

fcc-hcp Transition in Solid Orthohydrogen

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(Received 8 September 1971)

The cluster-variation method is applied to calculate the orientational ordering of *o*-H₂ molecules on fcc and hcp lattices. The *Pa3*, *Pca2₁*, and *P2₁/c* structures are examined. A fcc-hcp structural transition very near to an orientational ordering transition is predicted. These transitions result because of the anisotropic intermolecular interactions. The isotropic interactions are expected to play only a very minor role.

We wish to report the results of a calculation of the molecular ordering which occurs in the cubic and hcp phases of pure *o*-H₂ and *p*-D₂ near the first-order crystalline phase transition. This transition has been observed in the specific heat,^{1,2} NMR splittings,³⁻⁵ $(\partial p/\partial T)_V$ measurements,⁶⁻⁹ and x-ray diffraction.¹⁰ It has commonly been supposed that what is seen is a cooperative orientation of molecules resulting mainly from electrostatic quadrupole-quadrupole (EQQ) interactions. Closely associated with the molecular ordering transition is a change in the crystal structure from fcc to hcp as the temperature is raised. The ordering transitions have been described by molecular field theories using rigid lattice models with various space groups.¹¹⁻¹³ These theories predict that the "λ transition" in *o*-H₂ consists of a first-order transition from an orientationally ordered phase with fcc lattice to an orientationally ordered hcp phase, followed by one or more transitions on the hcp lattice with the molecular orientations ultimately becoming disordered. The ordering transition can also be discussed as the temperature at which the librational excitations become unstable. This soft-mode treatment must again assume librational oscillations about certain equilibrium orientations, such as *Pa3* for the fcc case. These treatments become increasingly complicated as the temperature is raised, because of the large anharmonic libron-libron interactions.¹⁴

Another approach to a theoretical description of the "λ transition" has been by cluster-variation expansions.^{15,16} These expansions, when applied to order-disorder phenomena, give reasonably accurate descriptions near the order-disorder transitions but fail at low temperatures.¹⁷⁻²⁰ The cluster-variation methods have the advantage

of accounting for both the alignment of small clusters of molecules, which occurs at high temperatures, and the possibility of attaining a state with long-range order below the transition. The molecular arrangements in small clusters are significantly different from the ultimate arrangement in a long-range ordered structure such as *Pa3*.²¹ This effect gives rise to the bad quantitative predictions of the molecular field theories as well as the large anharmonic terms arising in the libron theories.

We have extended our previous three-molecule cluster calculations¹⁶ to describe the ordering transitions on fcc and hcp lattices. It has been shown²² that the interactions between phonons and molecular rotations lead only to a renormalization of the EQQ interactions which does not affect their angular dependence. Apart from this renormalization we completely ignore phonons and treat the molecules as if they were on rigid lattices. For computational simplicity we consider only nearest-neighbor interactions. The space groups considered here are *Pa3*, *Pca2₁*, and *P2₁/c*. The *Pa3* structure is the one observed at low temperatures.^{10,23} The space groups *Pca2₁* and *P2₁/c* are two four-sublattice configurations of hcp lattices with relatively low free energies.^{12,24} Molecular field calculations¹² have indicated that one or both of these structures could become stable near the "λ transition." The molecular equilibrium orientations for the hcp structures were found to be slightly temperature dependent.¹² In the present work the molecules were assumed to be aligned along their zero-temperature directions.^{12,24}

The application of the three-molecule cluster-variation approximation to solid *o*-H₂ has already been described briefly.¹⁶ A detailed account will

be given elsewhere. Here we assume EQQ interactions between molecules described by the Hamiltonian

$$\mathcal{H} = \sum_{i,j} \sum_{m,n} \gamma_{ij}^{mn} O_i^m O_j^n, \quad (1)$$

$$\begin{aligned} \frac{-\beta F_{(3)}}{N} = & \frac{1}{2}(z-1)(z-2) \ln \sum_{l=1}^3 e^{-\beta \kappa_l + \frac{1}{2}z(z_1 - 2z + 3)} \sum_k a_k \ln \sum_{l=1}^9 e^{-\beta \nu_l(k)} \\ & + \frac{1}{2}z(z-z_1-1) \sum_m b_m \ln \sum_{l=1}^{27} e^{-\beta \lambda_l(m)} + \frac{1}{3!} z z_1 \sum_n c_n \ln \sum_{l=1}^{27} e^{-\beta / \mu_l(n)}. \end{aligned} \quad (2)$$

