. Fairbairn, in Proceedings of the Conference on the Many-Body Problem, Manchester, 1964 (unpublished).

site. This energy is minimized for a hcp lattice when (i) all sites are equivalent, (ii) superlattice ordering occurs in planes perpendicular to an axis of threefold symmetry of the crystal,[12] the minimization defining consistent axes of quantization at each lattice site. The former case reproduces a result which could be obtained by using a fixed axis of quantization, but the second case gives an ordered state with energy much lower than any found for orientational distributions in models using a fixed quantization axis.

The zeroth-order theory of the second-order transition into this state is discussed, using a simplified model which is defined in Sec. IV, below. We find that this transition occurs at a temperature of 2.91°K, in close agreement with the extrapolated value of the critical temperature determined by Smith and Housley.[4]

II. THE CONFIGURATIONAL ENERGY

The rotational wave function ψ_R for a molecule of orthohydrogen can be approximated well at low temperatures by the function which describes a rigid rotator with spin $J=1$. We can write

$$\psi_R(i)=\sum_M c_M(i)\,Y_{1M}(\theta_i,\phi_i), \qquad (2.1)$$

where the molecule occupies the site i and $M=0, \pm1$. It should be noted that the reference axis for the angles θ_i, ϕ_i in (2.1) is arbitrary: This is the direction which defines the quantum number M. If the reference axis is rotated to a new position, described by the spherical polar angles (θ_0, ϕ_0) with respect to the original axis, then the wave function becomes

$$\sum_{M'} c_{M'}'(i)\,Y_{1M'}(\theta_i', \phi_i'),$$

where

$$c_{M'}'(i)=\sum_M \mathfrak{D}_{M'M}^{(1)}(\theta_0,\phi_0,0)\,c_M(i),$$

$\mathfrak{D}^{(1)}$ being the usual three-dimensional representation of the rotation group R_3. Thus, as expected, the rotation of the reference axis alters the expectation value of M but leaves J unchanged.

On normalizing $\psi_R(i)$ we can write

$$\begin{aligned} c_{-1}(i)&=e^{i\delta_-}\sin\alpha\,\sin\beta,\\ c_0(i)&=\cos\alpha,\\ c_1(i)&=e^{i\delta_+}\sin\alpha\,\cos\beta, \end{aligned} \qquad (2.2)$$

where, since the over-all phase is arbitrary, we have chosen c_0 to be real. Also we can impose the restrictions $0\leq\alpha\leq(\pi/2)$, $0\leq\beta\leq(\pi/2)$, $-\pi<\delta_-\leq\pi$, $-\pi<\delta_+\leq\pi$. If, and only if, either $\beta=(\pi/4)$ and $(\delta_++\delta_-)=\pm\pi$ or $\alpha=0$ then $\psi_R(i)$ is of the form $Y_{10}(\theta,\phi)$ with respect to an axis defined by the angles $[\alpha, \frac{1}{2}(\pi-\delta_++\delta_-)]$ and therefore represents a molecule in a pure $M=0$ state. Thus the molecule of orthohydrogen is only in a pure $M=0$ state with respect to some axis if $c_{-1}=-c_1^*$ with respect to any, and therefore every, axis. A special case of this arises when $\alpha=0$ so that the molecule has $M=0$ with respect to the initial axis.

The energy due to the interaction between the electric quadrupole moments Q of molecules on sites i and j is of the form

$$w(ij)=\sum_{m_1m_2} A(m_1, m_2{:}r_{ij})\,B_{m_1}(i)\,B_{m_2}(j) \times Y_{4,-(m_1+m_1)}(\theta_{ij},\phi_{ij}), \qquad (2.3)$$

where

$$A(m_1, m_2{:}r_{ij}) =(20\pi/9)(70\pi)^{1/2}(-1)^{m_1+m_2}\,C(224;\,m_1m_2)\chi,$$

$$B_m(i)=\sum_{M'M} c_{M'}^*(i)\,c_M(i)\int Y_{1M'}^*\,Y_{2m}\,Y_{1M}\,d\Omega,$$

$$\chi=6Q^2/25r_{ij}^5,$$

and $(r_{ij}, \theta_{ij}, \phi_{ij})$ define the length and orientation of the line joining the centres of the two molecules, the axis of reference still remaining arbitrary. The total quadrupole energy of the assembly of molecules is obtained from (2.3) by summing over all pairs (i,j). It is realistic to limit this summation to nearest neighbors for which $r_{ij}=r_0$, thus obtaining

$$E_Q=\tfrac{1}{2}\sum_i\sum_{m_1m_2} A(m_1, m_2{:}r_0)\,B_{m_1}(i)\sum_{j(n,n)} B_{m_2}(j) \times Y_{4,-(m_1+m_2)}(\theta_{ij},\phi_{ij}). \qquad (2.4)$$

This equation determines the energy of the system due to the electric quadrupole interaction between orthohydrogen molecules in terms of the rotational wave function of each molecule, and of the lattice parameters. All orientations are defined relative to an arbitrary axis, so that (2.4) is invariant under rotation of the axis of reference.

