



DOE Hydrogen Program

**NIST**

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

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## Timeline

- Project start FY10
- Project end determined annually by DOE

## Budget

- FY12 \$200K
- FY13 \$200K

NIST continues to provide access to neutron facilities and FTEs for the DOE Hydrogen Storage Projects.

## NIST Associates

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Matt Hudson

## Barriers addressed

- A. System Weight and Volume
- P. 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, 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.

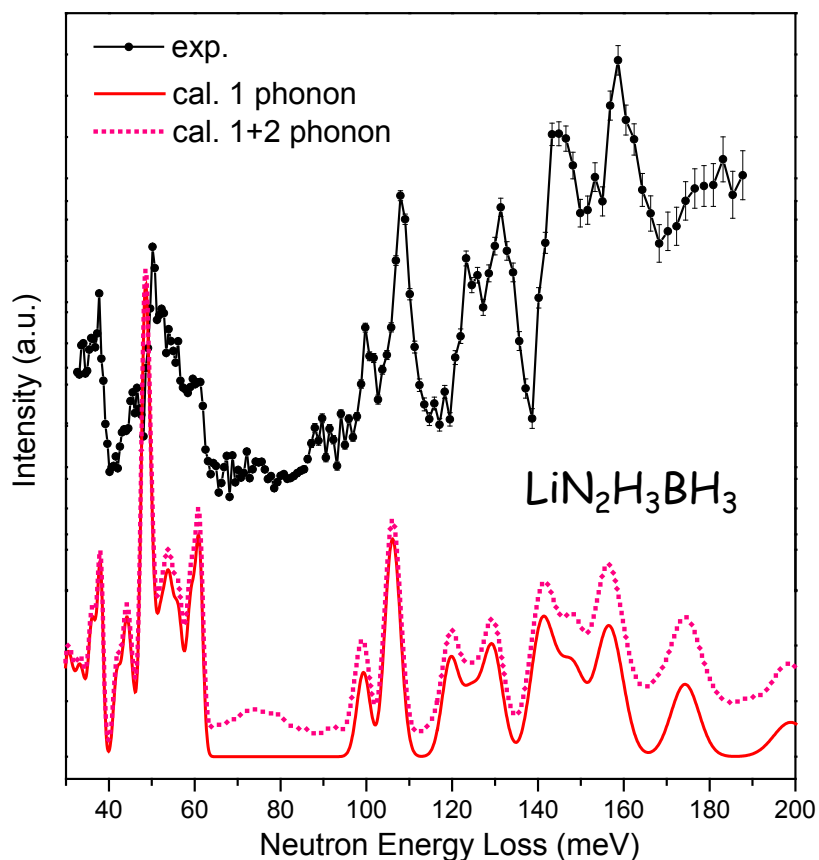
- Direct partner synthesis efforts based on the understanding gained through the use of these methods.
- Demonstrate the fundamental characteristics of useful hydrogen-storage materials.

## Neutron methods

- determine elemental compositions of materials (prompt- $\gamma$  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)

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

Motivation: synthesizing new compounds potentially promising for hydrogen storage

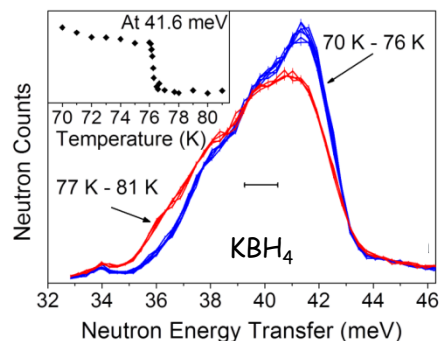


DFT phonon simulations are in good agreement with neutron vibrational spectra for the recently synthesized lithium hydrazinoborane ( $\text{LiN}_2\text{H}_3\text{BH}_3$ ).

$\text{LiN}_2\text{H}_3\text{BH}_3$  exhibits dramatically improved properties over the pristine hydrazine borane ( $\text{N}_2\text{H}_4\text{BH}_3$ ) with nearly complete dehydrogenation in a mild temperature range (50-225 C) and high-purity  $\text{H}_2$  release.

