



Effect of Trace Elements on Long-Term Cycling and Aging Properties of Complex Metal Hydrides

Dhanesh Chandra

University of Nevada, Reno (*UNR*)

June 12, 2008



ST 37

Timeline

Project start date – FY05

Project end date – FY10

Percent complete – ~60%

Budget

**Total project funding (5yrs.) : \$ 1.5 M
(Requested)**

DOE share (5yrs.) : \$ 1.2 M

Contractor share (5yrs.) : \$ 301 K

**Funding received in FY07 : \$ 520 K
(Includes funding for major equipment)**

Funding received in FY08 : \$ 250 K

Barriers Addressed

- **The effect of trace impurities on materials**
- **Poor mechanistic understanding of some materials**
- **Lack of characterization of material volatilization**

Partners

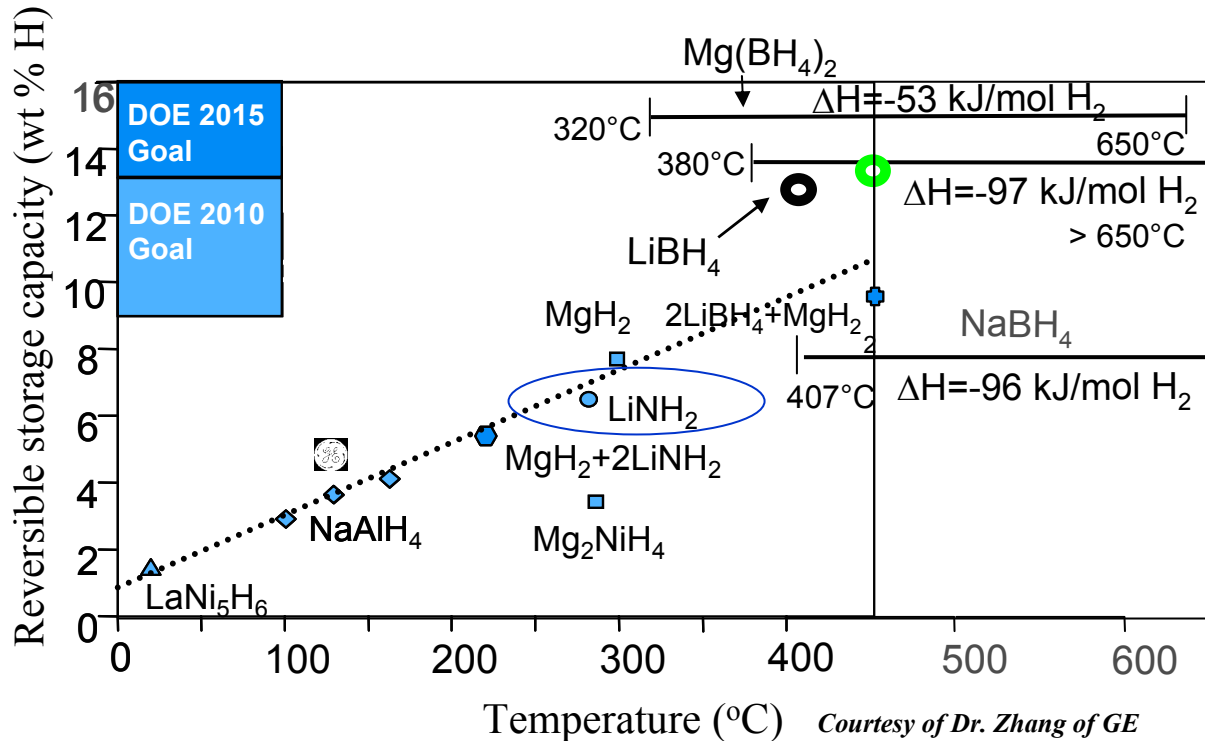
- **SNL – Ewa Rönnebro**
- **GE – Dr. J.C. Zhao (Now at Ohio State)**
- **ESRF, Grenoble , France – Yaroslav Filinchuk**
- **Univ. of Utah, - Dr. Z. Fang**

<p>Overall Objective</p>	<p><u>UNR's Focus Areas:</u></p> <ul style="list-style-type: none"> ➤ I. The primary objective of the UNR Project is to <u>determine the effects of gaseous trace impurities</u> such as O₂, CO, H₂O, CH₄ etc. in H₂ on long-term behavior of the complex hydrides/precursors by pressure cycling and/or thermal aging with impure H₂. ➤ II. Secondary related objectives: (a) Vaporization behavior of hydrides (b) Crystal Structure studies
<p>2006</p>	<ul style="list-style-type: none"> ➤ Constructed high pressure (up to 100 bar) cycling equipment. ➤ Performed hydrogen cycling studies on amide-imide and mixed alanates. ➤ Vapor pressure behavior of Li₃N and Mg(BH₄)₂ initiated. ➤ HP DSC experiments, in-situ neutron, and x-ray diffraction studies
<p>2007 (May, 15 2007- April 1, 2008)</p>	<ul style="list-style-type: none"> ➤ <i>Thermodynamic Studies:</i> <ul style="list-style-type: none"> A. <u>Extrinsic Hydrogen Charging/Discharging effects:</u> Determined the effects of gaseous impurities in hydrogen on Li₂NH-LiNH₂ and other systems. B. <u>Vaporization Thermodynamics:</u> Worked on Mg Borohydride, and identified vapor species at moderate temperatures. ➤ <i>Crystal Structure Studies:</i> In-situ phase transformation studies on Ca(BH₄)₂

Significance of Amide-Imide Studies

1. $\text{Li}_2\text{NH-LiNH}_2 \rightarrow$ total capacity of ~ 10.5 wt.% hydrogen, but currently ~ 5.6 wt.% is reversible. Further studies may lead to increased capacities
2. $\text{LiNH}_2\text{-Li}_3\text{AlH}_6 \rightarrow$ Mixed Amide-Alanates

are important because of their theoretical ~ 7 wt.% hydrogen storage capacity



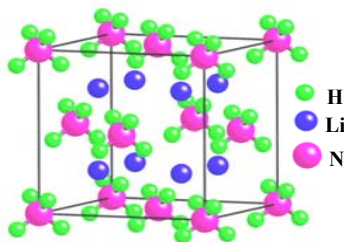
Significance of $\text{Mg}(\text{BH}_4)_2$ and $\text{Ca}(\text{BH}_4)_2$ Studies

1. $\text{Mg}(\text{BH}_4)_2 \rightarrow$ ~ 15 wt.% H_2 capacity with $\Delta\text{H} \sim -53$ kJ/mol
2. $\text{Ca}(\text{BH}_4)_2 \rightarrow$ Potential candidate for hydrogen storage candidate
3. $\text{Mg}(\text{BH}_4)_2$ and $\text{Ca}(\text{BH}_4)_2 \rightarrow$ Vapor Pressures are important to understand vaporization during evacuation cycle of the hydriding/dehydriding.

