First-Principles Computational Search for Reversible Room-Temperature Hydrides

Vidvuds Ozolins

University of California, Los Angeles

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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 H_2 density
    - 2.0 kWh/kg & 1.5 kWh/L
  - H2 Delivery Temperature Range
    - -40 to +85 ^{o}C
  - Cycle life (thermodynamic modeling)

Partners

- UOP LLC
- Ford
- Hawaii Hydrogen Carriers
- Striatus

Objectives

- ✓ Using first-principles computational modeling, identify new H_2 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-H_2 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% H_2

– 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 $X_nY_m(BH_4)_p(AlH_4)_{n+m-p}$, 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.% H_2 (theoretical)

  – ΔH in the 30-40 kJ/mol-H_2 range

– Optimize these materials for lower ΔH and/or higher ΔS:

  – Mixing/Alloying

  – Destabilized reactions

FUTURE WORK:

– Complete material optimization

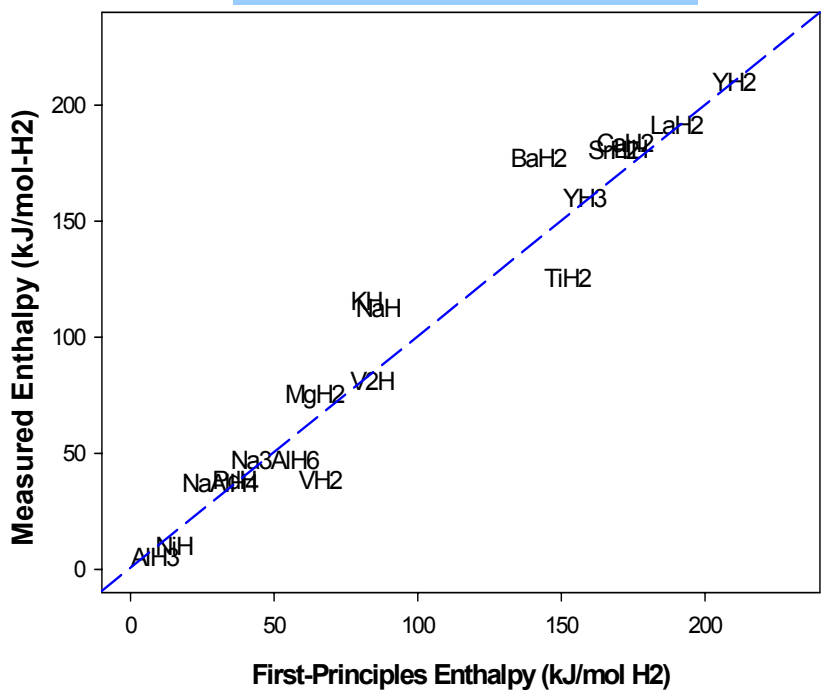
– Complete searching of phase space

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.

$$MH_x \rightarrow M + \frac{x}{2} H_2$$



Wolverton, Ozolins, and Asta, 2004

Highlights

First-principles can steer us *away* from certain regions:

- ✓ Investigated mixtures of alanates and borohydrides ($LiAlH_4$-XBH_4, where *X*=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 alanates 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

Compounds

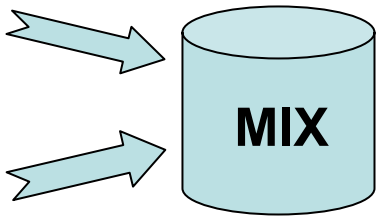
	LiAlH4	*NaAlH4*	*KAlH4*	*LiBH4*	*NaBH4*	*KBH4*
LiAlH4	0.0	4.0	12.2	8.3	21.0	7.3
NaAlH4	6.1	0.0	8.7	13.8	10.3	10.2
KAlH4	8.1	2.4	0.0	24.2	11.9	12.0
LiBH4	4.9	10.0	4.2	0.0	18.8	4.6
NaBH4	10.2	0.0	0.9	2.7	0.0	0.0
KBH4	10.7	18.3	0.8	13.9	0.0	0.0

