

HySCORE: Technical Activities at NIST

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National Renewable Energy Laboratory & National Institute of Standards and Technology

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Timeline and Budget

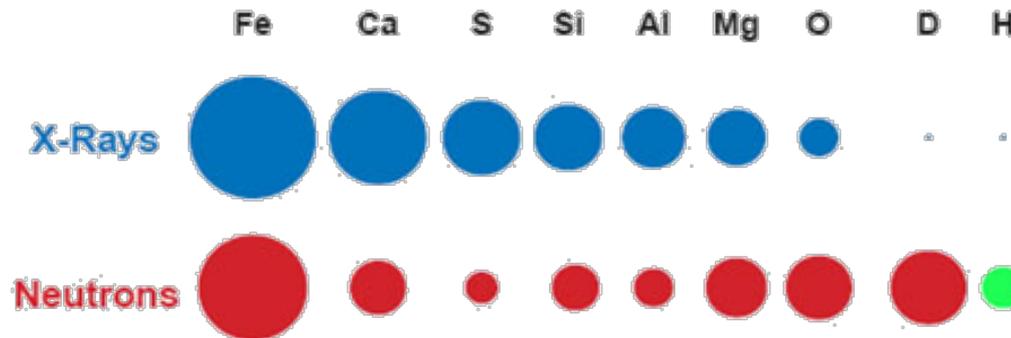
- **Timeline:**
 - Project Start:** 10/1/2015
 - End:** Project continuation determined by DOE. Currently scheduled through 9/30/18 (*previously a component of NREL's materials development program and supported annually since 2006)
- **Budget:**
 - Total Team Budget: (HySCORE): \$8.2M
 - Federal Share:
 - NREL: \$2.6M
 - LBL: \$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 Chemisorption;
 - 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)

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)

- 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>

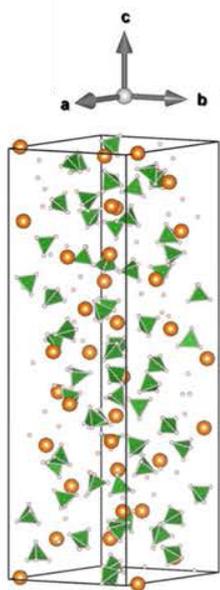
Utilize neutrons to characterize and validate hydrogen storage media

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

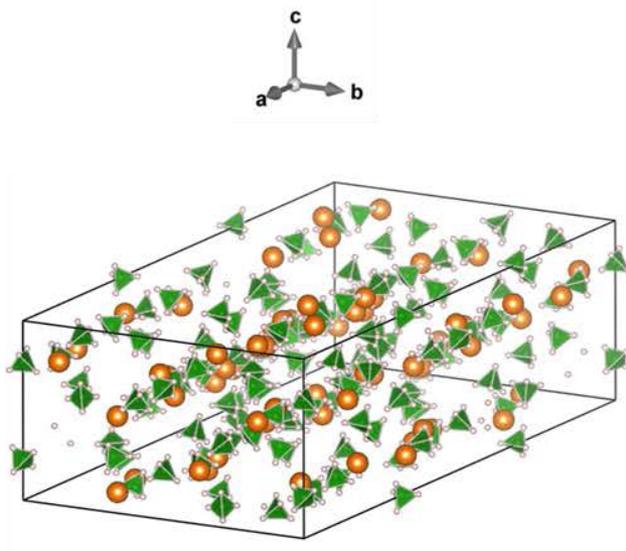
- $\text{Mg}(\text{BH}_4)_2$
 - MgB_2 and $\text{M}_2\text{B}_{12}\text{H}_{12} + \text{MH}$ hydrogenations
 - Li_3N hydrogenation in nanoporous C
 - $\text{Mg}(\text{BH}_4)_2 \cdot x\text{THF}$
 - H_2 in $\text{Mn}_2(\text{dsbdc})$ and $\text{Co}_2(m\text{-dobdc})$ MOFs
 - LiBH_4 in N-functionalized nanoporous C —
- HyMARC (SNL/LLNL)
- HySCORE (PNNL/LBNL/NREL)
- UMSL Project

Accomplishments and Progress: Mg(BH₄)₂ polymorphs

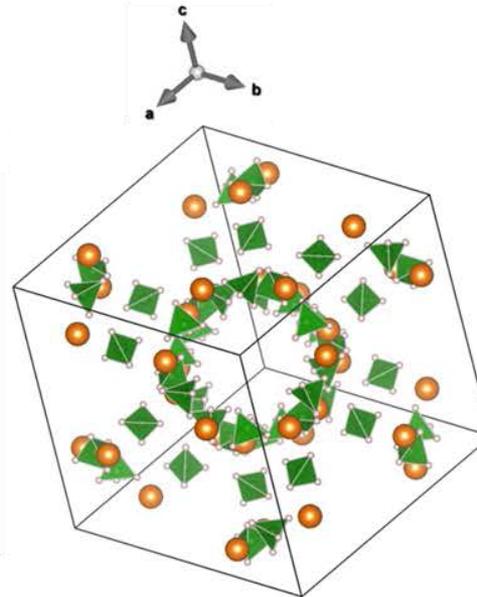
- Collaboration with Vitalie Stavila (SNL, HyMARC)
- **Develop spectral signatures for different Mg(BH₄)₂ polymorphs**



