

## IV.A.1k Neutron Characterization and Calphad in Support of the Metal Hydride Center of Excellence

Terrence J. Udovic (Primary Contact),  
Ursula R. Kattner  
National Institute of Standards and Technology (NIST)  
NIST Center for Neutron Research  
100 Bureau Dr., MS 6102  
Gaithersburg, MD 20899-6102  
Phone: (301) 975-6241; Fax: (301) 921-9847  
E-mail: udovic@nist.gov

DOE Technology Development Manager:  
Ned Stetson  
Phone: (202) 586-9995; Fax: (202) 586-9811  
E-mail: Ned.Stetson@ee.doe.gov

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### Objectives

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

### Technical Barriers

This project addresses the following technical barriers from the Storage section of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

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

### Technical Targets

We support the development of hydrogen-storage materials by providing timely, comprehensive characterization of Metal Hydride Center of Excellence (MHCoe)-developed materials and storage systems using state-of-the-art neutron methods and Calphad. This characterization helps speed the development and optimization of storage materials that can meet the following 2010 DOE hydrogen-storage system capacity targets:

- 6 wt% H
- 45 g H/l

### Accomplishments

Key accomplishments for Fiscal Year 2009 are listed in the following for hydrogen-storage materials of interest to the MHCoe: (For more details, see the Results section.)

- The structures of  $\text{Li}_2\text{B}_{12}\text{H}_{12}$ ,  $\text{Na}_2\text{B}_{12}\text{H}_{12}$ , and  $\text{CaB}_{12}\text{H}_{12}$  were solved by a combination of X-ray diffraction (XRD), neutron vibrational spectroscopy (NVS), and density functional theory (DFT) calculations.
- NVS and nuclear magnetic resonance (NMR) data hint at the formation of a new  $\text{Ca}(\text{AlH}_4)(\text{BH}_4)$  compound via ball-milling  $\text{LiBH}_4 + \text{LiAlH}_4 + \text{CaCl}_2$ .
- NVS and neutron prompt-gamma activation analysis (PGAA) indicate nontrivial amounts of  $\text{sp}^2$ -bonded residual H in carbon aerogels.
- Confined  $\text{Li}_3\text{BN}_2\text{H}_8$  in nanoporous carbon materials was shown to be partially reversible.
- Decreasing the filling of a 13 nm carbon aerogel with  $\text{LiBH}_4$  increased the fraction that exhibited non-bulk-like  $\text{BH}_4^-$  reorientational dynamics.
- Neutron imaging techniques were shown to provide in situ, real-time diagnostics of practical hydrogen-storage beds.
- Neutron reflectivity measurements were found to be sensitive to the hydrogen profile formed within a single thin-film Mg layer during hydrogen cycling.
- The thermodynamic Calphad database for Li-Mg-Ca-B-Si-N-H was expanded to include more gas phase species and ternary hydride phases.



### Introduction

In search of a hydrogen-storage medium that meets the DOE technical targets, the MHCoe has been investigating various materials, such as light-metal hydrides, borohydrides, and borohydride-amide mixtures. Moreover, considerable efforts have been focused on understanding the borohydrides' decomposition pathways in order to improve their hydrogen-cycling properties and enhance their reversibility. Using neutron-based probes, NIST has provided structural and/or spectroscopic

characterization of such materials as  $\text{RbMgH}_3$ ,  $\text{RbCaH}_3$ ,  $\text{NaBH}_4$ ,  $\text{KBH}_4$ ,  $\text{LiK}(\text{BH}_4)_2$ ,  $\text{Ca}(\text{BH}_4)_2$ ,  $\text{Ca}(\text{AlH}_4)(\text{BH}_4)$ ,  $\text{Li}_2\text{B}_{12}\text{H}_{12}$ ,  $\text{Na}_2\text{B}_{12}\text{H}_{12}$ ,  $\text{CaB}_{12}\text{H}_{12}$ ,  $\text{MgB}_{12}\text{H}_{12} \cdot x\text{H}_2\text{O}$  and both  $\text{LiBH}_4$  and  $\text{Li}_3\text{BN}_2\text{H}_8$  nanoconfined in carbon aerogels. Such detailed information is important for a more thorough understanding of these materials and their hydrogen-storage properties. In addition, neutron reflectometry has been used to characterize hydrogen-concentration profiles within light-metal thin films during hydrogen cycling in order to understand the fundamental hydrogen diffusion mechanisms during hydrogenation and dehydrogenation. Finally, the usefulness of neutron imaging techniques has been explored for obtaining in situ, real-time diagnostics of practical hydrogen-storage beds.

