

Reversible Hydrogen Storage Materials – Structure, Chemistry and Electronic Structure

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University of Illinois

***A Participant in the DOE Metal Hydride
Center of Excellence***

DOE 2006. Hydrogen Program Annual Review, Washington, D.C., 2007

Overview

Timeline

Start date: FY 05

End Date: FY 09

Percent Complete:

Budget

- **Total project funding**
 - \$1,566,746
 - DOE Share: \$1,253,396
 - UIUC Share: \$ 313,350
- Funding for FY 05: \$150,000
Funding for FY 06: \$175,000
Funding for FY 07

Barriers addressed

- Optimization of absorption /desorption kinetics of solid-state storage systems.
- Theoretical modeling to guide material development.
- Improve understanding of fundamental processes impacting alloy development that surpass targets.

Partners

The *DOE Metal Hydride Center of Excellence* participants, specifically *Sandia National Labs, HRL, U. of Hawaii, U. of Pittsburgh, CMU, General Electric.*

Objectives

Overall	<p>Support and guide development of complex metal hydrides to meet systems requirements by</p> <ul style="list-style-type: none">• providing center partners with structural and chemical insight of candidate systems.• providing experimentally based and validated theoretical modeling.
2007	<ul style="list-style-type: none">• providing modeling to guide materials development.• providing understanding of role of catalysts and determine nature, state and effect of surface contaminants on uptake and release.
2008	<ul style="list-style-type: none">• providing theoretical and experimental insight to reactions and processes that occur on and in near surface regions and could limit kinetics.• understanding how to optimize materials processing routes.

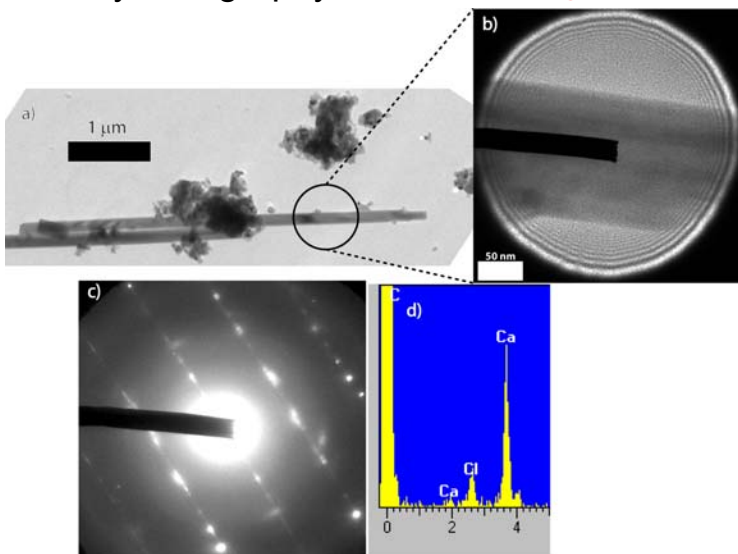
Approach overview

Our approach combines use of advanced characterization capabilities with first-principles electronic and thermodynamic calculations.

Structural/chemical information

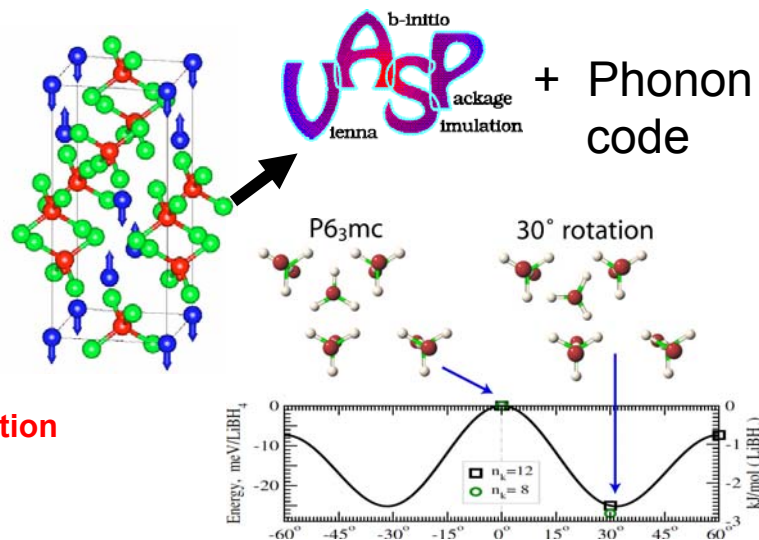
TEM – structure and crystallography

EDS and EELS – chemical and bonding information



Provides Needed information

First-principles calculations of thermodynamic properties



Aids interpretation

TEM, EDS, EELS – Robertson, UIUC
 X-ray diffraction – Clemens, Stanford
 Neutron diffraction – Udovic, NIST
 TEM – Ahn, Cal Tech

DFT D.D. Johnson, UIUC
 Monte Carlo Majzoub, SNL
 DFT K. Johnson, U. Pitt.
 DFT D. Sholl, CMU