Pressure Cycling Li-N-H

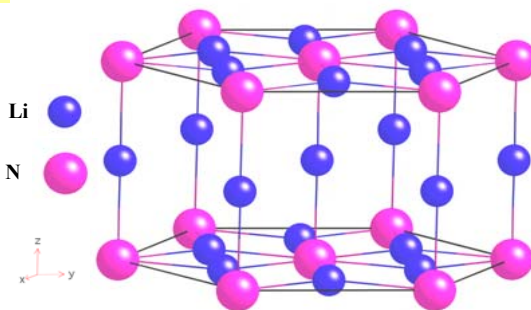
Li_2ND - Cubic - $\text{Fm-}3\text{m}$ - $Z = 4$
 $a = 5.0476 \text{ \AA}$, $\text{Vol} = 128.602 \text{ \AA}^3$

Li_2NH

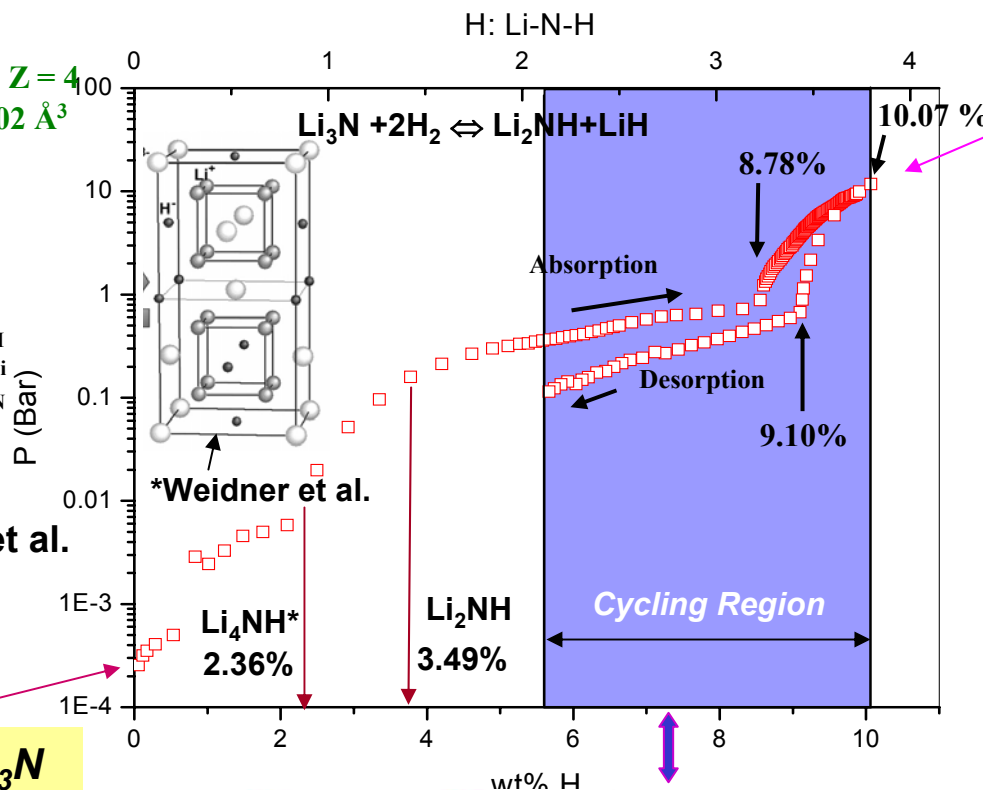


T. Noritake, Orimo, et al.
J. Alloys Compds.
 393 (2005),
 264-268.

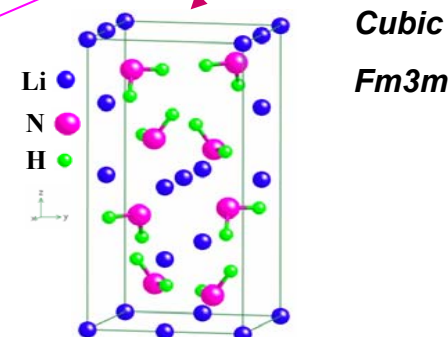
Li_3N



$\alpha\text{-Li}_3\text{N}$ - Hexagonal
 $\text{P6}/\text{mmm}$ - $Z = 1$
 $a = 3.6587 \text{ \AA}$, $c = 3.876 \text{ \AA}$
 $\text{Vol} = 44.933 \text{ \AA}^3$



$\text{LiNH}_2 + \text{LiH}$

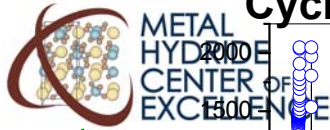


LiNH_2 - BCTI-4 - $Z = 8$
 $a = 5.0695 \text{ \AA}$,
 $c = 10.2599 \text{ \AA}$
 $\text{Vol} = 263.68 \text{ \AA}^3$

K. Miwa, N. Ohba, S. Towata, Y. Nakamori, and S. Orimo
Physical Review,
 B71(2005), 195109.

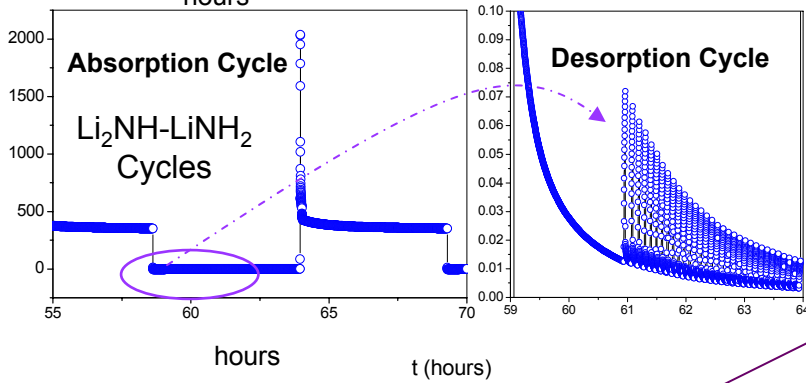
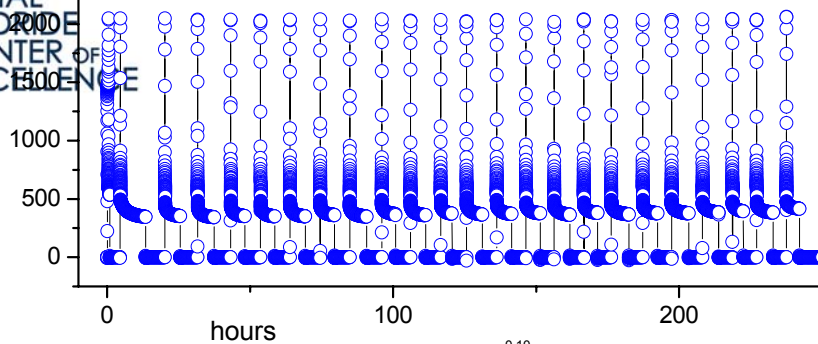
*Weidner, E., D.K. Ross, et al. *Chemical Physics Letters*, 2007. 444(1-3): p. 76-79.

Cycling Data of Imide-Amide with 100 ppm CH₄ in UHP Hydrogen



This cycling data from CH₄ - H₂

Pressure (bar)

