HyMARC: LLNL Technical Activities

2018 DOE Hydrogen Annual Merit Review

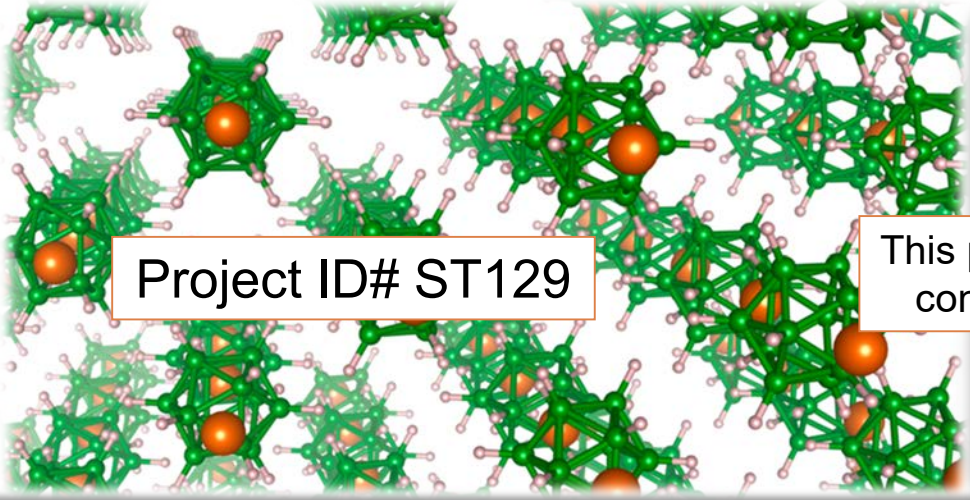
June 14, 2018

PI: Brandon C. Wood, LLNL

HyMARC Hydrogen Materials Advanced Research Consortium

Enabling **twice the energy density** for onboard H_2 storage

Team: T.W. Heo, S. Kang, S. Wan, T. Ogitsu, S. Bonev, J.R.I. Lee, M. Lefcochilos-Fogelquist, A. Baker, P. Shea, K. Ray, P. Campbell, T. Baumann



Project ID# ST129

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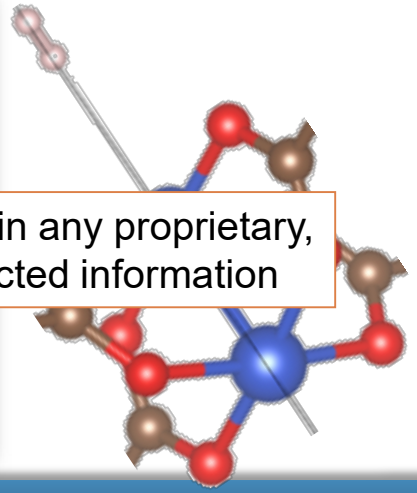

LLNL-PRES-750732

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Lawrence Livermore National Laboratory

Overview

Timeline

Project start date: 9/17/2015

Phase I end date: 9/30/2018

Barriers addressed

- **Lack of understanding of hydrogen physisorption and chemisorption (Barrier O)**
- System weight and volume (Barrier A)
- Charge/discharge rate (Barrier E)

Budget

FY17 DOE Funding: $855K

FY18 DOE Funding: $1100K

Total Funds Received: $3140K

Team

Funded Partners:

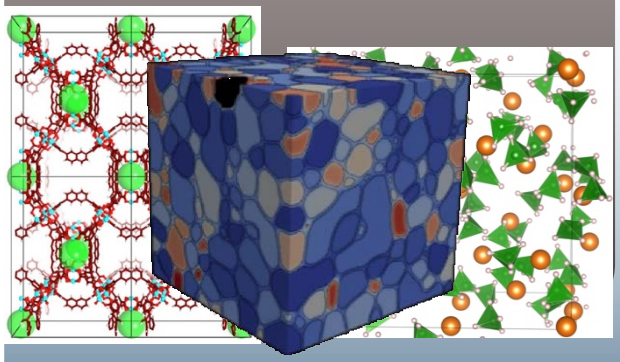
Sandia National Laboratories (lead)

Lawrence Berkeley National Laboratory

Relevance

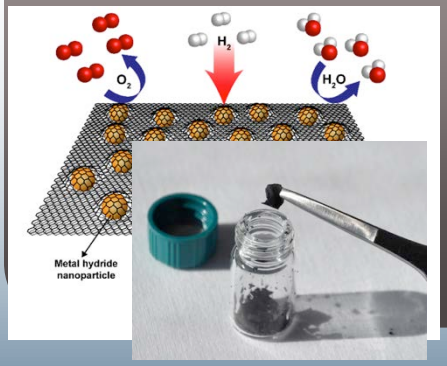
HyMARC provides community tools and foundational understanding of phenomena governing thermodynamics and kinetics to enable solid-phase hydrogen storage materials

Theory, simulation, data



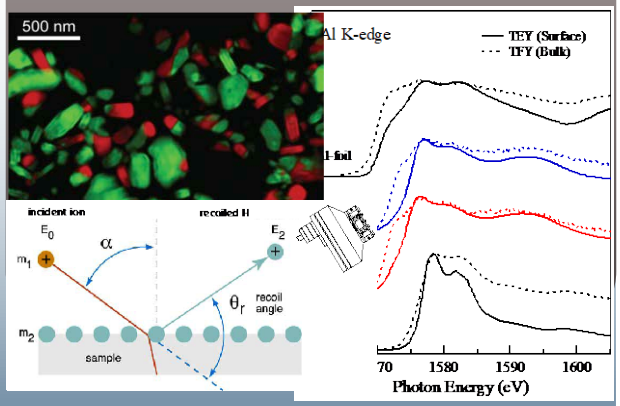
- High-accuracy physisorption
- *Ab initio* thermodynamics
- *Ab initio* molecular dynamics for bulk/surface/interface chemistry
- Multiscale non-equilibrium mass transport
- Phase-field models for solid-state phase transformation kinetics
- Semiempirical kinetic modeling
- Community software & databases

Controlled synthesis



- Functionalized carbon and porous nanoconfining media

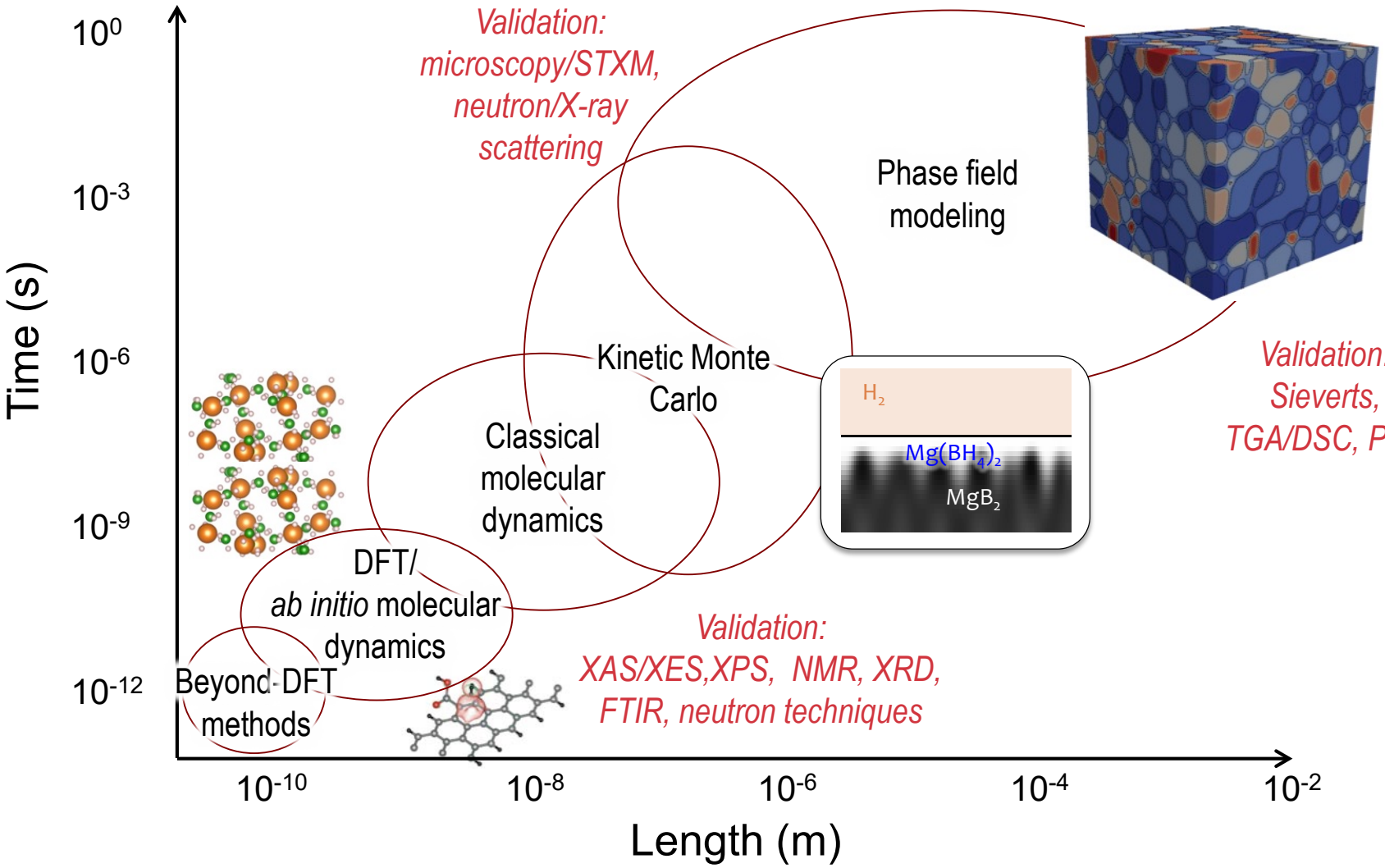
In situ characterization



- Soft X-ray absorption and emission spectroscopy
- X-ray spectromicroscopy

Approach: Validated multiscale modeling

Modeling approach prioritizes (1) bridging scales via multiscale integration; (2) improving descriptions of "real" materials; and (3) leveraging experiment-theory feedback



Approach: Investigate key phenomena via model materials

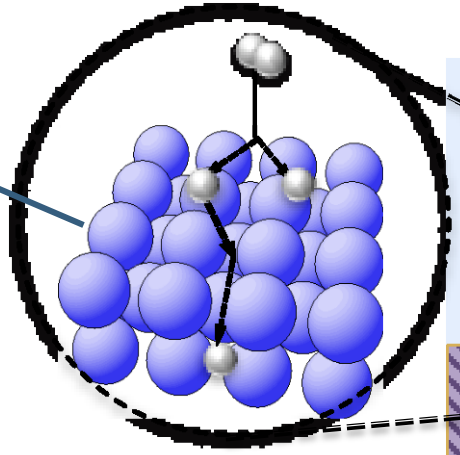
We choose model systems that allow us to isolate different physical factors & mechanisms

