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

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ST067

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Overview

Timeline

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

*Project continuation and direction determined annually by DOE

Budget

- FY13 DOE Funding: $200K
- Planned FY14 DOE Funding: $200K
- Total DOE Project Value: $600K

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

NIST Associates

Nina Verdal
John J. Rush
Matt Hudson
Zeric Hulvey
Hui Wu
Wei Zhou
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

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)

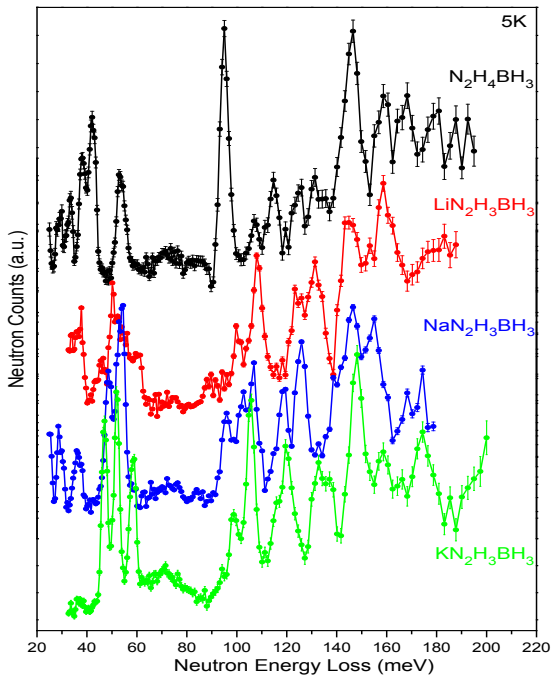
Technical Accomplishments

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

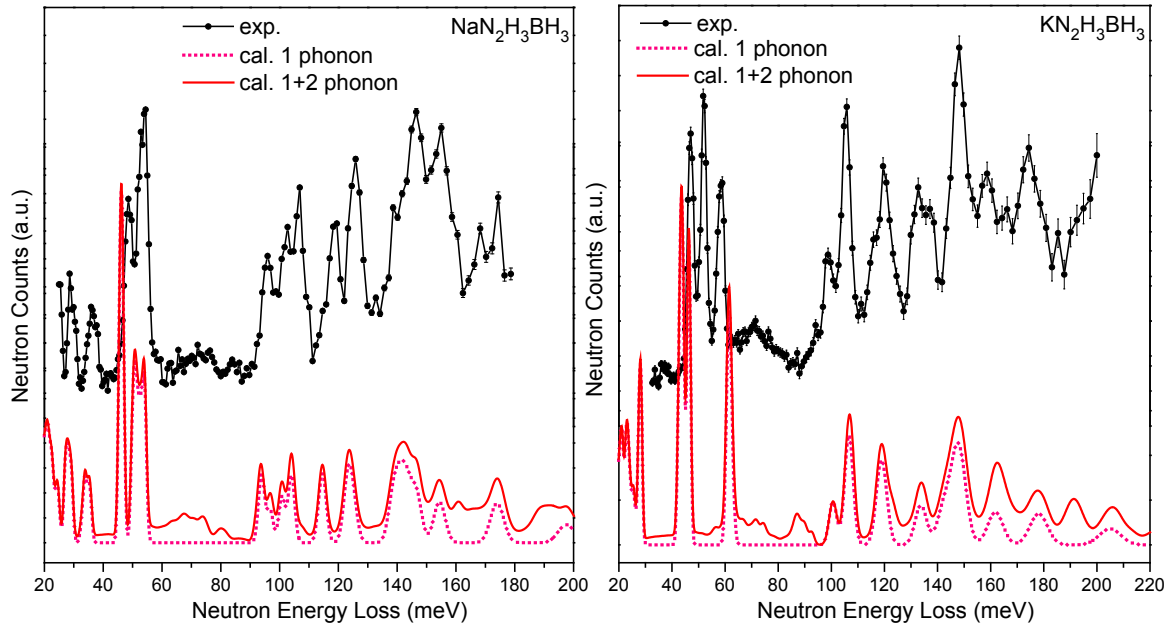
Synthesis and Characterization of Novel Compounds

Collaboration with Maryland, GM, Dalian Institute of Chemical Physics, Sichuan University

Motivation: synthesizing new compounds potentially promising for hydrogen storage



Comparison of neutron vibrational spectra for $N_2H_4BH_3$ and $AN_2H_3BH_3$ (A = Li, Na, K)



DFT phonon simulations are in agreement with neutron vibrational spectra for the recently synthesized $NaN_2H_3BH_3$ and $KN_2H_3BH_3$.

