Unique Structures in Yttrium Trihydride at High Pressure

In rare-earth metal hydrides, it is an important problem to determine the roles interstitial hydrogen (H) atoms play in structural and electronic properties. For yttrium hydrides, YH_x, as a prototypical example, various studies have been performed. Yttrium trihydride, YH_3, exhibits a hexagonal metal lattice, which contains three H atoms per metal atom in the interstitial spaces under ambient conditions. Two H atoms are located at the tetrahedral (T) sites and the remaining H atom is located near the Y metal plane in the octahedral (O) sites. On the other hand, dihydride YH_2 has an fcc metal lattice in which the T sites are filled with H atoms. YH_x exhibits a gradual opening of the band gap during hydrogenation over x=2 with a structural change from cubic to hexagonal. Hexagonal YH_3 eventually becomes transparent at a gap of 1.8 eV. Upon dehydrogenation into YH_2, insulating YH_3 transforms into metallic YH_2 with a reversible hexagonal-cubic structural transition. It is considered that the interstitial H atoms, especially the O-site H atoms, play a dominant role in the hydrogen-induced band-gap opening as well as in the structural transition. Band structure calculations have been performed in an attempt to give a clear-cut explanation for the unusual metal-insulator transition, but the origin of the large band-gap opening seems still controversial.

At a highly densified state, which is realized under high pressure, the hydrogen-metal (H-M) and H-H interactions are thought to play an essential role in the structural and physical properties. Previous high-pressure X-ray diffraction experiments have revealed that hexagonal YH_3 sluggishly transforms into cubic YH_3 upon an increase in pressure from about 10 to 20 GPa, suggesting the existence of an intermediate structure bridging the hexagonal and cubic structures [2]. On the other hand, a rapid decrease in the optical gap on compression has been observed for this intermediate phase by optical absorption measurements in the visible region [3]. The electronic band structure of the intermediate phase is very sensitive to pressure. This is in strong contrast to the behavior of insulating hexagonal YH_3, which has a band gap that remains approximately constant with changing pressure. The structural investigation of the intermediate phase is crucial for understanding the mechanism of the hexagonal-cubic structural transition and the band gap closing mechanism for YH_3. In this work, we propose a candidate structural model for the intermediate state [1].

A diamond anvil cell (DAC) was used for the high-pressure hydrogenation of Y metal and successive X-ray diffraction measurements on the hydride. Synchrotron radiation X-ray diffraction patterns were measured at pressures of up to 30 GPa at ambient temperature using a diffractometer for the DAC that was constructed at beamline **BL22XU**. The diffraction pattern of hexagonal YH_3 exhibits significant changes at about 12 GPa on compression. Some of the reflection peaks split into several peaks and new peaks appear. The diffraction pattern becomes simple with gradual peak merging on further compression, and the observed major reflection peaks are eventually indexed with an fcc lattice above 22 GPa. Hexagonal YH_3 transforms to the cubic structure through an intermediate state that exists over a wide pressure range of 10 GPa. These structural changes are reversible; the fcc structure reverts to the hexagonal structure through the intermediate phase with hysteresis as the pressure is released.

The diffraction patterns of the intermediate state are complicated, as shown, for example, in the pattern obtained at 14.0 GPa on the top of Fig. 1, and cannot be interpreted using the two-phase coexisting model or other structures reported for rare-earth metals such as Sm-type (9*R*) or dhcp (4*H*) structures. We speculate that the intermediate structure consists of stacked metal layers with partial hexagonal-type and fcc-type sequences along the *c*-axis of the hexagonal unit cell. Starting with this structural model, we searched for a suitable candidate structure.

Powder diffraction profiles are simulated for various candidate structural models by systematically changing the numbers of hexagonal-type (*ABA*-type) and fcc-type (*ABC*-type) layers contained in a unit cell.

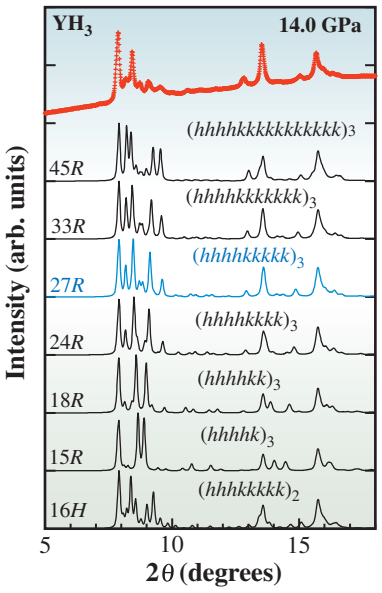

Fig. 1. Simulated patterns of the long period stacking structures (solid curves). Top pattern is the experimental one measured at 14.0 GPa (crosses).

