HyMARC: LLNL Technical Activities

2019 DOE Hydrogen Annual Merit Review

May 1, 2019

PI: Brandon C. Wood, LLNL

HyMARC
Hydrogen Materials Advanced Research Consortium

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

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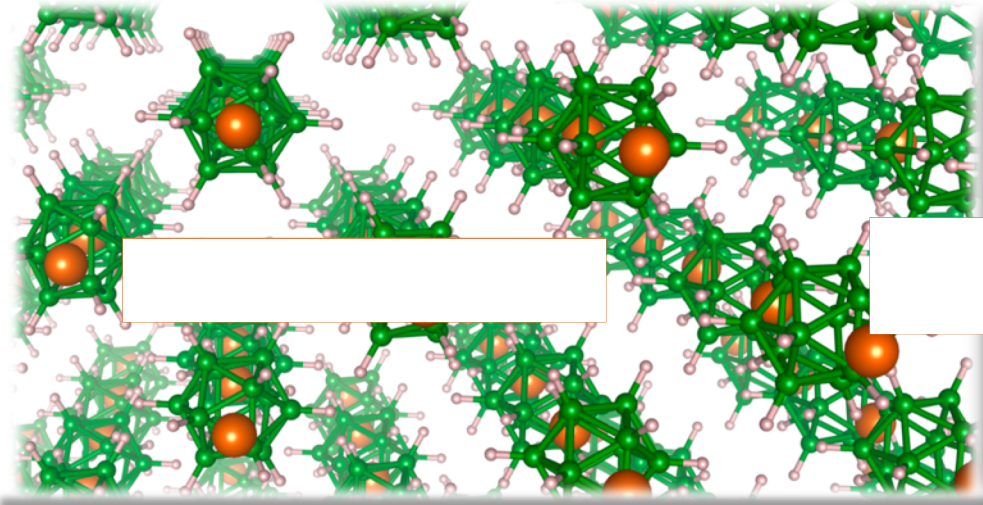
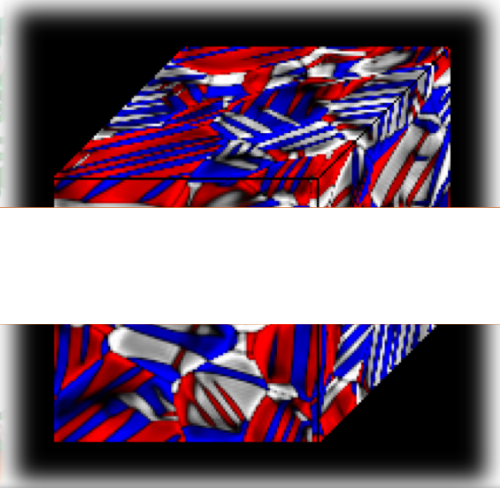
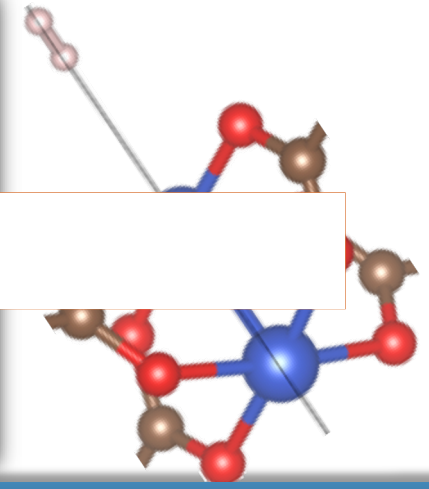






Overview

Timeline

Phase II start date: 10/1/2018

Phase II end date: 9/30/2022

Barriers addressed

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

Budget

FY18 Phase I funds: $800K

FY18 Phase II funds: $750K

FY19 funds through 3/31/19: $450K

Partners

Sandia (lead)

NREL (lead)

PNNL

LBNL

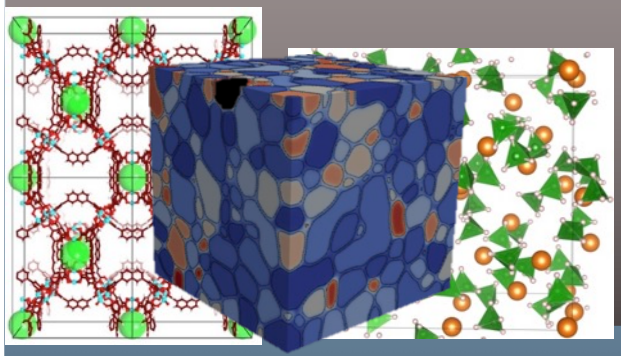
NIST

SLAC

ORNL

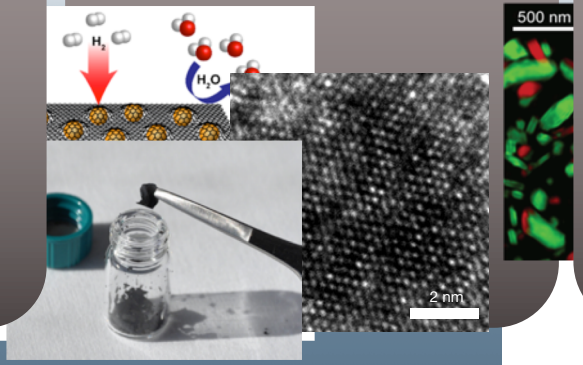
Relevance

HyMARC improves understanding of underlying thermodynamic and kinetic lim and explores new concepts to accelerate development of storage materials an



- High-accuracy physisorption
- Phase diagram prediction
- Catalyst pathway and microkinetic models
- *Ab initio* molecular dynamics and spectroscopy modeling for chemistry
- Non-equilibrium mass transport
- Nanoconfinement and interface effects
- Phase-field models for phase transformation kinetics
- Semiempirical kinetic analysis
- Community software & databases

Controlled synthesis



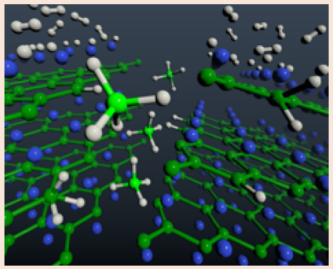
- Functionalized carbon and porous nano-confining media

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

Relevance: HyMARC modeling and simulation strategy

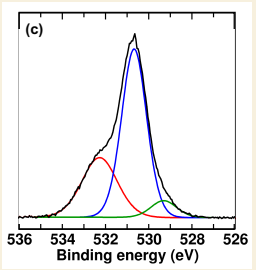
Realistic multiscale modeling and theory-experiment integration aid materials understanding and design

Assess



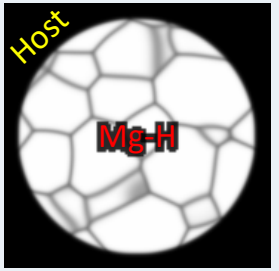
Isolate limiting factors in known materials

Interpret



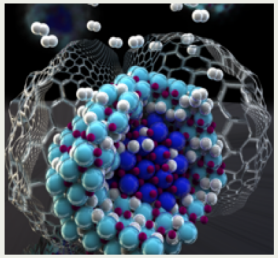
Aid experimental interpretation

Model



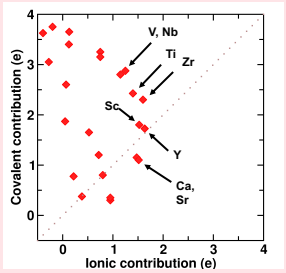
Develop and train models on surrogate materials

Understand



Investigate origins of demonstrated improvement strategies

Design



Define theoretical ranges of improvement and design parameters

Approach: Realistic modeling informs improvement strategies

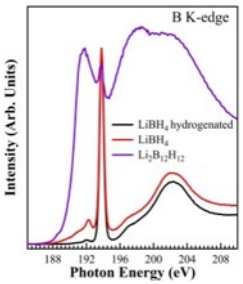
Phase II Tasks

- 2A: Comprehensive phase diagrams for hydride materials
- 2B: Interrogating complex solid interfaces and surfaces
- 2D: Nanoscaling to improve thermodynamics and kinetics
- 3C: Eutectic systems as hydrogen carriers

- 2B: Interrogating complex solid interfaces and surfaces
- 2C: Activating B-B & B-H bonds
- 2D: Nanoscaling to improve thermodynamics and kinetics
- 2E: Microstructural impacts on metal hydride reactions
- 3H: Catalyst stability

Approach: Simulation of hydrides at multiple scales

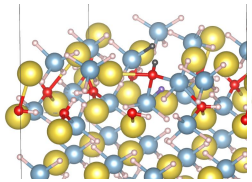
Atomic/molecular (0 – 1 nm)

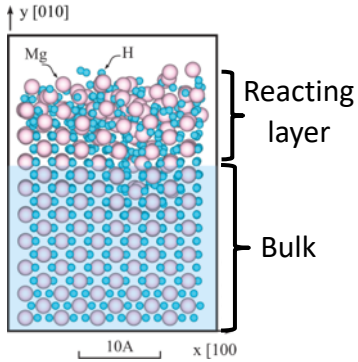


Computational Spectroscopy

Hydrogen physisorption

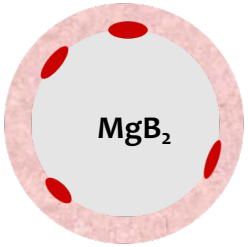
Molecular/micro (0.5 – 2 nm)

