Current Challenges and Needs in Metal Hydride Research

Ewa Rönnebro

Sandia National Laboratories
Livermore, CA, USA

NIST Gaithersburg, MD, November 5, 2008

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MHCoE Contributions from…

UMSL: Eric Majzoub
HRL: John Vajo
U. Pitt.: Karl Johnson
GT: David Sholl
UIUC: Duane Johnson, Dennis Graham
Sandia: Rich Behrens
OSU: J.-C. Zhao
UNR: Dhanesh Chandra
UH: Craig Jensen

Funding provided by U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy under the Hydrogen Storage Grand Challenge, Metal Hydride Center of Excellence (MHCoE) within DOE's National Hydrogen Storage Project

MHCoE Project Structure

DOE

Coordinating Council (2007-2008)

Bruce Clemens (Stanford, POC A), Ewa Rönnebro (SNL, POC B), Zak Fang (Utah, POC C), Jim Wegrzyn (BNL, POC D), Don Anton (SRNL, POC E), Craig Jensen (UH), Jay Keller (SNL) and Lennie Klebanoff (SNL)

Project Groups

A

Destabilized Hydrides

- **Stanford (POC)**
- Caltech
- JPL
- UIUC
- U. Hawaii
- U. Pitt/CMU
- HRL
- U. Utah
- Intematix
- NIST

B

Complex Anionic Materials

- **SNL(POC)**
- GE
- U. Hawaii
- UIUC
- JPL
- ORNL
- NIST
- UNR
- Utah
- UTRC

C

Amides/ Imides (M-N-H)

- **Utah (POC)**
- GE
- UNR
- ORNL
- U. Hawaii
- JPL
- Caltech
- SRNL

D

Alanes (AlH_3)

- **BNL(POC)**
- SRNL
- U. Hawaii
- SNL
- UIUC
- UNB

E

Engineering Analysis & Design

- **SRNL(POC)**
- NIST
- JPL
- GE
- SNL

MHCoE Budget: ~ $8.6M FY'07

Contents

- Materials within MHCoE
- Synthesis methods
- Characterization methods
- High-capacity borohydride related materials
- Computational Materials Screening
- Summary challenges and needs

Approach to Technical Targets

H Capacity: 2010 System Targets: 6 wt. %, 45gH_2/L vol. density

- Synthesize and characterize hydride materials with high hydrogen capacity and favorable thermodynamics. Use state-of-the-art theory to guide materials discovery effort.

Charge/Discharge Rates: 2010 Sys. Target: 3 min. system fill (5kg)

- Develop materials that are fully reversible, catalysts that aid reversibility, assess nanoengineering promotion of kinetics, and investigate role of contamination on reaction rates

Hydrogen Purity (from Storage) : 2010 Target: 99.99% pure

- Assess release of NH_3, B_2H_6 and other volatile species from metal hydrides during desorption and cycling

Cycle Life: 2010 Target: 1000 Desorption/Adsorption Cycles

- Investigate durability of materials, cycling behavior, effects of contaminants, structural stability, release of volatiles

Challenges to Discover and Develop High-Capacity Materials

Kinetics:

The adsorption/desorption kinetics of metal hydrides are typically too slow. We are using nanoconfinement and catalysts to increase kinetic performance.

Thermodynamics:

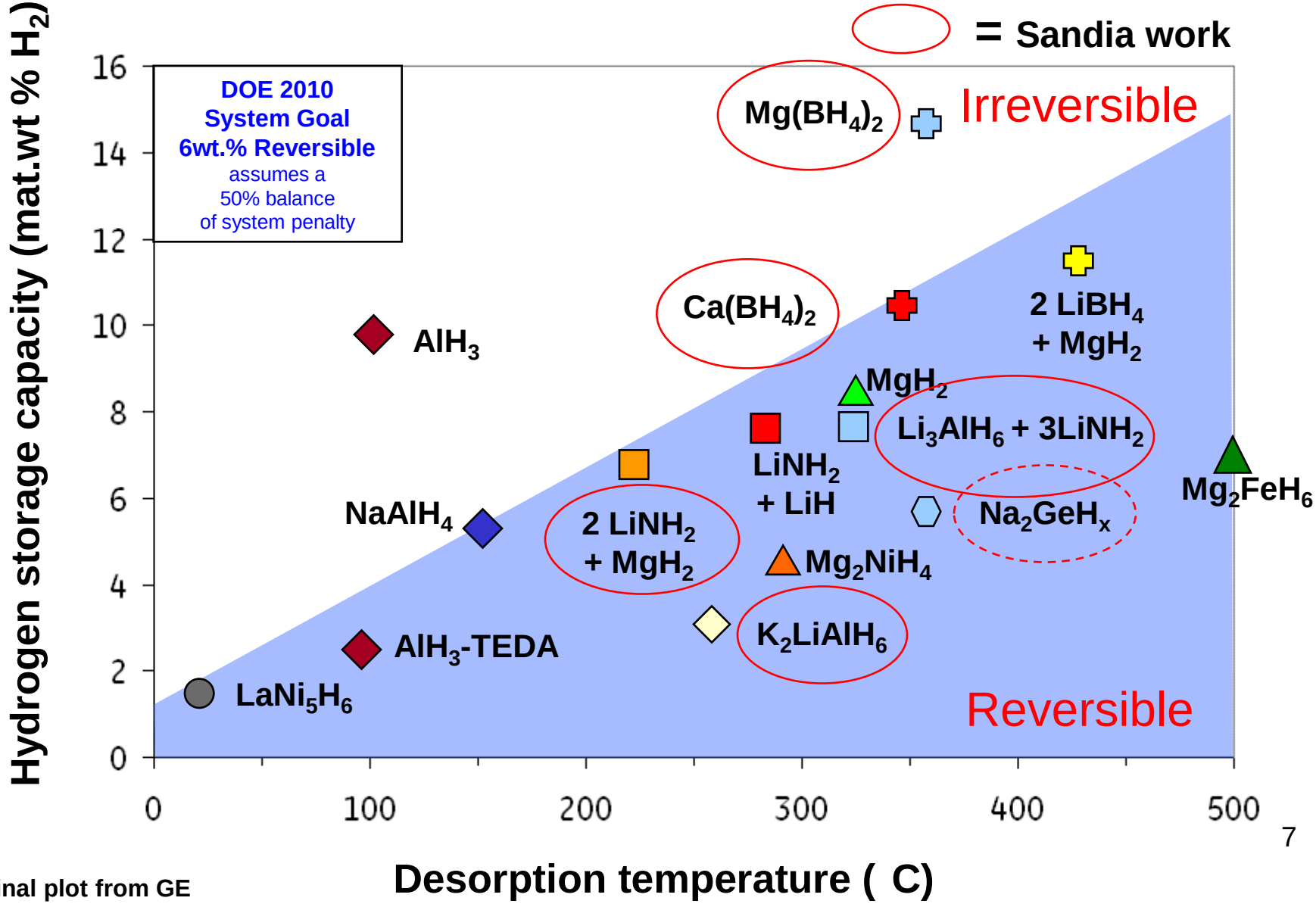
The enthalpies of reaction and activation barriers for metal hydrides are typically too high, requiring desorption temperatures in excess of PEM fuel cell operating temperatures.

