Improving the Kinetics and Thermodynamics of Mg(BH$_4$)$_2$ for Hydrogen Storage

2017 DOE Hydrogen Annual Merit Review

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Project ID# ST118

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Lawrence Livermore National Laboratory

Overview

Timeline

Project start date: 07/01/2014
Project end date: 07/01/2017

Barriers addressed

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

Budget

Total project budget: $1.2M
Total federal share: $1.2M

Total received: $200K (FY14), $400K (FY15), $400K (FY16), $200K (FY17)
Total funds spent (as of 3/17): $937K
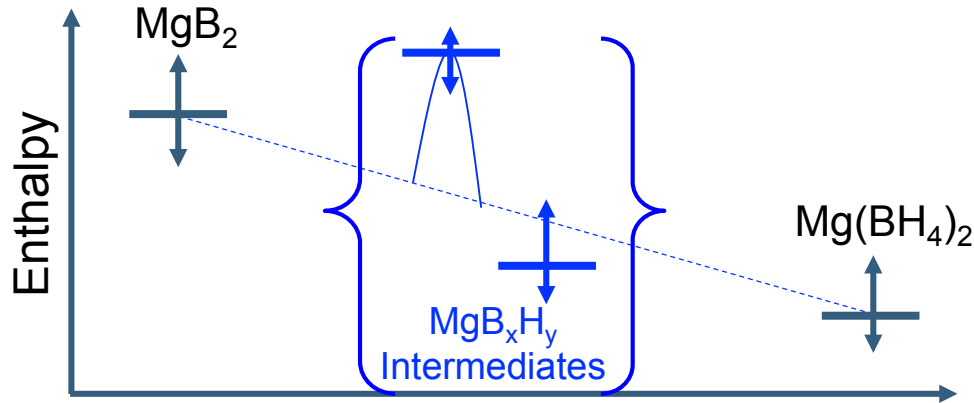
Team

Project Lead:
Lawrence Livermore National Laboratory

Funded Partners:
Sandia National Laboratories
University of Michigan

Relevance and approach

We integrate theoretical and experimental tools to probe mechanisms and pathways in MgB_2/$Mg(BH_4)_2$ towards rational tuning of the energy landscape

How, when, and why can these help?

- *Nanoscaling*
- *Additives*
- Microstructure (physical arrangement)
- State (crystal/amorphous/molecular)
- Mechanical effects/confinement (stress)
- High H_2 pressure (far from equilibrium)

| Phase I: Thermodynamics	Phase II: Bulk & nanoscale kinetics	Phase III: Additives & optimization
Predict thermodynamics of (de)hydrogenation	**Understand mechanisms & kinetic pathways**	**Assess how energy landscape can be tuned**
• *Baseline bulk phase diagram and phase fraction prediction by high-level computation* • *Validation and calibration from testing and literature data*	• *Study initial hydrogenation (single-phase) and deeper hydrogenation (multiphase)* • *Use theory, spectroscopy, and kinetic rate analysis*	• *Investigations focused on nanoscaling and additives* • *Theory studies of mechanical and microstructural effects* • *Identify & test promising improvement strategies*

Approach: Combining chemistry and materials science

Our approach adapts tools from chemistry and materials science, with particular emphasis on less-well-understood rehydrogenation
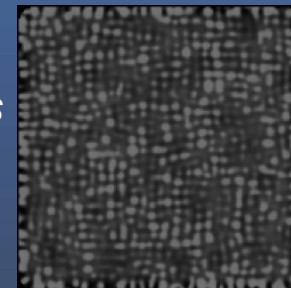
Local chemistry of B_xH_y complexes

- *Single-phase reactions*
- *DFT/ab initio molecular dynamics*
- *Soft X-ray spectroscopy & NMR*
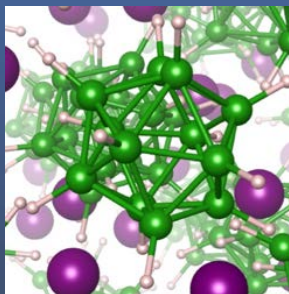
Evolution of solid phases

- *Multi-phase reactions*
- *Ab initio thermodynamics and phase-field models*
- *Phase identification via XRD, NMR, FTIR*

Multiscale Theory

Validation

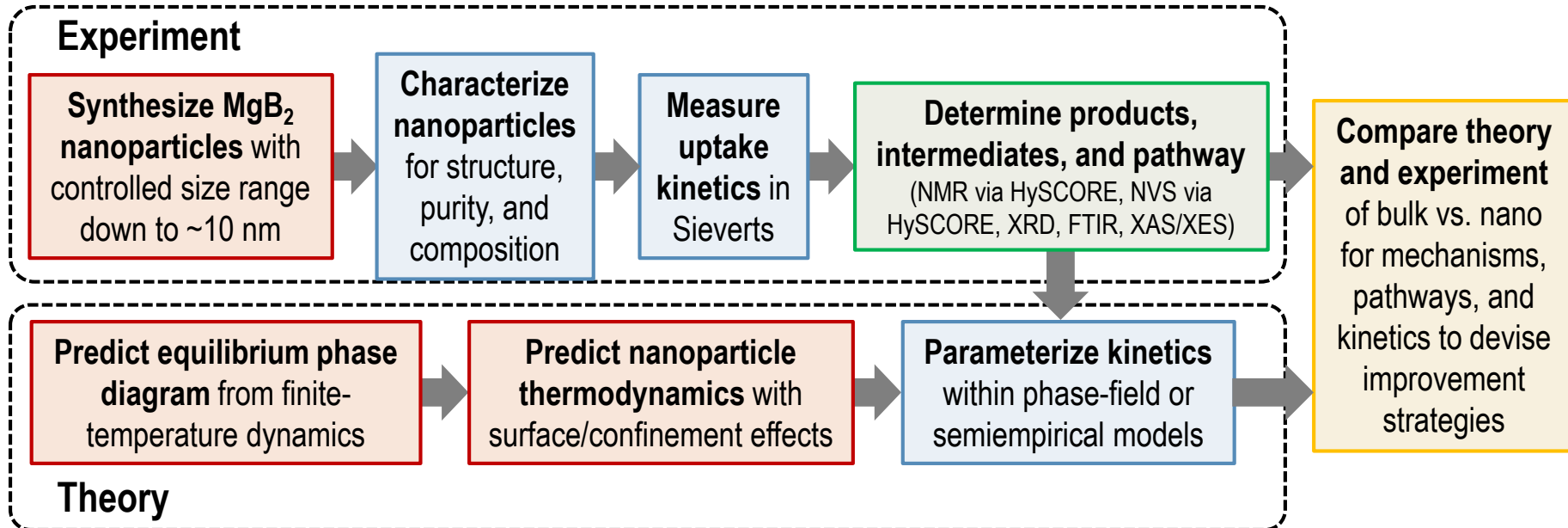Characterization

Parameterization

Controlled Synthesis

- *Bulk materials*
- *Unconfined size-selected nanoparticles*
- *Additives/catalysts*

Tightly integrated with efforts on the Mg-B-H system within HyMARC (theory tools & high-pressure testing) and HySCORE (B_xH_y dehydrogenation chemistry & NMR)

Approach: MgB_2 nanoparticle synthesis and understanding

To boost capacity and isolate size effects without confinement, we use unique nanoparticle synthesis that integrates with theory for mechanistic insight and improvement strategies
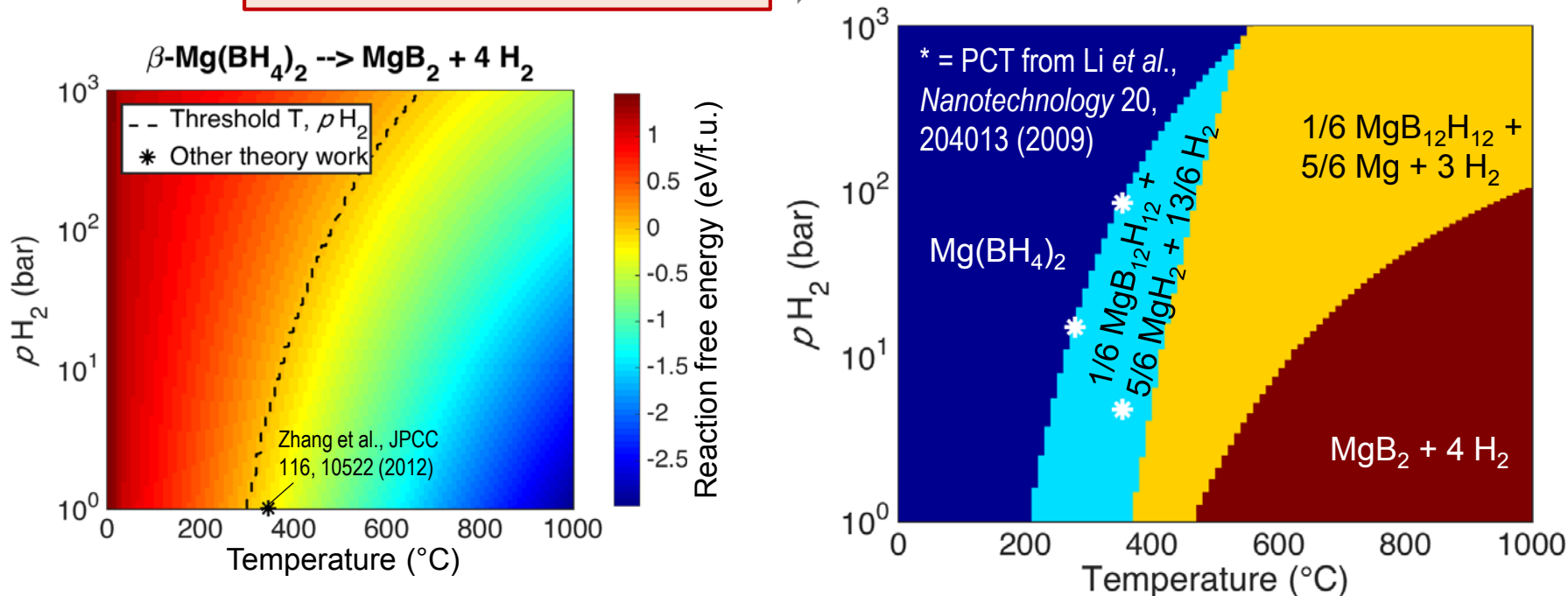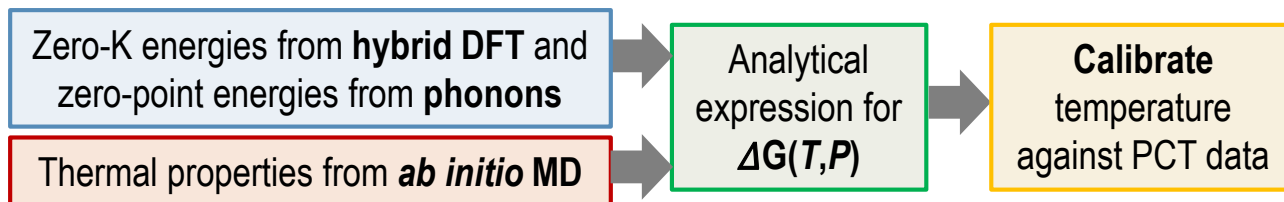
Experiment