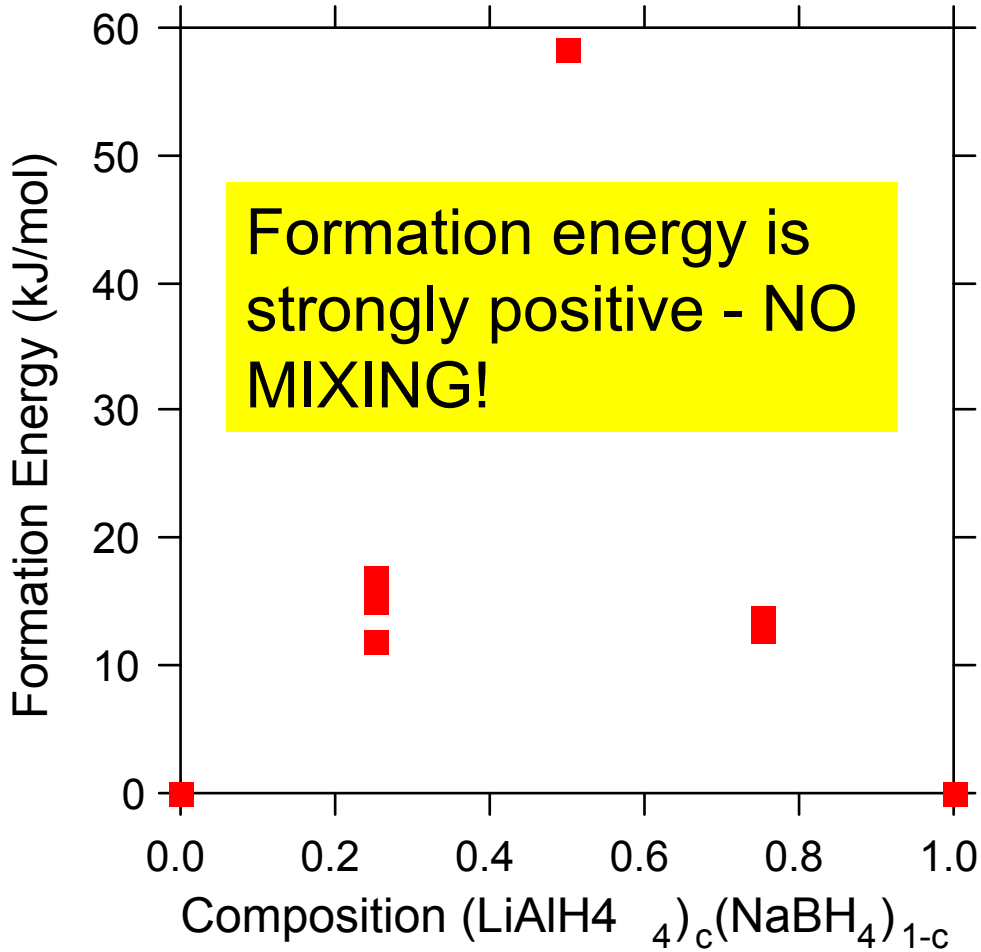
Pick trial crystal structures with low values of $\Delta E_X(Y)$ for *all* end-compounds!

Mixed Alanates-Borohydrides

Calculated ΔH (in kJ/mol H_2)

LiBH4	81.3
NaBH4	106.8
KBH4	133.0
LiAlH4	11.3
NaAlH4	36.8
KAlH4	60.1
Mg(AlH4)2	0
Ca(AlH4)2	11.7