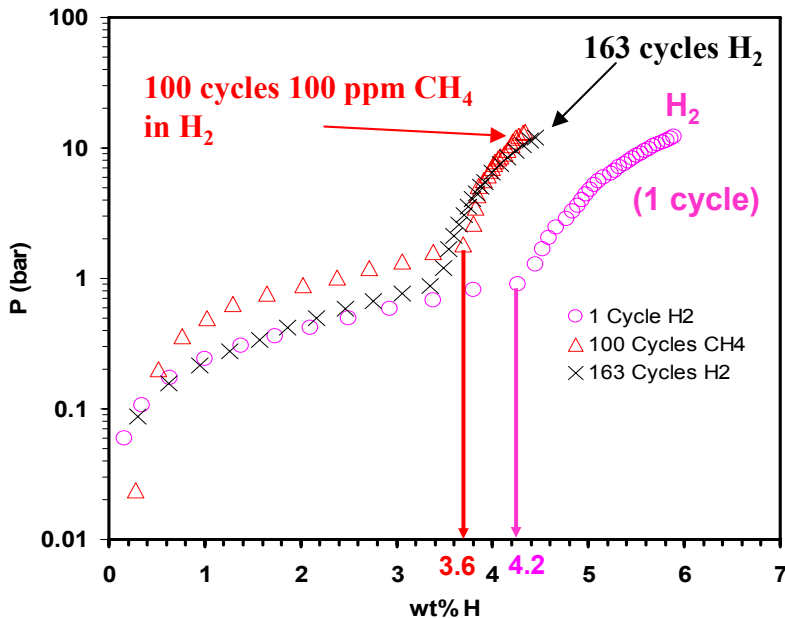


Objective

To assess Loss in Hydrogen Capacity after Pr. cycling Nominally for ~100 cycles

Experiments

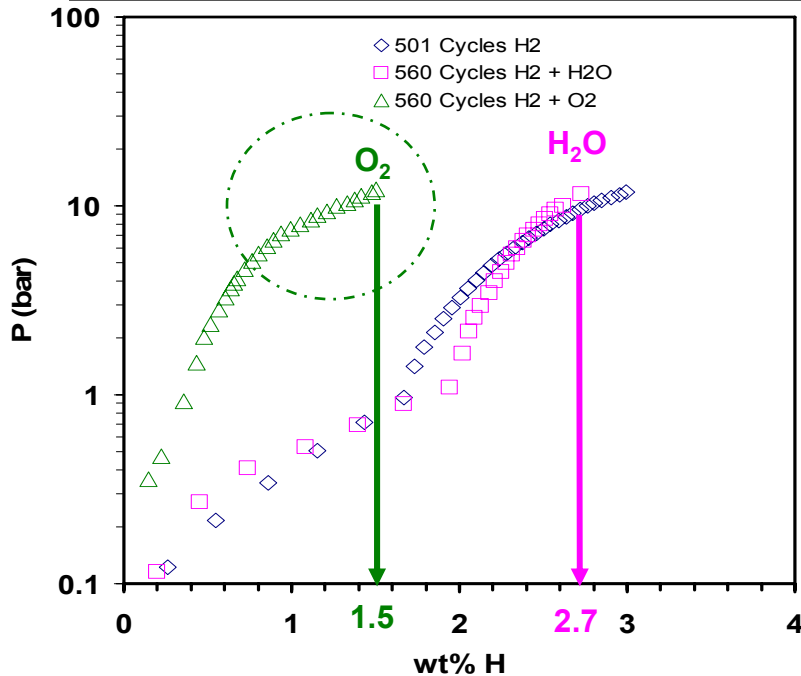
1. Li₂NH ↔ LiNH₂ Pressure Cycled ~ 20 atm/vacuum at 225°C. Top-left
2. Absorption/desorption Isotherms (up to ~12 bar) using the Sieverts apparatus



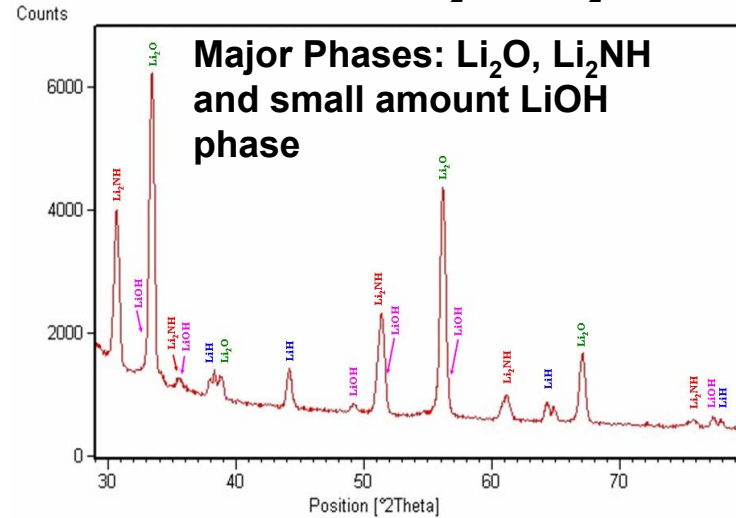
Summary

➤ **Effect of 100 ppm CH₄ in H₂ :**
 About 0.7 wt.% H₂ capacity was lost after 100 pressure cycles.
 There was virtually no change in kinetic behavior

Effect of O₂ and H₂O in H₂ Cycling between Li₂NH-LiNH₂



X-ray Diffraction Pattern - 560 Cycles with 100 ppm H₂O in H₂



Li₂NH: Cubic (Fm-3m)

LiH: Cubic (Fm-3m)

Li₂O (MAJOR): Cubic (Fm-3m)

LiOH (small Fraction): Tetragonal (P4/nmm)

Results:

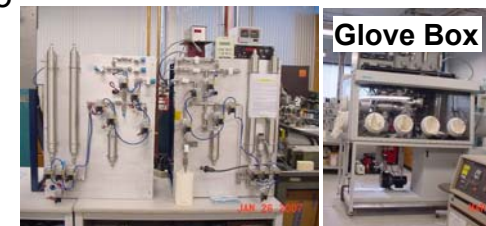
➤ **Thermodynamics:** After ~500 Pressure cycles at 225°C → remaining Hydrogen capacity is 1.5wt.% (with O₂ additions) and 2.7 wt.% out of ~5.6 wt.% with H₂O (total reversible capacity).

➤ **Cycling of Li₂NH ↔ LiNH₂ with Industrial hydrogen** Water ~32 ppm, O₂~10ppm showed ~2.6% hydrogen loss (500 cycles under similar cycling conditions)

