Japan Geoscience Union Meeting 2012
(May 20-25 2012 at Makuhari, Chiba, Japan)

SMP48-P01 Room:Convention Hall Time:May 23 17:15-18:45

High pressure NMR of high density liquid molecular hydrogen

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Microscopic dynamics of molecular hydrogen in liquid state is important for understanding its transport properties. Nuclear magnetic relaxation times of compressed liquid molecular hydrogen were measured at room temperature using a diamond anvil cell. We determined spin relaxation times of molecular hydrogen at pressures up to 1.8 GPa at 294+/-1 K temperature, where active dynamics of the molecules are quantitatively described from the observed results [1]. The dynsmics of molecules in highly-compressed hydrogen is in reasonable agreement with the standard kinetic theory assuming hard-sphere molecules.

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SMP48-P02 Room:Convention Hall Time:May 23 17:15-18:45

First principles molecular dynamics study on filled ice hydrogen hydrate under pressure

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We present a study on the structural and vibrational properties of filled ice C2 hydrogen hydrate under compression by first principles molecular dynamics (FPMD). It is essential to note that the experimentally reported cubic Fd-3m (space group) C2 phase reflects the symmetry at high (room) temperature when the hydrogen bond network is disordered and the hydrogen molecules are orientationally disordered. In this sense, the "cubic" symmetry would definitely be lowered at low temperature where the hydrogen bond network is ordered and the hydrogen molecules are aligned. Indeed, we found tetragonal symmetry (P41212 and Pna21 space group) in our FPMD at low temperature. This finding demonstrates that the thermal effects play an essential role in stabilizing the structure to appear as cubic below 40 GPa. We also observed an indication of transition to an unknown high pressure phase above 40 GPa which is consistent with the experimental findings. Moreover, we extend our efforts to determine the phase boundary line between hydrogen bond ordered (disordered) phases and the H2 rotation and non-rotation phases at a rough approximation. The vibrational frequencies are extracted from Fourier analysis of the MD trajectories, which are in good agreement with experimental data. Hydrogen bond is predicted to symmetrize below 60 GPa based on the analysis of O-H stretching frequencies and radial distribution function g(OH). In comparison with the pure ice VII, the hydrogen bond symmetrization pressure in C2 hydrogen hydrate is much lower as reduced by a factor two.

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Keywords: hydrogen, hydrate, high pressure, phase transition, molecular interaction, molecular dynamics

Japan Geoscience Union Meeting 2012
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SMP48-P03 Room:Convention Hall Time:May 23 17:15-18:45

Changes in lattice parameters of filled ice Ih structure of methane hydrate under high pressure

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In our previous Raman study, orientaional ordering of guest methane molecules in a filled ice Ih structure of methane hydrate was observed above15 to 20GPa. Also, Sasaki's group reported clear change in lattice vibration mode of the structure at around 15GPa by Raman spectroscopy, showing a certain change in state of the structure. However, change in a fundamental structure has not yet been observed at the pressure range by X ray diffractometry. In this study, the lattice parameters of the filled ice Ih structure were carefully measured at room temperature up to 40GPa. The results showed that axes ratios changed at around 15 GPa, although the fundamental structure was maintained. The similar changes in the axes ratios were observed at low temperatures and also for denudated-water methane hydrate. The relationship of the axes-ratio change to the orientational ordering of methane molecules in the filled ice Ih structure was discussed.

Keywords: Methane Hydrate, X ray diffraction, high pressure, Raman spectroscopy

Japan Geoscience Union Meeting 2012
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SMP48-P04 Room:Convention Hall Time:May 23 17:15-18:45

Stabilities of filled ice II structure of hydrogen and helium hydrates at low temperatures and high pressures

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High pressure and low temperature experiments with filled ice II structures of hydrogen hydrate and helium hydrate were performed by using diamond anvil cells and a helium-refrigerator cryostat. The experimental conditions were in a region of 0.2 to 4.5 GPa and 130 to 300 K for the former hydrate and of 0.2 to 5.0 GPa and 200 to 300 K for the latter one, respectively. X-ray diffractometry for hydrogen hydrates revealed a series of phase change from sII to filled ice Ic via filled ice II. Change in a/c ratio was observed at approximately 2 GPa, and Raman spectroscopy also showed changes in frequencies of vibron and OH vibration mode at around 2 GPa within the filled ice II structure. For helium hydrate, X-ray diffractometry showed that the filled ice II structure did not transformed to filled ice Ic structure in this study, being contrary to the previous prediction, but decomposed into helium and ice VI or VIII. Difference in compressibility between both hydrates was examined in relation to their stabilities.

