Structures and phase transitions of ScH_3 under high pressure*

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(Received 26 July 2012; revised manuscript received 18 October 2012)

The structures and the phase transitions of ScH_3 under high pressure are investigated using first-principles calculations. The calculated structural parameters at zero pressure agree well with the available experimental data. With increasing pressure, the transition sequence hcp (GdH_3-type)→ $C2/m$ →fcc→hcp (YH_3-type)→$Cmcm$ of ScH_3 is predicted first; the corresponding transition pressures at 0 K are 23 GPa, 25 GPa, 348 GPa, and 477 GPa, respectively. The $C2/m$ symmetry structure is a possible candidate but not a good one as the intermediate state from hexagonal to cubic in ScH_3. On the other hand, via the analysis of the structures of hexagonal $ScH_{2.9}$, cubic ScH_3, and cubic ScH_2, we find that the repulsive interactions of H–H atoms must play an important role in the transition from hexagonal to cubic.

Keywords: *ab-initio* calculations, phase transitions, high pressure

PACS: 71.15.Pd, 65.40.–b, 62.50.+p **DOI:** 10.1088/1674-1056/22/5/057102

1. Introduction

Systems of rare-earths with hydrogen have increasingly attracted scientists' attention since the discovery of the switching properties of Y and La hydride films in 1996.[1,2] In such systems, the physical properties of most hydrides are extremely sensitive to the variations in the hydrogen concentration. Particularly, a metal–insulator transition occurs when the hydrogen concentration changes from 2 to 3 (per metal), below which the hydride is conductive and reflective, and above which it is insulating and transparent. Moreover, unlike other metal–insulator transitions, the transition in rare-earth hydrides occurs at room temperature in the visible part of the spectrum, and is smooth and reversible as a function of the hydrogen concentration.[3–5] This makes them very attractive for application as optical switches.[6–8] In addition to the interesting optical properties, RH_x (R=Sc, Y, Sm, Gd, Tb, Dy, Ho, Er, Tm, Lu) displays an intriguing structural behavior as a function of the H concentration. At a low H concentration, it has the same hexagonal structure as its matrix. Increasing H concentration, RH_x ($x \approx 2$) stabilizes the cubic CaF_2-type structure. At an even higher H concentration, RH_x ($x \approx 3$) becomes again of the hexagonal type instead of the cubic type.[9,10] On the other hand, with increasing pressure, rare-earth trihydride RH_x ($x \approx 3$) is expected to undergo a structural transition from hexagonal to cubic[2] and the insulator–metal transition in association with the gap closure, which is also of much interest in the sense of 1s metal realized by the metallization of the hydrogen sublattice and in superconductivity realized by the strong electron–phonon coupling.[11–13] Consequently, it is not surprising that these materials have become a subject of recent and current interest, and have drawn much attention both in the experimental and the theoretical working groups.[1–27]

In researching these materials, the structural, electronic, superconductive properties and the phase transition[11–22] of YH_3 have been studied most intensely. Recently, we also systematically investigated the structures, structural relative stabilities, pressure-induced phase transitions (hcp→fcc), and equations of state for lanthanide trihydrides RH_3 (R=Sm, Gd, Tb, Dy, Ho, Er, Tm, Lu) by using the *ab-initio* calculations.[23] However, there should be some differences in the properties of different rare-earth trihydrides. Scandium (Sc) is the lightest element with the smallest ionic radius among rare-earth metals; at the same time, it is adjacent to rare earth element Yttrium (Y). But in experiment, substoichiometric $ScH_{2.9}$ was shown to have a crystal structure with $P6_3/mmc$ symmetry in 2006,[24] which differs from the HoH_3-type structure with $P\bar{3}c1$ symmetry proposed for YH_3[14] and for other rare-earth metal trihydrides.[25] The hydrogen atoms in the octahedral sites occupy randomly one of the two equivalent positions near the metal basal planes in the $P6_3/mmc$ structure.[24] Those in the $P\bar{3}c1$ structure regularly occupy three positions: one in the metal planes and two above and below the metal planes.[14,25] However, in theory,[17–19] the $P6_3cm$ symmetry structure (a broken symmetry structure of the $P\bar{3}c1$ structure) was considered as the most possible structure for YH_3. This not only came from the energy calculation,[17] but also came from the results of the calculated phonon spectra[18] and electric-field gradients.[19] So the ground state structure of $ScH_{2.9}$ is particu-