Agreement between neutron vibrational spectroscopy and density functional theory corroborates structures determined by diffraction methods.

Y. S. Chua *et al.*, J. Phys. Chem. C (submitted).

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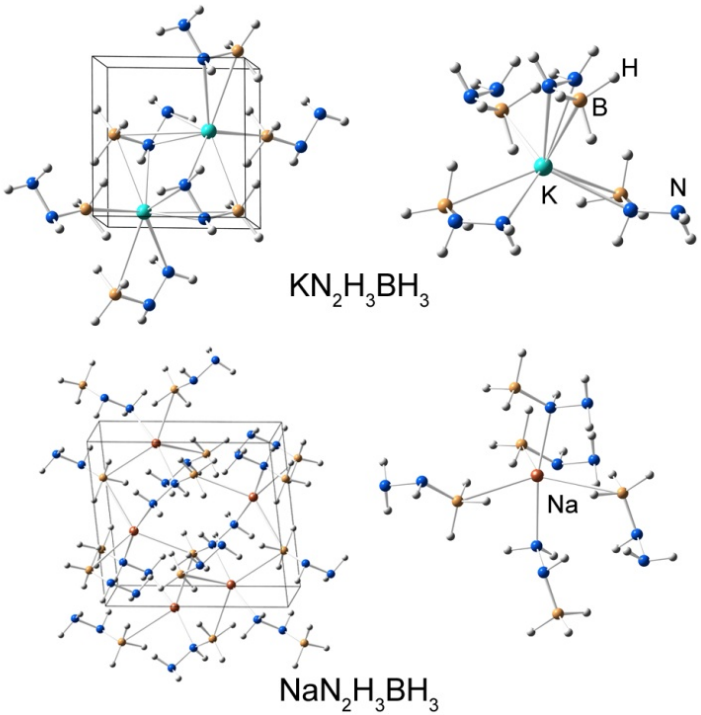
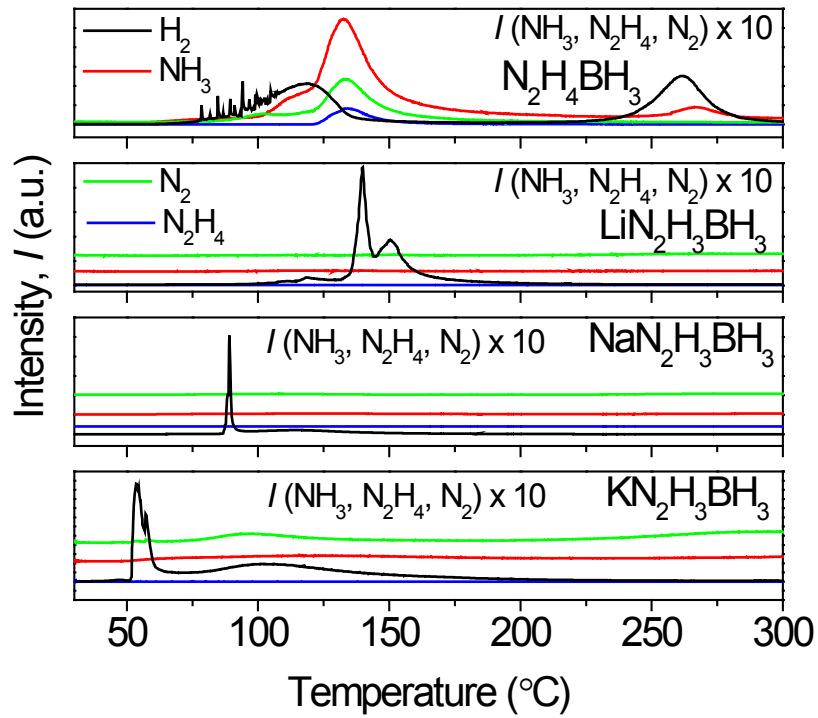


