

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

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

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

Contract Number: DE-AI-01-05EE11104

Project Start Date: April 1, 2005
Project End Date: October 1, 2010

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 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

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 H₂/L

Accomplishments

Key accomplishments for Fiscal Year (FY) 2010 are listed below for hydrogen-storage materials of interest to the MHCoe:

- The structures of SrB₁₂H₁₂ and BaB₁₂H₁₂, heavier alkaline-earth analogs to MgB₁₂H₁₂, were solved by a combination of X-ray diffraction (XRD), neutron vibrational spectroscopy (NVS), and density functional theory (DFT) calculations.
- NVS measurements of amorphous, partially solvated MgB₁₂H₁₂ yield a vibrational density of states suggestive of the predicted stable crystalline structure.
- Quasielastic neutron scattering (QNS) measurements of NaBH₄, KBH₄, and Cs₂B₁₂H₁₂ allowed us to characterize, in detail, the rotational dynamics of the corresponding BH₄⁻ and B₁₂H₁₂²⁻ anions.
- NVS measurements of the direct high-pressure hydrogenation of Li₂B₁₂H₁₂ + 10LiH and Na₂B₁₂H₁₂ + 10NaH mixtures indicate the near complete formation of LiBH₄ and NaBH₄, respectively.
- Small-angle neutron scattering (SANS) measurements of partially LiBH₄-loaded carbon aerogels are consistent with the preferential filling of smaller pores and/or surface film formation.
- The structures of two new synthesized complex hydrides, Li₂(BH₄)₂NH₃BH₃ and Ca(BH₄)₂(NH₃BH₃)₂, were solved by XRD.
- Neutron reflectometry of dehydrogenated MgH₂ thin films suggests the formation of porous Mg.
- The thermodynamic Calphad database for Li-Mg-Ca-B-Si-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 NaBH_4 , KBH_4 , $\text{SrB}_{12}\text{H}_{12}$, $\text{BaB}_{12}\text{H}_{12}$, $\text{MgB}_{12}\text{H}_{12} \cdot x\text{THF}$ (THF = tetrahydrofuran), $\text{Li}_2(\text{BH}_4)_2\text{NH}_3\text{BH}_3$, $\text{Ca}(\text{BH}_4)_2(\text{NH}_3\text{BH}_3)_2$, and LiBH_4 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.

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, 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 continued our collaboration

with Sandia National Laboratories (SNL), the Jet Propulsion Laboratory, the California Institute of Technology (Caltech), and the University of Maryland to investigate the structures and bonding in the alkali and alkaline-earth dodecahydro-*closo*-dodecaborates, which are possible intermediates in borohydride decomposition. Adding to our previously determined $\text{Li}_2\text{B}_{12}\text{H}_{12}$, $\text{Na}_2\text{B}_{12}\text{H}_{12}$, and $\text{CaB}_{12}\text{H}_{12}$ structures, we have solved the isomorphous *P31c* structures of the heavier alkaline earth analogs of $\text{MgB}_{12}\text{H}_{12}$, namely $\text{SrB}_{12}\text{H}_{12}$ and $\text{BaB}_{12}\text{H}_{12}$, by a combination of XRD, NVS, and DFT calculations. The $\text{MgB}_{12}\text{H}_{12}$ structure still eludes us since it has been impossible as of yet to synthesize the totally anhydrous compound. NVS results for $\text{MgB}_{12}\text{H}_{12}$ partially solvated by ~ 0.5 THF/ $\text{MgB}_{12}\text{H}_{12}$ suggests some similarity with the predicted structure of Ozolins, et al., [1] but definitive results await a solvent-free sample.

We have collaborated with SNL and Caltech to investigate the hydrogenation behavior of $\text{A}_2\text{B}_{12}\text{H}_{12} + 10\text{AH}$ mixtures (A=Li and Na) because of the $\text{A}_2\text{B}_{12}\text{H}_{12}$ intermediate's high stability during the cycling of alkali-metal borohydrides. Spectral comparison by NVS 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 LiBH_4 and NaBH_4 compounds indicates that 773 K and 90 MPa H_2 is sufficient to transform the reactant mixtures into the pure borohydride compounds.

