

Neutron Characterization in support of the DOE Hydrogen Storage Sub-Program

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Timeline

- Project start date: 10/2010
- Project end date: 10/2014*

*Project continuation and direction determined annually by DOE

Budget

- FY14 DOE Funding: \$200K
- Planned FY15 DOE Funding: \$200K
- Total DOE Funds Received to Date: \$800K

[NIST continues to provide access to neutron facilities and FTEs for the DOE Hydrogen Storage Projects.](#)

NIST Associates

John J. Rush	Hui Wu
Matt Hudson	Wei Zhou
Zeric Hulvey	Wan Si Tang

Barriers addressed

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

Partners

Caltech, Delaware, GM, HRL, Maryland, Michigan, Missouri-St. Louis, Molecular Foundry, NREL, Ohio State, Penn, Penn State, RCB Hydrides, Sandia, UC Berkeley, Utah, Washington U.-St. Louis

Overall: 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.

Neutron methods

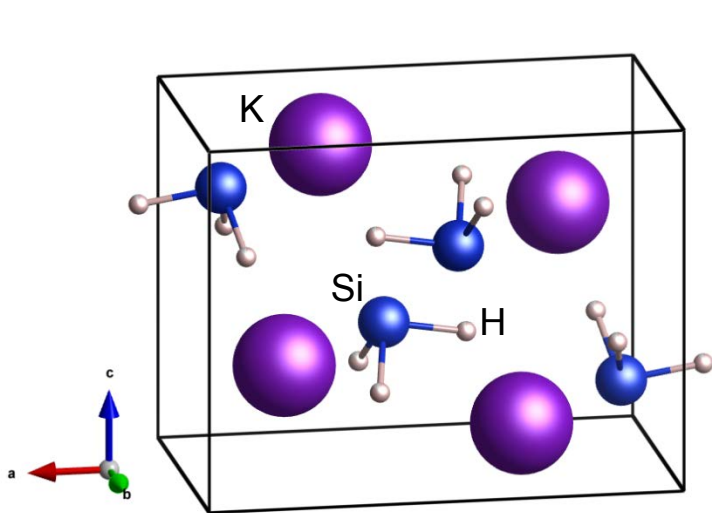
- determine elemental compositions of materials (prompt- γ activation analysis and neutron reflectometry of H stoichiometries and profiles)
- determine location of H and crystal structures of materials (neutron diffraction superior to XRD for “seeing” light H and D)
- determine bonding of absorbed H (unlike IR and Raman, neutron vibrational spectroscopy “sees” all H vibrations for straightforward comparison with first-principles calculations)
- elucidate H diffusion mechanisms (faster dynamics timescale of neutron quasielastic scattering complements NMR; transport mechanisms gleaned from momentum transfer dependence)

Technical Accomplishments

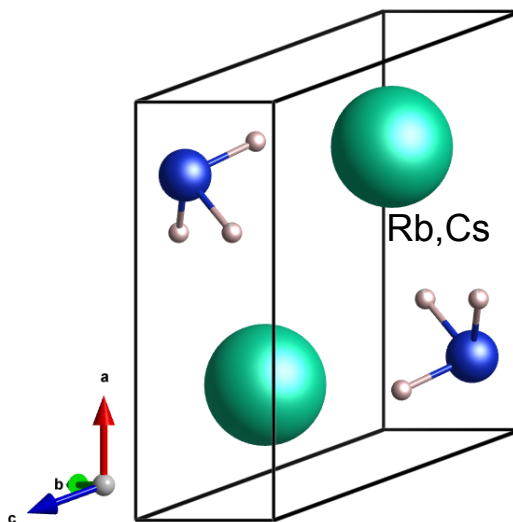
Neutron methods, synthesis expertise, and DFT computations were used to further the goals of the DOE Hydrogen-Storage Sub-Program.

Motivation: investigating new materials potentially promising for hydrogen storage

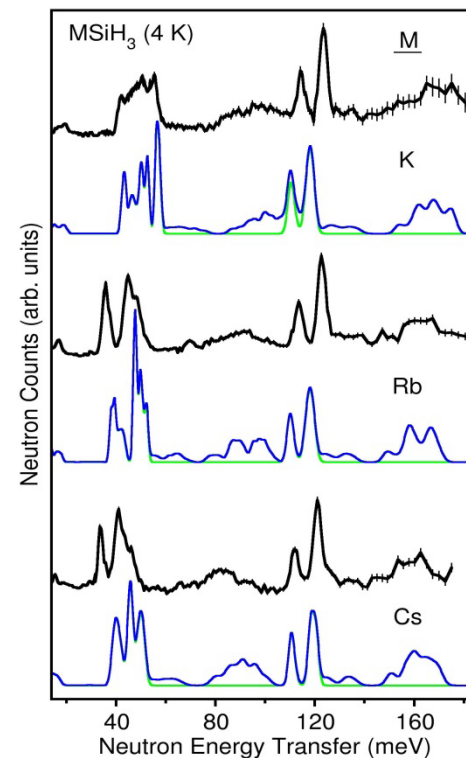
MSiH_3 (M=K, Rb, Cs) stores hydrogen reversibly through an MSi/MSiH_3 equilibrium, yielding a 0.1 MPa H_2 equilibrium pressure at ~ 410 K.



