# STRUCTURAL STUDIES OF MATERIALS FOR HYDROGEN STORAGE

**High Resolution SR-PXD measurement: 01-01-679 (April 2006 and February 2007) Beamline BM01B**

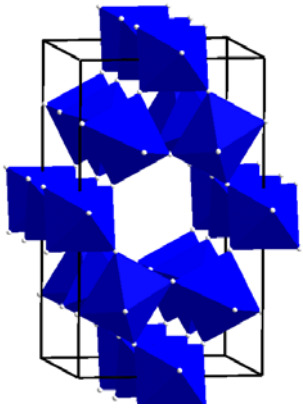
M. H. Sørby, H.W. Brinks, H. Grove, S. Deledda, M.D. Riktor and B. C. Hauback,

Physics Department, Institute for Energy Technology, P. O. Box 40, NO-2027 Kjeller, Norway.

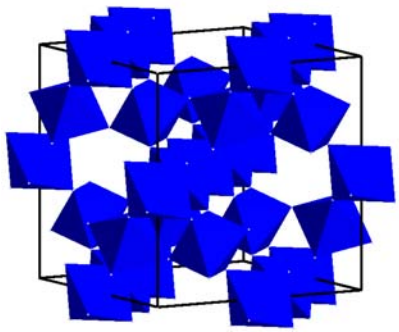
## $AlD_3$

$AlH_3$ ("alane") has been shown considerable interest as a possible hydrogen storage material the last few years due to its high H content (10 wt% H) and favourable desorption properties. $AlH_3$ exhibits as many as 7 structure modifications whereof only one ($\alpha$-$AlH_3$) was structurally characterized prior to our investigations.

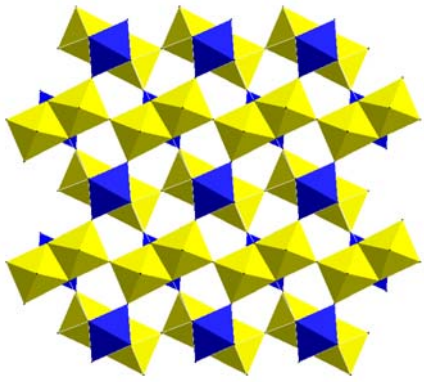
Deuterated samples containing $\alpha$'-$AlD_3$, $\beta$-$AlD_3$ and $\gamma$-$AlD_3$ were synthesised for crystal structure determination. The data analysis was particularly challenging since the samples always contained a mixture of several $AlD_3$ modifications and sometimes synthesis by-products. Still, successful indexing of the three modifications was possible with high-resolution synchrotron diffraction data from BM01B. The data were combined with powder neutron diffraction data from our home source (PUS diffractometer at JEEPII) to solve and refine the crystal structures. The crystal structure of the $\alpha$' modification is published (H.W. Brinks, A.I. Lem, B.C. Hauback, J. Phys. Chem. B 110 (51) (2006) 25833-25837) and the $\beta$ and $\gamma$ modifications are accepted for publication as two separate papers in Journal of Alloys and Compounds.



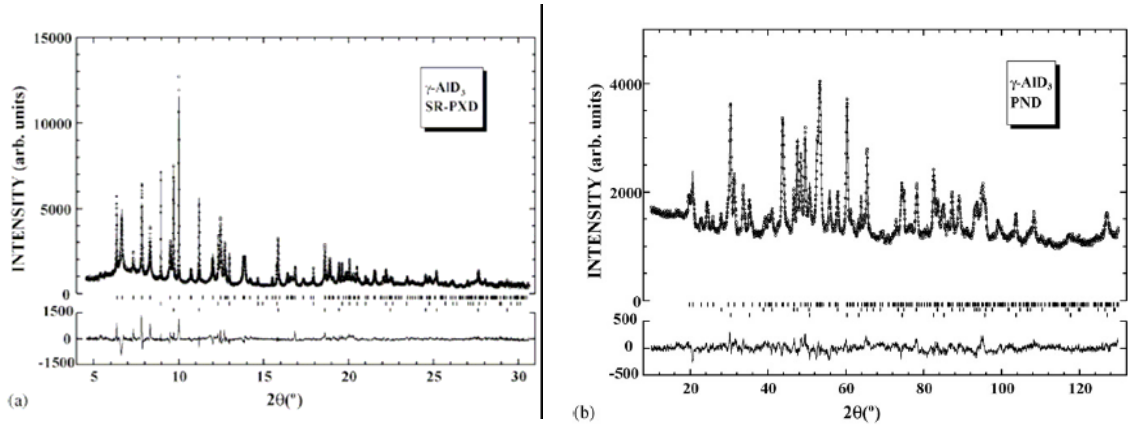
$\alpha$'-$AlD_3$ (*Cmcm*)