Synthesize MgB_2 nanoparticles with controlled size range down to ~10 nm	**Characterize nanoparticles** for structure, purity, and composition	**Measure uptake kinetics** in Sieverts	**Determine products, intermediates, and pathway** (NMR via HySCORE, NVS via HySCORE, XRD, FTIR, XAS/XES)	**Compare theory and experiment** of bulk vs. nano for mechanisms, pathways, and kinetics to devise improvement strategies
Predict equilibrium phase diagram from finite-temperature dynamics	**Predict nanoparticle thermodynamics** with surface/confinement effects	**Parameterize kinetics** within phase-field or semiempirical models		

Theory

Nanoparticle synthesis approach:

1. *Use **"surfactant-assisted" ball milling** to create unconfined MgB_2 nanoparticles (Y. Wang et al., Nanotechnology **18**, 465701 (2007))*

2. *Employ solvent dispersion techniques to separate out nano and micro size fractions*

3. *Remove surfactants and solvents from the nanoparticle material*

# Accomplishment: Reference phase diagram of Mg-B-H

Used combined computational-experimental approach to obtain a reliable baseline phase diagram for further thermodynamic predictions

Zero-K energies from **hybrid DFT** and zero-point energies from **phonons**

Thermal properties from *ab initio* MD

→ Analytical expression for $\Delta G(T,P)$

→ **Calibrate** temperature against PCT data

β-Mg(BH$_4$)$_2$ --> MgB$_2$ + 4 H$_2$

- - Threshold T, p H$_2$
* Other theory work

Reaction free energy (eV/f.u.)

Zhang et al., JPCC 116, 10522 (2012)

pH$_2$ (bar)

Temperature (°C)

* = PCT from Li *et al.*, *Nanotechnology* 20, 204013 (2009)

Mg(BH$_4$)$_2$

1/6 MgB$_{12}$H$_{12}$ + 5/6 MgH$_2$ + 13/6 H$_2$

1/6 MgB$_{12}$H$_{12}$ + 5/6 Mg + 3 H$_2$

MgB$_2$ + 4 H$_2$

pH$_2$ (bar)

Temperature (°C)

- **MgB$_{12}$H$_{12}$ is stable over a wide (P,T) range, but other MgB$_x$H$_y$ intermediates are not stably formed as isolated solid phases and must exist as molecules or at interfaces**
- **Including thermal anharmonic effects dramatically changes behavior for T > 300°C**
- **Density affects anharmonic modes, suggesting a new pathway for tuning thermodynamics**

Accomplishment: Validation experiments at high H_2 pressure

Successfully validated predicted phase fractions under high-pressure H_2 with levels of MgB_xH_y intermediates depending on (T,P) conditions
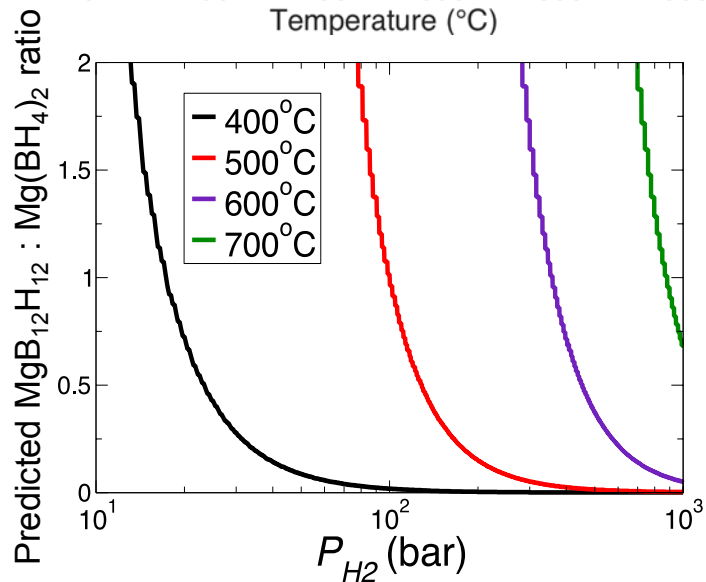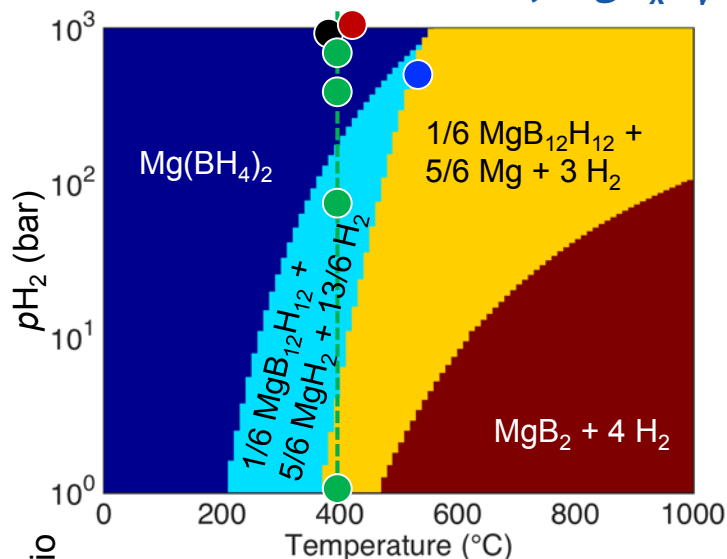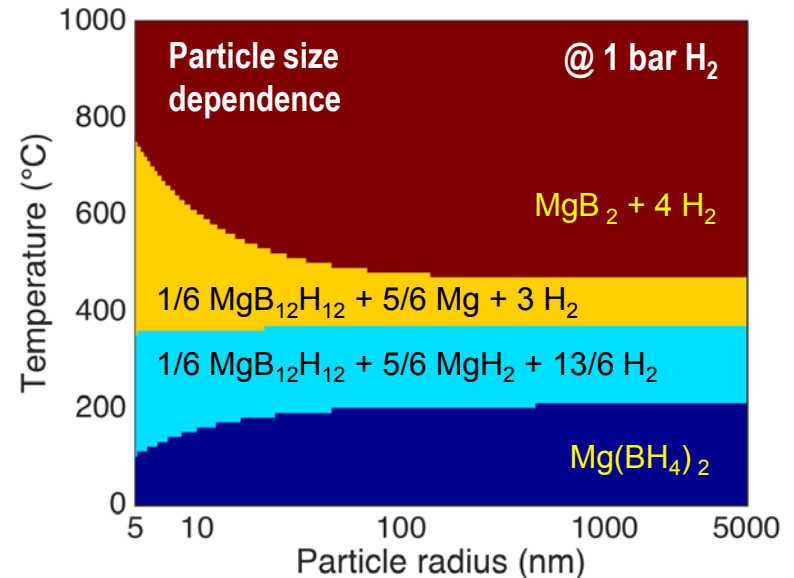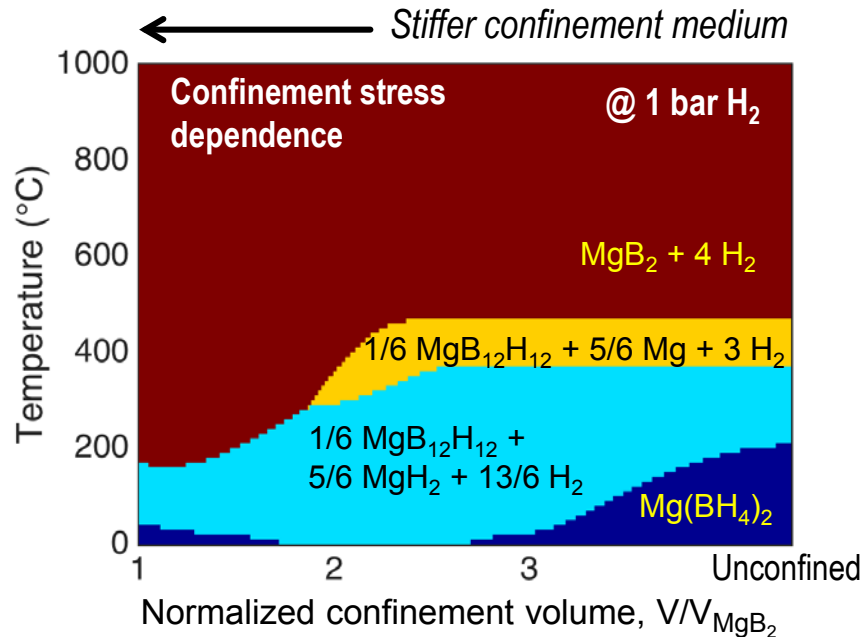

