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ORIENTATIONAL ORDERING IN SOLID HYDROGEN

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Résumé. — L'établissement des états d'ordre orientationnel dans l'hydrogène solide est étudié en fonction de la concentration X des espèces J = 1 (ortho-hydrogène, para-deutérium) par la méthode des traces restreintes. Les calculs des températures critiques montrent qu'en dessous d'une certaine concentration critique $X_c \approx 0.5$ il n'est plus possible de maintenir un état d'ordre orientationnel à longue portée. Ce résultat est en accord qualitatif avec les résultats expérimentaux.

Abstract. — The phenomenon of orientational ordering in solid hydrogen is studied as a function of the concentration X of the J = 1 species using Kirkwood's technique of restricted traces. Calculations of the critical temperatures as a function of X demonstrate a behaviour in qualitative agreement with the experimental observation that a long range orientation order cannot be maintained in samples for which $X \leq X_c \approx 0.5$.

1. Introduction. — At low temperatures the homonuclear isotopes of hydrogen undergo phase transitions to orientationally ordered structures in which the molecules are aligned parallel to specific crystalline axes. The experimental evidence for these structures includes observation of anomalies in the specific heat curves [1-4] the appearance of Pake doublets in the NMR absorption spectra [5-10] and thermodynamic measurements [11-13]. The transition temperatures $T_c$ depend on the concentration of the J = 1 component (ortho-H$_2$, para-D$_2$) and for large concentrations ($> 60\%$) the empirical results are given to a good approximation by the linear relations,

$$T_c^{H_2}(X) = 4.79 X - 1.80 \pm 0.03 \text{ K}$$
$$T_c^{D_2}(X) = 6.48 X - 2.43 \pm 0.03 \text{ K}$$

where X is the fractional concentration of the J = 1 species.

The studies carried out at elevated temperatures ($T \gtrsim 0.45 \text{ K}$) as limited by refrigerating techniques showed no evidence of ordered structures for concentrations less than a so-called critical value ($X_c^{H_2} \approx 0.59, X_c^{D_2} \approx 0.55$) [11]. The slope $\partial T_c(X)/\partial X$ increases rapidly as $X < X_c$ (as shown in figure 1) and the variation of the order parameter has led to the conjecture [14] that the behaviour near $X_c$ was analogous to that observed for dilute antiferromagnets. The critical percolation concentrations [15] are however much smaller (by almost a factor of 3) than the $X_c$ observed for the hydrogen alloys.

Subsequent studies of the order parameter at very low temperatures and at reduced ortho-concentrations [16-18] have now demonstrated that ordered phases can exist for $X < X_c$ if the cubic structure is maintained (e.g. by aging the specimens at low temperatures). The variation of $T_c$ as a function of concentration is however, very different for $X < X_c$. 

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**Fig. 1.** — Observed dependence of the critical temperatures $T_c(X)$ on the concentration X of the J = 1 species for (a) solid hydrogen (the open circles are taken from ref. [12] and the solid circles from ref. [17]) and (b) solid deuterium for which the open triangles are taken from reference [13].
and for solid hydrogen [17] it is given approximatively by $T_c = 0.54 X \pm 0.06 \text{ K}$ although systematic studies of the phase diagram in this region have not been carried out.

It is generally believed that the ordering in solid hydrogen is determined largely by the quadrupolar interaction between the $J = 1$ molecular species [19] and that the configuration with the lowest free energy is given by the space group $\text{Pa}3$: a f.c.c. lattice with four distinct simple cubic sublattices such that in each sublattice the equilibrium direction of the molecules is aligned along a three-fold axis, the body diagonal of the f.c.c. lattice. (These become the quantisation axes for the sublattices.) The electric field at a given molecular site due to the quadrupoles of its neighbours has axial symmetry thereby removing the degeneracy of the $J = 1$ state.

Neutron diffraction [20] and infra-red absorption studies [21] have verified this structure and although the solid crystallizes in the h.c.p. structure, the orientational transition is accompanied by a structural transition to the cubic phase on cooling, while on warming the thermodynamic studies of Meyer et al. [12, 13] reveal that orientational disordering precedes the structural transition (f.c.c. $\rightarrow$ h.c.p.). Hysteresis effects observed on thermal cycling and related evidence [22] suggest that the structural transition may be Martensitic in character.

