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# Orientational Order in fcc Solid Ortho-$H_2$: Effect of the Spin-Lattice Coupling

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The technique of temperature-dependent Green's functions, as applied in a previous paper, to a molecular-field model of the ordering of ortho-$H_2$ molecules on a rigid face-centered-cubic molecular lattice, is extended to include the effects of the interaction between the rotational motions of the molecules and the lattice vibrations on both the nature of the order-disorder transition and the value of the transition temperature for face-centered-cubic solid ortho-hydrogen. This "spin-lattice" coupling, resulting from the anisotropic van der Waals forces, is taken to be of the form proposed for hexagonal close-packed hydrogen. This interaction is found to lead to an additional, temperature-independent splitting of the $J=1$ rotational level. Depending on the sign and magnitude of this splitting, it is shown that either a first-order, a second-order, or no transition is obtained.

## I. INTRODUCTION

Solid hydrogen can exist in two phases, the cubic close-packed (fcc) phase, stable at low temperatures, and the hexagonal close-packed (hcp) phase, stable at higher temperatures.[1–4] The fcc-hcp transition temperature depends on the ortho-$H_2$ concentration and occurs at temperatures very near those of the anomaly in nuclear magnetic resonance,[5–7] and the λ anomaly in the specific heat.[8,9] Analogous behavior is observed for deuterium.[10–12]

A theoretical discussion of the ordering of ortho-$H_2$ molecules on both fcc and hcp *rigid* lattices, based on the assumption that the orientational coupling of the molecules arises from the quadrupole-quadrupole interaction, has been given by Raich and James[13] in terms of a molecular-field approximation. The technique of temperature-dependent Green's functions has been applied to this molecular-field model of the orientational order-disorder transition for ortho-$H_2$ molecules on a rigid fcc lattice by Raich and Etters.[14] (For convenience, this paper will be referred to as I). For the case of a rigid fcc lattice with quadrupole-quadrupole coupling, the calculations in I show that the molecular-field approximation leads to a first-order phase transition between an orientationally ordered phase, stable at low temperatures, and an orientationally disordered phase, stable at higher temperatures.

Recently, Van Kranendonk and Sears[15] have investigated the effects of the interaction between the rotational motion of the molecules and the lattice vibrations in solid hydrogen, resulting from the anisotropic van der Waals forces. It is found that the result of these "spin-lattice" coupling effects is a shift plus a small, temperature-independent splitting of the $J=1$ rotational level of the ortho-$H_2$ molecules.

A complete theoretical discussion of the combined fcc-hcp, order-disorder transition in solid hydrogen of arbitrary ortho-para composition is necessarily complicated by changes in the free energy associated with the change in molecular lattice and the resulting change in density.[16] A calculation of these free-energy changes could at present give at most only order-of-magnitude estimates because of the uncertainty in the values of the parameters characterizing the isotropic and anisotropic parts of the intermolecular potential for solid hydrogen. Also the equilibrium molecular orientations for ortho-$H_2$ molecules on a fcc molecular lattice have been determined both experimentally[10] and theoretically,[13,17,18] which is not the case for ortho-$H_2$ molecules on a hcp lattice.[17] Therefore, the purpose of this paper is to give only a discussion of the effect of the spin-lattice coupling on both the order of the phase transformation and the transition temperature for ortho-$H_2$ molecules on a *nonrigid* fcc molecular lattice. The results obtained here are thus only valid for ortho-

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hydrogen below the fcc-hcp phase transition. The discussion is presented in terms of an analysis of the conditions for phase transformations of the first and second order as given by Strässler and Kittel.[19]

The Green's-function method developed by the authors to treat the order-disorder transition of ortho-$H_2$ molecules on a rigid fcc lattice can also be applied here. It is shown that a very small splitting (compared to the quadrupole-quadrupole splitting at low temperatures) of the $J=1$ rotational level in ortho-hydrogen, due to the anisotropic van der Waals forces has a marked effect on both the nature of the transition and the value of the transition temperature.

