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Phase stability of some rare earth trihydrides under high pressure



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ABSTRACT

Phase stability of lanthanum, gadolinium and erbium trihydides have been studied at high pressure in diamond anvil cell. Raman high pressure studies up to 40 GPa of lanthanum trihydride and deuteride have shown more complex spectra than one can expect from the factor group analysis for stoichiometric LaH₃. Our studies have shown that the stoichiometric lanthanum trihydride and deutride undergo pressure induced phase transformation presumably of hydrogen ordering origin.

Investigations of the phase stability of erbium and gadolinium trihydrides have been performed using argon as pressure transmitting medium in Raman scattering method. The same medium has been used for X-ray diffraction analysis under pressure for erbium trihydride. Significant difference in the transition pressure as compared to earlier results obtained in quasi hydrostatic conditions has been noticed both in X-ray and Raman scattering measurements. Deviatoric stresses present in earlier nonhydrostatic measurements can be blamed for its discrepancy.

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Introduction

Hydrogen-rich materials have attracted a lot of attention in the last decades mainly as potential hydrogen storage materials. As an important class of such compounds, metal hydrides have been considered. Beyond being regarded for hydrogen storage, metal hydrides offer the attractive physical properties to be potentially used in the electronics and other applications.

In this respect the family of rare earth hydrides seems to be very promising, especially that the physical properties of these hydrides can be tuned by hydrogen concentration from the metallic to semiconductors behavior. Reaction of hydrogen saturation is reversible, so the switching for metal to isolator and vice versa can be realized by changing hydrogen pressure over the metals. This phenomenon has been presented by Griessen et al. in their famous Nature paper [1].

Another stimulus for the study of these systems was the discovery of pressure induced phase transformation in a row of rare earth trihydrides [2], which attracted a lot of attention from both experimentalists and theoreticians as well [3–10]. It is commonly accepted that the pressure induced structural transformation in this trihydrides is result of the hydrogen-hydrogen interaction in metal lattice in accordance with Switendick criteria [11]. Mechanism of this transformation has been described in details by Machida et al. [9] as a result of long-period stacking structures that consist of cubic and hexagonal planes. Rare earth hydrides quite recently became

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the object of investigations as a components of complex hydrides for hydrogen storage [12,13].

Lanthanum trihydride has been selected for the measurements because to our knowledge Raman scattering under pressure has not been performed so far on this stoichiometric compound. Lanthanum trihydride has cubic, sometimes referred to as BiF₃ structure according to [14]. Therefore, according to group factor analysis only one Raman active mode should be present. Our preliminary measurements have shown quite rich Raman spectrum coming from LaH₃ sample. It should be mentioned that the X-ray diffraction study by Boroch et al. [15] preformed on stoichiometric lanthanum trihydride has shown additional to the peaks indexed as fcc structure quite intense peaks of unknown origin.

Our preliminary study of high pressure Raman scattering study on lanthanum trihydride have shown interesting phase transition unknown up to now. We suggest that this transition could be similar to that observed in the heat capacity measurements at low temperature [16]. The superstructure lines in the neutron diffraction pattern and X-ray measurements of stoichiometric LaD₃ has been reported also by Udovic et al. [17,18] for stoichiometric lanthanum trideuteride at temperature about 260 K. These results suggest the appearance of a low temperature phase transformation presumably of the second type of order which was interpreted as due to an ordering of the D atoms on off-centre positions in the octahedral interstices of the metal atom network. It was also postulating that a long-range-ordered pattern of displacements of the La metal atoms from the ideal fcc symmetry was occurring in addition to long-range-ordered displacements within the D sublattices.

As it is commonly known that the value of transition pressures depend on the hydrostaticity within diamond anvil cell, we decided to check how the transmitting media influence the determination of transition pressures of erbium and gadolinium trihydrides by using gaseous argon loaded at high pressure together with the corresponding specimens.

Materials and methods

Samples of trihydrides and lanthanum deuteride, gadolinium and erbium trihydides were obtained from nominally 99.9% pure metals by direct absorption under the gaseous hydrogen and deuterium pressure of 15.0 MPa and 300 °C during 4 h in a high pressure Sieverts apparatus as described earlier [19]. The purity and predicted structure of the samples used for high pressure studies have been confirmed by powder X-ray diffraction and elemental analysis before loading in diamond anvil cell (DAC).

Initial sample has been analyzed using X-ray diffraction method while composition has been determined by weighting sample of about 1.5 g before and after charging it with hydrogen. Value of 3.00 ± 0.03 in atomic ratio H/La has been obtained. X-ray diffractogram of lanthanum trihydride is shown in Fig. 1. Similar pattern was obtained for lanthanum deuteride. According to Klavins et al. [20] lattice parameter determined in our measurements as equal 5.619 Å corresponds to stoichometric trihydride of lanthanum.