Experimental validation at high *P*

Sample	Method	T (°C)	pH$_2$ (bar)	Relative mole fractions of products (%)		
				MgB$_x$H$_y$	Mg(BH$_4$)$_2$	
● Severa (2010)[1]	^{11}B NMR	390	900	7	93	
● SNL #1	^{11}B NMR	420	1000	13	87	
● SNL #2	^{11}B NMR	540	500	53	47	
				Mg(BH$_4$)$_2$	MgB$_2$	MgH$_2$
● SNL/HyMARC #3 (White/Stavila)	XRD	400	1	75	25	0
		400	70	0	10	90
		400	350	66	34	0
		400	700	84	16	0

[1]Severa *et al.*, *Chem. Commun.* **46**, 421 (2010)

- **Predicted phase diagram and phase fractions are in excellent agreement with NMR & XRD**
- **Meets Go/No-Go for theory-experiment agreement**
- **Method for phase fraction prediction published as cover article in *Adv. Mater. Interfaces***

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Accomplishment: Predicted nanosizing/confinement effects on pathway

Theory predicts that nanosizing increases prevalence of $MgB_{12}H_{12}$ intermediate, inhibiting full cycling but decreasing onset temperature/pressure for partial (de)hydrogenation

Stiffer confinement medium →

Confinement stress dependence — @ 1 bar H_2

$MgB_2 + 4 H_2$
$1/6\ MgB_{12}H_{12} + 5/6\ Mg + 3\ H_2$
$1/6\ MgB_{12}H_{12} + 5/6\ MgH_2 + 13/6\ H_2$
$Mg(BH_4)_2$

Temperature (°C) vs Normalized confinement volume, V/V_{MgB_2} (Unconfined)

Particle size dependence — @ 1 bar H_2

$MgB_2 + 4 H_2$
$1/6\ MgB_{12}H_{12} + 5/6\ Mg + 3\ H_2$
$1/6\ MgB_{12}H_{12} + 5/6\ MgH_2 + 13/6\ H_2$
$Mg(BH_4)_2$

Temperature (°C) vs Particle radius (nm)

- **Trends explain published dehydrogenation data showing nanoconfinement has biggest destabilizing effect on larger H-rich phases**
- **Nano-MgB_2: Higher thermodynamic driving force will aid partial rehydrogenation kinetics**
- **Confinement in very stiff medium could be thermodynamically beneficial**

Reaction (@ 1 bar H_2)	Exp. ΔT upon nanoconfinement	
	@ 2 nm (DSC)[1]	@ 4 nm (TPD)[2]
$Mg(BH_4)_2 \rightleftharpoons (MgB_{12}H_{12}, MgH_2, H_2)$	-20 °C	-94 °C
$(MgB_{12}H_{12}, MgH_2, H_2) \rightleftharpoons (MgB_{12}H_{12}, Mg, H_2)$	-5 °C	~0 °C

[1]Fichtner et al., Nanotechnology 20, 204029 (2009)
[2]Wahab et al., J. Mater. Chem. A 1, 3471 (2013)

Accomplishment: Developed synthesis procedure for MgB$_2$ nanoparticles

TEM confirms successful synthesis of MgB$_2$ nanoparticles that are < 50 nm in diameter

Procedure:

1. Combine high-purity MgB$_2$ with heptane, oleic acid, and oleylamine in Ar glovebag

2. Use tungsten carbide milling pot and milling balls to ball mill for 20 hrs (for 2 hr increments with 1 hr rest in between)

3. Disperse product in heptane, ultrasonicate, and filter out insolubles (bulk particles)

4. Centrifuge at 5000 rpm for 25 minutes, producing deposit and remaining solution

5. Remove material that deposits (d > 200 nm) coated with surfactant

6. Recover particles from solution (d < 50 nm) by washing 3x with EtOH

d < 50 nm

100 nm

100 nm
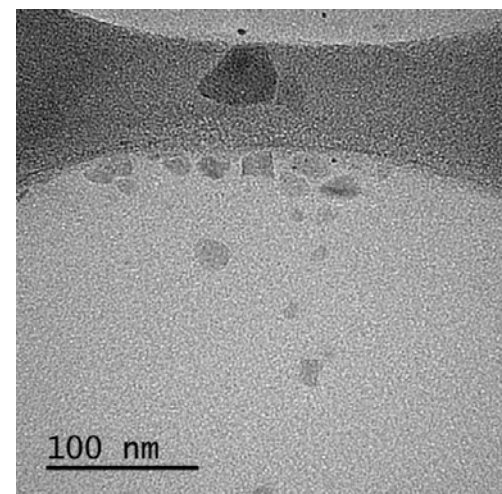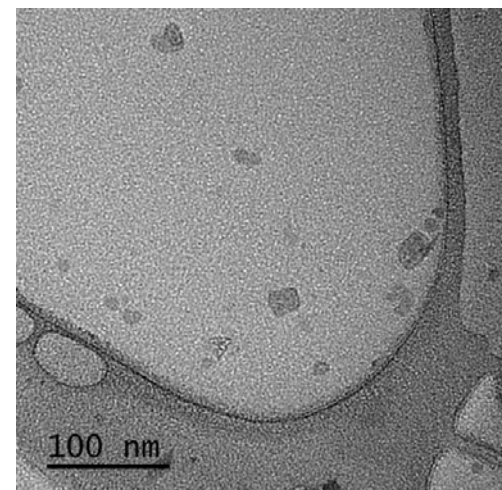
- **Can now synthesize gram-level amounts to study kinetics and pathways jointly w/ theory**
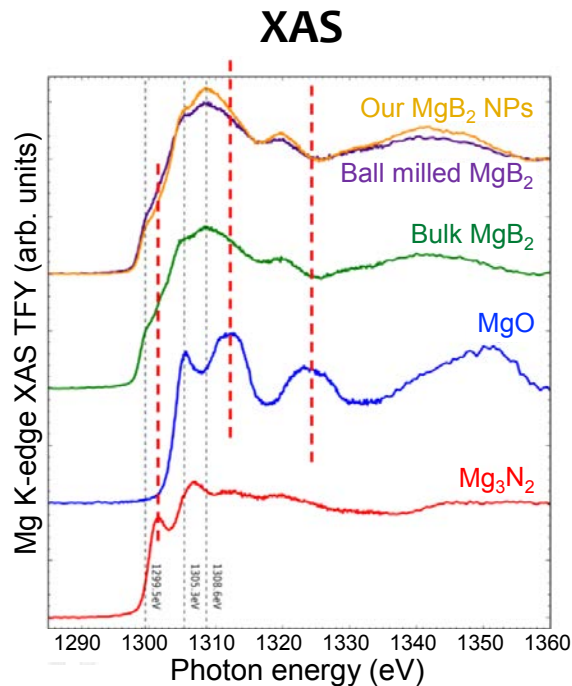- **Enables Phase III: including additives with the MgB$_2$ nanoparticles**

FTIR shows that NP synthesis removes oleic acid and oleyl amine surfactants, dispersion solvent (heptane), and recovery solvent (ethanol), while avoiding B oxidation
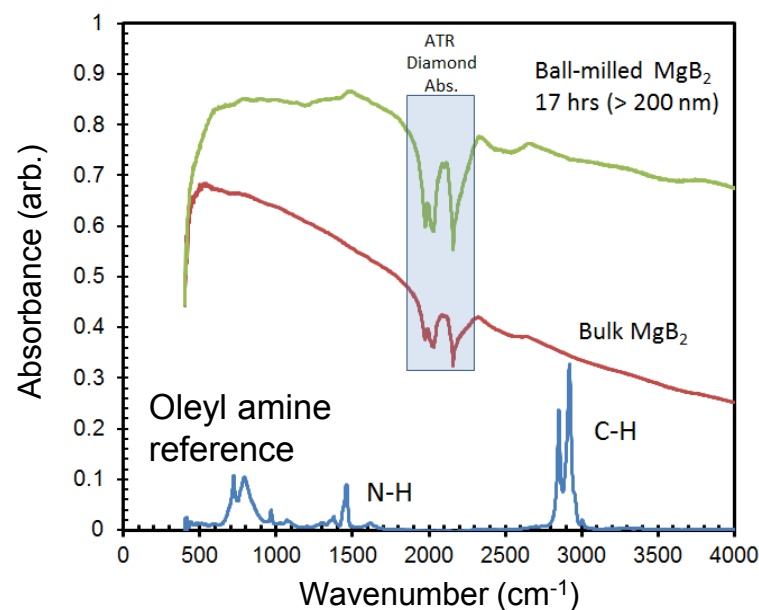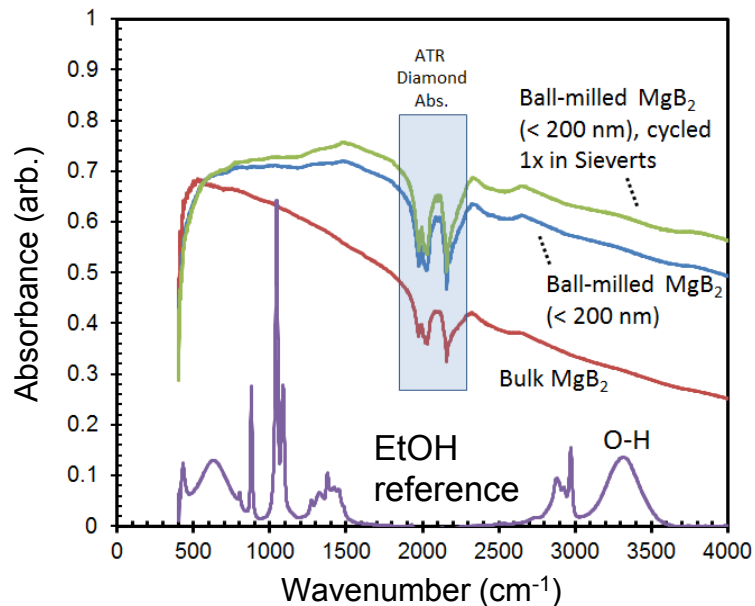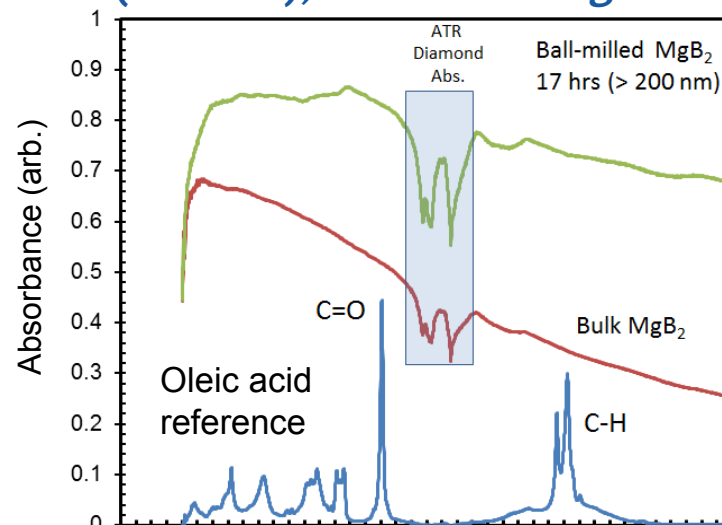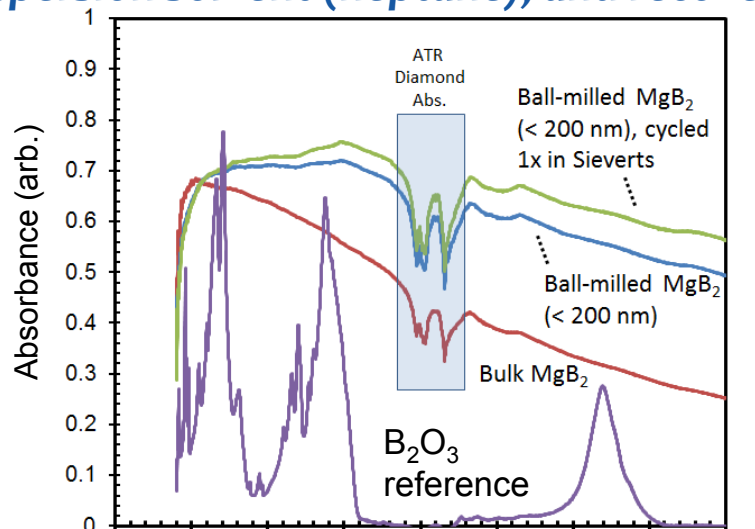
Accomplishment: Confirmed purity of synthesized MgB$_2$ nanoparticles

