

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

Terrence J. Udovic
Ursula R. Kattner



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

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ST067

Timeline

- Project start FY05
- Project end FY10
- 100% complete

Budget

<u>FY</u>	<u>HSCoE</u>	<u>MHCoE</u>
• FY09	\$234K	\$298K
• FY10	\$235K	\$299K

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

NIST Associates

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

Barriers addressed

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

MHCoE 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 and thermodynamic evaluations (Calphad) in support of the Center's go/no-go analysis

Month/Year	Milestone
Sep-09 (Complete)	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 $\text{CaAlH}_4\text{BH}_4$)
Apr-09 (Complete)	Develop descriptions for borane gas species and the Mg-B-H system including the $\text{Mg}(\text{BH}_4)_2$ compound.
Sep-09 (Complete)	Develop descriptions for Ca and Mg hydro- <i>closo</i> -borates.

- **Neutron methods**

- determine elemental compositions of materials (prompt- γ 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 5

Neutron methods, synthesis expertise, and Calphad and DFT computations were used to further the goals of the MHCoe.

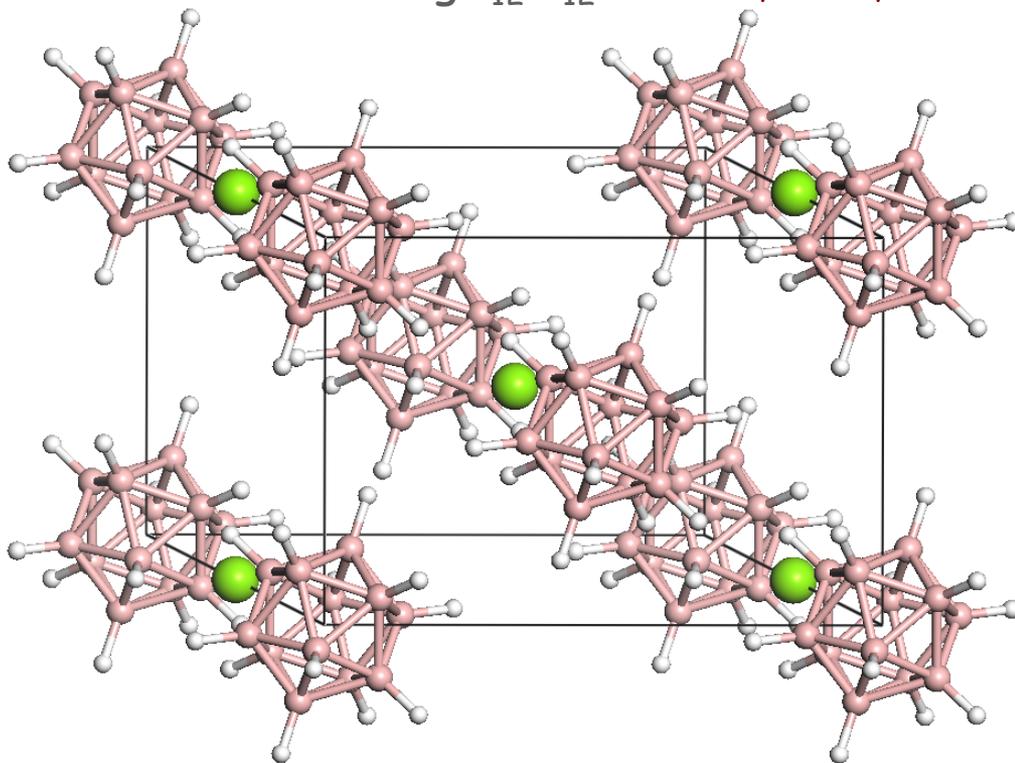
- We characterized the structure, dynamics, thermodynamics, and reactivity of various $M_xB_{12}H_{12}$ compounds because they are potentially key intermediates in the hydrogen cycling of the borohydrides.
- We characterized the rotational dynamics of BH_4^- and $B_{12}H_{12}^{2-}$ anions in bulk compounds as a baseline for comparison with the dynamics found for nanoconfined compounds. Changes in rotational dynamics reflect changes in thermodynamic properties.
- We continued to characterize various aspects of nanoconfinement in an attempt to understand its effect on the hydrogen cycling of $LiBH_4$.
- We synthesized new mixed-anion complex hydrides that have potentially favorable cycling behavior for hydrogen storage.
- We characterized the hydrogen cycling of Mg thin films to understand the fundamental mechanisms involved.
- We continued to expand our Calphad thermodynamic database to include new compounds of importance to hydrogen storage research.

Technical Accomplishment

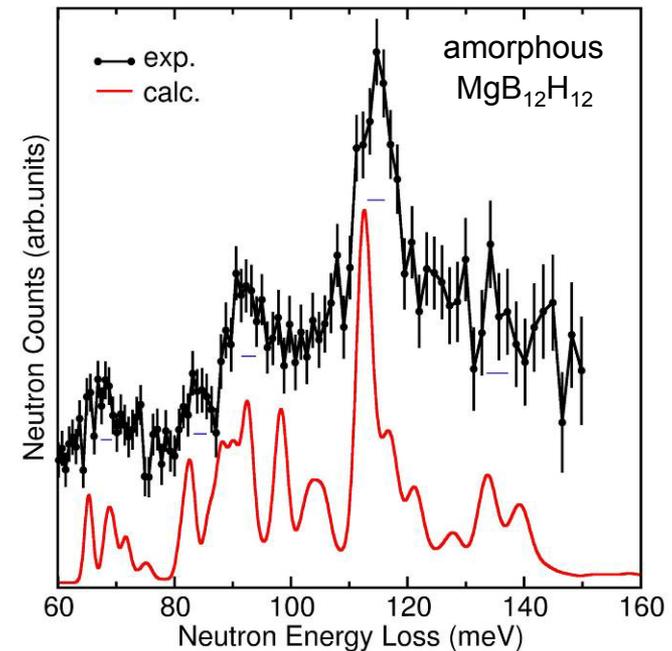
Collaboration with Sandia, JPL, Caltech, and Maryland

