Crystal-Structure Changes in Hydrogen and Deuterium*

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The hexagonal-to-cubic-to-hexagonal structure changes in hydrogen and deuterium were studied by x-ray diffraction over many cycles of the transitions for orthohydrogen and paradeuterium concentrations up to 95%. Results of the x-ray study can be closely correlated with those of infrared, neutron-diffraction, heat-capacity, nuclear-magnetic-resonance, and volume-change measurements. The structure changes take place by a shifting of the hexagonal nets, which appears to be incomplete after the first transition and may cause intermediate close-packed structures to form. Repeated cylcing through the transition stabilizes the cubic structure, possibly because orientation of the $J=0$ molecules takes place.

I. INTRODUCTION

THE discovery of ortho and para modifications of hydrogen in the late 1920's presented scientists with intriguing material for experimental and theoretical study. During the intervening years, investigations of the influence of ortho and para states on the behavior of solid hydrogen and deuterium have produced puzzling results. There has been a renewed interest in the subject in the past few years and, although our understanding of the hydrogen problem is still incomplete, many of the experimental results can at present be correlated and hopefully will stimulate further theoretical treatment of the problem.

In 1930, Simon, Mendelssohn, and Ruhemann[1] found that the heat capacity of ortho-rich hydrogen, after following the Debye curve down to 11°K, anomalously rose with decreasing temperature down to 3°K. Pauling[2] and Simon[3] discussed such an anomaly in terms of hindrance to rotation of the orthomolecules. Much later Hill and Ricketson[4] found that for mixtures of 66 and 74% orthohydrogen the rise in heat capacity upon cooling climaxed in a sharp maximum of the λ type around 1.5°K. They attributed the entire anomalous behavior to ordering of the rotational state of orthohydrogen which in its lowest level has $J=1$ unit of angular momentum. For samples with orthohydrogen concentration less than ∼60%, no spike in the heat-capacity curve down to 0.2°K was observed.[5]

Nuclear-magnetic-resonance (NMR) studies also disclosed anomalies in crystals of high orthohydrogen concentration. In 1949 Hatton and Rollin[6] observed in normal hydrogen below 11°K a rapid increase in resonant linewidth. In the neighborhood of 1.5°K, the line

split into two peaks. Reif and Purcell[7] found a hysteresis effect such that the temperature at which the side peaks appeared on cooling was considerably lower than that at which they disappeared on warming. Smith and Housley[8] studied the NMR anomaly over a wide range of orthohydrogen concentrations and their results showed that the anomaly occurs at temperatures near the λ transition in heat capacity.[4,5]

A similar lambda transition[9] and NMR anomaly[10] have been observed in paradeuterium, which is the form of that isotope for which the lowest rotational level is $J=1$.

The cause of the strange behavior of both isotopes has received much attention from experimentalists[4-15] and theoreticians.[16-23] It has commonly been supposed that what is seen is a cooperative orientation of the molecules resulting mainly from an electric quadrupole-quadrupole interaction. Until recently theoretical treatments of this and other models have been handicapped by a lack of knowledge and some confusion concerning the crystal structures of the hydrogen isotopes.

In 1930 Keesom, De Smedt, and Mooy[24] determined the structure of parahydrogen to be close-packed hexagonal from x-ray measurements at liquid-helium temperature. Sometime later a body-centered tetragonal structure was proposed but was later withdrawn. Recently it was shown by x-ray photographs at Los

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Alamos[25,26] that hydrogen and deuterium first crystallize in the hexagonal close-packed form regardless of the ortho-para ratio. However, solids containing about 70% of the $J=1$ component were found to change their structure to cubic closest packing of molecules in the neighborhood of 1.5°K. The crystal-structure change has been confirmed by other diffraction studies using x rays,[27] electrons,[28] and neutrons.[29]

The H₂ molecule is a poor scatterer of x rays and consequently only a few reflections can be recorded. While these few diffraction peaks are sufficient to locate the center of gravity of the molecules, they are not sufficient to locate the atoms. In the final analysis it is the location of the atoms which determines the structure. It is understood that the fcc and hcp structures that are reported for H₂ and D₂ are those the isotopes would have if the molecules were spherically symmetric.

Neutrons, however, are scattered fairly well by deuterium. The neutron-diffraction study[29] made on deuterium showed evidence of weak diffraction peaks in the cubic phase which could be indexed as the {210} and {211} reflections from a cell more complex than cubic closest packing. Such reflections would be expected if the D₂ molecules were oriented along the body diagonals of a cubic structure in space group $Pa3$. Positional ordering of atoms in hexagonal deuterium however has not been observed.[30] As in the case of x rays, the diffraction of neutrons by H₂ is so poor that the atoms have not been located on lattice sites. One can only infer from the deuterium results that cubic hydrogen may also take on the $Pa3$ space group.

