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Density-Functional Calculations of New Alanates

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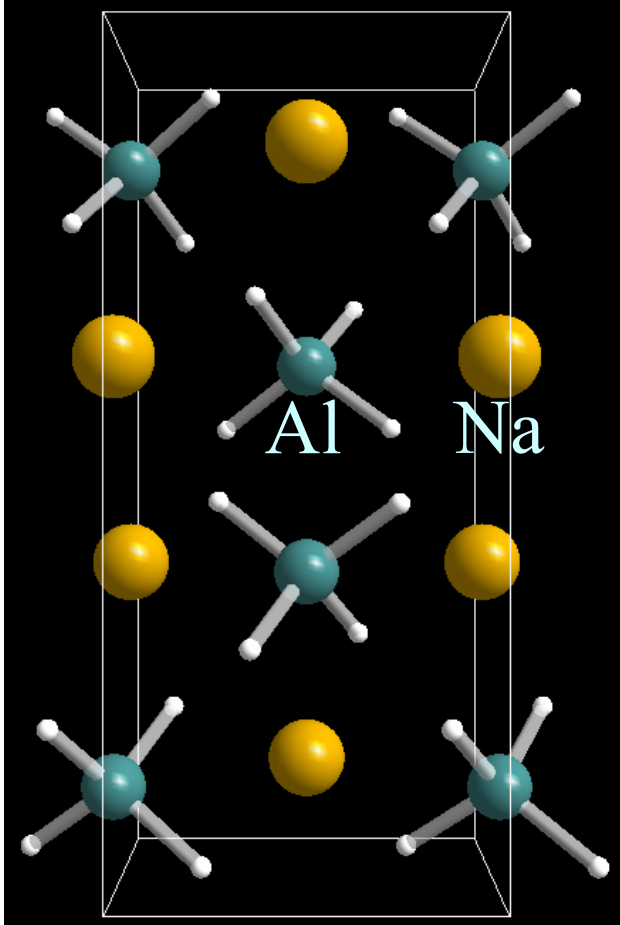
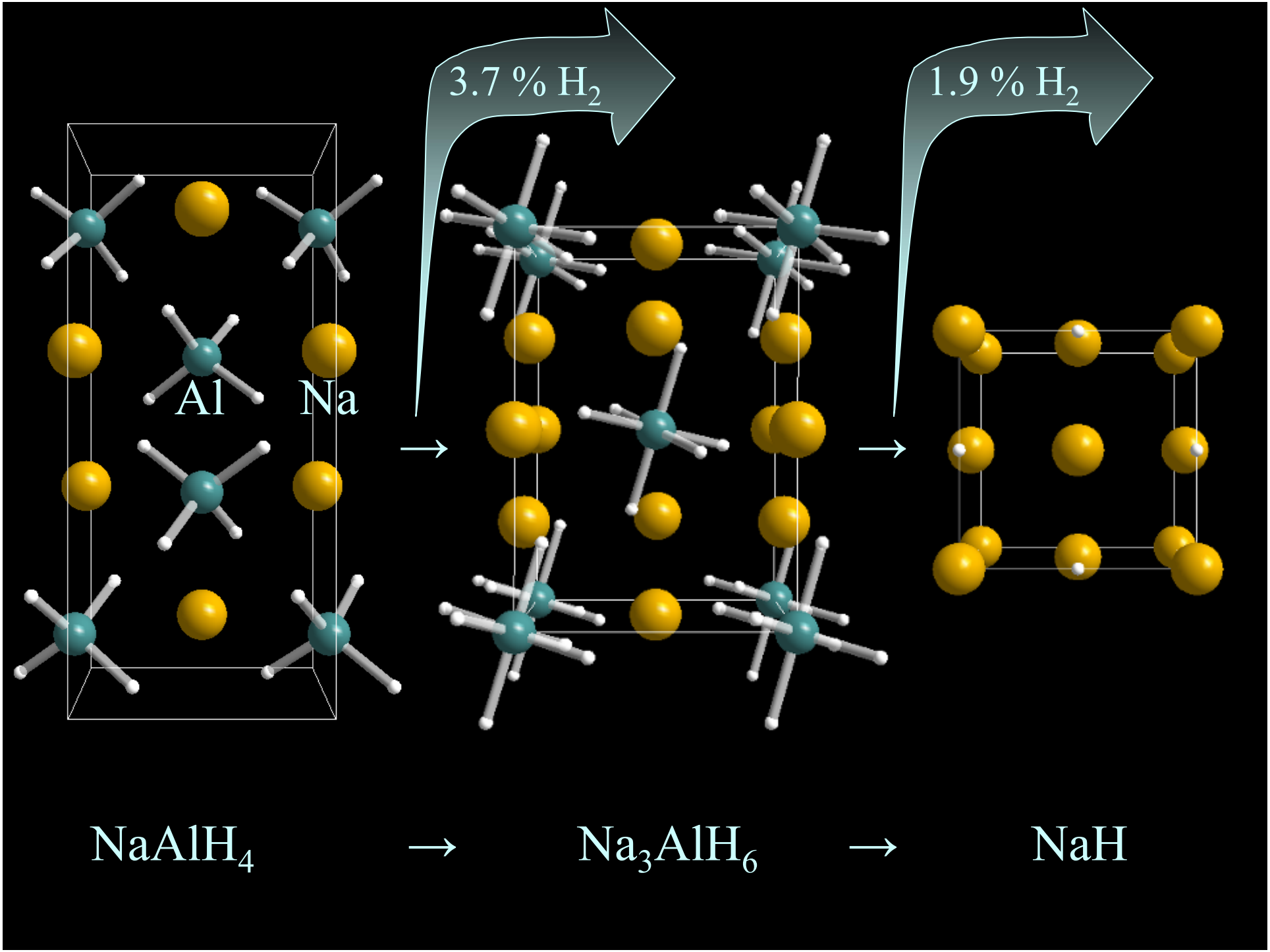
United Technologies



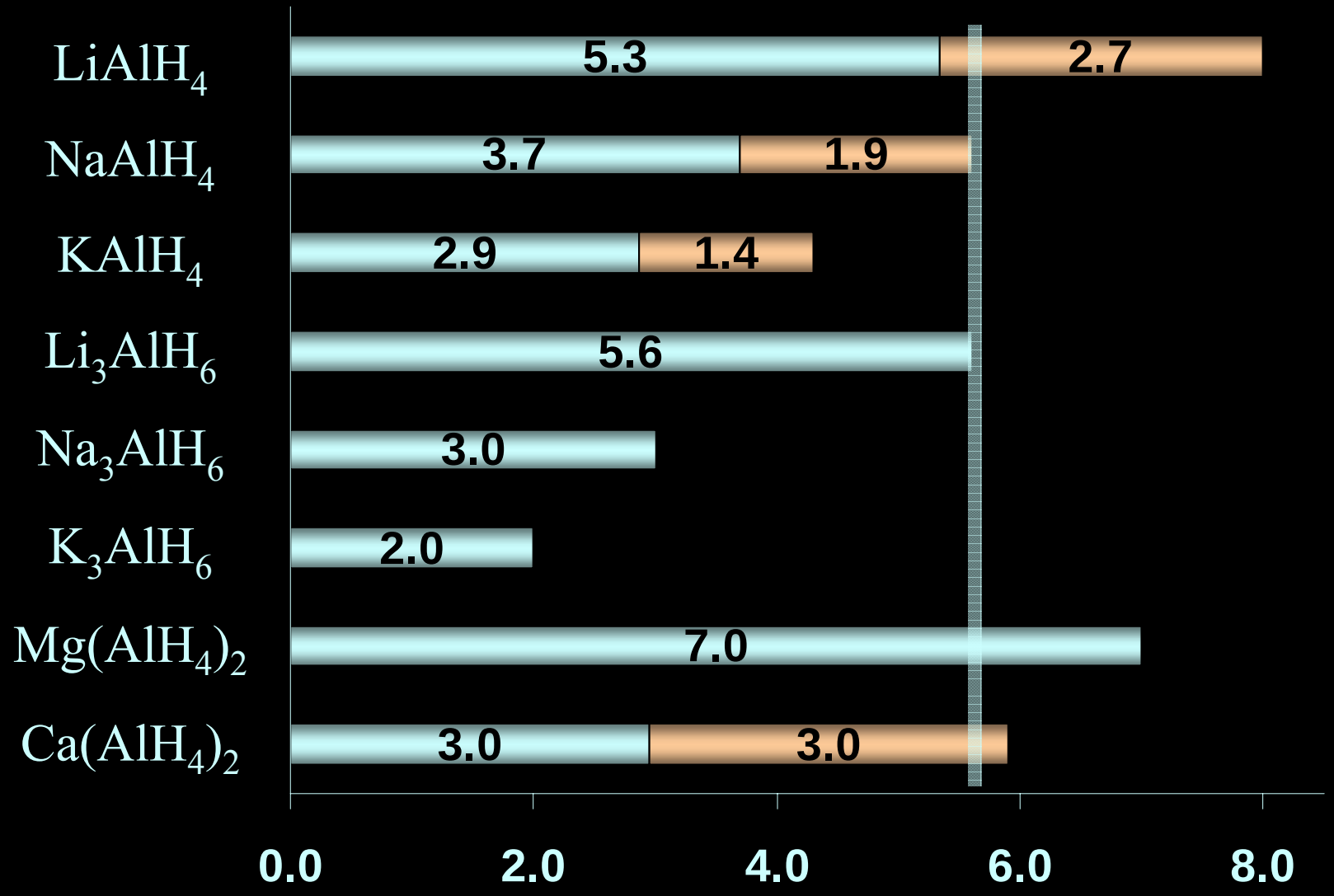
Alanates for hydrogen storage

- First alanate shown to be reversible: $NaAlH_4$.
- Any other (lighter) reversible alanates?
- What can we learn from the crystal structures and electronic structures?
- The role of Ti?