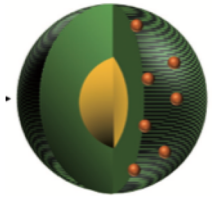




Surface/interface chemistry

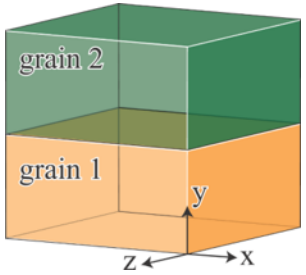
Mesoscale (2 - 100 nm)





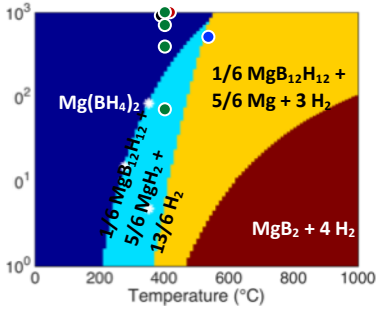
Nucleation kinetics
Phase microstructures

Grains (≤ 10 µm)



Grain boundaries
Particle size effects
Stress/strain

Macroscale/Bulk



Thermodynamics
Mixing

10^{-10} 10^{-8} 10^{-6} 10^{-4} 10^{-2}

Length (m)

Progress towards FY19 milestones with key LLNL activities

FY19Q2: Generate DFT training set for B_xH_y-cation interactions to formulate pair potentials (70%)

- *Formulated basic molecular training set and initiated three complementary strategies for pair potentials*

FY19Q4: Perform molecular dynamics of surfaces of complex hydrides (20%)

- *Generated static surface models to be used as inputs for dynamics simulations*

FY19Q3: Develop computational approach for screening additives to activate B-B bonds in MgB_2 (80%)

- *Preparing publication on B-B bond interactions in MgB_2 with metal additives; currently validating with experiments*

FY19Q4: Determine theoretical limits of confinement-induced enthalpy and entropy changes (50%)

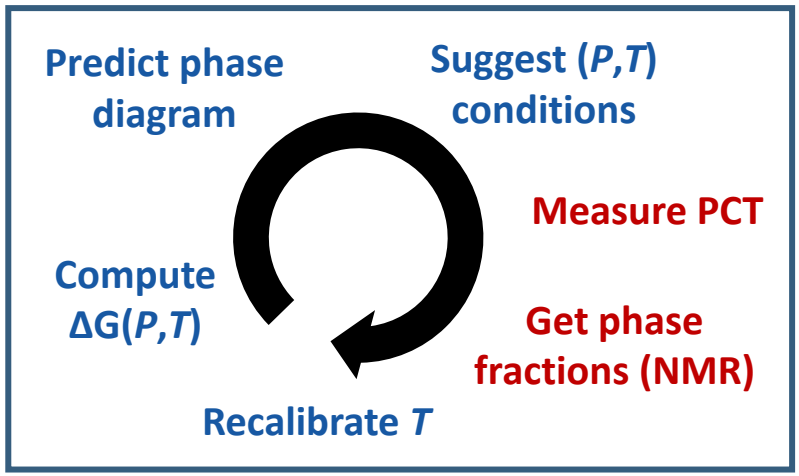
- *Surface energies computed; entropy will follow upon completion of surface dynamics*

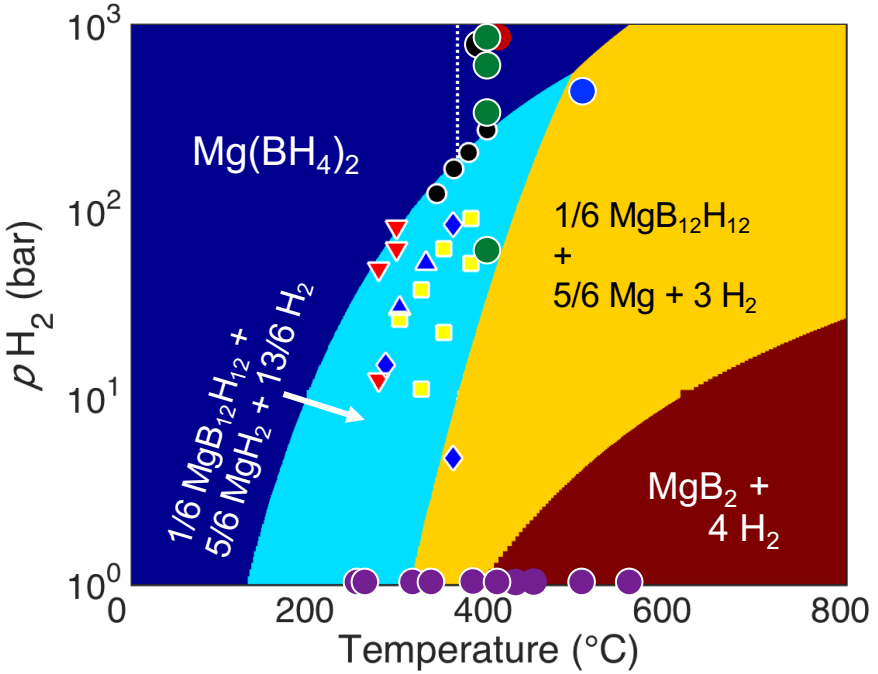
FY19Q4: Predict possible microstructure morphologies based on nucleation model and compare with STXM to elucidate kinetic pathways (70%)

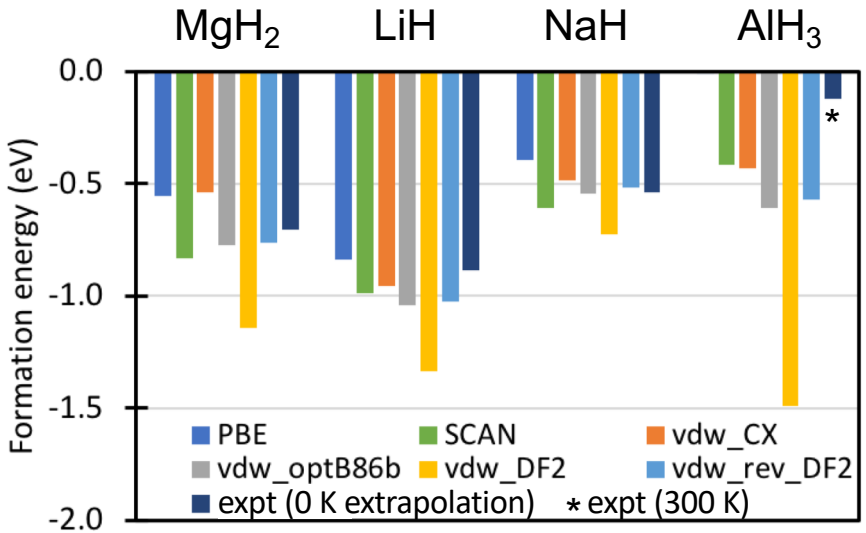
- *Determined three unique microstructures based on barriers in multi-stage nulceation*

