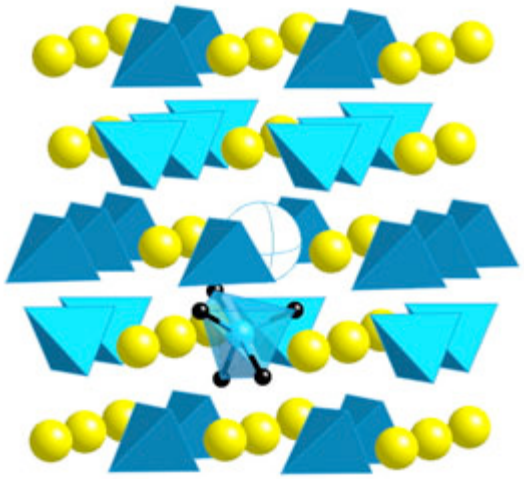
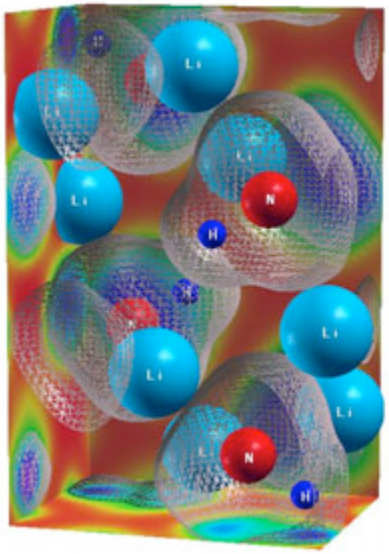
Prediction of New Hydrogen Storage Compounds and Mixtures



Vidvuds Ozoliņš
UCLA



Research supported by DOE grants No. DE-FG02-05ER46253 and DE-FC36-04GO14013

Sponsored Projects

Discovery of Novel Complex Metal Hydrides for Hydrogen Storage Through Molecular Modeling and Combinatorial Methods

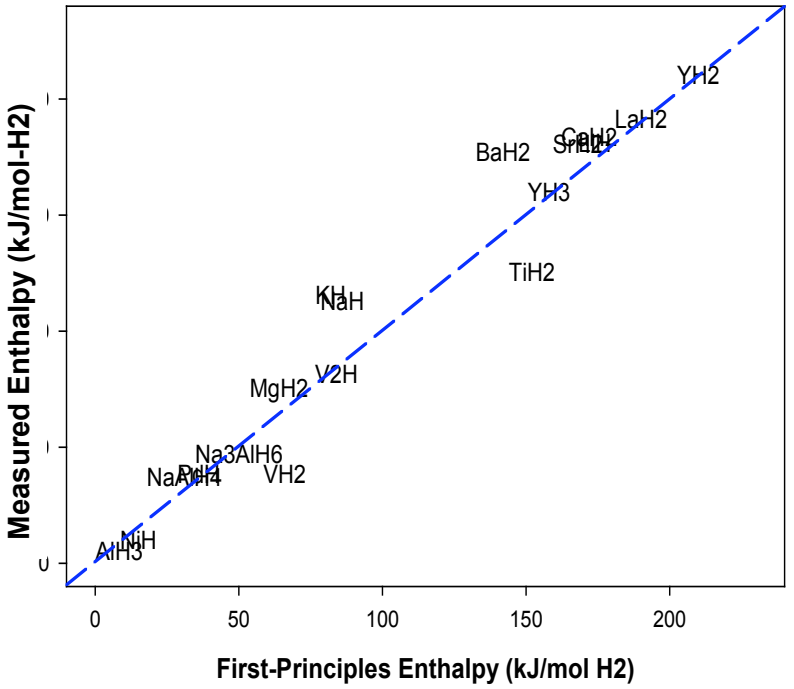
DOE BES: Theory and Modeling of Materials for Hydrogen Storage
PIs: Gerbrand Ceder (MIT), Nicola Marzari (MIT), Vidvuds Ozoliņš (UCLA)

Accuracy of DFT

First-Principles provides accurate predictions of decomposition enthalpies for *known* compounds.

This provides confidence in predictions of thermodynamics for *unknown* compounds.

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



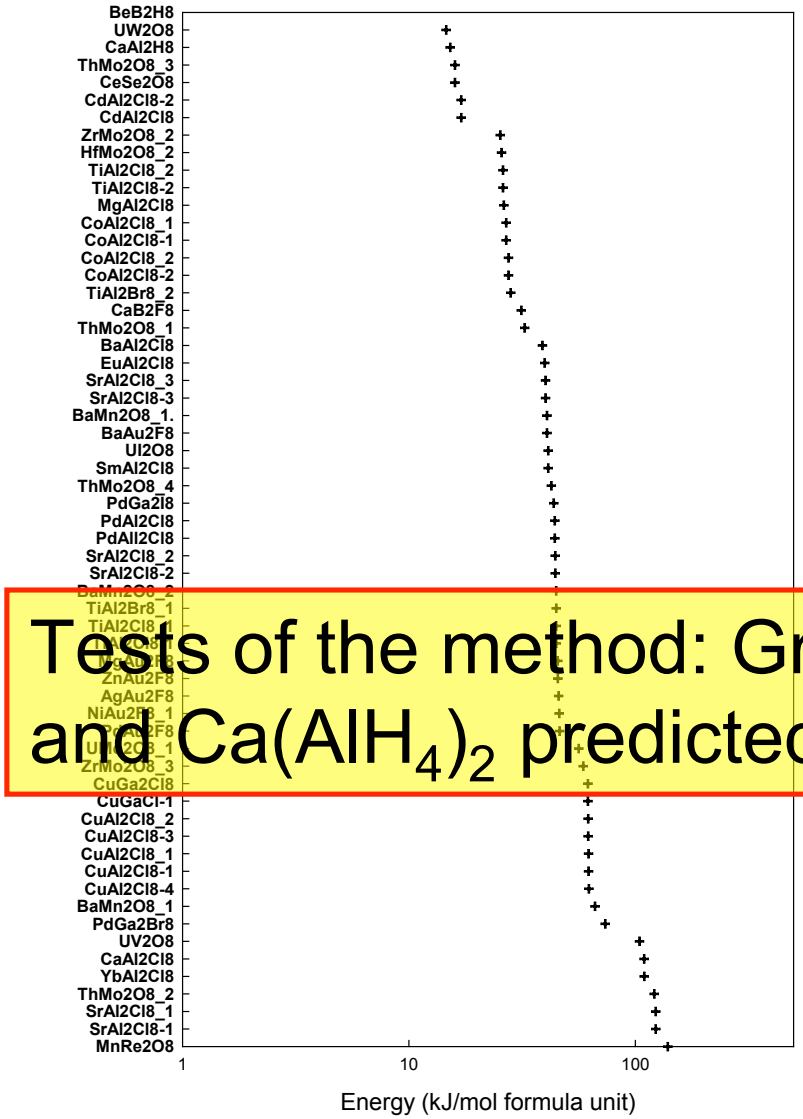
Wolverton, Ozolins, and Asta, 2004

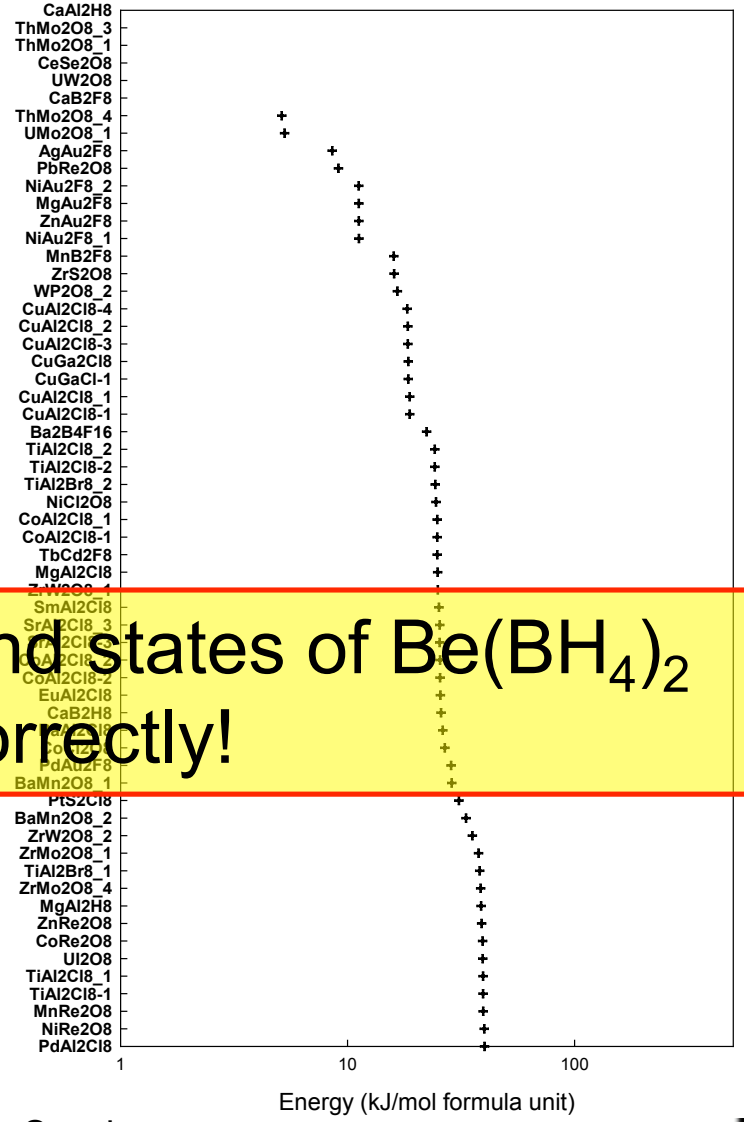
Overview

- Problem: Crystal structures of hydrides often not known
- Methods for predicting crystal structures
  - Structure database search (e.g., ICSD) [with Chris Wolverton]
  - Structure enumeration [with Blanka Magyari-Köpe, Ali Akbarzadeh, and Chris Wolverton]
  - Cluster expansion [Tim Mueller and Gerd Ceder (MIT)]
  - Fixed-lattice electrostatic models [with Blanka Magyari-Köpe and Chris Wolverton]
  - Off-lattice global optimization [with Eric Majzoub]

Part I: "ICSD search"