$\beta\text{-KSiH}_3$
(*Pnma*)



$\beta\text{-RbSiH}_3, \beta\text{-CsSiH}_3$
(*P2₁/m*)

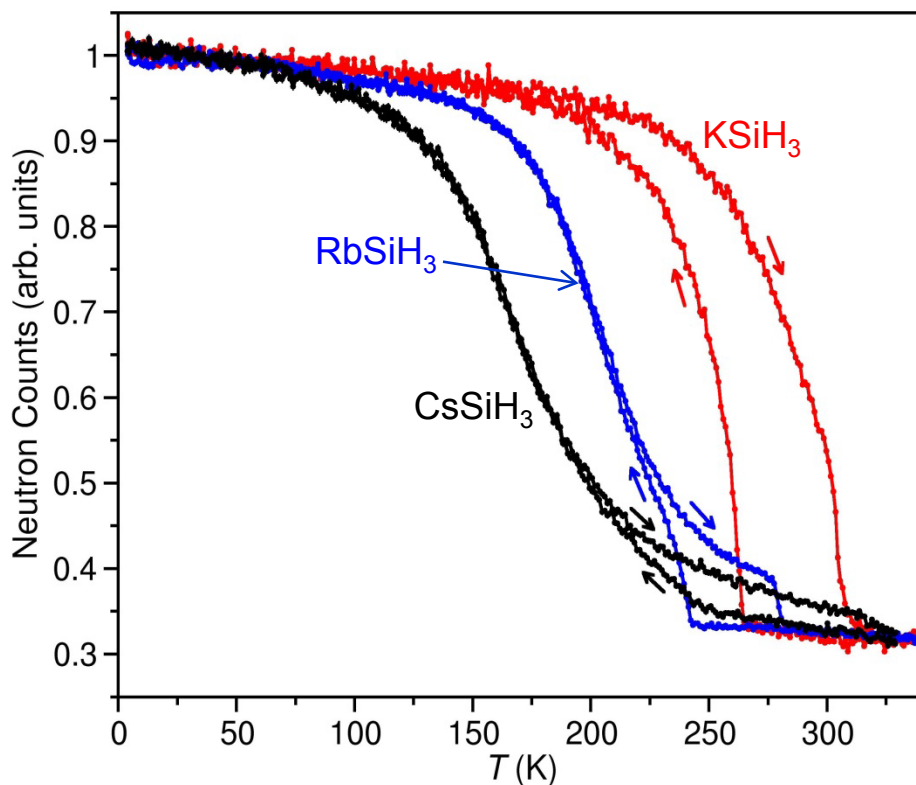


DFT phonon simulations (blue) are in agreement with neutron vibrational spectra (black) for the MSiH_3 compounds.

Agreement between neutron vibrational spectroscopy and density functional theory corroborates $\beta\text{-MSiH}_3$ structures determined by diffraction methods.

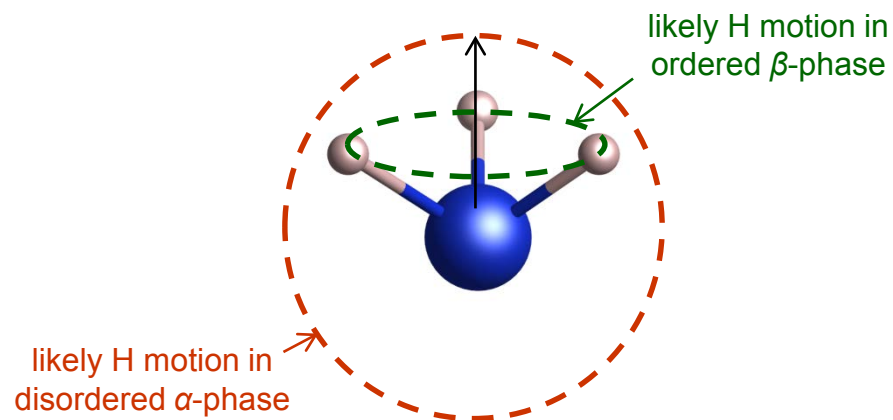
Motivation: investigating new materials potentially promising for hydrogen storage

