Project ID: ST135

HySCORE

HySCORE: Technical Activities at NIST

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National Renewable Energy Laboratory & National Institute of Standards and Technology

2017 DOE Annual Merit Review: June 8th, 2017

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BERKELEY LAB

Pacific Northwest NATIONAL LABORATORY

NIST Center for Neutron Research

Timeline and Budget

- **Timeline:**

  Project Start: 10/1/2015

  End: Project continuation determined by DOE. Currently scheduled through 9/30/18 (*previously a component of NREL's materials development program and supported annually since 2006)

- **Budget:**

  Total Team Budget: (HySCORE): $8.2M
  Federal Share:
  NREL: $2.6M
  LBNL: $2.4M
  PNNL: $2.4M
  NIST: $0.8M
  NIST Funds Spent: ~$0.35M
  (Estimated as of 3/31/17)

- **Barriers Addressed:**

General:
A. Cost; B. Weight and Volume; C. Efficiency;
E. Refueling Time;
Reversible Solid-State Material:
M. Hydrogen Capacity and Reversibility;
N. Understanding of Hydrogen Physi- and Chemi-sorption;
O. Test Protocols and Evaluation Facilities;

- **Collaborators**
  - LBNL – Jeff Long, Martin Head-Gordon
    PNNL – Tom Autrey, Mark Bowden
  - HyMARC - Vitalie Stavila (SNL), Brandon Wood (LLNL)
  - HyMARC seedling - Eric Majzoub (Univ. Missouri-St. Louis)

Relevance: Project Objectives

HySCORE

An NREL-led National Laboratory collaboration and synergistic research effort between:

NREL, LBNL, PNNL, NIST

- To *Develop* and *Enhance* Hydrogen Storage Core Capabilities, i.e. Characterization Techniques
- To *Validate* claims, concepts, and theories of hydrogen storage materials
- To *Double* hydrogen storage energy density (increase from 25g/L to 50 g/L)

Relevance: Impact of Neutron Analyses

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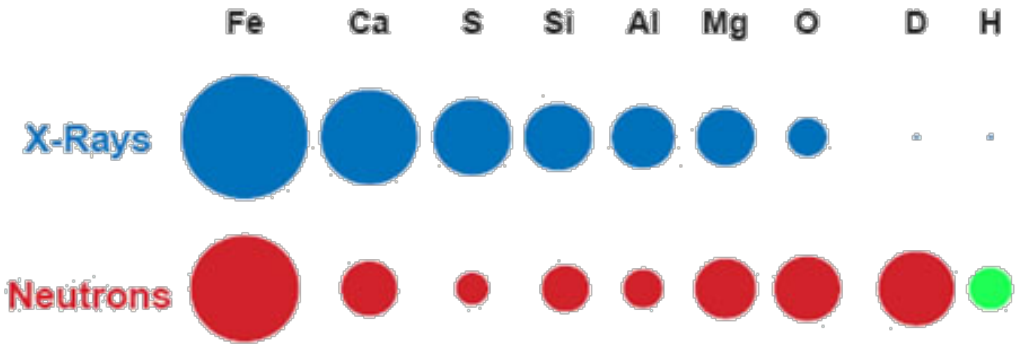
- Neutrons provide unique specificity towards determination of hydrogen properties
  - Enables identification of isotopically-labelled hydrogen location within complex structures
  - Enables identification of hydrogen dynamics within complex structures



http://www.ne.ncsu.edu/nrp/npdf.html

Approach: Neutron Scattering

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Utilize neutrons to characterize and validate hydrogen storage media

NIST provides neutron-scattering-based characterization of materials of interest within HySCORE and other DOE-funded projects

- $Mg(BH_4)_2$
- MgB_2 and $M_2B_{12}H_{12}$+MH hydrogenations
- Li_3N hydrogenation in nanoporous C

HyMARC (SNL/LLNL)

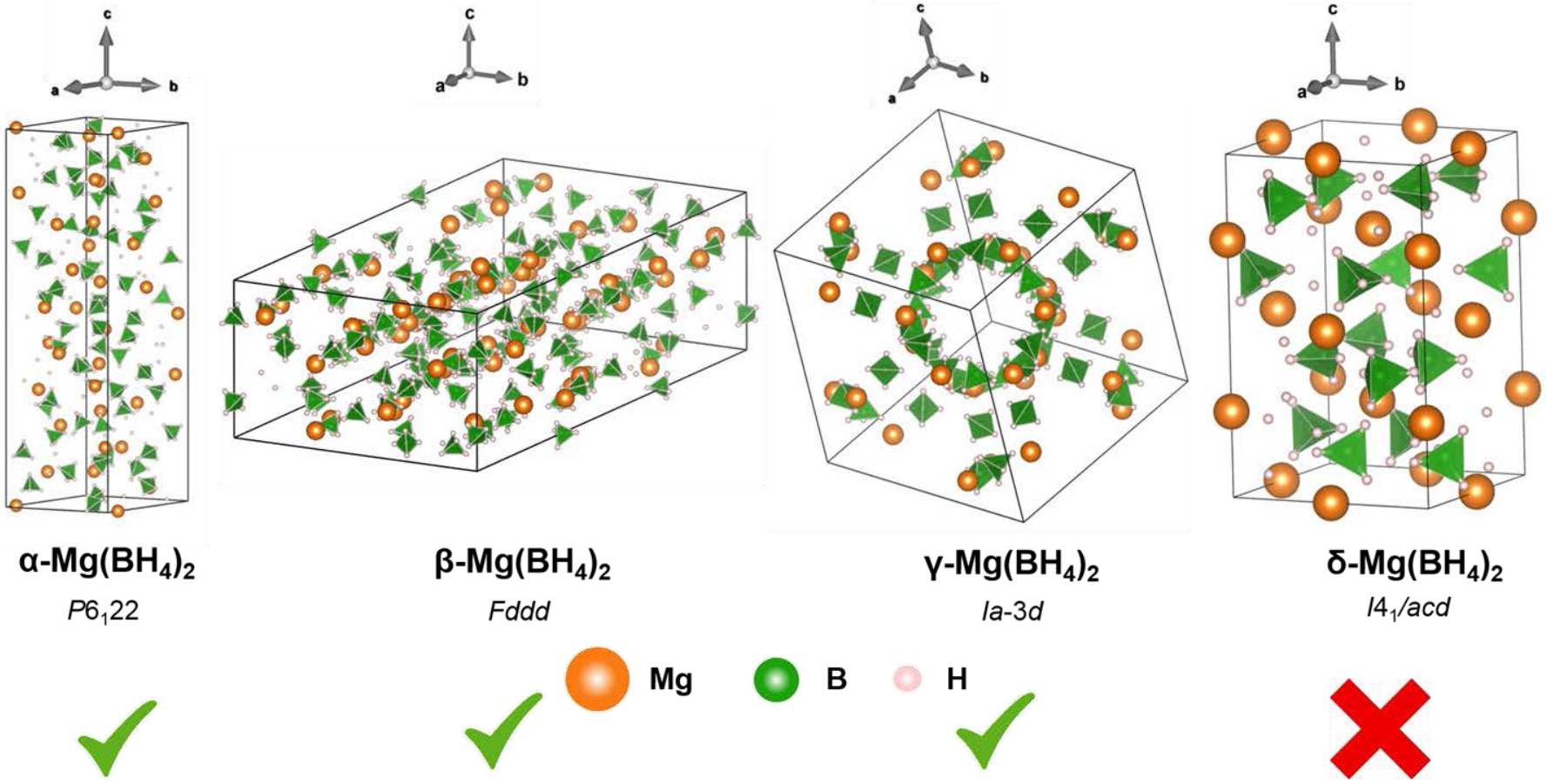
- $Mg(BH_4)_2 \cdot xTHF$
- H_2 in Mn_2(dsbdc) and Co_2(*m*-dobdc) MOFs

HySCORE (PNNL/ LBNL/NREL)

