

IV.D.3 Neutron Characterization in Support of the DOE Hydrogen Storage 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) 2014 Objectives

- Synthesize and characterize the structure and dehydrogenation properties of the Na and K analog compounds of lithium hydrazinoborane, $\text{LiN}_2\text{H}_3\text{BH}_3$.
- Investigate how halide substitution in NaBH_4 perturbs the parent structure and BH_4^- anion mobilities.
- Complete our investigations concerning previously unknown order-disorder phase transitions in LiBH_4 and NaBH_4 dehydrogenation by-products $\text{Li}_2\text{B}_{12}\text{H}_{12}$ and $\text{Na}_2\text{B}_{12}\text{H}_{12}$.
- Elucidate the conductivities of disordered, cation-vacancy-rich $\text{Li}_2\text{B}_{12}\text{H}_{12}$ and $\text{Na}_2\text{B}_{12}\text{H}_{12}$.

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 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 2014 Accomplishments

- Manuscript published on two alkali metal hydride modifications of hydrazine borane for improved dehydrogenation properties.
- Manuscript published on detailed quasielastic neutron scattering (QENS) study of confinement effects on LiBH_4 nanosequestered in both ordered (columnar-pore) carbon frameworks and carbon aerogels.
- Four manuscripts published on the structural modifications, anion and cation dynamics, and cationic conductivity associated with the order-disorder phase transitions in $\text{Li}_2\text{B}_{12}\text{H}_{12}$ and $\text{Na}_2\text{B}_{12}\text{H}_{12}$.
- Manuscript published on the structure and spectroscopy of H_2 adsorbed in a nickel metal-organic framework (MOF).



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 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, 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 the University of Maryland, Dalian Institute of Chemical Physics, and Sichuan University, two new alkali metal hydrazidotrihydridoborates, $\text{NaN}_2\text{H}_3\text{BH}_3$ and $\text{KN}_2\text{H}_3\text{BH}_3$, were synthesized via a liquid approach [1]. The crystal structures were determined by X-ray diffraction and corroborated by neutron vibrational spectroscopy (NVS) measurements of the phonon densities of states in conjunction with density functional theory (DFT) calculations (Figure 1). There was a clear correlation between the sizes of the metal cations and their corresponding melting and dehydrogenation temperatures. Upon approaching the melting points, alkali metal hydrazidotrihydridoborates dehydrogenated rapidly in the first step, giving rise to the formation of intermediates that possessed N_2BH_2 , N_2BH , and NBH_3 species. Further increases in temperature led to the release of additional H_2 and the formation of N_2BH species. Compared to pristine $\text{N}_2\text{H}_4\text{BH}_3$, the alkali-metal-substituted hydrazidotrihydridoborates showed markedly improved dehydrogenation behavior with no N_2H_4 emission and greatly suppressed NH_3 release.

In collaboration with the University of Maryland and the Institute of Metal Physics-Ekaterinburg, the effect of partial Cl^- anion substitution in NaBH_4 on the reorientational dynamics of the BH_4^- anions was investigated by QENS. 1:1 $\text{Na}^{11}\text{BH}_4\text{-NaCl}$ solid solutions were made by ball-milling the pure components. The elastic incoherent structure factor