The theoretical treatments of the orientational ordering based on molecular field models [23, 24] do account for some of the general qualitative features characterising the ordered phases but they do not describe the observed concentration dependence. The molecular field results

$$T_c^D[X] = 4.48 \times 10^3 \text{ K}$$

$$T_c^D[X] = 6.37 \times 10^3 \text{ K}$$

disagree with the experimental results by a factor of approximately two (at $X \approx 1$) and offer no identical results are given by more elaborate non-linear wave (librons) treatments [25].

First order approximations such as the Bethe-Peierl's approximation [26] suggest critical concentrations of $\sim 1/2$ but the $T_c$ are otherwise identical to the molecular field values for large $X$.

Following a brief outline of the molecular field treatment we report calculations of the transition temperature using Kirwood's method of restricted traces [27] and compare the results with previous first order approximations.

2. Zeroth order molecular field approximation. —

Adopting the notation of Raich and Etters [25], we write the electric quadrupole Hamiltonian $\mathcal{K}_Q$ as

$$\mathcal{K}_Q = \frac{1}{2} \sum_{i,j} \sum_{m,n} \xi_{ij}^{mn} \theta_i^m \theta_j^n$$

where $\theta_i^m$ are the operator equivalents of the spherical harmonics in the manifold $J = 1$:

$$\theta_i^0 = \frac{1}{2} (3 J_i^2 - 2)$$

$$\theta_i^{\pm 1} = \pm 2^{-1/2} (J_i J_{z_i} \pm J_{z_i} J_i)$$

$$\theta_i^{\pm 2} = \frac{1}{2} (J_i)^2 .$$

The coefficients $\xi_{ij}^{00}$ have been conveniently tabulated for nearest neighbour interactions in the $\text{Pa}3$ structure by Berlinsky and Harris [28].

In the internal field approximation the fluctuation terms are discarded to retain the truncated form

$$\mathcal{K}_Q = \frac{1}{2} \sum_{i,j} \xi_{ij}^{00} \theta_i^0 \theta_j^0 ,$$

where for nearest neighbours $\xi_{ij}^{00} = - 19 \Gamma_{12}/8$.

$$\Gamma_{12} = 6 e^2 Q^2/25 R_{12}^3$$

and $Q$ is the molecular quadrupole moment and $R_{12}$ designates the inter-molecular separation.

The energy levels of a given pair of molecules $i,j$ are given (within this approximation) by

$$\omega_{ij}^{00} = - \frac{19 \Gamma}{8} \langle \theta_i^0 \theta_j^0 \rangle$$

and a molecule can exist in one of two states $| \mu \rangle$, $| \lambda \rangle$ with degeneracies $\delta_\mu$, $\delta_\lambda$ respectively. If we represent the number of molecules in these states by $N_\mu$ and $N_\lambda$; then denoting the number of nearest neighbour site pairs by $N_{\mu\lambda}$ we have

$$N_{\mu\mu} + 2 N_{\mu\lambda} = Z N_\mu$$

$$N_{\lambda\mu} + 2 N_{\lambda\lambda} = Z N_\lambda$$

where $Z$ is the total number of occupied crystalline nearest neighbour sites and $N$ is the total number of lattice sites each of which has an equal probability $X$ of occupation. The energy of the lattice distribution $\{ N_{\mu}, N_{\lambda} \}$ is given by

$$E \{ N_{\mu}, N_{\lambda} \} = \frac{1}{2} \sum_{x \neq x'} N_{x \beta} \omega_{x \beta} + \sum_x N_{x \alpha} \omega_{x \alpha}$$

$$= \left( N_{\mu\lambda} + \frac{1}{2} Z N_\mu \right) \omega_0 + \frac{1}{2} Z N_{\lambda \lambda} \omega_{\lambda \lambda}$$

where

$$\omega_0 = \omega_{\mu\lambda} - \delta (\omega_{\mu\mu} + \omega_{\lambda\lambda}) = \frac{1}{2} (\omega_{\mu\mu} - \omega_{\lambda\lambda}) = 19 \Gamma_{12}/16 .$$

The partition function is

$$Q(T) = (g_{\mu} g_{\lambda})^{N/2} (g_{\mu} g_{\lambda})^{(N_{\mu} - N_{\lambda})/2} \times \sum_{N_{\mu},N_{\lambda}} g(N_{\mu}, N_{\lambda}) e^{-\beta E \{ N_{\mu}, N_{\lambda} \}}$$

where $g(N_{\mu}, N_{\lambda})$ represents the number of configurations having a given set of values $(N_{\mu}, N_{\lambda})$

$$g(N_{\mu}, N_{\lambda}) = N ! / N_{\mu} ! N_{\lambda} ! .$$

The immediate environment of a given molecule (in the state $| \mu \rangle$, for example) is represented by the
fraction of its nearest neighbours in the state \( | \lambda \rangle \), i.e. by
\[
N_{\mu\lambda}/ZN_{\mu}
\]
and can be related to a short range order parameter \( \sigma \) defined by
\[
N_{\mu\lambda}/(\frac{1}{2} ZN) = (1 + \sigma)/2
\]
(4)