- $LiBH_4$ in N-functionalized nanoporous C — **UMSL Project**

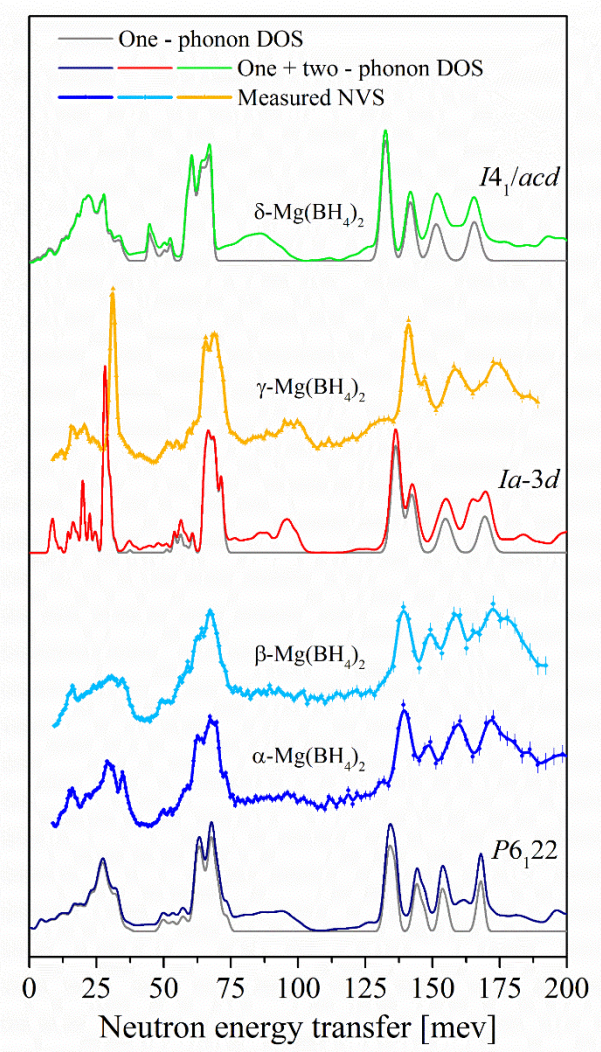
Accomplishments and Progress: $Mg(BH_4)_2$ polymorphs

- Collaboration with Vitalie Stavila (SNL, HyMARC)
- **Develop spectral signatures for different $Mg(BH_4)$ polymorphs**



M. Dimitrievska, *et al.*, Phys. Chem. Chem Phys. **18,** 25546 (2016).

Accomplishments and Progress: $Mg(BH_4)_2$ polymorphs

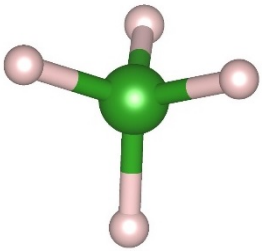


Neutron vibrational spectroscopy

- No selection rules
- H-weighted PDOS dominated by the optical phonons involving large-amplitude H motions

BH_4^- vibrational modes

T_d symmetry



Neutron vibrational spectra of the α-, β- and γ-$Mg(BH_4)_2$ phases at 4 K compared to the simulated one-phonon and one+two-phonon densities of states from first-principles phonon calculations of the DFT-optimized 0 K structures.

M. Dimitrievska, *et al.*, Phys. Chem. Chem Phys. **18,** 25546 (2016).

Accomplishments and Progress: $Mg(BH_4)_2$ polymorphs

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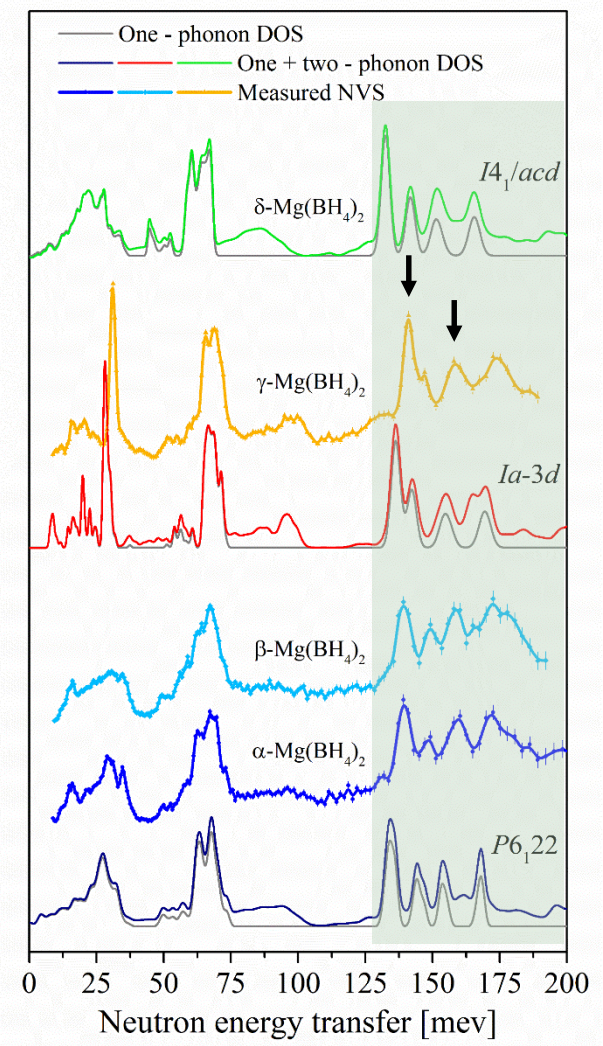
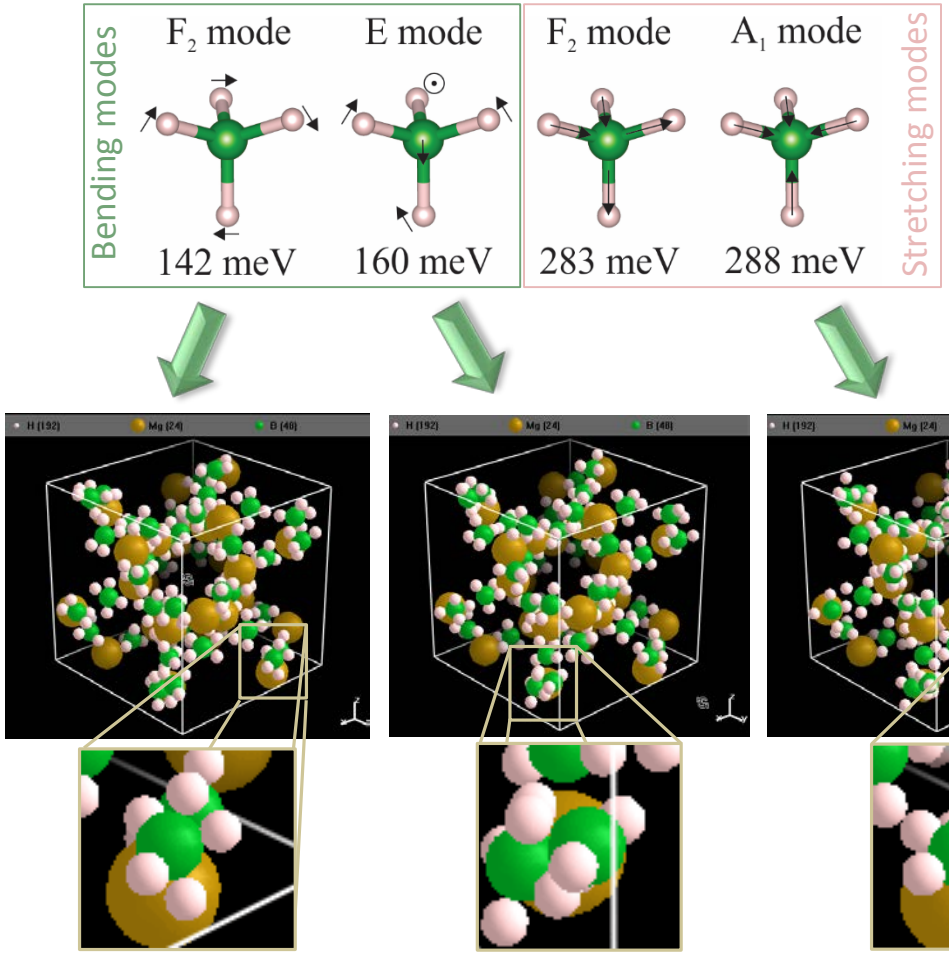