Loss in Capacity due to formation Li₂O, and LiH and LiOH

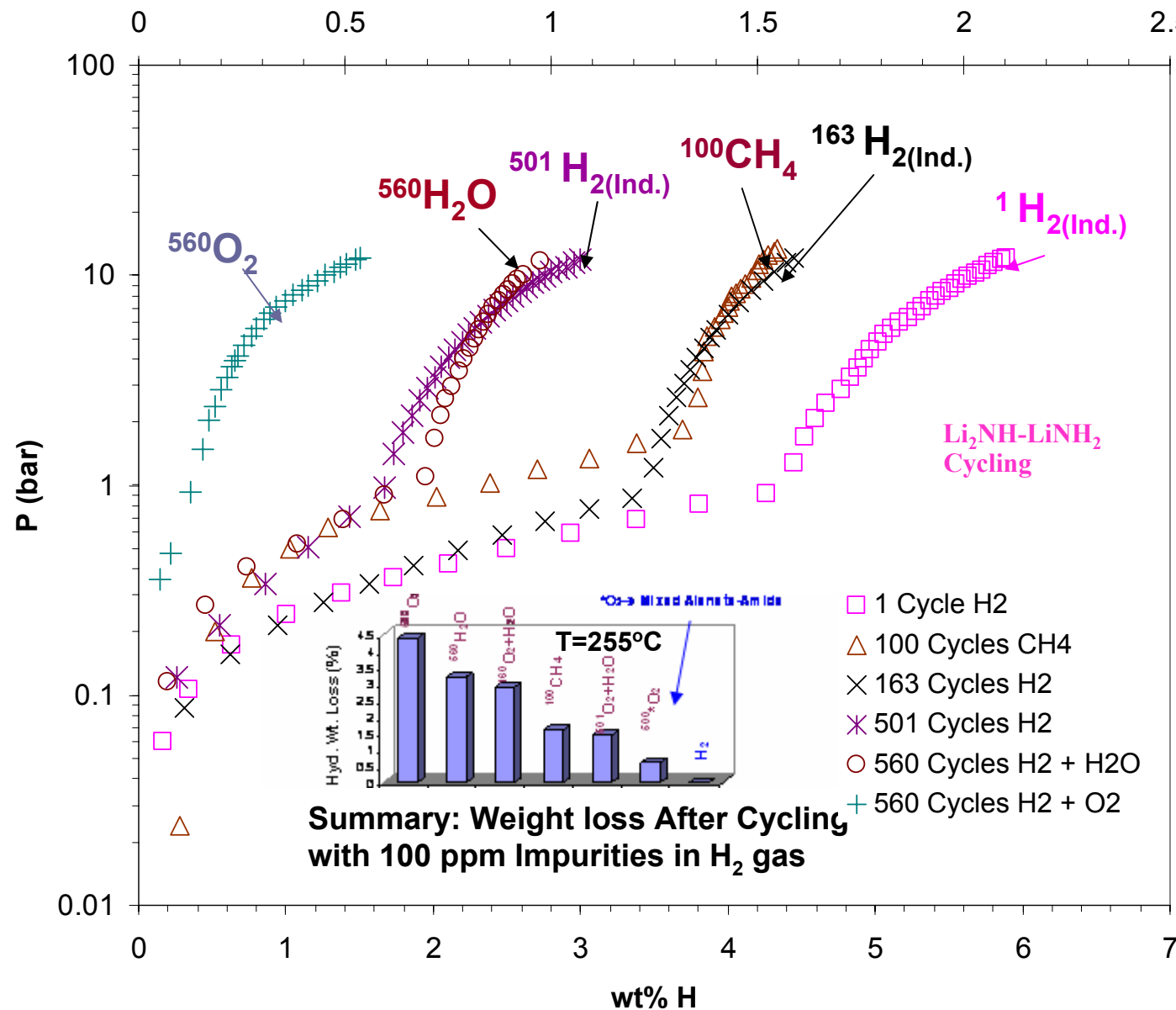
➤ **Importance:** Presence of water in H₂ is expected to have more impact on the loss of hydrogen capacity but it appears that there is greater loss observed when the experiments were conducted with O₂ impurity in H₂

Dual Combined 100 bar H_2 Cycling and Sievert's apparatus



Glove Box

H/Li-N-H

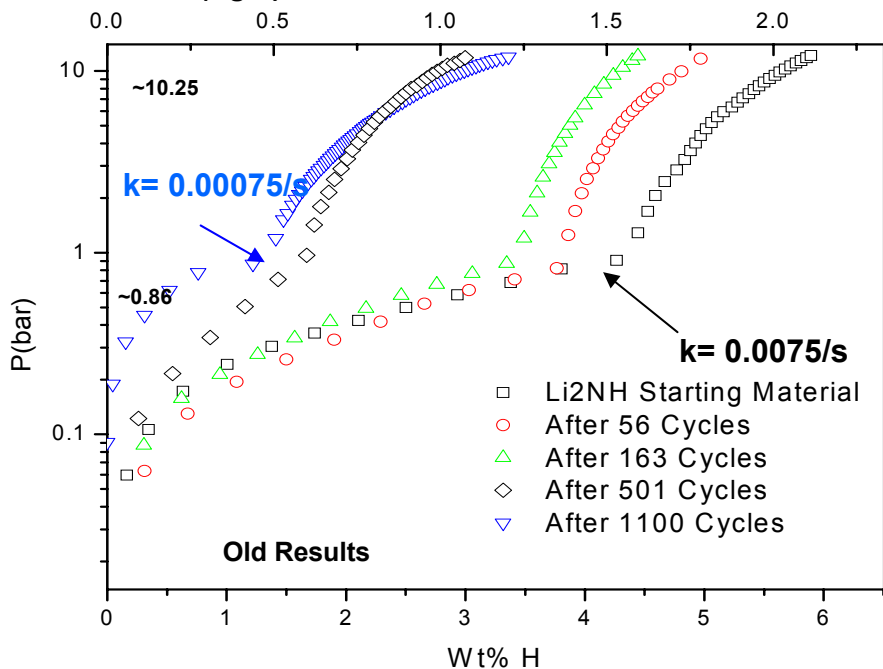


Results:
Pressure Cycling :
 Significantly more losses with O_2 and H_2O impurities.
 (Desorption cycles not shown for clarity)
Thermal aging: 100 ppm CO with H_2 → very little loss in H_2 capacity for the imide-amide system (results not shown)
XRD results show that there is residual Li_2NH along with Li_2O (major phases) and LiH phase.

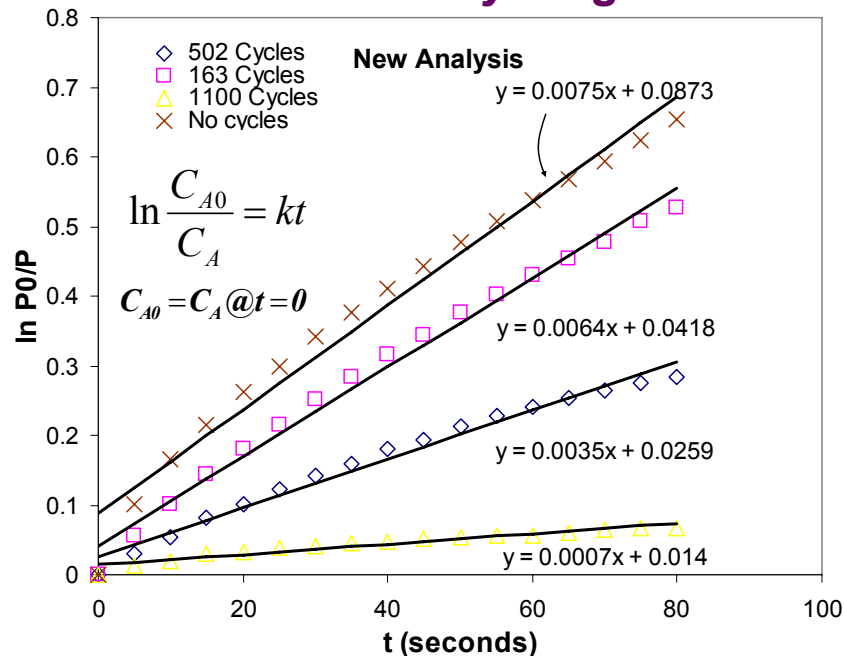
Imide/amide Pr. Cycling with Industrial H₂ containing small levels* of O₂ and H₂O

Li₂NH ↔ LiH ↔ LiNH₂ Cycle
2 Bar - Industrial Hydrogen @T= 255°C

The PCI's were shown before (as a reference), and the kinetic data (right) is new H: Li-N-H



Kinetic Plot for Cycling Data



C_{A0} = Initial Conc. of Hyd. in gas - reaction
 C_A = Concentration at time (t) & $C_{A_0} = C_A @ t = 0$

Rate Constant for the Hydriding reaction:

Cycles	k (1/s)
1	0.0075
163	0.0064
502	0.0035
1100	0.00075

***Please note:** Note that cycling Li₂NH ↔ LiNH₂ in Industrial hydrogen Water ~32 ppm, O₂~10ppm and others showed ~3.2% (out of ~4.4%) hydrogen loss after 1100 cycles under similar cycling conditions

Pressure Measurements

- Torsion effusion system, available at UNR used to determine total equilibrium pressure we use the following Eq.: ('K'=Fiber Constant)