Here N is the total number of lattice sites, z is the number of nearest neighbors, z_1 is the number of nearest neighbors which two nearest neighbors have in common, and $\beta = 1/kT$. The quantities κ_l , $\nu_l(k)$, $\mu_l(n)$, and $\lambda_l(m)$ are the eigenvalues of $\mathcal{H}_{(1)}$, $\mathcal{H}_{(2)}$, $\mathcal{H}_{(3)}$, and $\mathcal{H}_{(3)}^{(2)}$, respectively. These quantities can be found from Eqs. (32), (51), (66), and (67) of Ref. 17 by the substitutions of \bar{O}_i , \bar{O} , and γ_{ij}^{mn} for \bar{S}_i , \bar{S} , and J_{ij} , respectively. In addition, the scalar product $J_{ij} \bar{S}_i \cdot \bar{S}_j$ is replaced by $\sum_{m,n} \gamma_{ij}^{mn} O_i^m O_j^n$. Here \bar{O} is the expansion parameter of the cluster-variation theory. The κ_l arise from single molecules, the ν_l from pairs, the λ_l from one type of triplet (V 's of nearest neighbors), and the μ_l from the other type of triplet (triangles of nearest neighbors).¹⁷ If all pairs, V -linked clusters ($m = i, j, k$ with i, k being nearest neighbors of j , but not each other), and triangles ($n = i, j, k$ with i, j, k all being nearest neighbors) were equivalent, the sums over k, m, n would only contain one term each and $a_1 = b_1 = c_1 = 1$. However, in general, there are several nonequivalent clusters of each type, so the sums over k, m, n are over all nonequivalent clusters with the coefficients a_k , b_m , and c_n giving the weights of the k th, m th, and n th cluster, respectively. For example, for the $Pa3$ structure all pairs are equivalent, but there are two nonequivalent triangles, and seven nonequivalent V -linked clusters. Equation (2) gives the variational free energy as a function of the effective field parameter \bar{O} . The best value of \bar{O} is found by minimizing $F_{(3)}$ with respect to \bar{O} . The long-range order parameter $\langle O_i^0 \rangle$ is then calculated from the equilibrium free energy in the usual manner.¹⁷

We have calculated $F_{(3)}$ for the space groups $Pa3$, $Pca2_1$, and $P2_1/c$. The results for the minima of the respective free energies are shown in Fig. 1 as a function of the reduced temperature T/T_b . Here $T_b = 19\Gamma/3$, where Γ is the ef-

fective EQQ coupling constant.^{14,22,23} The present treatment thus predicts the $Pa3$ structure to be stable at low temperatures, and an ordering based on the space group $P2_1/c$ to give the lowest free energy at higher temperatures. The $Pca2_1$ structure is never stable. A fcc-hcp transition is predicted to occur at $T_c/T_b \cong 0.71$, which is substantially below the molecular field value of 1.082.¹¹⁻¹³ For o -H₂, using $\Gamma = 0.539 \text{ cm}^{-1}$,²³ $T_c = 3.49 \text{ K}$, while for p -D₂ where $\Gamma = 0.736 \text{ cm}^{-1}$,²⁴