$\beta$-$AlD_3$ (*Fd*3*m*)



$\gamma$-$AlD_3$ (*Pnnm*)

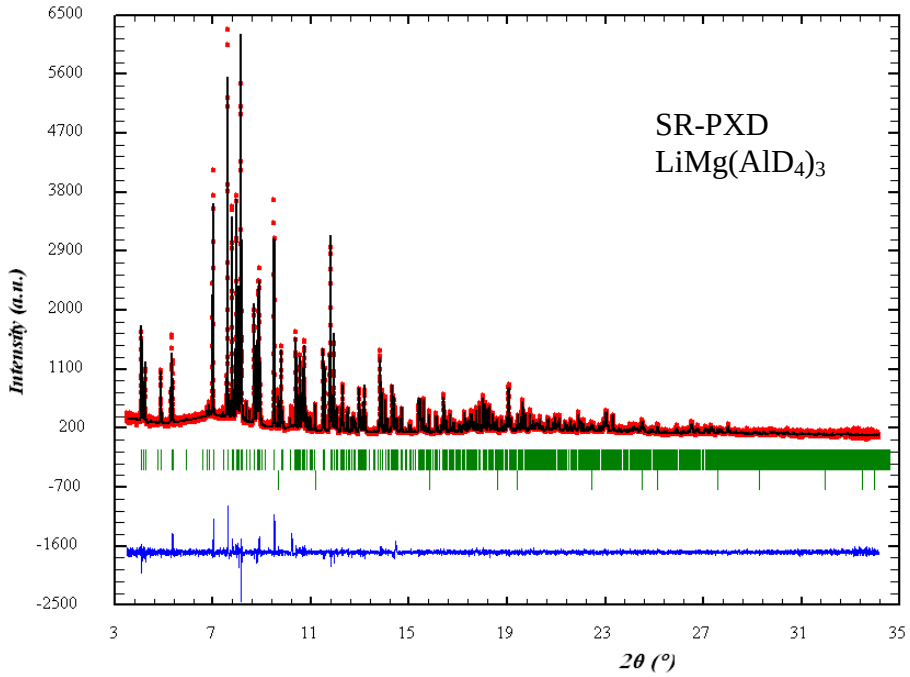



*Fits from combined SR-PXD and PND refinement of the crystal structure of γ-$AlD_3$. The sample also contains α-$AlD_3$ and LiCl.*

