

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

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Project End Date: Project continuation and direction determined annually by DOE

### Overall 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.

### Fiscal Year (FY) 2013 Objectives

- Complete our investigations and publish results concerning how  $\text{LiBH}_4$  nanosequestration in various carbon scaffolds affects the nature of tetrahydroborate ( $\text{BH}_4^-$ ) anion mobilities.
- Complete our investigations and publish results concerning how iodide substitution in  $\text{LiBH}_4$  perturbs the parent structure and  $\text{BH}_4^-$  anion mobilities.
- Elucidate the nature of the mobile hydrogenous species previously observed in  $\text{NaAlH}_4$  using neutron spectroscopic techniques.

### 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-funded projects using neutron-scattering measurements to understand and characterize hydrogen-substrate interactions of interest in a variety of materials ranging from  $\text{H}_2$  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 2017 storage targets:

- Specific energy: 1.8 kWh/kg
- Energy density: 1.3 kWh/L
- Cost: \$12/kWh

### FY 2013 Accomplishments

- Manuscript published concerning the utility of neutron scattering fixed-window scans for characterizing the relative reorientational mobilities of  $\text{BH}_4^-$  anions in various environments.
- Two manuscripts published concerning the nature of the subtle order-disorder phase transitions of some heavier alkali-metal borohydrides.
- Manuscript published on joint nuclear magnetic resonance (NMR)/quasielastic neutron scattering (QENS) study of  $\text{BH}_4^-$  translational/reorientational dynamics in  $\text{LiBH}_4$  infiltrated in 4-nm pore size ordered-pore carbon.
- Manuscript submitted on detailed QENS study of confinement effects on  $\text{LiBH}_4$  nanosequestered in both ordered (columnar-pore) carbon frameworks and carbon aerogels.
- Manuscript published on  $\text{BH}_4^-$  reorientational mechanism in a hexagonal  $\text{LiBH}_4$ -LiI solid solution.
- Manuscript published concerning the nature of the mobile Al-containing species previously observed in  $\text{NaAlH}_4$ .



## 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 govern 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.

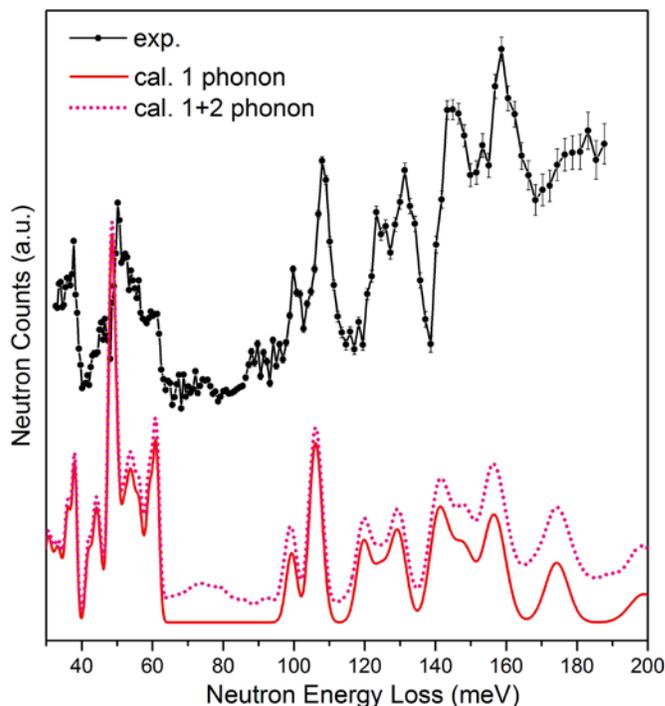
## APPROACH

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 (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

In collaboration with University of Maryland, University of Pennsylvania, and General Motors, the phonon density of states of the recently synthesized metal hydrazinoborane,  $\text{LiN}_2\text{H}_3\text{BH}_3$ , was measured by neutron vibrational spectroscopy (NVS). Agreement with the simulated spectrum from density functional theory (DFT) phonon calculations (Figure 1) corroborated the proposed structure based on X-ray diffraction results.

