

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

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NIST

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

May 19, 2009

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## Timeline

- Project start FY05
- Project end FY10
- 80% complete

## Budget

<u>FY</u>	<u>HSCoE</u>	<u>MHCoE</u>
• FY08	\$225K	\$287K
• FY09 (planned)	\$234K	\$298K

NIST continues to provide access to neutron facilities and FTEs for the HSCoE and MHCoE.

### NIST Associates

Jae-Hyuk Her	Muhammed Yousufuddin
Wei Zhou	Hui Wu
Nina Verdal	John J. Rush

## Barriers addressed

- A. System Weight and Volume
- P. Lack of Understanding of Hydrogen Physisorption and Chemisorption

## Partners

- Caltech, GM, HRL, JPL, Lawrence-Livermore, Maryland, Michigan, Missouri-Columbia, Ohio State, Penn, Sandia, Stanford
  - Neutron-based Characterization
- Georgia Tech, Illinois, Missouri-St. Louis, Pittsburgh, Sandia
  - Calphad Calculations
- Sandia
  - Project Lead

**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. Use this information to speed the development and optimization of storage materials that can meet the 2010 DOE system goals of 6 wt% and 45 g/L capacities.

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

## *Detailed neutron studies in support of the Center's go/no-go analysis*

Month/Year	Milestone
Apr-08 <b>(Complete)</b>	Evaluate structural and bonding properties of new materials selected through discussions with the leadership of the Center and coordinating council and establish a high-pressure hydrogenation system to complement SNL work. (Complete for $\text{Li}(\text{BH}_4)_x(\text{NH}_2)_{1-x}$ , $\text{NaMgH}_3$ , $\text{Li}_2\text{B}_{12}\text{H}_{12}$ , $\text{Ca}(\text{BH}_4)_2$ , and $\text{LiKBH}_4$ .)
Sep-08 <b>(Complete)</b>	A thorough analysis as needed of the materials that have favorably passed the Phase 1 go/no-go decisions and show the most promise of achieving the DOE 2010 targets (e.g., other nano-confined borohydrides).
Sep-09	Evaluate structural and bonding properties of new materials selected through discussions with the leadership of the Center and coordinating council (e.g., $\text{Na}_2\text{B}_{12}\text{H}_{12}$ , $\text{CaB}_{12}\text{H}_{12}$ , and $\text{CaAlH}_4\text{BH}_4$ )

## *Thermodynamic evaluations (Calphad)*

Month/Year	Milestone
Apr-08 <b>(Complete)</b>	Refine descriptions of constituent binary Ca-systems.
Sep-08 <b>(Complete)</b>	Develop description of the Ca-B-H system including the $\text{Ca}(\text{BH}_4)_2$ compound.
Apr-09	Develop descriptions for borane gas species and the Mg-B-H system including the $\text{Mg}(\text{BH}_4)_2$ compound.
Sep-09	Develop descriptions for Ca and Mg hydro- <i>c</i> l <sub>o</sub> so-borates.

- **Neutron methods**

- determine elemental compositions of materials (prompt- $\gamma$  activation analysis and neutron reflectometry of H stoichiometries and profiles)
- 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)

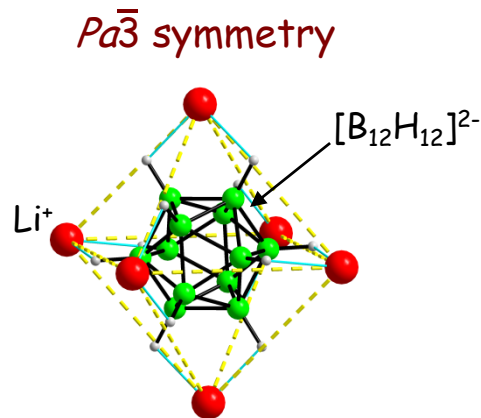
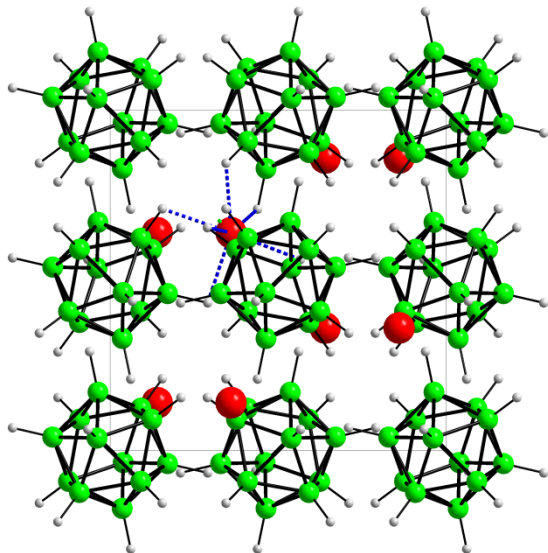
- **Calphad methods**