*Project supported by the National Natural Science Foundation of China (Grant No. 11174214), the Specialized Research Fund for the Doctoral Program of Higher Education, China (Grant No. 20090181110080), the National Basic Research Program of China (Grant No. 2011CB808201), the Special Project for Research Conditions of High-level Talents of Guizhou Province, China (Grant No. TZJF-2008-42), and the Science Foundation of Education Bureau of Guizhou Province, China (Grant No. 2010053).

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lar and interesting. However, with increasing pressure, hexagonal $ScH_{2.9}$/ ScH_3 was also found to transform to the cubic (face-centered cubic) structure in a synchrotron X-ray diffraction (XRD) experiment using a diamond anvil cell (DAC) in 2007.[26] In that experiment, the transition was found to begin at 30 GPa and finish at 46 GPa. Recently, Kume *et al*.[27] investigated not only the structural transition but also the insulator–metal transformation in ScH_3 via the measurements of Raman, infrared, and visible absorption spectroscopy, and the hcp-intermediate-fcc phase transitions were observed at 25 GPa and 46 GPa; the energy gap of ScH_3 was 1.7 eV in ambient conditions and was closed at around 50 GPa. Meanwhile, the recent theoretical studies[28] have shown that potential superconductivity applications of the high pressure cubic phase of stoichiometric ScH_3 may also exist like in the case of YH_3.[13] However, the theoretical research of the structural, electronic properties and the pressure-induced phase transitions in ScH_3 has been absent until now. An appropriate theoretical investigation of the electronic properties of ScH_3 or the other rare-earth metal trihydrides is still a special challenge; the general density functional theory,[4,9] the advanced *GW* calculations,[20] or combining the dynamical mean field theory (DMFT) with the electronic structural calculation based on the density approximation[29] may solve the problem.

The main aim of this paper is to explore the structures and the phase transitions of ScH_3 under high pressure, and to provide a comparative and complementary study via the density functional theory. From the calculated results, the phase transition mechanism of hexagonal $ScH_{2.9}$/ScH_3 under pressure is discussed. Particularly, whether ScH_3 has the similar transition sequence to YH_3 under high pressure is presented. The rest of the paper is organized as follows. In Section 2, we give the detail of the computational method. The results and discussion for the structures and the phase transitions of ScH_3 under high pressure are presented in Section 3. Concluding remarks can be found in the last section.

2. Theoretical methods

We calculated the electronic structures of ScH_3 using the plane-wave pseudopotential density functional theory method through the Cambridge Serial Total Energy Package (CASTEP) code,[30,31] together with the generalized gradient approximation (GGA-PBE)[32] for the exchange–correlation function. The Kohn–Sham equation was solved by means of the ultrasoft pseudopotentials introduced by Vanderbilt.[33] Pseudo-atomic calculations were performed for Sc $3s^2 3p^6 3d^1 4s^2$ and H $1s^1$. A plane-wave basis set with energy cut-off at 450 eV was applied. For Brillouin zone sampling, we used 13×13×13, 11×11×8, 9×9×7, 10×10×6 Monkhorst–Pack meshes respectively for the face-centered cubic (fcc), hexagonal close-packed (hcp), $C2/m$ (primitive cell), *Cmcm* (primitive cell) structures of ScH_3. The self-consistent convergence of the total energy was 10^{-6} eV/atom. A full optimization of the cell structure was performed to acquire the equilibrium structure and enthalpy at each target external pressure, and the optimizing method adapted the Broyden–Fletcher–Goldfarb–Shenno (BFGS) minimization technique.[34,35]