New $NaN_2H_3BH_3$ and $KN_2H_3BH_3$ structures determined from diffraction data



TPD-MS measurements of $N_2H_4BH_3$, $LiN_2H_3BH_3$, $NaN_2H_3BH_3$ and $KN_2H_3BH_3$

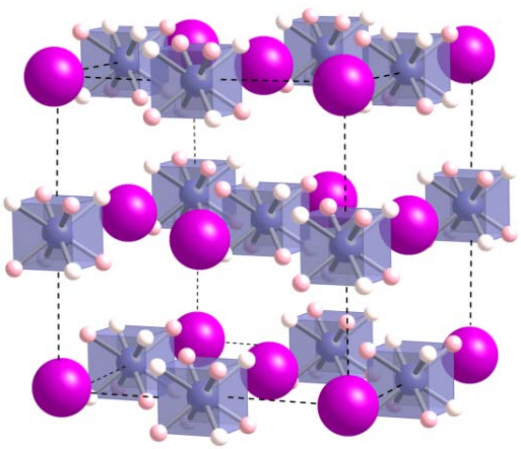
Compared to $N_2H_4BH_3$, the alkali-metal substituted hydrazidotrihydridoborates display improved dehydrogenation behavior with no N_2H_4 emission and greatly suppressed NH_3 release.

Y. S. Chua *et al.*, J. Phys. Chem. C (submitted).

Subtle Borohydride Phase Transitions

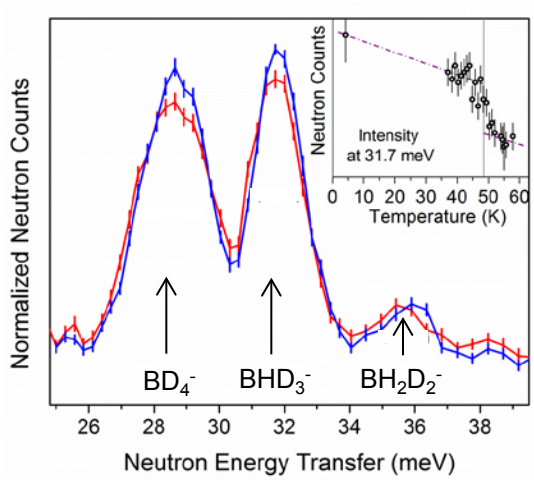
Collaboration with Maryland, Michigan, Delft University

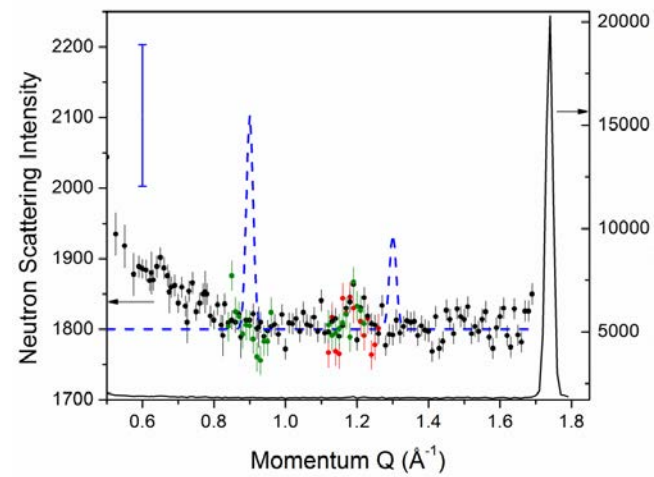
Motivation: characterizing the bonding in borohydride materials



A disordered $RbBD_4$ structure was determined from NPD data at both 5 K and 60 K.

Neutron vibrational spectra of torsions in $RbBD_4$ (with 4 % H) at 38 K (blue) and 55 K (red). Inset: neutron scattering intensity at 31.7 meV vs. temperature, denoting the phase transition at 48.5 K.