Neutron-Elastic-Scattering Fixed-Window Scans



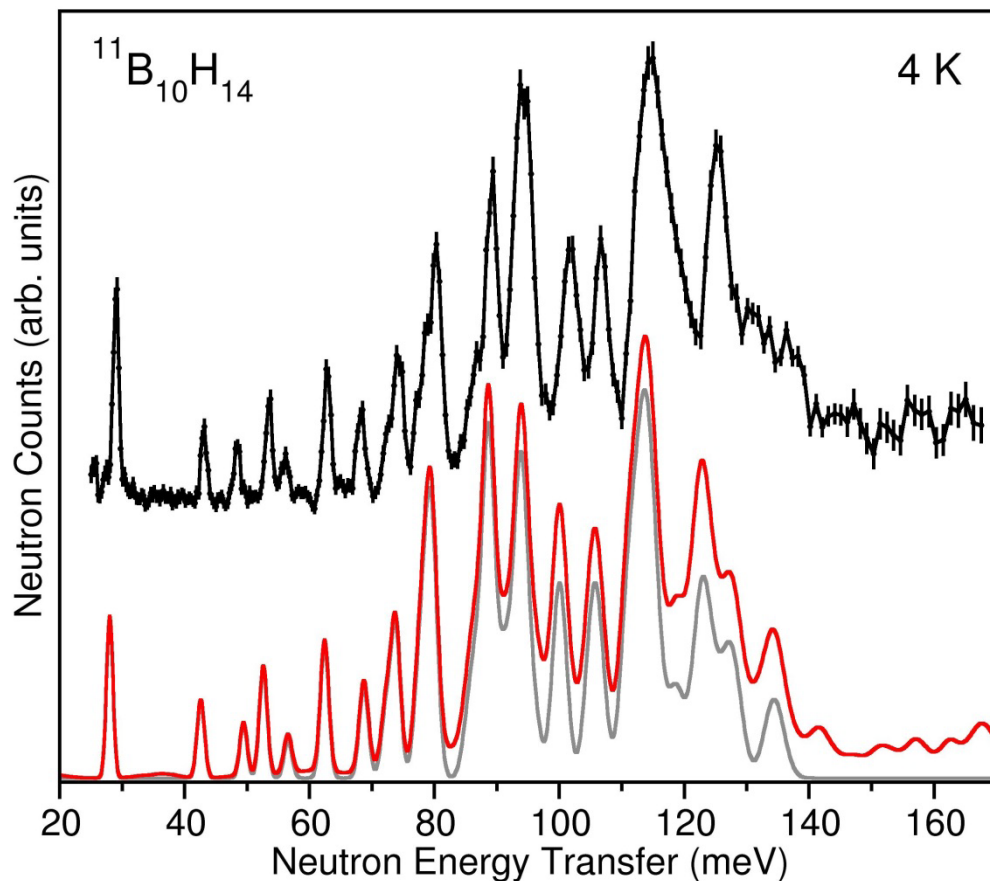
Fixed-window scans indicate that:

- SiH_3^- anions attain high reorientational mobilities ($\gg 10^{10}$ H jumps/s) that increase with cation size
- there are hysteretic order-disorder phase changes that affect the SiH_3^- reorientation mechanism and mobilities.



Quasielastic neutron scattering data for CsSiH_3 corroborate the change to a more three-dimensional SiH_3^- reorientation mechanism upon transformation to the disordered cubic α -phase.

Motivation: Determining the chemical nature of thermally treated decaborane

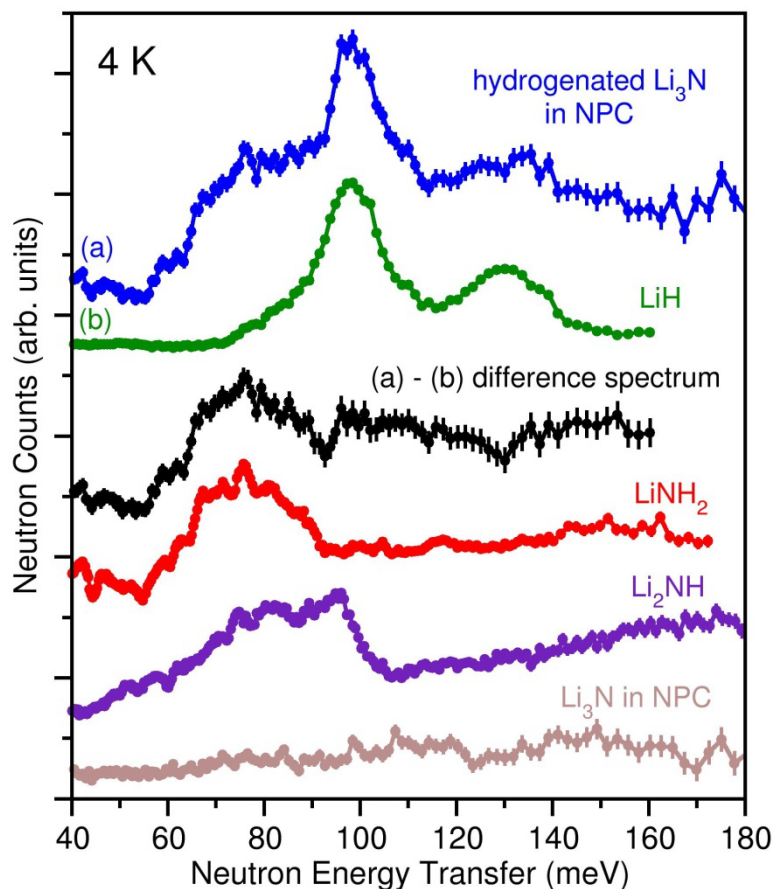


The neutron vibrational spectrum of $^{11}\text{B}_{10}\text{H}_{14}$ (black) is in good agreement with the DFT-simulated 1-phonon (gray) and 1+2-phonon (red) spectra.

Currently, neutron prompt-gamma activation analysis is being used to obtain B/H ratios in different thermally treated samples of $\text{B}_{10}\text{H}_{14}$.

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.

