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Pressure induced phase transformation of REH_3

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Abstract

High-pressure X-ray diffraction studies of the number of rare earth trihydrides (REH_3) have been carried out in a diamond anvil cell up to 30 GPa at room temperature. This includes the family of rare earth trihydrides that possess hexagonal structure at ambient conditions. A reversible structural phase transformation from the hexagonal to cubic phase has been observed for the Sm, Gd, Er, Ho and luthetium trihydrides. The same type of phase transition has been found also for yttrium trihydride. The lattice parameters of the new cubic phases and the volume changes at transition points were determined for the all compounds investigated. The parameters of the equation of state for all the hexagonal and cubic phases have been determined in the pressure range up to 30 GPa. The role of H–H repulsive interaction as a probable promoter of the transition and a systematics of transition are discussed.

Keywords: High pressure; Phase transformation; Rare earth hydrides

1. Introduction

There has been much interest in rare-earth metal hydrides in the last few years, for several reasons. Among the most interesting reasons are:

- Metal-insulator transitions, first discovered almost 50 years ago [1] and recently demonstrated by Griessen and coworkers [2] on the optical properties of yttrium and lanthanum hydrides. Spectacular changes from light reflecting to transmitting behaviour of thin films of hydrides caused by changes of hydrogen concentration have been shown. This phenomenon – called “switchable mirrors” – is believed to have potential application in the electronic industry.
- Magnetic and structural properties strongly dependent on the hydrogen content.
- The variety of electronic states in these hydrides makes them very attractive objects for theoretical calculations.
- Volume changes as a function of hydrogen concentration could be attributed to the bonding character between the corresponding metal and hydrogen.
- Possibility of structural and insulator-to-metal transitions under pressure predicted by theory.

Although yttrium hydrides are among the most investigated trivalent hydrides, the results could be attributed to the whole family of rare earth hydrides due to their similar properties, with the exception of europium and ytterbium.

The first suggestions on the possibility of structural transformation induced by pressure were reported by Ponaytovsky and coworkers on samarium and gadolinum trihydrides about 30 years ago [3]. The resistometric measurements of these hydrides under high pressure revealed anomalies which were interpreted as being the result of possible transitions from the hexagonal to cubic phases, although no structure determination was carried out. About 20 years later a number of theoretical calculations on yttrium trihydrides were carried out employing the local density approximation method, assuming different crystal structures [4]. Although rather conflicting results regarding the ground state of YH_3 were reported and some attempts were undertaken to improve these calculations [5], the possibility of transformation to the cubic phase was strongly postulated. However, X-ray high pressure investigations performed in a diamond anvil cell up to 25 GPa on thin film of yttrium hydride have not shown structural change to the fcc phase in this pressure range [6]. We have observed the first reversible hexagonal to cubic phase

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transformation induced by pressure on the bulk erbium trihydride by X-ray “in situ” diffraction study [7]. Our project has been stimulated by Sandia’s report in which signs of cubic phase has been detected during the sputtering of erbium in a hydrogen atmosphere [8] on cold deposit. As the sputtering technique inevitably involves creation of high stresses we decided to check the structural properties and existence of the fcc phase of erbium trihydrides under well controlled pressure conditions in a diamond anvil cell. It has also been reported that the insulating fcc yttrium trihydride can be obtained during hydrogenation of a magnesium–yttrium mixture [9]. No clear explanation of this behaviour has been given except for the involvement of high stresses during both hydrides formation. Whether or not the fcc structure of $YH_{3-\delta}$ is stable under normal conditions is not clear either. However, optical and electrical resistance measurements confirmed the insulating state of the fcc yttrium trihydrides phase, contrary to the predictions by some theoretical calculations [4].

In the present paper we report the experimental results of high pressure diffraction measurements carried out on the six trihydrides exhibiting similar phase transitions from a hexagonal to a cubic structure. The systematics of the reported phase transitions will be postulated.

Recently our results have been confirmed by Japanese group who preformed high pressure optical [10] and X-ray diffraction measurements [11] on yttrium trihydride. Beyond confirmation of structural transition from hexagonal to cubic structure their optical results strongly suggest insulator to metal transition within cubic phase at pressure about 25 GPa supporting earlier theoretical predictions.

