

Neutron Characterization and Calphad in support of the Metal Hydride Center of Excellence

Terry Udovic
Ursula Kattner



National Institute of Standards and Technology
Technology Administration, U.S. Department of Commerce

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STP-38

Timeline

- Project start FY05
- Project end FY09
- 50% complete

Budget

- FY05 \$125k
- FY06 \$156k
- FY07 \$276k
- FY08_(req.) \$287k

Barriers addressed

- Characterization of structures and hydrogen bonding in new storage materials
- Lack of phase diagram data on potential new storage materials

Partners

- **MHCoE** -Sandia, JPL, HRL, GE, Caltech, Hawaii, Stanford, Nevada-Reno, Illinois, Carnegie Mellon, Pittsburgh, Utah, ORNL, BNL, SRNL, Intematix

NIST has provided over 420 instrument days to date and 2 FTE's/year for the HSCoE and MHCoE combined.

Overall: Support the development of hydrogen storage materials by providing timely, comprehensive characterization of Center-developed materials and storage systems using state-of-the-art neutron methods and Calphad. Help speed the development and optimization of storage materials that can meet the 2010 DOE system target of 6 wt% and 45 g/L capacities.

- Characterize structures, compositions, and absorption site interaction potentials for hydrogen in candidate materials .
- Provide Calphad calculations of phase relationships of potentially promising hydrides.

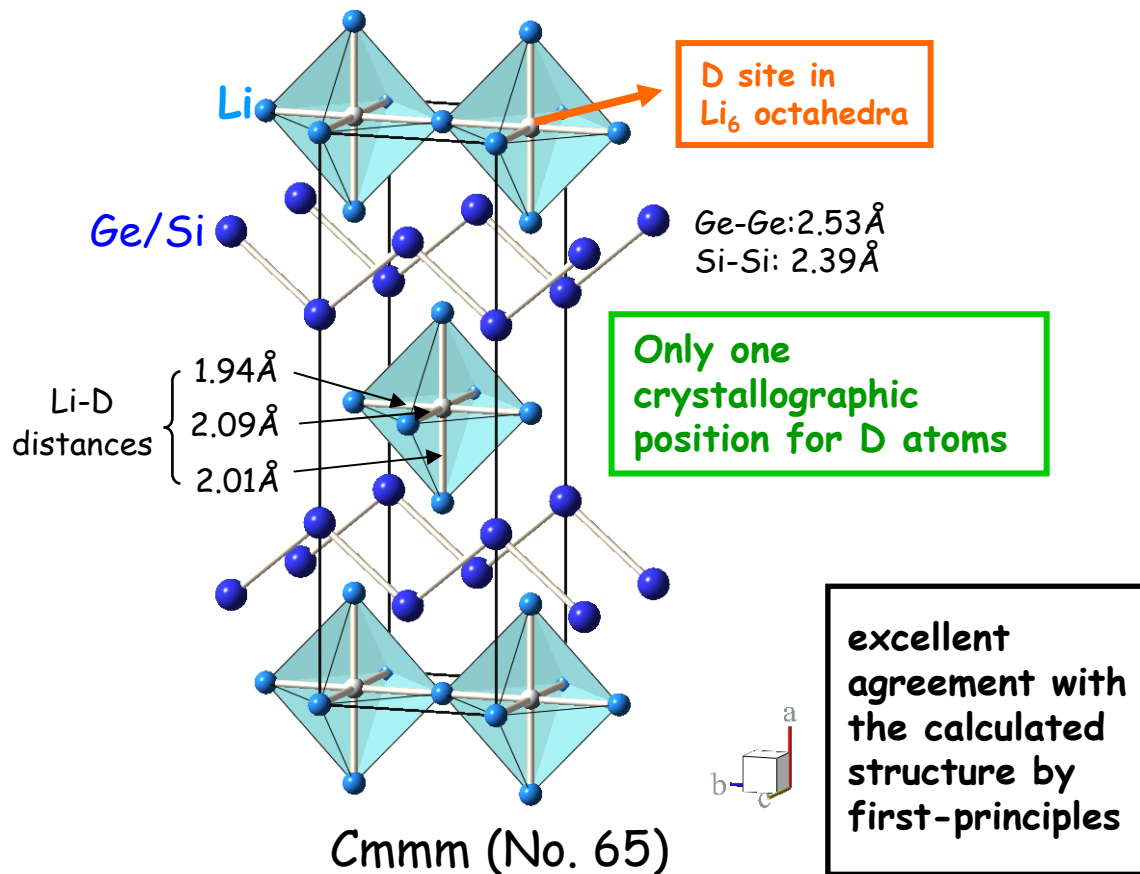
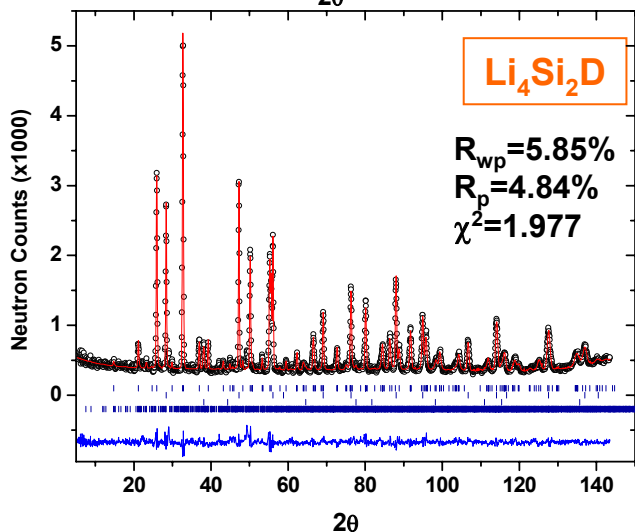
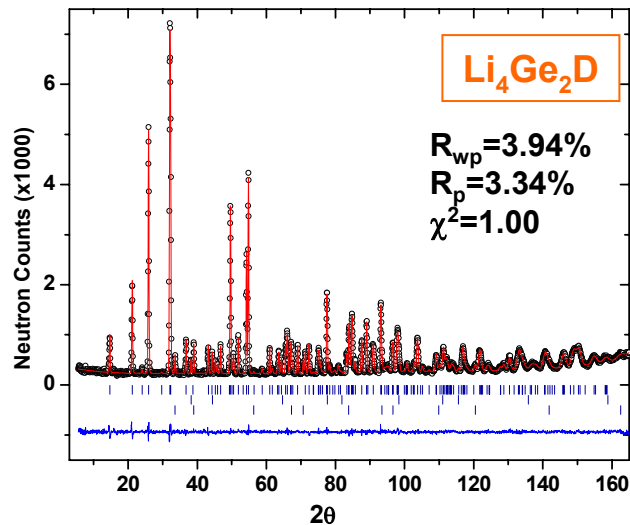
- **Neutron methods**

