

Pressure-induced structural change from hexagonal to fcc metal lattice in scandium trihydride

A. Ohmura^{a,*}, A. Machida^a, T. Watanuki^a, K. Aoki^a, S. Nakano^b, K. Takemura^b

^a Synchrotron Radiation Research Center, Japan Atomic Energy Agency (JAEA), 1-1-1 Sayo, Sayo, Hyogo 679-5148, Japan

^b Advanced Nano Materials Laboratory, National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan

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Abstract

We synthesized scandium hydrides by hydrogenation of a scandium foil with hydrogen fluid under high pressure at ambient temperature. Scandium dihydride (ScH_2) and trihydride (ScH_3) were prepared near 4 and 5 GPa, respectively. The hydrogenation process and pressure-induced structural changes in ScH_3 were investigated by synchrotron radiation X-ray diffraction measurements up to 54.7 GPa. A structural transition from hexagonal to the fcc lattice began at 30 GPa and was completed at 46 GPa via an intermediate state similar to those reported for other hexagonal trihydrides. The intermediate state was not interpreted in terms of a coexisting state for the low-pressure hexagonal and the high-pressure fcc structures. The onset transition pressure of ScH_3 supported the previously proposed relation that the hexagonal–fcc transition pressure is inversely proportional to the ionic radius of the trihydride.

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1. Introduction

Rare-earth metals exhibit successive hydride forms from a solid solution MH_x ($x < 2$) to a trihydride, MH_3 , via the dihydride, MH_2 , as the hydrogen concentration increases [1]. Yttrium (Y) and other rare-earth metals tend to form hexagonal metal lattices in the trihydride, while lanthanum (La) forms an fcc one. Hydrogen atoms occupy the tetrahedral and octahedral interstitial sites in each metal lattice. It has been reported that trihydrides with hexagonal lattices show structural changes to fcc lattices at pressures of several tens gigapascals [2–5]. The initial hexagonal lattices have relatively large c -axis values and consequently, the c/a ratios are around 1.8, which deviate largely from the ideal hcp lattice value of 1.63. The large c/a ratios lead to an expectation that the lattice gradually approaches the ideal hcp lattice or transforms into the fcc lattice, another closed packed structure, upon compression. The observed hexagonal–fcc transitions are characterized as

first-order transitions with a 10–15% reduction in volume, and proceed gradually through hexagonal–fcc coexisting [3] or intermediate states [5].

Scandium (Sc) is the lightest element with the smallest ionic radius among rare-earth metals. Sc forms a solid solution (ScH_x , $x \leq 0.43$), a dihydride (ScH_2), and a trihydride (ScH_3) [6–10]. The crystal structure and electrical properties of ScH_3 are not well studied because a high hydrogen gas pressure is required for trihydrogenation, and ScH_3 reversibly decomposes into the dihydride upon releasing hydrogen gas pressure. However, ScH_3 has a hexagonal metal lattice [8]. The detailed crystal structure, including hydrogen positions, has been recently determined by neutron diffraction measurements [11]. Substoichiometric $\text{ScH}_{2.9}$ is shown to have a crystal structure with $P6_3/mmc$ symmetry, which differs from the HoH_3 -type structure with a $P\bar{3}c1$ symmetry proposed for YH_3 [12] and other rare-earth metal trihydrides. The hydrogen atoms in the octahedral sites occupy randomly one of two equivalent positions near the metal basal planes in the $P6_3/mmc$ structure, while those in the $P\bar{3}c1$ structure occupy regularly the three positions: one in the metal plane and two above and below the metal plane.

Hexagonal- ScH_3 has a c/a ratio of 1.8 and should undergo a pressure-induced structural change to an fcc metal lattice. The

* Corresponding author at: Institute for Materials Research, Tohoku University, Katahira 2-1-1, Sendai 980-8577, Japan. Tel.: +81 22 215 2093; fax: +81 22 215 2091.

E-mail address: ohmura@imr.tohoku.ac.jp (A. Ohmura).

hexagonal–fcc transition pressure tends to be inversely proportional to the ionic radius of constituting metal atom: 5 GPa for GdH_3 with an ionic radius of 0.94 Å, and 12 GPa for LuH_3 with 0.85 Å. Hence, ScH_3 , which has an approximate radius of 0.72 Å, should have a much higher transition pressure. The hexagonal–fcc transition pressure, if observed, would play a key role in establishing the trend for rare-earth metal hydrides and would provide a clue to the ionicity dependence.

