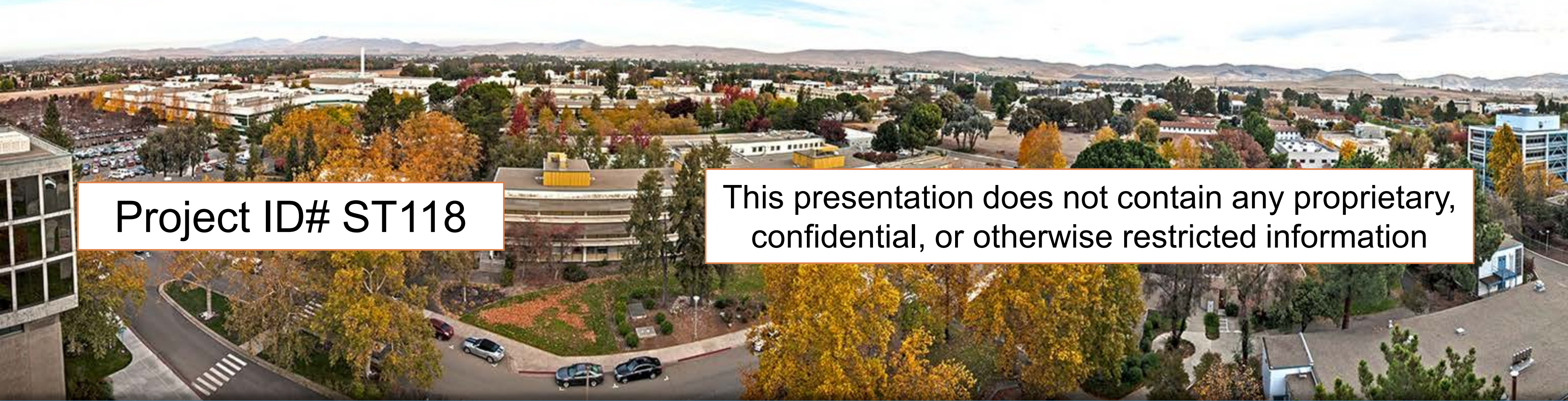
Improving the Kinetics and Thermodynamics of $Mg(BH_4)_2$ for Hydrogen Storage

2016 DOE Hydrogen Annual Merit Review
June 8, 2016

PI: Brandon C. Wood, LLNL

Lawrence Livermore National Laboratory (B.C. Wood, T.W. Heo, K. Ray, J. Lee)
Sandia National Laboratories (L. Klebanoff, V. Stavila)
University of Michigan (K. Thornton)



Project ID# ST118

LLNL-PRES-XXXXXX
This work was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under contract DE-AC52-07NA27344. Lawrence Livermore National Security, LLC

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)
Total funds spent (as of 3/16): $681K

Team

Project Lead:
Lawrence Livermore National Laboratory

Funded Partners:
Sandia National Laboratories
University of Michigan

Relevance

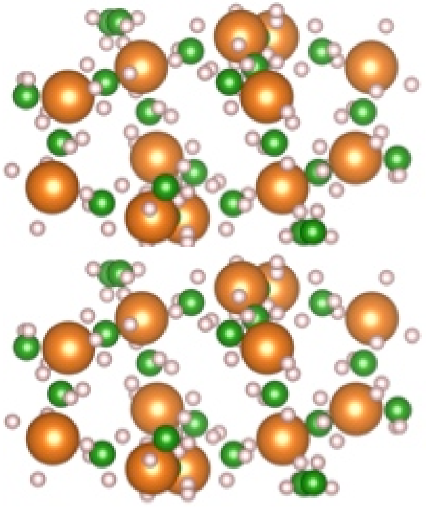
$Mg(BH_4)_2$ is attractive for compact, lightweight solid-state hydrogen storage that could meet ultimate DOE targets, but it suffers from poor kinetics and undesirable intermediates

Overall project objectives:

- Combine **theory, synthesis, and characterization** techniques at **multiple length/time scales** to understand kinetic limitations and possible improvement strategies in $Mg(BH_4)_2$
- Deliver a **flexible, validated, multiscale theoretical model** of (de)hydrogenation kinetics in “real” Mg-B-H materials **beyond idealized theoretical descriptions**

Current project year objectives:

- Synthesize MgB_2 nanoparticles with < 10 nm diameter
- Measure X-ray absorption and emission spectra for bulk $MgB_2/Mg(BH_4)_2$ during stages of (de)hydrogenation
- Compare measured and simulated spectra on informed models to determine local chemical pathways

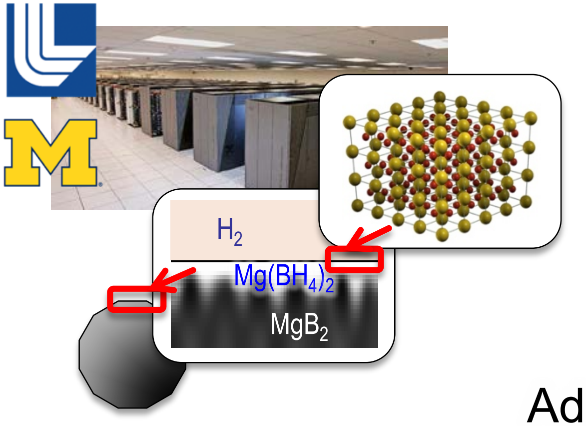


> 15 wt.%H

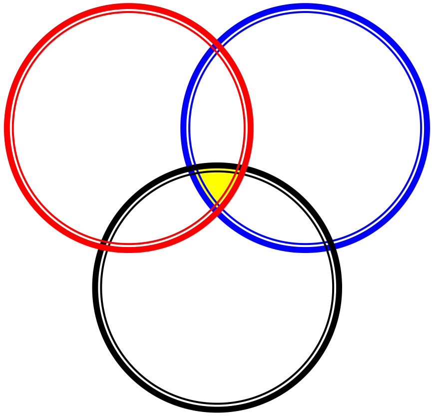
Approach: Integrated experiment-theory framework

Dehydrogenation kinetics of $Mg(BH_4)_2$ *have previously demonstrated susceptibility to improvement via* ***structural (nanosizing)*** *and* ***chemical (doping)*** *changes*

