

IV.C.3 Neutron Characterization in Support of the DOE Hydrogen Storage Sub-Program

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

Overall Objectives

- Support the DOE-EERE-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

Fiscal Year (FY) 2015 Objectives

- Investigate structural and dynamical properties of alkali (*A*) and alkaline-earth (*Ae*) metal decahydro-*closo*-decaborates $A_2B_{10}H_{10}$ and $AeB_{10}H_{10}$
- Start characterization work on new hydrogenated metal silicides ($M_x[SiH_3]_y$)
- Start characterization work on hydrogenated/dehydrogenated Li_3N in nanoporous carbon, hydrogenated metal borides, and decaborane-based materials

Technical Barriers

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

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

Technical Targets

NIST provides important materials metrologies for DOE-EERE-funded projects using neutron scattering measurements to understand and characterize hydrogen-substrate interactions of interest in a variety of materials ranging from H_2 adsorbed in nanoporous materials to hydrogen 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 2020 storage targets:

- Specific energy: 1.8 kWh/kg
- Energy density: 1.3 kWh/L
- Cost: \$10/kWh

FY 2015 Accomplishments

- Manuscript published on kinetic trapping of D_2 in MIL-53(Al)
- Two manuscripts published on the effects of partial halide anion substitution on BH_4^- reorientational motion in $NaBH_4$
- Manuscript published on the structural properties of modified $A_2B_{12}H_{12}$ compounds
- Manuscript published on the room-temperature $Li_2B_{10}H_{10}$ structure and thermal behavior
- Manuscript published on the correct room-temperature monoclinic $Na_2B_{10}H_{10}$ structure
- Manuscript published on the high-temperature disordered structure and conductivity of $Na_2B_{10}H_{10}$



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 projects using neutron-scattering measurements to probe the amount, location, bonding states, dynamics, and morphological aspects of (1) molecular hydrogen in carbon-based materials such as polymers, metal organic frameworks (MOFs), and carbonaceous materials such as carbon nanohorns; and (2) 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

In collaboration with University of Maryland and the Université de Picardie Jules Verne, we investigated the spectroscopic and dynamical properties of various alkali-metal silanides $MSiH_3$ ($M=K, Rb, Cs$), which store hydrogen reversibly through an $MSi/MSiH_3$ equilibrium, yielding a 0.1 MPa H_2 equilibrium pressure at ~ 410 K. Hence, these materials, comprised of M^+ cations and SiH_3^- anions, are potentially promising for hydrogen storage applications. They typically undergo order-disorder phase transitions by ~ 325 K. Agreement between neutron vibrational spectroscopy (NVS) and density functional theory (DFT) phonon calculations corroborated the ordered β - $MSiH_3$ structures determined by diffraction methods. Neutron-elastic-scattering fixed-window scans (FWSs) indicated that the pyramidal SiH_3^- anions attain high orientational mobilities ($\gg 10^{10}$ H jumps/s) that increase with cation size. Complementary quasielastic neutron scattering (QENS) data for $CsSiH_3$ confirmed a change to a more three-dimensional SiH_3^- reorientation mechanism upon transformation to the disordered cubic α -phase.

In collaboration with University of Maryland, HRL Laboratories, University of Missouri-St. Louis, and University of Utah, we started NVS measurements to assist in determining the chemical nature of thermally treated decaborane $B_{10}H_{14}$. We successfully established the baseline

spectroscopic signature for $B_{10}H_{14}$ (Figure 1) to be used later for comparison with polymerized versions after thermal treatments and potential lithiation. The neutron vibrational spectrum of $^{11}B_{10}H_{14}$ is in good agreement with the DFT phonon calculations. Neutron prompt-gamma activation analysis is currently being used to obtain accurate B/H ratios in different thermally treated samples of $B_{10}H_{14}$.

In collaboration with Sandia National Laboratories (SNL), Lawrence Livermore National Laboratory, and Mahidol University, Bangkok, we spectroscopically characterized the (de)hydrogenation of Li_3N in nanoporous carbon. NVS measurements associated with (de)hydrogenated nanoconfined Li_3N after five desorption/absorption cycles compared to reference spectra (Figure 2) indicated that relatively little H exists in the dehydrogenated state, whereas both $LiNH_2$ and LiH are present in the hydrogenated state, with no obvious presence of the Li_2NH intermediate phase. The lack of Li_2NH suggests a change in the expected reaction pathway.