XAS and elemental analysis further confirm surfactant/solvent removal and show we are not oxidizing or nitriding Mg, but there is ~ 5 mole % of inert C

XAS

Mg K-edge XAS TFY (arb. units) vs Photon energy (eV)

Our MgB$_2$ NPs
Ball milled MgB$_2$
Bulk MgB$_2$
MgO
Mg$_3$N$_2$

No evidence of N or O contamination of Mg

Elemental Analysis

Sample	C (mol.%)	H (mol.%)	N (mol.%)
MgB$_2$ nanoparticles (< 200 nm)	5.2	2.8	Not detected
MgB$_2$ nanoparticles (< 200 nm) after full cycle at 365 °C, 140 bar H$_2$	5.2	3.7	Not detected
Bulk MgB$_2$	Not detected	Not detected	Not detected

- **Erosion of milling balls (stainless steel or tungsten carbide) was initially a major problem, producing high levels (25 mol.%) of metal contamination**
- **Procedures were developed to reduce metal contamination to < 0.5 mol.%**
- **Remaining C contaminant is unaffected by cycling and therefore deemed inert**

Nano-MgB$_2$ shows reduction of activation barriers and significant kinetic improvement for initial hydrogen uptake (0.7 – 0.9 wt.%H)
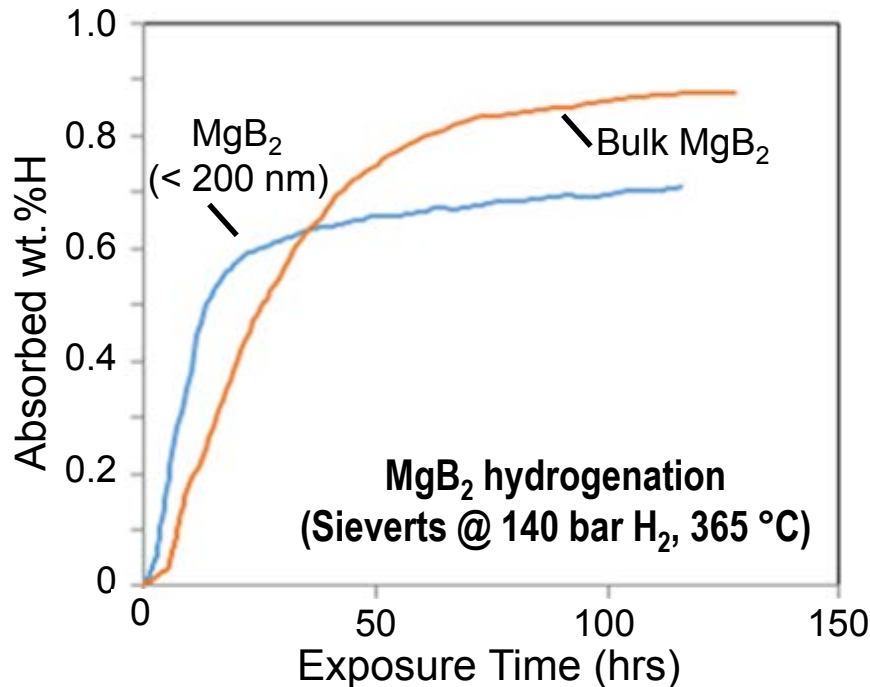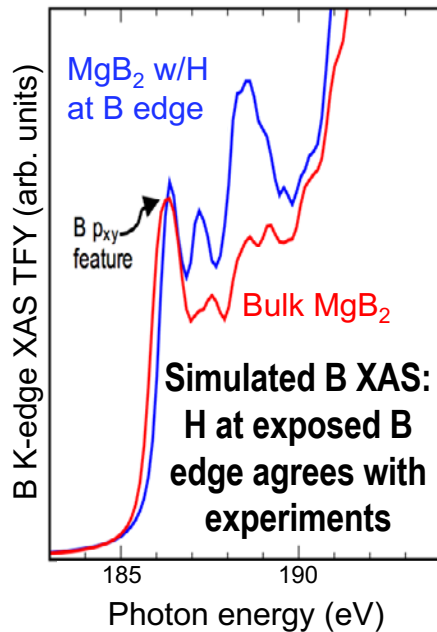

- **Nanosizing improves initial hydrogenation rates by ~2× and exhibits ~3× lower barriers**
- **Running higher-pressure uptake and chemical analysis via FTIR, XRD, and NMR (HySCORE)**
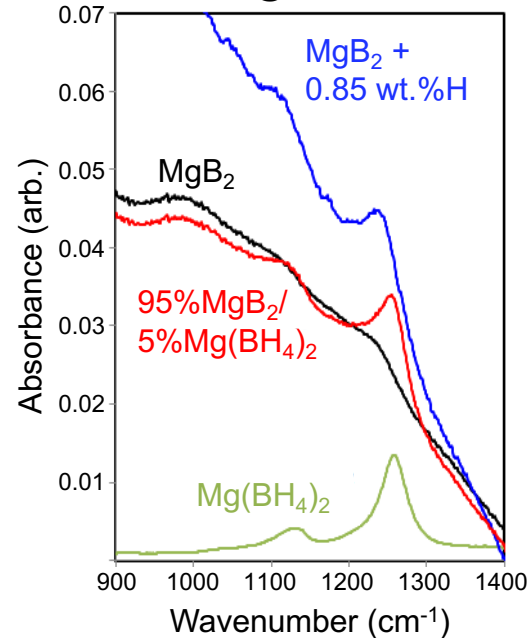- **Plan to check for agglomeration upon hydrogenation of nano-MgB$_2$**
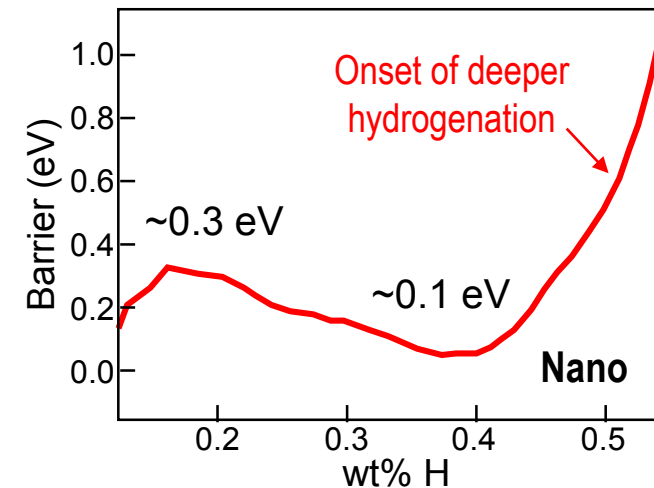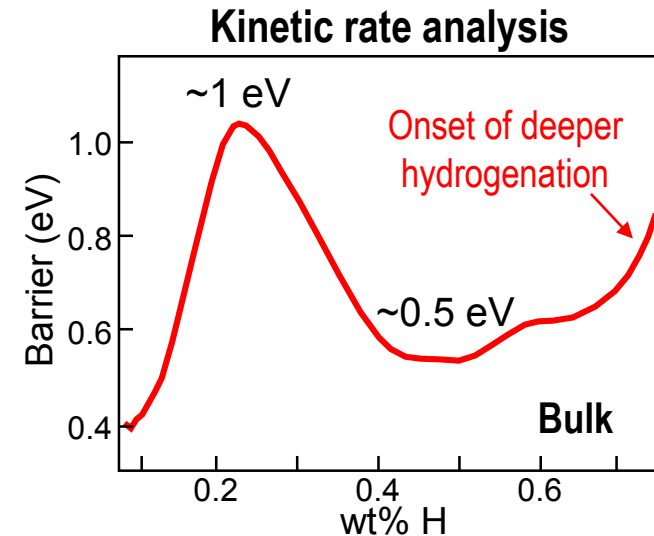
Accomplishment: Determined initial hydrogenation mechanism for MgB$_2$