- 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

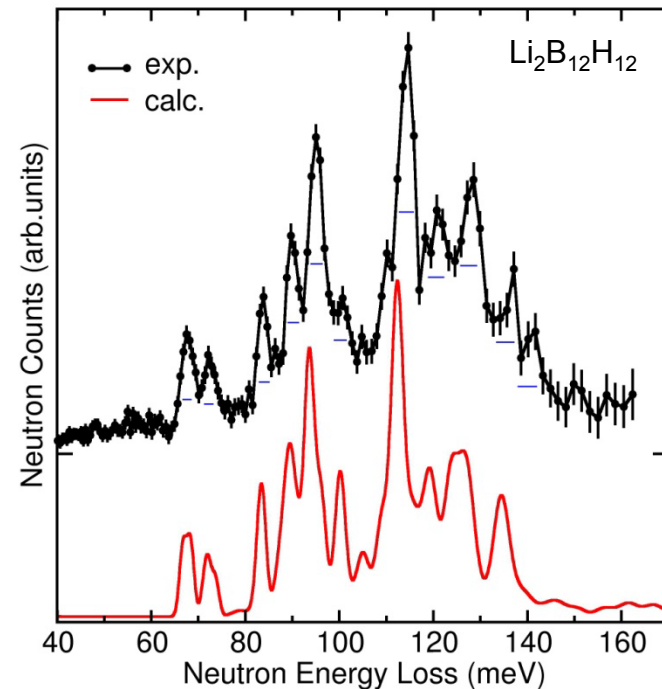
Collaboration with Sandia, JPL, Caltech, Maryland, and Missouri-Columbia

Motivation: to characterize hydrogen cycling intermediates in light-metal borohydrides, where structural and thermodynamic data are lacking.



The  $Li^+$  cation lies in a nearly trigonal planar site formed by three  $B_{12}H_{12}^{2-}$  anions, each of which resides in the octahedral cage defined by six  $Li^+$  cations.

Each  $[B_{12}H_{12}]^{2-}$  anion orients two H atoms to each of the  $Li^+$  cations, resulting in a strongly distorted octahedral coordination of the  $Li^+$  cation with six H atoms.



The NV spectrum and DFT calculations agree with the structural model from XRD.

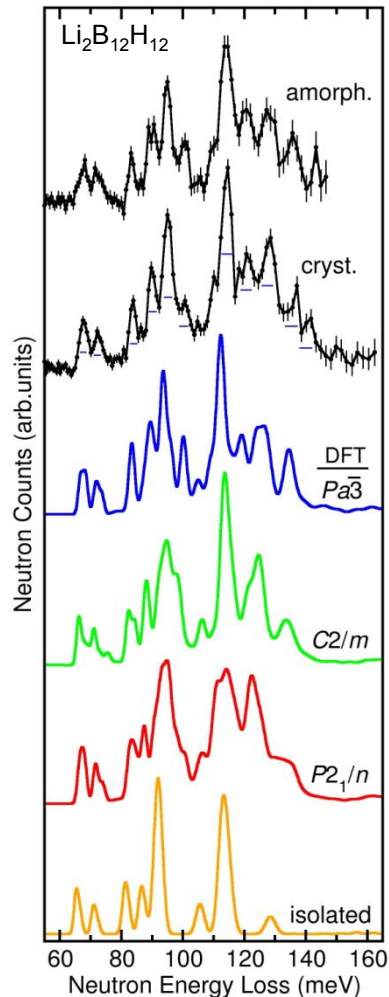
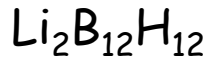
J.-H. Her *et al.*, *Inorg. Chem.* **47**, 9757 (2008)

\* The structure of  $Li_2B_{12}H_{12}$  was solved by a combination of XRD, neutron vibrational spectroscopy (NVS), and DFT calculations.



Technical Accomplishment

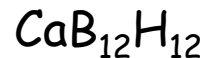
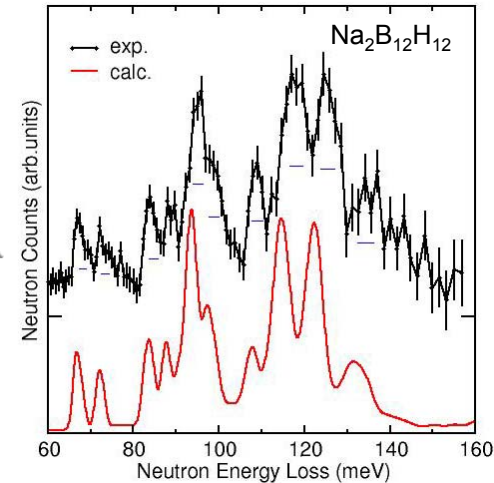
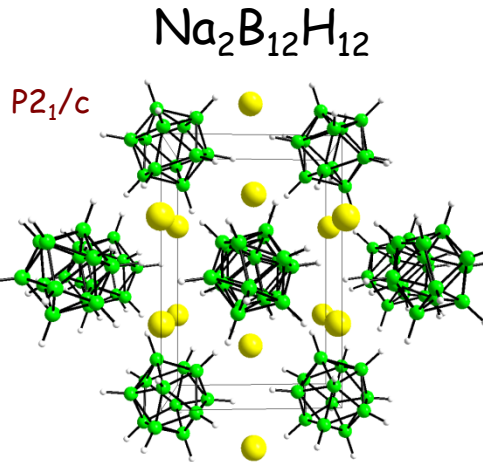
Collaboration with Sandia, JPL, Caltech, Maryland, and Missouri-Columbia



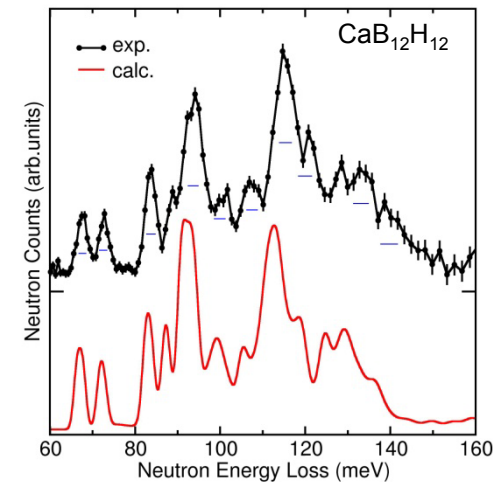
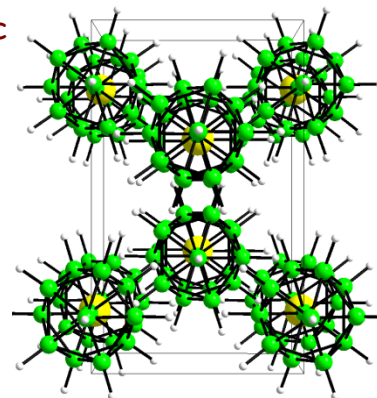
DFT calculations confirm that the phonon density of states for  $B_{12}H_{12}^-$ -based compounds is sensitive to the structure.