Calphad thermodynamic modeling provides critical assessments of hydrogen content, character and heats of reaction, and phase-reaction sequences during hydrogen charge-discharge cycling of MHCoe-developed metal-hydride systems. NIST has continued to update and expand the thermodynamic database, including the elements Li, Mg, Ca, B, Si, N, and H and their respective binary and ternary phases, for the Calphad modeling of metal-hydrogen systems. This database is being used to calculate the reactions in multi-component hydrogen systems. These results are the basis for the evaluation of dehydrogenation temperatures and pressures and the suitability of element additions for destabilization of the hydride phases.

## Approach

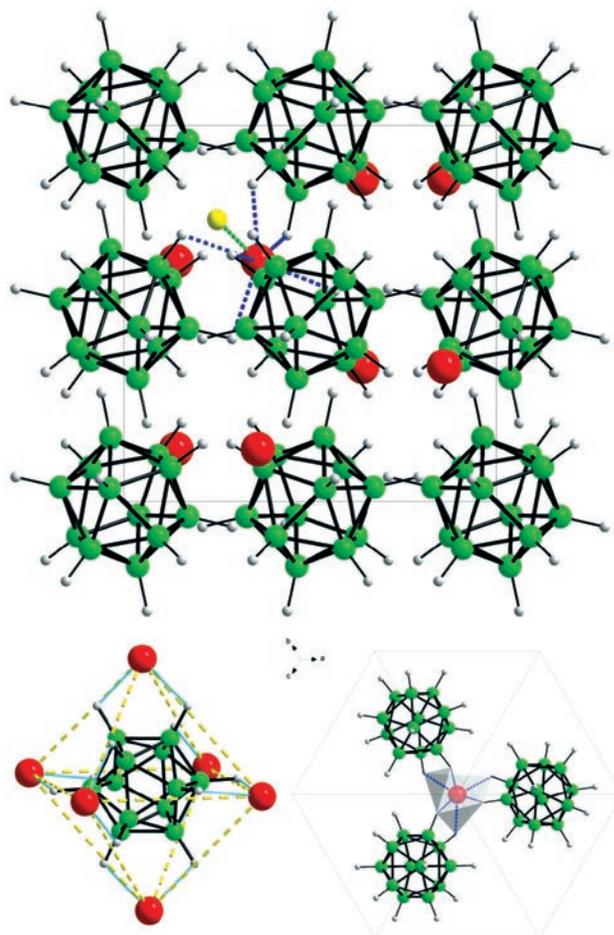
The key to improved hydrogen-storage materials is a detailed understanding of the atomic-scale locations and lattice interactions of the hydrogen. We are applying our state-of-the-art neutron measurement capabilities and expertise at the NIST Center for Neutron Research to the promising materials being developed by the MHCoe. This work enables MHCoe partners to obtain unique insights into the atomic- and molecular-scale properties that are responsible for the hydrogen-storage properties of these candidate materials.

In addition, we are performing Calphad thermodynamic modeling. The available literature is evaluated for thermodynamic data and analytical descriptions of the thermodynamic functions of the relevant phases. The data and functions are compiled into a consistent database describing the multi-component systems. Missing quantities are identified and descriptions are being developed in collaboration with MHCoe partners.

## Results

We have focused the majority of our neutron measurements on borohydride-based materials in order to provide structural and spectroscopic details where

lacking. For example, we have collaborated with Sandia National Laboratories (SNL), Jet Propulsion Laboratory (JPL), Caltech, Maryland, and Missouri-Columbia to investigate the structures and bonding in the alkali and alkaline-earth dodecahydro-*closo*-dodecaborates, which are possible intermediates in borohydride decomposition. The structures of  $\text{Li}_2\text{B}_{12}\text{H}_{12}$  (*Pa-3*),  $\text{Na}_2\text{B}_{12}\text{H}_{12}$  (*P2<sub>1</sub>/n*), and  $\text{CaB}_{12}\text{H}_{12}$  (*C2/c*), were solved by a combination of XRD, NVS, and DFT calculations. The vibrational density of states associated with the  $\text{B}_{12}\text{H}_{12}^{2-}$  anions proved to be sensitive to the crystal structure. For  $\text{Li}_2\text{B}_{12}\text{H}_{12}$  (see Figure 1) [1], the  $\text{Li}^+$  cation lies in a nearly trigonal planar site formed by three icosahedral  $\text{B}_{12}\text{H}_{12}^{2-}$  anions, each of which resides in the octahedral cage defined by six  $\text{Li}^+$  cations. Each  $\text{B}_{12}\text{H}_{12}^{2-}$  anion orients two H atoms to each of the  $\text{Li}^+$  cations, resulting in a strongly distorted octahedral coordination of the  $\text{Li}^+$  cation with six H atoms. For  $\text{Na}_2\text{B}_{12}\text{H}_{12}$  [2],

