LaD_2の圧力誘起相分離に伴う新規水素化物の形成

原子力機構量子ビーム（播磨）

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本研究の一部は「水素貯蔵材料先端基盤研究事業」のもと、（独）新エネルギー・産業技術総合開発機構（NEDO）の委託を受けて行われたものである。

Outline

1. Introduction
   - high pressure studies of structural properties of rare-earth metal hydrides

2. X-ray diffraction measurement on the phase separation of LaH_2
   - decomposition into two fcc phases with different unitcell volumes

3. Neutron diffraction measurement on the phase separation of LaD_2
   - formation of NaCl-type monohydride, LaD
   - hydrogen transfer from T-site to O-site

4. Thermodynamics of the phase separation
   - first-principle calculations of formation enthalpies and phonon dispersions

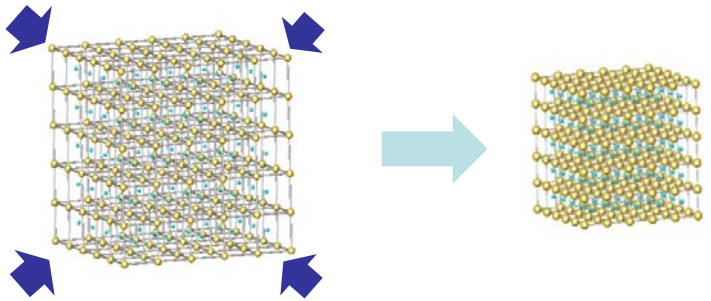
5. Summary

Introduction

High pressure for H-M systems

– key technique for studying M-H systems –

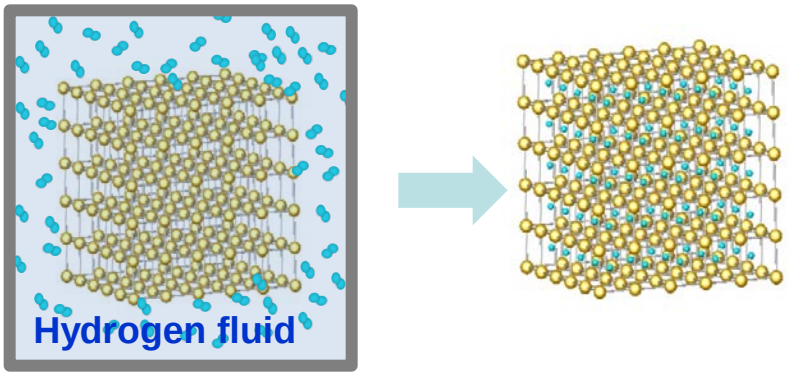
- **Produce highly densified state**



Change the M-H bondings without chemical substitution

Collapse of Westlake-rule (2Å-rule)

