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1968 J. Phys. A: Gen. Phys. 1 34

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Pca₂₁ ordering in a self-consistent model for solid orthohydrogen

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MS. received 24th August 1967, in revised form 23rd October 1967

Abstract. A self-consistent method, described by Bell and Fairbairn in 1967, is used to investigate Pca₂₁ ordering in solid orthohydrogen. It is shown that when the orientations of the orthohydrogen molecules are ordered in accordance with the Pca₂₁ structure a state of very low energy is produced. The zero-order statistical approximation is applied to the transition between this ordered state and the high-temperature disordered phase. It is found that a second-order transition occurs at a temperature of 3.6 °K.

1. Introduction

The behaviour of solid hydrogen has proved to be more complex than was at first imagined. Measurements of specific heat (Ahlers and Orttung 1964, Hill and Ricketson 1954) and data on nuclear magnetic resonance (Dickson and Meyer 1965, Reif and Purcell 1953, Smith and Housley 1960) indicate that, for sufficiently high orthohydrogen concentration, there is an order-disorder transition in solid hydrogen at a temperature which depends on the ortho-para ratio of the specimen. Recent infra-red absorption (Clouter and Gush 1965) and x-ray diffraction (Barrett *et al.* 1966, Mills and Schuch 1965) measurements suggest, in addition, that solid hydrogen undergoes a change of crystal structure (from hexagonal close-packed to face-centred cubic) at a temperature very close to the critical temperature for the order-disorder transition. However, the data do indicate that this structural change occurs at a temperature slightly below that at which ordering starts to take place. It is therefore realistic to assume that the ordering occurs initially on a hexagonal close-packed structure and that the change in crystal structure occurs after some ordering has taken place. Perhaps the ordering process triggers off the structural

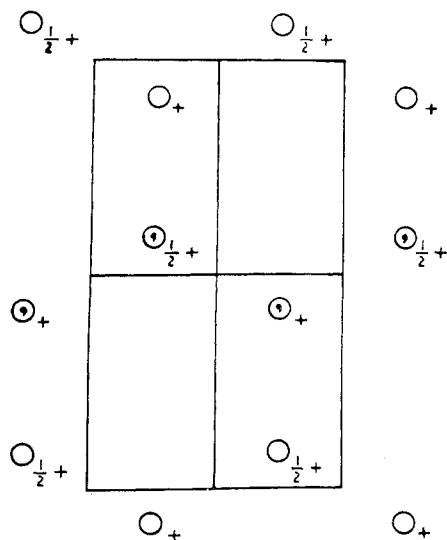


Figure 1. The Pca₂₁ lattice (Henry and Lonsdale 1952). The open circles represent the sites forming one sublattice, the remaining sites forming the second sublattice. Those sites labelled with suffixes $\frac{1}{2}$ lie in a plane at a distance $\frac{1}{2}c$ above the plane of the other sites. The c axis ($\theta = 0$) is normal to the plane of the figure.

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change. Electron diffraction data (Bostanjoglo and Kleinschmidt 1967, Curzon and Mascall 1965) also show the existence of the face-centred cubic phase, but at temperatures greater than the critical temperature for ordering. However, these effects are found only in thin films and do not seem to be typical of bulk solid hydrogen. They may be due to surface phenomena.

The classical discussion (Kitaigorodskii and Mirskaya 1965, Miyagi and Nakamura 1967) of the ordering of quadrupoles on the hexagonal close-packed structure and the fixed-axis models (Bell and Fairbairn 1961, 1962, 1964, Danielian 1965, Tomita 1955) for solid hydrogen both indicate that a most favourable superlattice structure is that denoted by Pca2₁, which is shown in figure 1.

In this paper we investigate the possible occurrence in orthohydrogen at low temperature of an ordered state with this superlattice structure. Using a self-consistent approach, we demonstrate that such a superlattice allows the existence of an ordered state of very low energy. The predicted orientations of the orthomolecules in this ordered state are derived in §2. In §3 we consider the transition which takes place between this orientationally ordered state and the completely disordered high-temperature state. A second-order transition is found to occur at a temperature of approximately 3.6 °K. This is reasonably close to that extrapolated from the available experimental data (Smith and Housley 1960).

