

## Nuclear Magnetic Resonance of Solid Hydrogen (67–86% Ortho) and Solid Deuterium (33% and 55% Para)

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Nuclear magnetic resonance studies on solid hydrogen ( $H_2$ ) of ortho concentrations from 67% to 86% and of solid deuterium ( $D_2$ ) with para concentrations of 33% and 55% are reported. The method of Cunningham, Chapin, and Johnston was used to produce the high concentrations ortho  $H_2$  and para  $D_2$ . The temperature ( $T_\lambda$ ) of appearance of side peaks associated with the removal of rotational degeneracy in  $H_2$  was found to shift to 2.18°K for 86% ortho as compared to a value of 1.6°K for the normal concentration. Our  $T_\lambda$  versus concentration data were found to join smoothly to the previous lower concentration work of Sugawara *et al.* In addition an interesting hysteresis phenomenon was observed for  $H_2$ . It was noted that the temperature of appearance of the side peaks when the  $H_2$  is cooled is some 0.15°K lower than the temperature of their disappearance when the temperature is slowly raised. In the case of deuterium, no peaks were observed for either 33% or 55% para  $D_2$  at temperatures down to 0.9°K.  $T_1$  was measured roughly for the two concentrations. For  $n$ - $D_2$ ,  $T_1$  was found to be  $7.6 \pm 3$  sec. This compares well with the theoretical value of 8 sec given by Moriya and Motizuki. For 55% para- $D_2$ , a value of  $3 \pm 1$  sec was found. The theory of Moriya and Motizuki gives 5 sec.

### INTRODUCTION

#### $H_2$

EVER since Hatton and Rollin<sup>1</sup> performed their pioneer experiments on solid hydrogen, the nuclear magnetic resonance (NMR) of solid  $H_2$  has been of considerable interest to solid-state physicists. Hatton and Rollin discovered the two line shape transitions—the self-diffusion transition at 10°K and the “rotation-libration” transition at about 1.5°K. The former transition at which the line broadens from less than 1 gauss to some 5–6 gauss, as temperature is lowered, is associated with the self-diffusion of the molecules through the lattice.<sup>1–4</sup> The transition takes place at higher temperatures as pressure is increased.<sup>4</sup>

At the lower transition, the threefold rotational degeneracy of the ortho molecule in its  $J=1$  state is removed by the crystalline potential of interaction and the lowest rotational level is preferentially populated. As a result there is an anomaly in the specific heat<sup>5,6</sup> which is accompanied by a change in the NMR line shape. The 5-gauss wide central absorption signal becomes small and side peaks of 40-gauss separation and humps 80 gauss apart appear. Reif and Purcell<sup>7</sup> have given an exact quantitative explanation of the line shape. Tomita<sup>8</sup> gives a treatment of the transition

as a cooperative phenomenon. Nakamura<sup>9</sup> investigated the nature of the interactions which produce the anomalous specific heat. Hill and Ricketson,<sup>5</sup> and Hill, Ricketson, and Simon<sup>6</sup> found that as the ortho concentration is decreased, the temperature of the specific heat maximum also decreases (see Fig. 1). The latter workers found that, for ortho concentrations less than 60%, the specific heat anomaly is no longer a sharp  $\lambda$ -like peak but becomes more like that of a Schottky function, though more complicated in nature. Sugawara<sup>10</sup> and his co-workers, investigating the NMR of solid hydrogen with various ortho concentrations, found that the temperature of appearance of side peaks decreases with decreasing ortho concentrations and obtained transition temperatures very close to those found from specific heat measurements. However, the NMR results form a curve which is concave toward the temperature axis while those of Hill, Ricketson, and Simon have the opposite curvature. McCormick and Fairbank<sup>11</sup> have reported the effect of pressure on the temperature  $T_\lambda$ .