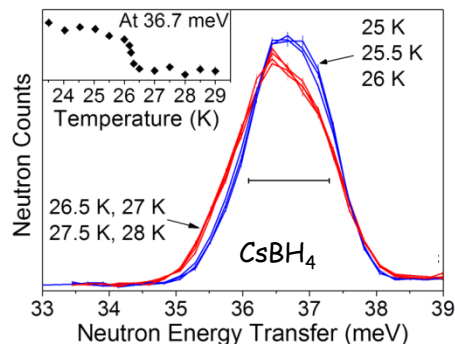
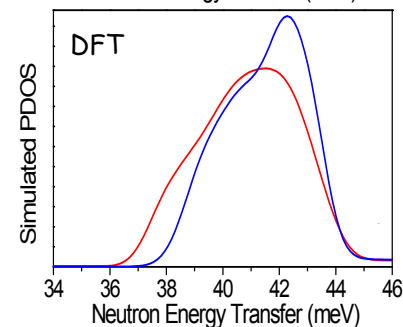
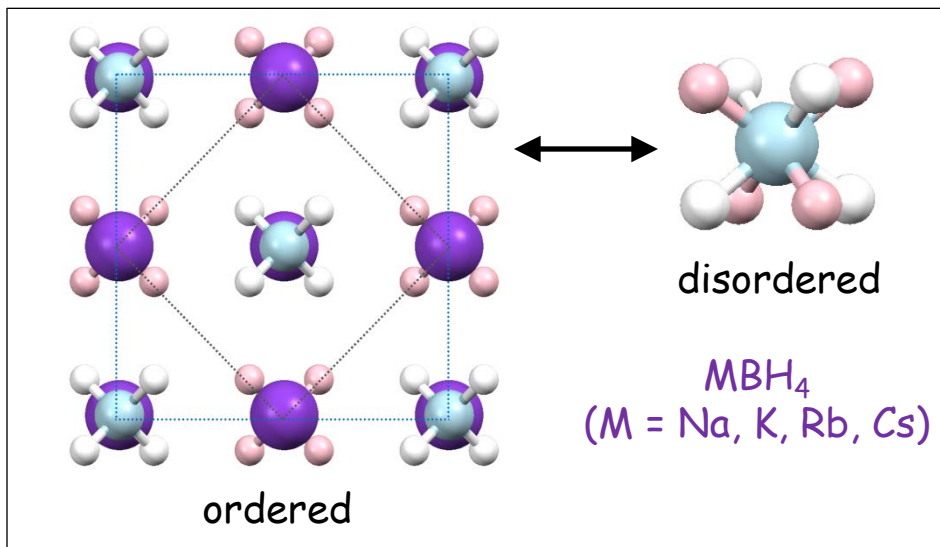
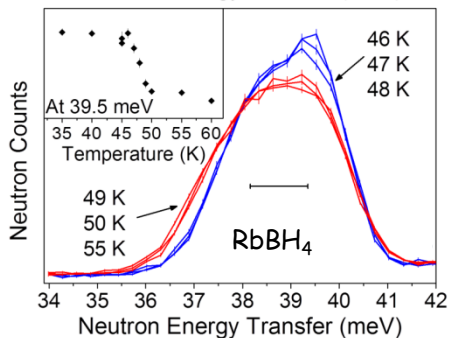
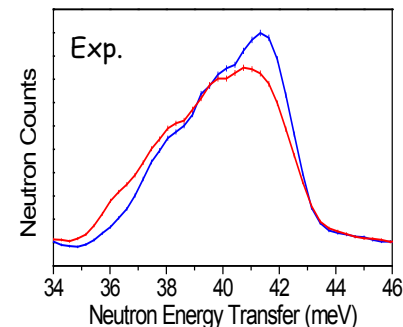
Agreement between neutron vibrational spectroscopy and DFT corroborates structure determined by diffraction methods.

## Motivation: characterizing the bonding in borohydride materials



Neutron vibrational spectra of  $\text{BH}_4^-$  torsional bands in  $\text{MBH}_4$  across the order-disorder phase transition.