3. Results and discussion

3.1. Ground state structure and *P–V* equation of state

At room temperature and ambient pressure, rare earth metal Sc is in hexagonal structure with space group $P6_3/mmc$ (No. 194),[36] and its dihydride ScH_2 is in cubic structure with space group $Fm\bar{3}m$ (No. 225);[37] while its trihydride $ScH_{2.9}$ is again in hexagonal structure with space group $P6_3/mmc$ (No. 194).[24] The ground state structure of $ScH_{2.9}$ is very interesting because of its difference from the other rare-earth trihydrides, as mentioned above. But it is difficult to simulate the substoichiometric experimental structure $ScH_{2.9}$. In the experimental $P6_3/mmc$ structure ($ScH_{2.9}$),[24] two Sc atoms reside at 2*c* (0.3333, 0.6667, 0.25) sites, four H atoms reside at 4*e* (0, 0, 0.21) sites (O sites), the other four H atoms reside at 4*f* (0.3333, 0.6667, –0.088) sites (T sites); here T sites are the tetrahedral sites, O sites are the octahedral sites. It is important to note that there are two Sc atoms and eight H atoms in the unit cell, so the formula unit in theory is ScH_4 for general understanding, although Antonov *et al*.[24] reported the corresponding formula unit in experiment should be $ScH_{2.9}$. This will lead to theoretical difficulties for the study of the structure of ScH_3 as well as for the study of the pressure-induced phase transition of ScH_3. An LDA/GGA calculation to resolve this question would involve a very large supercell,[9] and this is outside the scope of this work. So, the present simulation considers only the stoichiometric trihydride ScH_3. Then we take the conventional $P6_3/mmc$ structure of RH_3 as the ideal $P6_3/mmc$ structure of ScH_3. In the literature, two types of $P6_3/mmc$ structures are proposed as the approximate structures of RH_3. One is YH_3,[38] where two Y atoms reside at 2*c* (1/3, 2/3, 1/4) sites, two H atoms reside at 2*a* (0, 0, 0) sites (O sites), and four H atoms reside at 4*f* (1/3, 2/3, 0.625) sites (T sites). The other is GdH_3,[39] where two Gd atoms reside at 2*c* (1/3, 2/3, 1/4) sites, two H atoms reside at 2*b* (0, 0, 0.25) sites (O sites), and four H atoms reside at 4*f* (1/3, 2/3, 0.58) sites (T sites). Obviously, the differences in these $P6_3/mmc$ structures mainly come from the locations of the H atoms on the octahedral sites. It seems that the GdH_3-type $P6_3/mmc$ structure is closer to the experimental one.[24] Indeed, the calculated structural parameters in the GdH_3-type $P6_3/mmc$ structure are $a = 3.361$ Å, $c = 6.104$ Å, and $c/a = 1.816$, which are very close to Antonov *et al*.'s[24] experimental data

($a = 3.373$ Å, $c = 6.121$ Å, $c/a = 1.815$). The relative errors for lattice constants a, c and ratio c/a are only 0.34%, 0.47%, and 0.11%, respectively, whereas, the optimized lattice parameters ($a = 3.356$ Å, $c = 5.56$ Å, $c/a = 1.56$) in the YH_3-type $P6_3/mmc$ structure have very large discrepancies compared to the experimental data.[24] Furthermore, the optimized total energy in the YH_3-type $P6_3/mmc$ structure is even much higher than that of the cubic structure. As the approximate structure of the experimental $ScH_{2.9}$, the YH_3-type $P6_3/mmc$ structure is naturally excluded, while the GdH_3-type $P6_3/mmc$ structure is a good approximation. With the approximate GdH_3-type $P6_3/mmc$ structure, the P–V curve of ScH_3 at 0 K is presented together with the experimental data at room temperature in Fig. 1. It is seen that the present results are in good agreement with Ohmura *et al.*'s[26] experimental data. This will support the following simulation of the pressure-induced phase transition in ScH_3.

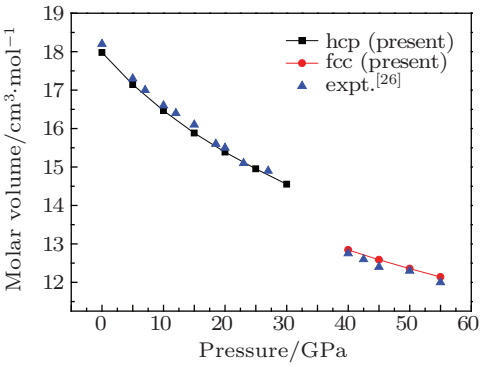


Fig. 1. (color online) Equation of state of ScH_3 at 0 K.