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

$\text{MgB}_{12}\text{H}_{12}$ ($C2/m$ symmetry)



predicted structure from Ozolins *et al.*, JACS 131, 230 (2009)



The NV spectrum of amorphous $\text{MgB}_{12}\text{H}_{12}$ and DFT phonon calculation for the predicted crystalline structure show significant similarities.

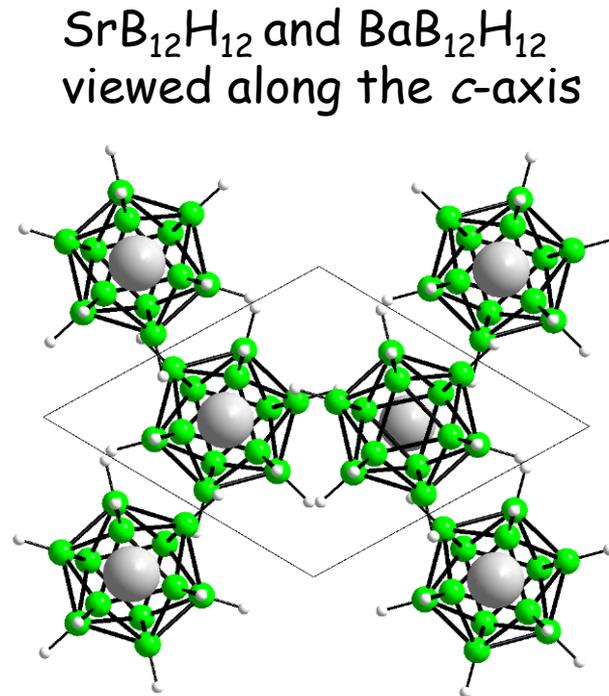
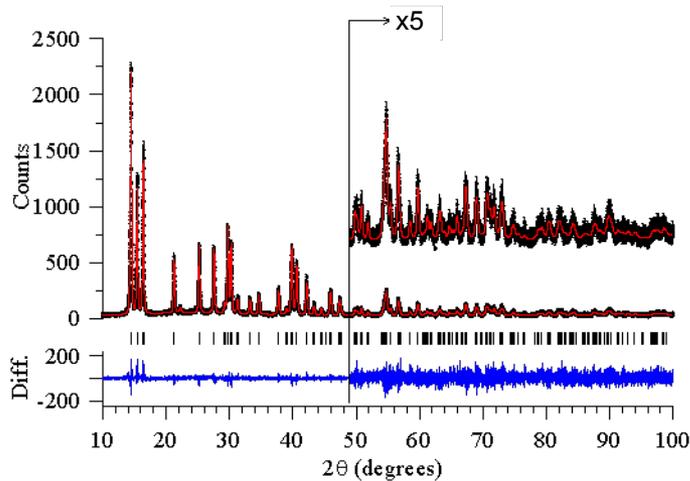
* The neutron vibrational spectrum of amorphous $\text{MgB}_{12}\text{H}_{12}$ suggests the presence of short-range order resembling the predicted crystalline structure.

Technical Accomplishment

Collaboration with Sandia, JPL, Caltech, and Maryland

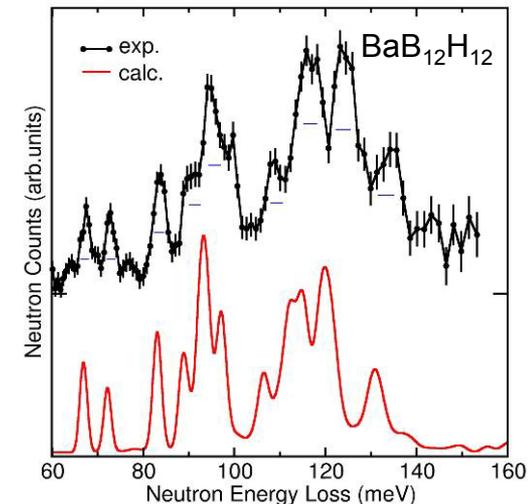
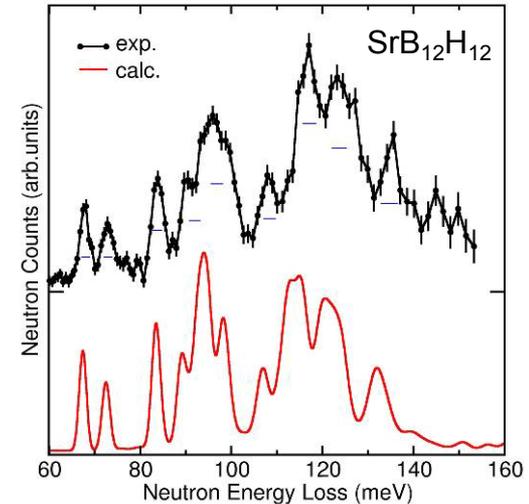
NVS, XRD, and DFT were used to determine the structures of the heaviest stable $MB_{12}H_{12}$ compounds