Bonding probes (FTIR, XAS/XES) w/distinct depth sensitivities (nm to mm) were combined with theory for mechanistic understanding of MgB$_2$ uptake within single-phase regime
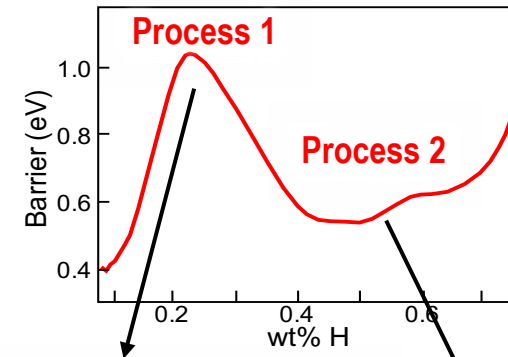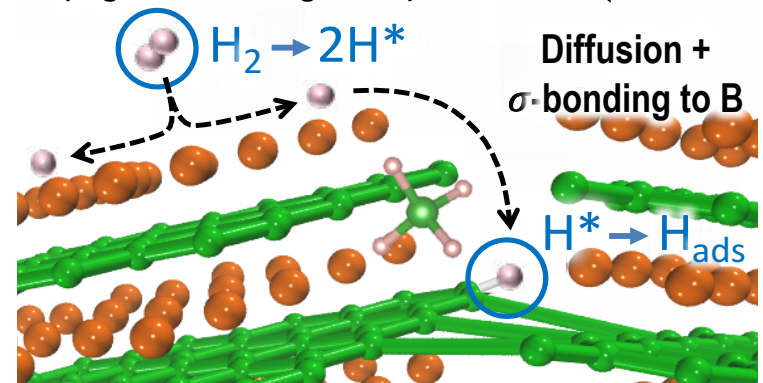
From 2016 AMR

MgB$_2$ w/H at B edge

B p$_{xy}$ feature

Bulk MgB$_2$

B K-edge XAS TFY (arb. units)

Simulated B XAS: H at exposed B edge agrees with experiments

Photon energy (eV)

FTIR: Direct formation of Mg(BH$_4$)$_2$ complexes without persisent intermediates @140 bar, 365 °C

MgB$_2$ + 0.85 wt.%H

MgB$_2$

95%MgB$_2$/ 5%Mg(BH$_4$)$_2$

Mg(BH$_4$)$_2$

Absorbance (arb.)

Wavenumber (cm^{-1})

Proposed mechanism

Process 1

Process 2

Barrier (eV)

wt% H

Dissociation on basal plane (high barrier, high rate)

$H_2 \rightarrow 2H^*$

Diffusion + σ-bonding to B

$H^* \rightarrow H_{ads}$

- **Direct chemical pathway to BH$_4^-$ is feasible**
- **DFT confirms pathway is energetically favorable**
- **Mechanism of H bonding to exposed B (at defects or edges) is uniquely consistent with all spectroscopy + simulations**

Accomplishment: Semi-empirical multiprocess kinetic modeling

Used energy landscape to parameterize kinetic model for validation of two-step mechanism

| **Create kinetic model** based on proposed mechanisms | → | **Inform model** from extracted barriers + energy calculations | → | **Fit prefactors** to calibrate kinetic model | → | **Compare behavior** to measurements for mechanism validation |

$$H_2(g) \leftrightarrow 2H^* \leftrightarrow 2H_{ads}$$

391 °C, 140 bar
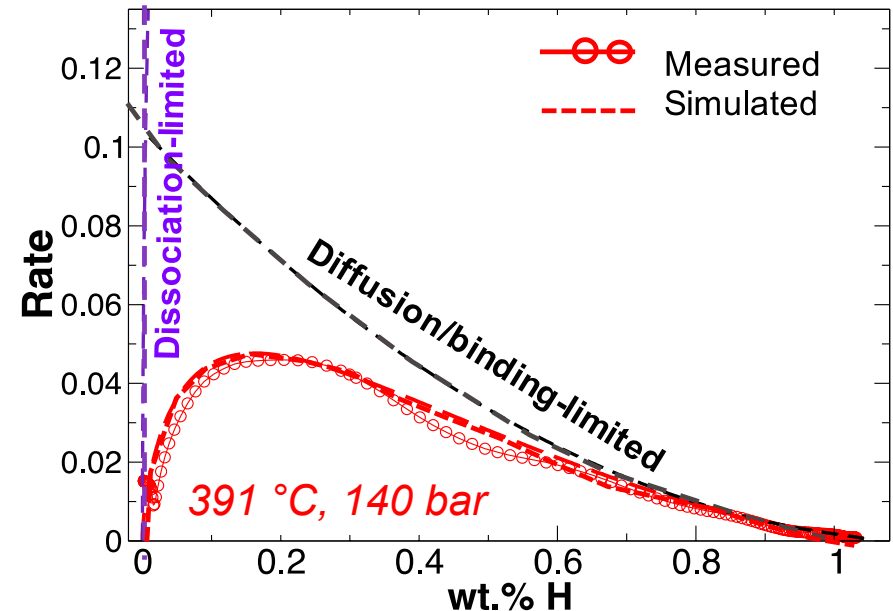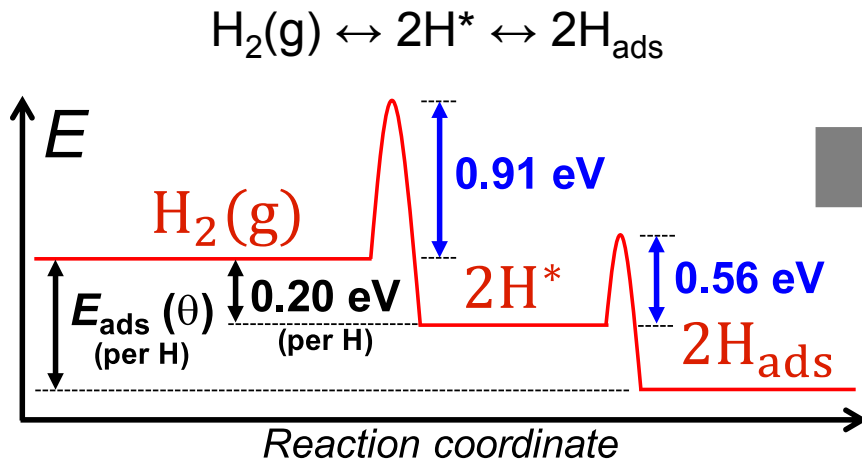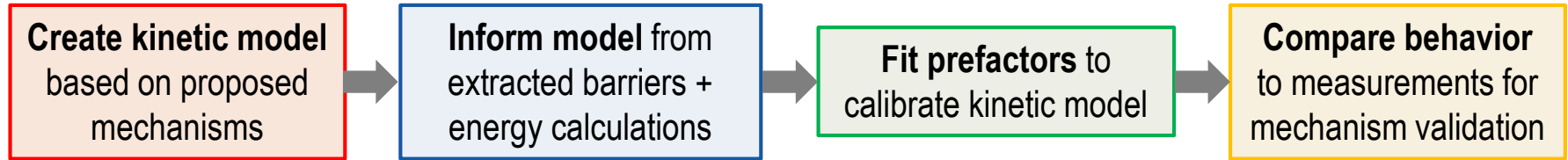
Dissociation

$$\frac{\partial c_{H^*}}{\partial t} = k_1 \cdot P_{H_2} - \tilde{k}_1 \cdot c_{H^*}^2 - \frac{\partial c_H^{ads}}{\partial t}$$

Surface diffusion/binding (modified Langmuir model)

$$\frac{\partial c_H^{ads}}{\partial t} = k_2 \cdot c_{H^*}^2 \cdot c_s^3 \cdot (1-\theta)^2 - \tilde{k}_2 \cdot c_s^3 \cdot \theta^2$$

- **Agreement with experiments confirms two-step dissociation + interface diffusion/ binding mechanism (manuscript submitted)**

- **Importance of interfaces explains why barriers are reduced for nano-MgB$_2$**

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Accomplishment: Phase-field simulation of $MgB_2 \leftrightarrow MgB_{12}H_{12}$ kinetics
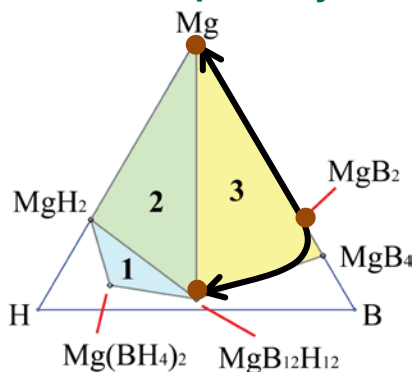
Performed first full phase-field simulation of (de)hydrogenation for H-poor reaction domain to explore kinetic effects under conditions where Sieverts cannot be performed
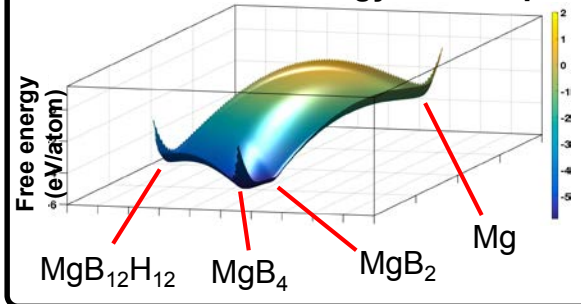
Faster diffusion of Mg and B