In collaboration with University of Maryland and SNL, we investigated the structural behavior of $Li_2B_{10}H_{10}$, another stable compound within the technologically relevant Li-B-H phase diagram. Based on X-ray powder diffraction and neutron powder diffraction (NPD), DFT calculations, and NVS, $Li_2B_{10}H_{10}$ was found to exhibit atypical hexagonal symmetry (Figure 3) to best stabilize the ionic packing of the relatively small Li^+ cations and large ellipsoidal $B_{10}H_{10}^{2-}$ anions [1]. Differential scanning calorimetry (DSC) and neutron-elastic-scattering FWSs suggested that $Li_2B_{10}H_{10}$ completes an order-disorder phase transition by ~ 680 K, similar to $Li_2B_{12}H_{12}$, concomitant with

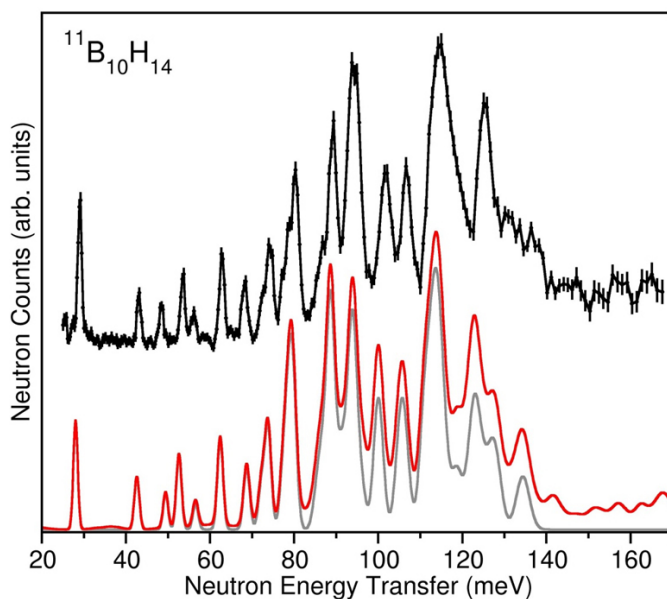


FIGURE 1. The neutron vibrational (NV) spectrum at 4 K of $^{11}B_{10}H_{14}$ (black) with the DFT-simulated 1-phonon (gray) and 1+2-phonon (red) spectra

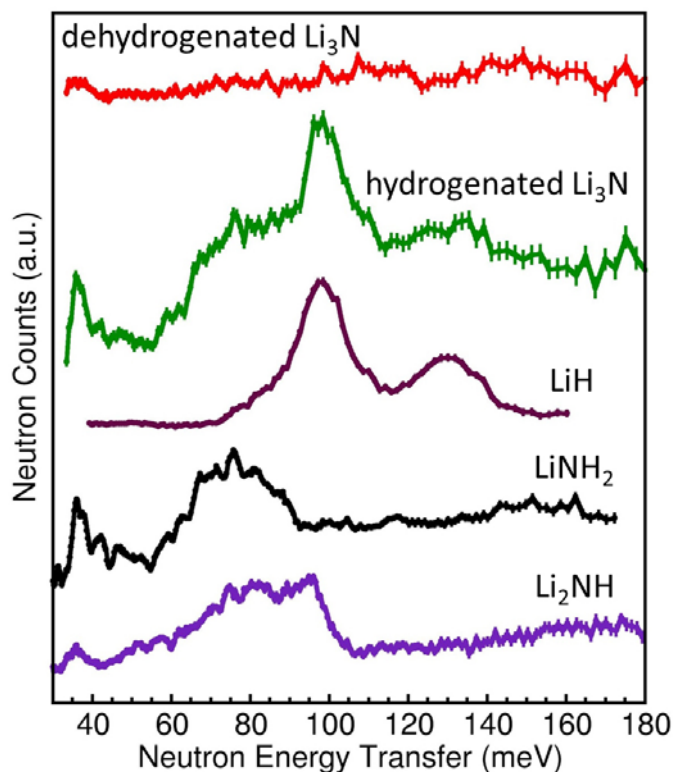


FIGURE 2. The NV spectra at 4 K associated with (de)hydrogenated Li_3N confined in nanoporous carbon after five desorption/absorption cycles, compared to reference spectra

enhanced anion orientational mobility. These results provide valuable structural information pertinent to understanding the potential role that $\text{Li}_2\text{B}_{10}\text{H}_{10}$ plays during LiBH_4 (de) hydrogenation.

