METAL HYDRIDE CENTER OF EXCELLENCE

DOE Hydrogen Program

NIST

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

Terry Udovic

Ursula Kattner

NIST

National Institute of Standards and Technology

Technology Administration, U.S. Department of Commerce

STP-38

May 16th 2007

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Overview

Timeline

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

Barriers addressed

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

Budget

- FY05 $125k
- FY06 $156k
- FY07 $276k
- FY08(req.) $287k

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.

Objectives

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.

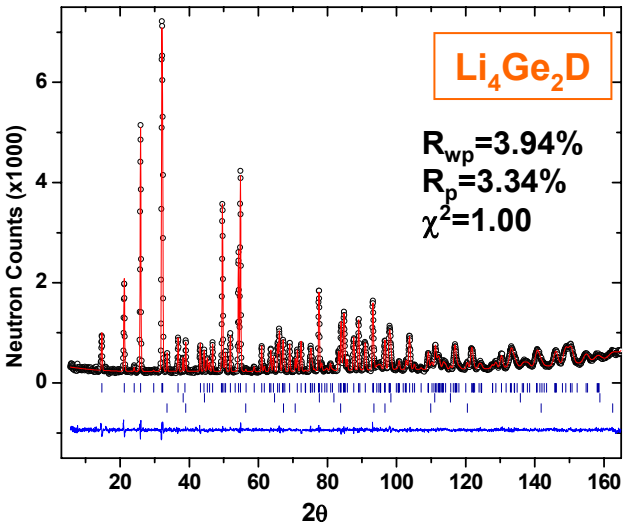
- Characterize structures, compositions, and absorption site interaction potentials for hydrogen in candidate materials .
- Provide Calphad calculations of phase relationships of potentially promising hydrides.

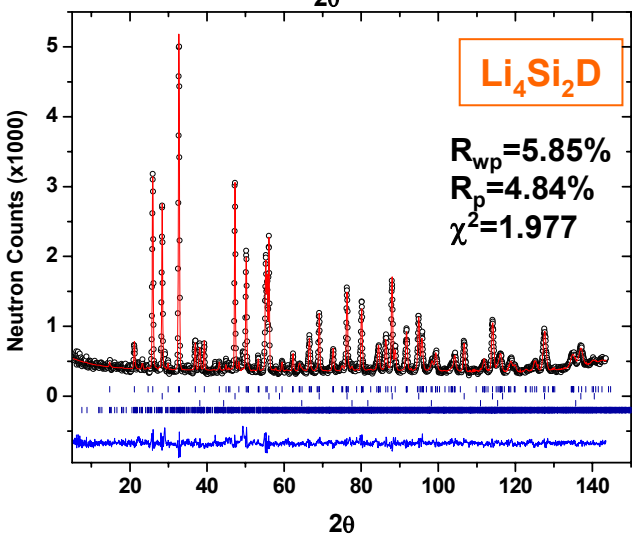
Approach

- **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.

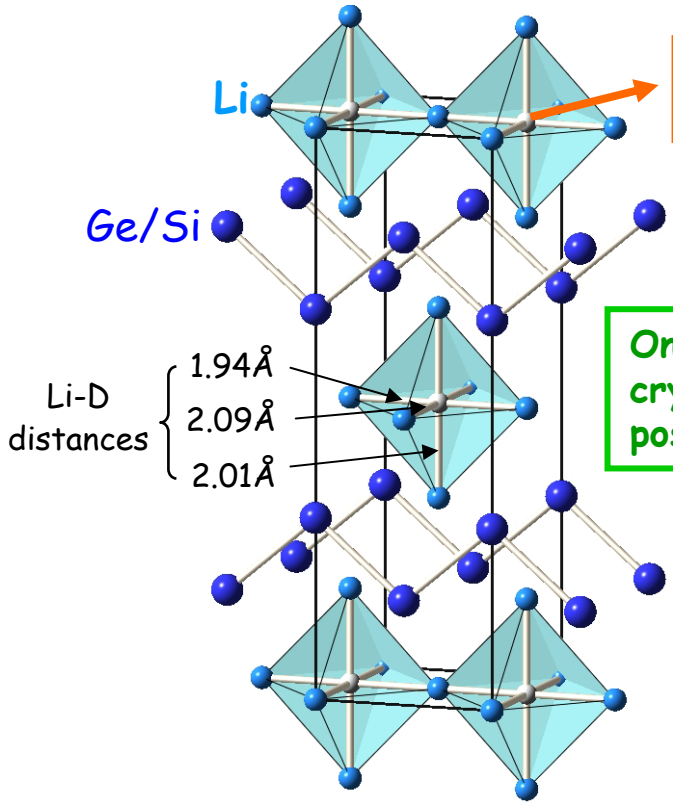
Technical Accomplishment

Structure Identification of Li_4Ge_2D and Li_4Si_2D





Acta. Cryst. B63, 63 (2007)