The present research was undertaken specifically to determine the crystal transition temperature as a function of the ortho-para ratio for both hydrogen isotopes and hopefully to gain an understanding of the way in which the transition takes place. Preliminary data for H₂ have already been reported.[31]

II. EXPERIMENTAL

A. General Technique

Previous x-ray diffraction photographs had been made[25,26] of hexagonal and cubic specimens of H₂ and D₂ contained in a Be cell. For both crystal forms the photographs showed a series of spots indicating that

the hydrogen isotopes solidified in a mass of crystallites. As reported by others,[27,28] there was a noticeable preference for the orientation of the hexagonal c axis to be approximately perpendicular to the cold cell wall. Both H₂ and D₂ gave strong {100}, {002}, and {101} reflections from hexagonal crystals and strong {111} and {200} reflections from cubic crystals. Values of the cell constants and planar spacings have been reported[25-29] at liquid-He temperatures.

It seemed feasible to observe the crystal-structure transition from hexagonal to cubic to hexagonal by measuring with a counter the intensity of an x-ray reflection, characteristic of either the hexagonal or cubic lattice, which emanated from a single crystallite of H₂ or D₂. In 1966 the method was demonstrated[31] for H₂ when the transition was studied by observing the hexagonal {101} and cubic {200} reflections.

In general, these strong reflections were used in the present work although on one occasion the transition in D₂ was measured by means of the hexagonal {100} reflection. Supplementary information was obtained by observing the strong {002} hexagonal reflection which transformed to the {111} cubic reflection with no apparent change of intensity. However, in one experiment the transition was observed through a unique {111} cubic reflection which did not transform to the {002} hexagonal reflection.

B. Apparatus

A Picker model x-ray diffractometer with a Geiger or scintillation counter was used to make the measurements. Copper radiation was focused on the specimen cell through a collimator which gave a beam that was large compared to the size of the crystallites in the cell. The reflected beam entered the counter through another collimator, receiving slit, and Ni foil to remove most of the Cu $K\beta$ radiation. The output from the counter went to a pulse-height analyzer, scaling circuit, and rate meter with a time constant typically 3 sec. The signal was displayed on a chart recorder running at a speed of $\frac{1}{2}$ in./min.

The cryostat was positioned in the diffractometer by a mounting table which could be translated in two horizontal directions, 90° to each other, and which could be raised and lowered relative to the x-ray beam. Coupled gear drives in the diffractometer allowed the counter to scan angles of 2θ horizontally and permitted the cryostat to rotate through an independent angle of ω. However, the Dewar design was such that changes in ω were limited to a total angle of 2θ, and only reflections lying close to the horizontal plane entered the counter.

A schematic diagram of the cryostat is shown in Fig. 1. Liquid N₂ in an upper container cooled a thermal radiation shield which surrounded the apparatus. The lower pot contained liquid He which filled a tubular extension of the Dewar and cooled the bottom end of

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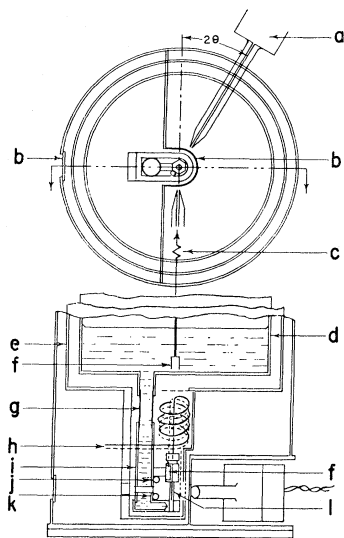
FIG. 1. Cryostat and x-ray cell showing top and sectional views: (a) counter; (b) Be window; (c) x-ray beam; (d) liquid He pot; (e) liquid N_2 shield; (f) vapor-pressure bulb; (g) thin-walled stainless steel; (h) fill lines; (i) Dewar extension; (j) cell heater; (k) carbon thermometer; (l) Be, x-ray cell.

the specimen cell and a surrounding thermal shield. The upper end of the cell was cooled by a copper bridge to the Dewar extension. In the path of the x-ray beam, thermal shields at liquid N_2 and He temperatures were made of 0.3-mil Al foil. To provide for cell temperatures up to 20°K, the Dewar extension was built with a thin-wall, stainless-steel section which could support a large temperature gradient when liquid He was flushed from the lower region with an electric heater. The cell heater was a 1-W, 10-Ω, metal film resistor attached to the Dewar extension. A 3-in.-He pumping line was joined to the top of the Dewar by means of a sliding O ring which permitted the cryostat to turn while maintaining a reduced vapor pressure. The x-ray beam entered the cryostat through a Be window large enough to allow the reflected beam to exit at nearly all angles of 2θ. A separate Be window in the vacuum jacket was used for transmitting the incident beam when the cryostat was rotated 90° for centering the specimen.

The specimen holder was machined from beryllium; it was cylindrical with an o.d. of 0.063 in., an i.d. of 0.020 in., and a useful length of about 0.25 in. The blind end of the cell was pressed into a mounting hole in the Dewar extension; the other end of the cell was sealed to the filling line with a nickel conical closure which was thermally anchored to the Dewar extension. The 0.010-in. stainless-steel filling capillary entered the experimental region at liquid N_2 temperature and was coiled inside the radiation shields, as shown in Fig. 1. Also coiled inside the shields was a larger capillary line connecting to a vapor-pressure bulb which was soldered to the cell closure nut and which could be filled with

either He^3 or He^4. A carbon resistance thermometer was mounted near the cell and a separate vapor-pressure bulb was immersed in the He^4 coolant bath near the bottom.

