DOE Hydrogen Program

NIST

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

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Overview

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
Hui Wu
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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

Objectives and Relevance

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.

Approach

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

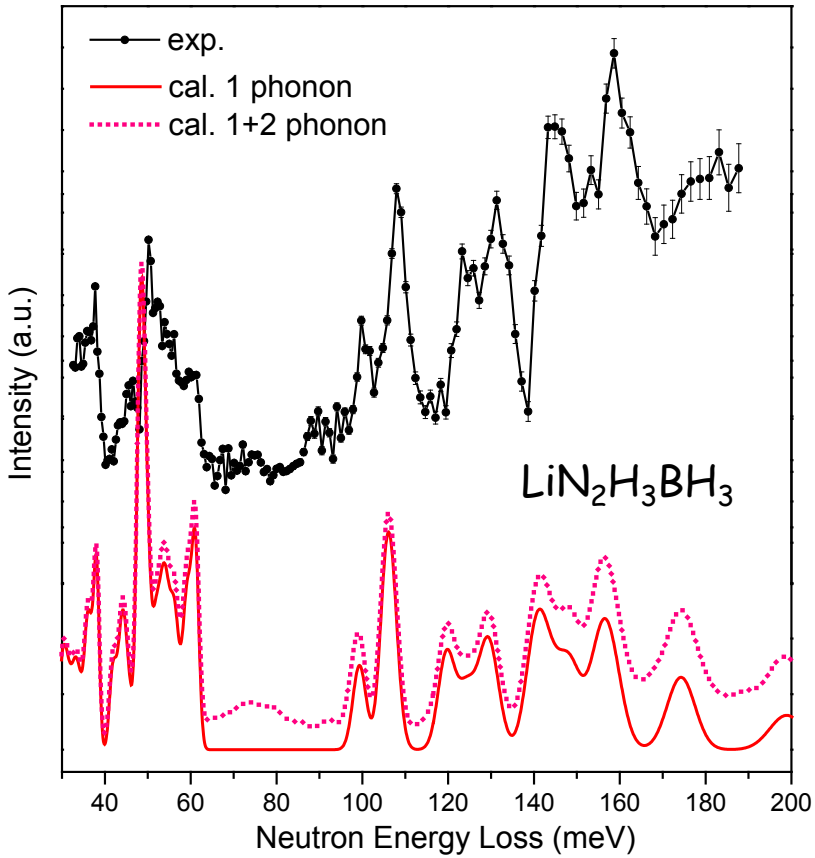
Neutron methods, synthesis expertise, and DFT computations were used to further the goals of the DOE Hydrogen-Storage Program.

Synthesis and Characterization of Novel Compounds

DOE Hydrogen Program

Collaboration with Maryland, GM

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 ($LiN_2H_3BH_3$).

$LiN_2H_3BH_3$ exhibits dramatically improved properties over the pristine hydrazine borane ($N_2H_4BH_3$) with nearly complete dehydrogenation in a mild temperature range (50–225 C) and high-purity H_2 release.

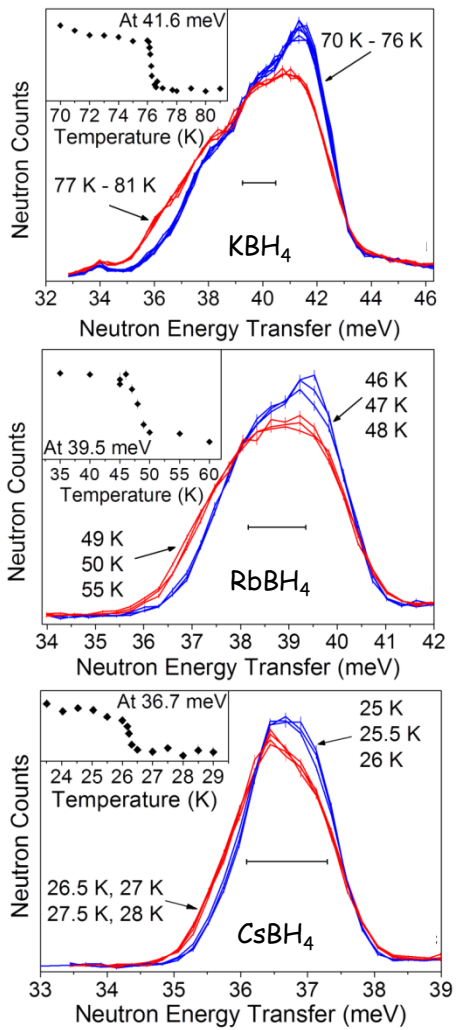
Agreement between neutron vibrational spectroscopy and DFT corroborates structure determined by diffraction methods.