#### $D_2$

Many of the magnetic resonance workers who have studied solid  $H_2$  have also investigated solid  $D_2$ .<sup>1,2,7,10</sup> Deuterium was found to have a self-diffusion transition<sup>2</sup> at about 13°K, but no rotational transition was found in any of the investigations down to temperatures as low as 1.1°K. This might be expected since the concentration of para-molecules, which would be the only ones to contribute to side peaks, is only 33%. This could mean that the transition occurs at a very low temperature, if at all. Since the ortho-deuterium also has a resonance, the contribution of the para-molecules

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<sup>1</sup> J. Hatton and B. V. Rollin, Proc. Roy. Soc. (London) **A199**, 222 (1949).

<sup>2</sup> R. V. Rollin and E. Watson, *Conférence de Physique des Basses Températures, Paris, 1955* (Centre National de la Recherche Scientifique, and UNESCO, Paris, 1956), No. 63.

<sup>3</sup> M. Bloom, *Physica* **23**, 767 (1957).

<sup>4</sup> G. W. Smith and C. F. Squire, *Phys. Rev.* **111**, 188 (1958).

<sup>5</sup> R. W. Hill and B. W. A. Ricketson, *Phil. Mag.* **45**, 277 (1954).

<sup>6</sup> Hill, Ricketson, and Simon, reference 2, No. 76.

<sup>7</sup> F. Reif and E. M. Purcell, *Phys. Rev.* **91**, 631 (1953).

<sup>8</sup> K. Tomita, Proc. Phys. Soc. (London) **A68**, 213 (1955).

<sup>9</sup> T. Nakamura, *Progr. Theoret. Phys. (Kyoto)* **14**, 135 (1955).

<sup>10</sup> Sugawara, Masuda, Kanda, and Kanda, *Sci. Repts. Research Inst. Tohoku Univ.* **7**, 67 (1955).

<sup>11</sup> W. D. McCormick and W. M. Fairbank, *Bull. Am. Phys. Soc.* **3**, 166 (1958).

to the signal strength is only  $\frac{1}{6}$  the total intensity for normal D<sub>2</sub>. The theoretical separation of the side peaks is 75.7 kilocycles per sec or some 116 gauss.<sup>12</sup>

$T_1$  for solid in  $n$ -D<sub>2</sub> was measured to be approximately 5 sec by Hatton and Rollin.<sup>1</sup> The theory of Moriya and Motizuki<sup>13</sup> predicts a value of 8 sec.

The present work was undertaken with a twofold purpose. We hoped to provide further experimental information on the rotational transition of solid H<sub>2</sub> by extending the  $T_\lambda$  versus concentration curve to values of ortho concentration greater than normal. Further, we felt that side peaks might then be found in D<sub>2</sub> with higher para concentrations and lower temperatures than previously used. The higher ortho hydrogen and para deuterium concentrations became feasible with the discovery of a technique for enrichment of these concentrations by Cunningham, Chapin, and Johnston.<sup>14</sup>

#### EXPERIMENTAL APPARATUS AND METHODS

The NMR spectrometer used was a Pound-Watkins<sup>15</sup> type manufactured by the Nuclear Magnetics Corporation. Frequencies of about 9 Mc/sec were used for both H<sub>2</sub> and D<sub>2</sub>. The magnetic field was supplied by a diesel generator powered electromagnet. Field instability was such that it was not possible to use the lock-in amplifier to trace derivatives. Therefore, absorption signals were observed visually on an oscilloscope. Usual cryogenic equipment made it possible to attain temperatures between 0.9°K and 4.2°K. Temperatures were determined from the vapor pressure of the liquid helium bath and from a carbon resistance thermometer calibrated against the bath.

Both H<sub>2</sub> and D<sub>2</sub> gas were obtained from cylinders. Water vapor was removed by liquid air traps in the line. Oxygen in the H<sub>2</sub> was removed by a Deoxo unit. The equipment and procedure used to produce high ortho H<sub>2</sub> and para D<sub>2</sub> concentrations were essentially those described in reference 14 with only minor changes. With a one stage enriching unit, we could produce up to 2 liters STP of 85.5% ortho H<sub>2</sub> or smaller amounts of higher concentration. The highest concentration ortho H<sub>2</sub> achieved was 91% ortho. A single run with D<sub>2</sub> produced an estimated 55% para D<sub>2</sub>.