\( N_{\mu} \) is independent of the number of nearest neighbour correlations excepting that it specifies the number of molecules in the state \( | \mu \rangle \) and can be related to a long range order parameter \( \rho \) given by
\[
N_{\mu}/N = (1 - \rho)/2.
\]
(5)

In the zeroth order approximation (Bragg-Williams approximation for binary alloys [29]), the short range order is assumed to be determined solely by the long range order
\[
N_{\mu\lambda}/\left(\frac{1}{2} ZN\right) \approx 2 N_{\mu}/N \cdot N_{\lambda}/N
\]
or
\[
\sigma \approx - \rho^{2}.
\]
(6)

The energy as a functional of the long range order parameter can therefore be written as
\[
E(\rho) = - \frac{ZN_{\omega_{0}}}{4} \left( \rho^{2} + \frac{2}{3} \rho \right)
\]
(7)
(constant terms have been omitted).

The value \( \bar{\rho} \) of \( \rho \) which minimises the free energy
\[
\beta = - k_{B} T \log Q(T)
\]
is found to satisfy
\[
\log \left[ \frac{2(1 + \rho)}{(1 - \rho)} \right] = \beta Z_{\omega_{0}} \left[ \bar{\rho} + \frac{1}{3} \right].
\]

As \( T \rightarrow 0 \), \( \bar{\rho} \rightarrow +1 \), corresponding to a fully ordered configuration with all molecules occupying the ground state \( | \lambda \rangle \) (i.e. with \( J_{z} = 0 \)) which has the lowest energy. As the temperature increases \( \bar{\rho} \) decreases smoothly until the critical temperature \( T_{c} \) is reached where there is a discontinuity in the solution for \( \bar{\rho} \); and for \( T > T_{c} \), only the trivial solution \( \bar{\rho} = - \frac{1}{3} \) exists. The critical temperatures are given by
\[
k_{B} T_{c}^{MF} \approx \frac{Z_{\omega}}{3 \log 2}
\]
\[
= \frac{19 \Gamma_{12}}{4 \log 2}.
\]
(8)

This molecular field result differs by only a few per cent from that obtained by Raich and Etters [25] using a librational wave calculation. Since these treatments consider only the long range order they cannot be expected to provide a reliable description of the system near the transition temperature if the short range correlation effects are at all significant.

The neglect of specific short range order in the zeroth order approximation can be improved by the use of Bethe-Peierl's technique [26]. In this method one considers a cluster of molecules consisting of a central molecular site together with its nearest neighbours as one element with the rest of the structure providing a background field which is then determined self-consistently.

In contrast to the molecular field approach one finds that there is no first order transition [30] and only a rapid variation of the order parameter for
\[
k_{B} T \approx 19 \Gamma_{12} X/3.
\]
(9)

The absence of a first order transition is believed to result from the neglect of correlation effects and it has been shown by a cluster variational method [31] that a discontinuous transition between the orientationally ordered and disordered phases is predicted for pure solid orthohydrogen only if one includes the anisotropic (or fluctuation) terms in the quadrupolar interaction; i.e. the terms \( m, n \neq 0 \) in eq. (1). The importance of the correlations resulting from these terms has been emphasised by Englman and Friedman [32] who pointed out that while the fractional correction of the mean field approximation is of the order of \( Z^{-1} \) for the isotropic Hamiltonian, the correction is approximately 0.4 for the full quadrupolar interaction (for pure orthohydrogen) and the neglect of the anisotropic terms is not justified.

It should be noted that straightforward symmetry arguments [33] can be used to demonstrate the existence of a third order invariant in the orientational free energy (expressed in terms of a set of order parameters which transform according to the irreducible representations of the relevant space group). Following Landau's theory of phase transitions this implies that the transition should be first order as indicated by the experimental results.

3. The method of restricted traces. — In an attempt to improve on the theoretical treatments of the concentration dependence of the transition temperatures \( T_{c}(X) \) we now consider the technique of restricted traces proposed originally by Kirkwood [27] for the study of co-operative ordering in solid binary solutions. This has been applied to Heisenberg's model of ferromagnetism [34, 35] and with a certain degree of success in the theory of nuclear antiferromagnetism [36].