Outcome: Provides guidance for new candidates with improved properties

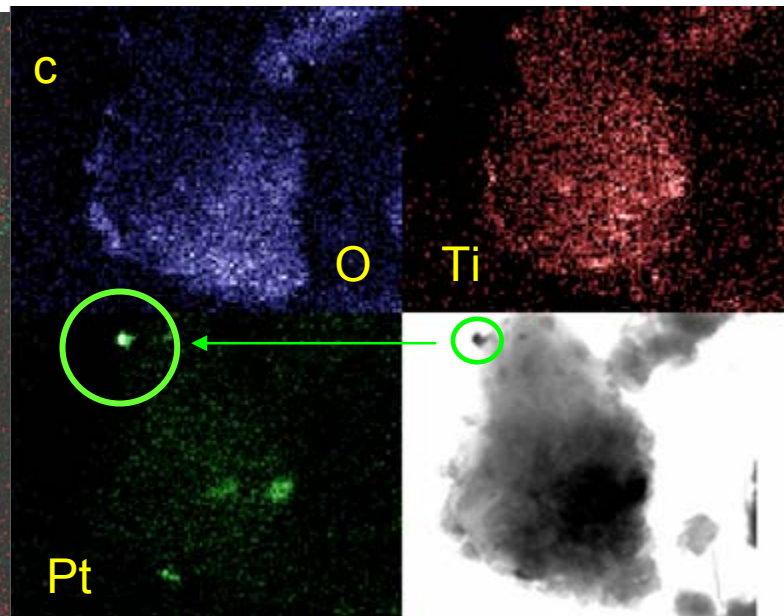
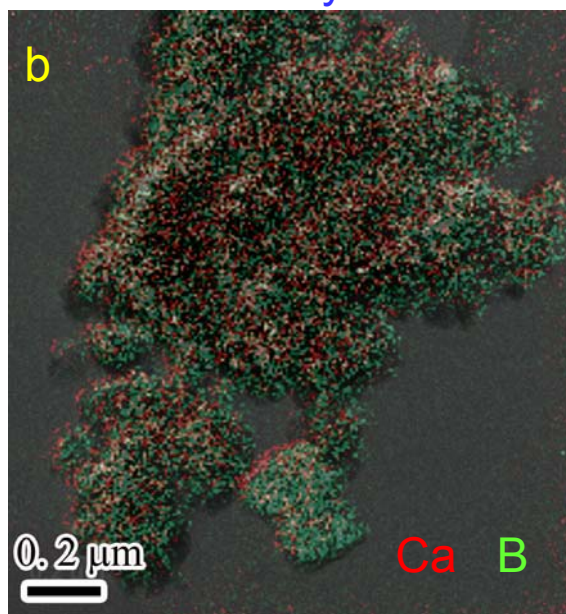
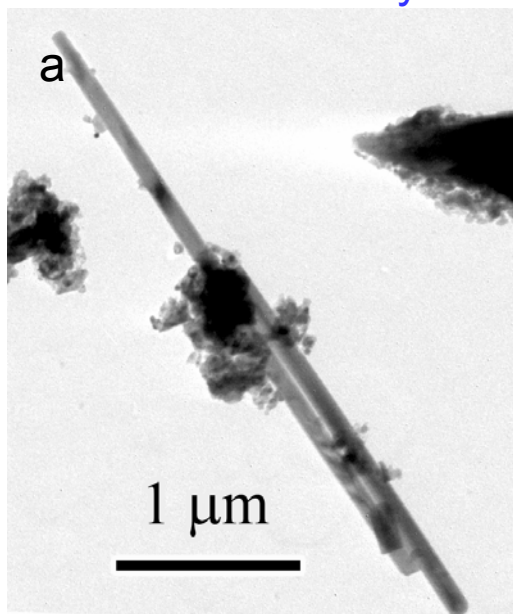
Microchemistry and Structure of Calcium Borohydride systems with different catalysts



4 mol % TiCl_3
Condition: 3-cycle

4 mol % V_2O_5
2-cycle

1 mol % TiF_3 and Pt
as-milled

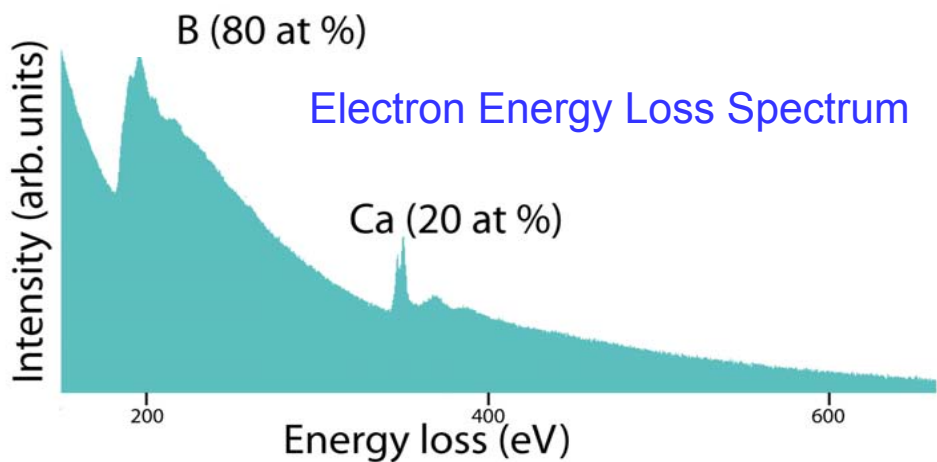
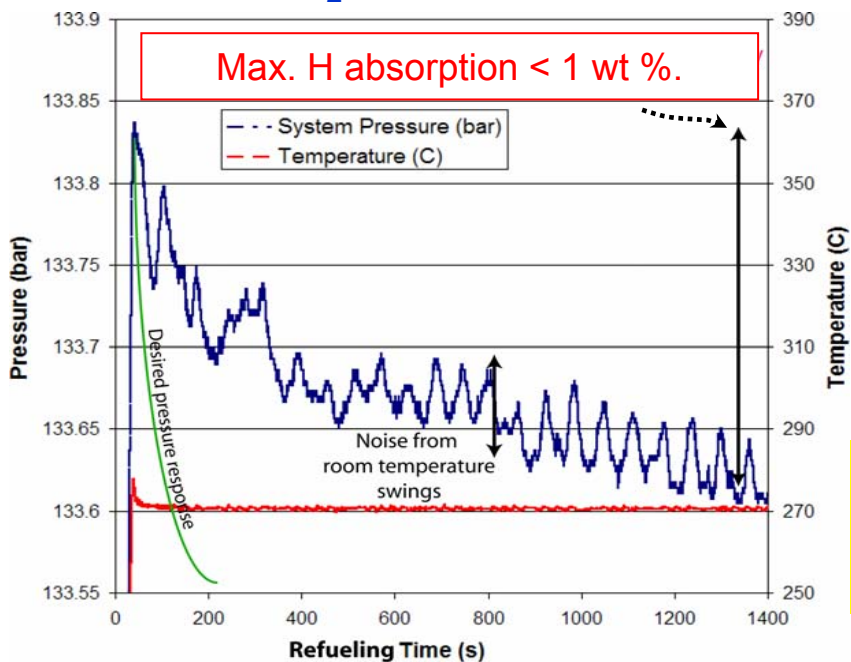


