NIST Center for Neutron Research

HySCORE: Technical Activities at NIST

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National Renewable Energy Laboratory & National Institute of Standards and Technology

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Project ID: ST135

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Overview

Timeline and Budget

- **Timeline:**
  - Project Start Date: October 2015
  - Project End Date: TBD
  - % Complete FY 18: ~65%

- **Budget:**
  - Funding FY17: $1,444,792
  - Funding FY18: $750,000
  - Total Multi Performer Project Funding FY18: $3.625M

Barriers

- **Barriers Addressed:**
  - A. System Weight and Volume
  - O. Understanding of Hydrogen Physi- and Chemisorption

- **Partners**
  - NIST – Craig Brown, Terry Udovic
  - PNNL – Tom Autry, Mark Bowden
  - LBNL – Jeff Long, Martin Head-Gordon

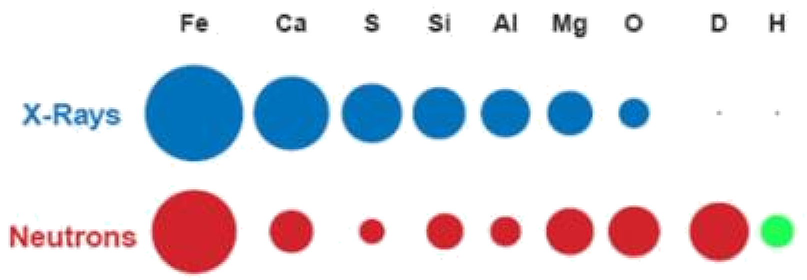
Relevance: Project Objectives

- **NREL leads a collaborative research effort involving NIST, LBNL and PNNL**
  - Seek to employ and develop characterization capabilities at each facility to understand and enhance hydrogen storage media
  - Leverage each institute's unique strengths to jointly validate hydrogen storage claims and design strategies

Relevance: Impact

- **We provide neutron-scattering-based characterization of materials of interest within HySCORE and HyMARC**
- **Neutrons provide unique specificity towards determination of hydrogen properties**
    - Enables identification of isotopically-labelled hydrogen location within complex structures
    - Enables identification of hydrogen dynamics within complex structures

Relative comparison of scattering strength for x-rays and neutrons



Approach: Neutron Scattering

- **Neutron Powder Diffraction (NPD)**: Determine where the atoms are located
- **Quasielastic Neutron Scattering (QENS)**: Diffusional and reorientational dynamics
- **Inelastic Neutron Scattering (INS)** as a sensitive probe of local structure/potential

Isotopes have different scattering powers

H_2

Incoherent

- Does not 'see' neighbor atoms

SPECTROSCOPY

D_2

Coherent

- 'Sees' neighbor atoms

STRUCTURE

Approach: Neutron Scattering

- **Utilize neutrons to characterize and validate hydrogen storage media**
  - Neutron powder diffraction with precise D_2 loading at $T > 4$ K and $P < 100$ bar
    - Elucidate crystal structure of storage materials
    - Harness isotopic sensitivity of elastically scattered neutrons to locate chemi- and physisorption sites of deuterium
  - Inelastic and quasielastic neutron spectroscopy with precise H_2 loading at $T > 4$ K and $P < 100$ bar
    - Harness isotopic sensitivity of inelastically and quasielastically scattered neutrons to identify local environment for complex hydrides and chemi- and physisorbed hydrogen