We have collaborated with the universities of Maryland and Michigan to unravel the details of BH_4^- rotational dynamics in both the ordered and disordered phases of NaBH_4 and in the disordered phase of KBH_4 by QNS [2]. Model fits of the QNS data indicate that the BH_4^- tetrahedron in the NaBH_4 ordered phase rotates with a combination of two-site and three-site reorientations that preserve its crystallographic orientation. Data for the disordered phases are well described by a model assuming nearest-neighbor BH_4^- jumps from one corner to another of a cube formed by eight hydrogen positions of half occupancy. Distinguishing between likely mechanisms for reorientation was made possible by collecting data at sufficiently high Q values. The derived activation energies for reorientation for the NaBH_4 low-temperature and high-temperature phases are 13.4 ± 0.8 and 11.9 ± 0.5 kJ/mol, respectively, and 14.6 ± 0.5 kJ/mol for the KBH_4 high-temperature phase.

We have collaborated with HRL Laboratories, Lawrence Livermore National Laboratory, and the universities of Maryland, and Michigan to characterize the properties of LiBH_4 nanoconfined in carbon aerogels. SANS measurements for LiBH_4 -filled and partially-filled 13 nm aerogels (Figure 1) indicate significant scattering differences at the higher momentum transfer (Q) values and similar scattering behavior at intermediate Q values. This suggests that the smallest pores fill first with no change in apparent mesopore geometry with filling. Although NVS indicates

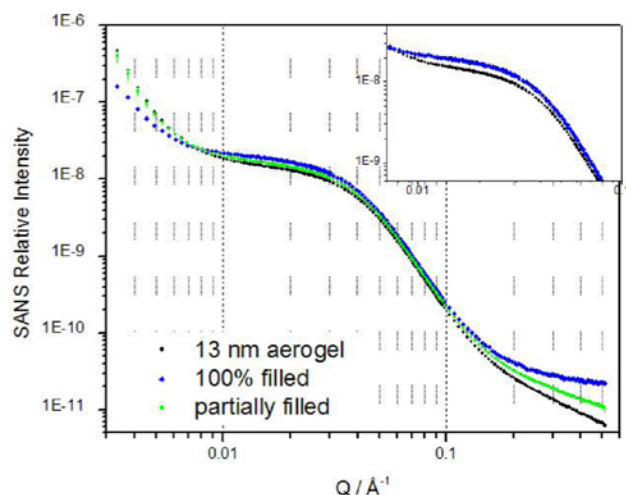


FIGURE 1. SANS Data for Nanoconfined LiBH_4 in 13 nm Carbon Aerogel

that the vibrational modes for LiBH_4 in a 13 nm carbon aerogel exhibit only a minor ($\sim 10\%$) broadening compared to those for bulk LiBH_4 . QNS measurements of the BH_4^- rotational jump frequency for nanoconfined LiBH_4 (Figure 2) indicate a step at ~ 360 K denoting the orthorhombic-to-hexagonal phase transition, which is nearly 30 K lower than the transition temperature for bulk LiBH_4 . This suggests that nanoconfinement perturbs bulk thermodynamic properties.

We have collaborated with the University of Maryland and General Motors to synthesize and evaluate two new borohydride-ammonia borane complex hydrides, $\text{Li}_2(\text{BH}_4)_2\text{NH}_3\text{BH}_3$ (Figure 3) and $\text{Ca}(\text{BH}_4)_2(\text{NH}_3\text{BH}_3)_2$ [3]. Their structures were determined using a combination of XRD and DFT calculations. Both structures are composed of alternating layers of borohydride anions and ammonia borane. Examination of bond lengths indicates ammonia borane ligands are stabilized in the structures mainly via dihydrogen bonding and interactions with their surrounding cations. Our experimental results show that more than 10 wt% and 11 wt% hydrogen can be released from $\text{Li}_2(\text{BH}_4)_2\text{NH}_3\text{BH}_3$ and $\text{Ca}(\text{BH}_4)_2(\text{NH}_3\text{BH}_3)_2$, respectively. Negligible ammonia was detected compared to ammonia borane and its amidoborane derivatives. Further improvements are needed to reduce borazine emission. Cycling studies show that $\text{Li}_2(\text{BH}_4)_2\text{NH}_3\text{BH}_3$ and $\text{Ca}(\text{BH}_4)_2(\text{NH}_3\text{BH}_3)_2$ can be partially rehydrogenated under hydrogen pressures at high temperatures.