XRD refinement for $SrB_{12}H_{12}$



$P31c$ symmetry

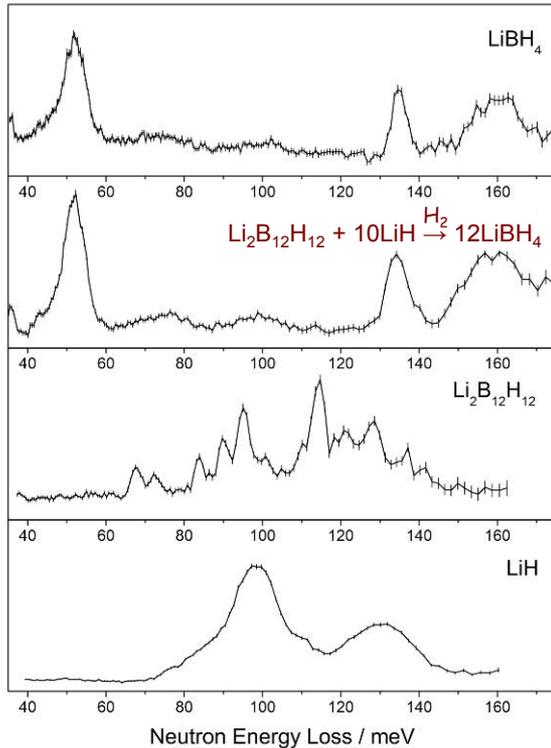
Neutron vibrational spectra are consistent with the observed and calculated structures.



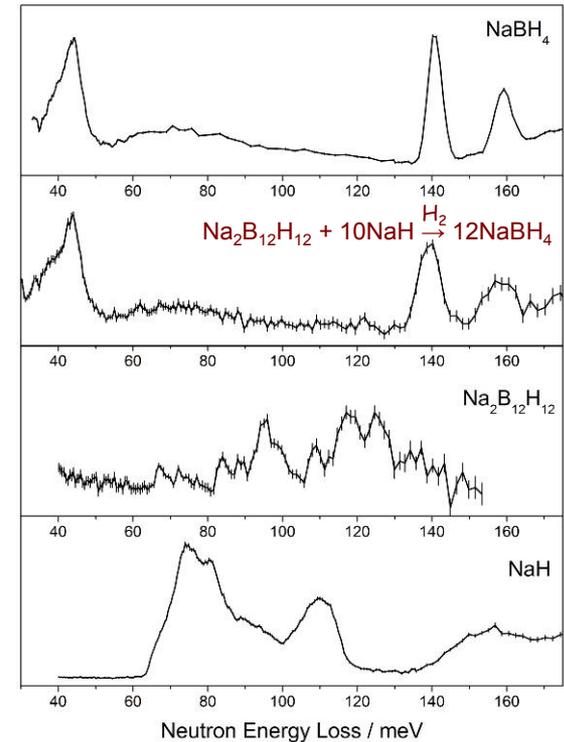
* Two other relevant $MB_{12}H_{12}$ structures were solved by XRD, NVS, and DFT.

Motivation: to investigate the hydrogenation behavior of $\text{A}_2\text{B}_{12}\text{H}_{12} + 10\text{AH}$ mixtures, intermediates in the cycling of alkali-metal borohydrides

NV spectral comparison of hydrogenated $\text{Li}_2\text{B}_{12}\text{H}_{12} + 10\text{LiH}$ and $\text{Na}_2\text{B}_{12}\text{H}_{12} + 10\text{NaH}$ mixtures with pure compounds



Hydrogenations of $\text{A}_2\text{B}_{12}\text{H}_{12} + 10\text{AH}$ mixtures were performed at 500°C and 90 MPa H_2 .



Comparison of NV spectra indicate that these hydrogenations produced the corresponding ABH_4 compounds.

* The hydrogenation of these intermediates is possible under the right conditions.

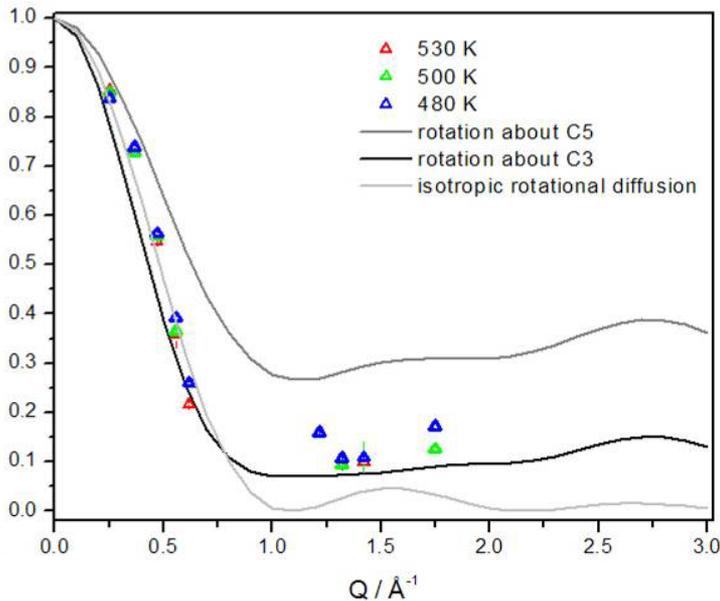
Technical Accomplishment

Collaboration with Sandia and Maryland

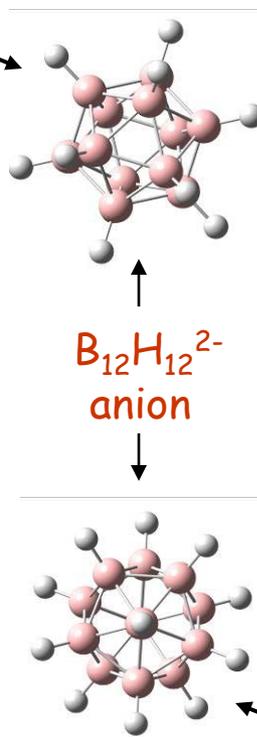
Motivation: to help characterize the dynamics of borohydride intermediates

Quasielastic neutron scattering (QENS) data for $Cs_2(^{11}B)_{12}H_{12}$ was measured near 500 K.