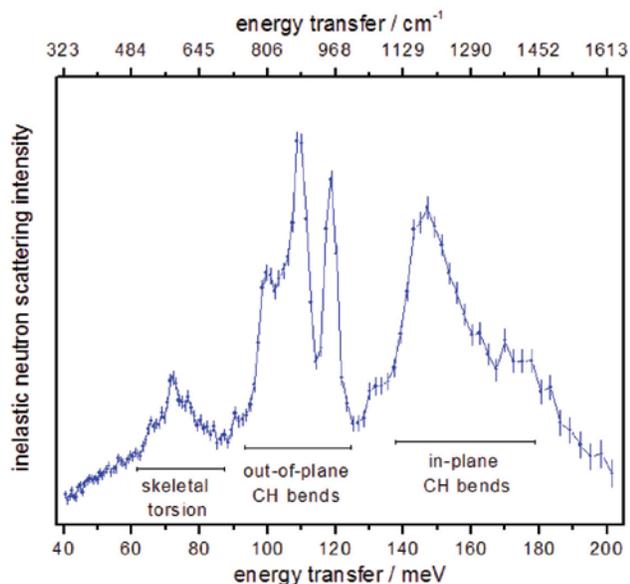


**FIGURE 1.** (top) The structure of  $\text{Li}_2\text{B}_{12}\text{H}_{12}$  viewed along the (100) direction. The  $\text{Li}^+$  cation position deviates from the ideal tetrahedral site (yellow ball) toward the near-trigonal-planar site along the body diagonal direction. (bottom left) Configuration of the six nearest  $\text{Li}^+$  cations around the  $\text{B}_{12}\text{H}_{12}^{2-}$  anion. (bottom right) Triangular arrangement of the  $\text{B}_{12}\text{H}_{12}^{2-}$  anions surrounding a  $\text{Li}^+$  cation. Li: red, B: green, H: silver.

each  $B_{12}H_{12}^{2-}$  anion is surrounded by eight  $Na^+$  cations, while each  $Na^+$  cation interacts with four near-neighbor  $B_{12}H_{12}^{2-}$  anions via nine H atoms. For  $CaB_{12}H_{12}$ , each  $Ca^{2+}$  cation is surrounded by five  $B_{12}H_{12}^{2-}$  anions. Three  $B_{12}H_{12}^{2-}$  anions form the triangular equatorial plane centered on each  $Ca^{2+}$  cation, while the other two  $B_{12}H_{12}^{2-}$  anions are located in axial positions. Each  $Ca^{2+}$  cation interacts with eight neighboring H atoms from the five  $B_{12}H_{12}^{2-}$  anions.

We have collaborated with SNL, JPL, Caltech, and Maryland to help characterize new MHCoe compounds such as novel borohydrides.  $Ca(AlH_4)(BH_4)$  was predicted to be a potentially stable compound. Its possible synthesis via ball-milling of  $LiAlH_4 + LiBH_4 + CaCl_2$  was studied by NVS and NMR. The resulting “amorphous” compound + LiCl indicated some spectroscopic similarities with  $Ca(AlH_4)_2$ ,  $Ca(BH_4)_2$ , and  $LiBH_4$ , but clear differences exist. It appears that longer ball-milling times may be required to complete the reaction. Proper interpretation requires DFT phonon calculations, which are in progress.

We have collaborated with HRL Laboratories, Lawrence Livermore National Laboratory (LLNL), and Maryland to investigate the amount and nature of hydrogen in carbon-aerogel nanoscaffold materials. NVS and PGAA indicate nontrivial amounts of residual H (approaching  $\sim 0.1$  H/C) in carbon aerogels, even after evacuation at 1,073 K. A typical spectrum (see Figure 2) reveals that the H is  $sp^2$ -bonded to edge carbons, presumably as in coronene. We need to understand the effect of this H on the nanostructure of the aerogel as well as on the measurements and cycling properties of nanoconfined storage materials.