3.2. Pressure-induced phase transition in ScH_3

At 0 K, the Gibbs free energy is equal to enthalpy H, expressed as $H = E + PV$. Then the transition pressure at 0 K can be estimated from the condition of equal enthalpies. The enthalpy–pressure curves for the hexagonal $P6_3/mmc$ (GdH_3-type), monoclinic $C2/m$, and cubic (fcc) structures of ScH_3 are presented in Fig. 2. It is seen that the stable pressure range for the GdH_3-type hexagonal structure is about from 0 GPa to 23 GPa. The theoretical result is very close to the recent Kume *et al.*'s[27] experimental data (0–25 GPa), but is smaller than Ohmura *et al.*'s[26] experimental data (0–30 GPa). In fact, according to the opinion of Kume *et al.*,[27] Ohmura *et al.*[26] must have overestimated the stable range because of a larger volume fraction of ScH_2 as well as the migrations of H atoms.[10,27] It is also noted that the theoretical transition pressure from hexagonal to cubic is larger than that of YH_3 (13 GPa[22]) or LuH_3 (20 GPa).[23] While the molar volume of ScH_3 is the smallest among these rare-earth trihydrides RH_3 (R=Sc, Y, Sm, Gd, Tb, Dy, Ho, Er, Tm, Lu), so the present theoretical results support the previous proposed relation for rare-earth metal hydrides that the transition pressure from hexagonal to cubic is inversely proportional to the ionic radius.[2]

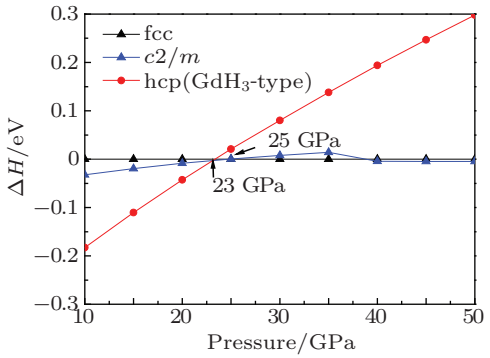


Fig. 2. (color online) Enthalpy as a function of pressure for the $P6_3/mmc$ (GdH_3-type), $C2/m$, and fcc structures of ScH_3 at 0 K, taking that of the cubic structure as reference.

In the cases of hexagonal SmH_3, GdH_3, and HoH_3, Palasyuk and Tkacz[2] have suggested that the repulsive interactions of H–H atoms may play an important role in the structural phase transition from hexagonal to cubic in terms of their measurements and analysis of the structures in the vicinity of the phase transition. In the real $ScH_{2.9}$ structure,[24] the shortest distance of H–H at ambient pressure and room temperature is 1.983 Å, which is a little smaller than the theoretical value (2.061 Å) of the cubic structure at zero pressure. With increasing pressure, the shortest distance of H–H atoms in the real $ScH_{2.9}$ structure will become shorter and shorter and the increasing H–H repulsive interactions will force it to transform into another structure, as dictated by the 2-Å rule (2-Å is the smallest distance for the stability of many hydrides. The exact value of the crucial distance for rare-earth hydrides may decrease appropriately and limitedly with decreasing ionic radius because of the decreasing electronegativity.[2]).[40] The shortest H–H distance of the cubic ScH_3 structure at the beginning transition pressure (about 30 GPa[26]) is 1.936 Å, which is smaller than 2 Å. While the shortest H–H distance of cubic ScH_2 at 50 GPa (3.752 Å) is also much larger than 2 Å. Therefore, in Ohmura *et al.*'s[26] experiment, their X-ray diffraction data alone were unable to conclude that the cubic ScH_3 was formed, and the possibility of a back transformation to cubic ScH_2 in association with dehydrogenation remained. So according to the 2-Å rule, a transition mechanism similar to those of hexagonal SmH_3, GdH_3, HoH_3 should exist for the hexagonal $ScH_{2.9}$.