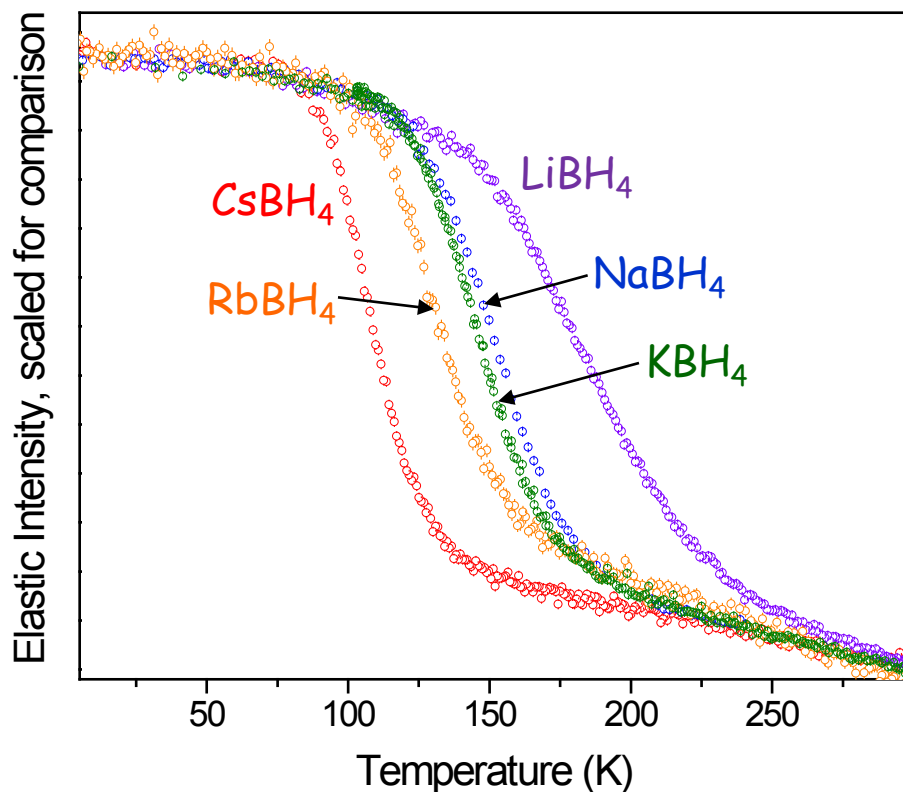
Comparison of observed and simulated  $\text{BH}_4^-$  torsional bands in  $\text{KBH}_4$  for the ordered (blue) and disordered (red) phases.



Neutron diffraction and spectroscopy indicate that the anion-ordered phases in  $\text{RbBH}_4$  and  $\text{CsBH}_4$  do exist but are short-ranged.

Motivation: understanding  $\text{BH}_4^-$  rotational dynamics in  $\text{MBH}_4$

## Neutron-Scattering Fixed-Window Scans for $\text{MBH}_4$ Compounds



As the cation size increases:

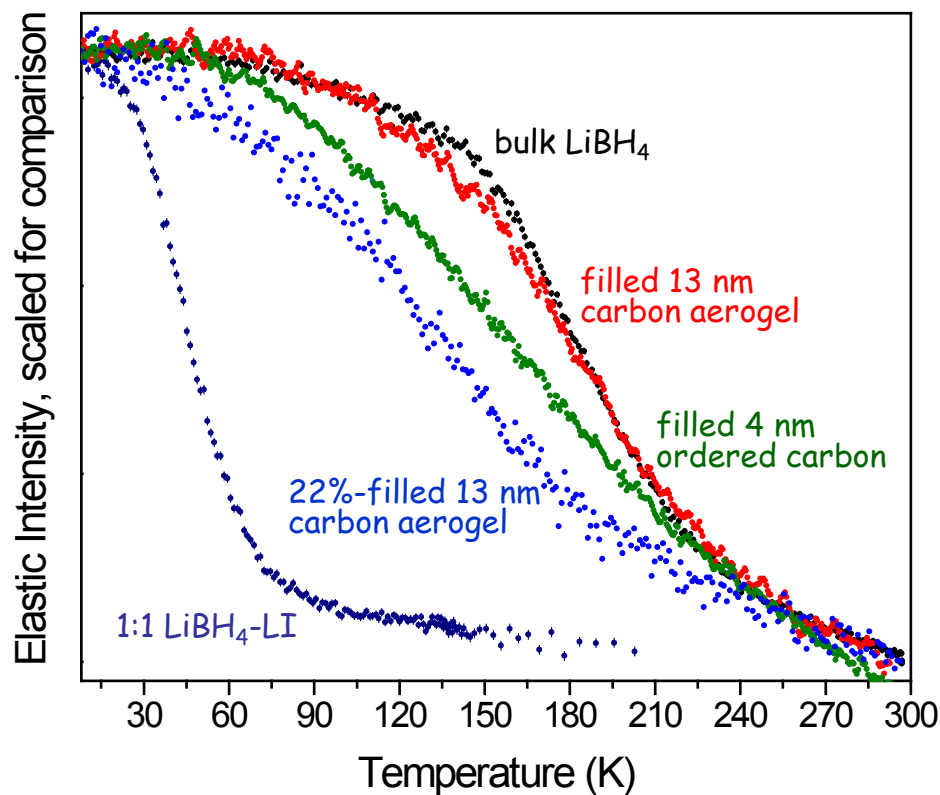
- the rotational jump rate increases at a given temperature.
- the temperature corresponding to the onset of rapid rotations decreases.

