

## IV.A.9 Neutron Characterization in Support of the DOE Hydrogen Storage Sub-Program

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Project Start Date: June 2010  
Project End Date: Project continuation and  
direction determined annually by DOE.

- Specific energy: 1.5 kWh/kg
- Energy density: 0.9 kWh/L
- Cost: \$4/kWh net

### FY 2011 Accomplishments

- Uptake, neutron powder diffraction (NPD), and neutron vibrational spectroscopy (NVS) measurements of H<sub>2</sub> in Fe-MOF-74 indicate even closer contacts between H<sub>2</sub> molecules compared to other MOF-74 variants.
- Robust yet low uptakes of H<sub>2</sub> in model zeolite compounds were characterized by NPD and NVS, marking the first time that H<sub>2</sub> adsorption sites were identified in a zeolite.
- Surfaces areas of synthesized amorphous metal-organic gels were found to be comparable to those of crystalline parent materials.
- NVS measurements of spillover hydrogen on activated carbons indicate excess-hydrogen modes at room temperature.
- The structure of the newly synthesized mixed-metal amidoborane Na<sub>2</sub>Mg(NH<sub>2</sub>BH<sub>3</sub>)<sub>4</sub> was solved by X-ray diffraction (XRD), characterized by NVS, and found able to release 8.4 wt% hydrogen with significantly less toxic gases.
- NVS measurements of novel complex borohydrides NaB<sub>3</sub>H<sub>8</sub>, NH<sub>4</sub>B<sub>3</sub>H<sub>8</sub>, and NH<sub>3</sub>B<sub>3</sub>H<sub>7</sub> indicated only limited agreement with density functional theory (DFT) phonon calculations, suggesting that the DFT descriptions of the bonding interactions need to be improved.
- Quasielastic neutron scattering (QENS) measurements of Cs<sub>2</sub>B<sub>12</sub>H<sub>12</sub> allowed us to characterize, in detail, the rotational dynamics of the B<sub>12</sub>H<sub>12</sub><sup>2-</sup> anions, a by-product of borohydride dehydrogenation.
- QENS and NVS measurements of LiBH<sub>4</sub> sequestered in 2-nm-pore carbon scaffolds indicated that the LiBH<sub>4</sub> is disordered and exhibits significant non-bulk-like behavior with respect to BH<sub>4</sub><sup>-</sup> rotational dynamics.

### Fiscal Year (FY) 2011 Objectives

- Support the DOE-funded hydrogen storage projects by providing timely, comprehensive characterization of materials and storage systems using state-of-the-art neutron methods.
- Direct partner synthesis efforts based on the understanding gained through the use of these methods.
- Demonstrate the fundamental characteristics of useful hydrogen storage materials.

### Technical Barriers

This project addresses the following technical barriers from the Storage section (3.3) of the Fuel Cell 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

NIST provides important materials metrologies for Center partners using neutron-scattering measurements to understand and characterize hydrogen-substrate interactions of interest in a variety of materials ranging from H<sub>2</sub> adsorbed in nanoporous materials to H chemically bonded in complex-hydride materials. Insights gained from these studies will be applied toward the design and synthesis of hydrogen storage materials that meet the following DOE 2011 storage targets:



### Introduction

To obtain the DOE levels of hydrogen storage in a timely manner, it is imperative that trial-and-error testing of materials be avoided. Thus, the focus must be upon the rational design of new systems. From a thorough understanding of the physics and chemistry that governs the hydrogen-substrate interactions, we will be able to make a more concerted effort to push the frontiers of new materials.

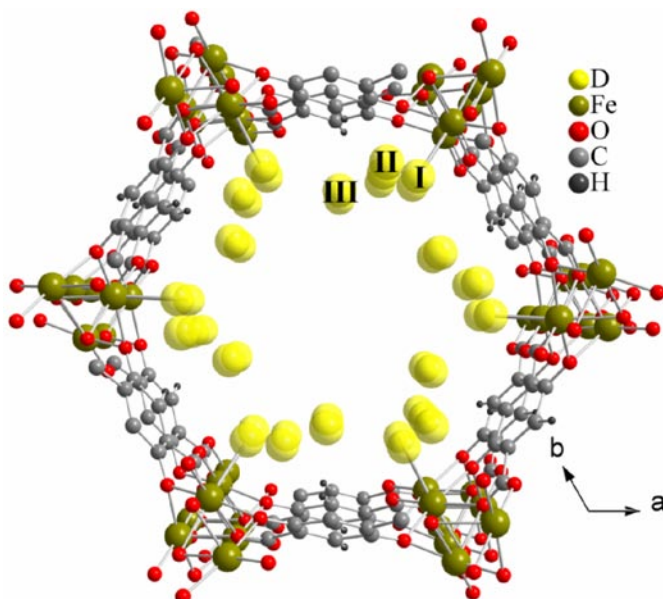
The key to improving materials is a detailed understanding of the atomic-scale locations of the hydrogen and determining how it gets there and how it gets out. Neutron scattering is perhaps the premier technique for studying hydrogen and the NIST Center for Neutron Research is currently the leading facility in the U.S. for studying these materials.