Neutron powder diffraction data for $RbBD_4$ at low Q below (4 K, green; 38 K, black) and above (58 K, red) the phase transition. Dashed lines represent previously suggested superlattice peaks at 4 K.

Neutron diffraction/spectroscopy suggest that only short-range BD_4^- order exists in $RbBD_4$.

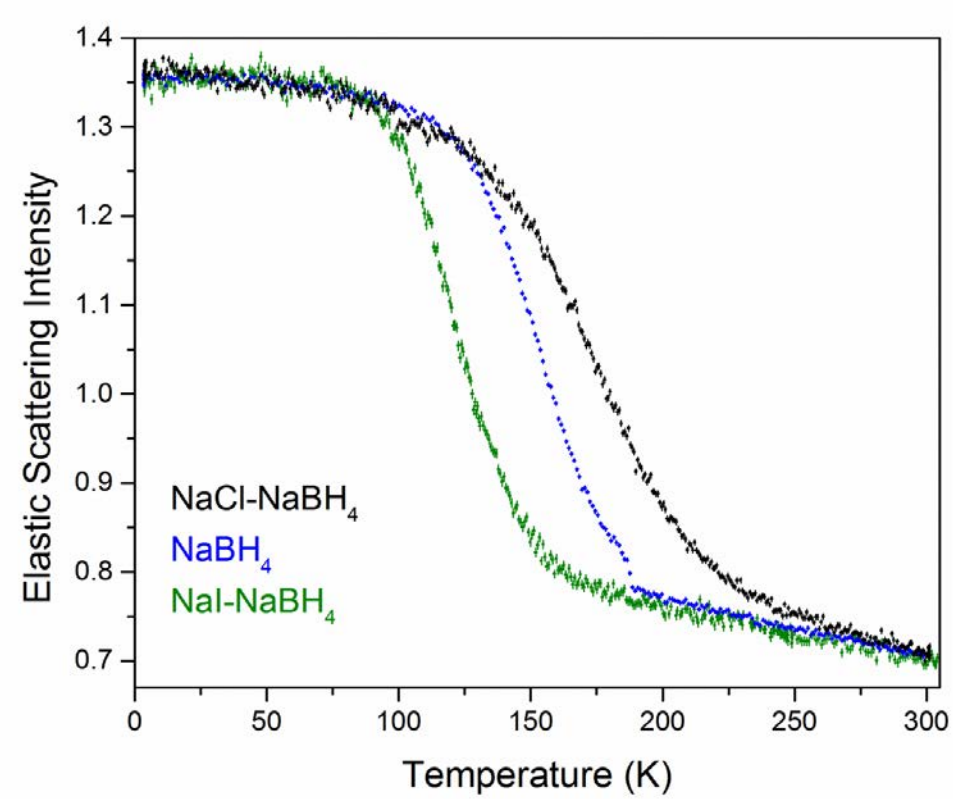
B. B. Kitchen *et al.*, J. Solid State Chem. **203**, 51-54 (2013).

BH_4^- Dynamics of Modified $NaBH_4$ Phases

Collaboration with Maryland, IMP Ekaterinburg

Motivation: understanding BH_4^- rotational dynamics in modified $NaBH_4$

Neutron-Scattering Fixed-Window Scans for Bulk and Halide-Anion-Substituted $NaBH_4$



Anion Sizes

$I^- > BH_4^- > Cl^-$

As the average anion size increases:

- The BH_4^- rotational jump rate increases at a given temperature.
- the temperature corresponding to the onset of rapid rotations decreases.