Accomplishments: $Mg(BH_4)_2 \cdot x$THF

decomposition

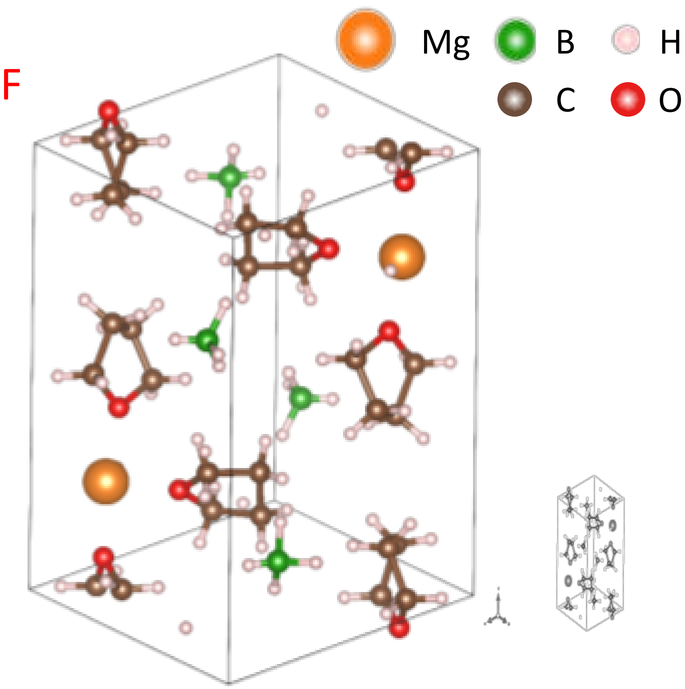
$$Mg(BH_4)_2 \xrightarrow[\text{200 °C}]{\text{5 weeks}} 1/3\ Mg(B_3H_8)_2 + 2/3\ MgH_2 + 2/3\ H_2$$

$\downarrow$ **L**

$$Mg(BH_4)_2 \bullet L \xrightarrow[\text{200 °C}]{\text{24 h}} 1/5\ MgB_{10}H_{10} \bullet L + 4/5\ MgH_2 + 11/5\ H_2$$

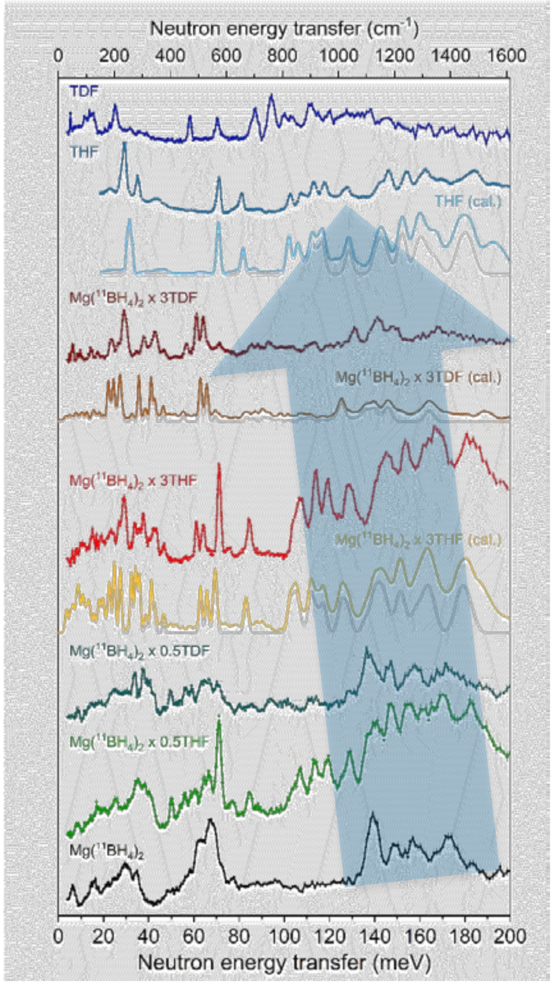
L – solvent: tetrahydrofuran (THF)

$Mg(BH_4)_2 \cdot 3THF$



Objective: Look into the fundamental properties of $Mg(BH_4)_2 \cdot L$ and try to explain how the solvent coordination might have the beneficial effect of enhancing dehydrogenation kinetics. (HySCORE/PNNL)