Bulk phase diagram prediction and validation

We continue to refine phase diagrams through experiment-theory feedback cycle





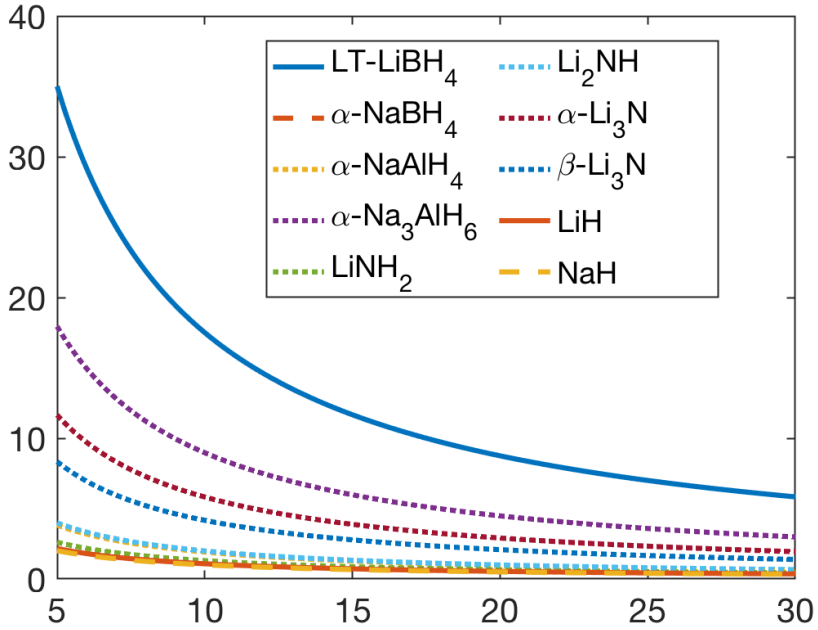


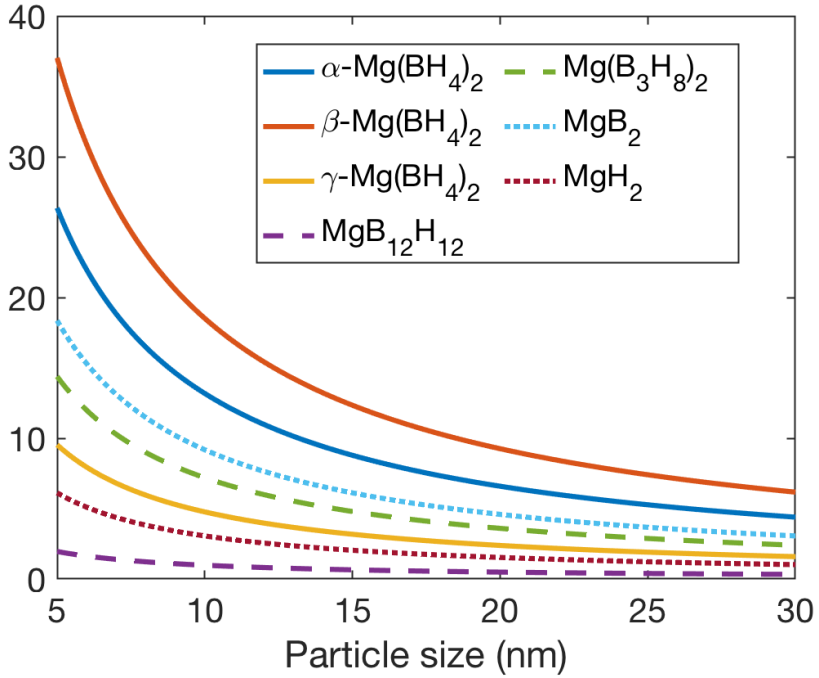
Entropy is predicted to within experimental accuracy using our latest approach, but we are pursuing higher accuracy for enthalpy

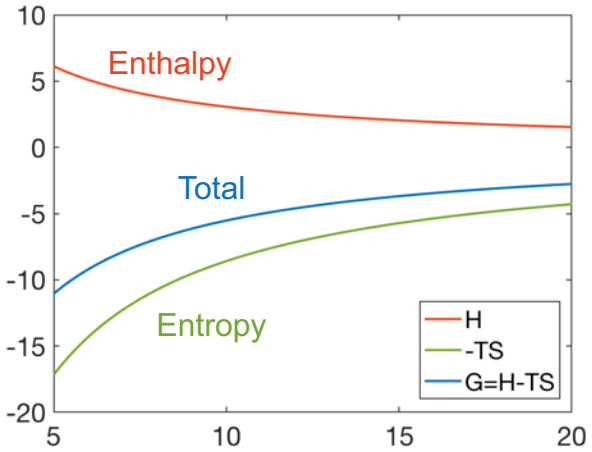
- Data-driven corrections
- New density functionals

Assessing effects of nanoscaling on thermodynamics

We are using surface enthalpy and entropy to predict tunability limits of nanoscaling



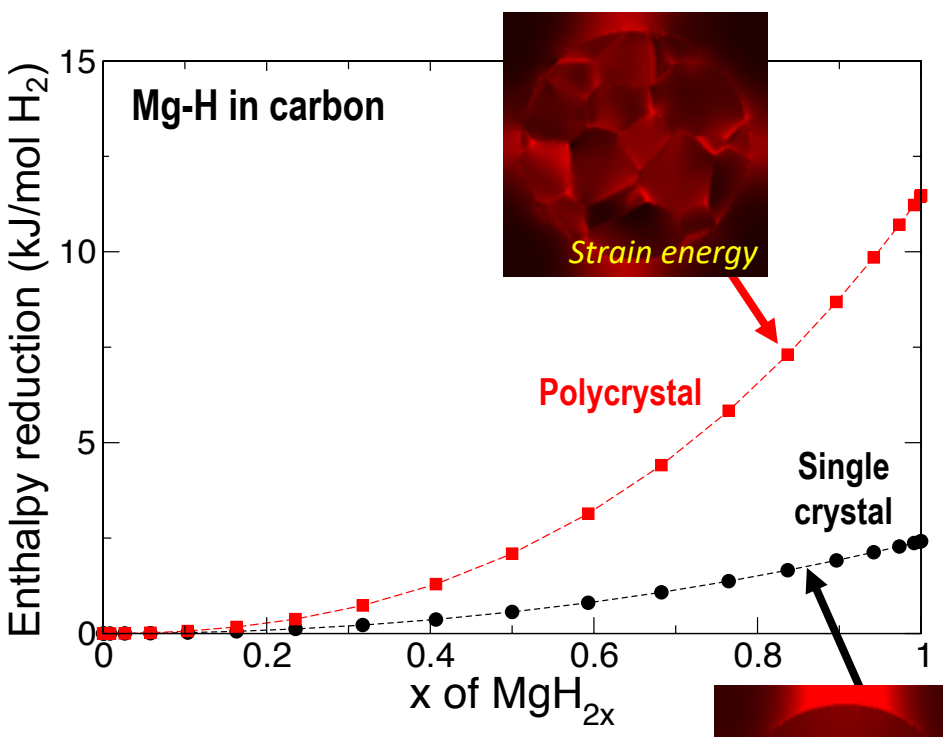




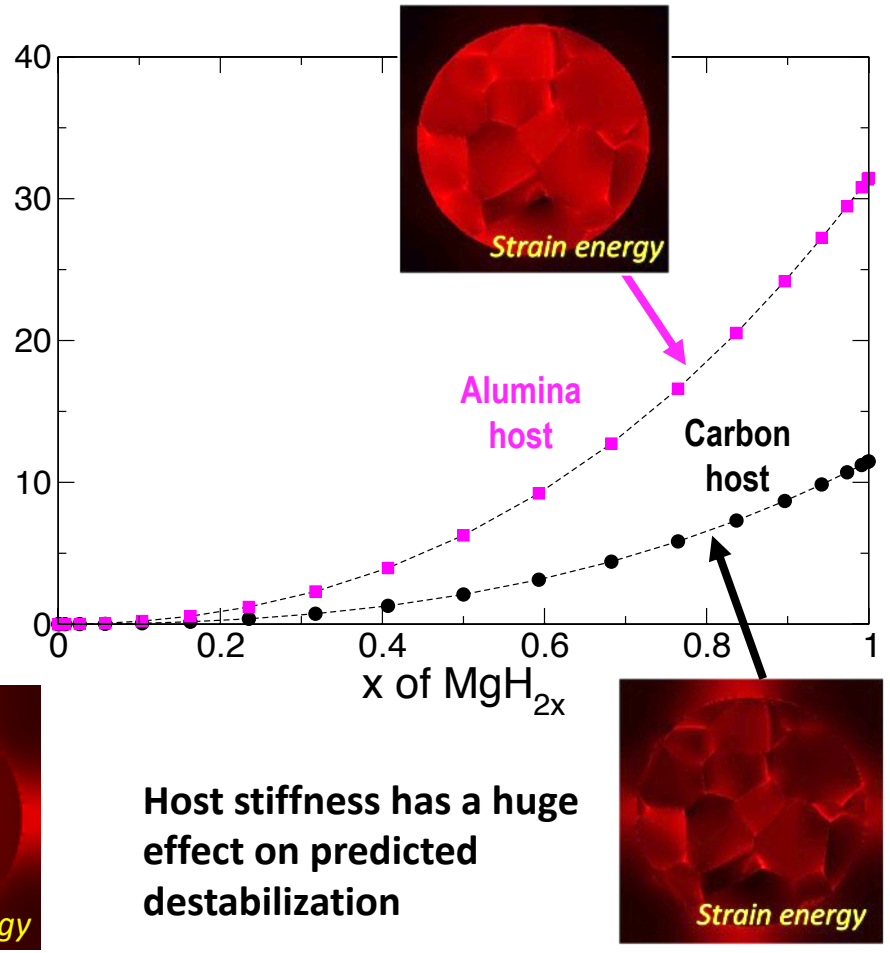
Excess surface entropy explains enthalpy-entropy compensation effect in nanoscale metal hydrides

Confinement stress: Promising strategy for destabilizing hydrides

We enhanced our confinement stress model to account for more realistic microstructures and variable host elasticity, which show large effects on thermodynamics and kinetics



Polycrystalline systems exhibit much higher local stresses, which can enhance local kinetics