In order to measure the hydrogen and deuterium ortho/para ratios we used the Pirani bridge of Grilly<sup>16</sup> with small changes, the most important of which was the use of a bridge current of 0.65 amp for greater sensitivity. Our bridge was calibrated with H<sub>2</sub> of 75%, 62.5%, 50%, and 0% ortho. The calibration of Grilly when normalized to one of our data points, fit the

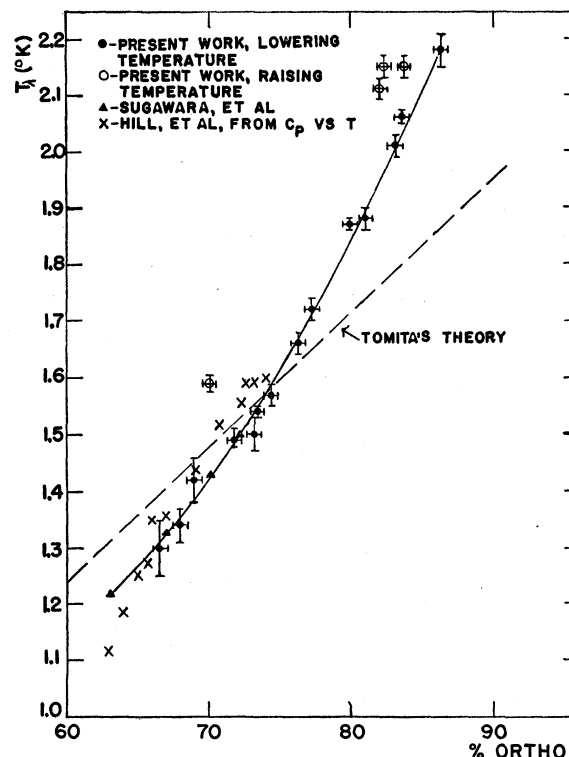


FIG. 1.  $T_\lambda$  versus concentration for solid hydrogen as determined by various workers. The points marked  $\circ$  taken on warming up are the temperatures of disappearance of the side peaks, while those marked  $\bullet$  were found with decreasing temperatures and represent the first appearance of the side peaks. The hysteresis is about 0.15°K. The dashed line is the Bethe-Peierls type theory of Tomita.

others to better than 1%. We found that a curve of the form

$$d = K(75 - c)/(\Delta - c) \quad (1)$$

fit our data and that of Grilly to better than 1%. In this equation  $d$  is the bridge unbalance in  $\mu\text{a}$ ,  $c$  is the ortho concentration in percent, and  $K$  and  $\Delta$  are constants. For 0% ortho  $d$  was  $+43.7 \mu\text{a}$  in our case.

Using this equation we could then calculate  $c$  for ortho concentrations greater than normal. For 85% ortho,  $d = -8 \mu\text{a}$ . We conservatively estimate that we could determine the ortho concentration of a given sample of hydrogen to  $\pm 0.5\%$ . Our calibration for D<sub>2</sub> was not so accurate, perhaps no better than  $\pm 5\%$ .

During an experimental run, hydrogen (or deuterium) was condensed in the rf sample chamber by cooling slowly until the gas condensed and then solidified. Since a single H<sub>2</sub> run lasted as much as 12 hours, during which time a conversion of as much as 14% would take place, it was necessary to know the ortho concentration as a function of time. This was easily accomplished by measuring the initial and final concentrations and determining intermediate values from the well-known

<sup>12</sup> F. Reif, thesis, Harvard University, 1953 (unpublished).

<sup>13</sup> T. Moriya and K. Motizuki, Progr. Theoret. Phys. (Kyoto) **18**, 183 (1957).

<sup>14</sup> Cunningham, Chapin, and Johnston, J. Am. Chem. Soc. **80**, 2382 (1958).

<sup>15</sup> G. D. Watkins, thesis, Harvard University, 1952 (unpublished).