- TEM shows each crystal's external morphology.
Long crystals in (a) from environmental exposure and have ~80 at.% Ca and ~20 at.% Cl; crystal not yet identified.
- EDS for V_2O_5 and TiF_3 +Pt shows Pt does not disperse like TiF_3 and TiCl_3 .

Microchemistry and Structure of Calcium-Borohydrides

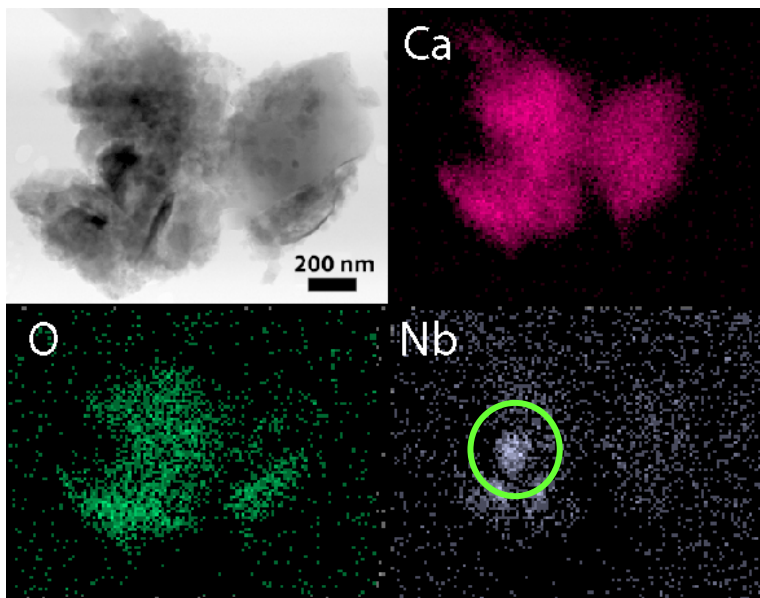
- $\text{Ca}(\text{BH}_4)_2$ can potentially store 11 wt % H_2 .
- Dehydrided forms of $\text{Ca}(\text{BH}_4)_2$ created by ball-milling CaB_6 , CaH_2 + catalyst.
- Catalysts selected for initial study were Nb_2O_5 , V_2O_5 , TiCl_3 and Pt.
- Working with Sandia, total H adsorption found to be < 1 wt % H_2 (P vs t).
- High-pressure reversibility demonstrated, but no low-pressure found yet.

$\text{CaB}_6 + 2 \text{CaH}_2 + 0.04 \text{Nb}_2\text{O}_5$ at
134 bar H_2 (~2000 psi); 270 °C.



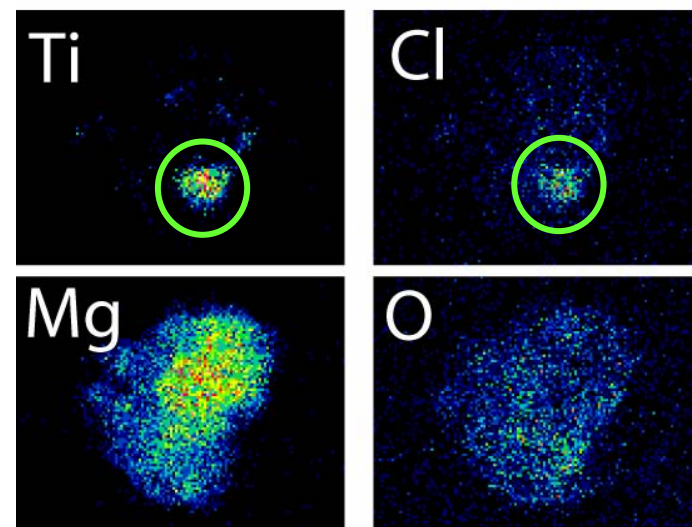
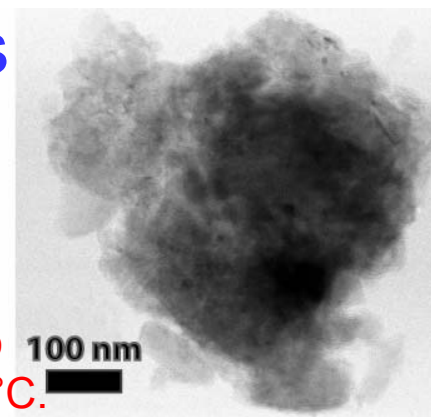
- Quantitative EELS detects isolated regions of CaB_6 that should be hydrided $\text{Ca}(\text{BH}_4)_2$.
- EELS confirms that hydrogenation does not occur.