## Approach

NIST provides important materials characterization for DOE-funded, hydrogen storage sub-program partners using neutron-scattering measurements to probe the amount, location, bonding states, dynamics, and morphological aspects of (i) molecular hydrogen in carbon-based materials such as polymers, metal organic frameworks (MOFs), and carbonaceous materials such as carbon nanohorns, and (ii) atomic hydrogen in a variety of complex hydride materials including those containing boron and nitrogen, as well as their intermediates and by-products. NIST works directly with DOE and other partners that produce novel hydrogen storage materials to analyze the most promising samples and to help determine and resolve the fundamental issues that need to be addressed.

## Results

MOFs have recently come under intense investigation for gas storage and separation applications, owing to their high internal surface areas, convenient modular synthesis, and chemical tenability. Previously, we have reported a number of MOFs in which removal of a solvent molecule from the coordination sphere of the framework metal cations yielded strong adsorption sites for H<sub>2</sub>. One possibility for improving the isosteric heat of adsorption within this structure type would be through constructing the structure with M<sup>2+</sup> cations having a smaller radius. The greater charge density of the exposed metal cations on the framework surface should then be more effective at inducing a dipole in H<sub>2</sub>, leading to stronger binding. In collaboration with University of California, Berkeley, the M<sup>2+</sup>-MOF-74 (M<sup>2+</sup>=Mg, Co, Ni, Zn) series of MOFs was extended to include Fe-MOF-74. With a high surface area measured at 1,300 m<sup>2</sup>/g, and five-fold coordinated metal ions decorating the inside of the one-dimensional hexagonal pores, we have expanded the family as well as allowed ourselves to probe the extent of hydrogen interactions with the system incorporating magnetic ions. Neutron diffraction reveals three different adsorption sites as a function of increased loading (see Figure 1). The D<sub>2</sub>-Fe<sup>2+</sup> interaction is characterized by a relatively close 2.46 Å distance, with the higher loading sites interacting at a short van der Waals distance of 3.22 Å to 3.24 Å. This results in even closer contacts between hydrogen molecules, providing a very dense monolayer packing in the pore with inter-molecular distances from 2.86 Å to 3.07 Å. Further studies are ongoing.

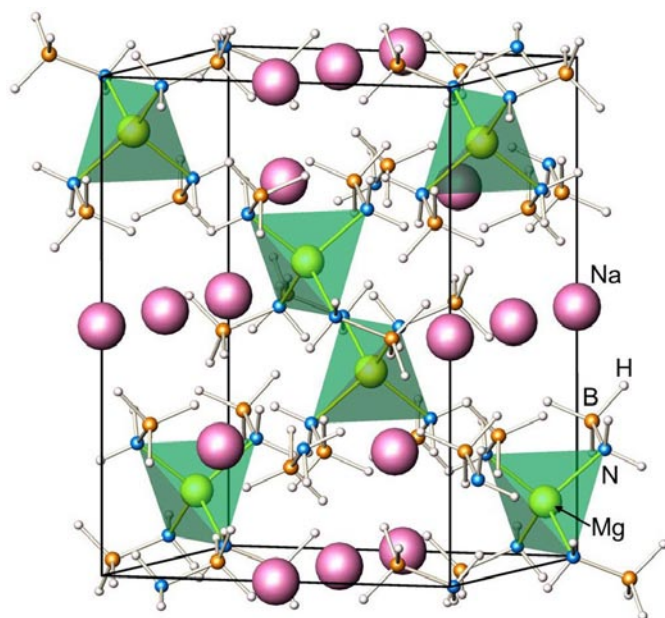


**FIGURE 1.** Neutron Diffraction Allows the Identification of Three Different D<sub>2</sub> Adsorption Sites in Fe-MOF-74

In collaboration with University of Maryland and University of Delaware, NPD and NVS measurements of hydrogen adsorption in Cu-SSZ-13 zeolite located two binding sites, one at the 8-member ring window and another near the Cu<sup>2+</sup> cation. The Cu<sup>2+</sup> site is not occupied at low hydrogen loadings but fully occupied at moderate pressures. The H<sub>2</sub> adsorption for the Cu<sup>2+</sup>-exchanged zeolite is enhanced (by ≈4% at 1 bar) over H-SSZ-13 due to the extra Cu<sup>2+</sup> binding sites. At 77 K and 1 bar, the mass ratios of adsorbed H<sub>2</sub>/zeolite for H-SSZ-13 and Cu-SSZ-13 are relatively low, 1.38 g/kg and 1.48 g/kg, respectively.