- determine elemental compositions of materials (non-destructive prompt-gamma activation analysis of H stoichiometries)
- determine location of H and crystal structures of materials (neutron diffraction superior to XRD for “seeing” light H and D)
- determine bonding of absorbed H (unlike IR and Raman, neutron vibrational spectroscopy “sees” all H vibrations for straightforward comparison with first-principles calculations)
- elucidate H diffusion mechanisms (faster dynamics timescale of neutron quasielastic scattering complements NMR; transport mechanisms gleaned from momentum transfer dependence)

- **Calphad methods**

- develop a thermodynamic database from the available literature and first-principles calculations
- incorporate database into an overall temperature-pressure-composition framework for multicomponent metal-hydrogen systems.

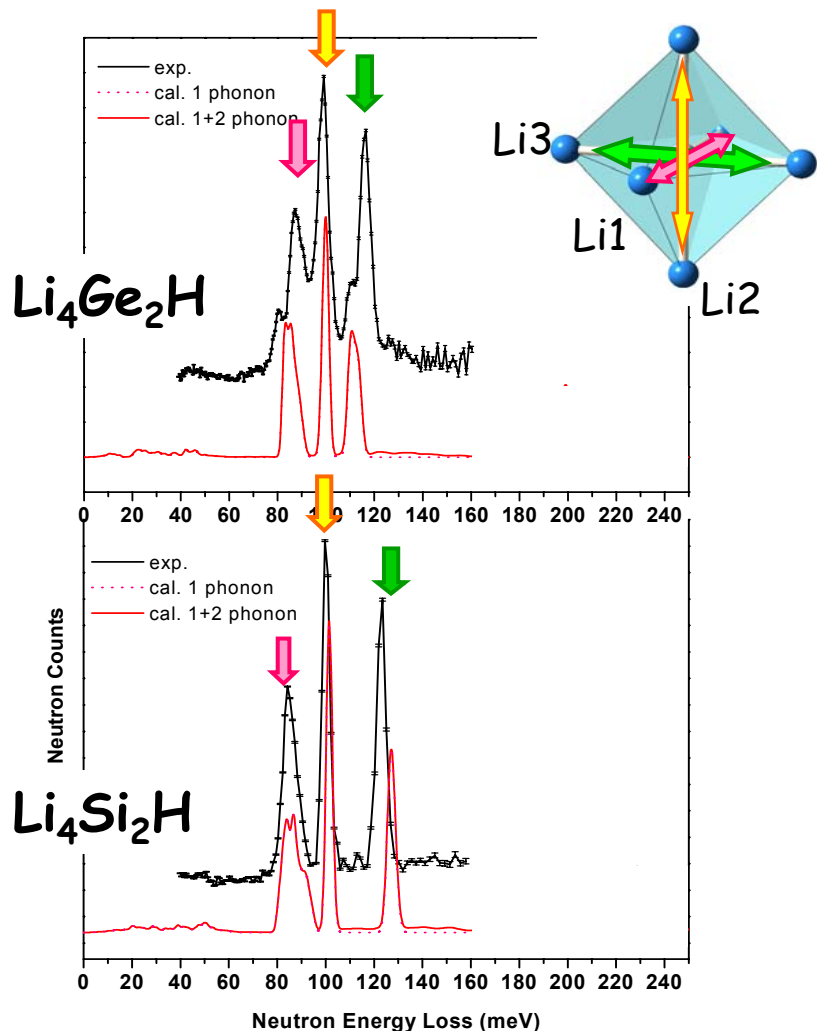
Structure Identification of $\text{Li}_4\text{Ge}_2\text{D}$ and $\text{Li}_4\text{Si}_2\text{D}$