The complete partition function as a functional of some suitable long range order parameter \( s \) is given by
\[
Z = \sum_{\text{full } I\text{-space}} e^{-\beta \mathcal{H}}
\]
\[
= \sum_{\{s\}} \sum_{\text{states of } \text{fixed } S} e^{-\beta \mathcal{H}}
\]
\[
= \sum_{\{s\}} \text{tr}_{s}(e^{-\beta \mathcal{H}})
\]
(10)
where \( \{ s \} \) denotes the range of the parameter \( s \).

Since the above sum is sharply peaked at the correct value of \( s \), namely that which minimises the free energy, we can to a good approximation consider only the contribution for the correct \( s \); i.e. we consider

\[
\log Z = \log (\text{tr} e^{-\beta E}) + O(\log N)
\]

where

\[
\frac{\delta}{\delta s} \left( \log Z \right) = 0.
\]

Introducing a normalisation factor we can write

\[
\log Z = \log \frac{\text{tr} e^{-\beta E}}{\text{tr} 1} + \log (\text{tr} 1) = \log \left< e^{-\beta E} \right>_s + \log W(s).
\]

(11)

\( W(s) \) is the number of configurations having fixed \( s \).

In view of the form of the quadrupolar Hamiltonian given above it is convenient to choose as a parameter of long range order, the variable

\[
s = \left< 3 J^2 - 2 \right>.
\]

(12)

\( W(s) \) may be calculated by introducing a Lagrange multiplier and calculating the sum, or alternatively, we may deduce \( W \) from the expression given in section 2 above for \( g(N_u, N_o) \).

The result is

\[
\log W(s) = \frac{NX}{3} \left[ s \log 2 - (1 - s) \log (1 - s) - (2 + s) \log (2 + s) + 3 \log 3 + 2 \log 2 \right].
\]

The temperature dependent term in \( \log Z \) can be expanded to obtain the cumulant expression

\[
\log Z = \log W + \sum_{n=1}^{\infty} (-\beta)^n M_n/n !
\]

(13)

where the first two cumulants (or semi-invariants) are

\[
M_1 = \left< \mathcal{K} \right>,
\]

\[
M_2 = \left< \mathcal{K}^2 \right> - \left< \mathcal{K} \right>^2.
\]

Since the interaction varies as \( R^{-5} \) we will consider only nearest neighbour interactions between molecules distributed at random over the possible sites given by the four interpenetrating sublattices of the \( \text{Pa}_3 \) structure.

The first order semi-invariant. — The first order invariant is

\[
M_1 = \sum_{i<j} \sum_{m,n} \sum_{ij} \left< \sigma_{mn}^o \sigma_{ij}^o \right>
\]

(14)

and since the molecules on sites \( i \) and \( j \) belong to different sublattices (only nearest neighbour pairs \( ij \)) are considered we may vary \( \left< \sigma_{mn}^o \right> \) and \( \left< \sigma_{ij}^o \right> \) independently in the calculation of the trace \( \left< \sigma_{mn}^o \sigma_{ij}^o \right> : \)

\[
\left< \sigma_{mn}^o \sigma_{ij}^o \right> = \frac{1}{9} s^2 \quad \text{for} \quad m = n = 0
\]

\[
= 0 \quad \text{otherwise}
\]

\[
M_1 = \frac{1}{9} e^{\alpha_0} s^2 \sum_{i \neq j} P_i P_j
\]

where \( P_i \) and \( P_j \) represent the probabilities that sites \( i \) and \( j \) are occupied by ortho molecules and the sum \( \sum_{i \neq j} \) is restricted to nearest neighbour sites. Since there are twelve nearest neighbour lattice sites we find

\[
\sum_{i \neq j} P_i P_j = 6 NX^2 + O(1) + O(\mathcal{N}^{-1})
\]

The result for \( M_1 \), correct to order \( N \), is therefore

\[
M_1 = 6 NX^2 \gamma^2
\]

(15)

\( \gamma = \frac{e^{\alpha_0}}{s^2} = - \frac{19}{72} \gamma_{12} \)

\( (N \) is the total number of lattice sites and the total number of ortho molecules is \( NX \).