Vapor pressures were read with Wallace-Tiernan gauges which were calibrated periodically with a Texas Instrument quartz helix gauge. Temperatures were computed from the vapor pressures on the 1962 He^3 scale[32] and the 1958 He^4 scale.[33] In an auxiliary experiment where the specimen cell itself served as a vapor-pressure thermometer, it was demonstrated that the cell temperature was the mean between the bulb temperature in the bath and the bulb temperature at the capillary end of the cell. With He I as a coolant, the capillary end of the cell was warmer than the bath by 100 mdeg or more, but when He II formed in the bath the cell end suddenly cooled to within 20 mdeg of the bath. It is estimated that cell temperatures were known to ±10 mdeg except near the He I–He II transition.

The carbon resistance thermometer was calibrated *in situ* at He temperatures and at the boiling and freezing points of H_2 and D_2. It was read with an ohmmeter and was used to indicate cell temperatures between 4 and 20°K at times when the cell heater was on and liquid coolant was prevented from flowing into the Dewar extension. Because of gradients set up by the electric heater, temperatures in this range are subject to an error of $\sim5\%$.

Samples enriched in orthohydrogen and paradeuterium were prepared by preferential adsorption of the $J=1$ component of normal gas on aluminum oxide at liquid H_2 temperatures. A multistage system, similar to that of Cunningham, Chapin, and Johnston,[34] was used initially. However, increasing the number of adsorption columns beyond about four failed to give an enrichment of paradeuterium greater than 87% because the operation was so time consuming that back conversion to orthodeuterium proceeded to an appreciable extent. A simplified method was devised[35] employing a single column $\frac{1}{2}$ in. in diameter and 1 m long, packed with aluminum oxide pellets, which could be inserted through the gland nut of a standard hydrogen-transfer Dewar. Normal gas at 50-mm pressure flowed down the column over the cold absorbent and up through a small concentric tube in the center. After a monolayer of adsorbed gas had formed and reached equilibrium with flowing normal gas, the inlet was closed and the column was slowly withdrawn from the bath. As the upper section warmed, desorbed gas was forced to

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circulate down the tube and to exchange with the remaining adsorbed gas on the column, continually enriching it. A concentration of 99% paradeuterium or orthohydrogen in usable quantity appeared in the final fraction of desorbed gas. Samples of smaller concentrations of paradeuterium or orthohydrogen were prepared by diluting the rich material with normal gas in a volumetric apparatus. After mechanical mixing of the gas, an ortho-para analysis was made.

The ortho-para content of the H_2 and D_2 samples was determined before and after the x-ray experiments. The analyses were carried out in a thermal-conductivity apparatus operating at 75°K, similar to that described by Grilly.[36] At this temperature the heat-capacity ratio of ortho to para D_2 is at a maximum and the gas is quite sensitive to measurement. However, at 75°K the sensitivity for ortho-para H_2 analysis is only about $\frac{1}{4}$ that for D_2. The optimum temperature for analyzing H_2 is 140°K but attempts to thermostat the apparatus in this region were unsuccessful. In an effort to increase the H_2 sensitivity at 75°K, the bridge current was raised from 300 to 350 mA, but convection currents developed in the gas and caused slightly unstable readings which resulted in reduced accuracy in the H_2 analysis. The o-H_2 and p-D_2 concentrations were known to about 0.8 and 0.4%, respectively.

The D_2 used in the experiments came from the Union Carbide Company and contained only 0.6% HD and a smaller amount of H_2, almost all of which was removed during the para enrichment process. Pure H_2 gas was obtained as boiloff from the liquid phase; it was allowed to convert to normal hydrogen prior to further ortho enrichment in the adsorption apparatus.

C. Procedure

The Be cell at 4°K was centered in the x-ray beam by translating the cryostat table in two directions at right angles to each other while observing the x-ray intensity with the counter set at zero 2θ. A narrow beam and 2-mil receiving slit were used. Contrast of the cell edges was made sharp by filling the cell with solid xenon, which was quite opaque to the beam. It was possible to determine the usable length of the cell by raising and lowering the cryostat table while scanning with x rays through the empty cell.

Prepared samples of H_2 and D_2 were stored at pressures varying from 1 to 5 atm in clean Cu cylinders which were attached to the cell filling manifold and which contained enough gas to charge the cell many times. The cell was filled with hexagonal solid by slowly transferring liquid He into the Dewar and cooling very slowly through the liquefaction and solidification temperatures of H_2 or D_2 while regulating the cell heater to avoid plugging the fill line with solid. The final cell pressure varied from 0 to 1.5 atm.