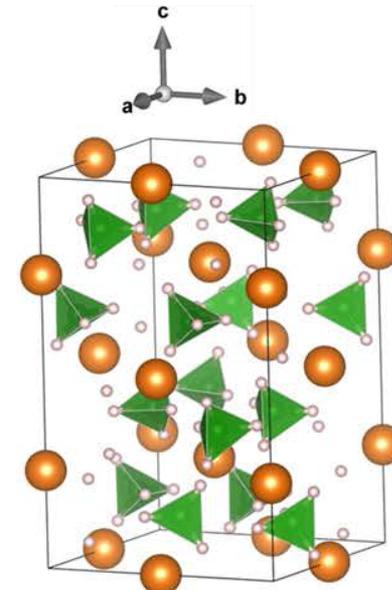
α -Mg(BH₄)₂
P6₁22



β -Mg(BH₄)₂
Fddd



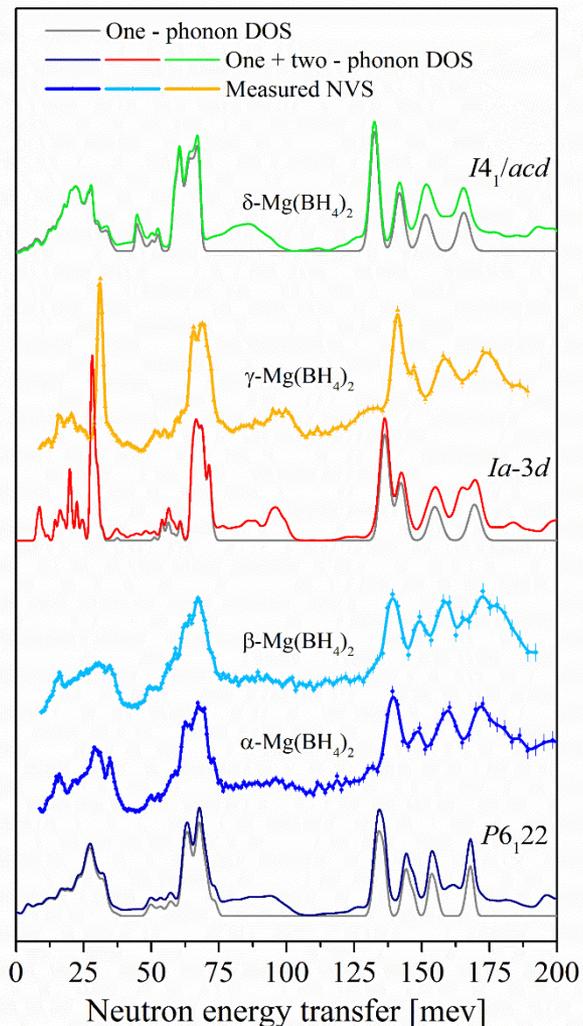
γ -Mg(BH₄)₂
Ia-3d



δ -Mg(BH₄)₂
I4₁/acd



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



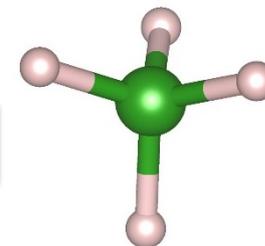
Neutron vibrational spectroscopy

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



BH₄⁻ vibrational modes

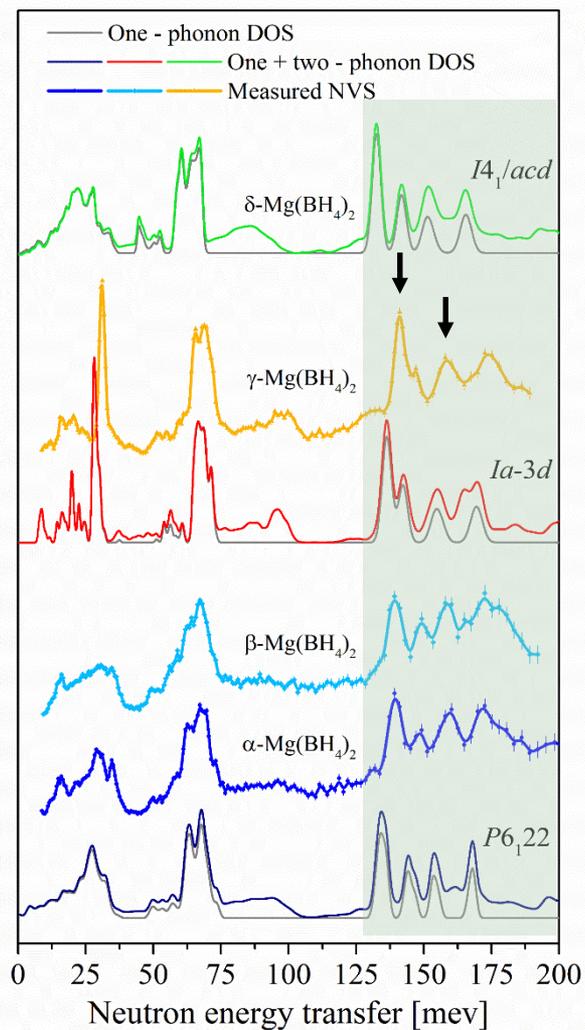
T_d symmetry



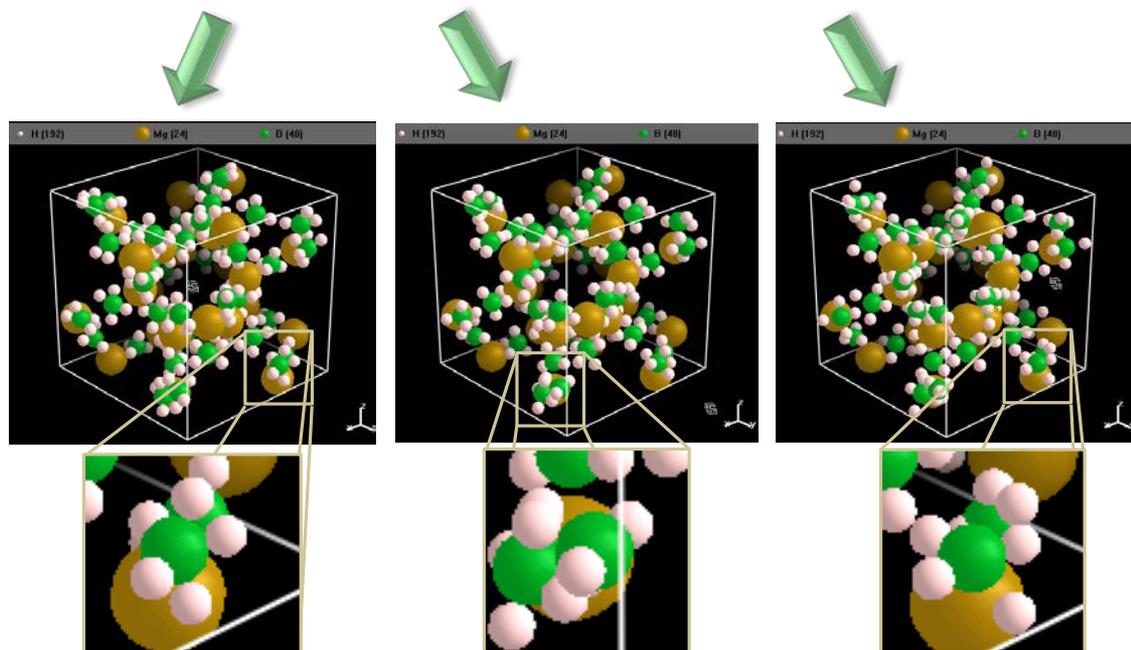
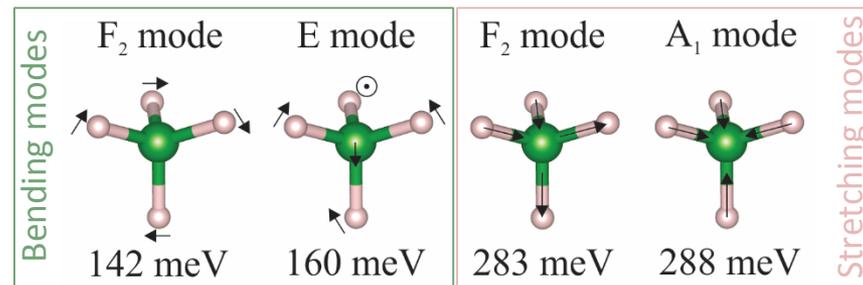
Neutron vibrational spectra of the α -, β - and γ -Mg(BH₄)₂ phases at 4 K compared to the simulated **one-phonon and one+two-phonon densities** of states from first-principles phonon calculations of the DFT-optimized 0 K structures.

