

## Ordering in Solid Hydrogen†

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It is shown that in the case of the model for solid ortho-hydrogen considered, the ground-state superlattice structure, produced by the electrostatic quadrupole interactions, may be derived exactly. It consists essentially of two unequal sublattices: one consisting of molecules  $A$  in the state  $M=0$  and the other consisting of molecules  $B$  in either of the states  $M=\pm 1$ , the latter being twice as many as the former. The configuration on each triangular plane, normal to the axis of symmetry of the lattice, is such that each  $A$  molecule is surrounded by six  $B$  molecules, and each  $B$  molecule is surrounded by three  $A$  molecules and three  $B$  molecules. The transition temperature of the system is found to be  $5.8^\circ\text{K}$  in the zeroth approximation and  $3^\circ\text{K}$  in a tetrahedral approximation, the latter being in agreement with the experimental estimate.

## INTRODUCTION

THE specific-heat measurements of Mendelssohn *et al.*,<sup>1</sup> Hill and Ricketson,<sup>2</sup> and lately Ahlers and Orttung,<sup>3</sup> have established that solid hydrogen with a high ortho-hydrogen concentration ( $>62\%$ ) exhibits a  $\lambda$  anomaly at about  $1.6^\circ\text{K}$ . These, together with nuclear-magnetic-resonance experiments,<sup>4-6</sup> indicate that solid hydrogen undergoes a co-operative transition at this temperature. This transition is due to the ortho-component of hydrogen, since the specific-heat anomaly is not observed at low concentrations, and only its nucleus (with  $I=1$ , as distinct from para-hydrogen with  $I=0$ ) could be responsible for the nuclear-resonance absorption. The mechanism by means of which the ortho-hydrogen molecules cause this transition† is considered to be basically the removal of their rotational degeneracy in  $J=1$  by the crystal field, resulting in general in three distinct states  $M=0$ ,  $M=\pm 1$ .<sup>5,7,8</sup> It has been shown that at normal pressure only electrostatic quadrupole-quadrupole interactions need be considered between neighboring molecules.<sup>8,9</sup> Thus it may be concluded that the transition is effected through a co-operative ordering process, in which the elements are molecules in the states  $M=0$ ,  $M=\pm 1$ , respectively, and the configurational energy is determined by the quadrupolar interactions.<sup>7,10</sup> Thus above the transition temperature there will be a random distribution of the elements whereas below the transition temperature an ordered array will appear,

the ultimate form of which will be determined by the lowest configurational energy.

In this paper, the case of pure ortho-hydrogen is considered. It is a convenient starting point from the theoretical point of view before proceeding to the study of lower concentrations (i.e., diluted with para-hydrogen). Besides, with the development of promising experimental techniques, pure ortho-hydrogen is no longer such a hypothetical substance as it has been until relatively recently. It is shown that given the crystal structure and the interactions between neighboring molecules considered here, the ground-state superlattice structure can be derived exactly and the thermodynamic properties of the system evaluated using well-known statistical-mechanical methods. In the following, the theoretical model used is described and the ground-state configuration derived; subsequently, the transition temperature is calculated. This theoretical model has already been investigated by Bell and Fairbairn<sup>10</sup>; however, they performed their calculations on a conjectured superlattice structure which is very different from the exact ground-state configuration derived here.

## THE GROUND STATE

The basic features of our theoretical model for pure ortho-hydrogen are as follows: (a) the crystal structure is hexagonal-close-packed; (b) the intermolecular interaction is purely an electrostatic quadrupole-quadrupole interaction; (c) the axis of quantization is parallel to the axis of threefold symmetry of the lattice; (d) the crystal field is axially symmetric, so that each molecule is in one of two states:  $A$ , with  $M=0$  or  $B$ , with  $M=\pm 1$ . These postulates have already been discussed in the literature.<sup>5,7-10</sup>

In Fig. 1 a section of a hexagonal-close-packed lattice is shown with the axis of symmetry normal to the paper and consisting of two consecutive plane triangular layers: one in full lines and the other above it in broken lines; this latter could just as well represent the layer immediately beneath the former. The whole lattice is a repetition of the scheme shown: Sites on alternate layers are vertically aligned, and each site is in a vertical line passing through the center of a