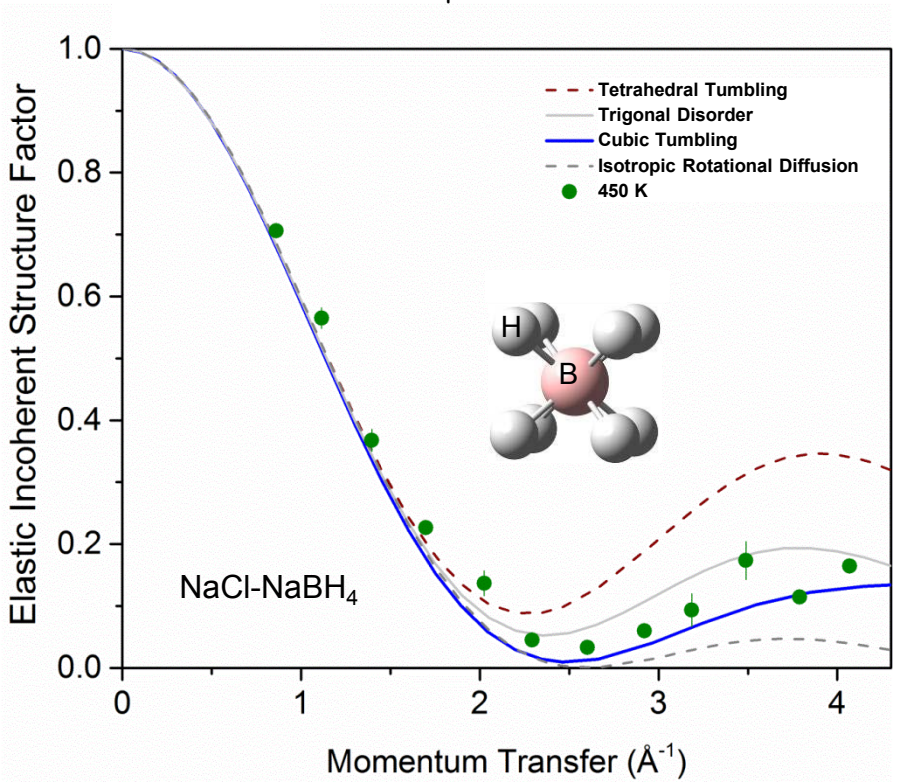
Fixed-window scans allow for a relative comparison of BH_4^- anion rotational mobilities.

BH_4^- Dynamics of Modified $NaBH_4$ Phases

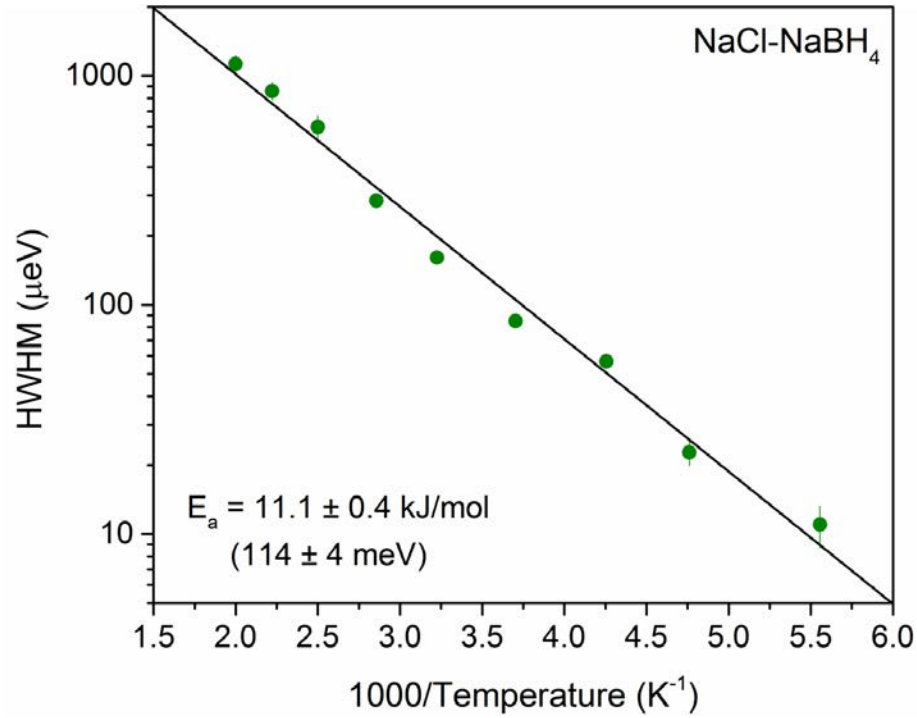
Collaboration with Maryland, IMP Ekaterinburg

Motivation: understanding BH_4^- rotational dynamics in modified $NaBH_4$

Elastic Incoherent Structure Factor (EISF) data for NaCl-$NaBH_4$



The activation energy for BH_4^- reorientation is similar to that for bulk $NaBH_4$.