← Si (39.6wt%) Note: LiH (Li-H ~ 2.038 Å)

Strong Li-H binding in $\text{Li}_4\text{Ge}_2\text{H}$ and $\text{Li}_4\text{Si}_2\text{H}$ is primarily responsible for the stabilization of these hydrides. 5

Hydrogen Bonding Potentials in $\text{Li}_4\text{Ge}_2\text{H}$ and $\text{Li}_4\text{Si}_2\text{H}$

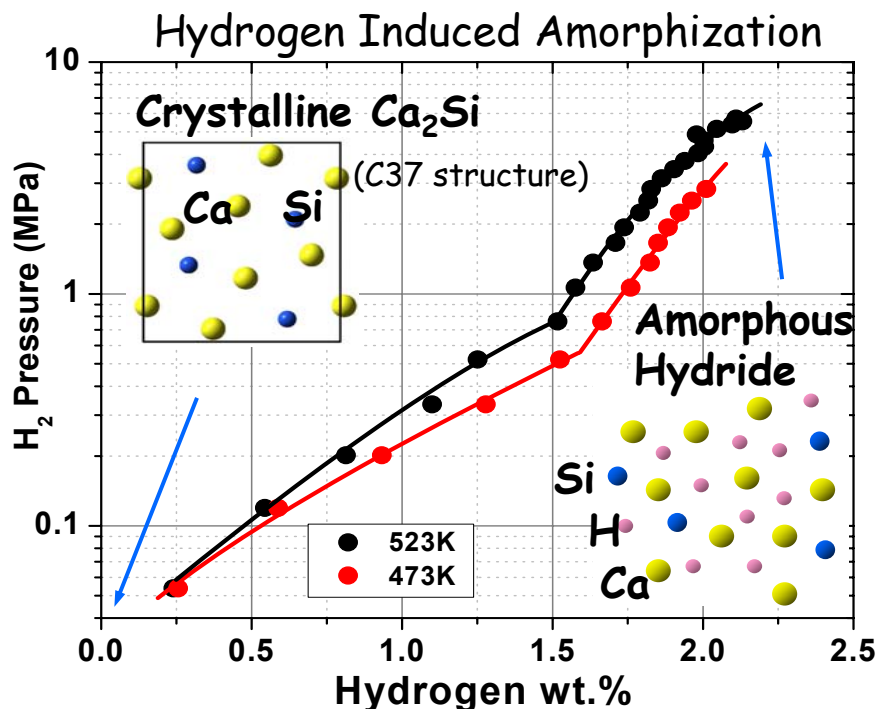
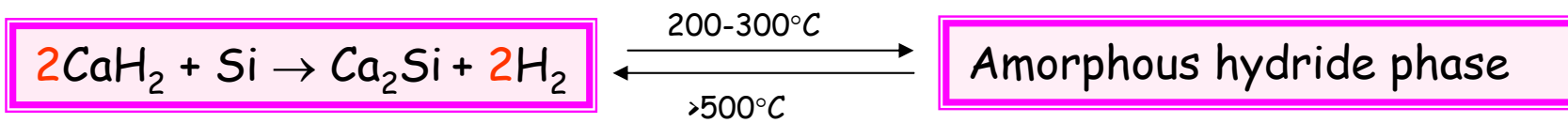


(in preparation 2007)

- Measured neutron vibrational spectra for $\text{Li}_4\text{Ge}_2\text{H}$ and $\text{Li}_4\text{Si}_2\text{H}$
- Characterized the phonon modes with first-principles phonon calculations
- Assignments of the phonon modes are consistent with NPD-observed Li-H bond lengths and the corresponding bond strength.