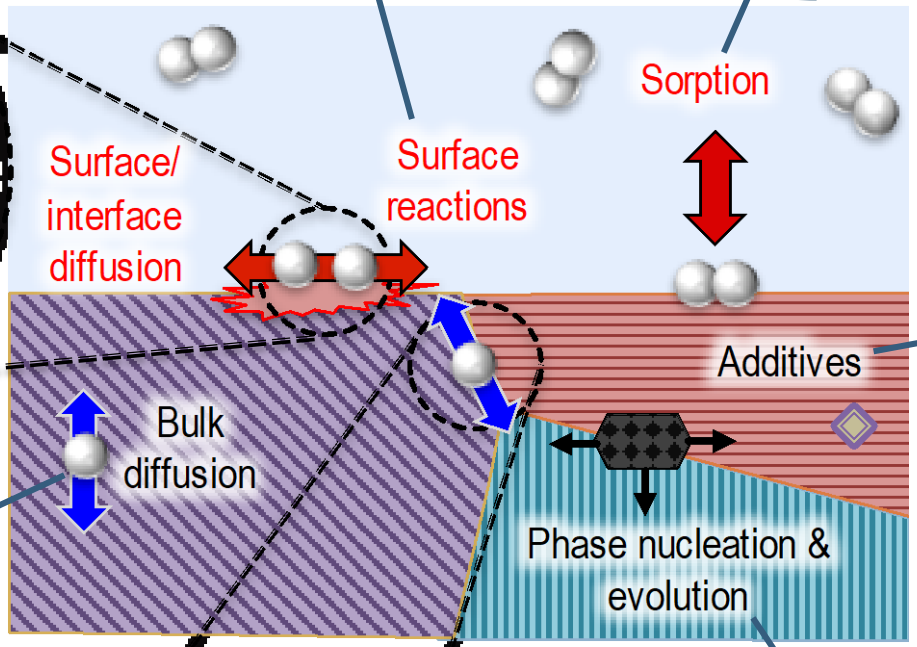
Thermodynamics:
- Mg-B-H, Li-N-H, Na-B-H, Li-B-H, Na-Al-H

- Oxidation ($NaAlH_4$, $Mg(BH_4)_2$)
- H_2 dissociation (Mg, MgB_2)
- H_2 formation ($NaAlH_4$)

- MOF-74, CuBTC
- COFs
- Graphene (doped/ functionalized)

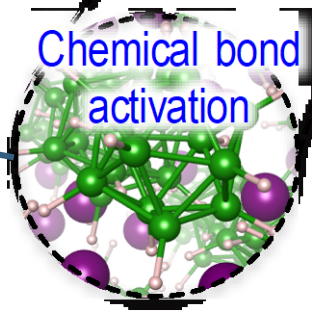
- LEIS on Mg and $NaAlH_4$





- TiF_3/$TiCl_3$
- Ti in $NaAlH_4$, MgB_2/$Mg(BH_4)_2$
- Etherates
- Simple hydrides

- Isotropic interstitial diffusion (PdH_x)
- Anisotropic vacancy diffusion (MgH_2)
- Complex hydride diffusion ($Mg(BH_4)_2$)



- Borohydride decomposition pathways in MgB_xH_y

- Interstitial topotactic interface (Pd/PdH_x)
- Simple structural transformation (Mg/MgH_2)
- Complex reactive interface (MgB_xH_y /MgB_nH_m)

LLNL contributions to HyMARC

Multiscale modeling

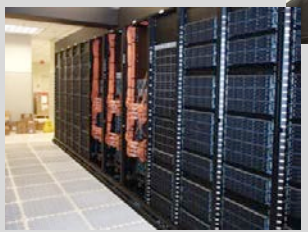
Multiscale integration: Brandon Wood

Ab initio molecular dynamics: Tadashi Ogitsu

Mesoscale phase-field kinetic modeling: Tae Wook Heo

Ab initio free energy: Stanimir Bonev

Postdocs: ShinYoung Kang, Sabrina Wan, Keith Ray, Patrick Shea



Porous carbon synthesis

Ted Baumann

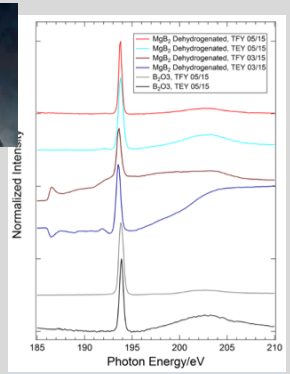
Pat Campell

Marcus Worsley

X-ray absorption/emission

Jon Lee

Alex Baker



Progress towards milestones with key LLNL activities

FY17Q2: Go/No-Go: Rank improvement strategies for enthalpy increases in sorbents (100%)

- *Provided theory data for aid in ranking strategies, submitted sorbent review for publication*

FY17Q4: Prototype hydride surface/interface chemistry kinetic models (100%)

- *Models completed and tested for Mg-B-H (diffuse reactive interface), Mg-H (interface with structural transformation), and Pd-H (interface without structural transformation)*

FY18Q1: Amorphous phases and defects model formalism (100%)

- *Completed computational study of tendency for model complex hydrides to form amorphous phases and their effect on ΔH*

FY18Q2: Compute H_2 binding with different computational methods for model MOFs to establish protocol for accurate physisorption calculations (70%)

- *Working with LBNL to assess finite-size/extended system corrections based on MOF-74*

FY18Q2: Sensitivity analysis of morphology and microstructure (100%)

- *Completed predictions of likelihood for different morphologies for model complex hydrides*

FY18Q2: Go/No-Go: Rank improvement strategies for enthalpy decreases in hydrides (50%)

- *Nanoscaling and confinement stress predicted to have the largest effects*

FY18Q3: Parameterize integrated kinetic model for representative B/N/Al hydrides (75%)

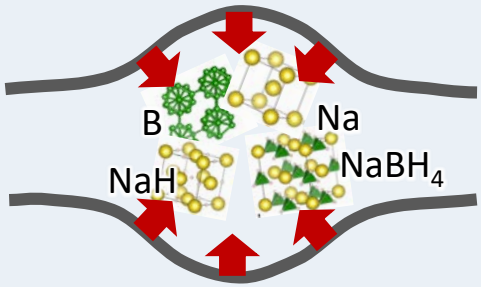
- *Necessary thermodynamic parameters have been computed, along with some kinetic parameters for Mg-B-H and Na-Al-H*

FY18Q4: Evaluate additive/composite strategies for improving effective ΔE (75%)

- *Evaluation of multiple strategies in progress*

Moving the bar

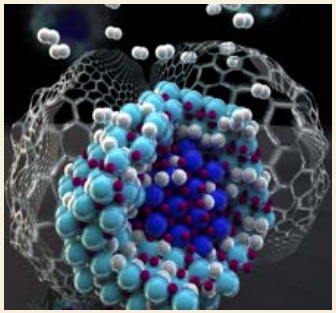
New tools & capabilities



- Improved accuracy in phase diagram prediction
- Predicted morphology of metastable intermediates
- Improved confinement stress calculation
- Developed new nucleation model for borohydrides
- Demonstrated XPS+AIMD for interrogating surface chemistry

ANL, UH seedlings

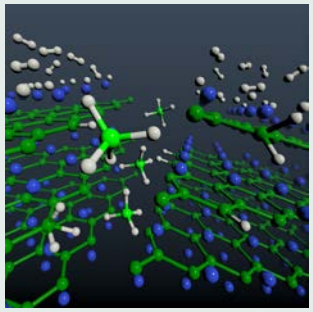
Materials tunability & design



- Quantified potential effect of confinement stress on thermodynamics and diffusion
- Computed functionalization effect on COF sorption
- Assessed tunability of vibrational entropy in hydrides
- Assessed effect of metal hydride additives

ANL, NREL seedlings

New foundational understanding

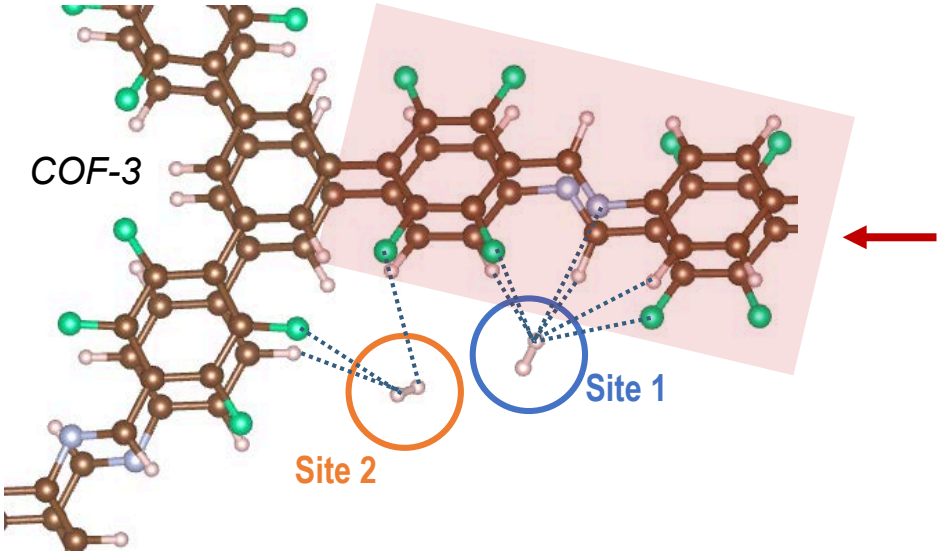


- Elucidated decomposition mechanism of MgB_2
- Explored relationship between charge and chemistry
- Simulated interaction of ether and metal hydride additives with surfaces
- Determined new role of surface oxide

UH, NREL seedlings

Accomplishment: MOF and COF sorbent calculations

Working with core team and NREL seedling to understand H_2 sorption on COFs and MOFs



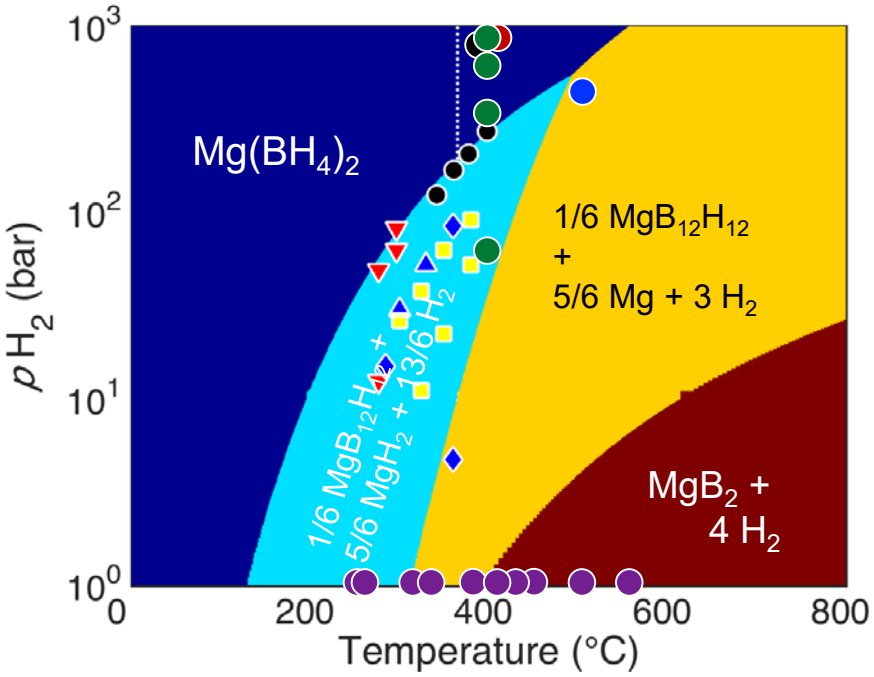
H_2 binding enthalpy vs. Base-COF (kJ/mol)	Site 1	Site 2
Base-COF	0	0
OH-COF	−2.198	−0.403
FASt-COF	−0.893	−0.941
F-COF	−0.459	−0.909
F-OH-COF	−0.461	−1.325