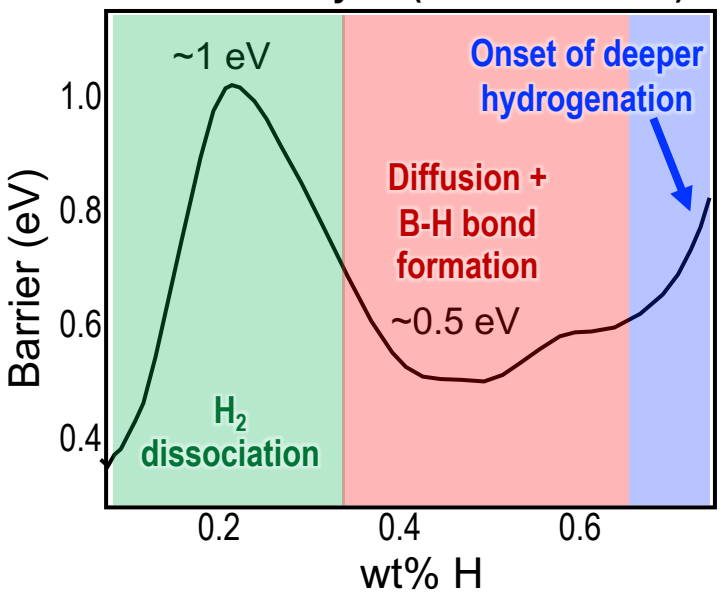


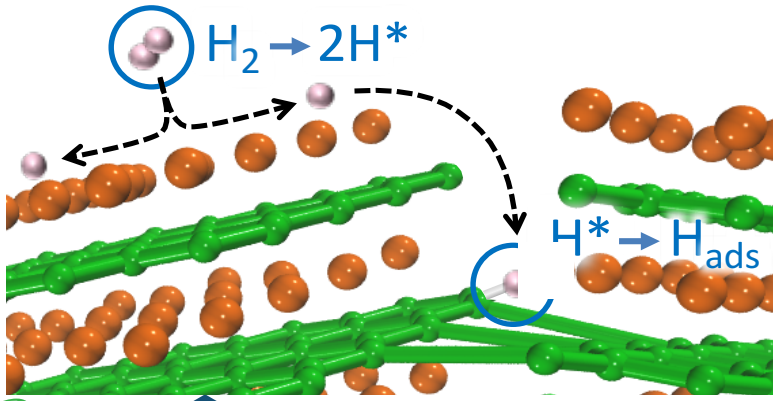
Host stiffness has a huge effect on predicted destabilization

Understanding and accelerating MgB_2 decomposition

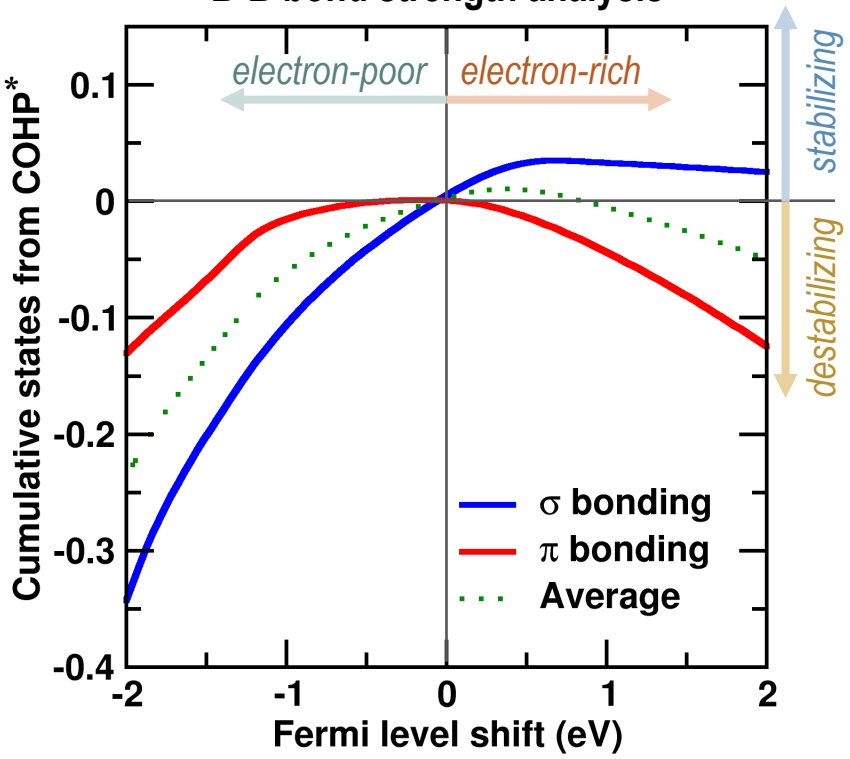
Hydrogenation beyond ~0.8 wt.% H is not limited by B-H bond formation or H_2 dissociation (confirmed by H-D isotope exchange); instead, likely limitation is from B-B bond cleavage

Kinetic analysis (from 2018 AMR)





B-B bond strength analysis



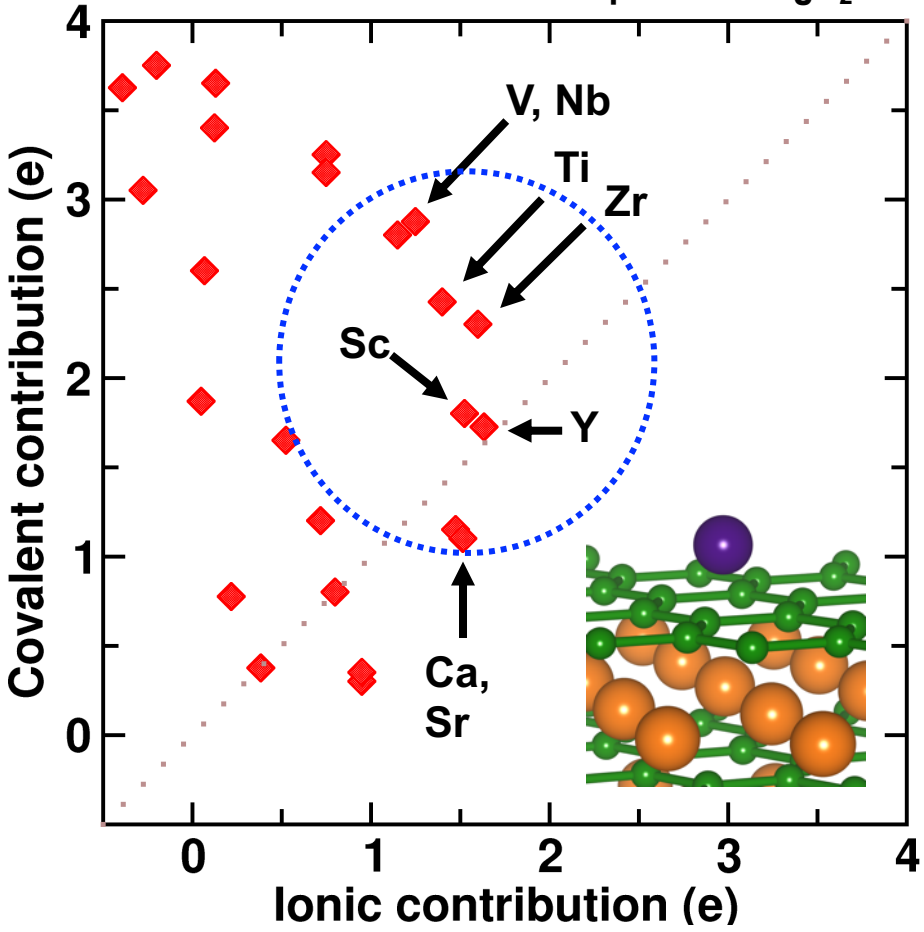
B-B bonds are weakened by charge donation/ depletion and/or changes to σ-bonding states.

Similar effect can be achieved by extracting Mg^{2+}, which may explain functionality of solvents.

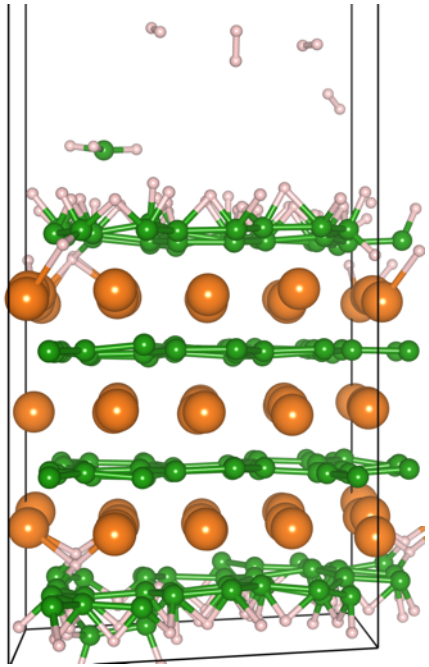
Screening metal dopants with mixed ionic-covalent character

Metal dopants for accelerated MgB_2 decomposition should mix charge donation (ionic bonding) with covalency to alter σ-bonding states

Bonding contributions for alkali, alkaline earth, & 3d/4d transition metal dopants on MgB_2



Changes in B-B XAS bond signature for MgB_2 ball-milled with dopants provide validation (early results on Ti vs. Li agree with predictions)

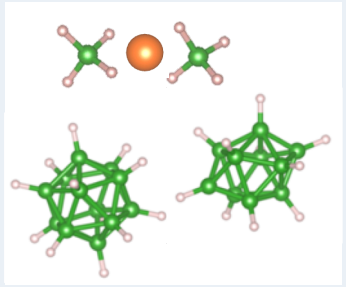


Effect on hydrogenation is being investigated via Sieverts testing and ab initio MD

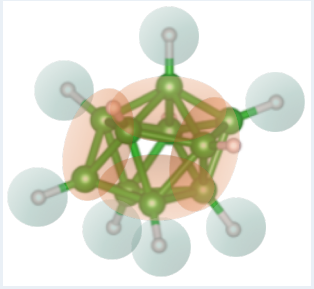
Complex hydrides: *ab initio* calculations inform scalable methods