← Experimental structure

← Reported theoretical structures



Agrees with theoretical structure



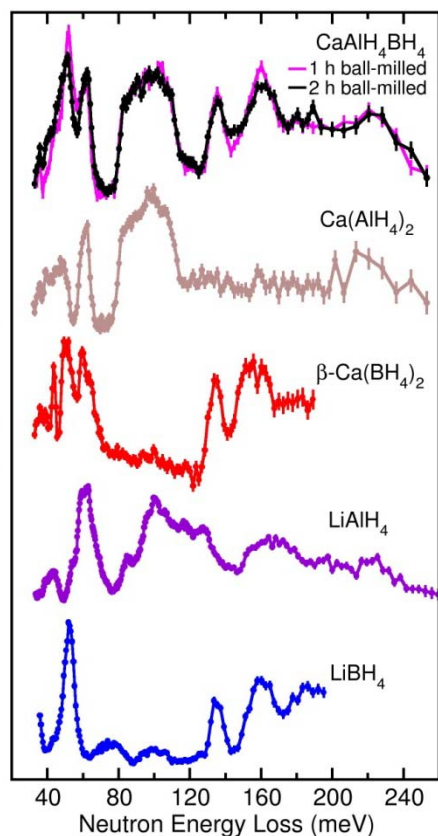
- \* Two other relevant  $M_xB_{12}H_{12}$  structures were solved by XRD, NVS, and DFT.
- \* Spectroscopy may be useful to test predicted structures, even for "amorphous" samples.

Technical Accomplishment

Collaboration with Sandia, JPL, Caltech, Maryland

Motivation: to help characterize new MHCoe compounds such as novel borohydrides

Possible synthesis of  $\text{Ca}(\text{AlH}_4)(\text{BH}_4)$  via ball-milling of  $\text{LiAlH}_4 + \text{LiBH}_4 + \text{CaCl}_2$

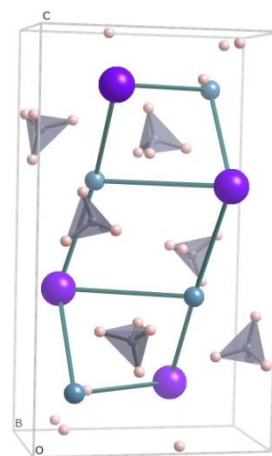


NVS (left) and NMR of the "amorphous" compound + LiCl indicate some spectroscopic similarities with  $\text{Ca}(\text{AlH}_4)_2$ ,  $\text{Ca}(\text{BH}_4)_2$ , and  $\text{LiBH}_4$ , but clear differences exist.

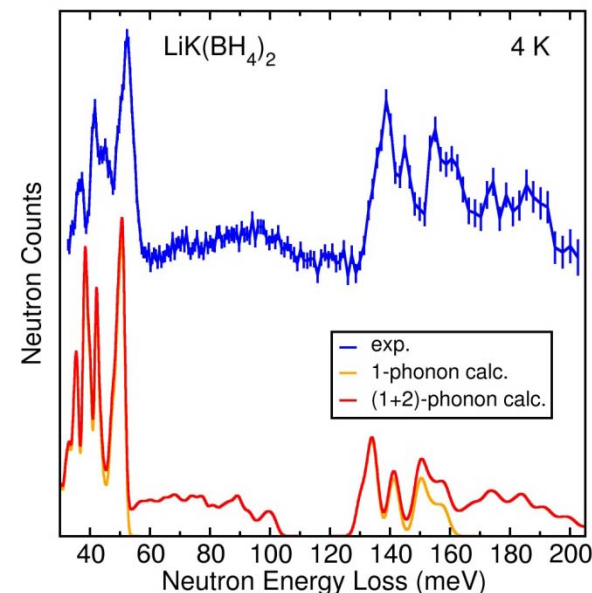
Theory predicts a possible stable structure. DFT phonon calculations are in progress.

\* NVS data may reflect a new compound.

Spectroscopic analysis of  $\text{LiK}(\text{BH}_4)_2$  synthesized via ball-milling of  $\text{LiBH}_4 + \text{KBH}_4$



*Pnma* structure from *Angew. Chem. Int. Ed.* 47, 2817 (2008)



NV spectrum of  $\text{LiK}(\text{BH}_4)_2$  synthesized at SNL agrees well with DFT phonon calculations of the optimized  $\text{LiK}(\text{BH}_4)_2$  structure.

\* NVS data and DFT corroborate  $\text{LiK}(\text{BH}_4)_2$  formation.

