

First-Principles Computational Search for Reversible Room-Temperature Hydrides



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Los Angeles*

**Project ID #
STP44**

Overview

Timeline

- Start Date: 5/1/2004
- End date: 4/30/2007
- % complete: 67

Budget

- Total project funding
 - DOE: \$2,000,000
 - UOP: \$2,910,618
 - Ford: \$75,000
- DOE FY05: \$604,423
- DOE FY06: \$525,032

Barriers

- Barriers addressed
 - Useable H₂ density
 - 2.0 kWh/kg & 1.5 kWh/L
 - H₂ Delivery Temperature Range
 - -40 to +85 °C
 - Cycle life (thermodynamic modeling)

Partners

- UOP LLC
- Ford
- Hawaii Hydrogen Carriers
- StriatuS

Objectives

- ✓ Using first-principles computational modeling, identify new H₂ storage materials that can enable the DOE 2010 targets in storage density (weight and volumetric) and operating temperatures
- ✓ Provide accurate reaction enthalpies for combinatorial material optimization at UOP LLC
- ✓ Provide leads for experimental testing/refinement using high-throughput combinatorial setup at UOP LLC

Approach

Use first-principles density functional calculations to obtain electronic, structural and crystal bonding properties of complex hydrides.

– Known complex hydrides:

- Input:
 - Chemical composition
 - Crystal structure type & symmetry
- Results of calculations:
 - Structural properties (e.g., volumetric densities)
 - Thermodynamic & vibrational properties
 - Reaction enthalpies ΔH and entropies ΔS

– New (unknown) complex hydrides:

- Develop and apply methods for determining crystal structure
- Calculate thermodynamics properties (ΔH and ΔS)
- Screen for materials with enthalpies in the 20-50 kJ/mol-H₂ range

Overview of Progress

1st YEAR

2nd YEAR

3rd YEAR

Validated approach on known hydrides

- Refinement of technical methods
- Literature search
- Calculations for all known materials with >6 wt% H₂
- Large database of reaction enthalpies
- Initial screen for new mixtures of materials

Expand to new materials with unknown crystal structures

COMPLETED WORK:

- Mixtures of alanates:
 - Stable compounds not found
 - **Not promising**
- Mixtures of alanates and borohydrides $X_n Y_m (BH_4)_p (AlH_4)_{n+m-p}$, where X and Y are monovalent cations (Li, Na, K):
 - Formation enthalpies positive
 - **Not promising**

CURRENT WORK:

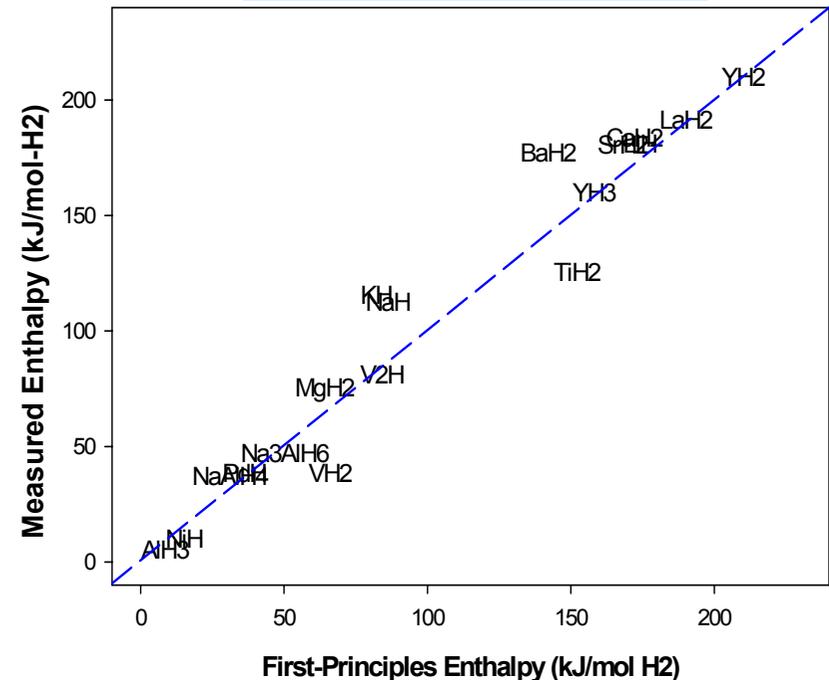
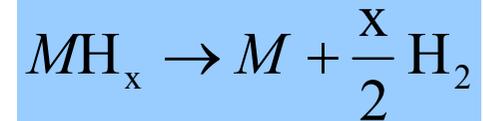
- Expanded search to new material classes:
 - Identified materials with 10-15 wt.% H₂ (theoretical)
 - ΔH in the 30-40 kJ/mol-H₂ range
- Optimize these materials for lower ΔH and/or higher ΔS :
 - Mixing/Alloying
 - Destabilized reactions

