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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% H₂
- 45 g H₂/L

Accomplishments

Key accomplishments for Fiscal Year 2008 are listed below for hydrogen-storage materials of interest to the MHCoe. (For more details, see the Results section.):

- Quasielastic neutron scattering (QENS) studies of LiBH₄ nanoconfined in 13 nm and 4 nm pore-size carbon aerogels indicated a significantly higher BH₄⁻ rotational mobility than in the bulk with a significantly reduced rotational activation energy (~4.5 kJ/mol compared to 14.6 kJ/mol).
- Neutron diffraction measurements of Li[BH₄]_x[NH₂]_{1-x} compounds indicated that they can be viewed as 3-dimensional (3-D) frameworks built by corner- and face-shared Li⁺[BH₄]_n[NH₂]_{4-n} tetrahedra.
- Based on neutron diffraction results, the origin of enhanced H mobility in NaMgH₃ (compared to MgH₂), was attributed to the decreasing lattice distortion with increasing temperature.
- Neutron vibrational spectroscopy (NVS) corroborated the formation of Li₂B₁₂H₁₂ during the partial dehydrogenation of LiBH₄, suggesting that the (B₁₂H₁₂)²⁻ anion is a common intermediate species during the dehydrogenation of the majority of borohydrides.
- The synthesis by Sandia National Laboratories (SNL) of the novel LiK(BH₄)₂ borohydride was confirmed by neutron vibrational spectroscopy and first-principles phonon calculations.
- The thermodynamic Calphad database for Li-Mg-Ca-B-Si-H was updated with improved descriptions for the binary Ca-B and Ca-H systems.



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 NaMgH₃, LiBH₄, LiK(BH₄)₂, Ca(BH₄)₂, LiBH₄-LiNH₂ mixtures, Li₂B₁₂H₁₂, and LiBH₄ 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 updated the thermodynamic database, including the elements Li, Mg, Ca, B, Si, and H and their respective binary phases, for the Calphad modeling of metal-hydrogen systems. This database is being used to calculate the reactions in ternary hydrogen systems. These results are the basis for the evaluation of dehydrogenation temperatures and pressures and the suitability of third-element additions for destabilization of the binary hydrides.

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 Center 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 HRL and Lawrence Livermore National Laboratory to investigate the effects of nanoconfinement on LiBH_4 dynamics. NVS indicated minor broadening of phonon modes for LiBH_4 nanoconfined in carbon aerogels with average pore sizes below 25 nm. QENS of isotopically enriched, bulk ${}^7\text{Li}{}^{11}\text{BH}_4$ indicated BH_4^- two-fold jump rotation near 200 K (see Figure 1) with an activation energy of ~ 14.6 kJ/mol, while at 290 K and 325 K, an additional three-fold rotation component with an activation energy of ~ 19 kJ/mol was needed to fit the

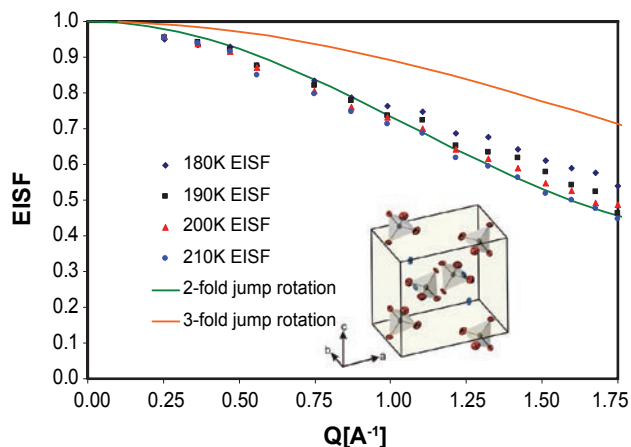


FIGURE 1. The momentum transfer (Q) dependence of the elastic incoherent structure factor (EISF) observed for ${}^7\text{Li}{}^{11}\text{BH}_4$ near 200 K, confirming that the BH_4^- undergoes two-fold jump rotations in this temperature region.

data. In contrast, QENS of nanoconfined ${}^7\text{Li}{}^{11}\text{BH}_4$ (in 13 nm and 4 nm carbon aerogels) suggested a significant reduction in the BH_4^- two-fold rotational activation energy to ~ 4.5 kJ/mol. More measurements are needed to confirm this surprising result, since there is a possibility that minor decomposition during aerogel loading may have potentially complicated the data analysis.