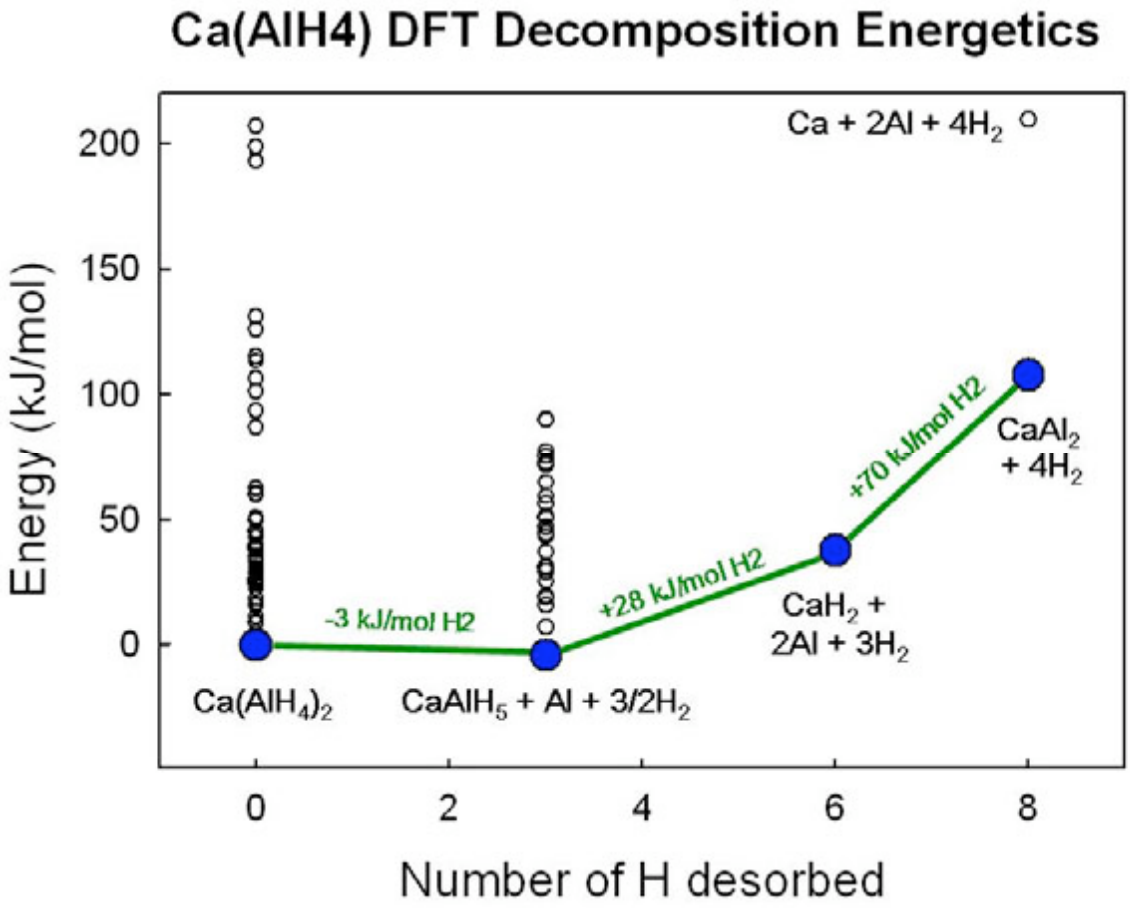
1. Identify compounds in crystallographic databases (e.g., ICSD) with the correct chemical formula and the correct ionic coordination
2. Obtain a set of *N* structures (*N* is usually between a few and a few hundred)
3. Run first-principles DFT calculations for the material *X* in all *N* structures, relaxing all structural degrees of freedom
4. Pick the lowest energy structure to get an estimate of the crystal structure and hydriding enthalpy
5. Calculate phonons
6. If dynamically unstable, run simulated annealing and go to Step 4. If needed, increase the supercell size
7. If stable, get an estimate of the hydrogenation enthalpy





Tests of the method: Ground states of $Be(BH_4)_2$ and $Ca(AlH_4)_2$ predicted correctly!

Ca Alanate Decomposition



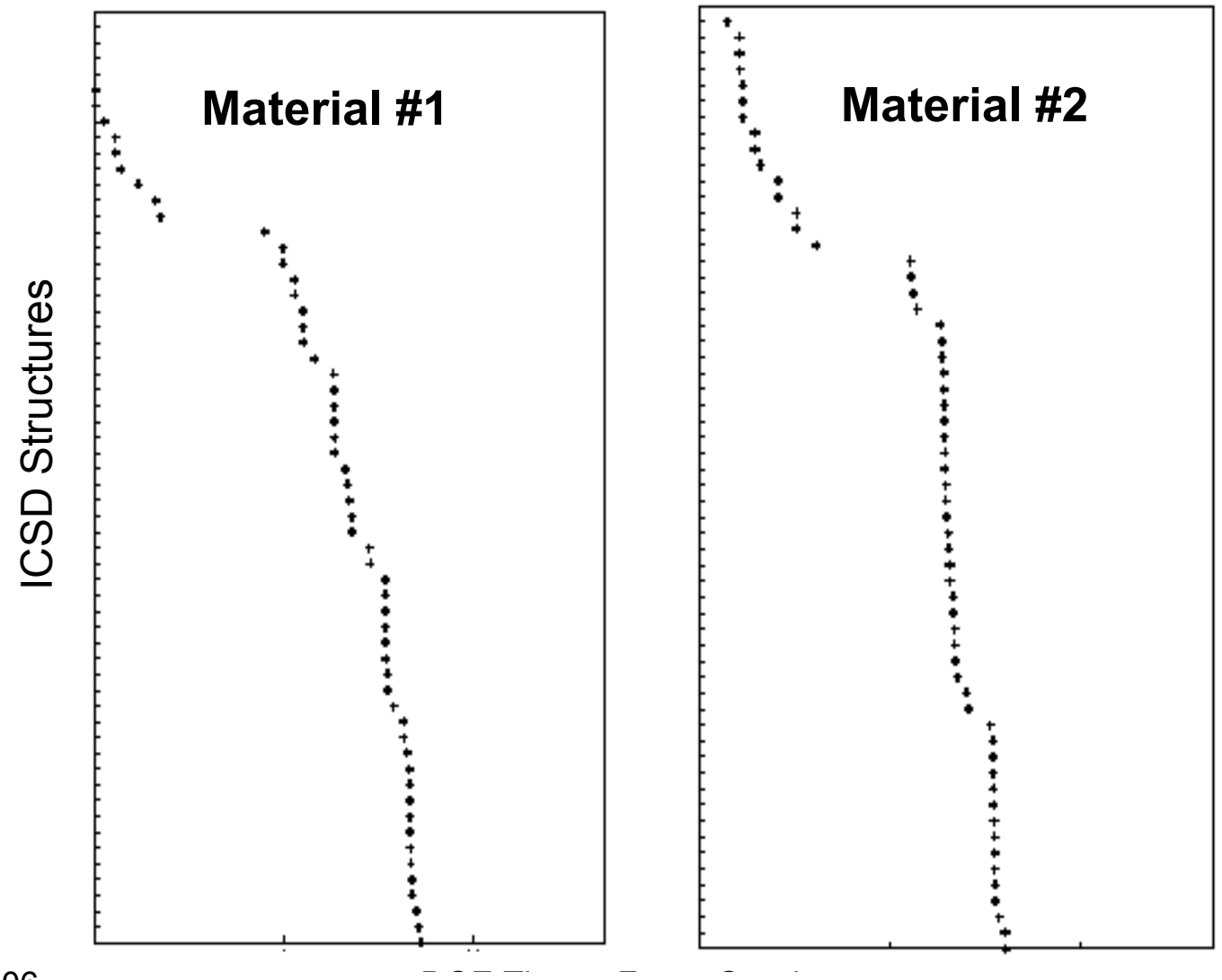
Experiment (Bogdanovic et al): -7.4/-7.6 and +31.6 kJ/mol-H_2

Vibrational Contributions

Reaction	Reaction enthalpy ΔH (kJ/mol H_2)				ΔS_{vib} (k_B/H_2)
	Static, PAW	Static, US	With ZPE	T=300 K	T=300 K
$Ca(AlH_4)_2 \rightarrow CaAlH_5 + Al + 3/2\ H_2$	-2.8	-2.1	-8.9	-5.2	-4.2
$CaAlH_5 \rightarrow CaH_2 + Al + 3/2\ H_2$	+27.8	+27.8	+14.2	+21.6	-1.1
$CaH_2 + 2\ Al \rightarrow CaAl_2 + H_2$	+70.3	+70.9	+64.2	+72.4	-0.2

Experiment (Bogdanovic et al): -7.4/-7.6 and +31.6 kJ/mol-H_2

New Material Predictions



New First-Principles Predicted High Density Storage Reactions with ΔH~40 kJ/mol H_2

- These materials can be used in several reactions
- 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

Part II: Enumeration Methods (Structure of Li_2NH)

$$Li_3N + 2H_2 \leftrightarrow Li_2NH + H_2 \leftrightarrow LiNH_2 + LiH$$

Stores ~11 wt.% H_2 and occurs at 200 to 300 ^oC.

Imide-to-amide reaction stores 6.5 wt.% H_2

Enthalpy of the imide-amide reaction is:

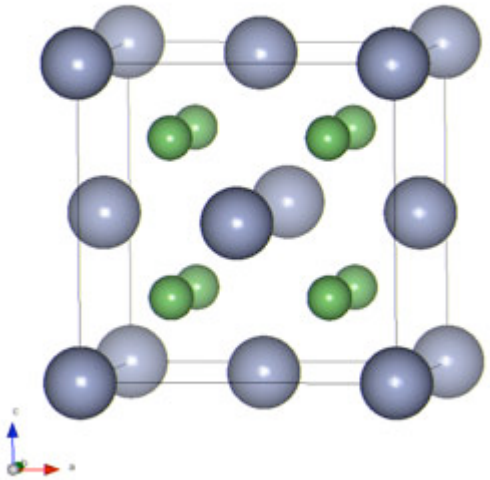
- ΔH = 64.5 kJ/mol H_2 (Chen et al, 2002),
- ΔH = 66 kJ/mol H_2 (Kojima & Kawai, 2005)

Chen, P.; Xiong, Z. T.; Luo, J. Z.; Lin, J. Y.; Tan, K. L. *Nature* **2002**, *420*, 302.