2. Experimental

The samples of trihydrides were prepared from nominally 99.9% pure metals by direct absorption under the gaseous hydrogen pressure of 15.0 MPa and 300 °C in a high pressure Sievert’s type apparatus. Elemental and X-ray diffraction analyses confirmed a composition close to trihydride stoichiometry for all the compounds.

The pressure-dependent X-ray measurements were performed using the energy dispersive X-ray diffraction method (EDXD) in a diamond anvil cell (DAC). A tungsten target tube operating at 40 keV and 25 mA was used as the X-ray source. The acquisition time of about 20 h was the same for all experimental points. The diffraction angle was determined by measurements with a copper sample placed in the diamond anvil cell instead of the hydride. The angle value has been chosen to display all the main diffraction lines with reasonable resolution. We have to admit that for the hexagonal structure, due to the limited resolution of the energy dispersive method, some of the weaker diffraction lines are not detected, and indices given in the figures correspond to the strongest ones. The gasket with a 300 μm-drilled hole was made of Inconel. The incident X-ray beam was collimated down to 0.12 mm to avoid diffraction from the gasket material. The gasket hole was loaded with a sample and a ruby chip. The shift of the ruby fluorescence lines was used for the measurement of pressure according to the pressure scale proposed earlier [12].

3. Results

As an example of results obtained we present energy dispersive X-ray diffraction (EDXRD) spectra of gadolinium and holmium trihydrides collected over 24 h, each for different pressures are shown in Fig. 1.

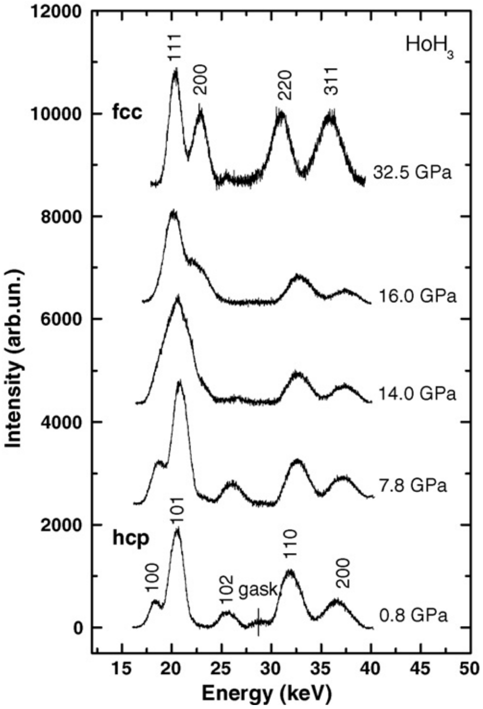

Fig. 1. EDXRD spectra of HoH_3 for different pressures indexed for both the initial hexagonal and high pressure phases. Index {2 0 0} in the initial hexagonal structure represents strongest diffraction line in the quadrupole set of peaks.

Holmium and other heavy rare earths metals form trihydrides by filling tetrahedral sites in the fluorite structure of dihydride with hydrogen atoms, similarly as light rare earths elements do, but before reaching trihydride composition, a lattice transformation to a hexagonal structure takes place, while hydrides of light rare earth elements remain cubic.

At lower pressures all trihydrides investigated exhibit a hexagonal structure with all the diffraction lines available at given diffraction angle. When pressure was increased, new lines appeared in the spectra and they grew in intensity with increasing pressure, eventually sweeping out the initial hexagonal structure. The new lines have been identified as belonging to the cubic fcc structure. During the decrease of pressure the samples remained cubic well below the transition point exhibiting a relatively wide hysteresis, eventually reaching structure of the initial hexagonal phase. The only difference in the behaviour of these hydrides is the value of transition pressures.

3.1. Systematics of the hcp–fcc transition in REH_3 (RE = Sm, Gd, Ho, Er, Lu, and Y)

Experimental data related to the crystal structure of hexagonal and a new cubic phases of lanthanide and yttrium trihydrides are collected in Table 1.

The molar volume of the hexagonal rare earth trihydrides decreases with increasing atomic number as a result of the decrease of the atomic radius commonly known as lanthanide contraction.