Evaluation of borohydride materials



$\text{CaB}_6 + 2 \text{CaH}_2 + 0.04 \text{Nb}_2\text{O}_5$ shows poor distribution of Nb-oxide catalyst particles.

Mg-borohydride with TiCl_3 catalysts gave no reversibility up to 200 °C.

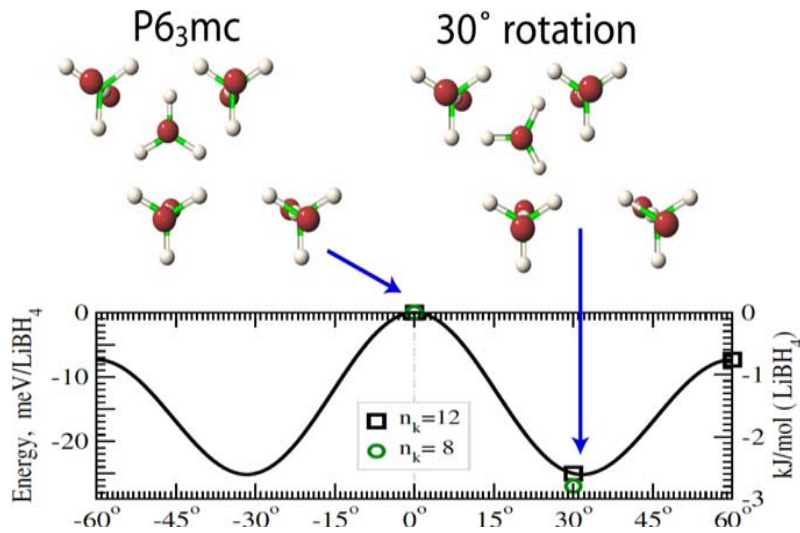


- *No reversibility* at low pressure using catalysts successful in Mg-based systems.
- *Highly uneven distribution of catalysts* always found.
- *Barrier to reversibility at low pressure is currently unknown*, possibly from “accidental” catalysis by undesirable CaO that we have tried to avoid.
- Proposal: *Re-evaluate modeling (E. Majzoub, SNL) that suggested this system, due to possible underestimate of enthalpy from assuming a structure for $\text{Ca}(\text{BH}_4)_2$.*

Ab Initio MD to Determine High-T Structure of LiBH₄

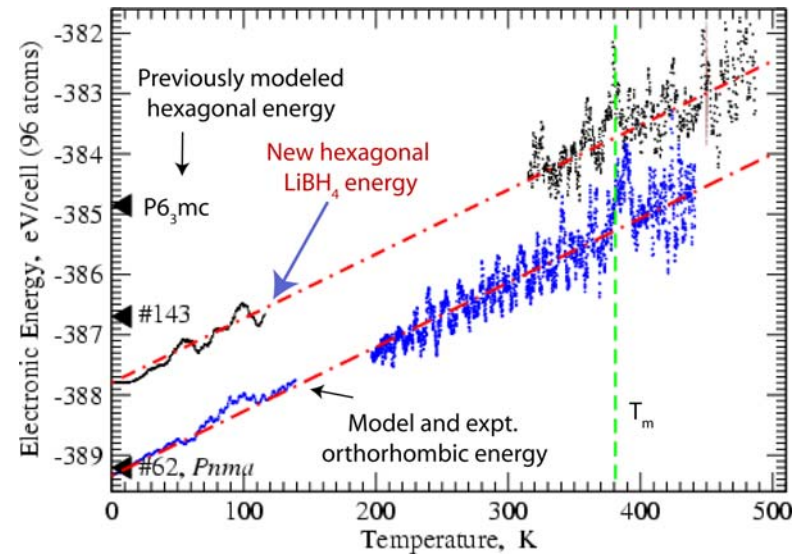
- We calculated barriers and performed *ab initio* molecular dynamics to ascertain the structure and stability of the *high-T LiBH₄* (*relevant phase for H release*) because standard harmonic phonon approximation is generally invalid for these systems.
- We predict the correct high-T hexagonal phase by accounting for rotation of BH₄ units.