- **Synthesize novel hydrides**

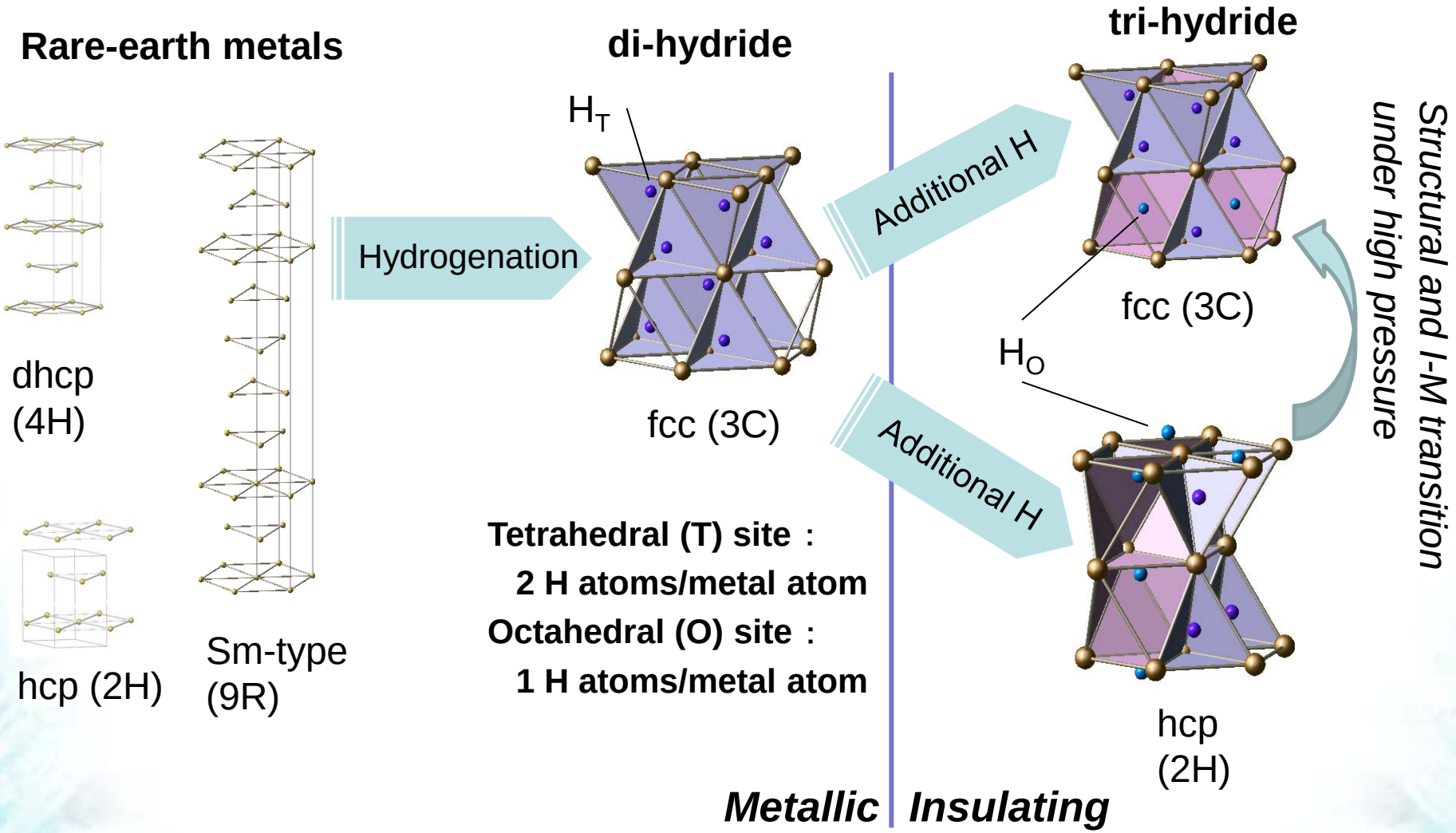


Synthesis of high density hydrogen storage materials

Hydrogenation reaction of hard hydrogenation materials

Rare-earth Material Hydrides

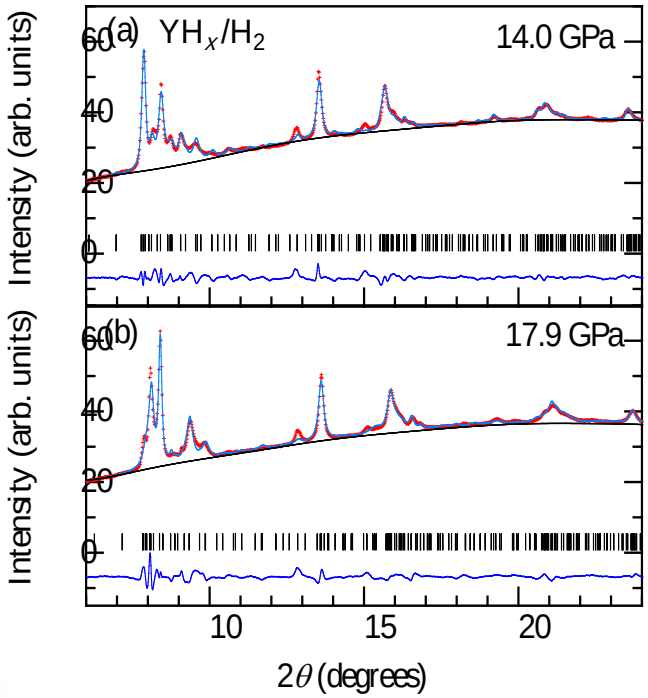
- Suitable compounds for studying the M-H interaction -



Intermediate structure bridging hex. and cubic structures of fully occupied hydrides