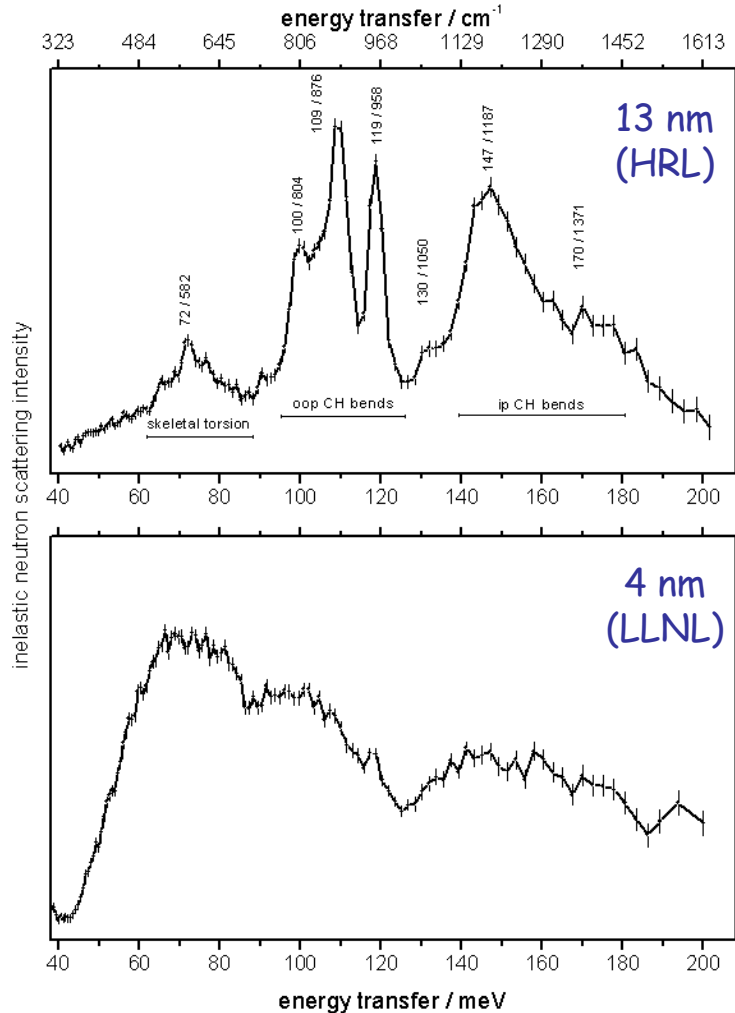


Technical Accomplishment

Collaboration with HRL and Lawrence Livermore

Motivation: to investigate the properties of nanoscaffold materials

We measured NV Spectra of Carbon Aerogels to probe the nature of residual H



Close resemblance of these features to those of nanotube and coronene hydrogen suggests  $sp^2$ -hybridized C-H edge groups.

Neutron prompt-gamma activation analysis (PGAA) for both indicates  $\sim 0.1$  H/C.

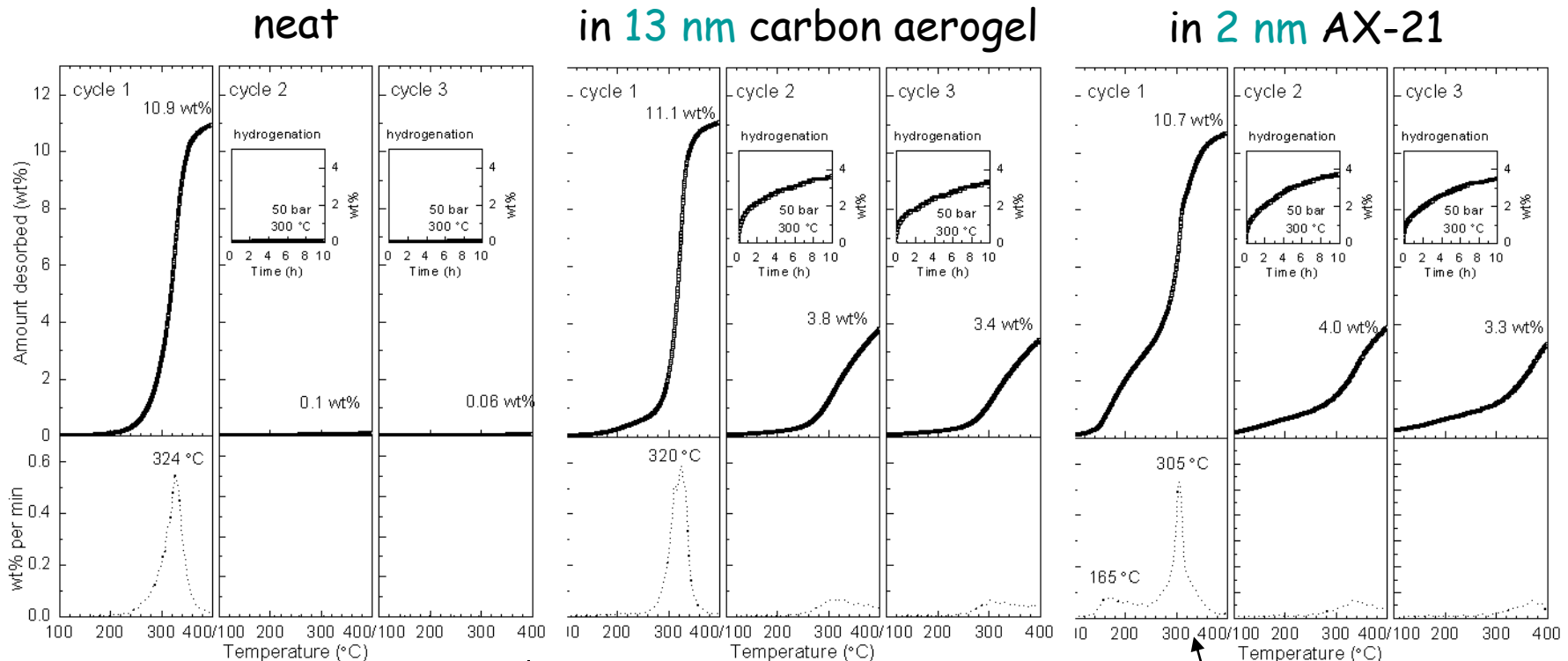
Spectrum indicates very little  $sp^2$ -hybridized C-H edge groups. H signal appears water-like.