	Ge	Si
H-Li1:	2.091 Å	2.087 Å
H-Li2:	2.007 Å	2.016 Å
H-Li3:	1.939 Å	1.881 Å

Destabilization of the $2\text{CaH}_2 / \text{Si}$ system



NPD, NVS, and Isotherm Results

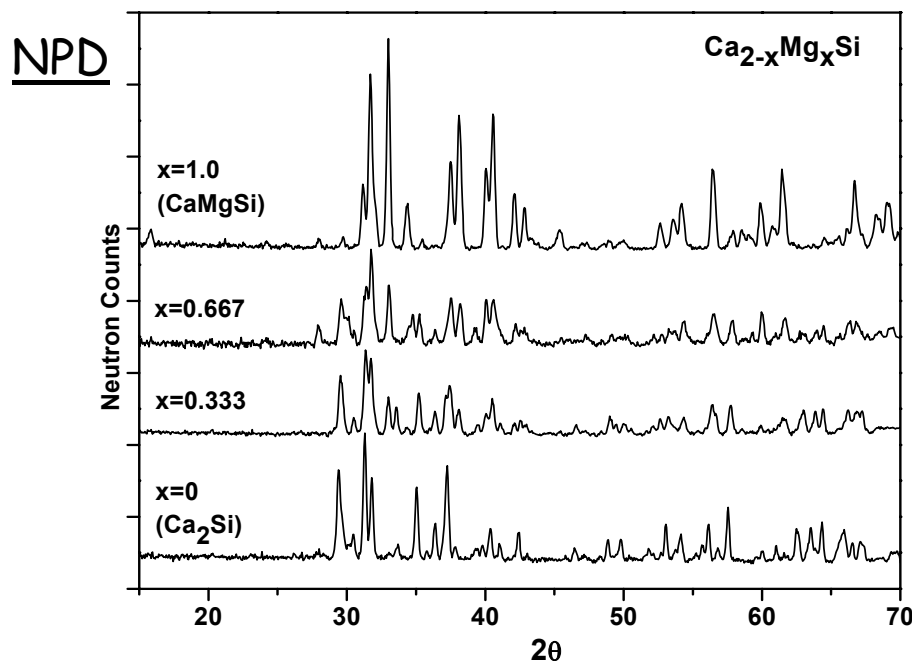
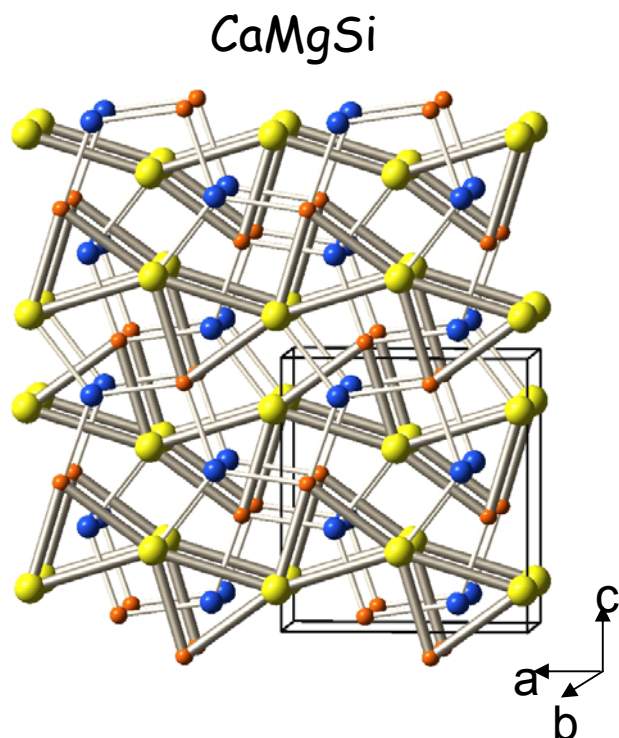
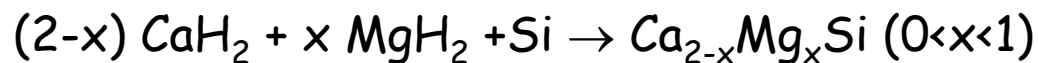
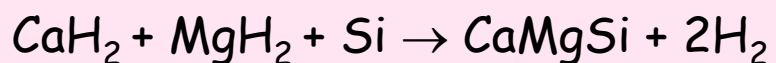
- Ca_2Si readily absorbs H_2 at $P < 1$ atm.
- Quite rapid absorption kinetics (few min)
- No obvious pressure plateau
- Formation of amorphous hydride upon hydrogenation

Easy H_2 absorption compared to hard-to-hydride Mg_2Si at $200-300^\circ\text{C}$.

“Amorphization” could be a way to accelerate the hydrogenation kinetics.