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

Accomplishments and Progress: Mg(BH₄)₂ polymorphs



BH₄⁻ vibrational modes

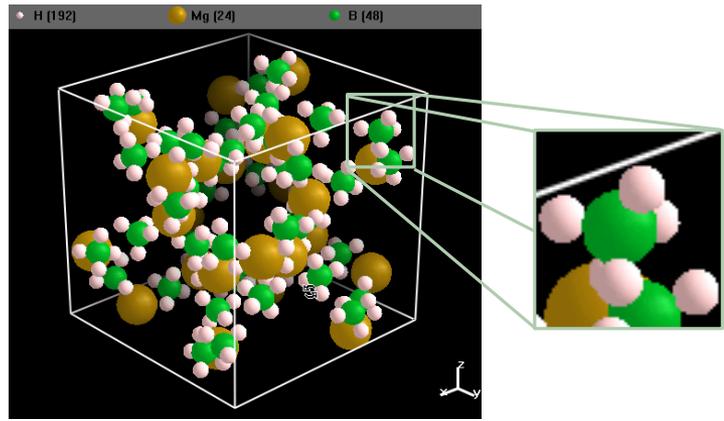
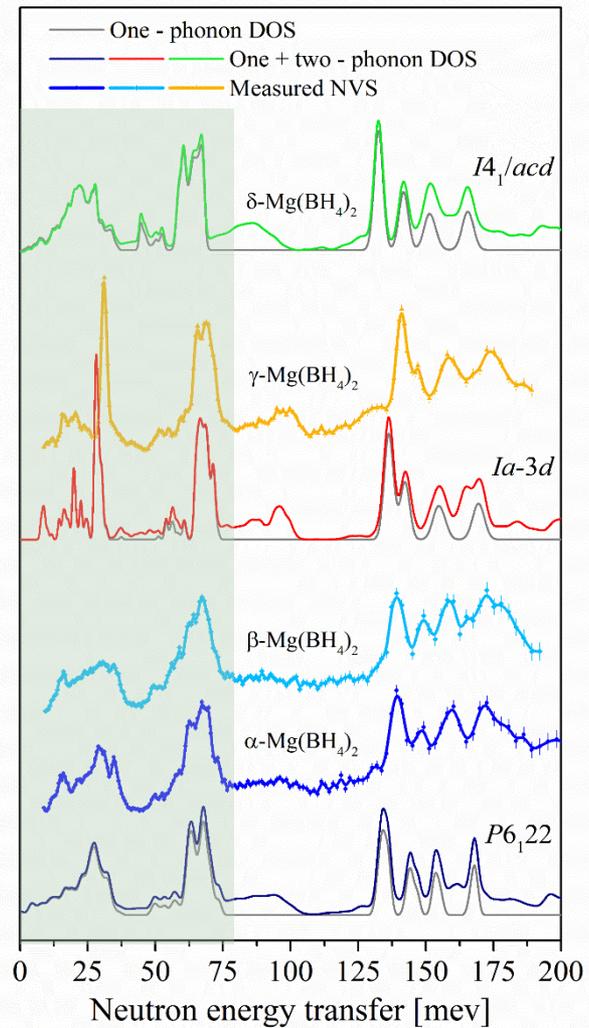


M. Dimitrievska, *et al.*, Phys. Chem. Chem Phys. **18**, 25546 (2016).

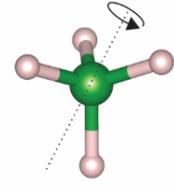
Accomplishments and Progress: Mg(BH₄)₂ polymorphs

BH₄⁻ vibrational modes

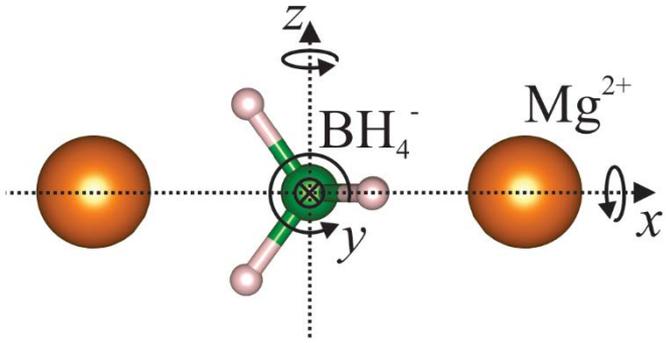
Librational (torsional) modes
(not usually observed in Raman spectra)



Libration



< 80 meV

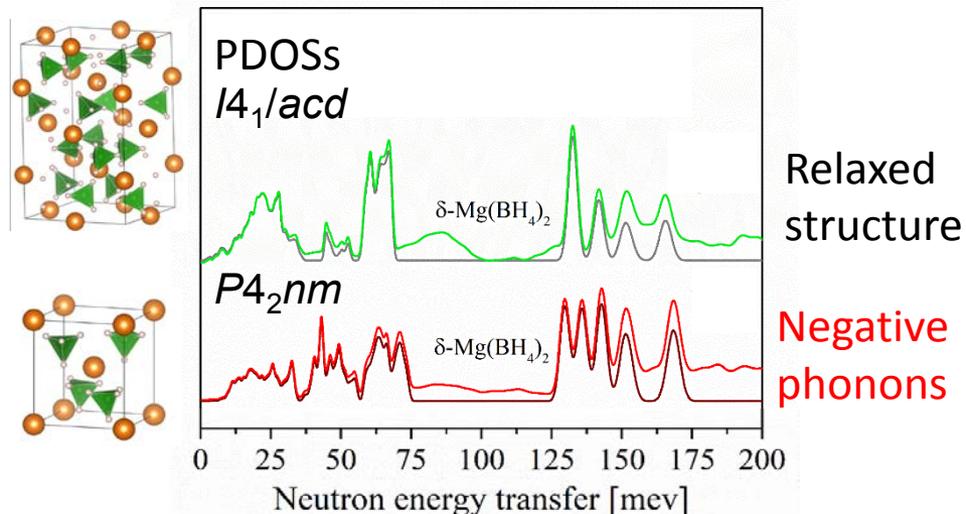


Orientation of the
BH₄⁻ anions and
possible librational
motions in the γ -
Mg(BH₄)₂ phase.