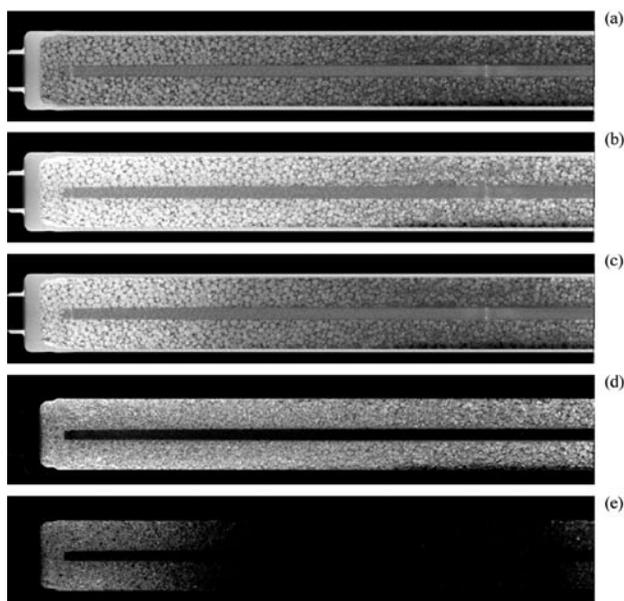
**FIGURE 2.** Typical Neutron Vibrational Spectrum of  $sp^2$ -Bonded Hydrogen in 13 nm Carbon Aerogel at 4 K

We have collaborated with HRL, General Motors, Maryland, and Pennsylvania to study the effect of nanoconfinement on the cycling properties of  $Li_3BN_2H_8$ , which is a mixture of  $(2/3)Li_4BN_3H_{10} + (1/3)LiBH_4$  with 11 wt% H and minimized  $NH_3$  formation [3]. In contrast to the irreversibility of  $Li_3BN_2H_8$  in bulk form, we have shown that its confinement in nanoporous carbon materials (*i.e.*, 13 nm carbon aerogel and 2 nm AX-21) renders it partially reversible. Moreover, a reduced desorption temperature occurs in the 2 nm AX-21 compared to in the 13 nm aerogel and in the bulk. Unfortunately, nanosequestration results in enhanced  $NH_3$  formation, compared to the bulk, during dehydrogenation.

We have collaborated with HRL, LLNL, Maryland, and Michigan to study the effect of  $LiBH_4$  fill fraction in carbon aerogels on  $BH_4^-$  dynamical properties. A comparison of  $LiBH_4$  in 13 nm carbon aerogels (4% and 100% filled) was undertaken by quasielastic neutron scattering. The data suggest that partially-filled samples exhibit an increased fraction of  $LiBH_4$  displaying faster, non-bulk-like  $BH_4^-$  reorientational dynamics. This may reflect preferential filling of smaller pores and/or surface film formation.

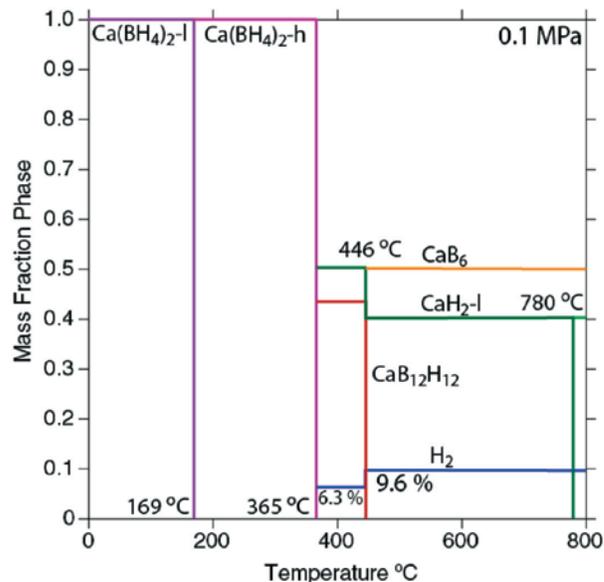
We have collaborated with JPL and Maryland to study the feasibility of using in situ neutron imaging techniques to map out the H distribution and transport in prototype hydrogen-storage beds, since such diagnostic tools are lacking. We simulated such a bed using an  $LaNi_{4.78}Sn_{0.22}$ -based hydride compressor element identical to those used on JPL's Planck Sorption Cryocooler [4]. The  $LaNi_{4.78}Sn_{0.22}$  powder was dispersed in a 10% dense Al foam in an annular bed geometry with an outer bed diameter of  $\approx 3$  cm. Hydrogen was added and removed through a central porous filter tube. Figure 3 displays some tomographic results using deuterium instead of hydrogen. Despite the non-uniform  $LaNi_{4.78}Sn_{0.22}$  powder distribution, the D content of the filled bed is rather uniform. During desorption,  $D_2$  preferentially escapes from the powder-depleted region, though this is likely due to the thermal control of the bed during desorption. (The heater does not reach to the end of the bed, and this cold region will be slower to desorb than the rest of the bed.) Such results confirm that the much lower total neutron cross section for D compared to H enables the probing of much thicker storage beds.