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With the counter set at the proper 2θ angle to receive the hexagonal {101} reflection, the cryostat at 4°K was slowly rotated through a maximum angle of about 35 deg. This procedure was repeated for different elevations of the cryostat until a crystallite was located at the correct Bragg angle to cast a usable reflection into the counter. On occasion it was necessary to melt and refreeze the crystallites several times before a suitable reflection could be found. However, once located, the crystallite was quite stable and did not change position throughout the experiments. The same procedure was used to find other hexagonal reflections and to find cubic reflections below the transition temperature. Reflected intensities up to many hundred counts per second, above a background of about 5 counts per sec, were observed.

To initiate an experiment the He bath pressure was slowly lowered and the specimen was cooled through the transition temperature at a rate of 5 to 30 mdeg/ min. Readings of the vapor-pressure thermometers were recorded on the chart along with the intensity of the hexagonal {101} reflection. Following the disappearance of the reflection at the transition, the bath was slowly warmed with an immersed electric heater until the reflection reappeared. Thermal cycling was repeated until the reflection became too weak to observe or, in the case of orthohydrogen which converted steadily to parahydrogen, until the transition temperature had shifted below the limit of the cryostat, about 1.2°K.

Similar cycles were made while observing the cubic {200} reflection from a different crystallite, and it was often possible to alternate between observations of the hexagonal and cubic reflections of the two crystallites during cycling. After a series of cycles through the transition, the same crystallites could be annealed near the melting point to initiate a fresh series of measurements. Having predetermined the location of a cubic spot, one could then observe, by means of the cubic reflection, the transition accompanying the first cooldown. Occasionally the {100} and {002} reflections from an hexagonal crystal and the {111} reflection from a cubic crystal were studied during the course of the same thermal cycle.

At the conclusion of an experiment, the filling line was evacuated and the sample was vaporized, collected, and analyzed for ortho-para content.

The scattered x-ray intensities were computed on a percentage basis of the maximum intensity observed in each experiment and a plot of the percent maximum intensity versus cell temperature was made. The temperature at which the scattered intensity reached half its full value for a given cycle was taken as the transition temperature.
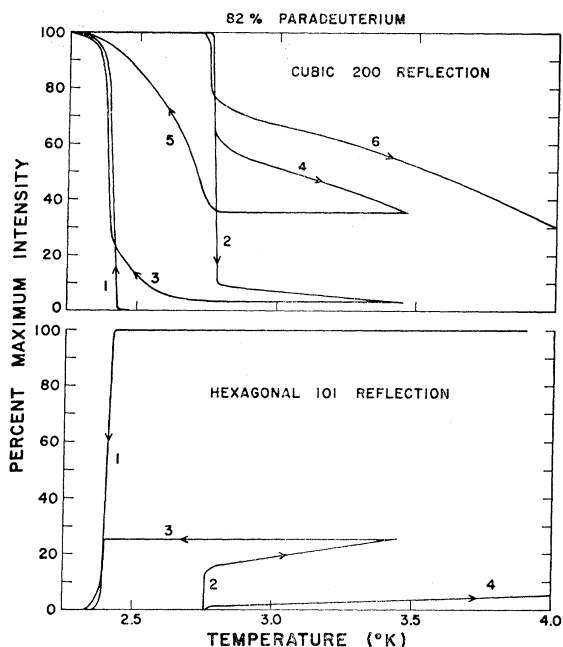
FIG. 2. Intensity of x-ray reflection as a function of temperature for 82% paradeuterium. Upper graph, {200} reflection from cubic crystallite; lower graph, {101} reflection from hexagonal crystallite. Directions of transitions and path numbers are indicated by arrows and numerals.

III. RESULTS

A. Self-Conversion

In solid hydrogen the self-conversion of ortho- to parahydrogen proceeds fairly rapidly according to the rate expression

$$-d[o-H_2]/dt = k[o-H_2]^2, \qquad (1)$$

where $[o-H_2]$ is the mole fraction of orthohydrogen and k is determined to be 0.019 ± 0.001 h^{-1} from the present experiments.[31] The self-conversion rate of para- to orthodeuterium in the solid is about an order of magnitude slower than that for hydrogen and follows the expression

$$-d[p-D_2]/dt = k_1[p-D_2]^2 + k_2[p-D_2][o-D_2], \qquad (2)$$

where the constants k_1 and k_2 have been given[37] as 0.00127 and 0.00178 h^{-1}, respectively.

Because of the relatively fast para conversion in solid H_2, each successive cycle through the crystal transition was made at a noticeably lower ortho concentration. While this facilitated measurements of the transition temperature as a function of orthohydrogen concentration, it was difficult to separate effects that were due to cycling from those that were caused by the varying ortho concentration. Deuterium, on the other hand, could be cycled through the transition many times at essentially constant para concentration.

[37] K. Motizuki, J. Phys. Soc. Japan **17**, 1192 (1962).

It was, however, expedient to make up new mixtures in order to study the transition in D_2 at various para concentrations. For the sake of clarity the D_2 results on cycling are presented first.