III. SELF-CONSISTENT ORIENTATIONAL ORDERING

The expression (2.4) which determines the configurational energy of the system of N molecules is a complicated function of degree four in $3N$ complex variables $c_M(i)$, $i=1, 2, \cdots, N$ and $M=-1, 0, 1$. By the normalization condition and by (2.2) it is, in fact, a function of the $4N$ real variables α_i, β_i, $\delta_-(i)$, $\delta_+(i)$ with $i=1, \cdots, N$. Because of the mathematical difficulties involved in minimizing this function—the task is even greater when the free energy is considered—it is unavoidable that some type of spatial ordering be assumed. The stability of various superlattices is examined at $T=0$°K using E_Q, and the transition from the high-temperature disordered state into such an ordered

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[12] The calculations are being extended to the superlattice structure $Pca2_1$ considered by Raich and James (Ref. 10) and previously, using a fixed axis of quantization, by Bell and Fairbairn [II and III (Ref. 7)].

state is investigated using the configurational free energy of the assembly. The former is considered in this section, the latter problem being investigated in Secs. IV–VI using a zeroth-order statistical approximation.

To demonstrate the method, we examine first the simple case in which all sites on the lattice are equivalent. There is no spatial ordering and $c_M(i)$ is, therefore, independent of i. Using (2.2) with the same values of α, β, δ_+ and δ_- for all i, a straightforward calculation gives

$$E_Q/N=\tfrac{7}{12}\chi\{13\sin^4\alpha+2\sin^4\alpha\sin^2\beta\cos^2\beta-16\sin^2\alpha+8\sin^2\alpha\cos^2\alpha\sin\beta\cos\beta\cos\lambda+4\},$$

where $\lambda=(\delta_++\delta_-)$, the c axis of the hcp structure being chosen as reference axis. On minimizing with respect to the three variables (α,β,λ), the value $E_Q=-\chi N$ is obtained: This corresponds to $\beta=\pi/4$, $\lambda=\pm\pi$ and $\alpha=\sin^{-1}(2/\sqrt{7})=49°\ 6'$. Thus the configuration, which has minimum energy at $T=0°\mathrm{K}$ subject to the constraint that all lattice sites are equivalent, has all molecules in the state $M=0$ with respect to an axis making an angle $\sin^{-1}(2/\sqrt{7})$ with the c axis. This value obtained for E_Q is lower than that found previously $(7\chi N/12)$ for a fixed axis of quantization, but not as low as that obtained below with spatial ordering present.

The simplest type of spatial ordering for the hcp structure is of the layer type, with the superlattice structure formed by planes perpendicular to the c axis. This amounts to taking the two sites in the unit cell to be inequivalent. The molecules in alternate planes are on equivalent lattice sites, and we introduce two distinct sets of coefficients $c_M^{(1)}$ and $c_M^{(2)}$. On writing $c_{-1}^{(k)}=\exp[i\delta_-(k)]\sin\alpha_k\sin\beta_k$, $c_0^{(k)}=\cos\alpha_k$, $c_1^{(k)}=\exp[i\delta_+(k)]\sin\alpha_k\cos\beta_k$, $k=1,2$, the configurational energy for N lattice sites is given by

$$\begin{aligned}E_Q/N=\tfrac{1}{48}\chi\{&\sum_{k=1,2}27(13\sin^4\alpha_k+2\sin^4\alpha_k\cos^2\beta_k\sin^2\beta_k-16\sin^2\alpha_k+8\sin^2\alpha_k\cos^2\alpha_k\cos\beta_k\sin\beta_k\cos\lambda_k+4)\\&-26(9\sin^2\alpha_1\sin^2\alpha_2-6\sin^2\alpha_1-6\sin^2\alpha_2+4+2\sin^2\alpha_1\sin^2\alpha_2\sin\beta_1\cos\beta_1\sin\beta_2\cos\beta_2\cos\lambda)\\&+104\sin\alpha_1\cos\alpha_1\sin\alpha_2\cos\alpha_2[\cos\beta_1\cos\beta_2\cos\tfrac{1}{2}(\lambda_1-\lambda_2-\lambda)+\sin\beta_1\sin\beta_2\cos\tfrac{1}{2}(\lambda_1-\lambda_2+\lambda)\\&-\cos\beta_1\sin\beta_2\cos\tfrac{1}{2}(\lambda_1+\lambda_2-\lambda)-\sin\beta_1\cos\beta_2\cos\tfrac{1}{2}(\lambda_1+\lambda_2+\lambda)]\},\qquad(3.1)\end{aligned}$$

where $\lambda=\{\delta_+(1)-\delta_-(1)\}-\{\delta_+(2)-\delta_-(2)\}$. For fixed values of α_k, β_k, the expression (3.1) is a minimum when $\cos\lambda_1=\cos\lambda_2=-\cos\lambda=-1$ and $\cos\frac{1}{2}(\lambda_1+\lambda_2\pm\lambda)=-\cos\frac{1}{2}(\lambda_1-\lambda_2\pm\lambda)=1$. These relations have the solution $\lambda_1=\lambda_2=\pi$ and $\lambda=2\pi$ (or, equivalently, $\lambda_1=\lambda_2=-\pi$ and $\lambda=-2\pi$). On minimizing further with respect to α_k, β_k, the minimum energy is obtained when $\beta_k=\pi/4$ and $453\sin^2\alpha_k=244$ (i.e., $\alpha_k\simeq 47°\ 13'$) for $k=1, 2$. This minimum value is $E_Q=-3.143\chi N$, which is much lower than that attained in the orderings discussed previously.

