

 <b>MLF Experimental Report</b>	提出日 Date of Report 2012/07/05
課題番号 Project No. 2011B0062 実験課題名 Title of experiment The phase transition phenomena of water molecular assemblies which have different sizes in carbon nanospaces 実験責任者名 Name of principal investigator Taku Iiyama 所属 Affiliation Faculty of Science, Shinshu University	装置責任者 Name of responsible person Toru Ishigaki 装置名 Name of Instrument/(BL No.) BL20 実施日 Date of Experiment 2012/04/14-2012/04/16

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.

A new designed measurement cell for the connecting with cryostat of BL20 was used. The ground activated carbon fiber A25 (Ad' all Co.; pore width is 1.36 nm) were introduced in the cells, and preheated for 4 h at 393 K and 1 mPa before the measurements. We measured the neutron diffractions of vacant vanadium cell (for BG), A25 in vacuum ( $\phi = 0$ ), and D<sub>2</sub>O adsorbed A25( $\phi = 0.9$ ). Adsorbed amount of  $\phi = 0.9$  sample was controlled at saturated adsorbed amount (1000 mg/g). The measurement time is 2 h with 200 kW pulsed neutron beam, at double-flame mode. ND were measured for vacant vanadium cell (for BG) at 20, 200, 225, 250, 298 K, activated carbon A25 in vacuum ( $\phi = 0$ ) at 20, 225, 298 K, and D<sub>2</sub>O adsorbed activated carbon A25 ( $\phi = 0.9$ ) at 20, 200, 225, 250, 298 K

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.

We measured ND of activated carbon (AC) and D<sub>2</sub>O adsorbed AC at low temperature for elucidation of the phase transition phenomena of water in hydrophobic nanospace. The adsorbed amount of D<sub>2</sub>O was controlled near of saturated adsorbed amount in this experiment. For the reducing the recoil effect, D<sub>2</sub>O (Cambridge Isotope Laboratories, D = 99.9 %) was used as adsorbate water. The AC samples were preheated in the cell, and then D<sub>2</sub>O vapor was introduced. Equilibrium time was 2 day. A new designed cell (Fig.1, by the corporation of Prof. Hoshikawa, MLF) can be connected with cryostat for controlling temperature, and can be keep the hermetically closed condition by the closing plug. We confirmed that the ability of this cell (temperature control and pressure keeping) was enough to this adsorption measurement in low temperature by this experiment.

Fig.1  
 Measurement Cell

Fig. 2 shows the structure factors of adsorbed D<sub>2</sub>O obtained by the subtracting NDs of AC in vacuum and D<sub>2</sub>O adsorbed AC. In high-Q region ( $>15 \text{ \AA}^{-1}$ ),

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

corresponding to the intra-structure of D<sub>2</sub>O mainly, the broad peaks whose positions coincide with bulk D<sub>2</sub>O data were shown. The profile in this region does not change with temperature decreasing even at 20 K. On the other hand, the profile in low-Q region (<15 Å<sup>-1</sup>) show the dramatically changing with *T*. Fig. 3 shows the structure factors at low-Q region. At first, at low temperature below 225 K, the sharp peaks appeared. The positions of these sharp peaks are coincided with the bulk ice crystal I<sub>h</sub>. These peaks shift to the high-Q side with the temperature decreasing. It comes from the thermal expansion of ice crystal. These peaks disappear at 250 K which is lower than the bulk melting point.

The broad feature at low-Q region (Fig. 3) shows also significant change with temperature, it gave the so important information about the unique phase transition phenomena of water in small hydrophobic spaces. The main peak at  $Q = 1.9 \text{ \AA}^{-1}$  shows the ①intensity increasing, ②shape sharpening, and ③low-Q shifting at low temperature. ① and ② indicates the forming of the ordered structure of water at low temperature. ③ indicates the increasing the average distance of water molecules. Therefore, this data suggested that the water shows the negative thermal expansion in the hydrophobic nanospace. Furthermore, the profiles change continuously with temperature. It suggests that the water in the hydrophobic small space does not have the clear phase transition point. In the middle-Q region show also the continuous changing with temperature. At 20 K, the new broad peaks appeared at  $Q = 2.8, 3.4, 4.3 \text{ \AA}^{-1}$ . The positions of these peaks are corresponding to the metastable phase, ice I<sub>c</sub> (the position of  $Q = 3.4 \text{ \AA}^{-1}$  peak is different little bit with I<sub>c</sub>). The formation of I<sub>c</sub> was reported in mesoporous silicas. This experiment suggests that the I<sub>c</sub> formation occur by the size-effect, because the I<sub>c</sub> formation is confirmed in the hydrophobic nanospace of AC. These results are important for the understanding of the phase transition behavior of water in the extremely small spaces.

We can confirm that the structure change of AC itself with temperature is small as expected. We obtained the data from all measurement banks such as LA15, 25, 35, SE, BS. We will compare these for improving the data accuracy and removing recoil factor. Especially, data from LA15 will contain the information about the density of adsorbed water. We will discuss it in near future.

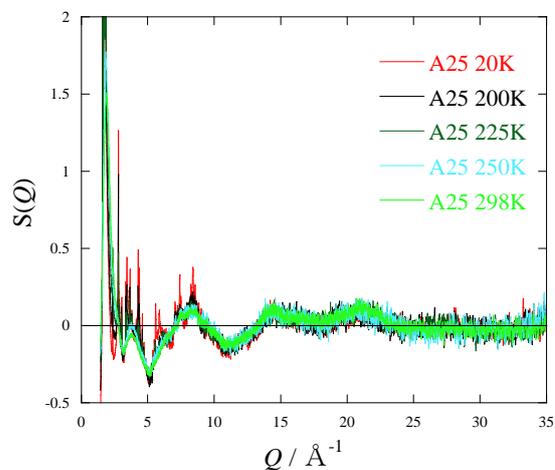


Fig.2 Structure functions of adsorbed water

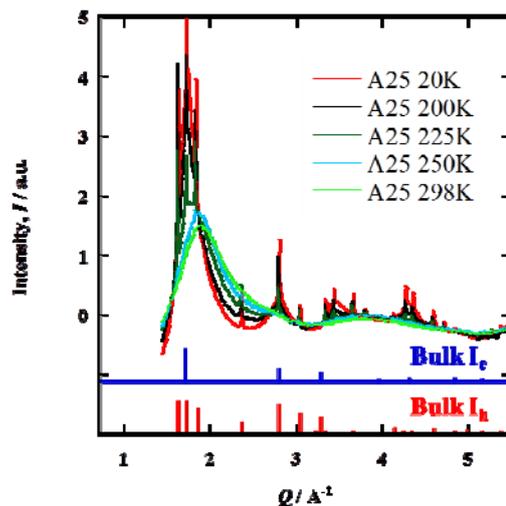


Fig. 3 Structure factors of adsorbed water on low-Q region and peaks of bulk crystals