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

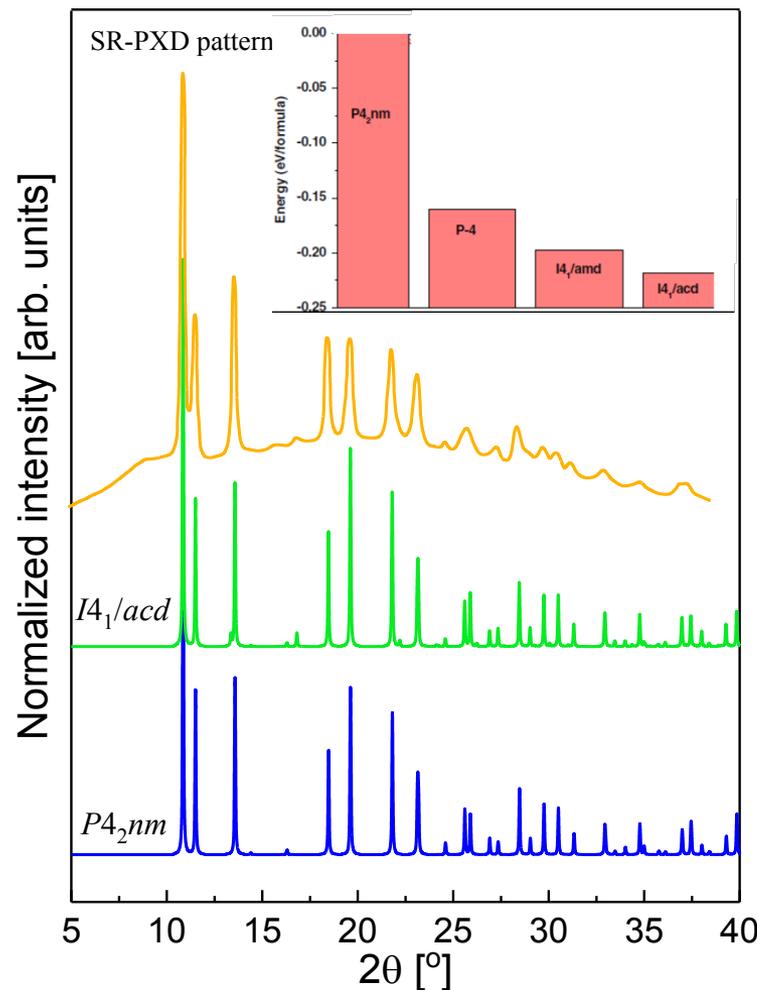
Accomplishments and Progress: Mg(BH₄)₂ polymorphs

problematic δ -phase

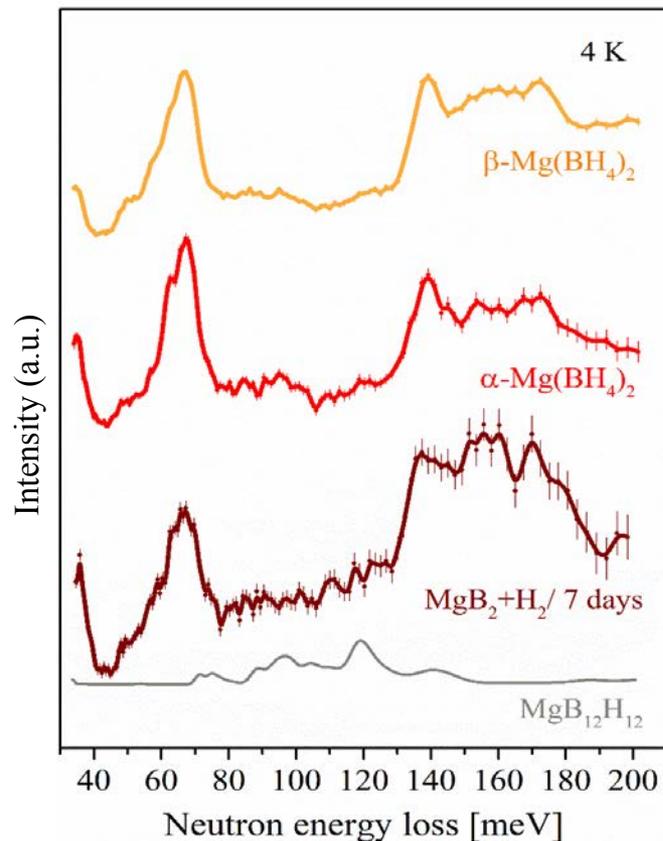


Optimization of the δ phase structure:

- 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).

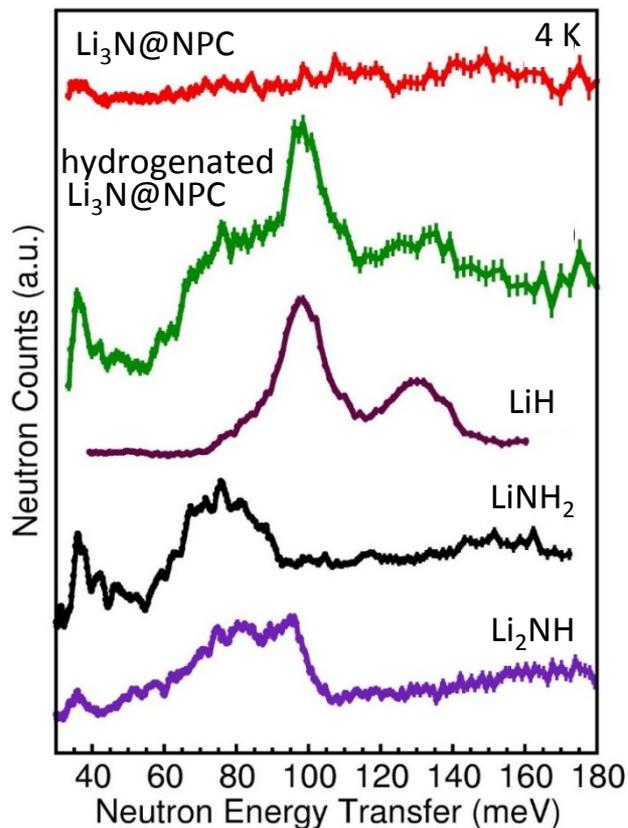


Neutron vibrational spectrum of hydrogenated MgB₂ (7 d, 380°C, 700 bar H₂) compared to those for α- and β-Mg(BH₄)₂ and the DFT-simulated MgB₁₂H₁₂ spectrum.