B. Transition in Deuterium

More than 35 runs using various specimens of D_2 were made during which the structure change was observed about 200 times. For paradeuterium concentrations of 71, 82, and 95%, the transition was studied in detail by observing both cubic and hexagonal reflections through many thermal cycles. In Fig. 2 the experimental data are shown for 82% p-D_2. The x-ray intensities from cubic and hexagonal crystallites have been plotted versus a common temperature scale for comparison. To make the comparison quantitative, the intensity scale is such that 100% corresponds to maximum intensity of the cubic or hexagonal reflection. In the following discussion, the relative intensity will be treated simply as an index of the amount of hexagonal or cubic solid present.

1. First Cycle, Hexagonal to Cubic to Hexagonal

On first cooling freshly prepared solid D_2 of 82% para content along path 1 of Fig. 2, one observes that the hexagonal form disappears completely over a range of about 100 mdeg, almost all of the change taking place over a ΔT of 20 mdeg centered around a transition temperature $T_{h-c} = 2.41°K$. Cubic D_2 appears quantitatively during the structure change and apparently no intermediate crystal forms are involved. On warming the solid over path 2, one observes no change in x-ray intensity as the temperature is first raised above T_{h-c}. Then sharply over a 20-mdeg range centered around $T_{c-h} = 2.77°K$, approximately 90% of the cubic form disappears while only 15% of the hexagonal reappears, leaving $\sim$75% of the solid material that must be assumed to exist in intermediate crystal forms. Further warming to 3.5°K destroys another 7% of the cubic form which reappears semi-quantitatively as hexagonal.

2. Second Cycle

With decreasing temperature (path 3 in Fig. 2) the cubic content remains constant at $\sim$3% then begins to increase slowly at T_{c-h} while the percentage of hexagonal holds at $\sim$25%. As T_{h-c} is approached, the cubic percentage grows at an ever increasing rate. Since the hexagonal content remains constant during this portion of the cool-down, it is apparent that cubic D_2 is being generated from the intermediate forms. At $T_{h-c}\cong 2.4°K$ the hexagonal D_2 suddenly transforms quantitatively to the cubic form, producing 100% cubic and 0% hexagonal D_2. On warming along path 4, no change occurs in the solid up to T_{c-h} where again there is a sharp transformation, but during this part of the

cycle only about 40% of the cubic disappears, $\sim$1% of the hexagonal reappears, and 39% of the total material is in forms other than hexagonal or cubic. Further warming to 3.5°K destroys more cubic, only a small fraction of which reappears as hexagonal.

3. Third Cycle

As the temperature decreases along path 5, the cubic fraction holds at $\sim$35% down to T_{c-h} where more cubic reforms. During this cycle the rate of cubic growth is quite rapid just below T_{c-h} and decreases as T_{h-c} is approached. Although not shown in Fig. 2, at T_{h-c} the existing small percentage of hexagonal form disappears, presumably generating finally 100% cubic D_2. On warming back to T_{c-h}, path 6, the behavior is similar to that during the second cycle except that $\sim$25% of the cubic disappears sharply and no detectable amount of hexagonal reappears.

4. Additional Cycles

On additional cycling the behavior is similar to that of the third cycle except that more and more cubic material is retained at T_{c-h}. As before, all of the cubic form is regenerated on cooling between T_{c-h} and T_{h-c}.

5. Annealing Temperature

The hexagonal form, which is completely destroyed by successive cycling through T_{h-c} and T_{c-h}, can be regenerated fairly rapidly at temperatures well above 4°K. At about 9°K the hexagonal solid begins to reappear; at 12°K most of the original hexagonal x-ray intensity is recovered. If the sample is not raised to this annealing temperature but is held in the neighborhood of 4°K, the growth of the hexagonal form at the expense of the cubic is very slow. Only a small increase of hexagonal deuterium was observed during a 12-h hold at 4°K.

6. Effect of Para Concentration

Experiments similar to those described above were carried out on 71 and 95% paradeuterium during which both cubic and hexagonal reflections were observed. The over-all behavior was much like that shown in Fig. 2 for 82% p-D_2. However, several effects could be attributed to the different para concentrations.

For the 71% mixture the transition temperatures T_{h-c} and T_{c-h} were shifted down to $\sim$1.8 and 2.2°K, respectively. The structure changes were spread over a wider ΔT and were therefore not as sharp. Also there was a more complete recovery of hexagonal and disappearance of cubic structure at 4°K than for the 82% para mixture.