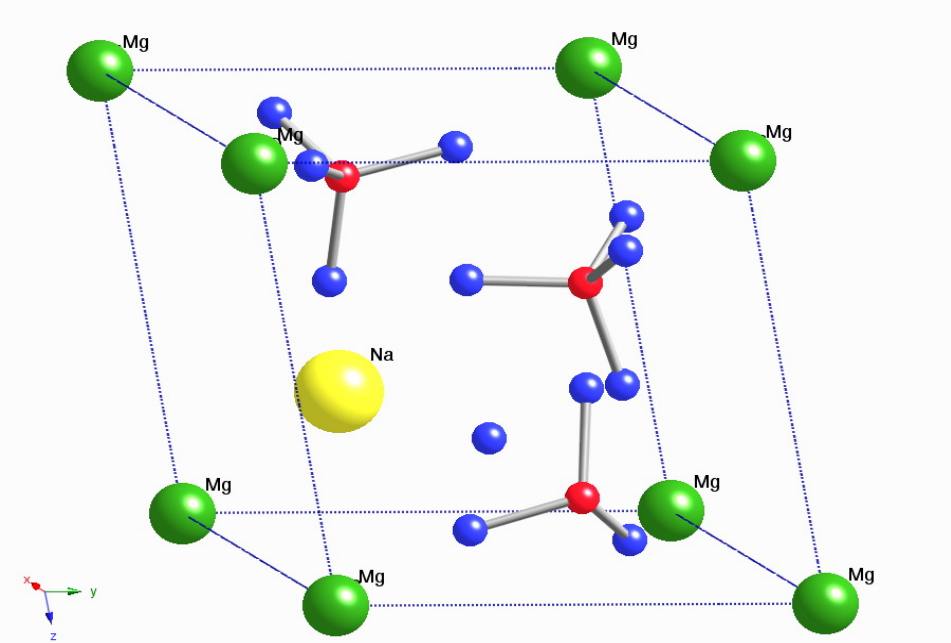




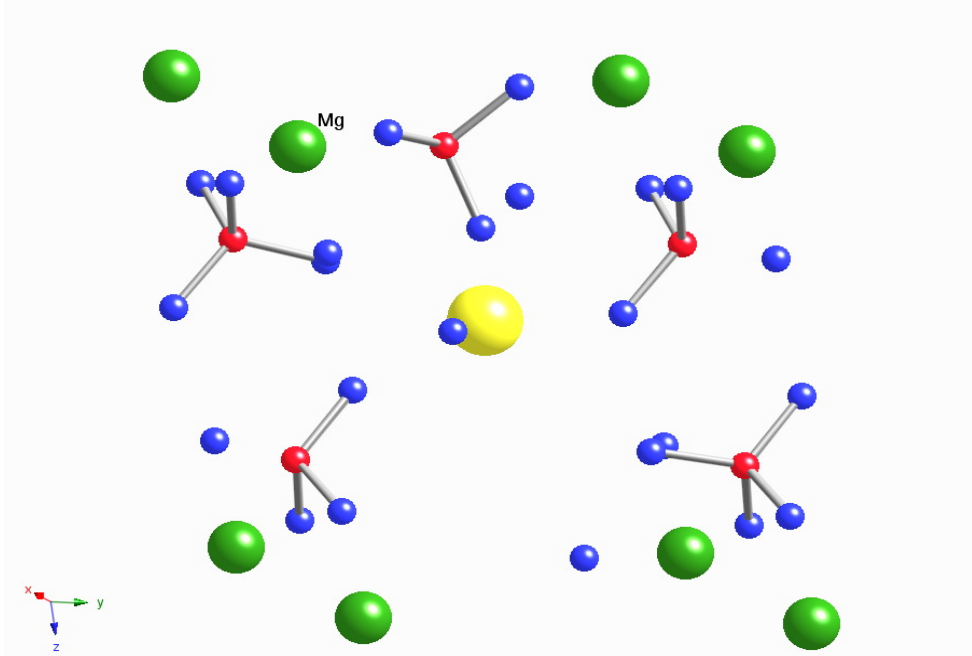
ΔH for $LiAlH_4$ is too low. Try mixing with $NaBH_4$ to increase ΔH.