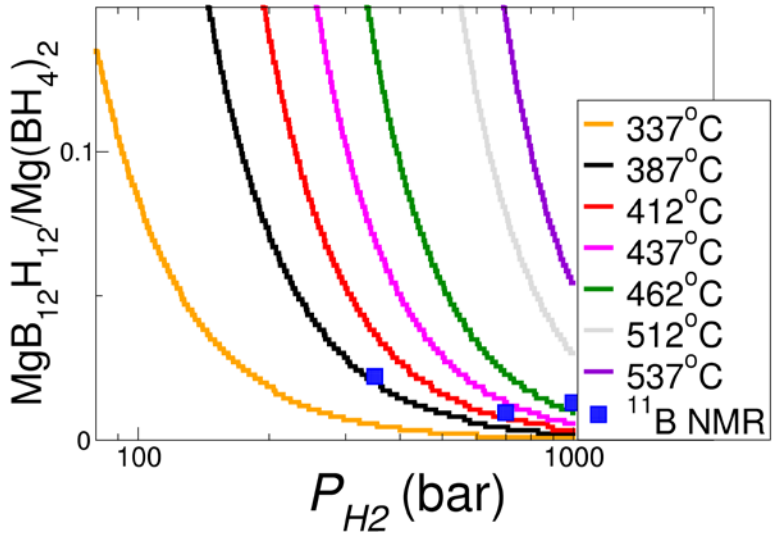
O F N

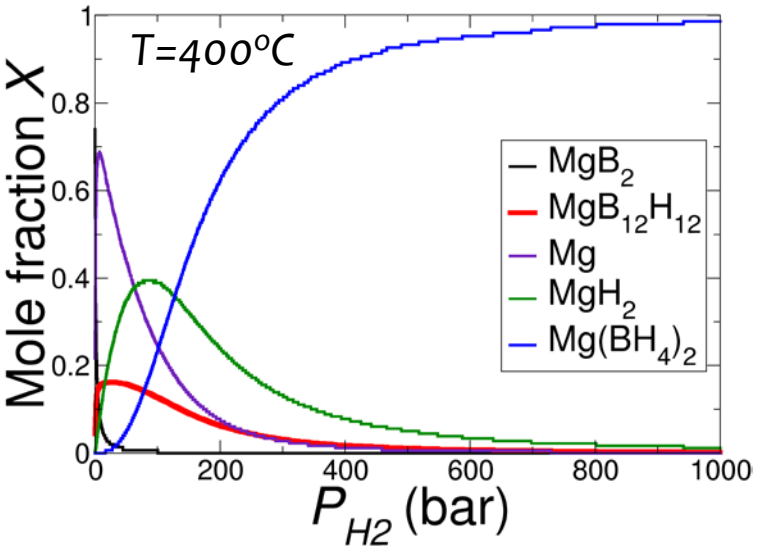
- Alternating stacking structure in COF-3 found to increase COF crystallinity and formation enthalpy (paper submitted)
- Functionalization predicted to increase H_2 binding enthalpy by up to 2.2 kJ/mol H_2 versus Base-COF

Accomplishment: Accurate Mg-B-H phase diagram prediction

LLNL is working with SNL and PNNL to predict, measure, and validate phase diagram of Mg-B-H, focusing on high-pressure regime



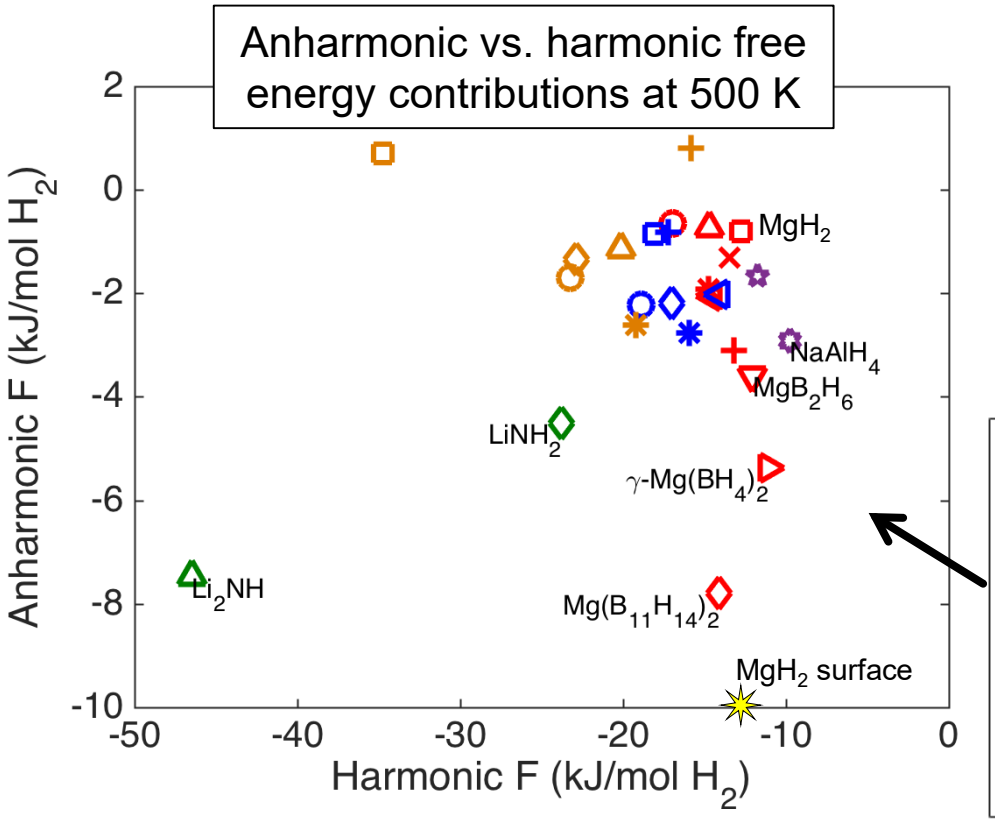


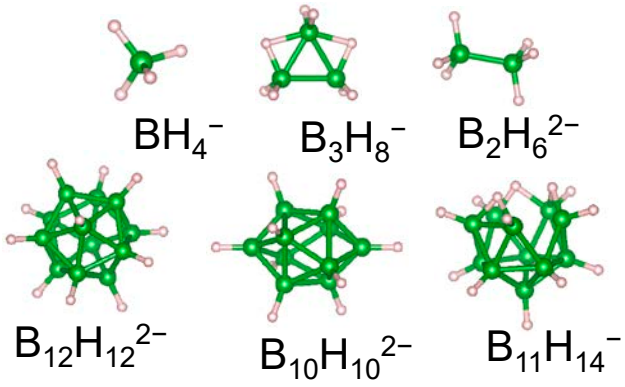


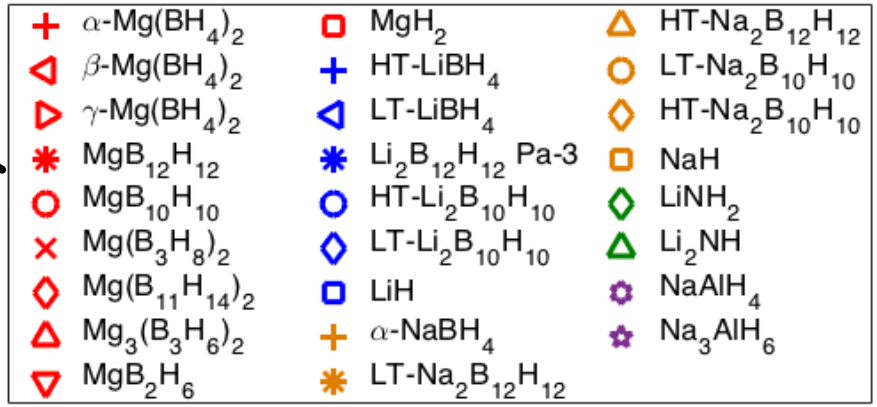
- **Compared to SNL PCT, we predict ΔS with 97% agreement and ΔH with 88% agreement (versus 89% and 50% for standard DFT)**
- **Phase equilibrium between $Mg(BH_4)_2$ and $MgB_{12}H_{12}$ is correctly predicted to within 10 °C!**

Accomplishment: Assessed entropy tunability

New method for accurately computing anharmonic entropy shows tunability of up to 8 kJ/mol H_2 for bulk materials at 500 K (more for surfaces and higher T)