A. Machida et al., PRB **76**, 052101

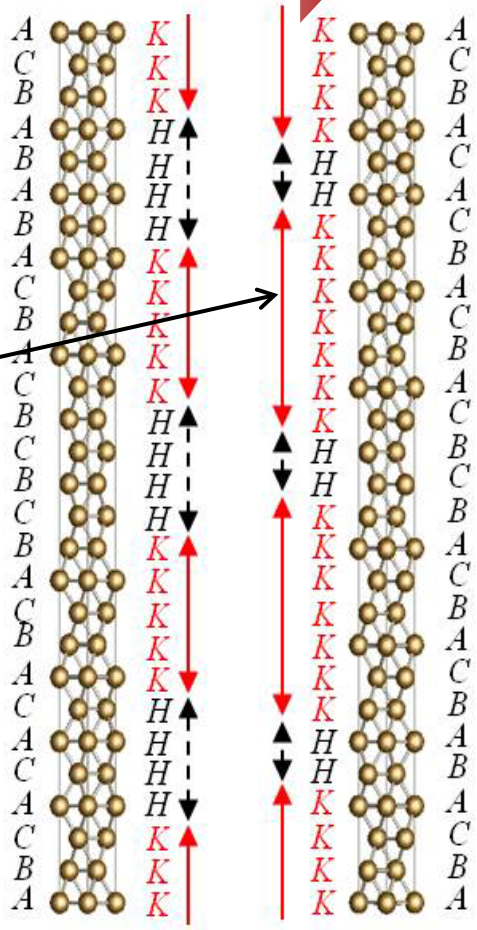
T. Kume et al., PRB**76,** 024107(2007).



High pressure

$(HHHHKKKKK)_3$

$(HHKKKKKKK)_3$

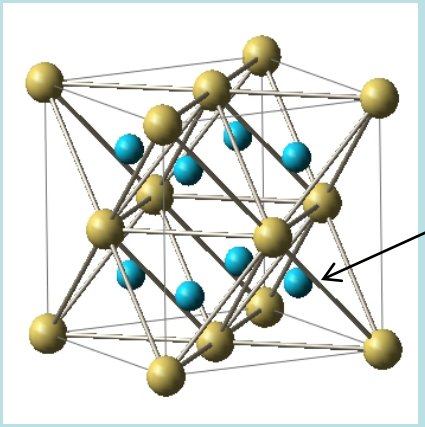


The intermediate structure is most likely a long-period metal lattice with periodic arrangements of hexagonal- (*H*-) and cubic- (*K*-) type stacking layers.

The O-site H-atoms plays essential roles in the formation of the long period structures.

Explore transition in metal hydrides accommodating hydrogen atoms partially in the interstitial sites

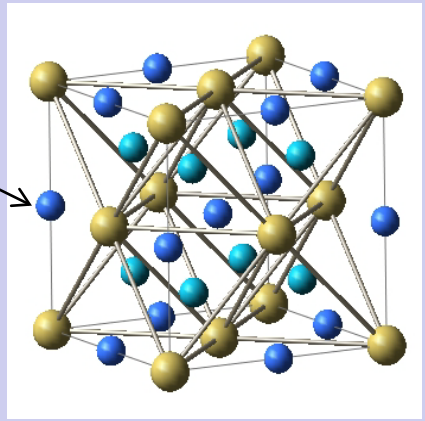
Hydrogen in FCC metal lattice



H^T

Additional H

H^O



Partially occupied di-hydride RH_2

Metal

Fully occupied tri-hydride RH_3

Insulator

High pressure

Hydrogen transfer between the T-sites and O-sites?

Lattice deformation from the cubic lattice?

Experimental –SR XRD @ SPring-8–

To investigate the variations of metal lattice

Diffractometer for Diamond Anvil Cell

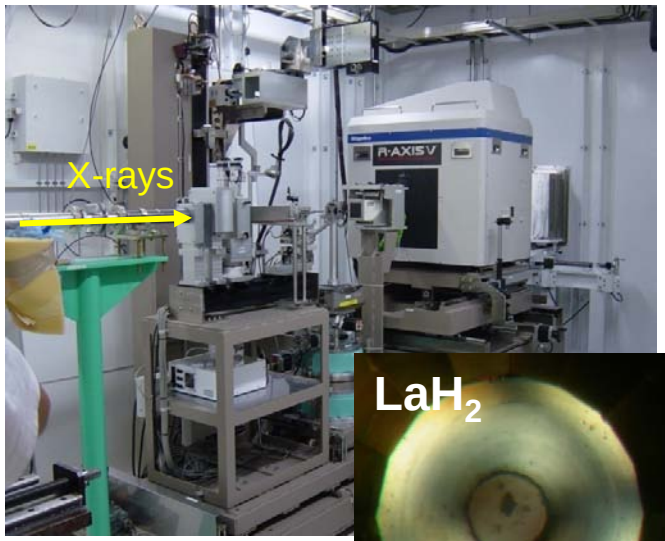
BL22XU Exp. Hutch1

Detector

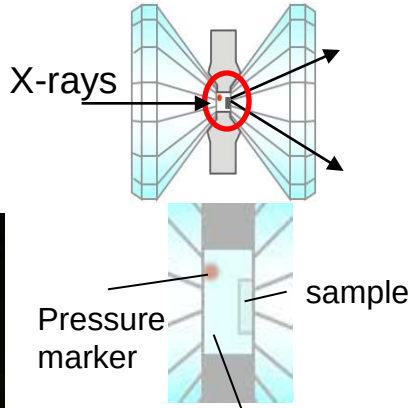
Imaging Plate (R-AXIS V, Rigaku Co.)