Classical B_xH_y potentials

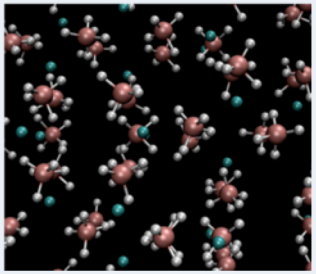
Rigid pair potentials (w/Sandia)



SAPT potentials (w/Georgia Tech)



Machine learning from dynamics trajectories (w/Tennessee State)

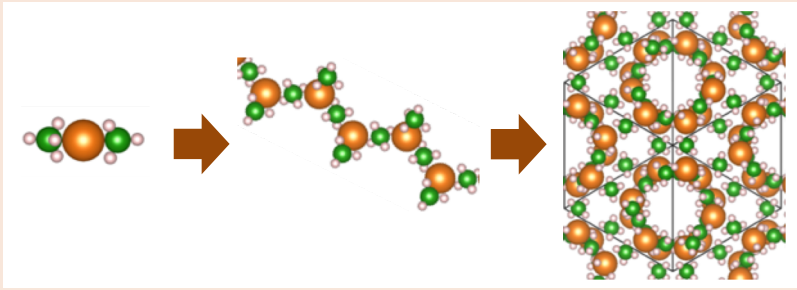


Will be used to compute energetics of:

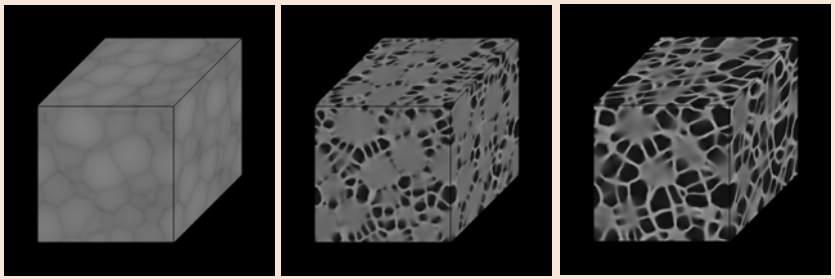
- *Complex interfaces*
- *Mixtures/alloys*
- *Amorphism*
- *Polymorphism*

Parameterized mesoscale simulations

Nucleation kinetics



Interfacial energies & solid mechanics

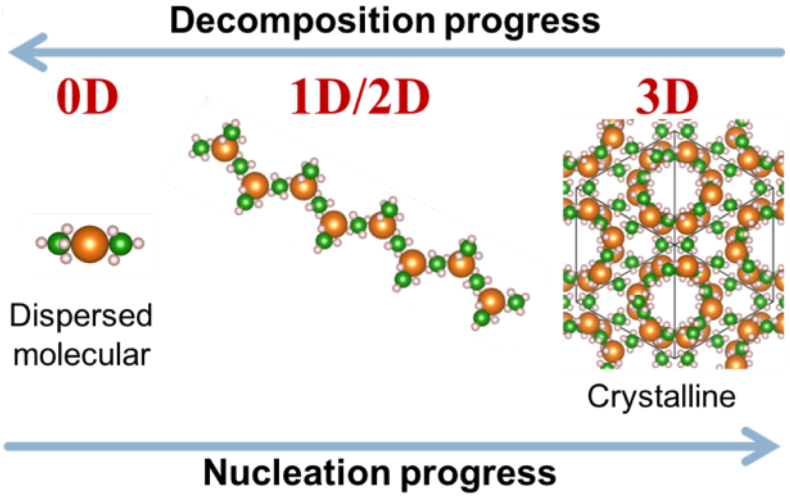


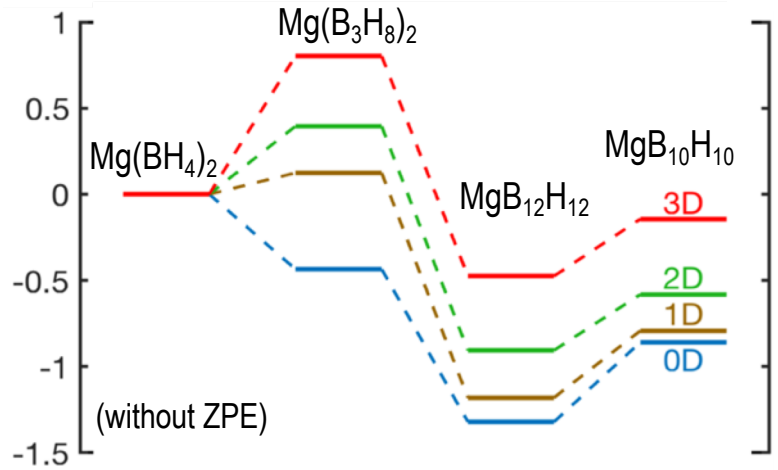
Will be used to compute kinetics of:

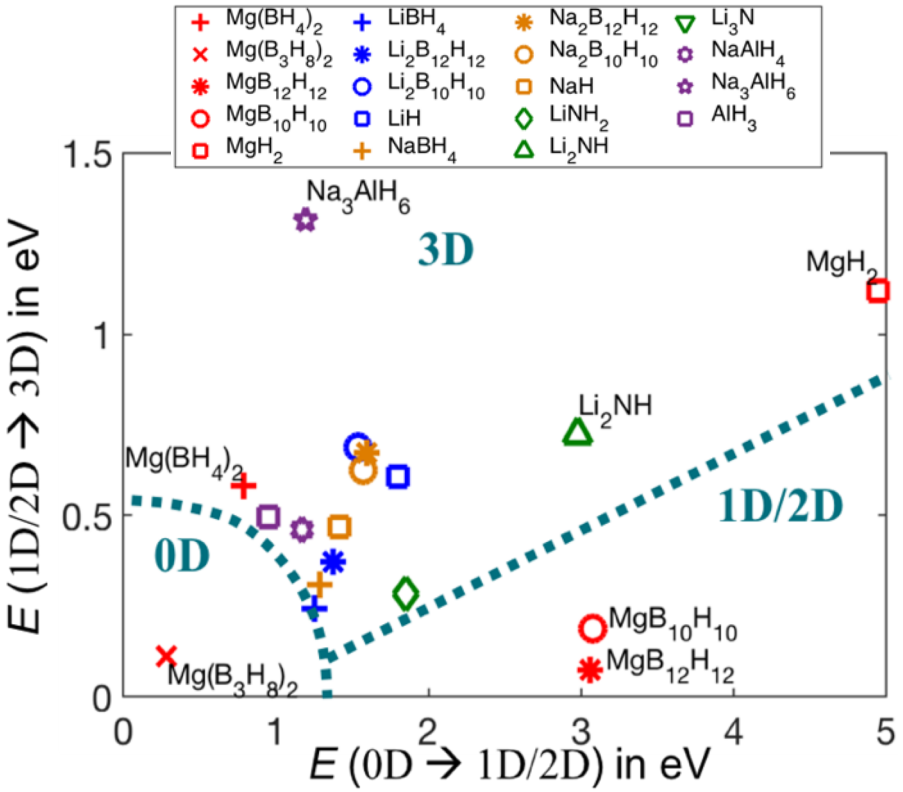
- *Isotherm uptake*
- *Microstructure evolution*
- *Mass transport*

Clustering and nucleation of intermediates

Comparisons of energetics at different "dimensionalities" from molecular to crystalline provide insights into nucleation and how reaction pathways can be tuned by morphology







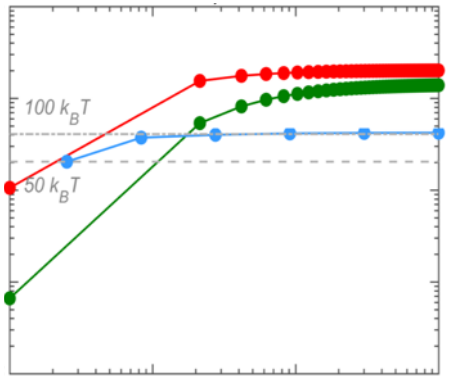
Driving force for crystallization relates to chance of forming solid solution with faster phase kinetics

Explains observations of metastable intermediates (e.g., $Mg(B_3H_8)_2$) that do not appear as crystalline

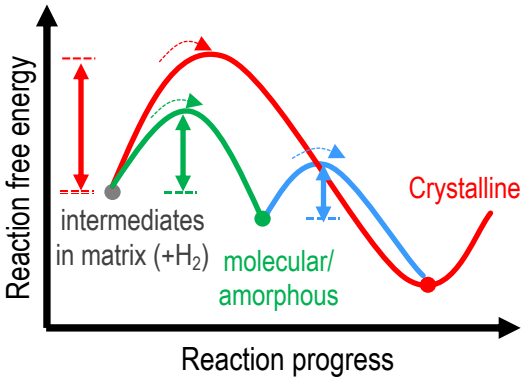
Nucleation kinetics models reveal solid phase pathways

Kinetics favor two-step condensation-crystallization mechanism of $Mg(BH_4)_2$ formation with pressure-dependent rate limitation