2. The ordered state

It has been shown (Bell and Fairbairn 1967, to be referred to as BF) how a self-consistent set of molecular wave functions can be defined for a crystal of solid hydrogen. The rotational part of the molecular wave function is written in the form

$$\psi_{\mathbf{R}}(i) = \sum_{JM} a_{JM}(i) Y_{JM}(\theta_i, \phi_i) \quad (2.1)$$

where i denotes the lattice site, the coefficients a_{JM} may be complex and the angles (θ_i, ϕ_i) define the orientation, with respect to an arbitrary axis, of the symmetry axis of the molecule at site i . For the temperature range over which the order-disorder transition takes place it is sufficient to restrict the summation in (2.1) to terms with $J = 0$ for paramolecules and with $J = 1$ for orthomolecules. Thus, if we consider crystals which are composed entirely of orthomolecules, the rotational wave function for the molecule at lattice site i is

$$\sum_M a_M(i) Y_{1M}(\theta_i, \phi_i). \quad (2.2)$$

For Pca2₁ type of ordering there are two sublattices (see figure 1), which we shall label by 1 and 2. In the ordered state the rotational part of the molecular wave function, defined by the coefficients $a_M(i)$ in (2.2), is identical for molecules on the same sublattice. We define therefore two sets of coefficients $a_M^{(1)}$ and $a_M^{(2)}$, where the superscripts refer to the sublattices and where we should expect $a_M^{(1)} = a_M^{(2)}$ (all M) for temperatures greater than T_c , the critical temperature for ordering, but $a_M^{(1)} \neq a_M^{(2)}$ for at least one value of M below T_c .

The equilibrium state of the system is determined by the minimum value of the free energy $F = E_Q - TS$. The energy E_Q is obtained by summing the interaction energies of the molecules forming the crystal and is restricted to contributions from the quadrupole-quadrupole force between nearest neighbours (BF, equation (2.4)). We consider a crystal containing N lattice sites, so that there are $\frac{1}{2}N$ sites on sublattice 1 and $\frac{1}{2}N$ on sublattice 2. If we neglect surface effects each molecule has twelve nearest neighbours, six on the same sublattice and six on the other. If we choose the arbitrary axis of reference to be the c axis of the hexagonal close-packed structure, then the direction $(\theta^{(rs)}, \phi^{(rs)})$ of the line joining a site on sublattice r ($= 1, 2$) to a nearest-neighbour site on sublattice s ($= 1, 2$) is given in table 1.

At absolute zero ($T = 0$) the free energy F of the system is equal to the energy E_Q . First, we discuss the orientation of the orthohydrogen molecules in the completely ordered

state for the structure Pca2₁ at $T = 0$. This orientational distribution is obtained by minimizing $F \equiv E_Q$ as a function of the variables $a_M^{(1)}$ and $a_M^{(2)}$.

Table 1

$\theta^{(11)} = \theta^{(22)};$	$\phi^{(11)} = \phi^{(22)}$	$\theta^{(12)} = \theta^{(21)};$	$\phi^{(12)} = \phi^{(21)}$
$\cos^{-1}(\pm\sqrt{\frac{2}{3}});$	$-\frac{1}{3}\pi$ and $-\frac{5}{6}\pi$	$\cos^{-1}(\pm\sqrt{\frac{2}{3}});$	$\frac{1}{2}\pi$
$\frac{1}{2}\pi$;	0 and π	$\frac{1}{2}\pi$;	$\pm\frac{1}{3}\pi$ and $\pm\frac{2}{3}\pi$