On the other hand, Ohmura *et al.*[26] pointed out that there appears to be an intermediate state in the transition process (30–46 GPa) from hexagonal to cubic for ScH_3. This intermediate state is not a state of coexisting hexagonal and cubic phases, but is to be interpreted in terms of a successive rearrangement of the metal layer sequence as reported for the hexagonal to cubic transition of YH_3. In a recent experiment, Kume *et al.*[27] also pointed out that the intermediate

phase of ScH_3 is very similar to that of YH_3 by the measurements of Raman and infrared spectroscopy. In the case of YH_3, the ambient-pressure hexagonal structure was shown to transform to the cubic (fcc) structure in the pressure range from about 9 GPa to 24 GPa.[41] The nature of the intermediate state of YH_3 has been studied by Yao and Klug.[22] They obtained a phase transition sequence for YH_3 using the VASP code and projector-augmented plane wave (PAW) potentials, together with the generalized gradient approximation (GGA-PBE) for the exchange–correlation function. The phase transition sequence was $P3c1 \rightarrow C2/m \rightarrow$ fcc $\rightarrow$ hcp (YH_3-type)$\rightarrow Cmcm$, and the corresponding transition pressures were 12 GPa, 38 GPa, 200 GPa, and 214 GPa, respectively. The $C2/m$ structure was suggested as the intermediate state in the transition process from hexagonal to cubic for YH_3. Does the intermediate phase of ScH_3 also actually belong to the $C2/m$ structure? In Fig. 2, it is seen that the $P6_3/mmc$ (GdH_3-type) structured ScH_3 transforms to the $C2/m$ structure at about 23 GPa. At that pressure, the optimized structural parameters for the $C2/m$ structure are Sc1: 4*i* 0.3333, 0, 0.206; Sc2: 2*c* 0, 0, 0.5; H1: 8*j* 0.1676, 0.2491, 0.2739; H2: 4*i* 0.3317, 0.5, 0.2701; H3: 2*d* 0, 0.5, 0.5; H4: 4*g* 0, 0.2425, 0 with $a = 11.133$, $b = 4.632$, $c = 3.636$ Å, and $\beta = 72.83°$. With further increasing pressure, the $C2/m$ structure transforms to the fcc structure at about 25 GPa. The stable range for the $C2/m$ structure is different compared with the experimental one, which is about from 30 GPa to 46 GPa for the intermediate phase connecting the ambient-pressure phase and the fcc phase.[26] In the case of YH_3, the theoretical stable range (12–38 GPa) for the $C2/m$ structure[22] is more reasonable compared with the experimental stable range (9–24 GPa).[41] In order to compare them more effectively, we apply similar parameters to optimize the corresponding structures of YH_3 using the CASTEP code. In Fig. 3, it is seen that the stable range for the $C2/m$ structure of YH_3 is from 13 GPa to 50 GPa. The result is basically consistent with another theoretical result (12–38 GPa).[22] Therefore, in contrast to the case of YH_3, the $C2/m$ structure is only a possible candidate but not a good one for the intermediate state from hexagonal to cubic in ScH_3, and a continued search for other new phases is expected. The hexagonal phase of ScH_3 has a structure similar to but different from that of YH_3,[24] and the intermediate phase from hexagonal to cubic in ScH_3 also may be different from that of YH_3. This opinion has a certain discrepancy with the speculation and judgment of both Ohmura *et al.*'s[26] and Kume *et al.*'s[27] experiments. However, Kume *et al.*'s[27] experiment could not confirm that the intermediate phase of ScH_3 is the $C2/m$ structure. So more advanced and actual experiments are needed to conclude the symmetry structures of the intermediate phases of ScH_3 and YH_3.

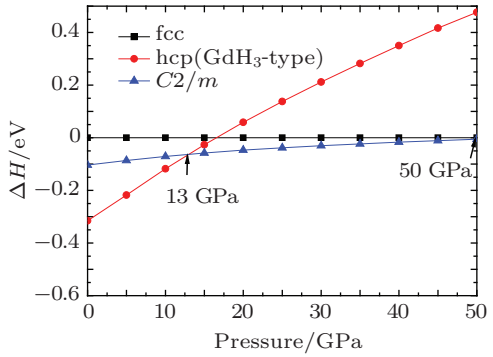


Fig. 3. (color online) Enthalpy as a function of pressure for the $P6_3/mmc$ (GdH_3-type), $C2/m$, and fcc structures of YH_3 at 0 K, taking that of the cubic structure as reference.