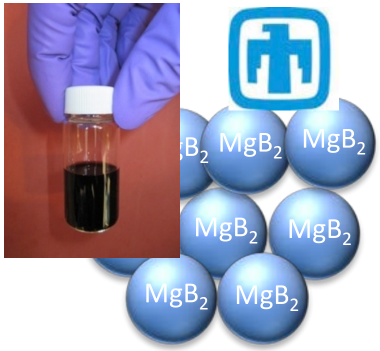
Predictive Theory



Multiscale "beyond-ideal" simulation



Controlled Synthesis & Testing



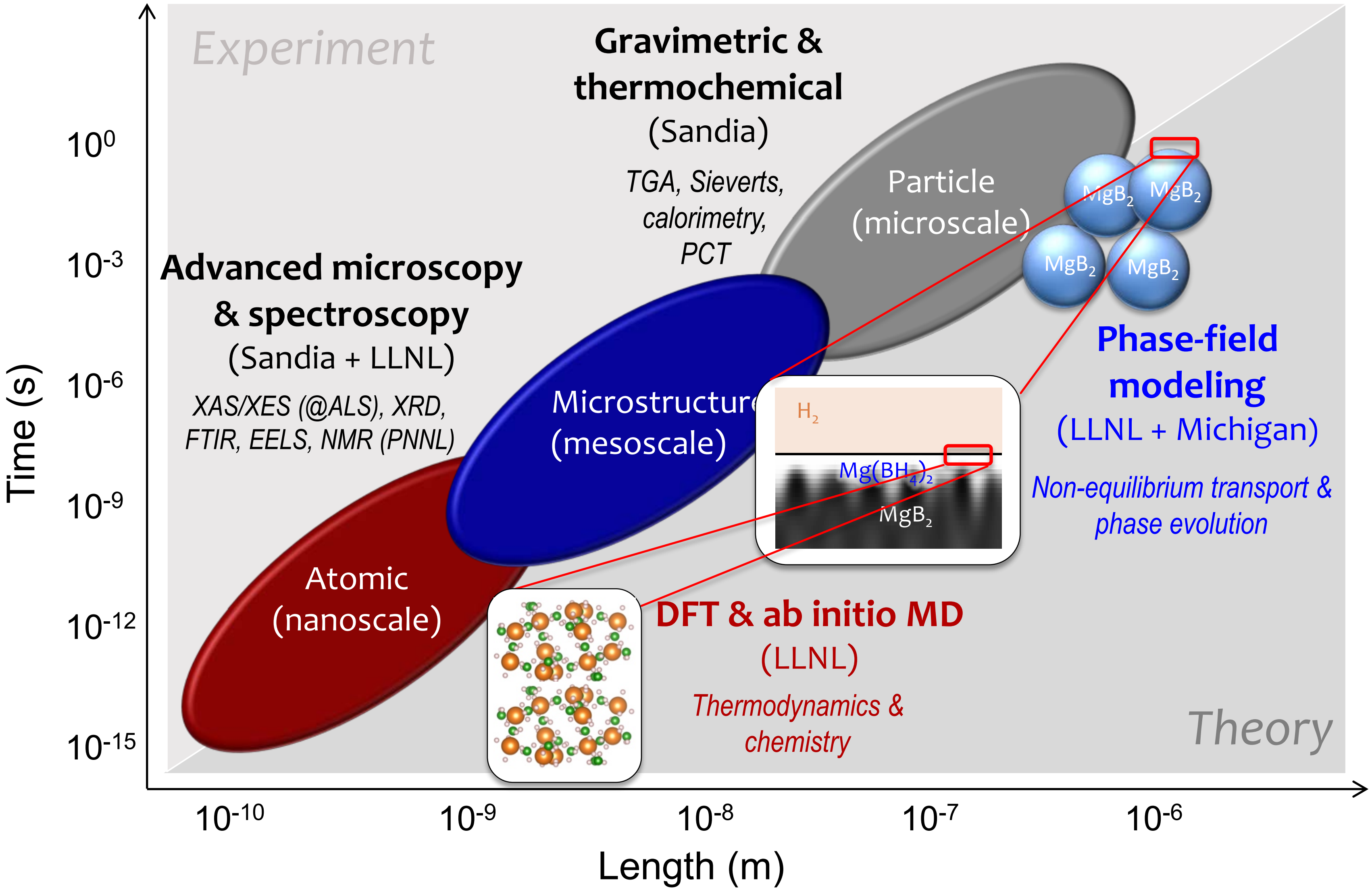
Size-selected nanoparticle synthesis & catalytic doping

Advanced Characterization

Spectroscopy, microscopy

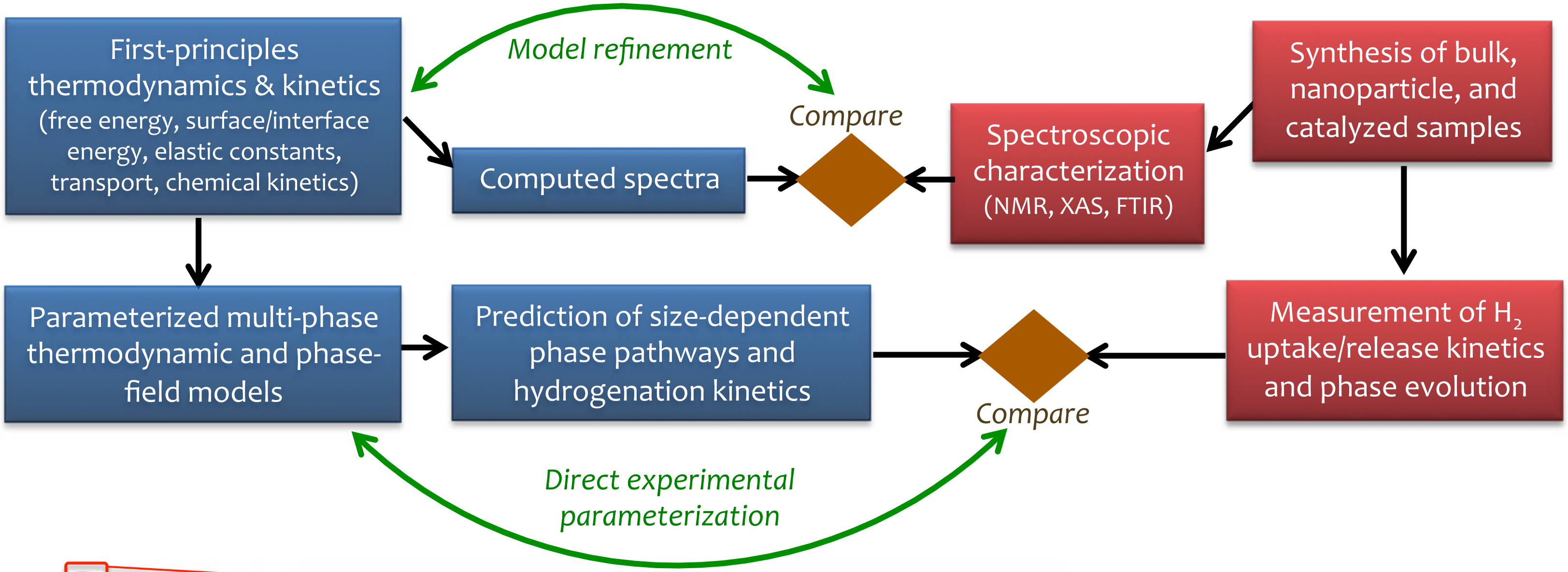
Our project integrates theory, synthesis, and characterization to understand limitations and discover how, why, and when these improvement strategies help

Approach: Multiscale characterization and modeling



Approach: Feedback cycle for modeling diverse processes

Experiment-theory feedback cycle allows modeling of complex surface and interface processes under non-equilibrium (de)hydrogenation conditions



First-principles thermodynamics & kinetics
(free energy, surface/interface energy, elastic constants, transport, chemical kinetics)

Model refinement

Computed spectra

Compare

Spectroscopic characterization
(NMR, XAS, FTIR)