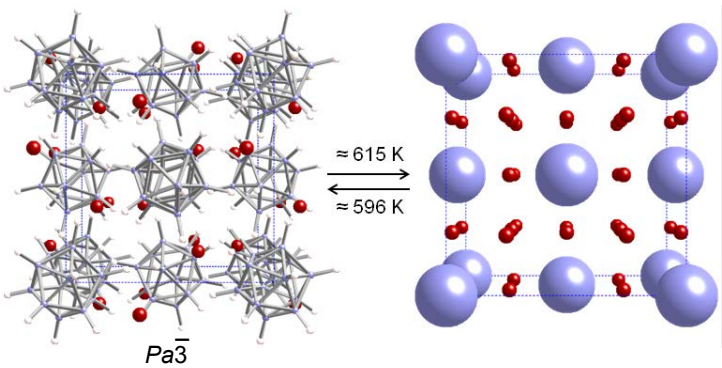
The cubic tumbling mechanism, where the H atoms jump to the eight corners of a cube, is in best agreement with the EISF data.

$Li_2B_{12}H_{12}$ and $Na_2B_{12}H_{12}$ Phase Transitions

Collaboration with Maryland, GE, Sandia, IMP Ekaterinburg

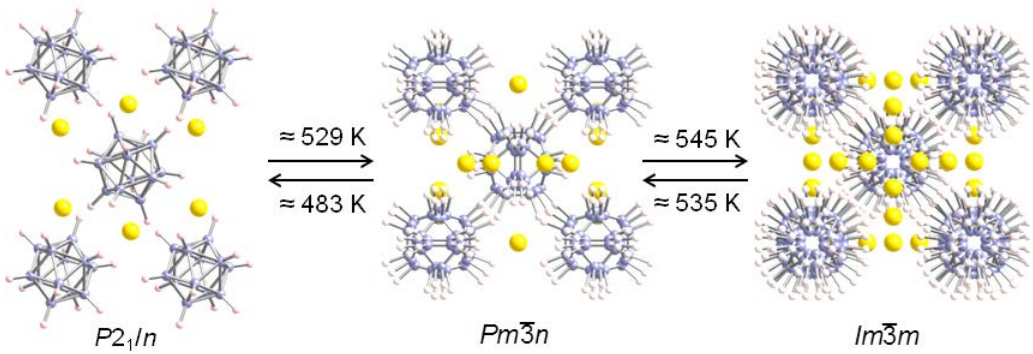
Motivation: characterizing borohydride dehydrogenation products

X-ray and neutron powder diffraction were used to elucidate the structures of $Li_2B_{12}H_{12}$ and $Na_2B_{12}H_{12}$ below and above their phase transitions near 615 K and 529 K, respectively.



$Na_2B_{12}H_{12}$ transition from an ordered monoclinic structure to a sequence of (anion and cation) disordered quasi-body-centered-cubic structures

Proposed $Li_2B_{12}H_{12}$ transition from an ordered cubic structure to an orientationally disordered anion sublattice harboring disordered cation sites



Both $Li_2B_{12}H_{12}$ and $Na_2B_{12}H_{12}$ undergo order-disorder phase transitions resulting in orientationally mobile anions and vacancy-rich cation sublattices.