Fig. 2 presents the change of the molar volume of both hexagonal and cubic phases of lanthanide trihydrides with the

Table 1
Lattice parameters and molar volume of hexagonal and cubic phases of different rare earth trihydrides

Hydride	Lattice parameters (Å)		Molar volume (cm^3/mol)	
	Hexagonal	Cubic[a]	Hexagonal	Cubic[a]
SmH_3	$a = 3.77 \pm 0.01$; $c = 6.77 \pm 0.02$	5.37 ± 0.02	25.1 ± 0.2	23.3 ± 0.2
GdH_3	$a = 3.75 \pm 0.02$; $c = 6.69 \pm 0.02$	5.36 ± 0.02	24.5 ± 0.3	23.2 ± 0.2
HoH_3	$a = 3.64 \pm 0.01$; $c = 6.57 \pm 0.02$	5.25 ± 0.02	22.7 ± 0.2	21.8 ± 0.2
ErH_3	$a = 3.62 \pm 0.01$; $c = 6.53 \pm 0.02$	5.23 ± 0.02	22.3 ± 0.2	21.5 ± 0.2
LuH_3	$a = 3.57 \pm 0.01$; $c = 6.41 \pm 0.02$	5.12 ± 0.02	21.3 ± 0.2	20.2 ± 0.2
YH_3	$a = 3.67 \pm 0.02$; $c = 6.62 \pm 0.02$	5.28 ± 0.02	23.3 ± 0.2	22.2 ± 0.2

[a] Estimated from the two-phase region at ambient pressure.

corresponding atomic number. The molar volumes of cubic phases at ambient pressure are estimated by extrapolation of the fit of the Murnaghan equation.

The procedures of extrapolation along with the procedure of deconvolution were discussed earlier [13]. One can see that the molar volumes of high pressure cubic phases of lanthanide hydrides nicely follow the trend initiated by cubic lanthanide hydrides which are stable at ambient pressure, such as LaH_3, CeH_3 and PrH_3.

In search of other parameters, which would describe the high-pressure behaviour of YH_3 along with other lanthanide trihydrides, we plotted the dependence of the transition pressure on the molar volume of initial hexagonal phases.

As can be seen in Fig. 3 this tendency includes all the trihydrides investigated and this relationship can be used for prediction of transition pressures for other, not studied yet rare earth trihydrides as indicated for Tr, Dy and Tm.

For the analyses the shortest H–H distances in both structures were chosen. As a reminder—the hydrogen positions in the initial hexagonal structure are well determined within the HoD_3 structure while in the fcc structure hydrogen species are assumed to occupy ideal tetrahedral and octahedral sites. The minimal H–H distance before (for hexagonal structure) and after (for cubic structure) the transition has been analyzed (Fig. 4).

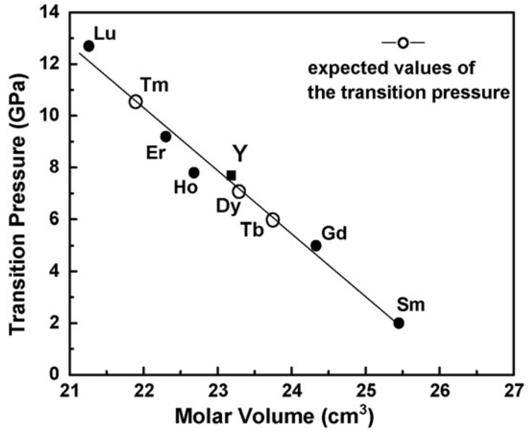

Fig. 3. Transition pressure as a function of the molar volume of the initial hexagonal phase.

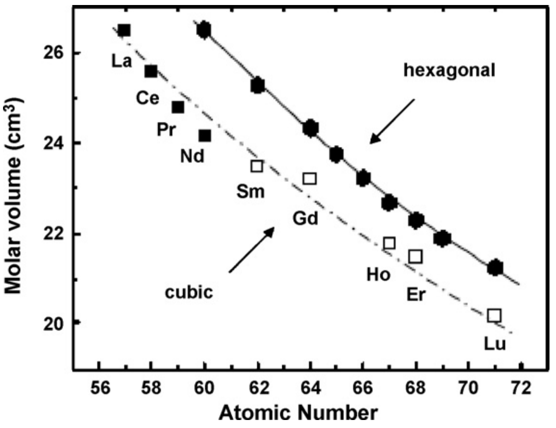

Fig. 2. Molar volume of different forms of lanthanide trihydrides as a function of atomic number. Solid and dotted lines are eye-guides only.