Synthesis of bulk, nanoparticle, and catalyzed samples

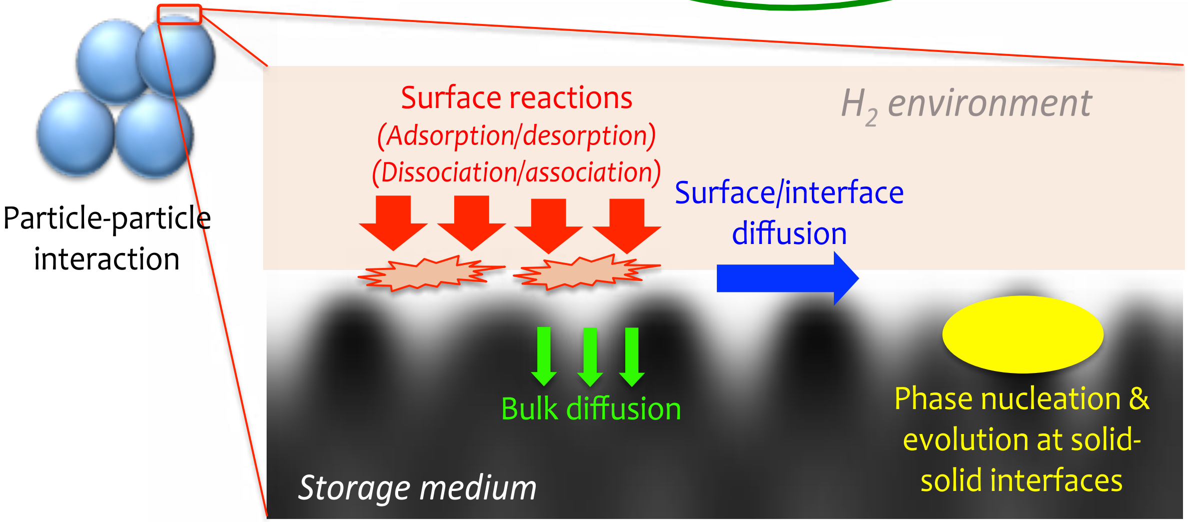
Parameterized multi-phase thermodynamic and phase-field models

Prediction of size-dependent phase pathways and hydrogenation kinetics

Compare

Measurement of H_2 uptake/release kinetics and phase evolution

Direct experimental parameterization



Particle-particle interaction

Surface reactions
(Adsorption/desorption)
(Dissociation/association)

H_2 environment

Surface/interface diffusion

Bulk diffusion

Phase nucleation & evolution at solid-solid interfaces

Storage medium

Also makes extensive use of HyMARC capabilities to model & characterize phase stability, evolution, and local chemistry

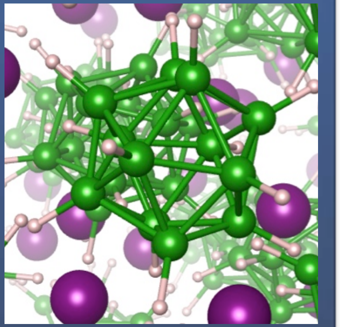
Approach: Combining chemistry and materials science

Three project phases adapt tools from chemistry and materials science

Phase I: *(De)hydrogenation thermodynamics in bulk $Mg(BH_4)_2/MgB_2$*
Phase II: *Nanoscale properties and kinetics*
Phase III: *Catalyst additives and optimization*

Local chemistry of defects and B_xH_y molecular complexes

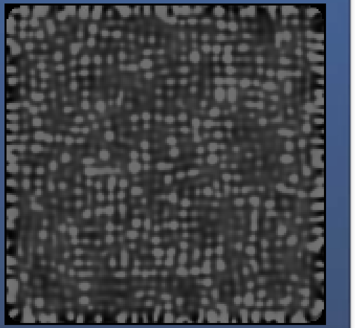
- *Focus on single-phase portions of reaction pathway*
- *Combine DFT/ab initio MD with chemically sensitive spectroscopy (XAS, NMR, FTIR, NVS)*



- *Collaboration on boron chemistry with T. Autrey, PNNL*

Evolution of solid phases

- *Focus on multiphase portions of reaction pathway*
- *Combine phase-field modeling with uptake kinetics measurements and diffraction*



- *Thermodynamic analysis based on DFT simulations within assumed microstructure*

Progress on FY16 and post-AMR FY15 milestones (as of 3/16)

Phase I

- Initial XAS/XES spectroscopy of bulk $Mg(BH_4)_2$ and bulk MgB_2 **(complete)**
- Initial theoretical calculations of XAS/XES spectroscopy and electronic structure of bulk $Mg(BH_4)_2$ and bulk MgB_2 **(complete)**
- Identify intermediate bulk phases during dehydrogenation of bulk $Mg(BH_4)_2$ and rehydrogenation of bulk MgB_2 **(complete)**
- Calculate energetics of B-H and B-B bond breaking and forming in $Mg(BH_4)_2/MgB_2$ **(complete)**
- ***Go/No-Go: Interpret intermediate chemical species in bulk MgB_2, $Mg(BH_4)_2$, and partially (de)hydrogenated samples, and show < 1 eV agreement between measured and computed XAS/XES spectra (complete)***

Phase II

- Compute thermodynamics of surfaces and interfaces of nanoscale $MgB_2/Mg(BH_4)_2$ and measure absorption/desorption rate **(75% complete)**
- Establish modeling framework for surface chemical reactions and calculate surface-dependent thermodynamics, migration, and dissociation **(25% complete)**

On track to meet all key FY16 milestones

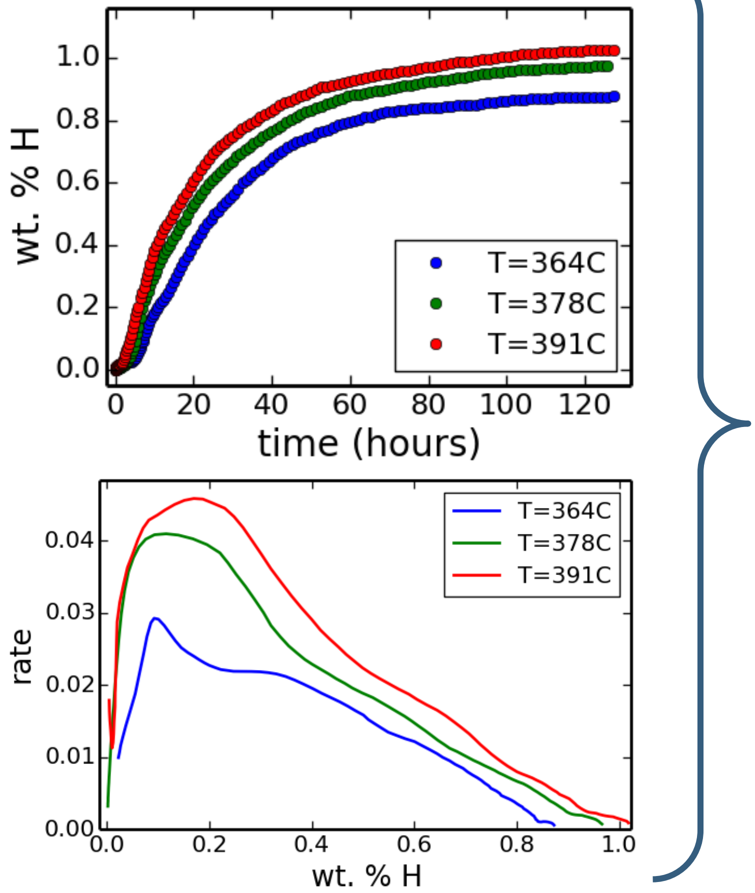
Additional key technical accomplishments this year

- Showed that high-pressure hydrogenation of MgB_2 can lead to direct conversion to $Mg(BH_4)_2$, suggesting it is possible to suppress intermediates
- Compared spectroscopic data with *ab initio* computations and kinetic analysis to show that hydrogenation of MgB_2 likely initiates at interfaces and defect sites
- Demonstrated size-selective synthesis of MgB_2 nanoparticles with diameter < 10 nm

