

## Orientational order in solid hydrogen at reduced ortho concentration\*

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The splitting of the NMR line in solid hydrogen has been observed during 145 h while it aged at temperatures below 0.1°K. For ortho-hydrogen mole fractions  $X$  less than 0.55, the NMR splitting is present but disappears abruptly at transition temperatures fitting a straight line  $T_c = (0.54 \pm 0.06)X + (0.02 \pm 0.02)$ . The concentration dependence of the splitting is compared to a model which includes only a zero-point admixture to the  $J_z = 0$  ground state from the  $J_z = \pm 1$  wave functions of the libron band, and a zero-point admixture of the  $J = 3$  state, both of which admixtures scale according to the observed concentration dependence of the transition temperature.

### I. INTRODUCTION

Studies of solid hydrogen at low temperatures by means of NMR at high magnetic fields have shown<sup>1</sup> that the ordered state of the magnetic ortho-hydrogen molecules persists into fractional ortho concentrations  $X$  well below 0.56. Earlier experiments had generally found that the temperature of the transition to the ordered state decreased approximately linearly with  $X$ , extrapolating to a temperature of zero at  $X \approx 0.56$ .<sup>2-4</sup> In the NMR experiments we reported earlier, the structured NMR line, characteristic of the ordered state, was observed at various times as the sample aged while continuously held at a low temperature and, owing to ortho-para conversion,  $X$  decreased to about 0.43. The measured decreasing frequency difference between the two main cusps of the structured line, a "Pake doublet" attributed to the dipole-dipole intramolecular interaction, was interpreted there as indicating that the energy gap to the excited libron band of molecular excitations decreased with  $X$  but became constant at about 0.24°K at  $X \leq 0.56$ .

Similar measurements have more recently extended the data downward in  $X$  to about 0.25. The apparatus and technique employed were the same as in the earlier report. The new observations, added to the earlier ones, suggest a different model. The primary dependence of the splitting on  $X$  over the extra range is now proposed to arise in ortho-concentration-dependent distortions (mixing) of the primarily  $J_z = 0$  ground-state molecular wavefunction, rather than in thermal excitation of the libron modes. At the temperature  $T \approx 0.085$ °K of the measurements, even at the lowest values of  $X$ , only zero-point effects are important.

### II. ORDER-DISORDER TRANSITION VERSUS $X$

As the frozen hydrogen ages at a temperature normally held continuously below 0.1°K, the derivative of the NMR line was sampled occasionally. As shown in Fig. 1, variations of the line intensity observed throughout the run were consistent with

the assumption of ortho-para conversion according to the accepted rate

$$\dot{X} = -kX^2 \text{ or } X^{-1} = kt + \text{const},$$

with  $k = 0.019$  per hour.<sup>5</sup> On several occasions, in the course of the aging, the temperature was raised briefly through a value that resulted in the abrupt disappearance of the doublet structure with a concomitant reduction in line breadth. In this way, the open circular points plotted on the phase diagram of Fig. 2 were obtained. The solid points in Fig. 2 represent quite similar data for  $X < 0.5$  recently reported by Ishimoto *et al.*<sup>6</sup> For  $X > 0.55$ , the line drawn is based on the data reported by Jarvis *et al.*<sup>4</sup> for the transition with increasing temperature, observed as a change of pressure at constant volume. Data for the warming transition from x-ray diffraction for a part of the range of concentration<sup>3</sup> and from NMR<sup>2</sup> fall close to the line.