BH_4^- vibrational modes



M. Dimitrievska, *et al.*, Phys. Chem. Chem Phys. **18,** 25546 (2016).

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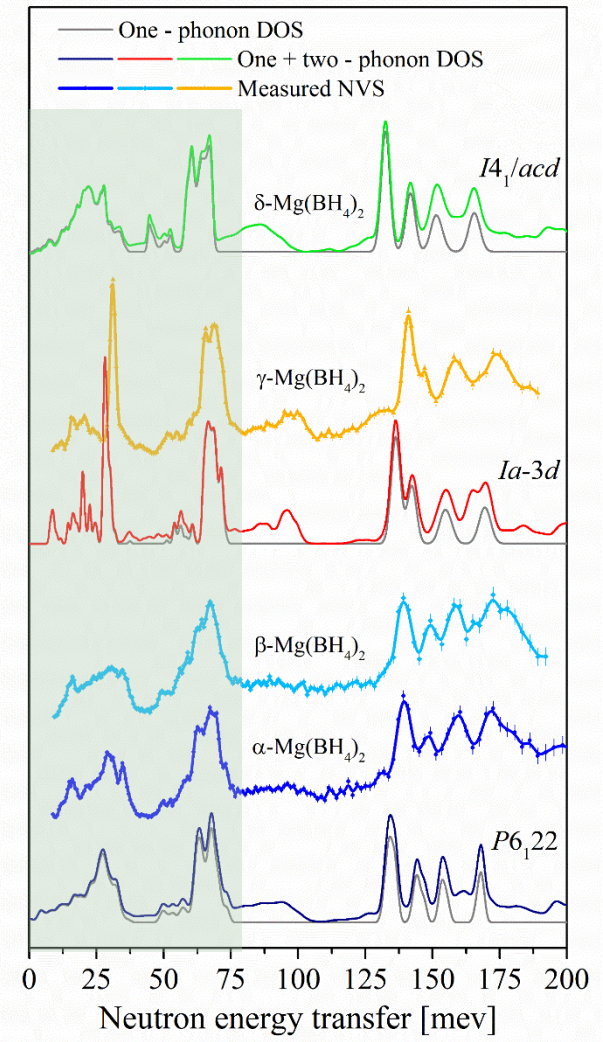
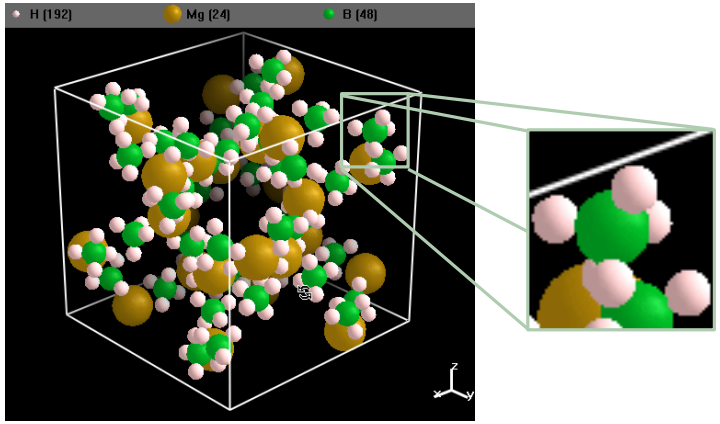
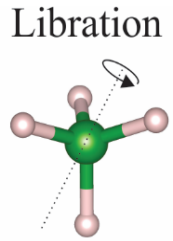
Accomplishments and Progress: $Mg(BH_4)_2$ polymorphs

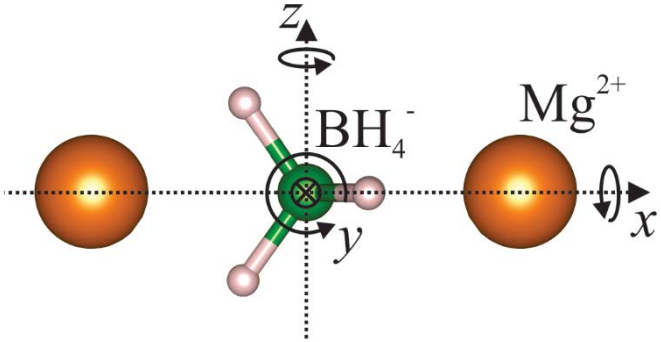


BH_4^- vibrational modes

Librational (torsional) modes
(not usually observed in Raman spectra)







Orientation of the BH_4^- anions and possible librational motions in the γ-$Mg(BH_4)_2$ phase.

M. Dimitrievska, *et al.*, Phys. Chem. Chem Phys. **18,** 25546 (2016).

Accomplishments and Progress: $Mg(BH_4)_2$ polymorphs

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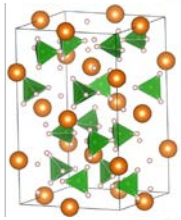
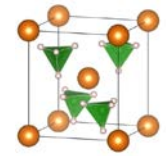
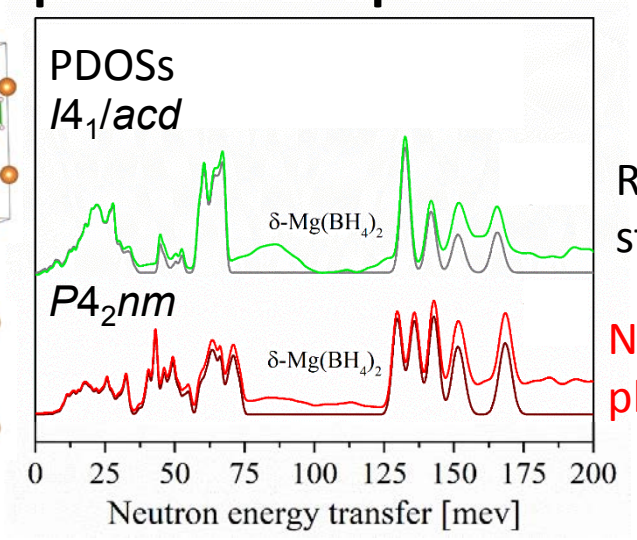
problematic δ-phase