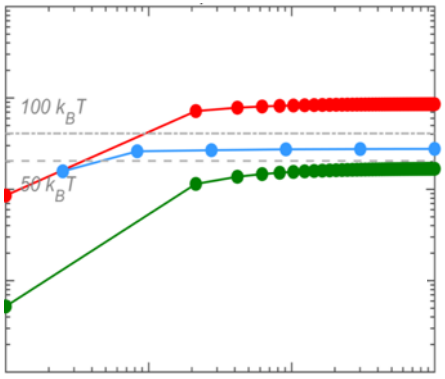
Low H_2 pressure: Chemical kinetics limit rate



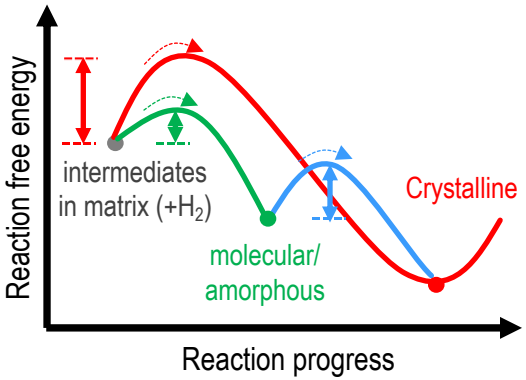
Particle radius (nm)



High H_2 pressure: Crystallization limits rate



Particle radius (nm)

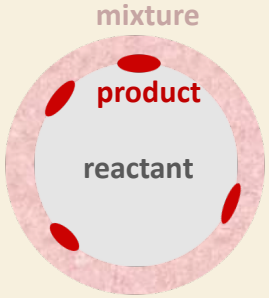


Identified three different microstructures generated by different energy landscapes

Unstable intermediates

High barrier for decomposing intermediates

High barrier for forming intermediates

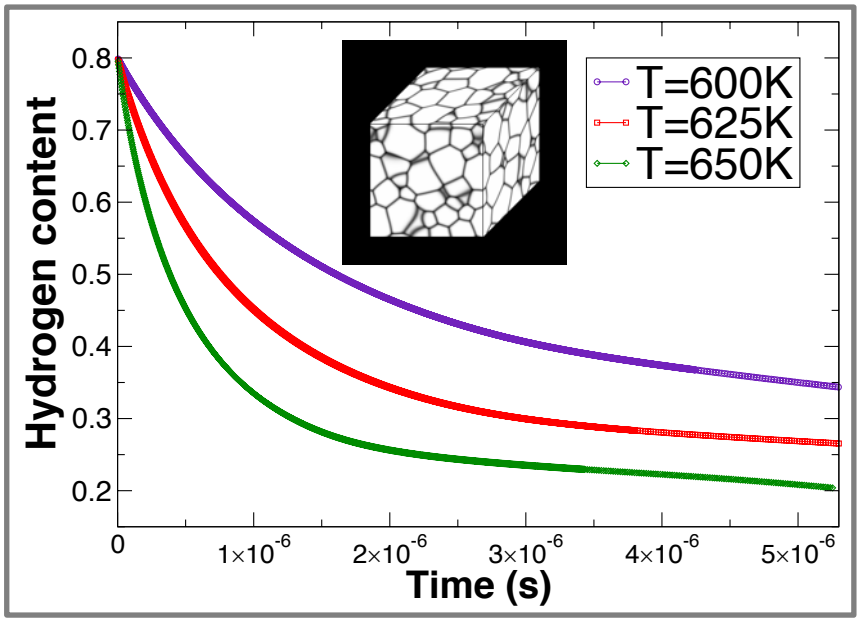


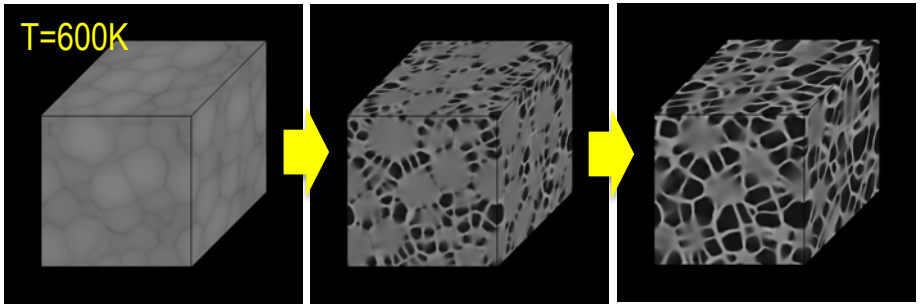
Comparisons with STXM on Li-N-H and Mg-B-H are underway

DRINK model progress: PdH_x dehydrogenation kinetics

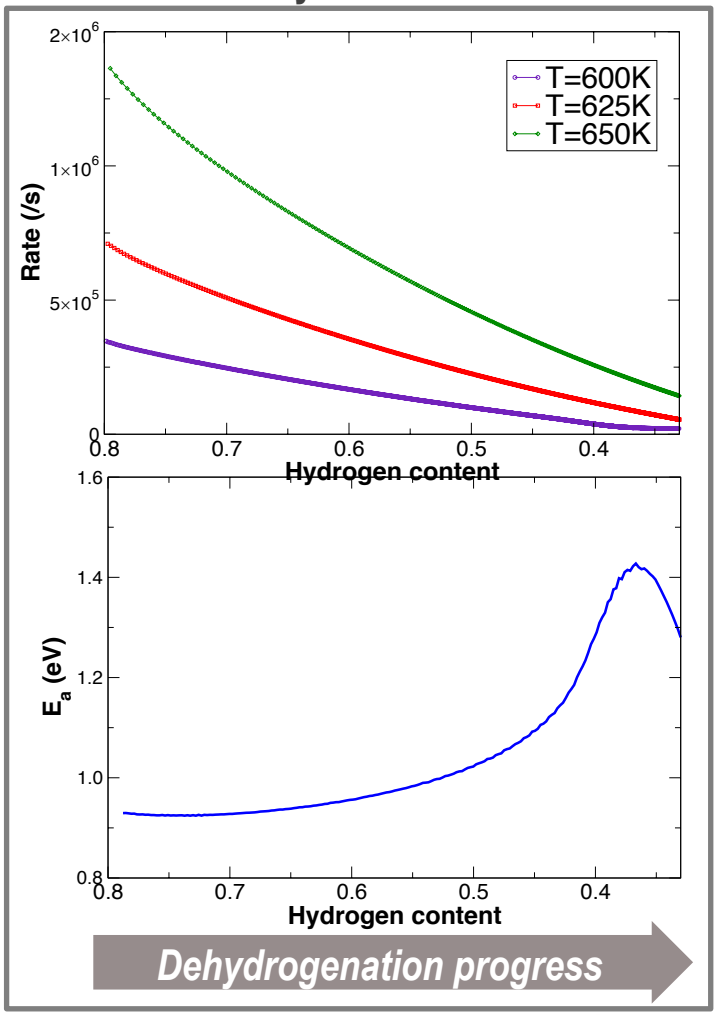
Diffuse Reactive Interface Nonlinear Kinetics model integrates chemistry, diffusion, stress, and phase transformations to simulate full reaction and identify rate-limiting factors

Simulated dehydrogenation





Kinetic analysis of simulations



Highlights of interactions with seedlings

Severa, U. Hawaii
(MgB_2/ethers)

- Regular monthly meetings
- Discovered mechanism of MgB_2 decomposition
- Investigated anthracene, THF, and inorganic additives

Christensen, NREL
($Mg(BH_4)_2$ @ ALD oxides)

- Hosted in-person meeting 11/18
- Estimated stiffness-dependent confinement and showed faster rates are from oxide reactions
- Follow-up simulations planned

Johnson, NREL
(COFs)

- Regular monthly meetings
- Computed functionality-dependent H_2 binding and structural stability in COFs

Vajo, LiOx/Caltech
(Electrolyte + hydrides)

- Phase II kickoff web meeting 1/2019
- Possible origins of solvent effects on MgB_2 decomposition
- Planned simulations of MgB_2 with iodide salts

Collaborations

HyMARC collaborations

- *Multi-lab working group focus areas on Mg-B-H system and nanoconfined hydrides*
- *Extensive collaborations on all topics (see lab logos on slides)*

U.S. collaborations

Michigan State (Prof. Hui-Chia Yu)
- *Energy landscape interpolation for phase-field model development*

Georgia Tech (Prof. Jesse McDaniel)
- *Symmetry-adapted perturbation theory (SAPT) potential development for $B_xH_y^{n-}$*

Tennessee State (Prof. Lizhi Ouyang)
- *Machine learning for structure prediction and potential development for Li/Na/MgB_xH_y compounds*

U. South Carolina (Prof. Morgan Stefik)
- *Confinement stress effects on hydride thermodynamics*
- *New NSF partnership with HyMARC*

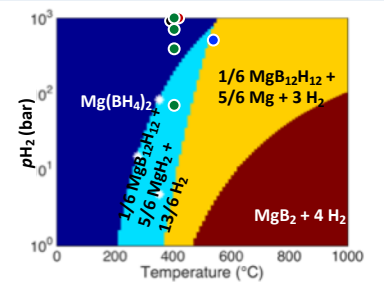
Foreign collaborations

KAIST, Korea (Profs. Eun Seon Cho, Seung Min Han, and Bong Jae Lee)
- *Microstrain and thermal transport in confined metal hydrides*
- *Multi-institutional partnership launched in September 2018*
- *Held workshop in October 2018 to draft CRADA*