Using the values obtained for λ_1, λ_2, β_1, and β_2, the ordered state of the system is one in which each molecule is in the $M=0$ state with respect to an axis. This is inclined at the angle $\alpha_1=\alpha_2=\alpha=47°\ 13'$ to the c axis for all molecules but, because $\lambda=2\pi$, the axis for the molecules in one set of planes is on the opposite side of the c axis (rotated through 180° about the c axis) to that for the molecules in the alternate planes. For this ground-state configuration, every molecule is in a definite state. On lowering the temperature, the transition from the high-temperature state, which is completely disordered, to the ground state is accompanied by an entropy loss of $\mathbf{k}\ln 3$ per orthomolecule ($\mathbf{k}$ being Boltzmann's constant), as has been found experimentally.[1] Many previous theoretical orientational orderings have failed to satisfy this criterion.

IV. SIMPLIFIED MODEL

We have indicated above the existence of a low-energy spatially ordered state at $T=0°\mathrm{K}$. To discuss the system at finite temperatures we require the configurational free energy. For convenience, and to obtain appropriate mathematical expressions for the free energy in the two phases under consideration, we use a simplified model in which the axes of the orthomolecules in the ordered phase are inclined at the angle 45° to the c axis rather than at the angle $\alpha=47°\ 13'$ derived above. This simplification allows the use of the same set of axes for the disordered phase and for both sets of planes in the ordered phase. This right-handed set of rectangular axes consists of the two quantization axes (01 and 02) for the sets of alternate planes and the direction (03) perpendicular to both of them, this third axis lying in the plane normal to the c axis.

Let N_1, N_2, and N_3 designate the numbers of molecules on the lattice which are oriented along the axes 01, 02, and 03, respectively. If $N_1^{(k)}$, $N_2^{(k)}$, and $N_3^{(k)}$ designate the corresponding numbers of molecules on sublattice k, then the completely ordered phase is defined by $N_1^{(1)}=\frac{1}{2}N=N_2^{(2)}$, or $N_2^{(1)}=\frac{1}{2}N=N_1^{(2)}$. This state has configurational energy $E_Q=-3.115\chi N$, which corresponds to an error of less than 1%, compared with the ordering using axes inclined at angle $\alpha=47°\ 13'$ obtained in Sec. III.

At nonzero temperatures, the minimum energy state is disturbed by thermal motion and all types of nearest-neighbor pairs occur in proportions determined by the equilibrium conditions. Let the unit vector $\mathbf{u}_{ij}$ represent the direction, specified by polar angles θ_{ij} and ϕ_{ij}, from site i to nearest-neighbor site j, and let $w_{kl}(\mathbf{u}_{ij})$ denote the interaction energy of a pair of molecules, the molecules on sites i and j being respectively oriented along the (quantization) axes $0k$ and $0l (k, l=1, 2, 3)$. Then, from (2.3),

$$\begin{aligned}
w_{11}(\mathbf{u}_{ij})/\chi &= \tfrac{1}{48}P_4^4(\cos\theta_{ij})\ \cos 4\phi_{ij} - \tfrac{1}{6}P_4^2(\cos\theta_{ij})\ \cos 2\phi_{ij} + \tfrac{3}{2}P_4(\cos\theta_{ij}),\\
w_{22}(\mathbf{u}_{ij})/\chi &= \tfrac{1}{48}P_4^4(\cos\theta_{ij})\ \cos 4\phi_{ij} + \tfrac{1}{6}P_4^2(\cos\theta_{ij})\ \cos 2\phi_{ij} + \tfrac{3}{2}P_4(\cos\theta_{ij}),\\
w_{33}(\mathbf{u}_{ij})/\chi &= 4P_4(\cos\theta_{ij}),\\
w_{12}(\mathbf{u}_{ij})/\chi = w_{21}(\mathbf{u}_{ij})/\chi &= -\tfrac{1}{48}P_4^4(\cos\theta_{ij})\ \cos 4\phi_{ij} + \tfrac{1}{2}P_4(\cos\theta_{ij}),\\
w_{13}(\mathbf{u}_{ij})/\chi = w_{31}(\mathbf{u}_{ij})/\chi &= \quad \tfrac{1}{6}P_4^2(\cos\theta_{ij})\ \cos 2\phi_{ij} - 2P_4(\cos\theta_{ij}),\\
w_{23}(\mathbf{u}_{ij})/\chi = w_{32}(\mathbf{u}_{ij})/\chi &= - \tfrac{1}{6}P_4^2(\cos\theta_{ij})\ \cos 2\phi_{ij} - 2P_4(\cos\theta_{ij}).
\end{aligned} \tag{4.1}$$