A straightforward, but laborious, calculation using the angles $\theta^{(rs)}$ and $\phi^{(rs)}$ shown in the table gives $E_Q(a_M^{(1)}, a_M^{(2)})$. Since normalization implies

$$\sum_M a_M^*(i)a_M(i) = 1$$

we can use the substitutions

$$\begin{aligned} a_{+1}^{(1)} &= \sin \alpha_1 \cos \beta_1 \exp(i\delta_+), & a_0^{(1)} &= \cos \alpha_1 \exp(i\delta_0), & a_{-1}^{(1)} &= \sin \alpha_1 \sin \beta_1 \exp(i\delta_-) \\ a_{+1}^{(2)} &= \sin \alpha_2 \cos \beta_2 \exp(i\gamma_+), & a_0^{(2)} &= \cos \alpha_2 \exp(i\gamma_0), & a_{-1}^{(2)} &= \sin \alpha_2 \sin \beta_2 \exp(i\gamma_-) \end{aligned}$$

together with the notation $\chi = 6Q^2/25r_0^5 = 0.654k$, where Q is the electric quadrupole moment of a hydrogen molecule and r_0 is the nearest-neighbour distance of the hexagonal close-packed structure, to obtain

$$E_Q(\alpha_1, \alpha_2, \beta_1, \beta_2, \delta_+, \delta_0, \delta_-, \gamma_+, \gamma_0, \gamma_-)$$

$$\begin{aligned} &= \frac{\chi N}{144} [\{13 \sin^4 \alpha_1 + 2 \sin^4 \alpha_1 \sin^2 \beta_1 \cos^2 \beta_1 - 16 \sin^2 \alpha_1 \\ &\quad + 8 \sin^2 \alpha_1 \cos^2 \alpha_1 \sin \beta_1 \cos \beta_1 \cos(\delta_+ + \delta_- - 2\delta_0) + 4\} \\ &\quad + 40\{5 \sin^4 \alpha_1 \sin \beta_1 \cos \beta_1 \cos(\delta_+ - \delta_-) - 4 \sin^2 \alpha_1 \sin \beta_1 \cos \beta_1 \cos(\delta_+ - \delta_-) \\ &\quad + \sin^2 \alpha_1 \cos^2 \alpha_1 \{\sin \beta_1 \cos 2(\delta_- - \delta_0) + \cos \beta_1 \cos 2(\delta_+ - \delta_0)\}\}] \\ &\quad + 560 \sin^4 \alpha_1 \sin^2 \beta_1 \cos^2 \beta_1 \cos 2(\delta_+ - \delta_-) \\ &\quad + \text{same terms with } 1 \rightarrow 2 \text{ and } \delta \rightarrow \gamma \\ &\quad + 82[9 \sin^2 \alpha_1 \sin^2 \alpha_2 - 6 \sin^2 \alpha_1 - 6 \sin^2 \alpha_2 + 4 \\ &\quad + 2 \sin \alpha_1 \cos \alpha_1 \sin \alpha_2 \cos \alpha_2 \{\sin \beta_1 \cos \beta_2 \cos(\delta_- - \delta_0 + \gamma_+ - \gamma_0) \\ &\quad + \sin \beta_1 \cos \beta_2 \cos(\delta_+ - \delta_0 + \gamma_- - \gamma_0) \\ &\quad + \cos \beta_1 \sin \beta_2 \cos(\delta_+ - \delta_0 + \gamma_- - \gamma_0) + \cos \beta_1 \sin \beta_2 \cos(\delta_- - \delta_0 + \gamma_+ - \gamma_0) \\ &\quad - 2 \sin \beta_1 \sin \beta_2 \cos(\delta_- - \delta_0 - \gamma_- + \gamma_0) - 2 \cos \beta_1 \cos \beta_2 \cos(\delta_+ - \delta_0 - \gamma_+ - \gamma_0)\}] \\ &\quad + 2 \sin^2 \alpha_1 \sin^2 \alpha_2 \sin \beta_1 \cos \beta_1 \sin \beta_2 \cos \beta_2 \cos(\delta_+ - \delta_- - \gamma_+ + \gamma_-)] \\ &\quad + 20[\sin^2 \alpha_1 (3 \sin^2 \alpha_1 + 3 \sin^2 \alpha_2 - 4) \sin \beta_1 \cos \beta_1 \cos(\delta_+ - \delta_-) \\ &\quad + \sin^2 \alpha_2 (3 \sin^2 \alpha_1 + 3 \sin^2 \alpha_2 - 4) \sin \beta_2 \cos \beta_2 \cos(\gamma_+ - \gamma_-) \\ &\quad + 4 \sin \alpha_1 \cos \alpha_1 \sin \alpha_2 \cos \alpha_2 \{\sin \beta_1 \sin \beta_2 \cos(\delta_- - \delta_0 + \gamma_- - \gamma_0) \\ &\quad - \sin \beta_1 \cos \beta_2 \cos(\delta_- - \delta_0 - \gamma_+ + \gamma_0) - \cos \beta_1 \sin \beta_2 \cos(\delta_+ - \delta_0 - \gamma_- + \gamma_0) \\ &\quad + \cos \beta_1 \cos \beta_2 \cos(\delta_+ - \delta_0 + \gamma_+ - \gamma_0)\}] \\ &\quad - 1120 \sin^2 \alpha_1 \sin^2 \alpha_2 \sin \beta_1 \cos \beta_1 \sin \beta_2 \cos \beta_2 \cos(\delta_+ - \delta_- + \gamma_+ - \gamma_-)]. \quad (2.3) \end{aligned}$$

