

THE STRUCTURE TRANSITION IN HYDROGEN BELOW 1 K<sup>†</sup>

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Résumé.- Les transitions de phases cfc à hcp et hcp à cfc dans les monocristaux d'hydrogène ont été étudiées en utilisant la diffraction des rayons x. La température de transition,  $T^*$ , est tracée comme fonction de la concentration d'orthohydrogène, X, dans la région  $0,13 \text{ K} < T < 1,5 \text{ K}$  et  $0,48 < X < 0,7$ .

Abstract.- The cfc to hcp and hcp to cfc phase transition in single crystals of hydrogen have been studied using x-ray diffraction techniques. The transition temperature,  $T^*$ , is mapped as a function of orthohydrogen concentration, X, in the region of  $0.13 \text{ K} < T < 1.5 \text{ K}$  and  $0.48 < X < 0.7$ .

Solid hydrogen is known to exist in different phases of crystal structure and molecular orientation. The transition between two phases is pressure temperature and orthohydrogen concentration dependent. Several experimental techniques have been used to study the transition temperatures,  $T^*$ , at zero pressure as a function of ortho concentration, X. It was found that the transition temperature and concentration dependence of the changes in the cw NMR line shape /1,2/, specific heat /3/,  $(dP/dT)_V$  /4/, and x-ray /5/ studies closely agreed. The x-ray work identified the crystal structure to be hexagonal close packed (hcp) for  $T > T^*$  and cubic face centred (cfc) for  $T < T^*$ . In addition the NMR line shape revealed the cfc structure to be associated with a rotationally ordered state while in the hcp structure the molecules were rotationally disordered.

With the exception of the  $(dP/dT)_V$  work these forementioned experiments were limited to  $X > 0.67$  for which  $T^* > 1 \text{ K}$ . The  $(dP/dT)_V$  results extended to  $T^* > 0.6 \text{ K}$  and  $X > 0.56$ . Recent NMR (cw /6,7/, pulsed /8/ and  $T_1$  /9/ measurements, utilizing dilution refrigerators, have studied the concentrations to values as low as  $X=0.1$  with a resulting  $T^*$  in the range of 0.05 to 0.2 K. Although the low temperature ( $T^* < 0.5 \text{ K}$ ) and low concentration ( $X < 0.55$ ) NMR results are not self-consistent, it has been believed that the

transition is similar to the high temperature results. Due to the close agreement between x-ray and NMR changes for  $X > 0.65$ , it has been implicitly assumed and explicitly stated that the low concentration ordered state was also cfc. It is the purpose of the present work to test this assumption.

The cfc to hcp and hcp to cfc transitions have been observed by watching the disappearance and reappearance, respectively, of the Cu K $\alpha$  (200) Bragg reflection from a single cfc hydrogen crystal. The intensity of the Bragg peak was monitored on a position sensitive detector as a function of time and temperature. The detector allows one to observe the peak position, shape, amplitude and integrated intensity simultaneously.

The samples were prepared from high purity H<sub>2</sub> gas. An initial ortho concentration of 0.75 was obtained by storing the gas in stainless steel cell filled with a catalyst, iron oxide, for three days at room temperature. An adequate volume was insured by pressurizing this cell to 10 MPa. At time equal to zero the storage cell was opened to the sample cell which was in the precooled cryostat at  $40 \text{ K} < T < 80 \text{ K}$ . The temperature of the cryostat was then lowered and liquid condensed into the sample cell. At some point the fill line would plug near the <sup>4</sup>He reservoir allowing the crystal to grow near zero pressure. As the temperature of the sample cell approached the solidification temperature of H<sub>2</sub>, 14 K, the

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appropriate temperature gradients and controllers were initialized which allowed for the growth of a single crystal from the liquid.

After solidification and modest annealing the temperature of the sample was lowered to  $T < T^*$ . A series of Laue pictures were then taken in the cfc phase. Once the crystal had been oriented, a 40 cm radius three circle diffractometer was aligned on the (200) Bragg peak.

Data were taken on six samples by raising and lowering the temperature through the transition. The temperature was stepped, in increments in the range 20 to 100 mK, in time intervals of 7 to 15 min. This allowed for the sample cell to come to thermal equilibrium with the germanium thermometers and two Bragg peaks at each temperature to be obtained. The transition temperature was defined as the temperature at which the integrated peak intensity was half the difference between maximum and minimum. The analysis of peak amplitude, raw integrated intensity and integrated intensities from curve fitted peaks yielded the same transition temperatures and times. The time was then converted to concentration using the well established conversion rate,  $dX/dt = -kX^2$ ,  $k = 0.019 \text{ hr}^{-1}$ . The results are shown in figure 1.

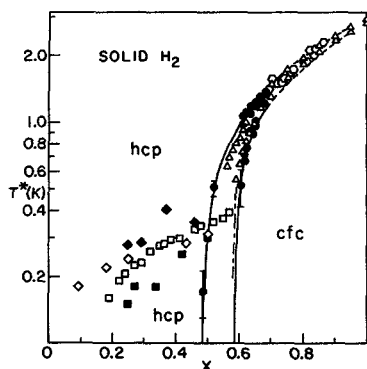


Fig. 1 :  $T^*$  versus concentration for solid  $H_2$ . ● -x-ray this work ; ---- x-ray Ref. /5/ ;  $\Delta$  - $(dP/dT)$  Ref. /4/ ;  $\circ$  -NMR(cw) Ref. /2/ ;  $\square$  -NMR(cw) Ref. /7/ ;  $\blacksquare$  -NMR(cw) Ref. /6/ ;  $\blacklozenge$  -NMR(pulsed) Ref. /8/ ;  $\diamond$  -NMR( $T_1$ ) Ref. /9/ ; - - - lower limit for hcp to cfc transition ; solid line is to guide the eye only. Upper curve is cfc to hcp transition and the lower curve is hcp to cfc transition.

The error bars are indicative of the uncertainty in thermometry and in temperature gradients between the sample and the thermometers. The hcp to cfc transition occurs at a lower temperature than the cfc to hcp transition. The dashed line represents the highest concentration-temperature path for which the specimen failed to reenter the cfc phase.

One can also cross the cfc to hcp phase transition by holding the temperature constant and changing the concentration as a function of time. A point at high temperature was taken in this manner and is indistinguishable from the rest of the data. The point at  $X=0.49$  was also taken in this manner. The thermometers were at  $T=0.13 \text{ K}$  with a little cooling power left in the dilution refrigerator. It is thought that the placement of the point on figure 1 at 0.17 K is an extreme. This point was taken twice, on two different sample, with the same results.

The present observations of a crystal structure change in solid hydrogen at low temperatures do not contradict previous analysis of NMR data. However, they do strengthen two findings from analysis of the NMR line shapes in the limit of  $T$  tending to zero as a function of concentration. First, it had been found /10/ that the zero point motion correction factor to the splitting in the peak derivative line shape was slightly different for  $X < 0.5$  than for  $X > 0.5$ . Second, it appears /7/ the long range rotational order found for  $X > 0.5$  is lost for  $X < 0.5$ . Neither of these results is surprising in view of the change in crystal structure and loss of inversion symmetry in going from the cfc to the hcp lattice.

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