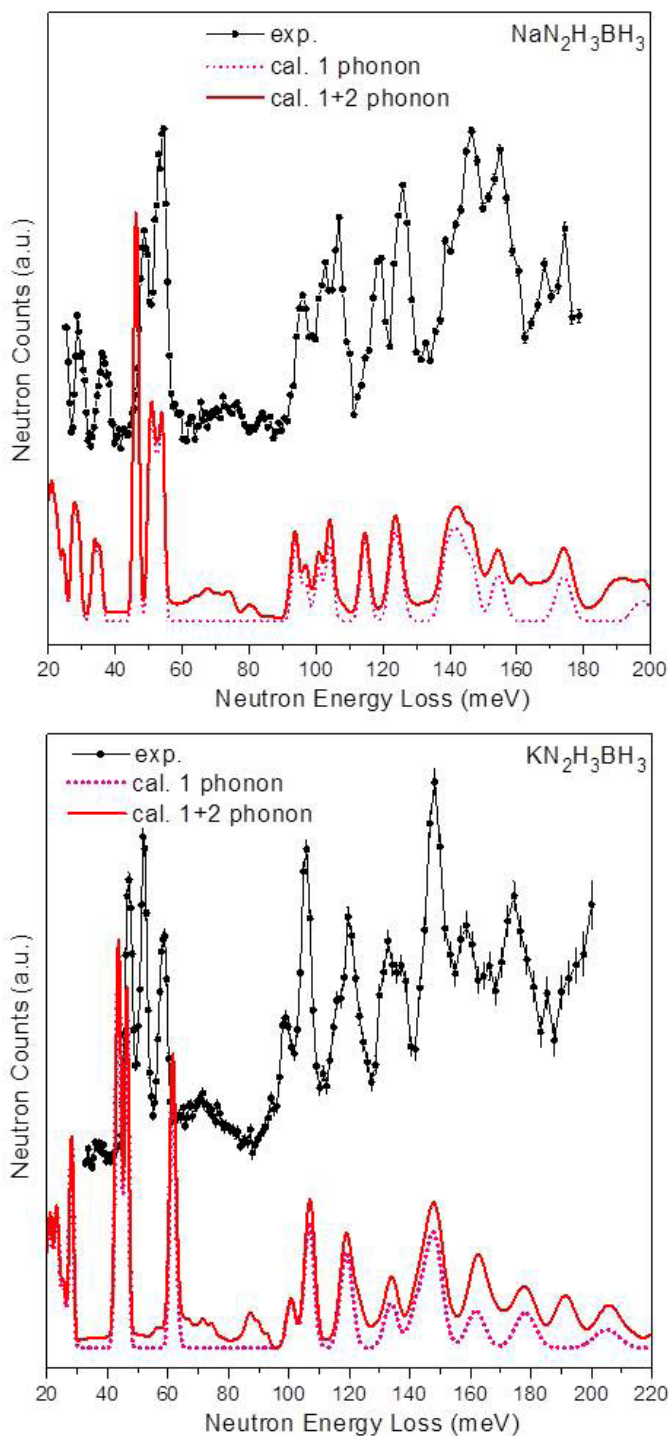


FIGURE 1. The NVS-measured (4 K) and DFT-calculated vibrational spectra for $\text{NaN}_2\text{H}_3\text{BH}_3$ and $\text{KN}_2\text{H}_3\text{BH}_3$ (from Ref. 1).

behavior with neutron momentum transfer Q at 450 K (Figure 2) indicated that the BH_4^- anions in the disordered structure were undergoing reorientational “cubic” tumbling motions such that the four H atoms associated with each B atom were visiting all eight corners of a cube. Since Cl^-

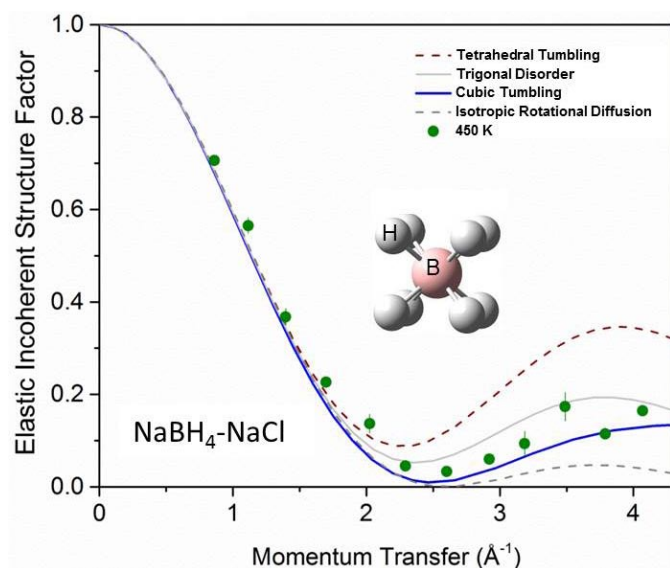


FIGURE 2. EISFs derived from QENS measurements for NaBH₄-NaCl at 450 K (green circles) compared with several BH₄⁻ reorientational jump models. A schematic of BH₄⁻ disordered cubic site geometry is depicted in the inset.

anions are smaller than BH₄⁻ anions, the mixed compound had a reduced lattice constant, and thus a smaller lattice volume, to accommodate each BH₄⁻ anion and lower anion rotational mobility compared with pristine NaBH₄. The activation energy for reorientation for NaBH₄-NaCl was found to be 114(4) meV which is similar to that observed for NaBH₄. Preliminary neutron elastic scattering fixed-window scans indicated that replacing Cl⁻ with the relatively larger I⁻ anion results in a BH₄⁻ rotational mobility surpassing that of both NaBH₄-NaCl and NaBH₄.