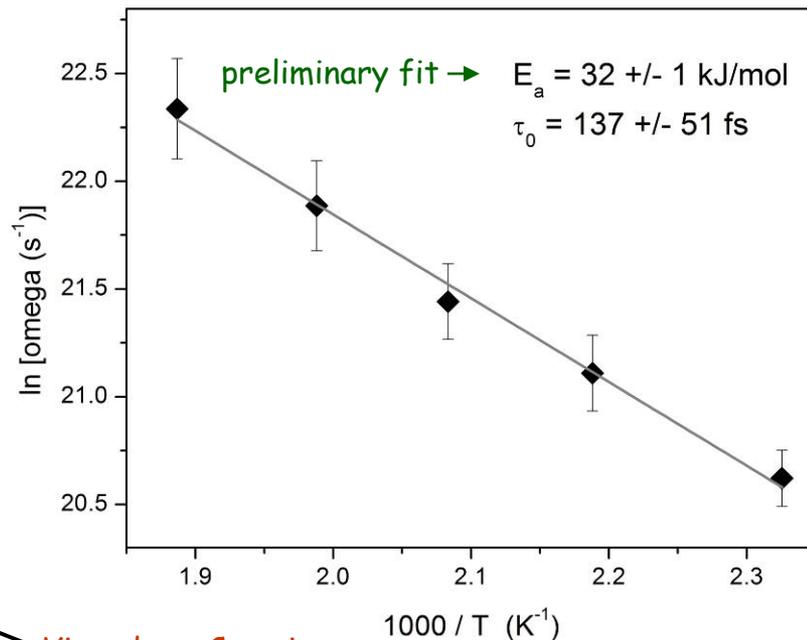
View down C_3 -axis



Comparison of QENS data for $Cs_2B_{12}H_{12}$ to different rotational models



Arrhenius plot for $[B_{12}H_{12}]^{2-}$ anion rotation from preliminary QENS data



View down C_5 -axis

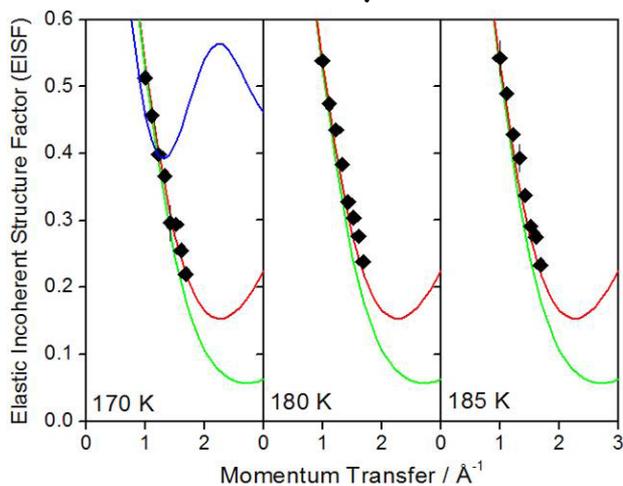
* QENS data suggest that the $[B_{12}H_{12}]^{2-}$ anion prefers C_3 -axial rotation near 500 K. 10

Technical Accomplishment

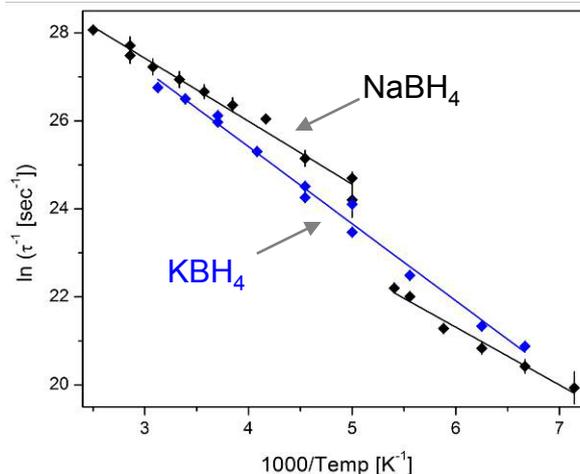
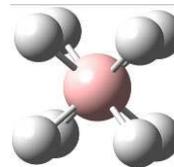
Collaboration with Maryland and Michigan

Motivation: to investigate BH_4^- rotational dynamics in light-metal borohydrides