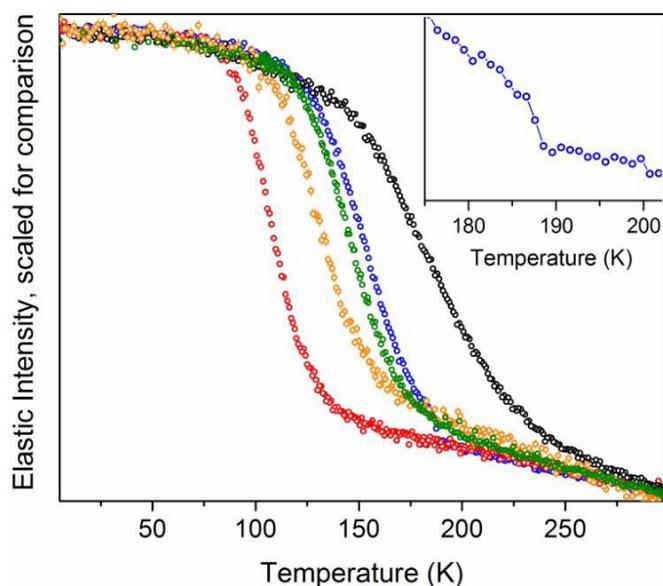
In collaboration with University of Maryland, University of Michigan, Delft University of Technology, HRL Laboratories, and the Institute of Metal Physics-Ekaterinburg, the reorientational dynamics of  $\text{BH}_4^-$  anions in a variety of environments were measured as a function of temperature via neutron scattering fixed-window scans (FWSs) at zero energy transfer using a neutron backscattering spectrometer [1]. The temperature dependence of the FWS was found to be a useful indicator of the relative reorientational mobilities of  $\text{BH}_4^-$  anions in the various alkali-



**FIGURE 1.** The NVS-measured (4 K) and DFT-calculated vibrational spectra for  $\text{LiN}_2\text{H}_3\text{BH}_3$ .

metal borohydride compounds  $\text{MBH}_4$  ( $M=\text{Li, Na, K, Rb, Cs}$ ),  $\text{LiBH}_4$  nanoconfined in carbon scaffolds, and  $\text{LiBH}_4$ -LiI solid solutions. Figure 2 displays the FWSs for the family of alkali-metal borohydrides between 4 K and 300 K. Although in this temperature range, the orthorhombic structure for  $\text{LiBH}_4$  is atypical of the face-centered-cubic structure observed for  $\text{NaBH}_4$ ,  $\text{KBH}_4$ ,  $\text{RbBH}_4$ , and  $\text{CsBH}_4$ , its FWS indicates that it possesses the least rotationally-mobile  $\text{BH}_4^-$  anions of all alkali-metal analogs, which is in line with the overall observed trend that mobility increases with cation size. The onset temperatures of observable motion (on the order of  $10^8$  jumps/s) are approximately 150 K for  $\text{LiBH}_4$ , 120 K for  $\text{NaBH}_4$  and  $\text{KBH}_4$ , 100 K for  $\text{RbBH}_4$ , and 80 K for  $\text{CsBH}_4$ . Likewise, the temperatures where motion starts becoming too rapid (surpassing  $10^{10}$  jumps/s) to be easily observed are approximately 270 K for  $\text{LiBH}_4$ , 200 K for  $\text{NaBH}_4$  and  $\text{KBH}_4$ , 190 K for  $\text{RbBH}_4$ , and 170 K for  $\text{CsBH}_4$ .

In collaboration with University of Maryland, University of Michigan, and Delft University of Technology, neutron vibrational spectra were measured for the alkali borohydrides  $\text{KBH}_4$ ,  $\text{RbBH}_4$ , and  $\text{CsBH}_4$  to probe the low-temperature phase transitions previously identified using thermodynamic and/or crystallographic techniques [2]. The  $\text{BH}_4^-$  torsional band for each compound changed noticeably across its corresponding phase transition. Previous neutron powder diffraction (NPD) measurements showed that the transitions for both  $\text{NaBH}_4$  and  $\text{KBH}_4$  are order-disorder transitions involving the relative orientations of the  $\text{BH}_4^-$  anions.

