# In situ neutron diffraction measurements on the crystal structures of bcc, dhcp and fcc $FeD_x$ at the triple point

National Institutes for Quantum and Radiological Science and Technology Hiroyuki Saitoh

## 1. Introduction

When a metal is exposed to hydrogen atmosphere, hydrogen molecules ($H_2$) dissociate into atoms (H) on the metal surface and the dissociated hydrogen atoms dissolve into interstitial sites of a metal lattice to form a solid solution or stoichiometric hydride. Iron (Fe), which is a prototype of 3*d* transition metals, is a hydrogen resistant metal; the hydrogen solubility in Fe is limited to ppm order at ambient temperature and hydrogen pressure. Under high hydrogen pressures of several gigapascals, the solubility increases by several orders and even hydrogen rich monohydride FeH is formed. The phase diagram of the Fe–H system has been intensively studied for a *T*–*P* region of below 2000 K and 10 GPa, showing a variety of states created by dissolved hydrogen: ferromagnetism, superabundant vacancies, minimum melting point etc [1].

There are two major subjects still remaining unsolved in the phase diagram of the Fe–H system; the crystal structures of fcc and dhcp $FeH_x$ coexisting at a triple point located at around 550 K and 5 GPa and the magnetic structure of dhcp FeH. The hydrides are thermodynamically stable only at high pressures and rapidly decompose to Fe metal and molecular hydrogen under ambient conditions. In situ neutron diffraction measurement is indispensable for determining the crystal and magnetic structures of the iron hydrides.

## 2. Experiment

We employed a high-pressure neutron diffraction beamline named PLANET constructed at J-PARC, Tokai, Japan. A compacted iron disc, 3 mm in diameter and 2.5 mm in height, was prepared by pressing iron flakes in a piston-cylinder type mold. The iron specimen was placed at the center of a NaCl capsule (5.5 mm in diameter and 8 mm in height) together with internal deuterium sources of $AlD_3$ pellets placed above and below the Fe disc. The NaCl capsule was inserted in a cylindrical graphite heater and embedded in a pressure-transmitting medium made of MgO (17-mm-edge cube). The details of the cell assembly and high-pressure apparatus used for neutron diffraction were described in the previous paper [1].

The reaction cell containing the Fe specimen and deuterium sources was compressed to 5. 8 GPa at 300 K and then heated to ~1000 K. During heating the internal deuterium sources decomposed to supply deuterium fluid, which reacted with the Fe specimen to form fcc $FeD_x$. The temperature was decreased to 603 K and further to 300 K, where diffraction profiles were taken with six hours integration. A neutron source was operated at a power of 300 kW. Observed diffraction profiles were analyzed by using Z-Rietveld (version 0.9.42.2) [2]

## 3. Results

Diffraction peaks from dhcp, fcc and hcp $FeD_x$ were observed at 603 K and 4.8 GPa. Preliminary Rietveld analysis was made for each deuteride, yielding mass ratios of 0.58, 0.16 and 0.252 for the dhcp, fcc and hcp deuteride, respectively. The hcp structure is not present in the Fe–H phase diagram, but appeared as a metastable state during cooling of the fcc deuteride. A deuterium composition $x$ was determined to be 0.53 for the dhcp deuteride and 0.45 for the fcc deuteride. For the hcp deuteride $x = 0.38$ was obtained. Mono deuteride of dhcp FeD

maintains up to ~60 GPa at 300 K and has been expected to stably exist also over a wide high temperature range. The present results indicate that dhcp deuteride is essentially a solid solution, becoming monodeuteride with a saturated deuterium composition of $x = 1.0$ at low temperatures or high pressures.

Diffraction peaks from a dominant component of dhcp deuteride, a slight amount of metastable fcc deuteride and precipitated bcc Fe were observed at 300 K and 4.2 GPa. The profile of the dhcp deuteride is being analyzed. It turned out that the profile was reproduced by taking into account scatterings from magnetic moments in addition to those from Fe and D nuclei.

