

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

<http://193.49.43.2:8080/smis/servlet/UserUtils?start>

Reports supporting requests for additional beam time

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.


Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.



	Experiment title: In-situ diffraction studies of the borohydride system LiBH_4 , and In-situ diffraction study of the phase diagram of $\text{Mg}(\text{NH}_2)_2 + \text{LiH}$.	Experiment number: ME1172 and 01-01-701
Beamline: BM01B	Date of experiment: from: 21 st Sep 05 to: 16 th Nov 05	Date of report:
Shifts: 15, 15	Local contact(s): Hermann Emerich	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Dr M.P. Pitt Institute for Energy Technology, Kjeller, Norway Dr M.H. Sørby Institute for Energy Technology, Kjeller, Norway		

Report:

This is a combined report for ME1172 (15 shifts) and 01-01-701 (15 shifts), both experiments conducted on BM01B. Both of these experiments were conducted as part of the principal proposers (Dr M.P. Pitt) Norwegian Research Council (NRC) project “High capacity Hydrogen Storage Materials studied by X-ray synchrotron diffraction”, which requires a minimum of 6 months contact time at ESRF during the 3 year contract period. ME1172 and part of 01-01-701 were conducted during a 2 month attachment at SNBL.

Several problems, both logistical and technical were encountered which prevented the original experiments outlined in ME1172 and 01-01-701 being conducted as specified.

ME1172 : This particular experiment must be conducted at $>360^\circ\text{C}$ at ca. 15 bar H_2 pressure to achieve greater than 8wt% H capacity, requiring a high temperature, high pressure cell. Part of the LiBH_4 is also melted under these conditions. Currently, the proposers existing in-situ cell (SS flanges with Be windows, allowing a ca. 1mm sample space) is rated to 300°C and 100 bar, and derating the pressure against temperature shows that the cell is easily capable of mechanically achieving the conditions of 360°C and 15 bar, however, the kalres o-ring seal cannot be taken beyond 312°C , otherwise it will begin to evolve organic vapours, and easily be destroyed, thereby destroying the sample through atmosphere exposure. Further, under these conditions of high temperature, it is likely the sample will react with the Be windows. These problems were understood at the time of submitting the proposal, and a higher temperature version of our existing cell, with a mechanical seal was being designed and proofed by Griffith University, Australia (where our original cell was designed and purchased), however, this design has proven problematic, and certainly not straightforward in material design terms. The high temperature cell will be available in the future, however, the present prototype requires further design refinement and pressure proofing at high temperatures.

01-01-701 : This particular experiment was plagued by sample synthesis problems. Synthesis of $3\text{Mg}(\text{NH}_2)_2 + 12\text{LiH}$ requires ball milling $4\text{Li}_3\text{N} + \text{Mg}_3\text{N}_2$, annealing the mixture at 600°C under ca. 3 bar N_2 , and then hydriding the annealed powder at 250°C under 350 bar H_2 . While we managed to successfully complete the annealing step, at the time, we had only 100 bar of H_2 bottle pressure available, and our efforts to hydride the sample resulted in only ca. 1/3 of full capacity, and only intermediate concentration H phases, rather than the fully saturated amide $\text{Mg}(\text{NH}_2)_2$.