AIST, Japan (Minoru Otani)
- *Hybrid quantum-classical simulations of catalytic interfaces for hydrogen carriers*

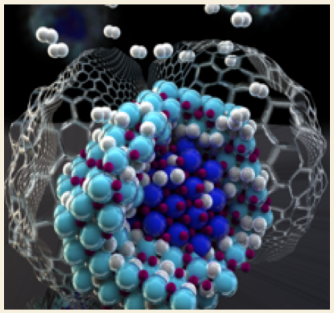
Helmholtz Zentrum Geesthacht (Martin Dornheim, Anna-Lisa Chaudhary)
- *Mixed metal hydride reactions and phase evolution*
- *Held workshop in December 2018 to identify research partnerships*

Proposed future work



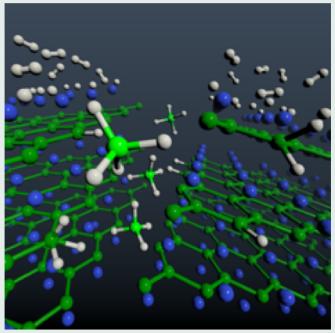
Phase diagram prediction/validation

- Establish **best practices** for DFT enthalpy predictions across multiple hydrides
- Complete **surface entropy** calculations for computation and validation of **size-dependent phase diagrams**



Tuning thermodynamics

- Apply new potentials to predict free energies of Li/Na/MgB_xH_y **eutectic mixtures**
- Estimate and validate potential of **amorphization** to alter ΔH and ΔS
- Validate size-dependent tunability for key hydrides by deconvoluting contributions of **surfaces and confinement stress**

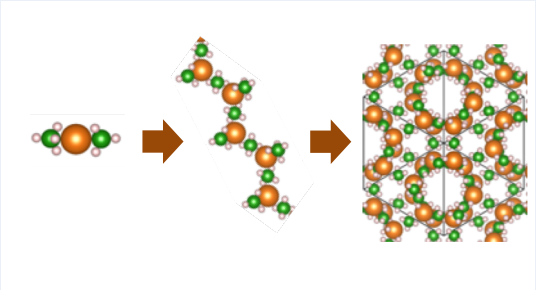


Tuning kinetics

- Extend **additives** study to dehydrogenation and continue model validation alongside direct *ab initio* molecular dynamics simulations
- Compute **Lewis acid/base interactions** with oxide hosts
- Compute **nucleation barriers** for Li-N-H and compare **microstructures** with STXM
- Parameterize **DRINK model** for partial hydrogenation of complex hydride
- Compute reaction landscape and catalyst stability for **formate and formic acid** electrocatalysis (H_2 carriers)

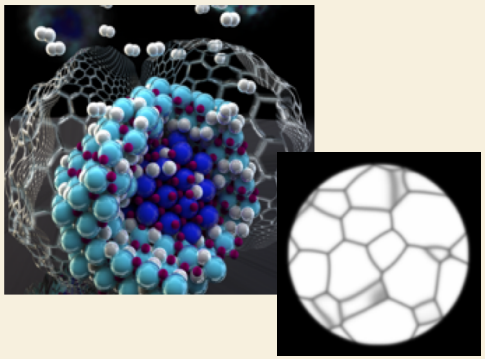
Summary: Moving the bar on metal hydrides

New tools & capabilities



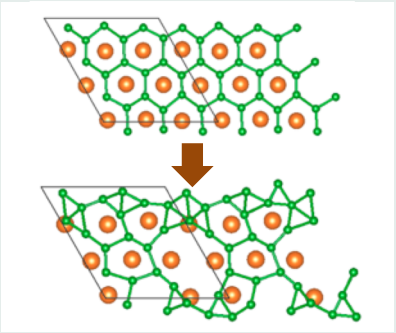
- Clustering and crystallization energies from morphology-dependent thermodynamics
- Advanced nucleation model
- Diffuse Reactive Interface Nonlinear Kinetics (DRINK) model

Materials tunability & design



- Quantified surface influence on nanoscale hydride enthalpy
- Assessed effects of crystallinity and host stiffness on confinement enthalpy
- Screened metal additives for effect on MgB_2 destabilization

New foundational understanding



- Showed origin of enthalpy-entropy compensation for nanoscale hydrides
- Demonstrated charge-reactivity interplay in MgB_2
- Determined link between nucleation pathways and microstructure

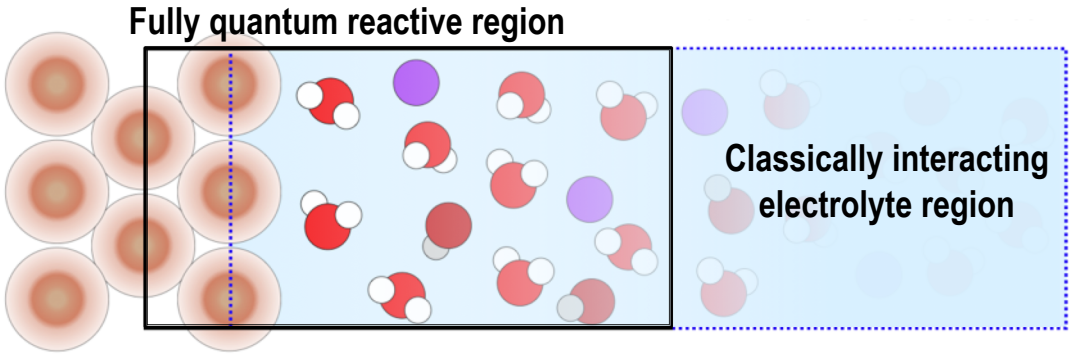
Also authored theory sections in new reviews on nanoscale hydrides and sorbents

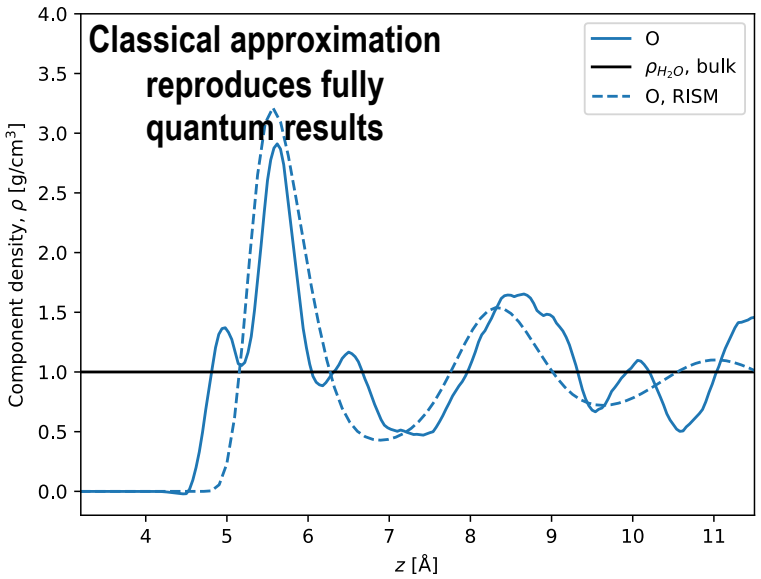
Technical backup slides

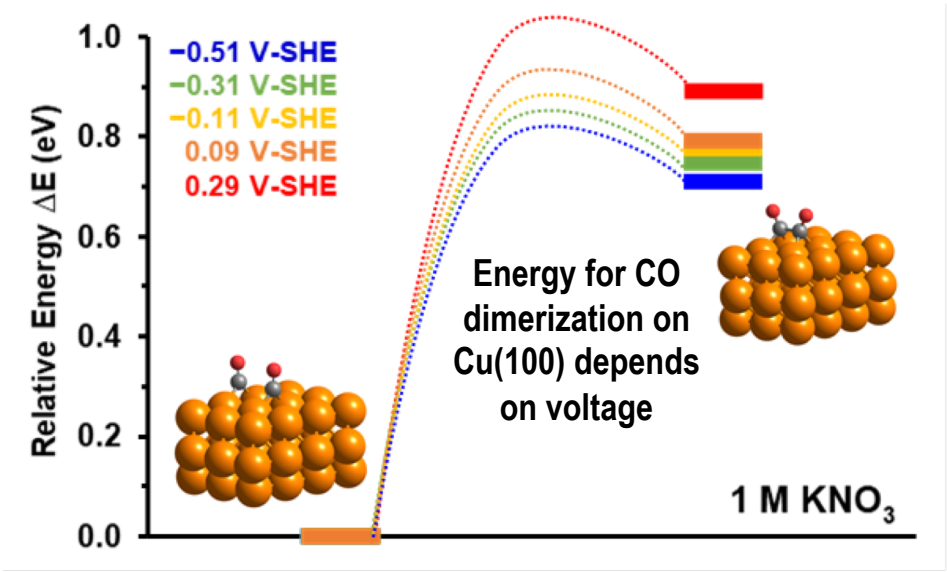
Benchmarking theory for electrocatalysis of H_2 carriers

We are exploring quantum-classical hybrid approaches for computing electrocatalytic overpotentials and voltage/temperature effects on formate and formic acid production