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triangle formed by sites on its neighboring layer, thus forming a tetrahedron (e.g., sites 1, 2, 3, 4, and 1, 5, 6, 4). In a given triangular layer, every alternate triangle is the base of two tetrahedra, the vertex of one being a site on the triangular layer immediately above it, and the vertex of the other being a site in the layer immediately beneath it. Each site has twelve nearest neighbors; six are in its own triangular layer, three form a triangle on the layer immediately above it, and the remaining three form a triangle on the layer immediately beneath it. It will be necessary to classify nearest-neighbor bonds into two types: "in" bonds, meaning bonds which are in one of the triangular layers, e.g., 1-5, 1-6; and "off" bonds, meaning bonds which are off the triangular layer; e.g., 1-4, 1-2. Since the axis of quantization is chosen parallel to the axis of symmetry, it follows that the "in" and "off" bonds form angles of  $\pi/2$  and  $\cos^{-1}(\pm\sqrt{3}/3)$ , respectively, with the axis of quantization. The other observation which will be required is the fact that if the lattice consists of  $N$  sites, then it can be subdivided into  $N$  tetrahedra of sites, such that each nearest-neighbor bond is found on one tetrahedron only. Such a set of tetrahedra may be obtained by taking either all tetrahedra the vertices of which point upwards, or all tetrahedra the vertices of which point downwards (the vertical direction in Fig. 1 is normal to the paper). This means that half the total number of tetrahedra on the lattice are considered; also each tetrahedron is symmetrical with respect to the axis of quantization.

The quadrupole-quadrupole interactions  $\omega$  between a neighboring pair of molecules can be shown to reduce to the following<sup>10</sup>:

$$\begin{aligned} \omega_{AA} &= 4\lambda P_4(\cos\theta), \\ \omega_{AB} &= -2\lambda P_4(\cos\theta), \quad \lambda = \frac{6e^2 Q^2}{25r_0^5}, \\ \omega_{BB} &= \lambda P_4(\cos\theta); \end{aligned} \tag{1}$$

where  $A$  and  $B$  refer to the two molecular species  $M=0$  and  $M=\pm 1$ , respectively,  $\theta$  is the angle between the axis of quantization and the line joining the pair of molecules,  $Q$  is the quadrupole moment of the molecule,  $r_0$  the intermolecular distance, and  $e$  the charge of the electron.

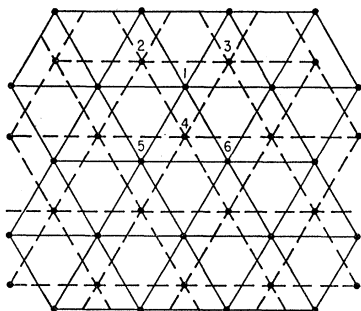


FIG. 1. Two consecutive plane triangular layers of a hexagonal-close-packed lattice. The axis of threefold symmetry is normal to these planes.

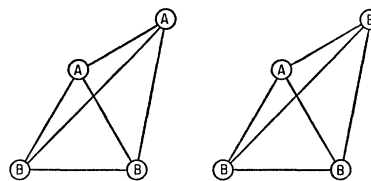


FIG. 2. The two possible ground-state tetrahedral configurations of  $A$  ( $M=0$ ) and  $B$  ( $M=\pm 1$ ) ortho-hydrogen molecules with quadrupolar interactions and the axis of quantization normal to the base triangles.

We now determine the ground configurational state of the system. The total interaction energy  $E$  is

$$E = \sum_{\langle i,j \rangle} \omega_{l,m}{}^{i,j}, \quad (l=A,B; m=A,B), \tag{2}$$

the summation being over all nearest-neighbor molecular pairs,  $\langle i,j \rangle$  on the lattice. Since the lattice may be subdivided into  $N$  tetrahedra such that each nearest-neighbor bond is found on one tetrahedron only,  $E$  may be expressed in the form

$$E = \sum_{i=1}^N \epsilon_i; \quad \epsilon_i = \sum_{\langle i,j \rangle} \omega_{l,m}{}^{i,j}; \tag{3}$$

where  $\epsilon_i$  represents the total interaction energy of a single tetrahedron, summed over its six bonds. It is obvious that

$$E \geq N\epsilon_0, \tag{4}$$

where  $\epsilon_0$  is the minimum total interaction energy for a single tetrahedron.