Reversibility:

Many thermodynamically-promising metal hydride systems are either not reversible, or reversible only under impractical conditions.

… in addition to cycle life, H_2 capacity, hydrogen purity….

Some Materials of Interest



Original plot from GE

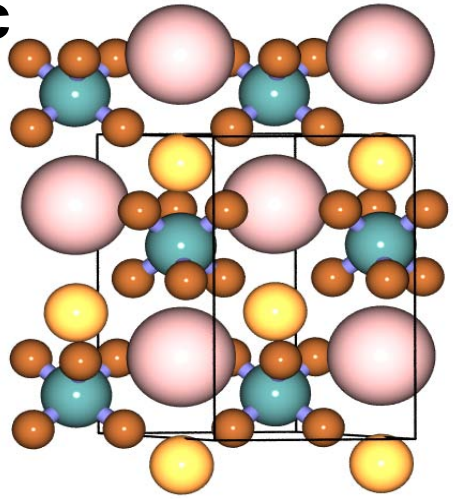
Synthesis Methods

Screening for New H-storage Materials

- **High-pressure synthesis (<2000bar, 500°C) and mechanical alloying (E. Rönnebro)**

- **Theory guidance: Prototype Electrostatic Ground State Search (PEGS) provides minimum energy structures for subsequent enthalpy estimates (E.H. Majzoub and V. Ozolins, PRB, in press)**

- **Examples of potential structures:**
  - **Metal borohydrides; $Mg(BH_4)_2$ and $Ca(BH_4)_2$**
  - **$AB(BH_4)_x$ (bialkali borohydrides)**
  - **Alkali transition metal borohydrides**



PEGS-generated Structure

Solid-State Synthesis of Complex Metal Hydrides

'Hot-sintering' under H_2-pressures

- **Metal + Binary Hydride + H_2 → Complex Hydride**
- Hydrogen pressure <100 bar in an autoclave
- Temperature <600°C
- Reaction time: several hours to several days
- Most known complex metal hydrides have been made by hot-sintering

The sintering technique is also used by groups at: U. Geneva (Switzerland), MPI (Germany), Stockholm University (Sweden), IFE (Norway), SRNL (USA), U. Tohoku, AIST (Japan)

Mechanical Alloying

Mechanical alloying

- Ball milling in Argon or H_2 atmosphere
- Reaction time: several minutes to several hours
- Some complex metal hydrides have been made by this method
- Sometimes necessary before further heat treatment to form materials of interest

High-pressure Station for Medium-Throughput Screening

Commercial autoclave with 6 steel crucibles

Metal + Binary Hydride + H_2 → Complex Hydride
Boride + Binary Hydride + H_2 → Metal Borohydride

Established a synthesis route that combines high-energy milling (SPEX) followed by hot-sintering under high H_2-pressures (in-house station)

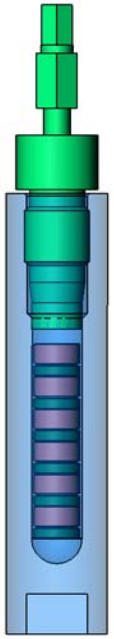
We can test six samples per experiment at a certain P, T and reaction time. Screening involves both searching for new materials and catalysts

Normal Run:
<700bar H_2-pressure, <450ºC

Why high-pressures?

Not so practical for applications, but:

- Reaction times shortened
- To screen for new materials: start at high pressures and if a hit, go to lower pressures (and temperatures) to optimize reaction conditions
- Utilizing six sample holders per run gives a moderate throughput
  - Six different molar ratios per run, or
  - Six different additives per run



Synthesis NH_3 complexes of metal borohydrides

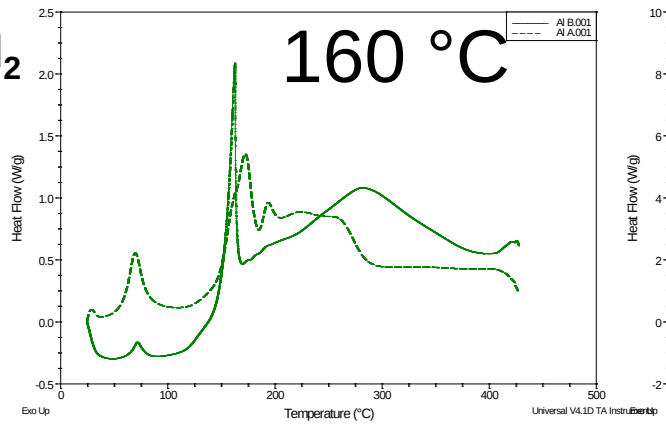
J.-C. Zhao, OSU

$$MCl_n + (2+n)\,LiBH_4 \xrightarrow[\text{3 hrs}]{Et_2O} Li_2M(BH_4)_2 \xrightarrow[\text{-30 °C}]{NH_3} M(BH_4)_n{\cdot}6NH_3 + 2\,LiBH_4$$