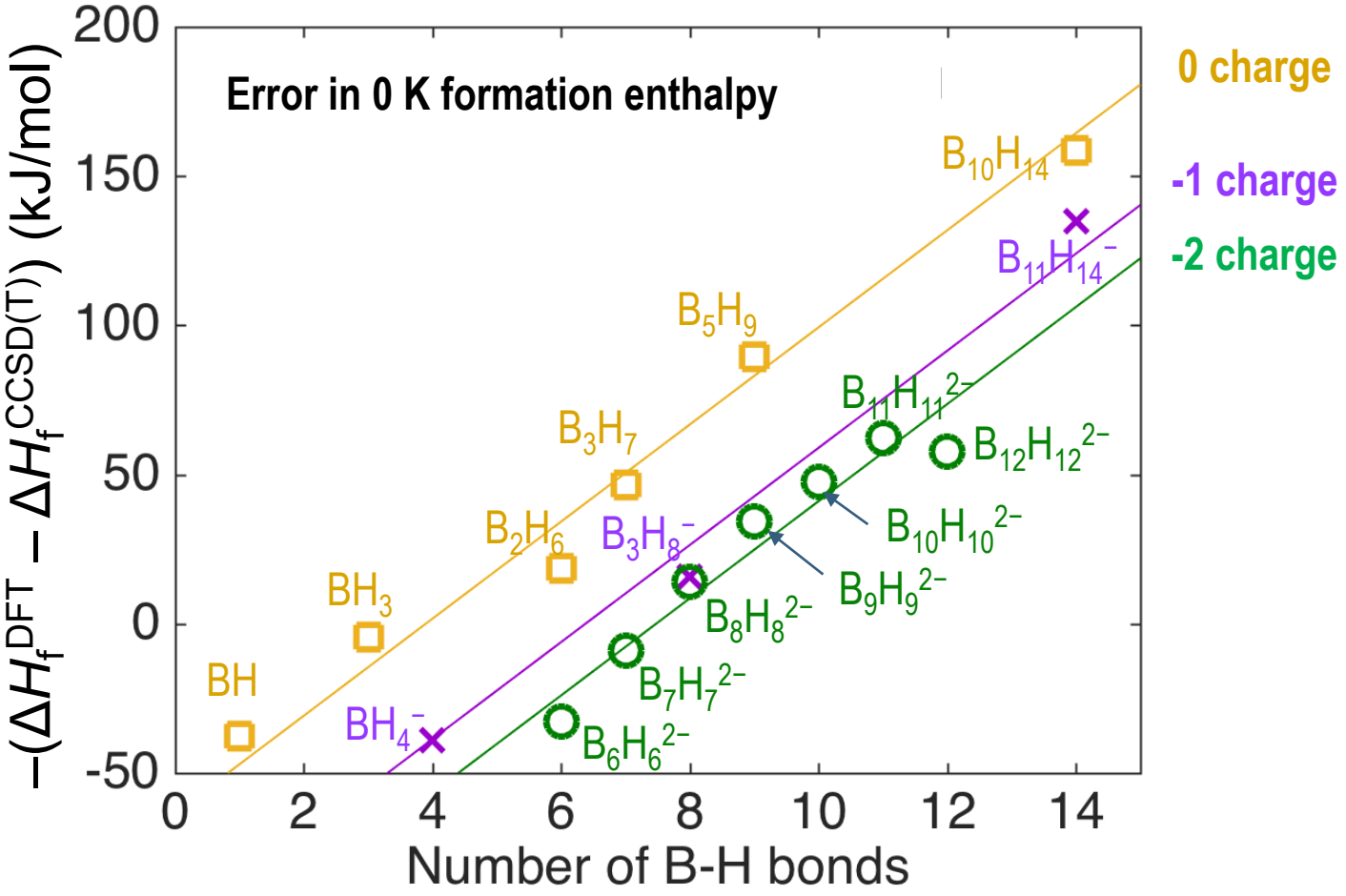


- **Surface anharmonicity from molecular rotations explains reductions in ΔS from nanoconfinement**
- **"Freezing" anharmonic rotations by binding with confining medium could destabilize complex hydrides by > 10 kJ/mol H_2**

Used ~ 4000 cpu-years on LLNL supercomputers!

Accomplishment: Data-driven corrections to DFT enthalpy

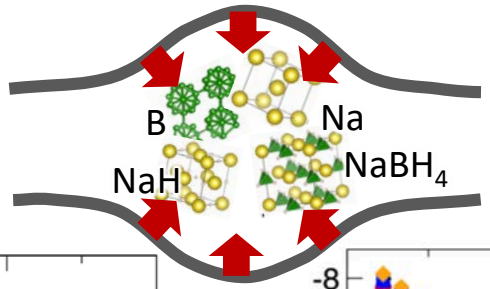
Errors in DFT enthalpy predictions are traceable to internal molecular energies of B_xH_y



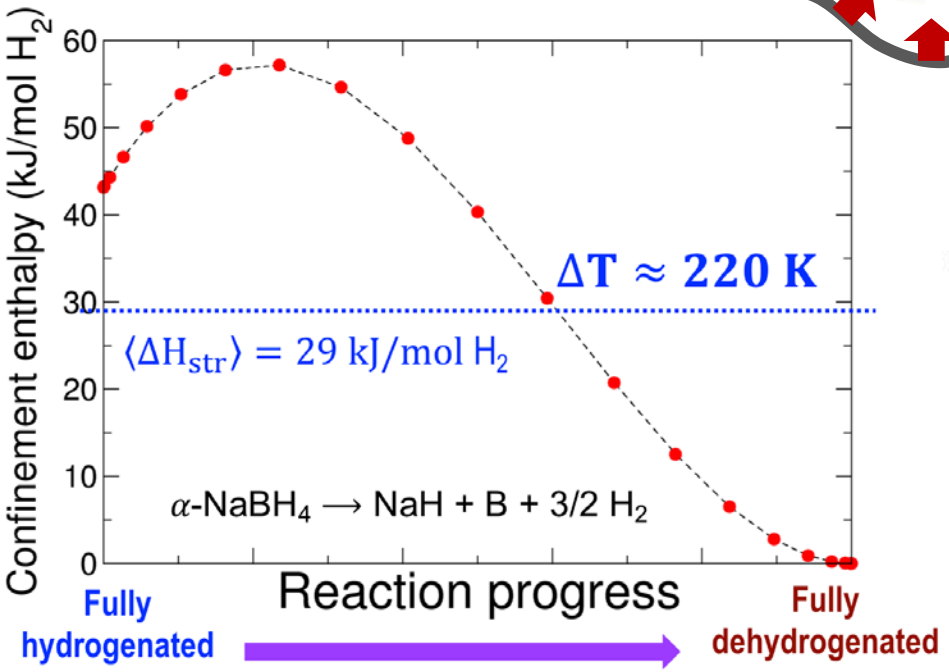
- **Average error in DFT enthalpy of B_xH_y molecules are reduced from ~66 kJ/mol to < 9 kJ/mol by applying systematic corrections based on data-driven trends**

Accomplishment: Assessed stress/strain tunability

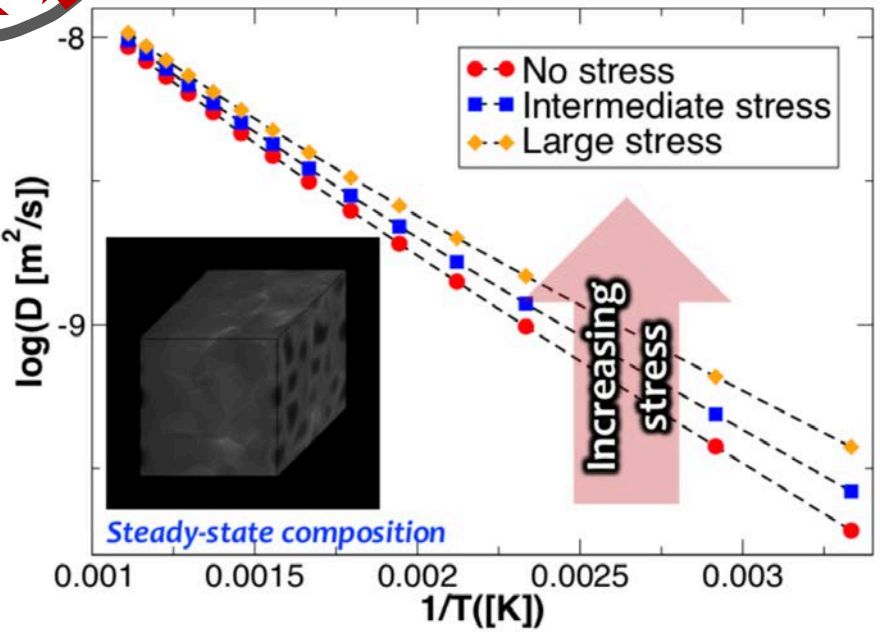
New method for quantifying the confinement stress effects on thermodynamics and diffusion kinetics suggests large changes can be induced mechanically



Impact on $NaBH_4$ thermodynamics



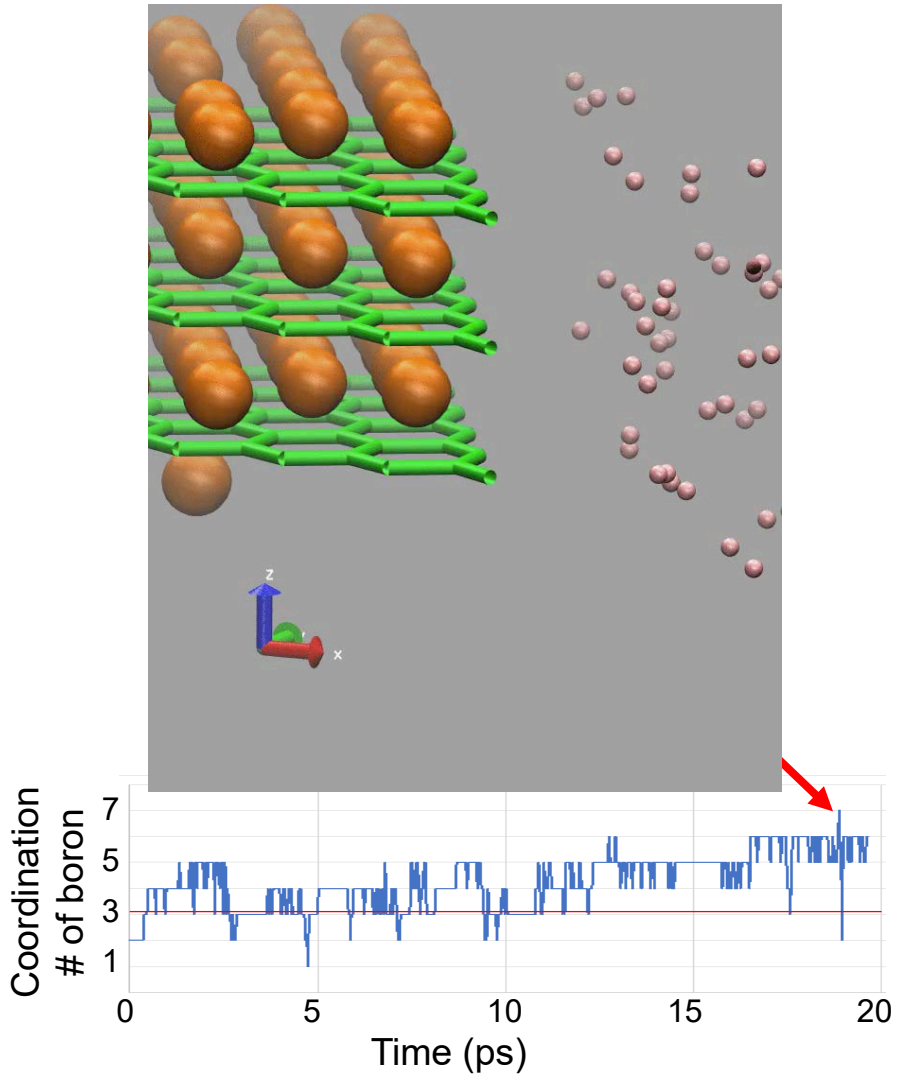
Impact on MgH_2 diffusion kinetics

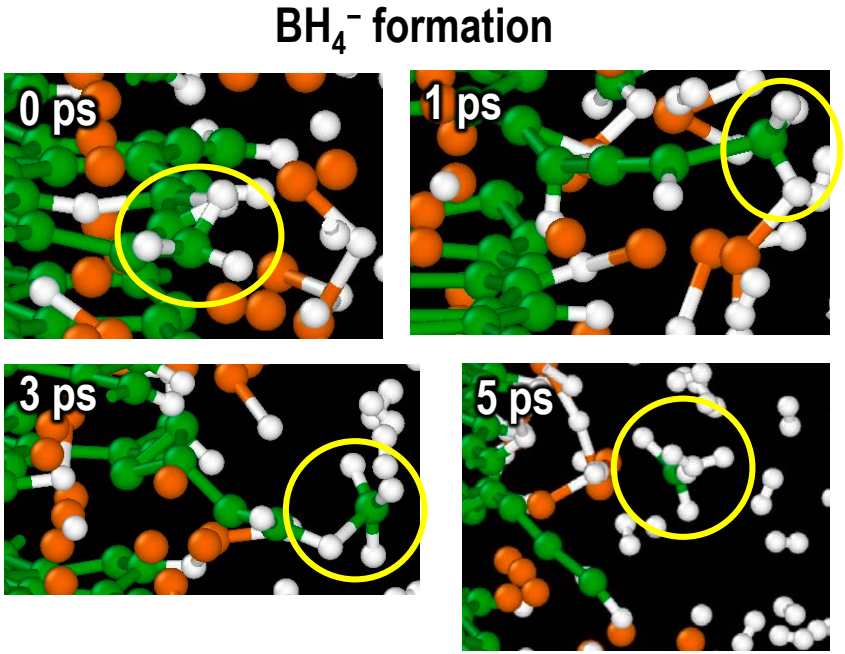


- **Predicted reduction in enthalpy of ~29 kJ/mol H_2 for 30 nm $NaBH_4$ upon nanoconfinement is in excellent agreement with Argonne seedling data (compare to < 2 kJ/mol H_2 for surface effect!)**