In collaboration with Lawrence Livermore National Laboratory, we additionally attempted to synthesis amorphous MOF gels in an effort to further increase MOF surface areas and micropore volumes. Reaction of iron nitrate and benzenetricarboxylic acid in ethanol produced the desired short-range-ordered material, but with a low surface area of 280 m<sup>2</sup>/g. The surface area increased to 510 m<sup>2</sup>/g after annealing to 120°C, and was further improved to 1,300 m<sup>2</sup>/g upon drying in supercritical CO<sub>2</sub>. This is still a relative low surface area and would need to be improved upon. For this material, the increasing surface area is not reflected in the hydrogen uptake increases expected and speculate that the access for hydrogen is unhindered relative to nitrogen.

In collaboration with University of Maryland and General Motors, the first example of a mixed-metal amidoborane Na<sub>2</sub>Mg(NH<sub>2</sub>BH<sub>3</sub>)<sub>4</sub> was successfully synthesized, and its structure (Figure 2) and bonding were characterized by XRD and NVS [1]. It forms an ordered arrangement in cation coordinations, i.e., Mg<sup>2+</sup> bonds solely to N<sup>-</sup> and Na<sup>+</sup> coordinates only with BH<sub>3</sub><sup>-</sup>. Compared

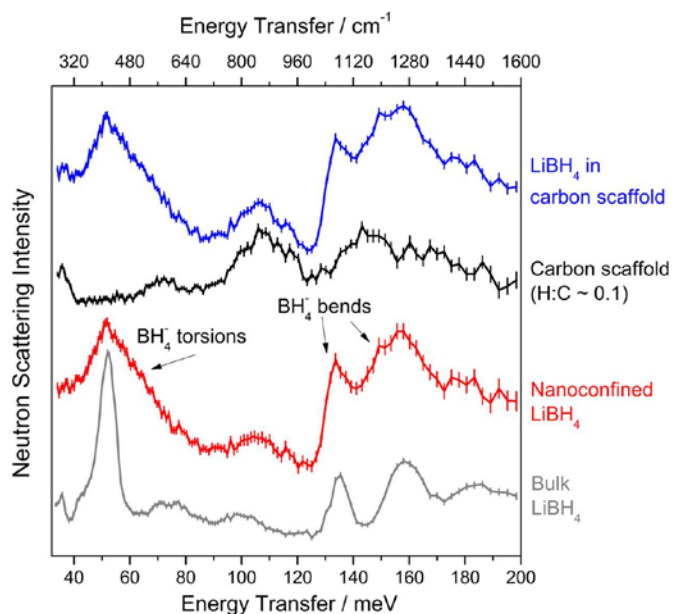


**FIGURE 2.** The Structure of  $\text{Na}_2\text{Mg}(\text{NH}_2\text{BH}_3)_4$

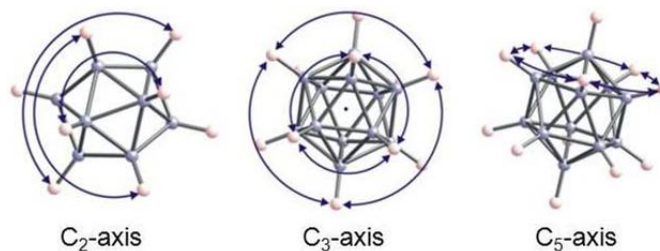
to ammonia borane and monometallic amidoboranes,  $\text{Na}_2\text{Mg}(\text{NH}_2\text{BH}_3)_4$  can release 8.4 wt% hydrogen with significantly less toxic gases, such as ammonia and borazine, and no detectable diborane. This study suggests that hydrogen-release properties of amidoboranes can be rationally and significantly improved by tuning the atomic interactions and thus producing more desired structures through the formation of mixed-metal amidoboranes.