For the $x\text{LiBH}_4 + (1-x)\text{LiNH}_2$ system, inaccurate structural parameters reported for different phases prompted a need for neutron powder diffraction (NPD) measurements with ${}^7\text{Li}$, ${}^{11}\text{B}$, and D-enriched compounds. We synthesized and used ${}^7\text{Li}{}^{11}\text{BND}_6$ to determine the $R\bar{3}$ crystal structure of Li_2BNH_6 by NPD [1]. Unlike previous results, a nearly ideal configuration was found for both BH_4^- and NH_2^- with a mean B-D distance of 1.208 Å and a mean N-D distance of 1.012 Å. Li_2BNH_6 neutron vibrational (NV) spectra and calculated phonon modes for the optimized structure were in agreement. Similarly, NPD results for synthesized ${}^7\text{Li}_3{}^{11}\text{BN}_2\text{BD}_8$ confirmed that $\text{Li}_3\text{BN}_2\text{BH}_8$ is not a single phase, but rather a combination of $I213$ -symmetric $\text{Li}_4\text{BN}_3\text{H}_{10}$ and LiBH_4 [1]. Again, unlike previous results, a nearly ideal configuration was found for both BH_4^- and NH_2^- with a mean B-D distance of 1.195 Å and a mean N-D distance of 1.009 Å. Similarly, $\text{Li}_4\text{BN}_3\text{H}_{10}$ NV spectra and calculated phonon modes for the optimized structure were consistent. Based on the structural results, $\text{Li}[\text{BH}_4]_x[\text{NH}_2]_{1-x}$ compounds can be viewed as 3-D frameworks built by corner- and face-shared $\text{Li}^+[\text{BH}_4]_n[\text{NH}_2]_{4-n}$ tetrahedra (see Figure 2). For Li_2BNH_6 , it is noteworthy that $\text{Li}^+[\text{NH}_2]_2[\text{BH}_4]_2$ tetrahedra are avoided due to steric instabilities. In general, BH_4^- -rich quaternaries are also not observed for the same reason.