Fixed-window scans allow for a relative comparison of  $\text{BH}_4^-$  anion rotational mobilities.



Motivation: understanding  $\text{BH}_4^-$  rotational dynamics in modified  $\text{LiBH}_4$

## Neutron-Scattering Fixed-Window Scans for Bulk and Destabilized $\text{LiBH}_4$



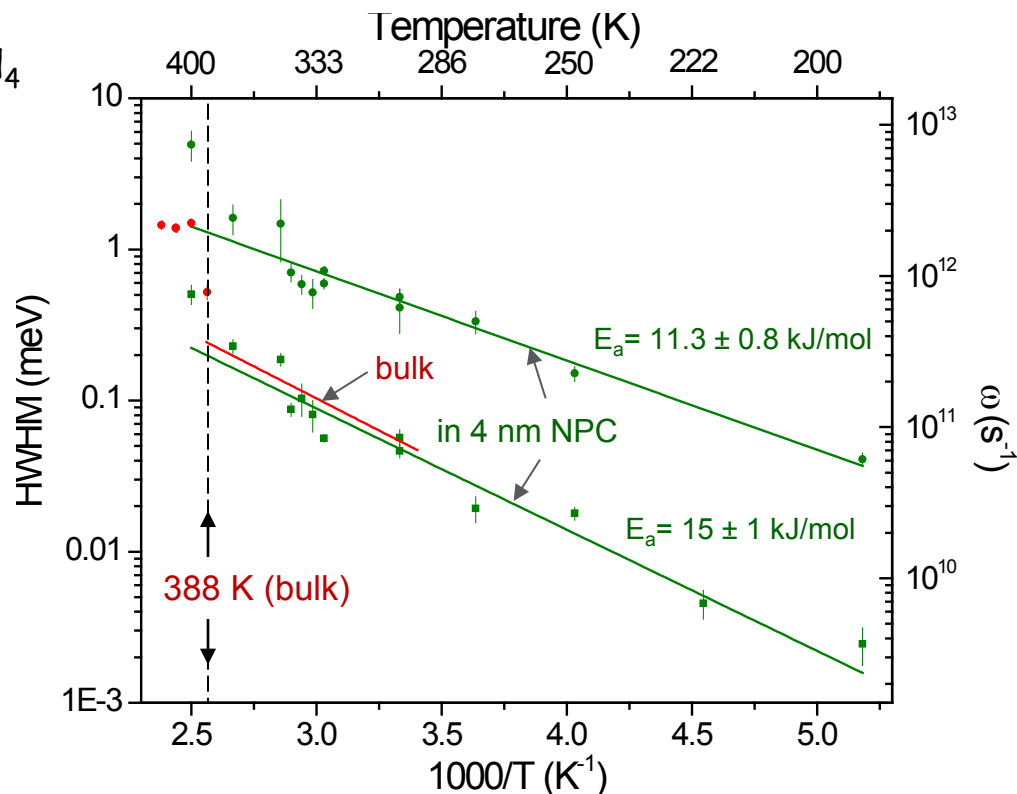
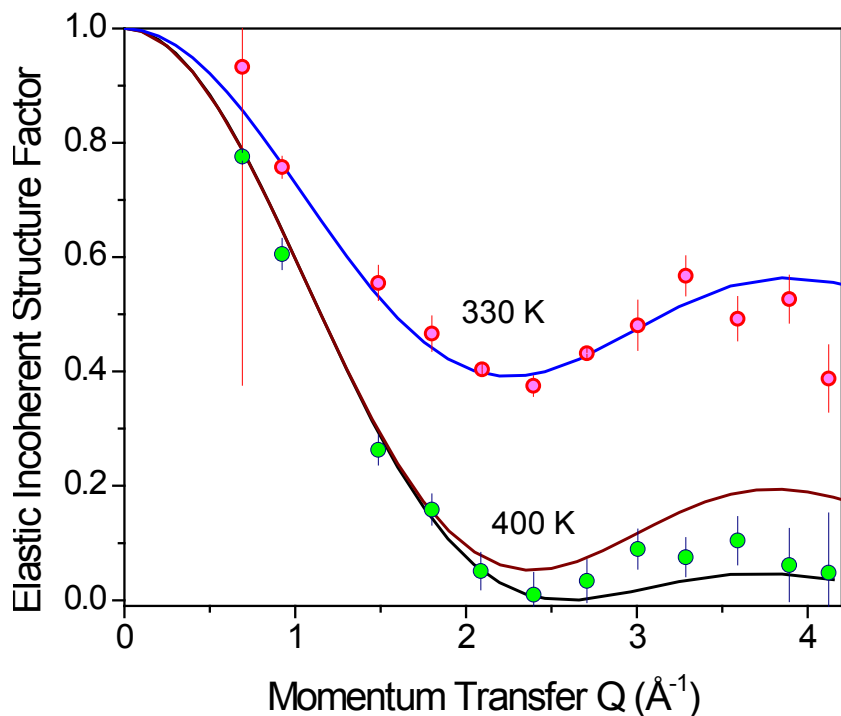
Compared to the bulk, the average  $\text{BH}_4^-$  rotational jump rate in nanoconfinement increases with decreasing pore size.