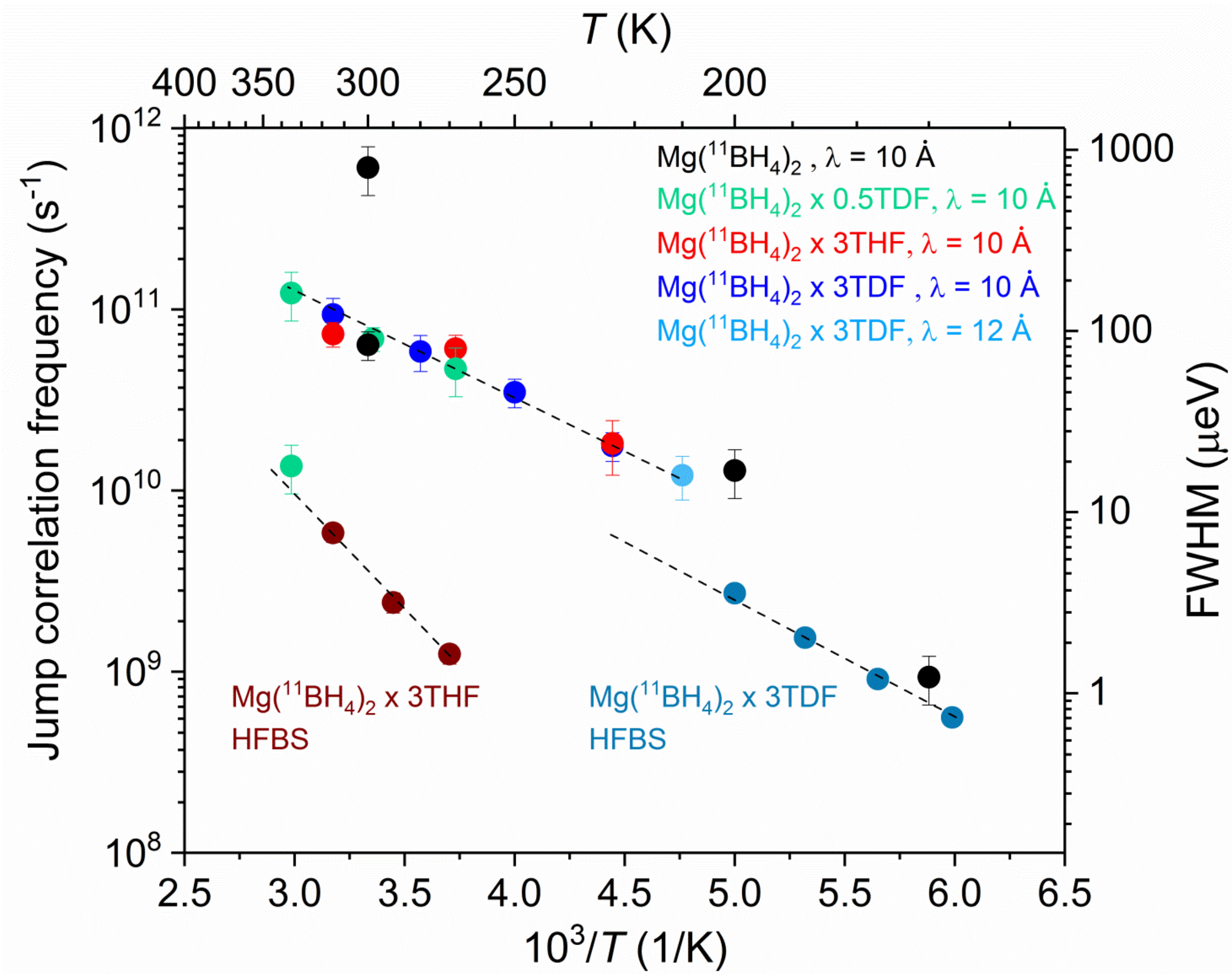
Accomplishments: $Mg(BH_4)_2 \cdot x$THF INS



- Calculated NVS spectra are in good agreement with the experimental results.
- For $Mg(BH_4)_2 \cdot 3$THF, sharp additional peaks attributed to discrete BH_4^- librational modes are observed near 500 cm^{-1}, which are unlike the more smeared out modes in α-$Mg(BH_4)_2$.
- **Intensity decrease** for the samples containing TDF (efficiently canceling the solvent scattering)

Red shift in the band energies of the BH_4^- librational and bending modes with increasing THF concentration as a result of changes in the bond lengths and force constants.