FUTURE WORK:

- Complete material optimization
- Complete searching of phase space

Highlights

- First-Principles provides accurate predictions of decomposition enthalpies for *known* compounds. This provides confidence in predictions of thermodynamics for *unknown* compounds.
- ✓ In FY 2004, constructed a large database of first-principles calculated structural and thermodynamic properties of known alanates, borohydrides and amides. It is being used to screen for new reactions and materials.



Wolverton, Ozolins, and Asta, 2004

Highlights

First-principles can steer us away from certain regions:

- ✓ Investigated mixtures of alanates and borohydrides ($\text{LiAlH}_4\text{-XBH}_4$, where $X=\text{Li, Na, K}$). All studied compounds had positive formation enthalpies, *indicating that mixed alanates and borohydride-alanate compounds will decompose into constituent hydrides exothermically.*

First-principles can guide us toward promising reaction classes:

- ✓ We have predicted novel materials/reactions with targeted thermodynamics (material-only, theoretical)* :
 - ✓ 7-15 wt. %
 - ✓ ~120 g/L volumetric H_2 densities
 - ✓ 30-40 kJ/mol- H_2 , including vibrational contributions

**Theoretical first-principles work done in collaboration with Ford*

Structural Energies

- ✓ Ordered compounds are constructed from the known crystal structures of aluminates and borohydrides
- ✓ Which ones to pick?
- ✓ Answer: Use $\Delta E_x(Y)$, the excess energy of compound X (e.g., LiAlH_4) in the crystal structure Y (e.g., of NaAlH_4). Energies given in kJ/mol:

Structures

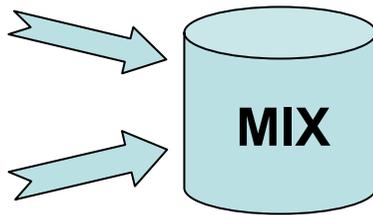
	<i>LiAlH₄</i>	<i>NaAlH₄</i>	<i>KAlH₄</i>	<i>LiBH₄</i>	<i>NaBH₄</i>	<i>KBH₄</i>
LiAlH ₄	0.0	4.0	12.2	8.3	21.0	7.3
NaAlH ₄	6.1	0.0	8.7	13.8	10.3	10.2
KAlH ₄	8.1	2.4	0.0	24.2	11.9	12.0
LiBH ₄	4.9	10.0	4.2	0.0	18.8	4.6
NaBH ₄	10.2	0.0	0.9	2.7	0.0	0.0
KBH ₄	10.7	18.3	0.8	13.9	0.0	0.0

Pick trial crystal structures with low values of $\Delta E_x(Y)$ for all end-compounds!