H. Wu *et al.*, Energy Environ. Sci. 5, 7531 (2012).

Subtle Borohydride Phase Transitions

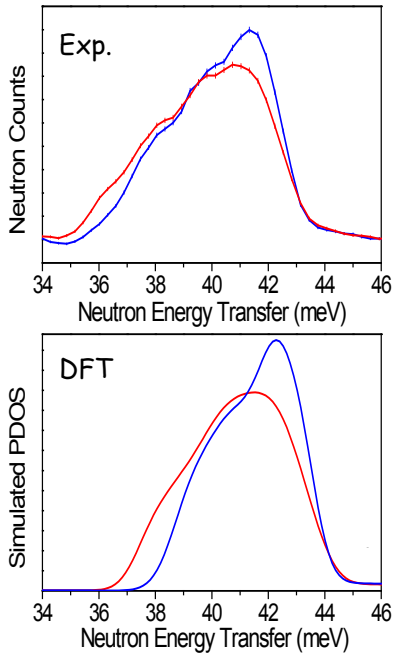
Collaboration with Maryland, Michigan, Delft University

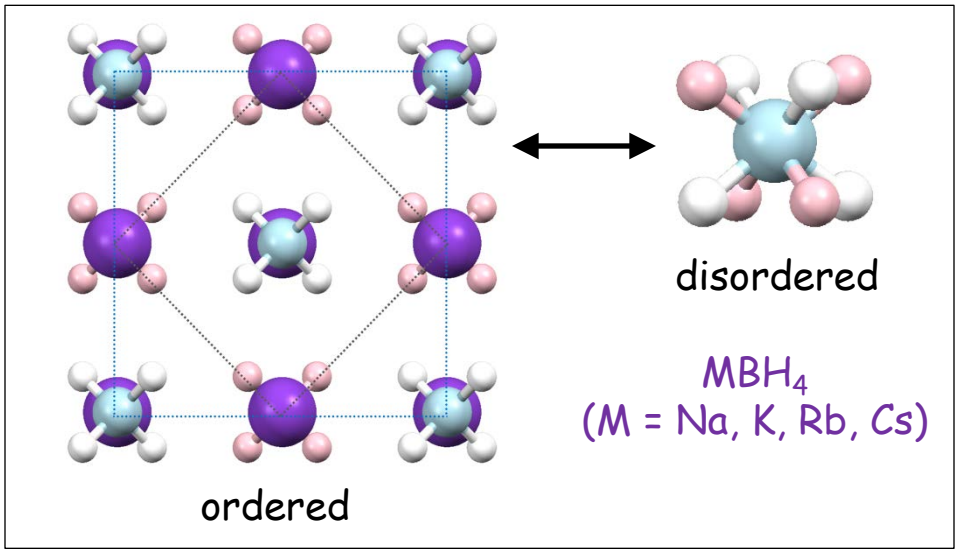
Motivation: characterizing the bonding in borohydride materials



Neutron vibrational spectra of BH_4^- torsional bands in MBH_4 across the order-disorder phase transition.

Comparison of observed and simulated BH_4^- torsional bands in KBH_4 for the ordered (blue) and disordered (red) phases.





Neutron diffraction and spectroscopy indicate that the anion-ordered phases in $RbBH_4$ and $CsBH_4$ do exist but are short-ranged.