In collaboration with Ohio State University, we used NVS to characterize the bonding associated with the novel lightweight borohydride materials  $\text{NaB}_5\text{H}_8$ ,  $\text{NH}_4\text{B}_3\text{H}_8$ , and  $\text{NH}_5\text{B}_3\text{H}_7$ . The limited agreement between the vibrational spectra and DFT phonon calculations suggested that the DFT descriptions of some weak bonding interactions present may be somewhat lacking. This reinforces the reality that there is a need to develop more accurate DFT descriptions of weak bonding potentials, such as associated with hydrogen-bonding interactions.

In collaboration with University Missouri-St. Louis, a comparison was made between  $\text{LiBH}_4$  sequestered inside 2 nm ordered pores of a carbon scaffold [2] and bulk  $\text{LiBH}_4$ . Using QENS, the relative mean square displacement of H atoms determined from a neutron fixed-window scan shows that the onset of  $\text{BH}_4^-$  rotational motion occurs  $\sim 100$  K lower for the nanoconfined material than for bulk  $\text{LiBH}_4$ . From NVS measurements (Figure 3), it is clear that the nanoconfined  $\text{LiBH}_4$  exhibits a much broader  $\text{BH}_4^-$  torsion peak (at 52 meV or  $419\text{ cm}^{-1}$ ) compared with bulk  $\text{LiBH}_4$ . In contrast, the  $\text{BH}_4^-$  bending modes are little perturbed by nanoconfinement. Hence, although the bending modes are fairly insensitive to near-neighbor interactions, NVS indicates a large inhomogeneity in the rotational potentials experienced by the nanoconfined  $\text{LiBH}_4$ . Overall, compared



**FIGURE 3.** NV spectra of nano-sequestered  $\text{LiBH}_4$  + carbon scaffold (with 2 nm pores), the corresponding bare carbon scaffold, and bulk  $\text{LiBH}_4$ . The spectrum of the nano-sequestered  $\text{LiBH}_4$  with the carbon scaffold spectrum subtracted is also shown.



**FIGURE 4.** Possible Rotational Jumps of the  $\text{B}_{12}\text{H}_{12}^{2-}$  Anion with Respect to its Local Axes of Symmetry

to prior results using carbon scaffolds with pores larger than 4 nm, nanoconfinement in the smaller 2 nm pores appears to more dramatically perturb the bulk thermodynamic properties of  $\text{LiBH}_4$ .

In collaboration with Sandia National Laboratories and University of Maryland, we used QENS to investigate the rotational dynamics of  $\text{B}_{12}\text{H}_{12}^{2-}$  anions (Figure 4), which are by-products of borohydride dehydrogenation. Elastic incoherent structure factor data for the prototypical  $\text{Cs}_2(^{11}\text{B})_{12}\text{H}_{12}$  were measured from 430 K to 530 K [3], suggesting that the  $\text{B}_{12}\text{H}_{12}^{2-}$  anion (encaged in a cube defined by eight  $\text{Cs}^+$  cations) changes from uniaxial ( $\text{C}_3$ -axis or  $\text{C}_5$ -axis) rotational jumps near 430 K to a combined mechanism involving, on average, independent two-axis ( $\text{C}_3$ -axis and/or  $\text{C}_5$ -axis) rotational jumps between 480 K and 530 K. Alternatively, if one assumes that the anions are undergoing temperature-dependent rotational trapping, then

the elastic incoherent structure factor is also consistent with a jump model involving a temperature-dependent mobile fraction of anions statistically tumbling between discrete crystallographic sites.

## Conclusions and Future Directions

- Neutron methods have provided crucial, non-destructive characterization tools for the DOE Hydrogen Storage sub-program.
- Fe-MOF-74 behaved similarly to other MOF-74 variants with respect to H<sub>2</sub> adsorption sites, with a relatively closer H<sub>2</sub>-M<sup>2+</sup> distance compared to other larger-cation variants.
- The observed H<sub>2</sub>-Cu<sup>2+</sup> interactions in Cu-SSZ-13 zeolite illustrate the need to better understand the relationship between accessible ions and hydrogen-storage characteristics in porous storage materials.
- The specific surface areas of synthesized amorphous metal-organic gels could not be enhanced relative to their crystalline parent materials.
- We synthesized the first mixed-metal amidoborane, one of a class of tailored compounds that may potentially have more favorable cycling behavior for hydrogen storage.
- The limited agreement between DFT phonon calculations and NV spectra for novel borohydride compounds reflects the need for better DFT descriptions of weak bonding interactions.
- We continued to characterize various aspects of nanoconfinement in an attempt to understand its effect on the hydrogen cycling of LiBH<sub>4</sub> and indeed observed more pronounced non-bulk-like effects as the pore size was decreased to 2 nm.
- We characterized the rotational dynamics of B<sub>12</sub>H<sub>12</sub><sup>2-</sup> anions in the prototypical Cs<sub>2</sub>B<sub>12</sub>H<sub>12</sub> compound. Ongoing work will investigate the dynamics of this anion in the lighter alkali-metal variants, Li<sub>2</sub>B<sub>12</sub>H<sub>12</sub> and Na<sub>2</sub>B<sub>12</sub>H<sub>12</sub>.
- We will continue to support the DOE Hydrogen Storage sub-program where needed.