The transition temperatures T_{h-c} and T_{c-h} for 95% paradeuterium appeared at 3.5 and 3.7°K, respectively, and were quite sharp. At the end of the first
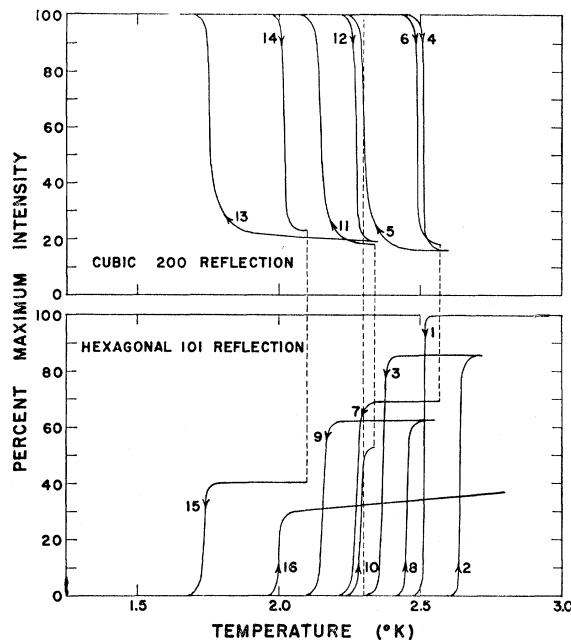

FIG. 3. Intensity of x-ray reflection as a function of temperature for enriched orthohydrogen. Upper graph, {200} reflection from cubic crystallite; lower graph, {101} reflection from hexagonal crystallite. Directions of transitions and path numbers are indicated by arrows and numerals. Orthohydrogen concentration varies from 95% (path 1) to 81% (path 16).

cycle from hexagonal to cubic to hexagonal, there remained about 40% cubic structure at 4°K compared to only a few percent cubic in the case of 82% paradeuterium. In part a larger amount of cubic structure is retained at 4°K because this temperature is not far from $T_{c-h}=3.7$°K.

C. Transition in Hydrogen

Thirty runs were made on H_2 samples of various ortho concentrations and the transition was observed about 200 times. For hydrogen the study of the effect of cycling on the transition is complicated by the relatively rapid rate of ortho-para conversion which constantly shifts the transition to lower and lower temperatures. In Fig. 3 is illustrated the effect of cycling on the transition in hydrogen. During the experiment the ortho concentration changed from 95 to 81%. Along paths 1 to 3, 7 to 10, 15, and 16 the hexagonal {101} reflection was observed. Along the other paths the {200} cubic reflection from a different crystallite was observed.

It can be seen that for hydrogen the upper and lower transitions are more clearly defined than they are for deuterium. Also for hydrogen, relatively more of the hexagonal structure is recovered at the upper transition temperature. After three cycles almost no hexagonal deuterium is recovered whereas for hydrogen about 70% of the original hexagonal reappears. In the cooldown leg the slight increase in intensity of the cubic
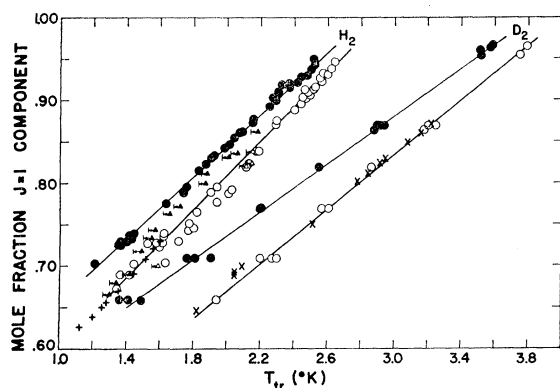
FIG. 4. Transition temperature as a function of orthohydrogen and paradeuterium concentration. Closed circle, T_{h-c} transition hexagonal to cubic, temperature falling; open circle, T_{c-h} transition cubic to hexagonal, temperature rising; plus and cross, λ spike in heat capacity (temperature rising) for H_2 (Ref. 4) and D_2 (Ref. 8), respectively; closed triangle and open triangle, anomaly in NMR Ref. 7 temperature falling and rising, respectively. Arrows shift points to center of transition.

reflection at T_{c-h} indicates the presence of a small amount of intermediate structures.

For both isotopes the hexagonal-to-cubic phase change goes to completion at T_{h-c}; for neither isotope does the cubic-to-hexagonal structure change go to completion at T_{c-h}, although for hydrogen the change is relatively greater. For both isotopes thermal cycling causes smaller amounts of the hexagonal structure to be recovered at T_{c-h}. Indeed after only a few cycles for deuterium no hexagonal structure reappears. This behavior on cycling was more pronounced when the concentration of orthohydrogen and paradeuterium was high. After eight complete cycles through the transition for hydrogen, the recovered hexagonal intensity was about $\frac{1}{3}$ that at the beginning. However raising the temperature to 4°K brought the intensity back to $\frac{1}{2}$ and a further temperature increase to ~ 12°K restored the original intensity.

In Fig. 4 are shown the cubic-to-hexagonal and hexagonal-to-cubic transition temperatures versus the concentration of orthohydrogen and paradeuterium.

IV. DISCUSSION

A. Comparison with Previous Measurements

1. Transition Temperatures

The first evidence of a structure change in normal hydrogen came from the infrared measurements of Clouter and Gush.[12] Their evaluations of the upper and lower transition temperatures for 72–75% orthohydrogen concentrations agree within 20 mdeg with the curves of Fig. 4.

For deuterium a determination of the hexagonal-to-cubic transition temperature was made by neutron diffraction[29] on a sample of 83% paradeuterium and produced a value of T_{h-c} which lies about 50 mdeg

above the curve of Fig. 4. On the warming cycle the neutron data were not taken in sufficient detail to show the existence of T_{c-h}.