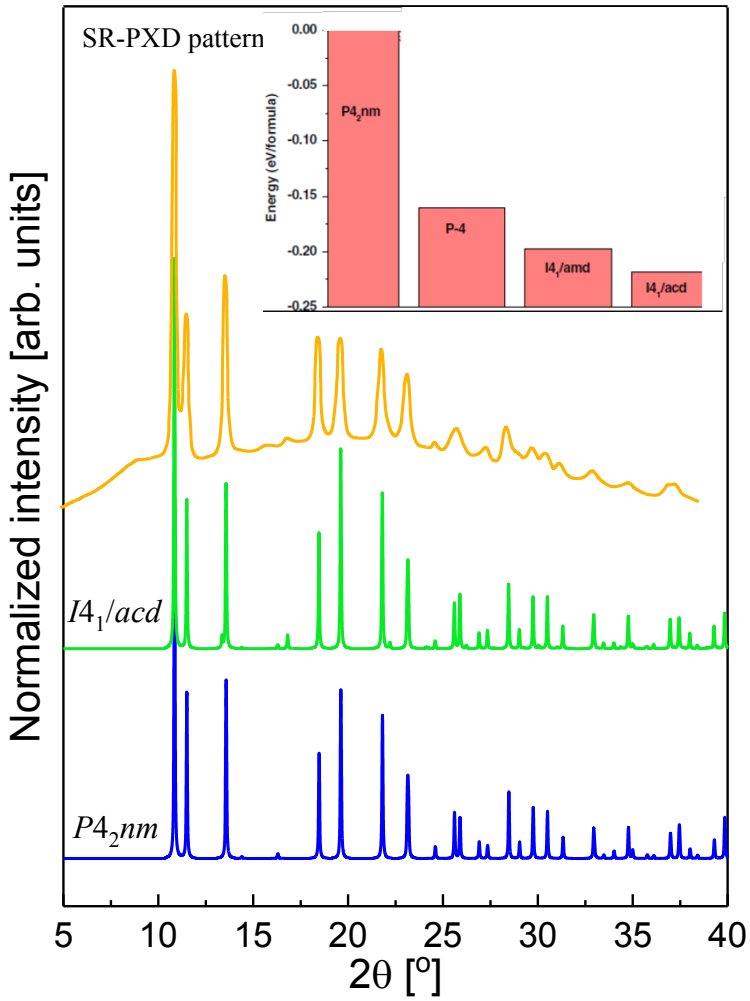






Relaxed structure

Negative phonons

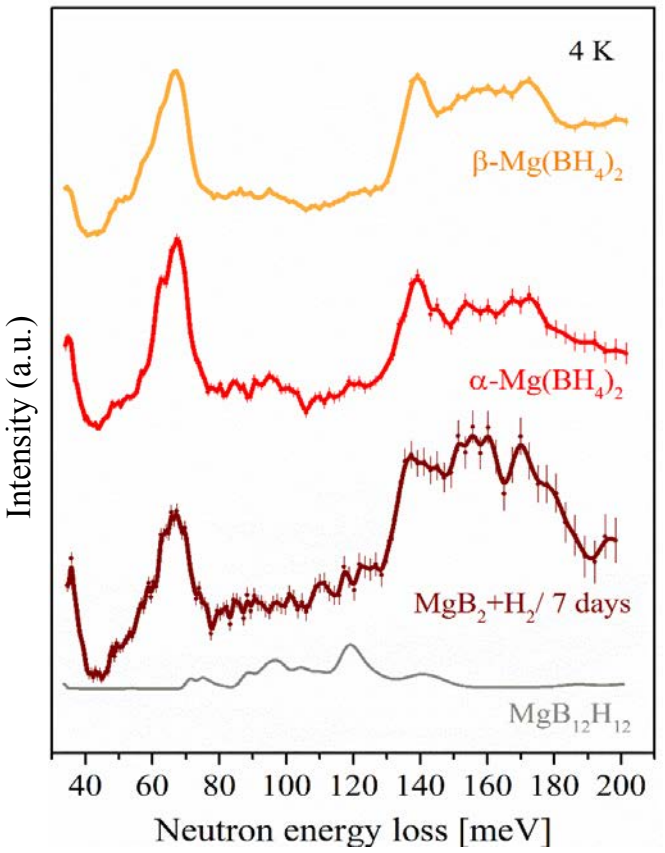


Optimization of the δ phase structure:

- DFT calculations of the PDOS using the previously reported $P4_2nm$ symmetry confirmed dynamical instability, with some of the modes having significantly negative frequencies.
- The alternative optimized $I4_1/acd$-symmetric structure proved to be more dynamically stable.

M. Dimitrievska, *et al.*, Phys. Chem. Chem Phys. **18,** 25546 (2016).

Accomplishments and Progress: MgB_2 and $M_2B_{12}H_{12}$+MH hydrogenations



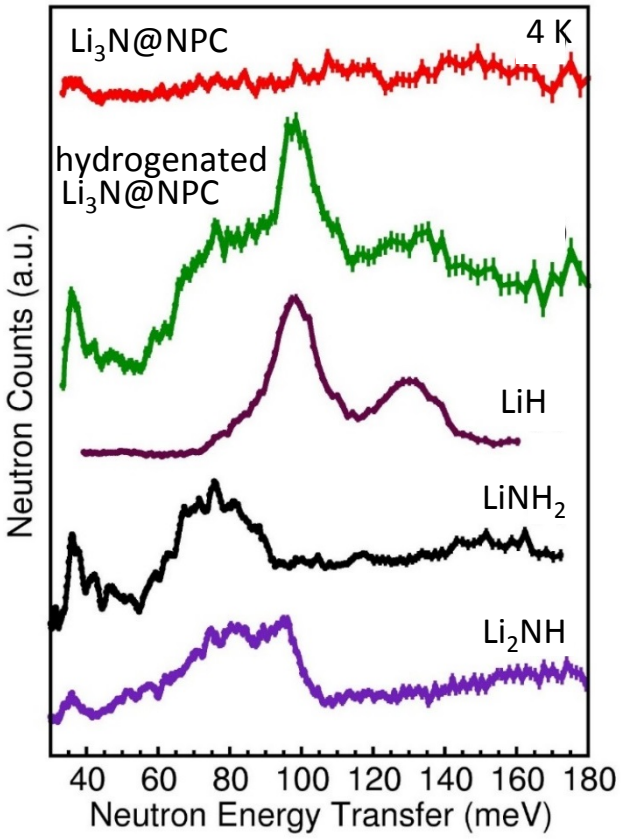
Neutron vibrational spectrum of hydrogenated MgB_2 (7 d, 380°C, 700 bar H_2) compared to those for α- and β-$Mg(BH_4)_2$ and the DFT-simulated $MgB_{12}H_{12}$ spectrum.

- NVS indicated the formation of α- and/or β-$Mg(BH_4)_2$ plus an additional hydrogenous phase consistent with $MgB_{12}H_{12}$ or a similar stabilized borohydride cluster.
- **Neutron prompt-γ activation analysis (PGAA)** indicated a H:B ratio of 1.8 after 7 d MgB_2 hydrogenation.

- **Neutron prompt-γ activation analysis (PGAA):**
  - Neutron based measurement technique for nondestructive bulk elemental analysis
  - Determining the presence and amount of many elements simultaneously in samples ranging in size from micrograms to many grams

Range (μg)	Elements
0.01 - 0.1	B, Cd, Sm, Gd
0.1 - 1	H, Cl, In, Nd
1 - 10	Na, S, K, Sc, Ti, V, Cr, Mn, Co, Ni, Cu, Ge, As, Se, Br, Mo, Ag, Te, I, Au
1 - 100	Mg, Al, Si, P, Ca, Fe, Zn, Ga, Rb, Sr, Y, Zr, Nb, Sb, Ba, La
100 - 1000	C, N, F, Sn, Pb

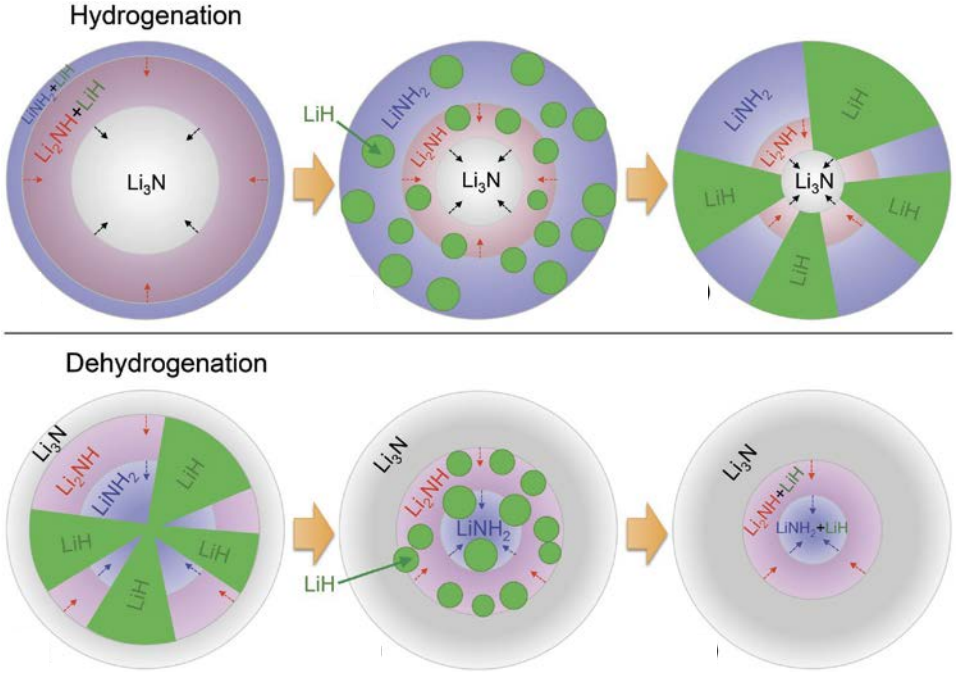
Accomplishments and Progress: Li_3N Hydrogenation in Nanoporous Carbon