Pressure Equation

$$P_T = \frac{K(2\theta)}{(a_1 f_1 d_1) + (a_2 f_2 d_2)}$$

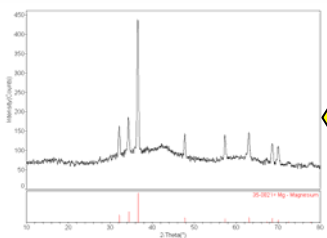
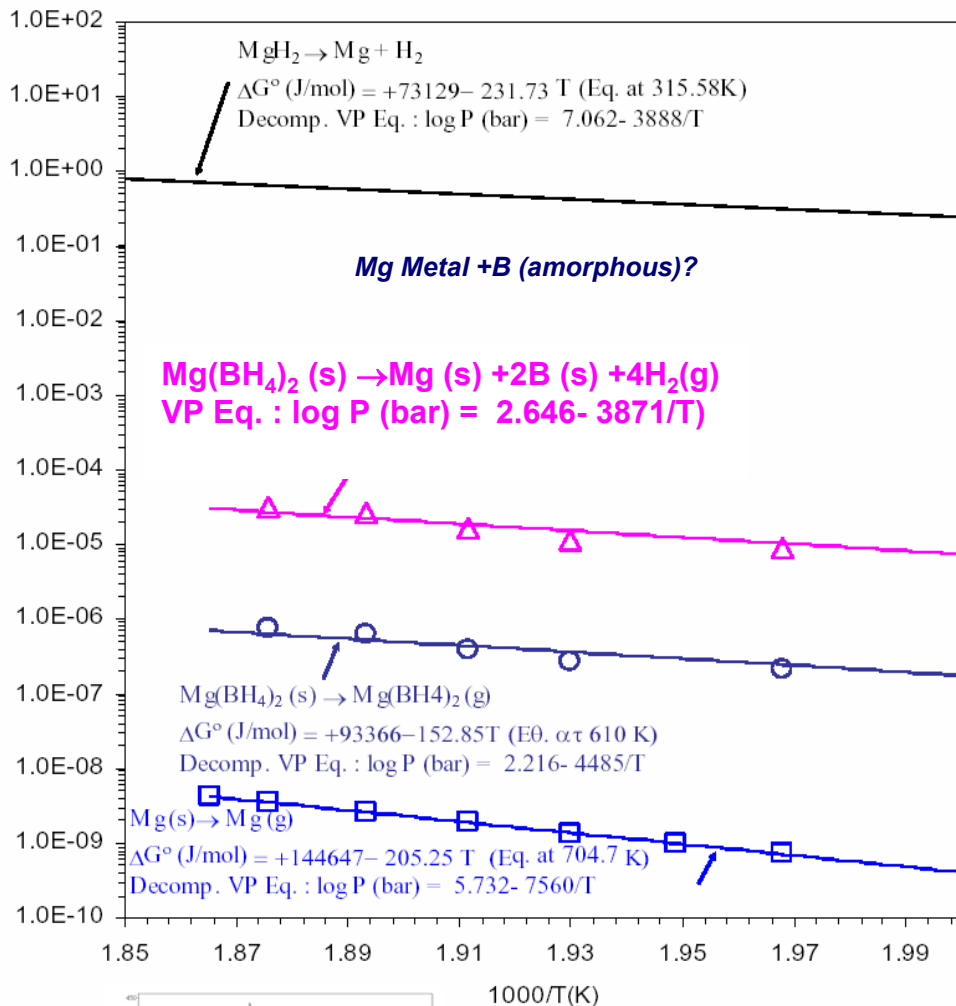
Typical Pr. Temp. and Sample Size:

- Turbo Pump vacuum ($<10^{-5}$ Torrs)
- ~ 1 gram
- Temperature capability: -20°C to $600-700^\circ\text{C}$
- Tungsten Knudsen Cells Used

Molecular Weight Measurements of Vapors

- Determined by rate of weight loss (TGA)
- Disproportionation equations (below) in the vapor phase determined by equating the experimental M_{AVG} to the theoretical Mol. Wt. of the effusing gas species:

$$M_{\text{AVG}} = \frac{2\pi RT}{(2K)^2} \cdot \left(\frac{(dw/dt)}{\theta} \right)^2 \left[\frac{(a_1 f_1 d_1) + (a_2 f_2 d_2)}{(a_1 c_1) + (a_2 c_2)} \right]^2 = \sum_{i=1}^n [m_i M_i^{1/2}]^{-2}$$



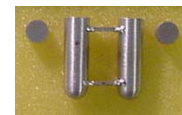
XRD Pattern Showing Mg Metal (residual sample)