$\text{BH}_4^-$  rotates extremely rapidly in the LiI-stabilized hexagonal phase

Fixed-window scans suggest that smaller pores fill first in partially loaded samples.

Motivation: characterizing BH<sub>4</sub><sup>-</sup> dynamics in nanoconfinement

Average EISF's for all BH<sub>4</sub><sup>-</sup> anions from LiBH<sub>4</sub> in 4-nm-diameter cylindrical-pore NPC



Arrhenius plot of QENS linewidths for bulk and nanoconfined BH<sub>4</sub><sup>-</sup> anions

On average, BH<sub>4</sub><sup>-</sup> anions go from uniaxial 3-fold jump rotations at 330 K to more multi-axis diffuse rotations at 400 K, with no obvious phase transition.

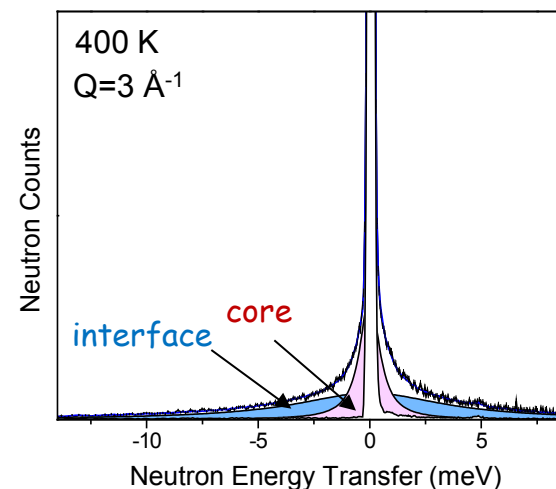
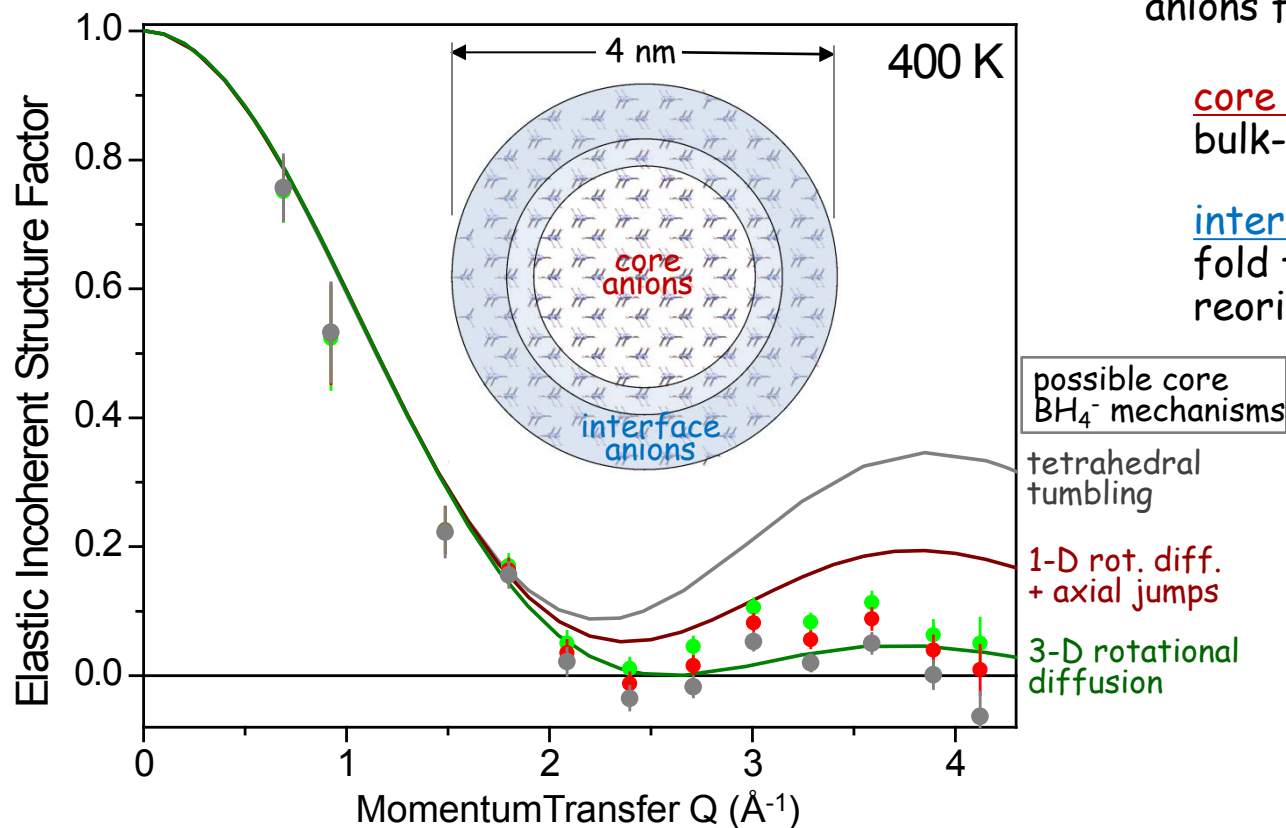
## Motivation: characterizing BH<sub>4</sub><sup>-</sup> dynamics in nanoconfinement

EISF's at 400 K for interface BH<sub>4</sub><sup>-</sup> anions assuming different mechanisms for core anions

QENS suggests that there are two dynamically distinct groups of BH<sub>4</sub><sup>-</sup> anions for nanoconfined LiBH<sub>4</sub>:

core BH<sub>4</sub><sup>-</sup> anions with slower, bulk-like, jump reorientations