\*We need to understand the effect of residual H on the measurements and cycling properties of nanoconfined storage materials.

Technical Accomplishment

Collaboration with HRL, GM, Maryland, and Penn

Motivation: to investigate the use of nanoconfinement to enhance the kinetics and reversibility of  $\text{Li}_3\text{BN}_2\text{H}_8$  [a mixture of  $(2/3)\text{Li}_4\text{BN}_3\text{H}_{10} + (1/3)\text{LiBH}_4$ , 11 wt% H]



irreversible  $\longleftrightarrow$  partially reversible

indicates a reduced desorption temperature compared to neat and 13 nm nanoconfinement

H. Wu *et al.*, Nanotechnology (in press 2009)

\* Nanoconfinement of  $\text{Li}_3\text{BN}_2\text{H}_8$  renders it partially reversible.

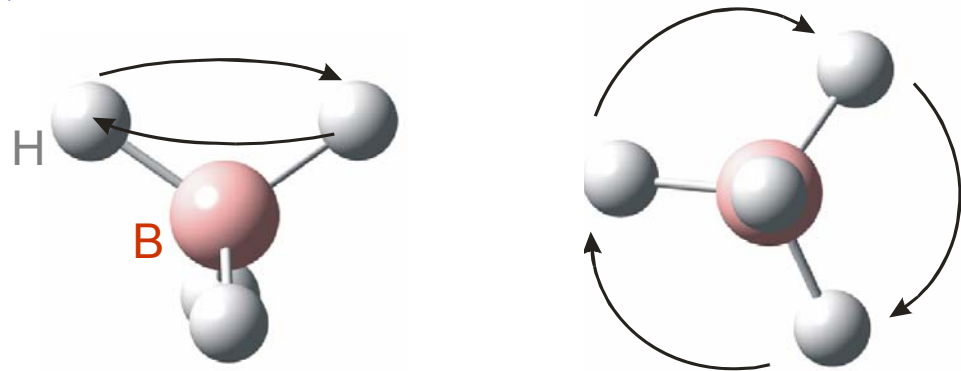
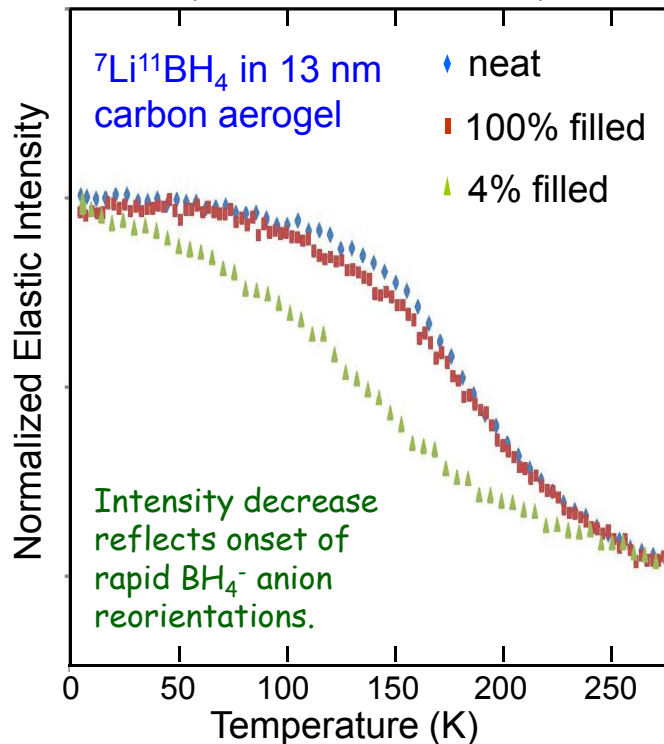
Technical Accomplishment

Collaboration with HRL, Lawrence Livermore, Maryland, and Michigan

Motivation: to investigate borohydride dynamics perturbations in carbon aerogels

We studied the effect of  $\text{LiBH}_4$  fill fraction in a 13 nm carbon aerogel on the reorientational dynamics of  $\text{BH}_4^-$  anions.

Neutron Backscattering Data  
(Fixed Window Scan)



two-fold jumps

three-fold jumps

For 4% filling, the onset of rapid  $\text{BH}_4^-$  anion reorientations shifts to much lower temperature.

Does this behavior reflect preferential filling of smaller pores and/or surface film formation?