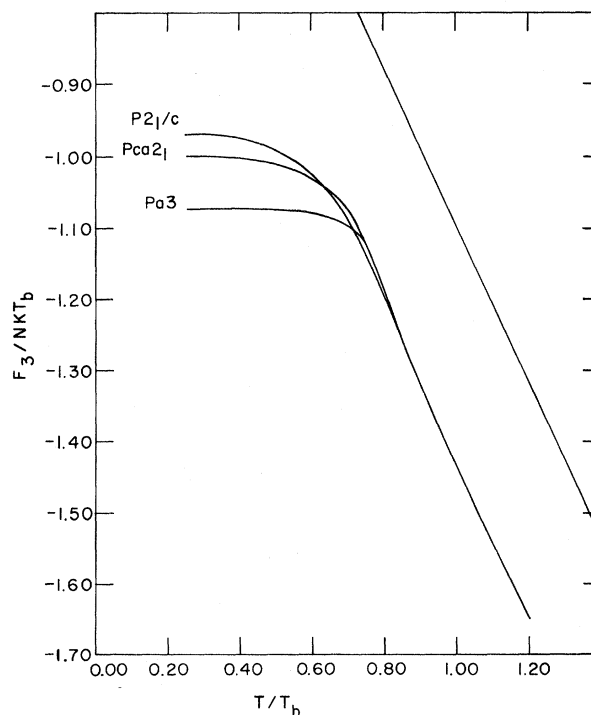


FIG. 1. The contribution of the orientational coupling to the three-molecule cluster free energy $F_{(3)}$. The disordered free energy $-kT \ln 3$ is shown by the straight line. The values for $F_{(3)}$ for the $Pa3$, $Pca2_1$, and $P2_1/c$ structures are given.

we find $T_c = 4.76$ K. The extrapolated experimental values are 2.9 and 3.9 K for *o*-H₂ and *p*-D₂, respectively.¹⁻¹⁰ A sizable hysteresis effect is present.

The corresponding values of the order parameter $\bar{n} = \frac{1}{2}(1 + \frac{1}{3}\langle O^0 \rangle)$ are given in Fig. 2. Here $\bar{n} = 0$ corresponds to perfect long-range order, or no librational excitations, and $\bar{n} = \frac{1}{3}$ represents complete disorder with respect to the *Pa3* or *P2₁/c* alignments. As the temperature is raised a first-order transition from an ordered fcc to an ordered hcp phase takes place at $T_c/T_b = 0.71$. Shortly thereafter, at $T/T_b = 0.79$ there occurs a transition to a disordered hcp phase which is stable at all higher temperatures considered in this work. A detailed examination of the free energy in the temperature region from $T/T_b = 0.71$ to $T/T_b = 0.79$ reveals a transition between two ordered hcp phases as illustrated in Fig. 2. However, this transition is not expected to remain when other possible space groups are examined. A considerable amount of short-range order does remain even in the "disordered" phase, as is evidenced by the large orientational free energies remaining above the transitions.

The difference in the free energies of the *Pa3* and *P2₁/c* structures slightly above the transitions at $T/T_b = 0.72$ is $\Delta F/NkT_b \cong 0.0405$ or $\Delta F/N \cong 0.199$ K for *o*-H₂. Here we have considered only the contributions of the orientational coupling to the free energy of the system. The total free energy of the real crystal includes other terms that depend on whether the lattice is cubic or hcp, on the isotropic intermolecular forces, and on the translational lattice vibrations. However, the difference in the isotropic fcc and hcp ground-state energies for solid H₂ is estimated at only about 10⁻³ K, with the hcp phase lower.²⁶ We thus find that the fcc-hcp transition is primarily due to the anisotropic intermolecular EQQ interactions which contribute only about 3% to the total energy per molecule.

It should be pointed out that the present calculations consider only nearest-neighbor interactions. Molecular field treatments have shown that nearest-neighbor models could lead to anomalous and perhaps unphysical behavior in the transition region.¹²⁻¹³ In addition, only three possible space groups were considered here. The introduction of the *P2₁/c* structure was found to reduce markedly the region where d^2F/dT^2 is positive. This region was previously explained as being a result of the competition of two ordering arrangements: small clusters and the even-

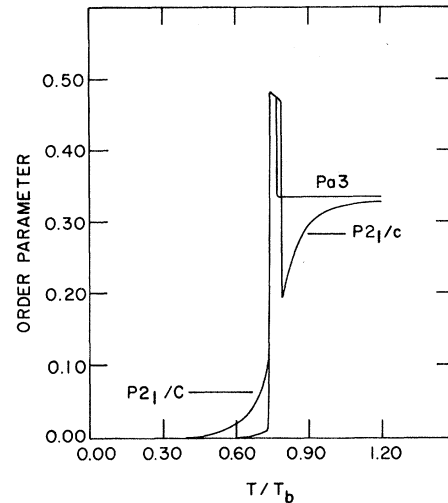


FIG. 2. The long-range order parameter $\bar{n} = \frac{1}{2}(1 + \frac{1}{3}\langle O^0 \rangle)$ versus the reduced temperature for the *Pa3* and *P2₁/c* structures.

tual alignment on a *Pa3* basis.¹⁶ Consideration of other fcc¹³ and hcp¹² structures in the transition region is expected to lead to further improvement. An extension of this work to further neighbor interactions, other possible space groups, and the *o*-H₂ concentration dependence of the "λ transition" is under way.