In collaboration with the University of Maryland, GE, Sandia National Laboratories, the Institute of Metal Physics-Ekaterinburg, and Tohoku University, we discovered by X-ray diffraction and neutron powder diffraction that Li₂B₁₂H₁₂ and Na₂B₁₂H₁₂ undergo phase transitions at ~615 K and 529 K, respectively, upon heating from known low-temperature ordered structures to high-temperature, entropically-driven, highly-disordered cubic structures with orientationally mobile anions and vacancy-rich cation sublattices [2]. These new high-temperature structures have to be considered in any future thermodynamic analyses of Li-B-H and Na-B-H systems. The disordered Na₂B₁₂H₁₂ phase (Figure 3) was found to be stable and more amenable to study than the disordered Li₂B₁₂H₁₂ phase. Nuclear magnetic resonance (NMR) and QENS studies [2-4] were performed to characterize the Na⁺ cation translational mobility and the B₁₂H₁₂²⁻ anion reorientational mobility of the disordered Na₂B₁₂H₁₂ phase. Measurements of the ²³Na NMR spectra and spin-lattice relaxation rates showed that the transition from the ordered to the disordered phase of Na₂B₁₂H₁₂ was accompanied by the onset of fast translational

diffusion of the Na⁺ cations. Just above the phase transition, the lower limit of the Na⁺ jump rate was estimated to be ~2×10⁸ s⁻¹, and the corresponding activation energy for Na⁺ diffusion was ~410 meV. QENS and NMR measurements also indicated a two-orders-of-magnitude enhancement in B₁₂H₁₂²⁻ anion reorientational mobility upon transitioning to the disordered phase, with a reorientational jump rate on the order of 10¹¹ s⁻¹. The predominant mechanism at 580 K appeared to be small-angle, uniaxial reorientational jumps, with the best overall fit to the elastic incoherent structure factor at high temperature being six-fold or greater reorientations around one of the anion C₃ symmetry axes. The average activation energy for reorientation was determined to be about 770(20) meV for the ordered phase and about 260(20) meV for the disordered phase. Subsequent AC impedance measurements [5] (Figure 3) confirmed that disordered Na₂B₁₂H₁₂ was superionic, with a conductivity of about 0.1 S cm⁻¹ near 550 K, which greatly exceeds that of all other complex-hydride materials to date. This conductivity rivals that of sodium beta alumina, the current commercial electrolyte for Na-ion batteries operating in this temperature region. It is believed that the overly large anions facilitate the high conductivity by providing large intralattice diffusion pathways for the much smaller cations.

In collaboration with the University of Delaware, University of Maryland, Oak Ridge National Laboratory, and University of St. Andrews, the structure of the MOF, Ni₂(dobdc) (dobdc = 2,5-dioxido-1,4-benzenedicarboxylate), as a function of D₂ adsorption was determined by in situ neutron powder diffraction, and the local adsorption potential for hydrogen at each site was probed using NVS [6]. At the lowest loadings, the D₂ molecules were located 2.20(1) Å from the open metal centers. The Ni²⁺ variant showed the shortest D₂-metal distance in the M₂(dobdc) series (M = Mg, Zn, Co, Fe) studied thus far and is consistent with the high initial H₂ adsorption enthalpy of 13.5 kJ mol⁻¹. The secondary adsorption sites were located close to the framework oxygen and carbon, respectively. NVS revealed detailed interactions of the adsorbed para-H₂ with the framework and its response to further H₂ adsorption. The adsorbed H₂ interconverts between ortho- and para-H₂, depending on the sample temperature. The transitions between rotational energy levels were determined for the three adsorption sites, with the transitions shifting slightly with increased adsorption levels.