## II. CALCULATIONS

The main contribution to the anisotropic interaction between molecules in solid ortho-hydrogen at low temperatures is the quadrupole-quadrupole interaction.[20] In addition, there exists an anisotropic interaction between a pair of molecules which consists of terms that depend on the orientation of only one of the molecules. This part can also be expanded in spherical harmonics, and the leading part can be written as a crystalline field effective for a molecule on site $i$,[15]

$$V_i^a=(4\pi/5)\epsilon_{2c}(i)\,Y_{20}(\mathbf{\Omega}_i), \tag{1}$$

where $\mathbf{\Omega}_i$ denotes the orientation of molecule $i$ relative to the crystal axis. The crystalline-field constant $\epsilon_{2c}$ is given by

$$\epsilon_{2c}(i)=\sum_j g(R_{ij})\,Y_{20}(\mathbf{\Omega}_{ij}), \tag{2}$$

where $\mathbf{R}_{ij}$ is the vector connecting the central site $i$ with the site $j$. For the radial part $g(R)$ one adopts an exp-6 model

$$g(R)=\epsilon_i \exp[-\eta(R-a)/a]-\epsilon_2(a/R)^6, \tag{3}$$

where the parameters $\epsilon_1$, $\epsilon_2$, $\eta$, and $a$ have been estimated by Van Kranendonk and Sears.[15]

For a rigid, undistorted fcc or hcp lattice the crystalline-field constant (2) vanishes when only nearest neighbors are considered in the sum in Eq. (2), and the contributions from the more distant shells alternate in sign. However, Van Kranendonk and Sears[15] have shown that for the case of a hcp lattice the zero-point vibrations should lead to a deviation from the ideal hcp structure with $c/a=(\frac{8}{3})^{1/2}$, and thus to a nonvanishing of the crystalline field (1). This fact has been confirmed by x-ray diffraction studies of solid hcp nitrogen, where the intermolecular forces are of the same nature as in solid hydrogen. A small deviation from the ideal $c/a$ ratio was found.[21,22] For the fcc phase there is also some evidence, for hydrogen as well as nitrogen, of a small distortion from a lattice described by the space group $Pa3$ to one described by $P2_13$.[10,22] A distortion of this nature would also lead to a finite contribution to the crystalline field (1).

It is seen from the calculations of Van Kranendonk and Sears, for dilute solutions of ortho-hydrogen in solid hcp para-hydrogen, that the effect of the spin-lattice coupling, resulting from the crystalline field (1), is a shift plus a small splitting of the $J=1$ rotational level of ortho-hydrogen. Leaving off the over-all shift, the effective crystalline field for the spin-lattice coupling for an ortho-molecule can be written in operator form in the subspace of $J=1$ [15]

$$V_i^a=(\Delta/3)[3(J_i^z)^2-2], \tag{4}$$

where $\mathbf{J}_i$ is the angular momentum operator for an ortho-molecule on site $i$, with the $z$ axis taken along the threefold symmetry axis. Here $\Delta$ is the effective splitting of the $J=1$ rotational level. $\Delta$ is independent of the temperature and the ortho-$H_2$ concentration. If $\Delta$ is positive the degenerate $M=\pm1$ level lies above the $M=0$ level, and vice versa for $\Delta$ negative. Van Kranendonk and Sears estimated $\Delta\simeq-0.2$ cm$^{-1}$. Again, this can only be an order-of-magnitude estimate because of the uncertainty of the parameters that specify the anistropic intermolecular potential. This estimate agress, except for possibly the sign, with recent experimental results, which showed a splitting between 0.3 and 0.4°K.[23,24]