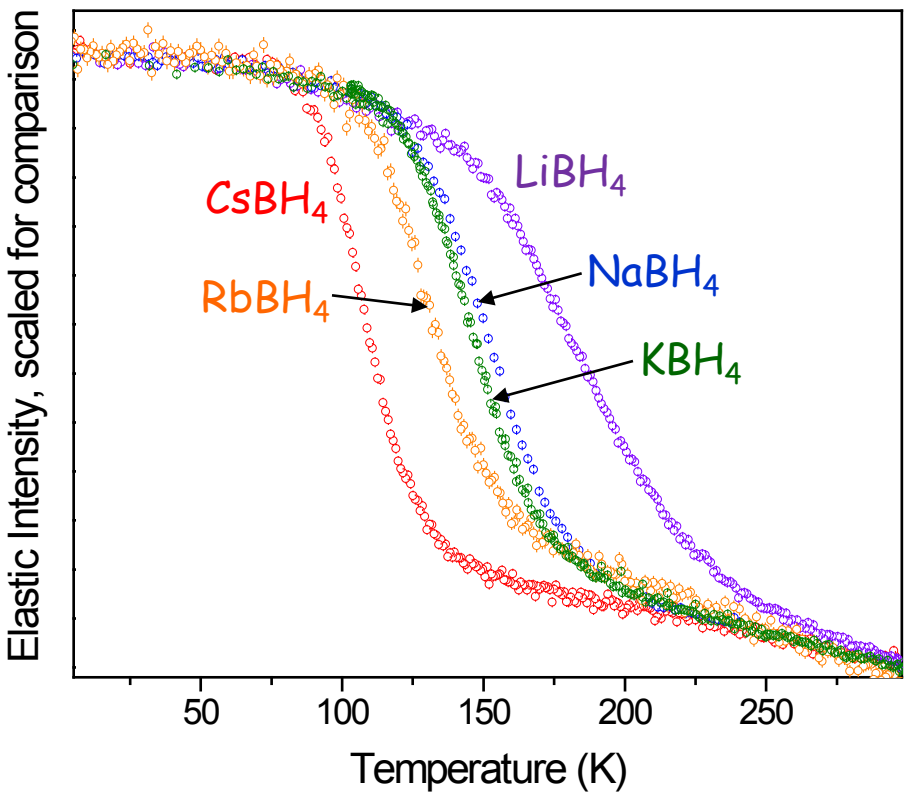
N. Verdal *et al.*, J. Phys. Chem. C 117, 876(2013).

The Rotational Dynamics of BH_4^- Anions

Collaboration with Maryland, Michigan, Delft University

Motivation: understanding BH_4^- rotational dynamics in MBH_4

Neutron-Scattering Fixed-Window Scans for 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 BH_4^- anion rotational mobilities.