Cmmm (No. 65)

Only one crystallographic position for D atoms

excellent agreement with the calculated structure by first-principles

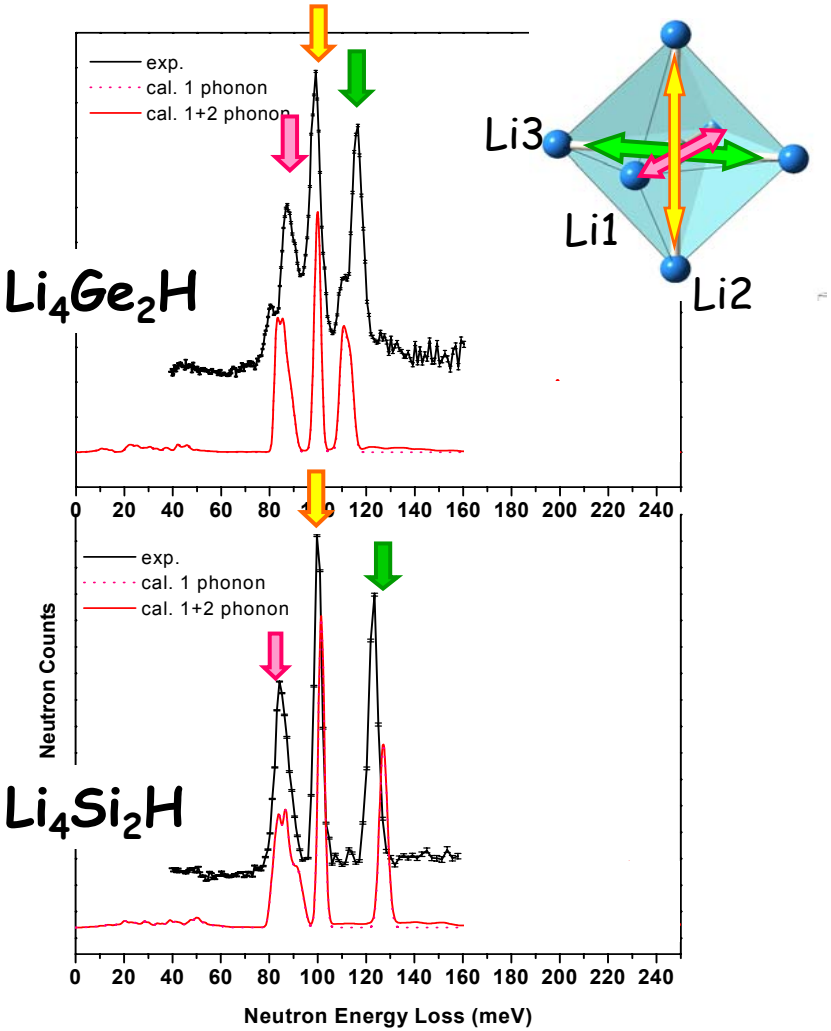
←Si (39.6wt%)

Note: LiH (Li-H ~ 2.038Å)

Strong Li-H binding in Li_4Ge_2H and Li_4Si_2H is primarily responsible for the stabilization of these hydrides.

Technical Accomplishment

Hydrogen Bonding Potentials in Li_4Ge_2H and Li_4Si_2H



(in preparation 2007)