The temperatures of the transitions we observed in the range  $0.55 > X \geq 0.25$  make a least-squares fit to a line  $T_c = (0.54 \pm 0.06)X + (0.02 \pm 0.02)$ . Ishimoto *et al.* express their data by a line  $T_c = (0.3 \pm 0.1)(0.5 + X)$ .<sup>7</sup> The disagreement between these results may reflect differences in the techniques employed in the two experiments. In the Japanese work, free-induction decays were observed and the transition temperatures were defined as those corresponding to the appearance of a "complete beat structure" in the decays as the temperatures were lowered. The samples were frozen from gaseous mixtures prepared with particular values of  $X$ . The transitions resulting from decreasing temperatures were observed, whereas ours were with increasing temperatures. Hysteresis in the transition itself should render their temperatures less than ours rather than greater, as reported. However, our samples, being the remainder after the conversion away of some of the ortho-hydrogen component, could have less than a purely random number of regions of high ortho concentration because these regions should convert

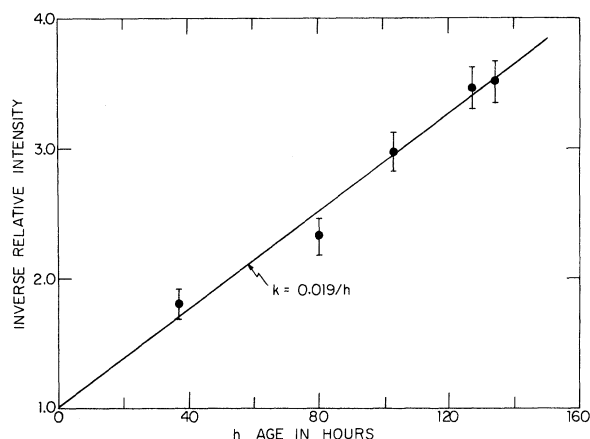


FIG. 1. Inverse of the relative intensity of the NMR signals vs time. The solid line corresponds to the ortho-para conversion constant  $k = 0.019 \text{ h}^{-1}$ .

first. In that event, the transition could be less easily nucleated than in random mixtures. Schmidt<sup>5</sup> finds that diffusion and the ortho-ortho molecular quadrupole interaction result, at  $1.57^\circ\text{K}$ , in more clustering than in a random sample, however. The difference between Ishimoto's samples and ours is underlined by our observation that with  $X \leq 0.5$ , after several hours aging at  $T \sim 1^\circ\text{K}$ , no evidence of fine structure was seen on subsequent cooling to  $85 \text{ m}^\circ\text{K}$ . We suggest that the molecular order-disorder transition we observe, via the line-shape change, occurs, when the temperature excursion is suitably restricted, without a corresponding change from the face-centered cubic structure of the low-temperature phase. The shapes of our NMR lines gave no evidence of coexistence of the ordered and the disordered phases as the transition was traversed. Aging at very low temperatures may produce such complete conversion to the cubic crystal structure that the hcp form cannot easily reappear in association with the transition to disorder. On the other hand, if we raise the temperature sufficiently to convert fully to the hexagonal structure, that structure apparently becomes metastable and we cannot recover the fcc phase by reducing the temperature. In contrast, it may be that, in the samples used by Ishimoto *et al.*, the existence of regions of large ortho concentration in the crystals frozen directly from the gas phase provides the centers needed to nucleate the transition to the fcc structure and to the ordered state within it. Another possible source of the different behavior comes from the fact that Ishimoto *et al.* froze their mixtures on silver wires. There is evidence that hydrogen freezes on some metal substrates directly into the fcc phase at relatively high temperatures.<sup>8-11</sup>

### III. PARAMETER OF ORIENTATIONAL ORDER

In Fig. 3 are reproduced points representing the data on the frequency difference  $\nu_{DD}$  between the main extrema of the "derivative" line of the "Pake doublet" structure vs  $X$  as reported earlier and as now extended. Ishimoto *et al.*<sup>6</sup> have given only one value for the splitting,  $149 \text{ kHz}$  at  $X = 0.50$  and at  $0.2^\circ\text{K}$ . It generally supports our data, falling only slightly below our points. At the temperatures involved,  $0.085^\circ\text{K}$ , effects of thermal excitations are negligible unless an energy gap as small as the  $0.24^\circ\text{K}$  invoked to fit the earlier data were present. Evidence against such a small energy gap comes from the observation that the splitting was not so strongly temperature dependent as such a model would require. The extended range of  $X$  below  $0.55$  makes the continued slow decrease of the splitting in that range very much more evident. Consequently we are now led to propose mechanism wherein mainly "zero-point" admixtures to the ground-state wave function are involved. The amounts of these are suggested to vary with  $X$  in the same manner as does the orienting mechanism itself, as revealed in the dependence of the observed transition temperature on ortho concentration. A similar analysis was made by Meyer *et al.*<sup>12</sup> to fit the splitting observed for para concentrations greater than  $0.55$  in solid  $\text{D}_2$  and for the limited ortho range  $0.7 \leq X \leq 0.87$  in solid  $\text{H}_2$ .