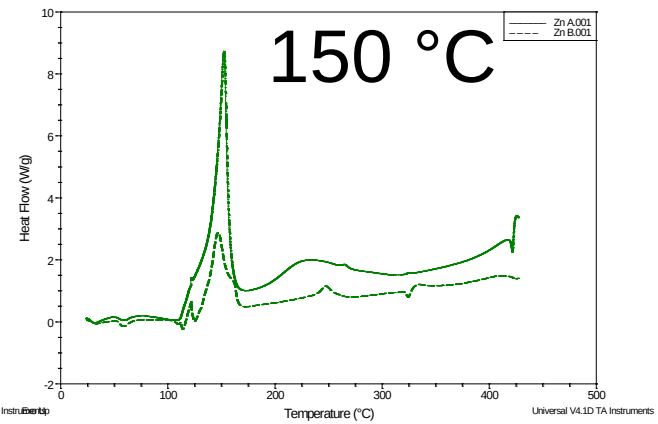
$$Li_2M(BH_4)_2 \rightarrow 2\,LiCl$$

$$M(BH_4)_n{\cdot}6NH_3 \rightarrow \boxed{M(BH_4)_n{\cdot}2NH_3}$$

$M(BH_4)_n{\cdot}2NH_3$	wt % H_2
$Mg(BH_4)_2{\cdot}2NH_3$	16.0
$Zn(BH_4)_2{\cdot}2NH_3$	10.9
$Al(BH_4)_3{\cdot}2NH_3$	17.1
$Ti(BH_4)_3{\cdot}2NH_3$	14.3



$Al(BH_4)_3{\cdot}2NH_3$



$Zn(BH_4)_2{\cdot}2NH_3$

- NH_3 complexes of other metal borohydrides synthesized
- Aluminum and zinc borohydrides have low H_2 desorption temp

NH_3 complexes make $Al(BH_4)_3$ and $Zn(BH_4)_2$ more stable and $Mg(BH_4)_2$ less stable
→ provides another way to fine tune thermodynamics

High-capacity borohydride related materials

Reversibility of Metal Borohydrides

- By hydrogenating decomposition products, reversibility is shown:

For example:

$CaB_6 + 2CaH_2 + 10H_2 + 2mol\%\ additive \rightarrow 3Ca(BH_4)_2$

Patent filed: Rönnebro and Majzoub

- Only feasible at higher H_2-pressures, i.e. ca 700bar (at ca 350C). We are utilizing our six sample autoclave to screen for feasible reactions/additive

- But, the challenge is that there can be competing reactions…

Reaction mechanism of $Ca(BH_4)_2$

- Competing decomposition reactions:
  - $3Ca(BH_4)_2 \rightarrow CaB_6 + 2CaH_2 + 10H_2$ (9.6 wt%)
  - $6Ca(BH_4)_2 \rightarrow CaB_{12}H_{12} + 5CaH_2 + 13H_2$ (6.3 wt%)
    - $\Delta H^{300K} \sim 40$kJ/mol (Ozolins, Majzoub, Wolverton, submitted 2008)

- MAS NMR (JPL/Caltech) indicated intermediate species
- We are underway characterizing $CaB_{12}H_{12}$ and comparing with decomposition products in collaboration with NIST, Caltech and others

New Materials Discovery
Need for effective screening

- Synthesis of Ternary Borides:
  - Metal or Transition metal(s) + boride
  - Prepared by solid state reactions
  - Need to screen through all transition metals
- Hydrogenation of Ternary Borides:
  - Within 150bar H_2-pressure range, or,
  - Within 2000bar range (Sandia's HP-station)

HRL: John Vajo and SNL: Ewa Ronnebro

Other Borohydride Related Materials

- Examples:
  - $Mg(BH_4)(NH_3)_x$
  - $Ca(BH_4)(AlH_4)$
- Challenge is that these materials may need multiple solution based reaction steps to form

Characterization

Characterization of Metal Hydrides

- Powder XRD: metal atom structures
  - Often first thumbprint if material is crystalline
- Neutron Diffraction: H/D atoms located
- Synchrotron XRD: Crystal structure, H atoms located
- Raman Spectroscopy, FTIR
- NMR
- STMBMS (Simultaneous thermo-gravimetric modulated-beam mass spectrometer)
- TEM: morphology, studies of additive dispersion
- Thermodynamics and kinetics studies

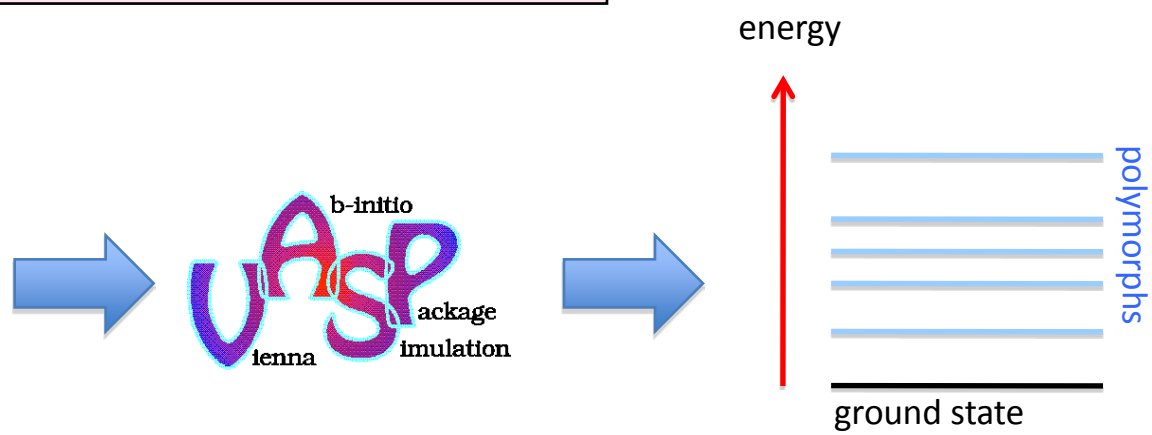
Computational Materials Screening

Computational Materials Screening

Determine structures and polymorphs

Competing Structures

- database (ICSD)
- structure search (PEGS)