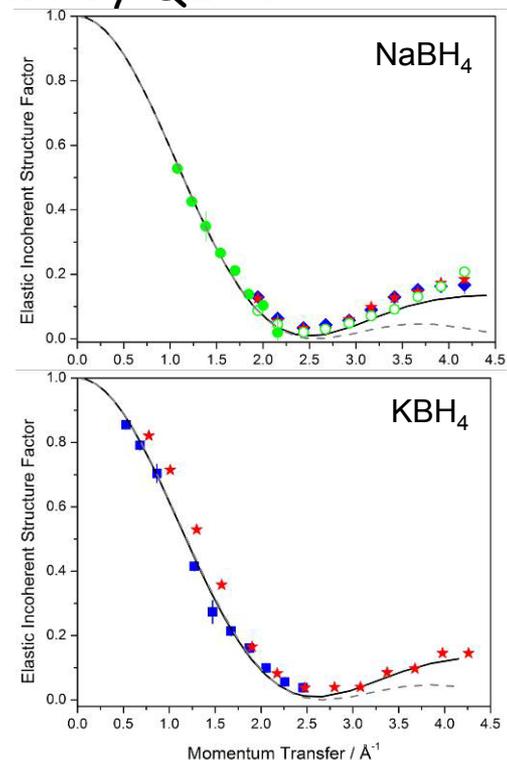
Rotational dynamics for NaBH_4 and KBH_4 were characterized by QENS



The BH_4^- hydrogen atoms in the high-T cubic phases reorient by jumping to the corner positions of a cube

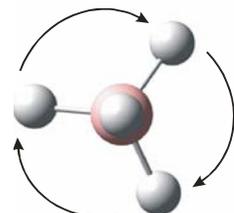
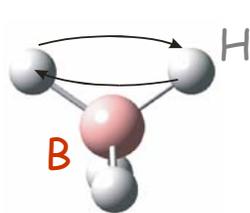


Activation energies determined from Arrhenius plots of quasielastic linewidths:
 13.4 ± 0.8 kJ/mol NaBH_4 (low-T phase)
 11.9 ± 0.5 kJ/mol NaBH_4 (high-T phase)
 14.6 ± 0.5 kJ/mol KBH_4 (high-T phase)



EISFs at different T compared to models for jumps along the C_4 -axes (solid line) and for isotropic rotational diffusion (dashed line)

QENS data for the low-T ordered phase of NaBH_4 , indicating BH_4^- rotations occur by a combination of two- and three-fold jumps



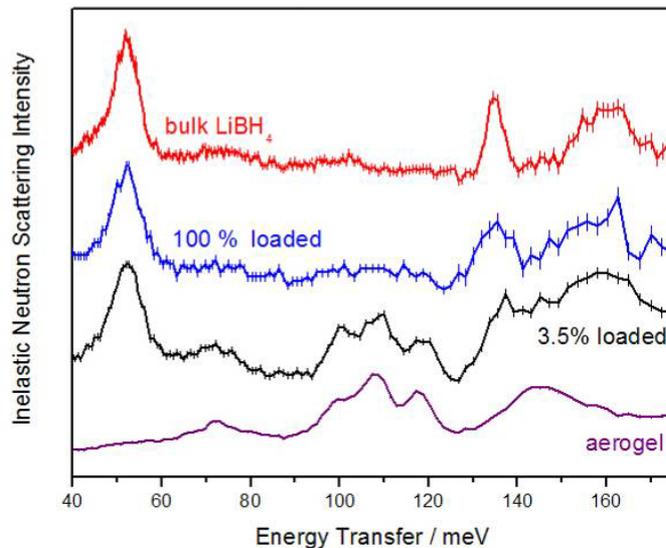
two-fold jumps

three-fold jumps

*The extended momentum transfer range is necessary to distinguish between different reorientational models.

Motivation: to characterize the properties of nanoconfined LiBH_4

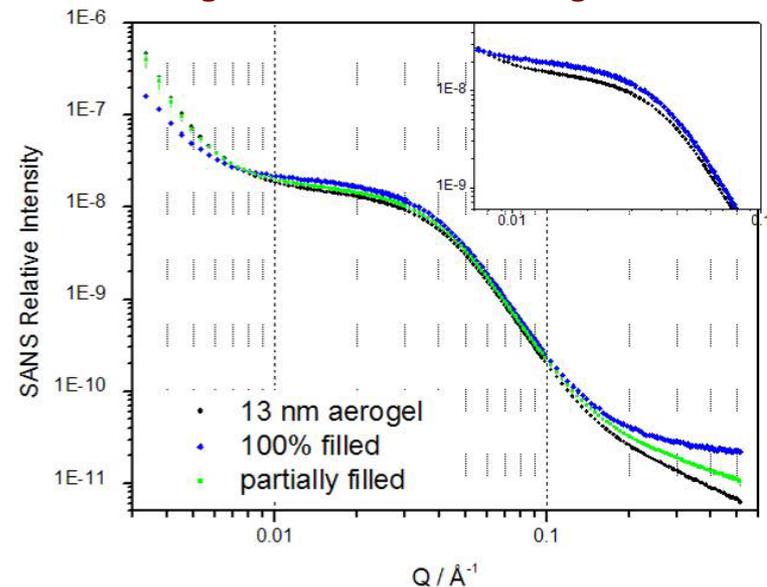
NV spectra of LiBH_4 in 13 nm carbon aerogels



LiBH_4 vibrational modes in the carbon aerogel exhibit a minor ($\sim 10\%$) broadening compared to bulk LiBH_4 modes

SANS suggests that the smallest pores fill first, and there is no change in apparent mesopore geometry with filling