We measured the X-ray diffraction patterns of a scandium–hydrogen system at high pressures up to 54.7 GPa at ambient temperature. The hydrogenation process observed during compression of a Sc foil with hydrogen fluid and a structural transition toward the fcc structure, which appeared upon further compression beyond 30 GPa, are presented.

2. Experimental

We used a diamond anvil cell (DAC) to synthesize ScH_x by hydrogenation of a scandium foil reacted with hydrogen fluid at high pressure and room temperature. A fragment of scandium (nominal purity 99.9%) was lightly pressed between the opposed diamond anvils to make the foil thinner. The metal fragment, which had a diameter of approximately 60 μm and thickness of 15 μm , was placed into a sample chamber (120 μm in diameter and 42 μm thick) made by drilling a small hole in a tungsten gasket. The DAC containing the sample was filled with a hydrogen fluid compressed to 180 MPa [13]. Then the scandium foil was treated in an argon atmosphere to prevent surface oxidation.

Hydrogen fluid/solid acted as a hydrogen source during the hydrogenation reaction, which was induced at relatively low pressures, and served as a quasi-hydrostatic pressure medium for the structural investigation at high pressures above several gigapascals up to 55 GPa. The pressure in the sample chamber was monitored by measuring the fluorescence spectra [14] from ruby balls pressurized with the sample in the hydrogen medium. X-ray diffraction measurements were conducted at beamline BL22XU, SPring-8 [15,16]. The incident beam, monochromatic X-rays tuned to 25.06 keV (wave length $\lambda = 0.4948$ Å), was collimated to 20 $\mu\text{m} \times 20 \mu\text{m}$ so that just the sample area was irradiated to obtain a high S/N ratio or high quality diffraction data. Diffraction patterns were recorded using an imaging plate (400 mm \times 400 mm area) with an exposure time of 18 min.

3. Results and discussion

Fig. 1 shows the diffraction patterns measured for the hydrogenation process at pressures from 0.43 to 7.2 GPa. The initial state at 0.43 GPa exhibits a typical hexagonal pattern with lattice parameters of $a_h = 3.3058(1)$ Å and $c_h = 5.249(1)$ Å. It is known that the solid solution phase, ScH_x , exists up to $x \sim 0.43$ at ambient temperature and has a hexagonal metal lattice [17]. The hexagonal lattice expands slightly as the hydrogen concentration increases. The reported lattice constants of $\text{ScD}_{0.33}$ are $a_h = 3.338(2)$ Å and $c_h = 5.299(8)$ Å, while those of the pure metal are $a_h = 3.3088(2)$ Å and $c_h = 5.2680(3)$ Å [17]. The lattice constants a_h and c_h obtained at 0.43 GPa are slightly smaller than the values for the pure metal, suggesting that the host metal lattice contains only a small amount of hydrogen atoms and shrinks slightly upon compression to 0.43 GPa.

The diffraction patterns indicate that dihydride ScH_2 and trihydride ScH_3 are formed at 4.1 and 5.3 GPa, respectively. As shown in the 4.1 GPa pattern, new peaks appear on the right side of the 100 and 101 reflections, and on the left side of the 110 reflection from the solid solution ScH_x , which are