We can choose, without loss of generality, $\delta_0 = \gamma_0 = 0$, and therefore the equilibrium state is defined by the minimum of a function of eight real variables.

The stationary points of this function are determined by the eight trigonometric equations obtained on equating to zero the first-order partial derivatives of E_Q . A value of E_Q obtained in this way is $E_Q = -25\chi N/144$, for the values of $\beta_1 = \beta_2 = \frac{1}{4}\pi$,

$\alpha_1 = \alpha_2 = \cos^{-1}(0.88) = 28.5^\circ$ and $\delta_+ = \gamma_+ = \delta_- = \gamma_- = \frac{1}{2}\pi$ (or $\frac{3}{2}\pi$). However, this state corresponds to $a_M^{(1)} = a_M^{(2)}$, all M , and therefore to ordering on the lattice without superlattice formation. Also the value obtained for E_Q is not as low as that found below.

As has been shown previously (BF), the molecule at a particular site is in an $M = 0$ state with respect to some axis, provided that $\beta = \frac{1}{2}\pi$ and $\delta_+ + \delta_- = \pm\pi$: equivalently $a_{+1}^* = -a_{-1}$. Because the ordered phase corresponds to each molecule being in a unique state, the internal field at any site must define an axis with respect to which the $M = 0$ state for the molecule at that site has lowest energy. Therefore we impose the conditions that $\beta_1 = \beta_2 = \frac{1}{2}\pi$, $\delta_1 = \pm\pi - \delta_+$, $\gamma_- = \pm\pi - \gamma_+$, which reduce the energy (2.3) to a function of four real variables α_1 , α_2 , δ_+ and γ_+ . This ensures that the ordered state is non-degenerate.

If, in addition, we wish the superlattice to correspond to Pca2₁ ordering, then $\alpha_1 = \alpha_2 = \alpha$ and $\gamma_+ = \pi - \delta_+$. The energy is a function of two real variables α and $\delta = \delta_+$:

$$E_Q(\alpha, \delta) = \frac{\chi N}{144} \{336 + (-864 + 816 \cos 2\delta) \sin^2 \alpha + (333 - 816 \cos 2\delta + 321 \cos 4\delta) \sin^4 \alpha\}. \quad (2.4)$$

For stationary values $\partial E_Q / \partial \alpha = 0 = \partial E_Q / \partial \delta$. However, these equations have no solution which gives a minimum for $E_Q(\alpha, \delta)$ and for which α and δ are both real. It follows that the minimum value of (2.4) occurs somewhere on the boundary of the physical region, defined by $|\cos 2\delta| \leq 1$ and $|\sin \alpha| \leq 1$. This minimum occurs where $\cos 2\delta = 0$, $\cos 4\delta = -1$ and $\sin^2 \alpha = 1$. The corresponding value of E_Q is $-43\chi N/12 = -3.583\chi N$. This value is to be compared with that found for layer-type ordering, viz. $-3.143\chi N$ (BF), and also it is appreciably lower than the values obtained for the various ordered ground states of fixed-axis models or calculated for the disordered state of any model. This low-energy state is chosen to be that into which the orthohydrogen molecules will order as the temperature is lowered.