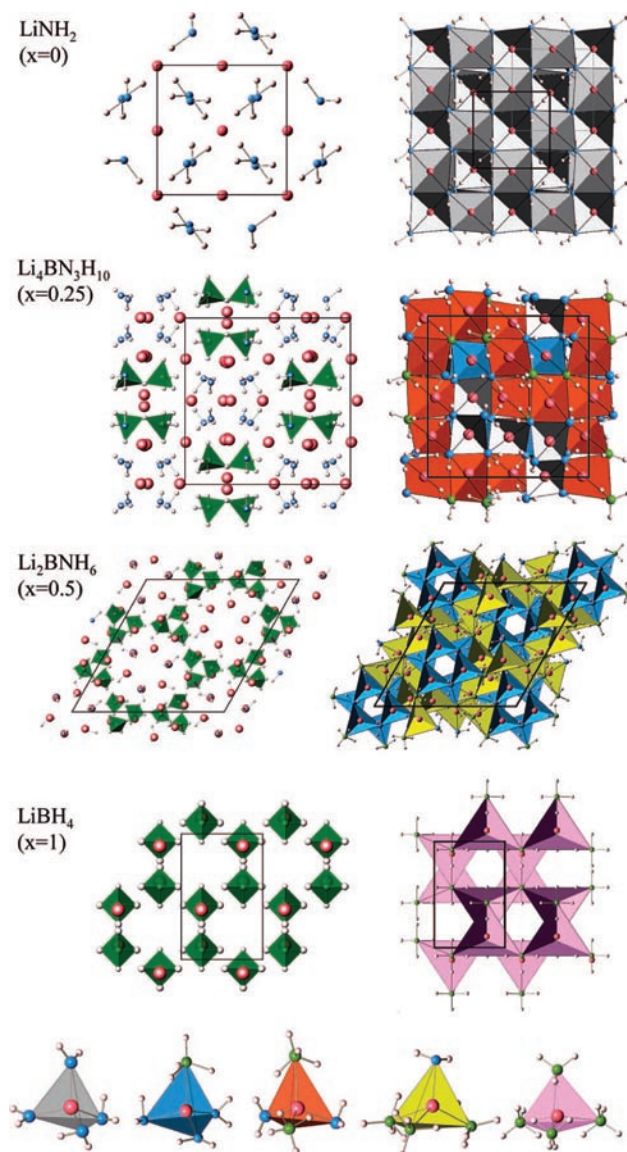


FIGURE 2. $\text{Li}[\text{BH}_4]_x[\text{NH}_2]_{1-x}$ compound structures shown in ball-and-stick views containing BH_4^- units (in green) and NH_2^- units, and as polyhedral diagrams of 3-dimensional frameworks built by corner- and face-shared $\text{Li}^+[\text{BH}_4]_n[\text{NH}_2]_{4-n}$ tetrahedra colored according to the different coordination environments of Li (see bottom row).

We have collaborated with the Jet Propulsion Laboratory (JPL) to investigate the origin of enhanced H mobility in NaMgH_3 (compared to MgH_2), a light-metal hydride with 6 wt% H. We determined the GdFeO_3 -type orthorhombic perovskite structure using NPD [2]. A non-ideal size ratio between Na and Mg led to lattice distortion and MgH_6 octahedral tilting. Despite lattice distortion, nearly ideal MgH_6 octahedra were maintained, in contrast to previous results in the literature. The refined structure was confirmed by density functional theory (DFT) structural optimization and bond valence calculations. The calculated phonon spectrum were consistent with the measured NV

spectrum. No phase transition was observed in the 5-370 K range. We observed a decrease in octahedral tilting angle with increasing temperature. This is similar to the behavior observed in the structurally analogous perovskite oxygen ionic conductors. In these materials, an undistorted structure has the most open pathway for oxygen anion diffusion, maximizing the ionic mobility. The emergence of high H mobility in NaMgH_3 observed by NMR with increasing temperature (H hopping rate $\approx 3 \times 10^5 \text{ s}^{-1}$ at 573 K) is consistent with decreasing lattice distortion and octahedral tilting. Also, H motions with the lowest activation energy are expected to result from the smallest tilting angle. Although the H desorption temperature is still too high for practical applications, improving H mobility in this class of hydrides can potentially be accomplished by (i) decreasing the lattice distortion and octahedral tilting via more favorable cation substitutions or other combinations of light elements and (ii) increasing the concentration of H vacancies via substitutional doping of Mg sites with monovalent cations.

We have collaborated with JPL and Caltech to investigate dehydrogenation intermediates in light-metal borohydrides. NMR has shown that the $(\text{B}_{12}\text{H}_{12})^{2-}$ anion is a common intermediate species during the dehydrogenation of borohydrides. We have used NVS to identify the presence of an $\text{Li}_2\text{B}_{12}\text{H}_{12}$ intermediate during the partial dehydrogenation of LiBH_4 (i.e., 30% dehydrogenated at 703 K into a fixed volume) by making comparisons with the phonon spectrum for pure $\text{Li}_2\text{B}_{12}\text{H}_{12}$. We plan to investigate the presence of $(\text{B}_{12}\text{H}_{12})^{2-}$ species along the dehydrogenation pathways of other borohydride materials.