It is convenient to list here the directions from a given site i to its twelve nearest-neighbor sites j; these are

(a) on the same sublattice:

$$\theta_{ij} = (\pi/6),\ (\pi/2),\ (5\pi/6);\ \phi_{ij} = -(\pi/4),\ (3\pi/4) \qquad \text{(6 sites)};$$

(b) on the other sublattice:

$$\theta_{ij} = \cos^{-1}(1/\sqrt{3}),\ \phi_{ij} = (\pi/4), (5\pi/4) \qquad \text{(2 sites)};$$

$$\theta_{ij} = \cos^{-1}(-1/2\sqrt{3}), \qquad \phi_{ij} = \alpha - (\pi/4),\ (3\pi/4) - \alpha,\ -\alpha - (\pi/4),\ \alpha - (5\pi/4); \qquad \alpha = \tan^{-1}(2\sqrt{2}/\sqrt{3}) \qquad \text{(4 sites)}.$$

It should be noted that $w_{kl}(\mathbf{u}_{ji}) = w_{kl}(-\mathbf{u}_{ij})$ denotes the interaction of the same pair as $w_{lk}(\mathbf{u}_{ij})$. Hence, since by (3.1) $w_{kl}(\mathbf{u}_{ij}) = w_{lk}(\mathbf{u}_{ij})$, it is necessary for consistency that $w_{kl}(\mathbf{u}_{ij}) = w_{kl}(-\mathbf{u}_{ij})$. Equations (4.1) satisfy this criterion since the changes $\theta_{ij} \to \pi - \theta_{ij}$, $\phi_{ij} \to \pi + \phi_{ij}$ leave the expressions on the right-hand side unaltered.

V. THE CONFIGURATIONAL ENERGY AND FREE ENERGY

Let $N_{kl}^{(11)}(\mathbf{u}_{ij})$, $N_{kl}^{(22)}(\mathbf{u}_{ij})$ denote the numbers of k-l nearest-neighbor pairs at orientation $\mathbf{u}_{ij}$ with both sites on sublattices 1 and 2, respectively. Note the identities

$$\begin{aligned}
N_{kl}^{(11)}(-\mathbf{u}_{ij}) &= N_{lk}^{(11)}(\mathbf{u}_{ij}),\\
N_{kl}^{(22)}(-\mathbf{u}_{ij}) &= N_{lk}^{(22)}(\mathbf{u}_{ij}),
\end{aligned} \tag{5.1}$$

where both sides of each relation refer to identical types of pairs. Also, let $N_{kl}^{(12)}(\mathbf{u}_{ij'})$ denote the number of k-l nearest-neighbor pairs at orientation $\mathbf{u}_{ij'}$ with the molecules in the k and l states on sublattices 1 and 2, respectively. When the number of lattice sites is large these pair numbers obey the conditions

$$\begin{aligned}
N_{kk}^{(11)}(\mathbf{u}_{ij}) + \sum_{l\neq k} N_{kl}^{(11)}(\mathbf{u}_{ij}) &= N_k^{(1)},\\
N_{kk}^{(22)}(\mathbf{u}_{ij}) + \sum_{l\neq k} N_{kl}^{(22)}(\mathbf{u}_{ij}) &= N_k^{(2)}, \quad \text{all } j;
\end{aligned} \tag{5.2}$$

$$\begin{aligned}
N_{kk}^{(12)}(\mathbf{u}_{ij'}) + \sum_{l\neq k} N_{kl}^{(12)}(\mathbf{u}_{ij'}) &= N_k^{(1)},\\
N_{kk}^{(12)}(\mathbf{u}_{ij'}) + \sum_{l\neq k} N_{lk}^{(12)}(\mathbf{u}_{ij'}) &= N_k^{(2)}, \quad \text{all } j'.
\end{aligned} \tag{5.3}$$

Adding the two relations of (5.3),

$$2N_{kk}^{(12)}(\mathbf{u}_{ij'}) + \sum_{l\neq k} \{N_{kl}^{(12)}(\mathbf{u}_{ij'}) + N_{lk}^{(12)}(\mathbf{u}_{ij'})\} = N_k, \quad \text{all } j'. \tag{5.4}$$