CONCLUSIONS AND FUTURE DIRECTIONS

- Neutron methods have provided crucial, non-destructive characterization tools for the DOE Hydrogen Storage Program.
- Agreement between NVS and DFT corroborates the recently synthesized NaN₂H₃BH₃ and KN₂H₃BH₃ structures that were determined by diffraction methods.

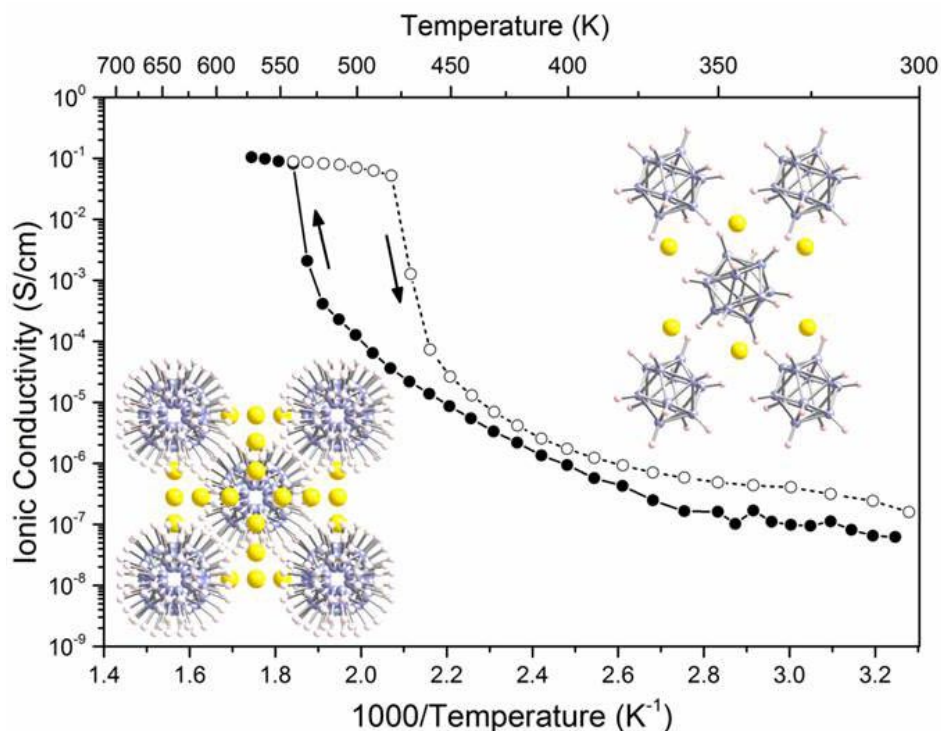


FIGURE 3. Depictions of the low-temperature ordered and high-temperature disordered structures of $\text{Na}_2\text{B}_{12}\text{H}_{12}$ and the corresponding Na^+ conductivity behavior vs. temperature upon heating and cooling. Conductivity hysteresis coincides with the observed order-disorder structural hysteresis (from Ref. 5).

- Compared to $\text{N}_2\text{H}_4\text{BH}_3$, the alkali-metal substituted hydrazidotrihydridoborates display improved dehydrogenation behavior with no N_2H_4 emission and greatly suppressed NH_3 release.
- Neutron-scattering fixed-window scans are shown to be valuable for making relative comparisons of BH_4^- anion rotational mobilities in bulk and halide-substituted NaBH_4 .
- The cubic tumbling mechanism, where the H atoms jump to the eight corners of a cube, is in best agreement with the QENS data for NaCl-NaBH_4 solid solution above room temperature.
- $\text{Li}_2\text{B}_{12}\text{H}_{12}$ and $\text{Na}_2\text{B}_{12}\text{H}_{12}$ undergo order-disorder phase transitions at ~ 615 K and 529 K, respectively, resulting in orientationally mobile anions and vacancy-rich cation sublattices.
- $\text{Na}_2\text{B}_{12}\text{H}_{12}$ exhibits dramatic superionicity above its order-disorder phase transition, aided by the large mobile anions and the appearance of cation vacancies.
- The Ni^{2+} variant in the MOF $\text{M}_2(\text{dobdc})$ series ($\text{M} = \text{Mg}, \text{Zn}, \text{Co}, \text{Fe}$) displayed the shortest adsorbed D_2 -metal distance ($2.20[1] \text{ \AA}$) of all studied variants, which is consistent with the high initial H_2 adsorption enthalpy.
- We will start characterization work on new hydrogenated metal silicides ($\text{M}_x[\text{SiH}_3]_y$).
- We will investigate properties of alkali (A) and alkaline-earth (Ae) metal decahydro-*closo*-decaborates $\text{A}_2\text{B}_{10}\text{H}_{10}$ and $\text{AeB}_{10}\text{H}_{10}$.
- 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.