We have collaborated with SNL and JPL to help characterize various newly-synthesized light-metal borohydrides. For example, Figure 3 shows the NV spectrum of $\text{LiK}(\text{BH}_4)_2$ prepared at SNL, compared to those of LiBH_4 and KBH_4 . First-principles phonon calculations are found to be consistent with the optimized $\text{LiK}(\text{BH}_4)_2$ structure reported in the literature [3]. In another example, NV spectra of different $\text{Ca}(\text{BH}_4)_2$ samples from SNL clearly show the sensitivity of BH_4^- torsional mode energies to the particular $\text{Ca}(\text{BH}_4)_2$ polymorph. $\text{Ca}(\text{BH}_4)_2$ is being intensively studied because it is the borohydride that currently shows the most promise for reversibility.

We have collaborated with Stanford to help characterize hydrogen concentration profiles in thin Mg films. We have measured neutron reflectivity profiles of a thin-film multilayer comprised of 10 stacked Pd/Mg bilayers (50 Å/200 Å) on a sapphire substrate. Four measurements were made: (i) the as-received film, (ii) after 7.5 bar D_2 exposure, (iii) after room-temperature evacuation of the deuterated film, and (iv) after 353 K evacuation of the deuterated film. The multilayer did not go back to the as-received state after 353 K evacuation. Reasonable agreement was achieved using

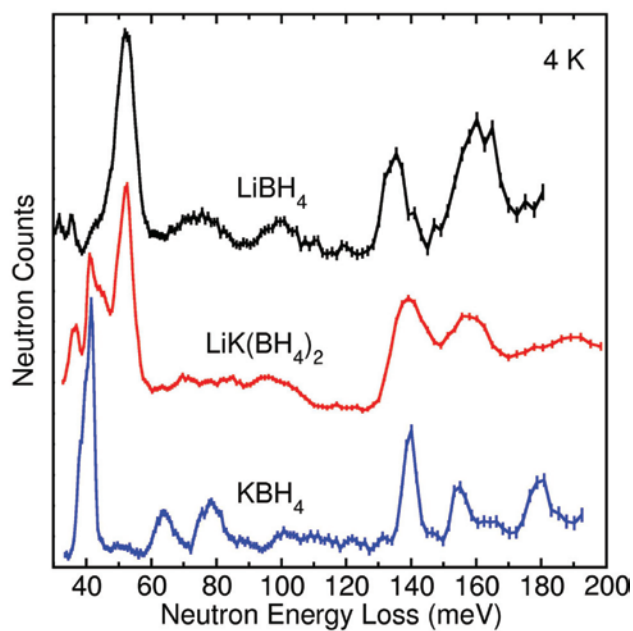


FIGURE 3. Comparison of NV Spectra for LiBH_4 , $\text{LiK}(\text{BH}_4)_2$, and KBH_4 at 4 K

a model in which the amount of D in the Mg layers at room temperature increased linearly with layer number starting at the substrate, transforming to a more even distribution of D in the Mg layers after heating to 353 K. This indicates that diffusion dominates over desorption at this temperature.

The thermodynamic Calphad database has been updated. The preliminary description of the Ca-B binary system has been replaced with a new description from the literature [4]. A refined description for the Ca-H binary system is under development. The assessment of the available data showed that the current Gibbs energy function for hcp-Ca [5] is not compatible with the Ca-H binary phase diagram. The data [6] for the CaH_2 compound indicate that this compound undergoes a solid-liquid phase transformation on heating before decomposing. However, thermochemical data indicate that higher pressures may be needed to observe this phase transformation. An accurate description of the phases in the Ca-H binary system is crucial for reliable calculations of candidate storage materials containing Ca and, therefore, a detailed evaluation of all original experimental data and further refinement of the thermodynamic description are necessary. A thermodynamic description for the ternary $\text{Ca}(\text{BH}_4)_2$ compound is under development. The University of Missouri – St. Louis calculated the thermodynamic properties of this compound with DFT relative to the *Fddd* ground state at 0 K. Since DFT calculations of the temperature dependence of thermodynamic functions are time-consuming, heat capacities obtained from the Neumann-Kopp rule were compared to the DFT values,