Destabilization of the CaH_2 / MgH_2 / Si system

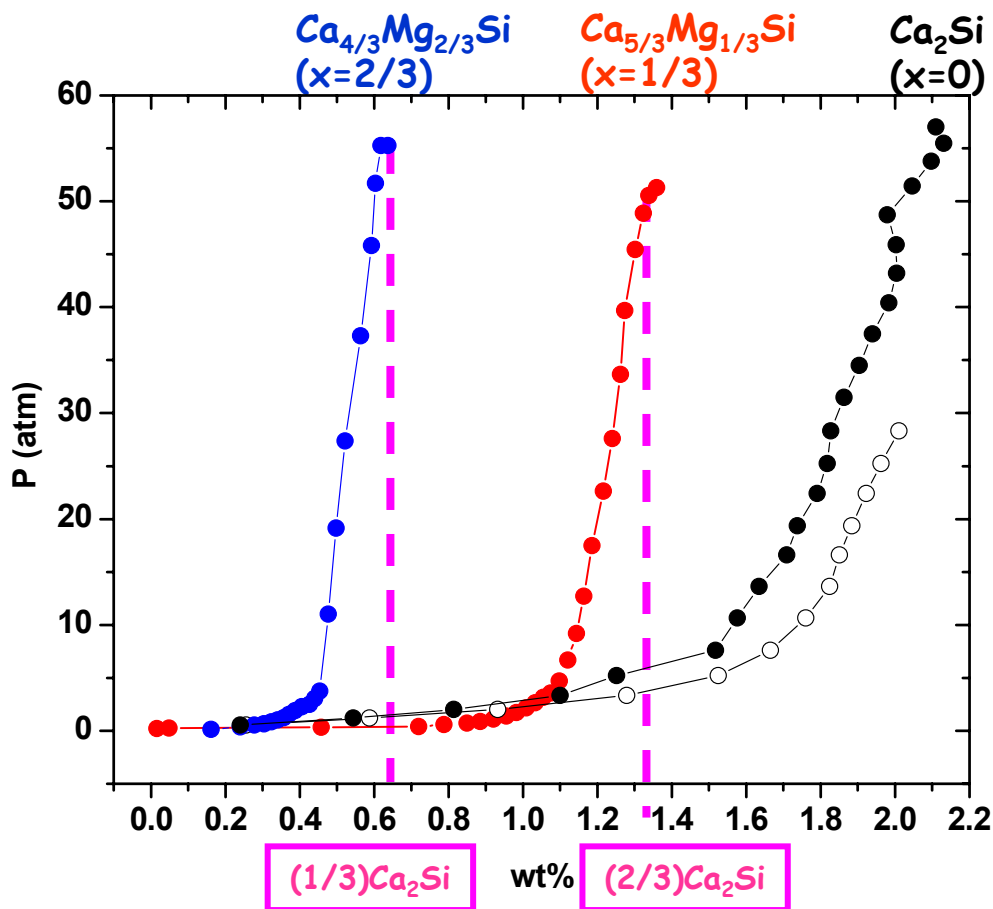
- Add MgH_2 (higher H_2 storage capacity); possibly improve slow Mg_2Si kinetics
- Single-phase solid solution $\text{Ca}_{2-x}\text{Mg}_x\text{Si}$ observed in $(1-x)\text{Ca}_2\text{Sn}-(x)\text{Mg}_2\text{Sn}$ system



Hydrogenation Properties of $\text{Ca}_{2-x}\text{Mg}_x\text{Si}$

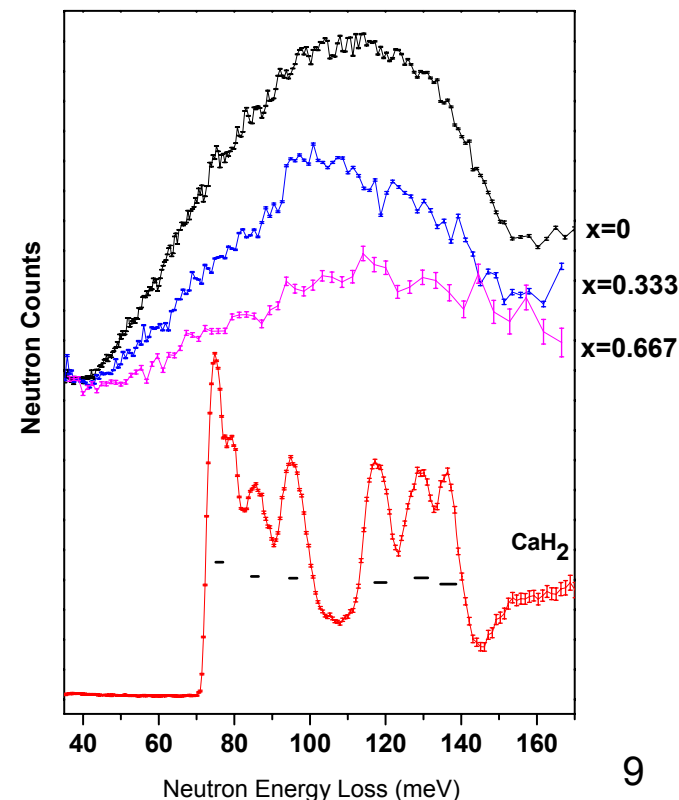
- CaMgSi hardly absorbs H_2 under 0-70 atm at 200-300°C.
- Hydrogenation behavior of $(1-x)\text{Ca}_2\text{Si}-x\text{CaMgSi}$ compositions is dominated by Ca_2Si .