Size : 400×400mm²
100×100μm²/pixcel

Sample-IP distance: 200mm-730mm



DAC



Pressure medium

Helium・・・
hydrostaticity

Samples

LaH_2 (40μm*20μm*10μmt)

LaD_2 (35μm*25μm*10μmt)

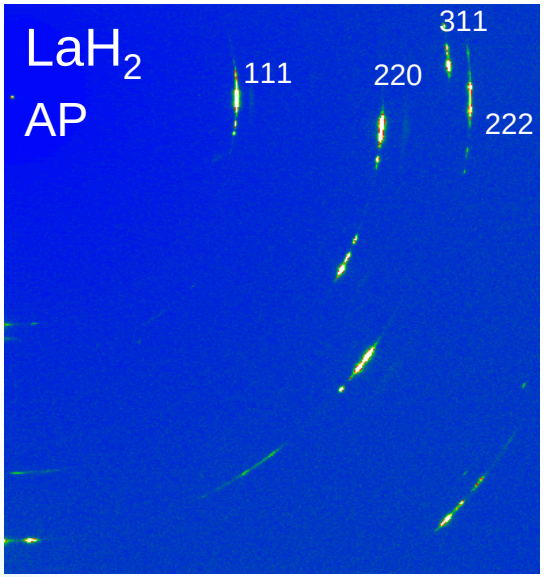
T. Watanuki, et al., Philos. Mag. **87**, 2905 (2007).

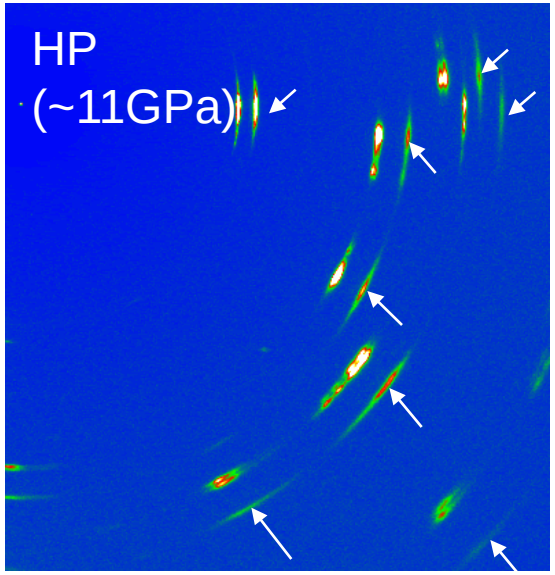
Phase separation from LaH_2 into $LaH_{2+\delta}$ and LaH_x

A. Machida et al., Phys. Rev. B **83**,054103 (2011).
Y. Sakurai et al., Solid State Commun. **151**, 815 (2011).

X-ray diffraction experiments

Additional Bragg spots appeared just outside of the original ones.





Formation of small-fcc lattice

Volume reduction ~ -17%

Ratio of reflection intensities I^s_{hkl} / I^o_{hkl} becomes almost constant above ~14 GPa.

Phase separation!

Pressure induced phase separation of LaH_2

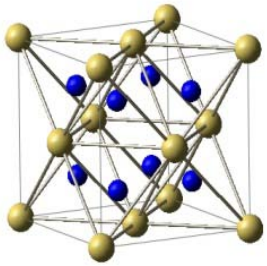
$$LaH_2 \rightleftarrows (1-\eta)LaH_{2+\delta} + \eta LaH_x$$

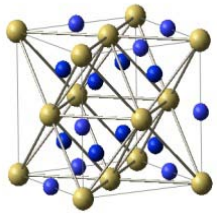
LaH_2 (metallic)

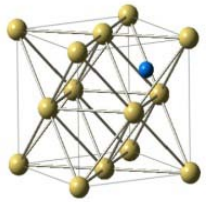
P

H rich (insulating)

H poor (metallic?)