The second order semi-invariant. — In order to evaluate the second order semi-invariant, which was defined as

\[
M_2 = \left< \mathcal{K}_1^2 \right> - \left< \mathcal{K}_1 \right>^2
\]

it is convenient to write out the full expression for \( M_2 \) in terms of the operators \( \sigma_{mn}^o \). Using the expression given by eq. (1) for the quadrupolar Hamiltonian we obtain

\[
M_2 = \frac{1}{4} \sum_{(ijkl)} \sum_{m,n,m',n'} \sum_{ij} \sum_{kl} e^{\alpha_{mn}} e^{\alpha_{m'n'}} \times
\]

\[
\times \{ \left< \sigma_{mn}^o \sigma_{ij}^o \sigma_{m'n'} \sigma_{kl}^o \right> - \left< \sigma_{mn}^o \sigma_{ij}^o \right> \left< \sigma_{m'n'} \sigma_{kl}^o \right> \}.
\]

(16)

Since we consider only nearest neighbour interactions the sum over the lattice indices \( (ijkl) \) is restricted to nearest neighbour crystalline sites \( (ij)_a \) and \( (kl)_a \), which are occupied by ortho molecules. (Note that for the \( \text{Pa}_3 \) structure, the site \( i \) and \( j \) of a nearest neighbour pair \( ij \) belong to distinct sublattices.)

Three types of terms arise:

a) all indices different, \( (ij) \neq (kl) \); 
b) one pair of indices equal, \( i = k, j \neq l \) (or \( i \neq k, j = l \)); and 
c) two pairs equal, \( i = k \) and \( j = l \).

These different terms are illustrated by the four particle, the three particle and the two particle diagrams shown in figures 2a, 2b and 2c respectively.

The anisotropic terms \( (m, n, m', n' \text{ not all zero}) \)
contribute only for the two particle terms and will be considered separately. The evaluation of the isotropic terms proceeds as follows.

\[ i \quad j \quad k \quad l \]
\[ i \quad j \quad i \quad j \]
\[ i \quad j \]

(a) (b) (c)

Fig. 2. — Diagrammatic representation of (a) the four particle terms, (b) the three particle terms, and (c) the two particle terms, that occur in the evaluation of the second order semi-invariant.

a) Four particle terms \((ij) \neq (kl)\). — For these terms the curly bracket in eq. (16) vanishes except for correction terms of order \(N^{-1}\) which occur in the evaluation of the trace \(\langle \theta_1^0 \theta_2^0 \theta_3^0 \theta_4^0 \rangle\) when the pair \((ik)\) and/or the pair \((jl)\) belong to the same sublattice. In these cases \(\langle \theta_1^0 \rangle\) and \(\langle \theta_4^0 \rangle\) cannot be varied independently and one finds by direct calculation that

\[ \langle \theta_1^0 \theta_4^0 \rangle = \left[ s^2 - \frac{4}{NX} (2 - s - s^2) \right] / 9 \]

\((N/4\) is the number of sites associated with each sublattice).

This correction of order \(1/N\) was omitted in a similar calculation performed by Homma and Nakano [37] for pure orthohydrogen.

Since the four sublattices of the \(Pa_3\) structure are interpenetrating, three distinct types of arrangements can occur for the four particle terms:

i) all four sites refer to different sublattices,

ii) one pair belongs to a given sublattice while the others are associated with different sublattices, and

iii) two pairs belonging to two different sublattices.

These different types of configurations and their corresponding traces are summarised in table I where the numbers \(1\), \(2\), \(3\) and \(4\) refer to the different sublattices.

On counting the total number of configurations that can occur, we find with the aid of table I that the contribution of the four particle diagrams is given by

\[ -144 \frac{N}{N} X^3 \gamma^2 s^2 (2 - s - s^2) \]

(terms of order unity have been dropped). The dependence on \(N X^3\) arises from the fact that there are \(36 N^2\) four particle terms for which each of the four sites may be occupied with a probability \(X\). The lattice sum therefore yields a term proportional to \(N^2 X^4\) while the non-vanishing traces are proportional to \((NX)^{-1}\).

b) Three particle terms; \(i = k, j \neq l\) (or \(i \neq k, j = l\)). — Since the number of terms is of order \(N\) we may neglect corrections of order \(N^{-1}\) in the evaluation of the traces and write the three particle terms in eq. (16) as

\[ \sum_i \sum_j \sum_k \langle \theta_1^0 \theta_i^0 \theta_j^0 \theta_k^0 \rangle \langle \theta_1^0 \rangle \langle \theta_i^0 \rangle \langle \theta_j^0 \rangle \]

\[ = 132 \frac{N}{N X^3} \gamma^2 s^2 (2 - s - s^2) \]