3.7 % H_2
1.9 % H_2
Al
Na
$NaAlH_4$ → Na_3AlH_6 → NaH

Alanates for hydrogen storage

- Accessible hydrogen wt%:

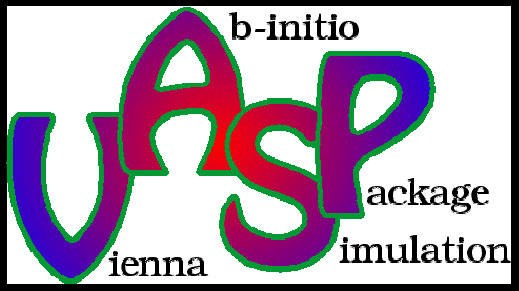


Crystal structure predictions

- E.g. Na_3AlH_6: Seven representative systems
- Full relaxation; allows to leave space group/symmetry

Space group	#	Type	# atoms	Model system
P-1	2	Triclinic	20	Ti_3NiS_6
$P2_1/n$	14	Monoclinic	20	$K_3Fe(CN)_6$
$P2_1/n$	14	Monoclinic	20	Na_3AlF_6 (α)
$Pna2_1$	33	Orthorhombic	40	Li_3AlF_6
Immm	71	Tetragonal	20	Na_3AlF_6 (β)
R-3	148	Rhombohedral	20	Ti_3NiS_6
Fm-3*m*	225	Cubic	40	K_3MoF_6

Calculation details



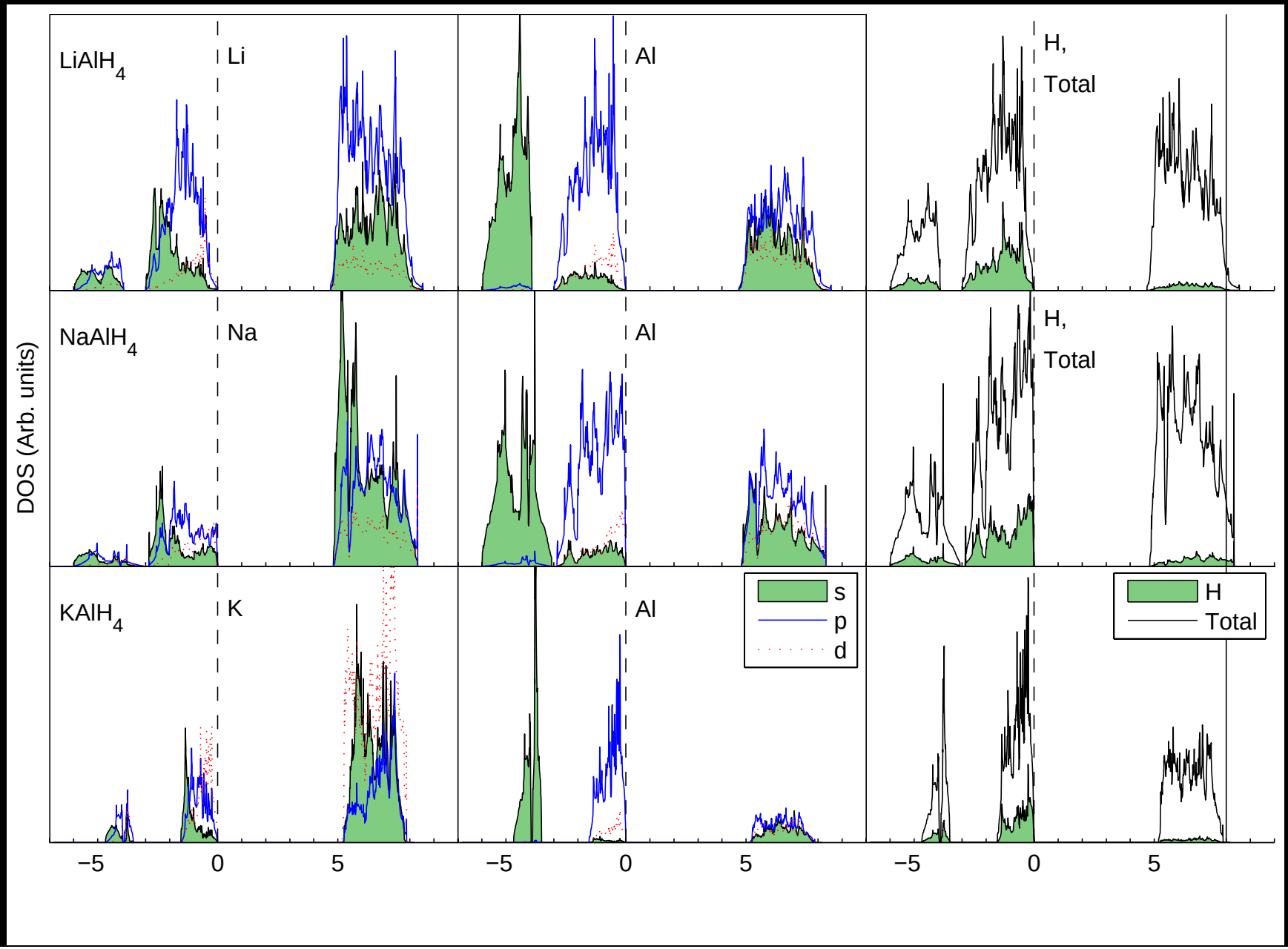
- Band-structure DFT
- VASP
- Generalized gradient appr. (GGA) PW91
- Projector augmented wave (PAW) method
- Spin polarization allowed
- Cut-off energy 780 eV
- Overall convergence: ~1 meV (0.01 kJ/mol)/unit cell

Predicted crystal structures

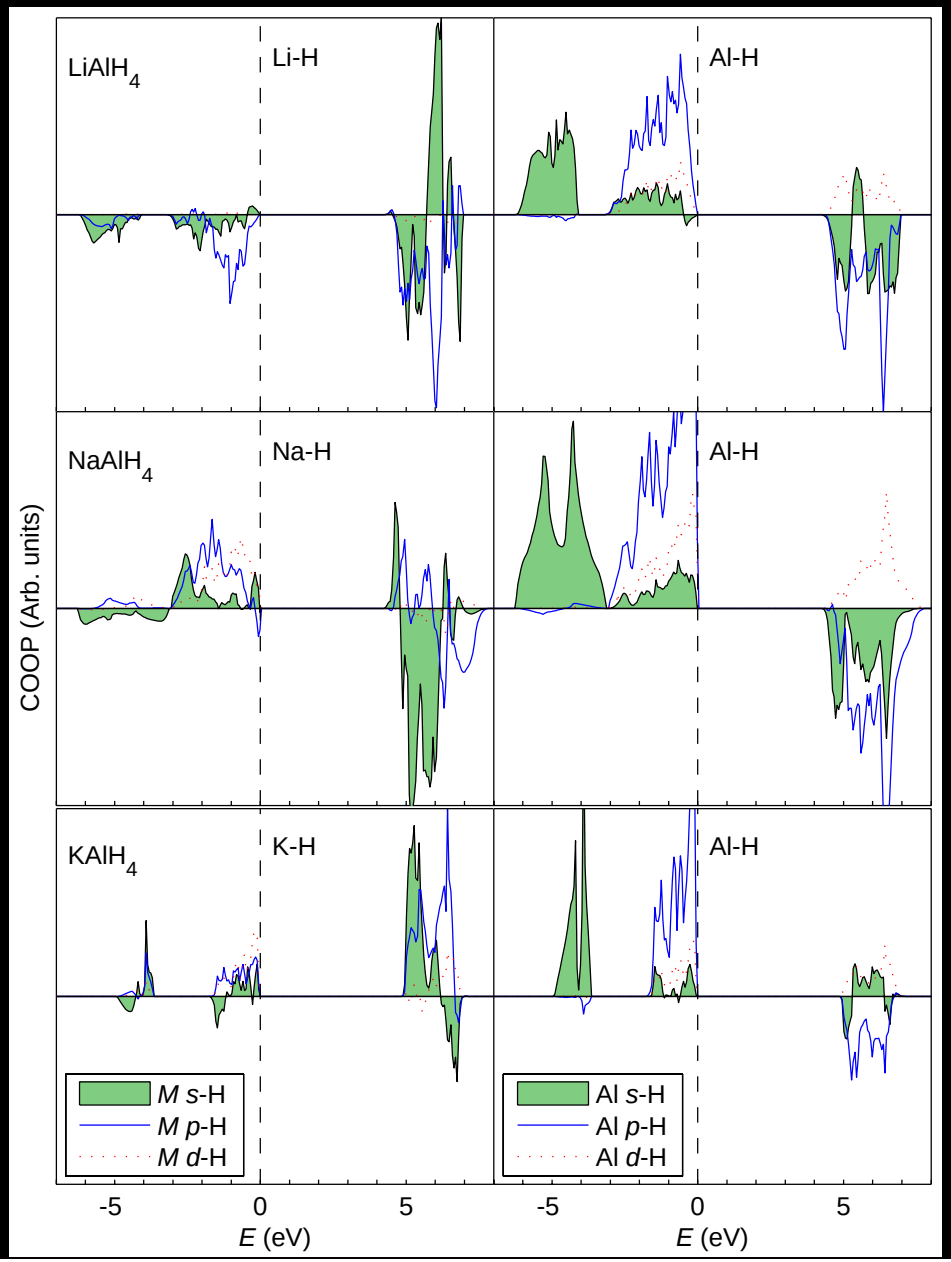
Compound	Predicted structure	Expt. structure
$LiAlH_4$	$P2_1/c$	$P2_1/c$
$NaAlH_4$	$I4_1/a$	$I4_1/a$
$KAlH_4$	*Pnma*	*Pnma*
Li_3AlH_6	*R*–3	*R*–3
Na_3AlH_6	$P2_1/n$	$P2_1/n$
K_3AlH_6	$P2_1/n$	
$Mg(AlH_4)_2$	*P*–3*m*1	*P*–3*m*1
$Ca(AlH_4)_2$	*Pbca*	

- O. M. Løvvik, S. M. Opalka, H. W. Brinks, B. C. Hauback, Phys. Rev. B **69** (2004) 134117).
- O. M. Løvvik, O. Swang, Europhys. Lett. **67** (2004) 607.
- O. M. Løvvik, Phys. Rev. B. **71** (2005) 144111.
- O. M. Løvvik, O. Swang, J. Alloys Comp. **404-406** (2005) 757-761.
- O. M. Løvvik, P. N. Molin, Phys. Rev. B. **72** (2005) 073201.
- O. M. Løvvik, O. Swang, S. M. Opalka, J. Mater. Res. **20** (2005) 3199 (Invited paper).

Electronic density of states



Crystal orbital overlap populations



Stability of alkali alanates

- Electronic (ground state) formation enthalpy:

$$H_{\text{form}}(M_n\text{AlH}_{(n+3)}) = E(M_n\text{AlH}_{(n+3)}) - n\,E(M) - E(\text{Al}) - (n+3)/2\,E(\text{H}_2)$$

Compound		$LiAlH_4$	$NaAlH_4$	$KAlH_4$	Li_3AlH_6	Na_3AlH_6	K_3AlH_6
H_{form}	(kJ/mol H_2)	-55.5	-54.9	-70.0	-102.8	-69.9	-78.5

Stability of alkaline earth alanates

- Electronic formation enthalpy:

$$\Delta H_{\mathrm{Form}}(Ae(\mathrm{AlH_4})_2) = E(Ae(\mathrm{AlH_4})_2) - E(Ae) - 2E(\mathrm{Al}) - 4E(\mathrm{H_2})$$

- Electronic reaction enthalpy:

$$\Delta H_{\mathrm{React}}(Ae(\mathrm{AlH_4})_2) = E(Ae(\mathrm{AlH_4})_2) - E(Ae\mathrm{H_2}) - 2E(\mathrm{Al}) - 3E(\mathrm{H_2})$$

kJ/mol H_2	Formation enthalpy	Reaction enthalpy
$Mg(AlH_4)_2$	-21.1	-6.2
$Ca(AlH_4)_2$	-59.4	-20.7

Why are not Li and Mg alanates reversible?

- Na and K alanates exhibit reversible hydrogenation, Li and Mg alanates not.
- Indicators of reversibility from calculations?
- Electronic structure: no clear signs.
- Crystal structure: Li_3AlH_6 stands out.
- Thermodynamic stability: Li_3AlH_6 stands out.
- The reason: Li small enough for Li_3AlH_6 to attain the *R*–3 structure, making Li_3AlH_6 too stable.
- Similarly: Mg alanate too unstable.
- No easy generalization to other materials.

Prediction of new mixed alanate phases

- O. M. Løvvik, O. Swang, Europhys. Lett. 67 (2004) 607.