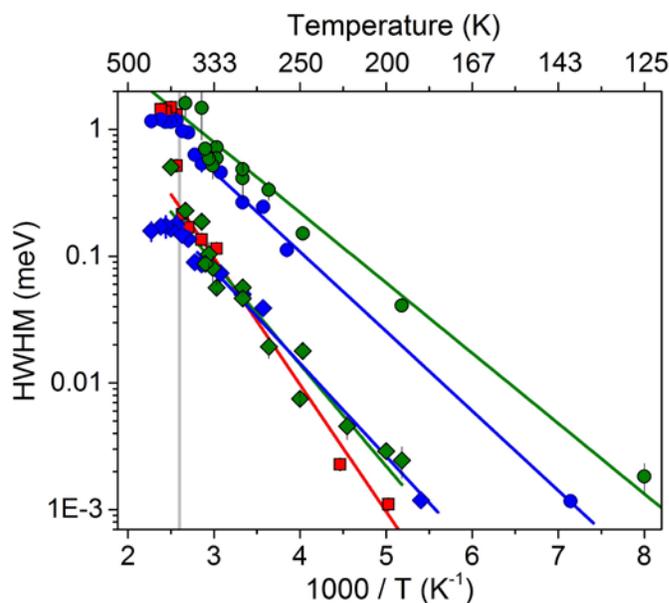


**FIGURE 2.** FWSs for  $\text{BH}_4^-$  anions in  $\text{MBH}_4$  compounds (from right to left,  $M = \text{Li, Na, K, Rb, and Cs}$ ) as a function of temperature. The inset shows evidence of the order–disorder phase transition of  $\text{NaBH}_4$  just below 190 K.

However, diffraction measurements for both  $\text{RbBH}_4$  and  $\text{CsBH}_4$  failed to unequivocally identify long-range-ordered phases below their transitions [3]. The NVS measurements of  $\text{BH}_4^-$  torsional as well as translational optic bands across the transitions, corroborated by DFT phonon calculations, suggested that the subtle  $\text{RbBH}_4$  and  $\text{CsBH}_4$  transitions are indeed analogous to those observed for  $\text{NaBH}_4$  and  $\text{KBH}_4$ , but of shorter range.

Continuing a collaboration with University of Missouri-St. Louis, Washington University-St. Louis, Sandia National Laboratories, and California Institute of Technology, a further dynamical comparison was made between bulk  $\text{LiBH}_4$  and  $\text{LiBH}_4$  sequestered inside both ordered-nanopore carbon (NPC) scaffolds and carbon aerogels. QENS measurements of  $\text{LiBH}_4$  sequestered in either ordered NPCs (with either 2-nm or 4-nm pore sizes) or carbon aerogels (with 13-nm average pore size) indicated similar dynamical results: i.e.,  $\text{BH}_4^-$  anions in the core regions of the pores undergo slower, bulk-like reorientations, and  $\text{BH}_4^-$  anions near the pore walls undergo order-of-magnitude faster reorientations. The data for the NPCs suggest that both types of dynamically distinct anions undergo single  $C_2$  or  $C_3$  axis reorientational jumps below 330 K. By 400 K (which is above the bulk phase transition temperature), both reorient more diffusively around multiple axes. Figure 3 compares the Arrhenius-like temperature dependence of the QENS linewidths for bulk  $\text{LiBH}_4$ ,  $\text{LiBH}_4$  in a 4-nm NPC, and  $\text{LiBH}_4$  in a 13-nm carbon aerogel.

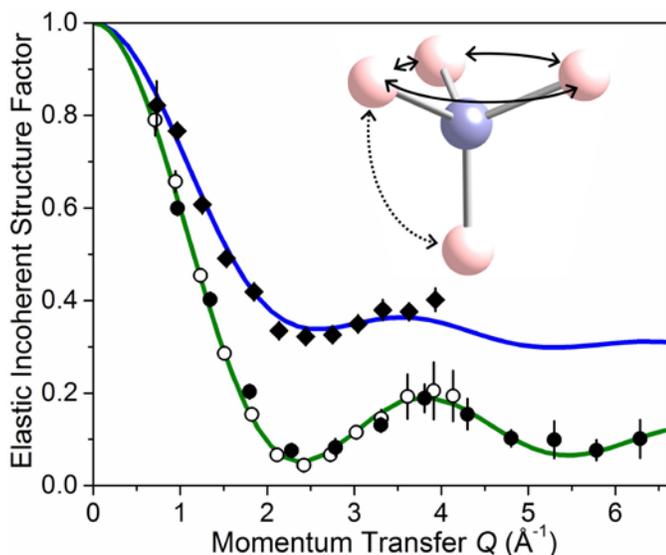
In collaboration with University of Maryland and the Institute of Metal Physics-Ekaterinburg, the reorientational dynamics of  $\text{BH}_4^-$  anions in the hexagonal 1:1  $\text{LiBH}_4\text{-LiI}$