The effect of the spin-lattice coupling has not been explicitly calculated for the case of fcc ortho-hydrogen, however, this calculation would be similarly limited by our inaccurate knowledge of the parameters specifying the anistropic intermolecular potential. Because of the change in the molecular lattice the splitting of the $J=1$ rotational level cannot be expected to be entirely independent of the ortho concentration. However, the crystalline field (1) does not depend on either the orientations or the rotational states of the molecules surrounding the site $i$, in contrast to the quadrupole-quadrupole interaction, but only on the type of molecular lattice and the orientation of the central molecule. Thus, for the case of fcc ortho-$H_2$, if there is indeed a small distortion to a molecular lattice described by the space group $P2_13$, it is reasonable to assume that this distortion also arises because of a nonvanishing of a crystalline field of the form (1), which would result in a splitting of the $J=1$ rotational level of the same nature as for the hcp case. We therefore include the spin-lattice effects (plus any other interaction leading to a $Pa3\rightarrow P2_13$ distortion of the fcc molecular lattice) by adding a crystalline field of the form (1) to the Hamiltonian of the system, as given by Eq. (I,1), with

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a value of $\Delta$ of perhaps the same order of magnitude as the value estimated for the hcp case.[15,23,24]

Thus, the Hamiltonian for the model applied here to describe the ordering of ortho-$H_2$ molecules on a nonrigid fcc molecular lattice, including both the quadrupole-quadrupole interactions and the anisotropic van der Waals forces, is

$$H=\tfrac{1}{2}\sum_{i,j}V_{ij}{}^{QQ}+\sum_{i}V_{i}{}^{a}, \tag{5}$$

where the sums range over all sites of the fcc lattice. Here $V_{ij}{}^{QQ}$ is the quadrupole-quadrupole interaction between molecules $i$ and $j$ as given by Eq. (I,2), and $V_i{}^a$ is the effective crystalline field given by Eq. (4). Even though it satisfies Laplace's equation, the quadrupole-quadrupole interaction $V_{ij}{}^{QQ}$ also leads to a spin-lattice coupling effect due to the anisotropy of the self-energy.[15] This particular spin-lattice coupling would lead to a correction to the temperature-dependent quadrupole-quadrupole splitting of the $J=1$ rotational level of an ortho-$H_2$ molecule as calculated in I, and can thus be included in an "effective" quadrupole moment for hydrogen molecules in the solid state. Preliminary calculations show that this effect is very small, of the order of a few percent of the quadrupole-quadrupole interaction as discussed in I.

Following the development in I, it is seen that utilizing the fact that there exists a threefold axis of symmetry for each molecule, a fact which holds for the space group $P2_13$ as well as for $Pa3$, the Hamiltonian (5) in the subspace $J=1$ can be written in operator form:

$$H=\sum_{i,j}\gamma_{ij}[3(J_i{}^z)^2-2][3(J_j{}^z)^2-2] +(\Delta/3)\sum_{i}[3(J_i{}^z)^2-2], \tag{6}$$

where $\mathbf{J}_i$ is the angular momentum operator for a molecule on site $i$, with the $z$ axis taken along the threefold symmetry axis for that molecule. Here $\gamma_{ij}=-(19/144)\Gamma_{ij}$, where $\Gamma_{ij}=6e^2Q^2/(25R_{ij}{}^5)$, with $Q$ the molecular quadrupole moment and $R_{ij}$ the $ij$ intermolecular distance. One now applies the technique of temperature-dependent Green's functions, as illustrated in I, to calculate the correlation functions $\langle J^z\rangle$ and $\langle(J^z)^2\rangle$ for the model specified by the Hamiltonian (6). It is seen that the calculations become identical to those in I if one makes the replacement

$$E_0=6\sum_{i}\gamma_{ig}(3\langle(J^z)^2\rangle-2)\rightarrow E_0{}' =6\sum_{i}\gamma_{ig}(3\langle(J^z)^2\rangle-2)+\Delta. \tag{7}$$