<sup>16</sup> E. R. Grilly, Rev. Sci. Instr. **24**, 72 (1952).

relation<sup>17</sup>

$$dc/dt = -kc^2. \quad (2)$$

Our conversion rate during a given run was nearly constant at about 1% per hour. Values of  $k$  for three runs were  $2.88 \times 10^{-6}$ ,  $3.08 \times 10^{-6}$ , and  $3.07 \times 10^{-6}$  all in units of (percent-min)<sup>-1</sup>. These values compare well with the result of  $2.92 \times 10^{-6}$  found by Cremer and Polanyi<sup>17</sup> and the theoretical value of  $3.24 \times 10^{-6}$  of Motizuki and Nagamiya.<sup>18</sup> As many as six or seven data points were taken during a single run. By knowing the concentration as a function of time, we then knew the concentration for each data point to within  $\pm 0.5\%$ .

During a hydrogen run two quantities were of interest to us: the temperature of appearance of the side peaks upon cooling down and the temperature of their disappearance upon warming up. The procedure in each case was to cool or warm a few hundredths of a degree every few minutes until the transition was observed to take place on the scope. Temperatures were held constant at each point for as much as several minutes to produce thermal equilibrium. Side peaks could be ascertained in this manner when their amplitude was less than 1/100 of the total central peak height. Measuring the ratio of the side peak height to that of the central peak as a function of  $T$  and extrapolation to zero offered a check on this method in some cases. Errors in determining lower transition temperatures were larger than those for higher  $T$  due to the fact that the side peak amplitude stayed small over a wider range of temperature. The above procedure was used to take from three to six acceptable cool-down transition points during each of our three successful H<sub>2</sub> runs and a total of four valid warm-up points.

In the case of D<sub>2</sub> a search was made for side peaks down to lowest temperatures for the two concentrations. Also crude determinations of  $T_1$  were made by partially saturating the signal and watching it grow upon reduction of the saturating field.

TABLE I.  $T_\lambda$  of solid H<sub>2</sub>, as determined by appearance of side peaks as temperature is lowered.

$c$ (% Ortho)	$T_\lambda$ (°K)
86.3 $\pm$ 0.5	2.18 $\pm$ 0.03
83.2	2.01 $\pm$ 0.02
81.1	1.88 $\pm$ 0.02
83.6	2.06 $\pm$ 0.01
80.0	1.87 $\pm$ 0.01
77.3	1.72 $\pm$ 0.02
76.3	1.66 $\pm$ 0.02
74.4	1.57 $\pm$ 0.02
73.2	1.50 $\pm$ 0.03
73.4	1.54 $\pm$ 0.01
71.8	1.49 $\pm$ 0.02
69.0	1.42 $\pm$ 0.04
68.0	1.34 $\pm$ 0.03
66.6	1.30 $\pm$ 0.05

<sup>17</sup> E. Cremer and M. Polanyi, *Z. physik Chem.* **B21**, 459 (1933).

<sup>18</sup> K. Motizuki and T. Nagamiya, *J. Phys. Soc. (Japan)* **11**, 93 (1956).

## RESULTS

### H<sub>2</sub>

Our results for  $T_\lambda$ , the temperature of appearance of side peaks upon cooling as a function of ortho concentration,  $c$ , are given in Table I. The temperature of disappearance of the side peaks upon warming are given in Table II.

Our data, as well as those of Hill and Ricketson,<sup>5</sup> Hill, Ricketson, and Simon,<sup>6</sup> and Sugawara *et al.*<sup>10</sup> are plotted in Fig. 1. It can be seen that our NMR results join smoothly to those of Sugawara. However, our large error at the low concentrations does not eliminate the possibility that the  $T_\lambda$  curve determined from NMR may bend down toward the  $c$ -axis like the specific heat curve.

It can be seen from our data that a sizeable hysteresis effect, previously unreported, exists in the NMR transition temperature. The temperature of disappearance of the side peaks is some 0.15°K higher than the temperature of their appearance. The existence of such a hysteresis is not surprising considering the cooperative nature of this transition.