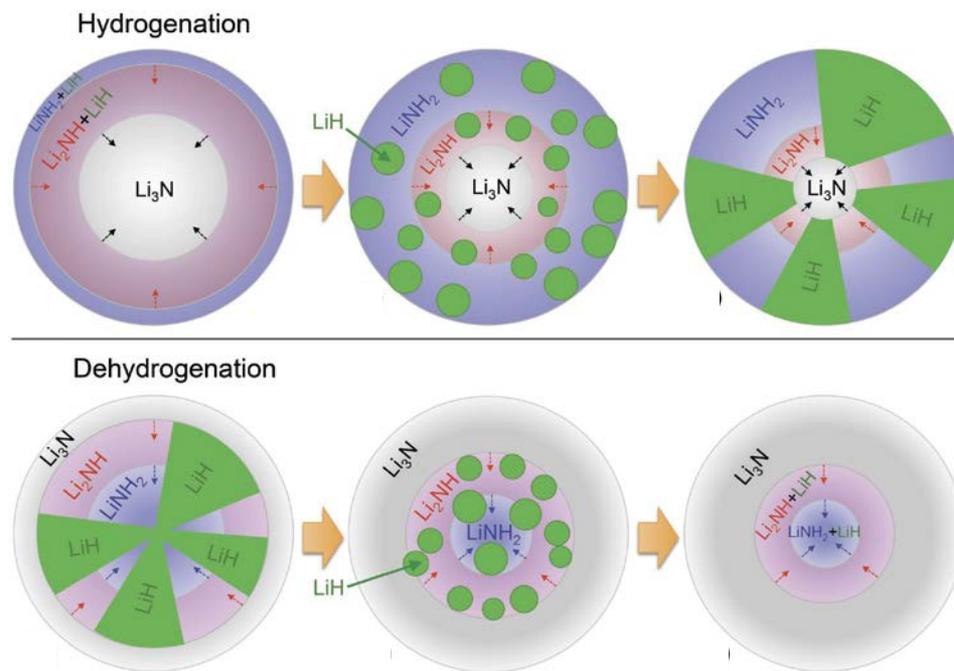
- NVS indicated the formation of α- and/or β-Mg(BH₄)₂ plus an additional hydrogenous phase consistent with MgB₁₂H₁₂ or a similar stabilized borohydride cluster.
- Neutron prompt-γ activation analysis (PGAA)** indicated a H:B ratio of 1.8 after 7 d MgB₂ hydrogenation.
- Neutron prompt-γ activation analysis (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: Li₃N Hydrogenation in Nanoporous Carbon



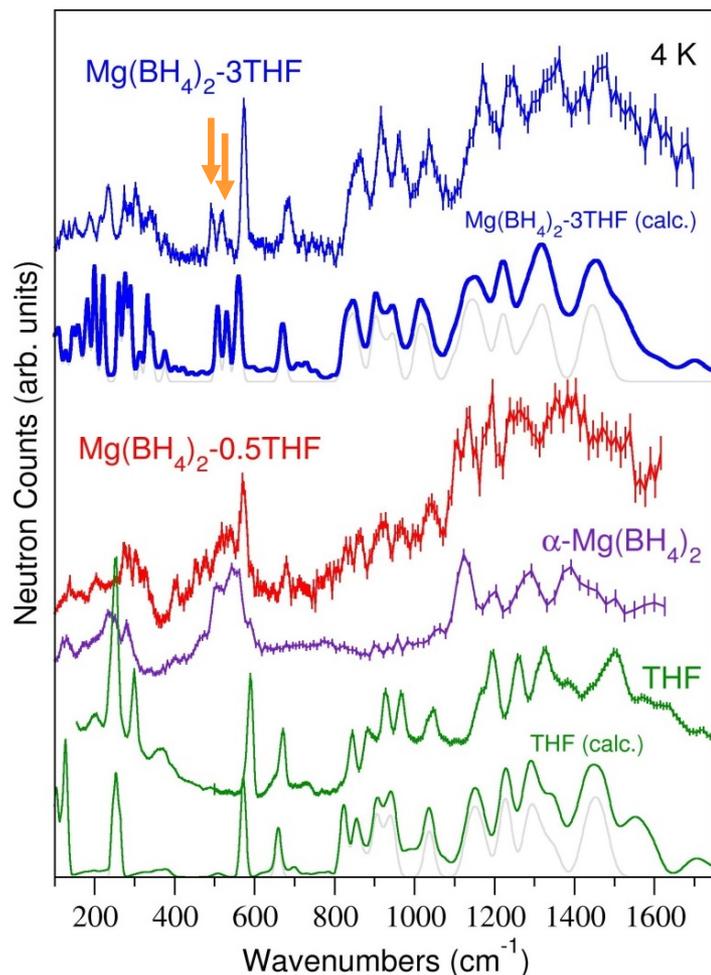
- Collaboration with Brandon Wood (LLNL) and Vitalie Stavila (SNL) to identify hydride phases
- NVS confirmed that both LiNH₂ and LiH are hydrogenation products from carbon-nanoconfined Li₃N, with no obvious presence of Li₂NH.



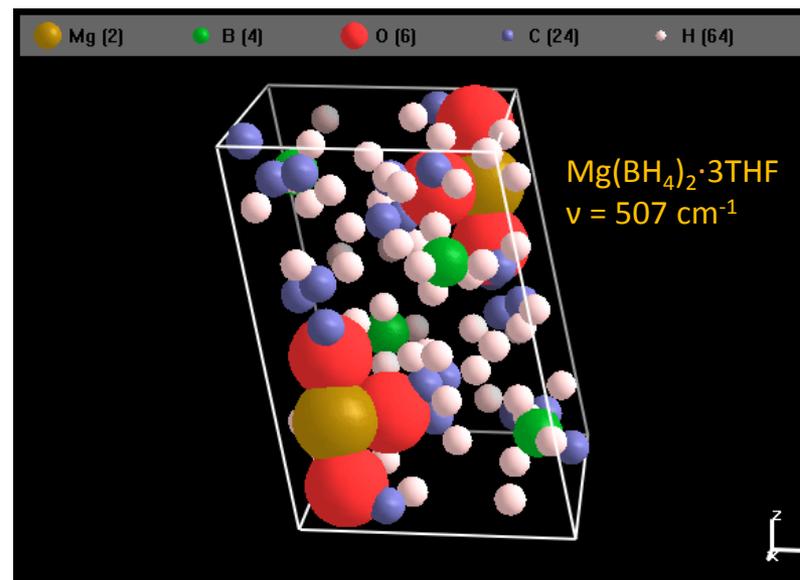
Neutron vibrational spectra associated with hydrogenated Li₃N confined in nanoporous carbon (NPC) after 5 desorption/absorption cycles compared to reference spectra

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

Accomplishments and Progress: Neutron studies of $\text{Mg}(\text{BH}_4)_2 \cdot x\text{THF}$