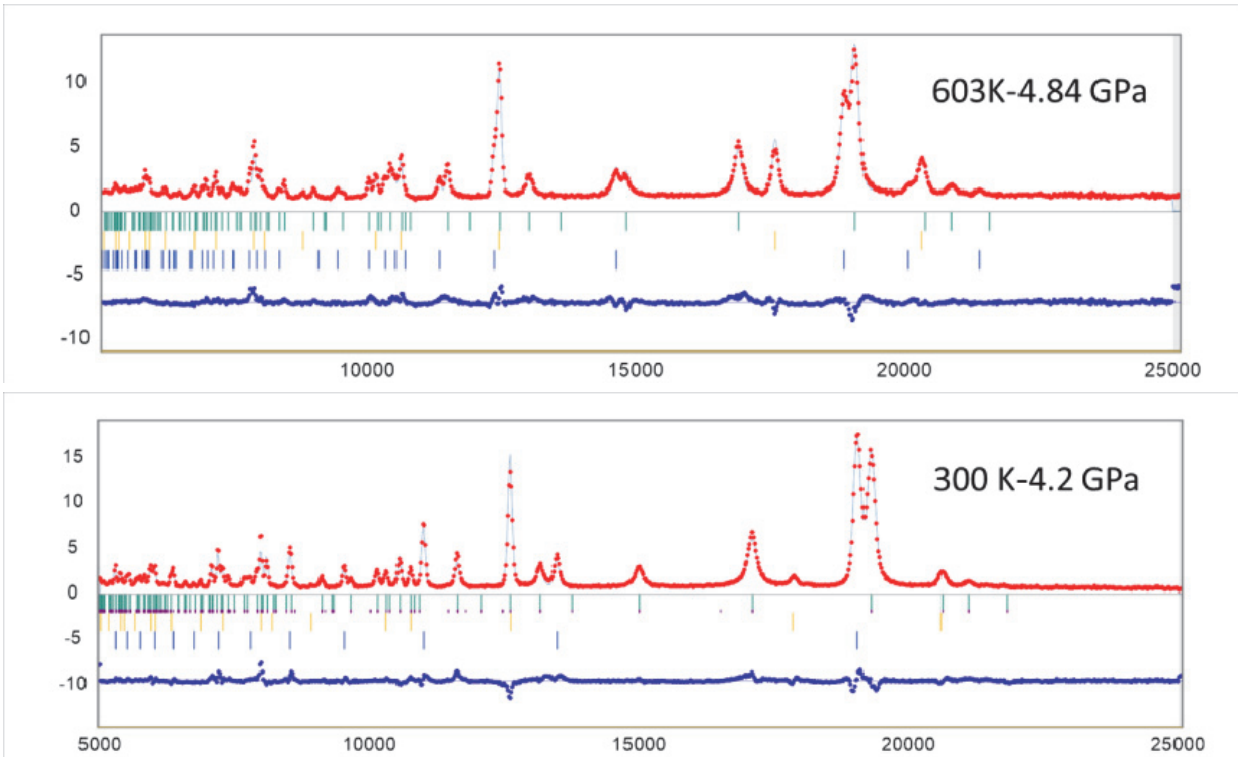


Fig.1 Neutron diffraction profiles taken at 603 K and 4.8 GPa (top) and 300 K and 4.2 GPa (bottom). Abscissa denotes time of flight in μs and vertical axis intensity in arbitrary unit.

## 4. Conclusion

The crystal structures of dhcp and fcc iron deuterides at 603 K and 4.8 GPa near the triple point in the Fe–H phase diagram were determined by in situ neutron diffraction measurement. The dhcp $FeD_x$, which has been believed to be present as a monodeuteride over the whole stable *T*–*P* region, was shown to become solid solution at high temperatures. The obtained data enables us to analyze the magnetic structure of dhcp FeD at 300 K and 4.2 GPa.

## References

1. Machida, A. *et al*. Site occupancy of interstitial deuterium atoms in face-centred cubic iron. *Nat. Commun.* **5**, 5063 (2014).
2. Oishi, R. *et al.* Rietveld analysis software for J-PARC. *Nucl. Instrum. Methods, Phys. Res. Sect. A* **600**, 94–96 (2009).