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†Work performed in part in the Ames Laboratory of the U. S. Atomic Energy Commission.

‡Work supported by National Science Foundation under Grant No. 22553.

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Noncollinear Spin Arrangement in Ultrafine Ferrimagnetic Crystallites

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(Received 30 August 1971)

Mössbauer-effect measurements on extremely small (~ 60 Å) crystallites of γ -Fe₂O₃ show that the spin configuration differs from the Néel type found in large crystallites. It is proposed that the ions in the surface layer are inclined at various angles to the direction of the net moment.

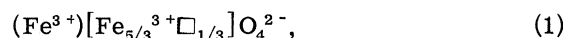
It is known that crystallites of γ -Fe₂O₃, small enough to be superparamagnetic, have a saturation magnetization which decreases abruptly with decreasing particle size.¹ It has been variously proposed that low moments in γ -Fe₂O₃ can be explained by nonmagnetic grain boundaries^{1,2} or the presence of hydrogen in the lattice.³ We have established that neither explanation can account for the magnetization of a sample of ultrafine γ -Fe₂O₃, and that such small ferrimagnetic particles have a different spin structure from bulk material. Values of the saturation magnetization measured in bulk materials cannot, therefore, be expected to apply to very small particles.

The sample was prepared by precipitation from a solution of ferrous and ferric chloride, and subsequent oxidization in air.⁴ It was identified as γ -Fe₂O₃ from its Mössbauer spectra and its x-ray powder pattern which showed eleven low-angle spinel-structure lines. Examination of the powder in an electron microscope showed that it consisted of agglomerates 10^3 – 10^4 Å across, which were composed of roughly spherical particles, 50–75 Å in diameter.

The material was superparamagnetic at room temperature in both magnetization and Mössbauer measurements, and the shape of the spectrum corresponded to a relaxation time of 2×10^{-9} sec. An effective anisotropy constant $K = 1.2 \times 10^6$ erg/cm³ was deduced.^{4,5} The stable ferrimagnetic fraction was obtained from the ratio of the rema-

nence to the saturation magnetization, as a function of temperature, and the particle-size distribution of Fig. 1 was obtained. $\int_0^D \phi(D) dD$ is the fraction of the sample composed of particles with a diameter less than D . According to this distribution, the average particle size is 59 Å, and 40% of the iron ions lie in the surface layer.

γ -Fe₂O₃ is usually supposed to have the formula



where the different brackets denote the A and B sites of the spinel lattice. Iron ions on the two sites are aligned antiparallel,⁶ and the formula gives a spin-only moment of 87.4 emu/g. The moment of our sample, obtained by extrapolation

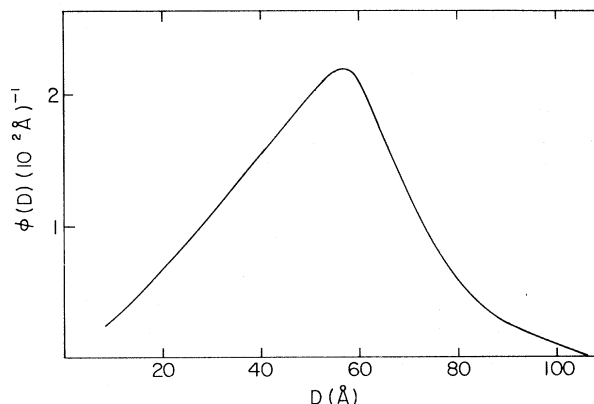


FIG. 1. Particle-size distribution of ultrafine γ -Fe₂O₃ crystallites.