ESRF	**Experiment title:** Novel superhydrides of rubidium and cesium	**Experiment number**: HC-4878
Beamline: ID27	**Date of experiment**: from: 20/07/22 to: 23/07/22	**Date of report**: 05/09/22
Shifts: 9	**Local contact(s)**: Bjorn Wehinger	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

KUZOVNIKOV Mikhail*

HOWIE Ross*

PENA-ALVAREZ Miriam

Centre for Science at Extreme Conditions, Erskine Williamson Building, University of Edinburgh

EH9 3FD Edinburgh UK

Report:

Goals

In this experiment, we planned to study the crystal structures, $V(P)$ equations of states, and pressure domains of stability of novel superhydrides in the Rb-H and Cs-H systems under high hydrogen pressures up to 100 GPa. Previously, DFT-based ab initio calculations predicted that RbH_9 [J. Hooper and E. Zurek, Chem. Eur. J. 18, 5013–5021 (2012)] and CsH_6 [A. Shamp et al, Inorg. Chem. 51, 9333−9342 (2012)] should form already at 2 GPa, and a cascade of phase transformations is predicted with gradually increasing hydrogen content, eventually reaching H/Me = 16 at 100 GPa.

Experimental results

The Rb-H system

We prepared four diamond anvil cells with $Rb+H_2$ samples, called S354, S361, SB085 and 7VAS. After exposing Rb to an H_2 atmosphere at room temperature in all cells we observed a formation of RbH-II (CsCl-type) with some traces of RbOH-II(*Cmcm*), as demonstrated in Fig.1a.

Cell SB085 was compressed to 20 GPa, and laser heating broke the diamond anvil.

Cells S361 and S354 were laser heated at 23 and 30 GPa, respectively, which resulted in a formation of Rb superhydrides with hexagonal close packed (hcp) and primitive simple hexagonal (sh) metal lattices, respectively. The XRD pattern of the former phase is shown in Fig.1b. The latter phase arguably matches the RbH_9 predicted in [hooper2012]. These phase transformations were accompanied by a volume increase ΔV of 30.2 and 27.9 Å^3 per Rb atom, respectively. On the basis of le Chatelier's principle, the lower bound on the hydrogen content of both phases can be set at $H/Rb > 1 + 2\Delta V/V(H_2) = 8.3$, using the volume $V(H_2)$ of pure H_2 from the literature [P.Loubeyre et al, Nature 383 (1996) 702]. Most likely, these hydrides have H/Rb = 9.

Upon compression above 15 GPa, the crystal structure of hcp-$RbH_{\sim 9}$ in cell S361 gradually develops a distortion with the *Cmcm* subgroup. After second laser heating at 24 GPa, it converts into a mixture of sh-$RbH_{\sim 9}$ and another superhydride with a diamond-like metal lattice (Fig.1c). The volume effect of this transformation is ΔV = +40.4 Å^3 per Rb atom, which corresponds to an increase in H/Rb ratio by at least 9.9.

During decompression the diamond-like-$RbH_{\sim 19}$ phase decomposes at about 15 GPa into sh-$RbH_{\sim 9}$, which in its turn decomposes at about 9 GPa into a mixture of RbH-II(sc) and hcp-$RbH_{\sim 9}$, which in its turn decomposes at around 7 GPa into pure RbH-II(sc).

The RbH-II(sc) monohydride in cell 7VAS persisted upon room-temperature compression to 94 GPa. Laser heating at 98 GPa transformed this sample into a new superhydride with orthorhombically distorted diamond-like metal lattice (Pearson symbol oI4, space group *Imma*), as shown in Fig.1d. The volume effect of this transformation is ΔV = +8.4 Å^3 per Rb atom, which implies that the H/Rb content of the new phase is at least 4.6. Decompression to about 21 GPa resulted in a decomposition of this phase into a mixture of RbH-II(sc) and sh-$RbH_{\sim 9}$, which in its turn decomposed at about 8 GPa into pure RbH-II(sc) upon further decompression.

Apart from sh-RbH_9 no other superhydrides can be matched with the predictions [hooper2012].