Since each molecule is in one of the states  $A$  or  $B$ , it follows that each tetrahedron has  $2^4=16$  configurational states. Using expression (1) and bearing in mind that the axis of quantization is the same for all tetrahedra, one can evaluate  $\epsilon$  for each one of these states. We find that  $\epsilon_0 = -(9/8)\lambda$  and is given by two configurations shown in Fig. 2. The base of each tetrahedron is a triangle in the plane triangular layer of the lattice, i.e., normal to the axis of quantization. It is seen that in the minimum energy state the base triangle must have the configuration: two  $B$  molecules and one  $A$  molecule. The fourth molecule on the tetrahedron may be  $A$  or  $B$ . It now follows that the minimum energy  $E$  of the lattice is obtained if each one of the  $N$  tetrahedra is in one of the configurations of Fig. 2. This leads to the following requirement for the lattice as a whole: Each triangle on any of the plane triangular layers which is the base of a tetrahedron must have two  $B$  molecules and one  $A$  molecule. This is shown in Fig. 3, and the over-all pattern is clear: each  $A$  site is surrounded by six  $B$  sites; each  $B$  site is surrounded by three  $A$  sites and three  $B$  sites, and the ratio of  $A$  to  $B$  is 1:2. That the pattern is unique may be seen by denoting any site  $A$  and completing the rest according to the above requirement. It follows that every triangular layer in the lattice must have the configurational pattern shown

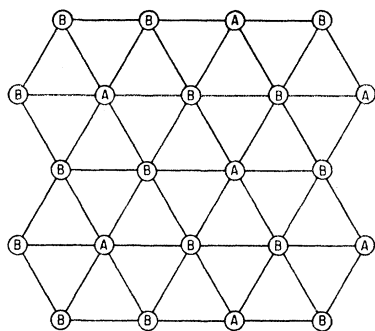


FIG. 3. The ground-state configuration of  $A$  ( $M=0$ ) and  $B$  ( $M=\pm 1$ ) ortho-hydrogen molecules on a plane triangular layer of a hexagonal-close-packed lattice normal to the axis of quantization.

in Fig. 3. Therefore, in order to construct the ground state of the three-dimensional lattice, one has to superpose such triangular layers. In Fig. 4 two such layers are shown. The circles at the centers of the alternate triangles represent the vertices of the tetrahedra based on those triangles (e.g., 8023) and form the next triangular layer (either beneath or above). It is clear that in the scheme described every tetrahedron in the lattice will be in one of the states shown in Fig. 2.

Looking at the lattice as a whole, in the ground configurational state the lattice consists of triangular layers (normal to the axis of symmetry), each following the scheme of Fig. 3. This does not lead to a strictly unique arrangement because each time one places the  $(n+1)$ th layer, one has the option of having a site (e.g., "8" of Fig. 4)  $A$  or  $B$  since this will not change the energy of the tetrahedron (0238). But, once any one site on the  $(n+1)$ th layer has been determined as  $A$ , then the configuration of that layer is determined and will follow the pattern shown in Fig. 3. This degeneracy, however, does not affect the basic configurational scheme of the lattice which may be described (looking downwards at Fig. 4) as chains of  $A$  sites running roughly along the axis of symmetry, surrounded

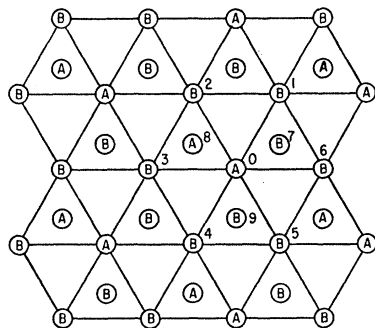


FIG. 4. The ground-state superlattice structure of  $A$  ( $M=0$ ) and  $B$  ( $M=\pm 1$ ) ortho-hydrogen molecules on a hexagonal-close-packed lattice. The circles at the centers of the triangles represent two other triangular layers: one above and the other beneath the triangular layer shown. Each one of the three layers has the configurational pattern of Fig. 3.

entirely by similar chains of  $B$  sites: thus "0, 8" is part of an  $A$  chain and "9, 5" part of one of the surrounding  $B$  chains. The only consequence of the degeneracy is that the  $A$  chain could have run along "0, 7" or "0, 9".

We can now conclude that in the ground state of solid ortho-hydrogen, two sublattices are formed: "1" comprising one-third of the total number of lattice sites occupied by  $A$  molecules in the state  $M=0$ ; and "2" comprising two-thirds of the sites occupied by  $B$  molecules in either of the states  $M=\pm 1$ . Of the twelve sites neighboring a site on sublattice "1", ten are on sublattice "2," and two on sublattice "1"; on the other hand, a site on sublattice "2" has seven neighbors on sublattice "2" and five on sublattice "1" (see Fig. 4, where  $A$  sites denote sublattice "1" and  $B$  sites sublattice "2").