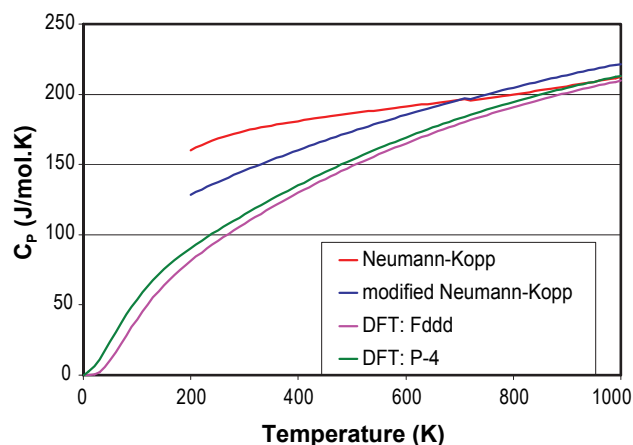


FIGURE 4. Calculated Heat Capacity Data of $\text{Ca}(\text{BH}_4)_2$

and are shown in Figure 4. Although the heat capacities from the DFT calculations and the Neumann-Kopp rule agree in the order of magnitude, there is a significant difference in the temperature dependence. This difference may be the result of using the heat capacity of gaseous H_2 in the application of the Neumann-Kopp rule. Komada and Westrum [7] found that vibrations of polyatomic ions are relatively isolated from their environments and should be relatively independent of the other components in the compound. Based on this, the heat-capacity contribution of the BH_4^- anion was extracted from the heat capacity data of LiBH_4 , NaBH_4 , and KBH_4 . This heat capacity contribution and the heat capacity of elemental Ca were used to calculate the heat capacity of $\text{Ca}(\text{BH}_4)_2$. The heat capacity data obtained from this modified Neumann-Kopp rule are also shown in Figure 4. The agreement with DFT data is significantly improved compared to the data from the original Neumann-Kopp rule. The modified Neumann-Kopp rule can be used to efficiently obtain heat capacity data for new compounds with hydride complexes.

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.
- QENS studies of LiBH_4 nanoconfined in carbon aerogels indicated a higher BH_4^- rotational mobility than in the bulk with a significantly reduced rotational activation energy. Further studies will investigate the effect of both aerogel pore size and LiBH_4 fill fraction on mobility and will be used to develop a fundamental understanding of the relationship between nanoconfinement and improved cycling kinetics.

- ^7Li , ^{11}B , and D labeled samples were needed to accurately solve the crystal structures of Li_2BNH_6 and $\text{Li}_4\text{BN}_3\text{H}_{10}$. $\text{Li}_3\text{BN}_2\text{H}_8$ was found to be a mixture of $\text{Li}_4\text{BN}_3\text{H}_{10}$ and LiBH_4 . Nearly ideal configurations found for both BH_4^- and NH_2^- anions clarify the large discrepancies in prior reports on artificial anion distortions and inaccurate bond distances. Due to their promising H densities, further work will focus on their cycling properties under nanoconfinement.
- Combined neutron and first-principles studies revealed the correct orthorhombic perovskite structure for NaMgH_3 . Enhanced H mobility at elevated temperatures could be correlated with decreased lattice distortion and tilting of the MgH_6 octahedra. Future focus will be on adjusting the structural characteristics so as to further increase H mobility.
- Neutron spectroscopy corroborated the formation of $\text{Li}_2\text{B}_{12}\text{H}_{12}$ during the partial dehydrogenation of LiBH_4 . Based on neutron and complementary NMR studies, the $(\text{B}_{12}\text{H}_{12})^{2-}$ anion appears to be a common intermediate species during the dehydrogenation of other investigated borohydrides. We are in the process of solving the unknown crystal structure of $\text{Li}_2\text{B}_{12}\text{H}_{12}$.
- Neutron reflectivity was shown to be sensitive to the hydrogen density profile through a thin Pd/Mg multilayer film on a sapphire substrate. Further studies will focus on determining the hydrogen density profiles associated with a single Mg layer during hydrogen cycling. This will give us a better handle on the fundamental mechanisms associated with H diffusion during hydriding.
- We plan to initiate feasibility studies of unique neutron imaging of H distribution and transport in storage beds for candidate materials.
- The thermodynamic database for Li-Mg-Ca-B-Si-H has been updated with improved descriptions for the binary Ca-B and Ca-H systems.
- A modified Neumann-Kopp rule has been successfully applied to obtain heat capacities for compounds with hydride complexes.
- We will refine the phase description in the Ca-H and $\text{Ca}(\text{BH}_4)_2$ systems and expand the thermodynamic database in conjunction with MHCoe partners.