Previously Proposed Structures

Anti-Fluorite

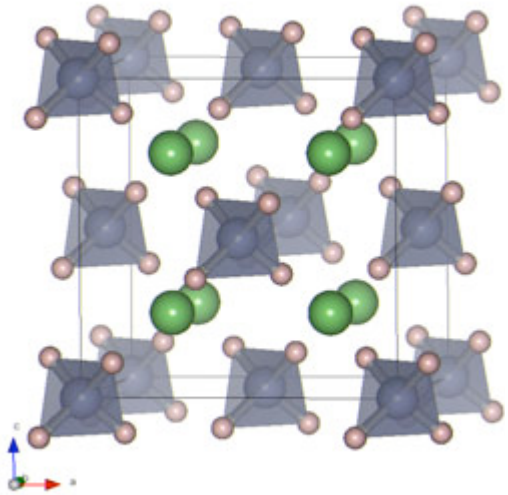
- $Fm\bar{3}m$
- Powder XRD
- 300K



R. Juza and K. Opp. *Zeitschrift für anorganische und allgemeine Chemie* **1951**, 266, 6, 325

1/4 Occupancy

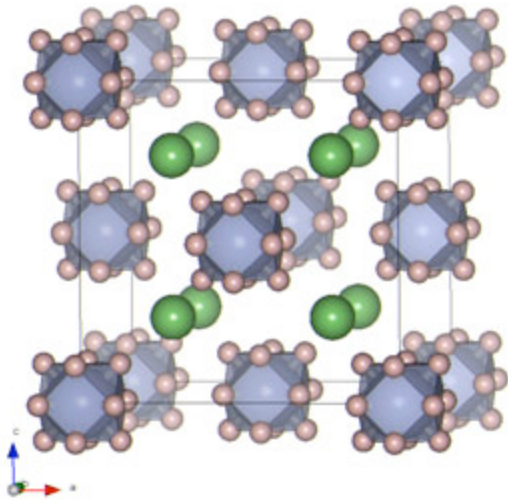
- $F\bar{4}3m$
- Neutron Powder Diffraction
- 10K – 300K



Ohoyama et al. *Journal of the Physical Society of Japan* **2005**, *74*, 483.

1/12 Occupancy

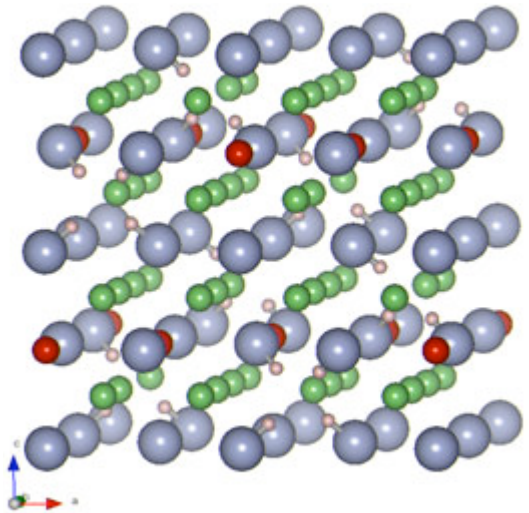
- $Fm\bar{3}m$
- Synchrotron Powder XRD
- 295K



Noritake et al. *Journal of Alloys and Compounds* **2005**, *393*, 264.

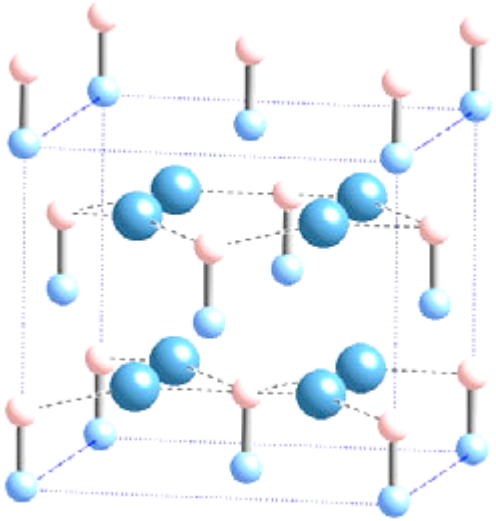
Octahedral Li

- $Ima2$
- Neutron Powder Diffraction
- 100K – 300K

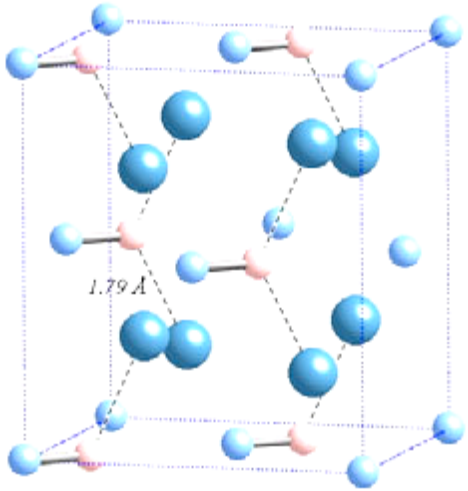


J. F. Herbst and L. G. Hector, Jr. *Physical Review B* **2005**, *72*, 125120.

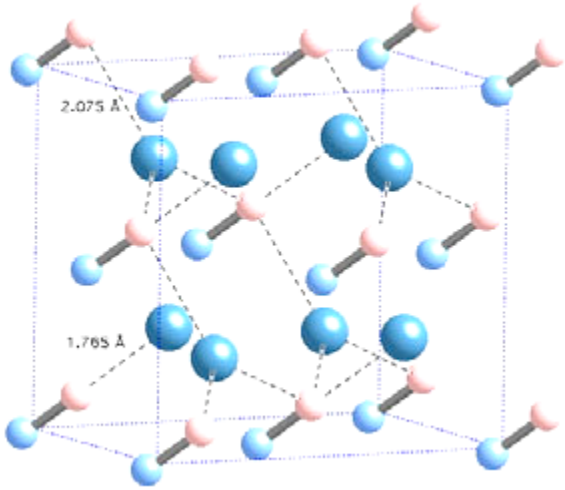
Parallel N-H Dimers



24e <001>
ΔE = +154 meV/f.u.
d(N-H)=1.039 Å
d(Li-H)=1.839 Å
d(Li-N)=2.176 Å

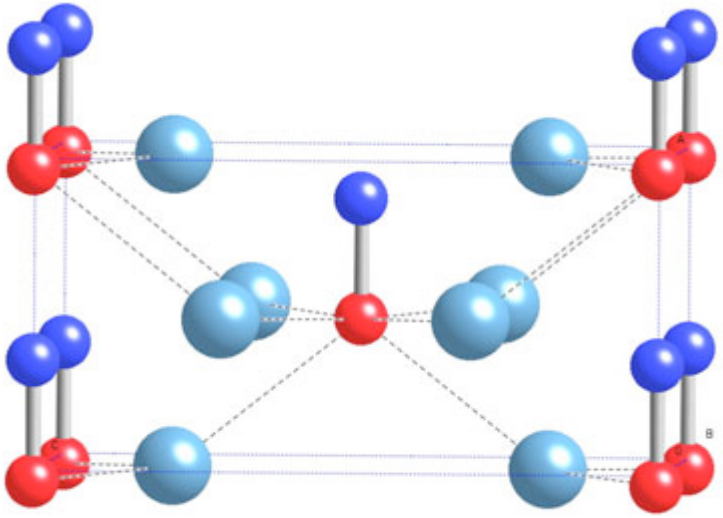


48h <110>
ΔE = +260 meV/f.u.
d(N-H)=1.033 Å
d(Li-H)=2.031 Å
d(Li-N)=2.213 Å

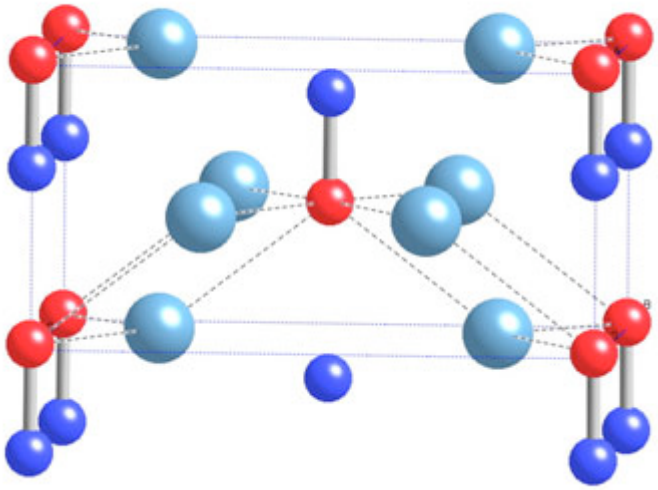


16e <111>
ΔE = +352 meV/f.u.
d(N-H)=1.028 Å
d(Li-H)=1.998 Å
d(Li-N)=2.246 Å

Antiparallel N-H Dimers



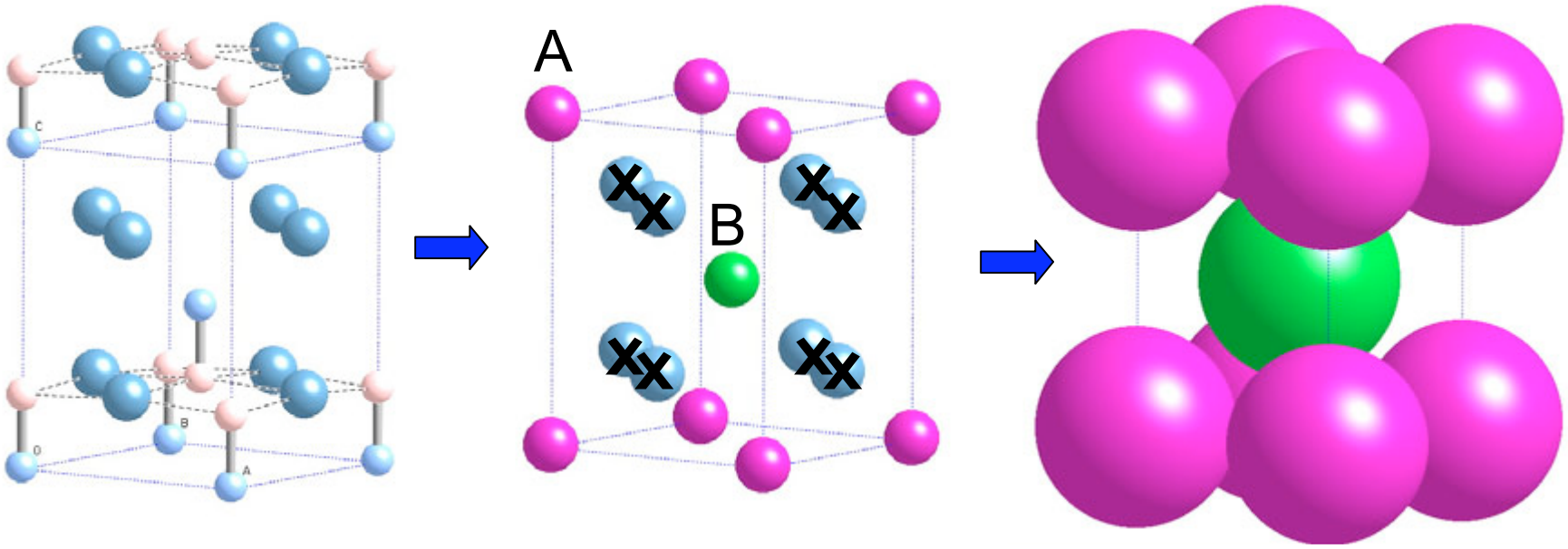
24e <001> parallel
ΔE = +154 meV/f.u.