Small-angle neutron scattering (SANS) data



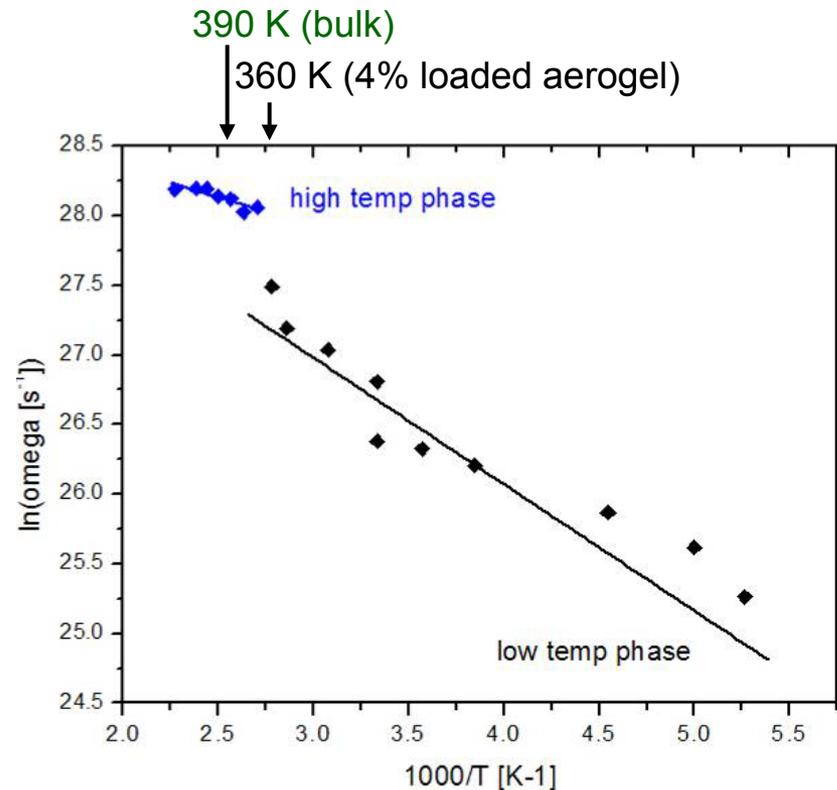
* We need to understand the relationship between pore morphology and filling behavior of nanoconfined storage materials.

Technical Accomplishment

Collaboration with HRL, Lawrence Livermore, Maryland, and Michigan

Motivation: to investigate borohydride dynamics perturbations in carbon aerogels

- Bulk LiBH_4 undergoes a phase transition at 390 K
- Under conditions of confinement, we observe indications of a phase transition at 360 K
- Low-temperature dynamics due to hydrogen reorientation appear on the nanosecond timescale at 200 K in the bulk and fully-loaded aerogel
- This temperature is decreased by 75 K in the partially-loaded carbon aerogel