Special Recognitions

1. T. J. Udovic -- Awarded a NIST Bronze Medal for leadership of neutron scattering studies of metal hydride systems for practical hydrogen storage, Dec. 2007.

FY 2008 Publications/Presentations

1. H. Wu, W. Zhou, and T. Yildirim, "Hydrogen Storage in a Prototypical Zeolitic Imidazolate Framework-8," *J. Am. Chem. Soc.* **129**, 5314 (2007).
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5. H. Wu, W. Zhou, T.J. Udovic, J.J. Rush, and T. Yildirim, "Crystal Chemistry of Perovskite-type Hydride NaMgH_3 : Applications for Hydrogen Storage," *Chem. Mater.* **20**, 2335 (2008).
6. H. Wu, "Structure of Ternary Imide $\text{Li}_2\text{Ca}(\text{NH})_2$ and Hydrogen Storage Mechanisms in Amide-Hydride System," *J. Am. Chem. Soc.* **130**, 6515 (2008).
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9. M.M. Barsan, I.S. Butler, D.F.R. Gilson, R.O. Moyer, Jr., W. Zhou, H. Wu, and T.J. Udovic, "Raman, FTIR, Photoacoustic-FTIR, and Inelastic Neutron Scattering Spectra of Alkaline Earth and Lanthanide Salts of Hexahydroruthenate(II), A_2RuH_6 , ($\text{A}=\text{Ca}, \text{Sr}, \text{Eu}$) and their Deuterides," *J. Phys. Chem. A* **112**, 6936 (2008).
10. H. Wu, W. Zhou, T.J. Udovic, J.J. Rush, T. Yildirim, and R. C. Bowman, Jr., "Neutron Scattering and First-Principles Calculations Study on Novel Metal-Hydride Systems for Hydrogen Storage," Gordon Research Conference on Hydrogen-Metals Systems, Colby College, Waterville, ME, Jul. 2007. (Poster).
11. T.J. Udovic, "Probing Structure, Bonding, and Dynamics in Hydrogen-Storage Materials by Neutron-Scattering Techniques," International Symposium on Materials Issues in a Hydrogen Economy, Richmond, VA, Nov. 2007.
12. H. Wu, "Crystal Chemistry of Several Quaternary/Ternary Metal Hydrides and Their Applications for Hydrogen Storage," NIST Metallurgy Division Seminar, Gaithersburg, MD, Dec. 2007.
13. W. Zhou, "First-Principles Modeling of Potential Hydrogen Storage Materials," NIST Metallurgy Division Seminar, Gaithersburg, MD, Feb. 2008.

14. H. Wu, W. Zhou, T. J. Udovic, J.J. Rush, and T. Yildirim, "Structures and Bonding of Li-B-N-H Quaternary Hydrides," American Physical Society March Meeting, New Orleans, LA, Mar. 2008.
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