Motivation: determining products of hydrogenated Li_3N in nanoporous carbon

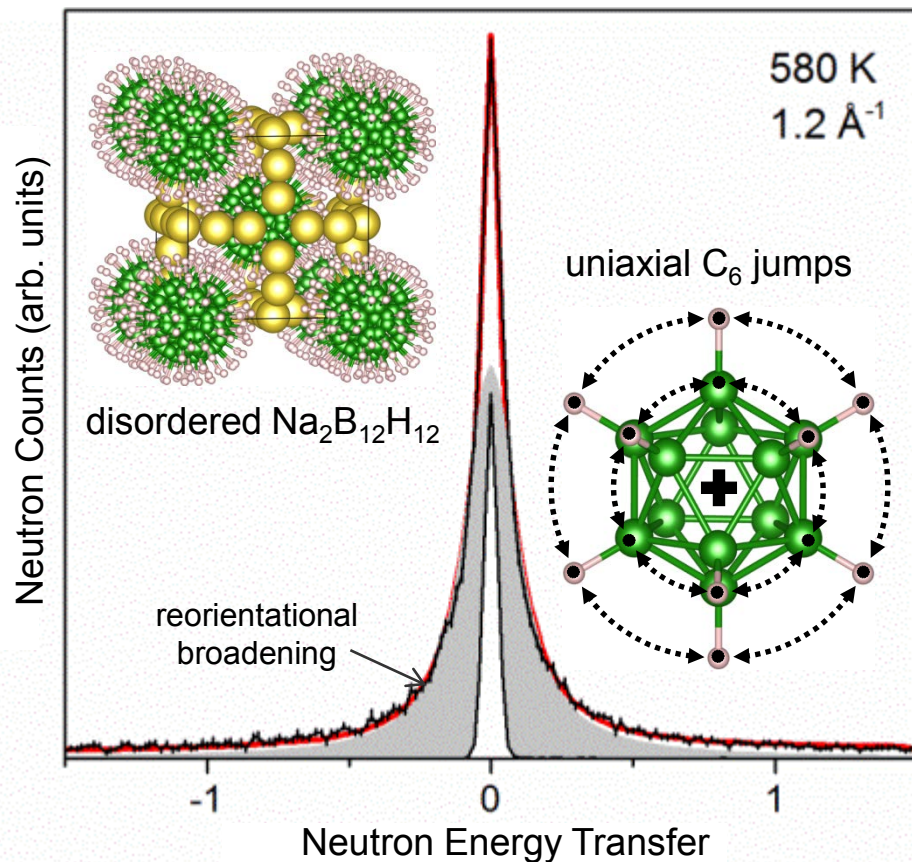


Neutron vibrational spectra associated with hydrogenated Li_3N confined in nanoporous carbon (NPC) after 5 desorption/absorption cycles compared to reference spectra indicate that:

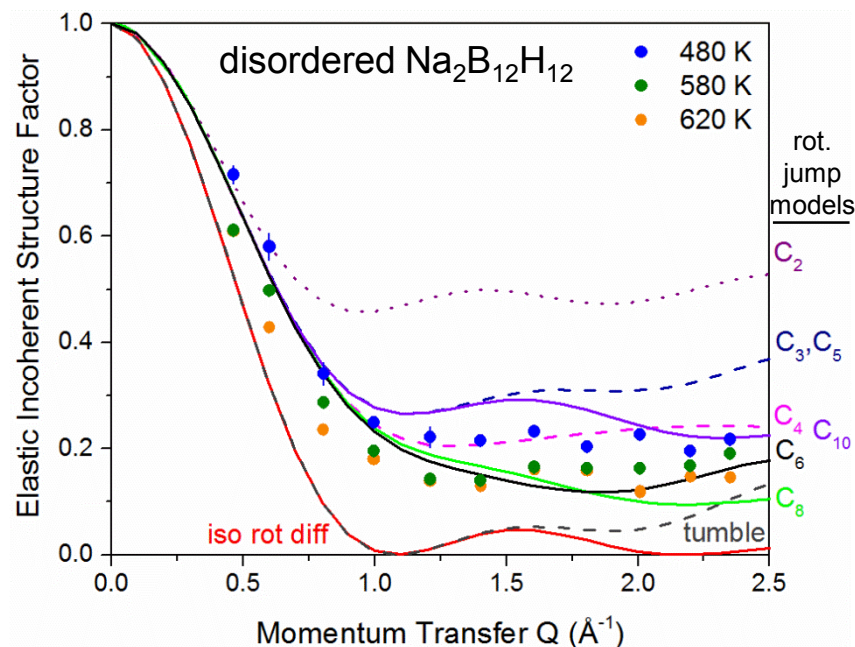
- relatively little H exists in the dehydrogenated spectrum (Li_3N in NPC)
- both LiNH_2 and LiH are present in the hydrogenated spectrum

Neutron vibrational spectroscopy confirms that both LiNH_2 and LiH are hydrogenation products from carbon-nanoconfined Li_3N , with no obvious presence of Li_2NH .