$LiAlH_4$

"Tetrahydrides"

- O. M. Løvvik, O. Swang, J. Alloys Comp. **404-406** (2005) 757-761

$Li_{0.75}Na_{0.25}AlH_4$

$K_{0.25}Li_{0.75}AlH_4$

- O. M. Løvvik, O. Swang, S. M. Opalka, J. Mater. Res. **20** (2005) 3199

$Li_{0.5}Na_{0.5}AlH_4$

$K_{0.5}Li_{0.5}AlH_4$

$Li_{0.25}Na_{0.75}AlH_4$

$K_{0.75}Li_{0.25}AlH_4$

$K_{0.25}Na_{0.75}AlH_4$

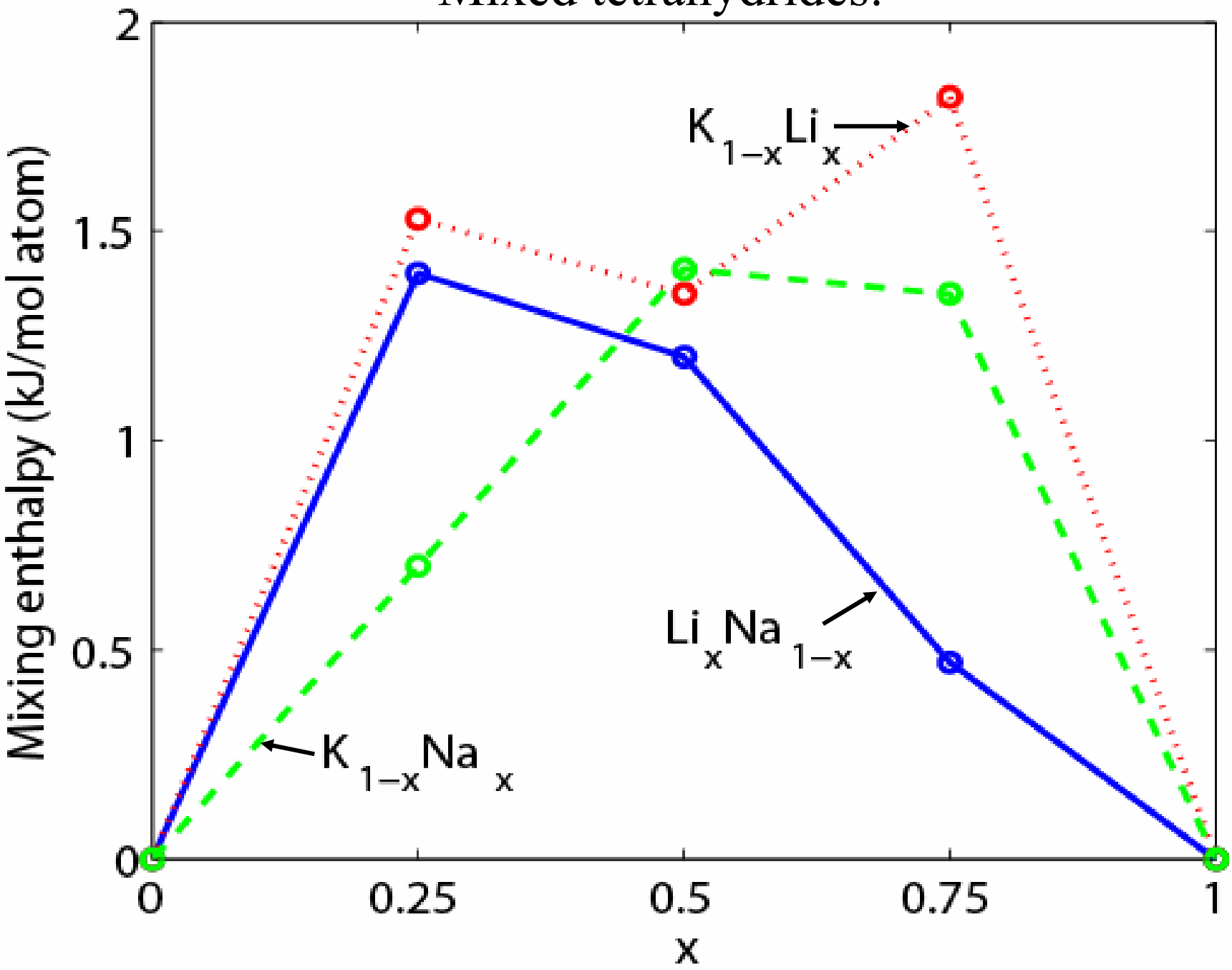
$K_{0.5}Na_{0.5}AlH_4$

$K_{0.75}Na_{0.25}AlH_4$

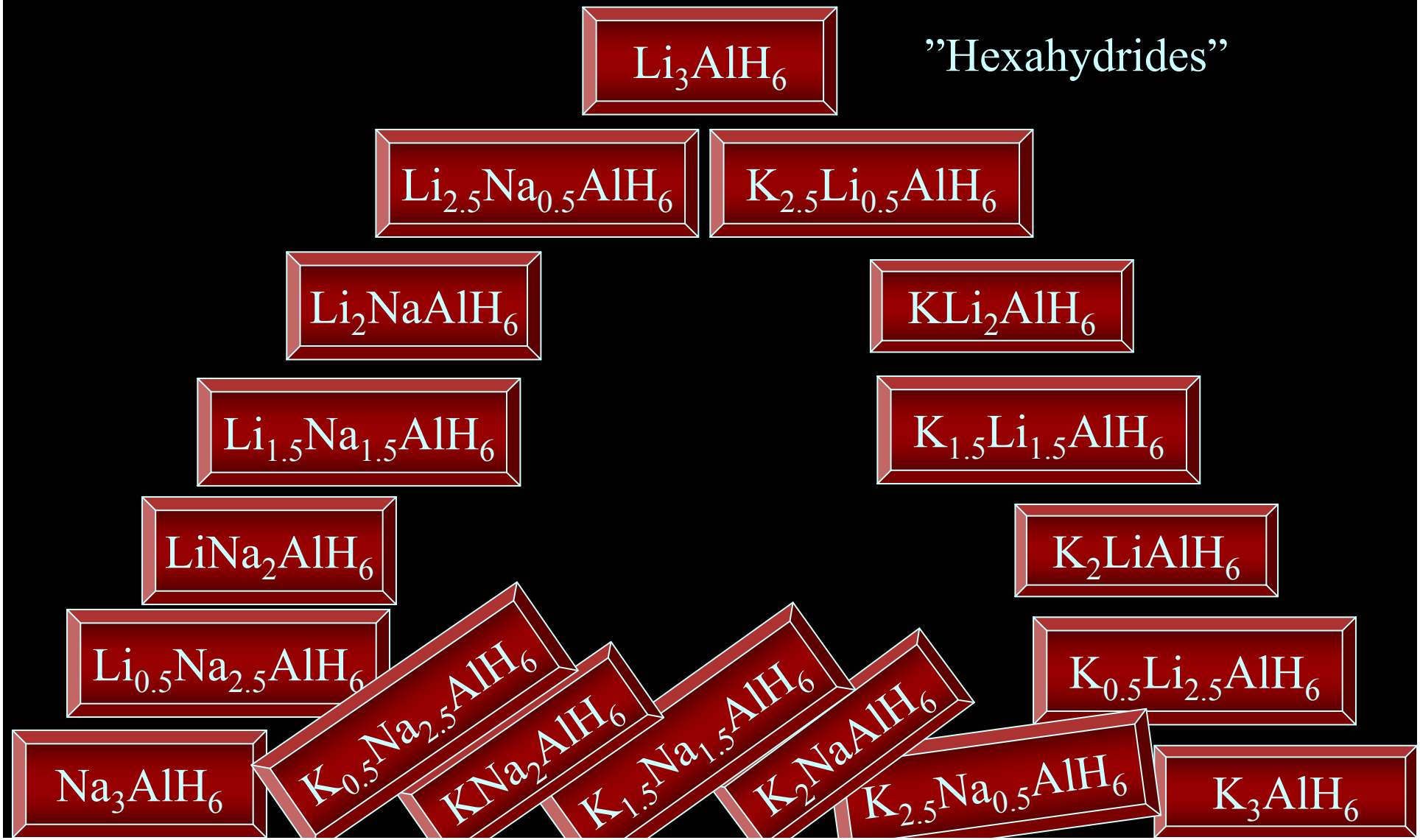
$NaAlH_4$

$KAlH_4$

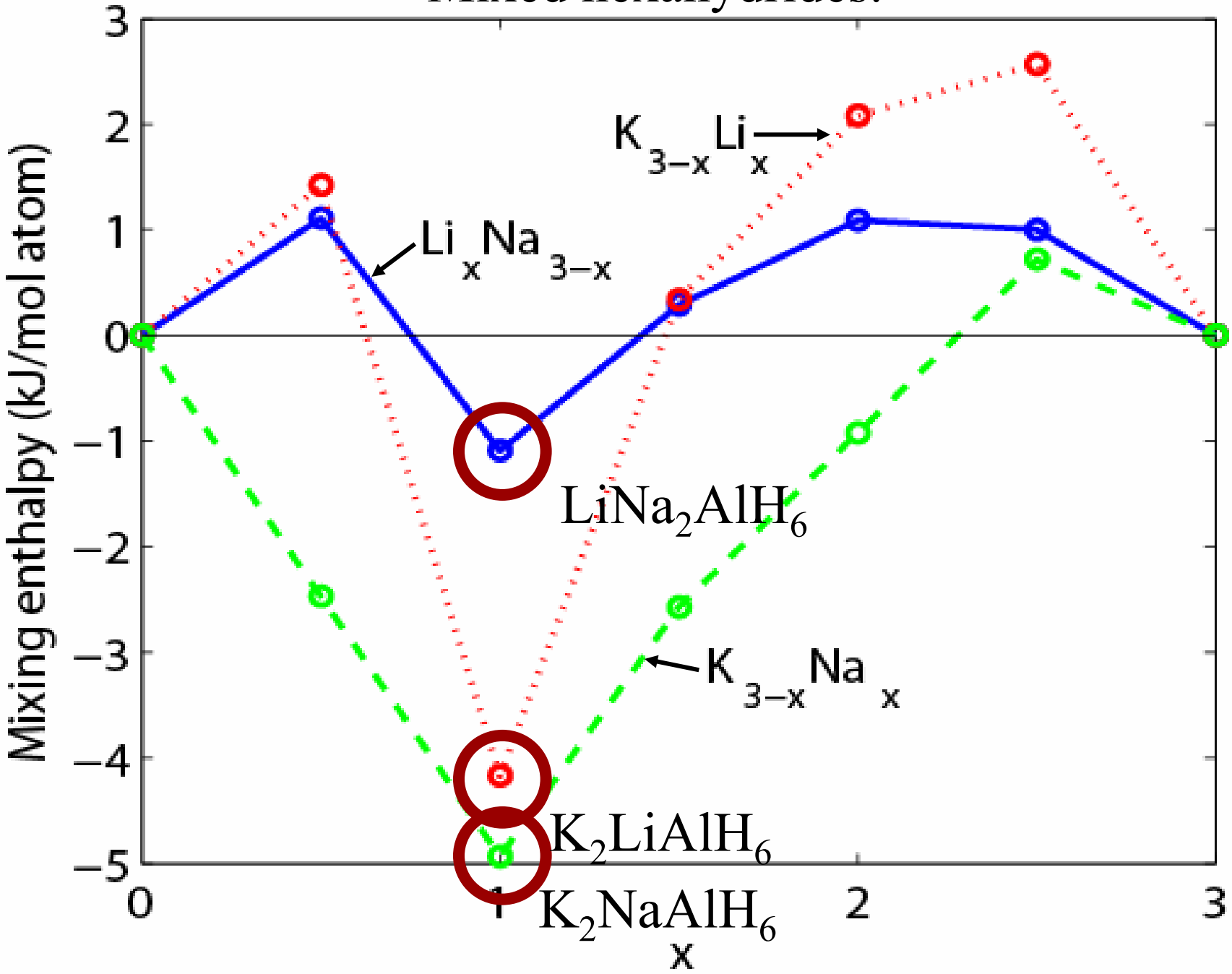
Mixed tetrahydrides:



Prediction of new mixed alanate phases



Mixed hexahydrides:



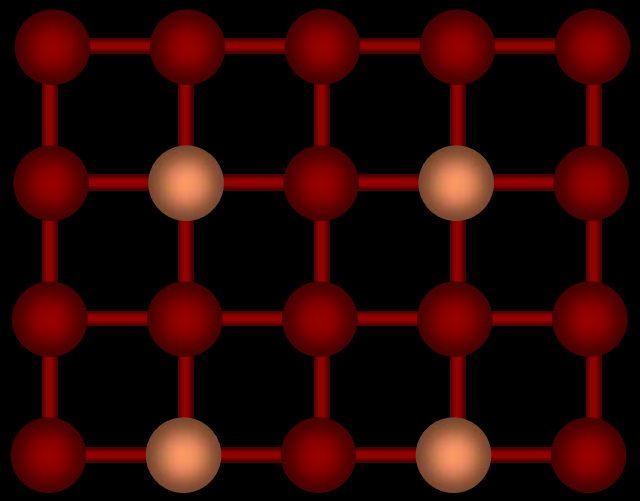
Thermodynamic properties

- How is the temperature and pressure dependence?
- Could mixtures be more attractive?
- Performed phonon calculations to assess thermodynamic properties of the Li-Na-Al-H system.

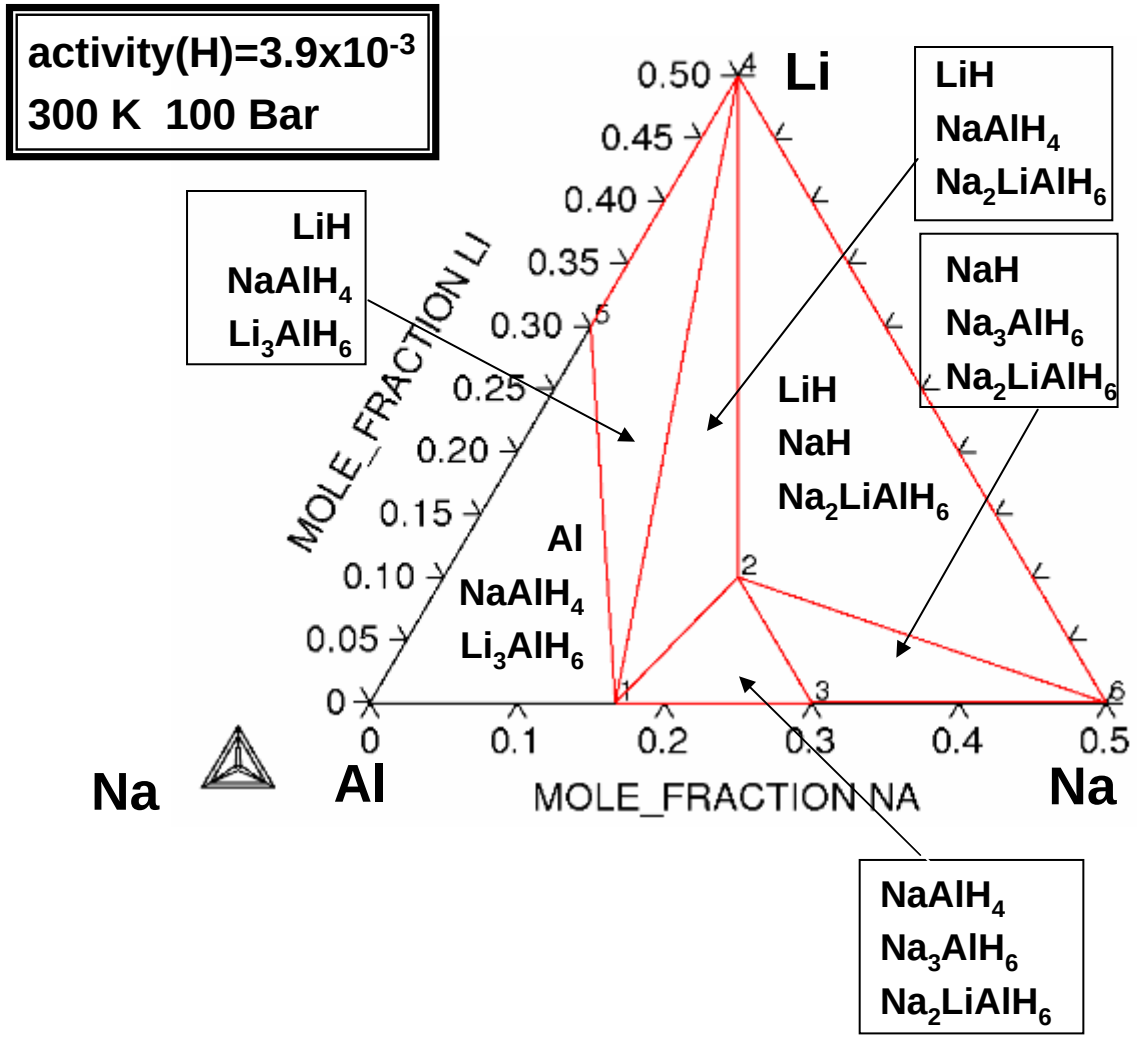
S. M. Opalka, O. M. Løvvik, H. W. Brinks, B. C. Hauback, In prep.

Phonon calculations

- Vibration frequencies from displacement calculations
- Phonon spectrum and partition function
- Integrated phonon density → Thermodynamics