### D<sub>2</sub>

No side peaks were observed for solid D<sub>2</sub> with para concentrations of 33% and 55% at temperatures as low as 0.9°K. These experiments were of an exploratory nature, however, and should be repeated, preferably with higher para concentrations and using improved techniques such as observation of the signal by means of a phase sensitive detector and lock-in amplifier.

Rough  $T_1$  measurements were made for both concentrations. For normal D<sub>2</sub>,  $T_1$  was found to be  $7.6 \pm 3$  sec. This compares well with the theoretical value of 8 seconds given by Moriya and Motizuki.<sup>13</sup> Their theory takes account of the intramolecular interaction, modulated by the intermolecular interaction. For 55% para, we measured  $T_1$  to be  $3 \pm 1$  sec. The theory of reference 13 gives 5 sec. The discrepancy may possibly be due to a paramagnetic impurity such as O<sub>2</sub> which could have been introduced in the enrichment process and condensed into the sample chamber when it was cooled.

## DISCUSSION AND CONCLUSIONS

Tomita<sup>8</sup> treats the rotational transition as a cooperative phenomenon from two viewpoints. A treatment similar to the Bragg-Williams theory for alloys yields

TABLE II. Temperature of disappearance of side peaks as temperature is raised.

$c$ (% Ortho)	$T$ (°K)
82.1 $\pm$ 0.5	2.11 $\pm$ 0.02
83.8	2.15 $\pm$ 0.02
82.4	2.15 $\pm$ 0.02
70.0	1.59 $\pm$ 0.01

a transition temperature which is linearly dependent upon the ortho concentration,  $c$ . A second method corresponds to the Bethe-Peierls theory for alloys. In this treatment Tomita considers only interactions between ortho-ortho pairs and assumes a uniform distribution of ortho-molecules through the crystal and takes into account the average number  $z$  of ortho-molecules on the twelve nearest neighbor sites. Thus  $z=12c/100$  in this theory. The theory gives for the concentration dependence of the transition temperature

$$\frac{(T_\lambda)(c)}{(T_\lambda)(c=100)} = \frac{0.201}{0.5 \ln(z^2 + z - 0.5) - \ln(z - 2)}. \quad (3)$$

This curve is concave toward the  $c$  axis at concentrations below 40%. The theory predicts no transition for concentrations less than 16.7% ortho.

By normalizing the above theoretical equation to  $T_\lambda = 1.60^\circ\text{K}$  at  $c = 75\%$  ortho, we obtain the dashed curve in Fig. 1. We conclude that the discrepancy between the theory and our experimental values for high concentrations is marked. The discrepancy at  $c = 62\%$  is also sizeable.

Comparison of our data with that of Sugawara *et al.* is satisfactory, for the two sets of data join quite smoothly. A comparison with the specific heat results is difficult, for the exact relation between the temperature of the specific heat maximum and the temperature of the appearance of the side peaks is not known. It appears that at higher concentrations, the side peaks do not appear until the temperature is below that of the specific heat maximum.

Additional work at both high and low ortho-hydrogen concentrations would be valuable in determining the exact shape of the  $T_\lambda$  versus  $c$  curve. An extrapolation of our work to higher concentrations would give about  $3^\circ\text{K}$  for  $T_\lambda$  at 100% ortho-hydrogen and a similar smooth extrapolation to lower temperatures and concentrations predicts about  $1.1^\circ\text{K}$  for  $T_\lambda$  at 55% ortho-hydrogen. Since 55% para-deuterium showed no transition at  $0.9^\circ\text{K}$  we must consider the following possibilities.

(a) The extrapolation to lower concentrations may be in serious error.

(b) The deuterium curve of  $T_\lambda$  versus concentration of para-deuterium may be considerably different from our Fig. 1 for hydrogen.

(c) The NMR techniques used by us in this work are not sensitive enough to detect the weak side peak signals expected for deuterium.

We hope to continue our NMR work on solid D<sub>2</sub> using a 12-inch Varian Magnet, more sensitive detection methods, and higher concentrations of para-deuterium. The use of a He<sup>3</sup> cryostat will permit even lower temperatures to be used.

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