Though the change of minimal H–H is almost the same (~0.22 Å) for all the hydrides, the relative change of this distance increases with the atomic number of the lanthanide element. That can partly account for the tendency of the transition pressure to increase within the trihydrides. Another observation is that the value of the H–H distance before the transition varies around 2 Å. This value was proved to be crucial for many stable hydrides of d-elements by Switendick [14] and it is believed that this is the minimal distance between two positively charged hydrogen particles in a stable hydride lattice. Later on in theoretical research on the stability of LiH [15] a similar value of the H–H distance that is about 2.1 Å, was calculated to correspond to the minimum energy of the crystal lattice. The author

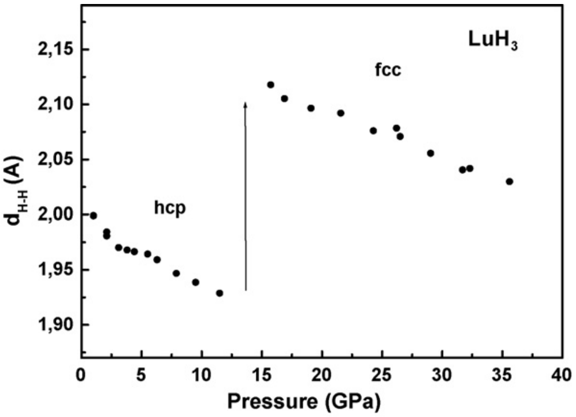

Fig. 4. The change of H–H distance ($d_{H–H}$) of LuH_3 during pressure increase.

of the research assumed a slightly negative charge for the hydrogen particles. Thus repulsive interactions increase dramatically if this distance is less than the critical one for either positively or negatively charged hydrogen particles. However the exact value of the crucial distance may vary and it is logical to assume that it may depend on the radius of the hydrogen particles. The smaller hydrogen particle can come closer to each other reaching the same repulsive effect. Lanthanide hydrides can be characterized as positively charged metal cations with negative hydrogen particles which occupy tetrahedral and octahedral interstices. The negative charge of hydrogen particles was observed earlier in electromigration measurements [16]. The fact that the minimal H–H distance before the transition is close to 2 Å can account for the instability of the initial hexagonal phase of the trihydrides under investigation.

The shortest hydrogen separation in trihydride of Y before and after the transition also follows the tendency of lanthanide hydrides. The change of minimal H–H is almost the same (~0.22 Å) for all the hydrides

3.2. Compressibility measurements

Before analyzing compressibility data it is worth mentioning a principal assumption and model used to evaluate equations of state (EOS). In search of the best fit, experimental data were fitted with different models. The main conclusion of such a procedure was that within the error bar all the models resulted in more or less the same fit, which was close to that of Murnaghan's EOS. In order to evaluate reasonable and comparable values of bulk modules (B_0) the assumption of a constant first pressure derivative of bulk modulus ($B'_0 = 4$) was made. Moreover we assumed that B'_0 did not change after structural transition. In the light of recent research on pressure transmitting media [17] all the assumptions made are justified for we have used mineral oil. As it was shown in that recent report, using mineral oil does not provide the perfect hydrostatic conditions, therefore compressibility data inevitably should be relatively less correct due to creation of stresses. While some reservations should be held for absolute values of bulk modulus generally they change little with atomic number of corresponding element. There is also an evident tendency of bulk modulus to increase after the transition. Though the values of bulk modulus of particular lanthanide trihydrides are different, the difference is almost negligible when we compare them with the bulk modulus of YH_3 (see Fig. 5 and Table 2).