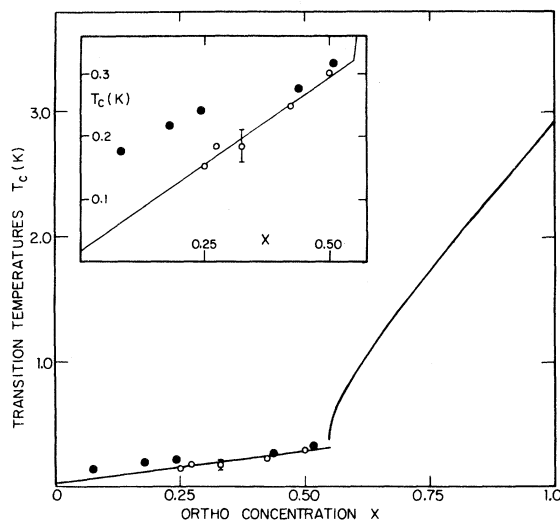


FIG. 2. Transition temperature vs ortho mole fraction  $X$ . The open circles are the present data. The solid circles are from Ishimoto *et al.* (Ref. 5). The segment for low concentration is replotted on an expanded scale in the insert. In the region  $X > 0.55$ , the line is drawn to fit data for the transition with increasing temperature from Ref. 4. For  $X < 0.55$  the line drawn is that giving a least-squares fit to the open circles,  $T_c = 0.54X + 0.02$ .

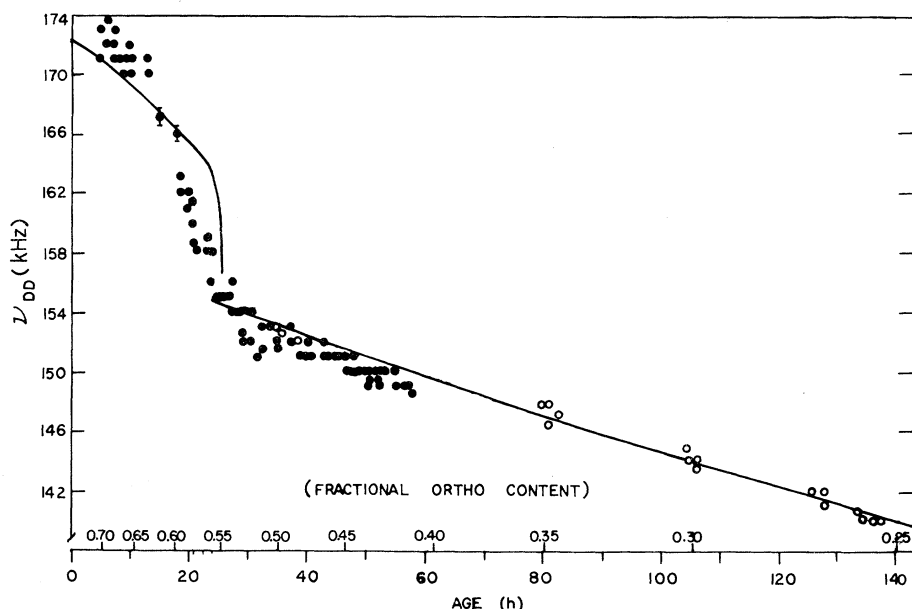


FIG. 3. Observed values in kHz of the frequency difference between points of maximum slope in the NMR line. Solid circles are those previously reported (Ref. 1), and the open circles are the extended data. Abscissa is ortho concentration  $X$ , assuming the normal conversion constant  $k = 0.019 \text{ h}^{-1}$ . The solid line corresponds to  $0.98(173, 0) \{ [1 + 0.0115 \times f^{-1}(X)]^{-1} + 0.049 f(X) \} + 1.4X$ . The last term accounts for intermolecular dipolar broadening, and  $f(X)$  is taken to represent  $T_c(X)/T_c(1)$ .

