

In-situ observation of hydrogen-bond symmetrization in δ -AlOOH and its isotope effect*Asami Sano¹, Takanori Hattori¹, Ken-ichi Funakoshi², Jun Abe², Shinichi Machida²

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Hydrogen bond is unique compared to the other covalent bond that makes a framework of minerals. Generally hydrogen bonds covalently to one side of oxygen while it forms hydrogen bond with the other side of oxygen, which is longer and soft bond. Applying pressure to this asymmetric geometry induces the decrease of O...O distance and results in various interactions with surrounding atoms. These changes are unquenchable to ambient pressure thus *in-situ* neutron diffraction experiment is indispensable to shed the light on hydrogen bond under high-pressure.

Aluminous hydrous mineral δ -AlOOH [1] has a strong hydrogen bond in its distorted rutile type structure at ambient conditions. Its stability field expands in wide pressure and temperature range, from 18 GPa to 134 GPa, and up to 2300 K [2] and considered as an important water carrier into the lower mantle. Ab-initio calculations pointed out that the hydrogen locates at the center between two oxygen atoms at high-pressure, which is so-called "symmetrization" of hydrogen bond [e.g. 3]. It is also suggested that the increase of bulk modulus is induced by the symmetrization. Subsequent X-ray diffraction study found that the bulk modulus increases at around 10 GPa for δ -AlOOH and 12 GPa for δ -AlOOD. Neutron diffraction study was conducted to 9.2 GPa but the hydrogen bond remains asymmetric in this pressure range [4].

To observe pressure-induced hydrogen-bond symmetrization directly, we conducted high-pressure neutron diffraction experiments to 18.1 GPa. The samples of δ -AlOOH and δ -AlOOD were synthesized at 18 GPa and 800-900 °C using a multi-anvil press. The synthesized sample and deuterated methanol-ethanol pressure-transmitting medium were loaded into a TiZr gasket in a Paris-Edinburgh press. Neutron diffraction patterns were corrected at the high-pressure neutron diffractometer "PLANET" in the MLF, J-PARC. The crystal structure including a hydrogen and deuterium position was refined by Rietveld method.

In δ -AlOOH, the disappearance of 021 reflection was observed at high-pressure. This observation can be attributed to the transition from the space group of $P2_1nm$ with asymmetric hydrogen bond to that of $Pnmm$ with disordered or symmetric hydrogen bond. The transition pressure of 8.4 GPa is consistent with our previous single crystal X-ray diffraction experiment. On the other hand the transition pressure of δ -AlOOD was determined to be 12.1 GPa, which is higher than that of δ -AlOOH. The O...O distance of hydrogen bond decreases significantly compared to other O...O distances below the transition but it becomes less compressible above the transition pressure. The result reveals that the small change of hydrogen position can induce the significant change of compression behavior. To discuss the detail hydrogen distribution in the $Pnmm$ structure, the difference Fourier map was obtained from the difference between the observed diffraction pattern and the refined model without hydrogen. The result will be presented in the paper.

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