We have collaborated with the universities of Stanford and Maryland to help characterize hydrogen concentration profiles in thin Mg films. We have continued our measurements of the hydrogen cycling of a single (25 nm Pd-capped) 100 nm Mg layer on a sapphire substrate. Under typical conditions of 343-373 K and 0.1 MPa H_2 , neutron reflectivity

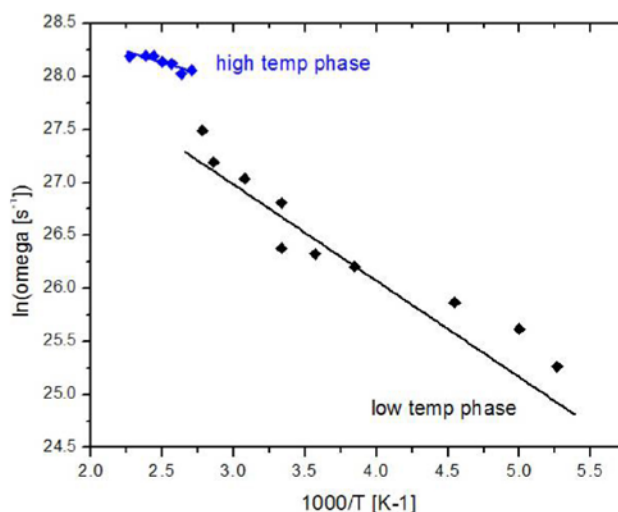


FIGURE 2. Temperature Dependence of the BH_4^- Rotational Jump Frequency (ω) for Nanoconfined LiBH_4 (25% loading) in 13 nm Carbon Aerogel, as Measured by QNS

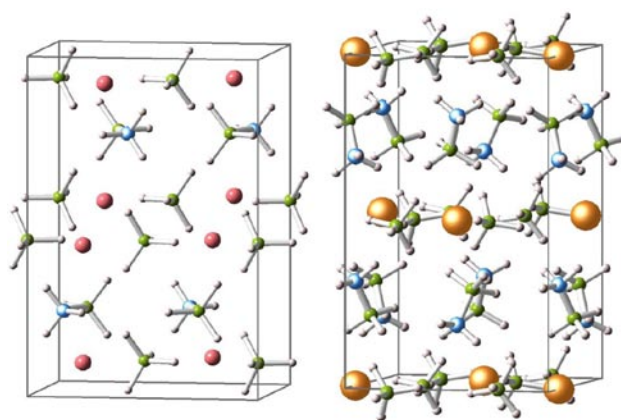


FIGURE 3. The Structures of the Borohydride-Ammonia Borane Compounds $\text{Li}_2(\text{BH}_4)_2\text{NH}_3\text{BH}_3$ (left) and $\text{Ca}(\text{BH}_4)_2(\text{NH}_3\text{BH}_3)_2$ (right). Li (red), Ca (orange), B (green), N (blue), and H (white)

results indicate an expansion of the Mg layer upon hydrogenation to MgH_2 . This expansion remains upon dehydrogenation of the MgH_2 layer, suggesting that the regenerated Mg layer possesses a porous morphology.

The thermodynamic Calphad database has been updated and expanded to include descriptions for the solid phases $\text{MgB}_{12}\text{H}_{12}$ and $\text{Li}_2\text{B}_{12}\text{H}_{12}$. Experimental data for the ternary hydride phases are extremely sparse. For developing the thermodynamic descriptions of these phases, data from first-principles calculations provided by members of the Theory Group were used to supplement the experimental data. 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

reported experimental dehydrogenation reactions differ greatly. This is caused by slow reaction kinetics and the potential for the formation of metastable reaction products. These complications result in reduced reliability of thermodynamic descriptions obtained from experimental desorption data. The dehydrogenation path of $\text{Mg}(\text{BH}_4)_2$ is depicted in Figure 4. The calculated reaction path of the desorption of $\text{Mg}(\text{BH}_4)_2$ gives an extremely favorable desorption temperature and released amount of hydrogen, however, this reaction has not been observed in experiments. This indicates that at least some of the reported dehydrogenation reactions are not equilibrium reactions.

The addition of nitrogen to the six component H-Ca-Mg-Li-B-Si databases results in the addition of 6 binary and 15 ternary sub-systems. The evaluation of the literature revealed that for the addition of nitrogen to the database, the descriptions of 49 intermediate phases and 16 gaseous species are needed, but very few data are available. Sufficient data are only available for 6 of the 49 intermediate compounds and 8 of the 14 gaseous species. The evaluation of the Gibbs energy functions of the complex borohydrides showed that the uncertainties from the experimental desorption data are significant. Similar or even larger uncertainties will affect the Gibbs energy functions of most of the nitrogen-containing phases. Therefore, the decision was made not to add nitrogen at this point to the database.