The recent measurements at Duke University[15] of the volume change which accompanies the transition in $< 75\%$ orthohydrogen gave transition temperatures during cooling and warming which agree within about 50 mdeg with the hydrogen curves of Fig. 4.

Shown also in Fig. 4 are temperatures at which anomalous peaks have been observed in the heat capacity of samples rich in orthohydrogen[5] and paradeuterium.[9] The heat-capacity data were taken with increasing temperature and therefore should be compared with the curves representing T_{c-h} for H_2 and D_2. The peaks occur at the cubic-to-hexagonal transition temperature within an average deviation of ± 25 mdeg.

The temperatures at which side peaks in the NMR curves for H_2 first begin to develop on cooling and finally disappear on warming[8] have been plotted in Fig. 4. These temperatures apparently are those at which the H_2 crystallite first starts to change from hexagonal to cubic on cooling and finally completes the transition from cubic to hexagonal on warming. When the NMR points are shifted downward in temperature by one-half the ΔT over which the crystal transition takes place, as indicated by the arrows, the agreement with T_{h-c} and T_{c-h} is quite satisfactory.

2. Character of Transition Curves

Through the first cycle, the transition curves observed in the infrared, x-ray-diffraction, neutron-diffraction, and volume-change studies all bear a striking resemblance to each other and to the entropy curve deduced from the heat-capacity work. The transitions all occur over a similar ΔT centered around a comparable temperature for a given orthohydrogen or paradeuterium concentration. The nature of the curves showing the growth of the NMR side peaks has not been reported.

B. Correlation of Data

It is evident from the general agreement of the various transition temperatures and the similar shapes of the transition curves that the structure change, the volume change, and the heat-capacity and NMR anomalies are all related.

The entropy change associated with the sharp heat-capacity peak in H_2 can be accounte dfor by the volume change and pressure dependence of the transition temperature, as demonstrated earlier[15,31] through the Clapeyron equation. However, the volume change decreases rapidly on cycling through the hydrogen transition and apparently disappears after several cycles.[15] Similarly, the heat-capacity spike is destroyed by cycling.[11] In contrast, the H_2 structure change, observed by x rays, shows only a partial decrease in effect through many cycles of the transition. It must

be concluded that, upon cycling, the crystal transition is accompanied by smaller and smaller volume and thermal effects. Both of these effects are reported to be restored to their original magnitude by warming the solid hydrogen to temperatures near the melting point. The x-ray studies show that a similar warming will regenerate the fraction of hexagonal hydrogen that is lost also through cycling.

The decrease in the volume change and thermal effect on cycling can be accounted for only partly by the fact that progressively smaller amounts of material transform from the cubic state, once it has been formed. Furthermore, the transition from one close-packed structure to another is expected to produce only a slight change in density and thermal properties. The large initial changes observed for H_2 can be explained in terms of the molecules being randomly oriented in the original hexagonal lattice and being fairly completely oriented in the cubic lattice. In the case of cubic D_2 it has been reported[29] that the molecules are aligned along the body diagonals of a cube giving space group $Pa3$. It may be that transitions from the cubic to the hexagonal phase produce hexagonal structures in which the molecules remain somewhat oriented and in which the orientation becomes more complete after repeated cycling through the cubic phase. The retained orientation would then be fairly stable until the crystal is warmed to the vicinity of 12°K where the molecules again become disoriented.

The multiple peaks that were observed in the heat-capacity data[11] on warming can not at present be correlated with the x-ray measurements, although they may result from positional reordering of the molecules or from intermediate close-packed structures. There is a need for more detailed heat-capacity measurements taken both with increasing and decreasing temperatures over many cycles of the transition for H_2 and D_2.

C. Nature of the Structure Change

Hexagonal and cubic closest packing are the most efficient and symmetric forms of packing hard spheres. The hexagonal and cubic unit cells are formed by the sequential stacking of two and three hexagonal nets, respectively. There are other ordered stackings of more layers with equally efficient packing, but they produce larger unit cells with fewer symmetry elements. Lastly, spheres can be packed by stacking hexagonal nets in a completely random fashion. Such a method gives a most unsymmetric but still an equally dense structure. Changing the stacking order will leave some diffraction reflections unchanged, will modify the intensity of others, and will cause still others to appear or disappear.

The structure change from hexagonal to cubic closest packing can be understood to take place by a simple sliding of the hexagonal nets relative to each other. The present observation that little or no in-

tensity change took place when the hexagonal {002} reflection became the cubic {111} reflection is in accord with the above view. These two reflections originate from the hexagonal nets themselves and the experimental evidence shows that the spacing between nets remains essentially constant through the transition.