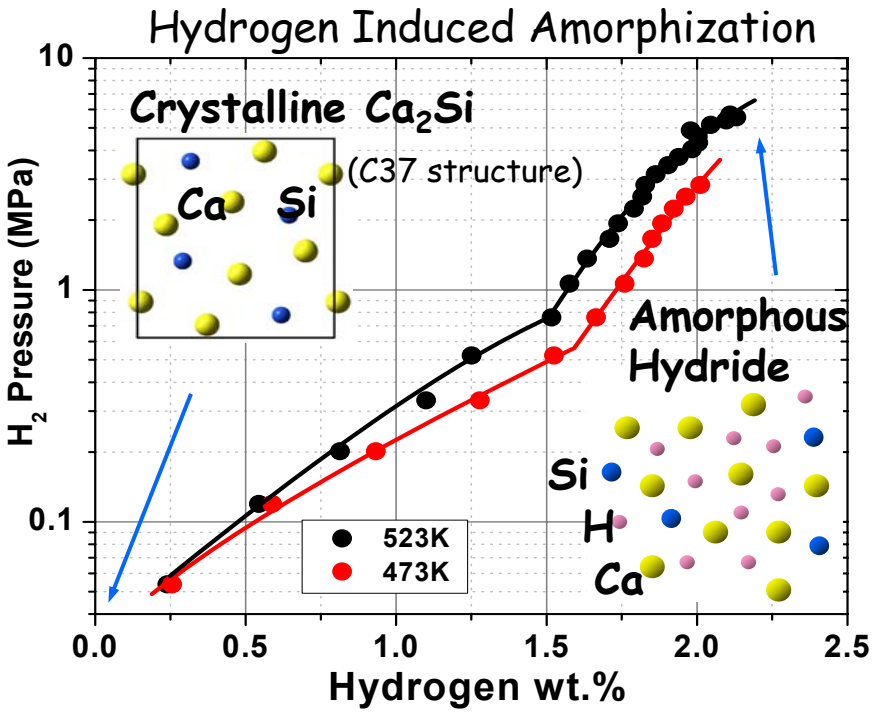
- Measured neutron vibrational spectra for Li_4Ge_2H and Li_4Si_2H
- Characterized the phonon modes with first-principles phonon calculations
- Assignments of the phonon modes are consistent with NPD-observed Li-H bond lengths and the corresponding bond strength.

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

Technical Accomplishment

Destabilization of the $2CaH_2$ / Si system

$$2CaH_2 + Si \rightarrow Ca_2Si + 2H_2 \underset{>500^\circ C}{\overset{200\text{-}300^\circ C}{\rightleftharpoons}} \text{Amorphous hydride phase}$$



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°C.

"Amorphization" could be a way to accelerate the hydrogenation kinetics.

Chem. Mater. 19, 329, (2007)

Technical Accomplishment

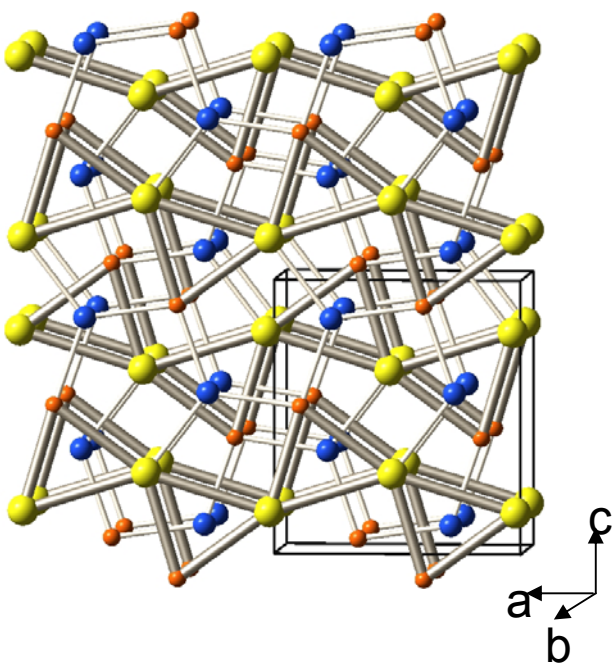
Destabilization of the CaH_2 / MgH_2 / Si system

- Add MgH_2 (higher H_2 storage capacity); possibly improve slow Mg_2Si kinetics
- Single-phase solid solution $Ca_{2-x}Mg_xSn$ observed in $(1-x)Ca_2Sn$-$(x)Mg_2Sn$ system