Portion of Glass tube with the baffles and Knudsen cell housing is shown

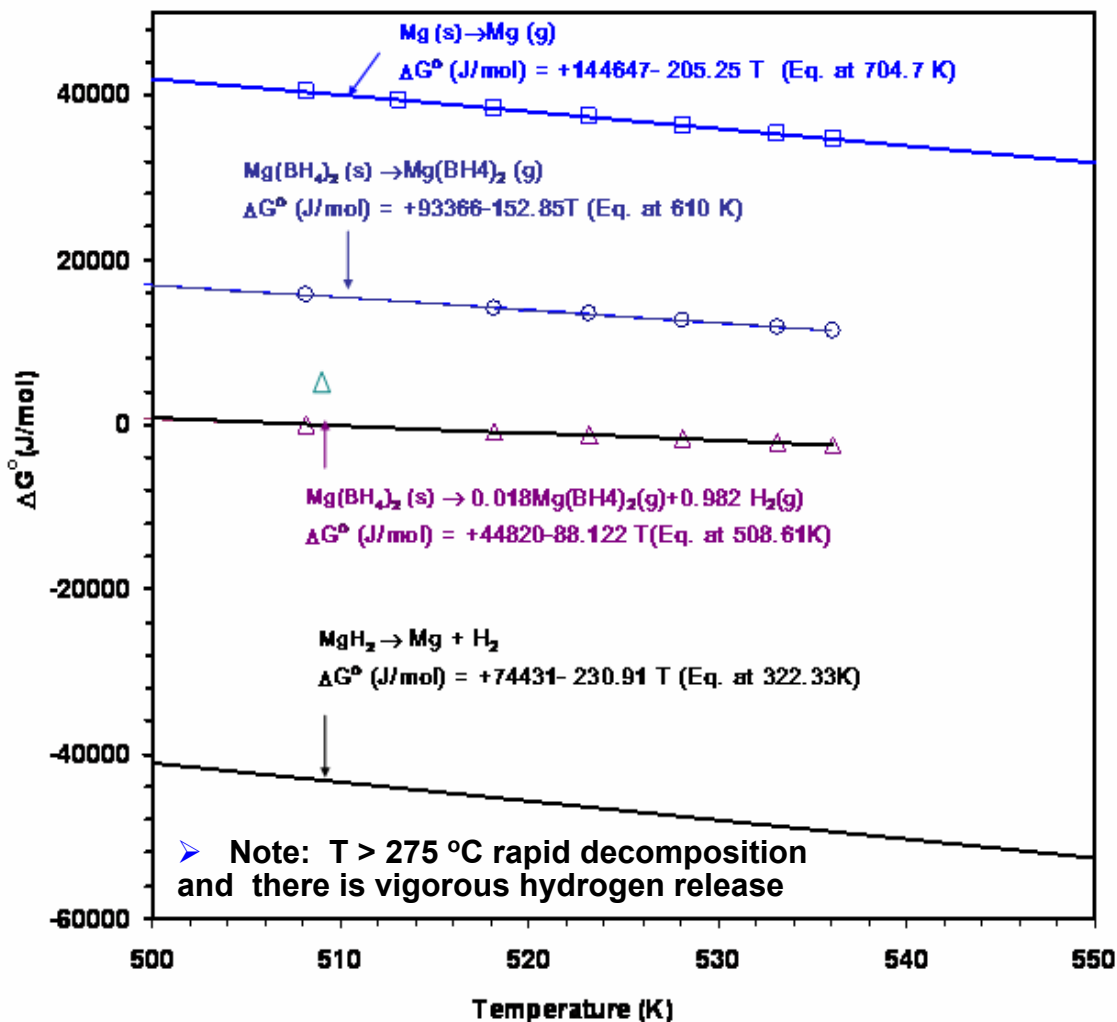


➤ *Knudsen Torsion Effusion apparatus used to measure thermodynamics*

➤ *V.P and Molecular weight of the effusing species.*



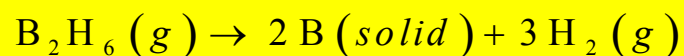
1. There are two principal reactions:
 $Mg(BH_4)_2(s) \rightarrow Mg(BH_4)_2(g)$(~ 2%)
 Eq. : $\log P$ (bar) = 2.216 - 4485/T
2. $Mg(BH_4)_2(s) \rightarrow Mg(s) + B(s) + 4H_2(g)$
 Eq. : $\log P$ (bar) = 2.646 - 3871/T
 thus Disproportionates.....(~98%)
3. The Average Mol. Wt. of effusing gas is 2.42 g/mol suggests that majority hydrogen is major component in vapor phase.



Issues related to formation solid or gaseous Boron (have significance in release of Borane gas)

Results:

- Vapor pressures of $Mg(s) \rightarrow Mg(g)$, and decomposition of MgH_2 to Mg metal and H_2
- Gibbs energy calculation of vaporization are listed in Figure
- At $225^\circ C$: $P_{H_2} = 8.8 \times 10^{-6}$ atm, and $P_{Mg(BH_4)_2} = 2.03 \times 10^{-7}$ atm
- No detrimental cations appear to be effusing out – stable
- Above 508 K ($233.1^\circ C$) the ΔG° becomes negative and vaporization does starts.

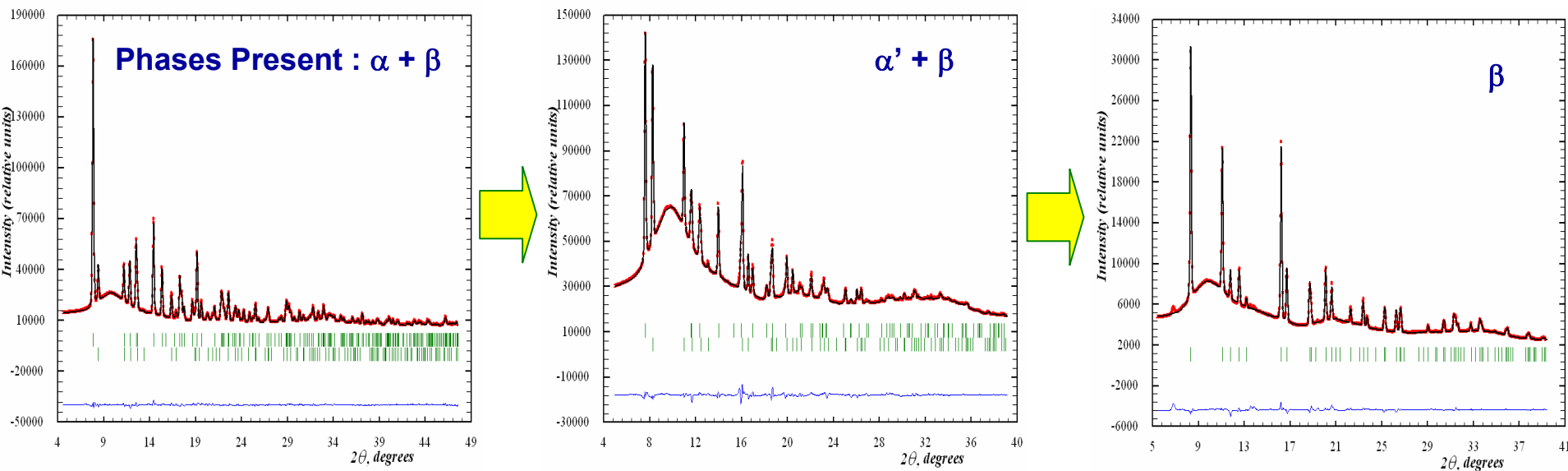


@ 298.15 K, 1 Bar $\Delta G_{RXN} = -87.6$ kJ/mol (Possible)

@ 298.15 K, 1 Bar $\Delta G_{RXN} = +1042.4$ kJ/mol (unlikely)

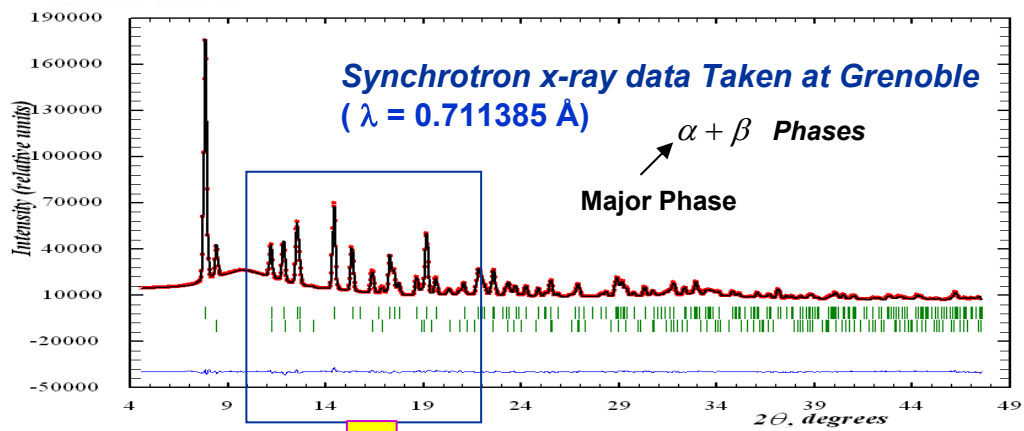
These studies were performed using High resolution and high temperature synchrotron x-ray diffraction at ESRF, Grenoble to understand the phase stability of $\text{Ca}(\text{BH}_4)_2$

Synchrotron Data from the $\text{Ca}(\text{BH}_4)_2$ Specimen



Summary

- The sample contains 87% α - $\text{Ca}(\text{BH}_4)_2$ and 13% β - $\text{Ca}(\text{BH}_4)_2$ phases at room temperature.
- Phase transition from $\alpha \rightarrow \alpha'$ occurred at 222°C (second order transformation)
- Then $\alpha' \rightarrow \beta$ occurred at 297°C
- Manuscript prepared: "Crystal Structures and Phase Transformations in $\text{Ca}(\text{BH}_4)_2$, Y. Filinchuk, E. Ronnebro and D. Chandra, 2008.