Accomplishments: $Mg(BH_4)_2 \cdot x$THF QENS



- Orientational mobilities of the BH_4^- anions: not sensitive to the amount of THF or TDF present (compare well with the mobilities of BH_4^- anions in unsolvated material)
- An abrupt change in the speed of the BH_4^- anions is observed at around 200 K (correlated with the phase change)

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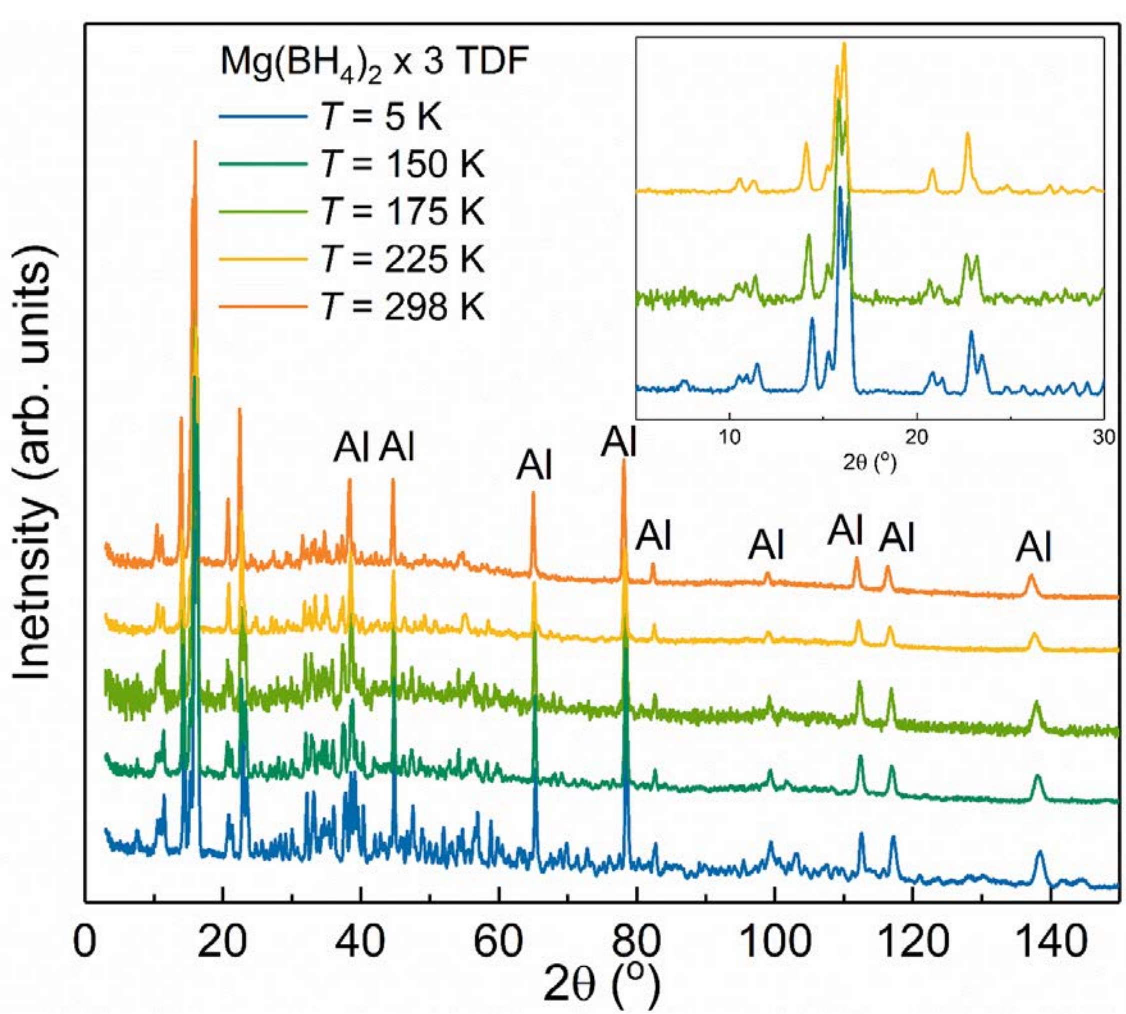
Accomplishments: $Mg(BH_4)_2 \cdot x$THF NPD



- An abrupt change in the speed of the BH_4^- anions is observed at around 200 K (correlated with the phase change)
- NPD patterns measured at different temperatures point to a phase transition occurring around 180 K
- High temperature structure has not been resolved