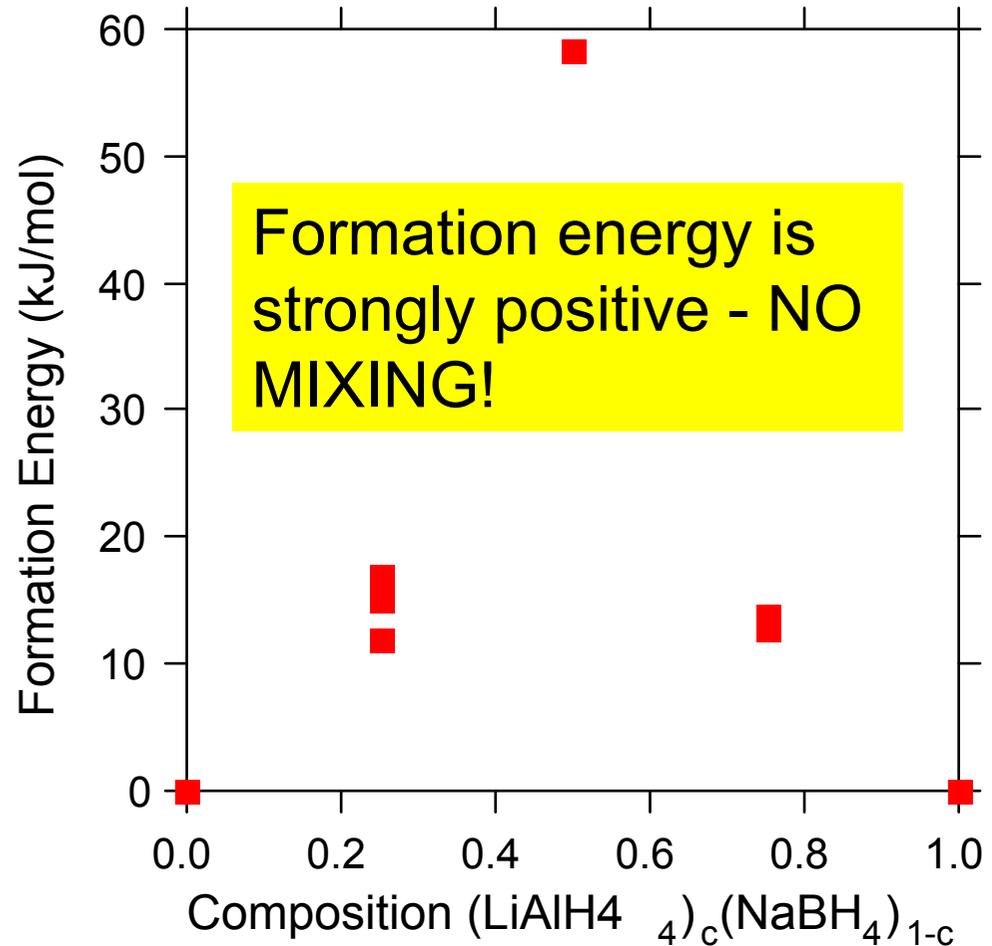
Mixed Alanates-Borohydrides

Calculated ΔH (in kJ/mol H_2)

LiBH ₄	81.3
NaBH ₄	106.8
KBH ₄	133.0
LiAlH ₄	11.3
NaAlH ₄	36.8
KAlH ₄	60.1
Mg(AlH ₄) ₂	0
Ca(AlH ₄) ₂	11.7

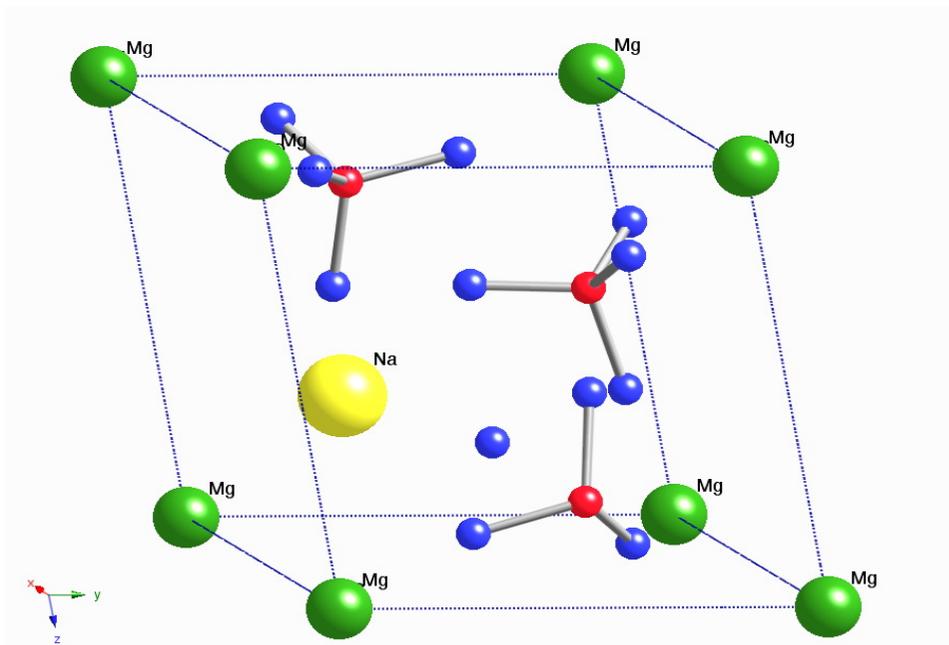


ΔH for LiAlH₄ is too low. Try mixing with NaBH₄ to increase ΔH .