In Table I further details which will be required in subsequent calculations are given. Finally, the ground-

TABLE I. The number  $n_{ab}$  of bonds of various types in the ground state of ortho-hydrogen molecules on a hexagonal-close-packed lattice with  $N$  sites. The bonds link a site on sublattice  $a$  with a nearest-neighbor site on sublattice  $b$  ( $a=1, 2$ ;  $b=1, 2$ ). "In" denotes bonds in the triangular planes normal to the axis of symmetry of the lattice and "off" those that are not. The sublattices are shown in Fig. 4, where  $A$  sites are on sublattice "1" and  $B$  sites on sublattice "2".

	"In"	"Off"	Total
$n_{11}$	0	$N/3$	$N/3$
$n_{22}$	$N$	$4N/3$	$7N/3$
$n_{12}$	$2N$	$4N/3$	$10N/3$
Total number of bonds = $6N$			

state energy  $E_0$  is

$$E_0 = N\epsilon_0 = -(9N/8)\lambda \quad (\lambda = 3.613 \times 10^{-16} \text{ erg}). \quad (5)$$

### EQUILIBRIUM PROPERTIES

In the previous section it was seen that in the ordered state, sublattice "1," comprising one-third of the sites, is occupied by  $A$  molecules ( $M=0$ ) and sublattice "2," comprising two-thirds of the sites, is occupied by  $B$  molecules ( $M=\pm 1$ ). In general, let  $n_A$  be the total number of  $A$  molecules,  $n_{A1}$  the number of  $A$  molecules on sublattice "1," and  $n_{A2}$  the number of  $A$  molecules on sublattice "2";  $n_B$ ,  $n_{B1}$ , and  $n_{B2}$  are similarly defined for  $B$  molecules. Hence, for a total number of sites  $N$ ,

$$\begin{aligned} n_{A1} + n_{B1} &= N/3, \\ n_{A2} + n_{B2} &= 2N/3, \\ n_{A1} + n_{A2} &= n_A, \\ n_{B1} + n_{B2} &= n_B, \\ n_A + n_B &= N. \end{aligned} \quad (6)$$

We now define two parameters,  $m$  and  $\alpha$  which

determine the ordering in the lattice:

$$m = (n_B - n_A)/N, \tag{7}$$

$$\alpha = \frac{n_{A1}}{\frac{1}{3}N} - \frac{n_{A2}}{\frac{2}{3}N} = \frac{n_{B2}}{\frac{2}{3}N} - \frac{n_{B1}}{\frac{1}{3}N}. \tag{8}$$

It follows that in the case of perfect order,  $m = \frac{1}{3}$  and  $\alpha = 1$ . The parameter  $\alpha$  determines the degree of sublattice ordering and varies between 1 in the ordered state and 0 when the sublattices are indistinguishable.

Using (6), (7), (8) we obtain:

$$\begin{aligned} N &= n_{A1} + n_{A2} + n_{B1} + n_{B2}, \\ Nm &= -(n_{A1} + n_{A2}) + n_{B1} + n_{B2}, \\ N\sigma &= -2n_{B1} + n_{B2}, \\ N\sigma &= 2n_{A1} - n_{A2}; \quad (\sigma = 2\alpha/3) \end{aligned} \tag{9}$$

from which one derives:

$$\begin{aligned} n_{A1} &= \frac{1}{6}N(1 - m + 2\sigma), \\ n_{A2} &= \frac{1}{3}N(1 - m - \sigma), \\ n_{B1} &= \frac{1}{6}N(1 + m - 2\sigma), \\ n_{B2} &= \frac{1}{3}N(1 + m + \sigma), \\ \sigma &= (2\alpha/3). \end{aligned} \tag{10}$$

The configurational energy  $E$  is given by

$$E = n_{AB}\omega_{AB} + n'_{AB}\omega'_{AB} + n_{AA}\omega_{AA} + n'_{AA}\omega'_{AA} + n_{BB}\omega_{BB} + n'_{BB}\omega'_{BB}, \tag{11}$$

where  $n_{AA}, n_{BB}, \dots$  denote the number of nearest-neighbor pairs of molecules  $AA, AB, \dots$  and  $\omega_{AA}, \omega'_{AB}, \dots$  the interaction energy between such pairs given by (1). The terms with a prime indicate pairs which are "off" the triangular planes normal to the axis of symmetry (e.g., "0,8" in Fig. 4) and the others indicate pairs "in" such planes (e.g., "0,1" in Fig. 4). This further classification is necessary because the interaction energy depends on the angle made by the pair with the axis of quantization.