DFT barriers for experimentally suggested high-T *P6₃mc* phase



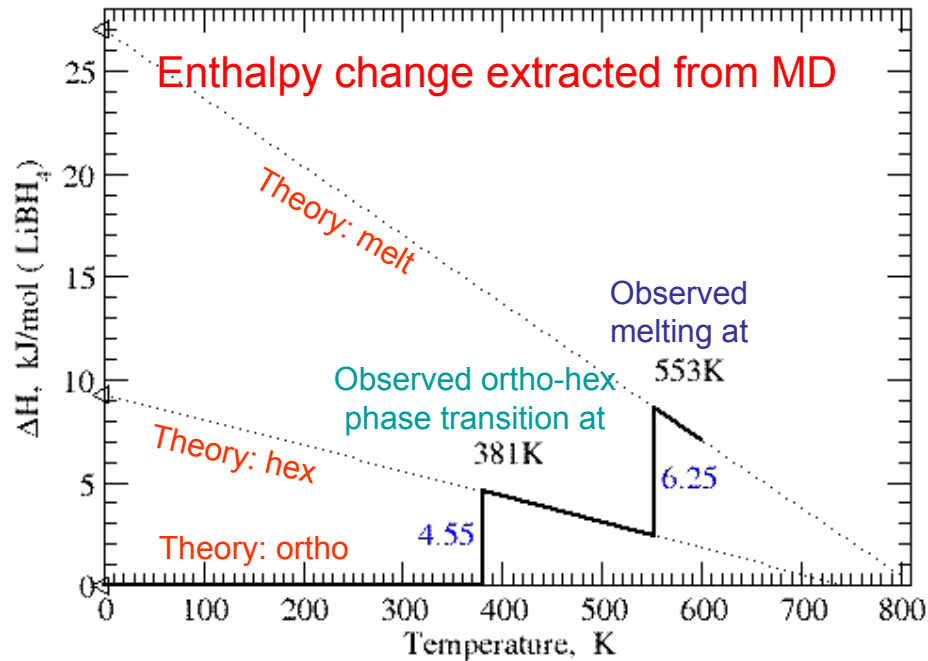
- Calculated barriers of experimentally suggested *P6₃mc* structure are negative, hence *P6₃mc* is unstable.
- Several hex-like structure are found due to rotations of BH₄ units that lower energy.

Ab initio MD in low-T ortho and high-T hex phases
Heavy B atoms fixed to observed positions



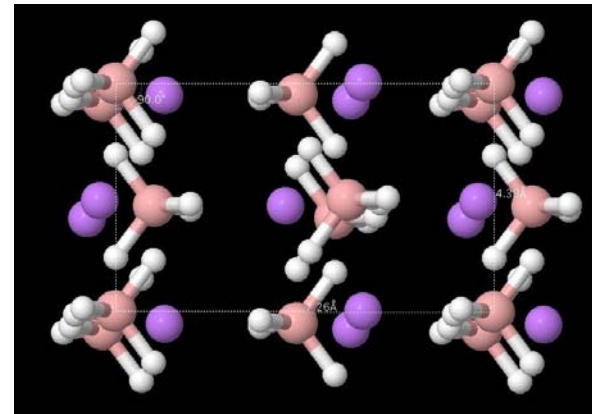
- Phase transition is marked (dashed green). No approximation to phonons made.
- As E vs T for phases are parallel, simple mode counting valid ($1/2 k_B T/\text{rot-mode}$).
- *P6₃mc* structure found to approximate incongruent melt phase in experiment.

Ab initio MD Predicted Transition Enthalpies for LiBH_4

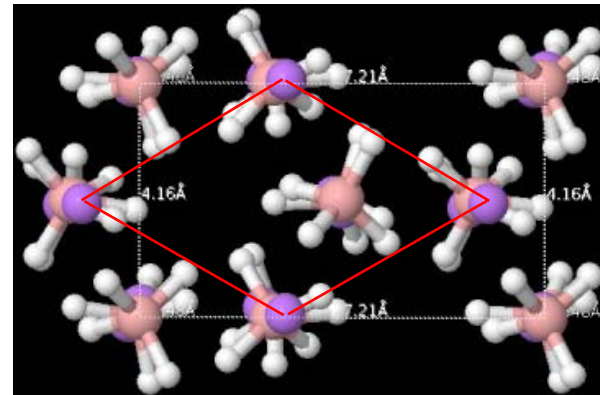


Enthalpy of transition, kJ/mol (LiBH_4)		
	Theory	Expt.
Solid-solid	4.55	4.3
Melting	6.25	6.9

Low-T (known) ortho structure.



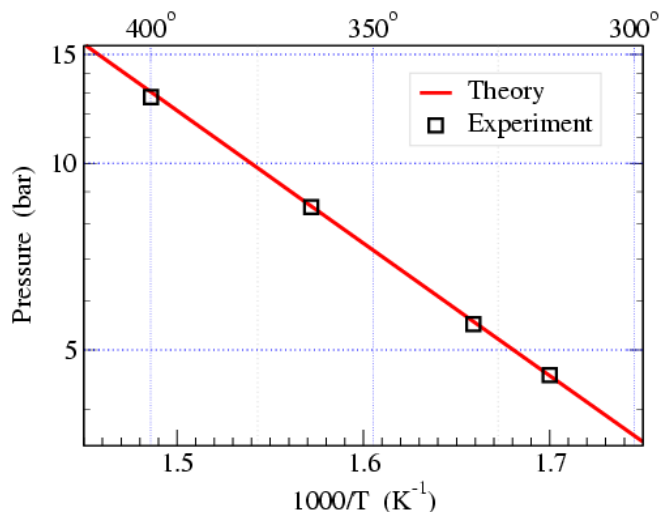
Proposed high-T hex structure



- Ab initio MD (beyond harmonic phonons) yields accurate enthalpies, whereas $T=0\text{K}$ DFT with harmonic phonons does not include rotational modes.