$CaH_2 + MgH_2 + Si \rightarrow CaMgSi + 2H_2$

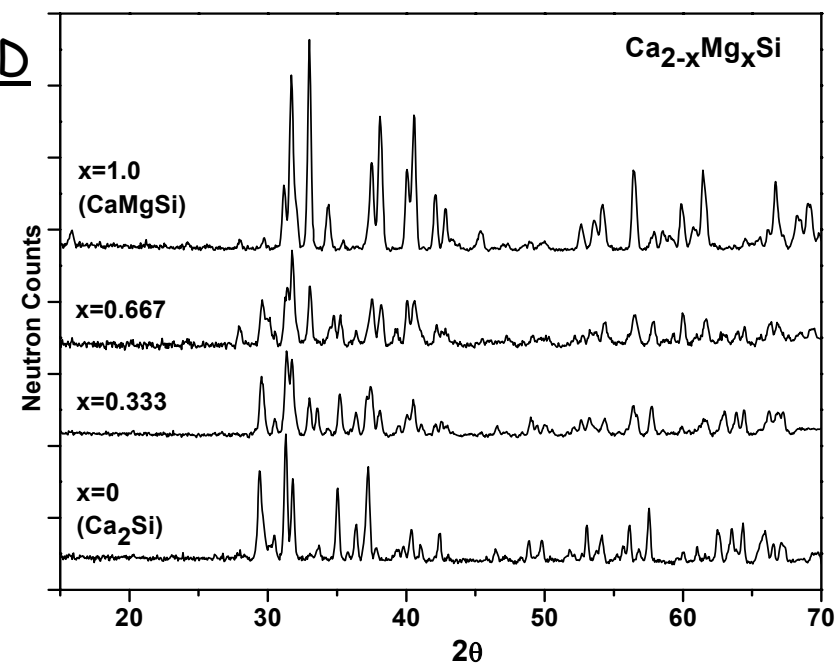
$(2-x)\ CaH_2 + x\ MgH_2 + Si \rightarrow Ca_{2-x}Mg_xSi\ (0<x<1)$

CaMgSi



J. Alloys Comp. in press (2007)

NPD



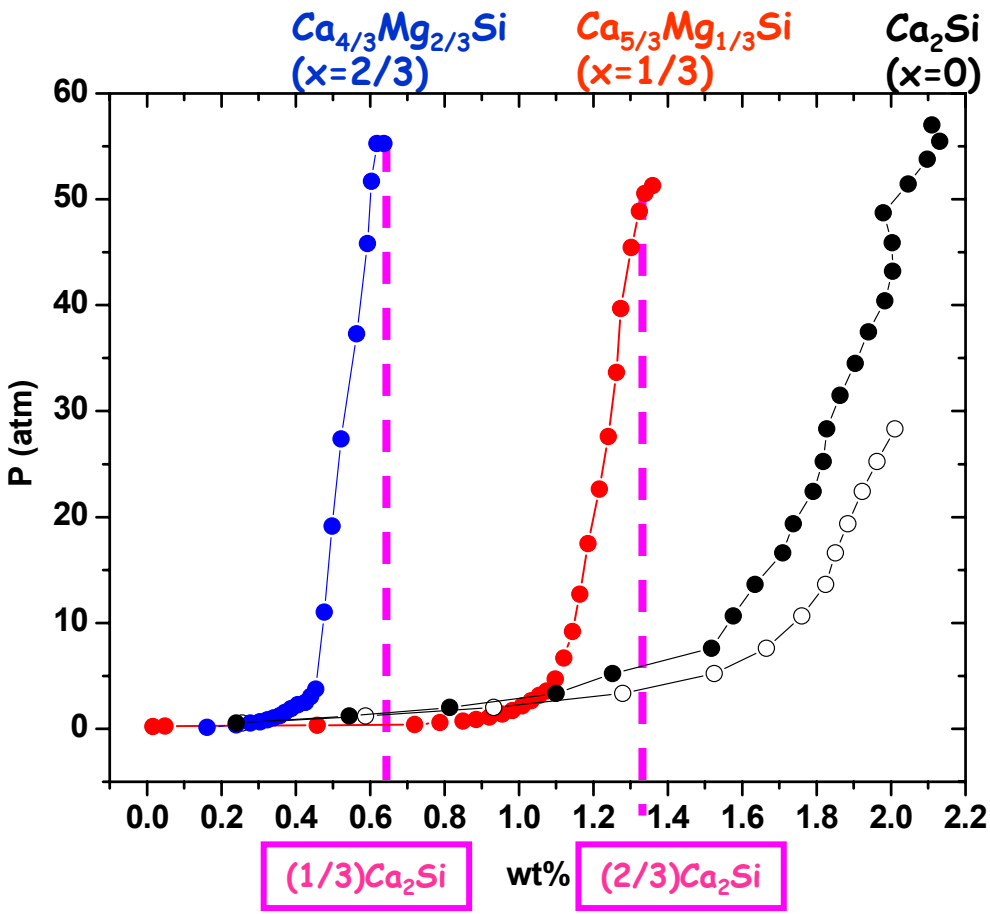
intermediate compositions are Ca_2Si/CaMgSi two-phase mixture (distinct from $Ca_{2-x}Mg_xSn$)