**$LiMg(AlD_4)_3$**

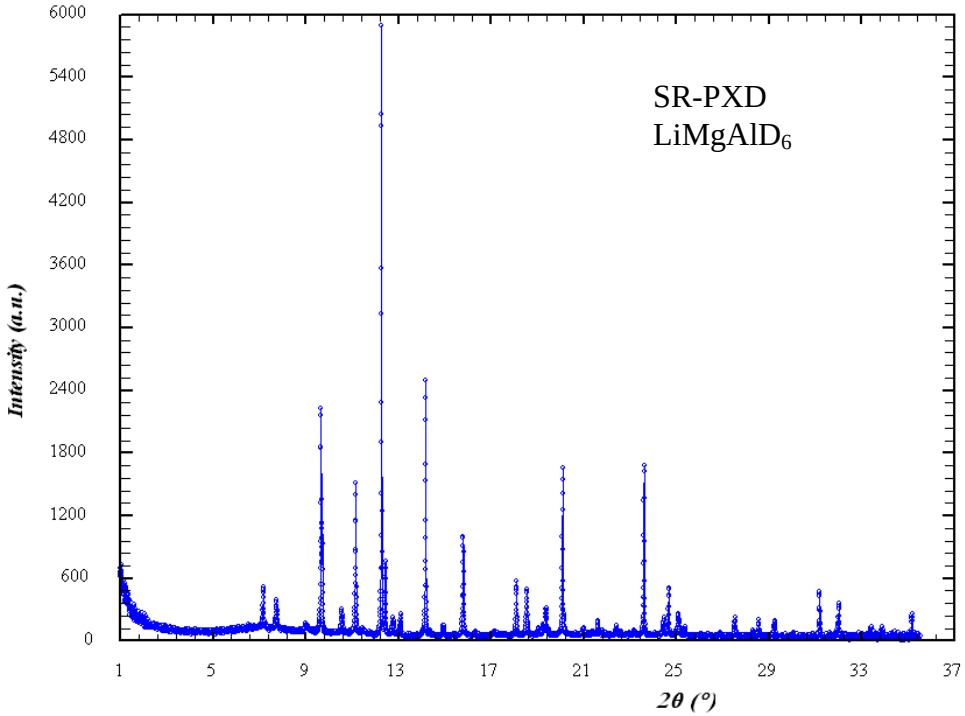
The previously unknown phase $LiMg(AlD_4)_3$ was synthesised by wet chemical methods. Recrystallization in ether/toluene yielded a well-crystalline product. The unit cell (a = 8.3711 Å b = 8.7391 Å c = 14.3012 Å β = 124.8308°) was obtained from high-resolution SR-PXD data with the program DICVOL. The global optimization program FOX was used to determine the position of the metal species.

Complementary powder neutron diffraction data from our home lab (PUS diffractometer at the JEEPII reactor) was used to determine the D positions. Both data sets were used in the structure refinement and the results are accepted for publication (H. Grove, H. W. Brinks, R. H. Heyn, F.-J. Wu, S. M. Opalka, X. Tang, B. L. Laube, B. C. Hauback, Journal of Alloys and Compounds, in press).