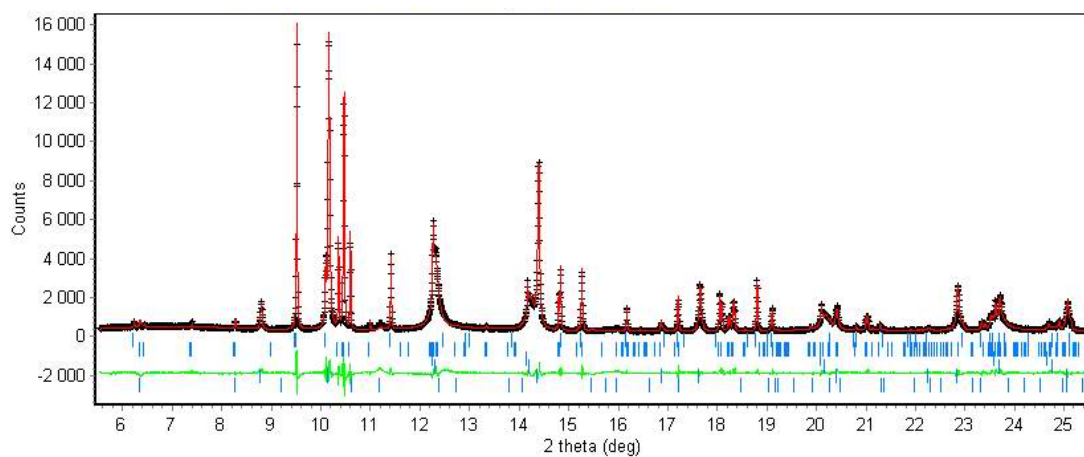
Despite these difficulties, rather than let the beam time for ME1172 and 01-01-701 lapse and not be used due to the difficulties outlined above, the beam time was used as efficiently as possible under the extenuating circumstances.

It was decided at the time to continue to attempt an in-situ experiment with the 100 bar 300°C cell in the spirit of the original proposals. This particular cell has already been used at SNBL on BM01B during the year 2000, so there was no question of its reliability. It was decided to attempt an in-situ isothermal phase diagram on the Ti enhanced NaAlH_4 (IFE has a large store of kg's of this powder) system. This in itself presented great logistical difficulties, as large quantities of loose powder were required to ball mill samples directly in the ESRF chemistry laboratory, so as to avoid disproportionation of the saturated Ti+ NaAlH_4 hydride during transport. The transport of these powders could not be by aircraft due to their sensitivity to atmosphere and potential fire hazard. Thus, road transport was a necessity, and at the beginning of the scheduled beam time period, the only transport company willing to undertake transportation of these powders as dangerous goods indicated a lengthy transport time on a scale of weeks, and finally, the principal proposer Dr Pitt had to transport these powders personally by boat from Oslo to Kiel, and then by car from Kiel to Grenoble. As the experimental equipment necessary for the in-situ setup (gas manifold, x-ray cell, temperature controllers, DVM/MUX etc) consumed a large volume, and could not be taken on the boat, it was transported by aircraft as a large crate on overnight delivery. Unfortunately, this crate was then stuck in French customs for an unacceptably long period of weeks, ruining the chance of initially conducting an in-situ experiment of any nature.

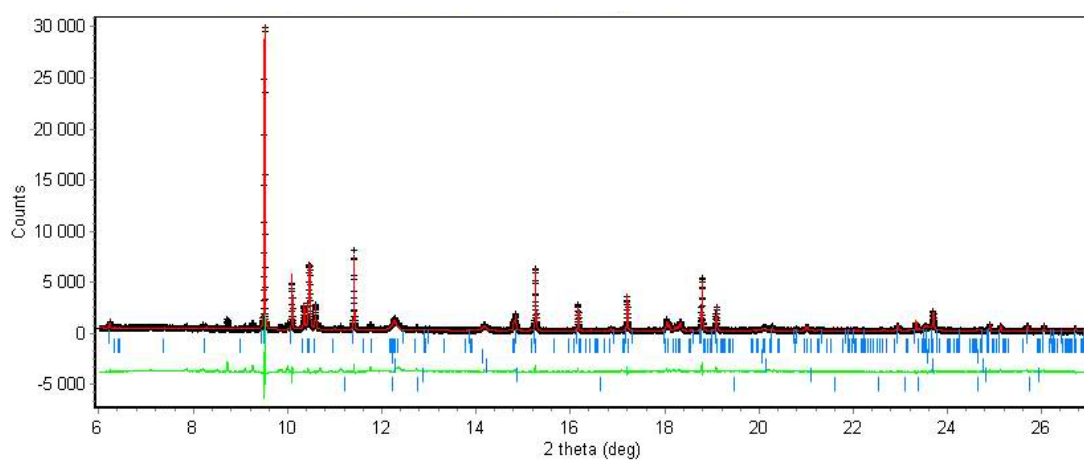
As the principal proposer had brought enough powder and a planetary ball mill by road transport, the beam time could still fortunately be filled by capillary based measurements. This was an immensely successful enterprise, and 50 samples were measured with the use of the planetary ball mill and regular access to the ESRF Chemistry Laboratory, and the able assistance of Dr Harald Mueller.