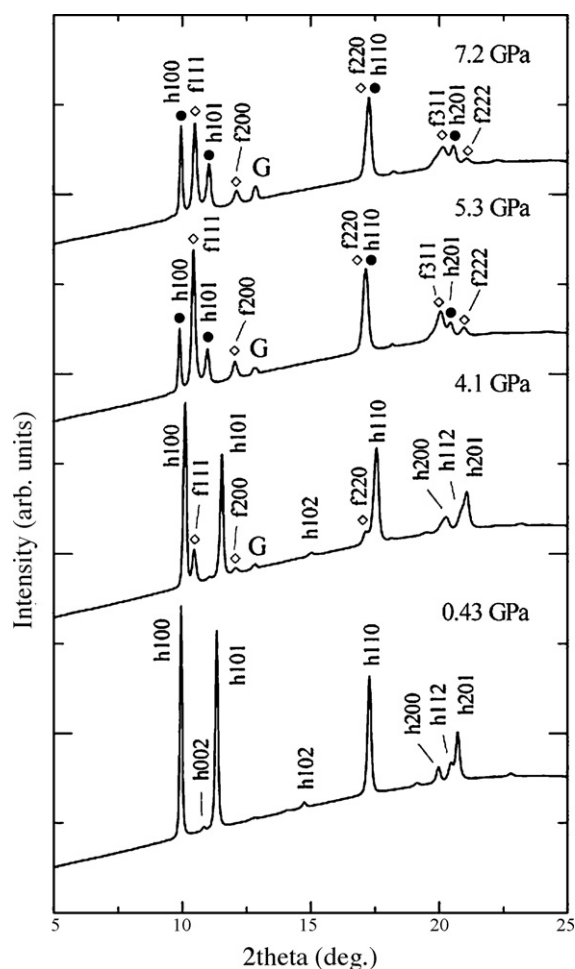


Fig. 1. X-ray diffraction patterns measured for the hydrogenation process of Sc metal upon compression from 0.43 to 7.2 GPa. Indices of the solid solution ScH_x , fcc- ScH_2 (\diamond) and hexagonal- ScH_3 (\bullet) are shown in each diffraction pattern. G denotes the reflection peak from the tungsten gasket.

assigned to the 111, 200, and 220 reflections, in the order of increasing two theta, from ScH_2 with an fcc lattice. Upon further increasing pressure to 5.3 GPa, the peaks of solid solution ScH_x disappear and are replaced by three peaks of ScH_3 . These three new peaks are indexed with a hexagonal lattice: 100, 101, and 201 reflections. The peaks of cubic ScH_2 remain. ScH_3 coexists with ScH_2 at 5.3 GPa. The lattice constants are $a_f = 4.727(1)$ Å for fcc- ScH_2 , and $a_h = 3.323(2)$ Å and $c_h = 5.979(8)$ Å for hexagonal- ScH_3 . These values are smaller than the ambient pressure values of ScH_2 [$a_f = 4.784(2)$ Å] and ScH_3 [$a_h = 3.380(3)$ Å and $c_h = 6.135(5)$ Å] by 1–3% [8] due to compression. Upon further compression, the remaining ScH_2 shows gradual hydrogenation to ScH_3 , which is completed near 20 GPa.

Fig. 2 shows selected diffraction patterns measured for the scandium–hydrogen system at pressures up to 54.7 GPa. The bottom spectrum, which was measured at 5.3 GPa, contains the diffraction peaks from fcc- ScH_2 and hexagonal- ScH_3 . The peak heights of the fcc lattice decrease as the pressure increases to 20.9 GPa, while those of the hcp lattice increase. ScH_2 is gradually hydrated to form ScH_3 . The integrated peak intensities

