


実験報告書様式(一般利用課題・成果公開利用)

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課題番号 Project No. 2013B0155 実験課題名 Title of experiment Structural change of liquid water under high-pressure and high-temperature conditions 実験責任者名 Name of principal investigator Yoshinori Katayama 所属 Affiliation Quantum Beam Science Center, Japan Atomic Energy Agency	装置責任者 Name of responsible person Takanori Hattori 装置名 Name of Instrument/(BL No.) PLANET/BL11 実施日 Date of Experiment 16-21, March, 2013 23-25, March, 2013

試料、実験方法、利用の結果得られた主なデータ、考察、結論等を、記述して下さい。(適宜、図表添付のこと)  
 Please report your samples, experimental method and results, discussion and conclusions. Please add figures and tables for better explanation.

1. 試料 Name of sample(s) and chemical formula, or compositions including physical form.
Heavy Water (D <sub>2</sub> O), liquid Vanadium(V), solid (rod)

2. 実験方法及び結果 (実験がうまくいかなかった場合、その理由を記述してください。) Experimental method and results. If you failed to conduct experiment as planned, please describe reasons.
To investigate pressure- and temperature-induced structural change of liquid water, we carried out <i>in-situ</i> neutron diffraction measurements on heavy water using a 6-axis press, ATSUHIME, installed on BL11. In 2013, we had measured neutron diffraction of liquid heavy water up to 473K and 0.8 GPa on BL11. Our initial plan was an extension of the temperature range from 473K to 673K at 0.8 GPa. To realize the high-temperature conditions, we designed a sample container made of Pt, which was chemically stable against hot water. We also succeeded in sealing the container filled with water by laser-welding technique. However it turned out that the deformation of the container was large under high pressures and it was not suitable for measurements. Therefore we changed our plan to an extension of pressure range from 0.8GPa to 2 GPa. The standard 6-6 method was adopted to generate pressure. The truncation size of each anvil was 10mm. Fig. 1 shows the sample assembly. It consisted of ZrO <sub>2</sub> cube, ZrO <sub>2</sub> end-plugs, a tube-type graphite heater, gold leads, ZrO <sub>2</sub> discs and tubes, and a sample container made of TiZr alloy filled with D <sub>2</sub> O. The sample size was 4.8mm in diameter and 1.1mm in height.

## 2. 実験方法及び結果(つづき) Experimental method and results (continued)

The pressure and temperature were estimated using load-pressure and heater power-temperature relations, respectively. These relations had been determined in previous calibration experiments using similar assemblies. The diffraction data were collected by two detector banks at  $2\theta\sim 90^\circ$ . To reduce scattering from the container, the size of the incident beam was reduced by slits. The opening was 0.6 mm in height and 2.2mm in width.

The sample assembly was slowly compressed to 0.8 GPa, which was below 1 GPa, the freezing pressure of water at room temperature. The sample was then heated to 373K and compressed to 2 GPa, to avoid possible breaking of the sample container due to a sudden volume change accompanying a pressure-induced freeze of the sample. Diffraction data were collected at 373K and 473K at 2 GPa.

We also measured neutron scattering of vanadium under high pressure using the same assembly in an independent run. The scattering from an empty sample container was measured at ambient conditions in an assembly with dimensions which are the same as those under high pressure. The data acquisition time of each measurement was about 20 hours. The scattering intensities were normalized by the beam current and scattering intensities of the water sample,  $I_{\text{sample}}(Q)$ , the vanadium sample,  $I_{\text{vanadium}}(Q)$  and the empty cell,  $I_{\text{empty cell}}(Q)$ , were obtained as a function of momentum transfer,  $Q$ . Because the data contain no diffraction peaks, scattering from the sample container and  $\text{ZrO}_2$  are negligible.

Figure 2 shows temperature variation of the normalized intensity,

$$I(Q) = (I_{\text{sample}}(Q) - I_{\text{empty cell}}(Q)) / (I_{\text{vanadium}}(Q) - I_{\text{empty cell}}(Q)).$$

While the oscillation above  $5 \text{ \AA}^{-1}$  changes little, the intensity around  $2 \text{ \AA}^{-1}$  increases and the first peak becomes broader upon heating. Because the oscillation in the high- $Q$  region is mainly caused by the intra-molecular correlation, the small change in the high- $Q$  region implies that the molecular shape does not change upon heating. On the other hand the change in the low- $Q$  region contains information on the inter-molecular correlations. A comparison between the present results and the results at ambient conditions and at 0.8 GPa indicates that the position of the first peak shifts to higher  $Q$ 's with increasing pressure. Further analysis is planned to clarify the change.

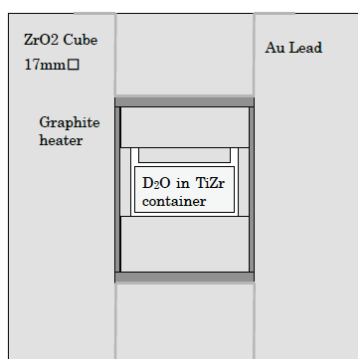


Fig.1 Sample assembly

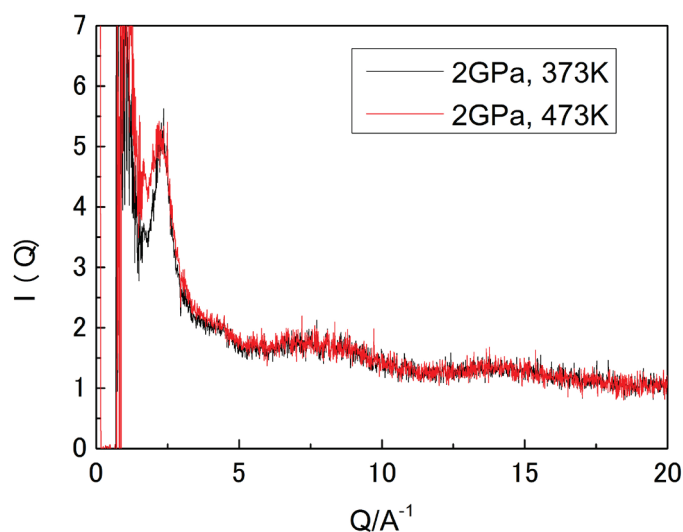


Fig. 2 Temperature variation of normalized intensity of heavy water at 2GPa