SPECIAL RECOGNITIONS & AWARDS/ PATENTS ISSUED

1. W.S. Tang: Highly Commended Poster Award for “Altering the Structural Properties of $\text{A}_2\text{B}_{12}\text{H}_{12}$ Compounds via Cation and Anion Modifications” at the 14th International Symposium on Metal-Hydrogen Systems: Fundamentals and Applications (MH2014), Manchester, UK.

FY 2014 PUBLICATIONS/PRESENTATIONS

1. C.M. Brown, A.J. Ramirez-Cuesta, J.-H. Her, P.S. Wheatley, and R.E. Morris, “Structure and Spectroscopy of Hydrogen Adsorbed in a Nickel Metal-Organic Framework,” *Chem. Phys.* 427, 3-8 (2013).

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3. X. Liu, E.H. Majzoub, V. Stavila, R.K. Bhakta, M.D. Allendorf, D.T. Shane, M.S. Conradi, N. Verdal, T.J. Udovic, and S.-J. Hwang, "Probing the Unusual Anion Mobility of LiBH_4 Confined in Highly Ordered Nanoporous Carbon Frameworks via Solid State NMR and Quasielastic Neutron Scattering," *J. Mater. Chem. A* **1**, 9935-9941 (2013).
4. N. Verdal, T.J. Udovic, J.J. Rush, X. Liu, E.H. Majzoub, J.J. Vajo, and A.F. Gross, "Dynamical Perturbations of Tetrahydroborate Anions in LiBH_4 due to Nanoconfinement in Controlled-pore Carbon Scaffolds," *J. Phys. Chem. C* **117**, 17983-17995 (2013).
5. A.V. Skripov, O.A. Babanova, A.V. Soloninin, V. Stavila, N. Verdal, T.J. Udovic, and J.J. Rush, "Nuclear Magnetic Resonance Study of Atomic Motion in $\text{A}_2\text{B}_{12}\text{H}_{12}$ (A = Na, K, Rb, Cs): Anion Reorientations and Na^+ Mobility," *J. Phys. Chem. C* **117**, 25961-25968 (2013).
6. N. Verdal, J.-H. Her, V. Stavila, A.V. Soloninin, O.A. Babanova, A.V. Skripov, T.J. Udovic, and J.J. Rush, "Complex High-Temperature Phase Transitions in $\text{Li}_2\text{B}_{12}\text{H}_{12}$ and $\text{Na}_2\text{B}_{12}\text{H}_{12}$," *J. Solid State Chem.* **212**, 81-91 (2014).
7. A.V. Skripov, V. Paul-Boncour, T.J. Udovic, and J.J. Rush, "Hydrogen Dynamics in Laves-Phase Hydride $\text{YFe}_2\text{H}_{2.6}$: Inelastic and Quasielastic Neutron Scattering Studies," *J. Alloys Compds.* **595**, 28-32 (2014).
8. Y.S. Chua, Q. Pei, X. Ju, W. Zhou, T.J. Udovic, G. Wu, Z. Xiong, P. Chen, and H. Wu, "Alkali Metal Hydride Modification on Hydrazine Borane for Improved Dehydrogenation," *J. Phys. Chem. C* **118**, 11244-11251 (2014).
9. N. Verdal, T.J. Udovic, V. Stavila, W.S. Tang, J.J. Rush, and A.V. Skripov, "Anion Reorientations in the Superionic Conducting Phase of $\text{Na}_2\text{B}_{12}\text{H}_{12}$," **118**, 17483-17489 (2014).
10. T.J. Udovic, M. Matsuo, A. Unemoto, N. Verdal, V. Stavila, A.V. Skripov, J.J. Rush, H. Takamura, and S.-I. Orimo, "Sodium Superionic Conduction in $\text{Na}_2\text{B}_{12}\text{H}_{12}$," *Chem. Commun.* **50**, 3750-3752 (2014).
11. M.R. Hudson, "In-situ Powder Diffraction for Industrial Gas Separations," User Science Lecture, Advanced Photon Source, Argonne National Laboratory, Argonne, IL, May 2013. (invited)
12. H. Wu, "Development of Novel Gas Storage Materials," Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, China, May 2013. (invited)