Since $\cos 4\delta = -1$, $\sin^2 \alpha = 1$ corresponds to $\alpha_1 = \alpha_2 = \frac{1}{2}\pi$, $\delta_+ = \frac{1}{4}\pi$ and $\gamma_+ = \frac{3}{4}\pi$, this ordered state is one in which all molecules are oriented so that they are in $M = 0$ states with respect to axes lying in planes normal to the c axis of the crystal. The axis for the molecules on one sublattice is at right angles to that for the molecules on the other because $\gamma_+ - \delta_+ = \frac{1}{2}\pi$, the orientations of the molecules on the two sublattices being mirror symmetrical in a plane through the c axis as required for the Pca2₁ structure.

3. The critical temperature

To calculate the critical temperature T_c at which the order-disorder transition takes place, we use the zero-order approximation for the entropy of the system. The three basic states of an orthohydrogen molecule are defined with reference to the set of axes determined by the completely ordered state: these are the two orthogonal axes (01 and 02) in the plane normal to the c axis, which were defined in the previous section, together with the c axis (03) of the hexagonal close-packed structure. We use the suffix $k = 1, 2, 3$ to denote those three directions. Let $N_k^{(1)}$ and $N_k^{(2)}$ be the number of molecules, on sublattices 1 and 2 respectively, which are in the $M = 0$ state with respect to axis $0k$. In the disordered phase

$$N_1^{(1)} = N_2^{(1)} = N_1^{(2)} = N_2^{(2)} = N_3^{(1)} = N_3^{(2)} = \frac{1}{3}N$$

and in the completely ordered state

$$N_1^{(1)} = N_2^{(2)} = \frac{1}{2}N, \quad N_2^{(1)} = N_1^{(2)} = 0, \quad N_3^{(1)} = N_3^{(2)} = 0.$$

The entropy S is given by

$$S = -k \ln g$$

where

$$g = \left(\frac{1}{2}N!\right)^2 \left\{ \prod_{k=1}^3 (N_k^{(1)}! N_k^{(2)}!) \right\}^{-1}$$

in zero-order approximation.

Using the variables σ and c (the order and the concentration parameters) and the averaged interaction energies ϵ_{kl} , ϵ_{kl}' , ϵ_k as defined by BF the rotational free energy of the crystal is

$$F = N(\epsilon_3 + c(\epsilon_1 - \epsilon_3) + \frac{3}{2}c^2\{(1 - \sigma^2)\epsilon_{12} + (1 + \sigma^2)\epsilon_{12}'\} + 6c(1 - c)(\epsilon_{13} + \epsilon_{13}') + kT[c \ln c + (1 - c) \ln(1 - c) + \frac{1}{2}c(1 + \sigma) \ln\{\frac{1}{2}(1 + \sigma)\} + \frac{1}{2}c(1 - \sigma) \ln\{\frac{1}{2}(1 - \sigma)\}]). \quad (3.1)$$

The differences between the zero-order analysis of the Pca2₁ superlattice ordering and that of layer-type ordering, discussed in BF (§ 6), are purely numerical. For the ordering considered in this paper

$$\begin{aligned} \epsilon_1 &= \epsilon_2 = 7\chi/8, & \epsilon_3 &= 7\chi/3 \\ \epsilon_{12} &= 558\chi/432, & \epsilon_{12}' &= -642\chi/432, \\ \epsilon_{13} &= \epsilon_{23} = 29\chi/96, & \epsilon_{13}' &= \epsilon_{23}' = -353\chi/288. \end{aligned}$$

The equilibrium state is defined by

$$\frac{\partial F}{\partial \sigma} = \frac{\partial F}{\partial c} = 0$$

from which conditions we obtain the simultaneous equations

$$\begin{aligned} \ln\left(\frac{1 + \sigma}{1 - \sigma}\right) - 6c\sigma\left(\frac{\epsilon_{12} - \epsilon_{12}'}{kT}\right) &= 0 \\ \ln\left(\frac{c}{2(1 - c)}\right) + \frac{21\chi}{2kT}(c - \frac{2}{3}) &= -\frac{1}{2} \ln(1 - \sigma^2). \end{aligned} \quad (3.2)$$

The disordered state, which is defined by $\sigma = 0$, $c = \frac{2}{3}$, is a solution of equations (3.2) at all T . The completely ordered state, $\sigma = 1$, $c = 1$, is a possible solution only at $T = 0$. It should be noted that $c \geq \frac{2}{3}$ and that the value $c = \frac{2}{3}$ occurs only when $\sigma = 0$.