Here, we adopt the Jagodzinski notation to describe the stacking sequence: symbols *h* and *k* denote the layers with hexagonal and cubic arrangements, respectively. According to Jagodzinski notation, the Sm-type (*ABABCBCAC*) and dhcp (*ABAC*) structures are described as $(khh)_3$, and $(kh)_2$, respectively. The subscripts indicate the number of times the sequence of layers must be repeated to complete the unit cell in the structure. The number of metal layers considered in the unit cell ranged from 9 to 51. In our simulation, only the lattice of Y metal is taken into account, because the contribution of the hydrogen atoms to the diffraction profile is neglected due to the small atomic scattering factor of hydrogen. Figure 1 shows typical examples of the simulated patterns. From 15*R* to 45*R*, the stacking sequences systematically change: the number of *k*-layers varies from 1 to 11 while the number *h*-layers remains unchanged. The profiles from 24*R* to 45*R* show good agreement with the experimentally obtained pattern, particularly in the high angle region. The high-angle peaks are less affected by extrinsic factors such as preferred orientation. By comparison with the simulated and experimental patterns, we find that the 27*R* $(hhhhkkkkk)_3$ structure well reproduces the overall profile.

The structural parameters are further refined by Rietveld analysis using RIETAN-2000 program. Figure 2 shows the results of Rietveld refinements using the 27*R* structural model. The space group *R*-3*m* is chosen and is assumed to be unchanged in the pressure range of 12-22 GPa in the fitting analysis. For 14.0 and 17.9 GPa patterns, different stacking sequences are examined. We correct the preferred orientation parameters as well as the atomic coordinates. The observed diffraction patterns are satisfactorily reproduced from the refined parameters.

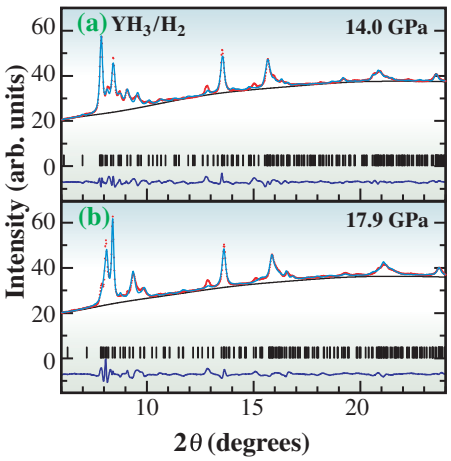

Fig. 2. X-ray diffraction patterns of YH_3 measured at 14.0 and 17.9 GPa. Solid curves are results of Rietveld refinements with the 27R structure models.

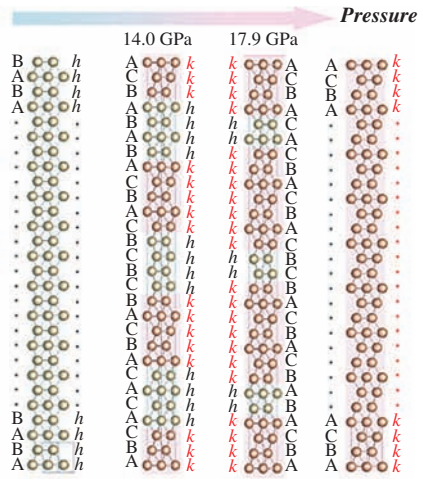

Fig. 3. Schematic illustrations of the long-period structures of the yttrium sublattices at 14.0 and 17.9 GPa. The hexagonal and cubic structures are also shown.

The intermediate structure is most likely to be a long-period metal lattice with a stacking sequence that successively changes toward the fcc structure upon compression.

Schematic illustrations of the long-period structures of the yttrium sublattices at 14.0 and 17.9 GPa are shown in Fig. 3. The hexagonal and cubic structures are also shown. Such stacking structures can be regarded as periodic arrangements of *h*-layer and *k*-layer domains. The 14.0-GPa structure consists of 4 *h*-layers and 5 *k*-layers, while the 17.9-GPa structure consists of 2 *h*-layers and 7 *k*-layers. The number of *k*-layers shows a tendency to increase with pressure as expected, and the full fcc stacking sequence is realized at about 22 GPa. In contrast with the parent metal, the hexagonal-cubic transition of YH_3 is slow and proceeds via an intermediate state in which the metal layer sequence gradually changes with increasing pressure. Such a transition process is considered to be characteristic of rare-earth metal hydrides and should be interpreted in terms of the H-H interactions and H-M bonding.

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References

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