13. C.M. Brown "Applications of Neutron Scattering to Understanding Structure and Gas Storage Properties of Metal-Organic Frameworks and Related Materials," American Chemical Society National Meeting, Indianapolis, IN, Aug. 2013. (invited)
14. H. Wu, "Novel Gas Storage Materials and Related Structural Studies," IUPAC 9th International Conference on Novel Materials and Synthesis (NMS-IX), Shanghai, China, Oct. 2013. (invited)
15. Y.S. Chua, Q. Pei, X. Ju, W. Zhou, T.J. Udovic, G. Wu, Z. Xiong, P. Chen, and H. Wu, "Alkali Metal Hydrazinoboranes for Hydrogen Storage," American Chemical Society Spring Meeting, Dallas, TX, Mar. 2014.
16. C.M. Brown, "Gas Adsorption in Microporous Materials," Chemistry Seminar, Drexel University, Philadelphia, PA, May 2014. (invited)
17. T.J. Udovic, C.M. Brown, D.A. Neumann, "Neutron Characterization in Support of the DOE Hydrogen Storage Sub-Program," DOE EERE Annual Merit Review, Washington, DC, Jun. 2014. (invited)
18. H. Wu, "Novel Complex Hydrides for Hydrogen Storage and Related Structural Studies," 14th International Symposium on Metal-Hydrogen Systems: Fundamentals and Applications (MH2014), Manchester, UK, Jul. 2014. (invited)
19. T.J. Udovic, N. Verdal, J.J. Rush, W.S. Tang, A.V. Skripov, and V. Stavila, "Probing Hydroborate Polyanion Reorientations via Quasielastic Neutron Scattering," 14th International Symposium on Metal-Hydrogen Systems: Fundamentals and Applications (MH2014), Manchester, UK, Jul. 2014. (invited)
20. C.M. Brown, "Neutron Studies of Hydrogen Adsorption in Porous Materials," 14th International Symposium on Metal-Hydrogen Systems: Fundamentals and Applications (MH2014), Manchester, UK, Jul. 2014. (invited)
21. S. Orimo, "Cool Hydrides! - Research Topics and Trends in Japan," 14th International Symposium on Metal-Hydrogen Systems: Fundamentals and Applications (MH2014), Manchester, UK, Jul. 2014. (plenary)
22. M. Matsuo, H. Oguchi, A. Unemoto, T. Ikeshoji, H. Takamura, T. Vegge, A. Remhof, A. Borgshulte, A. Züttel, T.J. Udovic, A.V. Skripov, and S. Orimo, "Fast Ionic Conduction in Complex Hydrides," 14th International Symposium on Metal-Hydrogen Systems: Fundamentals and Applications (MH2014), Manchester, UK, Jul. 2014. (invited)
23. A.V. Skripov, "Nuclear Magnetic Resonance Studies of Atomic Motion in Borohydride-Based Materials," 14th International Symposium on Metal-Hydrogen Systems: Fundamentals and Applications (MH2014), Manchester, UK, Jul. 2014. (invited)
24. W.S. Tang, T.J. Udovic, N. Verdal, J.J. Rush, A.V. Skripov, V. Stavila, M. Matsuo, and S. Orimo, "Altering the Structural Properties of $\text{A}_2\text{B}_{12}\text{H}_{12}$ Compounds via Cation and Anion Modifications," 14th International Symposium on Metal-Hydrogen Systems: Fundamentals and Applications (MH2014), Manchester, UK, Jul. 2014.
25. T.J. Udovic, "Sodium Superionic Conduction Discovered in Disordered Sodium Borohydride Compounds," IEA HIA Expert Meeting of Task 32 – Hydrogen-Based Energy Storage, Manchester, UK, Jul. 2014. (invited)

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