24e <001> antiparallel
ΔE = +35 meV/f.u.

Energy can be lowered significantly by anti-aligning the N-H dimers!

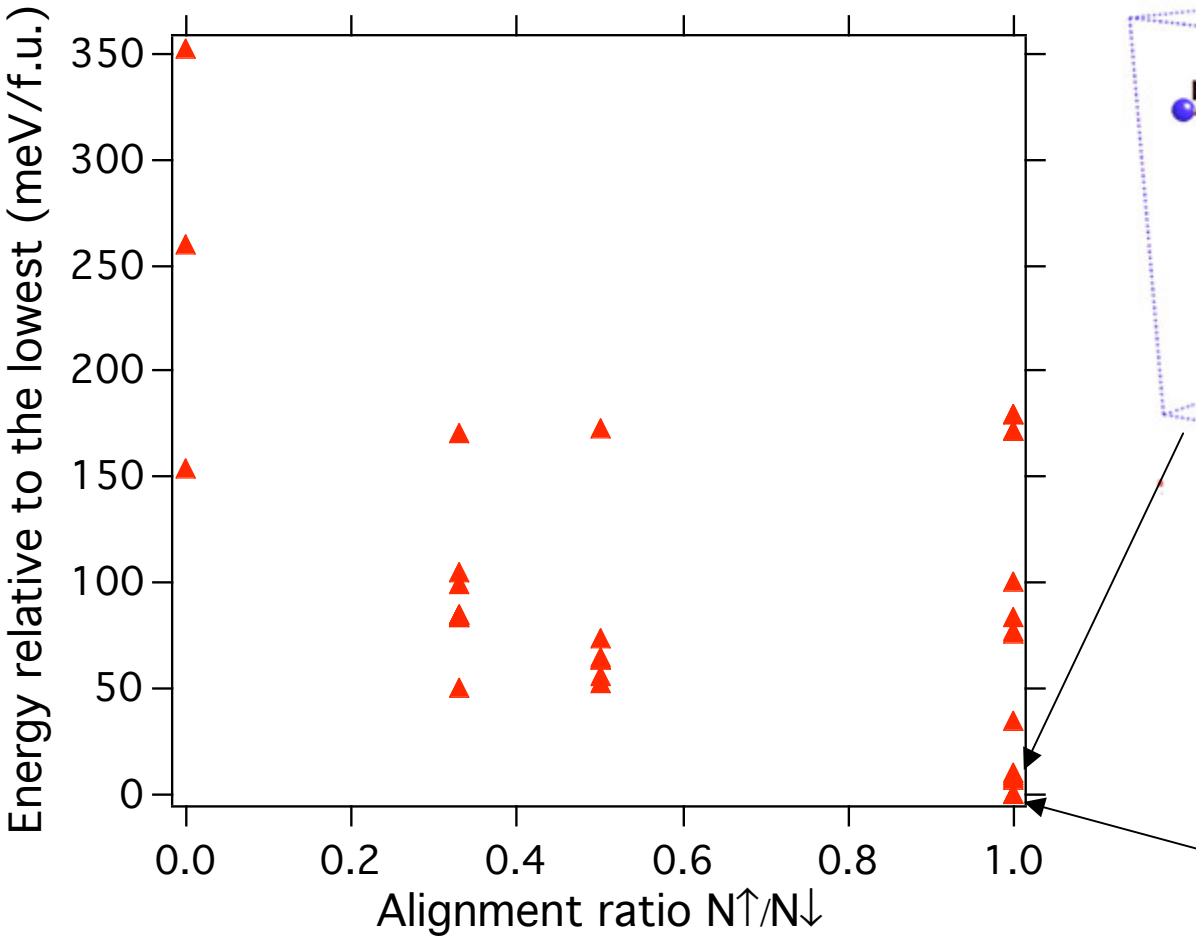
Relation to FCC Ordering

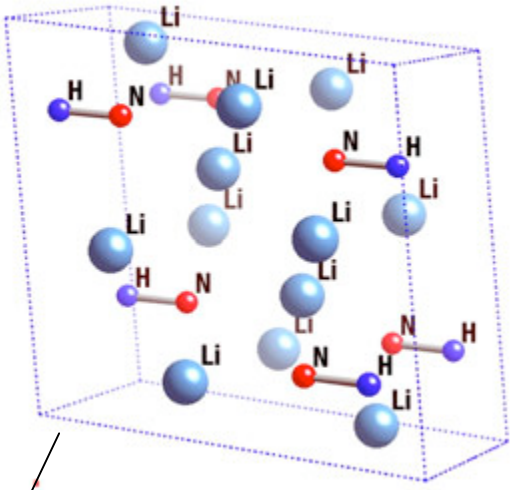


1. N-H along [001] - type A, along [00$\bar{1}$] - type B
2. Remove Li sublattice
3. Get AB in tetragonal $L1_0$ (Prototype CuAu)

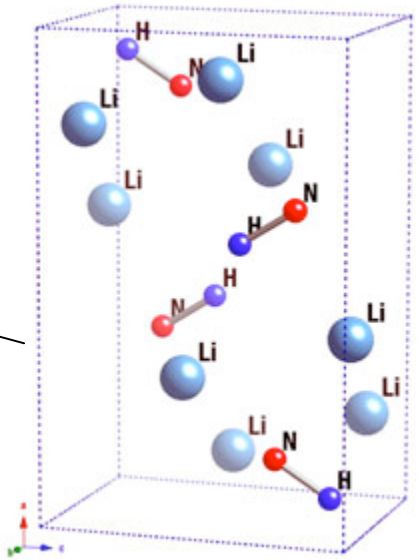
Li_2NH Energies

"Y2" is 4 kJ/mol lower than the structure proposed by Herbst et al





Pnma ("Y2")

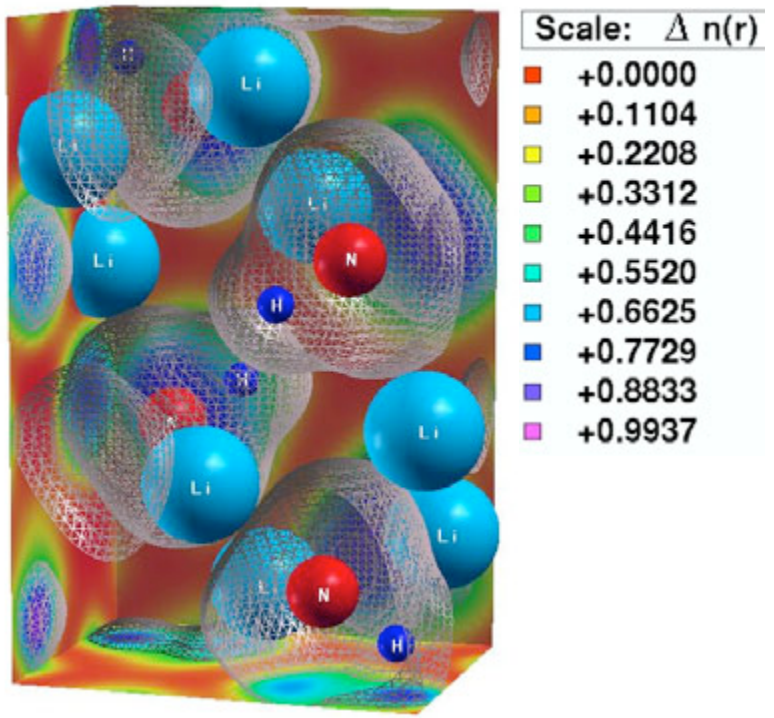


C2m ("W2")

Reaction enthalpy & ELF

$$LiNH_2 + LiH \rightarrow Li_2NH + H_2$$

T (K)	ΔH (kJ/mol-H_2)
0	64
300	75
400	77
500	80



Exp. : ΔH = 66 kJ/mol f.u.

Enumeration: Borohydride-Alanate Mixtures

- ✓ Ordered compounds are constructed from the known crystal structures of alanates and borohydrides
- ✓ Which ones to pick? 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

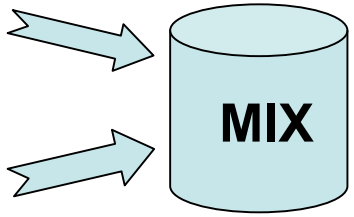
	LiAlH4	*NaAlH4*	*KAlH4*	*LiBH4*	*NaBH4*	*KBH4*
LiAlH4	0.0	4.0	12.2	8.3	21.0	7.3
NaAlH4	6.1	0.0	8.7	13.8	10.3	10.2
KAlH4	8.1	2.4	0.0	24.2	11.9	12.0
LiBH4	4.9	10.0	4.2	0.0	18.8	4.6
NaBH4	10.2	0.0	0.9	2.7	0.0	0.0
KBH4	10.7	18.3	0.8	13.9	0.0	0.0