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

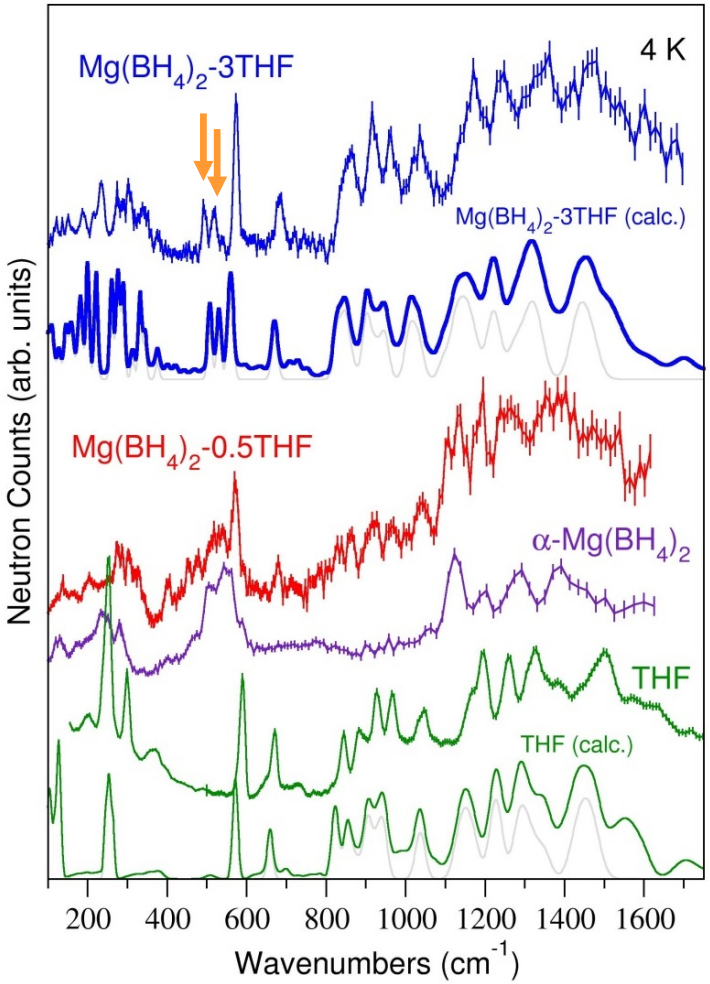
- Collaboration with Brandon Wood (LLNL) and Vitalie Stavila (SNL) to identify hydride phases

- NVS confirmed that both $LiNH_2$ and LiH are hydrogenation products from carbon-nanoconfined Li_3N, with no obvious presence of Li_2NH.



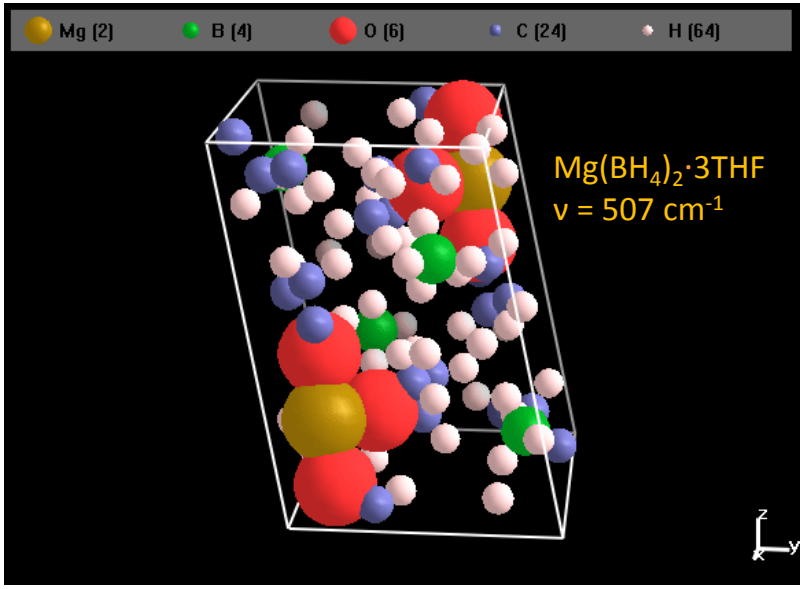
B. C. Wood, *et al.*, Adv. Mater. Interfaces **1600803** (2017).

Accomplishments and Progress: Neutron studies of $Mg(BH_4)_2 \cdot xTHF$



Neutron vibrational spectra for α-$Mg(BH_4)_2$, $Mg(BH_4)_2 \cdot 0.5THF$, $Mg(BH_4)_2 \cdot 3THF$, and THF compared to DFT calculations.

- Collaboration with Tom Autrey (PNNL) to characterize solvated $Mg(BH_4)_2$ compounds
- Calculated NVS spectra are in good agreement with the experimental results for $Mg(BH_4)_2 \cdot 3THF$.
- For $Mg(BH_4)_2 \cdot 3THF$, 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-$Mg(BH_4)_2$.



Accomplishments and Progress: Neutron studies of $Mg(BH_4)_2 \cdot xTHF$

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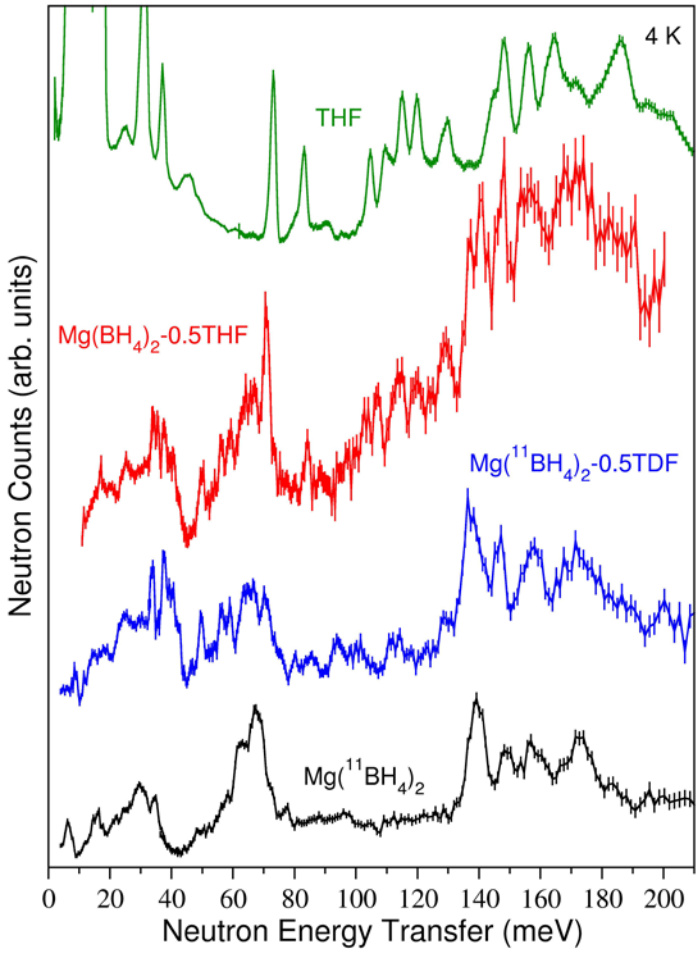
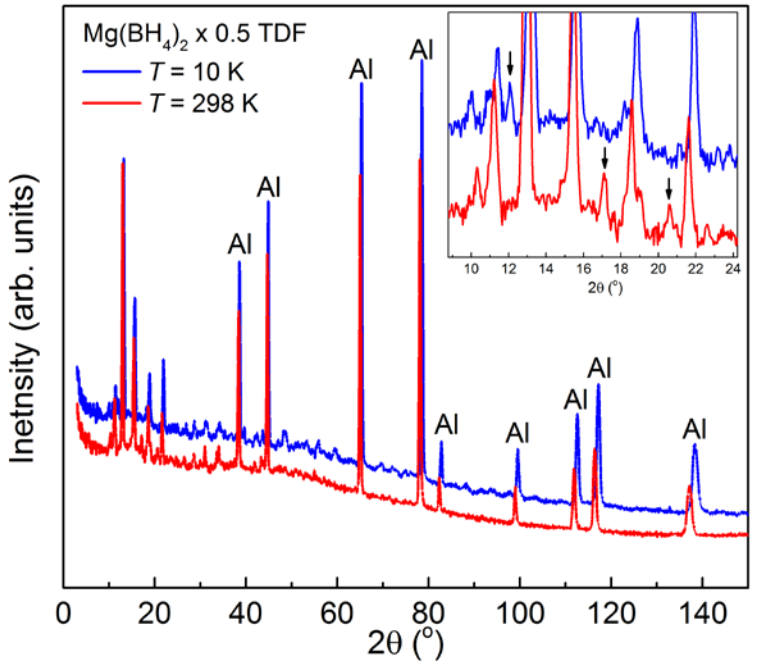