\(c) Two particle terms; i = k and j = l. \quad - For these terms the expression for \(M_2\) yields

\[ \frac{1}{2} \sum_{i \neq j} \langle \theta_1^0 \rangle^2 \langle \theta_i^0 \theta_j^0 \rangle^2 - \langle \theta_i^0 \theta_j^0 \rangle^2 \]

\[ = 6 N X^2 \gamma^2 (2 - s)^2 (2 - s - (2 X - 1) s^2) \]

The total contribution to the second order semi-invariant given by the sum of these three different types of terms for the isotropic interactions is then found to be

\[ M_2(\gamma) = 6 N X^2 \gamma^2 (2 - s - s^2) [2 - s - (2 X - 1) s^2] \]

(17)

### Table I

Summary of the traces occurring in the evaluation of the contribution of the four particle terms (Fig. 2a) to the second order semi-invariant. The numbers \(1\), \(2\), \(3\) and \(4\) refer to the four different sublattices of the \(Pa_3\) structure.

<table>
<thead>
<tr>
<th>Sublattice Configuration</th>
<th>Number of distinct terms</th>
<th>Trace</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 —— 2</td>
<td>6</td>
<td>81 { \langle \theta_1^0 \theta_2^0 \theta_3^0 \theta_4^0 \rangle - \langle \theta_1^0 \theta_2^0 \rangle \langle \theta_3^0 \theta_4^0 \rangle }</td>
</tr>
<tr>
<td>1 —— 2</td>
<td>24</td>
<td>0</td>
</tr>
<tr>
<td>1 —— 2</td>
<td>6</td>
<td>[ s^2 \left[ s^2 - \left( \frac{4}{NX} \right) (2 - s - s^2) \right] - s^4 ]</td>
</tr>
<tr>
<td>2 —— 1</td>
<td></td>
<td>[ \left[ s^2 - \left( \frac{4}{NX} \right) (2 - s - s^2) \right]^2 - s^4 ]</td>
</tr>
</tbody>
</table>
The anisotropic terms resulting from the two particle diagrams (Fig. 2c) are given by
\[
\sum_{ij \beta \epsilon} \sum_{m,n,m',n'} \zeta_{ij}^{mn} \zeta_{ij}^{m'n'} \langle \partial_\beta^m \partial_\epsilon^{m'} \partial_\beta^n \partial_\epsilon^{n'} \rangle = \sum_{ij \beta \epsilon} \sum_{m,n,m',n'} \zeta_{ij}^{mn} \zeta_{ij}^{m'n'} \langle \partial_\beta^m \partial_\epsilon^{m'} \partial_\beta^n \partial_\epsilon^{n'} \rangle
\]
\[= 0 \quad \text{for} \quad m + m' \neq 0 \quad \text{and} \quad n + n' \neq 0.\]

Since there can be no confusion with respect to the lattice indices, we can introduce the following abbreviated notation
\[
(mn) = \frac{\zeta_{12}^{mn}}{\zeta_{12}^{00}}, \quad (mn) = \frac{\zeta_{12}^{mn}}{\zeta_{12}^{00}}
\]
\[\langle mn \rangle = \langle \partial_\beta^m \partial_\epsilon^n \rangle, \quad \langle m\bar{n} \rangle = \langle \partial_\beta^m \partial_\epsilon^{\bar{n}} \rangle
\]
and write the above as
\[
\sum_{ij} (\zeta_{ij}^{00})^2 \sum_{m,n,m',n'} (mn) (m'n') \langle mn \rangle \langle mn' \rangle.
\]

On evaluating the summations we find
\[
M_{2}^{\text{aniso}} = 12 N X^2 (\gamma)^2 \left[ \begin{array}{c}
\{ (11)^2 + (1\bar{1})^2 \} \langle 1\bar{1} \rangle^2 \\
- \{ (12)^2 + (\bar{1}2)^2 + (21)^2 + (\bar{2}1)^2 \} \langle 1\bar{1} \rangle \langle 2\bar{2} \rangle \\
+ \{ (22)^2 + (\bar{2}2)^2 \} \langle 2\bar{2} \rangle^2 \\
- \{ (10)^2 + (01)^2 \} \langle 00 \rangle \langle 1\bar{1} \rangle \\
+ \{ (20)^2 + (02)^2 \} \langle 00 \rangle \langle 2\bar{2} \rangle
\end{array} \right]
\]
where we have used \((mn) = (-)^{m+n}(\bar{m}\bar{n})^*\).