Motivation: investigating potential borohydride dehydrogenation products



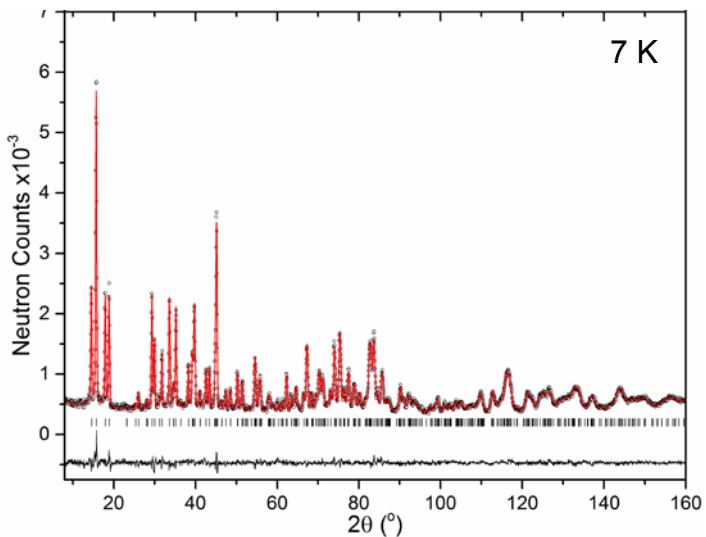
Elastic Incoherent Structure Factor (EISF) Models



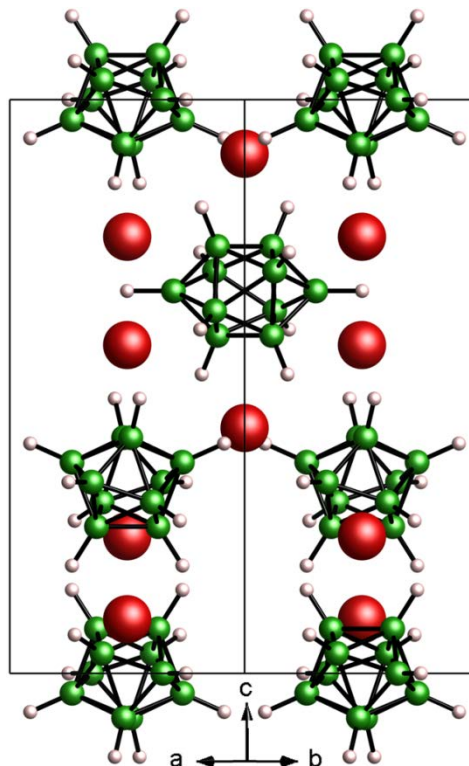
A comparison of the EISF data with different jump reorientation models suggests that $\text{B}_{12}\text{H}_{12}^{2-}$ anions undergo, on average, predominantly small-angle uniaxial jumps.

Quasielastic neutron scattering measurements of disordered $\text{Na}_2\text{B}_{12}\text{H}_{12}$ indicate rapid ($>10^{11}$ jumps/s), mainly (small-angle) uniaxial, reorientational motions of the $\text{B}_{12}\text{H}_{12}^{2-}$ anions. 10

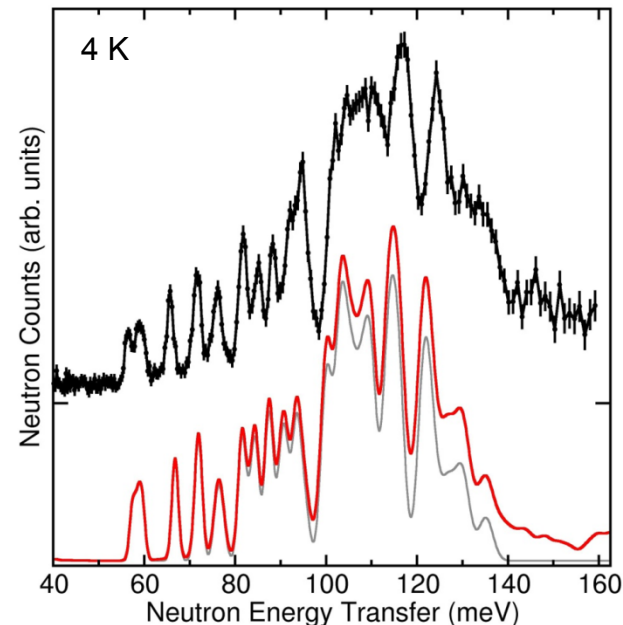
Motivation: investigating potential borohydride dehydrogenation products



Neutron powder diffraction pattern and fit for ${}^7\text{Li}_2{}^{11}\text{B}_{10}\text{D}_{10}^-$.