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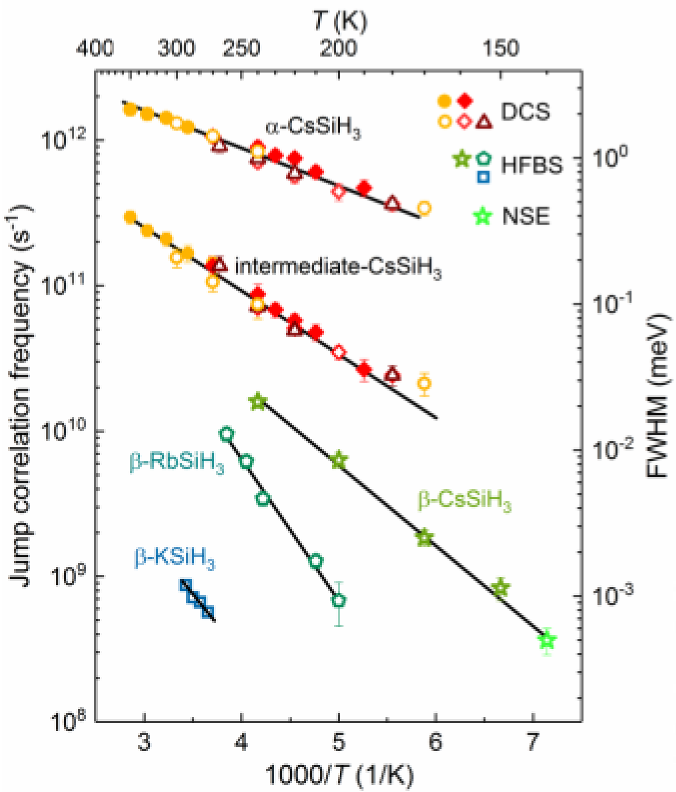
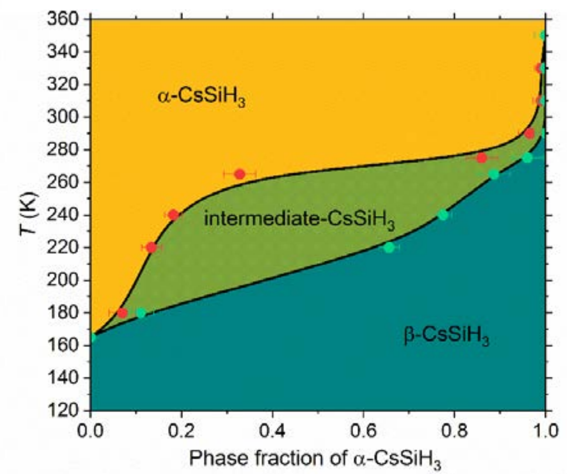
Accomplishments: $MSiH_3$



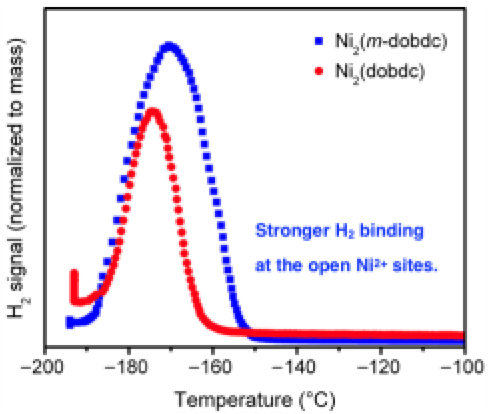
Anion jump correlation frequencies τ_1^{-1} vs. inverse temperature for $MSiH_3$

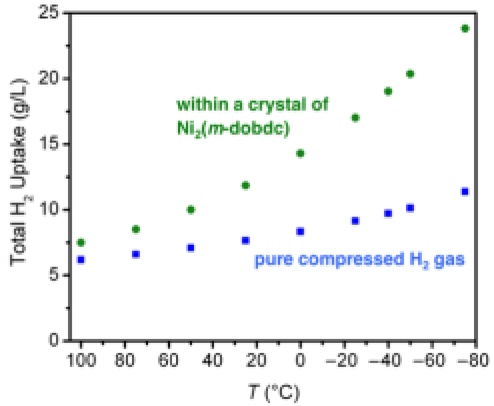
- Continuation of the study on $MSiH_3$, which will focus on the dynamics on the SiH_3- group in the low-temperature and high temperature phase
- The experiments were done on three different instruments (NSE, HFBS and DCS) extending the explored mobility range from 10^7 to 10^{12} s^{-1}.
- Dynamically distinct transitional state was observed upon transition from α-phase to β- phase, and vice versa. Future work will focus on the structural characterization (NPD) of this intermediate phase.
- This is an example of how dynamical measurements seem to predict an intermediate phase not yet observed by diffraction.