Determine reaction pathways

Using database structures, minimize reaction free-energy with stoichiometric constraints

$$G(T,p) = \sum_i x_i F_i(T) - \frac{\mu_{H_2}(T,p)}{2} \sum_i x_i n_i^H$$

Eric Majzoub, UMSL

PEGS Predicts Several New AlH_6-based Bialkali Hydrides*

Metropolis Monte Carlo + Potential Energy Smoothing

$$H = \sum_{i<j} \left(\frac{Z_i Z_j}{r_{ij}} + \frac{1}{r_{ij}^{12}} \right)$$

PEGS vs. ICSD: 2 f.u. AlH_6 alanate Comparison (energies kJ/mol)

System	Ground state	ICSD 2 f.u.	PEGS 2 f.u.
$LiMgAlH_6$	3 f.u.-$LiMnGaF_6$ (P321)	+5.8	+6.7
$NaMgAlH_6$	1 f.u.-$RbGeIO_6$ (P312)	0	0
$KMgAlH_6$	4 f.u.-$CsAgAlF_6$ (Pnma)	+3.9	+9.6
$LiCaAlH_6$	4 f.u.-$LiBaCoF_6$ ($P2_1/c$)	+12.1	+8.5
$NaCaAlH_6$	4 f.u.-$KNaSiF_6$ (Pnma)	+29.5	+13.1
$KCaAlH_6$	4 f.u.-$KNaSiF_6$ (Pnma)	+39.7	+22.2

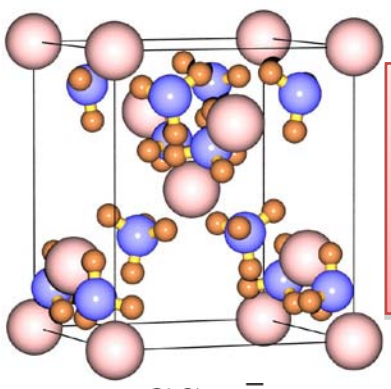
- PEGS outperforms database searching on a per f.u. basis
- PEGS predicts many observed structures: $NaAlH_4$, $Mg(AlH_4)_2$, K_2LiAlH_6, etc.
- $LiMgAlH_6$ prev. reported by Opalka, Mosher, et al.

*E.H. Majzoub and V. Ozolins, *Phys. Rev. B*, **77**, 104115 (2008)

PEGS Method Produces Best Candidate for $Mg(BH_4)_2$ Ground State

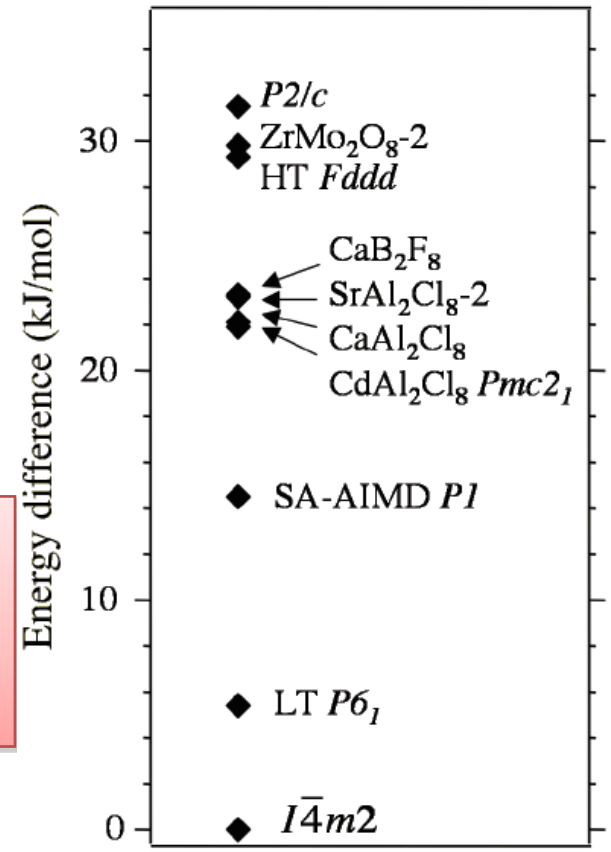
Eric Majzoub, UMSL

$Mg(BH_4)_2$ crystal structure from experiment
LT ($P6_1$) — 30 f.u./conv cell
HT (Fddd) — 64 f.u./conv cell
Her, et al., *Acta Cryst.*, **B63**, 561 (2007)



PEGS $I\bar{4}m2$

PEGS Prediction – LT (I-4m2)
4 f.u. primitive cell
V. Ozolins, E.H. Majzoub, C. Wolverton, *Phys. Rev. Lett*, in press



- PEGS static DFT total energy lower than expt observed structure
- New low energy structure with small unit cell allows DFT phonon calculations