Accomplishment: Understanding MgB_2 decomposition via AIMD

HPC-enabled capability to directly observe chemical reactions upon hydrogenation of MgB_2 edges under high pressure illustrates competing pathways for B_xH_y formation



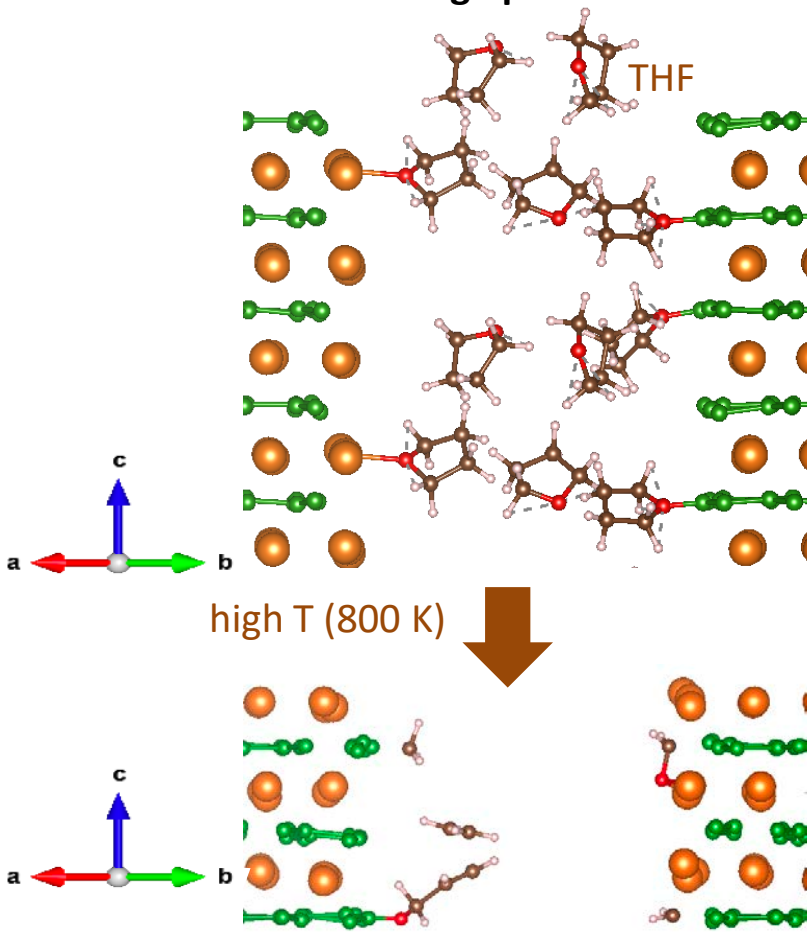


- Chemistry occurs at exposed edge planes, in agreement with Ray *et al.*, PCCP 19, 22646 (2017)
- Mg-rich edges lead to smaller molecules; B-rich edges lead to closo-borane formation

Accomplishment: Promoting MgB_2 decomposition

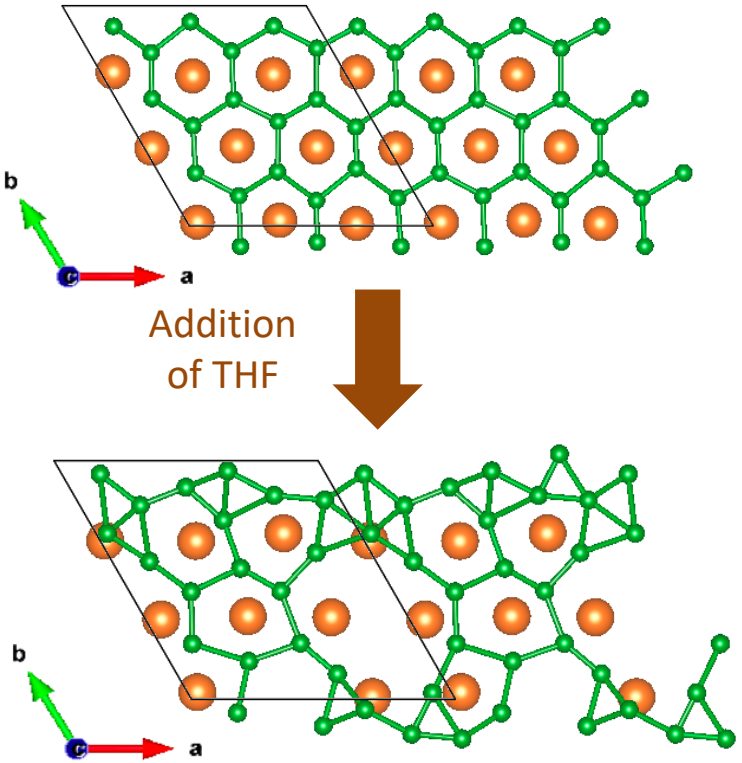
AIMD simulations in collaboration with U. Hawaii seedling reveal how THF interacts with MgB_2, activating B-B bonds in response to disruption of charge balance

edge plane



- **Reactive MgB_2 edge plane decomposes THF**

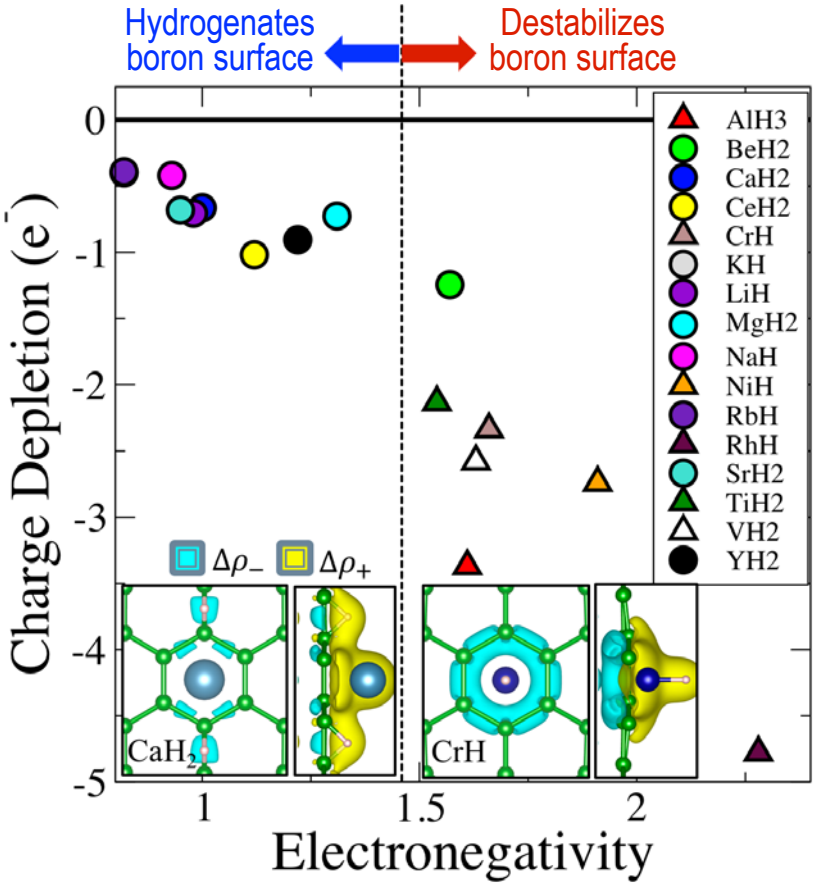
basal plane

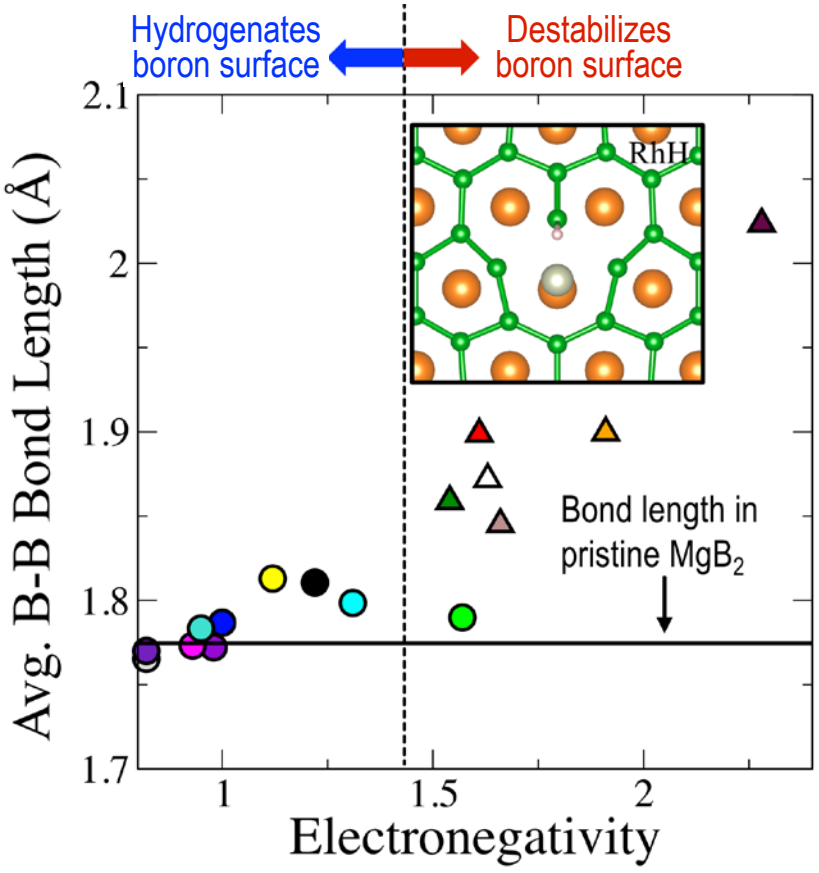


- **Etherates destabilize surface B sheet and create structural defects**
- **Origin of structural changes linked to charge redistribution**

Accomplishment: Metal hydride additives on MgB_2

Effect of metal hydride additives on B-B bond activation further demonstrates relationship between charge and B sheet stability in MgB_2 and suggests design rule