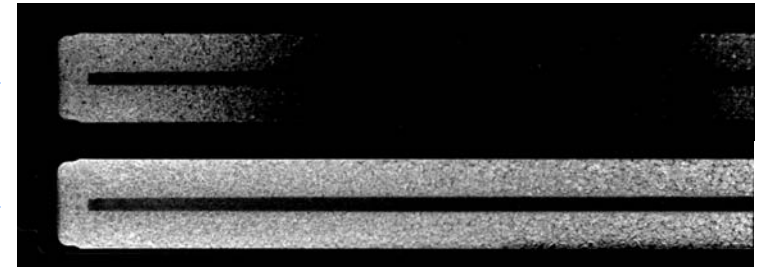
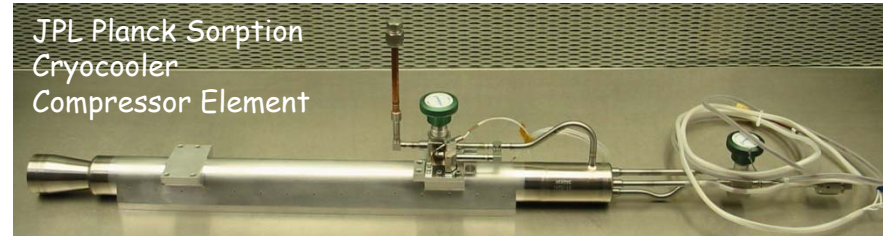
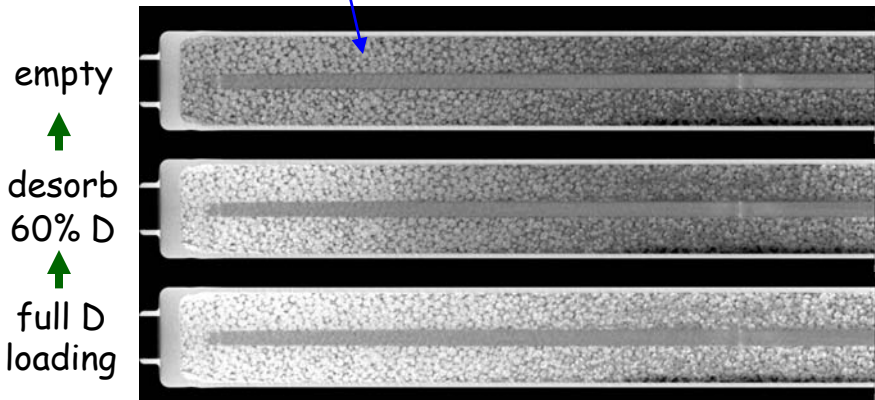
\*Partial filling enhances the  $\text{LiBH}_4$  fraction exhibiting non-bulk-like behavior.

Technical Accomplishment

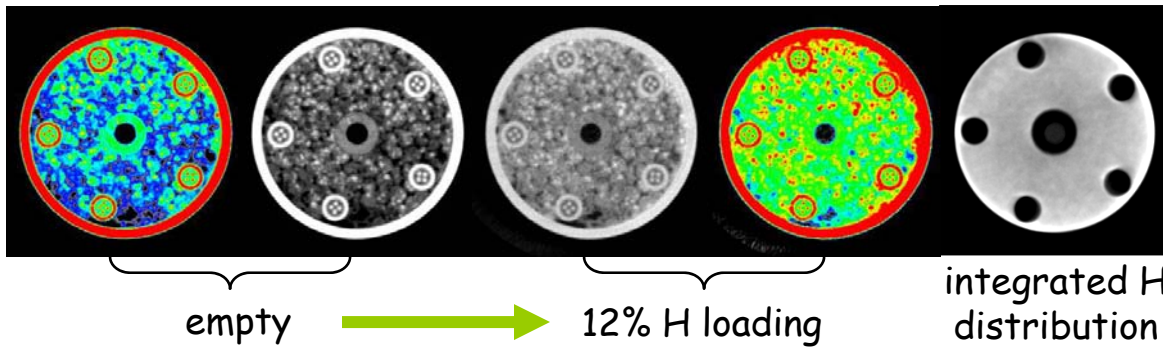
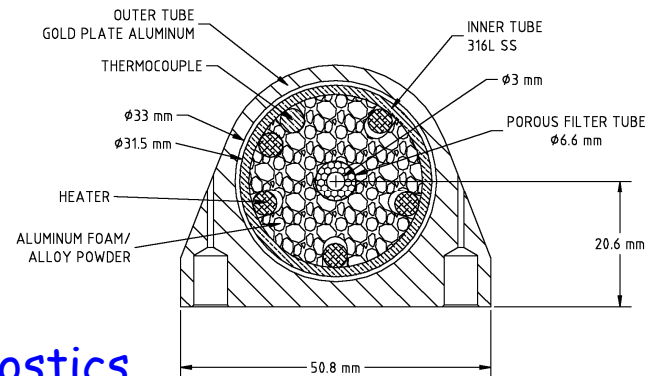
Collaboration with JPL and Maryland

Motivation: We need accurate *in-situ* diagnostics of practical hydrogen-storage beds

LaNi<sub>4.78</sub>Sn<sub>0.22</sub> powder in 10% dense Al foam



Deuterium difference images



\*Neutron imaging techniques can provide *in situ* diagnostics.  
 \*Using deuterium enables the imaging of thicker beds.

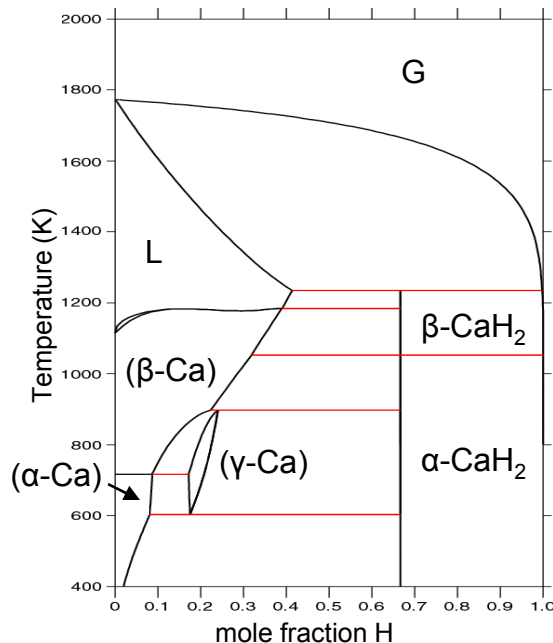
Technical Accomplishment Collaboration with Georgia Tech, Illinois, Missouri-St. Louis, Pittsburgh, Sandia