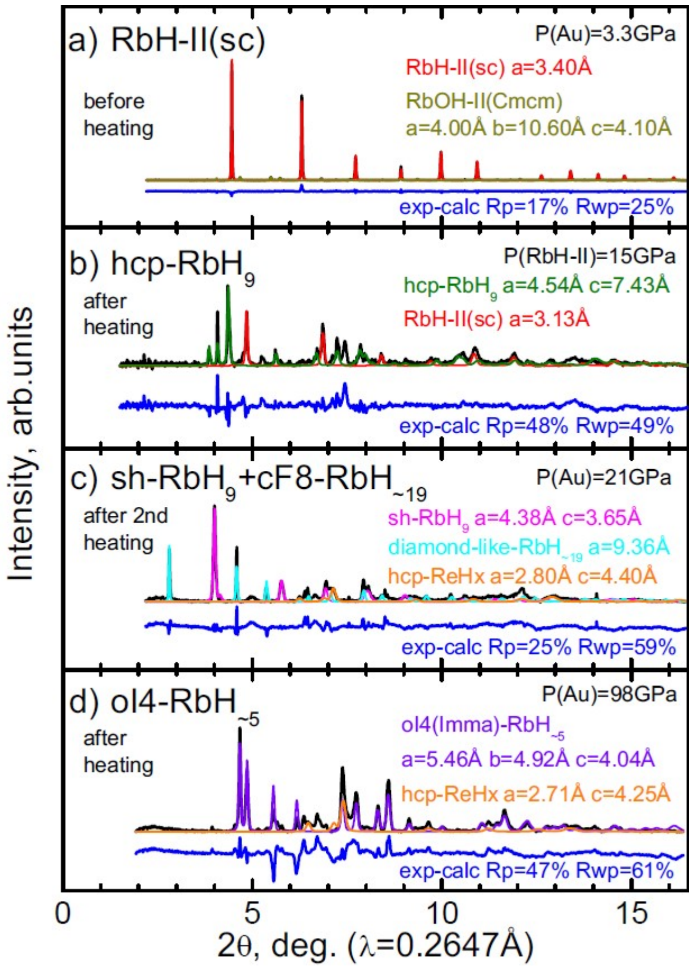

Fig.1. XRD patterns of presently studied $Rb+H_2$ samples (black curves), Rietveld refinement residuals (blue curves), and calculated contributions from individual phases (other colors). a) Typical XRD pattern of RbH-II(sc), formed after exposing Rb to an H_2 atmosphere at room temperature (cell SB085). b) XRD pattern of hcp-$RbH_{\sim 9}$, formed from RbH-II(sc)+H_2 after laser heating at 23 GPa in cell S361. c) A mixture of sh-RbH_9 + diamond-like-$RbH_{\sim 19}$, formed after laser heating the *oC*4-$RbH_{\sim 9}$(*Cmcm*) + RbH-II(sc) + H_2 mixture at 24 GPa in cell S361. d) Distorted diamond-like *oI*4-$RbH_{\sim 5}$ phase, formed from RbH-II(sc) + H_2 after laser heating at 98 GPa in cell 7VAS.

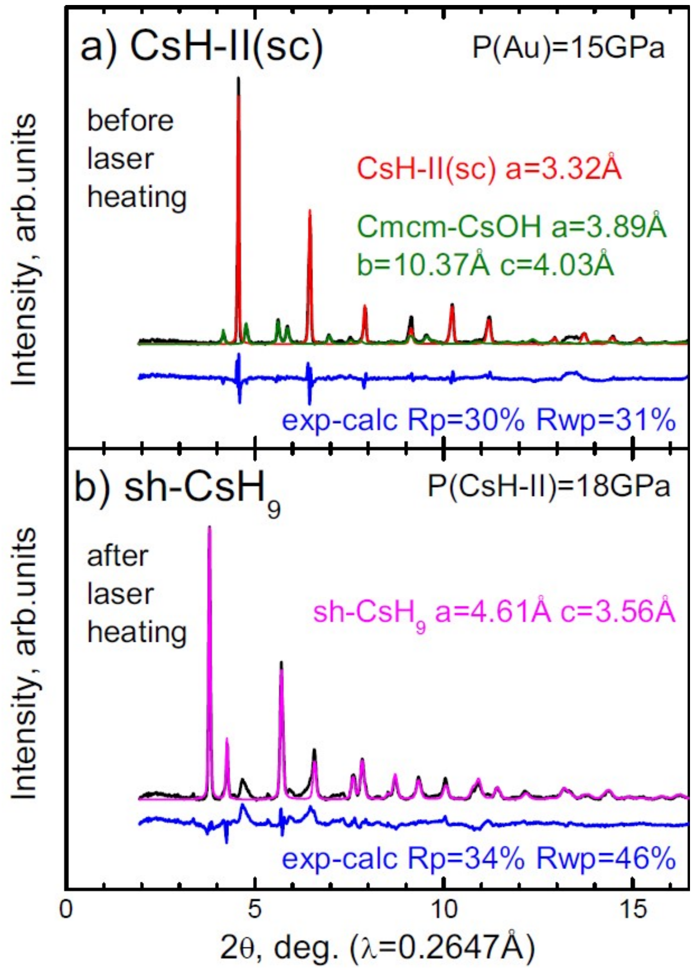

Fig.2. XRD patterns of presently studied $CsH+H_2$ sample in cell SB089 (black curves) before (a) and after (b) laser heating at 18 GPa. Rietveld refinement residuals are shown by the blue curves, and the calculated contributions from individual phases are shown by other colors.

The Cs-H system

We prepared two cells with $CsH+H_2$ samples, called SB089 and DC9. Initial samples contained CsH-II(sc) with trace amounts of CsOH-II(*Cmcm*), see Fig.2a. After compression and laser heating at 18 and 17 GPa, respectively, the samples in cells SB089 and DC9 converted into a new superhydride with primitive simple hexagonal (sh) metal lattice, see Fig.2b. The volume effect of this transformation, ΔV = +31 Å^3 per Cs atom, implies that the H/Cs content of this new phase is at least 7.9. The crystal stucture of this phase matches that of the CsH_9 predicted in [shamp2012] The sh-$CsH_{\sim 9}$ superhydride persisted during subsequent compression to 51 GPa in cell SB089, and decomposed into CsH-II(sc) after decompressing the cell DC9 to 3 GPa.