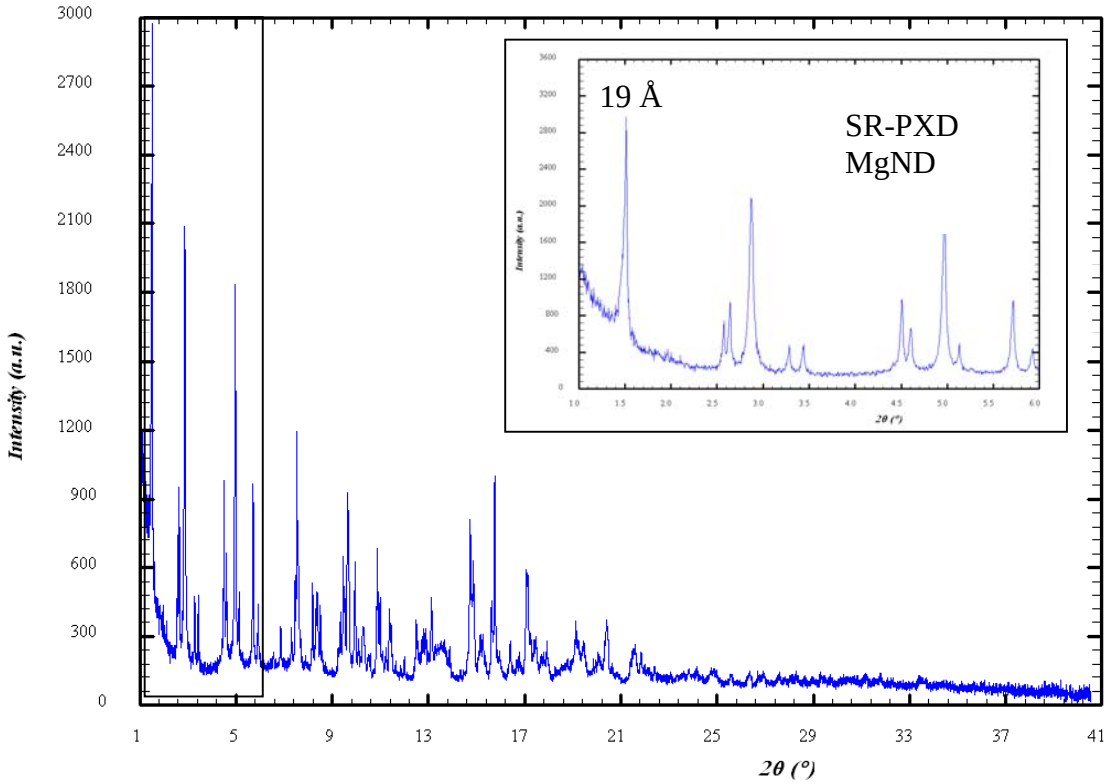

**$LiMgAlD_6$**

High resolution X-ray synchrotron data were also collected for a sample containing $LiMgAlD_6$. These data are still being analyzed, but the diffraction data show a well-defined diffraction pattern with narrow peaks and high intensity. The synchrotron powder X-ray diffraction data are in good agreement with a theoretically predicted structure for $LiMgAlD_6$ and the refined structure will be published.



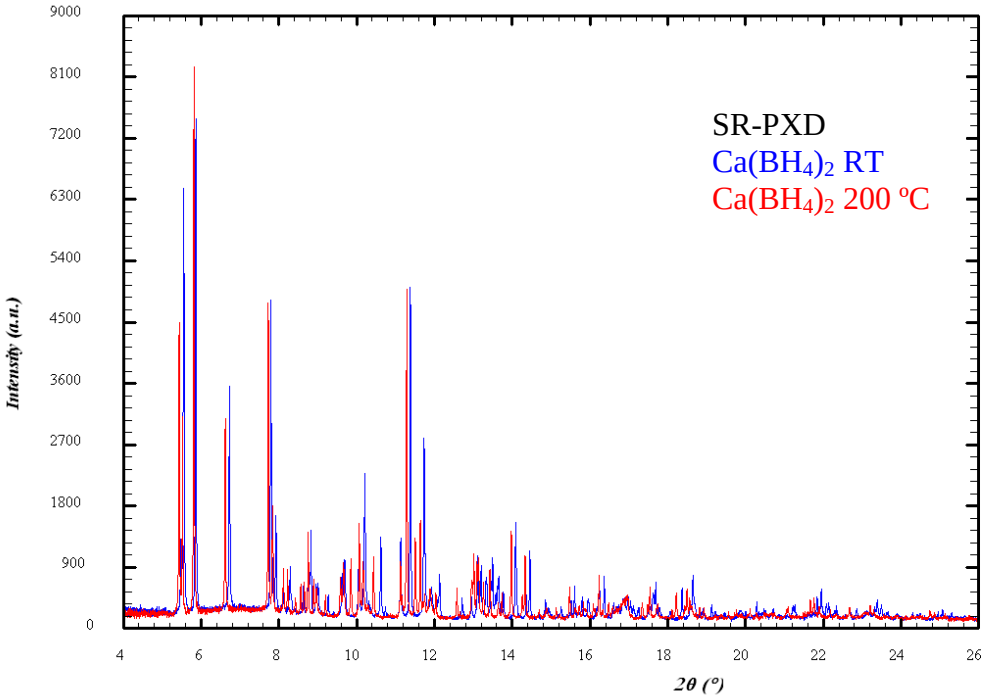
## MgND

The crystal structure of MgND appears to be far more complicated that previously assumed. A hexagonal unit cell with a = 11.58 Å and c = 3.667 Å has been suggested in the literature (Jacobs *et al*. 1969). However, our SR-PXD data show peaks at low angles corresponding to d-spacings up to about 19 Å. The sample was obtained by controlled decomposition of $Mg(ND_2)_2$ in ammonia atmosphere at the University of Hiroshima, which gave a sample with superior crystallinity compared to samples previously obtained by thermal decomposition in dynamic vacuum. Thus, the data are well suited for crystal structure determination. The work is in progress and the preliminary results indicate triclinic symmetry.