ESM+RISM Method (w/AIST Japan)

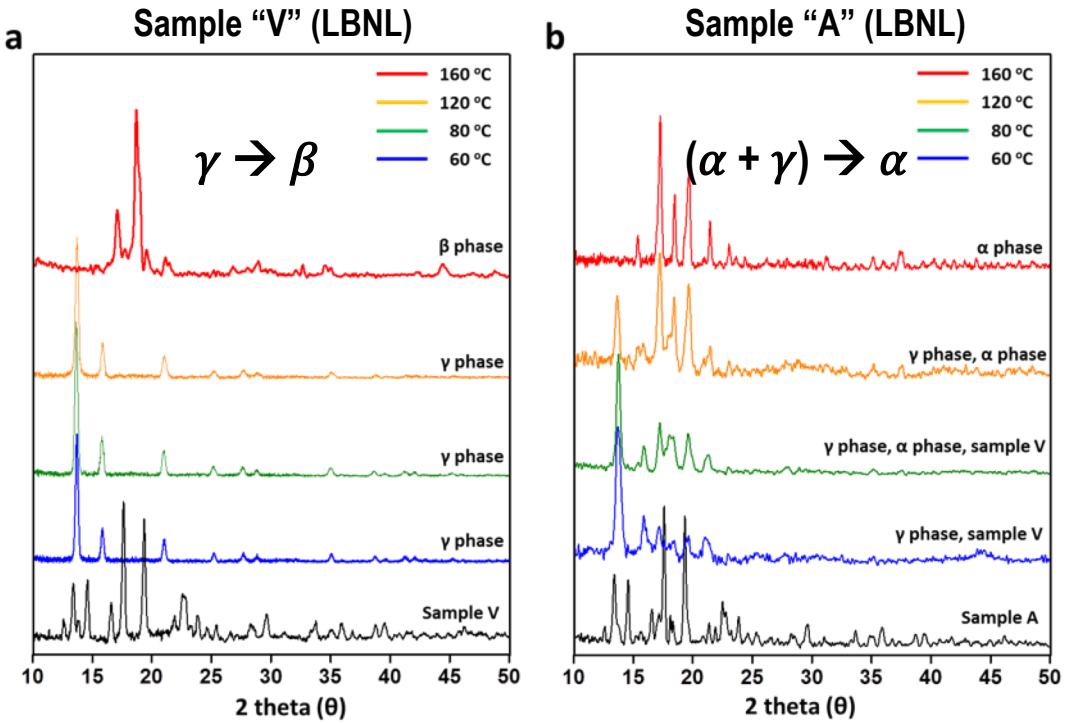


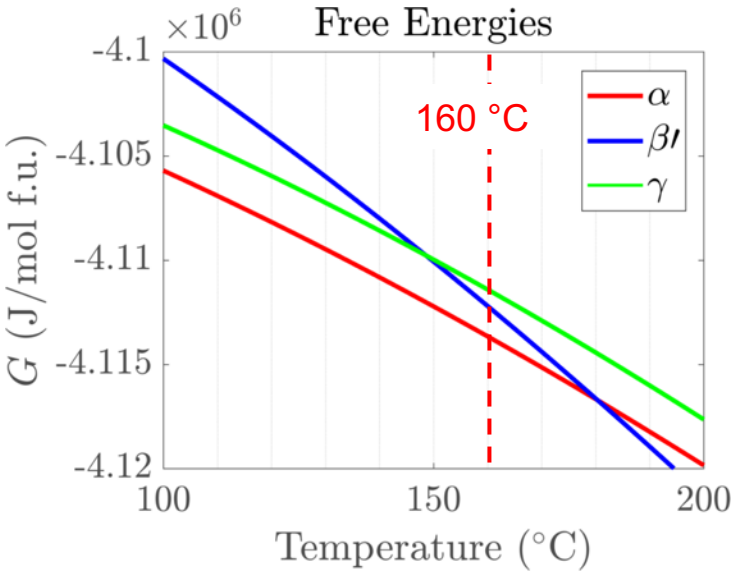




Tuning pathways via nucleation: Polymorphism in $Mg(BH_4)_2$

We are working with LBNL to understand polymorphic phase expression in $Mg(BH_4)_2$ under different synthesis conditions by applying our advanced nucleation model

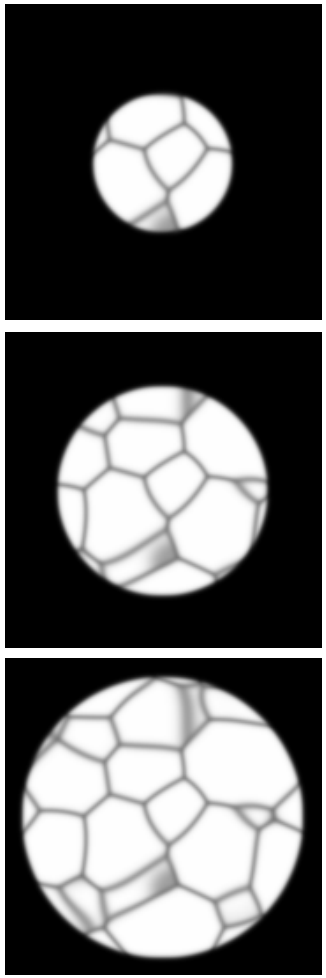


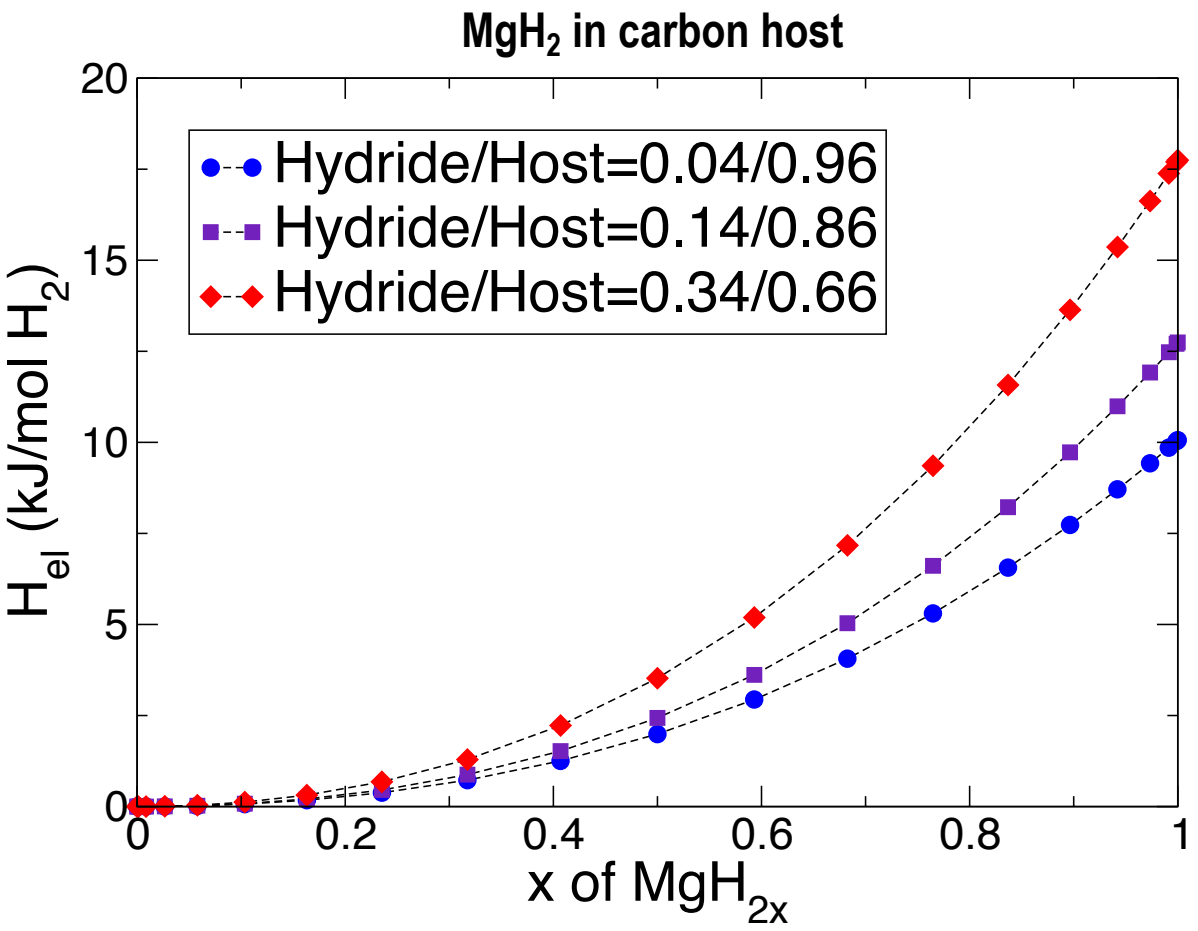


Different nucleation barriers for different polymorphs accounts for observed phase expression (manuscript in preparation)

Confinement stress: Effect of hydride loading

Higher hydride loading in carbon significantly enhances enthalpy destabilization





This same framework can be used to study the effects of powder packing density on hydride confinement stresses