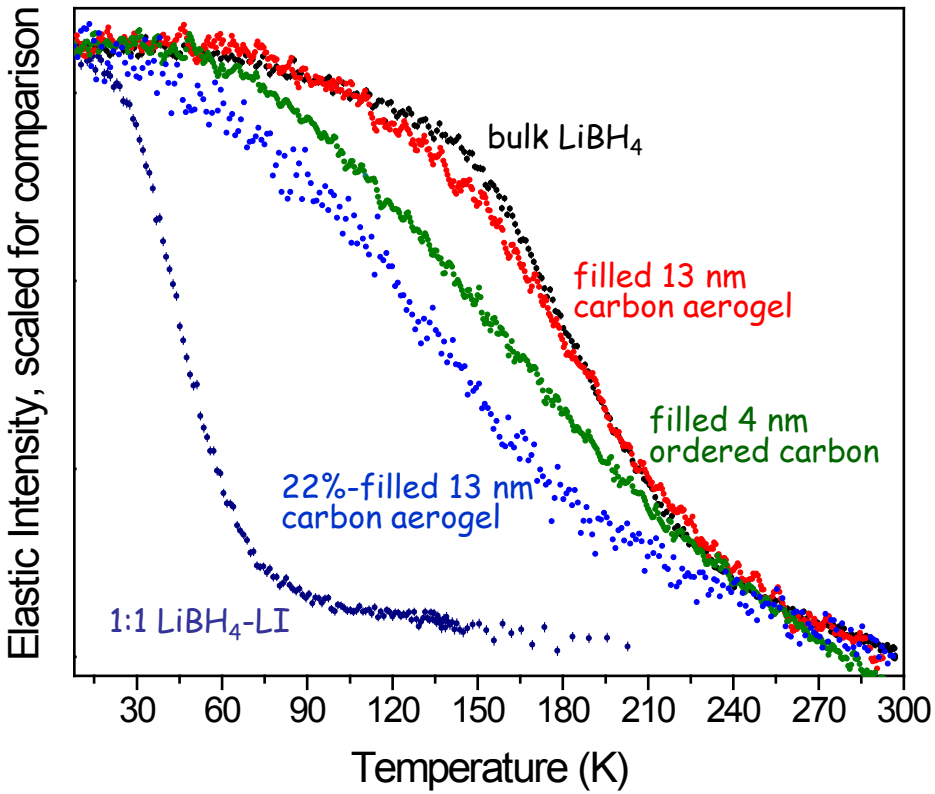
T. J. Udovic *et al.*, J. Alloys Compds. (in press 2013); http://dx.doi.org/10.1016/j.jallcom.2013.02.025

The Dynamics of Modified $LiBH_4$ Phases

Collaboration with Maryland, Michigan, HRL, IMP Ekaterinburg

Motivation: understanding BH_4^- rotational dynamics in modified $LiBH_4$

Neutron-Scattering Fixed-Window Scans for Bulk and Destabilized $LiBH_4$



Compared to the bulk, the average BH_4^- rotational jump rate in nanoconfinement increases with decreasing pore size.

BH_4^- rotates extremely rapidly in the LiI-stabilized hexagonal phase

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

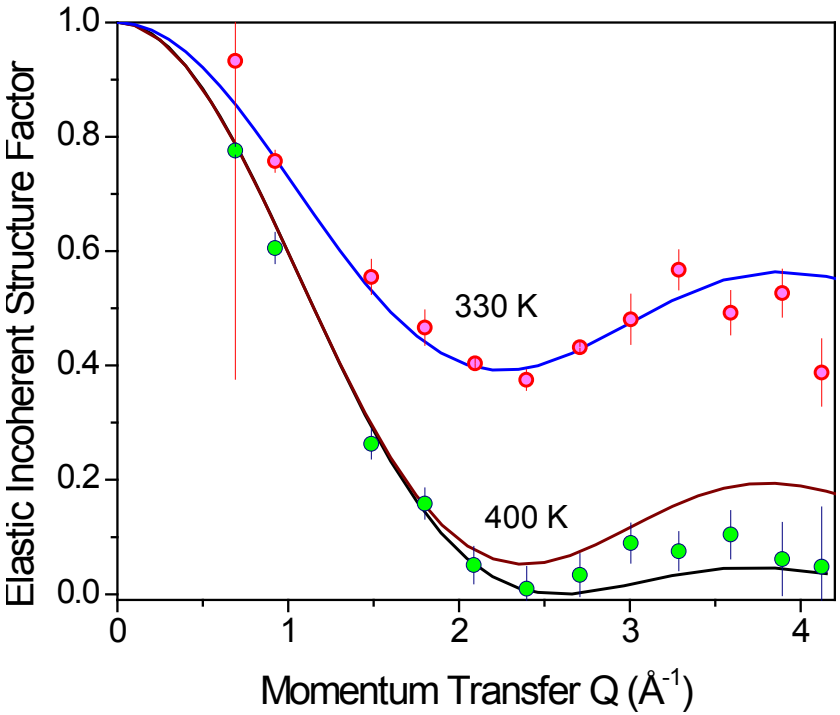
T. J. Udovic *et al.*, J. Alloys Compds. (in press 2013); http://dx.doi.org/10.1016/j.jallcom.2013.02.025