Microstructure

Mg

MgB_2
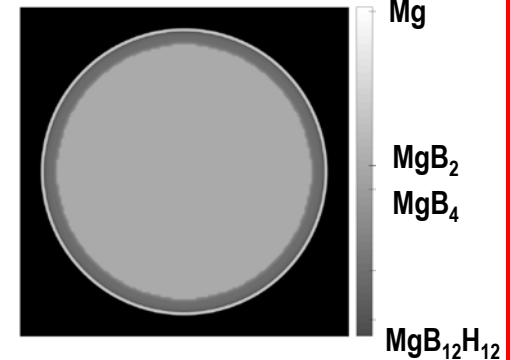MgB_4

$MgB_{12}H_{12}$
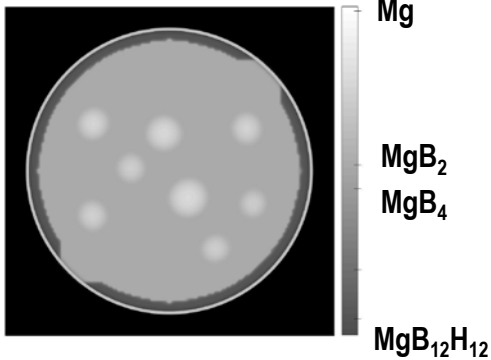
Kinetic pathway

DFT-based free energy landscape

$MgB_{12}H_{12}$ MgB_4 MgB_2 Mg
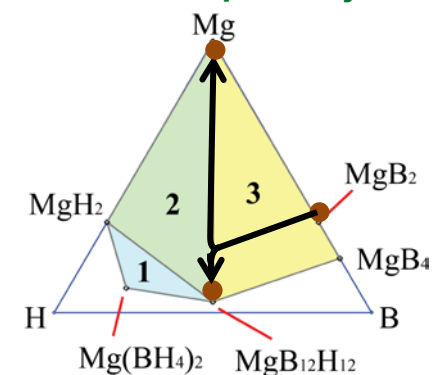
Relative hydrogen uptake kinetics

Slower diffusion of Mg and B

Microstructure

Mg

MgB_2
MgB_4

$MgB_{12}H_{12}$
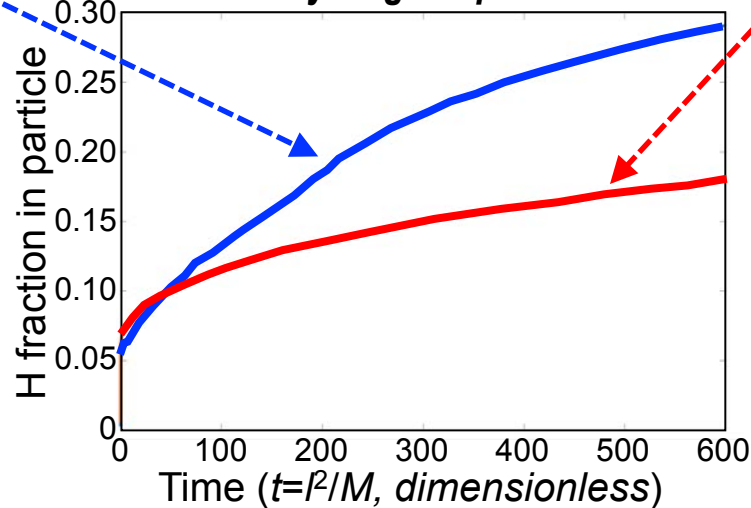
Kinetic pathway

- **Phase-field models reveal relationship between microstructure, pathway, and kinetics**
- **Faster mass transport of Mg is predicted to have a large effect on overall kinetics**

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# Accomplishment: Exploration of chemical pathways

Chemical pathways identified by HySCORE were explored using high-T/P ab initio molecular dynamics for additional mechanistic insight and model parameterization

Initial hydrogenation of MgB$_2$ (10$\bar{1}$0)

B-rich

Mg-rich
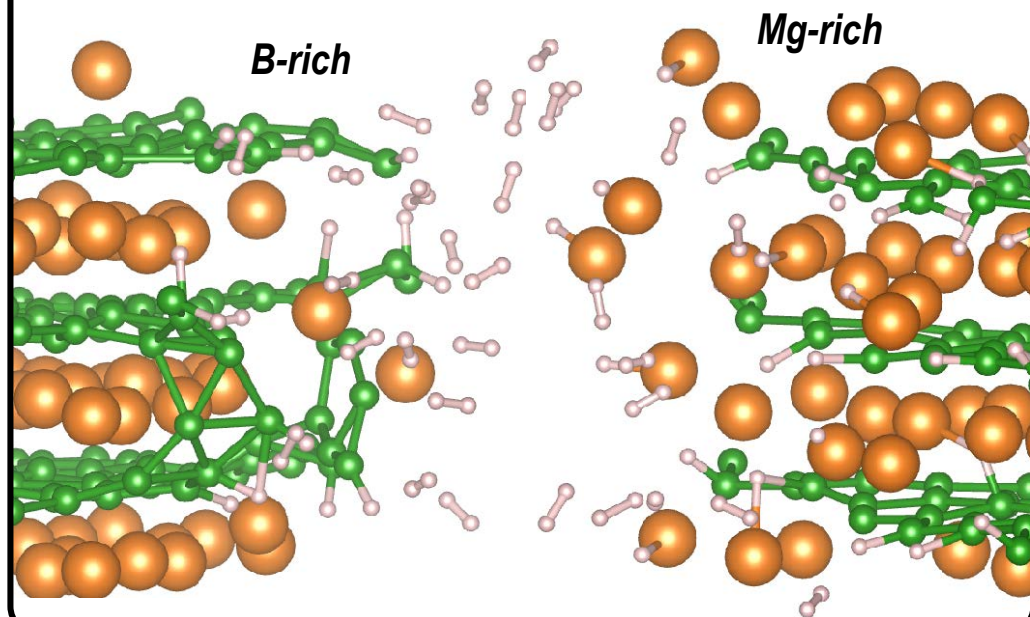
Initial dehydrogenation of Mg(BH$_4$)$_2$ (w/HySCORE)

Gas-phase ΔH courtesy of PNNL/HySCORE

$$BH_4^- + BH_4^- \xrightarrow{H^-} B_2H_7^- \xrightarrow{H_2} B_2H_5^-$$

+70.6 kJ/mol   +31.5 kJ/mol
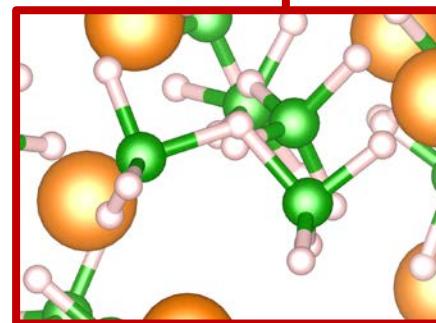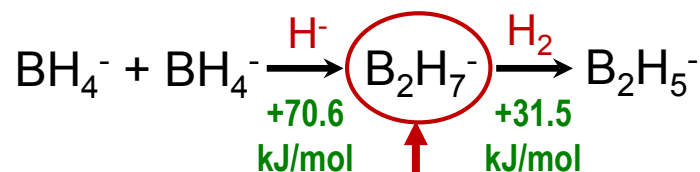
- **Simulations of MgB$_2$ hydrogenation show formation of B-H, B-B, and Mg-H bonds**
- **Closoborane formation during MgB$_2$ hydrogenation may arise from interactions between hexagonal B sheets upon removal and hydriding of Mg**
- **Can directly observe reaction pathways during dehydrogenation of Mg(BH$_4$)$_2$**
- **Changes in charge states induce boron chemistry and affect diffusion mobility**

Progress on FY17 and post-AMR FY16 milestones (as of 4/17)

Phase II

- Synthesize high-purity MgB_2 nanoparticles (~10 nm) **(complete)**

- Compute thermodynamics of surfaces and interfaces of nano-MgB_2/$Mg(BH_4)_2$ **(complete)**

- Establish modeling framework for surface chemical reactions and calculate surface-dependent thermodynamics, migration, and dissociation **(complete)**

- Measure hydrogen desorption/adsorption rate of nanoparticles and identify key intermediates **(75% complete; new samples sent to HySCORE for phase identification)**

- **Go/No-Go: Demonstrate 75% agreement between model predictions and observed phase diagram/phase fractions, and demonstrate scalable nanoparticle synthesis (complete)**

- Identify rate-limiting processes in hydrogenation of nano-MgB_2 **(75% complete)**

Phase III

- Measure hydrogen desorption/absorption in catalyst-modified nanoscale MgB_2 and identify intermediates **(25% complete)**

- Determine sensitivity of reaction kinetics on atomistic processes **(50% complete)**

- Compute hydrogenation/rehydrogenation kinetics using three-phase model **(75% complete)**

- Predict ideal particle shape, size, and stress state for optimized thermodynamics and kinetics **(20% complete)**

Remaining challenges/barriers & mitigation strategies

- **Nanosizing MgB_2 is unlikely to provide an ultimate solution on its own**
  - *Our predictions show that nanosizing helps kinetics but does not destabilize intermediates. Our Phase III study of nanoscale catalyzed MgB_2 will determine how additives might additionally help.*

- **Extracting barriers for inclusion in free energy landscape is challenging**
  - *We will work with HyMARC to improve the free energy landscape description via kinetics studies. We will also use time-dependent data from NMR analysis (HySCORE) of different exposure times at a variety of (T,P) to parameterize the landscape.*

- **Phase-field kinetic model should be applied to full reaction pathway**
  - *We started with the hydrogen-poor phases because the reaction chemistry is less complex, but the model can be extended to the full phase diagram.*

- **Need to translate mechanistic insights into rational design strategies for validation**
  - *Future activities will focus on use of mesoscale modeling framework to analyze sensitivity of kinetics to changes in materials properties and guide design, validated and informed by experiments.*