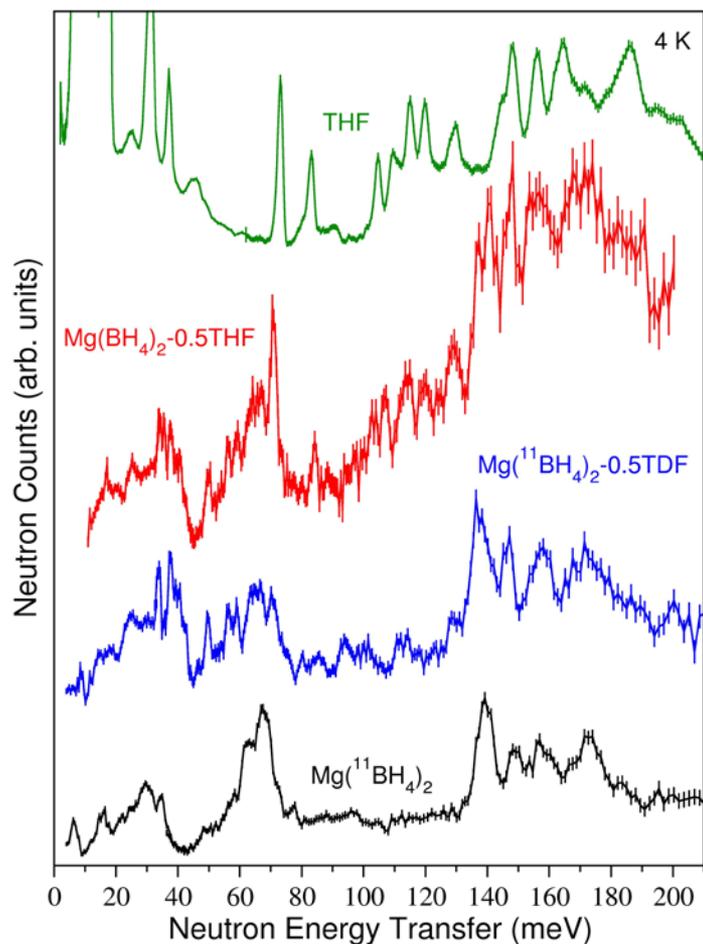


- Collaboration with Tom Autrey (PNNL) to characterize solvated $\text{Mg}(\text{BH}_4)_2$ compounds
- Calculated NVS spectra are in good agreement with the experimental results for $\text{Mg}(\text{BH}_4)_2 \cdot 3\text{THF}$.
- For $\text{Mg}(\text{BH}_4)_2 \cdot 3\text{THF}$, sharp additional peaks attributed to discrete BH_4^- librational modes are observed near 500 cm^{-1} , which are unlike the more smeared out modes in $\alpha\text{-Mg}(\text{BH}_4)_2$.



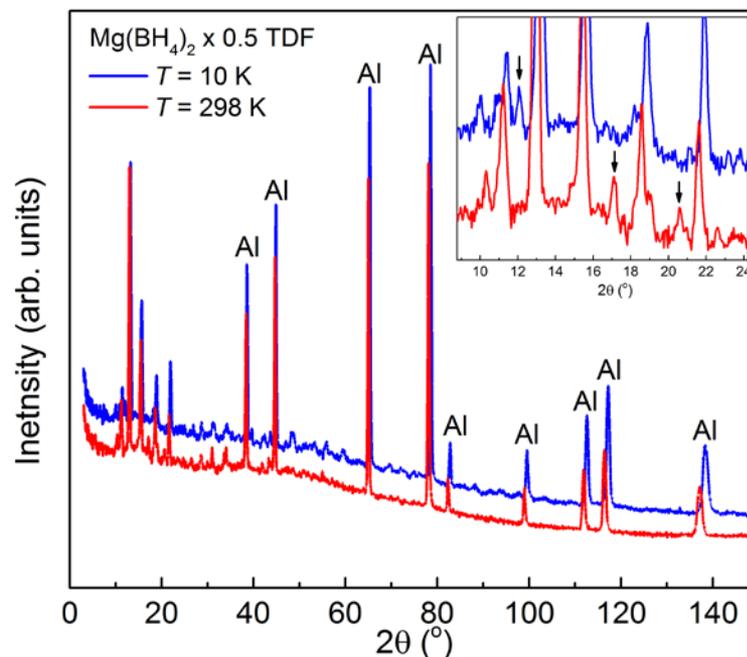
Neutron vibrational spectra for $\alpha\text{-Mg}(\text{BH}_4)_2$, $\text{Mg}(\text{BH}_4)_2 \cdot 0.5\text{THF}$, $\text{Mg}(\text{BH}_4)_2 \cdot 3\text{THF}$, and THF compared to DFT calculations.

Accomplishments and Progress: Neutron studies of $\text{Mg}(\text{BH}_4)_2 \cdot x\text{THF}$



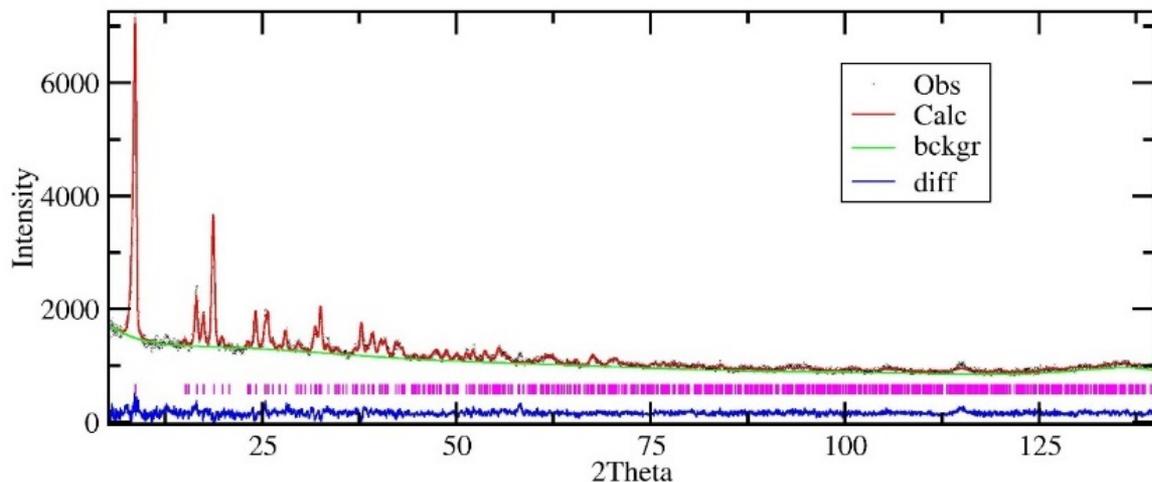
Neutron vibrational spectra for $\text{Mg}^{11}\text{BH}_4)_2$, $\text{Mg}(\text{BH}_4)_2 \cdot 0.5\text{THF}$, $\text{Mg}^{11}\text{BH}_4)_2 \cdot 0.5\text{TDF}$.

- Collaboration with Tom Autrey (PNNL) to characterize solvated $\text{Mg}(\text{BH}_4)_2$ compounds
- Selective deuteration is performed in order to exclude the effects of H coming from the THF groups during the neutron scattering measurements.