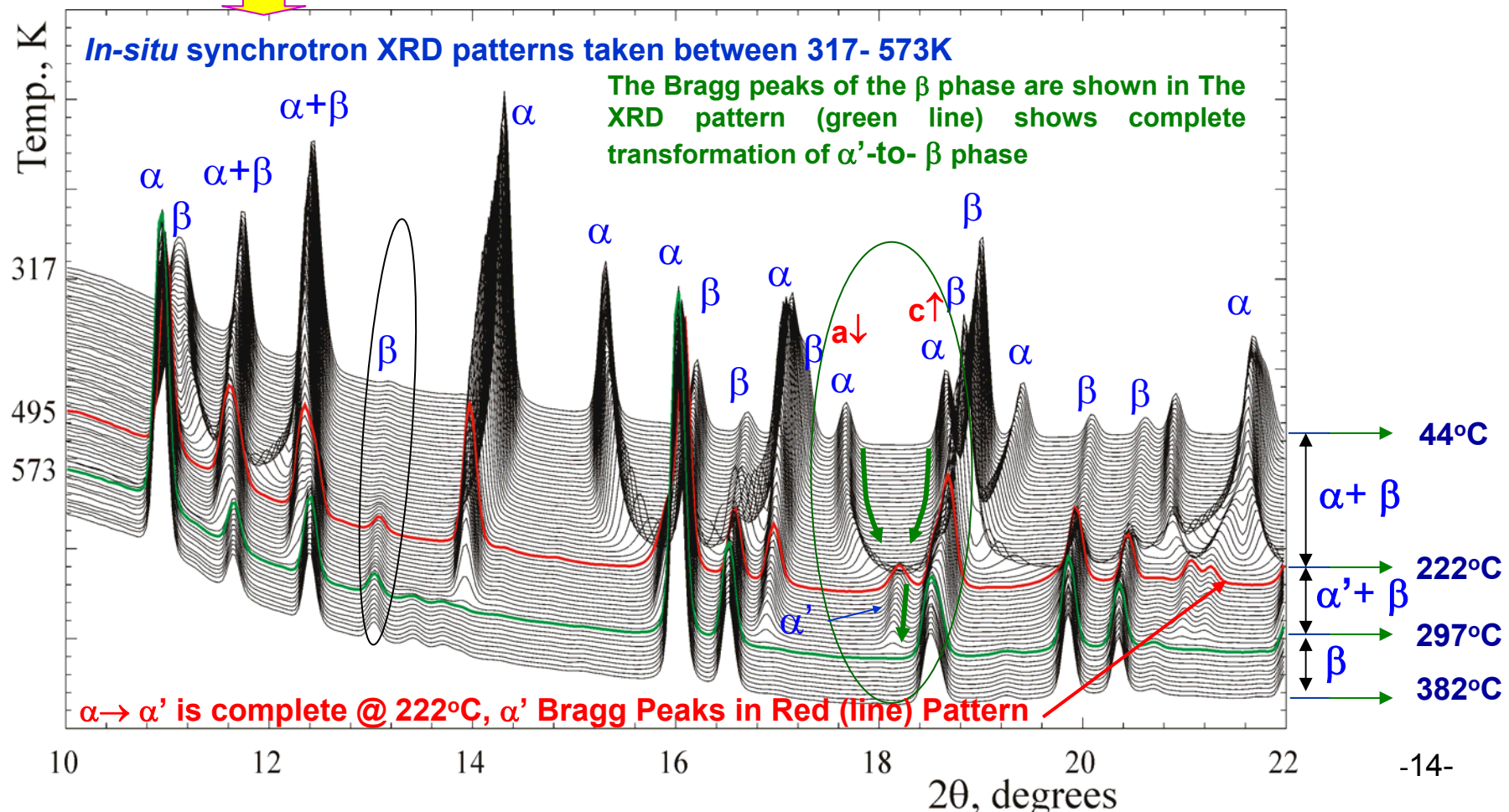
Summary of Phase Transitions

The following Phase transition were observed

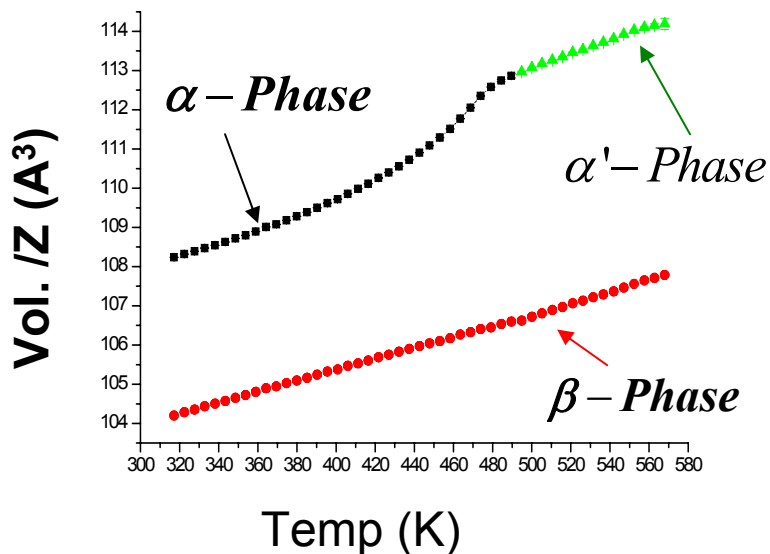
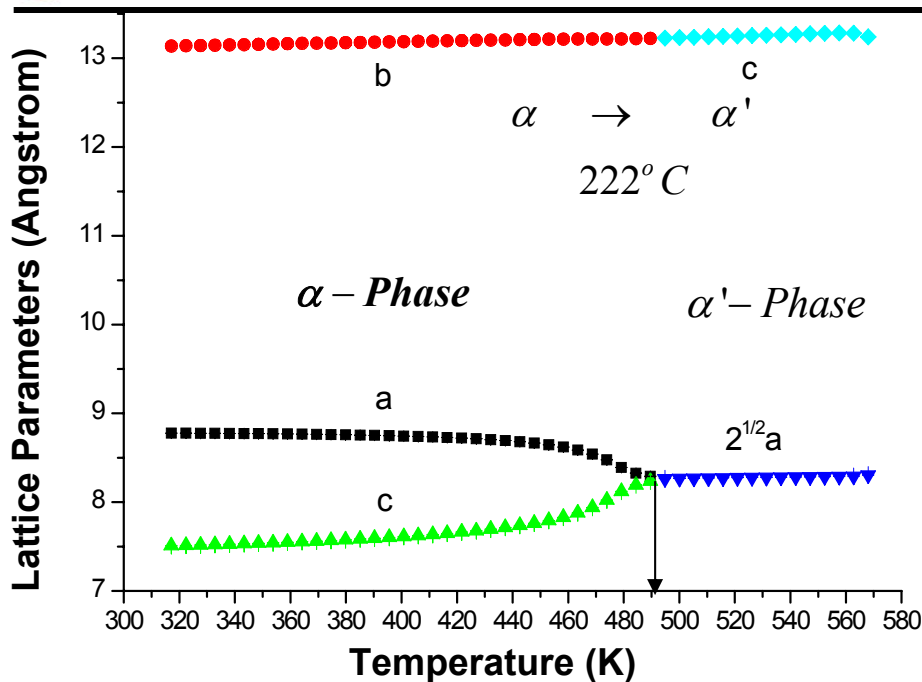
$$\alpha \xrightarrow{222^\circ\text{C}} \alpha' \xrightarrow{297^\circ\text{C}} \beta$$

$\alpha \rightarrow \alpha'$ (2nd order transition complete at 222°C)