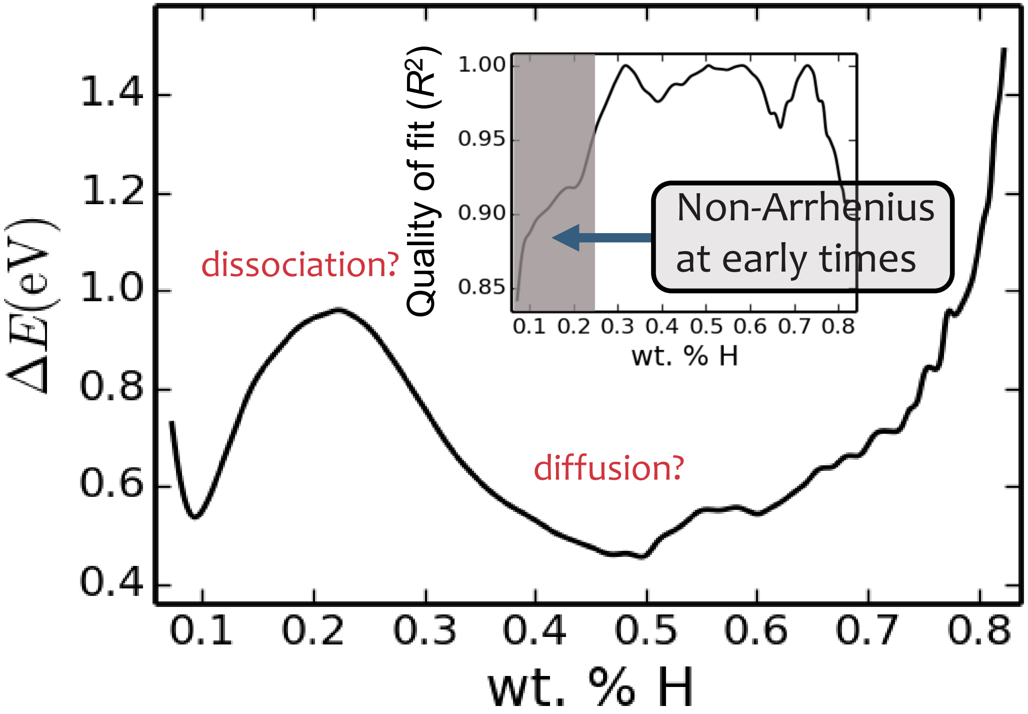
Accomplishment: Analysis of initial MgB_2 uptake kinetics

Analysis reveals multiple barriers corresponding to processes governing initial hydrogenation

MgB_2 hydrogenation @145 bar



Energy barriers from Arrhenius fits



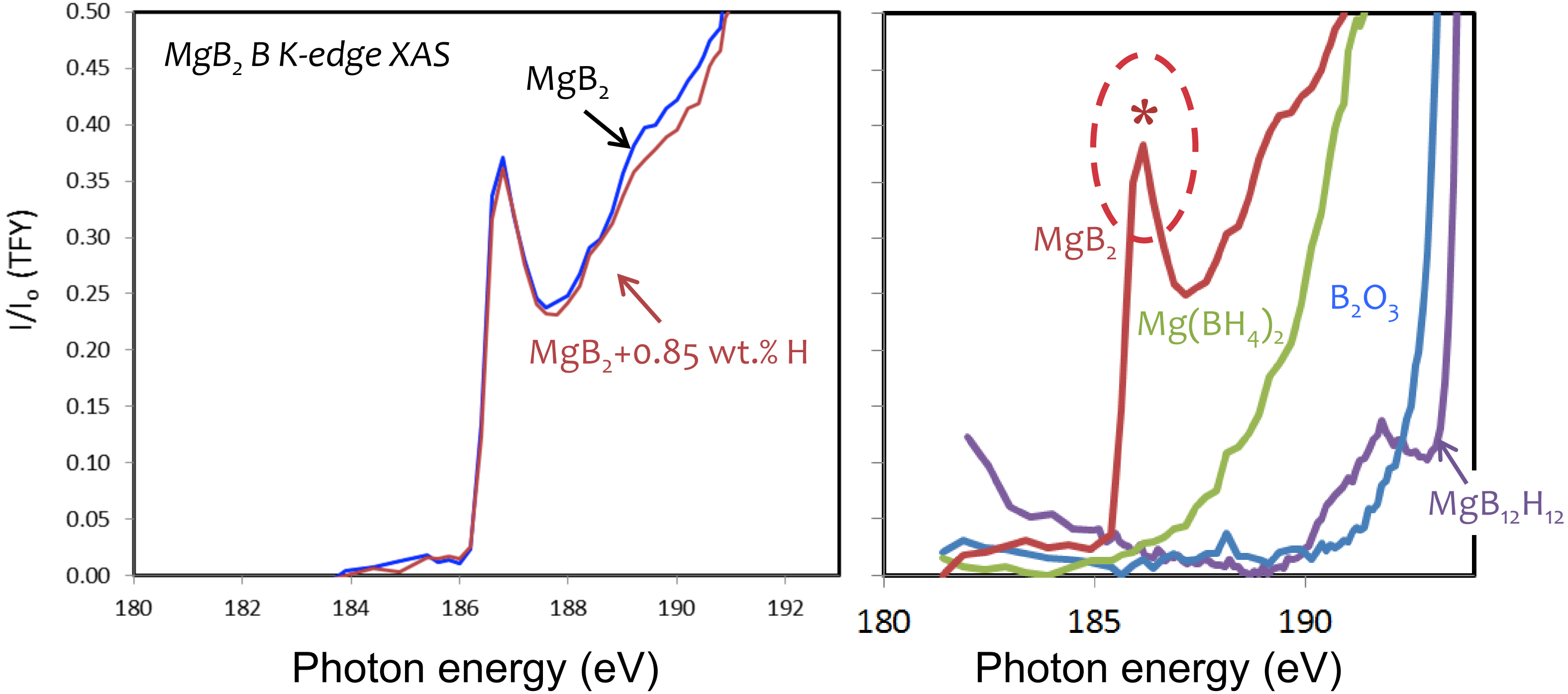
Computed dissociation barrier is 0.89 eV on pristine MgB_2(0001) from Wang et al., PRB 91, 155431 (2015)

Combined soft X-ray spectroscopy (+FTIR, NMR) with computational spectroscopy to probe mechanism of initial hydrogenation prior to any phase change

Accomplishment: Spectroscopy to probe local chemistry

After controlling for oxidation, no significant changes are observed in XAS/XES upon initial hydrogenation of MgB_2 up to 0.85 wt. % H ($MgB_2H_{0.39}$)

XAS total fluorescence yield, ~300 nm penetration



- *If MgB_2 becomes $MgB_{12}H_{12}$ or dispersed B-H bonds, expect 19.5% reduction in (*), inconsistent with the spectra*
- *Consistent with conversion into $Mg(BH_4)_2$ (4.9% expected reduction) or MgH_2 (almost no expected effect)*