Technical Accomplishment

Hydrogenation Properties of $Ca_{2-x}Mg_xSi$

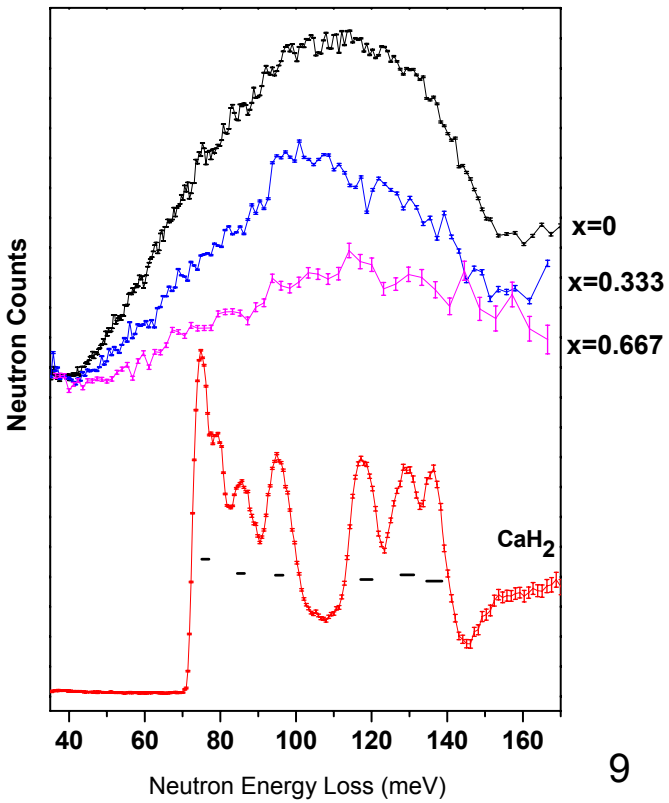
- CaMgSi hardly absorbs H_2 under 0-70 atm at 200-300°C.
- Hydrogenation behavior of (1-x)Ca_2Si-xCaMgSi compositions is dominated by Ca_2Si.

Isotherm measurements



NVS

(After hydrogenation at 200°C 50 atm)

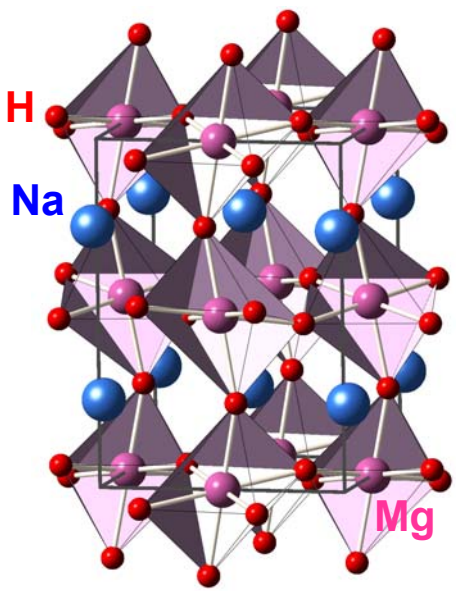


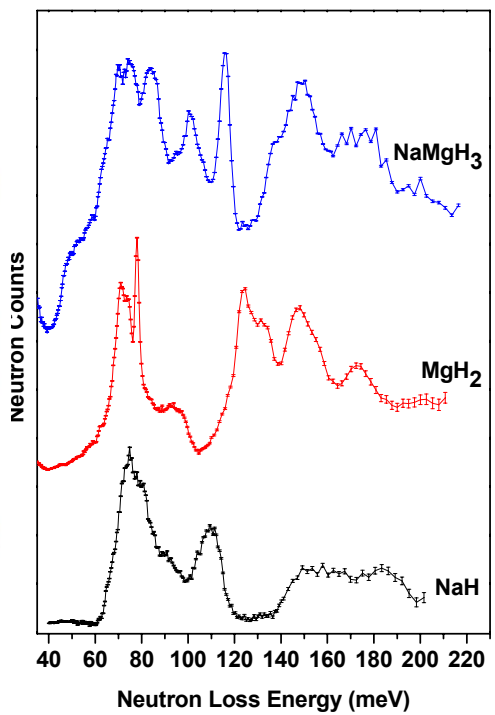
J. Alloys Comp. in press (2007)