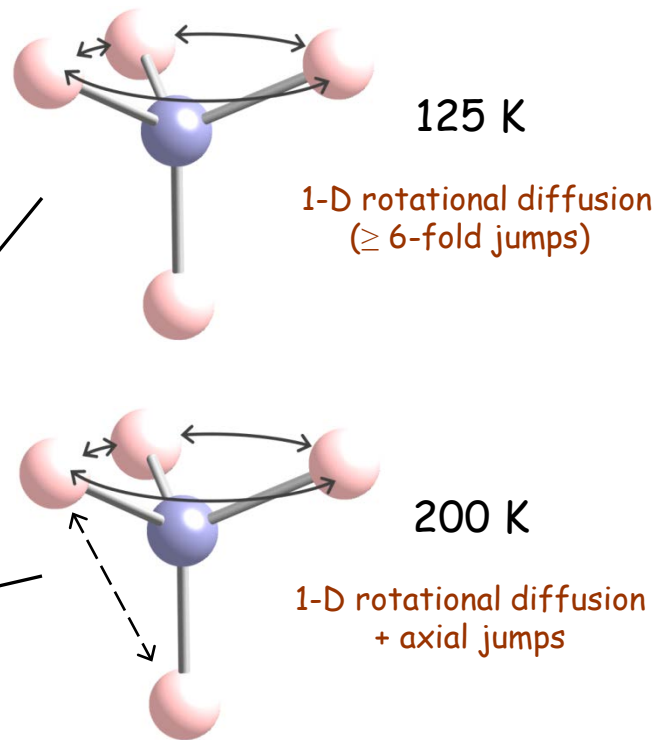
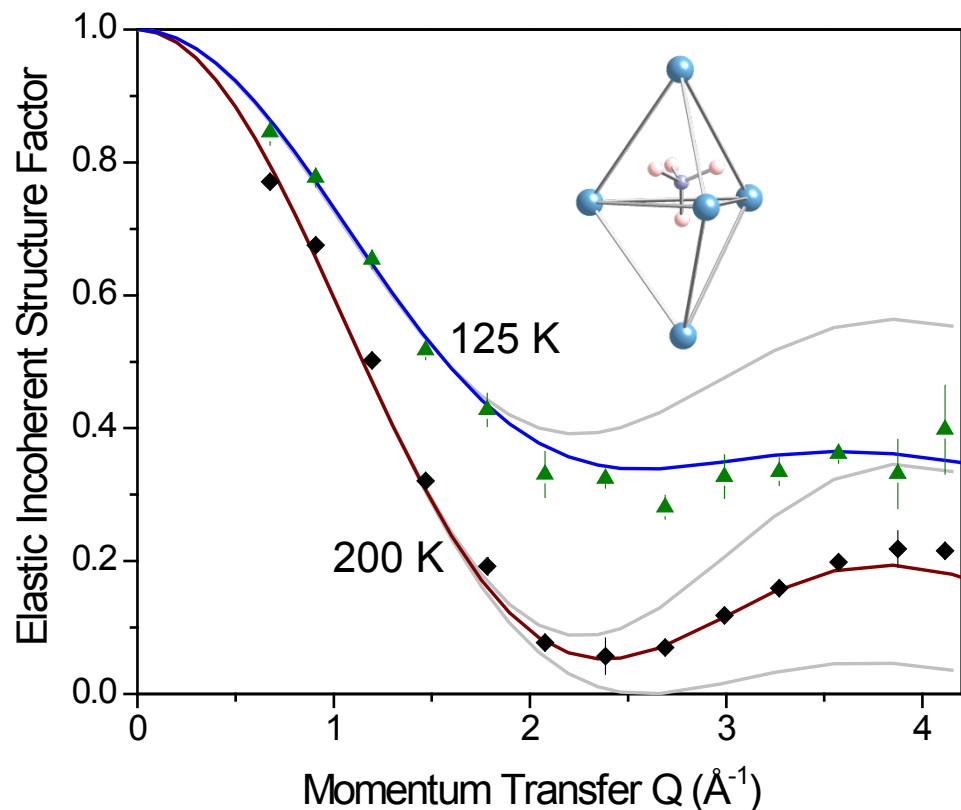
interface BH<sub>4</sub><sup>-</sup> anions with ten-fold faster, more disordered reorientations



The fraction of interface BH<sub>4</sub><sup>-</sup> anions increases somewhat with temperature.