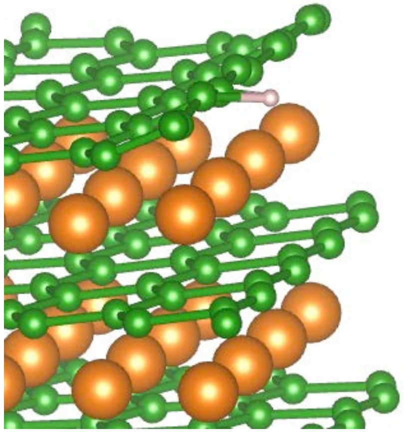
Relatively few B atoms are hydrogenated, suggesting a local concentration of highly coordinated BH_x or MgH_2 rather than $MgB_{12}H_{12}$ or uniformly dispersed B-H bonds

Accomplishment: Energetics of hydrogen in MgB_2

Computed binding energetics of hydrogen at sites in MgB_2

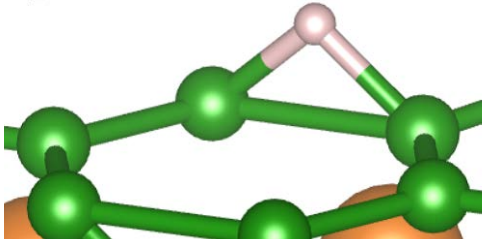
Binding energies (eV per H) with respect to H_2 (g):

H @ edges (favorable)



-0.8 eV per H

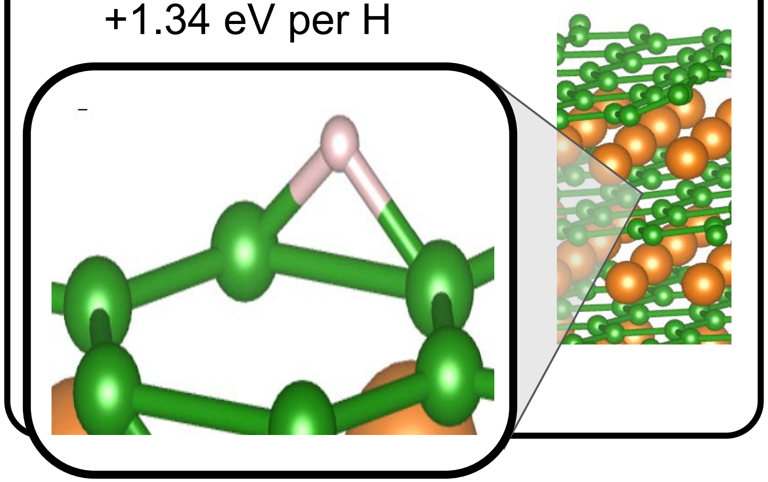
H @ basal plane (favorable)



-0.5 eV per H

H intercalation in bulk (unfavorable)

+1.34 eV per H

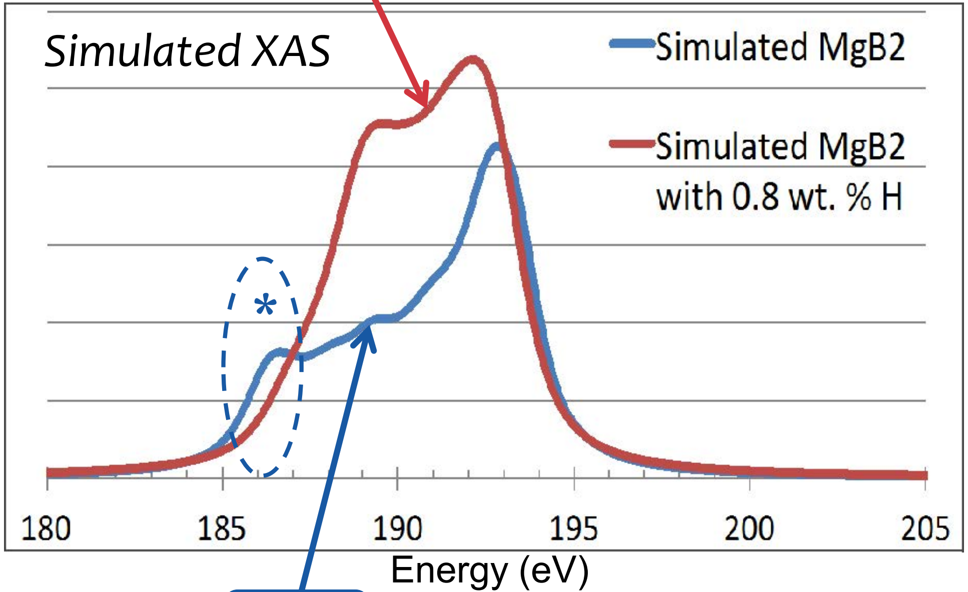


Unfavorable thermodynamics of dissociated hydrogen in bulk MgB_2 suggests hydrogen migrates to surfaces and interfaces

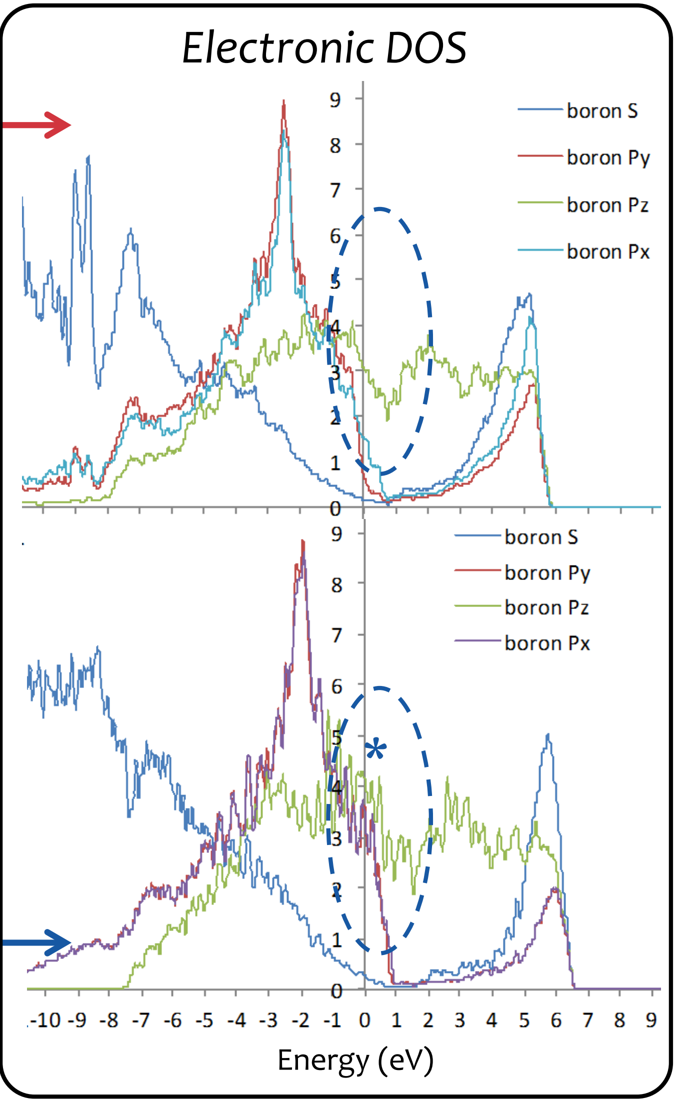
Accomplishment: Computational spectroscopy

Computed XAS spectra confirm H is not bulk-intercalated and does not further disrupt boron p_{xy} orbitals, suggesting it attacks high-energy defects and strained B-B bonds