Fig. 1 – XRD pattern of the initial LaH₃ sample (black), its Rietveld fit (red) and fit residue (blue). Ambient conditions, CuK α radiation. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

X-ray diffraction pattern of initial sample of erbium trihydrides taken outside of diamond anvil cell is shown in Fig. 2.

Lattice parameter shown in Fig. 2 is exactly the same as reported for stoichometric erbium trihydrides by Ref. [21] and no contamination of the sample has been noticed.

The high pressure X-ray diffraction studies were conducted at custom made facilitates that operates in energy dispersive X-ray diffraction mode.

Samples were loaded into 200 μm hole in the rhenium gasket preindented to a thickness of ~50 $\mu m,$ along with a



Fig. 2 – XRD pattern of the initial ErH_3 sample (black), its Rietveld fit (red) and fit residue (blue). Ambient conditions, CuK α radiation. Due to a strong texture the (002) peak was excluded from the refinement, as shown by the gray shadowed area. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

small ruby chip at the center of the sample. The pressures were then calculated using the ruby (R_1) fluorescence method.

Raman spectra were collected in backscattered geometry using custom designed setup for micro-Raman measurements based on monochromator Jobin Yvon THR1000 equipped with a single grating (with 1200 grooves mm^{-1}) giving a resolution of ~1 cm⁻¹, notch filters (Keiser Optical Systems) and thermoelectrically cooled (-65 °C) (Peltier effect) CCD (Horiba Synapse) detection. He-Ne laser (Melles-Griot) line 632.8 nm was used for sample excitation.

For the high pressure X-ray and Raman measurements performed on erbium and gadolinium trihydrides we used argon as a pressure medium inside diamond anvil cell using the method described earlier with starting pressure of about 0.5 GPa [22]. Measurements of lanthanum trihydride were done in paraffin oil which served both as a pressure medium and protection against oxidation. Lanthanum trihydride is most sensitive to oxygen and moisture among the rare earth trihydrides family.

Results and discussion

Raman studies on lanthanum trihydride and trideuteride at high pressure

The modes including acoustic and optical ones have been detected at ambient pressure for hydride and deuteride samples and are presented in Fig. 2. Whether or not these additional modes are hydrogen related we performed substitution of hydrogen by deuterium. Such a replacement should result in the shift of corresponding modes by quasi-harmonic factor of $\sqrt{2}$. All modes were identified as being hydrogen related as isotope effect shows value of 1.41 for optical part of spectrum as presented in Table 1.

Modes coming from possible surface contamination presumably by oxide layer should not display isotope effect. Data at ambient pressure were recorded outside of DAC.

Fig. 3 shows the spectra of LaH₃ and LaD₃ recorded at ambient condition. The modes below 250 cm⁻¹ were caused by the metal lattice vibrations due to the same locations in both hydride and deuteride. Specifically, the Raman modes which are labeled as 1 and 2 were attested to possessing the isotope shift by approximately $\sqrt{2}$. Since the Raman modes above 250 cm⁻¹ of LaH₃ presents the similar shape to that of LaD₃ and two modes possess the isotope shifts, the lines above 250 cm⁻¹ were confirmed to originate from hydrogen related vibrations. It is worth noting that the BiF₃- type structure ought to possess only one active Raman mode predicted by the factor group analysis. In the cases of LaH₃ and

Table 1 – Isotope effect of LaH_3 and LaD_3 at ambient condition.			
	ω_{LaH3}	ω_{LaD3}	$\omega_{LaH3}/\omega_{LaD3}$
Lattice modes	183.2	182.0	1.01
	111.5	111.3	1.00
	150.1	150.4	1.00
H modes	704.7	500.6	1.41
	1128.8	800	1.41



Fig. 3 – Raman Spectra of LaH_3 and LaD_3 at ambient condition.

LaD₃, many peaks are shown in the Raman spectra even though the peaks are considerably broadened due to the combination of several modes. Raman spectra of both LaH₃ and LaD₃ recorded at ambient and under high pressure are presented in Fig. 4. As always strong Raman signal of diamond at 1331 cm⁻¹ limits the region of data collection.