A solution other than $\sigma = 0$, $c = \frac{2}{3}$ can exist only when $3c(\epsilon_{12} - \epsilon_{12}') > kT$. Additional solutions occur in pairs: the value of c is the same for each member of the pair, but they have oppositely signed values of σ . At high temperatures the disordered state gives minimum free energy. The other solutions give a minimum when they exist, and then the disordered state is a maximum and therefore unstable. The critical temperature T_c is that at which the extra solutions of (3.2) appear. Thus

$$T_c = \frac{2}{k}(\epsilon_{12} - \epsilon_{12}') = \frac{50\chi}{9k} = 3.63^\circ\text{K}.$$

4. Discussion

The fixed-axis models for orthohydrogen demonstrate that the interaction between two electric quadrupoles can result in an orientational ordering process which occurs through a second-order transition, accompanied by the usual λ anomaly in the specific heat. In particular, the more sophisticated of those models were discussed by Bell and Fairbairn (1964) and by Danielian (1965). However, both models not only contain inconsistencies but also they predict critical temperatures which are too low. In addition, in Danielian's model the transition is of first order (Steel 1967).

In more recent communications (BF, Raich and James 1966, Raich and Eters 1966) there have been discussions of two methods for obtaining self-consistency in particular models. The present paper is an extension of the work of Bell and Fairbairn, in the sense that we have used their mathematical method to investigate what seems to be the most favourable superlattice for orientational ordering on the hexagonal close-packed structure. We have demonstrated the occurrence of a second-order transition at 3.63°K , a temperature which is to be compared with the extrapolated value of 3°K found by Smith and Housley (1960). Since a zero-order theory predicts too high a value for a critical temperature, a more refined statistical treatment of this model should give a value very close to that of

Smith and Housley for the critical temperature. Also the predicted transition is of second order, resulting in an entropy loss of $k \ln 3$ per orthomolecule on cooling.

The model discussed in BF differs from that of the present paper in the type of superlattice structure proposed. The energy of their completely ordered state of layer-type ordering is $-3.143\chi N$, which is greater than the value $-3.583\chi N$ obtained for Pca₂₁-type ordering; also their critical temperature of 2.91 °K is considerably lower. It is of interest to note that both self-consistent models which have been proposed require prior decision on a superlattice structure. Neither method can predict the type of spatial order which should take place.

There are other experimental data available, such as the variation of the critical temperature with the concentration of orthomolecules present in the system. Work is in progress to obtain the predictions of the present model when a mixture of ortho- and para-hydrogen is present. The experimental data give a cut-off for the second-order transition at a minimum concentration of orthohydrogen of about 60%.

The whole discussion of orientational ordering in solid hydrogen below the critical temperature will be complicated by the effect of the change in crystal structure. The critical temperature for the order-disorder transition is higher than that at which the change in structure takes place. Thus it is permissible to investigate the occurrence of orientational ordering on a fixed hexagonal close-packed structure, independently of the structural change. However, as the temperature is lowered and the degree of long-range order increases the crystal structure changes from hexagonal close-packed to face-centred cubic. This could be caused by the distortion of the hexagonal close-packed structure due to the orientational ordering: this has been suggested for the similar situation which occurs in solid deuterium (Mucker *et al.* 1966). Certainly any discussion of the change from hexagonal close-packed to face-centred cubic structure requires to take account of the existence of the long-range orientational ordering which has been discussed in this paper.

Acknowledgments

The authors wish to thank Professor G. M. Bell for his critical reading of the manuscript. One of us (M.R.S.) acknowledges the receipt of an Advanced Course Studentship from the Science Research Council.

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