A simple calculation shows that for a distorted fcc molecular lattice, specified by the space group $P2_13$, with molecular displacements $\delta$ along the threefold axis in the manner described by Streib *et al.*,[21,22] the sum $\sum_i\gamma_{ig}$ over nearest neighbors is

$$\sum_{i}\gamma_{ig}=\gamma' Z, \tag{8}$$

where

$$\gamma'=\gamma\{1-3.9(\delta/R_0)^2+O[(\delta/R_0)^4]\}. \tag{9}$$

Here Z is the number of nearest neighbors, twelve for the fcc lattice, $\gamma$ and $R_0$ are the values of $\gamma_{ij}$ and $R_{ij}$ for nearest neighbors $ij$ for the undistorted $Pa3$ lattice. For the case of nitrogen it is found that $(\delta/R_0)^2\sim10^{-3}$.[21,22] Assuming a similar value fo rthe distortion in hydrogen, it is seen that the correction terms to $\gamma$ as given by Eq. (9) are negligible, and at worst can be included in the constant $\gamma'$.

As a result of the nearest-neighbor approximation (8), $E_0{}'$ is written in the form

$$E_0{}'=6\gamma' Z(3\langle(J^z)^2\rangle-2)+\Delta. \tag{10}$$

A comparison with the Paper I then shows that the analogs of Eqs. (I,34) and (I,35) are

$$\langle J^z\rangle=0, \tag{11}$$

$$\beta(18\gamma' Z\langle(J^z)^2\rangle-12\gamma' Z+\Delta)-\ln2 =\ln[(1-\langle(J^z)^2\rangle)/\langle(J^z)^2\rangle], \tag{12a}$$

where $\beta=1/kT$. Equation (12a) reduces to Eq. (6) of Strässler and Kittel[19]:

$$\beta(\epsilon-\lambda\rho)+\ln\tfrac{1}{2}=\ln[(1-\rho)/\rho], \tag{12b}$$

with the substitutions

$$\begin{aligned}\rho&=\langle(J^z)^2\rangle,\\ \epsilon&=19\Gamma+\Delta,\\ \lambda&=(57/2)\Gamma,\end{aligned} \tag{13}$$

where $\Gamma$ is now $-(144/19)\gamma'$.

## III. RESULTS

Following the general treatment of Strässler and Kittel[19] it is seen that both the order of the transition and the transition temperature are dependent on the value of the anisotropic splitting parameter $\Delta$. There are three distinct cases to be considered:

(a) A first-order transition occurs at

$$kT_c=[(19/4)\Gamma+\Delta]/\ln2, \tag{14}$$

provided that $\Delta/\Gamma>(19/8)(3\ln2-2)$, supposing always that $\Delta/\Gamma>-19/4$.

(b) A second-order transition occurs at

$$kT_c=(57/8)\Gamma, \tag{15}$$

if $\Delta/\Gamma=(19/8)(3\ln2-2)$.

(c) For $\Delta/\Gamma<(19/8)(3\ln2-2)$ no transition occurs.

Figure 1 shows $\langle(J^z)^2\rangle$ as a function of $T/T_c$ for $\Gamma=0.654$°K for several values of $\Delta/\Gamma$. This value of $\Gamma$

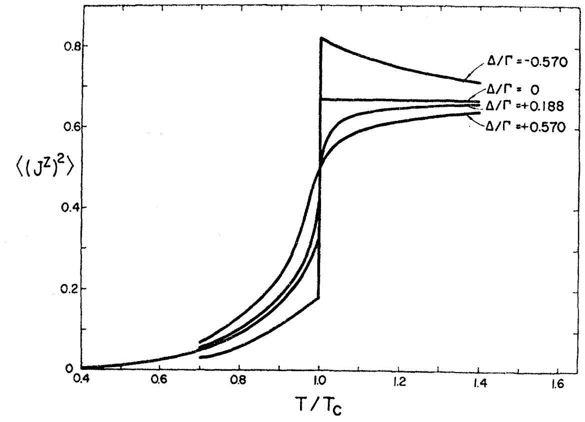

FIG. 1. The average value $\langle (J^z)^2 \rangle$ as a function of $T/T_c$ for several values of $\Delta/\Gamma$.

corresponds to the values of $Q=0.110\times10^{-16}$ cm$^2$,[25] $R_0=3.75$ Å, $(\delta/R_0)\sim10^{-3}$, and a negligible spin-lattice coupling effect due to the quadrupole-quadrupole interaction. For $\Delta/\Gamma=-0.57$ ($\Delta=-0.4$°K), the transition is first order. At $\Delta/\Gamma=+0.188$ ($\Delta=+0.123$°K), the transition is second order, while for $\Delta/\Gamma=+0.57$ ($\Delta=+0.4$°K), one obtains no transition. For $\Delta=0$, one finds a first-order transition as determined in I. As stated above these results are only applicable to solid ortho-hydrogen for $T<T_c$.