Isotherm measurements

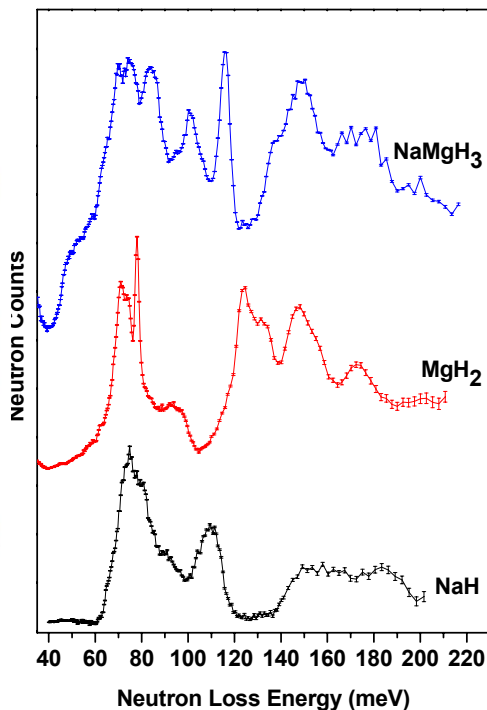
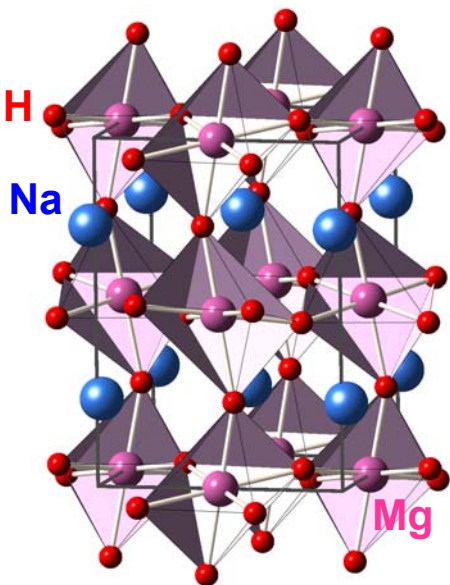


NVS

(After hydrogenation at 200°C 50 atm)



Quaternary System: Na-Mg-Si-H



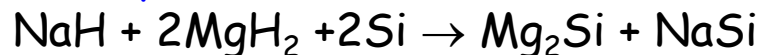
Reversible hydrogenation/dehydrogenation



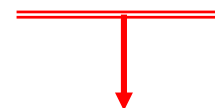
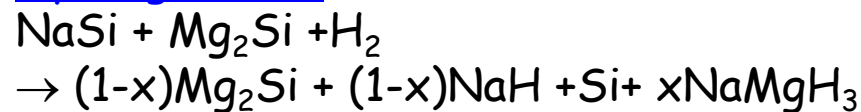
- MgH₂/Si system is hard to hydride
- NaH/Si system reversibly absorbs H₂
- NaH/MgH₂ forms a NaMgH₃ phase

So, we tried MgH₂/NaH/Si system

Desorption: 350°C evac.



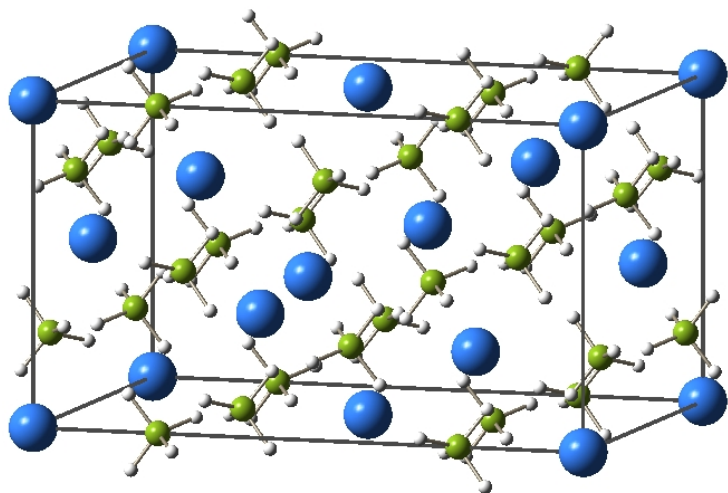
Hydrogenation: 350°C 50 atm



Mg₂Si can partially absorb H₂ through the formation of NaMgH₃

Spectroscopic Verification of $\text{Ca}(\text{BH}_4)_2$ Synthesis

$\text{Ca}(\text{BH}_4)_2$ Crystal Structure



RT structure

Space group: *Fddd* (No.70)