Proposed future work

- **Incorporate catalyst additives** ($TiCl_3/TiF_3$) into surfactant-assisted ball milling process for nanoparticles and test for kinetics and phase expression (underway)

- **Extend thermodynamic phase-fraction predictions** to account for other B_xH_y intermediates, including possible B_2H_6 formation

- **Extend phase-field kinetic model** to other regions of phase diagram (underway)

- **Inform free energy landscape** with more advanced interfacial reaction and transport models in collaboration with HyMARC and PNNL/HySCORE (underway)

- **Validate kinetic model** against phase expression from NMR, FTIR, XRD, XAS/XES in uncatalyzed and catalyzed nanoparticles as a function of exposure time

- **Use kinetic model to explore sensitivity of kinetics** to additives, nanosizing, and confinement to evaluate best strategies for optimization

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

Collaborations

Collaborations are crucial for realizing theory/characterization/synthesis partnership

Ab initio modeling/multiscale integration

- Dr. Brandon Wood (PI, LLNL)*
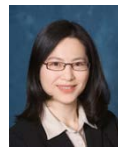- Dr. Keith Ray (LLNL)*
- Dr. ShinYoung Kang (LLNL)*

Mesoscale phase-field modeling

- Prof. Katsuyo Thornton
- Dr. Hui-Chia Yu (Univ. Michigan)**
- Dr. Tae Wook Heo (LLNL)*

HySCORE collaborations

- Borohydride chemistry and $Mg(BH_4)_2$ dehydrogenation pathways (PNNL)
- ^{11}B NMR (PNNL)
- Neutron vibrational spectroscopy (NIST)

Nanoparticle synthesis & testing

- Dr. Vitalie Stavila (Sandia)**

Characterization

- Dr. Lennie Klebanoff (Sandia)**
- Dr. Jonathan Lee (LLNL)*
- Dr. Alex Baker (LLNL)*

HyMARC collaborations

- Computational spectroscopy (LBNL)
- Free energy analysis for phase fraction prediction (LLNL)
- Diffuse reactive interface modeling (LLNL)
- High-pressure hydrogenation (SNL)
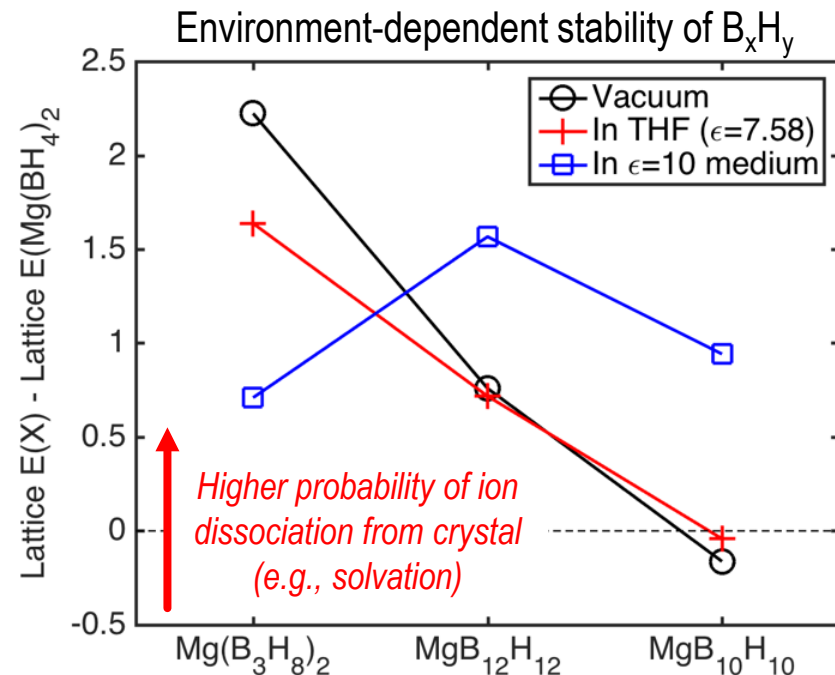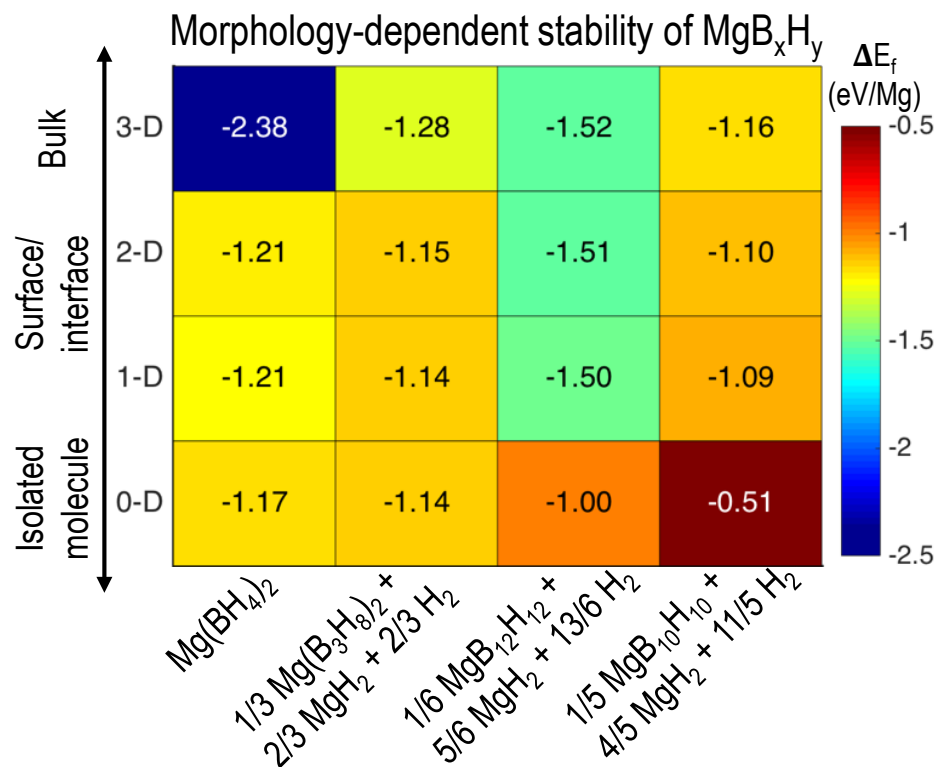- Nanoconfining carbons (LLNL)

*prime   **sub

Summary

Our theory/experiment approach informs mechanisms and improvement strategies

- **Validated and applied free energy landscape** within a mesoscale kinetic model to explore the sensitivity of H_2 uptake/release to specific kinetic processes

- **Demonstrated synthesis of high-purity MgB_2 nanoparticles without confinement**

- **Showed that it is possible chemically to create molecular $Mg(BH_4)_2$ directly from MgB_2** and determined associated atomistic mechanism with help from theory

- **Elucidated the role of anharmonic molecular rotations** in stabilizing $Mg(BH_4)_2$ and intermediates at higher T, suggesting a pathway for tuning thermodynamics

- **Showed that microstructure can play a key role in stability and kinetics**

  - *Most intermediates (e.g., $Mg(B_3H_8)_2$) are likely stabilized as molecules at reactive interfaces, so manipulating molecular vs. condensed-phase stability (e.g., via complexation with additives) is a promising strategy*

  - *For rehydrogenation of MgB_2, introducing interfaces and/or defects will create reaction sites that should aid kinetics (e.g., via ball milling, nanosizing, or additives)*

- **Predicted and demonstrated that nanosizing MgB_2 without confinement helps kinetics of partial uptake,** partly due to stronger thermodynamic driving forces, but it is not predicted to destabilize intermediates

Technical backup slides

Relative stability of MgB_xH_y intermediates depends strongly on environment & morphology

Morphology-dependent stability of MgB_xH_y

Environment-dependent stability of B_xH_y

Higher probability of ion dissociation from crystal (e.g., solvation)

- **MgB_2 and $Mg(BH_4)_2$ have a strong tendency to form bulk condensed phases, whereas other intermediates can form molecules or polymeric chains. This means manipulating molecular vs. condensed phase stability is a promising strategy, which may be one role of solvent additives.**

- **Of the common intermediates, $Mg(B_3H_8)_2$ most easily tolerates molecular dissociation (e.g., in THF), followed by $MgB_{12}H_{12}$, then $MgB_{10}H_{10}$ and $Mg(BH_4)_2$. This likely reflects the order of preference for interface segregation, so catalyst additives that segregate to grain boundaries and interfaces will preferentially target $MgB_{12}H_{12}$ and $Mg(B_3H_8)_2$.**

Backup: Influence of anharmonic modes on MgB$_2$ hydrogenation

At 390 °C, 900 bar (reaction conditions of Severa et al. (2010)), anharmonic B$_x$H$_y$ rotations are primarily responsible for converting MgB$_2$ to Mg(BH$_4$)$_2$ without significant intermediates
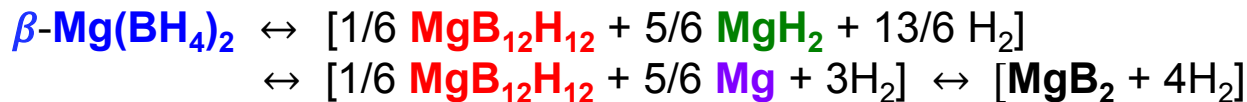
$$\beta\text{-Mg(BH}_4\text{)}_2 \leftrightarrow [1/6\ \text{MgB}_{12}\text{H}_{12} + 5/6\ \text{MgH}_2 + 13/6\ \text{H}_2]$$
$$\leftrightarrow [1/6\ \text{MgB}_{12}\text{H}_{12} + 5/6\ \text{Mg} + 3\text{H}_2] \leftrightarrow [\text{MgB}_2 + 4\text{H}_2]$$