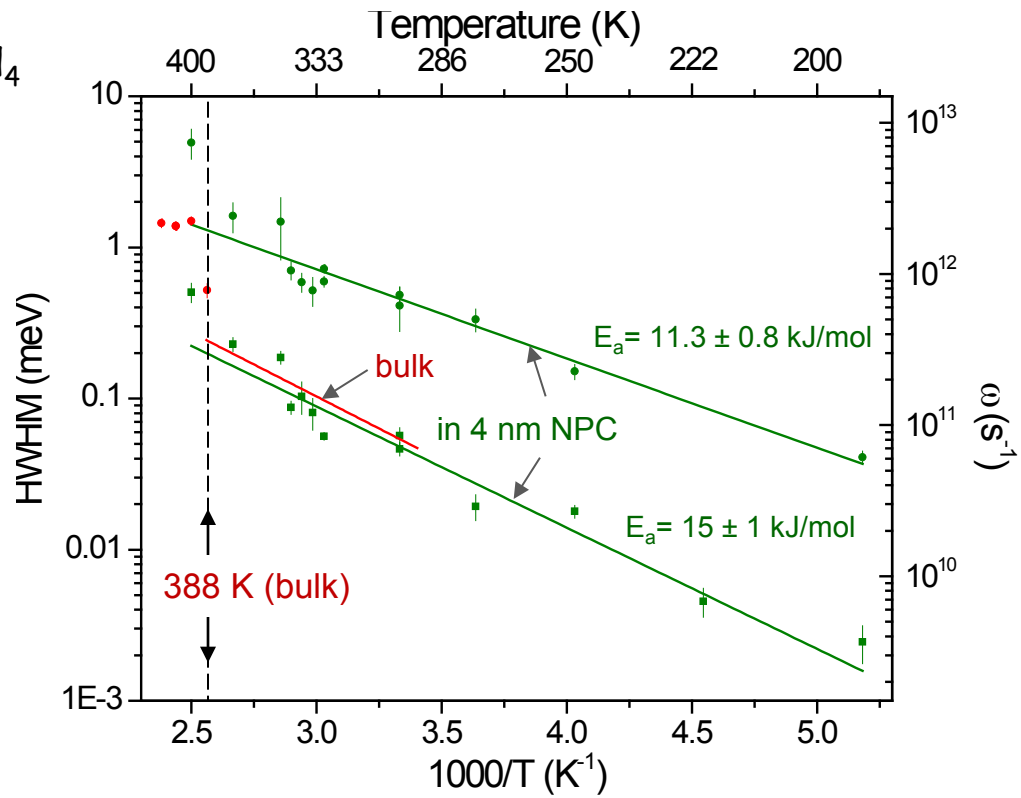
$LiBH_4$ in Ordered Nanoporous Carbon (NPC)

Collaboration with Maryland, Missouri-St. Louis, Washington U.-St. Louis, Sandia, Cal Tech

Motivation: characterizing BH_4^- dynamics in nanoconfinement

Average EISF's for all BH_4^- anions from $LiBH_4$ in 4-nm-diameter cylindrical-pore NPC