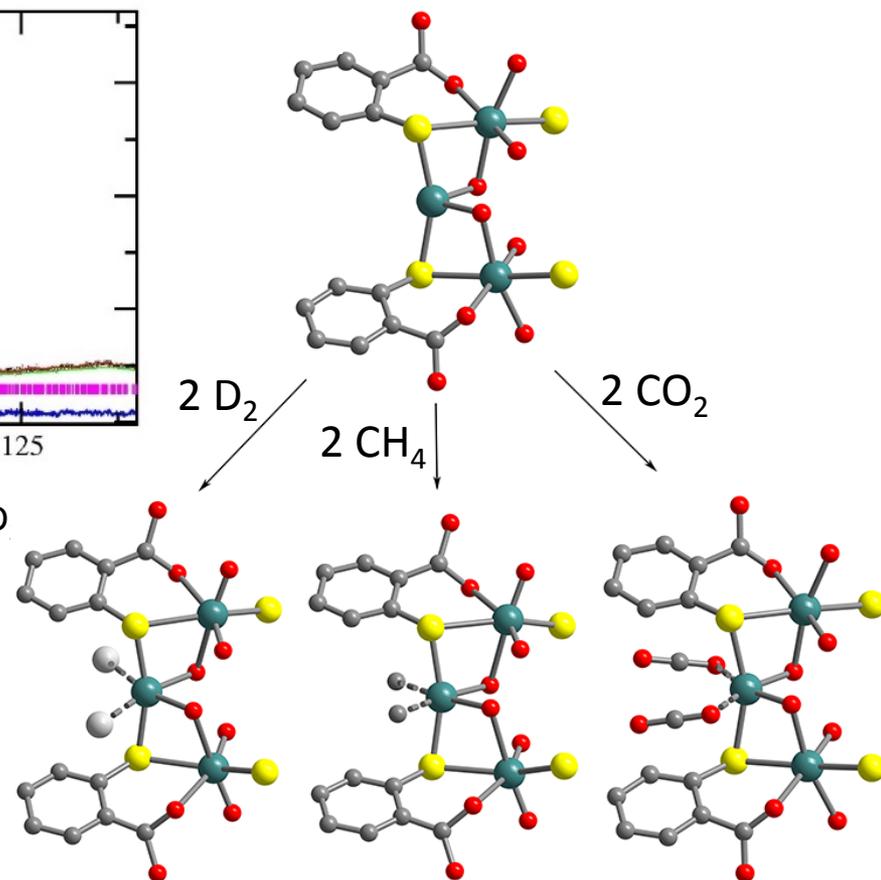
Neutron powder diffraction patterns for $\text{Mg}^{11}\text{BH}_4)_2 \cdot 0.5\text{TDF}$ at 10 and 298 K.

Accomplishments and Progress: Multiple H₂ binding at a metal site in a MOF



Rietveld refinement of neutron diffraction data for 0.75 D

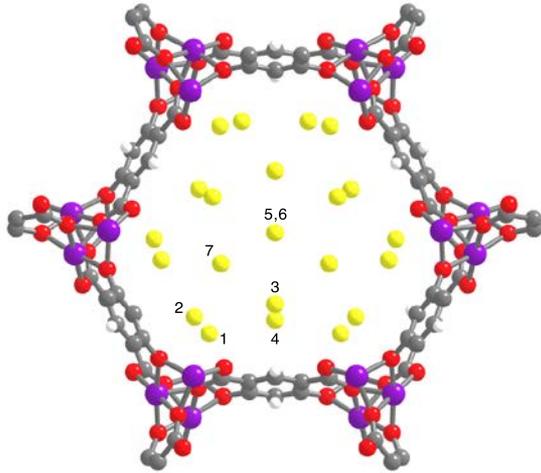
- Collaboration with Jeff Long (LBNL/Berkeley)
- Mn₂(dsbdc): a surprising MOF (Metal Organic Framework)
- Successful desolvation and activation
- X-ray and Neutron Diffraction; NVS
- D₂ and other gases have similar binding characteristics. Clear but weak interactions.



Mn²⁺ can bind multiple gases on one metal.

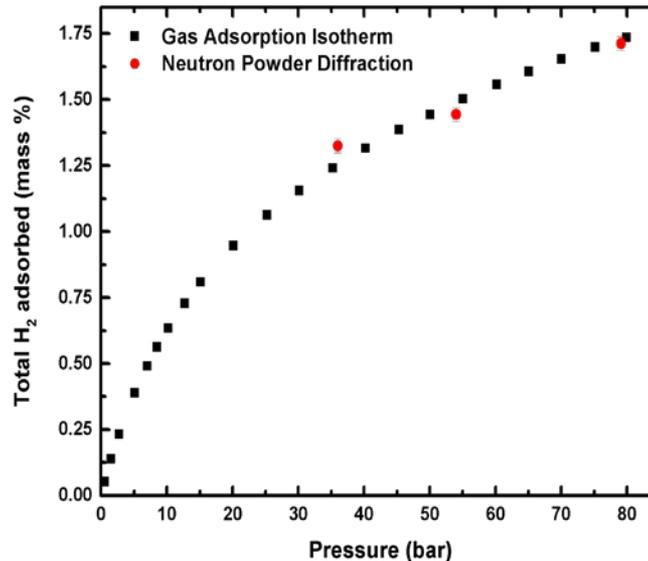
T. Runčevski, *et al.*, Chem. Commun. **52**, 8251 (2016).

Accomplishments and Progress: Evaluating MOFs for high-pressure H₂ storage



A single pore of Co₂(*m*-dobdc) showing the seven distinct D₂ binding sites within the pore at 77 K and 78 bar, with each D₂ shown as a yellow sphere.

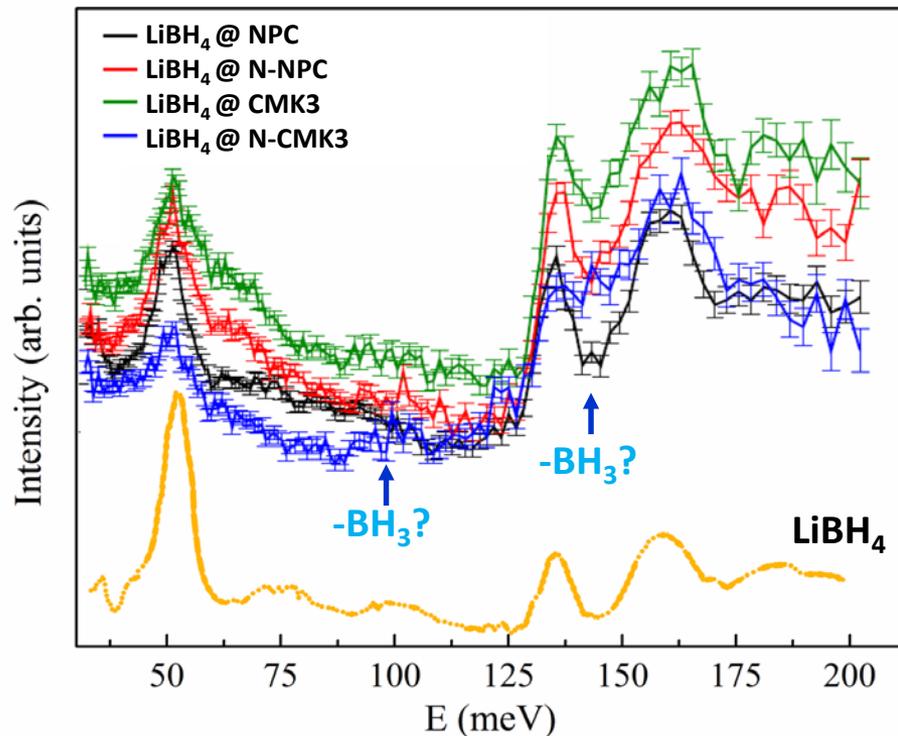
Volumetric adsorption isotherm for H₂ uptake in Co₂(*m*-dobdc) at 198 K compared to total H₂ uptake based on NPD data.