#### IV. THEORETICAL CONSIDERATIONS

In the orientationally ordered state, a sample containing randomly oriented microcrystals has a line shape with cusps, resulting from the intramolecular dipole-dipole interaction, separated in frequency by

$$\nu_{DD} = \frac{15}{4} d \langle 3 \cos^2 \theta_i - 1 \rangle_T,$$

where  $d = \frac{4}{3} h^{-1} \mu_p^2 r_0^{-3} = 57.68 \text{ kHz}$ ;  $\theta_i$  designates the angle between the  $i$ th molecular axis and the local axis of quantization,  $h$  is Planck's constant,  $\mu_p$  is the magnetic moment of the proton, and  $r_0^{-3}$  is the mean inverse cube of the internuclear separation in the free molecule.

In the manifold  $J = 1$ ,

$$\frac{5}{4} \langle 3 \cos^2 \theta_i - 1 \rangle_T = \langle 1 - \frac{3}{2} J_z^2 \rangle_T^{J=1} = S(T),$$

where  $S(T)$  is the order parameter at temperature  $T$ . However, as Reif and Purcell have first pointed out,<sup>13</sup> the same agency that produces the orientation of the molecule also can admix elements of higher rotational states, and therefore,  $J$  is not a "good quantum number." Accordingly, the wave function may be written

$$|10\rangle + \sum_{\substack{JM \\ (J \neq 1)}} \frac{|JM\rangle \langle JM|V|10\rangle}{E_{J=1} - E_J}.$$

Using the intermolecular electric quadrupole interaction<sup>14</sup> for  $V$  for  $X = 1$  (pure ortho-hydrogen) one finds the additional contribution comes only from the state  $J = 3$  and the result, in the lowest order, may be written

$$\frac{5}{4} \langle 3 \cos^2 \theta_i - 1 \rangle_T = \langle 1 - \frac{3}{2} J_z^2 \rangle_T^{J=1} + 4.4 \Gamma / B,$$

where the coefficient 4.4 is derived from the parallel detailed evaluation by Harris *et al.*<sup>15</sup> of the shift in the ground-state energy,  $\Gamma = 0.7 \text{ cm}^{-1}$  is the molecular quadrupole interaction constant,<sup>16</sup> and  $B = 59 \text{ cm}^{-1}$  is the molecular rotational constant for  $\text{H}_2$ .

Harris<sup>14,16</sup> finds that as a result of the interaction of the "zero-point" phonon modes with the librational degrees of freedom, the order parameter  $\langle 1 - \frac{3}{2} J_z^2 \rangle_T^{J=1}$  is reduced by a factor  $\xi = 0.98$  (a "dynamic renormalization")<sup>14</sup> and the orientational interactions (and therefore the effective value of  $\Gamma$ ) are further reduced by a factor  $\xi_{54} = 0.93$  (a "static renormalization").<sup>14</sup> If we include these effects, the angular average  $\frac{5}{4} \langle 3 \cos^2 \theta_i - 1 \rangle_T$  becomes  $\xi[S(T) + 4.1 \Gamma / B]$ .

Analogous to the "spin-wave" treatments of anti-ferromagnetism, the order parameter  $S(T)$  can be evaluated in terms of the spectrum of elementary excitations, the librational waves, and Raich and Eters show<sup>17</sup> that

$$S(T) = -2 + \frac{3S(T)}{4N} \sum_{\vec{k}, \mu} \frac{1 + \omega_\mu^2}{\omega_\mu} \coth(\frac{1}{2} \beta E_\mu),$$

where  $E_\mu(\vec{k}) = 19 \Gamma S \omega_\mu(\vec{k})$  is the excitation energy for a given mode  $\mu$  of wave vector  $\vec{k}$ . As described above, we are interested here only in the "zero-point" effects because we believe  $kT \ll E_{\text{min}}$ . In this approximation, and replacing the sum with an integral over  $g(\omega)$ , a "density of states," we find

$$S(0) = (1 + a)^{-1}, \quad a = \frac{3}{4} \int_0^\infty \frac{(\omega - 1)^2}{\omega} g(\omega) d\omega.$$