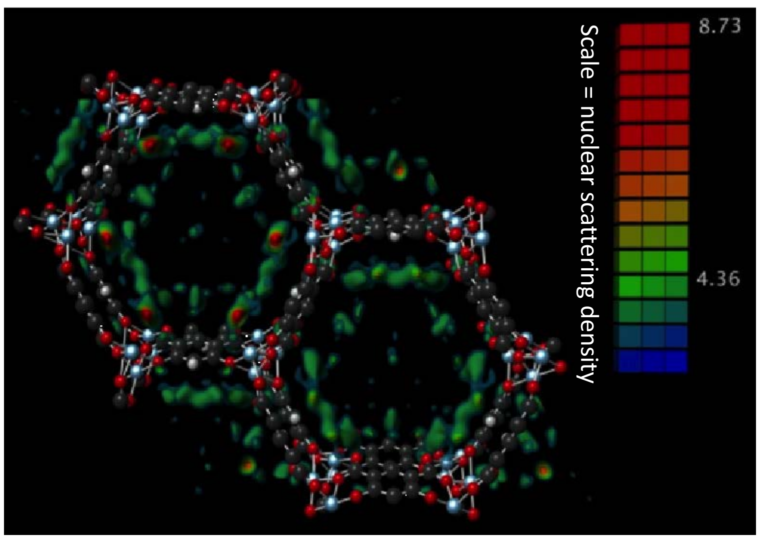


Phase diagram of $CsSiH_3$ made from the QENS analysis.

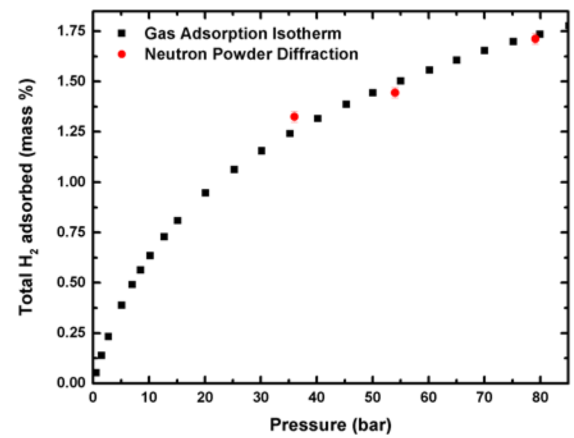
Accomplishments: High-pressure H_2 Storage in MOFS







- D_2 locations and compositions in Co_2(*m*-dobdc) probed at 77-298 K and 30-80 bar.
- D_2 content correlates with the low-temperature structures.
- Hydrogen content from NPD data matches the adsorption isotherm uptake values.
- Paper submitted: Berkeley/LBNL/NIST



Volumetric adsorption isotherm for H_2 uptake **in Co_2(*m*-dobdc)** at 198 K compared to total H_2 uptake based on NPD data.