Motivation: to develop thermodynamic database (using Calphad) for H-Li-Mg-Ca-B-Si, where experimental data are generally lacking

## We continued thermodynamic descriptions of the constituent subsystems

- Refined descriptions of constituent binary Ca systems
- Modified Neumann-Kopp rule for the prediction of heat capacities of complex metal-hydrides; developed description for  $\text{Ca}(\text{BH}_4)_2$
- Expanded database to include higher borane species in the gas-phase description

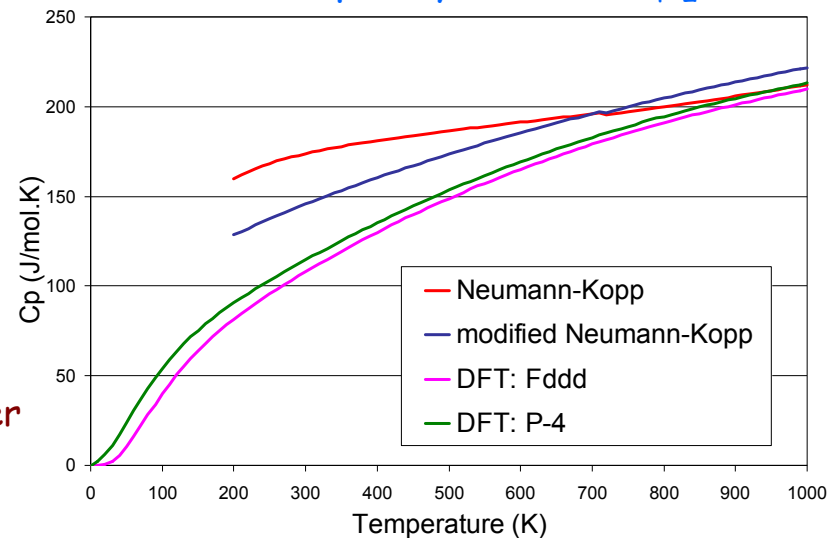
### Results: Refined description of Ca-H



Dissolution of H in terminal solution phases may significantly reduce available H

Modified Neumann-Kopp rule allows faster prediction of  $C_p$

### Heat capacity of $\text{Ca}(\text{BH}_4)_2$



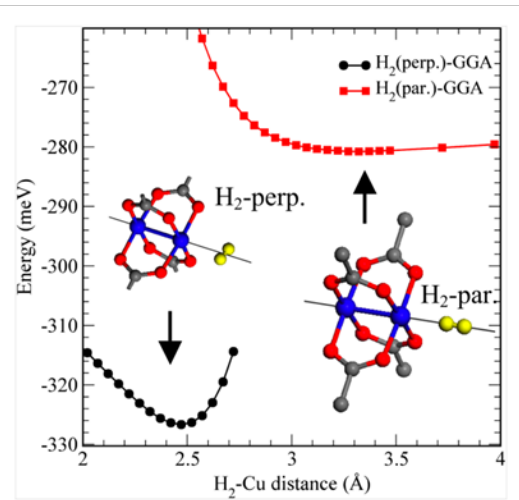
\*Results from Calphad computations give details of the reaction process, such as actual available H amount and species concentration in the gas phase.



Technical Accomplishment

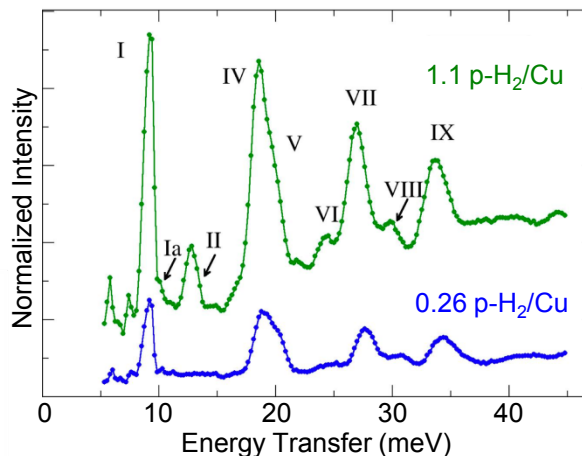
Collaboration with U. Sydney, Maryland, and Penn

Motivation: to understand the binding of  $H_2$  in paddlewheel-motif MOFs: HKUST-1



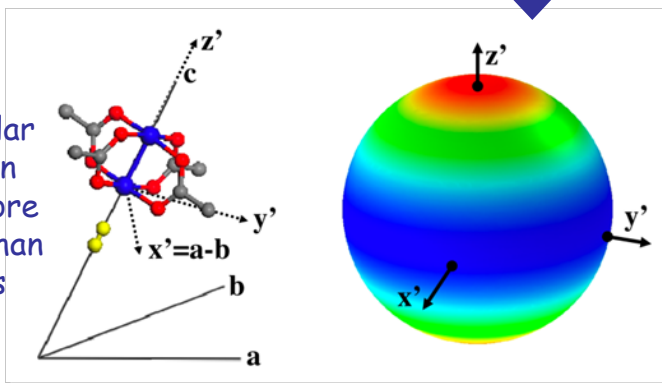
Brown, et al.  
Nanotechnology  
(in press 2009)

Calculate energy of  $H_2$  as a function of orientation in HKUST-1



Excellent agreement when compared to inelastic neutron data

Perpendicular orientation -78 meV more favorable than along axis



Solve rotational Schrödinger eqn.

phonon energies (meV)  
X = 9.56  
Y = 13.44  
Z = 22.87

Energy (meV)	$E_T - E_0$ (meV)	Major JM
-61.47	0	J=0, M=0
-51.85	9.61	J=1, M=+/-1
-51.71	9.76	J=1, M=-/+1
-25.39	36.08	J=2, M=+/-2
-25.39	36.08	J=2, M=-/+2
-24.20	37.27	J=1, M=0
-5.64	55.82	J=2, M=+/-1
-5.53	55.93	J=2, M=-/+2
9.95	71.41	J=2, M=0

- \* Interactions determined by Coulomb forces through weak electron overlap.
- \* Hydrogen rotations are quasi-2D.