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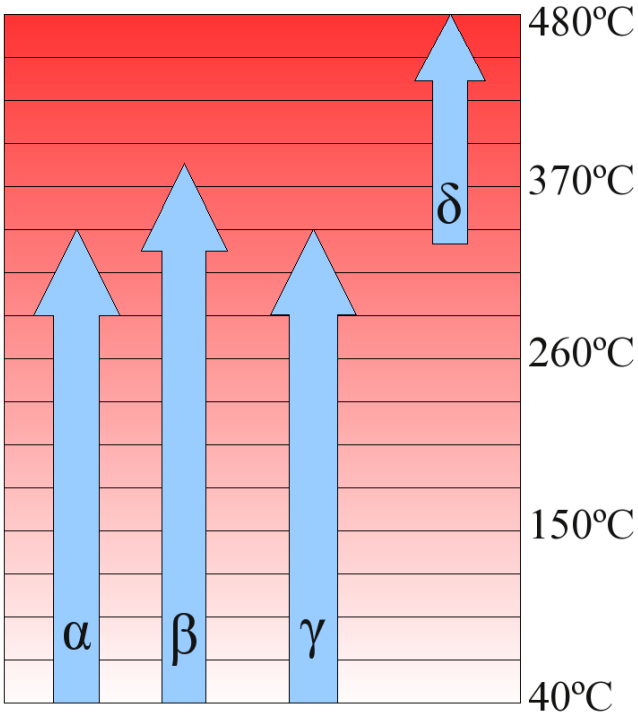
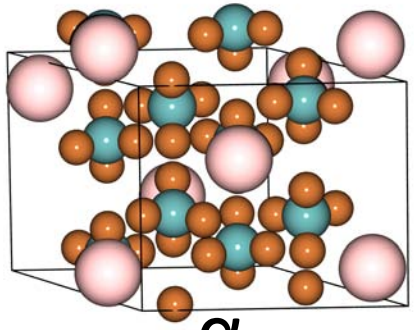
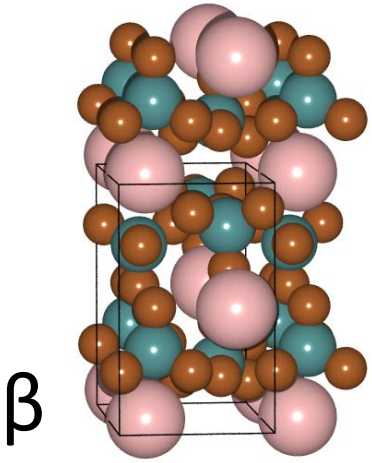
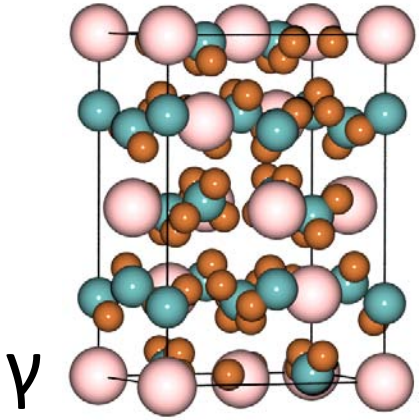
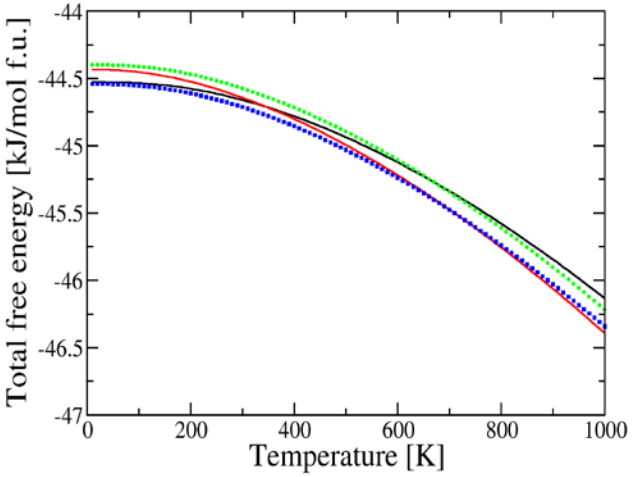
Combined Database Search and PEGS Finds Several Low-Energy $Ca(BH_4)_2$ Structures











- Four phases observed experimentally
- Identification debatable!

Majzoub, Rönnebro, submitted (2008)

Reaction Pathways Predicted for AlH_6-based Alanates

TABLE XI. Structural stabilities ΔH of the lowest-energy hexa-alanate structures identified in this study. The enthalpies are given relative to the energetically most favored phase separation products at each composition. Positive enthalpies indicate stable hexa-alanate compounds.

Compound	Prototype (symmetry)	Products	ΔH (kJ/mol)
$LiMgAlH_6$	$LiMnGaF_6$ ($P321$)	$\frac{1}{3}Li_3AlH_6+\frac{2}{3}MgAlH_5+\frac{1}{3}MgH_2$	+16.5
$NaMgAlH_6$	$RbGeIO_6$ ($P312$)	$NaAlH_4+MgH_2$	−2.5
$KMgAlH_6$	$CsAgAlF_6$ ($Pnma$)	$KAlH_4+MgH_2$	−2.1
$LiCaAlH_6$	$LiBaCoF_6$ ($P2_1/c$)	$LiH+CaAlH_5$	+4.1
$NaCaAlH_6$	$KNaSiF_6$ ($Pnma$)	$\frac{1}{3}Na_3AlH_6+\frac{2}{3}CaAlH_5+\frac{1}{3}CaH_2$	+9.0
		$NaAlH_4+CaH_2$	+9.1
$KCaAlH_6$	$KNaSiF_6$ ($Pnma$)	$KAlH_4+CaH_2$	+8.5

Majzoub, Ozolins, Phys. Rev. B, **77**, 104115 (2008)

Eric Majzoub, UMSL

Screening metal hydride mixtures for hydrogen storage using first-principles calculations

David S. Sholl, Ki Chul Kim
School of Chemical and Biomolecular Engineering, Georgia Tech