Arrhenius plot of QENS linewidths for bulk and nanoconfined BH_4^- anions

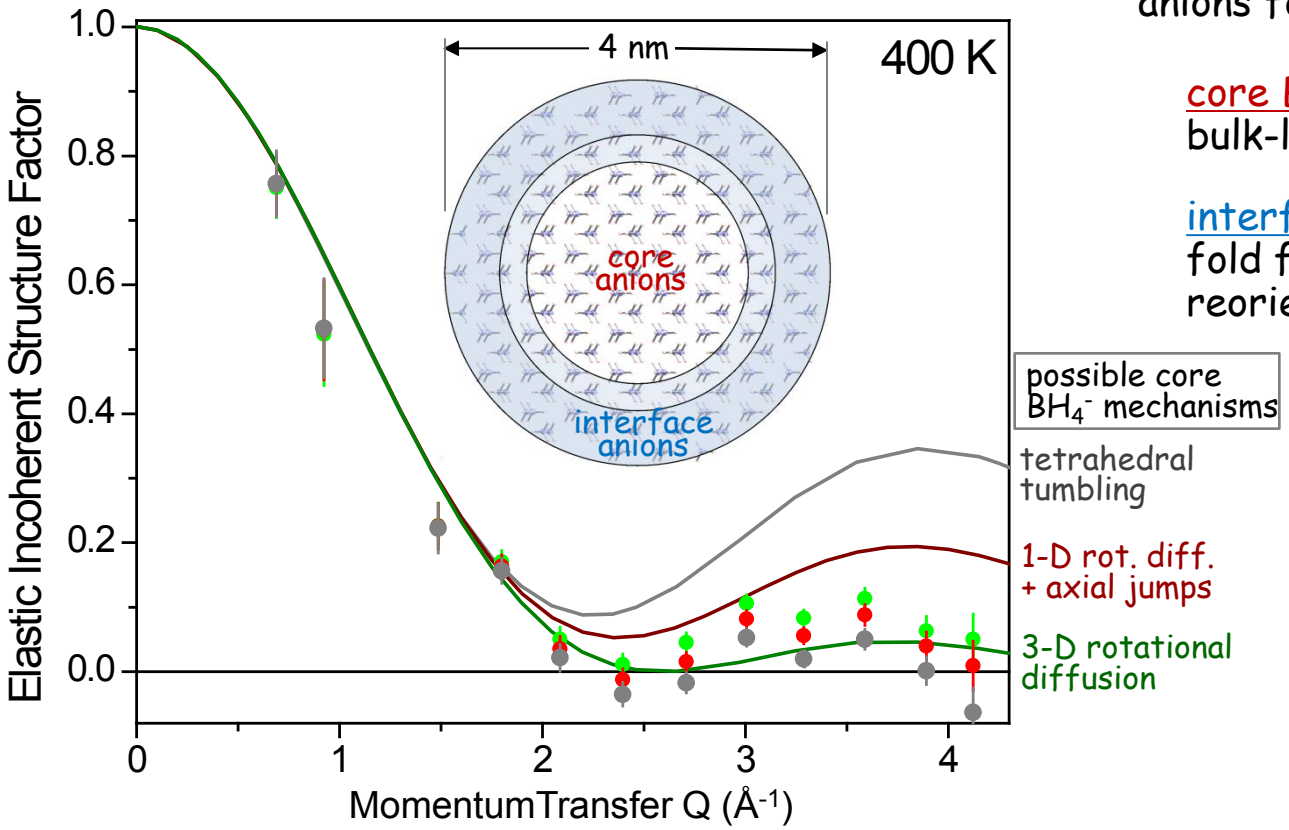
On average, BH_4^- anions go from uniaxial 3-fold jump rotations at 330 K to more multi-axis diffuse rotations at 400 K, with no obvious phase transition.

$LiBH_4$ in Ordered Nanoporous Carbon (NPC)

Collaboration with Maryland, Missouri-St. Louis, Washington U.-St. Louis, Sandia, Cal Tech

Motivation: characterizing BH_4^- dynamics in nanoconfinement

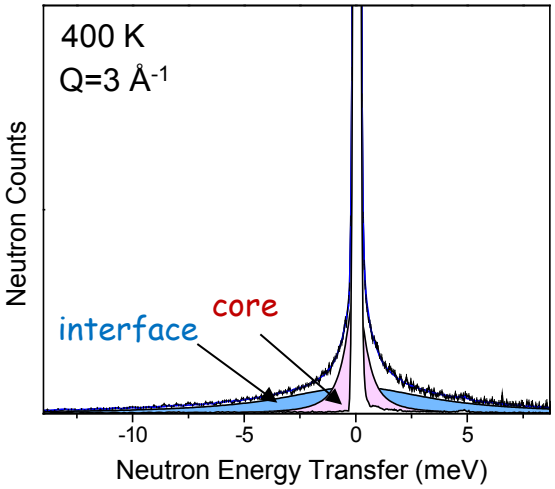
EISF's at 400 K for interface BH_4^- anions assuming different mechanisms for core anions