The configurational energy, which we assume is due solely to quadrupole-quadrupole interactions, is given by

$$E_Q = \tfrac{1}{2} \sum_{k=1}^{3} \sum_{l=1}^{3} \sum_{j=1}^{6} \{N_{kl}^{(11)}(\mathbf{u}_{ij}) + N_{kl}^{(22)}(\mathbf{u}_{ij})\} w_{kl}(\mathbf{u}_{ij}) + \sum_{k=1}^{3} \sum_{l=1}^{3} \sum_{j'=1}^{6} N_{kl}^{(12)}(\mathbf{u}_{ij'}) w_{kl}(\mathbf{u}_{ij'}), \tag{5.5}$$

where the summations with respect to j and j' are respectively over the nearest neighbors of a given site in the same sublattice and the other sublattice. The factor $\tfrac{1}{2}$ multiplying the first term corrects for the double counting of each pair in summing over all k, l, and j inside a given sublattice [see (5.1)]. Substituting from (5.2) and (5.4) in (5.5), and using (5.1), the configurational energy may be transformed to

$$E_Q = \sum_{k=1}^{3} N_k \epsilon_k + \sum_{k<l} \sum_{j=1}^{6} \{N_{kl}^{(11)}(\mathbf{u}_{ij}) + N_{kl}^{(22)}(\mathbf{u}_{ij})\} \epsilon_{kl}(\mathbf{u}_{ij}) + \sum_{k<l} \sum_{j'=1}^{6} N_{kl}^{(12)}(\mathbf{u}_{ij'}) \epsilon_{kl}(\mathbf{u}_{ij'}), \tag{5.6}$$

where

$$\begin{aligned}
\epsilon_k &= \tfrac{1}{2}\{\sum_{j=1}^{6} w_{kk}(\mathbf{u}_{ij}) + \sum_{j'=1}^{6} w_{kk}(\mathbf{u}_{ij'})\}, \qquad k=1, 2, 3\\
\epsilon_{kl}(\mathbf{u}_{ij}) &= w_{kl}(\mathbf{u}_{ij}) - \tfrac{1}{2}w_{kk}(\mathbf{u}_{ij}) - \tfrac{1}{2}w_{ll}(\mathbf{u}_{ij}) = \epsilon_{lk}(\mathbf{u}_{ij}), \qquad k\neq l
\end{aligned} \tag{5.7}$$

and $\epsilon_{kl}(\mathbf{u}_{ij'})$ is defined similarly. It will prove useful to define averaged energies,

$$\epsilon_{kl}=\epsilon_{lk}=\tfrac{1}{6}\sum_{j=1}^{6}\epsilon_{kl}(\mathbf{u}_{ij}), \qquad \epsilon_{kl}'=\epsilon_{lk}'=\tfrac{1}{6}\sum_{j'=1}^{6}\epsilon_{kl}(\mathbf{u}_{ij'}). \tag{5.8}$$

From (4.1) and (4.2),

$$\begin{aligned} &\epsilon_1=\epsilon_2=-91\chi/96, && \epsilon_3=7\chi/8,\\ &\epsilon_{12}=3\chi/2, && \epsilon_{13}=\epsilon_{23}=-33\chi/128,\\ &\epsilon_{12}'=-13\epsilon_{12}/27, && \epsilon_{13}'=\epsilon_{23}'=-13\epsilon_{13}/27. \end{aligned} \tag{5.9}$$

The equilibrium orientation distribution of the molecules on the lattice is found by minimizing the Helmholtz free energy

$$F_Q=E_Q-TS_Q=E_Q-\mathbf{k}T\ln g_Q, \tag{5.10}$$

where g_Q is the number of ways, consistent with given values of the nearest-neighbor pair numbers occurring in the expression (5.5) for E_Q, of arranging given numbers $N_k^{(1)}$ and $N_k^{(2)}$ of molecules in the states $k=1, 2, 3$ on the sublattices.

VI. ZEROTH-ORDER THEORY OF THE TRANSITION

Since the evaluation of g_Q presents formidable problems, we utilize the most elementary approach, that of the zeroth-order approximation in which it is assumed that the distribution within each sublattice is random so that

$$g_Q=\{(\tfrac{1}{2}N)!\}^2/\prod_{k=1}^{3}\{N_k^{(1)}!N_k^{(2)}!\}. \tag{6.1}$$

Also, from the assumption of randomness, the pair numbers are given by

$$\begin{aligned} N_{kl}^{(11)}(\mathbf{u}_{ij})&=N_k^{(1)}N_l^{(1)}/(\tfrac{1}{2}N),\\ N_{kl}^{(22)}(\mathbf{u}_{ij})&=N_k^{(2)}N_l^{(2)}/(\tfrac{1}{2}N),\\ N_{kl}^{(12)}(\mathbf{u}_{ij'})&=N_k^{(1)}N_l^{(2)}/(\tfrac{1}{2}N). \end{aligned} \tag{6.2}$$

Since these are now independent of j and j', respectively, the configurational energy will depend only on the averaged interaction energies ϵ_k, ϵ_{kl}, and ϵ_{kl}'. It is also assumed that the ordered state is symmetrical with respect to the two sublattices in a way consistent with the known low-energy state $N_1^{(1)}=N_2^{(2)}=\frac{1}{2}N$ and with the relations $\epsilon_{13}=\epsilon_{23}$, $\epsilon_{13}'=\epsilon_{23}'$ between the averaged interaction energies. Accordingly we set

$$N_1^{(1)}=N_2^{(2)}, \qquad N_1^{(2)}=N_2^{(1)}, \qquad N_3^{(1)}=N_3^{(2)}=\tfrac{1}{2}N_3, \tag{6.3}$$

and define parameters σ and c by

$$\begin{aligned} \sigma&=2(N_1^{(1)}-N_1^{(2)})/(N-N_3),\\ &=2(N_2^{(2)}-N_2^{(1)})/(N-N_3),\\ c&=(N-2N_3^{(1)})/N\\ &=(N-2N_3^{(2)})/N=(N-N_3)/N. \end{aligned} \tag{6.4}$$