Technical Accomplishment

Quaternary System: Na-Mg-Si-H

$NaH + MgH_2 \rightarrow NaMgH_3$ (350°C, 50bar H_2)





Reversible hydrogenation/dehydrogenation

$NaMgH_3 \leftrightarrow Na + Mg + 3/H_2$ (350°C)

- MgH_2/Si system is hard to hydride
- NaH/Si system reversibly absorbs H_2
- NaH/MgH_2 forms a $NaMgH_3$ phase

So, we tried MgH_2/NaH/Si system

Desorption: 350°C evac.

$NaH + 2MgH_2 + 2Si \rightarrow Mg_2Si + NaSi$

Hydrogenation: 350°C 50 atm

$NaSi + Mg_2Si + H_2$

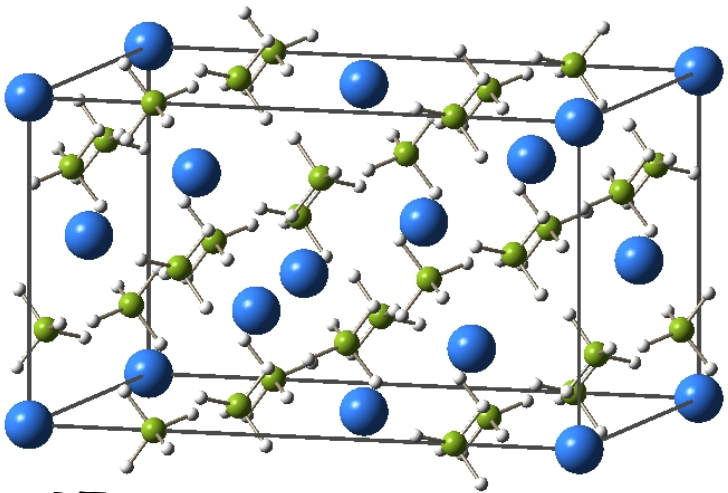
$\rightarrow (1-x)Mg_2Si + (1-x)NaH + Si + xNaMgH_3$

Mg_2Si can partially absorb H_2 through the formation of $NaMgH_3$

Technical Accomplishment

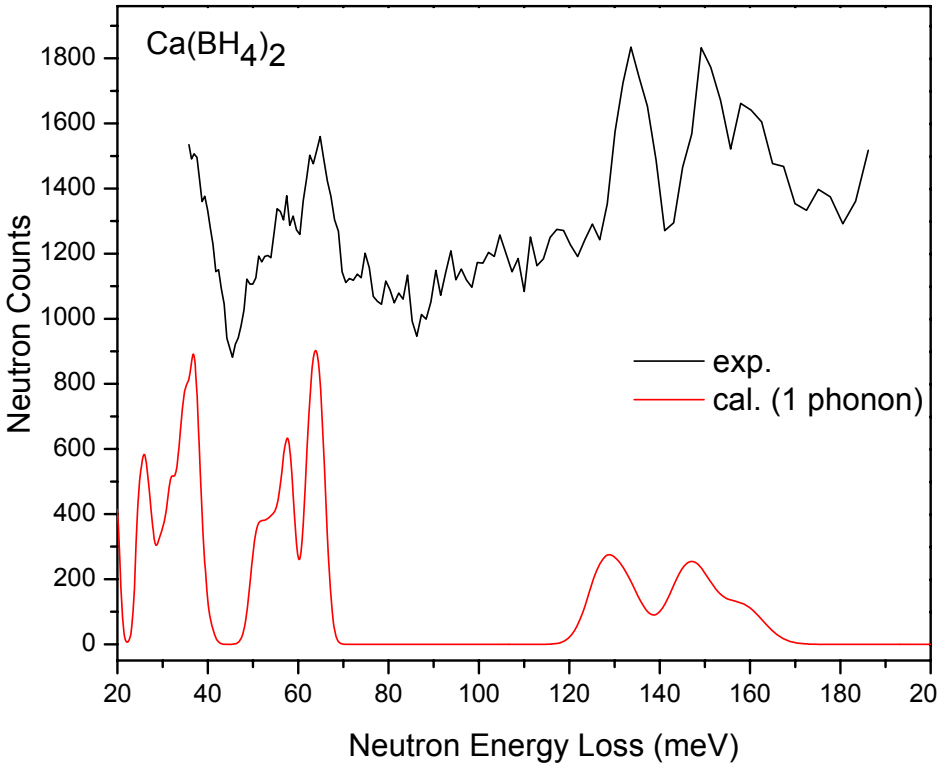
Spectroscopic Verification of $Ca(BH_4)_2$ Synthesis