## FY 2011 Publications/Presentations

1. N. Verdál, W. Zhou, V. Stavila, J.-H. Her, M. Yousufuddin, T. Yildirim, and T.J. Udovic, "Alkali and Alkaline-Earth Metal Dodecahydro-*Closo*-Dodecaborates: Probing Structural Variations via Neutron Vibrational Spectroscopy," *J. Alloys Compd.* (in press 2011).
2. K. Sumida, C.M. Brown, Z.R. Herm, S. Chavan, S. Bordiga, and J.R. Long, "Hydrogen Storage Properties and Neutron Diffraction Studies of Mg<sub>2</sub>(2,5-dioxido-1,4-benzenedicarboxylate)," *Chem. Commun.* 47, 1157 (2011).
3. V.K. Peterson, C.M. Brown, Y. Liu, and C. Kepert, "Structural Study of D<sub>2</sub> within the Trimodal Pore System of a Metal Organic Framework," *J. Phys. Chem. C* 115, 8851 (2011).

4. N. Verdál, T.J. Udovic, J.J. Rush, R. Cappelletti, and W. Zhou, "Reorientational Dynamics of the Dodecahydro-*Closo*-Dodecaborate Anion in Cs<sub>2</sub>B<sub>12</sub>H<sub>12</sub>," *J. Phys. Chem. A* 115, 2933 (2011).
5. S. Gadipelli, J. Ford, W. Zhou, H. Wu, T.J. Udovic, and T. Yildirim, "Nanoconfinement and Catalytic Dehydrogenation of Ammonia Borane by Magnesium-Metal-Organic Framework-74," *Chem. Eur. J.* 17, 6043 (2011).
6. J.A. Dura, S.T. Kelly, P.A. Kienzle, J.-H. Her, T.J. Udovic, C.F. Majkrzak, C.-J. Chung, and B. Clemens, "Porous Mg Formation upon Dehydrogenation of MgH<sub>2</sub> Thin Films," *J. Appl. Phys.* 109, 093501 (2011).
7. K. Sumida, J.-H. Her, M. Dinca, L.J. Murray, J.M. Schloss, C.J. Pierce, B.A. Thompson, S.A. FitzGerald, C.M. Brown, and J.R. Long, "Neutron Scattering and Spectroscopic Studies of Hydrogen Adsorption in Cr<sub>3</sub>(BTC)<sub>2</sub> - A Metal-Organic Framework with Exposed Cr<sup>2+</sup> Sites," *J. Phys. Chem. C* 115, 8414 (2011).
8. Y. Yang, C.M. Brown, C. Zhao, A.L. Chaffee, B. Nick, D. Zhao, P.A. Webley, J. Schalch, J.M. Simmons, Y. Liu, J.-H. Her, C.E. Buckley and D.A. Sheppard, "Micro-Channel Development and Hydrogen Adsorption Properties in Templated Microporous Carbons Containing Platinum Nanoparticles," *Carbon* 49, 1305 (2011).
9. H. Wu, W. Zhou, F.E. Pinkerton, M.S. Meyer, Q. Yao, S. Gadipelli, T.J. Udovic, T. Yildirim, and J.J. Rush, "Sodium Magnesium Amidoborane: The First Mixed-Metal Amidoborane," *Chem. Commun.* 47, 4102 (2011).
10. K. Sumida, S. Horike, S.S. Kaye, Z.R. Herm, W.L. Queen, C.M. Brown, F. Grandjean, G.J. Long, A. Dailly, and J.R. Long, "Hydrogen Storage and Carbon Dioxide Capture in an Iron-Based Sodalite-Type Metal-Organic Framework (Fe-BTT) Discovered via High-Throughput Methods," *Chemical Science* 1, 184 (2010).
11. D.L. Jacobson, D.S. Hussey, E. Baltic, T.J. Udovic, J.J. Rush, and R.C. Bowman, Jr., "Neutron Imaging Studies of Metal-Hydride Storage Beds," *Intl. J. Hydrogen Energy* 35, 12837 (2010).
12. N. Verdál, T.J. Udovic, J.J. Rush, R.L. Cappelletti, and W. Zhou, "Hydrogen Dynamics of the Dodecahydro-*Closo*-Dodecaborate Crystals," National Meeting of the American Chemical Society, Denver, CO (Aug. 2011).
13. C.M. Brown, "Determining Structures and Properties of Advanced Materials using Neutrons," U.C. Berkeley Chemistry Dept., Berkeley, CA (Apr. 2011).
14. C.M. Brown, "Applications of Neutron Scattering to Understanding Structure and Gas Storage Properties of Metal-Organic Frameworks and Related Materials," MRS Spring Meeting, San Francisco, CA (Apr. 2011).
15. W.L. Queen, C.M. Brown, M.R. Hudson, K. Sumida, E.D. Bloch, L.J. Murray, J.R. Long, D.K. Britt, and O.M. Yaghi, "Gas Adsorption Properties of Various Metal-Organic Frameworks with Coordinatively Unsaturated Metal Centers," 18<sup>th</sup> Annual Postdoctoral Poster Competition sponsored by the NIST chapter of Sigma Xi, Gaithersburg, MD (Feb. 2011).