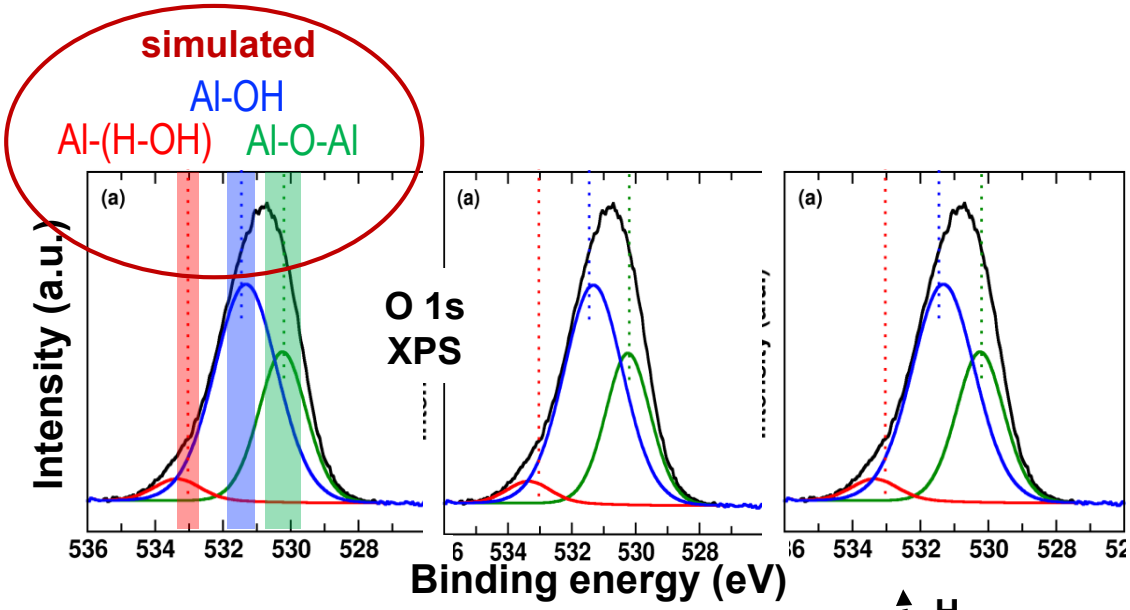


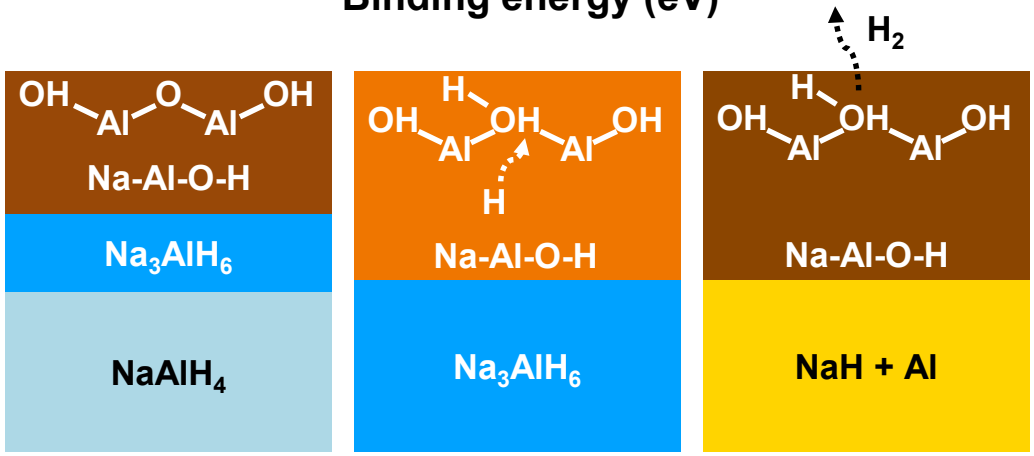


- **Boron plane in MgB_2 destabilized by charge loss or charge rearrangement in hexagonal rings**
- **Increasing electronegativity of metal additives leads to greater destabilization of boron plane**

Accomplishment: $NaAlH_4$ surface chemistry from AP-XPS

AIMD + XPS simulations (LLNL/LBNL collaboration) gives correct interpretation of SNL AP-XPS to understand how surface chemistry evolves

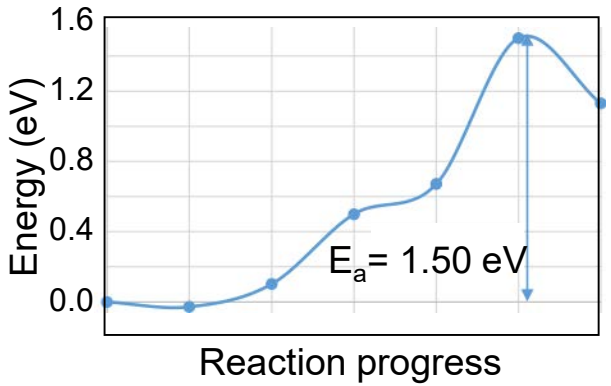




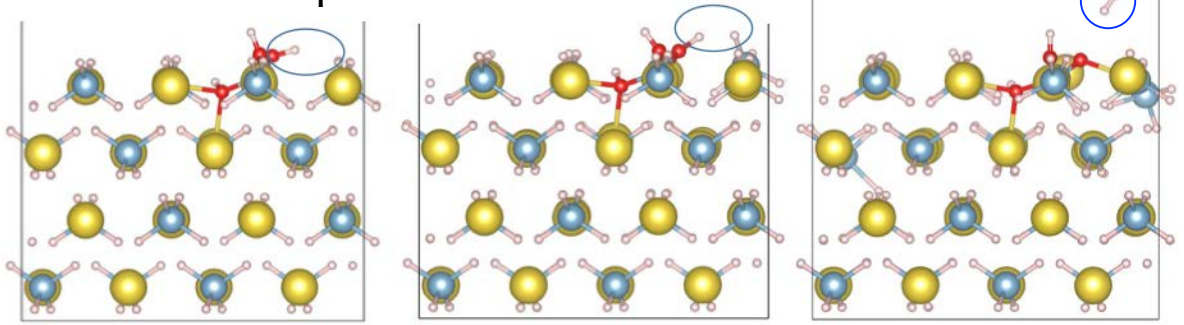
- Simulated XPS shows that past work has incorrectly assigned Al, $NaAlH_4$, and Na_3AlH_6 chemical species
- Initial oxide film on Na_3AlH_6 evolves as hydrogen enriches and depletes

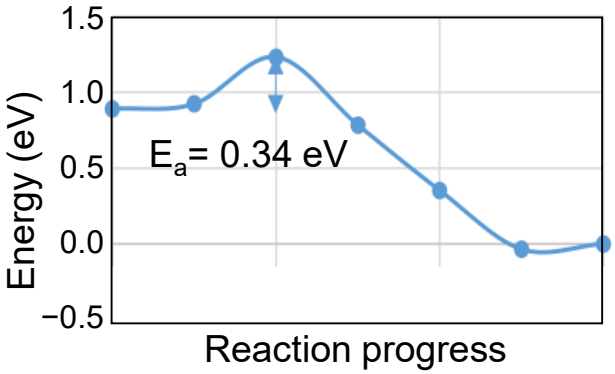
Accomplishment: Benefits of surface oxide for H_2 formation

Simulations show that oxide facilitates novel heterosynthetic pathway for H_2 formation upon dehydrogenation at $NaAlH_4$(001) surface

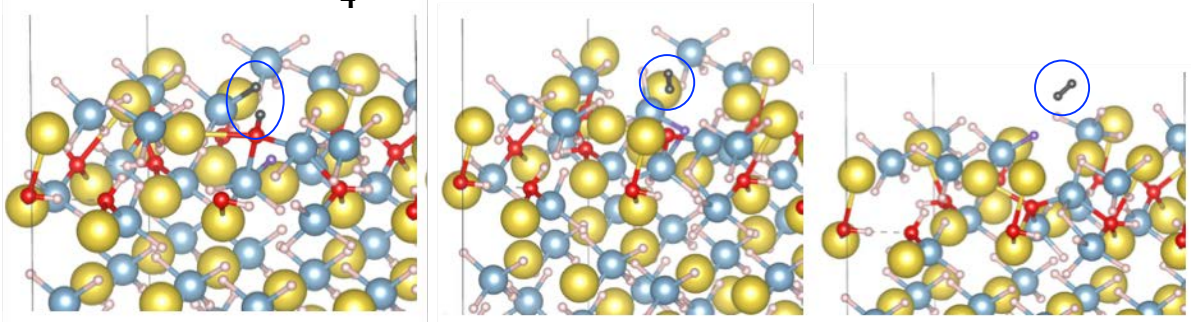


Pristine $NaAlH_4$ surface





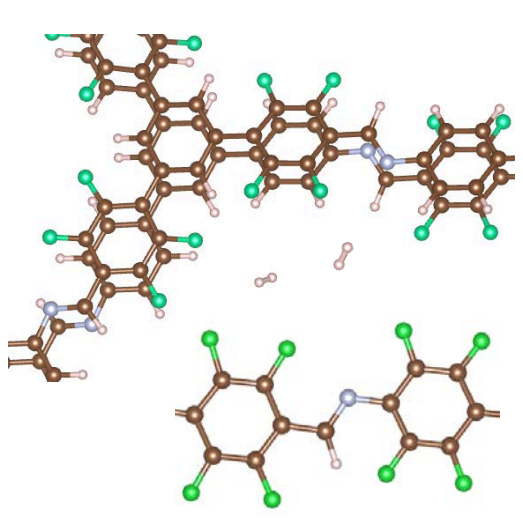
Oxidized $NaAlH_4$ surface



- **Oxide reduces barrier for H_2 formation by 4-5x!**
- **Thin oxide could be beneficial (results submitted for publication)**

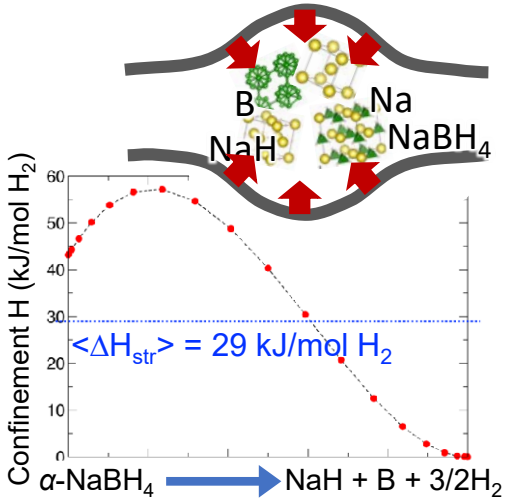
Highlights of interactions with seedlings

Johnson, NREL (MOFs, COFs)



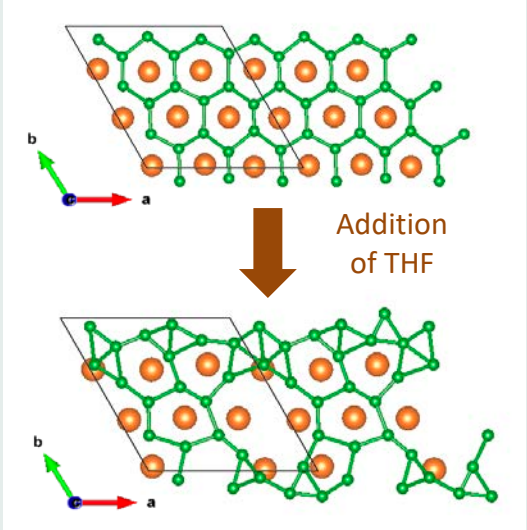
- Probed **functionality-dependent H_2 binding** and structural stability in COFs