From (1)

$$\begin{aligned} \omega_{AA} &= \frac{3}{2}\lambda, & \omega'_{AA} &= -(13/18)\lambda, \\ \omega_{AB} &= -\frac{3}{4}\lambda, & \omega'_{AB} &= (13/36)\lambda, \\ \omega_{BB} &= \frac{3}{8}\lambda, & \omega'_{BB} &= -(13/72)\lambda. \end{aligned} \tag{12}$$

The quantities  $n_{AA}, n_{BB}, n_{AB}$ , are of course not independent but are related as follows:

$$\begin{aligned} n_{AB} + 2n_{AA} &= 6n_A, & n'_{AB} + 2n'_{AA} &= 6n_A, \\ n_{AB} + 2n_{BB} &= 6n_B, & n'_{AB} + 2n'_{BB} &= 6n_B; \end{aligned} \tag{13}$$

which substituted in (11) give

$$E = \frac{3}{2}N(\omega_{AA} + \omega'_{AA} + \omega_{BB} + \omega'_{BB}) + \frac{3}{2}(n_B - n_A) \times (\omega_{BB} + \omega'_{BB} - \omega_{AA} - \omega'_{AA}) + n_{AB}\omega + n'_{AB}\omega', \tag{14}$$

where

$$\begin{aligned} \omega &= \omega_{AB} - \frac{1}{2}(\omega_{AA} + \omega_{BB}), \\ \omega' &= \omega'_{AB} - \frac{1}{2}(\omega'_{AA} + \omega'_{BB}). \end{aligned} \tag{15}$$

Hence, using (12) we have:

$$E/N\lambda = -(1/48)(81K - 39K' + 42m - 70), \tag{16}$$

where

$$K = n_{AB}/N \quad \text{and} \quad K' = n'_{AB}/N.$$

The total number of pairs  $N_{AB}$  of type  $AB$  comprises pairs of the types  $(A1)(B1), (A2)(B2), (A1)(B2)$ , and  $(A2)(B1)$  [( $A1$ ) means: molecule  $A$  on sublattice "1"]; therefore,

$$N_{AB} = N_{(A1)(B1)} + N_{(A2)(B2)} + N_{(A1)(B2)} + N_{(A2)(B1)} = n_{AB} + n'_{AB}. \tag{17}$$

Using Table I,

$$\begin{aligned} N_{AB} &= 2 \times \frac{N}{3} \times \frac{n_{A1}}{N/3} \times \frac{n_{B1}}{N/3} + 2 \times \frac{7N}{3} \times \frac{n_{A2}}{2N/3} \times \frac{n_{B2}}{2N/3} \\ &\quad + \frac{10N}{3} \left( \frac{n_{A1}}{N/3} \times \frac{n_{B2}}{2N/3} + \frac{n_{B1}}{N/3} \times \frac{n_{A2}}{2N/3} \right) \\ &= \frac{1}{N} \left[ 6n_{A1}n_{B1} + \frac{21}{2}n_{A2}n_{B2} \right. \\ &\quad \left. + 15(n_{A1}n_{B2} + n_{A2}n_{B1}) \right]. \end{aligned} \tag{18}$$

To obtain  $n_{AB}$  and  $n'_{AB}$  each term in (18) must be divided in the ratio given by Table I for "in" and "off" bonds; e.g., the term  $(A1)(B2)$  must be divided in the ratio 3:2 between  $n_{AB}$  and  $n'_{AB}$ . Hence,

$$\begin{aligned} n_{AB} &= \frac{1}{N} \left[ \frac{3}{7} \times \frac{21}{2} n_{A2}n_{B2} + \frac{3}{5} \times 15(n_{A1}n_{B2} + n_{A2}n_{B1}) \right] \\ &= \frac{9}{2N} [n_{A2}n_{B2} + 2n_{A1}n_{B2} + 2n_{A2}n_{B1}]. \end{aligned} \tag{19}$$

and

$$K = \frac{n_{AB}}{N} = \frac{9}{2} [P_{A2}P_{B2} + 2P_{A1}P_{B2} + 2P_{A2}P_{B1}], \tag{20}$$