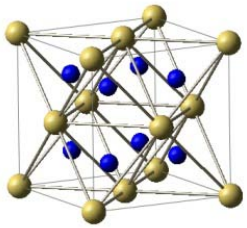


Phase diagram @AP → the solid solution phase.

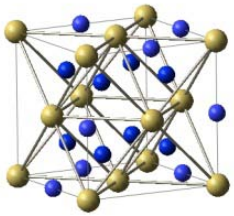
Volume difference → x~0.6, which is larger than solid solution limit (x~0.25)

Is the s-fcc phase solid solution phase?

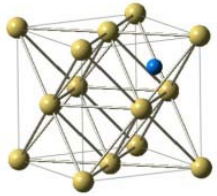
$LaH_2 \rightleftarrows (1-\eta)LaH_{2+\delta} + \eta LaH_x$



metallic

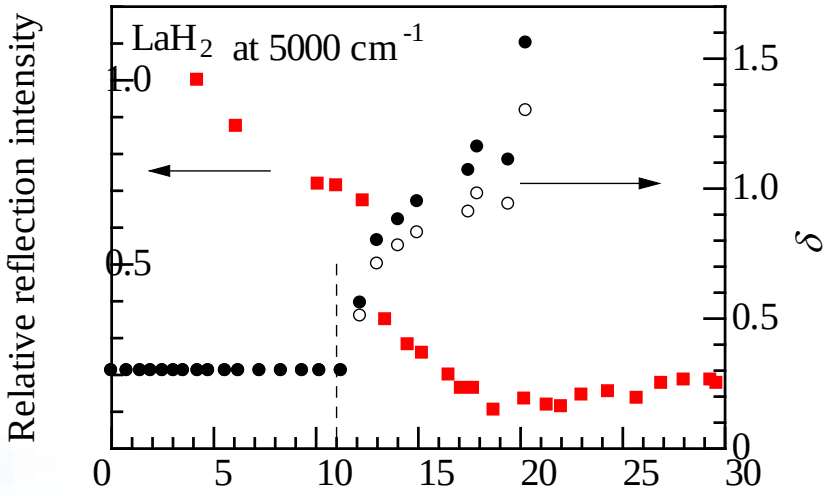


insulating



metallic?

XRD measurements are unable to determine the H-concentration and occupation sites.



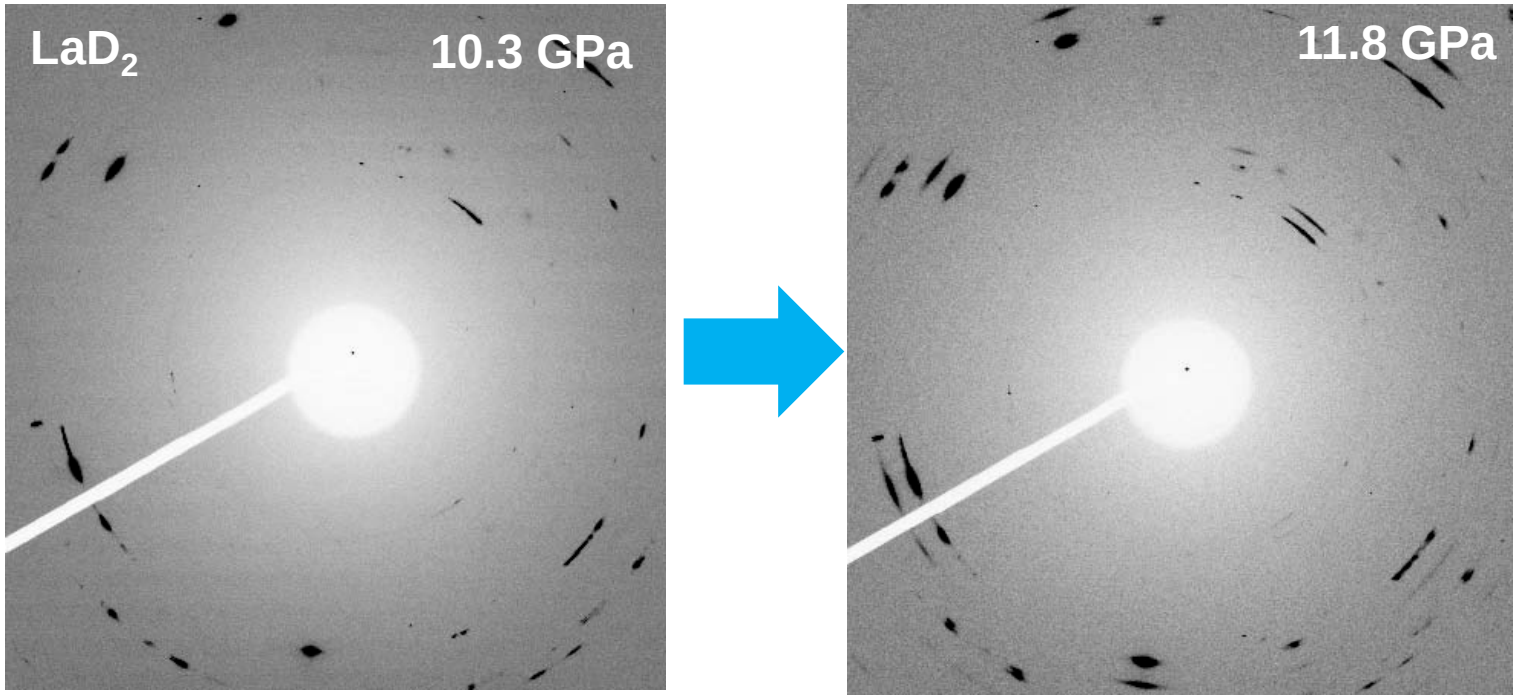
To clarify the H-states after phase separation, high pressure neutron diffraction experiments are performed.