We have collaborated with Stanford and Maryland to help characterize hydrogen concentration profiles in thin Mg films. We have extended our measurements to a single (25 nm Pd-capped) 100 nm Mg layer on a sapphire substrate. Preliminary neutron reflectivity results before and after partially hydrogenating/dehydrogenating the Mg layer to different degrees indicate that the instrument is fully capable of determining the hydrogen profile through such a layer.



**FIGURE 3.** Sagittal slices through the tomographic reconstructions of the  $\text{LaNi}_{4.78}\text{Sn}_{0.22}$ -based hydrogen-storage bed. The total attenuation coefficients of (a) the empty bed, (b) the bed filled with 100 L of  $\text{D}_2$ , and (c) the bed after desorbing about 60 L of  $\text{D}_2$ . In these images, black and white correspond to an attenuation coefficient of  $0 \text{ cm}^{-1}$  and  $1.0 \text{ cm}^{-1}$ , respectively. The large, open pore structure of the aluminum foam is clearly visible. Subtracting the empty bed attenuation coefficient yields the D content of the bed, which is shown in (d) after full absorption of about 100 L and (e) after desorption of about 60 L of  $\text{D}_2$ .

The thermodynamic Calphad database has been updated and expanded. The original version of the thermodynamic database had six borane species in the gas phase. However, more borane gas-phase species are known to exist, and their thermodynamic description should be included in the database for accurate calculations of the gas phase. Thermodynamic quantities for 16 additional borane species were found in a literature search, and the thermodynamic functions for these species were evaluated and added to the database. Calculations with this expanded database showed that significant borane amounts occur only if no condensed phases with boron are present. The database has been further expanded to include descriptions for the solid phases  $\text{Ca}(\text{BH}_4)_2$  (two polymorphs),  $\text{CaB}_{12}\text{H}_{12}$ ,  $\text{Mg}(\text{BH}_4)_2$ , and amorphous boron. Experimental thermochemical data for amorphous boron were found in the literature and used for the development of the thermodynamic function. Experimental data for the ternary hydride phases are extremely sparse. Experimental data are available for the transformation temperature of the  $\text{Ca}(\text{BH}_4)_2$  polymorphs and for the decomposition of the ternary hydride phases. For developing the thermodynamic descriptions of these phases, data from first-principles calculations provided by members of the Theory Group were used



**FIGURE 4.** Dehydrogenation Path of  $\text{Ca}(\text{BH}_4)_2$  from Calculations using the Calphad Database

to supplement the experimental data. When available, heat capacity data were used from first-principles calculations. Otherwise, the heat capacity was obtained from the previously developed modification of the Neumann-Kopp rule. The phase descriptions were refined by adjusting them to the available reaction enthalpies and temperatures. The dehydrogenation path of  $\text{Ca}(\text{BH}_4)_2$  is depicted in Figure 4. The path shows that the dehydrogenation occurs in two steps and that no solid elemental phases are formed during the dehydrogenation. Solid elemental phases, such as Ca, have a significant solubility for hydrogen and, therefore, can lower the amount of available hydrogen. The calculation also showed that the borane concentrations in the gas phase after dehydrogenation of the ternary phases is extremely small ( $<10^{-8} \%$ ).

## Conclusions and Future Directions

- Neutron methods and Calphad computations have provided crucial, non-destructive characterization and predictive tools for the MHCoe. We will continue these primary tasks in support of other MHCoe members.
- X-ray and neutron powder diffraction, neutron spectroscopy, and first-principles calculations provided a powerful combination for characterizing the structures and bonding of the dodecahydro-closo-dodecaborates. Spectroscopy was particularly useful to test predicted structures, even for “amorphous” samples. Work is still in progress to synthesize and characterize crystalline  $\text{MgB}_{12}\text{H}_{12}$ .