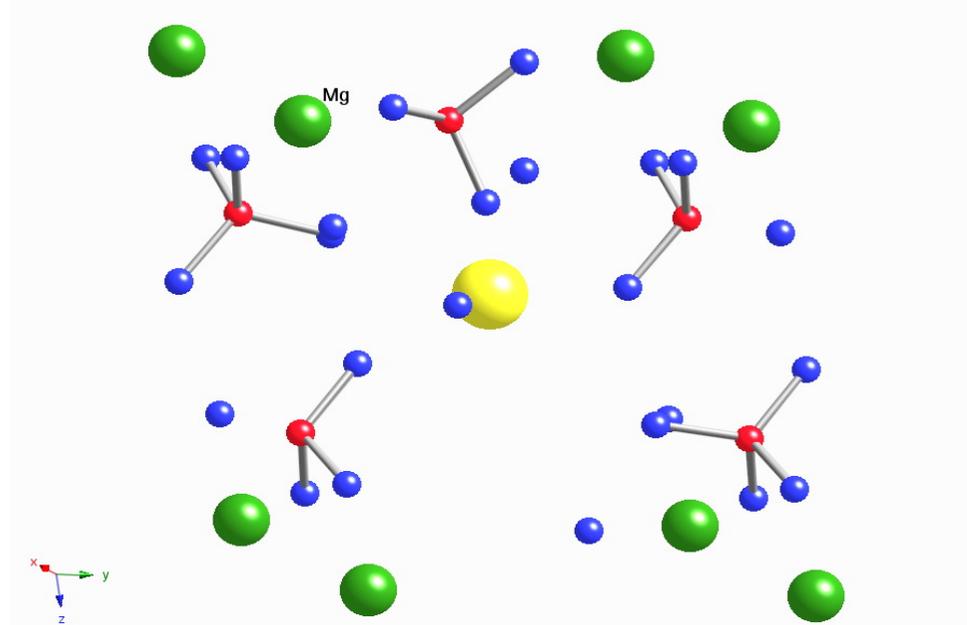


Mixing Alanates: $\text{MgNa}(\text{AlH}_4)_3$

Initial structure from electrostatic considerations

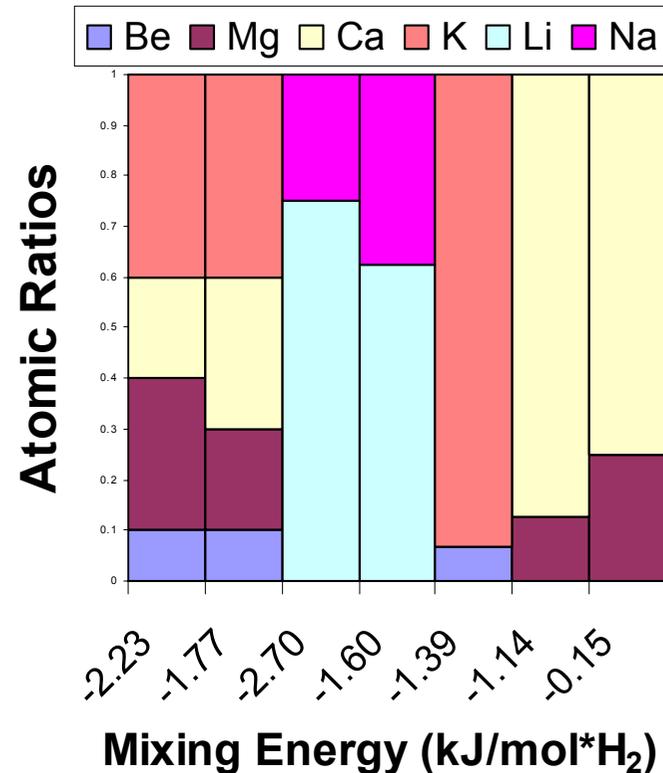
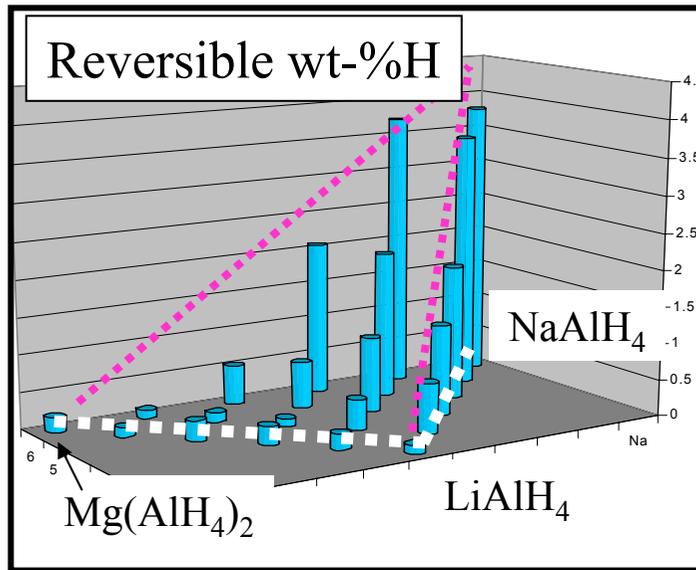