16. M.R. Hudson, W.L. Queen, C.M. Brown, D.W. Fickel, and R.F. Lobo, "CO<sub>2</sub> Separation and Hydrogen Storage Properties of Zeolites for Clean Energy Applications," 18th Annual Postdoctoral Poster Competition sponsored by the NIST chapter of Sigma Xi, Gaithersburg, MD (Feb. 2011).
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18. C.M. Brown, "Physical Aspects of Hydrogen Adsorption," Advances in Chemistry and Materials for Hydrogen Storage, Pacificchem Congress, Honolulu, HI (Dec. 2010).
19. C.M. Brown, "Understanding Hydrogen Storage in Microporous Materials using Neutrons," High Temperature Energy Materials Center Seminar, Korea Institute of Science and Technology, Seoul, South Korea (Nov. 2010).
20. C.M. Brown, "Understanding Hydrogen Storage in Microporous Materials using Neutrons," Department of Nuclear and Quantum Engineering Special Seminar, Korea Advanced Institute of Science and Technology, Daejong, South Korea (Nov. 2010).
21. C.M. Brown, "Studying Potential Hydrogen Storage Materials using Neutrons," Hanaro Symposium, Daejong, South Korea (Nov. 2010).
22. C.M. Brown, "Probing Adsorption in Microporous Materials using Neutrons," Spallation Neutron Source Seminar, ORNL, Oak Ridge, TN (Oct. 2010).
23. C.M. Brown, "Science as a Career," Mount St. Mary's College, Spinkhill, U.K. (Oct. 2010).
24. C.M. Brown, "Determining Structures and Properties of Advanced Materials," Bishop Justus C of E School, Bromley, U.K. (Sep. 2010).
25. C.M. Brown, "Application of Neutron Scattering to the Hydrogen Storage Problem," STAIR Graduate Student Seminar, U. Tennessee, Knoxville, TN (Sep. 2010).
26. N. Verdal, W. Zhou, V. Stavila, J.-H. Her, M. Yousufuddin, T. Yildirim, and T.J. Udovic, "Alkali and Alkaline-Earth Metal Dodecahydro-*Closo*-Dodecaborates: Probing Structural Variations *via* Neutron Vibrational Spectroscopy," MH2010 - International Symposium on Hydrogen-Metal Systems-- Fundamentals and Applications, Moscow, Russia (Jul. 2010).
27. C.M. Brown, "Understanding how Hydrogen Interacts with Materials using Neutrons," Award Presentation, American Conference on Neutron Scattering, Ottawa, Canada (Jun. 2010).
29. N. Verdal, T.J. Udovic, J.J. Rush, R. Cappelletti, and W. Zhou, "Reorientation Dynamics of the Hydrogen Storage Intermediate Dodecahydro-*Closo*-Dodecaborate," American Conference on Neutron Scattering, Ottawa, Canada (Jun. 2010).

## References

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2. X. Liu, et al., J. Phys. Chem. C **114**, 14036 (2010).
3. N. Verdal, et al., J. Phys. Chem. A **115**, 2933 (2011).