DFT Predicted Reaction Enthalpies and P-T curves for LiBH₄

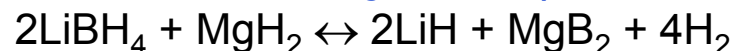
Van't Hoff P-T plot for high-T LiBH₄



We solve Gibbs

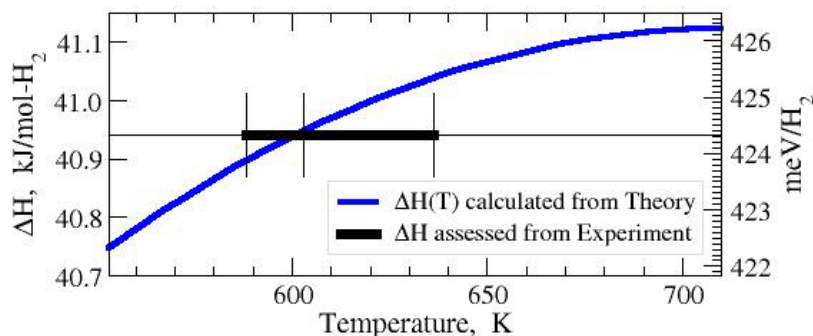
$$\ln P = -\frac{\Delta G_{elec+vibr}}{Nk_B T} + \frac{7}{2} \ln T - \frac{7}{2} + const$$

Reaction in high-T hex phase



LiBH₄ is melted above 553K.

Reaction Enthalpies for high-T LiBH₄



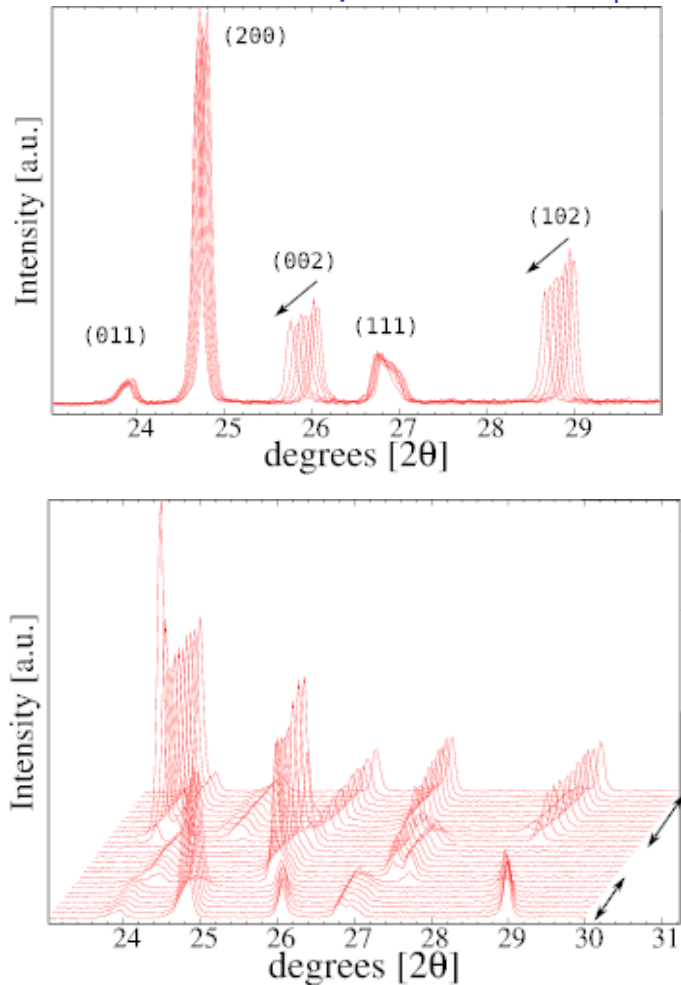
- ✓ Predicted enthalpy (and slope of P-T curve) at 600 K is 41 kJ/mol-H₂
- ✓ Now **theory** and **experiment** are in good agreement.

Measured data from J. Vajo, HRL.
With CMU and Sandia for Harmonic phonons calculations via PHONON code.

- Using the mode-counting within DFT that includes harmonic phonons is accurate, if *incongruent* melt phase (where dehydrogenation is measured) is approximated

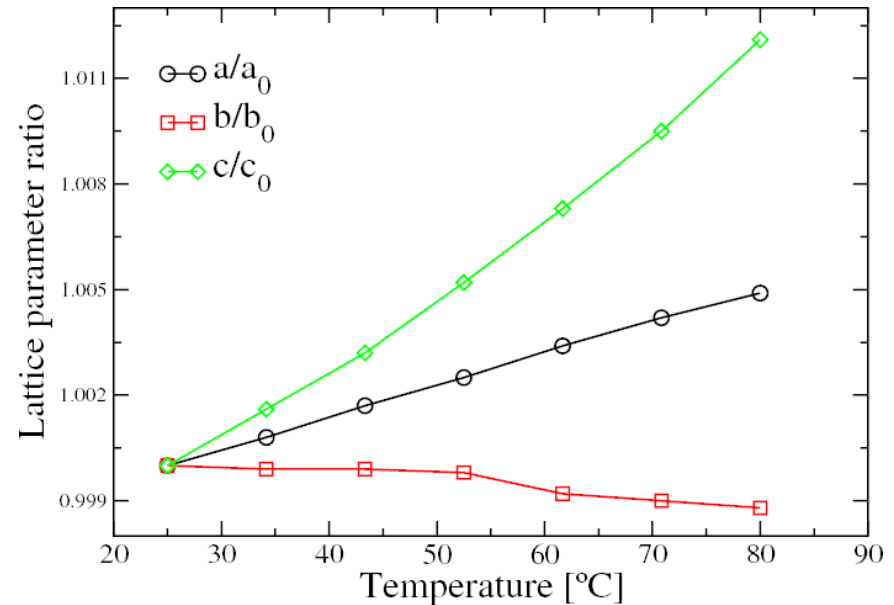
Modeling and X-ray Diffraction Investigations of Lithium-Based Hydrogen Storage Materials

XRD has T-dependent shift for low-T ortho phase of LiBH_4



Measured anisotropy (E. Majzoub, SNLL) gives **a-axis** as softest and **c-axis** as hardest direction.