With pure theoretical calculations, it is seen that the fcc structure of ScH_3 transforms to the hcp (YH_3-type) structure at about 348 GPa in Fig. 4. The transition pressure is much higher than that of YH_3 (205 GPa[22] or the present result 229 GPa shown in Fig. 5). Furthermore, the hcp (YH_3-type) structure in ScH_3 has a larger pressure range (348–447 GPa) than that of YH_3 (205–214 GPa[22] or the present result 229–239 GPa shown in Fig. 5). Above 447 GPa, the orthorhombic *Cmcm* structure becomes more stable in ScH_3. At 447 GPa, the optimized structural parameters for the *Cmcm* structure are Sc 4*c*: 0, 0.1185, 0.75; H1: 8*f* 0, 0.3932, 0.9188; H2: 4*c* 0, 0.1777, 0.25 with $a = 2.24219$, $b = 5.29266$, $c = 3.61326$.

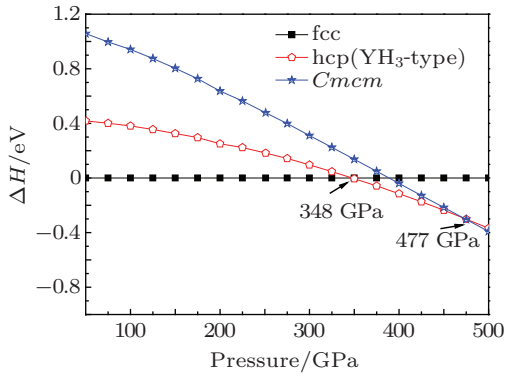


Fig. 4. (color online) Enthalpy as a function of pressure for the $P6_3/mmc$ (YH_3-type), *Cmcm*, and fcc structures of ScH_3 at 0 K, taking that of the cubic structure as reference.

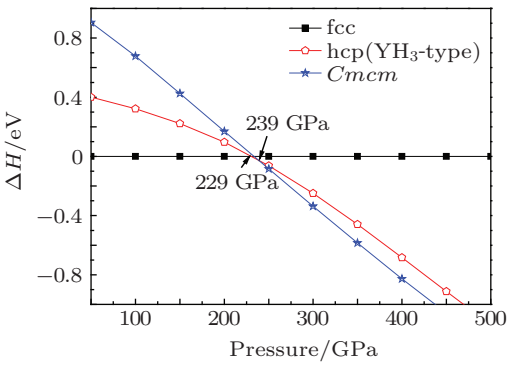


Fig. 5. (color online) Enthalpy as a function of pressure for the $P6_3/mmc$ (YH_3-type), *Cmcm*, and fcc structures of YH_3 at 0 K, taking that of the cubic structure as reference.

4. Conclusions

In summary, the structures and the phase transitions of ScH_3 under high pressure have been extensively investigated using the first-principles calculations. The structural parameters are predicted and compared with the available experimental data. The pure theoretical calculations predict the transition sequence hcp (GdH_3-type)→ $C2/m$ →fcc→hcp (YH_3-type)→$Cmcm$ of ScH_3 under high pressure; the corresponding transition pressures at 0 K are 23 GPa, 25 GPa, 348 GPa, and 477 GPa, respectively. In the transition sequence, the $C2/m$ symmetry structure is a possible (but not good) candidate of the intermediate state from hexagonal to cubic for ScH_3. The transition pressure from fcc to hcp (YH_3-type) or from hcp (YH_3-type) to $Cmcm$ structure is much larger than the corresponding one of YH_3. Furthermore, the hcp (YH_3-type) structure of ScH_3 has a larger pressure range than that of YH_3. On the other hand, via the analysis of the structures of hexagonal $ScH_{2.9}$, cubic ScH_3, and cubic ScH_2, the repulsive interactions of H–H atoms should play an important role in the transition from hexagonal to cubic and also explain why the experimental data could not conclude that cubic ScH_3 is formed and the possibility of a back transformation to cubic ScH_2 in association with dehydrogenation remains.

Acknowledgments

We acknowledge the support for the computational resources by the State Key Laboratory of Polymer Materials Engineering of China in Sichuan University.

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