**FIGURE 3.** Comparison of the temperature dependencies of the QENS linewidths for bulk  $\text{LiBH}_4$  (red),  $\text{LiBH}_4$  in a 4-nm NPC (green), and  $\text{LiBH}_4$  in a 13-nm carbon aerogel (blue). Vertical gray line marks the 385 K bulk phase transition temperature.

solid solution were characterized by QENS with results extended to high momentum transfers [4]. The high reorientational mobility compared to that for  $\text{BH}_4^-$  in other solid-state environments reflected a synergistic combination of the underlying hexagonal close-packed lattice and the unusually large  $\text{BH}_4^-$  crystallographic site stabilized by the presence of the  $\Gamma$  anions throughout the structure. Elastic incoherent structure factor (EISF) data (Figure 4) at 125 K revealed a dominant uniaxial reorientation mechanism consisting of rapid  $\text{BH}_4^-$  diffusive-like rotational motions of three H atoms in a ring around the  $c$ -directed trigonal B-H axis, with the fourth axial H atom remaining stationary (orbit model). By 200 K, this diffusive ring of three H atoms underwent additional noticeable jump exchanges with the axial H atom (orbit-exchange model), identical to what had been observed for  $\text{BH}_4^-$  reorientations in hexagonal  $\text{LiBH}_4$  at much higher temperature. The two separate mechanisms were consistent with the two reorientational motions revealed recently by NMR measurements. An average rotational activation energy of  $36 \text{ meV} \pm 1 \text{ meV}$  was derived over a wide temperature range.

In collaboration with Washington University-St. Louis, RCB Hydrides, University of Missouri-St. Louis, and Radboud University, we further investigated the newly discovered, mobile, Al-containing species termed S105 that was found to be present in certain  $\text{NaAlH}_4$  samples, with S105 a likely facilitator of Al-atom transport [5]. We found that hydroxide impurities played a crucial role in the formation of the species. Specifically, in bare  $\text{NaAlH}_4$ ,



**FIGURE 4.** EISFs derived from QENS measurements for  $\text{LiBH}_4\text{-LiI}$  at 125 K (black diamonds) and 250 K (black circles), compared with the orbit model (blue line) and the orbit-exchange model (green line). A schematic of  $\text{BH}_4^-$  reorientational jumps is depicted in the inset. The observed EISFs for hexagonal  $\text{LiBH}_4$  at 400 K (open circles) are shown for comparison.

S105 was present after melting (under sufficient hydrogen pressure to block the dehydriding reaction) only in samples either exposed to  $\text{H}_2\text{O}$  vapor or mixed with metal hydroxides. Moreover, both in situ NMR and NVS measurements indicated that S105 likely involved very (rotationally and translationally) mobile  $\text{AlH}_4^-$  tetrahedra. We proposed that hydroxide impurities promoted fast diffusion of nearby  $\text{AlH}_4^-$  units, similar to enhanced motions seen in  $\text{NaH}$ ; the hydroxides also reacted with  $\text{NaAlH}_4$  to form  $\text{NaH}$  and subsequently produce  $\text{Na}_3\text{AlH}_6$ , which was always found to accompany S105. Our measurements revealed that the only chemical components of S105-containing alanate apart from hydroxides were  $\text{NaAlH}_4$  and  $\text{Na}_3\text{AlH}_6$ . Presence of the S105 species in  $\text{NaAlH}_4$  samples also led to faster dehydriding in hot, undoped  $\text{NaAlH}_4$  solid, pointing to an enhancement of the hydrogen reaction kinetics by S105.

## 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 the recently-synthesized- $\text{LiN}_2\text{H}_3\text{BH}_3$  structure that was determined by diffraction methods.
- Neutron-scattering fixed-window scans are shown to be a valuable technique for making relative comparisons of  $\text{BH}_4^-$  anion rotational mobilities in a host of solid-state environments.