QENS suggests that there are two dynamically distinct groups of BH_4^- anions for nanoconfined $LiBH_4$:

core BH_4^- anions with slower, bulk-like, jump reorientations

interface BH_4^- anions with ten-fold faster, more disordered reorientations



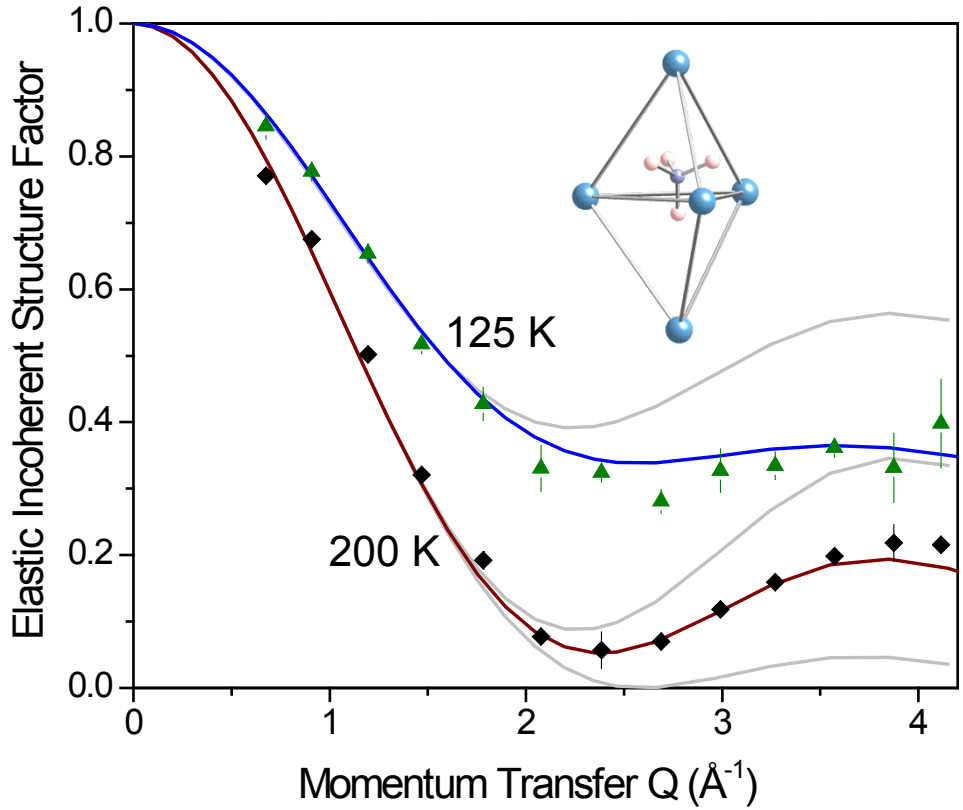
The fraction of interface BH_4^- anions increases somewhat with temperature.

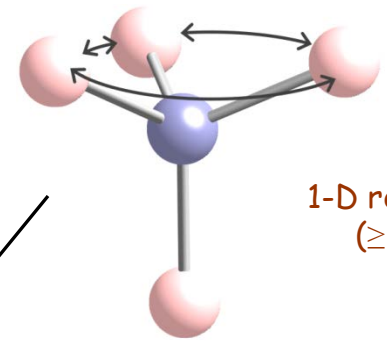
Characterization of $LiBH_4$-LiI Alloys

Collaboration with Maryland, IMP-Ekaterinburg

Motivation: understanding the effects of alloying $LiBH_4$ with LiI

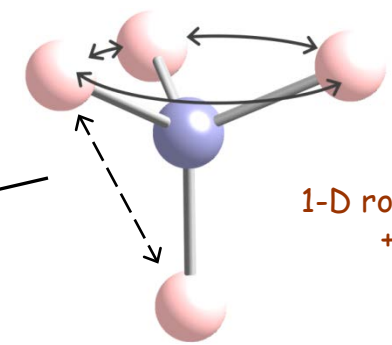
Neutron EISF's for 1:1 $LiBH_4$-LI (hexagonal phase)