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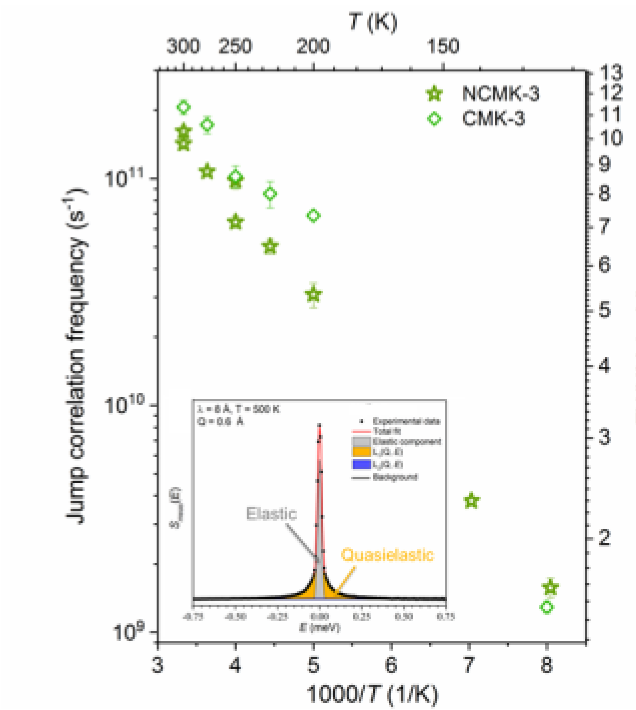
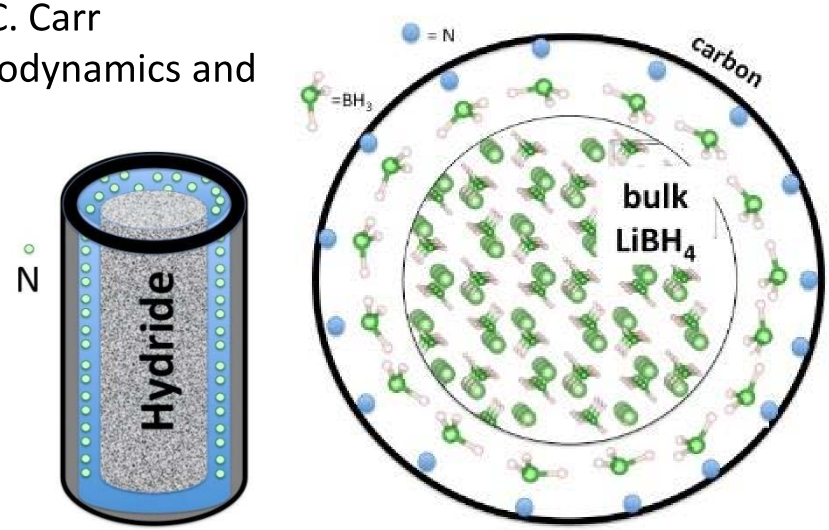
Accomplishments: $LiBH_4$ in N-doped Carbon Scaffolds

- With E. Majzoub (U. Missouri-St. Louis), PhD student C. Carr
- Studying the effect of nanoconfinement on the thermodynamics and kinetics properties of hydrogen storage materials



Comparison of orientational BH_4^- mobility for the N-doped (NCMK-3, 5nm pore) and undoped (CMK-3, 3.5nm pore) nanoporous carbon scaffolds



- NVS measurements show infiltration of $LiBH_4$ into all nanopore geometries.
- Some differences in the orientational mobility/activation energy
- The most N-doped scaffold (N-CMK-3) shows lower average mobility.

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Responses to Previous Year Reviewers' Comments

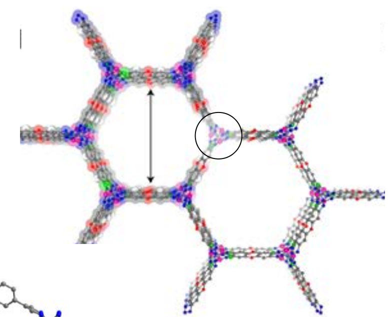
- **This project was not reviewed last year**

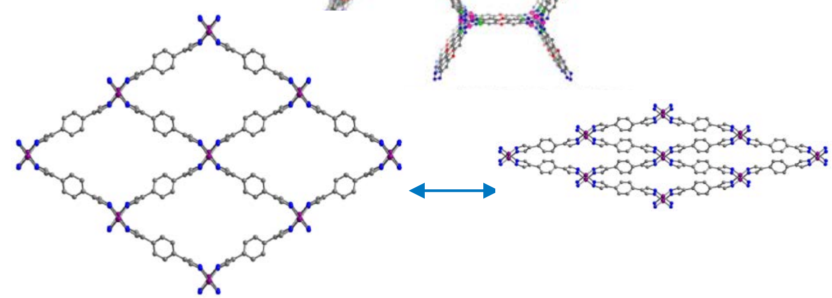
Collaborations

- **NREL/NIST collaboration**
  - Characterizing ultra-microporous materials using neutron diffraction and neutron spectroscopy
- **NREL/NIST collaboration with LBNL**
  - Characterizing hydrogen adsorption in metal organic framework materials using neutron diffraction and neutron spectroscopy
  - Characterizing various hydrogen storage materials at the Advanced Photon Source
- **NREL/NIST collaboration with PNNL**
  - Developing spectroscopic signatures for $Mg(BH_4)_2 \cdot x$THF
- **NREL/NIST collaboration with LLNL and SNL**
  - $MgB_2/MgBH_4$ hydrogenations/dehydrogenations
  - Catalytic dissociation of H_2/D_2
- **NREL/NIST collaboration with EPFL**
  - Characterizing new open-metal MOFS based on benzenetristriazolate and triazine-derivative ligands
  - Characterizing effect of induced framework polarization on hydrogen adsorption in zeolitic imidazolate frameworks

