ESRF	**Experiment title:** **Structural study of Lithium Borohydride at very high pressure.**	**Experiment number**: HC-2184
Beamline: ID27	**Date of experiment**: from: 13/12/2015 to: 16/12/2015	**Date of report**: 04/03/2016
Shifts: 9	**Local contact(s)**: Gaston Garbarino	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Adrien Marizy, CEA (France)*

Paul Loubeyre, CEA (France)

Report:

The aim of this proposal was to determine the equation of state of Lithium Borohydride at very high pressure (over 100GPa) with a pressure transmitting medium. So far, the structural investigation of $LiBH_4$ has been performed up to 50 GPa at 300K and three phases have been discovered [1,2]. Another phase transition has been predicted at 60GPa [3]. Our previous infrared measurements without pressure transmitting medium have revealed two possible phase transitions: one around 90GPa and another one around 130 GPa. A direct structural study was needed to confirm those findings.

Out of 3 DAC prepared beforehand in our laboratory, only one DAC with 300µm culets turned out not to be contaminated with water. Indeed $LiBH_4$ is highly hygroscopic and only a few ppm of water inside the gas used as pressure transmitting medium proved sufficient to hydrate our $LiBH_4$ samples and make them amorphous. Thus, we were forced to use the ESRF glovebox and gas loading system to try to load a DAC with anvils of 100µm culets (to raise the pressure over 100GPa) with helium while avoiding any contact with water. A huge part of our beam time was thus used to reload our cell with a $LiBH_4$ sample and to try to perfect our protocol in order to remove the remaining water inside the gas loading system which polluted the pressure medium. After an unsuccessful attempt, the second sample turned out to be free of water and gave us an XRD signal.
XRD was performed on ID27 at a fixed energy of 33keV and with a beam size of ~3x3µm² to minimize the signal of the rhenium gasket. The X-ray signal was collected with a MARCCD detector. Due to the low scattering power of the compound, an acquistion time of more than 200s was necessary. The pressure was determined thanks to the volume of a small piece of gold loaded next to the sample.

Culet diameter (µm)	Pressure medium	Pressure range (GPa)	Comments
300	Helium	5-60GPa	
100	Helium	39-133GPa	
100	No medium	-	Opening of the gasket

Table 1: Conditions of the experimental runs.

Finally, we managed to collect X-ray diffraction patterns up to 133GPa, which is the maximum pressure that the anvils could withstand. Helium was used as a pressure transmitting medium both for the 300µm culets

DAC and the 100µm culets DAC, allowing us to determine the equation of state (while increasing the pressure) of the known teragonal and cubic phases (respectively with space group $I4_1/acd$ and Fm-3m) of $LiBH_4$ under hydrostatic conditions. At ~60GPa, the 3 diffraction peaks of the cubic phase began to disappear while a new peak started to appear (figure 1) indicating a phase transition. Preliminary data analysis of this new phase seems to indicate that it could be the predicted phase VI [3] but the weak XRD signal collected for this phase makes any structure solving difficult.

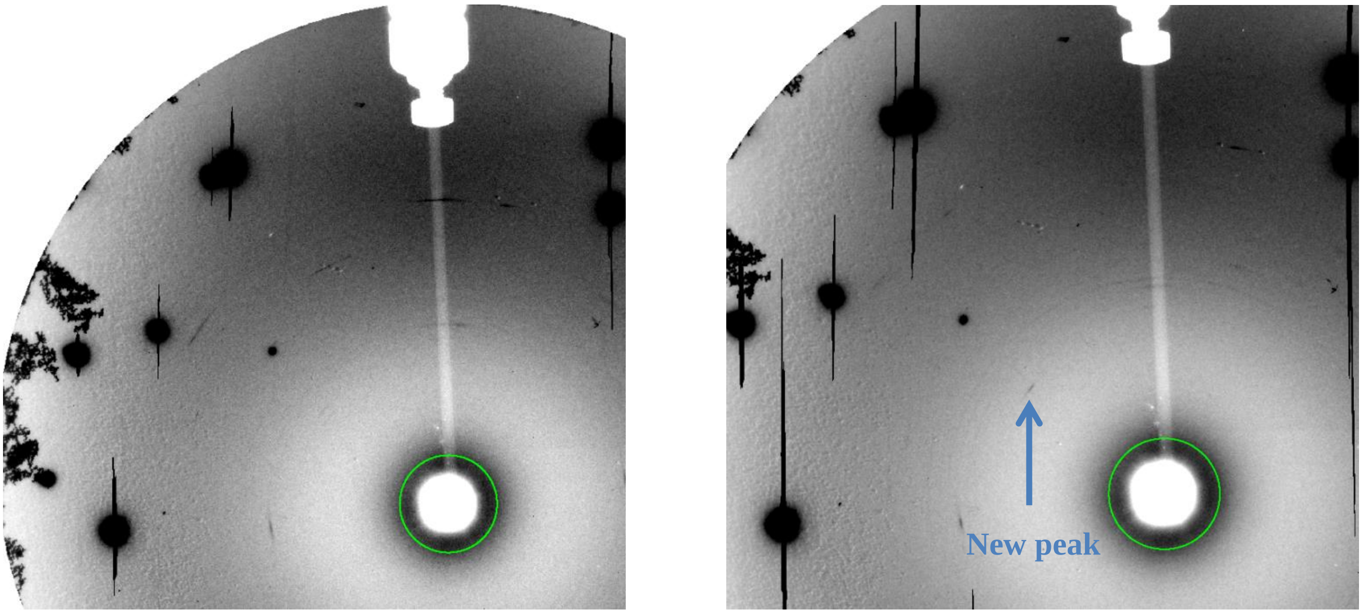

Fig1.: Recorded XRD images before (55GPa, left) and after (66GPa, right) the new phase transition for the DAC with 100µm culets.

References:

[1] Y.Filinchuk et al, Phys. Rev. B 76, 7 (2007).

[2] S. Nakano et al. J. Phys. Chem. (2015).

[3] Y. Yao and D. Klug. Phys. Rev. B 86, 064107 (2012).