Bing Dai, J. Karl Johnson
Department of Chemical and Petroleum Engineering, University of Pittsburgh

Sudhakar Alapati
Intel Corporation

Financial support: US DOE

METAL HYDRIDE CENTER OF EXCELLENCE

Using DFT Calculations to Examine Reaction Thermodynamics

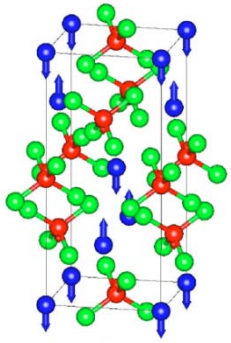
Plane wave Density Functional Theory (DFT) is well suited to characterizing reaction thermodynamics of crystalline materials

Planewave Pseudopotentials with PAW

- **gradient-corrected DFT (PW91)**
- **convergence reached with energy cutoff and *k*-space sampling**
- **all solid state structures fully optimized within experimental space group**

Enthalpy Changes (neglecting zero point energies)

ΔU_0



PHONON code direct lattice method

→ C_v **and Entropy** S →

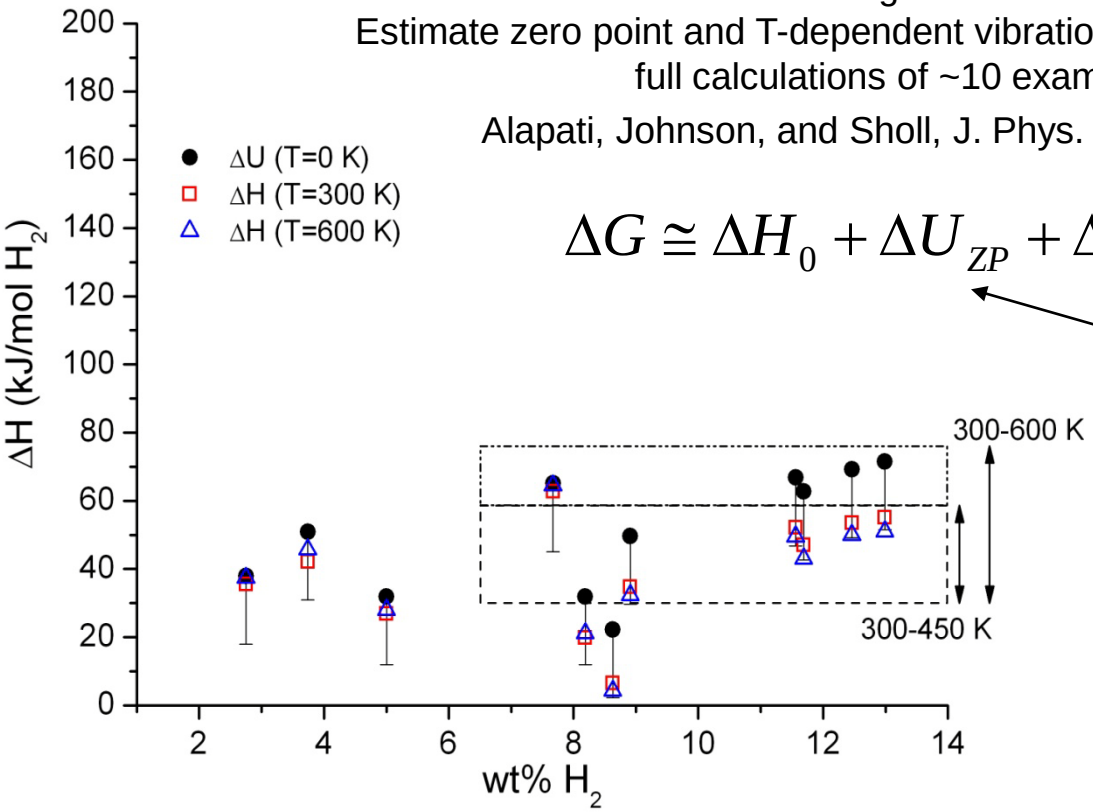
Changes in *Gibbs Free Energy* ΔG

"Simple" DFT Calculations Give Useful Predictions

Our ongoing work has used plane wave DFT calculations to screen materials for potential use in reversible on-board hydrogen storage applications

Can we screen based on free energies without calculating phonon DOS?
Estimate zero point and T-dependent vibrational contributions from full calculations of ~10 examples.

Alapati, Johnson, and Sholl, J. Phys. Chem. C 111 (2007) 1584



$$\Delta G \cong \Delta H_0 + \Delta U_{ZP} + \Delta U'_{vib}(T) - T\Delta S_{vib}(T) + \Delta(PV)$$

-20 to -10 kJ/mol H_2

Only gas phase H_2 significant

This approach does not identify any "interesting" reactions that were not also identified using only the T = 0 K result

Perform initial screening using (computationally cheaper) total energy calculations

Screening approach - outline

We have optimized the crystal structures of > 210 solid materials comprised of Al, B, Ca, Li, Mg, K, Na, Si, C, N, Sc, Ti, V or H (including all relevant materials from ICSD plus more recent examples from literature)

Screening from this catalog is performed using thermodynamic methods of Akbarzadeh et al., Adv. Mat. 19 (2007) 3233

Total energy calculations for known crystal structures

210+ structures
13 elements (+H)

Scan composition using ΔH_0
Catalog all observed rxns
(no explicit vibrational contributions)

286 three element spaces
715 four element spaces
> 16 million compositions

$\Delta G(T)$ outside bounds

Discard reaction

$\Delta G(T)$ inside bounds

Compute vibrational DOS for all compounds in reaction (when feasible)

40+ reactions

Assess P_{eq} at operating T of interest

Caveats:

This approach does not include non-stoichiometric or noncrystalline compounds.
Gaseous species other than H_2 (e.g. NH_3) are not included.
Thermodynamic calculations cannot allow conclusions about reaction kinetics.