where

$$P_{lm} = n_{lm}/N \quad (l=A,B; m=1,2). \tag{21}$$

Similarly,

$$\begin{aligned} n'_{AB} &= \frac{1}{N} \left[ 6n_{A1}n_{B1} + \frac{4}{7} \times \frac{21}{2} n_{A2}n_{B2} \right. \\ &\quad \left. + \frac{2}{5} \times 15(n_{A1}n_{B2} + n_{A2}n_{B1}) \right] \\ &= \frac{6}{N} [n_{A1}n_{B1} + n_{A2}n_{B2} + n_{A1}n_{B2} + n_{A2}n_{B1}]. \end{aligned} \tag{22}$$

and

$$K' = \frac{n'_{AB}}{N} = 6 [P_{A1}P_{B1} + P_{A2}P_{B2} + P_{A1}P_{B2} + P_{A2}P_{B1}]. \tag{23}$$

We have seen that for perfect order  $m=\frac{1}{3}$  and  $\alpha=1$ , i.e.,  $P_{A2}=P_{B1}=0$ ,  $P_{A1}=\frac{1}{3}$ , and  $P_{B2}=\frac{2}{3}$  [from (21) and (10)]. Substituting in (20) and (23) and subsequently in (16) gives

$$E/N\lambda = -9/8, \quad (24)$$

which is identical with (5). Similarly with  $\alpha=0$ , and  $m=\frac{1}{3}$  one obtains  $E=0$ , as expected in the disordered state.

The partition function  $\Omega$  of the system may be written

$$\Omega = C \sum 2^{n_B} g(n_A, n_B, n_{AB}, n'_{AB}) \exp(-E/kT), \quad (25)$$

where  $g(n_A, n_B, n_{AB}, n'_{AB})$  is the number of ways  $n_A$  and  $n_B$  molecules can be arranged to give  $n_{AB}$  and  $n'_{AB}$  pairs. The factor  $2^{n_B}$  is due to the twofold degeneracy of the  $B$  molecules ( $M=\pm 1$ ).

In the zeroth approximation,<sup>11</sup> the configurational free energy  $F_c$  is given by

$$F_c = -kT \ln g_0 - n_B kT \ln 2 + E, \quad (26)$$

together with the equilibrium equations,

$$\partial F_c / \partial m = 0, \quad \partial F_c / \partial \alpha = 0; \quad (27)$$

and

$$g_0 = \frac{(N/3)!(2N/3)!}{(n_{A1})!(n_{B1})!(n_{A2})!(n_{B2})!}. \quad (28)$$

Using Stirling's theorem, (10), (16), (20), (21), and (23), we obtain from (26), (27) and (28) the equilibrium equations of the system:

$$\begin{aligned} \frac{6}{NkT} \frac{\partial F_c}{\partial m} &= \ln \left[ \frac{P_{B1} P_{B2}^2}{8 P_{A1} P_{A2}^2} \right] - \frac{84\lambda}{16kT} (1-3m) \\ &= \ln \left[ \frac{(1+m-2\sigma)(1+m+\sigma)^2}{8(1-m+2\sigma)(1-m-\sigma)^2} \right] \\ &\quad - 84x(1-3m) = 0, \quad (29) \end{aligned}$$

and

$$\begin{aligned} \frac{3}{NkT} \frac{\partial F_c}{\partial \sigma} &= \ln \left[ \frac{P_{A1} P_{B2}}{P_{B1} P_{A2}} \right] - \frac{243\lambda}{16kT} \sigma \\ &= \ln \left[ \frac{(1-m+2\sigma)(1+m+\sigma)}{(1+m-2\sigma)(1-m-\sigma)} \right] \\ &\quad - 243x\sigma = 0, \quad (30) \end{aligned}$$

where  $x = \lambda / (16kT)$  and  $\sigma = \frac{2}{3}\alpha$ .

It is seen that Eqs. (29) and (30) are always satisfied by the solution  $m=\frac{1}{3}$  and  $\sigma=0$ —this is the disordered phase. (It may be noted here that  $m=\frac{1}{3}$  for perfect order also.) However, the solutions will not be stable at all temperatures, since a solution of (29) and (30) could equally give a maximum in  $F_c$ . We now seek the temperature range for which the solution  $m=\frac{1}{3}$ ,  $\sigma=0$ ,

gives a minimum in  $F_c$ . For this we further derive

$$\frac{6}{kTN} \frac{\partial^2 F_c}{\partial m^2} = \frac{1}{3} \left[ \frac{1}{2P_{A1}} + \frac{1}{2P_{B1}} + \frac{2}{P_{A2}} + \frac{2}{P_{B2}} \right] + 243x, \quad (31)$$