hexagonal $P6_422$ symmetry

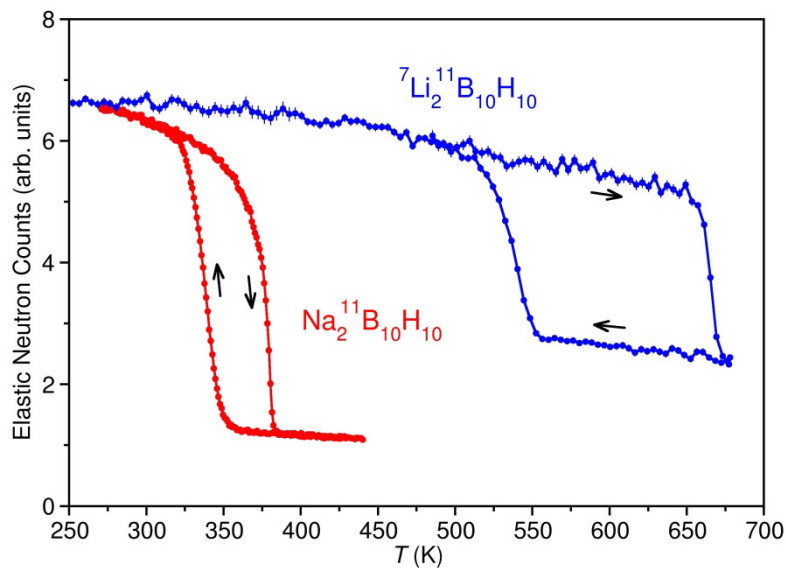


DFT phonon simulations (gray: 1-phonon, and red: 1+2-phonon) are in good agreement with the neutron vibrational spectrum (black) for ${}^7\text{Li}_2{}^{11}\text{B}_{10}\text{H}_{10}^-$.

$\text{Li}_2\text{B}_{10}\text{H}_{10}$ 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.

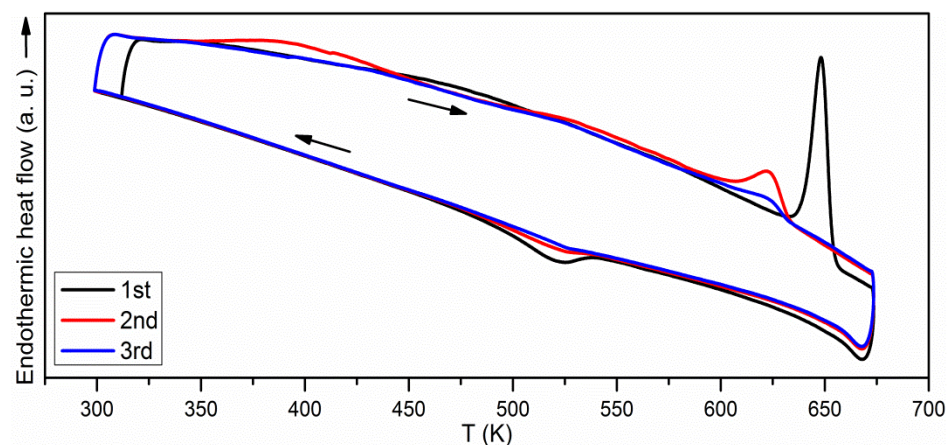
Motivation: investigating potential borohydride dehydrogenation products

Neutron-Elastic-Scattering Fixed-Window Scans



Fixed-window scans of ${}^7\text{Li}_2{}^{11}\text{B}_{10}\text{H}_{10}$ indicate a transition to an unknown phase by 680 K with highly reorientationally mobile $\text{B}_{10}\text{H}_{10}^{2-}$ anions, possibly similar in character to $\text{Na}_2\text{B}_{10}\text{H}_{10}$.

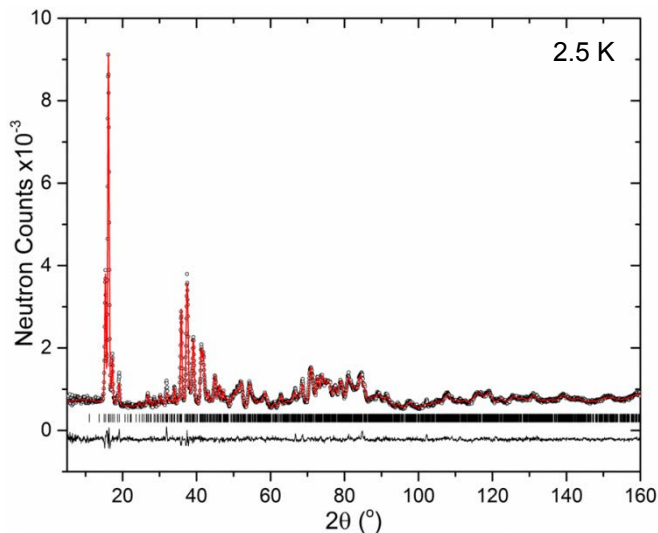
Differential Scanning Calorimetry for $\text{Li}_2\text{B}_{10}\text{H}_{10}$



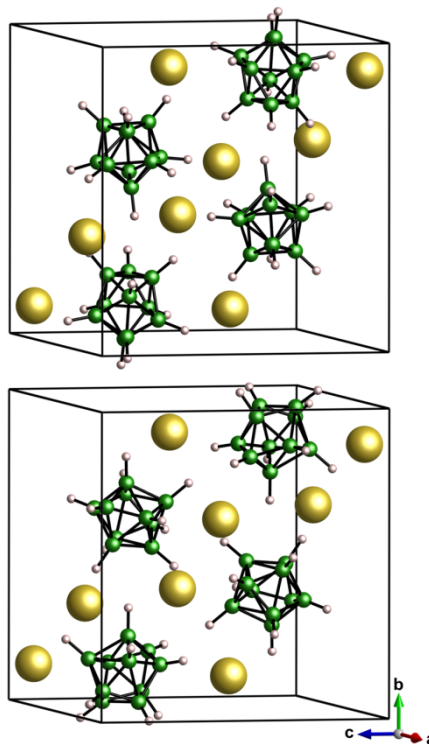
Multiple differential calorimetry scans for $\text{Li}_2\text{B}_{10}\text{H}_{10}$ suggest that this high-temperature phase is somewhat unstable.