The coefficients of the traces \(\langle mn' \rangle \langle mn' \rangle\) can be calculated from the values of \((mn)\) tabulated by Berlinsky and Harris [28]. The result is
\[
M_{2}^{\text{aniso}} = 12 N X^2 (\gamma)^2 \left[ \begin{array}{c}
0.176 \langle 1\bar{1} \rangle^2 - 1.280 \langle 1\bar{1} \rangle \langle 2\bar{2} \rangle \\
+ 0.545 \langle 2\bar{2} \rangle^2 - 0.612 \langle 00 \rangle \langle 1\bar{1} \rangle \\
+ 2.032 \langle 00 \rangle \langle 2\bar{2} \rangle
\end{array} \right].
\]

The traces are given by
\[
\langle 1\bar{1} \rangle = -(4 - s)/6
\]
\[\langle 2\bar{2} \rangle = (2 + s)/6
\]
\[\langle 00 \rangle = (2 - s)/9,
\]
and the contribution of the anisotropic terms to the second order semi-invariant is (apart from a constant) found to be
\[
M_Z(s) = 27 N X^2 \gamma^2 (0.884 s - 1.506 s^2).
\]

The orientational free energy
\[
\beta(s) = - k_B T \log Z(s)
\]
can be determined from the cumulant expansion given by eq. (13) for \log Z(s), and using the results for the first and second order semi-invariants we find
\[
\beta(s)(N X k_B T) = \frac{1}{4}[(1 - s) \log (1 - s) + (2 + s) \log (2 + s) - s \log 2] - 6 \beta | \gamma | X s^2 - 3 \beta^2 \gamma^2 X(2 - s - s^2) [2 - s - (2 X - 1) s^2] - 27 \beta^2 \gamma^2 X s(0.44 - 0.76 s)
\]
(19)
(additive constants have been omitted).
Typical plots of the free energy as a function of the order parameter for different temperatures are shown in figures 3 and 4 for concentrations $X = 1.0$ and $0.6$ respectively. Following the notation of Lee and Raich [31], the curves are labelled by the reduced temperatures $t = T/T_b$ where $k_B T_b = 19 \Gamma_{1/2}/3$.

At high temperatures the free energy has only one minimum which occurs for $s = 0$, corresponding to the disordered configuration. As the temperature is reduced two minima appear, one at $s = 0$ and another at $s = 3$ (for $0 < \beta < 2$), and the equilibrium configuration is determined by the free energy minimum which has the lowest value. The critical temperature $T_c$ is then identified as the temperature for which the free energies at the two minima have the same value. For $T < T_c$, $\beta(s = 0) > \beta(s = 3)$; and the equilibrium configuration is given by $s = 3$ which corresponds to an orientationally ordered configuration.

There is therefore a discontinuity in the equilibrium value of the order parameter at $T = T_c$ and the transition is first order. For $X = 1.0$,

$$T_c \approx 0.79 \ T_b \approx 0.73 \ T_b^{MF}$$  

where $T_b^{MF}$ is the molecular field solution (see eq. (8)).

As the temperature is further reduced, $\beta$ varies smoothly and for large ortho concentrations ($X > 0.6$) approaches the limiting value $\beta = 2$ as $T \to 0$.

It can be noted that at very low temperatures a minimum does appear for $s > 0$ (see Fig. 3) but it is the minimum at $s < 0$ which corresponds to the equilibrium configuration. The extrapolation of the results to temperatures $T < T_c$ is not really justified since the free energy expansion given by eq. (19) is a high temperature expansion and the theory is certainly not valid for temperatures for which

$$\beta_2 \left| M_2(s)/(NX) \right| \leq 1.$$  

This condition imposes a low temperature limit given approximately by

$$T > X^{1/2} \ T_b/4$$  

for the theory in its present form.

The temperature dependence of $\beta$ (the value of the order parameter for which the free energy is an extremum) is illustrated in figure 5 for several ortho concentrations. The value $s = 0$ also corresponds to an extremum and the vertical lines indicates the first order transitions for which the solution $s = 0$ corresponds to the equilibrium configuration for $T > T_c$. If the transverse correlation effects generated by the anisotropic terms in $M_2$ are suppressed (i.e. if one assumes $M_2^{aniso} = 0$) one finds that there is no first order transition (regardless of the value of $X$). The variation of $\beta$ as a function of the temperature is continuous as shown in figure 5 for the case $X = 1$ for which the slope $\partial \beta/\partial T$ is a maximum at $T = 1.07 \ T_b \approx T_b^{MF}$.  

$$T = 1.07 \ T_b \approx T_b^{MF}.$$

FIG. 3. — Calculated orientational free energies $\beta(s)$ as functions of the order parameter for $X = 1.0$ and for several temperatures near the transition temperature using the method of restricted traces. The reduced temperatures $t = T/T_b$ where $k_B T_b = 19 \Gamma_{1/2}/3$. A first order transition occurs at $t_c = 0.79$.