Mixing Alanates: $MgNa(AlH_4)_3$

Initial structure from electrostatic considerations



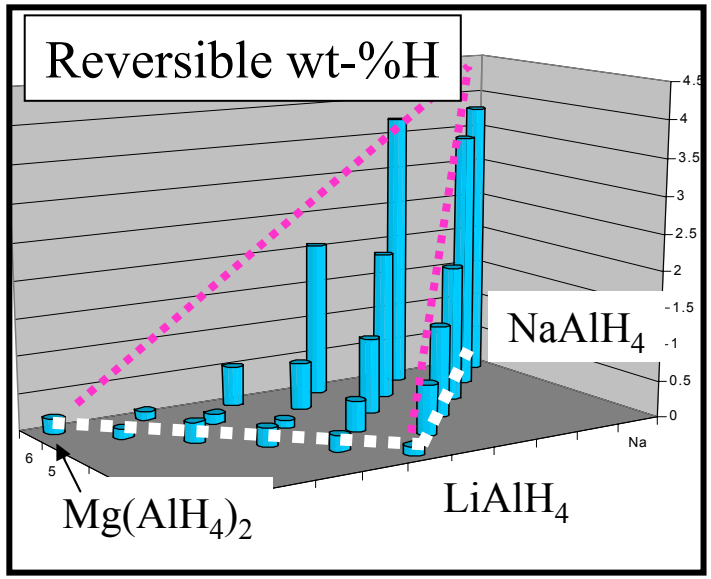
Relaxed structure from DFT

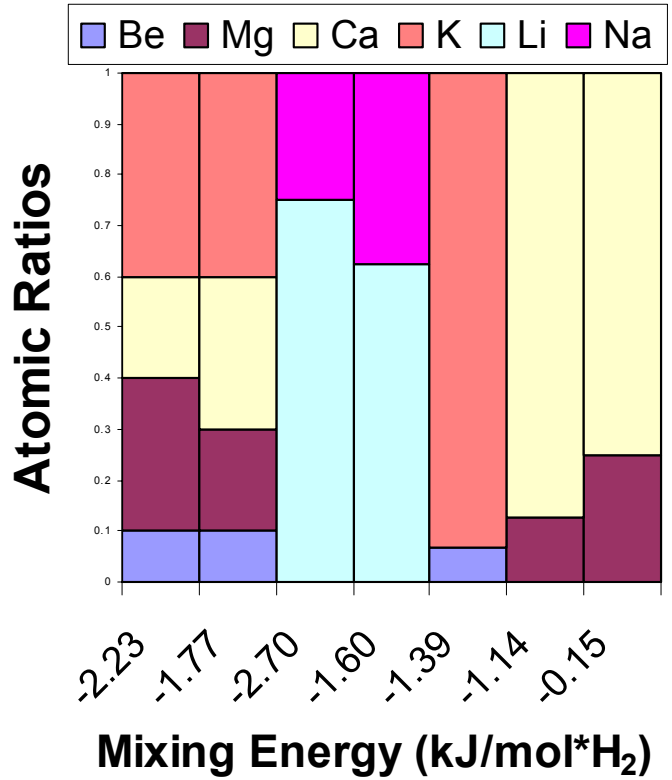


$$Mg(AlH_4)_2 + NaAlH_4 \rightarrow MgNa(AlH_4)_3 \qquad \Delta E = +10.7\ kJ/mol$$

Conclusion: $MgNa(AlH_4)_3$ 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.