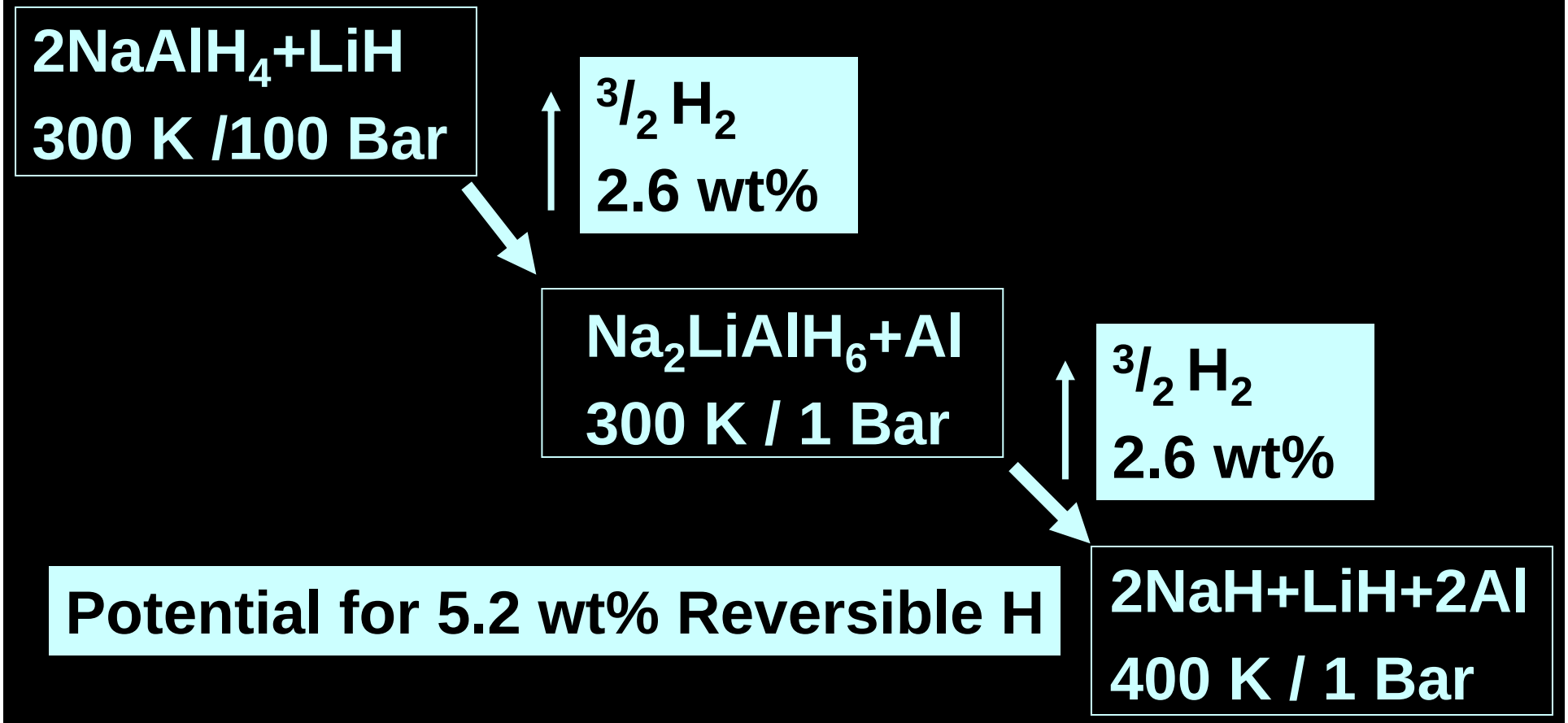


Thermodynamic predictions



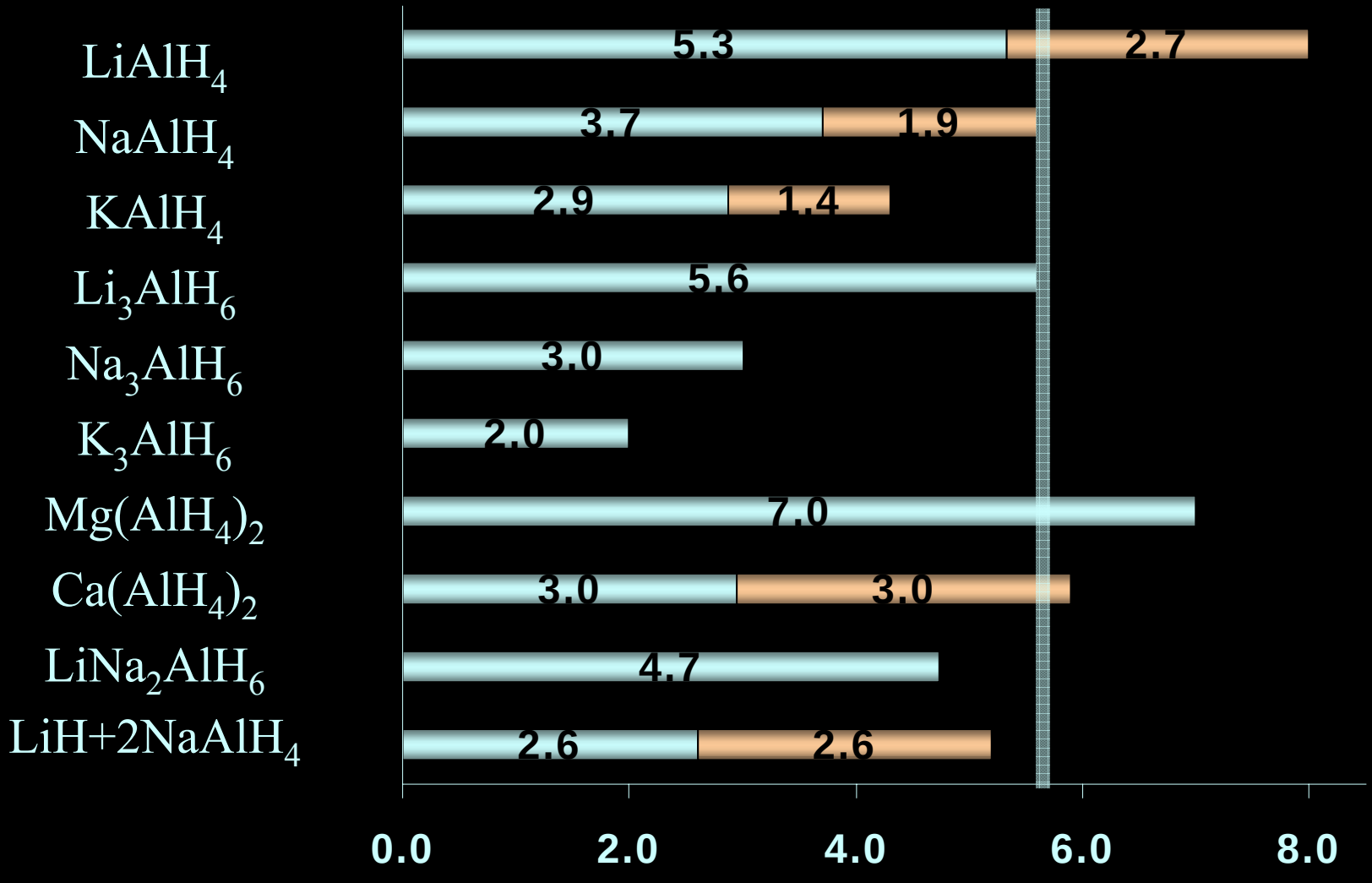
Optimum H reversibility

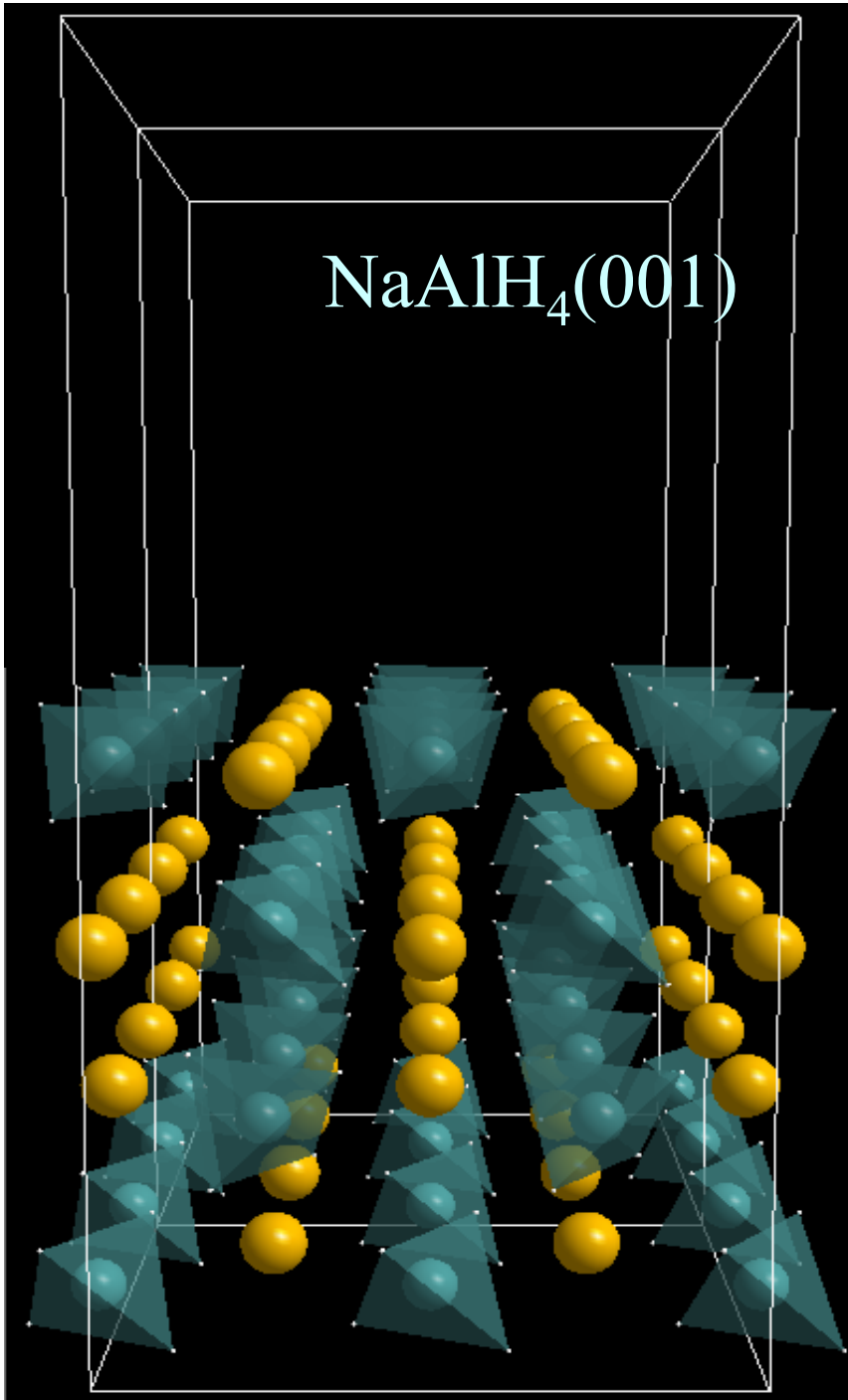
- {2Na : 1Li : 2Al : 9H}:



Alanates for hydrogen storage

- Accessible hydrogen wt%:





Alanate surfaces

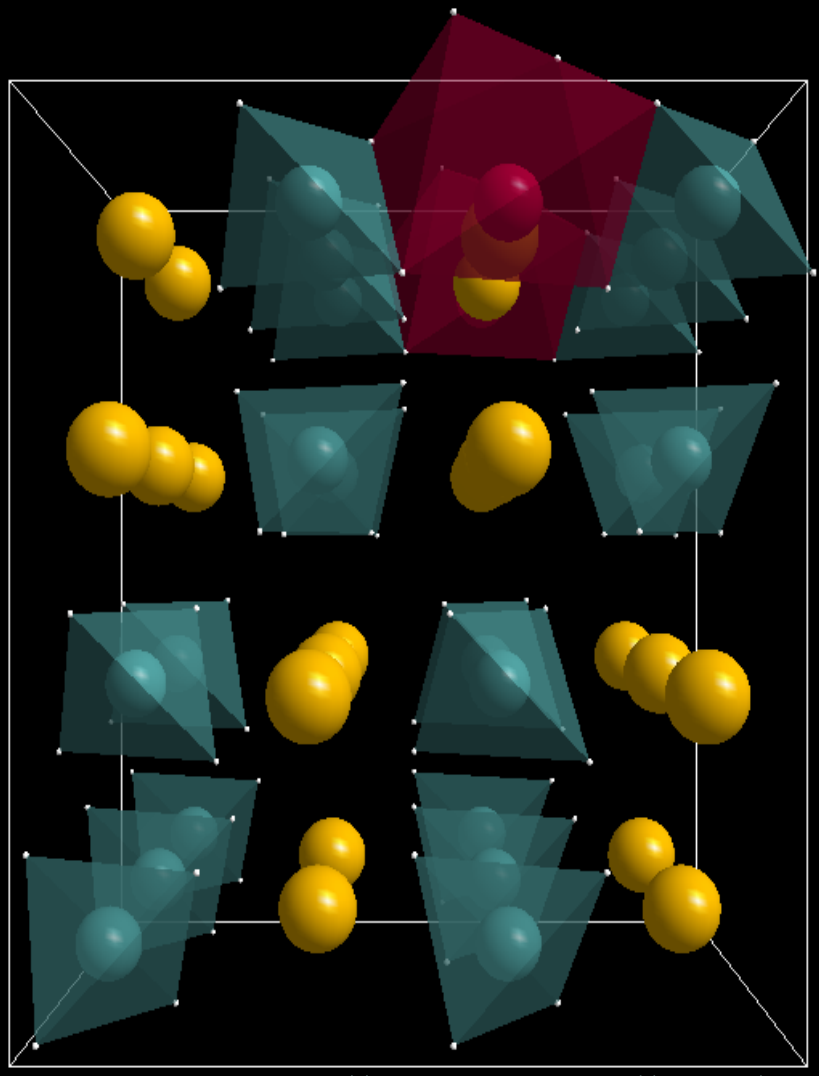
- $LiAlH_4$: The (010) surface most stable.
- $NaAlH_4$: The (001) surface most stable.
- $Mg(AlH_4)_2$: The (001) surface most stable.

- O. M. Løvvik, J. Alloys Comp. **356-357** (2003) 178.
- T. Frankcombe, O. M. Løvvik, J. Chem. Phys. B **110** (2006) 622.
- O. M. Løvvik, P. Molin, In prep.

Ti in $NaAlH_4$ – experimental status

- Nature of Ti additive not important ($TiCl_3$, TiF3, Ti powder, $Ti(OBu)_4$, etc.)
- Three different majority phases found:
  - Al_3Ti
  - Dispersed, amorphous $Al_{1-u}Ti_u$ (u = 0.07 – 0.15)
  - TiH_2
- Samples with different Ti majority phases have comparable kinetics
- Is there an active minority phase?
- Doping or catalysis?