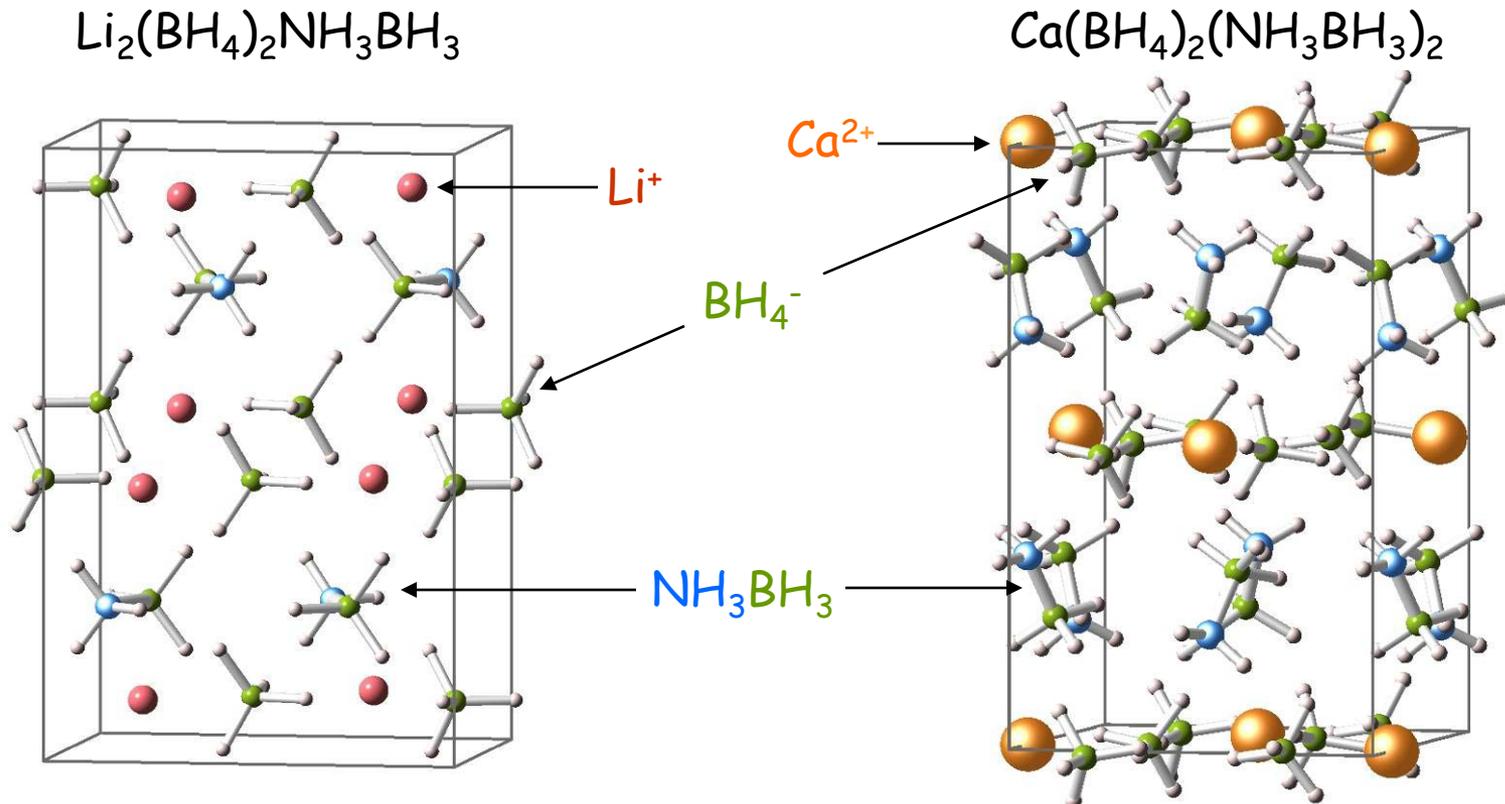


T dependence of BH_4^- rotational jump frequency for nanoconfined LiBH_4 (4% loading in carbon aerogel)

* Nanoconfinement appears to perturb the bulk thermodynamic properties

Motivation: to synthesize new compounds potentially promising for hydrogen storage

The structures of two new synthesized, mixed-anion complex hydrides were solved by XRD.

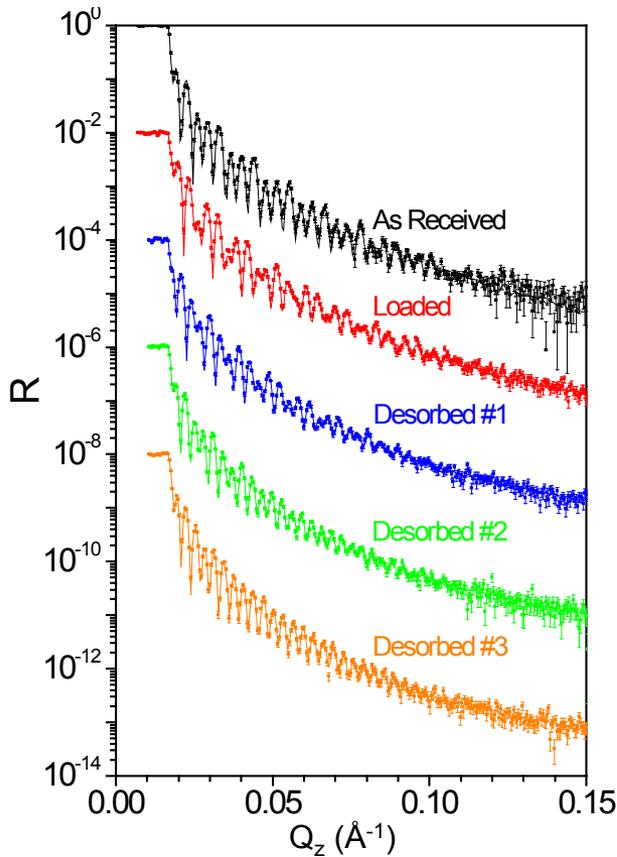


* The determination of the details of H_2 release is in progress.

Technical Accomplishment

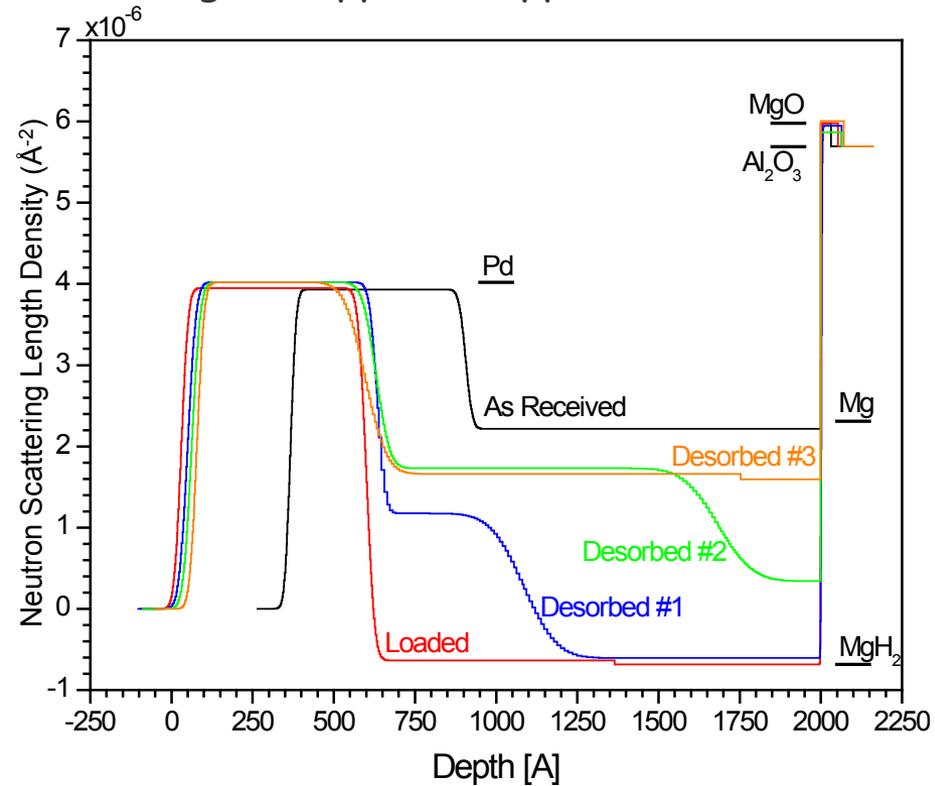
Collaboration with Stanford

Motivation: to probe the mechanisms of thin-film metal hydride cycling



Started with 100 nm Mg on sapphire capped with 50 nm Pd

Typical conditions:
 T ~ 70-100 C
 P ~ 0.1 MPa H₂



Neutron reflectivity (NR) data for hydrogenated and dehydrogenated Mg films on sapphire