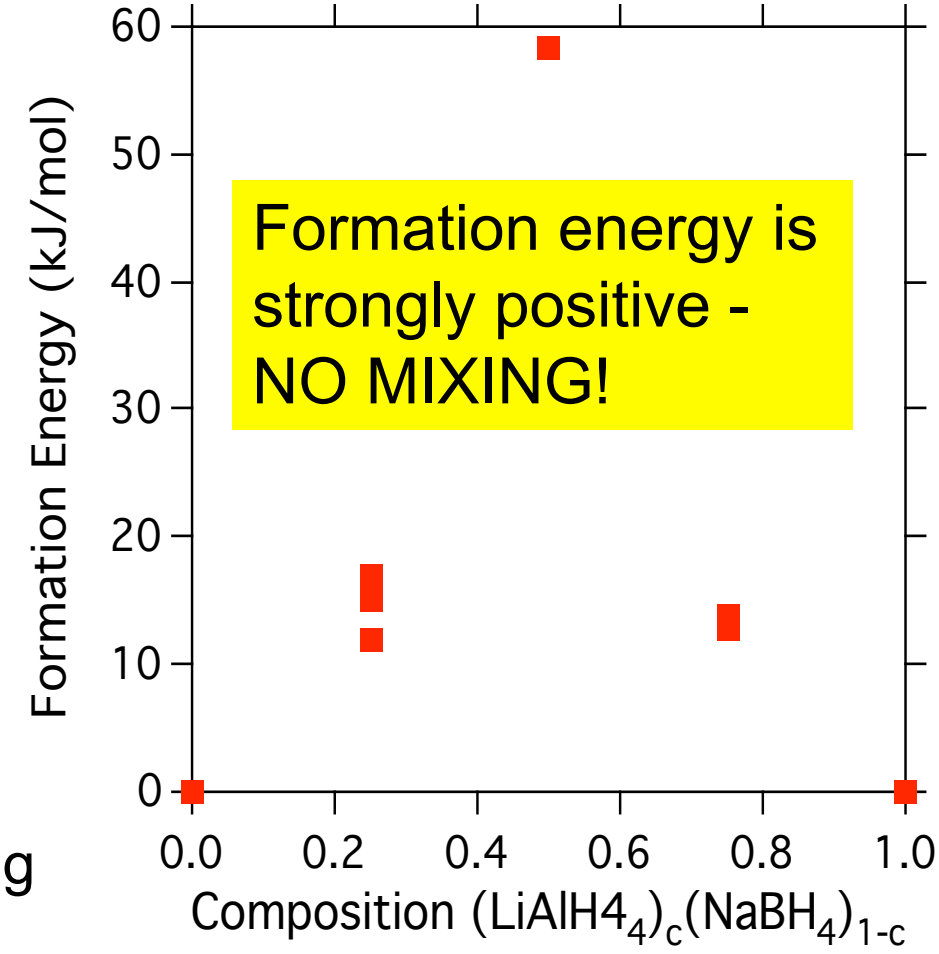
Pick trial crystal structures with low values of $\Delta E_X(Y)$ for *all* end-compounds!

Mixed Alanates-Borohydrides

Calculated ΔH (in kJ/mol H_2)

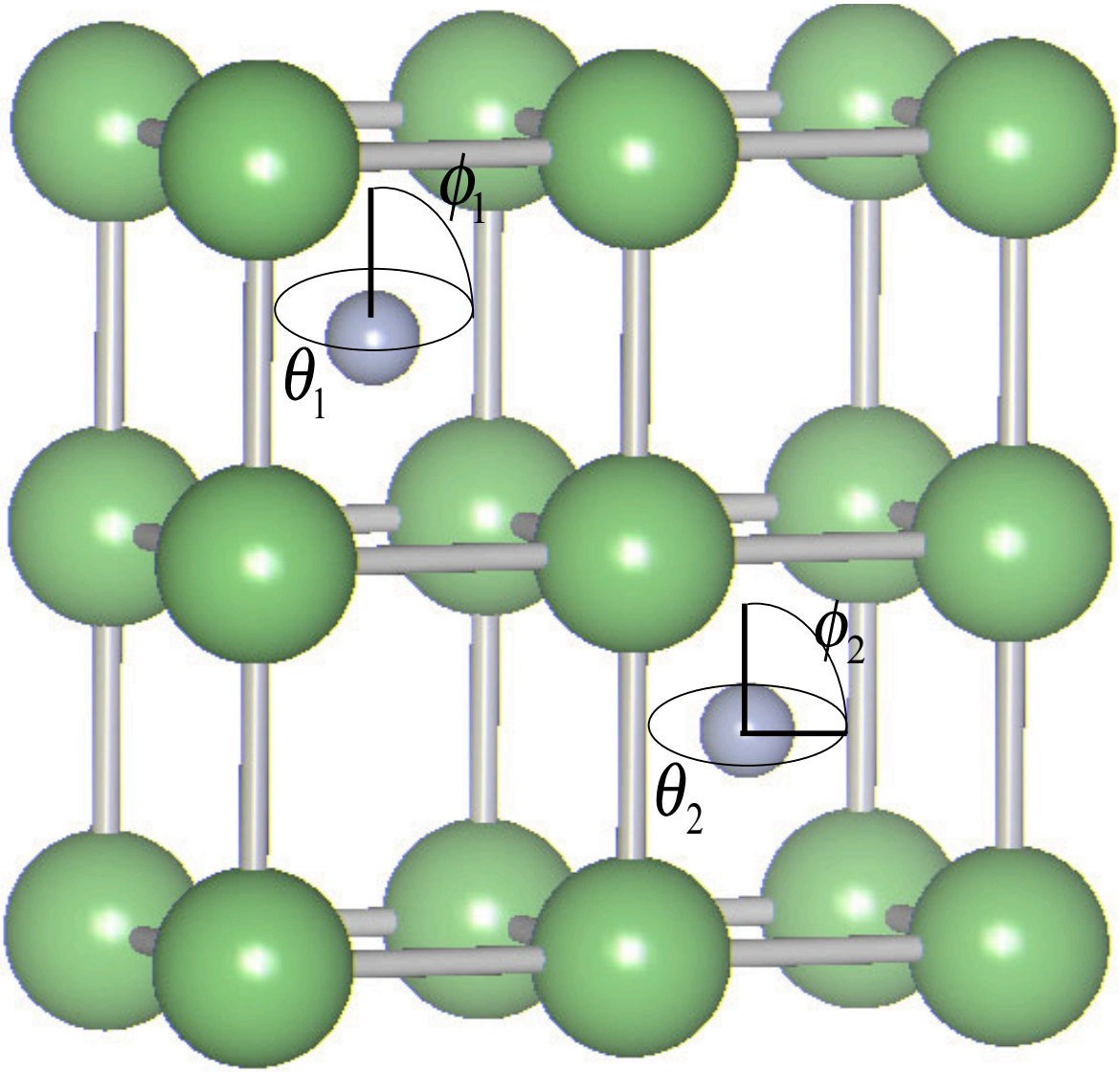
LiBH4	81.3
NaBH4	106.8
KBH4	133.0
LiAlH4	11.3
NaAlH4	36.8
KAlH4	60.1
Mg(AlH4)2	0
Ca(AlH4)2	11.7





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

PART III: CLUSTER EXPANSION



Cluster functions based on spherical harmonics.

Example:

$$Y_1^{-1}(\theta_1,\phi_1)Y_1^{0}(\theta_2,\phi_2)$$

Big Assumptions

Only N-H bond angle matters

Only need to expand local minima

UCLA

New Orthorhombic Structure

Library of 98 energies calculated using density functional theory

↓

Cluster expansion Hamiltonian

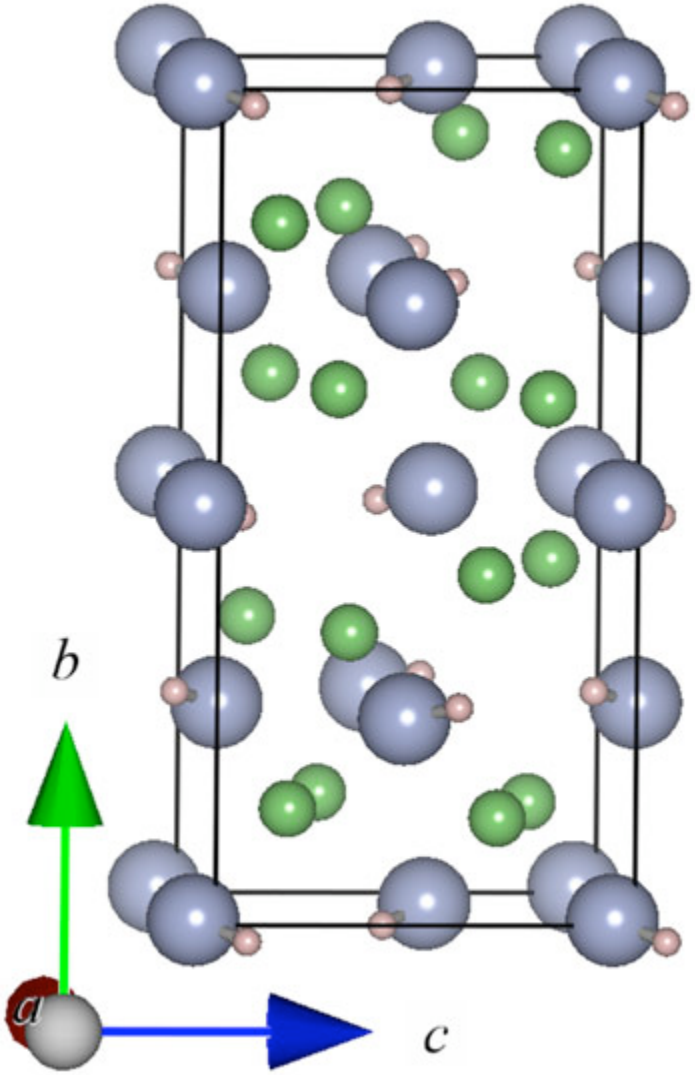
↓

Monte Carlo search for structures with low predicted energy

↓

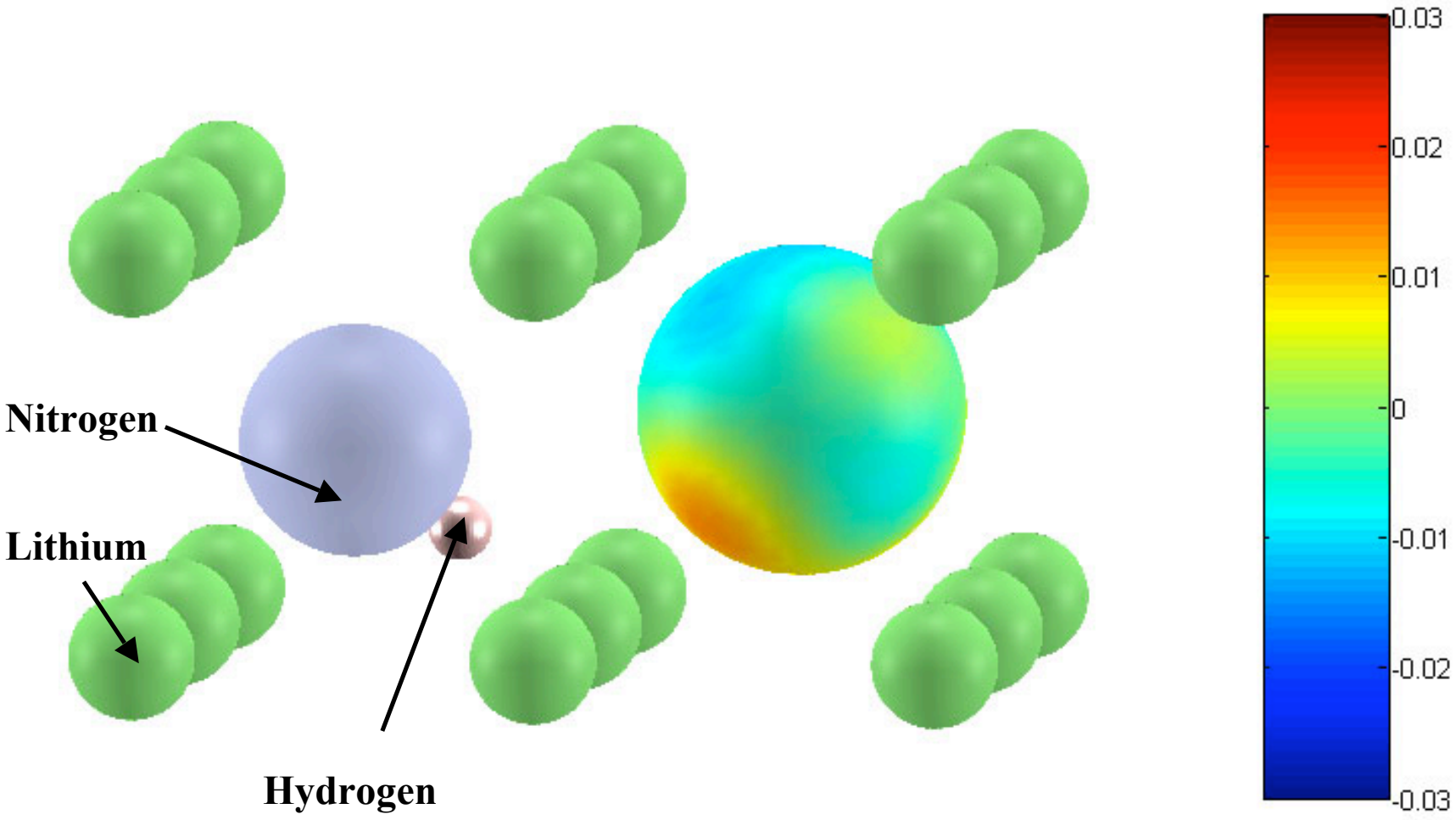
Verification of low-energy structure using Density Functional Theory

→



Lithium Nitrogen Hydrogen

Interaction between N-H dimers II



New Orthorhombic Structure

Lattice Parameters

a = 5.12 Å

b = 10.51 Å

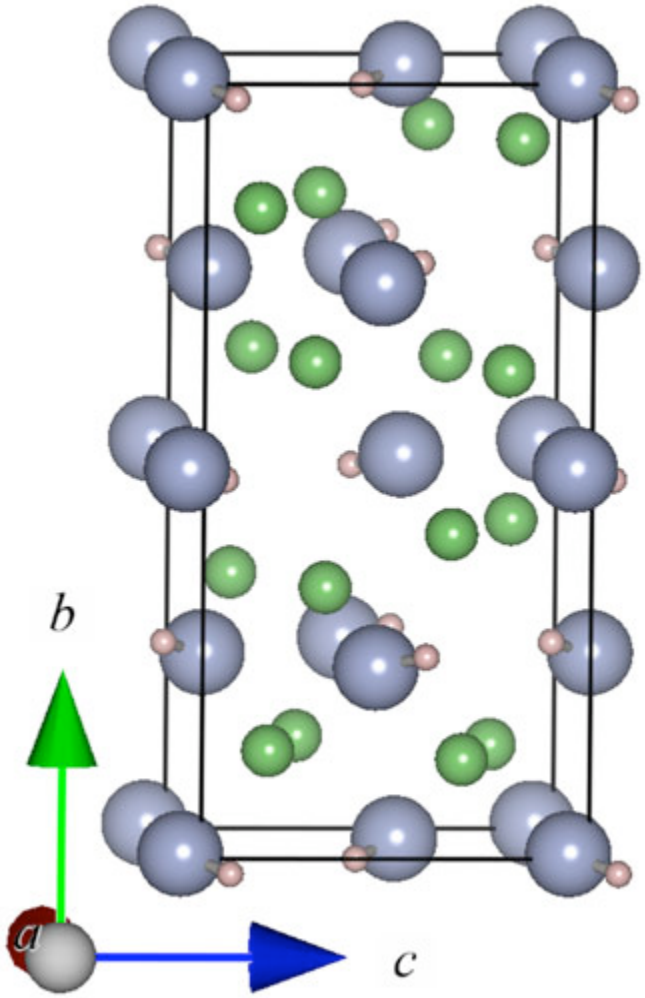
c = 5.27 Å

Calculated ΔH at 298K

-178.4 kJ/mol f.u.

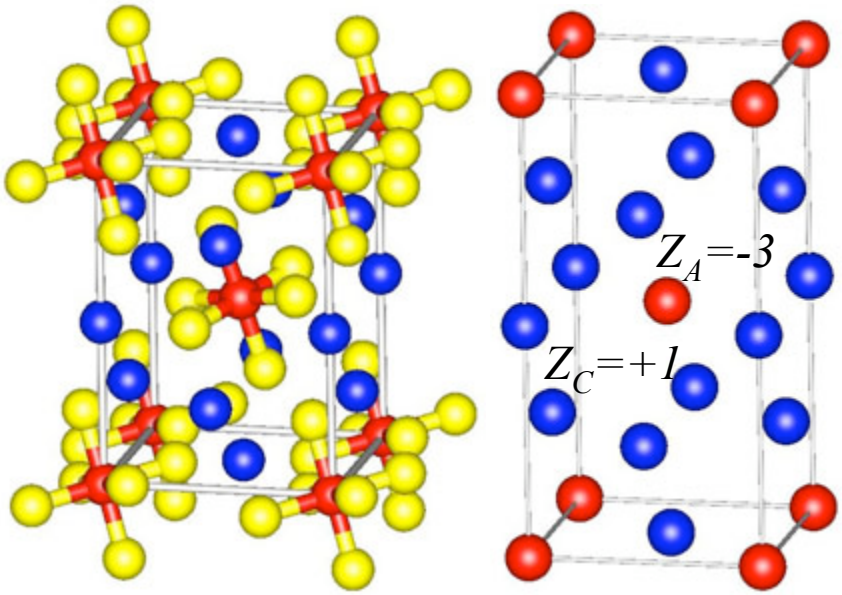
-1.849 eV/mol f.u.

