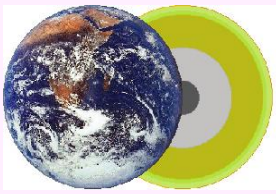
The 394th Geodynamics Seminar

Phase changes of deuterated hydrogen hydrate induced by guest orientational ordering

Dr. Hisako Hirai (Distinguished Professor, GRC)

Date: 07.25.2014 (Fri) 16:30 ~
Venu: Meeting Room #486, Science Research Bldg 1, Ehime Univ.

日時：2014年7月25日(金)16:30～
場所：愛媛大学 総合研究棟Ⅰ 4階共通会議室



EHIME UNIVERSITY GRC GEODYNAMICS RESEARCH CENTER

Abstract

Hydrogen and ice are the most abundant materials in the universe according to the cosmic abundance of the elements. Hydrogen hydrates have been reported to be potentially ubiquitous in space objects such as proto-stars, extrasolar planets, and their satellites. While, one type of hydrogen hydrates has recently received significant interest as an environmentally clean hydrogen storage material. Three hydrogen hydrate phases are known to be stable under high pressure: a clathrate structure II (sII) and two filled ice structures called C1 and C2. The filled ice structures are composed of host ice framework with guest molecules included in the voids of the host. The host of C2 is a diamond-like structure similar to ice Ic. In both clatherate and filed ice structures, guest molecules are randomly rotating with spherical symmetry. At room temperature, C1 forms above 0.9 GPa and transforms to C2 at ~2.5 GPa. Previously many studies have been made at room temperature, but low temperature and high pressure study above 5 GPa has not been reported. The host of C2 is ice Ic, so C2 has been thought to have a cubic symmetry. However, a theoretical study predicted that cubic to tetragonal transition occurs at low temperature and high pressure. And, we experimentally confirmed the transition to a tetragonal structure. Also, above the pressure region of the tetragonal phase, existence of another high pressure phase (HP-phase) was found.

Here next subjects rise to clarify the reason for forming tetragonal structure, and to infer the nature of the HP-phase. To examine these subjects, it is expected that deuterated sample gives suggestive information, because isotopic effects may affect phase transitions. Thus, we performed low temperature and high pressure experiments using D_2-D_2O hydrate samples, as well as H_2- H_2O samples for comparison. Raman spectroscopy revealed that a rotational mode, $S_0(0)$, split both for D_2O and H2O samples, which means lowering rotational symmetry of hydrogen molecules, e.g. from spherical symmetry to ellipsoidal one, probably due to orientational ordering. That lowering symmetry of the guest molecules may lead deformation of the cubic lattice to a tetragonal one. As for HP-phase, the phase appeared at lower pressures above 35 GPa for D_2-D_2O samples. The O-O distance at 35 GPa is too longer for symmetrization of hydrogen bond, thus the symmetrization is not appropriated for the formation. The vibration modes and rotation modes considerably changed for the HP phase. And, X-ray diffraction line of 111 was also split, indicating lowering lattice symmetry, too. Thus, it is suggested that the HP-phase is formed by further guest ordering or totally ordering. Hydrogen hydrate exhibits outstanding stability under high pressure. Such stability may substantiate by increasing interactions between the guest and host via the guest orientational ordering and the host symmetrization of hydrogen bonds.

詳細は当センターホームページ：http://www.ehime-u.ac.jp/~grc/をご覧ください
問い合わせ先： 出倉 春彦（TEL:089-927-8408, e-mail:dekura@sci.ehime-u.ac.jp）