Keywords: hydrigen hydrate, helium hydrate, filled ice II structure, stability

SMP48-P05 Room:Convention Hall Time:May 23 17:15-18:45

Vibrational properties of hydrous ringwoodite, first principles investigation

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Wadsleyite and ringwoodite are primary constituent minerals in the Earth's transition zone. These phases can contain up to a few wt% H_2O in the crystal structure and are thought to be the most important water reservoirs in the Earth. We have investigated the high pressure protonation sites in hydrous wadsleyite using first principles calculation and found that the oxygen O_1 site is the most favorable for protonation in wadsleyite because of the electric imbalance of this site. On the other hand, the crystal structure of ringwoodite does not have such peculiar protonation sites and the reason of such high retention of water in ringwoodite has been unclear so far. In present study, I have calculated the vibrational properties of hydrous ringwoodite under pressure with various protonation models by first principles. Comparing with the IR and Raman measurements, I will discuss the protonation sites in hydrous ringwoodite.

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Keywords: hydrous ringwoodite, first principles, vibrational property

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SMP48-P06 Room:Convention Hall Time:May 23 17:15-18:45

A high-temperature neutron difraction study on $Mg(OD)_2$

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The structure of deuterated brucite, $Mg(OD)_2$, was investigated by measuring neutron diffraction at high temperature and at atomospheric pressure to see the dynamic behavior of D atoms with increasing temperature. The neutron diffraction experiments from 202K to 600K were carried out at the beamline of Wide-Angle Neutron Difractometer (WAND) in the High Flux Isotope Reactor (HRIR), Oak Ridge National Laboratory, USA. Rietveld analysis was performed with both the single D site model and the three-site D model. D atom sits at a crystallographic $2d$ site on the 3-fold rotation axis in the single D site model and at a $6i$ site with occupation factor of 1/3 in the three-site D model. Analysis for 600 K data was not successful using the single D site model but was successfully converged using the three-site D model. This is possibly due to the strongly anisotropic D motion.

Keywords: brucite, Deuterium, high temperature, dynamic behavior, neutron diffraction

Japan Geoscience Union Meeting 2012
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SMP48-P07 Room:Convention Hall Time:May 23 17:15-18:45

Hydrogen solubility into Fe-C and Fe-Si alloys at high pressure

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The most of the Fe-Ni cores of terrestrial planets are considered to contain light elements, such as S, Si, O, C and H. Hydrogen is considered to be one of the plausible light elements in the planetary cores. It is important to understand the effect of coexisting light elements, i.e. C and Si, on the solubility of H into Fe. Here, we have carried out in-situ X-ray diffraction experiments on the Fe_3C-H and FeSi-H systems to investigate the solubility of hydrogen into Fe-C and Fe-Si alloys under high pressure.

The experiments were performed up to 19 GPa and 2073 K for FeSi-H system and up to 17 GPa and 1973 K for Fe_3C-H system. Hydrogen dissolved in FeSi and $FeSiH_x$ hydride was formed above 10 GPa. This hydrogenation pressure is much larger than that of Fe, suggesting that presence of Si in Fe metal increases the minimal pressure for H incorporation. Hydrogen content (x) increases from 0.07 to 0.22 with increasing pressure for $P > 10$ GPa and the H content in $FeSiH_x$ is lower than that in FeH_x. The effect of carbon on hydrogenation pressure and H solubility will also be discussed.

Keywords: Hydrogen, hydride, Fe-alloy, diffraction

Japan Geoscience Union Meeting 2012
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SMP48-P08 Room:Convention Hall Time:May 23 17:15-18:45

Hydrogen in the core inferred from high P-T reaction of Fe-Ni-Si-H2O

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Iron-nickel alloy containing some light elements is considered to be main constituent of the Earth core. We have reported the effect of nickel on iron-water reaction under high pressure and temperature at the Joint Meeting in 2010, which suggests a significant extending of oxyhydroxide phase to higher pressure than pure iron?water system. We have further studied the reaction of iron-nickel alloy and water by adding silicon which is one of the most plausible light elements of the core using a laser-heated diamond anvil cell combined with X-ray diffraction measurements at KEK-PF:AR-NE1A. The starting material of iron-nickel-silicon alloy was prepared in an arc furnace in a pure Ar atmosphere. The foiled iron-nickel-silicon alloy was loaded into the sample hole of Re gasket, with distilled water. Pressures were calculated using the equation of state of ice VII phase. The sample was heated with Nd:YAG laser using a double-sided heating techniques. The temperatures were determined by the thermal radiation from the heated sample. The experimental conditions were up to about 40GPa and 2000K. In situ observation at pressures and temperatures is essential to identify the reaction phase because the iron rich hydride produced in the reaction is unquenchable to the ambient condition. We observed the reaction between the iron-nickel-silicon alloy and water and phase transition of each phase at high pressure and temperature. In the present study, oxyhydroxide and metal hydride were stable to 38GPa and 1000K, while oxide and metal hydride was produced at higher pressure and 1650K. The stability field of oxyhydroxide expands more than Fe-Ni-water system to higher pressure of 42GPa. The produced hydride phase with a dhcp structure transformed to an fcc structure at higher temperature at 1900K 42GPa. The results indicate that hydrogen was much partitioned to mantle phase by silicon and nickel in the core material.