4.8 kJ/mol f.u. lower than the "Y2" structure

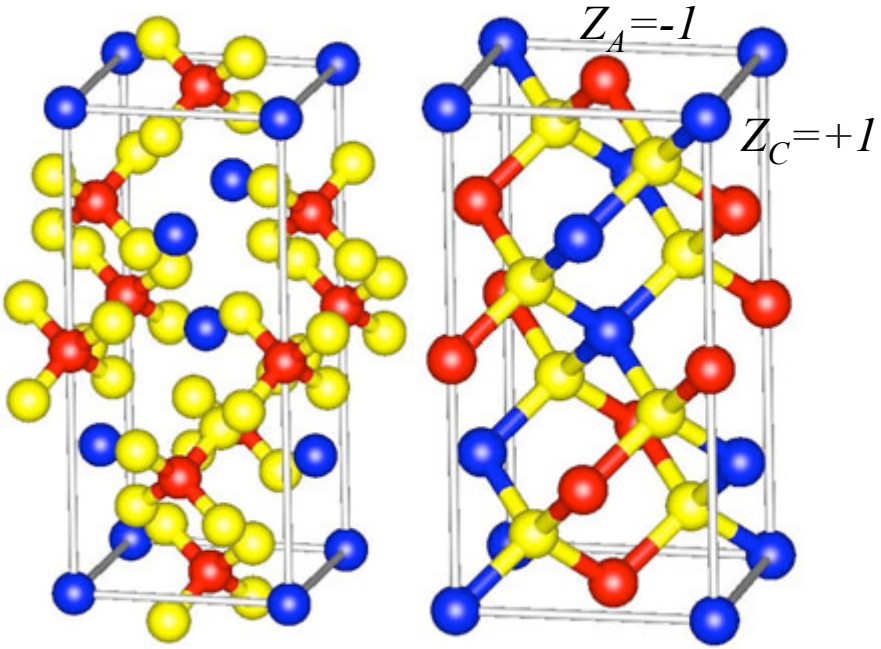


Part IV: Fixed-Lattice Electrostatic Models

Na_3AlH_6 and $TiAl_3$



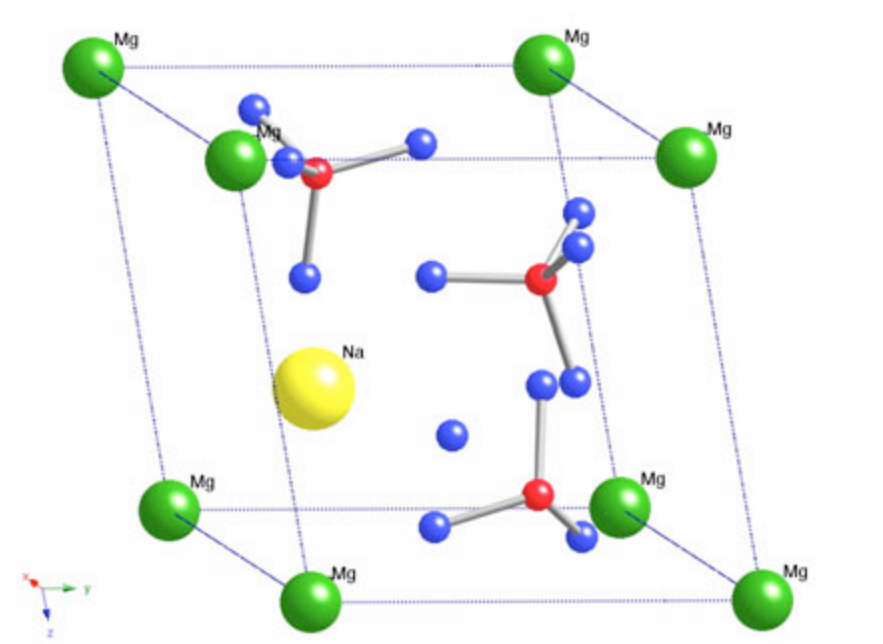
$NaAlH_4$ and $CuInSe_2$



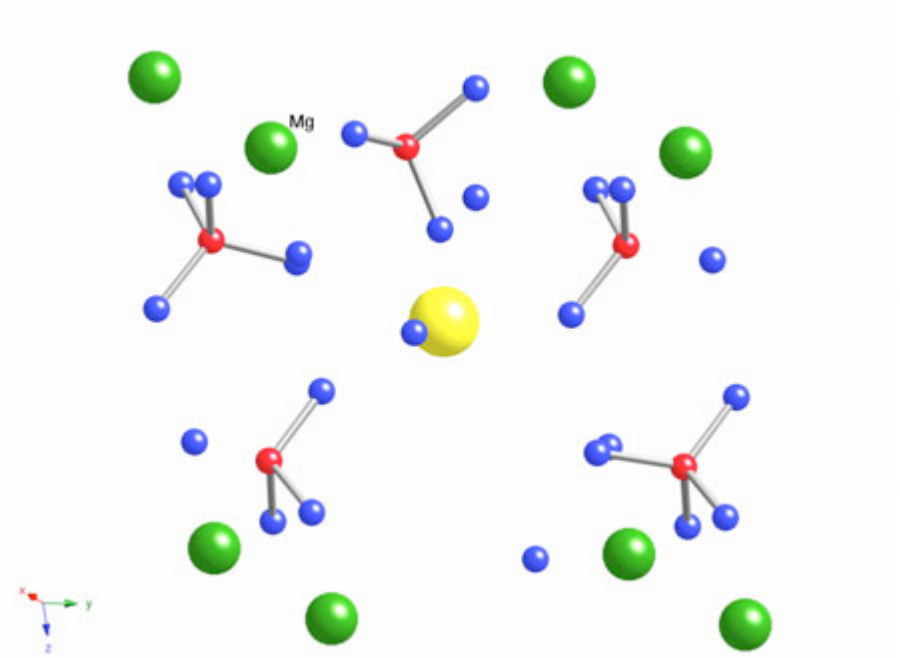
Na^+ and $AlH_n^{-(n-3)}$ units are arranged on the vertices of FCC lattice.
Among FCC-based structures, these have the lowest electrostatic energies!

Mixing Alanates: $MgNa(AlH_4)_3$

Initial structure from electrostatic



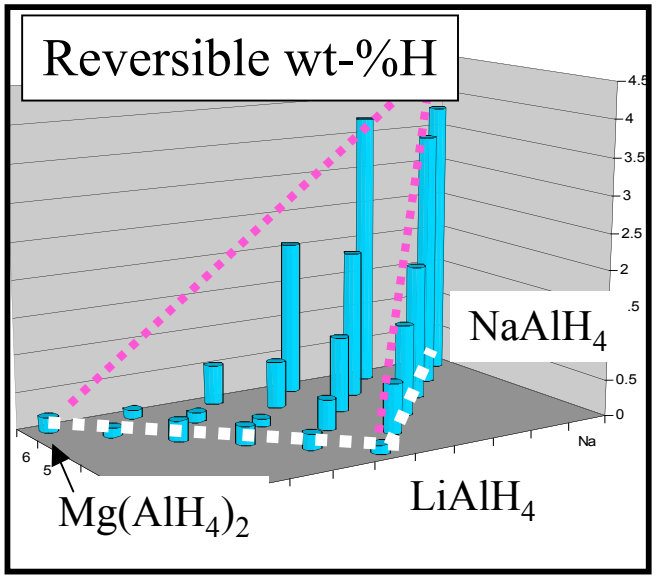
Relaxed structure from DFT



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

Conclusion: $MgNa(AlH_4)_3$ compounds will not form!

UOP Results for Mixed Alanates



- **First-Principles results agree with experimental combinatorial results at UOP LLC:**
  - Na-Li-Mg-Alanate phase diagram searched starting from hydrided side
  - No stable mixtures found under these conditions.

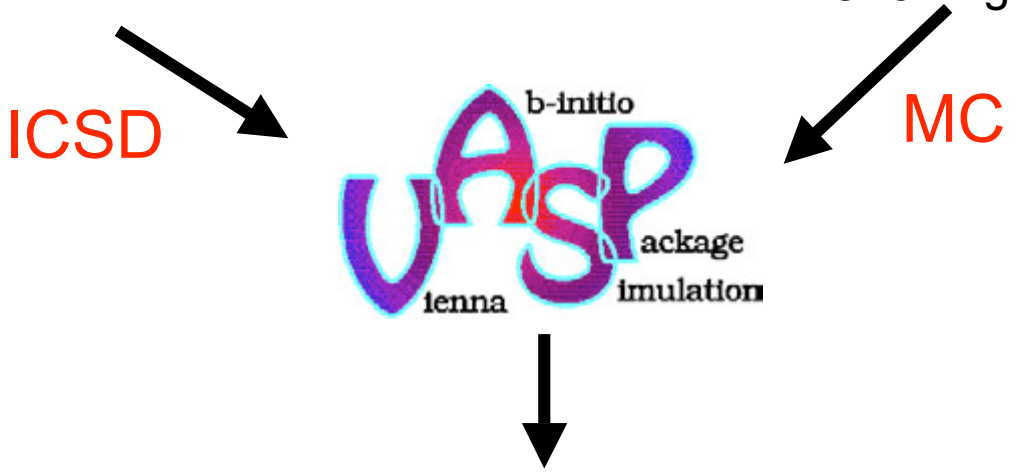
Part V: Off-Lattice Global Optimization

Database (Usual Suspects)

- Inorganic crystal structure database
- ICSD data base contains 80,000 inorganic structures
- looking for AB_2X_8 yields ~ 100 inequivalent test structures

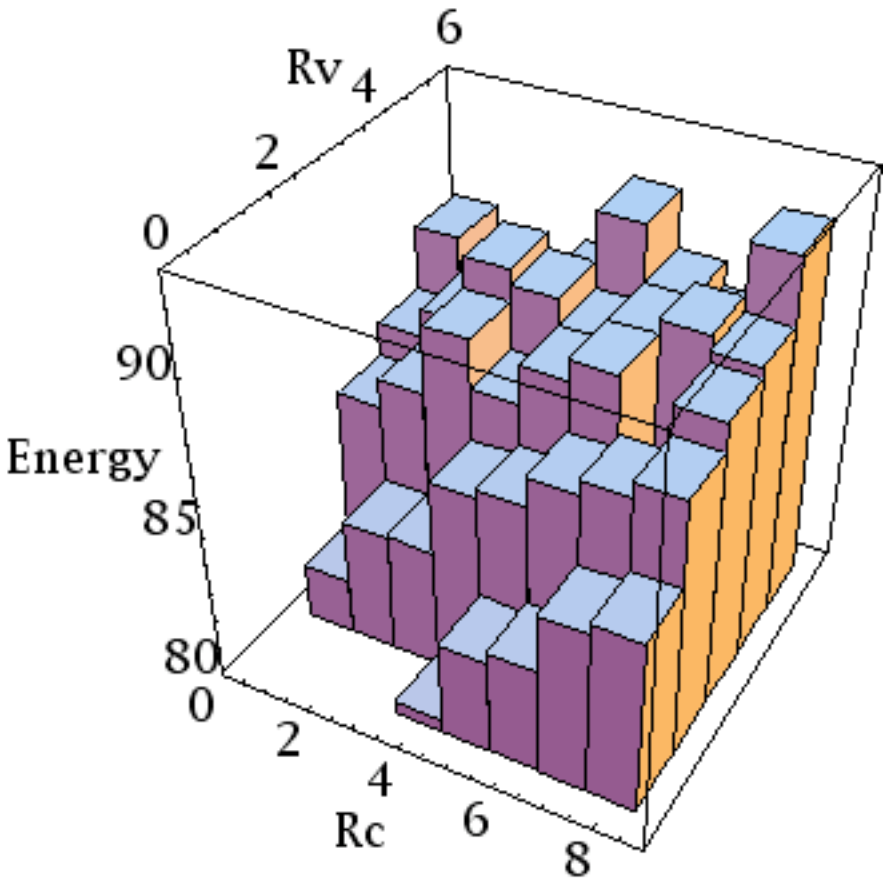
Monte Carlo Model

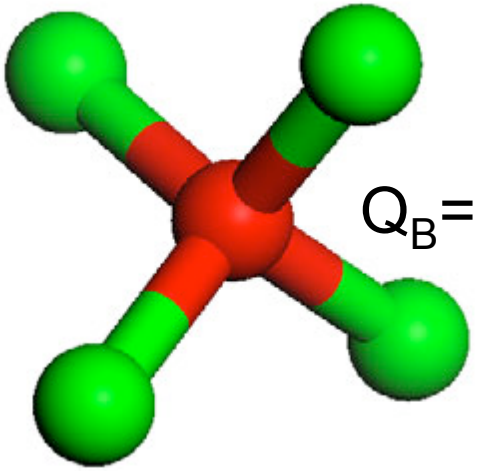
- electrostatic interactions
- soft-sphere repulsion
- MH_x anion is a rigid unit
- Perform global optimization