Y. Sakurai *et al.*, Solis State Commun., **151**, 815 (2011).

Confirmation of the isotope effect

X-ray diffraction experiments on LaD_2

(LaD_2 powder was prepared by Kojima Lab., Hiroshima Univ.)

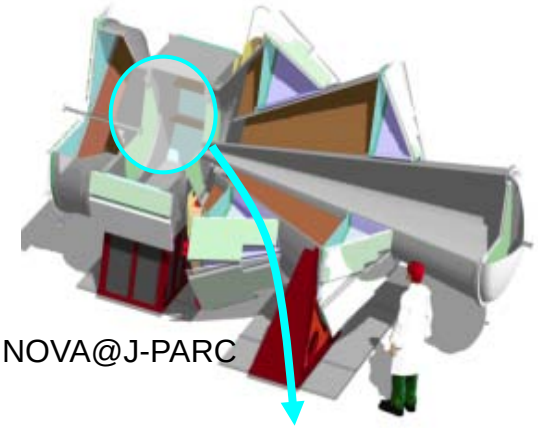


- P-induced phase separation has been observed in LaD_2.
- P_{PS} is same as the hydride.
- Structural changes is similar to the hydride.

H/D substitution does not influence the phase separation.

Experimental –NPD @ MLF, J-PARC–

To investigate the hydrogen positions

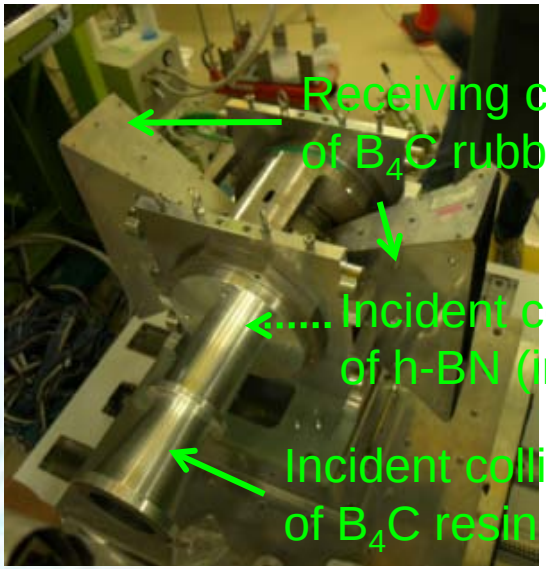


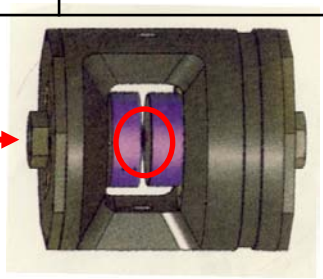
NOVA@J-PARC

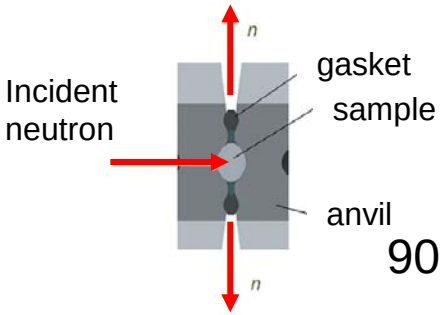
High Intensity Total Diffractometer (NOVA)

