ESRF	**Experiment title:** Search for new chromium hydrides under high pressure.	**Experiment number**: HC-3390
Beamline: ID27	**Date of experiment**: from: 16/12/2017 to: 18/12/2017	**Date of report**: 27/02/2018
Shifts: 12	**Local contact(s)**: V. Svitlyk and G. Garbarino.	*Received at ESRF:*

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Report:

Pressure is expected to favor the formation of polyhydrides. In the Cr-H system, various novel hydrides are predicted stable with a stoichiometry increasing under pressure: CrH, Cr_2H_3, CrH_2, CrH_3, CrH_4 and CrH_8 [1]. The formation mechanism for these polyhydrides is also interesting: after the formation of the well-known *hcp* ε-CrH, the hydrogen fills the interstitial sites of the chromium sublattice to form CrH_x with x up to 2 and then, higher stoichiometries are obtained through a complete reorganization of the Cr metallic framework, which enables CrH_8 to form at 130 GPa. The aim of this proposal was to observe and characterize the chromium hydrides synthesized directly under pressure out of $Cr+H_2$ samples from 1 GPa up to about 150 GPa to test these theoretical DFT predictions and compare the sequence of CrH_x hydrides to those discovered in the Fe-H system at high pressure [2, 3].

We performed a detailed structural study of the chromium hydrides synthesized directly under pressure by laser heating mixtures of $Cr+H_2$ up to 120 GPa. The Cr flake was always embedded in excess hydrogen to be sure to synthesize the Cr hydride with the highest stoichiometry at each pressure. We carried out three experiments at 300 K, over different pressure ranges. The sample was annealed using a YAG laser, at various pressures to overcome the kinetic barriers (see Table 1). The temperature reached was about 1300 K. The pressure was measured using either the gold volumic or the ruby luminescence gauges. The volume was measured using angular-dispersive x-ray diffraction. The conditions of the experiments are summarized in **Table 1**.

Name	Sample	Culet diameter (μm)	Pressure range (GPa)	T (K)	P laser annealing (GPa)
Run 1	$Cr+H_2$	400	0.5 – 32	300	0.5, 3, 31
Run 2	$Cr+H_2$	300	3.5 – 42 – 0	300	3.5, 41
Run 3	$Cr+H_2$	150	3 – 120	300	30, 100

Table 1: Conditions of the three experimental runs.

The measurements of *V* vs. *P* for chromium hydrides at 300 K are plotted in **figure 1**. CrH forms above 2 GPa. Below that pressure, laser-heating the chromium sample led to a single crystal of *bcc* chromium. CrH remained the only stable phase up to 19 GPa, and was found to be metastable upon decompression. A Rietveld refinement of the integrated x-ray diffraction pattern was successfully performed in the *P6₃/mmc* space group with Cr atoms in position 2c. Cr_2H_3 appeared spontaneously at 19 GPa, with a mixture of CrH and Cr_2H_3. It was obtained pure upon decompression from 24 GPa and a Rietveld refinement of the corresponding x-ray diffraction pattern was performed in the *C2/m* space group, with chromium atoms in

position 4i. CrH_2 was formed at 31 GPa, the H atoms filling the tetrahedral sites, and remained stable up to 120 GPa, contradicting the predictions that CrH_3 should appear around 80 GPa. A Rietveld refinement of the x-ray diffraction pattern was performed in the *Pnma* space group with chromium atoms in position 4c.
This experiment was successful, as we uncovered two new hydrides (namely Cr_2H_3 and CrH_2). Unfortunately, we did not witness any transition to hydrides with H:M ratios higher than 2:1, even though they had been predicted by *ab initio* calculations [1]. We suspect that the entropy contribution, not taken into account in T = 0 K DFT calcultions, could explain the enduring stability of CrH_2.
A more extended report of these results has been submitted as an article in Physical Review B.

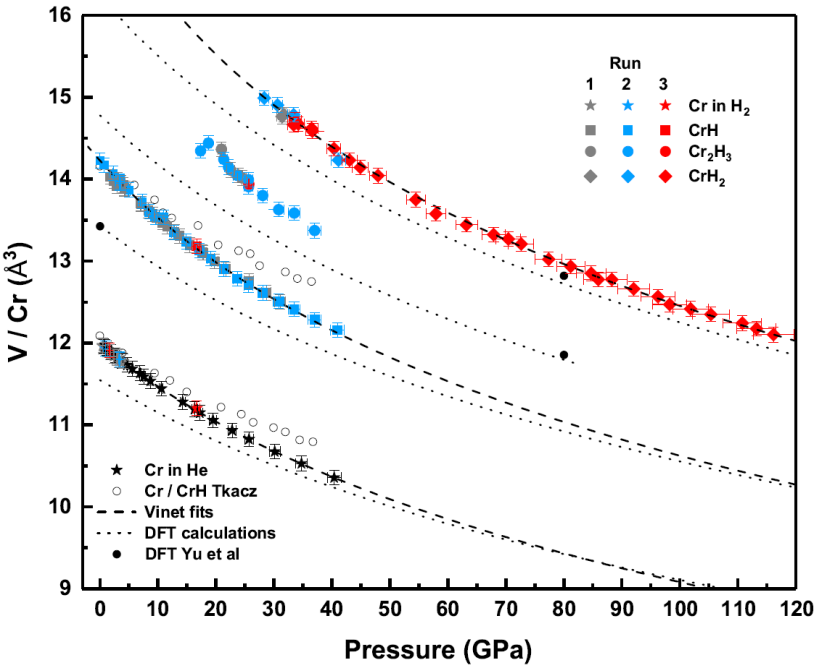

Figure 1: Evolution of the volume as a function of pressure for Cr (stars), CrH (squares), Cr_2H_3 (circles) and CrH_2 (diamonds) together with the Vinet fits of the data (dashed lines). Also presented are *ab initio* calculations (dotted lines), and data from refs 1 (calculations, black dots) and 4 (experimental, white dots).

References:

[1] S. Yu *et al.*, Scientic Reports 5, 17764 (2015)
[2] C. M. Pépin *et al.*, Physical Review Letters 113, 265504 (2014)
[3] C. M. Pépin *et al.*, Science 357, 382 (2017)