MgB_2 + 0.8 wt. % H intercalated in the bulk



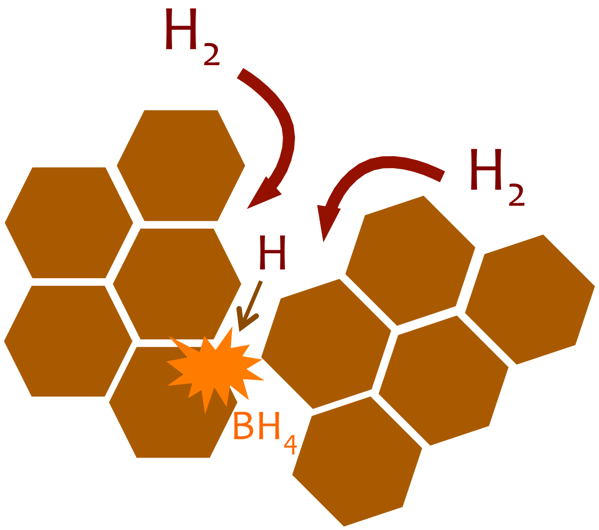
MgB_2


Electronic DOS

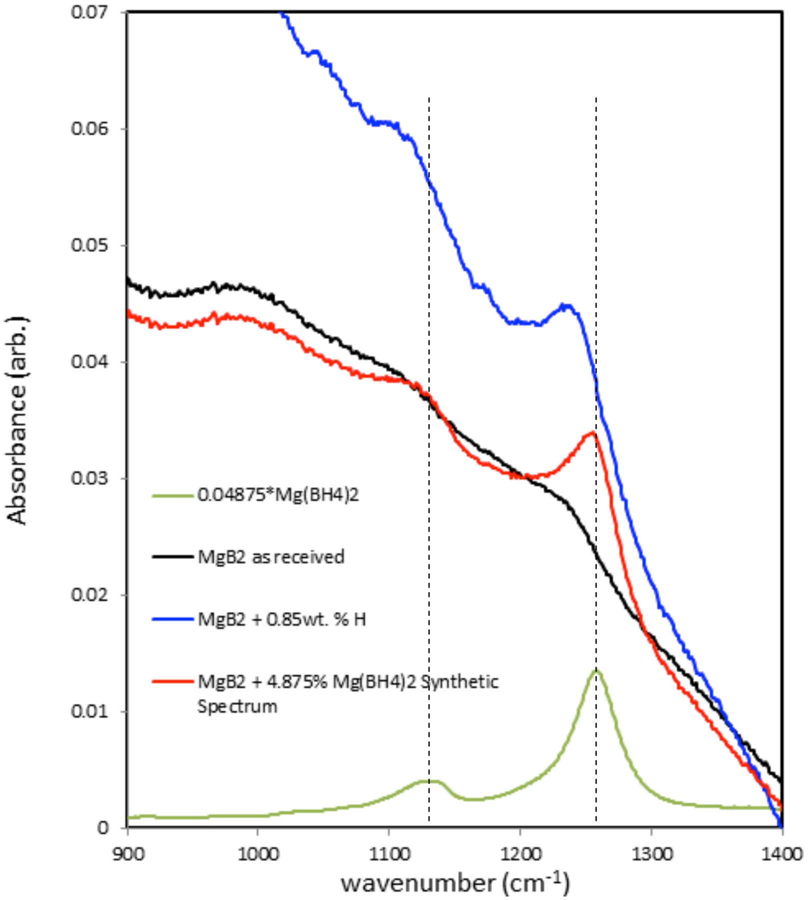
The * state is unoccupied B p_{xy}, a decrease in which signals charge donation to p_{xy} upon H bonding

Accomplishment: FTIR supports proposed uptake mechanism

FTIR spectra show features similar to $Mg(BH_4)_2$ but no $MgB_{12}H_{12}$ or B-H, supporting XAS interpretation of highly selective hydrogenation of B atoms concentrated at interfaces



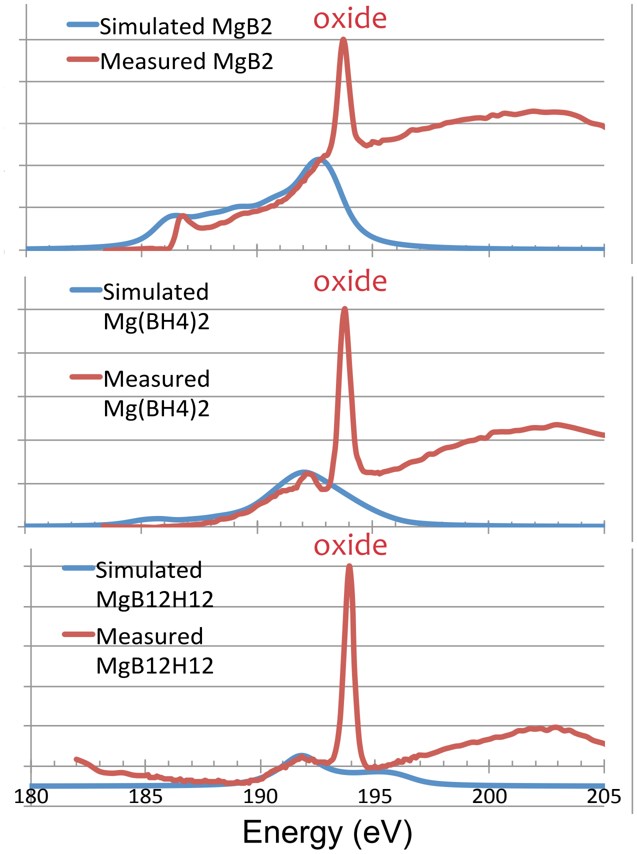
Evidence for higher hydrogenated BH_x ($x > 1$) also seen in solid-state NMR (T. Autrey, PNNL)

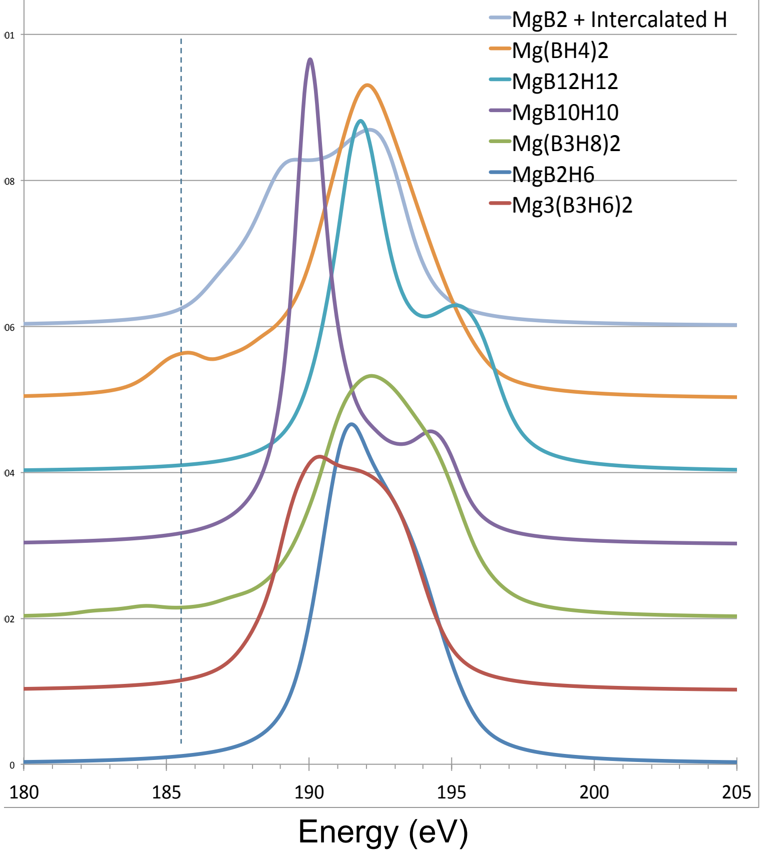


Suggests direct pathway for formation of BH_4-like species via hydrogenation of MgB_2 proceeding from interfaces and grain boundaries even at low pressure (140 bar)

