ESRF	**Experiment title: Structural determination of Phase II and Phase III of solid hydrogen by angle dispersive single crystal x-ray diffraction.**	**Experiment number**: HS- 1825
Beamline: ID30	**Date of experiment**: **8/03/02 to 13/03/02**	**Date of report**: 20/08/05
Shifts: 18	**Local contact(s)**: Mohamed Mezouar	*Received at ESRF:*

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Report:

Experiments: The aim of this proposal was to determine the structure of Phase II and Phase III of solid H2 and solid D2. From spectroscopic measurements, it was shown that phase II and phase III are orientationally ordered. The ordering objects in phase II are angular momenta of rotating molecules, whereas in phase III the molecules order themselves. The transition to phase II is a quantum orientational ordering whereas the transition to phase III is a classical orientational ordering. In particular, the transition to phase II occurs with a strong isotopic shift in the transition pressure, respectively 28 GPa for D2, 69 GPa for HD and 110 GPa for H2. The transition to phase III occurs about 160 GPa in both H2 and D2. These phase transition takes place at low temperature, below 100K.

The data were obtained by single-crystal x-ray diffraction with a focused monochromatic beam (wavelength 0.3738 Å) and a MAR Image Plate detector. The x-ray beam was focused to its minimum spot size on ID 30, that is around 20 µm. But with a sample chamber hole of 30 µm, the rhenium gasket diffraction rings on the image plates were much more intense than the sample diffraction spot and consequently, that prohibits long accumulation times (longer than 10 s). That is the reason why, the data collection and solid H2 could not be done above 100 GPa. Hence, no data could be taken in the interesting pressure range for the stability of phase II and phase III of solid H2. The beam time was then devoted to the structural determination of phase II of solid D2, which is stable above 28 GPa. Then, large sample chamber (larger than 50 µm in diameter) could be used and then almost no parasitic diffraction signal of the gasket was observed.

Four different D_2 crystals were studied by X-ray diffraction: two of them were embedded in helium pressure transmitting medium. The effect of the pressure hydrostaticity on the structural changes could then be tested. In one run, the single crystal of D_2 in helium was cooled at a constant pressure of 63.4 GPa and the (100), (101) and (002) reflections were measured. As seen in figure 1, a small positive discontinuity in the

lattice parameter c ($\Delta c/c=3\times10^{-4}$) was observed at 70 K. A negative discontinuity in the parameter a ($\Delta a/a=-6\times10^{-4}$) was also observed at 70 K. This gives a transition point to phase II that is in excellent agreement with previous spectroscopic studies. We note that the orthorhombic structures with the polar angle of the molecule almost in the a–b plane should give a negative discontinuity in c of about 1, whereas a positive discontinuity is observed here. Two other runs have followed the evolution of reflections of the [100] and [101] class by going up in pressure at 25 K. One crystal had helium as pressure transmitting medium and the other did not. As seen in figure 1, no discontinuity of the 100 d-spacing could be detected within the accuracy of the measurement. From X-ray measurements, we find that the I–II transition does not affect the diffraction peaks of the h.c.p. lattice, except for a very small volume discontinuity. Yet a transition was observed in both cases at around 16 GPa, as determined from the appearance of a superstructural peak.

These x-ray data were not sufficient to solve the structure of phase II. X-rays are almost insensitive to individual positions of the H(D) atoms in the molecules and to orientational ordering. The present X-ray data were combined to neutron study to solve the structure of phase II. For the neutron study, the crystal was oriented by X-ray diffraction. Combining the two techniques, an incommensurate structure with local orientational order was disclosed. This has been recently published :

Neutron and X-ray diffraction study of the broken symmetry phase transition in solid deuterium. I. Goncharenko and P. Loubeyre. Nature 435, 1206 (2005).

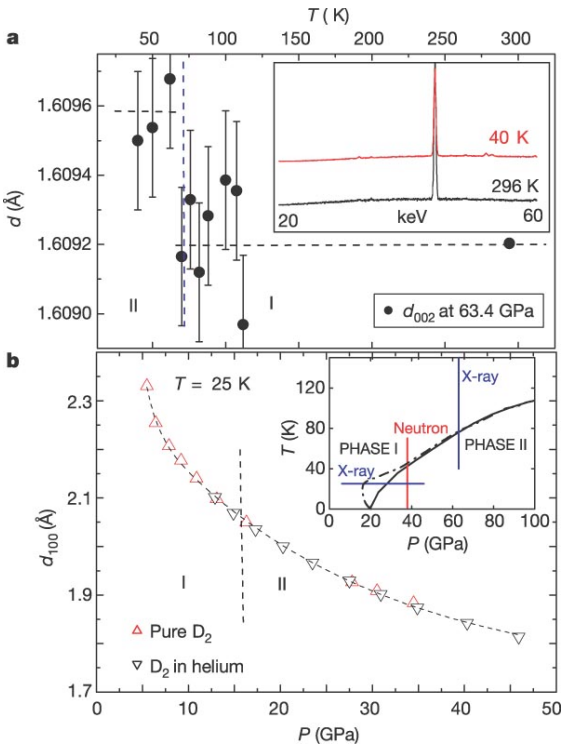

Figure 1 : **X-ray diffraction measurements at the I–II phase transition in solid D_2. a**, Evolution with temperature (T) of the d-spacing at 63.4 GPa. The inset shows the 002 peak measured in phase I at 296 K (black) and in phase II at 40 K (red). **b**, Evolution with pressure (P) of the d-spacing of the 100 reflections measured at 25 K. The black and red triangles indicate data from a single crystal of D_2 respectively with and without helium pressure transmitting medium. The inset shows the pressure–temperature domains of the X-ray (in blue) and neutron (in red) measurements in the phase diagram. The solid and dashed black lines show respectively the I–II boundary line as determined from spectroscopic measurements.

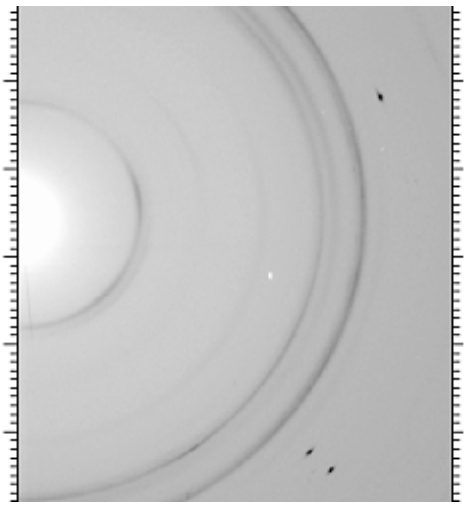

Figure 2 : Experimental evidence of a superstructure in phase II of D_2. The diffraction peaks are recorded on the Image Plate during an oscillation of the DAC.An incommensurate peak is observed along the 100 directio but not along the 010 one.