Paris-Edinburgh Press (VX4)

Anvil	single toroidal made of WC	double toroidal made of sintered diamonds
P-range	<10GPa	<20GPa
Sample volume	0.48cm^3	0.14cm^3
Measurement time	12h for 100kW	15-20h for 200kW



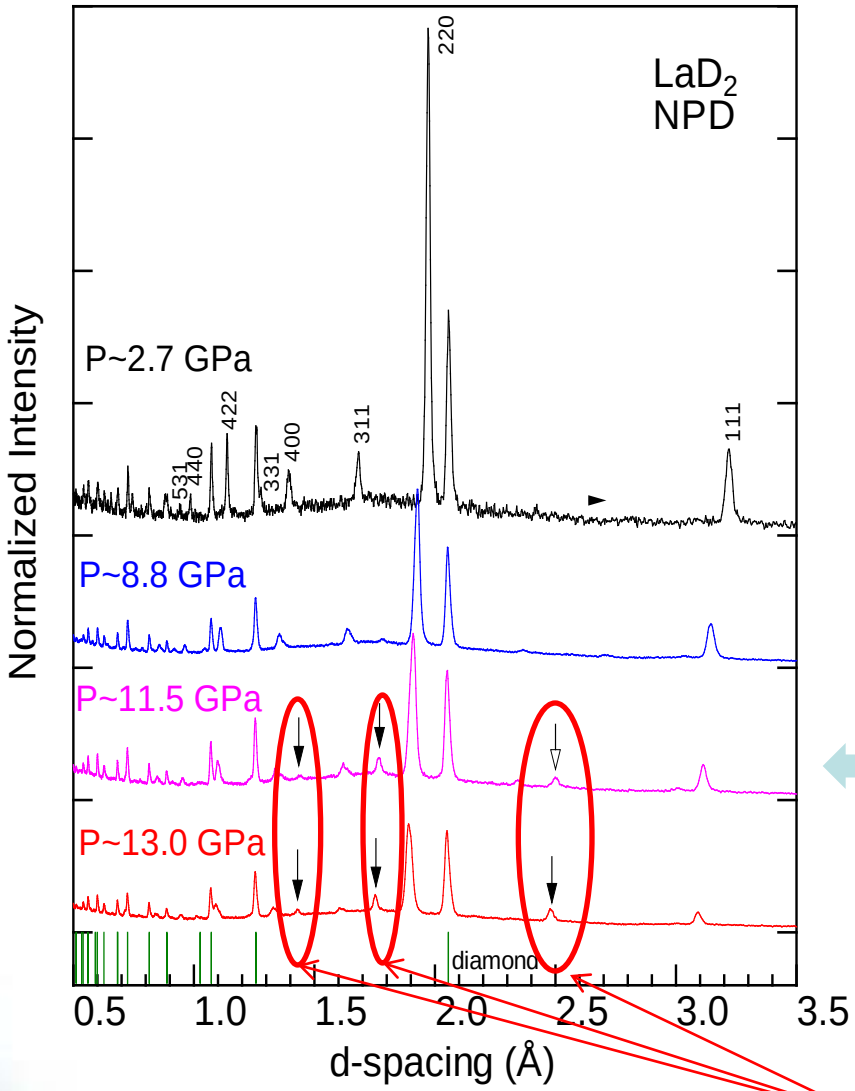




90 degrees scattering geometry

T. Hattori et al., J. Phys.: Conference Series **215**, 012024 (2010).

Pressure variation of NPD patterns of LaD_2



Anvil: double toroidal (sintered diamonds)