Conclusions and Future Directions

- Neutron methods and Calphad computations have provided crucial, non-destructive characterization and predictive tools for the MHCoe.

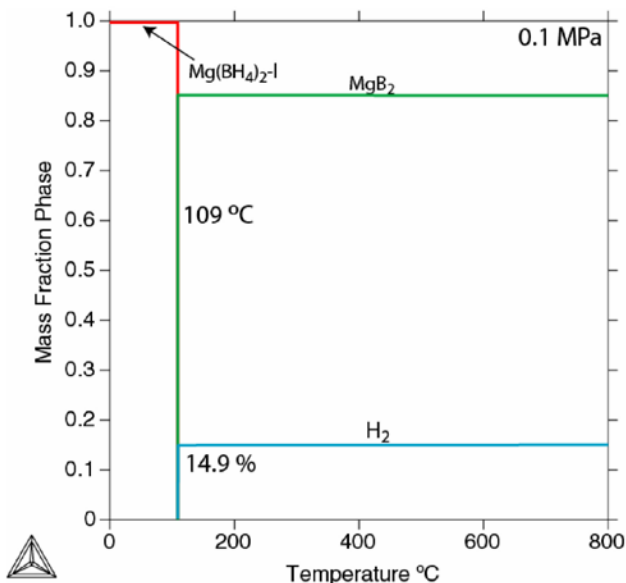


FIGURE 4. Dehydrogenation Path of $\text{Mg}(\text{BH}_4)_2$ from Calculations using the Calphad Database

- X-ray and neutron powder diffraction, neutron spectroscopy, and DFT calculations continued to provide a powerful combination for characterizing the structures and bonding of the dodecahydro-*closo*-dodecaborates. Spectroscopy was particularly useful to test predicted structures. Work is still in progress to synthesize and characterize anhydrous crystalline $\text{MgB}_{12}\text{H}_{12}$.
- We characterized the rotational dynamics of BH_4^- anions in bulk compounds as a baseline for comparison with the dynamics found for nanoconfined compounds. Changes in rotational dynamics due to nanoconfinement may signal 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 and indeed observed non-bulk-like effects. We will continue to use SANS to understand the relationship between pore morphology and filling behavior of nanoconfined storage materials.
- We synthesized two examples of a new family of complex hydrides, the borohydride ammonia boranes, that may have potentially favorable cycling behavior for hydrogen storage.
- We continued to characterize the hydrogen cycling of Mg thin films by neutron reflectometry to understand the fundamental mechanisms involved.
- The thermodynamic Calphad database for Li-Mg-Ca-B-Si-H was expanded to include more gas phase species and ternary hydride phases.
- Creating a database with Gibbs energy functions from first principles calculations and incorporating it with Calphad descriptions of solution phases will combine the strengths of both methods.

FY 2010 Publications/Presentations

1. H. Wu, W. Zhou, K. Wang, T.J. Udovic, J.J. Rush, T. Yildirim, L.A. Bendersky, A.F. Gross, S.L. Van Atta, J.J. Vajo, F.E. Pinkerton, and M.S. Meyer, "Size Effects on the Hydrogen Storage Properties of Nanoscaffolded $\text{Li}_3\text{BN}_2\text{H}_8$," *Nanotechnology* **20**, 204002 (2009).
2. M. Yousufuddin, J.-H. Her, W. Zhou, S.S. Jalisatgi, and T.J. Udovic, "Crystal Structure, Neutron Vibrational Spectroscopy, and DFT calculations of $\text{Li}_2\text{B}_{12}\text{H}_{12} \cdot 4\text{H}_2\text{O}$," *Inorg. Chim. Acta* **362**, 3155 (2009).
3. H. Wu, W. Zhou, T.J. Udovic, and T. Yildirim, "Crystal Chemistry and Dehydrogenation/ Rehydrogenation Properties of Perovskite Hydrides RbMgH_3 and RbCaH_3 ," *J. Phys. Chem. C* **113**, 15091 (2009).
4. J.-H. Her, W. Zhou, V. Stavila, C.M. Brown, and T.J. Udovic, "Role of Cation Size on the Structural Behavior of the Alkali-Metal Dodecahydro-*Closo*-Dodecaborates," *J. Phys. Chem. C* **113**, 11187 (2009).