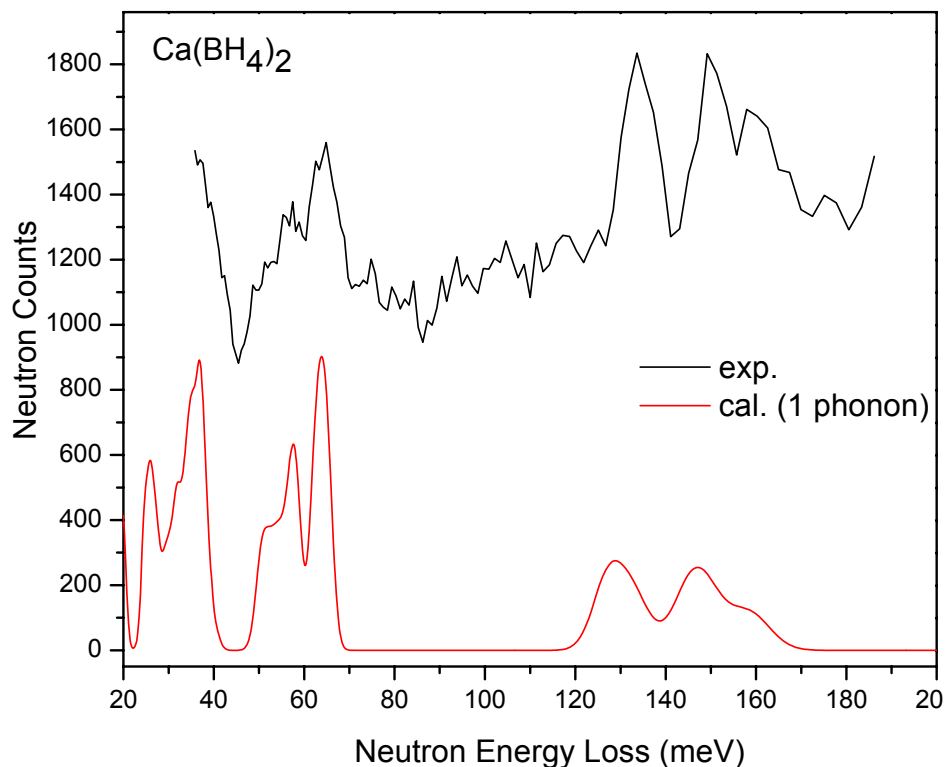
$a = 8.791 \text{ \AA}$

$b = 13.137 \text{ \AA}$

$c = 7.500 \text{ \AA}$

PRB 74, 155122 (2006)

$\text{Ca}(\text{BH}_4)_2$ Neutron Vibrational Spectrum



For $\text{Ca}(\text{BH}_4)_2$ synthesized at Sandia, the neutron vibrational spectrum is in agreement with first-principles phonon calculations based on the published $_{11}$ $\text{Ca}(\text{BH}_4)_2$ structure.

Destabilization of LiBH_4 with ScH_2 and CaH_2

- $2\text{LiBH}_4/\text{ScH}_2$

Isotherm proposed: $2\text{LiBH}_4 + \text{ScH}_2 \rightarrow \text{ScB}_2 + 2\text{LiH} + 4\text{H}_2\uparrow$ (8.9 wt%)

- Moderate desorption (~6 h to complete)

but: 1. dehydrogenation only above 380°C

2. no noticeable absorption observed during the rehydrogenation step

- $6\text{LiBH}_4/\text{CaH}_2$

Isotherm proposed: $6\text{LiBH}_4 + \text{CaH}_2 \rightarrow \text{CaB}_6 + 6\text{LiH} + 10\text{H}_2\uparrow$ (11.7 wt%)

- Moderate desorption (~2-3 h to complete)
- Complete rehydrogenation can be achieved at 380°C / 50 bar H_2