During this period of capillary based measurements, the crate finally cleared French customs, and the in-situ experimental equipment was able to be used toward the end of the principal proposers 2 month attachment to SNBL. During several attempts to mount the in-situ cell on the Huber, a mechanical problem was encountered on one flange of the cell, which required workshop time to re-bore the filter assembly seat, the data logging software required recoding to be able to read the pressure transducer, and finally, to anneal a fresh ball milled Ti+ NaAlH_4 sample, laboratory access could not be obtained at a logistically difficult period during weekend time. With only one single shift slot left at the very end of the 2 month attachment period, all of the bugs associated with the experimental setup were solved, however, nothing in-situ could be done in a single shift due to the slow kinetics of the sample, and several more relevant capillary samples were run instead.

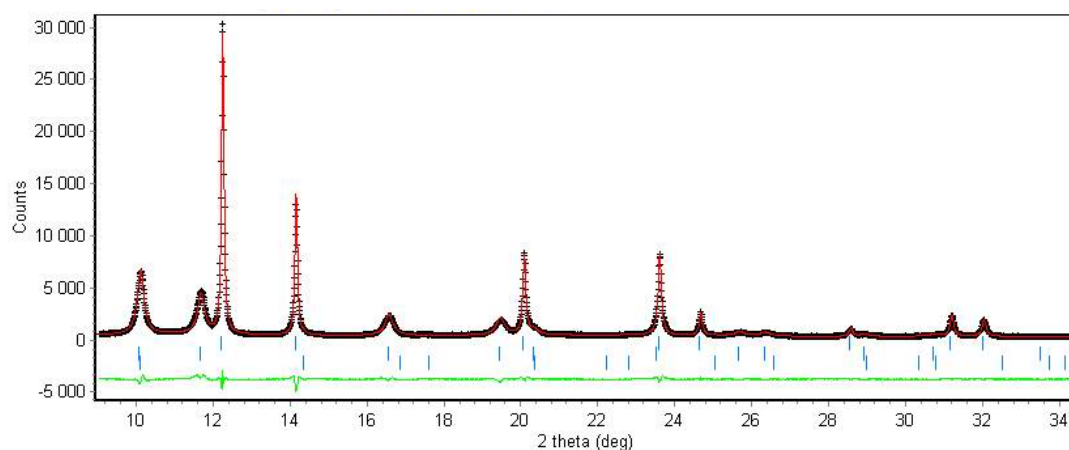
Rather than be seen as a litany of one logistical disaster after another, the beamtime used as outlined, has proven beyond extremely fruitful, with a major breakthrough in our understanding of the Ti enhanced NaAlH_4 system, which stands as the most pressing unsolved problem in the field of hydrogen storage research. This major breakthrough has encouraged the principal proposer to submit a long term proposal based on these exciting results alone, as a general study on the behaviour of transition metal additives in complex hydrides. The data obtained is highly sensitive, and the complete analysis cannot be shown here before publication. Already, the analysis of this data with combined TEM methodologies has been developed as a manuscript to be submitted to Physical Review B, and has been accepted as an important oral contribution at MH2006, the largest international metal-hydrogen conference. Some examples of the data quality and analysis are shown below.



a) 10% TiCl_3 doped, cycled 5 times



b) 10% $\text{Ti}_{13.6}\text{THF}$ doped, cycled 5 times



c) (NaH + Al) + 2% TiCl_3 , milled only.

50 data sets were collected on a wide variety of samples, including both milled and cycled samples, both saturated NaAlH_4 , and dehydrided NaH + Al, using a range of dopants, including TiCl_3 , $\text{Ti}_{13.6}\text{THF}$ clusters, and 65nm nanoscopic Ti.