0-D (point) defects

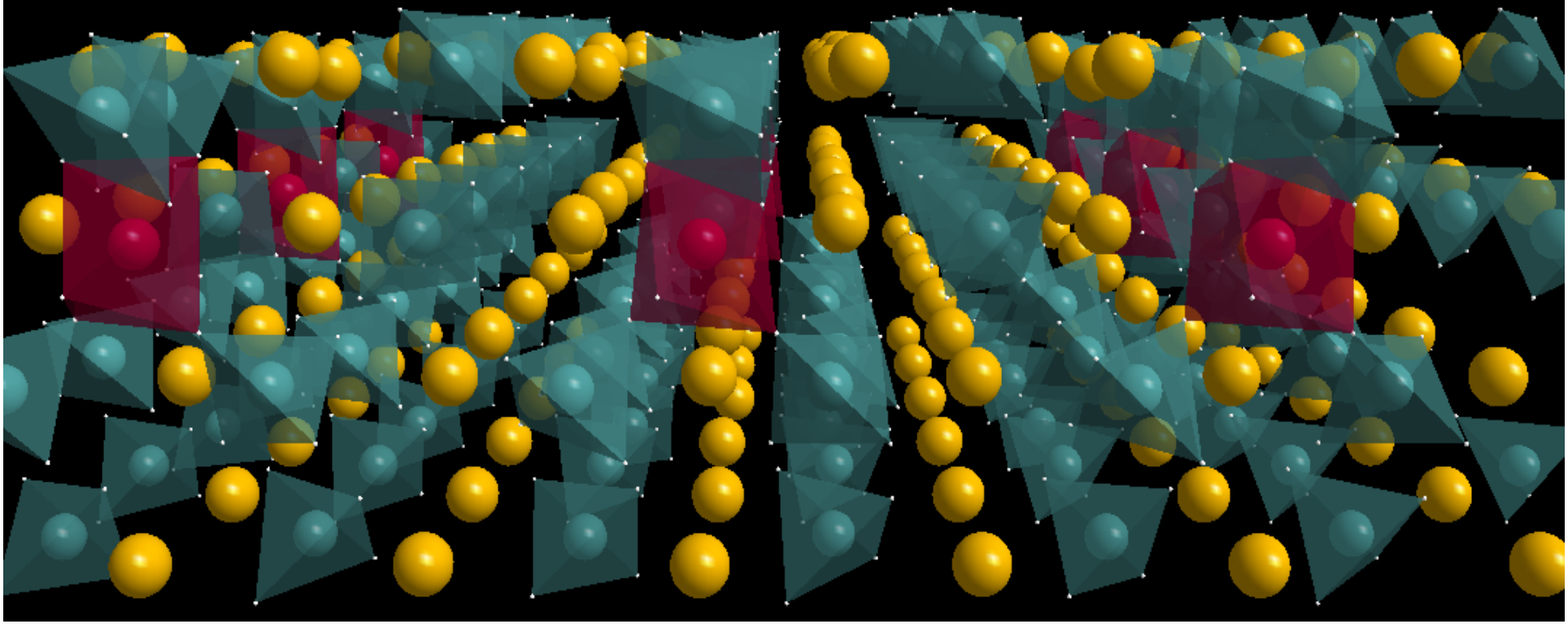


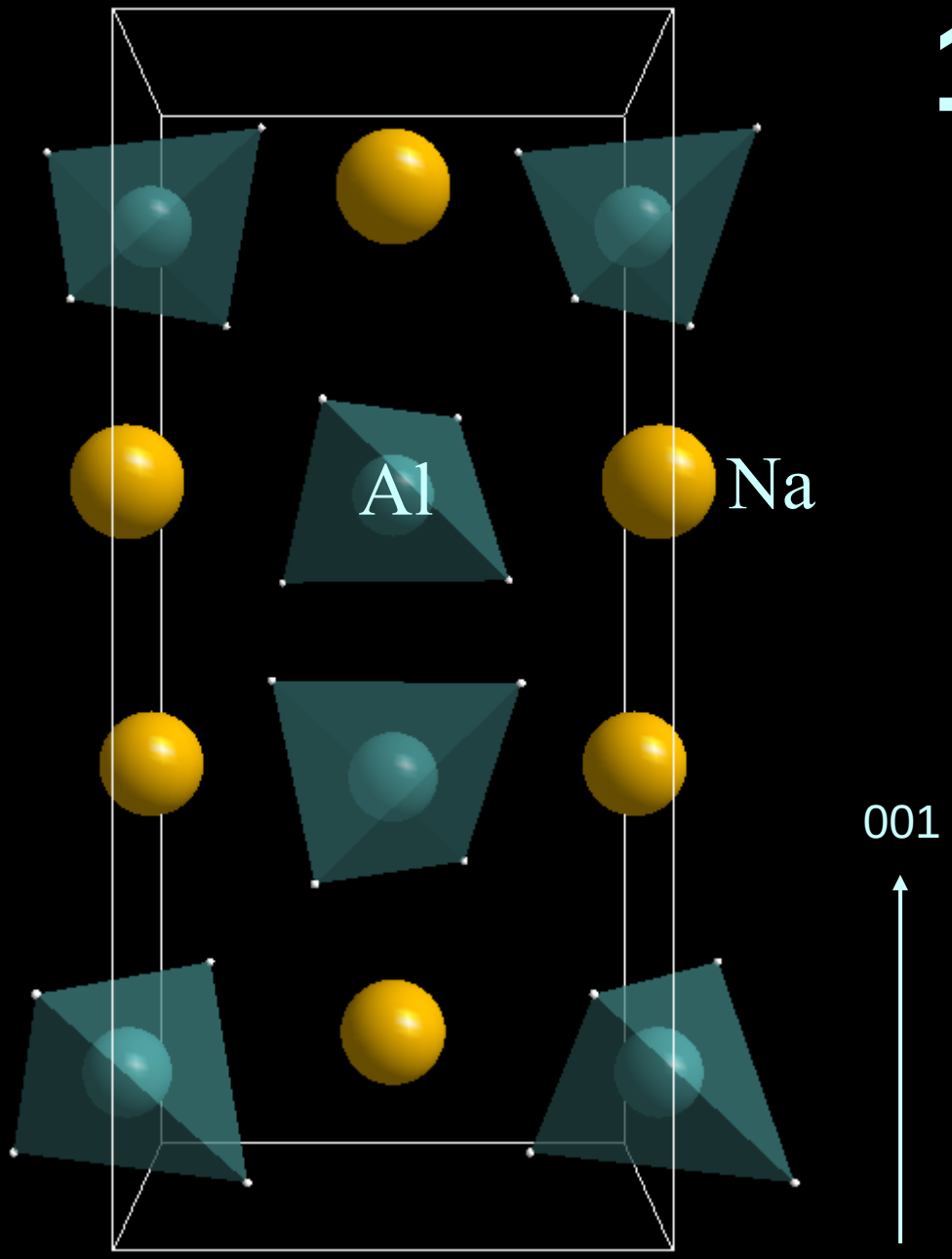
- Disregard majority phases
- If in the $NaAlH_4$ lattice:
  - Ti substituting Al or Na, or at interstitial sites.
  - Additional vacancies may be produced.
  - Surface or bulk?
- Full relaxation; lattice constants change?
- Reference: standard state or all relevant compounds

- O. M. Løvvik, S. M. Opalka, Phys. Rev. B. **71** (2005) 054103
- O. M. Løvvik, S. M. Opalka, Appl. Phys. Lett., **88** (2006) 161917

The most stable structure

- Ti: not in the bulk.
- If in the lattice: near the surface, replacing Al.
- Metastable at best.
- Large local distortions.
- Increased Ti-H coordination from 4 to 8.
- Weak Ti-H bonds.



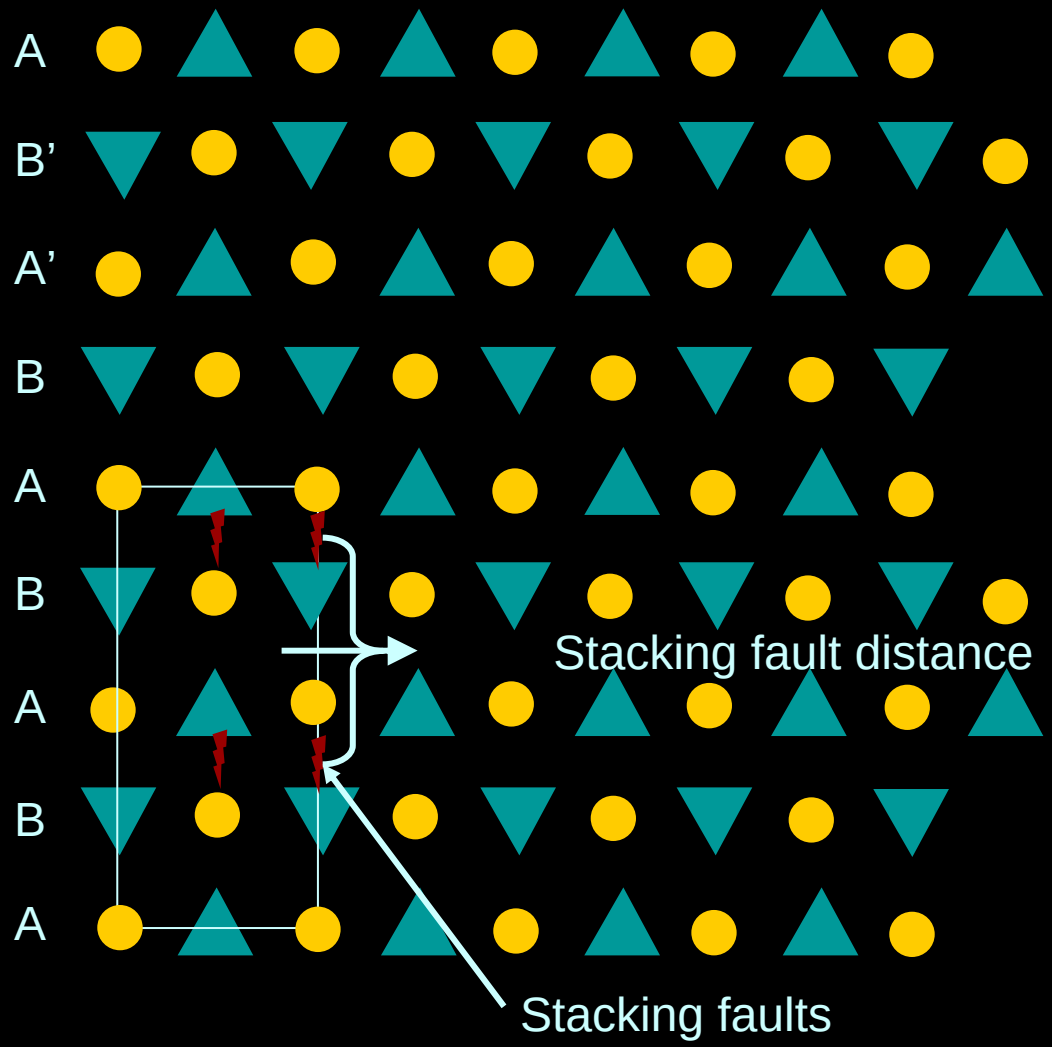


1-2D defects in $NaAlH_4$

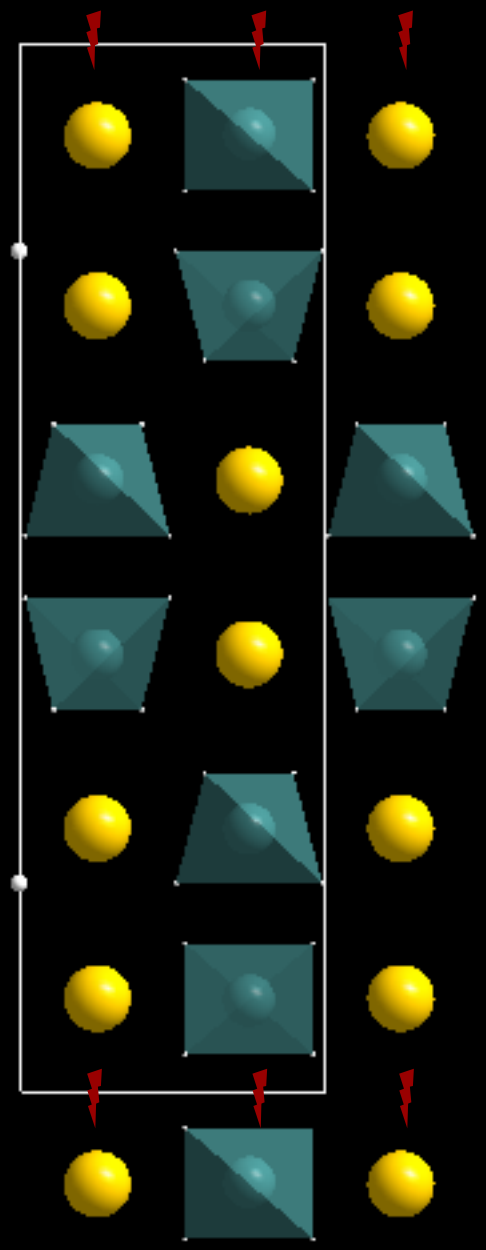
- Unknown if such defects exist.
- What are their energy costs?
- What are their effects?