Depth profiles for hydrogenated and dehydrogenated Mg films on sapphire

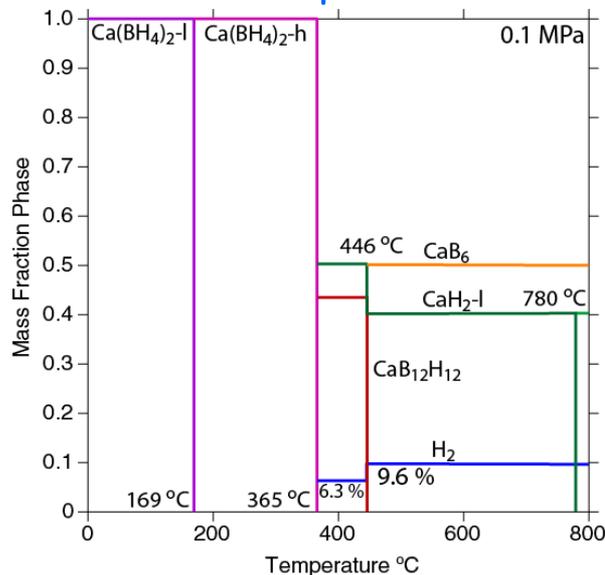
* NR data suggest porous Mg formation upon dehydrogenation of thin-film MgH₂

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

- Expanded database to include higher borane species in the gas-phase description.
- Expanded the modified Neumann-Kopp rule for the prediction of heat capacities for the hydro-*closo*-borates.
- Developed thermodynamic descriptions for Mg-B-H and Ca-B-H systems.

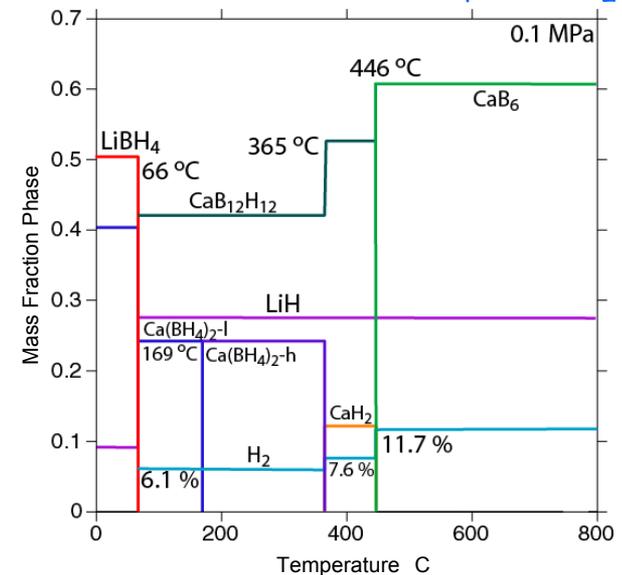
Results: Description of Ca-B-H



Reaction path of the dehydrogenation of $\text{Ca}(\text{BH}_4)_2$

In the original database, the higher-component compounds were not included, resulting in a predicted one-step dehydrogenation

Revised Reaction Path of $6 \text{LiBH}_4 + \text{CaH}_2$



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

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 complex hydrides

HRL (Industry/MHCoE): neutron measurements of aerogels and nanoconfined LiBH_4 ; cycling and kinetics studies and characterization of nanoconfined storage materials

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 storage materials

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

Michigan (Univ.): neutron measurements of 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 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 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 $\text{SrB}_{12}\text{H}_{12}$ and $\text{BaB}_{12}\text{H}_{12}$, heavier alkaline-earth analogs to $\text{MgB}_{12}\text{H}_{12}$, were solved by a combination of XRD, neutron vibrational spectroscopy (NVS), and DFT calculations.
- NVS measurements of amorphous, anhydrous $\text{MgB}_{12}\text{H}_{12}$ yield a vibrational density of states suggestive of the predicted stable crystalline structure.
- Quasielastic neutron scattering measurements of NaBH_4 , KBH_4 , and $\text{Cs}_2\text{B}_{12}\text{H}_{12}$ allowed us to characterize, in detail, the rotational dynamics of the corresponding BH_4^- and $\text{B}_{12}\text{H}_{12}^{2-}$ anions.
- NVS measurements of the direct high-pressure hydrogenation of $\text{Li}_2\text{B}_{12}\text{H}_{12} + \text{LiH}$ and $\text{Na}_2\text{B}_{12}\text{H}_{12} + \text{NaH}$ mixtures indicate the near complete formation of LiBH_4 and NaBH_4 , respectively.
- Small-angle neutron scattering measurements of partially LiBH_4 -loaded carbon aerogels are consistent with the preferential filling of smaller pores and/or surface film formation.
- The structures of two new synthesized, mixed-anion complex hydrides, $\text{Li}_2(\text{BH}_4)_2\text{NH}_3\text{BH}_3$ and $\text{Ca}(\text{BH}_4)_2(\text{NH}_3\text{BH}_3)_2$, were solved by XRD. The determination of the details of H_2 release is in progress.
- Neutron reflectometry of dehydrogenated MgH_2 thin films suggests the formation of porous Mg.
- Calphad thermodynamic descriptions were expanded to include higher borane gas-phase species and hydro-*closo*-borates.