In collaboration with University of Maryland, SNL, Institute of Metal Physics Ekaterinburg, and Tohoku University, we also investigated the structural behavior of $\text{Na}_2\text{B}_{10}\text{H}_{10}$. A modified structure [2] for monoclinic $\text{Na}_2\text{B}_{10}\text{H}_{10}$ with less-distorted and differently oriented $\text{B}_{10}\text{H}_{10}^{2-}$ anions than the previously published structure [3] (Figure 4) was determined from NPD measurements of $\text{Na}_2^{11}\text{B}_{10}\text{D}_{10}$ in conjunction with DFT computations. Compared to the previous structure, it is found to be lower in energy, exhibits more reasonable Na-H distances, and yields simulated phonon densities of states in better agreement with NVS data for both $\text{Na}_2^{11}\text{B}_{10}\text{H}_{10}$ and $\text{Na}_2^{11}\text{B}_{10}\text{D}_{10}$. Via a combination of DSC, NPD, QENS, nuclear magnetic resonance spectroscopy and ac impedance measurements, [4] $\text{Na}_2\text{B}_{10}\text{H}_{10}$ was found to form a disordered, face-centered-cubic phase above ~ 360 K, with a vacancy-rich Na^+ cation sublattice within the interstitial network formed by highly orientationally mobile anions. This liquid-like cation sublattice exhibits impressive superionic conductivity (e.g., $\sigma \approx 0.01$ S cm^{-1} at 383 K) to substantially lower temperatures than for $\text{Na}_2\text{B}_{12}\text{H}_{12}$.

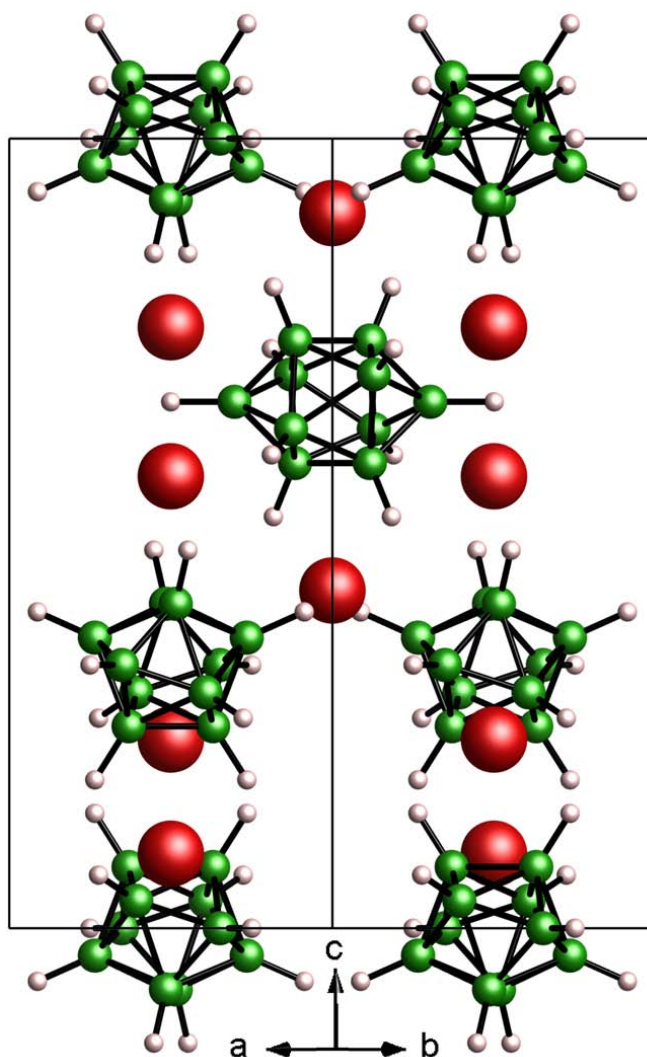


FIGURE 3. The structure of $\text{Li}_2\text{B}_{10}\text{H}_{10}$, with hexagonal $P6_22$ symmetry; red, green, and white spheres denote Li, B, and H atoms, respectively

CONCLUSIONS AND FUTURE DIRECTIONS

- Neutron methods have provided crucial, non-destructive characterization tools for the DOE Hydrogen Storage Sub-Program.
- Agreement between NVS and DFT corroborates $\beta\text{-MSiH}_3$ structures determined by diffraction methods.
- FWS/QENS data for CsSiH_3 corroborate the change to a more 3D SiH_3^- reorientation mechanism upon transformation to the disordered cubic α -phase.
- We successfully established the baseline spectroscopic signature for $\text{B}_{10}\text{H}_{14}$ to be used later for comparison with polymerized versions after thermal treatments and lithiation.