In prep.

1-2D defects in $NaAlH_4$

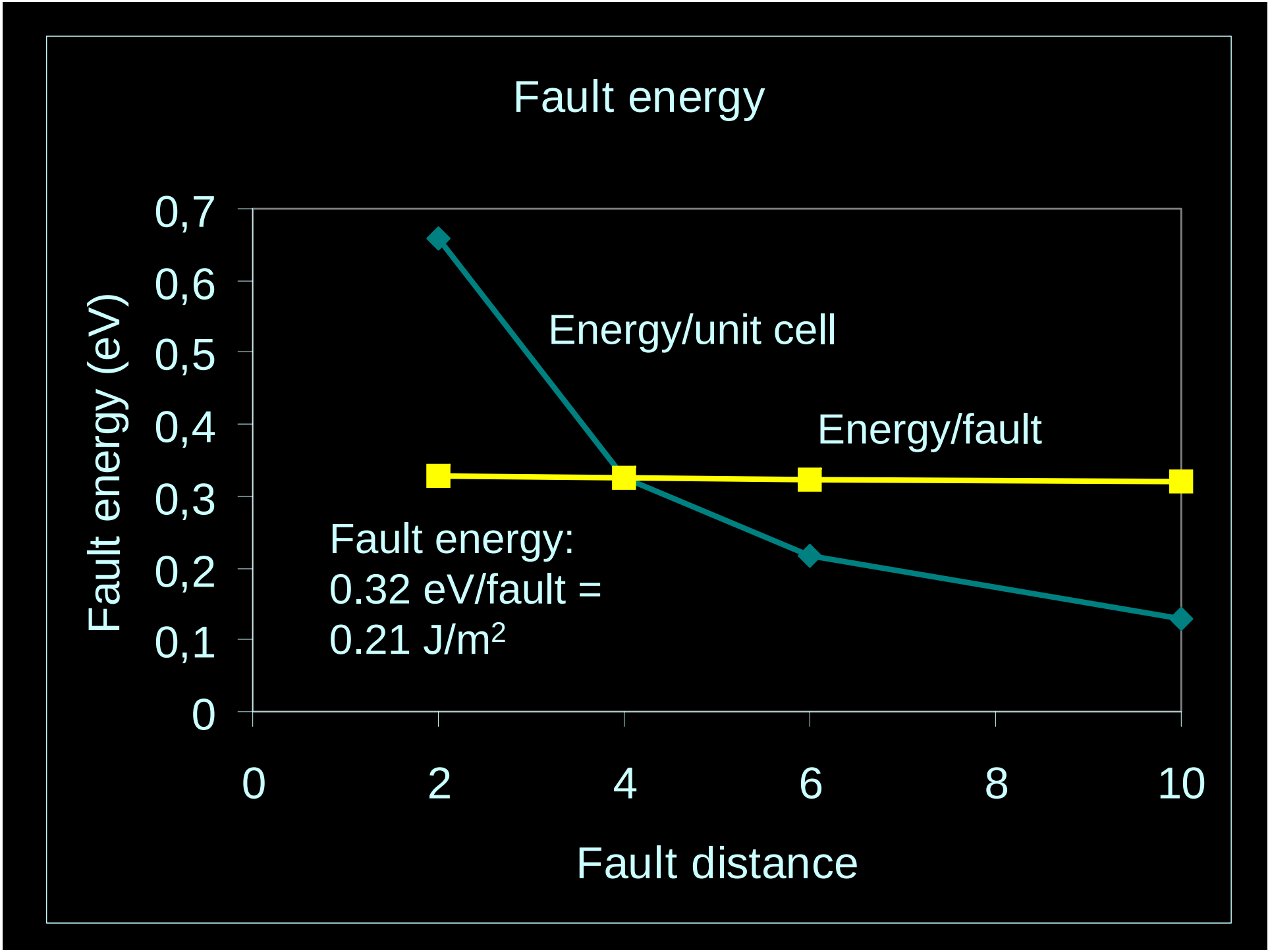


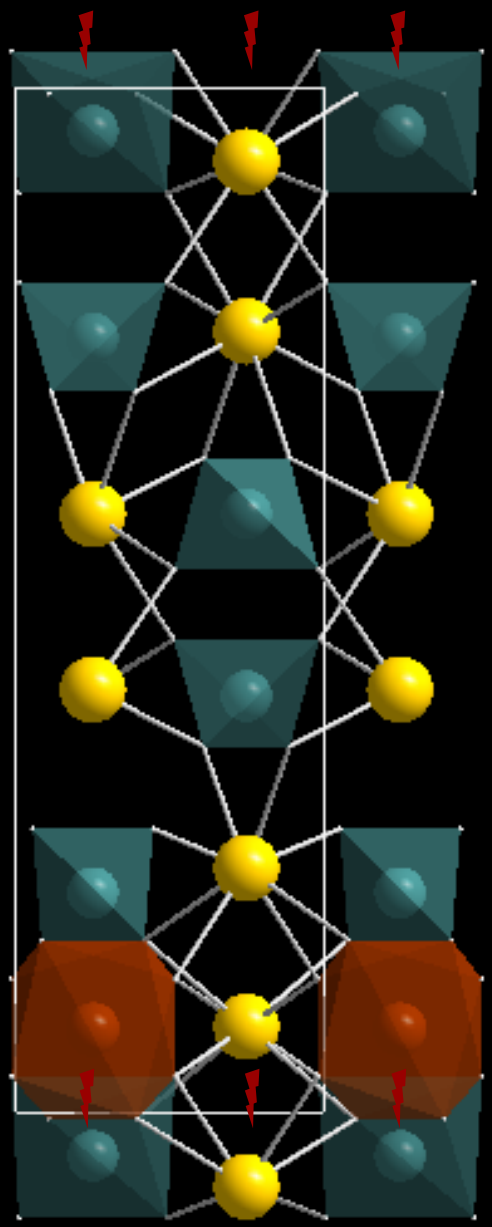
- 1D: dislocations.
- 2D: stacking faults, twins, anti-phase boundaries, grain boundaries.
- Unknown if such defects exist.
- What are their energy costs?
- What are their effects?



Relaxed structure

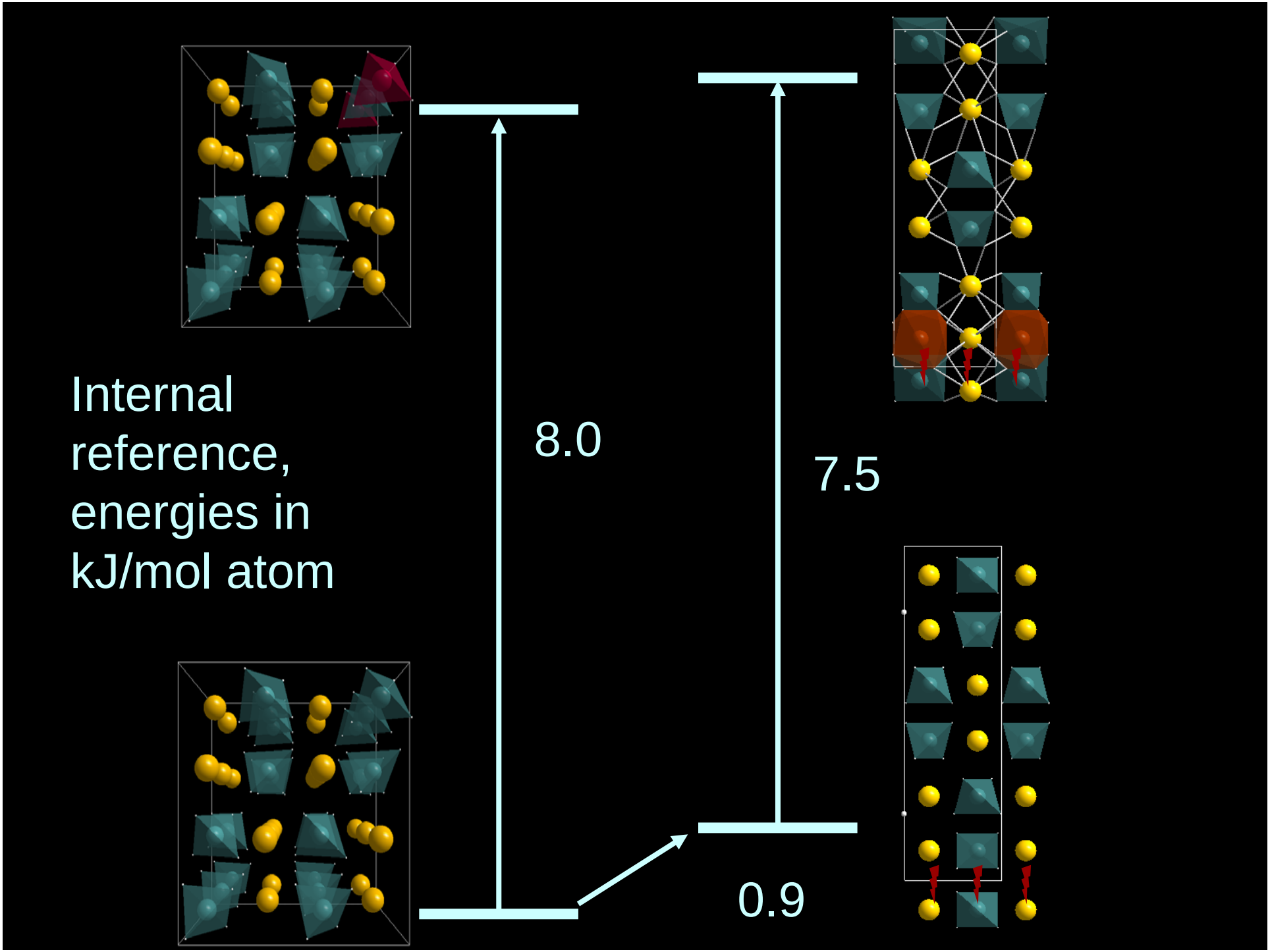
- Very similar to perfect lattice
- Main difference: Na-H coordination reduced from 8 to 6
- Possible to observe?