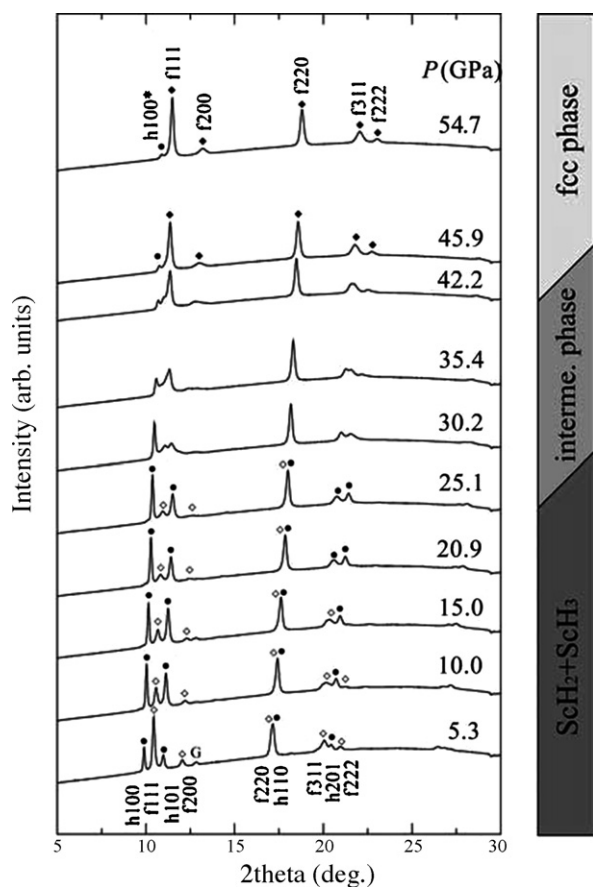


Fig. 2. Selected diffraction patterns measured for the Sc–H system up to 54.7 GPa (left), and a statement of scandium hydride on compression (right), indicating that fcc-ScH₂ coexists with hexagonal-ScH₃ up to 25.1 GPa, and the fcc phase appears above 45.9 GPa via the intermediate phase. Indices of fcc-ScH₂ (◇) and hexagonal-ScH₃ (●) are shown at 5.3 GPa, and fcc phase (◆) at 54.7 GPa. Small peak shown as an asterisk (*) in the fcc phase is most likely the surviving peak of hexagonal-ScH₃, the 1 0 0 reflection peak. *G* denotes the reflection peak from the tungsten gasket.

roughly estimated the volume fraction of the fcc-ScH₂ phase at 5.3 GPa to be 68%. It decreases to 25% at 20.9 GPa.

Structural changes from the hexagonal to an fcc begin near 30 GPa and are completed near 46 GPa. The 1 0 0 reflection from the hexagonal-ScH₃ gradually loses the peak intensity, while the 1 0 1 reflection peak of the hexagonal-ScH₃ and the 1 1 1 reflection peak of the fcc-ScH₂ seem to be merged into a single peak. Five reflection peaks are eventually observed at pressures above 45.9 GPa. They are indexed with an fcc unit cell. One small peak is additionally observed at $2\theta \sim 10.8^\circ$, which is assigned to the 1 0 0 reflection peak from unconverted hexagonal-ScH₃. The fcc phase persists up to 54.7 GPa, which is the maximum pressure achieved in this experiment.

Fig. 3(a) shows the interplanar spacings, d_{hkl} , plotted as a function of pressure. There are two characteristic features in the variation of the d -values at pressures between 30 and 46 GPa, which is the pressure region where the transition toward the fcc structure gradually occurs. First, the 1 0 1 reflection peak begins to split into a doublet at 30 GPa, but upon further increasing the pressure, the peaks shift continuously in opposite directions and eventually merge into the d -values of the 1 1 1 and

2 0 0 reflections near 46 GPa. Fig. 3(b) and (c) displays the 1 0 1 plane of the hexagonal lattice and the (1 1 1) and (2 0 0) planes of the fcc lattice, respectively. These planes are shown to be geometrically corresponding. The continuous conversion from the hexagonal 1 0 1 to the cubic 1 1 1 and 2 0 0 reflections in the d -value indicates that the shape of the metal plane is maintained during the transition. Second, the 1 1 0 reflection of hexagonal-ScH₃ is smoothly converted into the 2 2 0 reflection of the fcc structure without a discontinuity in the d -value. These reflections correspond to the interplanar spacings in the triangle lattice plane perpendicular to the c -axis of the hexagonal lattice and the (1 1 1) direction of the fcc lattice. These features indicate that the intermediate state between 30 and 46 GPa is not explained by a coexisting state of the low-pressure hexagonal and the high-pressure fcc structures.

Fig. 4 plots the molar volumes derived for the solid solution ScH_{*x*} ($x \leq 0.43$), fcc-ScH₂, hexagonal-ScH₃, and fcc phases. The compression curves are fitted with the Birch–Murnaghan equation of state [18]:

$$P = \frac{3}{2} B_0 \left\{ \left(\frac{V}{V_0} \right)^{-7/3} - \left(\frac{V}{V_0} \right)^{-5/3} \right\} \times \left[1 + \frac{3}{4} (B'_0 - 4) \left\{ \left(\frac{V}{V_0} \right)^{-2/3} - 1 \right\} \right],$$

where V_0 is the volume at ambient pressure, V the volume at pressure P given in gigapascals, B_0 the bulk modulus, and B'_0 is the pressure derivative. The equation of state provides $B_0 = 149 \pm 11$ GPa, $B'_0 = 1.3 \pm 0.5$, and $V_0 = 16.46 \pm 0.05$ cm³ for fcc-ScH₂, $B_0 = 103 \pm 10$ GPa, $B'_0 = 2.6 \pm 0.5$ and $V_0 = 18.16 \pm 0.10$ cm³ for hexagonal-ScH₃. The bulk moduli of the hydrides are larger by 40–80 GPa than that of 60 GPa reported for Sc metal [19,20]. Similar to reports for other rare-earth metals [2–5], the metal lattice is significantly hardened by hydrogenation. The volume reduction is estimated to be 13.1% for the hexagonal–fcc transition, which is consistent with the value of 13–14% predicted from the relation between the volume change and the ionic radius reported for other hexagonal trihydrides [4].