$Ca(BH_4)_2$ Crystal Structure



RT structure
Space group: *Fddd* (No.70)
a= 8.791Å
b=13.137Å
c= 7.500 Å PRB 74, 155122 (2006)

$Ca(BH_4)_2$ Neutron Vibrational Spectrum



For $Ca(BH_4)_2$ synthesized at Sandia, the neutron vibrational spectrum is in agreement with first-principles phonon calculations based on the published $Ca(BH_4)_2$ structure.

Technical Accomplishment

Destabilization of $LiBH_4$ with ScH_2 and CaH_2

- $2LiBH_4/ScH_2$

Isotherm proposed: $2LiBH_4 + ScH_2 \rightarrow ScB_2 + 2LiH + 4H_2\uparrow$ (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

- $6LiBH_4/CaH_2$

Isotherm proposed: $6LiBH_4 + CaH_2 \rightarrow CaB_6 + 6LiH + 10H_2\uparrow$ (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.

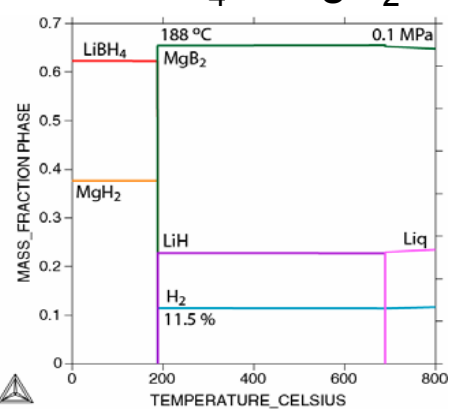
Technical Accomplishment

Calphad Computations

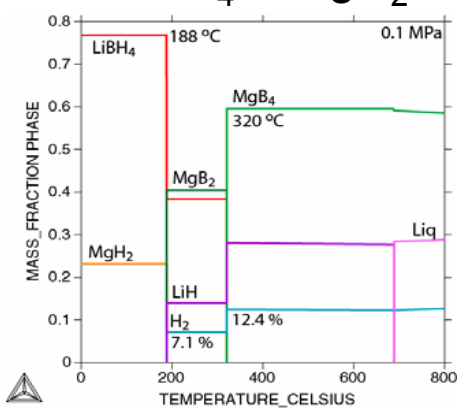
- Developing Calphad database for H-Li-Mg-Ca-B-Si with thermodynamic descriptions of the constituent subsystems
  - 15 binary total: 11 full descriptions available, 3 provisional in development, 1 under development
  - 20 ternary total: 2 full descriptions available,1 partial description available
-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

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

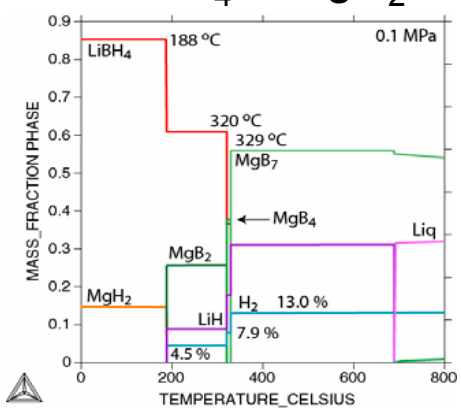
2 $LiBH_4$ + MgH_2



4 $LiBH_4$ + MgH_2



7 $LiBH_4$ + MgH_2



>> 2 $LiBH_4$ + MgH_2 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.

Future Work

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.

Summary

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 $Ca(BH_4)_2$ 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 $LiBH_4$ + MgH_2 is the most promising composition with respect to hydrogen availability and reaction temperature.