Neutron vibrational spectra for $Mg(^{11}BH_4)_2$, $Mg(BH_4)_2 \cdot 0.5THF$, $Mg(^{11}BH_4)_2 \cdot 0.5TDF$.

- Collaboration with Tom Autrey (PNNL) to characterize solvated $Mg(BH_4)_2$ compounds
- Selective deuteration is performed in order to exclude the effects of H coming from the THF groups during the neutron scattering measurements.



Neutron powder diffraction patterns for $Mg(^{11}BH_4)_2 \cdot 0.5TDF$ at 10 and 298 K.

Accomplishments and Progress: Multiple H_2 binding at a metal site in a MOF

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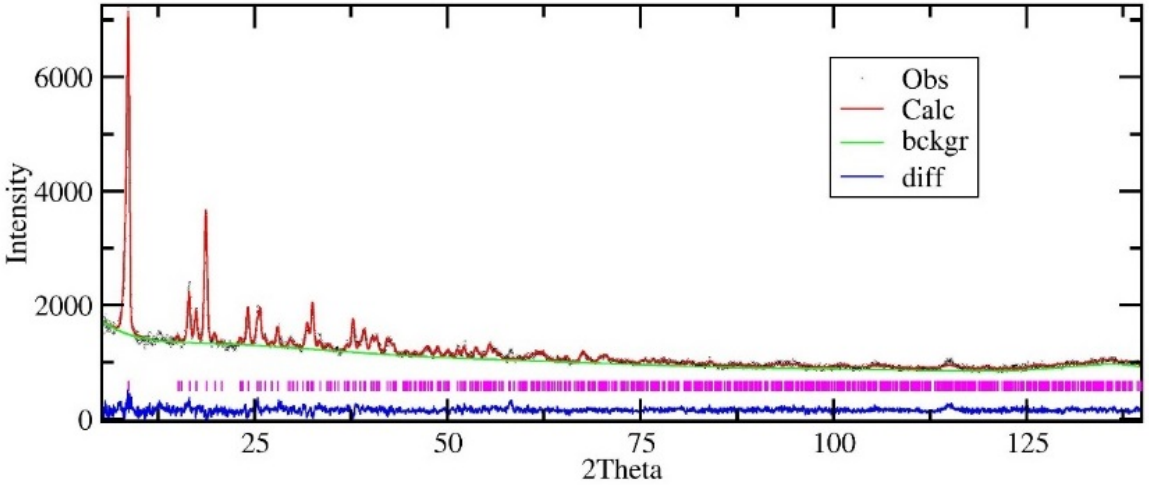
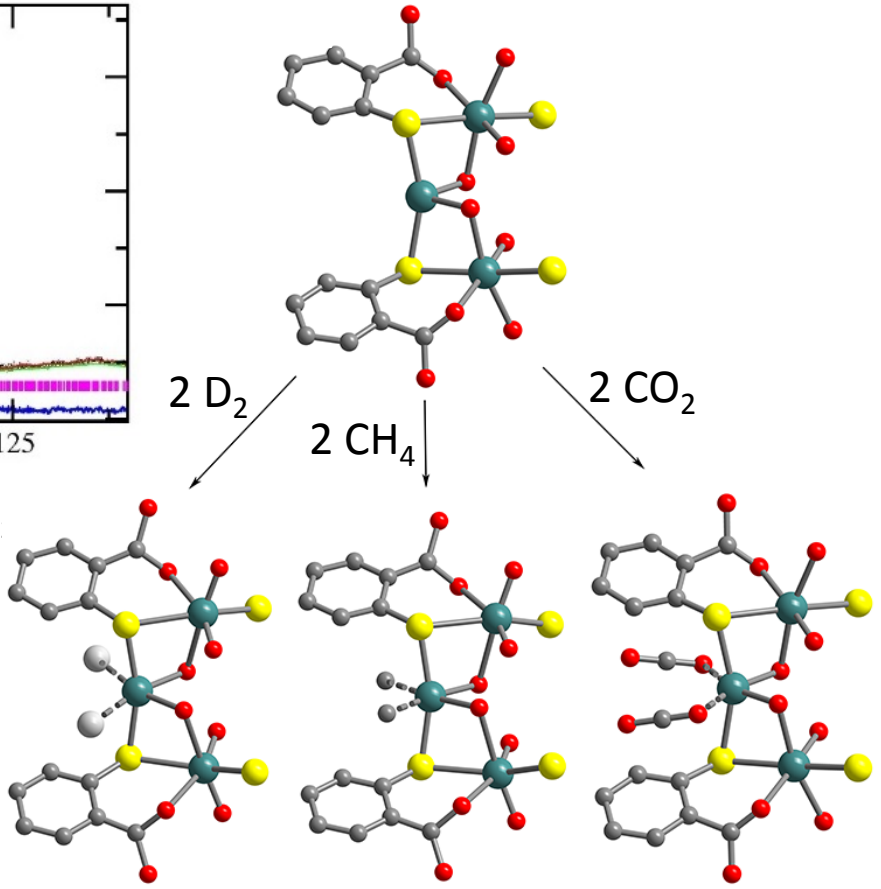


Rietveld refinement of neutron diffraction data for 0.75 D



- Collaboration with Jeff Long (LBNL/Berkeley)
- Mn_2(dsbdc): a surprising MOF (Metal Organic Framework)
- Successful desolvation and activation
- X-ray and Neutron Diffraction; NVS
- D_2 and other gases have similar binding characteristics. Clear but weak interactions.

Mn^{2+} can bind multiple gases on one metal.