Exploring MC Parameter Space

DFT Energy vs. R_H and R_C for $Ca(BH_4)_2$



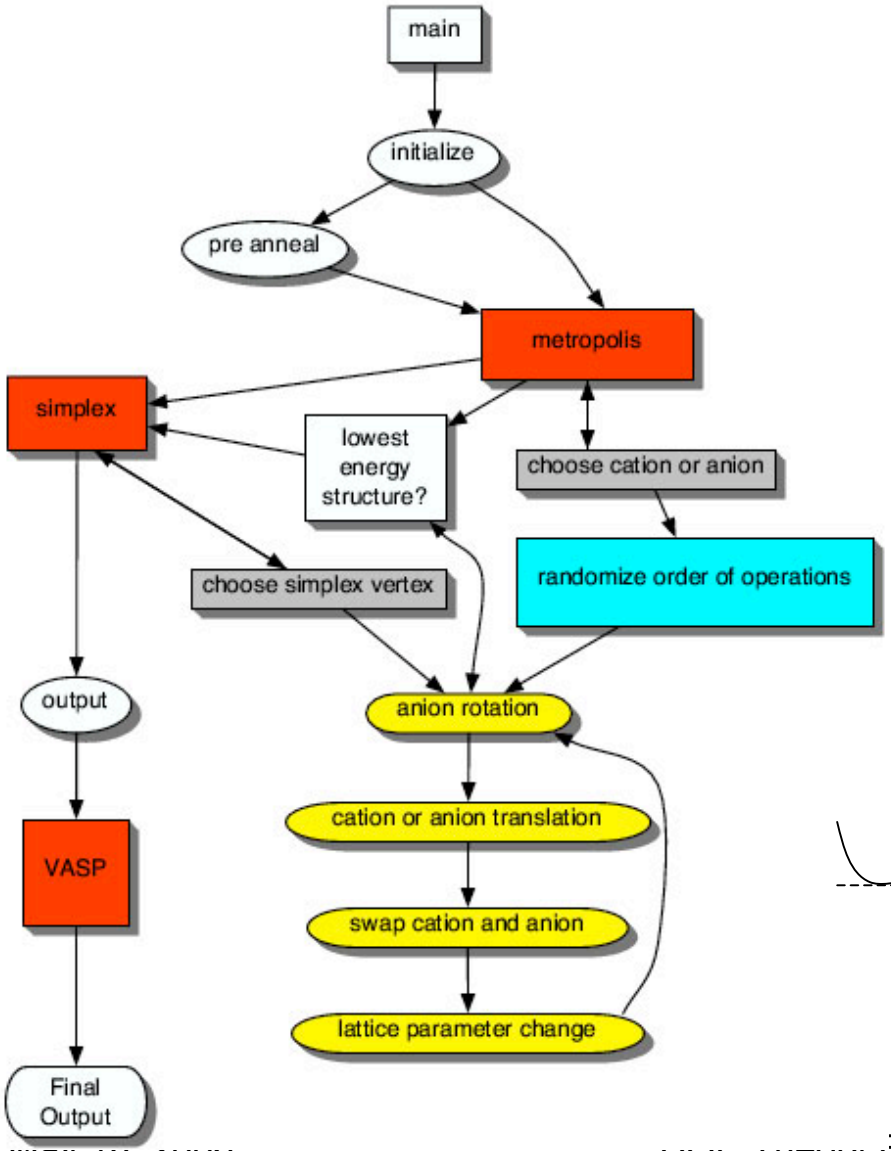


$Q_B=1-4Q_A$

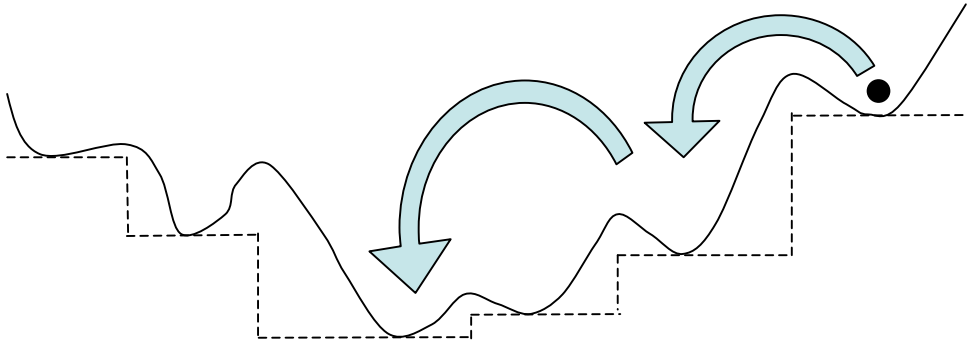
R_H, Q_H

R_C, $Q_C=+1$

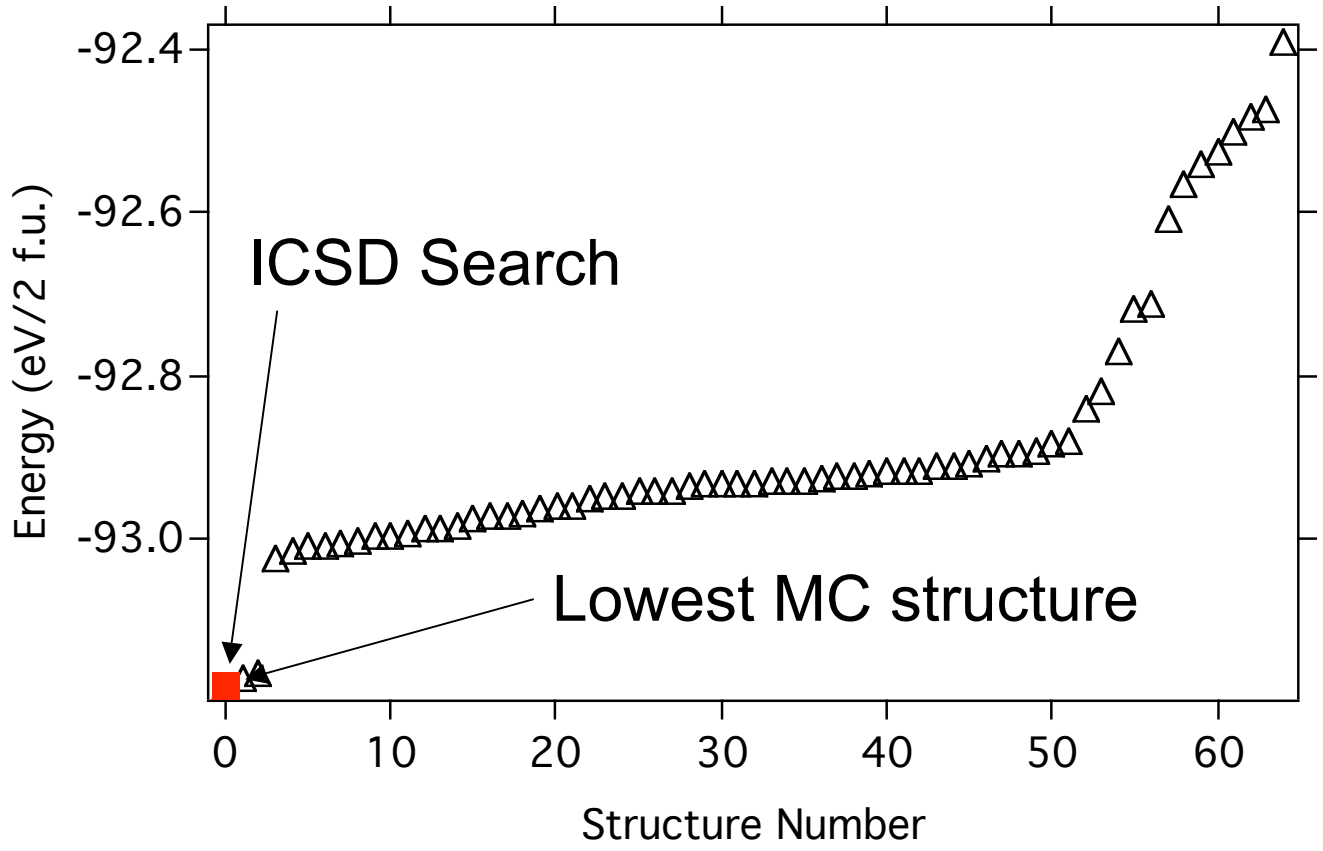
Monte Carlo Algorithm



- Metropolis Monte Carlo with Basin Hopping
- No restrictions on cell shape
- Model anions as rigid anionic units
- Key assumption: cohesive energy is dominated by electrostatics
- Forces: Ewald electrostatic energy and soft-sphere repulsion



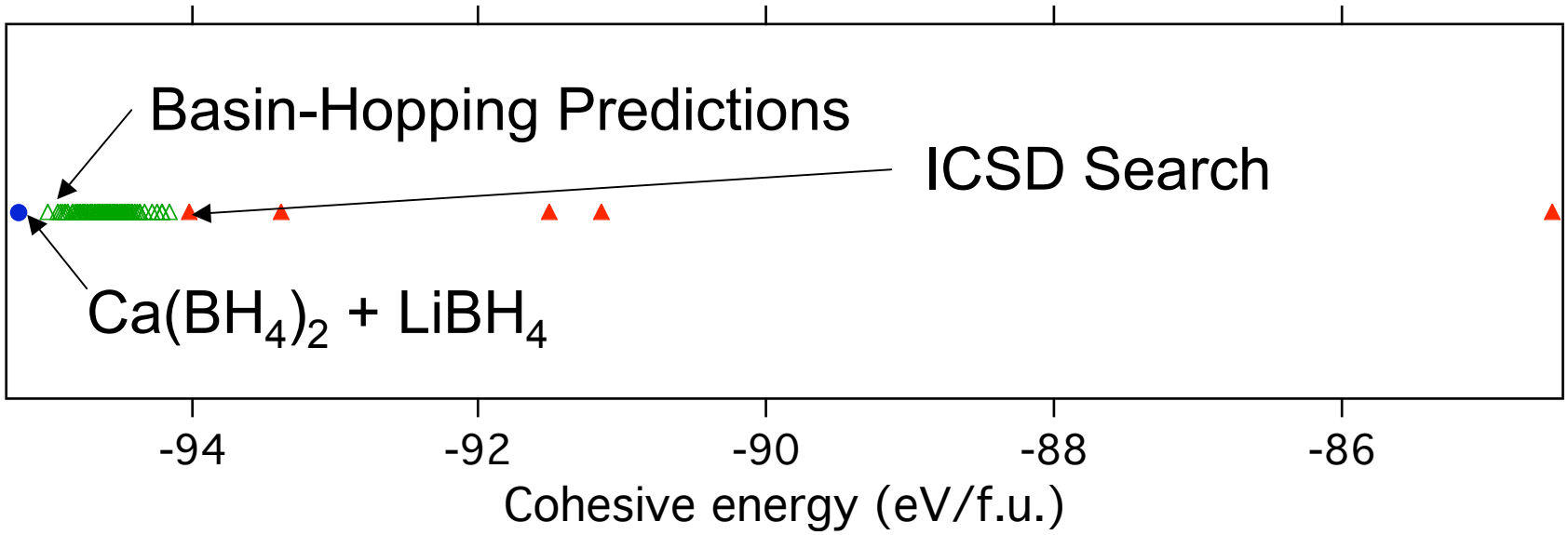
MC Results for $Ca(BH_4)_2$



Energy within 10 meV/f.u. of the best ICSD structure!

10 meV error = approx 1 kJ/mol, or 0.25 kJ/mol-H_2

Enthalpies of Compounds: $CaLi_2(BH_4)_4$



Monte Carlo basin hopping easily beats the ICSD search.

The lowest structure unstable w.r.t. to phase separation.

Summary & Outlook

- ICSD search seems to work well for common compositions (ABC_4, ABC_5 or AB_2C_8)
  - Predicted enthalpies within ~10 kJ/mol
  - Need experimental crystal structures to evaluate accuracy
- Enumeration and cluster expansion methods useful when common crystal lattice exists (imides/amides, alloys)
- Fixed-lattice electrostatics is reasonable for alanate and borohydride alloys
- Monte Carlo may have the greatest potential. But more work is needed:
  - Global Optimization methods to locate the true ground state
  - Applications to other systems