- We will continue to pursue the synthesis and characterization of a possible new hydrogen-storage compound,  $\text{Ca}(\text{AlH}_4)(\text{BH}_4)$ .
  - We will continue to investigate the importance of residual H in carbon aerogels on aerogel morphology and hydrogen cycling properties of nanosequestered storage materials by varying the aerogel pretreatment temperatures.
  - We will extend our studies of  $\text{Li}_3\text{BN}_2\text{H}_8$  and similar materials in nanoporous carbons by investigating the role of catalyst dopants on hydrogen cycling kinetics, reversibility, and  $\text{NH}_3$  formation.
  - We will continue to investigate the relationship between fill fraction and  $\text{BH}_4^-$  reorientational dynamics for  $\text{LiBH}_4$  and  $\text{NaBH}_4$  nanosequestered in carbon aerogels.
  - Feasibility studies of in situ neutron imaging of the H and D distribution and transport in a  $\text{LaNi}_{4.78}\text{Sn}_{0.22}$ -based hydrogen-storage bed proved to be highly successful. This technique should greatly benefit the Engineering Center of Excellence to study prototype storage beds.
  - Neutron reflectivity was shown to be sensitive to the hydrogen density profile associated with a single, Pd-capped, 100 nm Mg layer on sapphire during the different stages of hydrogen cycling. Detailed analysis of the reflectivity data is in progress.
  - The thermodynamic database for Li-Mg-Ca-B-Si-N-H has been expanded to include more gas phase species, amorphous boron, and ternary hydride phases.
  - We will continue to expand the database to include more ternary hydride phase descriptions, e.g.,  $\text{MgB}_{12}\text{H}_{12}$ , in collaboration with MHCoe partners.
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  15. U.R. Kattner, "Thermodynamics of Reactions in Metal-Hydrogen Systems," Materials Science and Technology '08, Pittsburgh, PA, Oct. 2008.
  16. M. Yousufuddin, "Neutron Diffraction Studies of Hydrogen Storage Materials," University of Texas at Arlington, Arlington, TX, Oct. 2008.

## Special Recognitions

1. J.-H. Her was awarded 1<sup>st</sup> place in the 16<sup>th</sup> annual Postdoctoral Poster Competition sponsored by the NIST chapter of Sigma Xi, Gaithersburg, MD, Feb. 2009.

## FY 2009 Publications/Presentations

1. J.-H. Her, M. Yousufuddin, W. Zhou, S.S. Jalisatgi, J.G. Kulleck, J.A. Zan, S.-J. Hwang, R.C. Bowman, Jr., and T.J. Udovic, "Crystal Structure of  $\text{Li}_2\text{B}_{12}\text{H}_{12}$ : a Possible Intermediate Species in the Decomposition of  $\text{LiBH}_4$ ," *Inorg. Chem.* **47**, 9757 (2008).
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19. J.-H. Her, Y. Liu, C.M. Brown, M. Yousufuddin, T.J. Udovic, D.A. Neumann, A. Dailly, S.S. Kaye, J.R. Long, and S.S. Jalisatgi, "Structural Studies on Various Hydrogen Storage Materials: MIL-53,  $K_2Zn_3[Fe(CN)_6]_2$  and  $Li_2B_{12}H_{12}$ ," 16<sup>th</sup> annual Postdoctoral Poster Competition sponsored by the NIST chapter of Sigma Xi, Gaithersburg, MD, Feb. 2009.
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22. J.-H. Her, "Powder Diffraction Studies for Hydrogen-Storage Materials," Korea Atomic Energy Research Institute, Daejeon, Korea, Jul. 2009.
23. J.-H. Her, V. Stavila, M. Yousufuddin, W. Zhou, S.S. Jalisatgi, E. Rönnebro, C.M. Brown, T.J. Udovic, "Crystal Structures of  $M_nB_{12}H_{12}$  ( $n=1,2$ ) Compounds – Possible Intermediate Species in the Decomposition of  $M_n(BH_4)_2$ ," 2009 American Crystallographic Association Meeting, Toronto, Canada, Jul. 2009.
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25. J.-H. Her, W. Zhou, V. Stavila, C.M. Brown, T.J. Udovic, "Crystal Structure of  $Na_2B_{12}H_{12}$  and the Role of Cation Size on the Structural Behavior of the Alkali-metal Dodecahydro-closo-dodecaborates," 238<sup>th</sup> American Chemical Society National Meeting, Washington, D.C., Aug. 2009.

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