T. Runčevski, *et al.*, Chem. Commun. **52**, 8251 (2016).

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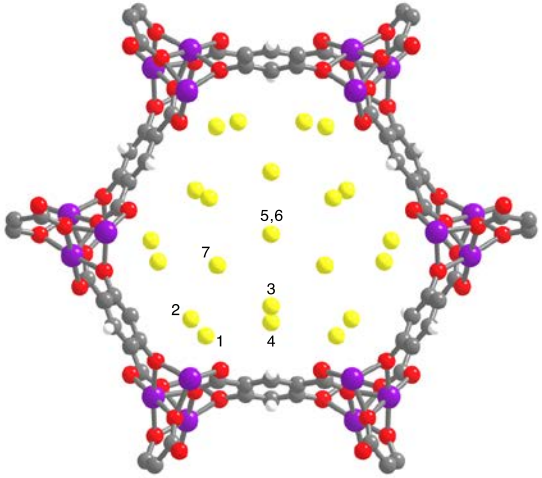
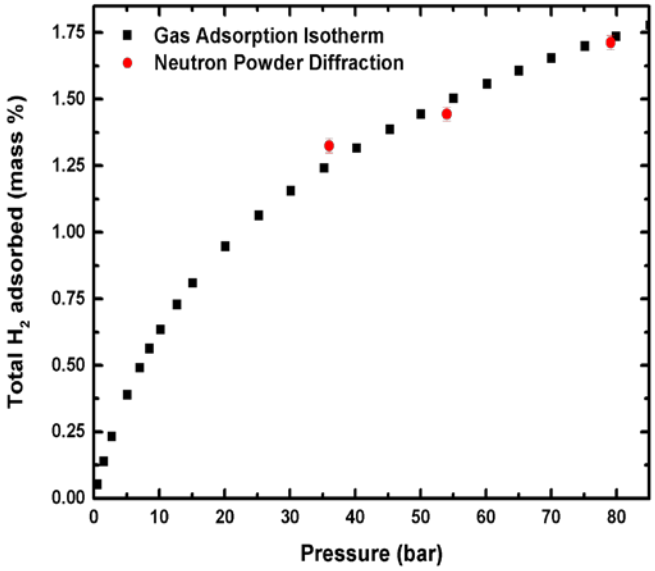
Accomplishments and Progress: Evaluating MOFs for high-pressure H_2 storage



A single pore of Co_2(*m*-dobdc) showing the seven distinct D_2 binding sites within the pore at 77 K and 78 bar, with each D_2 shown as a yellow sphere.



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.

- Collaboration with Jeff Long (LBNL/Berkeley) and Tom Gennett (NREL)
- D_2 locations and compositions in Co_2(*m*-dobdc) probed at 77-298 K and 30-80 bar.
- D_2 content correlated well with the low-temperature structures.
- Hydrogen content from NPD data matches the adsorption isotherm uptake values.

M. T. Kapelewski, *et al.*, in preparation (2017).

Accomplishments and Progress:
Vibrational and dynamical properties of nanoconfined $LiBH_4$ in controlled-pore, N-doped/undoped carbon scaffolds

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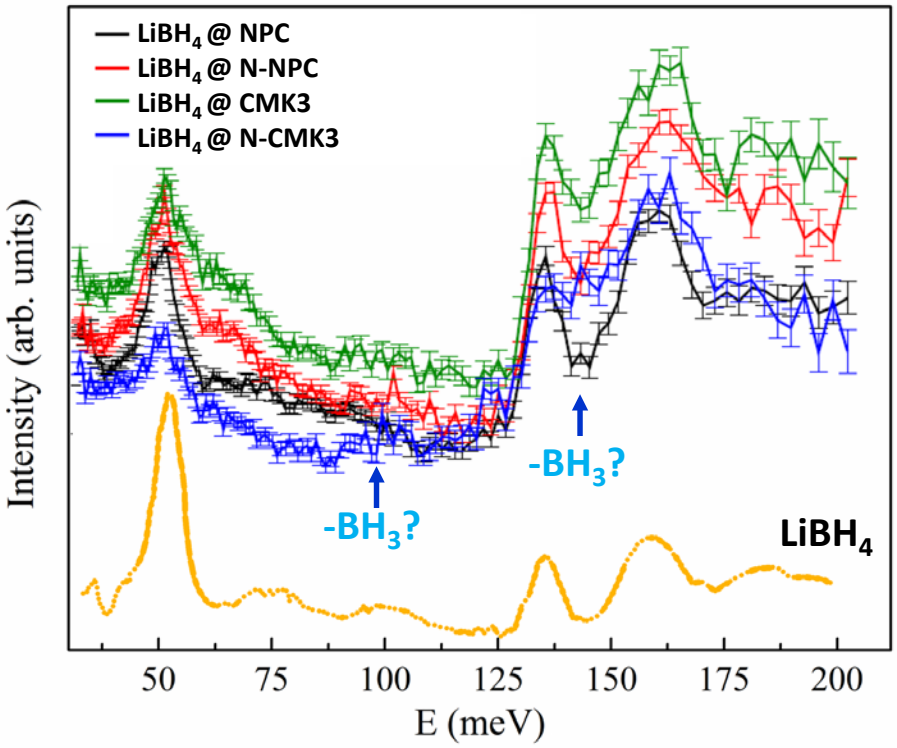
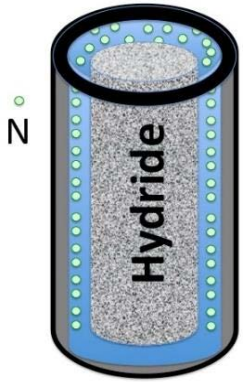
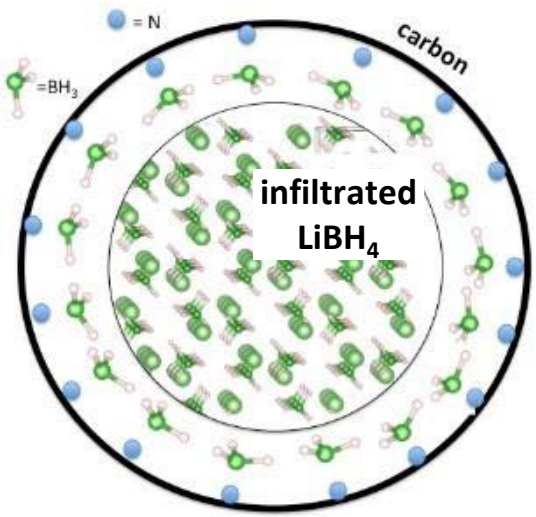
- Collaboration with Eric Majzoub (U. Missouri-St. Louis)
- Studying the effect of nanoconfinement on the thermodynamics and kinetics properties of hydrogen storage materials



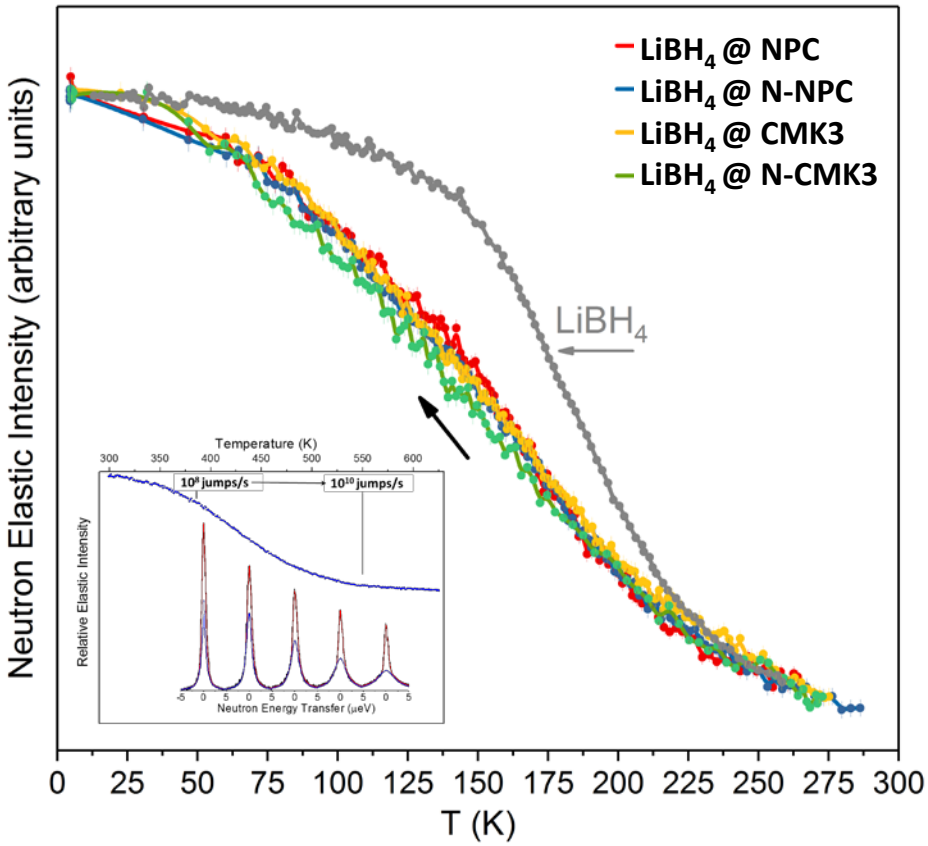
Neutron vibrational spectra at 4 K of $LiBH_4$ nanoconfined in N-doped/undoped carbon scaffolds with two geometries.