125 K

1-D rotational diffusion
(≥ 6-fold jumps)



200 K

1-D rotational diffusion
+ axial jumps

Relatively more rapid than in bulk hexagonal $LiBH_4$.

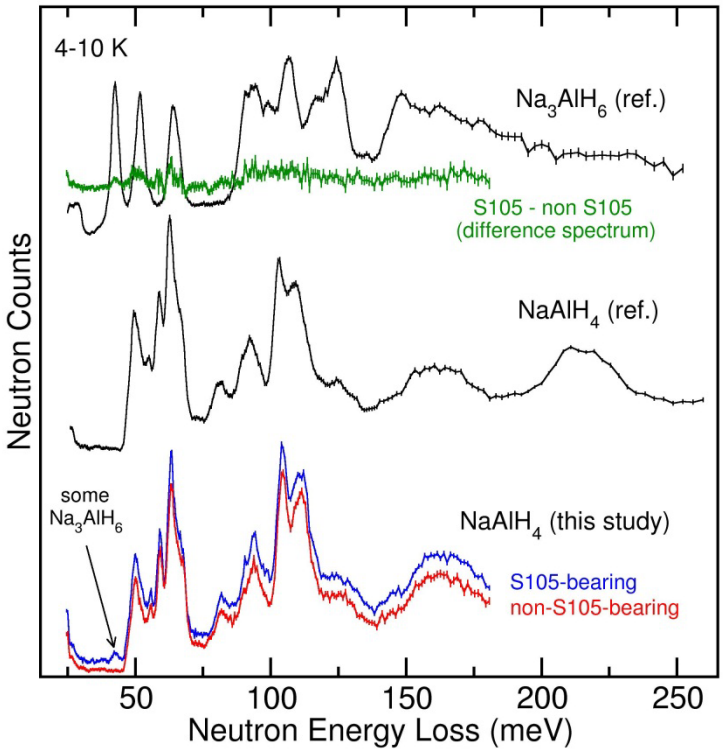
BH_4^- anions reorient predominantly around the *c*-directed B-H bond at 125 K. By 200 K, jump exchanges between the axial H and other three trigonal H's also occur.

Identity of AlH_x Species in $NaAlH_4$

Collaboration with Washington U.-St. L., Missouri-St. L., RCB Hydrides, Radboud University

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.

Collaborations

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 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.

Future Work

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 MgH_2-$LiBH_4$ and MgH_2-TiH_2 hybrid storage materials.

Summary

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 $LiN_2H_3BH_3$ structure that was determined by diffraction methods.
- Neutron diffraction and spectroscopy indicate that the anion-ordered phases in $RbBH_4$ and $CsBH_4$ do exist but are short-ranged, unlike the long-range order observed for the lighter $NaBH_4$ and KBH_4 compounds.
- Neutron-scattering fixed-window scans are shown to be a valuable technique for making relative comparisons of BH_4^- anion rotational mobilities in a host of solid-state environments.
- QENS measurements of $LiBH_4$ sequestered in 4-nm controlled-pore carbon scaffolds indicated two types of BH_4^- anions: core BH_4^- anions with slower, bulk-like, jump reorientations and interface BH_4^- anions with faster, more disordered reorientations.
- QENS measurements of BH_4^- anions in a 1:1 hexagonal $LiBH_4$-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 $LiBH_4$ at 400 K.
- NV spectra are consistent with NMR results suggesting that the unusual S105 species found in some pretreated $NaAlH_4$ samples involves mobile AlH_4^- tetrahedral anions whose formation is promoted by hydroxide impurities.