Crystal structures of novel lanthanum superhydrides

M. A. Kuzovnikov[1;2*], A. P. Drozdov[1], P. P. Kong[1], V. S. Minkov[1], S. P. Besedin[1], V. B. Prakapenka[3], E. Greenberg[3], D. A. Knyazev[1] and M. I. Eremets[1]

[1]*Max-Planck Institut für Chemie, Hahn-Meitner Weg 1, 55128 Mainz, Germany*
[2]*Institute of Solid State Physics RAS, Chernogolovka, Moscow District, 142432, Russia*
[3]*Center for Advanced Radiation Sources, University of Chicago, 5640 South Ellis Avenue, Chicago, Illinois, 60637, USA*

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*e-mail: m.kuzovnikov@mpic.de

After the discovery of the superconductivity in the sulphur-hydrogen system at temperatures as high as 200 K [1], there was a renewal of an interest towards the fundamental properties of hydrides, which are dominated by the presence of high-frequency optical phonons of hydrogen vibrations.

Until present, the highest hydrogen content among all hydrides was observed in the La-H system [2] for LaH_{10} superhydride. Fcc-LaH_{10} was proven to have exceptional superconductive properties, with claimed T_c value to be above 260 K [3], or about 250 K in later, more accurate measurements [4]. These observations confirmed earlier theoretical predictions of high-temperature superconductivity in fcc-LaH_{10} [5,6].

The calculations predicted that fcc-LaH_{10} is dynamically stable only at pressures above 210 GPa [6], and below this pressure there should be a rhombohedral distortion of the fcc crystal structure of LaH_{10}. Fcc-LaH_{10} was experimentally observed down to 160 GPa [2], and a distortion was observed in its crystal structure at lower pressures [2]. However, the suggested distortion scenario disagrees with the observed XRD data.

Apart from LaH_{10}, a series of other La superhydrides was synthesized in [2] at around 120-130 GPa. These include superhydrides with bcc and A15 (incorrectly identified as C2/m) crystal structures and at least two unidentified phases.

It should be noted that in the pressure range of interest the pressure scale used in [2], based on the edge of the Raman peak from the diamond anvil, systematically overestimates pressure by about 10-30 GPa comparing to the pressure scale, based on the H_2 [7] or D_2 [8] vibron frequency. We employed the latter pressure scales below. Presumably, pressure overestimation was the reason why the apparent lattice volume of fcc-LaH_{10} in [2] was the same as the sum of the volumes of La and $5H_2$, which would violate the le Chatelier's principle.

In present work we report on the XRD study of the La-H and La-D systems in pressure range 127-163 GPa, where we observed a number of $LaH(D)_x$ phases, with most of them being new. These include, in the order of decreasing H(D)/La content:

a) Distorted primitive simple cubic sc-$LaH_{\sim 12}$ with a=3.30Å at 159 GPa. This phase is semitransparent, and, judging from its Raman spectrum, it contains molecular H_2 units. The exact distortion nature is unclear, with the most affected by the distortion peaks being (100) and (200).

b) fcc-$LaD_{\sim 11}$ with a=5.26Å at 127GPa.

c) P4/nmm-LaD_{11}, which has a tetragonally distorted fcc lattice with a=3.73Å c=5.10Å at 142GPa, predicted in [5].

d) fcc-$LaH(D)_{10}$ with a=5.10Å at 150GPa, discovered in [2].

e) orthorhombically distorted fcc-LaD_{10} with a=3.74Å b=5.18Å c=3.60Å (tentative space group Pmmn, atomic coordinates La 2a (0 0 0.18)) at 131GPa. The distortion splits the (111) peak of fcc-LaD_{10}, similar to what was observed for LaH_{10} below 160GPa (diamond pressure scale) in [2].

f) hcp-$LaH(D)_{10}$ with a=3.62Å c=5.91Å at 150GPa.

g) hcp-II-$LaH(D)_{\sim 9\text{-}10}$ with a=3.75Å c=5.58Å and unusually small c/a≈1.49 ratio at 131GPa. Similar phase was recently observed in the Ce-H system [9].

h) I4/mmm-LaD_4 with a=2.77Å c=5.96Å at ~153GPa, predicted for LaH_4 in [6].

i) Cmcm-LaD_3 with a=2.8Å b=6.6Å c=4.5Å at ~153GPa, predicted for LaH_3 in [5].

j) fcc-LaH_3 with a=4.36Å at ~152GPa.

k) numerous unidentified phases, most of them irreproducible.

The volumes of all observed superhydrides are plotted below as a function of pressure.

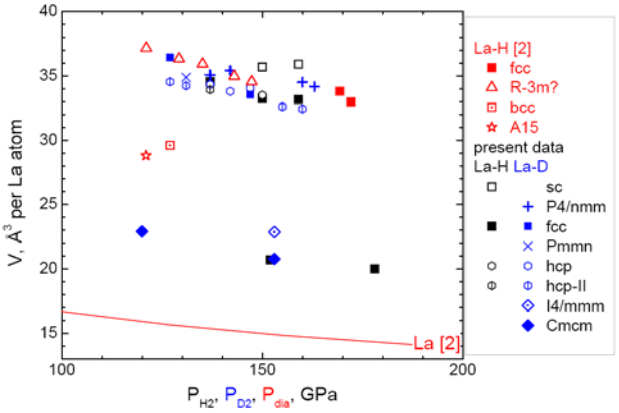

Figure 1. Volumes of various lanthanum superhydrides as a function of pressure. Please note that the pressures from [2] were likely overestimated by about 10-30GPa, and the corresponding data for La superhydrides (shown by the red symbols) should be shifted to the left with respect to the rest of data.

Cases h-k were observed in experiments with apparent H(D) deficiency after laser heating. Cases a-c were observed only in a presence of a large H(D) excess

over all sample surface. The rest of the phases were obtained in conditions when the samples were pressed between the anvils, and H(D) was present only at the sample outermost boundary. A large observed variety of superhydrides suggest that in most of the runs either $H_2(D_2)$ was in deficiency, or equilibrium was not reached.

We observed considerable difference between the La-H and La-D systems. Namely, cases a and j were observed only in La-H system, whereas cases b,c, h and i were observed only in the La-D one. We think that this dissimilarity is caused by the large difference in zero-point vibrational energies of H and D atoms in the interstitials of La lattice.

Above 150 GPa the highest observed hydride is sc-$LaH_{\sim 12}$. This puts the upper limit on the pressure, at which LaH_{10} is stable under hydrogen excess (if any). The highest deuterides, which were observed between 127-163 GPa were fcc and P4/nmm-LaD_{11}. Thus, fcc-LaD_{10} should be a metastable phase with respect to these higher deuterides in this pressure range, and, if LaD_{10} under deuterium excess has any stability field at all, this field should be located at lower pressures. Presently there is no consensus about the existence of the stability field of LaH_{10} in theory, with some ab-initio calculations [6] suggesting that LaH_{10} is stable, while the other [5] predict absence of such a stability field. No calculations were reported for the La-D system at present.

To summarize, we report on the synthesis of a series of new lanthanum superhydrides and superdeuterides under high pressure. The crystal structures of these new compounds in most cases were not predicted by theory, which suggests that more elaborate calculations are needed. We emphasize the need to distinguish between the La-H and La-D systems, which have different phase sequences. Taking into account the richness of the La-H(D) system under pressure, further experiments are needed to determine the sequence of stable phases and their stability fields, particularly, to determine if fcc-$LaH(D)_{10}$ has a stability field under $H_2(D_2)$ excess.

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