$\text{Li}_2\text{B}_{10}\text{H}_{10}$, similar to its polyhedral cousin $\text{Li}_2\text{B}_{12}\text{H}_{12}$, completes an order-disorder phase transition by ~ 680 K. This information further elucidates the important Li-B-H phase diagram.

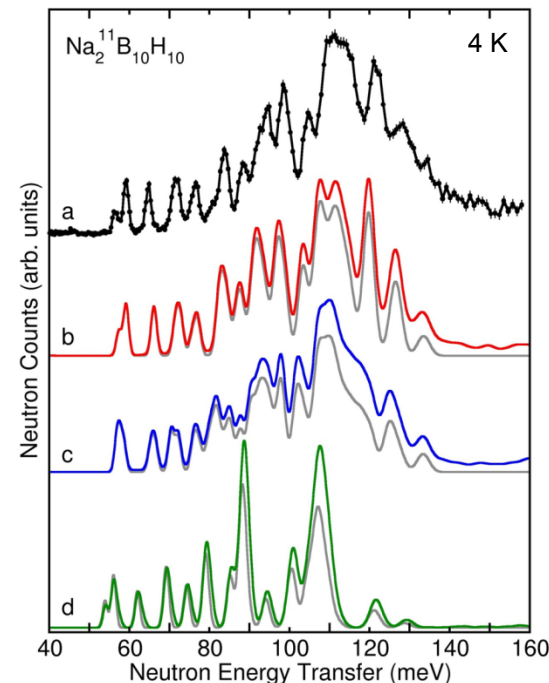
Motivation: investigating potential borohydride dehydrogenation products



Neutron powder diffraction pattern and fit for $\text{Na}_2^{11}\text{B}_{10}\text{D}_{10}$ at 2.5 K.



The corrected monoclinic $\text{Na}_2\text{B}_{10}\text{H}_{10}$ crystal structure (top) compared to the published structure (bottom).



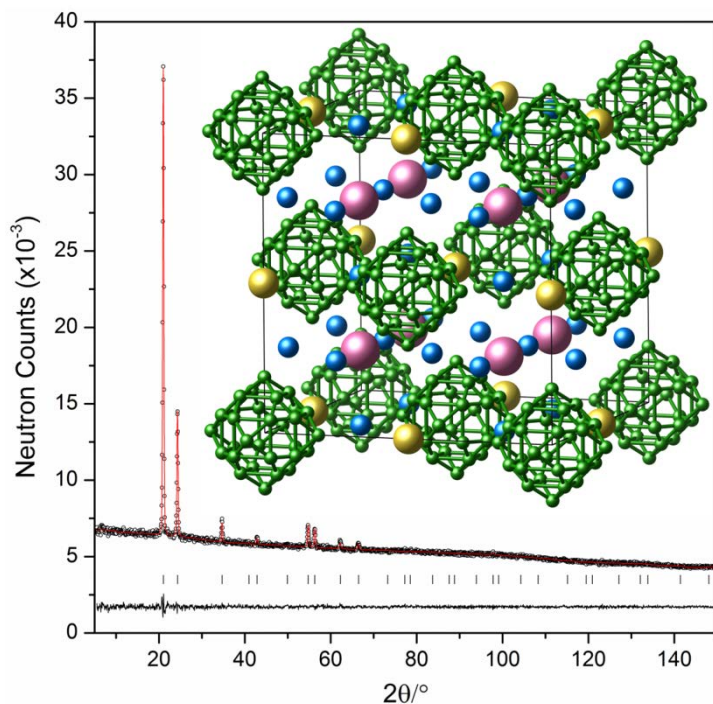
(a) Neutron vibrational spectrum of monoclinic $\text{Na}_2^{11}\text{B}_{10}\text{H}_{10}$ compared to DFT simulations for (b) the corrected structure, (c) the published structure, and (d) the isolated anion.

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.

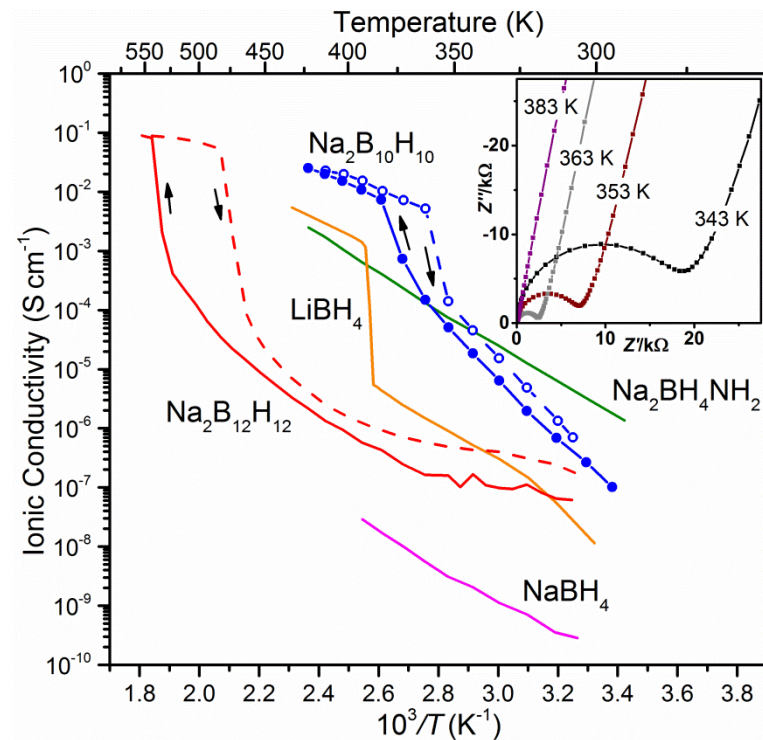
Sodium Superionic Conduction in $\text{Na}_2\text{B}_{10}\text{H}_{10}$