but: 1. dehydrogenation only above 380°C

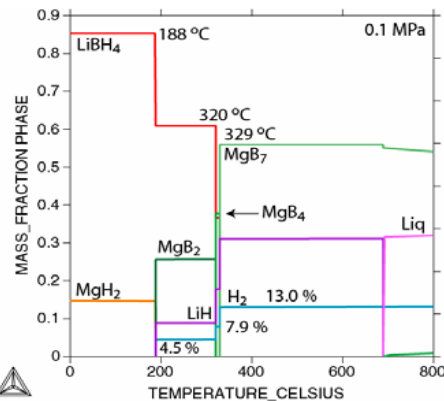
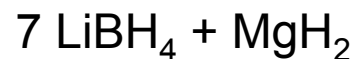
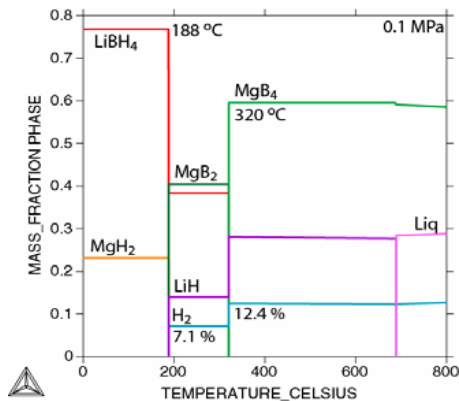
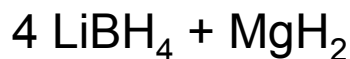
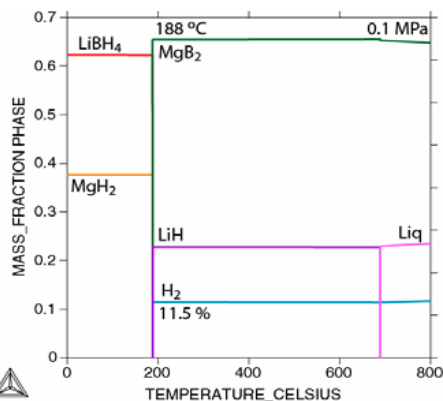
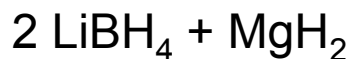
2. relatively slow hydrogenation kinetics (1 day to complete)

Subsequent results from other partners suggest that the dehydrogenation of the borates leads to elemental boron, not borides.

Calphad Computations

- Developing Calphad database for H-Li-Mg-Ca-B-Si with thermodynamic descriptions of the constituent subsystems
 - 15 binary total: 11 full descriptions available, 3 provisional in development, 1 under development
 - 20 ternary total: 2 full descriptions available, 1 partial description available
- Challenge: lack of available experimental data
 - Incorporate data from ab initio calculations by MHCoe partners

Results: Quaternary System: Mg-Li-B-H



» 2 LiBH₄ + MgH₂ is the most promising composition with a large amount of available hydrogen (11.5 %) at the lowest reaction temperature (188 °C).

We are currently in the process of expanding to include N in the overall database as well as to investigate Na-K-B-H phases.

Remainder of FY 2007:

- Scale up for higher hydrogenation pressure capability (<1000 atm) and use to investigate new ternary and quaternary systems via neutron methods.
- Continue thin-film characterizations using neutron reflectometry.
- Continue efforts to synthesize ^{11}B labelled hydrogen-storage materials.
- Complete thermodynamic assessments for systems with provisional descriptions (Li-B intermediate phases).
- Include descriptions for ternary and quaternary hydrides as data become available.
- Identify systems with MHCoe partners for future neutron scattering studies and Calphad database development.

FY 2008:

- Perform neutron scattering characterizations of new materials in conjunction with the needs of the other partners, emphasizing materials synthesized at high pressures.
- Continue to expand Calphad database (evaluate literature for data, identify data needs and systems with MHCoe partners for future database development).
- Initiate feasibility studies of unique neutron imaging of H distribution and transport in storage beds for candidate materials.

Neutron methods and Calphad computations provided crucial, non-destructive characterization and predictive tools for the Metal-Hydride Center of Excellence.

- Combined neutron and first-principles studies reveal novel ternary structures and H bonding for hydrided Li and Ca alloyed with Si (Ge). Nonetheless, the formation of these structures decreases the maximum H uptake expected for these destabilized materials. Also the H desorption temperature is still too high for practical applications.
- Hydrogen-induced amorphization (HIA) observed for Ca_2Si suggests a possible pathway for developing new hydride materials with improved absorption kinetics and warrants further examination.
- Attempts to make Mg_2Si more hydridable by alloying with Ca_2Si or NaSi were only partially successful. Although the CaMgSi alloy that routinely formed using Ca_2Si could not be hydrided under normal conditions, some of the Mg_2Si hydrided when NaSi was present to form NaMgH_3 . This suggests that proper doping of Mg_2Si with additional elements can render the Mg component more reactive.
- Neutron methods confirm the formation of $\text{Ca}(\text{BH}_4)_2$ from the high-pressure hydrogenation of CaH_2 and CaB_6 . These high-pressure syntheses may provide an alternate means of incorporating neutron-transparent ^{11}B into various borohydrides to enable better neutron measurements.
- Hydrogen cycling measurements of promising destabilizing combinations of LiBH_4 with ScH_2 and CaH_2 indicate that they may be hindered by the formation of elemental boron during dehydrogenation.
- A Calphad database for H-Li-Mg-Ca-B-Si-N with thermodynamic descriptions of the constituent subsystems is being developed from binary data from the literature and *ab initio* calculations. So far, $2 \text{LiBH}_4 + \text{MgH}_2$ is the most promising composition with respect to hydrogen availability and reaction temperature.