$$\frac{6}{kTN} \frac{\partial^2 F_c}{\partial m \partial \sigma} = -\frac{1}{3} \left[ \frac{1}{P_{A1}} + \frac{1}{P_{B1}} - \frac{2}{P_{A2}} - \frac{2}{P_{B2}} \right], \quad (32)$$

$$\frac{3}{kTN} \frac{\partial^2 F_c}{\partial \sigma^2} = \frac{1}{3} \left[ \frac{1}{P_{A1}} + \frac{1}{P_{B1}} + \frac{1}{P_{A2}} + \frac{1}{P_{B2}} \right] - 243x. \quad (33)$$

If

$$P = \partial^2 F_c / \partial m^2, \quad Q = \partial^2 F_c / \partial \sigma^2, \quad R = \partial^2 F_c / \partial m \partial \sigma;$$

then, as is well-known, the conditions for a minimum in  $F_c$  are

$$R^2 - PQ < 0, \quad P + Q > 0. \quad (34)$$

For  $m=\frac{1}{3}$ ,  $\sigma=0$ ,

$$R=0; \quad P = \frac{kTN}{6} \left( \frac{27}{4} + 243x \right) > 0, \quad (35)$$

and

$$Q = \frac{kTN}{3} \left( \frac{27}{4} - 243x \right).$$

Therefore, the condition for a minimum reduces to

$$Q > 0, \quad (36)$$

i.e.,

$$243x < 27/4 \quad \text{or} \quad kT/\lambda > 9/4. \quad (37)$$

This gives  $T > 5.8^\circ\text{K}$ . Therefore, the disordered state is stable for  $T > 5.8^\circ\text{K}$  and we conclude that  $T_c = 5.8^\circ\text{K}$  is the transition temperature.

It is necessary next to determine whether the transition point located above is of the first or second order. In the case of transitions of the first order there is another solution of the equilibrium equations at  $T=T_c$ , other than that of complete disorder ( $m=\frac{1}{3}$ ,  $\alpha=0$  in this case) and giving a second minimum in the free energy. This second solution with  $\alpha > 0$  is a more ordered phase. The transition at  $T=T_c$  involves a sudden jump from the disordered ( $\alpha=0$ ) solution, to the  $\alpha > 0$  solution which henceforward ( $T < T_c$ ) gives the minimum in the free energy while the  $\alpha=0$  solution becomes a maximum. This transition is accompanied by latent heat. On the other hand, in the case of transitions of the second order, there is no second solution at the transition temperature. At  $T=T_c$  the  $\alpha=0$  solution is at an inflexion point [ $(\partial^2 F) / (\partial \alpha^2) = 0$ ], changing from a minimum ( $T > T_c$ ) in the free energy to a maximum ( $T < T_c$ ). Henceforward ( $T < T_c$ ), the minimum in the free energy is at  $\alpha > 0$ , and the distinctive characteristic in this case is the continuous progression from the disordered state ( $\alpha=0$ ) to the ordered state ( $\alpha=1$ ) (see Refs. 11, 12).

In the case of Eqs. (29) and (30), there is another solution at  $T=T_c$  ( $m \approx 0.3085$ ,  $\sigma \approx 0.315$ ) but on

<sup>11</sup> E. A. Guggenheim, *Mixtures* (Oxford University Press, New York, 1952).

<sup>12</sup> L. D. Landau and E. M. Lifshitz, *Statistical Physics* (Pergamon Press, Ltd., London, 1959).

further examination it is found that it is not a minimum but a metastable state. It is therefore concluded that the system goes through a transition of the second order ( $\lambda$  type) at  $T=5.8^\circ\text{K}$ .

Bell and Fairbairn<sup>10</sup> obtained a practically identical result in their zeroth-order calculation but the superlattice structure they conjectured was configurationally a very different one from the exact ground state derived here. This can be seen immediately by comparing the values of  $m$ : they obtained  $m=\frac{1}{3}$  and  $m=0$  for the disordered and ordered phases, respectively; in our case  $m=\frac{1}{3}$  for both phases. This means that in their case the ratio of  $A$  molecules to  $B$  molecules changes from the statistically expected 1:2 to 1:1 and consequently, in addition to the configurational ordering of  $A$  and  $B$  molecules, one-quarter of the latter must be converted to the former. Since in our case  $m$  is the same, only ordering need take place.