Liu, ANL ($NaBH_4$@graphene)



- Quantified **enthalpy change by nanoconfinement**, explaining decreased dehydrogenation temperature

Godwin, U. Hawaii (MgB_2/ethers)



- Suggested **new structural defect model** for MgB_2 hydrogenation from simulations of MgB_2/ether interface

Additional interactions

- *Christensen, NREL: Joint development of foundational understanding of diffusion through ALD oxides*
- *Majzoub, UMSL: Provided computational resources for larger-scale sorbent medium interactions*

Collaborations

External collaborations

- Stress effects in confined metal hydrides: New multi-institutional HyMARC partnership with Prof. E. Cho in KAIST, Korea awarded in April 2018
- Phase-field model development: H.-C. Yu (Michigan State)
- Classical "SAPT" potential development for borohydrides: Prof. J. McDaniel (Georgia Tech)
- Hybrid quantum-classical simulations of borohydride interfaces: M. Otani (AIST, Japan)

HyMARC collaborations (outside of core labs)

- Mg-B-H chemistry, NMR, borohydride reaction modeling (T. Autrey et al., PNNL)
  - *Regular webinars plus bilateral visits*
  - *LLNL focuses on solid-state aspects and MgB_2 rehydrogenation; PNNL focuses on borohydride chemistry during $Mg(BH_4)_2$ dehydrogenation*
- DFT computations of H_2 physisorption on MOF-74 (M. Head-Gordon, LBNL)
  - *LLNL focuses on deriving corrections for extended systems using benchmark approaches; LBNL focuses on cluster chemistry*
- Neutron diffraction/spectroscopy of borohydrides (T. Udovic, NIST)

Also extensive collaborations within HyMARC core lab team

Remaining challenges/barriers & mitigation strategies

- **Thermodynamic predictions using conventional DFT have accuracy limitations**

  We have prioritized strategies for improving predictions of ΔH and ΔS by utilizing explicit dynamics approaches, data-driven corrections, and PCT-based calibration. Errors have now been reduced by severalfold compared to conventional DFT, and improvements continue to be made.

- **Difficult to paramaterize free energy landscape for amorphous materials**

  We continue to work with SNL to synthesize amorphous materials for testing. We have now devised a new method for predicting the relative metastability of amorphous materials, which will aid SNL's efforts towards validation in the coming months.

- **Microstructural information is needed for model validation**

  We have now started STXM measurements as part of our ALS Approved Program. This data is still very new, but interpreting it will be a key focus of the theory effort in the coming months.

Proposed future work (remainder of FY18)

Sorbents:

- *Complete calculations of H_2 physisorption and stability of functionalized COFs (w/NREL seedling)*
- *Establish "best practice" for DFT calculations of H_2 physisorption on MOF-74 (w/LBNL & SNL)*

Thermodynamics of metal hydrides:

- *Publish anharmonic free energy database for model complex hydrides*
- *Publish validated Mg-B-H phase diagram and phase fractions (w/SNL & PNNL)*

Chemistry of metal hydrides:

- *Track hydride intermediates within high-T AIMD of $NaAlH_4$ and $Mg(BH_4)_2$ with and without Ti*
- *Identify & validate pathways for closo-borane formation from MgB_2 (w/SNL & LBNL)*

Interfaces:

- *Publish LLNL multiscale modeling framework for hydriding kinetics (w/SNL)*
- *Compare nucleation model with STXM microstructures for Mg-B-H and Li-N-H (w/SNL & LBNL)*

Additives:

- *Extend metal hydride additive effort to include clusters and solid-state interfaces and compare w/SNL experiments*
- *Continue AIMD of Mg-B-H in ether and analyze coordination (w/U. Hawaii seedling)*

Standards and tools:

- *Complete MgB_xH_y spectroscopy standards study (w/PNNL, SNL, & LBNL)*
- *Continue building library of pairwise intermolecular potentials for B_xH_y (w/SNL)*

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

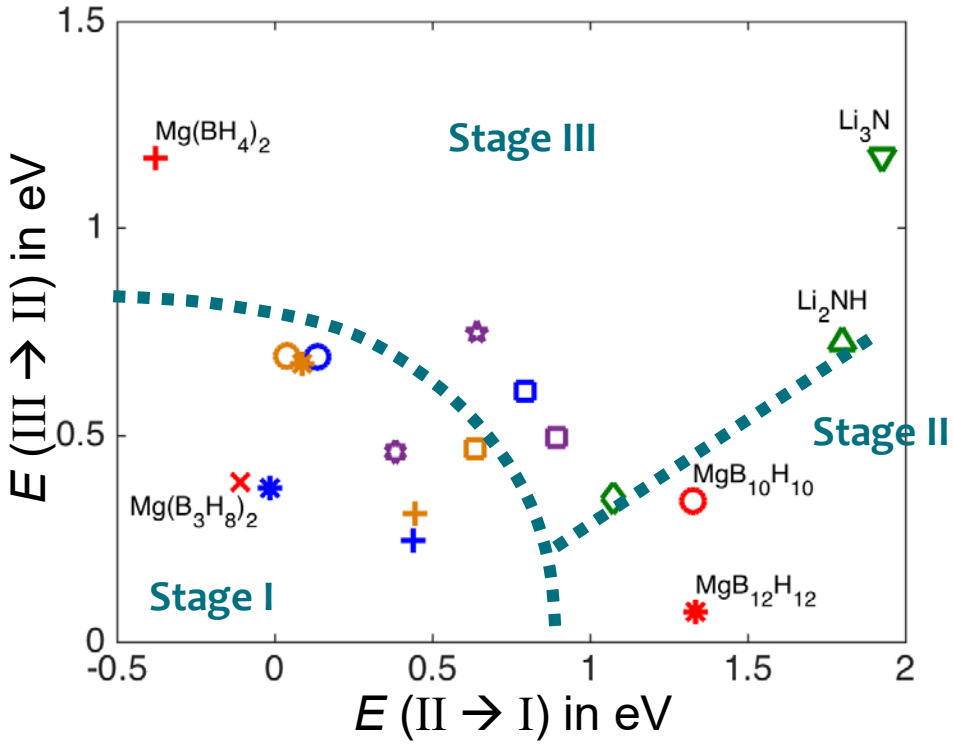
Summary

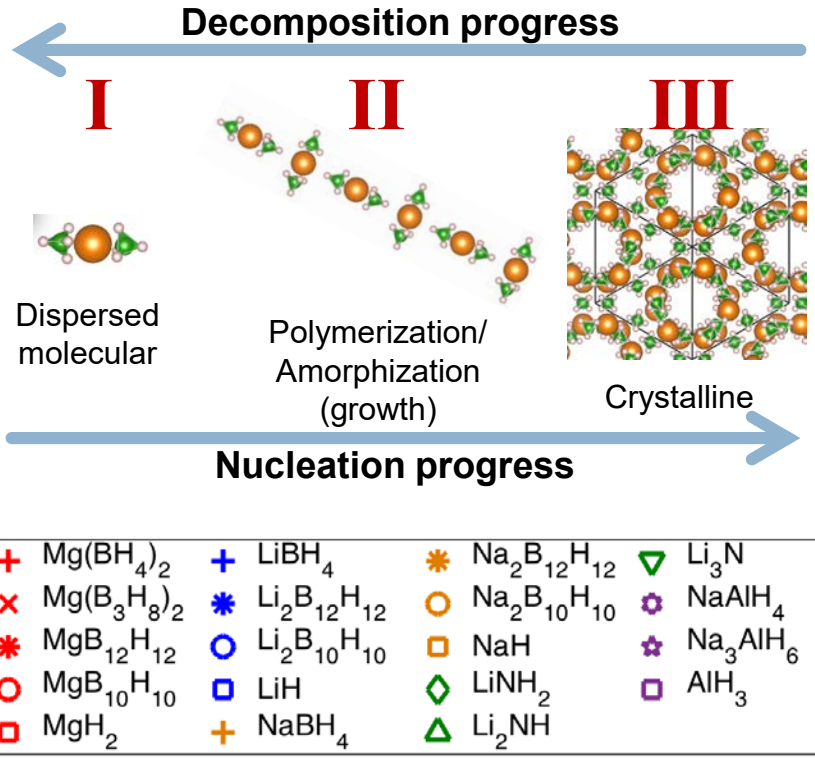
- Integrated **theory/synthesis/characterization** framework of HyMARC aims to provide foundational understanding and new tools for solid-state hydrogen storage
- LLNL modeling tasks broadly focused on **multiscale integration, experiment-theory feedback, and beyond-ideal materials modeling**
- **Developed & validated new capabilities** for describing thermodynamics of complex hydrides, stress effects, nucleation kinetics, and surface chemistry
- **Assessed tunability of materials thermodynamics and kinetics** by stress engineering, chemical functionalization, entropy, and additives
- **Established new foundational understanding** of surface oxidation and MgB_2 decomposition driven by charge reorganization
- **Applied tools for interaction with seedlings** to model thermodynamics and kinetics of confined hydrides and MgB_2 etherates, as well as H_2 physisorption on tailored sorbents

Technical backup slides

Accomplishment: Metastability of borohydride intermediates

New method estimates tendency of hydride intermediates to form amorphous and molecular morphologies before crystallizing, providing insights into microstructure