Keywords: Earth'S core, hydrogen, iron alloy, synchrotron X-ray, high pressure

Japan Geoscience Union Meeting 2012
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SMP48-P09 Room:Convention Hall Time:May 23 17:15-18:45

Developments of 6-6 type compression for high-pressure neutron diffraction at PLANET

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NA

Keywords: high-pressure neutron diffraction, 6-6 type compression, J-PARC

Japan Geoscience Union Meeting 2012
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Developments of pressure and temperature controlling system for x-ray and neutron scattering experiments

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Some polymorphs or amorphous phase of ice, for example, ice II, HDA, LDA, etc,, could only be accessible by compressing under low-temperature, and metastable ice phases like ice Ic, IV, XII, VII' are formed through HDA. Therefore, it is essentially important for the study of ices to control pressure and temperature individually. For x-ray study, diamond anvil cells (DACs) with helium-gas driven membrane have been widely used in synchrotron facilities so far, and the DAC often attaches to a helium compressor-type cryogenic system. The problems of cryostat are 1) generally too large and heavy, and 2) having noise and oscillation so that it is difficult to set it to laboratory based x-ray diffractometer. We have developed liquid-nitrogen circulating type cryogenic system with newly designed DAC with very large opening angle. The considerably small cryostat and the specially designed DAC allow us to conduct single crystal or powder x-ray diffraction experiments under pressure from 80 K to 473 K, and of course, pressure and temperature are individually controllable. Moreover, there is no oscillation thanks to removing pulsate compressor from the system.

On the other hand, for neutron experiments, high pressure (up to 2000 bar) helium-gas driven Paris-Edinburgh cells have been used in ISIS and ILL. Although this technic has been quite sophisticated at the moment, some technical difficulties like helium gas leaking and safety problems have still remained. Therefore, we again adopt liquid nitrogen circulating system for 100 ton opposed-type press for high pressure and low/high temperature neutron scattering experiments.

The p-T controlling system for x-ray has been now nearly perfected and that for neutron is going to be completed until March/2012. We reported the details of the systems and briefly introduce some preliminary studies using them.

Keywords: Low temperature, High pressure, ice, x-ray diffraction, neutron diffraction

SMP48-P11 Room:Convention Hall Time:May 23 17:15-18:45

Performance of PLANET beamline

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The powder diffractometer dedicated to high-pressure experiments (PLANET) is now being constructed on BL11 at the spallation neutron source of J-PARC. PLANET aims to study structures of hydrogen-bearing materials including dense hydrous minerals of the Earth's deep interior, magmas and light element liquids.Here we present design of neutron delivery system of PLANET and first results of beam characterization.

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6-rams Multi Anvil Press installed in BL11

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Neutron diffraction is a powerful tool to investigate hydrogen in minerals and rocks. New neutron diffraction beamline ”PLANET” is currently under construction at BL11 of Materials and Life Science Experimental Facility (MLF) at J-PARC, at Tokai, Ibaraki. One of the unique features of this beamline is that 6-rams multi-anvil high-pressure apparatus (ATSUHIME) is installed, to generate high pressure and high temperature conditions of earth's mantle. Maximum load of each hydraulic ram is 500-ton. Each rams are controlled independently by six plunger pumps. The press will be installed at experimental hutch at Feb. 2012. I will present the current status of the 6-rams multi-anvil apparatus.

Keywords: neutron diffraction, 6-rams press

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Neutron Camera Installed in BL11 ”PLANET” Beamline in J-PARC

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The neutron camera of the custom-made product by Toshiba Corp. was introduced in J-PARC BL11 ”PLANET” beamline on December 22, 2011. Various examinations have been made from several years before for the introduction.

In this talk, we will present the outline of the neutron camera, and report the result of the preliminary experiment conducted using a 45MeV pulsed neutron source of Hokkaido University (Hokkaido LINAC). Although it has not realized yet to conduct neutron imaging experiment in J-PARC BL11 ”PLANET” beamline using this camera because of the way of the beamline construction, it should be possible to conduct preliminary neutron imaging experiment by the presentation day. So, in addition, we will introduce the preliminary results in our beamline.

By introduction of this camera, it becomes possible to observe the various sample images under high pressure and high temperature using large-volume high pressure apparatus. Especially neutron has an advantage to detect hydrogen and water in samples, which is much different from X-ray. So our target is to see hydrogen-bearing sample by this camera. Still more, we are considering to conduct three-dimensional neutron tomography using this camera. Especially, when we use the Paris Edinburgh press, it will be possible to do tomography under high pressure and high temperature. So we are also doing this kind of development.

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Keywords: neutron imaging, water, the Earth’s interior, neutron camera