After the initial structure change from hexagonal to cubic to hexagonal, the cubic and hexagonal fractions no longer account for 100% of the material and this fact makes it attractive to postulate the existence of intermediate close-packed structures. Observations of the growth of the cubic {200} reflection on cooling between T_{c-h} and T_{h-c} tend to indicate that the intermediate forms return gradually to the cubic structure. Because there is no sharp transition temperature there may be a series of intermediates that vary in hexagonal- or cubic-like qualities. The first intermediates that form appear to be of an hexagonal nature since the bulk of them return to the cubic structure near T_{h-c} (see path 3 of Fig. 2). After several cycles the intermediates transform to the cubic structure almost reversibly on cooling at T_{c-h} and would seem to possess cubiclike qualities (see path 5 of Fig. 2).

Several of the more common close-packed structures are listed in Table I, where the indices of the strong reflections, the planar spacings, and the relative intensities are given for deuterium. The present x-ray apparatus was not suitable for identifying the possible intermediate structures. Future work with a cylindrical x-ray camera and oscillating cell may result in a clearer understanding of the problem. Attempts to grow large single crystals of orthohydrogen and paradeuterium for study by the Laue photographic technique have so far been unsuccessful.

It has been explained that the rotational ordering of the $J=1$ molecules is an increasing and cooperative process. Probably after a number of molecules are ordered, symmetry and energy considerations favor the cubic structure. Thereafter the crystalline field of the cubic lattice reacts with the $J=1$ molecules to promote spatial orientation. Thus a cooperative second-order transition can through mutual processes bring about a first-order phase change.

At the cubic transformation it is possible that, along with the $J=1$ molecules, some of the $J=0$ molecules for steric or better-packing reasons will also attain a fixed orientation. The orientation of the molecules may occur during the transition or it may occur with time after the cubic phase has formed. As mentioned, the x-ray data have given no information on the degree of orientation of the molecules. One can speculate that because of local temperature gradients or stresses there may be regions where the $J=0$ molecules become oriented sooner than those in other parts of the crystal. All of the aligned molecules would help stabilize the cubic structure. After warming to the upper transition temperature T_{c-h}, those domains con-

TABLE I. Planar spacings[a] and relative intensities[b] for various close-packed cells of deuterium.[c]

h hexagonal 2 molecules			hc double hexagonal 4 molecules			hch 9 molecules			hcc double cubic 6 molecules			c cubic 4 molecules		
hkl	d	I	hkl	d	I	hkl	d	I	hkl	d	I	hkl	d	I
100	3.12	7.5	100	3.12	1.4									
						101	3.10	6.1						
									101	3.07	2.5			
						102	3.03	2.4						
			101	3.01	5.3									
002	2.94	26.3	004	2.94	26.3	009	2.94	26.3	006	2.94	26.3	111	2.94	26.3
									102	2.94	6.7			
						104	2.82	18.2						
101	2.75	17.8	102	2.75	13.1				103	2.75	8.0			
						105	2.69	16.2						
									104	2.55	14.2	200	2.55	27.2
						107	2.46	1.5						
			103	2.44	3.3									
									105	2.34	1.3			
						108	2.27	3.0						
102	2.14	3.0	104	2.14	0.8									
						1010	2.02	2.1						
			105	1.88	1.5									
110	1.80	6.8	110	1.80	6.8	110	1.80	6.8	110	1.80	6.8	220	1.80	13.4

[a] Planar spacings, d, are given in angstroms.
[b] Intensities I have not been corrected for temperature and polarization effects.
[c] Molecules of D_2 are assumed to be spherical.

taining few oriented molecules would return to the hexagonal structure. In other domains where the molecules are better packed, the shifting of the hexagonal nets, by which the cubic structure changes to the hexagonal, would not be complete and an intermediate structure would result. Those domains containing many well oriented molecules would remain cubic at T_{c-h}.

Even in the absence of a phase change, one can expect the oriented molecules to retain their alignments for some time since energy is required to change them. Therefore the over-all effect of cycling between the two structures would be to increase the number of domains containing oriented molecules and thus increase the amount of cubic structure that is retained.

Thus far little has been said about the hysteresis in temperature that separates T_{h-c} and T_{c-h}. From the experimental data shown in Fig. 4 it appears that the hysteresis is greater for deuterium than it is for hydrogen and that the hysteresis for both isotopes is proportional to the concentration of $J=0$ species (parahydrogen or orthodeuterium). The possible orientation of $J=0$ molecules may confer stabilities on some of the structures which cause a hysteresis in the transition.

V. FUTURE WORK

The present results have suggested areas in which future experimental work on solid hydrogen and deuterium might prove fruitful. Neutron-diffraction measurements using the metallic sponge technique for preparing randomly oriented crystallites of D_2[29,30] may be capable of identifying the space groups which characterize the ordered hexagonal structure and intermediate close-packed cells that are indicated by the present x-ray study. Oscillation x-ray photographs of orthohydrogen and paradeuterium in various stages of the transition might give a clue to the intermediate structures. As mentioned earlier, detailed heat-capacity measurements both for increasing and decreasing temperatures through several cycles of the transition would be extremely interesting. Finally there is a need for additional NMR data on enriched paradeuterium. It is hoped that the present study will stimulate further theoretical work on the order-disorder transition in hydrogen and deuterium.