Here σ is the ordering parameter, and at $\sigma=0$ the distributions or the two sublattices are identical. The low-energy state is specified by $\sigma=c=1$. Substituting (6.2) in (5.6) and using definitions (6.4) we obtain

$$E_Q/N=\epsilon_3+c(\epsilon_1-\epsilon_3)+\tfrac{3}{2}c^2\{(1-\sigma^2)\epsilon_{12}+(1+\sigma^2)\epsilon_{12}'\}+6c(1-c)(\epsilon_{13}+\epsilon_{13}'). \tag{6.5a}$$

From (6.1) and (6.4), the configurational entropy is given by

$$S_Q/N=-\mathbf{k}[c\ln c+(1-c)\ln(1-c)+c\{\tfrac{1}{2}(1+\sigma)\ln(1+\sigma)+\tfrac{1}{2}(1-\sigma)\ln(1-\sigma)-\ln2\}]. \tag{6.5b}$$

For equilibrium F_Q must have a stationary value so that, using (5.10), (6.1), (6.4), and (6.5),

$$(N\mathbf{k}T)^{-1}\frac{\partial F_Q}{\partial\sigma}=\tfrac{1}{2}c\ln\frac{1+\sigma}{1-\sigma}-3c^2\sigma\frac{\epsilon_{12}-\epsilon_{12}'}{\mathbf{k}T}=0, \tag{6.6a}$$

$$\begin{aligned} (N\mathbf{k}T)^{-1}\frac{\partial F_Q}{\partial c}=\ln\frac{c}{1-c}&+\tfrac{1}{2}(1+\sigma)\ln\tfrac{1}{2}(1+\sigma)+\tfrac{1}{2}(1-\sigma)\ln\tfrac{1}{2}(1-\sigma)\\ &+(\mathbf{k}T)^{-1}[\epsilon_1-\epsilon_3+3c\{(1-\sigma^2)\epsilon_{12}+(1+\sigma^2)\epsilon_{12}'\}+6(1-2c)(\epsilon_{13}+\epsilon_{13}')]. \end{aligned} \tag{6.6b}$$

At $T=\infty$, the only solution of (6.6) is $\sigma=0$, $c=\frac{2}{3}$ which represents the completely disordered state

$$N_1^{(1)}=N_2^{(1)}=N_3^{(1)}=N_1^{(2)}=N_2^{(2)}=N_3^{(2)}=N/6.$$

If the expression for $\ln[(1+\sigma)/(1-\sigma)]$ supplied by (6.6a) is substituted in (6.6b), if both relations are simplified, and if the values (5.9) are used for the interaction energies, then we obtain the pair of simultaneous equations

$$\ln[(1+\sigma)/(1-\sigma)]-(40\chi/3\mathbf{k}T)c\sigma=0, \tag{6.7a}$$

$$\ln\{\tfrac{1}{2}c/(1-c)\}+(63\chi/16\mathbf{k}T)(c-\tfrac{2}{3})=-\tfrac{1}{2}\ln(1-\sigma^2). \tag{6.7b}$$

Since the left-hand side of (6.7b) is a monotonic increasing function of c while the right-hand side is never less than zero, the least possible value of c is $\frac{2}{3}$, attained only at $\sigma=0$. The solution $\sigma=0$, $c=\frac{2}{3}$ is clearly a possible one at all values of T, and any other solutions must exist in symmetrical pairs, since if σ_0, c_0 is such a solution then so is $-\sigma_0$, c_0. For a given value of c, it is easy to show that solutions other than $\sigma=0$ of (6.7a) exist only when

$$20\chi c>3\mathbf{k}T. \tag{6.8}$$

Hence the only temperature at which a second-order transition can occur by the separation of a pair of other solutions from the solution $\sigma=0$, $c=\frac{2}{3}$ is found by inserting $c=\frac{2}{3}$ in (6.8) and this we denote by T_c, so that

$$T_c=(20\chi/3\mathbf{k})(\tfrac{2}{3})=40\chi/9\mathbf{k}=2.9\text{°K} \tag{6.9}$$

(taking $4\chi=2.615\mathbf{k}$). Also since the maximum value of c is 1 it follows from (6.8) that the solution $\sigma=0$, $c=\frac{2}{3}$ is unique for $T>\frac{3}{2}T_c$. It can be shown that, in fact, the solution $\sigma=0$, $c=\frac{2}{3}$ is unique where $T\geq T_c$ and also is stable in the sense of giving the least value of F_Q, while the pair of solutions which separate at $T=T_c$ are stable for $T<T_c$. Hence T_c is a second-order transition temperature. Since the proof of these points requires some rather tedious algebra, it has been placed in the Appendix.