Fault energy
Fault energy (eV)
0,7
0,6
0,5
0,4
0,3
0,2
0,1
0
Energy/unit cell
Energy/fault
Fault energy:
0.32 eV/fault =
0.21 J/m2
0
2
4
6
8
10
Fault distance

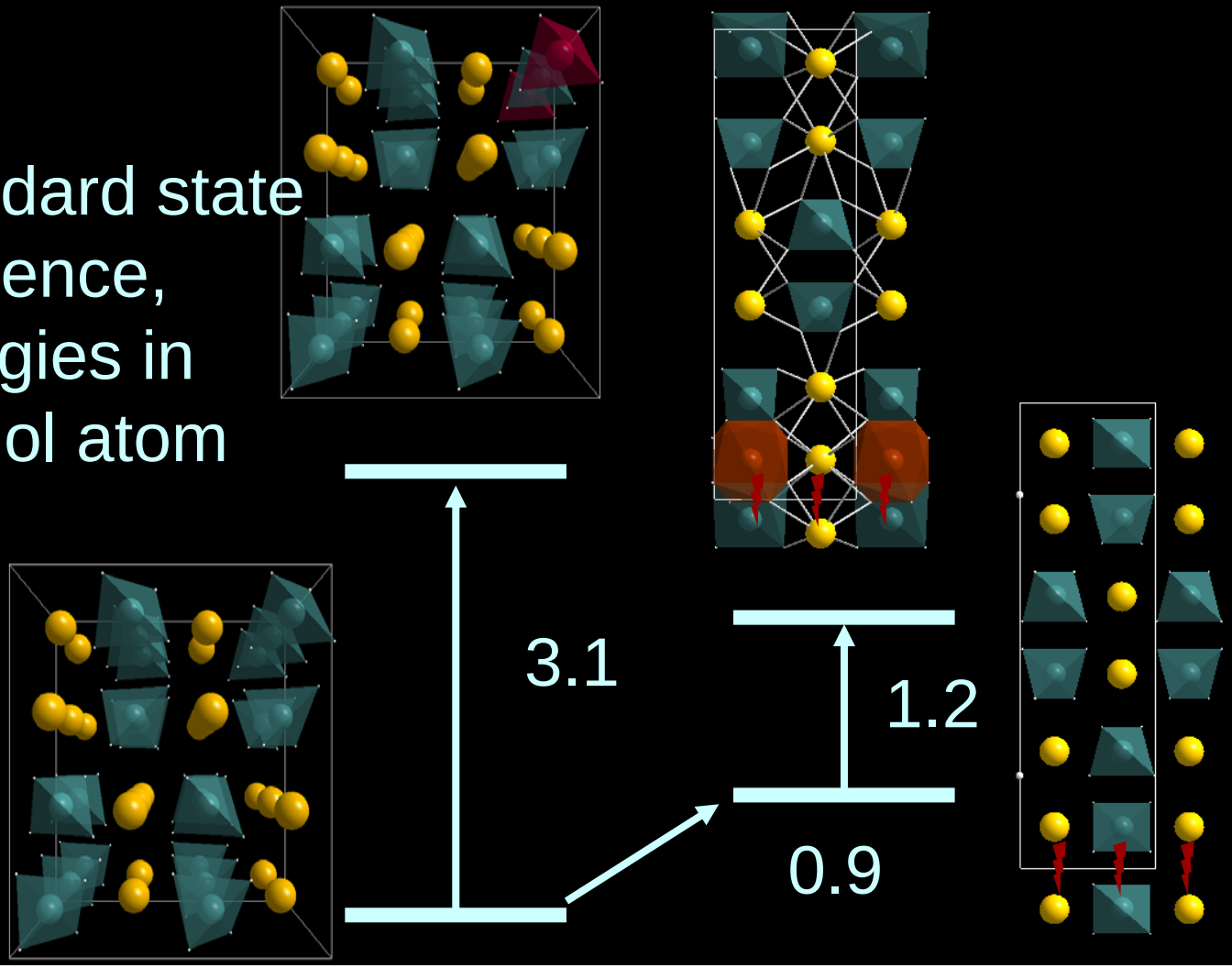


Ti substitution near faults

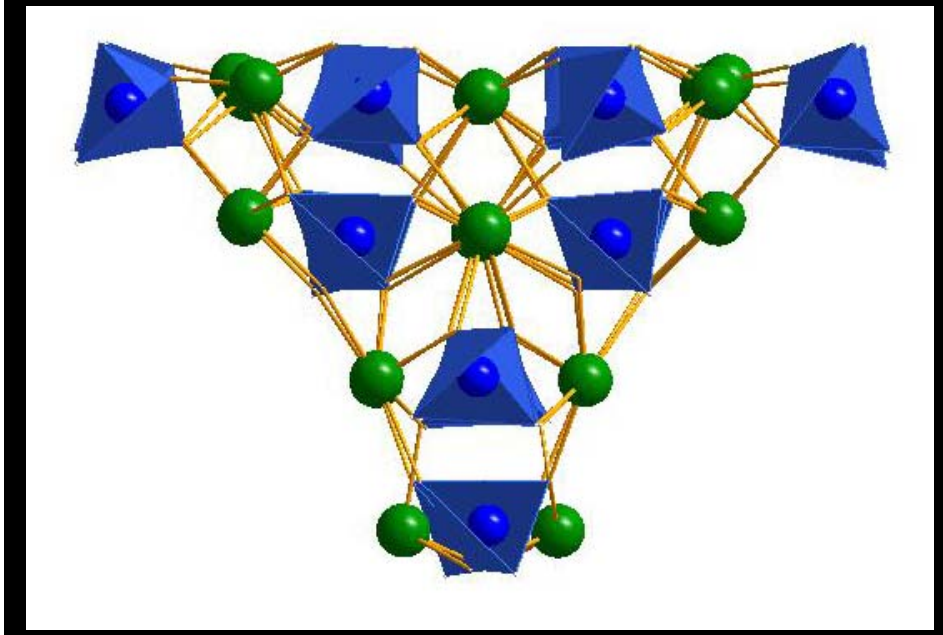
- Investigated Al→Ti, Na →Ti, and interstitial Ti
- Internal reference: Al →Ti most stable
- Ti-H coordination: 8
- Results for $Z = 6$; 16.7 % Ti.
- Interpolated values for defect-free models


Internal reference, energies in kJ/mol atom
8.0
7.5
0.9

Standard state reference, energies in kJ/mol atom



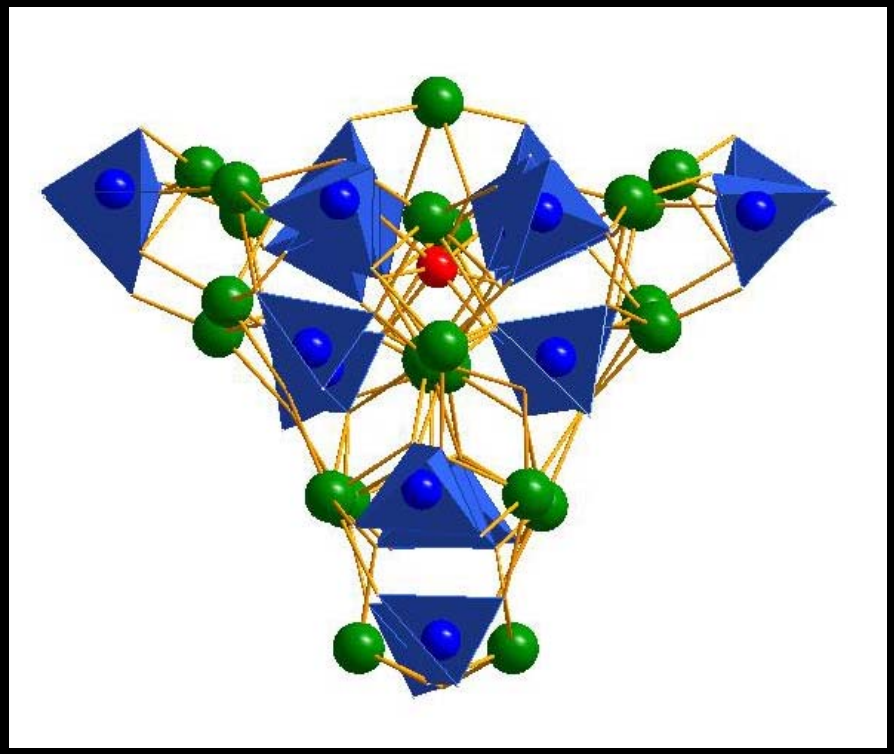
What about non-equilibrium structures?



- Suppose that mono-dispersed Ti is available.
- Investigated clusters with constant number of atoms.
- $\Rightarrow$ Reference is $NaAlH_4$ + Ti.

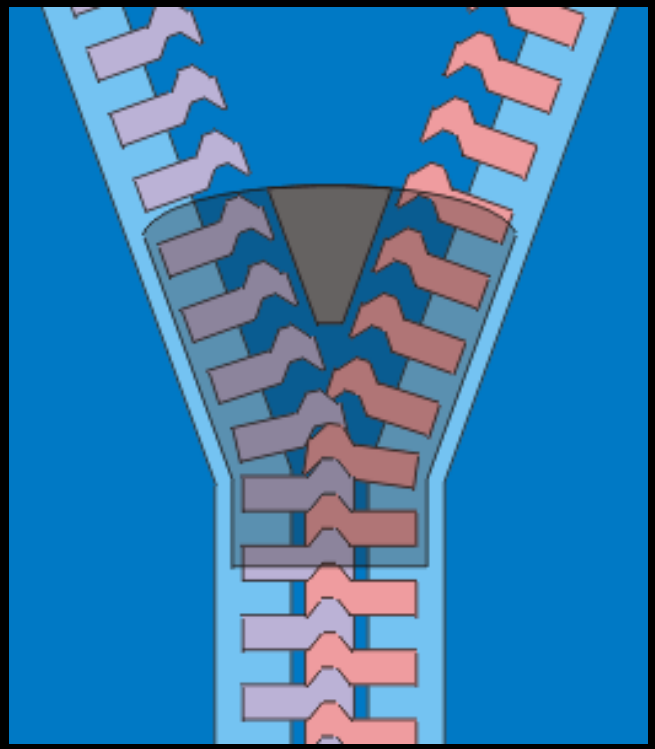
A. Marashdeh, R. A. Olsen, O. M. Løvvik, G.-J. Kroes, Chem. Phys. Lett. **426** (2006) 180–186; In prep.

The role of Ti?



- End point: Na ↔ Ti.
- Na out of the structure.
- Start of decomposition?

The role of Ti?



The ”zipper model”:

- Ti acts as a slider.
- Catalysis, but not traditional.
- May be combined with H_2 splitting in the absorption process.
- Promoted by 2D defects?

Summary

- Probably no better alanate than $NaAlH_4$.
- The LiH + 2 $NaAlH_4$ mixture is interesting. (And maybe $Ca(AlH_4)_2$.)
- Minority phase of Ti probably important in $NaAlH_4$ (de-)hydrogenation:
  - Ti substitution in bulk ruled out.
  - Ti substitution promoted by defects.
  - Non-equilibrium: Ti may enter lattice.
  - Proposed model: zipper model with Ti-slider.

Acknowledgements

- Coworkers:
  - Susanne Opalka, UTRC
  - Peter Molin, UiO
  - Bjørn Hauback *et al.*, IFE
  - Roar Olsen *et al.*, Leiden University
  - Ole Swang *et al.*, Sintef
  - Max Fichtner *et al.*, Forschungszentrum Karlsruhe
- Funding: Nanomat, NFR