From the discussions of nuclear magnetic resonance in solid hydrogen by Abragam[26] and Reif and Purcell[5] one finds that the splitting of the two side peaks of the NMR line of hydrogen is given by

$$\Delta_{\mathrm{NMR}}=3d(3\langle (J^z)^2\rangle-2), \tag{16}$$

where

$$d=(\tfrac{1}{5})(h\gamma_p^2/2\pi)\langle r^{-3}\rangle=57.68 \text{ kc/sec}, \tag{17}$$

in the notation of Abragam. A comparison of an experimental determination of $\Delta_{\mathrm{NMR}}$ with $\langle (J^z)^2\rangle$ as a function of temperature, using Eqs. (16) and (17) and Fig. 1, should give an estimate of both the sign and the order of magnitude of the splitting $\Delta$ for ortho-molecules on a fcc lattice.[27]

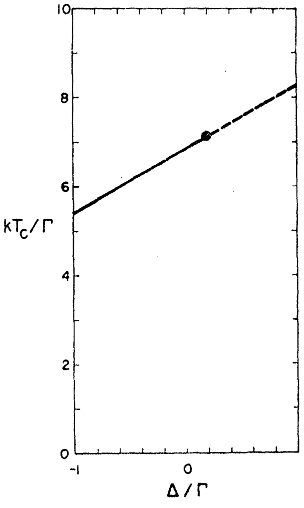

FIG. 2. The transition temperature in terms of $kT_c/\Gamma$ versus $\Delta/\Gamma$. First-order transitions are shown by the solid line, the second-order transition is shown by the point. The dashed line indicates gradual changes.

The dependence of the transition temperature on the parameter $\Delta/\Gamma$ is shown in Fig. 2. The solid line indicates first-order transitions, the dot shows the position of the second-order transition. For $\Delta/\Gamma<(19/8)(3\ln2-2)$, the transition temperature is defined as $T(\langle (J^z)^2\rangle=\frac{1}{2})$ and is shown by a dashed line. One may also plot the calculated transition temperature of ortho-para mixtures of solid fcc hydrogen versus ortho-$H_2$ concentration for several values of the parameter $\Delta/\Gamma$ on the basis of the molecular-field approximation, i.e., a random distribution of ortho- and para-molecules. The results are shown in Fig. 3.

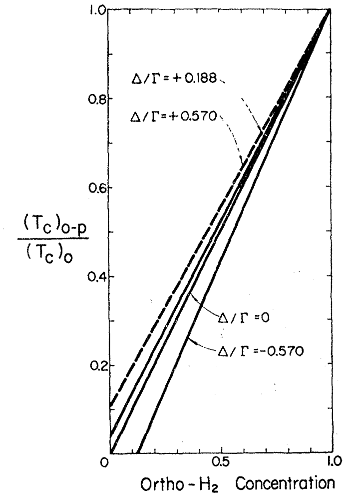

FIG. 3. The reduced transition temperature for ortho-para mixtures $(T_c)_{o-p}/(T_c)_o$, calculated on the basis of a molecular-field theory, versus the ortho-$H_2$ concentration.

Again we must point out that no attempt has been made to give a complete theoretical description of the observed fcc-hcp, order-disorder transition. Such a discussion would require not only an accurate knowledge of the parameters specifying both the isotropic and anisotropic parts of the intermolecular interaction, but also a description of the orientational ordering of ortho-$H_2$ molecules on a hcp lattice. The latter calculations are presently being carried out by James.[28]

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