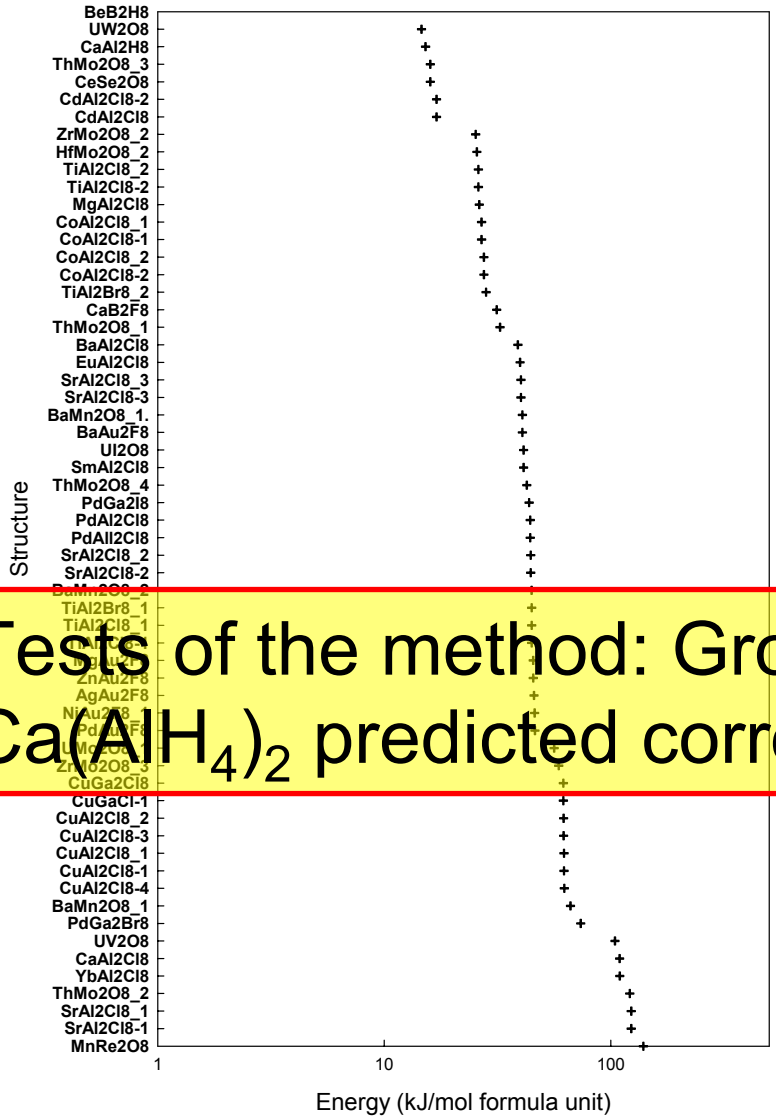
Crystal Structure Determination

- **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 hydriding enthalpy

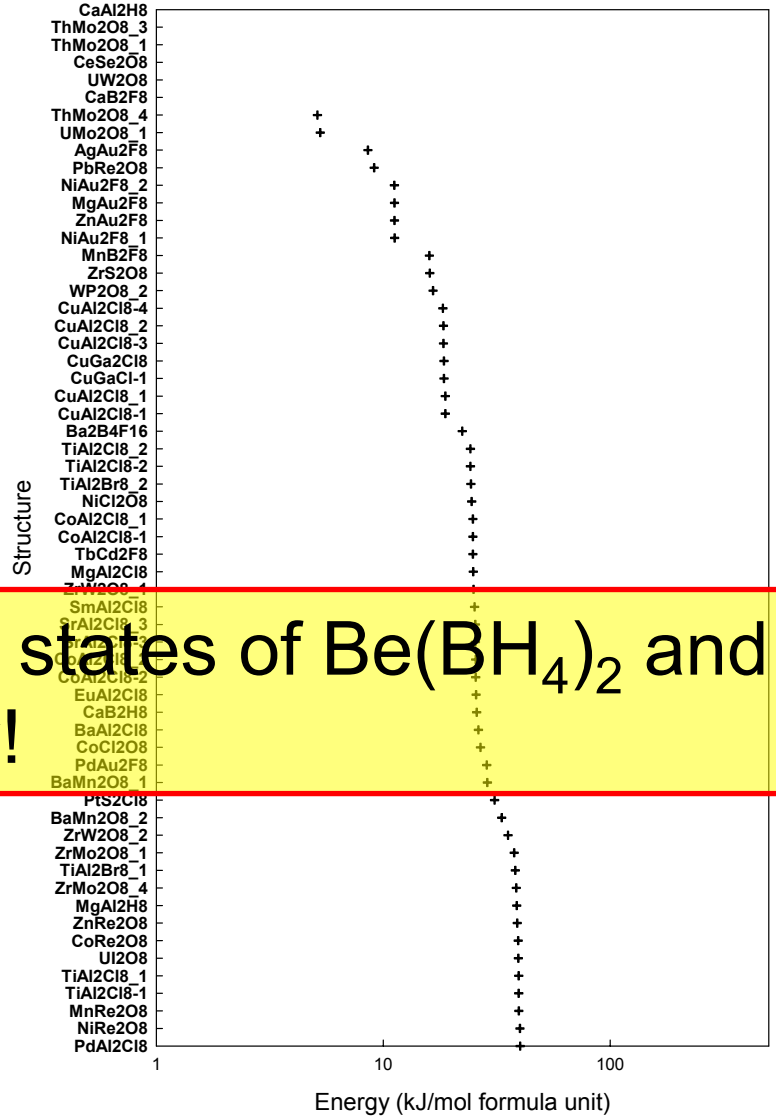
Be(BH4)2 Energetics

93 Structures
875 eV, 4x4x4 k-points
Structures initially relaxed from 400eV 2x2x2 calcs
Relaxation constrained to symmetry of original structure