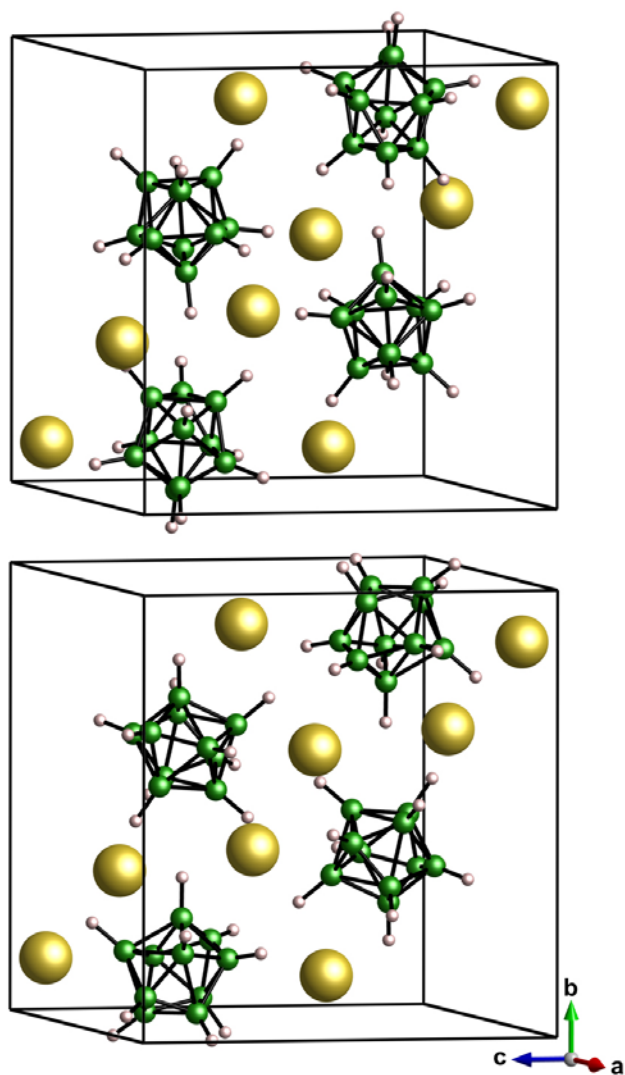


FIGURE 4. The corrected ($P2_1/n$) monoclinic $\text{Na}_2\text{B}_{10}\text{H}_{10}$ crystal structure (top) compared to the published structure (bottom); yellow, green, and white spheres denote Na, B, and H atoms, respectively

- NVS confirms that both LiNH_2 and LiH are hydrogenation products from carbon-nanoconfined Li_3N , with no obvious presence of Li_2NH .
- $\text{Li}_2\text{B}_{10}\text{H}_{10}$ was found to exhibit hexagonal symmetry to best stabilize the ionic packing of the relatively small Li^+ cations and large ellipsoidal $\text{B}_{10}\text{H}_{10}^{2-}$ anions.
- $\text{Li}_2\text{B}_{10}\text{H}_{10}$ completes an order-disorder phase transition by ~ 680 K concomitant with enhanced anion orientational mobility.
- Using neutron scattering methods in conjunction with DFT, we have corrected structural errors in the previously published, monoclinic ordered $\text{Na}_2\text{B}_{10}\text{H}_{10}$ structure.

- An improvement over $\text{Na}_2\text{B}_{12}\text{H}_{12}$, $\text{Na}_2\text{B}_{10}\text{H}_{10}$ exhibits dramatic superionicity above its ~ 360 K phase transition, aided by the large mobile anions and the appearance of cation vacancies.
- We will continue characterization work on hydrogenated metal borides and decaborane-based materials.
- We will start characterization work on mixed alkali metal silanides.
- We will continue to perform neutron based structural and spectroscopic characterizations of new materials in conjunction with the needs of the DOE-funded projects, including novel bulk and nanoconfined complex hydride materials.

FY 2015 PUBLICATIONS/PRESENTATIONS

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8. A. Unemoto, T. Ikeshoji, S. Yasaku, M. Matsuo, V. Stavila, T.J. Udovic, and S. Orimo, "Stable Interface Formation between TiS_2 and LiBH_4 in Bulk-Type All-Solid-State Lithium Batteries," *Chem. Mater.* (in press). doi: 10.1021/acs.chemmater.5b02110.
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10. H. Wu, “Neutron Studies in Complex Metal Hydrides,” Neutron Day: Symposium on Exploring Structure and Dynamics in Hard Matter with Neutrons, University of Maryland, College Park, MD, Oct. 2014.
11. C.M. Brown, “Structural Studies of Small Molecules in MOFs,” Telluride SRC Workshop, Telluride, CO, Jun. 2015.
12. S. Orimo, “Complex Hydrides: A New Series of Solid-State Electrolytes for Battery Devices,” Hydrogen-Metal Systems Gordon Research Conference, Stonehill College, Easton, MA, Jul. 2015.
13. A.V. Skripov, “NMR Approach to Study Atomic Jump Motion in Complex Hydrides,” Hydrogen-Metal Systems Gordon Research Conference, Stonehill College, Easton, MA, Jul. 2015.
14. W.S. Tang, M. Matsuo, H. Wu, W. Zhou, V. Stavila, T.J. Udovic, J.J. Rush, and S. Orimo, “Understanding Complex Hydride Materials as Fast-Ion Conductors,” Hydrogen-Metal Systems Gordon Research Conference, Stonehill College, Easton, MA, Jul. 2015.

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