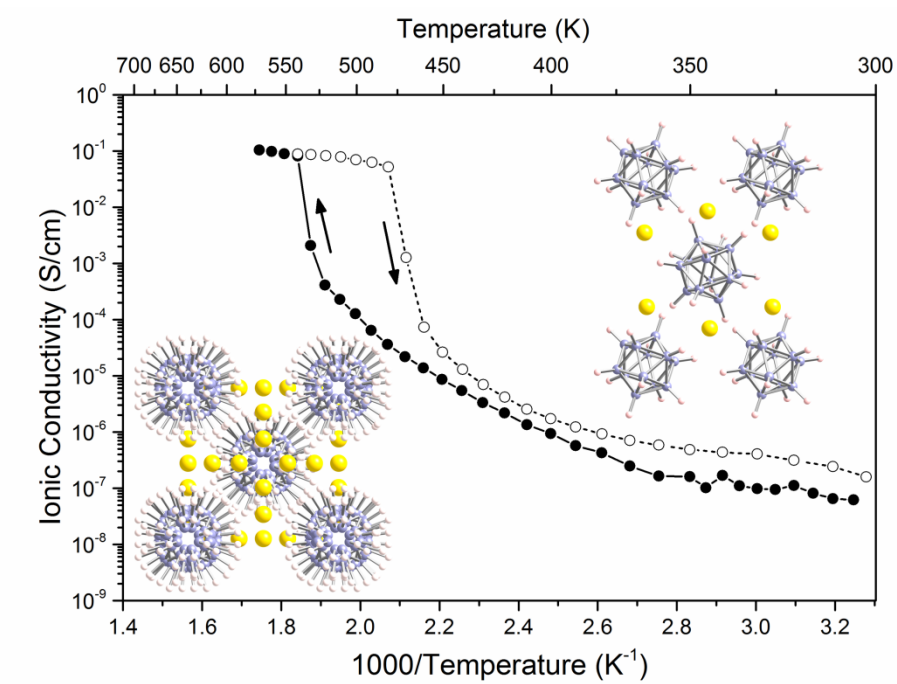
N. Verdal *et al.*, J. Solid State Chem. **212**, 81-91 (2014).

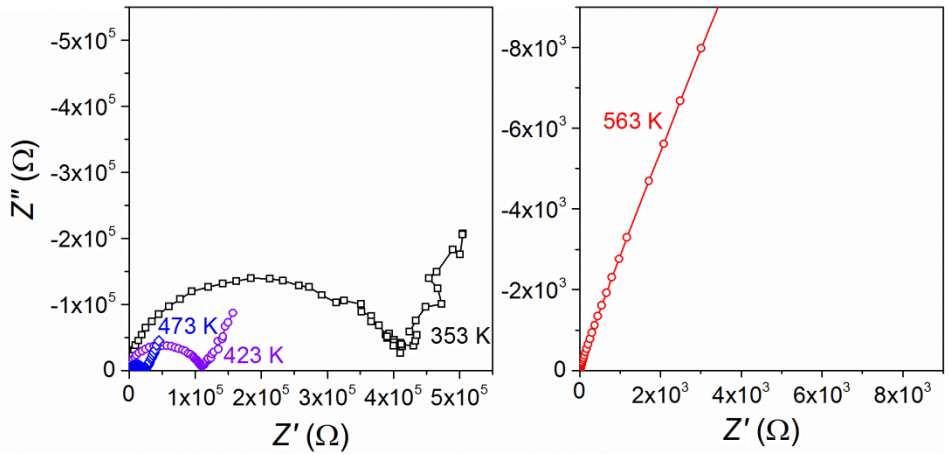
Sodium Superionic Conduction in $Na_2B_{12}H_{12}$

Collaboration with Maryland, GE, Sandia, IMP Ekaterinburg, Tohoku University

Motivation: characterizing conductivity properties of cubic $Na_2B_{12}H_{12}$

AC impedance measurements of $Na_2B_{12}H_{12}$ ionic conductivity vs. temperature





Complex impedance plots of $Na_2B_{12}H_{12}$ at various temperatures during heating run

$Na_2B_{12}H_{12}$ exhibits dramatic superionicity above its order-disorder phase transition, aided by the large mobile anions and the appearance of cation vacancies.