Relaxed structure from DFT



Conclusion: $\text{MgNa}(\text{AlH}_4)_3$ compounds will not form!

UOP Results for Mixed Alanates



- **First-Principles results agree with experiments and virtual high-throughput screening (VHTS) results at UOP:**
 - Na-Li-Mg-Alanate phase diagram searched starting from hydrided side
 - No stable mixtures found under these conditions.

Crystal Structure Determination

- **Problem:**
 - Crystal structure of material X is often not known
- **Strategy:**
 - Identify compounds in crystallographic databases (e.g., ICSD) with the correct chemical formula and the correct ionic coordination
 - Obtain a set of N structures (N is usually from five to a few hundred)
 - Run first-principles DFT calculations for the material X in all N structures, relaxing all structural degrees of freedom
 - Pick the lowest energy structure to get an estimate of the crystal structure and hydrating enthalpy

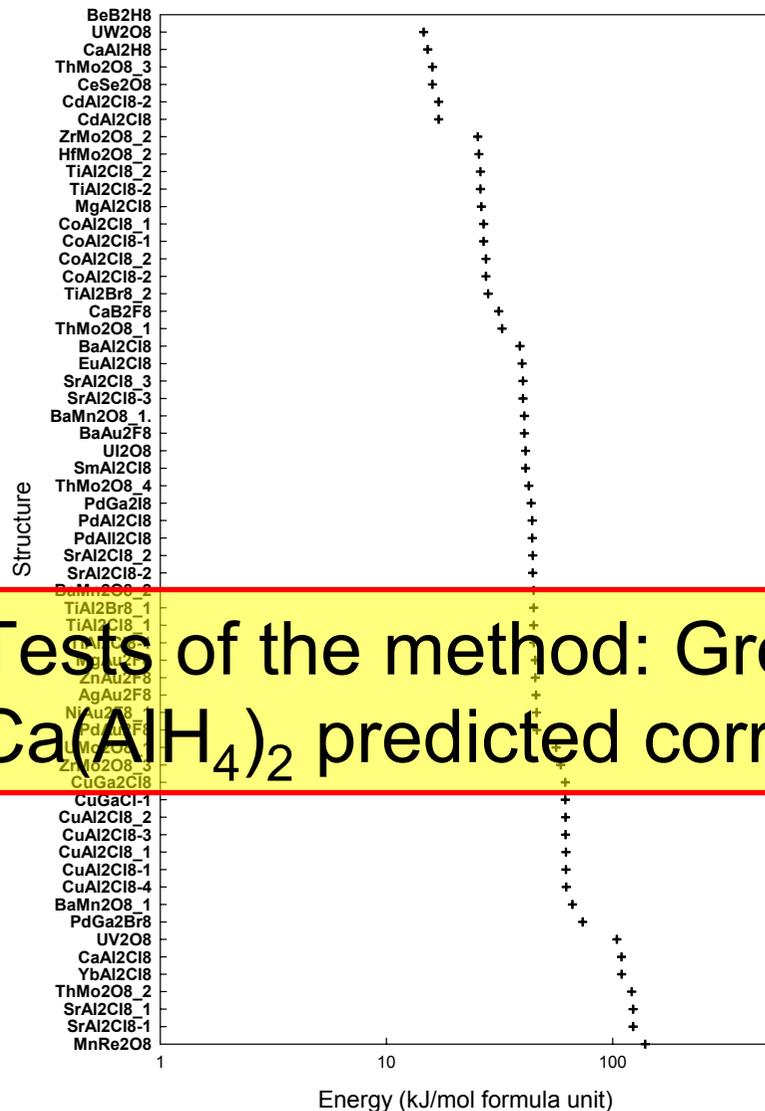
Be(BH₄)₂ Energetics

93 Structures

875 eV, 4x4x4 k-points

Structures initially relaxed from 400eV 2x2x2 calcs

Relaxation constrained to symmetry of original structure



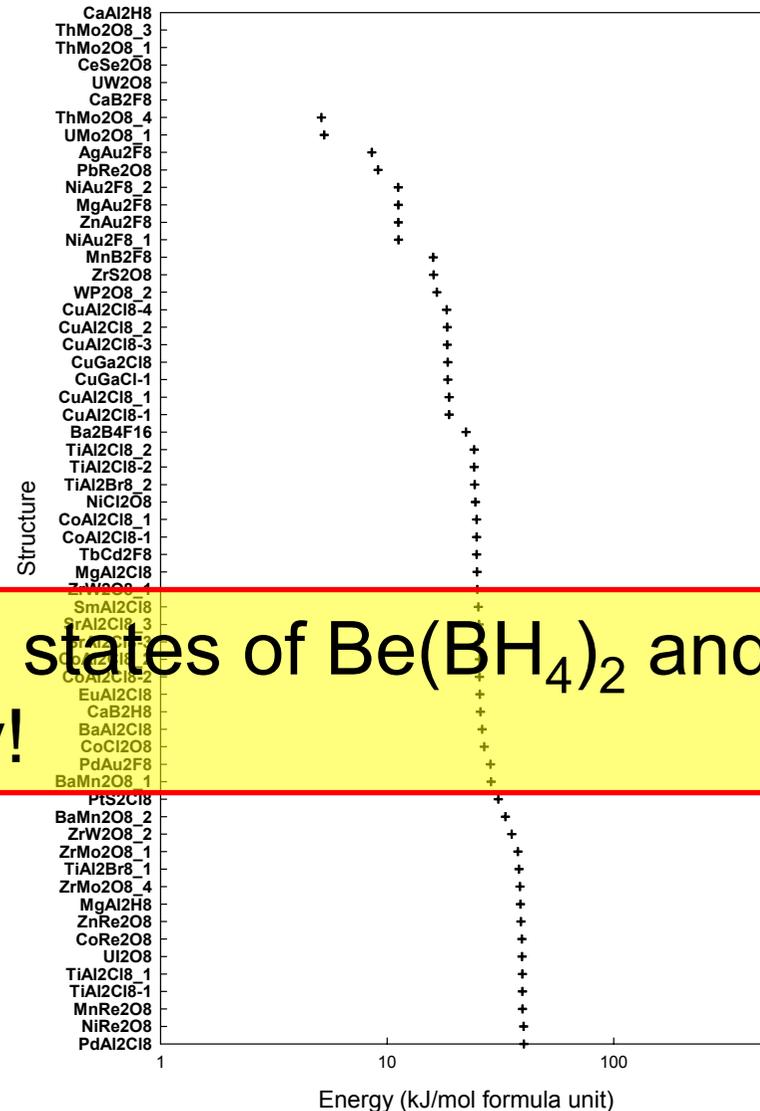
Ca(AlH₄)₂ Energetics

93 Structures

875 eV, 4x4x4 k-points

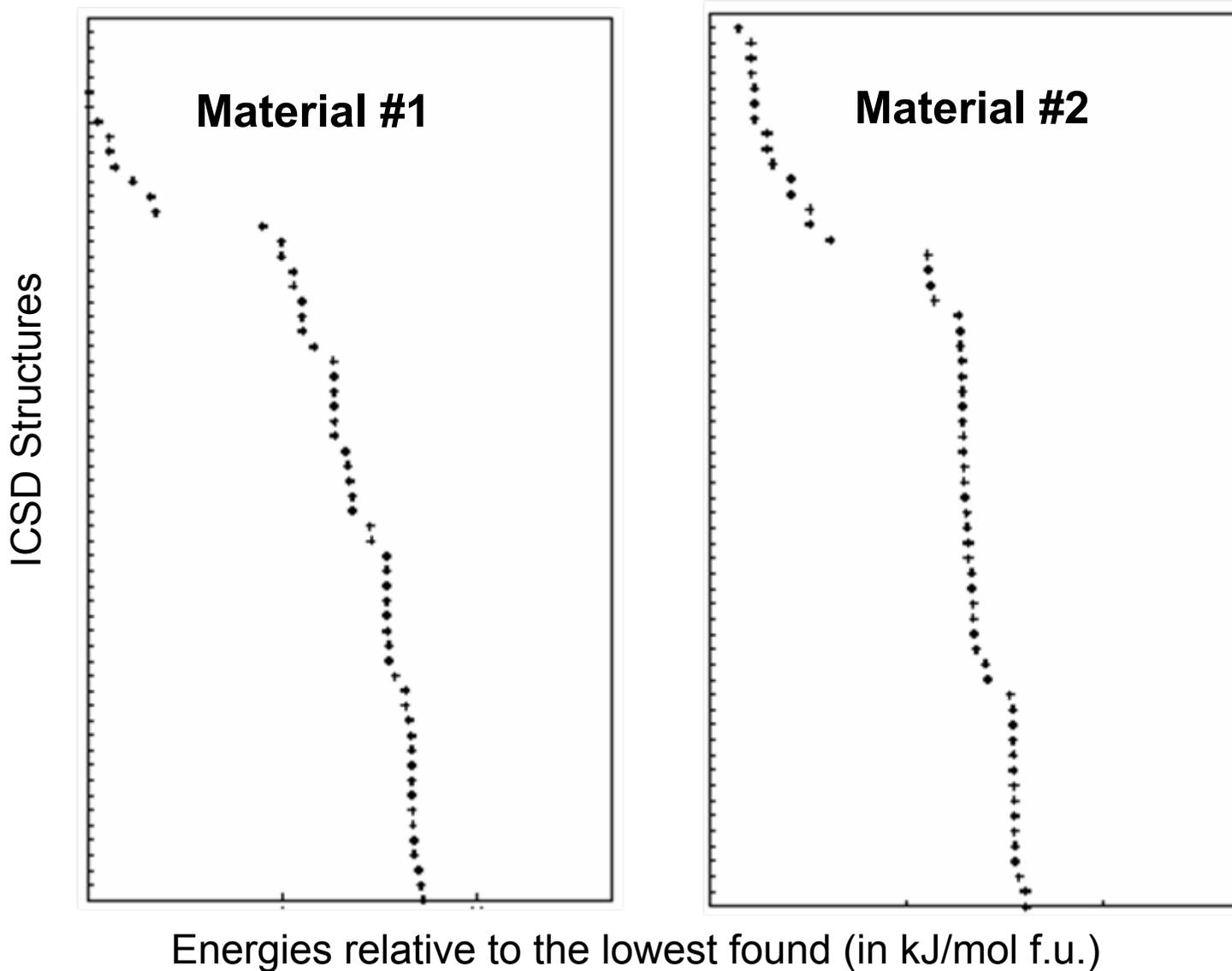
Structures initially relaxed from 400eV 2x2x2 calcs

Relaxation constrained to symmetry of original structure



Tests of the method: Ground states of Be(BH₄)₂ and Ca(AlH₄)₂ predicted correctly!

New Material Predictions



New First-Principles Predicted High Density Storage Reactions with $\Delta H \sim 30-40$ kJ

- These materials show several decomposition pathways.
- Good news: all H₂ should be released at one temperature!
- All reactions distinct from DFT predictions of the CoE (Alapati, Johnson, Scholl, 2006)
- All reactions involve experimentally-synthesized materials

Some Examples of Reactions:

REACTION	ΔH (kJ/mol -H ₂)			ΔS at 298 K [J/(K mol -H ₂)]	H ₂ Wt. % *	Volume density (g -H ₂ /L)*
	Static	With ZPE	T=300 K			
MATERIAL #1	57	35	41	111	10	125
MATERIAL #2, REACTION #1	51	31	38	117	15	120
MATERIAL #2, REACTION #2	52	31	37	115	13	120
MATERIAL #2, REACTION #3	53	31	38	114	12	120

* theoretical, material-only

Future Work at UCLA/Ford

- Search for ways to lower reaction enthalpies of materials #1 and #2 using:
 - Alloying
 - Destabilization (Vajo et al, 2004)
- Continue search for new materials/reaction based on complex hydrides
- Study/Optimize reaction enthalpies in the LiBH_4 - MgH_2 - LiNH_2 system in collaboration with UOP and Ford

Summary

- First-Principles modeling steers away from regions of phase space - e.g., mixtures of alanates and borohydrides are not promising
- First-principles modeling has identified materials with 10-15 wt. % theoretical H₂ capacity and ΔH in the 30-40 kJ/mol-H₂ range