5. N. Verdál, M.R. Hartman, T. Jenkins, D.J. DeVries, J.J. Rush, and T. J. Udovic “Reorientational Dynamics of NaBH_4 and KBH_4 ,” *J. Phys. Chem. C* **114**, 10027 (2010).
6. V. Stavila, J.-H. Her, W. Zhou, S.-J. Hwang, C. Kim, L.A. M. Ottley, and T. J. Udovic, “Probing the Structure, Stability, and Hydrogen Storage Properties of Calcium Dodecahydro-*Closo*-Dodecaborate,” *J. Solid State Chem.* **183**, 1133 (2010).
7. H. Wu, W. Zhou, F.E. Pinkerton, M.S. Meyer, G. Srinivas, T. Yildirim, T.J. Udovic, and J.J. Rush, “A New Family of Metal Borohydride Ammonia Borane Complex: Synthesis, Structures, and Hydrogen Storage Properties,” *J. Mat. Chem.* **20**, 6550 (2010).
8. T.M. Ivancic, S.-J. Hwang, R.C. Bowman, Jr., D.S. Birkmire, C.M. Jensen, T.J. Udovic, and M.S. Conradi, “Discovery of a New Al Species in Hydrogen Reactions of NaAlH_4 ,” *J. Phys. Chem. Lett.* **1**, 2412 (2010).
9. 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* (in press 2010).
10. N. Verdál, W. Zhou, J.-H. Her, M. Yousufuddin, V. Stavila, S.S. Jalihatgi, 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 2010).
11. J.-H. Her, “Understanding Hydrogen Storage Materials using Diffraction Techniques,” GE Global Research, Niskayuna, NY (Aug. 2009). (invited)
12. U.R. Kattner, “Thermodynamic Databases for Metal-Hydrogen Systems,” Materials Science and Technology 2009 Conference, Pittsburgh, PA (Oct. 2009). (invited)
13. N. Verdál, T.J. Udovic, “Characterization of Borohydrides as Hydrogen Storage Materials Using Neutron Scattering Techniques,” 17th annual Postdoctoral Poster Competition sponsored by the NIST chapter of Sigma Xi, Gaithersburg, MD (Feb. 2010).
14. V. Stavila, E.H. Majzoub, S. Hwang, R.J. Newhouse, M. Ulutagay-Kartin, W. Luo, J.G. Cordaro, T.J. Udovic, “Factors Affecting Hydrogen Release from Metal Borohydrides,” Materials Challenges in Alternative & Renewable Energy 2010, Cocoa Beach, FL (Feb. 2010).
15. N. Verdál, T.J. Udovic, M. Hartman, M. Bacon, J. Vajo, A. Gross, T. Baumann, J.J. Rush, “Characterization of Carbon Aerogels as Scaffolds for Hydrogen Storage Materials,” American Physical Society March Meeting, Portland, OR (Mar. 2010).
16. V. Stavila, R.J. Newhouse, S.-J. Hwang, M. Ulutagay-Kartin, J.-H. Her, T.J. Udovic “Hydrogen Storage in Alkali and Alkaline Earth Borohydrides: Probing the Role of Intermediate Species,” 239th American Chemical Society National Meeting, San Francisco, CA (Mar. 2010).
17. T.J. Udovic, “Neutron Metrology of Hydrogen in Bulk and Nanoconfined Metal-Hydride and Complex-Hydride Systems,” Task 22–Fundamental and Applied Hydrogen Storage Materials Development–IEA HIA Expert Meeting, Death Valley, CA (Apr. 2010). (invited)
18. U.R. Kattner, “Thermodynamic Databases for Metal-Hydrogen Systems,” CALPHAD XXXIX, Jeju, Korea (May 2010).
19. N. Verdál, J.J. Rush, and T.J. Udovic, “Reorientation Dynamics of the Hydrogen-Storage Intermediate Dodecahydro-*Closo*-Dodecaborate,” American Conference on Neutron Scattering 2010, Ottawa, Canada (Jun. 2010).
20. N. Verdál, W. Zhou, V. Stavila, J. H.- Her, M. Yousufuddin, T. Yildirim, J.J. Rush, and T.J. Udovic, “Alkali and Alkaline-Earth Metal Dodecahydro-*Closo*-Dodecaborates: Probing Structural Variations via Vibrational Spectroscopy,” MH2010 - International Symposium on Metal-Hydrogen Systems, Moscow, Russia (Jul. 2010).

References

1. V. Ozolins, *et al.*, *J. Am. Chem. Soc.* **131**, 230 (2009).
2. N. Verdál, *et al.*, *J. Phys. Chem. C* **114**, 10027 (2010).
3. H. Wu, *et al.*, *J. Mater. Chem.* **20**, 6550 (2010).