- NVS, NPD, and DFT indicate that the anion-ordered phases in  $\text{RbBH}_4$  and  $\text{CsBH}_4$  do exist but are short-ranged, unlike the long-range order observed for the lighter  $\text{NaBH}_4$  and  $\text{KBH}_4$  compounds.
- QENS measurements of  $\text{LiBH}_4$  sequestered in either ordered nanoporous carbons or carbon aerogels indicate similar dynamical results: core  $\text{BH}_4^-$  anions undergo slower, bulk-like, jump reorientations, and interface  $\text{BH}_4^-$  anions undergo order-of-magnitude faster, more diffusive reorientations.
- QENS measurements of  $\text{BH}_4^-$  anions in a 1:1 hexagonal  $\text{LiBH}_4\text{-LiI}$  alloy indicate  $\text{BH}_4^-$  reorientations predominantly around the  $c$ -directed B-H bond at 125 K with additional jump exchanges between the axial H and other three trigonal Hs occurring above this temperature, similar to what occurs for hexagonal  $\text{LiBH}_4$  at 400 K.
- Neutron vibrational spectra are consistent with NMR results suggesting that the unusual S105 species found in some pretreated  $\text{NaAlH}_4$  samples involves mobile  $\text{AlH}_4^-$  tetrahedral anions whose formation is promoted by hydroxide impurities.
- We will continue to support the DOE Hydrogen Storage Sub-Program where needed.

## FY 2013 PUBLICATIONS/PRESENTATIONS

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13. C.M. Brown, "Understanding Adsorption through Structure and Spectroscopy," American Chemical Society National Meeting, Philadelphia, PA, Aug. 2012. (invited)
14. C.M. Brown, "A View from the Inside: What We Understand about Adsorption in Porous Materials through Structure and Spectroscopy," Chemistry Seminar, Clemson University, SC, Sep. 2012. (invited)
15. T.J. Udovic, N. Verdald, J.J. Rush, and V. Stavila, "Reorientational Dynamics Studies of Various Hydroborate Anions using Quasielastic Neutron Scattering," International Symposium on Metal-Hydrogen Systems--Fundamentals and Applications, Kyoto, Japan, Oct. 2012. (invited)
16. T.J. Udovic, "NIST Center for Neutron Research Plans for International Collaborations in Task 32: Hydrogen-Based Energy Storage," IEA HIA Expert Meeting of Task 22 – Fundamental and Applied Hydrogen Storage Materials Development, Kyoto, Japan, Oct. 2012. (invited)
17. C.M. Brown, "A View from the Inside: What We Understand about Adsorption in Porous Materials through Structure and Spectroscopy," Physics Seminar, University of Missouri-Columbia, Oct. 2012. (invited)
18. C.M. Brown, "Understanding Adsorption in Porous Materials through Structure and Dynamics," Frontiers in Chemical Spectroscopy, Abingdon, Oxford, UK, Nov. 2012. (invited)
19. C.M. Brown, "Neutron Diffraction," 600 Seminar Series Lecture, University of Delaware, Wilmington, DE, Nov. 2012. (invited)
20. C.M. Brown, "Neutron Scattering," 600 Seminar Series Lecture, University of Delaware, Wilmington, DE, Dec. 2012. (invited)
21. H. Wu, "Novel Hydrogen Storage Materials and Related Structural Studies," Department of Materials Science and Engineering Seminar, University of Maryland, College Park, MD, Mar. 2013. (invited)
22. N. Verdald, T.J. Udovic, J.J. Rush, and A.V. Skripov, "Neutron Scattering Studies of Destabilized Lithium Borohydride," American Physical Society March Meeting, Baltimore, MD, Mar. 2013.
23. T.J. Udovic, "Neutron Metrology of Hydrogen in Bulk and Nanoconfined Metal-Hydride and Complex-Hydride Systems," IEA HIA Kickoff Expert Meeting of Task 32 – Hydrogen-Based Energy Storage, Heraklion, Crete, Greece, Apr. 2013. (invited)
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26. C.M. Brown, "Hydrogen Storage in Metal Organic Frameworks," DOE EERE Annual Merit Review, Arlington, VA, May 2013. (invited)
27. H. Wu, "Novel Hydride Materials for Hydrogen Storage," Gordon Research Conference on Hydrogen-Metal Systems, Lucca (Barga), Italy, Jul. 2013.
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