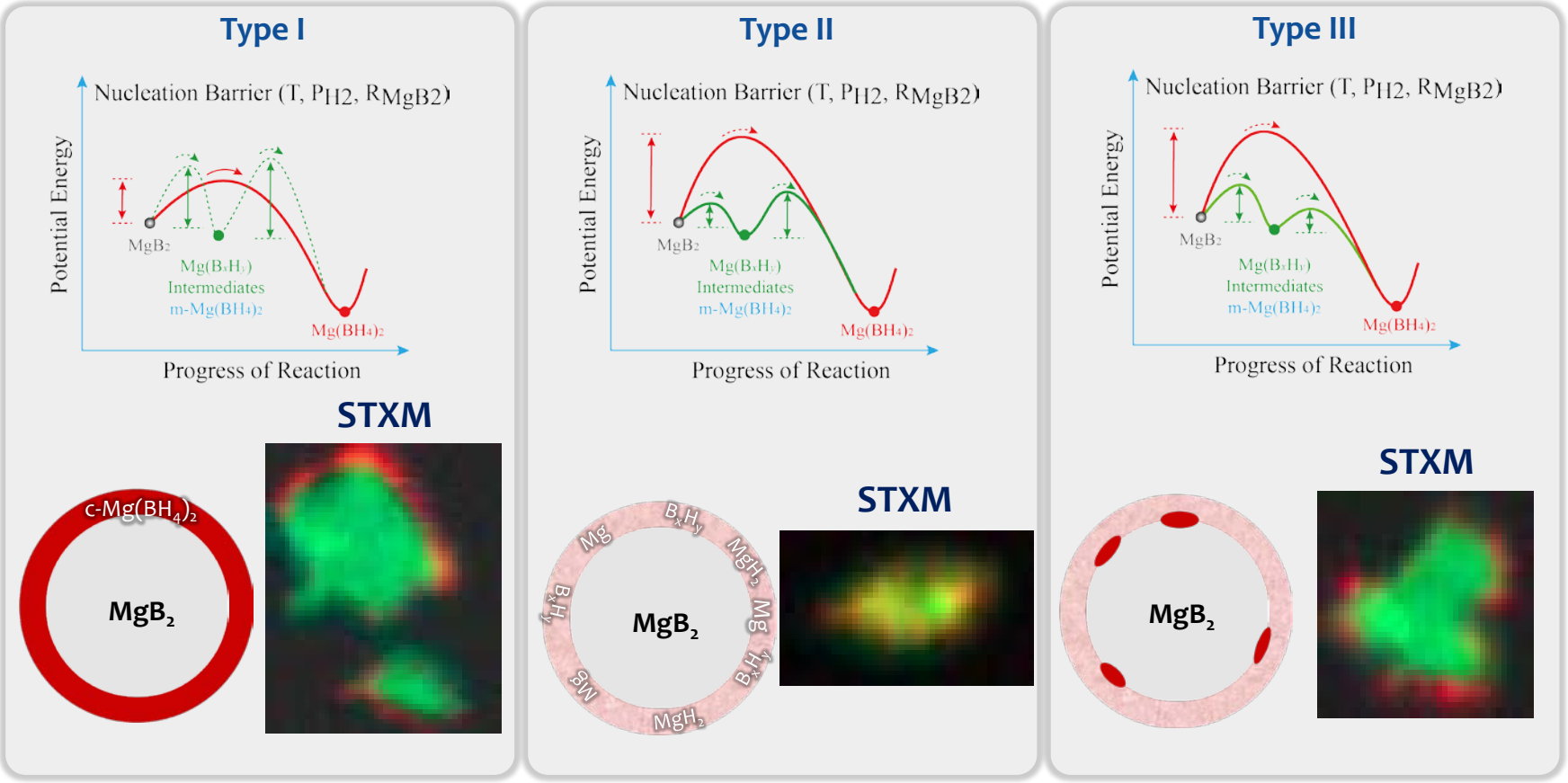


- **Explains known observations of intermediates that are not predicted as bulk stable but can readily exist as metastable molecular (e.g., $Mg(B_3H_8)_2$) or amorphous (e.g., $MgB_{10}H_{10}$) materials**
- **Intermediates with less driving force for crystallization have higher chance of forming solid solutions with faster phase kinetics; reversibility of these intermediates relies only on chemical destabilization**

**Relies on comparing enthalpies of 0D, 1D, 2D, and 3D in materials models*

Accomplishment: Advanced model for nucleation kinetics

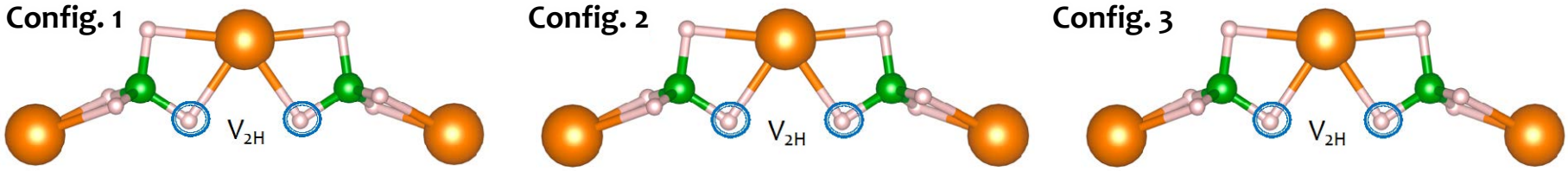
Advanced nucleation model identifies possible different pathways of phase formation

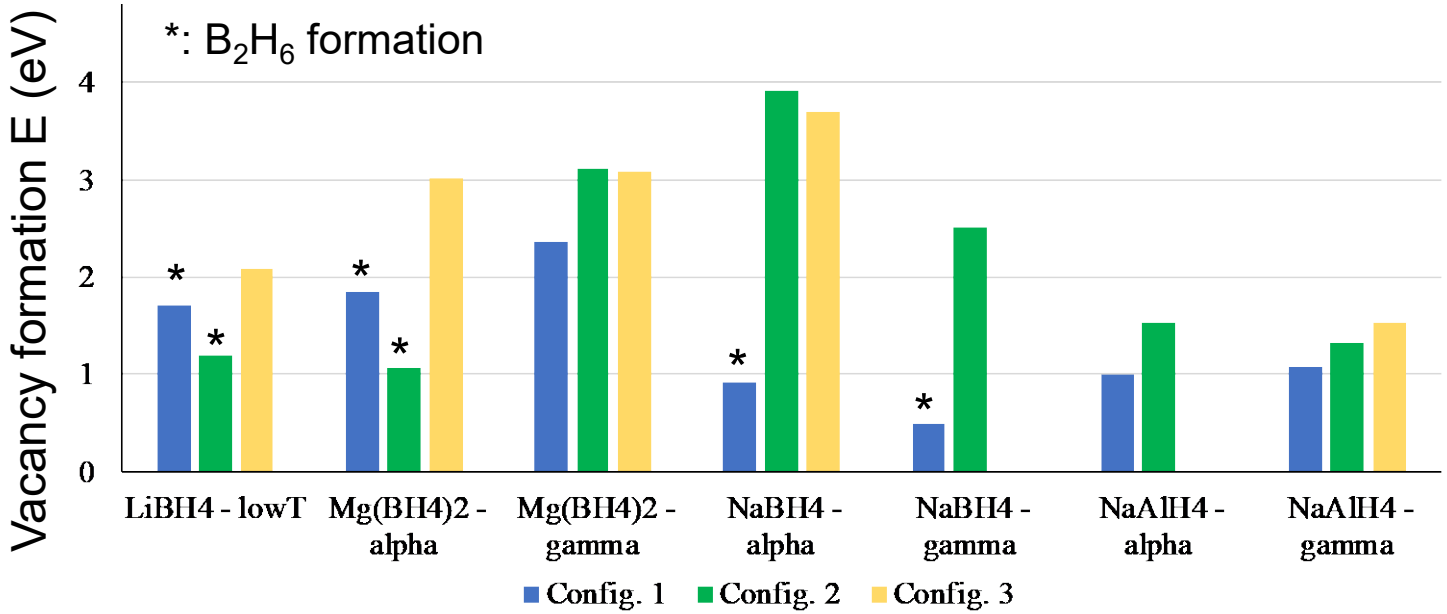


- **Advanced phase nucleation model predicts at least three types of possible kinetic pathways and corresponding phase microstructures**
- **We analyze predicted phase morphologies by comparing with STXM experiments (in progress)**

Accomplishment: Assessed B-H & Al-H bond strengths

Calculations of hydrogen di-vacancy formation energies are used to understand dehydrogenation chemistry of complex boro/aluminum hydrides

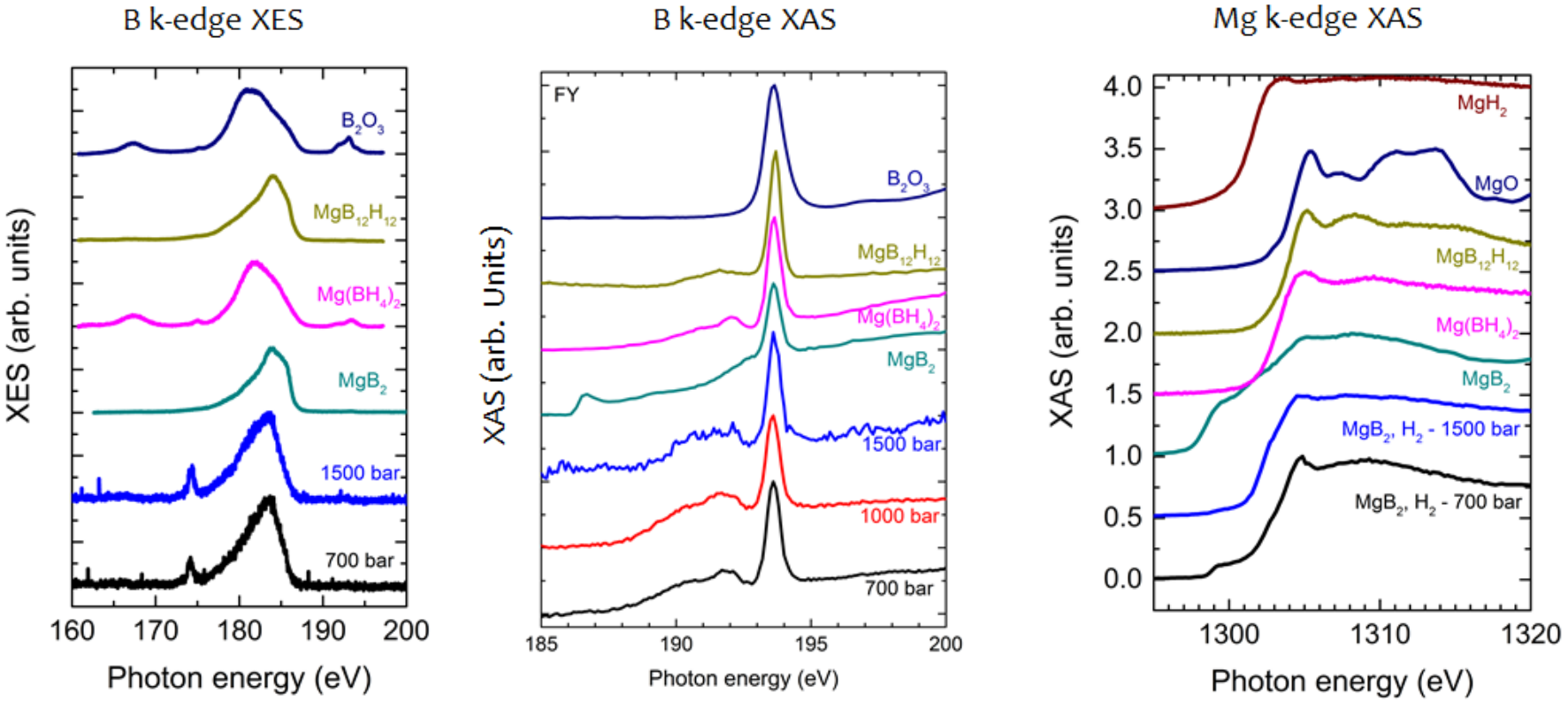




- **Configurations with similarly low vacancy formation energies (e.g., γ-$NaAlH_4$) are most likely to be favorable for hydrogen diffusion**

Accomplishment: XAS/XES for deep hydrogenation of MgB_2

Comparison with standards reveals transition from MgB_2 to $Mg(BH_4)_2$ as a function of pressure, along with the suppression of intermediaries such as $MgB_{12}H_{12}$



- **Strengthening of spectral features indicates more complete conversion to $Mg(BH_4)_2$ at higher pressures, providing fingerprint for suppression of $MgB_{12}H_{12}$**
- **Mg XAS shows evidence of MgH_2 alongside conversion from MgB_2 to $Mg(BH_4)_2$**

Accomplishment: Al 2p XPS simulations of oxidized Na-Al-H

XPS simulations show that assignment does not always follow oxidation state, establishing new standards for re-interpretation of current and past XPS spectroscopy