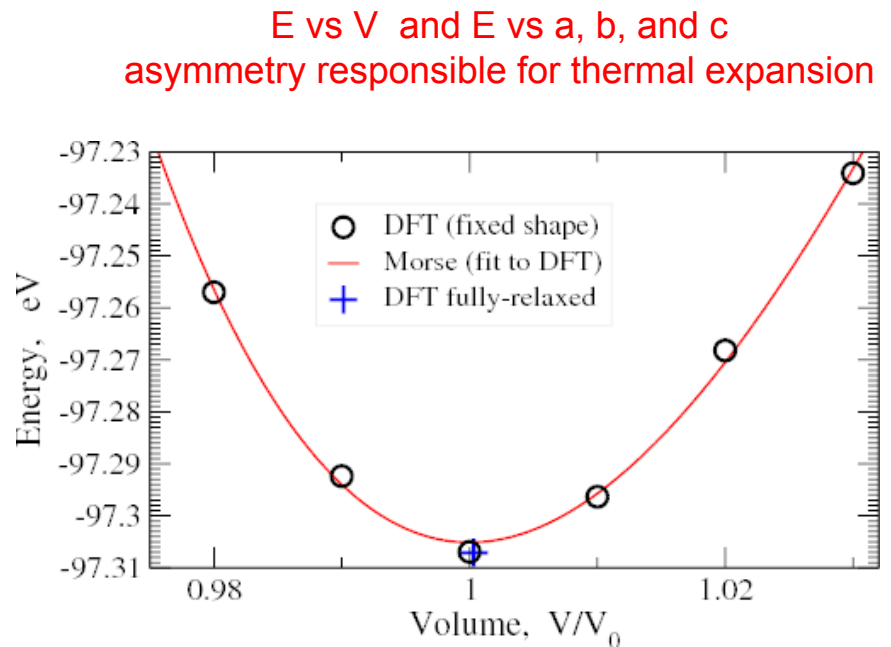
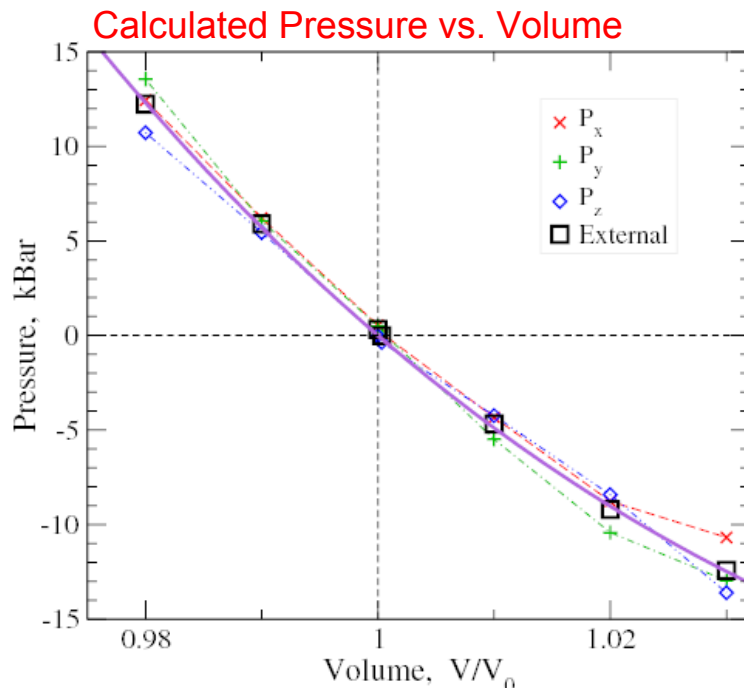
- No thermal expansion along **b-axis**.



• Shift in position and decrease in intensity consistent with DFT-predicted phase change.

Modeling and X-ray Diffraction Investigations of Lithium-Based Hydrogen Storage Materials

- Sandia/UIUC XRD data showed low-T and high-T structural changes to LiBH_4 .
- We have calculated the DFT enthalpy and lattice parameters and determined understand what causes the T-dependent shift in low-T XRD.



- LiBH_4 thermal expansion arises from asymmetry in potential giving pressure (stress) anisotropy (color coded to expt next slide).
- From DFT, z (a -axis) is softest and y (c -axis) is hardest, but we are currently finding the individual E vs a , b , and c curves for 1-to-1 comparison to XRD.

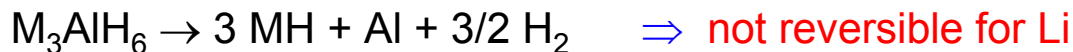
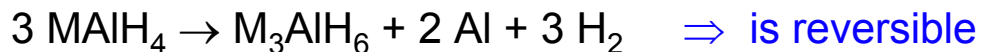
Reversibility and Poisoning of H-storage reactions in Alanates

- Observation of poisoning in secondary reactions that decrease yield.