FIG. 4. — Calculated orientational free energies $\beta(s)$ as functions of the order parameter for $X = 0.6$ and for several temperatures near the transition temperature using the method of restricted traces. The reduced temperatures $t = T/T_b$ where $k_B T_b = 19 \Gamma_{1/2}/3$. A first order transition occurs at $t_c = 0.40$. 

For the theory in its present form.
Calculations of the free energies for $X < 0.5$ show that the disordered configuration ($s = 0$) is the only equilibrium configuration for all temperatures for which the theory may be expected to be valid and this implies that no long range orientational order can be sustained in alloys having ortho concentrations less than a critical concentration of approximately 50\%.

The concentration dependence of the critical temperatures is shown in the phase diagram of figure 6 where we compare the present calculations with the experimental results for solid hydrogen. (A similar phase diagram would be obtained for solid deuterium.) As a result of various renormalisation factors \[38\] the absolute values of the effective interaction constants $\Gamma_{12}$ are rather uncertain, and in figure 6, we have used a recent experimental value of 0.58 cm\(^{-1}\) (observed for very pure solid ortho hydrogen \[39\]) in order to illustrate the different concentration dependences predicted by the theoretical estimates discussed in the text.

The improved qualitative agreement with the experimental data is striking and this is attributed to the inclusion of local (librational) correlations in the method of restricted traces. The correlation effects arising from the anisotropic terms in the quadrupolar Hamiltonian are of course only treated to lowest order in the present theory and in view of the considerable difference between the results for the isotropic and anisotropic models the detailed predictions for the temperature dependence of the order parameter may be quite misleading at low temperatures especially for concentrations close to $X_c$. For example, as shown in figure 5, the low temperature limit of $s$ for $X = 0.6$ is $-1.5$ rather than $-2$ as given by the low temperature NMR results \[17\].

If in addition we include a perturbation in terms of a crystalline field $V_i = \Delta \Omega_i$, resulting from anisotropic intermolecular interactions other than quadrupolar forces (e.g. anisotropic crystalline strains resulting from zero-point librational deviations as well as a coupling between the rotational motion and the lattice vibrations have been proposed by van Kranendonk and Sears \[40\] as possible origins of $\Delta$), one finds critical temperatures reduced by a factor of approximately $1 - 2 \Delta / T_b$. Theoretical evaluations of $\Delta$ are rather unreliable since the nature of these interactions is not really understood and although there is some experimental evidence for values as low as 0.02 K \[41\], van Kranendonk and Sears \[40\] estimated $|\Delta| \approx 0.15$ K. (Recent experiments at high densities \[42\] suggest that large values of $\Delta$ may occur in stressed samples.) In view of these uncertainties we have not included a crystalline field term in the present calculations although the critical temperatures could be modified by as much as 10\% if the theoretical estimates \[40\] are realistic.

In the limit of very low ortho concentrations ($X < X_c$), the elucidation of the nature of the anisotropic forces as well as the inclusion of the next nearest neighbour quadrupolar interactions may be necessary if ones wishes to understand the phase diagram for orientationally ordered states observed at low concentrations \[17, 18\]. While clustering effects may be expected to be important at low concentrations it should be noted that the growth of clusters in solid hydrogen \[43\] is neutralised to a large extent by the rapid ortho-para conversion rate.

4. Conclusion. — While first order approximations (such as the method due to Bethe-Peierls) beyond the molecular field treatment (zeroth order) of the orientational ordering of ortho hydrogen alloys fail to predict the general behaviour of the phase diagram...
(as a function of the concentration of the $J = 1$ species) it is shown that Kirkwood's treatment of restricted traces (limited to the second order invariant) does predict critical concentrations $X_c \approx 0.5$. Below these concentrations the alloys do not undergo phase transitions to orientationally ordered phases having a well defined long range orientational order. The treatment given here is very approximative since it only to lowest order, and next nearest neighbour interactions have been completely ignored. It will be important to include these higher order effects in future refinements of the calculation. The theory at this stage is not capable of elucidating the nature of the orientational ordering observed at very low temperatures for $X < X_c$ in what are probably metastable cubic structures.

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References