Future Work and Challenges

- Finish QENS measurements on $Mg(^{11}BH_4)_2 \cdot x$THF and $Mg(^{11}BH_4)_2 \cdot x$TDF materials (HySCORE)
- INS/QENS on MgB_2/$MgBH_4$ hydrogenations/dehydrogenations (HyMARC)
- Explore catalytic dissociation of H_2/D_2 using INS (HyMARC)
- Continue NPD/INS characterizations of new MOF materials (HySCORE)
  - Cu(I) MOF (Long)
  - V(II) MOF (Long)
  - Benzenedipyrazolate frameworks
  - Pore-opening frameworks
    - Develop 2 kbar H_2 pressure cell





Any proposed future work is subject to change based on funding levels

Summary

- **$Mg(BH_4)_2 \cdot x$THF Structure and Dynamics**
  - NPD/INS/QENS measurements are complete
  - Analysis ongoing, manuscript anticipated soon
- **$MSiH_3$ Dynamics**
  - QENS probed mobilities across 10^7-10^{11} s^{-1} range
  - Phase diagram developed
- **High-pressure H_2 Storage in MOFS**
  - NPD measurements are complete
  - Manuscript has been submitted
- **$LiBH_4$ in N-doped Carbon Scaffolds**
  - N-doping shown to suppress BH_4^- orientational mobility

Technical Backup Slides

Technical Slides: Sample preparation

- Samples activated by slowly heating to predetermined temperature in tube furnace under dynamic vacuum (~10^{-7} torr)
- Samples transferred to He-filled dry box with < 0.1 ppm H_2O and < 5 ppm O_2 and sealed in vanadium or aluminum sample cells
- Gas dosing sample cell permits delivery of D_2/H_2 to sealed sample
- Samples mounted onto closed cycle refrigerator
- Samples connected to gas delivery manifold of known volume when dosing with D_2/H_2
- Residual He removed using turbo molecular pump

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Technical Slides: Neutron Powder Diffraction

- **High resolution neutron powder diffraction data collected at 7 K using a Ge(311) monochromator with an in-pile 60' collimator**
  - Instrument: BT1
  - Corresponds to λ = 2.078 Å

- **Initial measurements collected on evacuated bare sample**

- **Volumetric gas dosing of D_2 performed above 20 K with incrementally increasing amounts**
  - Full adsorption ensured by letting pressure fall to zero

- **Sample cooled as low as 7 K for measurement**

Technical Slides: Inelastic Neutron Spectroscopy

- **Inelastic neutron spectra collected using the Filter Analyzer Neutron Spectrometer (FANS)**
- **Residual He removed using turbo molecular pump**
- **Spectra collected below 10 K using pyrolytic graphite (002) and Cu (220) monochromators**
  - Covers an energy range of 4.1 – 250 meV, resolution up to 1.1 meV
- **Volumetric gas dosing of H_2 performed above 20 K with incrementally increasing amounts**
  - Full adsorption ensured by letting pressure fall to zero
- **Sample cooled below 10 K for measurement**

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Technical Slides: Quasielastic Neutron Spectroscopy

- **Quasielastic neutron spectra collected using 3 complementary spectrometers:**
  - NGA Neutron Spin Echo Spectrometer (NSE)
    - 10^{-3} – 10^{2} ns time scales, 0.2 – 1.8 $Å^{-1}$ Q range
  - High-Flux Backscattering Spectrometer (HFBS)
    - 10^{-1} – 10 ns time scales, 0.25 – 1.75 $Å^{-1}$ Q range
  - Disk Chopper Spectrometer (DCS)
    - 10^{-4} – 1 ns time scales, 0.1 – 6 $Å^{-1}$ Q range

- **Volumetric gas dosing of H_2 performed above 20 K with incrementally increasing amounts**
  - Full adsorption ensured by letting pressure fall to zero

- **Temperature varied from 4 K to 680 K for measurement**

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