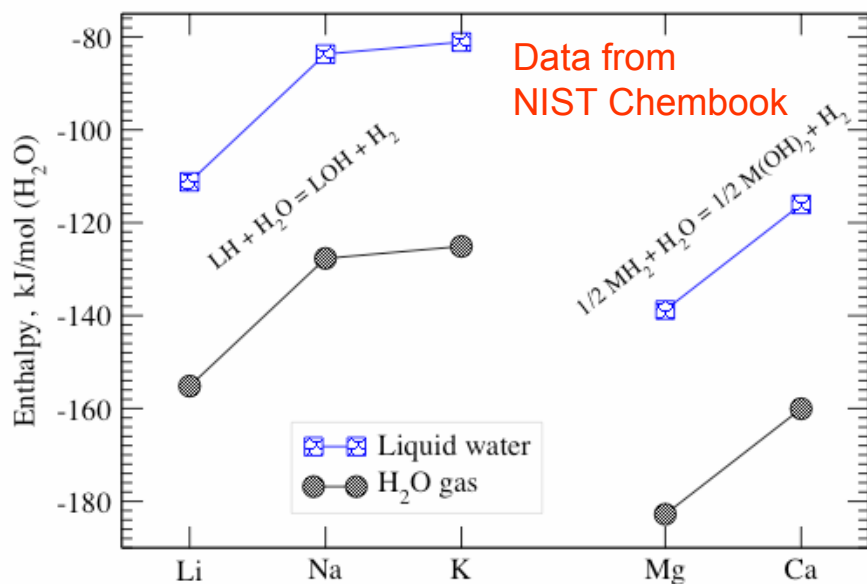
e.g., R. Ren et al., J. Phys. Chem. B 110 (2006) 10567-75.

By H_2O and O_2 at R.T. to form LiOH , and $\text{O}_2 > 55 \text{ C}$ to form Li_2O .

- With Pitt/CMU, address enthalpy related issues to help ameliorate possible issue.
- Focus on the 2-step reactions (M = Li, Na, K):



With O_2 , consider surface 2-step reaction: $\text{MH} + 1/2 \text{O}_2 \rightarrow 1/2(\text{M}_2\text{O} + \text{H}_2\text{O}) \rightarrow \text{MOH}$
 With H_2O , consider surface reaction: $\text{MH} + \text{H}_2\text{O} \rightarrow \text{MOH} + \text{H}_2 + E_{\text{ad}}$



- ✓ LiH is poisoned by LiOH.
- ✓ Mg stronger interactions with OH.
- Suggestion:** Getter OH via MgH_2 to prevent poisoning of LiH.
- ✓ Reversibility to be checked by experiment (SNL/CA).

The Structural Database: Data sharing amongst MHCoe



ORACLE® type database. N. Zarkevich and D.D. Johnson (2005)

All VASP structures (xyz), energies (ΔH), ... are stored into electronic Structural Database (<http://data.mse.uiuc.edu>)

Home Structures Lattices Symbols Elements Methods Authors Comments

Structures : Recently added : Other

First found 2 structures, displaying 1 through 35

	Name	Energy (eV/atom)	FE (eV/atom)	Error (eV/atom)	Pressure (kbars)	Stoichiometry	Composition	# Atoms	# Types	Author
<input type="checkbox"/>	LiBH4-hex	-4.190185	null	.01	-.67	2:8:2	B H Li	12	3	Nikolai Zarkevich
<input checked="" type="checkbox"/>	LiBH4-ort	-4.22446	null	.01	-.82	4:16:4	B H Li	24	3	Nikolai Zarkevich

e.g. "click" name, structure appears via Jmol® with xyz coordinates.

- All MHCoe collaborators (and others) access, download, and contribute by upload via scripts. No unnecessary repetition!
- Sandia MHCoe Theory people have contributor status.
- Systems MHCoe have explored are being upload. Database log errors are being fixed which slowed uploads due to disk filling.
- Visualization of all structures possible via Jmol® interface.
- Information to reproduce calculations are part of database.
- Upgrades to database for stability being made in summer 2008.
- Database will then be opened to all DOE, MIL, and EDU urls.

Future experiments and theory

FY08 Future Directions

- For FY 08 we will continue experimental studies of the microchemical and microstructural changes occurring in different candidate systems that are supplied by the various partners. In addition to diffraction and EDS analysis, electron energy loss spectroscopy will continue to be used to identify electronic states within the materials.
- The *Structural Database* will continue to be updated and used by partners.
- Further studies on the electronic-structure calculations on the bulk phase of LiBH_4 in the high-temperature hex-phase, along with H_2 , hexagonal MgB_2 , MgH_2 and LiH will be conducted with input from the HRL group.
- Kinetics and poisoning issues with OH^- and O^{2+} will be addressed to try to ameliorate problems within secondary reactions within Li-alanate to increase H_2 yield. Results of these studies may require experimental verification and we will collaborate with partners as appropriate.
- Additional calculations will be performed with input from partners regarding key issues.

Specific Efforts and collaborations

- Determine chemical and structural change occur during (de)hydriding cycles for different systems (with SNL, HRL, U Hawaii)
- Structure and energy of combined Mg-borohydrides.
- Complete study of $\text{CaH}_2/\text{CaB}_6$ (with SNL)
- Structure and chemistry of contaminant layers on (de)hydriding cycle (U. Nevada, SNL, CMU, U Pitt.)
- Evaluate overall effectiveness of ball-milling at distributing catalyst particles. (Cal Tech, HRL)