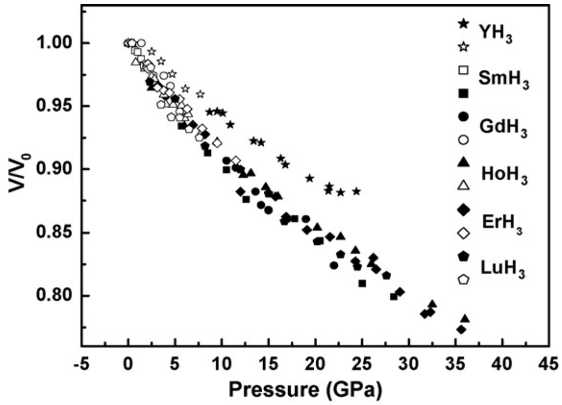

Fig. 5. Change of the reduced molar volume of yttrium and lanthanide trihydrides with pressure.

Note that YH_3 definitely does not follow the tendency of other lanthanide trihydrides. Its compressibility resembles the compressibility of d-metal hydrides. This is not surprising, since Y is a d-metal and unlike lanthanide elements does not possess an f-shell. Recent measurements have shown however that the compressibility of yttrium trihydride is more likely that of other rare earth hydrides. Whether it is results of nonhydrostatic conditions in our measurements or influence of hydrogen on the sample composition in the Japanese studies is not clear.

Empty symbols correspond to the hexagonal phase while solid ones to the cubic phases. The problem whether the new phases are metallic has been partially solved by Japanese group for the yttrium trihydride [11]. However a few question marks remain. First is why the closing optical gap is observed at the pressure of about 15 GPa above the transition point. Second concern the influence of hydrogen, used as a transmitting medium on the properties of new cubic phase, particularly on the hydrogen concentration in the sample. The measurements of electrical conductivity and reflectivity in a wide energy range, especially near the infra red region, should give more relevant information that could support their very interesting findings. The unit cell volume of the high pressure phase approaches the value of that for metallic dihydride that is only slightly higher than the volume predicted for metallic trihydride by theoretical studies acting in favour of this idea.

It is worth noting that the product of ΔV_p calculated at the transition points is almost the same for gadolinium, holmium and erbium and is equal to ~6.6 kJ mol^{-1} of hydride, while

Table 2
Transition pressure, parameters of equation of state and volume changes due to phase transition of the investigated trihydrides

Hydride	Pressure (GPa)	B_0 (GPa)		ΔV at transition (cm^3/mol)	ΔV up to transition (%)
		Hexagonal	Cubic		
SmH_3	~2.0	70 ± 4	80 ± 4	2.3	2.1
GdH_3 [10]	~5.0	80 ± 2	78 ± 4	1.3	6.5
HoH_3 [10]	~8.0	87 ± 3	90 ± 2	0.9	7.2
ErH_3[a]	~9.2	77 ± 4	81 ± 3	0.8	8.5
LuH_3 [10]	~12.0	90 ± 3	89 ± 4	1.2	9.6
YH_3 [9]	~7.7	142 ± 3	145 ± 5	1.0	4.5

[a] The values of transition pressure and parameters of EOS presented in our previous papers [18] and [19] were carefully revised.

for lutetium it is significantly higher (∼14.6 kJ mol^{-1}). At the moment no convincing explanation for this difference can be offered.

As for the investigations on the fcc trihydride formation by synthesis from the mixture of corresponding rare earth metal and magnesium [9] or by the sputtering technique [8], the striking feature is that these phases remain stable at normal pressure while our results clearly show the complete reversibility of the transition. How it is possible that the surroundings of magnesium hydride can locally sustain pressure of the order of GPa's to keep the grain of the fcc phase stable remains difficult to understand. If there are high activation barriers then annealing at higher temperature should cause the fcc phase to return to the hcp one. To our knowledge no such attempt has been undertaken so far. Another big question is how other properties of the fcc phase, like for instance optical properties, are affected by the presence of such huge stresses.

4. Summary

High-pressure X-ray diffraction studies of the number of hexagonal rare earth trihydrides (REH_3) have been carried out in a diamond anvil cell up to 35 GPa at room temperature. A reversible structural phase transformation from the hexagonal to cubic phase has been observed for the Sm, Gd, Er, Ho and luthetium trihydrides. The same type of phase transition has been found also for yttrium trihydride. The lattice parameters of the new cubic phases and the volume changes at transition points were determined for the all compounds investigated. The parameters of the equation of state for all the hexagonal and cubic phases have been determined in the pressure range up to 30 GPa. The role of H–H repulsive interaction as a probable promoter of the transition and a systematics of transition is discussed.

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