Accomplishment: Interpreting intermediates (Go/No-Go)

Compared calculations to measured spectra to aid interpretation of intermediates based on library of reference computed spectra for Mg-B-H compounds (completes Go/No-Go)


Simulated and measured spectra show similar resonances to within ~1 eV

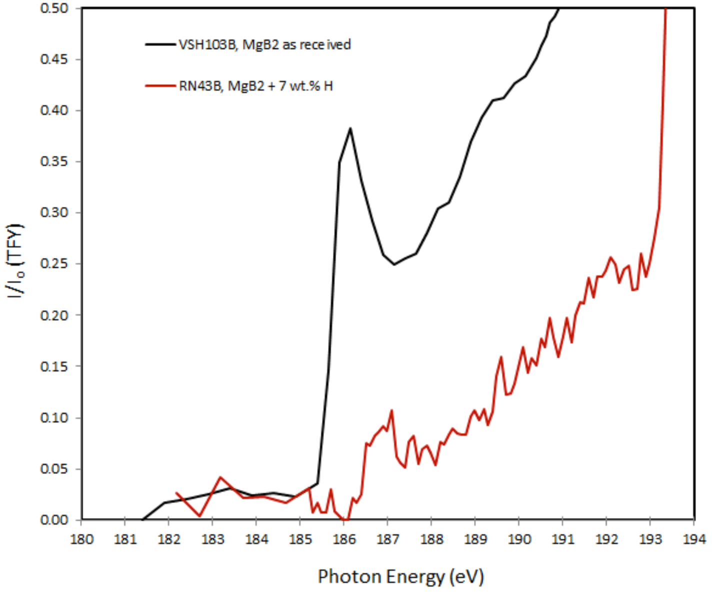

Calculated database of XAS/XES spectra for intermediate phases at 300 K (XAS shown)

Agreement between reference and computed spectra assures confidence in predicted models, which will be used to aid interpretation of (de)hydrogenation intermediates

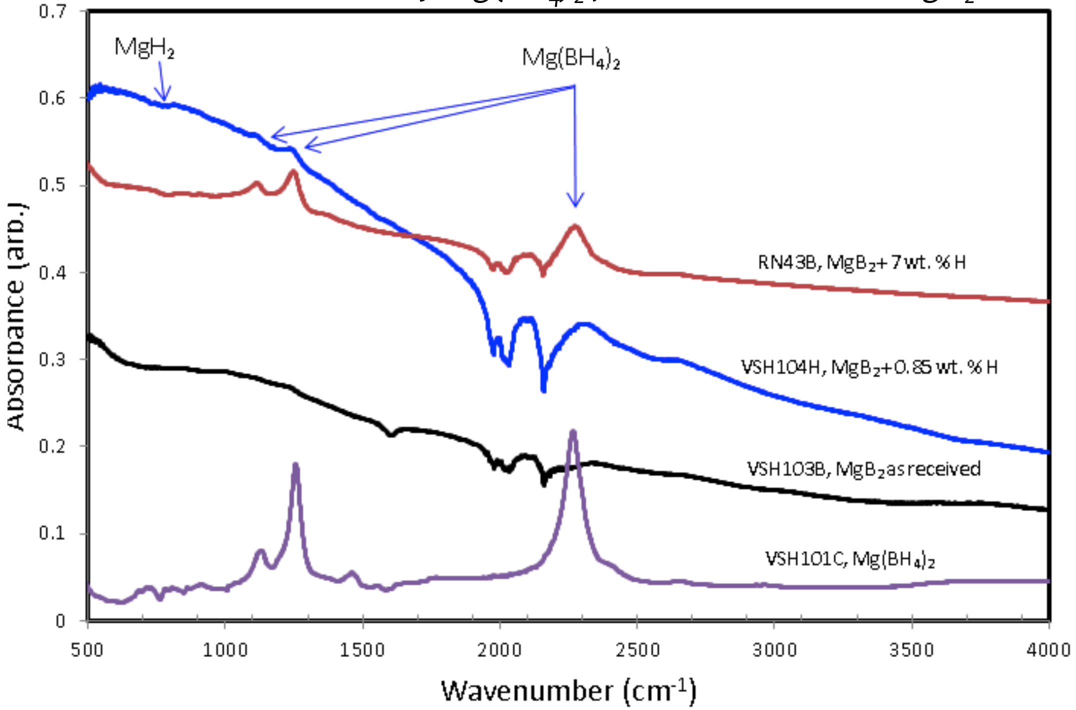
Accomplishment: Hysteresis in reaction pathway

XAS and FTIR near half hydrogenation (7 wt.% H) show results consistent with lower hydrogenation, with $Mg(BH_4)_2$-like features and no closoborane intermediates