The fcc phase appearing above 46 GPa is considered to be trihydride, ScH₃. The structural behavior of ScH₃ is similar to that of YH₃. The hexagonal-YH₃ shows a transition into the fcc structure via an intermediate structure, which exists over a wide pressure span from 12 to 22 GPa [5]. The fcc phase, which appears above 22 GPa, is confirmed to be trihydride or fcc-YH₃ by X-ray diffraction and infrared spectroscopy [5,21]. The present X-ray diffraction data alone is unable to conclude that fcc-ScH₃ is formed because the possibility of a back transformation to fcc-ScH₂ in association with dehydrogenation remains. However, the analogy of the observed structural behavior to that of the hexagonal-YH₃ leads to the transition from the hexagonal to fcc lattice in ScH₃ as the most likely structural change.

The difference in the structural change with pressure between hexagonal-ScH₃ and hexagonal-YH₃ is prominent in the variation of the c/a ratio. The c/a ratios of YH₃ and other rare-earth trihydrides with hexagonal metal lattices decrease upon com-

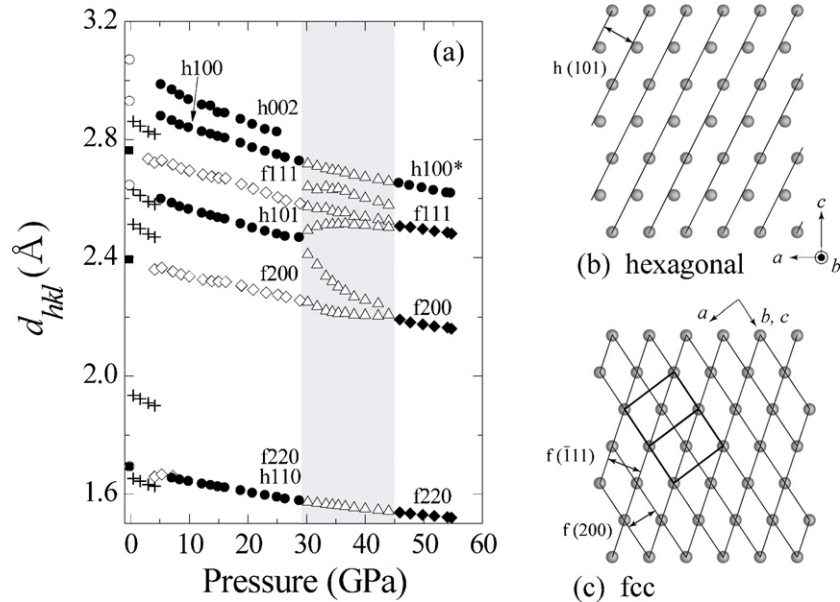


Fig. 3. (a) Interplanar spacings, d_{hkl} , plotted as a function of pressure: solid solution ScH_x (+), fcc- ScH_2 (◇), hexagonal- ScH_3 (●), intermediate phase (□), and the fcc phase (◆). Open circles (○) and solid squares (■) indicate those of fcc- ScH_2 and hexagonal- ScH_3 reported in the literature [8], respectively. The spacing shown as an asterisk (*) in the fcc phase is most likely the (100) plane of hexagonal- ScH_3 . Hatched area shows the region of the intermediate state. (b) and (c) The (101) planes in the hexagonal lattice and the (111) and (200) planes in the fcc lattice, respectively.

pressure [2,5]. The ratio of hexagonal- YH_3 decreases from 1.79 to 1.71 as the pressure increases from 0 to 10 GPa. In contrast, that of hexagonal- ScH_3 remains nearly constant at 1.8 for a wide

pressure range of 4–30 GPa, as shown in the inset of Fig. 4. The hexagonal lattice of ScH_3 is uniformly compressed, while those of YH_3 and other rare-earth trihydrides are predominantly compressed along the c -axis.