Phase transition connected with the hydrogen ordering similar to the low temperature phase transition reported in Ref. [16] is observed at pressure range from 6 to 11 GPa. This is clearly seen in Raman spectra evolution and from the shift of selected Raman modes as function of pressure as presented in Figs. 4 and 5, respectively. It should be pointed out that the earlier high pressure X-ray study on stoichiometric lanthanum trihydride [23] performed up to 25 GPa did not revealed any structural phase transition. Since the composition of both compounds have been determined as very close to stoichiometry the known tetragonal distortion notice at low temperature and high pressure should also be excluded as this transformation is restricted to the hydrogen concentration range from 2.65 to 2.90 in atomic ratio [20]. So the observed transition must originate from the hydrogen particles ordering rather than from the lattice rearrangement.

X-ray and Raman studies of erbium and gadolinium trihydrides

Fig. 6 shows the selected spectra of erbium trihydride under pressure taken in diamond anvil cell.

Initial spectrum taken at 0.6 GPa (black) is indexed as hexagonal phase and the highest spectrum indexed as cubic phase (red) was taken at pressure over 20 GPa. Clearly at the pressure of 12.6 GPa we have still almost pure hexagonal phase while at pressure above 18.5 GPa transition to cubic phase is completed. Transformation is reversible and hexagonal structure of the sample is recovered at ambient pressure.

As can be seen the hexagonal phase persists to pressure of about 13 GPa. This value is significantly higher than that



Fig. 4 - Raman Spectra of (a) LaH₃ and (b) LaD₃ at selected pressure during compression.



Fig. 5 – Pressure dependence of Raman frequencies of LaH₃ during compression.

(around 8 GPa) determined earlier where the paraffin oil was used in X-ray studies.

Raman studies on erbium and gadolinium trihydrides at high pressure

Raman scattering of erbium and gadolinium trihydrides have been performed up about 20 and 15 GPa respectively both on compression and decompression course. Phase transitions which were observed at about 14 and 5 GPa have appeared to be complete reversible. Evolution of Raman spectra for both compounds under pressure are shown in Fig. 7. As one can see the spectra consist of two parts one low energy side linked to the lattice modes and higher energy part which is hydrogen related oscillations located in tetra- and octahedral position in metal lattice. Interactions of the hydrogen in the metal lattice



Fig. 6 – Evolution of the X-ray diffraction patterns of ErH_3 for the selected pressures taken at room temperature. Peaks at low energy range correspond to the L-fluorescence lines of tungsten coming from the X-ray target tube used.

are responsible for the pressure induced phase transformation as discussed in Ref. [2]. Shift of these modes with pressure was used to determine region of phase stability of both compounds. Results are shown in Fig. 8 a and b.



Fig. 7 – Raman spectra of the sample ErH_3 and GdD_3 taken in argon as a pressure transmitting medium during both increasing and decreasing of pressure.



Fig. 8 – Pressure dependence of Raman frequencies of (a) ErH₃ and (b) GdH₃ during compression. Perpendicular dash dot lines indicate estimation of the transition pressures from hexagonal to cubic phases.

Transition pressure for erbium trihydrides estimated from X-ray diffraction measurements and Raman scattering are quite consistent giving average value of about 14 GPa as compared to 8 GPa determined from X-ray measurements preformed in paraffin oil [2]. As a transition pressure we consider pressure at which hexagonal symmetry is diminishing both in X-ray and Raman experiment. For gadolinium this pressure was estimated as equal of about 5 GPa.

If we compare these values with the results of earlier studies where the paraffin oil was used as transmitting medium we observe for erbium trihydride large difference in transition pressure while for gadolinium trihydride these values are almost the same. We think that the reason for such behavior is that the paraffin oil provides hydrostatic condition in the limited pressure range. Since the transition pressure for gadolinium is relatively low, about 5 GPa, paraffin oil remains relatively soft but for the pressure of about 14 GPa, required for the phase transition in erbium trihydride, it become stiffer resulting in the large deviatoric stresses across the sample. It is experimentally proved that the deviatoric stresses decreases transition pressure in many pressure induced phase transitions [24–27].

Conclusions

High pressure Raman measurements on lanthanum trihydride and deuteride have shown pressure induced phase transition at pressure range from 6 to 11 GPa. This transition can be compared to the similar phase transition observed in low temperature region by heat capacity, neutron and X-ray diffraction measurements performed on stoichiometric lanthanum trihydride and trideuteride.

Raman scattering method has been used for the investigations of phase stability at the high pressure in the erbium and gadolinium trihydrides. X-ray and Raman studies performed on erbium and gadolinium trihydrides at high pressure have also shown importance of the type of transmitting media used in diamond anvil experiments. Our data proved that the quasi hydrostatic conditions, in our case paraffin oil, decreased the pressure of phase transition observed in erbium trihydrides by about 5 GPa.

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