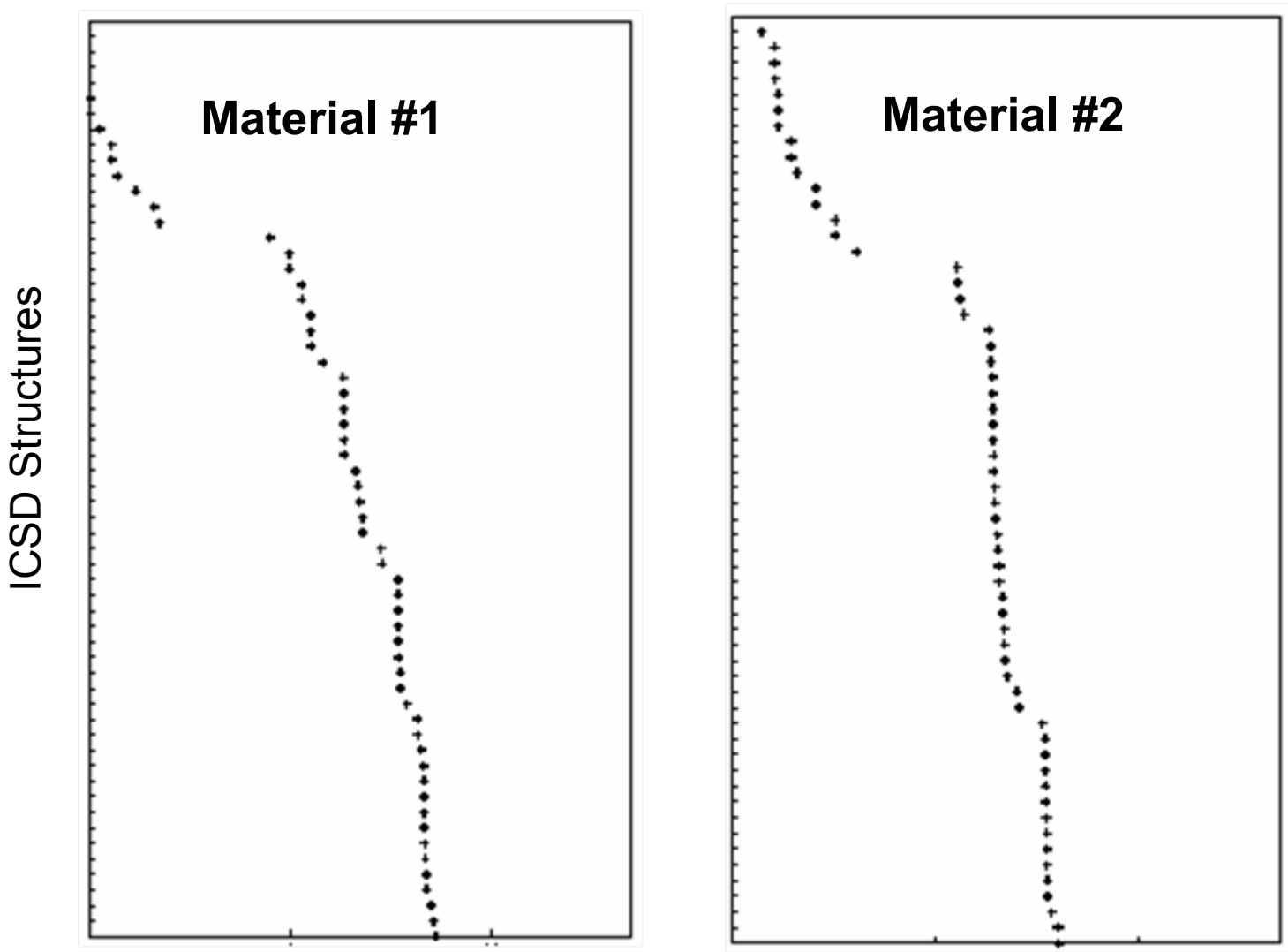
Ca(AlH4)2 Energetics

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 $Be(BH_4)_2$ and $Ca(AlH_4)_2$ predicted correctly!

New Material Predictions



New First-Principles Predicted High Density Storage Reactions with ΔH~30-40 kJ

- These materials show several decomposition pathways.
- Good news: all H_2 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 H_2 capacity and ΔH in the 30-40 kJ/mol-H_2 range