β Phase decomposes to unknown phases above 382°C



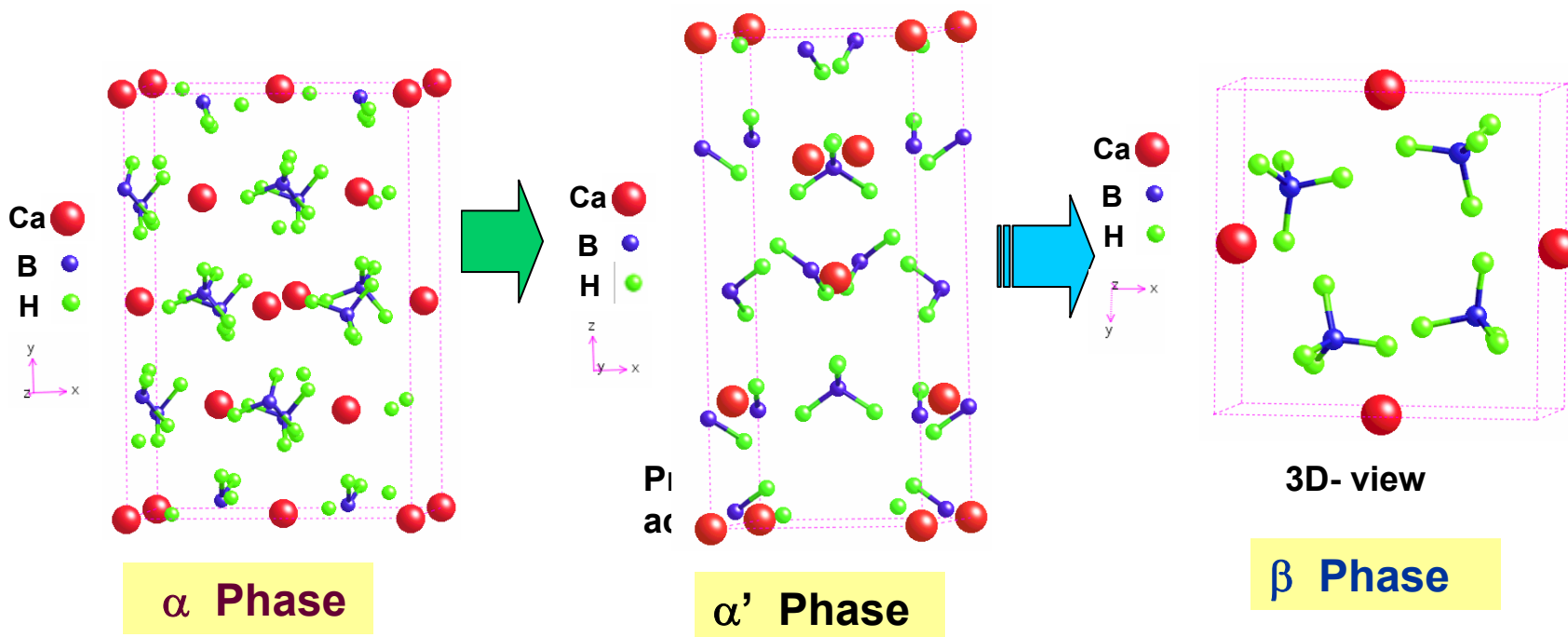
Variation of the Unit cell Parameters of α and α' - $\text{Ca}(\text{BH}_4)_2$ as a Function of Temperature



- ### Summary
- No change to lattice parameters of α phase until $\sim 165^\circ\text{C}$,
 - Unit cell volume per formula unit of the α and α' phases shows increases as temperature ramps up.
 - The volume of the unit cell of β phase shows linear increase during heating
 - Small amount of β phase are always present at the start of the experiment mixed with the α - phase

Volume of the $\text{Ca}(\text{BH}_4)_2$ / formula unit in the α , α' and β -polymorphs as a function of temperature

Structure determination in final Stages in Collaboration with ESRF (Grenoble) and Sandia National Laboratory



Summary

- New phase transitions were observed and crystal structures determined as shown above.
- Crystal Structures were determined in collaboration with Dr. Yaroslav Filinchuk (ESRF-Grenoble) and Dr. Ewa Ronnebro (Sandia National Laboratory).

Future Work on Complex Hydrides (FY '08 and Beyond)

- **1. Continue Work on Effect of Impurities on Specific Contaminants**
 - Pressure Cycling on mixed Mg-Li based complex hydrides
 - New 8 station combined cycling/Sievert's hydriding apparatus
 - Testing of hydrides developed by MHCoe partners
- **2. In-Situ Neutron and X-ray Diffraction Studies on Hydriding/Dehydrating**
 - Studies on Borohydride using X-ray and neutron diffraction
- **3. Vapor Pressure Studies on LiBH_4 and other Borohydrides**
 - Thermodynamics of vaporization of LiBH_4 and others
- **4. Phase Diagram Determination of Mixed Complex Hydrides**
 - Develop experimental non-equilibrium/equilibrium phase diagrams
 - CALPHAD modeling at UNR
- **5. High Pressure Differential Scanning Calorimetric Research**
 - Dynamic heating behavior at up to ~ 50 bar hydrogen
- **6. Hydrogen Lattice Dynamics Studies on Complex Hydrides- Prof. Cantelli, Univ. of Rome - IPHE Proposal**
 - "Hydrogen Dynamics, Lattice interactions, and Atomic-scale Structure of Complex/Chemical Hydrides"
 - Collaboration between Cantelli-Rome, Italy and Chandra-Jensen, USA
- **7. IEA/IPHE Collaborative Studies at Uni. of Geneva and CRNS (France)**
 - Proposal to study defect structures in the complex hydrides such as Li-Al hydrides , Mg-Li amides, and others

➤ Imide-Amide ($\text{Li}_2\text{NH-LiNH}_2$) Impurity Effects (UNR Sample)

- Studies on trace amounts of impurity gases (100 ppm) such as O_2 , CO , H_2O , and CH_4 , in H_2 and industrial hydrogen, up to ~1100 cycles.
- O_2 was most detrimental to the performance of amide-imide hydrides
- The kinetic analyses showed one order of magnitude change of the rate constants; from cycle 1 at $7.5 \times 10^{-3}/\text{sec}$ to $7.5 \times 10^{-4}/\text{sec}$. after 1100 cycles.

➤ Vapor Pressure Measurement of $\text{Mg}(\text{BH}_4)_2$ (Sample from GE)

- No significant vaporization of $\text{Mg}(\text{BH}_4)_2$. Below 233°C not possible to record any data.
- Above 233°C the ΔG° becomes negative and vaporization starts. ΔG° of $\text{Mg}(\text{BH}_4)_2$ was determined.
- Partial Pressures: $P_{\text{H}_2} = 8.8 \times 10^{-6} \text{ atm}$, $P_{\text{Mg}(\text{BH}_4)_2} = 2.03 \times 10^{-7} \text{ atm}$, at 225°C
- $\text{Mg}(\text{BH}_4)_2 (\text{s}) \rightarrow \text{Mg}(\text{BH}_4)_2 (\text{g})$ ($\Delta H = 93.4 \text{ kJ/mol}$) (only ~2% of the vaporization).
- The majority of the vaporization was due to disproportionation of $\text{Mg}(\text{BH}_4)_2 \rightarrow \text{Mg}(\text{s}) + \text{B}(\text{s}) + 4\text{H}_2(\text{g})$, $\Delta H = 44.82 \text{ kJ/mol}$ (~98%)

➤ Structure and Phase Transformations in $\text{Ca}(\text{BH}_4)_2$ (UNR-SNL Sample)

- in-situ synchrotron data showed two polymorphs of $\alpha\text{-Ca}(\text{BH}_4)_2$ and a small amount of β -phase formed upon removal of solvent from $\text{Ca}(\text{BH}_4)_2 \cdot 2\text{THF}$.
- A second order $\alpha \rightarrow \alpha'$ phase transition occurred at 222°C (confirmed by DSC).
- Another phase transition, $\alpha' \rightarrow \beta$ phase upon heating above 297°C and decomposes at 382°C into unknown products which according to TGA is associated with a weight loss, likely due to release of hydrogen.