The present results for ScH_3 provide a clue to systematical understanding the hexagonal–fcc transition in rare-earth metal hydrides. Fig. 5 plots the onset pressures for the hexagonal–fcc transitions against the ionic radii of rare-earth metals. The previously reported values of YH_3 , GdH_3 , HoH_3 , ErH_3 , and LuH_3 [2–5] show the tendency that the onset pressure, P_c , is inversely proportional to the ionic radius. P_c increases from 5 GPa (GdH_3) to 12 GPa (LuH_3) as the radius decreases from 0.94 to 0.85 Å. The result of ScH_3 provides a pressure of 28 GPa for a radius of 0.73 Å, which is located on the extrapolated line of the transition

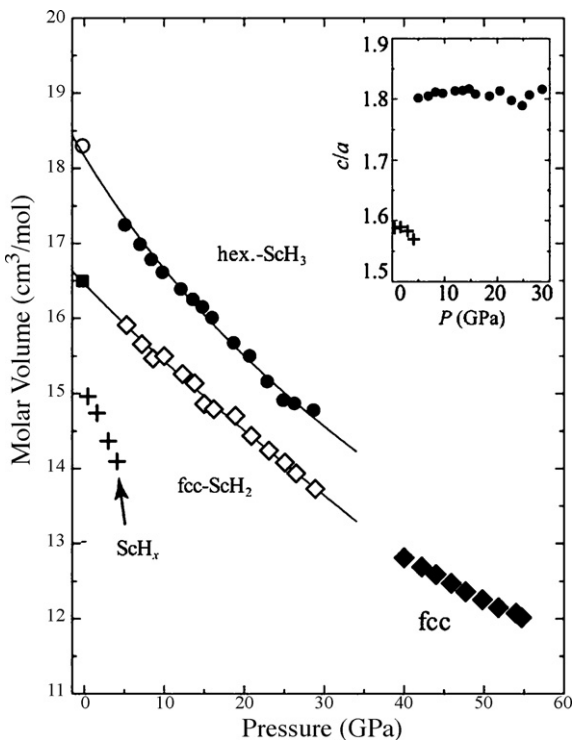


Fig. 4. Molar volumes for the solid solution ScH_x (+), fcc- ScH_2 (◇), hexagonal- ScH_3 (●), and the fcc phase (◆). Solid squares (■) and open circles (○) are the volumes of fcc- ScH_2 and hexagonal- ScH_3 calculated with the lattice constants reported in the literature [8], respectively. Inset shows the c/a ratios of the solid solution ScH_x (+) and hexagonal- ScH_3 (●).

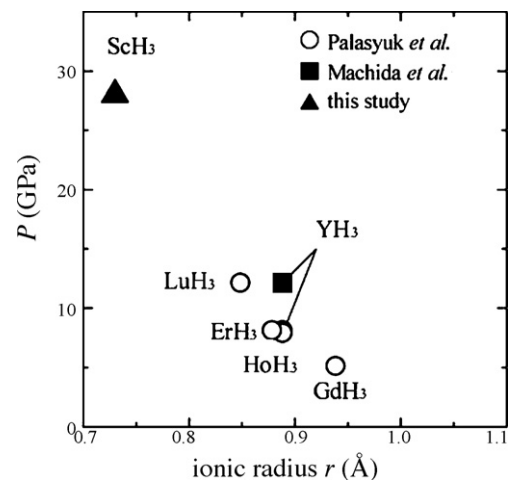


Fig. 5. Onset pressures of the hexagonal–fcc transition in rare-earth trihydrides plotted against the ionic radii of metals. Open circles (○) and solid square (■) are references from the literature [2–5].

pressure versus the ionic radius plot. Thus, the tendency for the onset pressure to be inversely proportional to the ionic radius is definitely confirmed.

4. Summary

Scandium hydrides were synthesized by compressing a scandium foil in hydrogen fluid/solid at ambient temperature. ScH₂ with an fcc metal lattice and ScH₃ with a hexagonal metal lattice formed at 4.1 and 5.3 GPa, respectively. Hexagonal-ScH₃ transformed to the fcc structure via an intermediate state, which appeared between 30 and 46 GPa. The intermediate state was not the coexisting state of the hexagonal and the fcc phases, but was interpreted in terms of the successive rearrangement of the metal layer sequence as reported for the hexagonal–fcc transition of YH₃. The present results confirmed the previously proposed relation for rare-earth metal hydrides that the hexagonal–fcc transition pressure was inversely proportional to the ionic radius. The bulk moduli of 149 ± 11 and 103 ± 10 GPa obtained for fcc-ScH₂ and hexagonal-ScH₃, respectively, were much larger than that of 60 GPa reported for Sc metal. In addition, a significant hardening by hydrogenation was confirmed for Sc metal.

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