Only Harmonic

Harmonic + Anharmonic
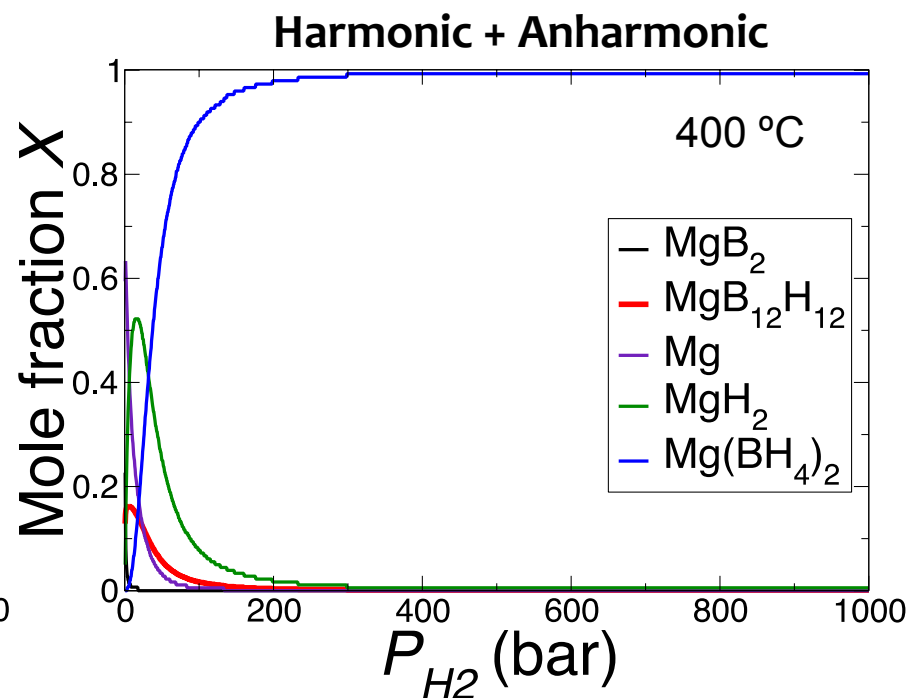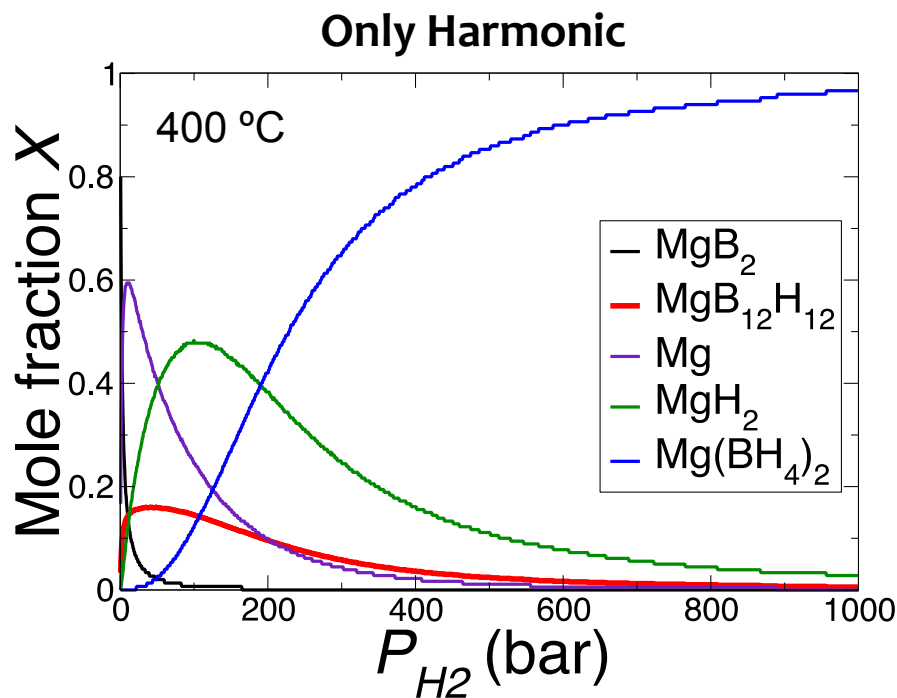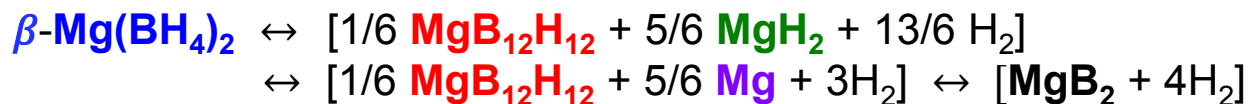
- **Anharmonic modes are strongly density dependent and may be enhanced by grain/phase boundaries or atom substitutions**

Computed phase fractions agree with experimental trends in intermediate expression
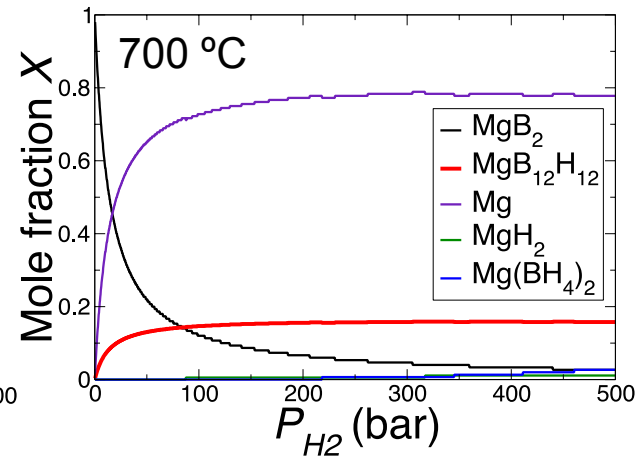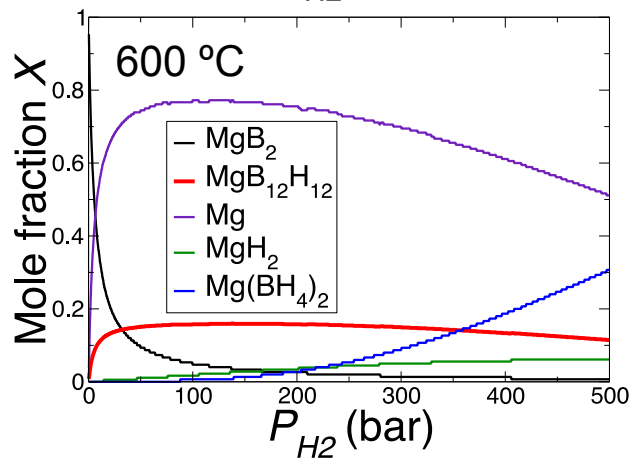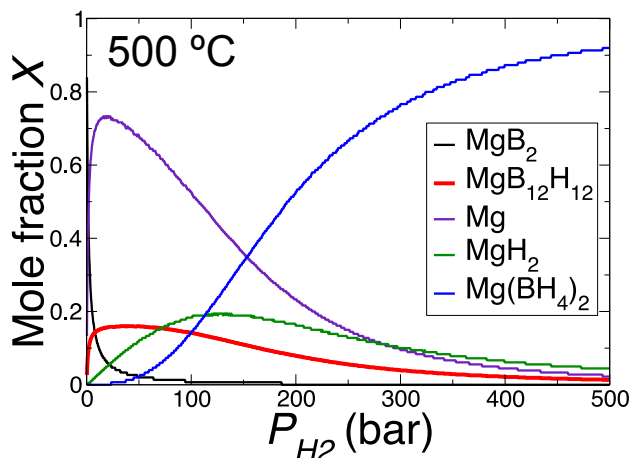
β-**Mg(BH$_4$)$_2$** $\leftrightarrow$ [1/6 **MgB$_{12}$H$_{12}$** + 5/6 **MgH$_2$** + 13/6 H$_2$]

$\leftrightarrow$ [1/6 **MgB$_{12}$H$_{12}$** + 5/6 **Mg** + 3H$_2$] $\leftrightarrow$ [**MgB$_2$** + 4H$_2$]

Our work on Li$_3$N demonstrating
the method made the cover of
Adv. Mater. Interfaces, 2017

Based on grand-canonical free
energy minimization plus
regular solution phase mixing

Amounts of MgB$_{12}$H$_{12}$ and
Mg(BH$_4$)$_2$ predicted to be
equal at 635 ℃ at 500 bar
(vs. ≳540 ℃ from NMR)
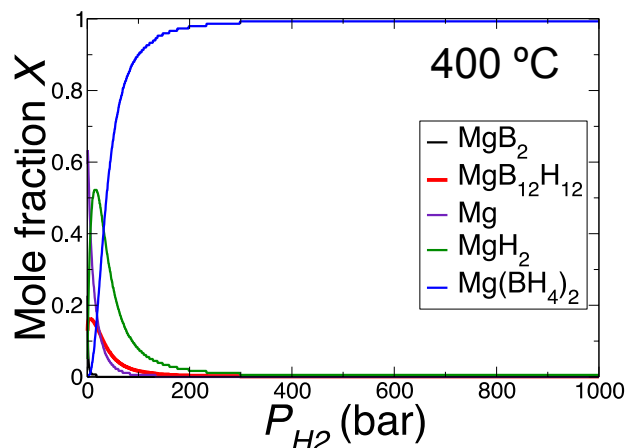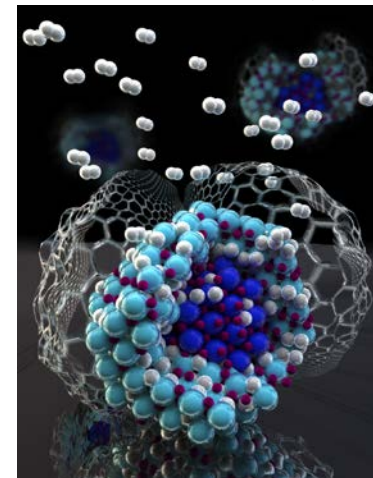
Meets second Go/No-Go (75% phase fraction theory-experiment agreement)

Under compressive stress

Particle size dependence