Note that, in the molecular-field approximation,  $\omega = 1$ ; so  $a = 0$  and  $S(0)_{\text{MF}} = 1$ . The zero-point deviation of the order parameter from the molecular field value is analogous to the "spin-deviation" of the zero-point sublattice magnetization of antiferromagnets.<sup>18</sup>

For pure ortho-hydrogen, Raich and Etters estimate that  $a = 0.02$ . (Ueyama and Matsubara<sup>19</sup> calculate a fractional zero-point deviation of  $-0.028$  for the quadrupolar energy.) For ortho-para mixtures one would naively expect the deviation  $a(X)$  to be proportional to the number of ortho-hydrogen nearest neighbors, and Coll and Harris<sup>20</sup> inferred a dependence of

$$S(0) = 1 - a_0 X^{-1} + \dots,$$

where  $a_0 = 0.025$ .

At very low temperatures where thermal excitations of the libron states can safely be ignored, one then expects

$$\nu_{DD} = 3d\xi[(1+a)^{-1} + C],$$

where  $C = 4.1\Gamma/B$ .

In the absence of a theoretical model that predicts the observed dependence of the transition temperature on  $X$ , and in recognition of the fact that both  $a$  and  $C$  are also manifestations of the strength of the intermolecular electric quadrupole interaction, we are led to use for the  $X$  dependence of both  $a$  and  $C$  a function of  $X$  chosen to resemble the  $X$  dependence of the transition temperature, normalized to unity at  $X$  equal to unity. For simplicity we assume that the functional dependence of  $C$  and  $a^{-1}$  on  $X$  is the same, although we note that this is not the case for the model of  $g(X)$  considered by Harris *et al.*<sup>15</sup> Thus we are led to consider a function

$$\nu_{DDa} = 3d\xi \left[ \left( 1 + \frac{a_0}{f(X)} \right)^{-1} + C_0 f(X) \right] + 1.4X,$$

where  $f(X)$  results from fitting the data of Fig. 2 for the order-disorder transition, and the term  $1.4X$  takes account of intermolecular dipole-dipole broadening. For  $X > 0.55$ ,  $f(X)$  is evaluated from the tabulated data of Jarvis *et al.*<sup>4</sup> For  $X \leq 0.55$ ,  $f(X)$  is taken from the fitted line normalized to  $T_c(X=1) = 2.92^\circ\text{K}$ .<sup>4</sup> Using the calculated value  $C_0 = 0.049$ , the curve drawn in Fig. 3 results for  $a_0 = 0.0115$ . If this model is the correct source of the fine-structure splitting, the zero-point librational contribution to the distortion of the wave function is somewhat less than one-half as large as the estimates to which reference has been made above, but the close agreement in form of the function calculated from the transition temperatures is striking. The value of  $a_0$  is dependent upon the detailed form of  $g(\omega)$ . In the similar fitting carried out by Meyer *et al.*<sup>12</sup> for  $\text{D}_2$ , a value of  $a_0 = 0.021$  was used. Analysis of their data using the corresponding value of  $C$  appropriate for  $\text{D}_2$  would lead to a reduction of their value of  $a_0$ .

Note that even if the conversion rate does not follow the simple quadratic dependence on concentration to such long times as 150 h, the interrelationship between the splitting and the transition temperature is still valid. The parameter  $X$  does not appear in the final fit. Slowing of the conversion at small  $X$  and low temperature could account for the inference from the fit that  $T_c(X=0) > 0$ . Schmidt observed an increased rate but at  $1.57^\circ\text{K}$  and after 200 h.<sup>5</sup> Molecular quadrupole interactions with next-nearest neighbors may play a major part in establishing the ordered phase for  $X \leq 0.5$  (Ref. 4).

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