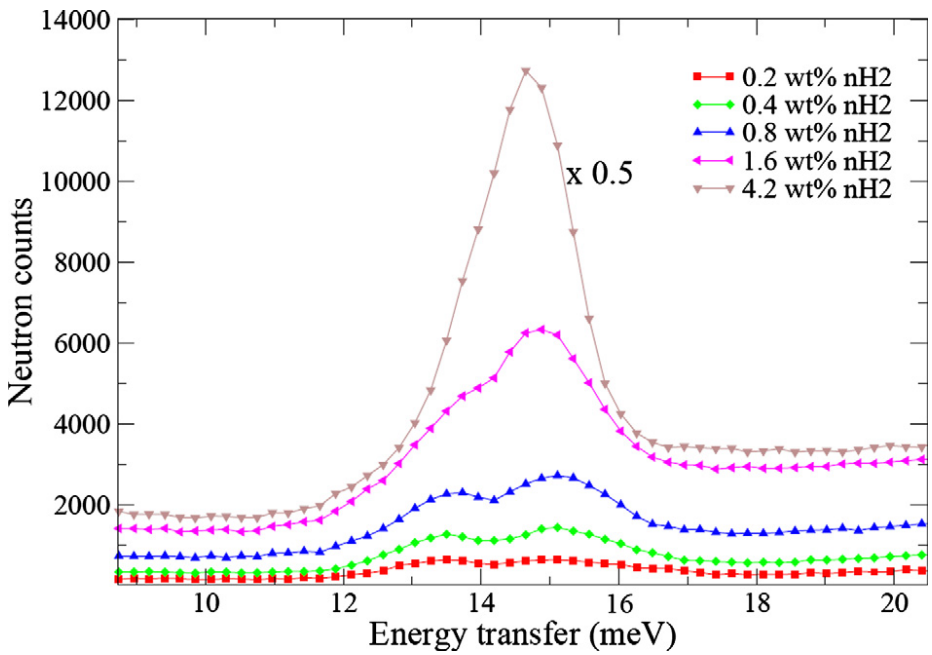
T. J. Udovic *et al.*, Chem. Comm. **50**, 3750-3752 (2014).

Surface Compression of C-nanoconfined H_2

Collaboration with Penn State, Delaware

Motivation: investigating surface compression effects in C nanopores

Neutron vibrational spectra at 4 K of normal H_2 adsorbed in polyfurfuryl-alcohol-derived nano-porous carbon (PFA-NPC40) at different loadings



The rotational tunneling behavior of adsorbed H_2 in this nanoporous carbon confirmed the hindrance to rotational motion.

Measurements using heavier gases showed similar changes in the nature of the lateral forces during adsorption. Lateral forces were attractive at low uptakes and pressures but became repulsive at higher uptakes and pressures.

Adsorbates at high uptakes can be in a highly compressed state with the appearance of repulsive lateral forces that significantly affect the energetics of adsorption.

A. Qajar, et al., Carbon **60**, 538-549 (2013).

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.

Future Work

Remainder of FY2014:

- 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, start characterization work on new hydrogenated metal silicides

Summary

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

- Agreement between NVS and DFT corroborates the recently synthesized $NaN_2H_3BH_3$ and $KN_2H_3BH_3$ structures that were determined by diffraction methods.
- Compared to $N_2H_4BH_3$, the alkali-metal substituted hydrazidotrihydridoborates display improved dehydrogenation behavior with no N_2H_4 emission and greatly suppressed NH_3 release.
- Neutron diffraction and spectroscopy indicate that BD_4^- anion ordering in $RbBD_4$ does exist but is short-ranged and does not involve any superlattice ordering.
- 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 quasielastic neutron scattering data for NaCl-$NaBH_4$ solid solution above room temperature.
- $Li_2B_{12}H_{12}$ and $Na_2B_{12}H_{12}$ undergo order-disorder phase transitions at ~615 K and 529 K, respectively, resulting in orientationally mobile anions and vacancy-rich cation sublattices.
- $Na_2B_{12}H_{12}$ exhibits dramatic superionicity above its order-disorder phase transition, aided by the large mobile anions and the appearance of cation vacancies.
- Molecular hydrogen and other gaseous adsorbates at high uptakes in nanoporous carbon can be in a highly compressed state with the appearance of repulsive lateral forces that significantly affect the energetics of adsorption.