It is important to note that from (6.1) and (6.4) the orientational entropy $\mathbf{k}\ln g_Q$ has the value $\mathbf{k}N\ln 3$ in the high-temperature state $\sigma=0$, $c=\frac{2}{3}$, while in the low-energy state $\sigma=c=1$ at $T=0$ it has the value zero. Hence the change in entropy per molecule of orthohydrogen is $\mathbf{k}\ln 3$ over the transition region.

VII. DISCUSSION

A theory of the second-order or λ transition in solid orthohydrogen should satisfy three conditions:

(1) The low-temperature state has a symmetry attainable by a second-order transition from the high-temperature state.

(2) The change in the entropy per orthohydrogen molecule over the transition range is equal to the observed value of $\mathbf{k}\ln 3$[1] (this condition can possibly be relaxed at lower mole fractions of orthohydrogen).[2]

(3) The calculated transition temperature should be of the same order of magnitude as the experimental one.

The earliest theory, due to Tomita,[6] failed to satisfy condition (1) and we showed in I[7] that the "orientational transition" he postulated does not occur. It was proved there that a model like Tomita's with no spatial order is equivalent to an Ising model ferromagnet in an "equivalent" external field which is a linear function of the temperature. Any transition which may occur is of the first order and is due to the equivalent field passing through the value zero at a temperature below the second-order transition temperature of the corresponding symmetrical or zero-field Ising model. (The first-order transition temperature obtained by Raich and James[10] in their discussion of an fcc model for solid orthohydrogen can easily be calculated in this way.) We concluded that the second-order transition in solid orthohydrogen is probably due to the onset of spatial ordering, and in II and III[7] discussed a type of ordering with two equivalent sublattices reached by a second-order transition. The same model based on single-particle rotational wave functions with quantization axis parallel to a threefold symmetry axis of the hcp lattice was used by Danielian,[8] who agreed that the transition is due to sublattice ordering. However, he demonstrated that the completely ordered state of II and III[7] lies slightly above the lowest quadrupole-quadrupole lattice energy state. Neither the theory in II and III[7] nor that of Danielian[8] satisfies condition (2). In the former case a half and in the latter two-thirds of the sites are occupied in the ground state by molecules for which $M=\mp1$, where M is the component along the symmetry axis of the rotational quantum number J, equal to 1 for orthohydrogen at low temperatures. Hence the changes in entropy per orthohydrogen molecule are, respectively, $\frac{1}{2}\mathbf{k}\ln 2$ and $\frac{2}{3}\mathbf{k}\ln 2$, less than the required value $\mathbf{k}\ln 3$. Also an error was made both in II and III and in Danielian, because the value of χ used was too large by a factor of four. The transition temperatures obtained should thus be divided by four and are then much lower than Smith and Housley's[4] estimate for pure orthohydrogen.

An improved treatment of the ground state is thus desirable, and this has been attempted in the present paper. We assume that in the temperature range where the λ transition in solid hydrogen is observed the lattice is of the hcp type, and that the transition represents the onset of spatial ordering with two equivalent sublattices consisting of layers perpendicular to an axis of threefold symmetry. Instead of using single-particle orientational wave functions for $J=1$ with arbitrary axes, we have carried out a variational process and minimized the quadrupole-quadrupole energy of the completed ordered state with respect to the axes of the wave functions. The ground-state energy produced is considerably lower than that of Danielian, $-3.14\chi N$ as compared with $-9\chi N/8$. Also the single-particle orientational wave functions of the molecules on the two sublattices have no degeneracy in the ground state so that condition (2) is now satisfied. To derive a transition temperature, we have used an orthogonal set of rotational wave functions of which two are approximately equivalent to the ground-state wave functions in the respective sublattices. With a zeroth-order statistical approximation, we find a second-order transition at 2.9°K so that conditions (1) and (3) are also satisfied. The calculated transition temperature is very close to Smith and Housley's[4] extrapolated experimental value of 3.0°K for pure orthohydrogen, but this close agreement may be fortuitous, since the zeroth-order statistical method gives rather high transition temperatures.[13] The accurate second-order transition temperature for our model is thus probably less than 3°K. This may be due to using wave functions in the statistical theory which are only approximately equivalent to the true ground-state single-particle wave functions, to the fact that a product of single-particle wave functions is itself an approximation, to inaccuracies in the lattice parameters assumed for pure orthohydrogen, to the neglect of interactions other than those of nearest-neighbor quadrupole-quadrupole type, and to the possible occurrence of a more complicated sublattice structure than that assumed.