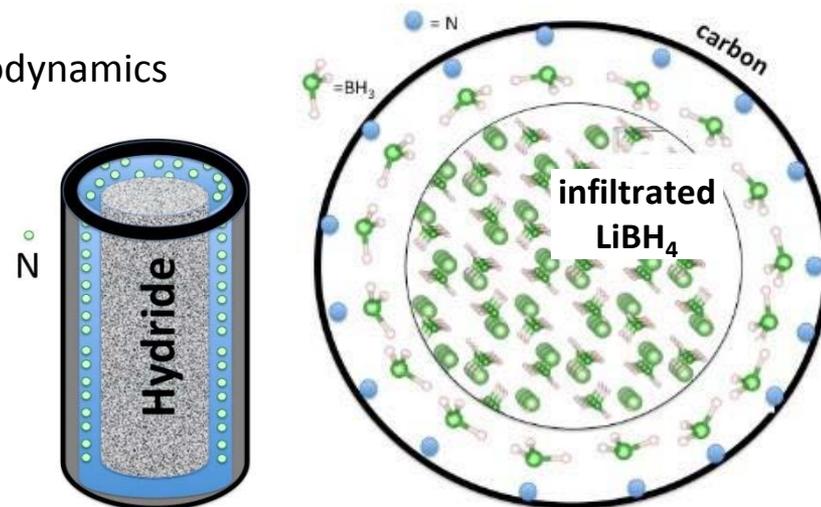
- Collaboration with Jeff Long (LBNL/Berkeley) and Tom Gennett (NREL)
- D₂ locations and compositions in Co₂(*m*-dobdc) probed at 77-298 K and 30-80 bar.
- D₂ content correlated well with the low-temperature structures.
- Hydrogen content from NPD data matches the adsorption isotherm uptake values.

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

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

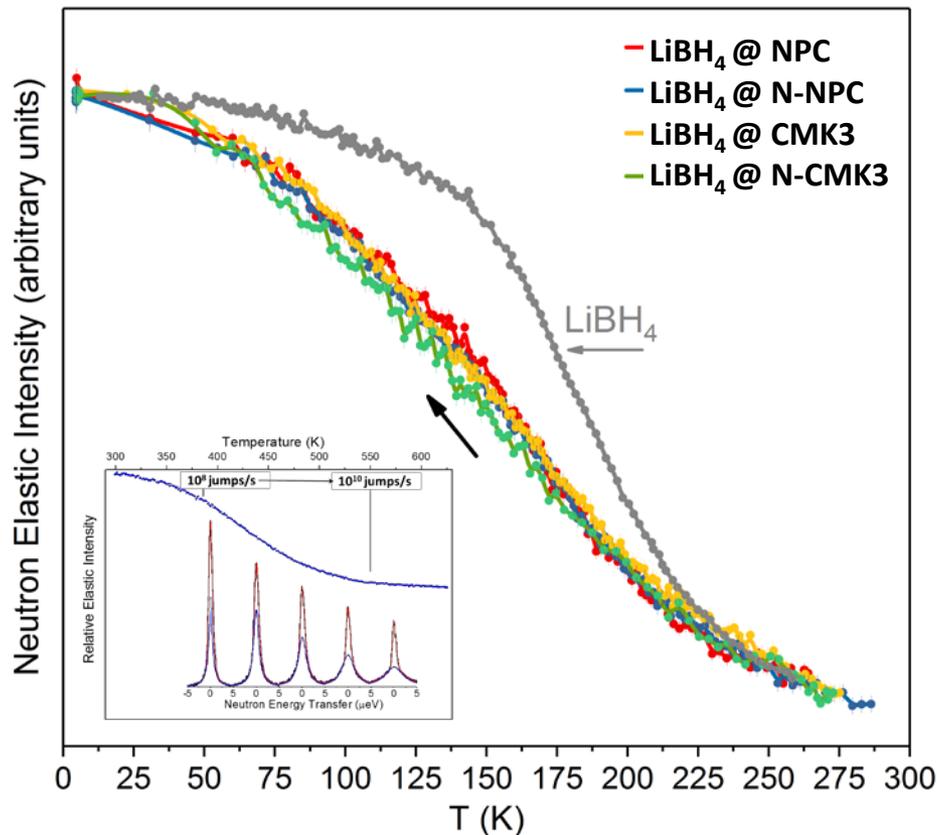


Neutron vibrational spectra at 4 K of LiBH_4 nanoconfined in N-doped/undoped carbon scaffolds with two geometries.



- 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 $-\text{BH}_3$ 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.

- 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 $\text{Mg}(\text{BH}_4)_2 \cdot x\text{THF}$
- NREL/NIST collaboration with SNL and LLNL (HyMARC)
 - $\text{Mg}(\text{BH}_4)_2$: Developing a neutron vibrational spectroscopy (NV) library of $\text{Mg}(\text{BH}_4)_2$ polymorphs (M. Dimitrievska, *et al.*, Phys. Chem. Chem Phys. 18, 25546 (2016))
 - MgB_2 and $\text{M}_2\text{B}_{12}\text{H}_{12} + \text{MH}$ 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

- Perform QENS measurements on recently synthesized $\text{Mg}(\text{}^{11}\text{B}\text{H}_4)_2 \cdot x\text{THF}$ and $\text{Mg}(\text{}^{11}\text{B}\text{H}_4)_2 \cdot x\text{TDF}$ materials to gain insights into the reorientation dynamics and mobilities of BH_4^- anions and provide more information on the interaction between THF and $\text{Mg}(\text{BH}_4)_2$.
- Perform QENS measurements of ${}^7\text{Li}{}^{11}\text{BH}_4$ 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.

- 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.

- 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.