Recent comparisons with experimental results

Both examples below are from experiments motivated by our earlier results

$CaH_2 + 6\ LiBH_4 \rightarrow CaB_6 + 6\ LiH + 10\ H_2$

This reaction observed recently by Goudy et al.

Experimentally observed and theoretically predicted P_{eq} in good agreement

$Ca(AlH_4)_2 + 2\ MgH_2$

Experiments by Hanada, Lohstroh, Fichtner (J. Phys. Chem. C, 112 (2008) 131)

Experiments and theory both show a multistep process:

$Ca(AlH_4)_2 \rightarrow CaAlH_5 + Al + 1.5\ H_2$

$CaAlH_5 \rightarrow CaH_2 + Al + 1.5H_2$

$12\ Al + 17\ MgH_2 \rightarrow Al_{12}Mg_{17} + 17\ H_2$

Theory predicts one more reaction at higher T:

$CaH_2 + Al_{12}Mg_{17} \rightarrow 17\ Mg + 6\ Al_2Ca + 6\ H_2$

Agreement is not observed with experiments in all cases. DFT predicts that

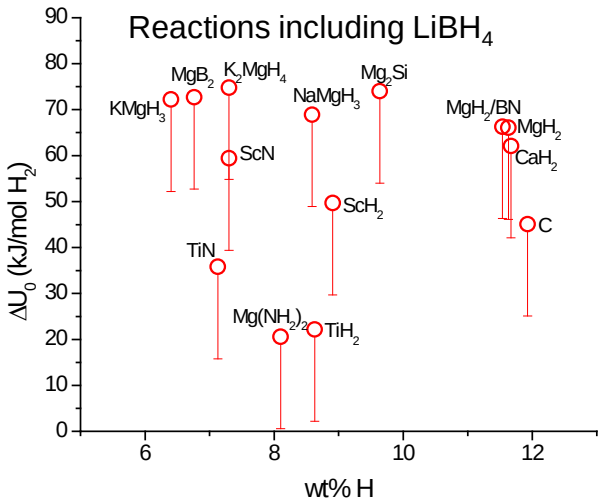
$ScH_2 + 2\ LiBH_4 \rightarrow ScB_2 + 2\ LiH + 4\ H_2$

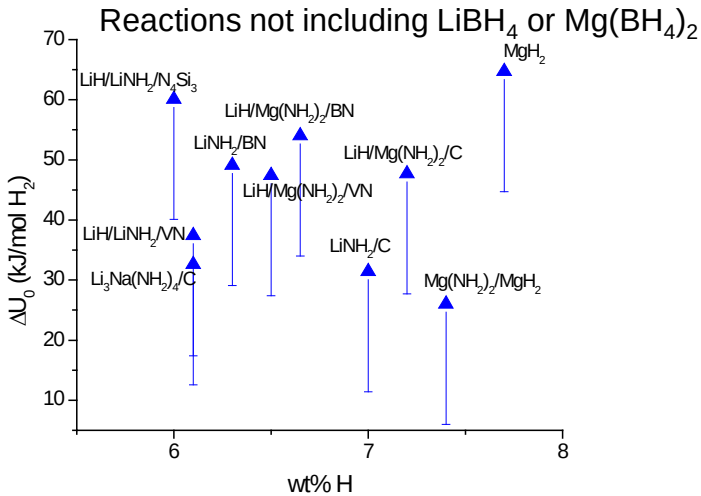
is thermodynamically favored near room temperature, but extensive Experiments by Bowman, Ahn et al. show no evidence for this reaction