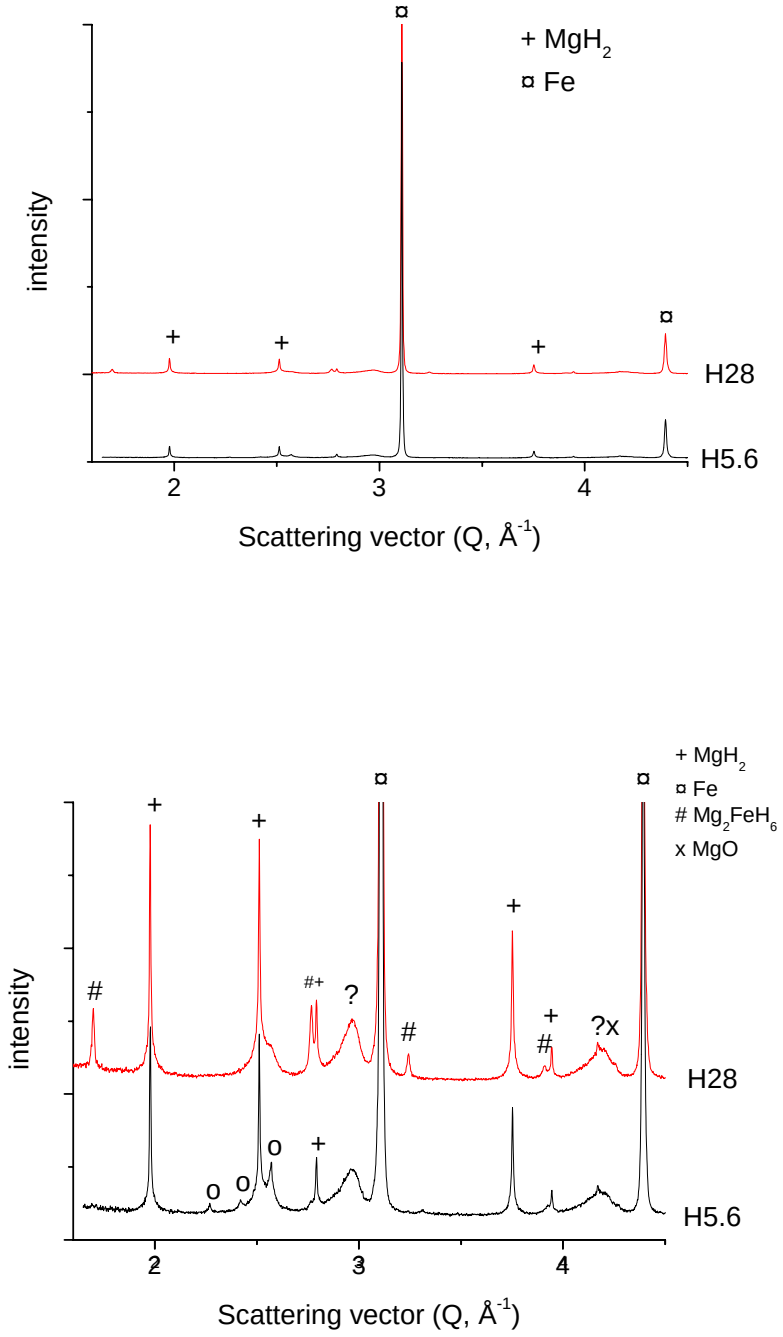

## $CaBH_4$

Borohydrides are for the time being one the "hottest" class of solid hydrogen storage materials. $CaBH_4$ undergoes a phase transition around 150ºC. Neither the low-temperature nor the high-temperature modification has a known crystal structure. Measurements were performed at ambient temperature and 200ºC using a heat blower. There are marked differences in the collected patterns. Data analysis is in progress.




**$2MgH_2$ + Fe**

The ternary hydride $Mg_2FeH_6$ was synthesized using three different milling methods. (1) Milling at room temperature under argon atmosphere and subsequent hydrogenation at 5.6 and 28 bar. (2) Milling at 77 K under argon atmosphere and subsequent hydrogenation at 5.6 and 28 bar. (3) Milling at room temperature under hydrogen pressure. The desired ternary phase was only formed in very small quantities, that would not have been identified with out the combination of good signal-to-noise ratio and excellent resolution offered by SR-PXD (see figure on next page).