- NVS measurements show infiltration of $LiBH_4$ into all nanopore geometries.
- Broadening and redshift of peaks is observed for confined $LiBH_4$ when compared to bulk $LiBH_4$.
- 52 meV peaks reflect BH_4^- librations, while peaks between 125 meV and 180 meV reflect BH_4^- bending vibrations.
- Is $-BH_3$ present?

- Neutron fixed-window scans suggest scaffold-dependent differences in the reorientational mobilities of the BH_4^- anion.



- BH_4^- orientational mobilities are enhanced in the nanopores compared to those in bulk $LiBH_4$.
- The most N-doped scaffold (N-CMK3) shows the highest average mobility.
- This may reflect the contribution from borane (BH_3) species present in the capping layer region.

Collaborations

- NREL/NIST collaboration (HySCORE)
  - Characterizing ultra-microporous materials using neutron diffraction and neutron spectroscopy
- NREL/NIST collaboration with LBNL and PNNL (HySCORE)
  - Characterizing hydrogen adsorption in metal organic framework materials using neutron diffraction and neutron spectroscopy
  - Characterizing various hydrogen storage materials at the Advanced Photon Source
  - Various neutron scattering characterization of $Mg(BH_4)_2 \cdot xTHF$
- NREL/NIST collaboration with SNL and LLNL (HyMARC)
  - $Mg(BH_4)_2$: Developing a neutron vibrational spectroscopy (NV) library of $Mg(BH_4)_2$ polymorphs (M. Dimitrievska, *et al.*, Phys. Chem. Chem Phys. 18, 25546 (2016))
  - MgB_2 and $M_2B_{12}H_{12}$+MH hydrogenations (NVS characterization) (J. L. White, *et al.*, J. Phys. Chem. C 120, 25725 (2016)).
  - Li_3N hydrogenation in nanoporous carbons (B. C. Wood, *et al.*, Adv. Mater. Interfaces 1600803 (2017))
- NREL/NIST collaboration with UMSL (HyMARC seedling)
  - Neutron scattering characterization of nano-confined $LiBH_4$ in N-functionalized nanoporous carbons

Proposed Future Work

- Perform QENS measurements on recently synthesized $Mg(^{11}BH_4)_2 \cdot x$THF and $Mg(^{11}BH_4)_2 \cdot x$TDF materials to gain insights into the reorientation dynamics and mobilities of BH_4^- anions and provide more information on the interaction between THF and $Mg(BH_4)_2$.
- Perform QENS measurements of $^7Li^{11}BH_4$ in N-doped/undoped nanoporous carbons to compare the BH_4^- reorientational dynamics.
- Continue neutron diffraction/NVS characterizations of new MOF materials

Any proposed future work will depend on the available funding.

Publications

1) *M. Dimitrievska, J. L. White, W. Zhou, V. Stavila, L. E. Klebanoff and T. J. Udovic, **Phys. Chem. Chem Phys.,** 18, 25546 (2016).

2) W. S. Tang, M. Dimitrievska, J.-N. Chotard, W. Zhou, R. Janot, A. V. Skripov, and T. J. Udovic, **J. Phys. Chem. C**, 120, 21218 (2016).

3) *A. V. Soloninin, M. Dimitrievska, R. V. Skoryunov, O. A. Babanova, A. V. Skripov, W. S. Tang, V. Stavila, S. Orimo, and T. J. Udovic, **J. Phys. Chem. C**, 121, 1000 (2017).

4) *W. S. Tang, K. Yoshida, A.V. Soloninin, R. V. Skoryunov, O. A. Babanova, A. V. Skripov, M. Dimitrievska, V. Stavila, S. Orimo, and T. J. Udovic, **ACS Energy Lett.**, 1, 659 (2016).

5) *J. L. White, R. J. Newhouse, J. Z. Zhang, T. J. Udovic, and V. Stavila, **J. Phys. Chem. C,** 120, 25725 (2016).

6) *B. Wood, T. W. Heo, K. G. Ray, L. E. Klebanoff, T. J. Udovic, J. R. I. Lee, N. Angboonpong, J. D. Sugar, P. Pakawatpanurut, **J Adv. Mater. Interfaces,** 1600803 (2017).

7) T. Runčevski, M. T. Kapelewski, R. M. Torres-Gavosto, J. D. Tarver, C. M. Brown and J. R. Long, **Chem. Comm.**, 53, 8251 (2016).

8) Y. Tulchinsky, C. H. Hendon, K. A. Lomachenko, E. Borfecchia, B. C. Melot, M. R. Hudson, J. D. Tarver, M. D. Korzynski, A. W. Stubbs, J. J. Kagan, C. Lamberti, C. M. Brown, M. Dinca, **J. Am. Chem. Soc.**, DOI: 10.1021/jacs.7b02161.

9) *H. Wu, W. S. Tang, W. Zhou, J. D. Tarver, V. Stavila, C. M. Brown, T. J. Udovic, **J. Solid State Chem.**, 243, 2015, 162-167.

Presentations

HySCORE

1) T. Udovic: "Materials Design for Novel Borohydride-based Li^+ and Na^+ Electrolytes for Solid-State Batteries," Annual Meeting of the Center for Research in Extreme Batteries, University of Maryland, College Park, MD, May, 2016.
2) T. Udovic: "Pertinence of Structural and Anion Dynamical Behavior to Super-Cationic Conductivity in the Hydro-*closo*-borate Salts of Sodium and Lithium Studied via Neutron Scattering Methods," 8th American Conference on Neutron Scattering (ACNS 2016), Long Beach, CA, July, 2016.
3) T. Udovic: "Anion Dynamical Behaviors in Super-Cationic-Conducting Hydro-*closo*-borate Salts of Lithium and Sodium Studied via Quasielastic Neutron Scattering," International Symposium on Metal-Hydrogen Systems--Fundamentals and Applications, Interlaken, Switzerland, August, 2016.
4) C. Brown: "Structural studies of adsorbates in metal-organic frameworks", PNNL, WA, USA, September, 2016.
5) C. Brown: "Neutron Scattering", Craig M. Brown, Graduate Chemistry Course, U. Del, DE, USA, November, 2016.
6) C. Brown: "Hydrogen and Hydrocarbons located in Co2(m-dobdc)", CGS EFRC presentation, U.C. Berkeley, CA, USA, November, 2016.
7) C. Brown: "Structural studies of metal-organic frameworks of adsorption and separation applications", Molecular Engineering and Sciences Seminar Series, U. Washington, WA, USA, September, 2016
8) C. Brown: "Structural and dynamical studies of small molecules in MOFs", European Spallation Source, Sweden, April, 2017.
9) M. Dimitrievska: "Anion Dynamical Behaviors and Their Possible Relationship to Superionic Conductivities in Hydro-Closo-Borate Salts of Lithium and Sodium", MRS Fall meeting, Boston, USA, December, 2016
10) M. Dimitrievska: "Neutron scattering applications in materials for hydrogen energy storage", 23rd ANNUAL SIGMA XI POSTDOCTORAL POSTER PRESENTATION, Gaithersburg, USA, February, 2017. (**The most outstanding poster award**)
11) J. Tarver: "Using Neutrons to Probe Hydrogen Storage in Metal Organic Frameworks", 11th Int. Symposium Hydrogen & Energy, Waikoloa, Hawaii, USA, March, 2017.