Collaboration with Maryland, Sandia National Laboratories, IMP Ekaterinburg, Tohoku University

Motivation: characterizing conductivity properties of cubic $\text{Na}_2\text{B}_{10}\text{H}_{10}$



NPD pattern for disordered cubic $\text{Na}_2\text{B}_{10}\text{H}_{10}$ at 410K and inset showing the orientationally disordered $\text{B}_{10}\text{H}_{10}^{2-}$ anions (H atoms omitted) and the array of partially occupied Na^+ cation sites (red, yellow, and blue).



AC impedance measurements for $\text{Na}_2\text{B}_{10}\text{H}_{10}$ and related materials vs. temperature.

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.

Collaborations

U.S. Partners (Type of Institution): What we provide to them

CalTech (Univ.): neutron measurements of various porous materials and borohydrides.

Delaware (Univ.): neutron measurements of various zeolites.

GE (Industry): neutron characterization of complex hydrides.

GM (Industry): neutron characterization of complex hydrides.

HRL (Industry) neutron measurements of BH_4^- dynamics in nanoconfined metal borohydrides.

Maryland (Univ.): neutron and x-ray measurements of alanates, borohydrides, and related materials.

Michigan (Univ.): neutron measurements of BH_4^- dynamics in neat and nanoconfined metal borohydrides.

Missouri-St. Louis (Univ.): neutron measurements of various alanates, borohydrides, and related materials.

NREL (Gov.): neutron measurements / isotherm measurements of various spillover related materials.

Ohio State (Univ.): neutron and x-ray measurements of borated compounds.

Penn (Univ.): neutron measurements of amidoboranes and other storage-related materials.

Penn State (Univ.): neutron measurements of various boron doped carbons.

RCB Hydrides (Industry): neutron and x-ray measurements and DFT calculations of various alanates, borohydrides, and related materials; neutron imaging of hydrogen-storage beds.

Sandia (Gov.): neutron measurements and DFT calculations of various alanates, borohydrides, and related materials.

Molecular Foundry (Gov.): neutron measurements of various metal-organic framework materials

U.C. Berkeley (Univ.): neutron measurements of various alanates, borohydrides, and related materials.

Utah (Univ.): neutron characterization of complex and metal hydrides.

Remainder of FY2015:

- 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.
- For example, continue characterization work on hydrogenated/dehydrogenated Li_3N in nanoporous carbon, metal borides, and decaborane-based materials (with Sandia National Laboratories, HRL, and U. Missouri-St. Louis); start characterization work on mixed-alkali-metal silanides.

Neutron methods continue to provide crucial, non-destructive characterization tools for the DOE Hydrogen-Storage Sub-Program.

- Agreement between neutron vibrational spectroscopy and density functional theory corroborates β -MSiH₃ structures determined by diffraction methods.
- Quasielastic neutron scattering data for CsSiH₃ corroborate the change to a more three-dimensional SiH₃⁻ reorientation mechanism upon transformation to the disordered cubic α -phase.
- We successfully established the baseline spectroscopic signature for B₁₀H₁₄ to be used later for comparison with polymerized versions after thermal treatments and lithiation.
- Neutron vibrational spectroscopy confirms that both LiNH₂ and LiH are hydrogenation products from carbon-nanoconfined Li₃N, with no obvious presence of Li₂NH.
- Quasielastic neutron scattering measurements of disordered Na₂B₁₂H₁₂ indicate rapid (>10¹¹ jumps/s), mainly (small-angle) uniaxial, reorientational motions of the B₁₂H₁₂²⁻ anions.
- Li₂B₁₀H₁₀ was found to exhibit hexagonal symmetry to best stabilize the ionic packing of the relatively small Li⁺ cations and large ellipsoidal B₁₀H₁₀²⁻ anions.
- Li₂B₁₀H₁₀, similar to its polyhedral cousin Li₂B₁₂H₁₂, completes an order-disorder phase transition by ~680 K. This information further elucidates the important Li-B-H phase diagram.
- Using neutron scattering methods in conjunction with DFT, we have corrected structural errors in the previously published, monoclinic ordered Na₂B₁₀H₁₀ structure.
- An improvement over Na₂B₁₂H₁₂, Na₂B₁₀H₁₀ exhibits dramatic superionicity above its ~360 K phase transition, aided by the large mobile anions and the appearance of cation vacancies.