## Partners (Type of Institution): What we provide to them

**CalTech** (Univ./MHCoE): neutron and x-ray measurements and DFT calculations of various alanates, borohydrides, and related materials

**Georgia Tech** (Univ./MHCoE): Calphad calculations of multicomponent light-element systems

**GM** (Industry): cycling and kinetics studies and characterization of nanoconfined  $\text{Li}_3\text{BN}_2\text{H}_8$

**HRL** (Industry/MHCoE): neutron measurements of aerogels and nanoconfined  $\text{LiBH}_4$ ; cycling and kinetics studies and characterization of nanoconfined  $\text{Li}_3\text{BN}_2\text{H}_8$

**Illinois** (Univ./MHCoE): Calphad calculations of multicomponent light-element systems

**JPL** (Fed./MHCoE): neutron and x-ray measurements and DFT calculations of various alanates, borohydrides, and related materials

**Lawrence-Livermore** (Fed./MHCoE): neutron measurements of aerogels and nanoconfined  $\text{LiBH}_4$

**Maryland** (Univ.): neutron and x-ray measurements of alanates, borohydrides, and related materials; neutron imaging of hydrogen-storage beds

**Michigan** (Univ.): neutron measurements of  $\text{BH}_4^-$  dynamics in neat and nanoconfined metal borohydrides

**Missouri-Columbia** (Univ.): neutron and x-ray measurements of  $\text{Li}_2\text{B}_{12}\text{H}_{12}$  compounds

**Missouri-St. Louis** (Univ./MHCoE): Calphad calculations of multicomponent light-element systems; neutron measurements of various alanates, borohydrides, and related materials

**Ohio State** (Univ./MHCoE): neutron and x-ray measurements of  $\text{MgB}_{12}\text{H}_{12}$  compounds

**Penn** (Univ.): neutron measurements of boranes, perovskite hydrides, and other storage-related materials

**Pittsburgh** (Univ./MHCoE): Calphad calculations of multicomponent light-element systems

**Sandia** (Fed./MHCoE): neutron measurements and DFT calculations of various alanates, borohydrides, and related materials; Calphad calculations of multicomponent light-element systems

**Stanford** (Univ./MHCoE): neutron reflectivity measurements of H profiles in H-cycled Mg thin films

## Remainder of FY 2009 and FY2010:

- Continue structural and spectroscopic characterizations of dodecahydro-*c*-*closo*-dodecaborates ( $M_xB_{12}H_{12}$ ). (with Sandia, Caltech, Maryland, Missouri-St. Louis, Ohio State)
- Continue rotational dynamics investigations of nanoscaffolded borohydrides. (with HRL, Lawrence Livermore, Michigan, Caltech)
- Continue Mg thin-film characterizations using neutron reflectometry. (with Stanford)
- Perform neutron scattering characterizations of new materials in conjunction with the needs of the other partners, including borohydrides and nanoscaffolded materials of interest.
- Continue feasibility studies using neutron imaging to probe H distribution and transport in storage beds for candidate materials. (with JPL, Maryland)
- Develop Calphad description of the Ca-B-H and Mg-B-H systems including the  $Ca(BH_4)_2$  and  $Mg(BH_4)_2$  compounds. (with MHCoe Theory Group)
- Continue to expand Calphad database (evaluate literature for data, identify data needs and systems with MHCoe partners for future database development).

## Neutron methods and Calphad computations continue to provide crucial, non-destructive characterization and predictive tools for the MHCoe.

- The structures of  $\text{Li}_2\text{B}_{12}\text{H}_{12}$ ,  $\text{Na}_2\text{B}_{12}\text{H}_{12}$ , and  $\text{CaB}_{12}\text{H}_{12}$  (possible intermediates in borohydride decomposition) were solved by a combination of XRD, neutron vibrational spectroscopy (NVS), and DFT calculations.
- NVS and NMR data are not inconsistent with the formation of a new  $\text{Ca}(\text{AlH}_4)(\text{BH}_4)$  compound via ball-milling  $\text{LiBH}_4 + \text{LiAlH}_4 + \text{CaCl}_2$ . Yet, it appears that longer ball-milling times are required to complete the reaction, and proper interpretation requires DFT phonon calculations.
- NVS and PGAA indicate nontrivial amounts of residual H in carbon aerogels. We need to understand the effect of this H on the measurements and cycling properties of nanoconfined storage materials.
- Confinement of  $\text{Li}_3\text{BN}_2\text{H}_8$  in nanoporous carbon materials renders it partially reversible.
- Only partially filling a 13 nm carbon aerogel with  $\text{LiBH}_4$  increases the fraction that exhibits non-bulk-like  $\text{BH}_4^-$  reorientational dynamics. This may reflect preferential filling of smaller pores and/or surface film formation.
- Neutron imaging techniques can provide *in situ*, real-time diagnostics of practical hydrogen-storage beds. Using deuterium enables the imaging of thicker beds.
- A Calphad database for H-Li-Mg-Ca-B-Si-N with thermodynamic descriptions of the constituent subsystems is being developed from literature data for the binary solution phases and intermediate compounds and data from first-principles calculations.
- The modified Neumann-Kopp rule allows fast prediction of the heat capacities of complex metal hydrides.