Gasket: Ti-Zr encapsulating

Pressure medium: methanol-ethanol 4:1 mixture

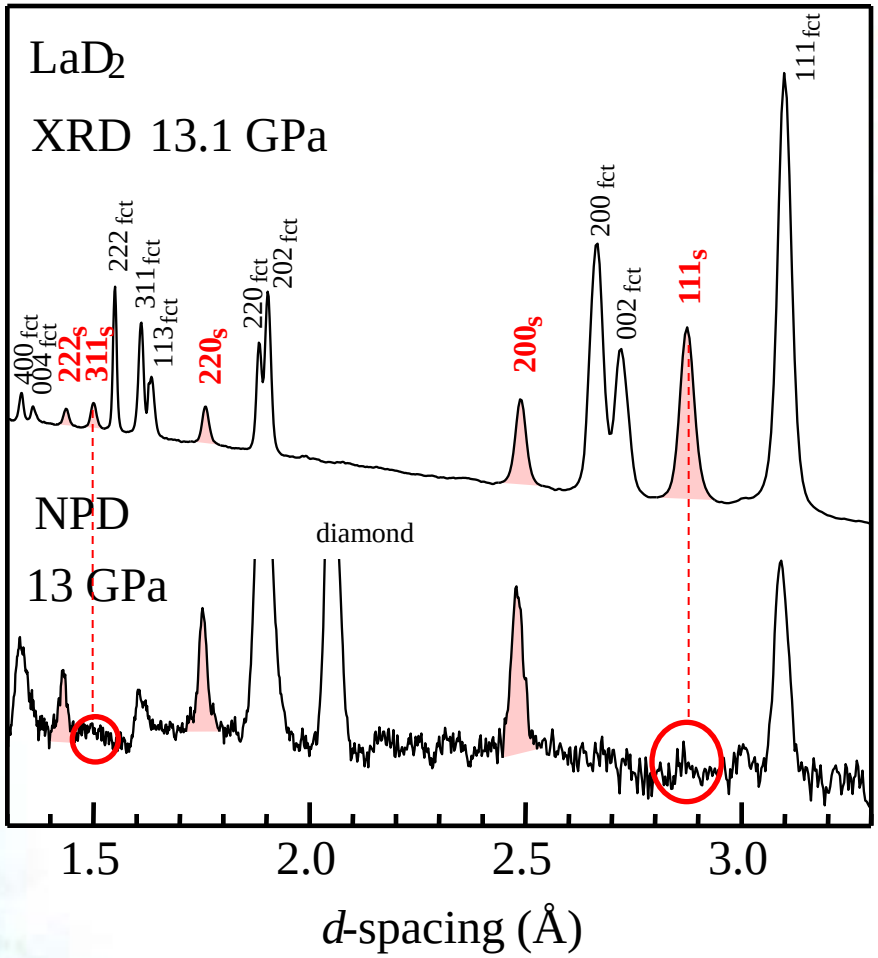
With increase of pressure, the each reflection peaks exhibit no significant broadening.

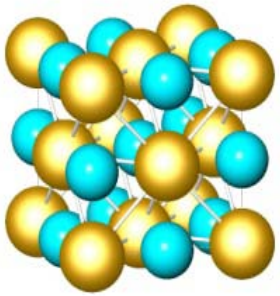
Pressurize under quasi-hydrostatic pressure

New reflection peaks appear and their intensities increase

Bragg reflections of small-fcc phase

Formation of NaCl type mono-deuteride





Occupy at O-sites only

Neutron scattering length

b_{La}=8.24 fm for La

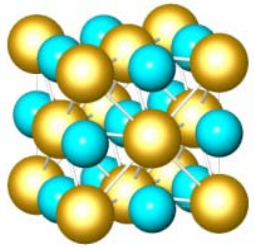
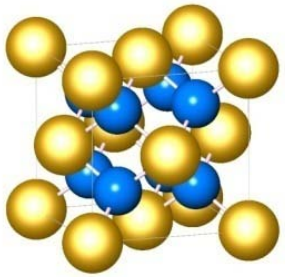
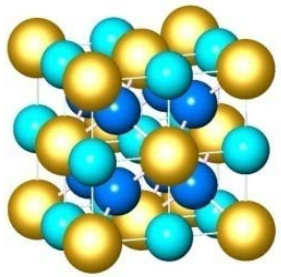
b_{D}=6.671 fm for D

Structure factor of NaCl-structure

$F_{hkl:odd}=4(b_{La}-b_{D})$ for
odd-numbers indexed peaks

$F_{hkl:even}=4(b_{La}+b_{D})$ for
even-number indexed peaks

Different concentration with common metal lattice

	LaH	LaH_2	LaH_3
Structure fcc metal lattice			
Occupation sites	O-site	T-site	O-site T-site
Nearest neighbor	H^O-La	H^T-La	H^T-La H^O-H^T

Different bonds should be made in the different state.

Summary

- LaH_2 (LaD_2) exhibits a pressure-induced phase separation starting at 11 GPa.
- The high pressure neutron diffraction experiments enable to determine the position and occupancy of the hydrogen atoms.
- Mono-hydride with the NaCl-type structure is found for the first time. (new phase in the rare-earth metal hydrides!)
- The phase separation is accompanied by the hydrogen transfer from the T-site to O-sites.
- The phase separation and stabilization of mono-hydride are well reproduced by a first-principle calculation.
- Line-up of mono-, di- and tri-hydrides opens a way to study the site-dependent bonding nature of metal hydrides.