These results are in the zeroth-order approximation and it is well known that such approximations predict too high values for the transition temperature. A higher-order analysis is being undertaken. Meanwhile a better estimate of the transition temperature may be obtained relatively easily using percolation-theory data. This has been found to be the case in other systems investigated, namely, magnetic spin systems.<sup>13</sup> In the present case, taking the tetrahedron as the basic unit of the system, the transition temperature is found to be  $3^\circ\text{K}$  (see Appendix). This is identical with the estimate of Smith and Housley<sup>6</sup> obtained by extrapolating their nuclear magnetic resonance measurements of the transition temperature at lower concentrations (<86%) to 100%.

It would be of great interest if direct experimental evidence of the properties of pure, or almost pure, ortho-hydrogen become available in the near future for comparison—in particular, as far as this paper is concerned, regarding its crystal structure, transition temperature, and superlattice structure. Other properties of the system, such as the dependence of the transition temperature and other thermodynamic quantities on the concentration of ortho-hydrogen, will be investigated in due course.

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#### APPENDIX

An outline only of the tetrahedral approximation is given here. A more detailed discussion of the general method will be published elsewhere.

<sup>13</sup> A. Danielian (to be published).

As in the text, the hexagonal-close-packed lattice ( $L$ ) is divided into  $N$  tetrahedra such that each nearest-neighbor bond is found on one tetrahedron only. Each tetrahedron can be in any one of the 16 states referred to in the text (second section), but as the temperature is lowered an increasing proportion will be in the ground state.

We now consider a second lattice ( $L'$ ), formed by joining the centres of the  $N$  tetrahedra of  $L$ .  $L'$  is also hexagonal-close-packed. Each site of  $L'$  is labeled 'A' or 'B' depending on whether the tetrahedron surrounding it is in its ground state or not. According to percolation theory,<sup>14</sup> if each site on a lattice can be 'A' or 'B' independently of the rest, then at a critical concentration of A's an infinite cluster of A's will be formed. If the tetrahedra of  $L$  are regarded as independent (this is the tetrahedral approximation) then the ideas of percolation theory may be applied to  $L'$  and it may be deduced that at a certain critical concentration  $p_c$  of A sites, an infinite cluster of A sites will be formed. Furthermore, if an A site denotes a tetrahedron of  $L$  in its ground state, then at this concentration it may be said that long-range order has set in (since a large section of the lattice  $L$  is now in the ground state) and the temperature at which this occurs is the transition temperature.

The final step consists in determining the temperature at which  $Np_c$  of the tetrahedra are in their ground states or, the equivalent, in determining the temperature at which the probability of a tetrahedron being in its ground state is  $p_c$ . Since the tetrahedra are regarded as independent, this may easily be obtained from the partition function  $Z_c$  of a tetrahedron as follows: if  $Z_c = \sum \exp(-\beta\epsilon_n)$ , [where  $\epsilon_n$  represents the eigenvalues of the tetrahedron ( $n=1 \cdots 16$ ) and  $\beta=1/kT$ ] and if  $\epsilon'_n$  is the lowest energy with degeneracy  $g'$ , then we have

$$g' \exp(-\beta\epsilon'_n)/Z_c = p_c, \quad (\text{A1})$$

for the probability of the tetrahedron being in the ground state  $\epsilon'_n$ . The temperature for which (A1) is satisfied will be the temperature required.

In the present case,

$$Z_c = y^{-134} + y^{-56} + y^{-53} + y^{-14} + 3y^{-13} + 3y^{26} + 6y^{27}, \quad (\text{A2})$$

where  $y = \exp(\beta\lambda/24)$  [see Eq. (1)] and  $p_c=0.2$  for a face-centered cubic lattice.<sup>15,16</sup> Assuming  $p_c$  is approximately the same for a hexagonal-close-packed lattice, we solve

$$2y^{27}/Z_c = 0.2, \quad (\text{A3})$$

and obtain  $y=1.037$ , hence  $T=3^\circ\text{K}$ .

<sup>14</sup> H. L. Frisch and J. M. Hammersley, *J. Soc. Ind. Appl. Math.* **11**, No. 4 (1963).

<sup>15</sup> M. F. Sykes and J. W. Essam, *Phys. Rev.* **133**, A310 (1964).

<sup>16</sup> H. L. Frisch, E. Sonnenblick, V. A. Vyssotsky, and J. M. Hammersley, *Phys. Rev.* **124**, 1021 (1961).