Motivation: understanding the effects of alloying LiBH<sub>4</sub> with LiI

Neutron EISF's for 1:1 LiBH<sub>4</sub>-LiI (hexagonal phase)

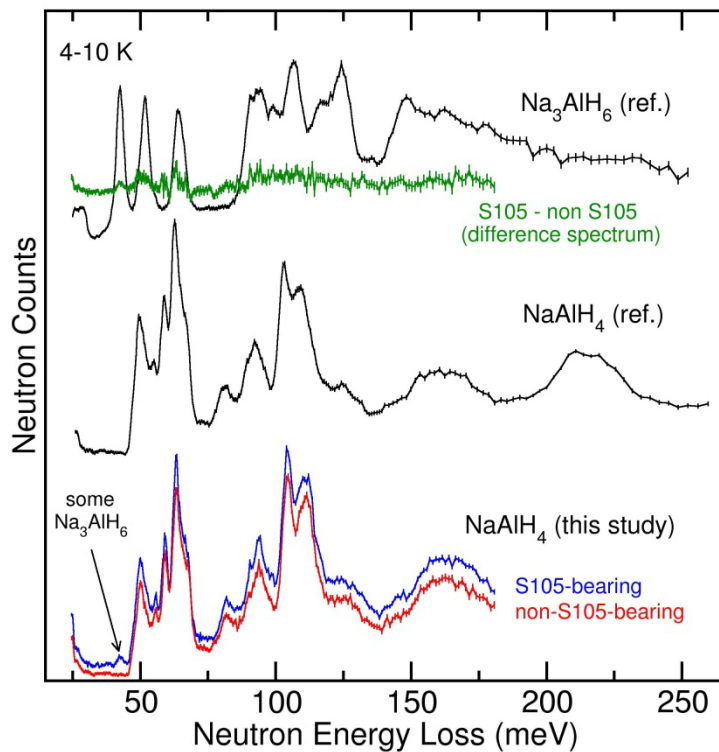


Relatively more rapid than in bulk hexagonal LiBH<sub>4</sub>.

BH<sub>4</sub><sup>-</sup> anions reorient predominantly around the *c*-directed B-H bond at 125 K. By 200 K, jump exchanges between the axial H and other three trigonal H's also occur.

Motivation: understanding the nature of mobile  $AlH_x$  species observed in  $NaAlH_4$

## Neutron Vibrational Spectra of pretreated $NaAlH_4$ vs. bulk $NaAlH_4$ and $Na_3AlH_6$



Recently, a new mobile  $AlH_x$  species (termed S105) was discovered in the hydrogen chemistry of  $NaAlH_4$  using *in situ* NMR. [J. Phys. Chem. Lett. 1, 2412 2010]

Besides  $NaAlH_4$  and trace amounts of  $Na_3AlH_6$ , NV spectra indicate no unusual hydrogenous species in S105-bearing samples.

NV spectra are consistent with NMR results suggesting that S105 involves mobile  $AlH_4^-$  tetrahedral anions whose formation is promoted by hydroxide impurities.

## Partners (Type of Institution): What we provide to them

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

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

**GM** (Industry): neutron characterization of complex hydrides.

**HRL** (Industry) neutron measurements of  $\text{BH}_4^-$  dynamics in nanoconfined metal borohydrides.

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

**Michigan** (Univ.): neutron measurements of  $\text{BH}_4^-$  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.

## Remainder of FY2013:

- Continue to perform neutron-based structural and spectroscopic characterizations of new materials in conjunction with the needs of the DOE-funded projects, including nanoporous materials, borohydrides, and nanoscaffolding materials of interest.
- For example, start characterization work on  $\text{MgH}_2\text{-LiBH}_4$  and  $\text{MgH}_2\text{-TiH}_2$  hybrid storage materials.

## Neutron methods continue to provide crucial, non-destructive characterization tools for the DOE Hydrogen-Storage 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 diffraction and spectroscopy 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.
- 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.
- QENS measurements of  $\text{LiBH}_4$  sequestered in 4-nm controlled-pore carbon scaffolds indicated two types of  $\text{BH}_4^-$  anions: core  $\text{BH}_4^-$  anions with slower, bulk-like, jump reorientations and interface  $\text{BH}_4^-$  anions with faster, more disordered reorientations.
- QENS measurements of  $\text{BH}_4^-$  anions in a 1:1 hexagonal  $\text{LiBH}_4$ -LiI alloy reorient predominantly around the *c*-directed B-H bond at 125 K with additional jump exchanges between the axial H and other three trigonal H's occurring above this temperature, similar to what occurs for hexagonal  $\text{LiBH}_4$  at 400 K.
- NV 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.