APPENDIX

First we investigate the possibility of solutions of Eq. (6.7) other than $\sigma=0$, $c=\frac{2}{3}$ in the temperature range $T>T_c$. Defining $y=\frac{1}{2}(3c-2)$, and T_c by (6.9) then, if $\sigma\neq 0$, Eq. (6.7a) gives

$$y=\frac{T}{2\sigma T_c}\ln\frac{1+\sigma}{1-\sigma}-1>\frac{1}{2\sigma}\ln\frac{1+\sigma}{1-\sigma}-1,\qquad \text{for } T>T_c. \tag{A1}$$

Thus the left-hand side of (6.7b), since $y>0$ for $\sigma\neq 0$, satisfies the inequality

$$\ln\frac{1+y}{1-2y}+\frac{189T_c}{320T}y>3y>\frac{3}{2\sigma}\ln\frac{1+\sigma}{1-\sigma}-3.$$

Since $(3/2\sigma)\ln\{(1+\sigma)/(1-\sigma)\}-3+\frac{1}{2}\ln(1-\sigma^2)$ is a monotonic increasing function of σ, it follows that

$$\ln\frac{1+y}{1-2y}+\frac{189T_c}{320T}y>-\tfrac{1}{2}\ln(1-\sigma^2) \tag{A2}$$

for $\sigma>0$, and hence by symmetry for all $\sigma\neq 0$. The inequality (A2) shows that Eq. (6.7b) has no solutions with $T>T_c$ and $\sigma\neq 0$. Hence the state defined by $\sigma=0$, $c=\frac{2}{3}$ (the disordered state) is the unique solution of the equilibrium conditions for temperatures $T>T_c$.

Secondly, for $T<T_c$, (6.7) can be solved for y and σ^2 as series in

$$\delta=(T_c-T)/T. \tag{A3}$$

The first-order terms are given by the simultaneous equations

$$y=-\delta+\tfrac{1}{3}\sigma^2,\qquad 1149y/320=\tfrac{1}{2}\sigma^2,$$

which have the solution, a good approximation when $\delta\ll 1$,

$$\sigma^2=1149\delta/223,\qquad y=160\delta/223. \tag{A4}$$

If a stationary point is to represent a possible equilibrium state, it must give a minimum of the $F_Q(\sigma,c)$ surface. From (6.6) and (5.9),

$$\frac{1}{N\mathbf{k}T}\frac{\partial^2F_Q}{\partial\sigma^2}=\frac{c}{1-\sigma^2}-\frac{3c^2T_c}{2T}, \tag{A5a}$$

$$\frac{1}{N\mathbf{k}T}\frac{\partial^2F_Q}{\partial\sigma\partial c}=\tfrac{1}{2}\ln\frac{1+\sigma}{1-\sigma}-\frac{3T_cc\sigma}{T}, \tag{A5b}$$

$$\frac{1}{N\mathbf{k}T}\frac{\partial^2F_Q}{\partial c^2}=\frac{1}{c(1-c)}+\frac{3T_c}{2T}\left[\frac{189}{320}-\sigma^2\right]. \tag{A5c}$$

Hence, when $\sigma=0$, $c=\frac{2}{3}$,

$$\frac{1}{N\mathbf{k}T}\frac{\partial^2F_Q}{\partial\sigma^2}=\frac{2}{3}\frac{T-T_c}{T},$$

$$\left(\frac{1}{N\mathbf{k}T}\right)^2\left\{\frac{\partial^2F_Q}{\partial\sigma^2}\frac{\partial^2F_Q}{\partial c^2}-\left(\frac{\partial^2F_Q}{\partial\sigma\partial c}\right)^2\right\}=3\frac{T-T_c}{T}\left(1+\frac{63T_c}{320T}\right), \tag{A6}$$

so that, where $T>T_c$, $F_Q(0,\frac{2}{3})$ is a minimum. In cooperative phenomena it is sometimes found that, though a disordered state gives a minimum on the free-energy surface down to a "second-order transition temperature," this transition is forestalled by a first-order transition at a higher temperature to a lower minimum of the free energy. This cannot happen in the present case, as we have shown that $\sigma=0$, $c=\frac{2}{3}$ is the unique stationary point of $F_Q(\sigma,c)$ when $T\geq T_c$. Hence the disordered state is stable down to $T=T_c$ and, again by (A6), it can be seen that it becomes a saddle point on the surface $F_Q(\sigma,c)$ and hence is unstable where $T<T_c$. To complete the demonstration that T_c is a second-order transition temperature, it is necessary to show that the pair of solutions which separate at $T=T_c$ represent minima on the surface $F_Q(\sigma,c)$ just below T_c. If only the terms of order δ are retained in (A5), and (A4) is substituted, then

$$\frac{1}{N\mathbf{k}T}\frac{\partial^2F_Q}{\partial\sigma^2}=\frac{4\sigma^2}{9}=\frac{1532\delta}{669},$$

$$\left(\frac{1}{N\mathbf{k}T}\right)^2\left\{\frac{\partial^2F_Q}{\partial\sigma^2}\frac{\partial^2F_Q}{\partial c^2}-\left(\frac{\partial^2F_Q}{\partial\sigma\partial c}\right)^2\right\}=\frac{1149\delta}{160}.$$

Hence the pair of symmetrical solutions which separate from $\sigma=0$, $c=\frac{2}{3}$ at $T=T_c$ are stable just below T_c. This, of course, does not preclude a further transition, caused, for example, by a change in lattice structure occurring at a finite interval below T_c.

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[13] C. Domb, Advan. Phys. 9, 245 (1960).