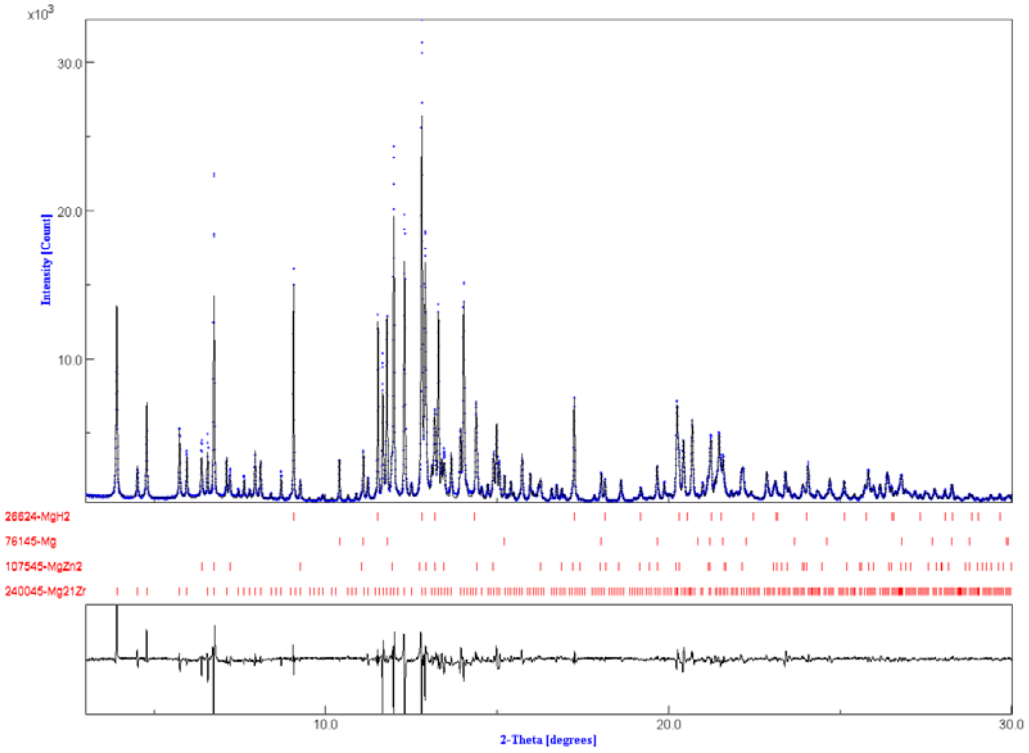



*SR-PXD data of $2MgH_2$ + Fe milled under argon atmosphere at 77 K and hydrogenated at 5.6 and 28 bar (top). Zooming in on the background reveals weak reflections from $Mg_2FeH_6$ (below).*

**Mg-Zn-H**

The hydrogenation and dehydrogenation of ball-milled $Mg_7Zn$ and $Mg_{51}Zn_{20}$ alloys has been investigated. Ball milling, which was carried out using different processing conditions, results in the formation of an amorphous Mg–Zn phase with a likely composition of about $Mg_{45}Zn_{55}$. Upon hydrogenation/dehydrogenation the amorphous phase crystallizes and the crystallization products were investigated by SR-PXD. It was found that the amorphous phase crystallizes polymorphously to $Mg_{21}Zn_{25}$. Upon

hydrogenation, the latter partially decomposes into $MgZn_2$ and $MgH_2$ (see figure belwo). These results were presented at the MH2006 International Symposium on Metal-Hydrogen Systems and are accepted for publication in the conference proceedings (Journal of Alloys and Compounds).




## General comments

There were no significant problems during the run in April 2006. However, there were considerable problems with the new double monochromator in February 2007. Most critically, we lost a factor 25 in beam intensity over the weekend due to mechanical drift. The peaks are also more asymmetrical than they were on with the old channel-cut monochromator. Several data sets were collected with the aim of extracting microstructural information (crystallite size for $NaAlH_4$ that cryomilled from 2 to 10 hours, size information for nano-Cu particles and dislocation density for cryomilled nano-Cu). However, the asymmetry obstructs accurate extraction of the desired information.