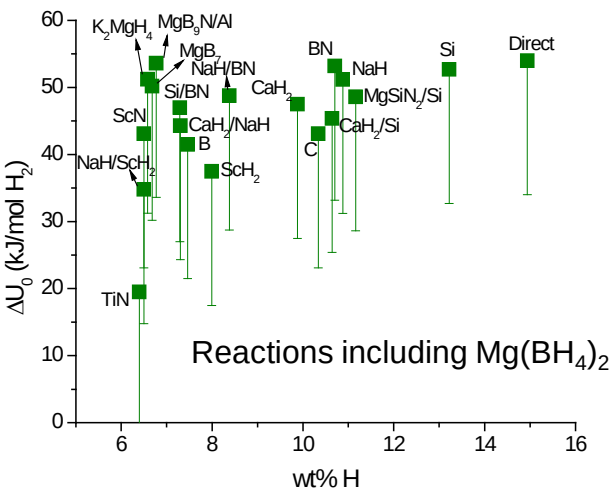
Predicted single step reactions

For details, see Alapati, Johnson, & Sholl, J. Phys. Chem. C 112 (2008) 5258

Only reactions with $15 < \Delta U_0 < 75$ kJ/mol H_2 and > 6 wt.% H retained





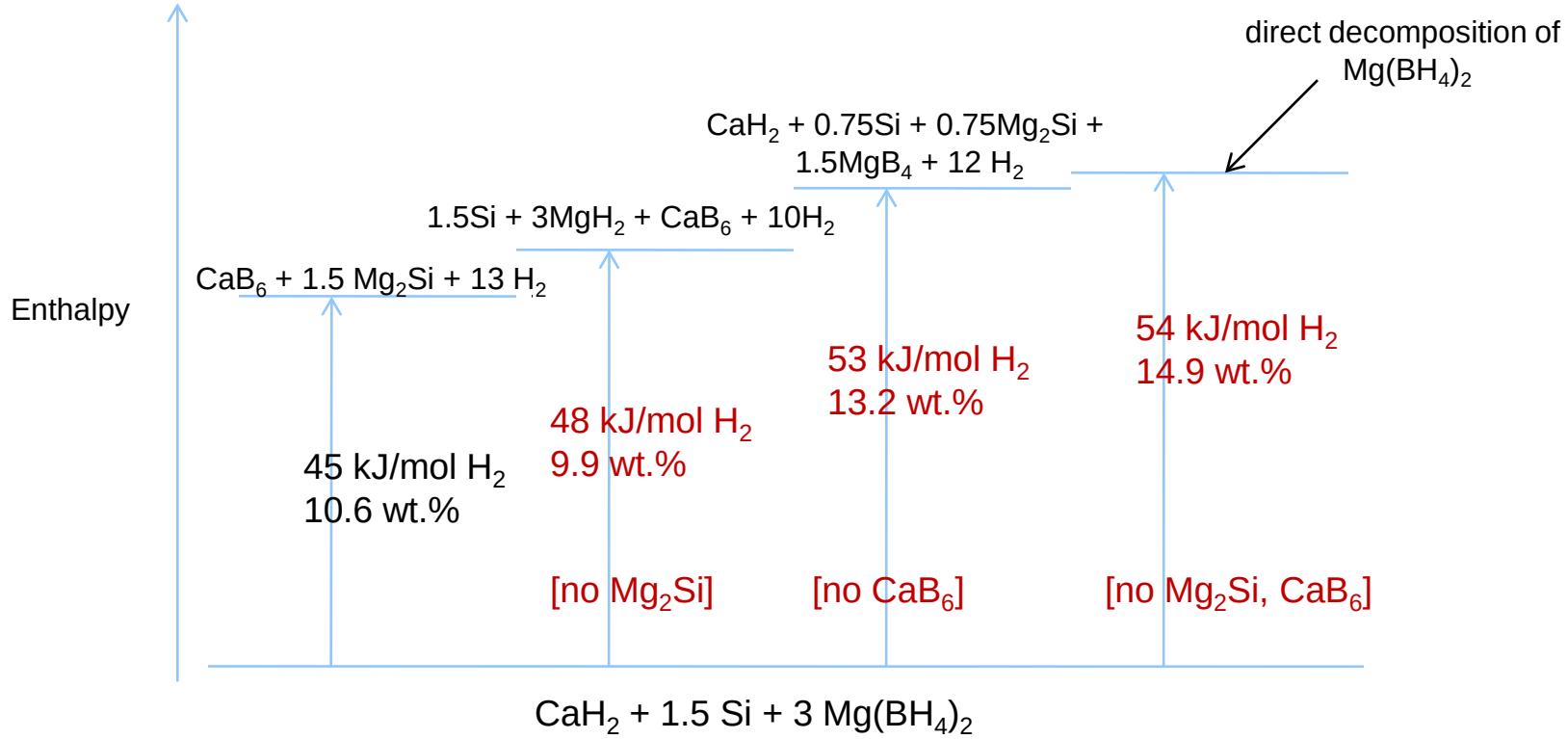


$Mg(BH_4)_2$ calculations do not include the amorphous phases observed experimentally, so results with enthalpies close to "direct" result are likely to proceed via decomposition into this amorphous material

Free energy calculations with $Mg(BH_4)_2$ (and several other compounds) are not currently feasible because of the large number of atoms in the unit cell

Metastable reactions

We have extended our thermodynamic analysis to consider metastable paths by repeating calculations using "restricted" versions of the full database of compounds



These results are with 0 K enthalpies – ordering could change when full free energy is considered ("entropic stabilization"). Of 43 single-step reactions, 28 have one (or more) alternate pathways within 10 kJ/mol H_2 other than direct decomposition of one reactant

Metastable reactions (cont.)

The 15 single step reactions below are predicted to have no metastable paths with reaction enthalpies within 10 kJ/mol H_2 of the stated reaction

$$LiBH_4 + C \rightarrow LiBC + 2H_2$$

$$6LiBH_4 + CaH_2 \rightarrow 6LiH + CaB_6 + 10H_2$$

$$2C + Mg(BH_4)_2 \rightarrow MgB_2C_2 + 4H_2$$

$$2LiBH_4 + ScH_2 \rightarrow 2LiH + ScB_2 + 4H_2$$

$$2LiBH_4 + TiH_2 \rightarrow 2LiH + TiB_2 + 4H_2$$

$$MgH_2 \rightarrow Mg + H_2$$

$$2MgH_2 + Mg(NH_2)_2 \rightarrow Mg_3N_2 + 4H_2$$

$$6LiBH_4 + 2ScN \rightarrow 6LiH + 2ScB_2 + 2BN + 9H_2$$

$$6LiBH_4 + 2TiN \rightarrow 6LiH + 2TiB_2 + 2BN + 9H_2$$

$$2LiNH_2 + C \rightarrow Li_2CN_2 + 2H_2$$

$$2LiH + LiNH_2 + BN \rightarrow Li_3BN_2 + 2H_2$$

$$4LiH + 3LiNH_2 + VN \rightarrow Li_7N_4V + 5H_2$$

$$10LiH + 5LiNH_2 + N_4Si_3 \rightarrow 3Li_5N_3Si + 10H_2$$

$$Mg(BH_4)_2 \rightarrow MgB_2 + 4H_2$$

$$MgB_7 + 1.5Mg(BH_4)_2 \rightarrow 2.5MgB_4 + 6H_2$$

Challenges and Needs…

- Solid state approach
  - Starting with anticipated decomposition products
  - Challenge is that synthesis depends on many reaction parameters
  - Need to screen for ternary metal borides
  - Need to screen for new borohydride related materials
- Solution based routes
  - Challenge is that the complex reaction routes involve several steps to make new materials
- Screening for reversibility
  - Need to screen for dopants/additives/catalysts and challenge is to effectively analyze thermodynamics and kinetics
- Need to fully understand reaction mechanism, and to improve reversibility, extensive analysis is needed
- Challenge is to incorporate in situ analysis to improve the throughput when often multiple tools are needed