XAS shows filling of B $2p_z$ state with deeper H absorption, but some remains



FTIR shows mostly $Mg(BH_4)_2$ features with some MgH_2



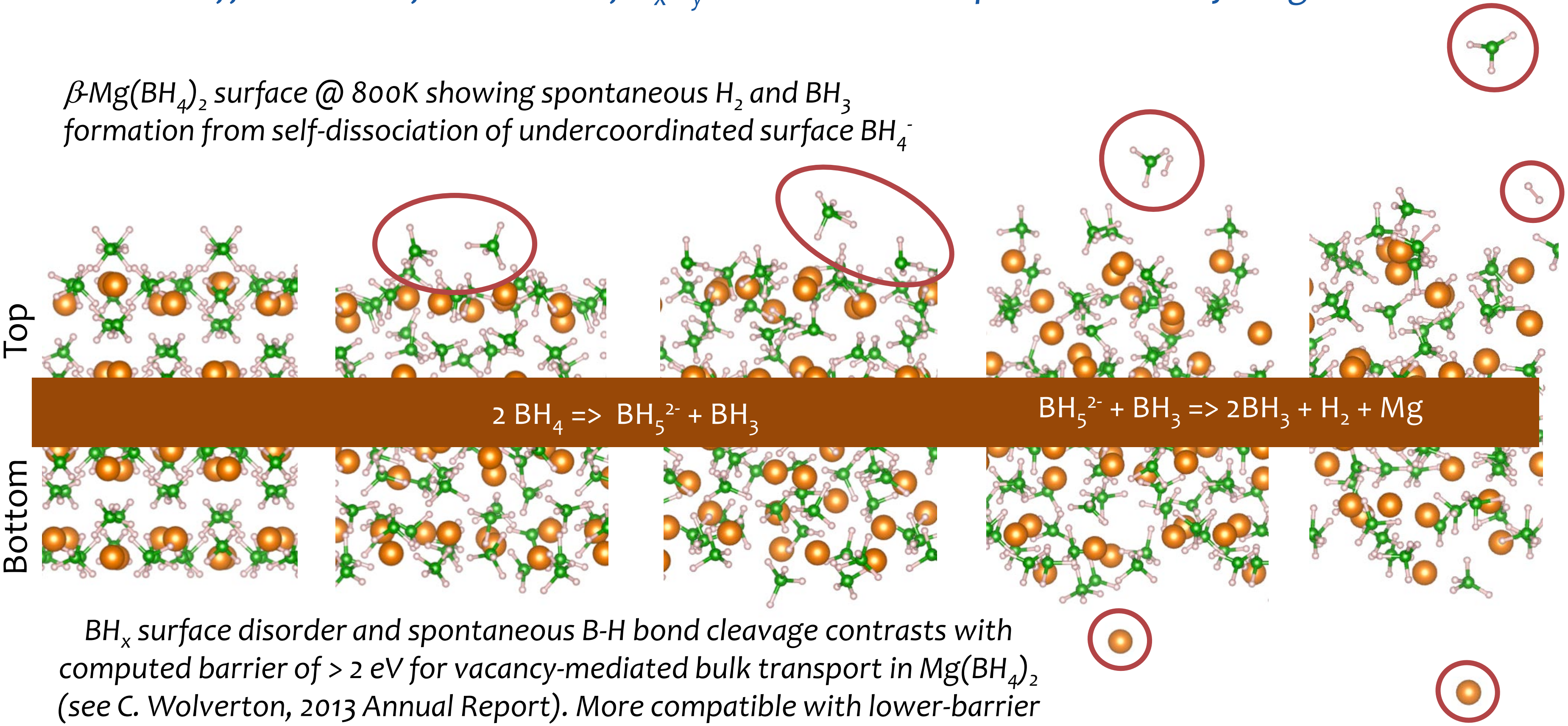
Collaborating with T. Autrey and M. Chong (PNNL) who are providing other suspected intermediates for us to characterize for deeper (de)hydrogenation studies: Et_4N salts of $B_{10}H_{10}$, B_3H_8, B_9H_{14} and $B_{11}H_{14}$

Differences between direct uptake pathway and known desorption pathway (via intermediates) highlight the solid-state nature of the MgB_2 hydrogenation reaction

Accomplishment: Local chemical pathways for BH_x formation

High-temperature ab initio molecular dynamics reveals possible chemical pathways for H diffusion and formation of B_xH_y intermediates upon initial dehydrogenation

β-$Mg(BH_4)_2$ surface @ 800K showing spontaneous H_2 and BH_3 formation from self-dissociation of undercoordinated surface BH_4^-



$2\ BH_4 \Rightarrow BH_5^{2-} + BH_3$

$BH_5^{2-} + BH_3 \Rightarrow 2BH_3 + H_2 + Mg$

BH_x surface disorder and spontaneous B-H bond cleavage contrasts with computed barrier of > 2 eV for vacancy-mediated bulk transport in $Mg(BH_4)_2$ (see C. Wolverton, 2013 Annual Report). More compatible with lower-barrier isotope-exchange measurements (Hagemann et al., JPCC 114, 10045 (2010))

Low-barrier H_2 formation and H transport can initiate at surfaces and interfaces of $Mg(BH_4)_2$ that contain undercoordinated BH_4^- units with higher entropy

Accomplishment: Improved thermodynamic predictions

Understanding reaction pathway and kinetics requires reconciliation of discrepancies between experiment and theory for stability of reaction intermediates

Why do theoretical and experimental pathways differ (e.g., stability of $Mg(B_3H_8)_2$)?

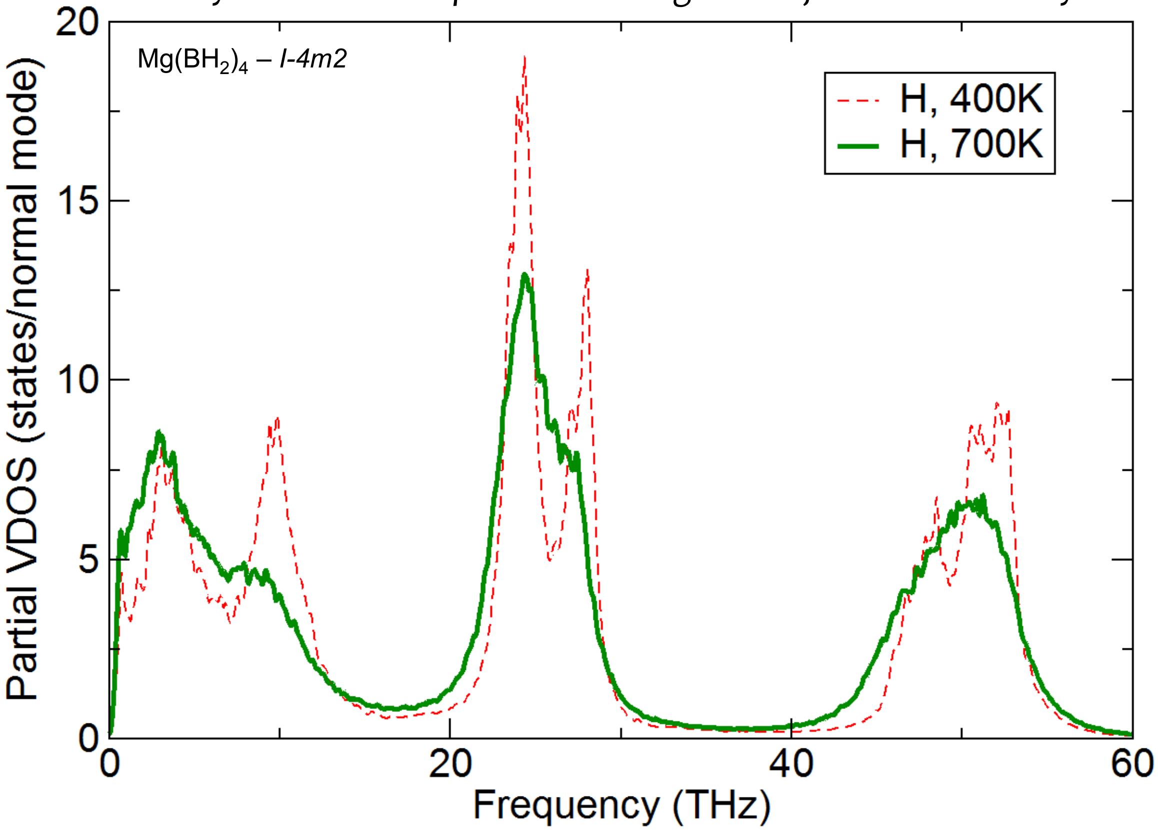
1) *Anharmonic contributions to free energy (due to B_xH_y molecular modes)*
2) *Microstructure (interface/surface contributions)*
3) *Kinetic differences (nucleation, transport, or chemical)*
4) *Non-crystalline phases (molecular defects vs. amorphous vs. polycrystalline)*

We have been evaluating possible relevance of each of the above factors, with plans to inform and validate models with nanoparticle experiments in Phase II

Accomplishment: Finite-temperature anharmonic contributions

Computed atom-resolved dynamical contributions based on ab initio molecular dynamics, including oft-neglected anharmonic contributions

Changes in the vibrational density of states (VDOS) of the H subsystem with temperature is a signature for anharmonicity



Anharmonic modes contribute anywhere between 1 and 12 kJ/mol to the free energy, and preliminary investigations indicate that values for surfaces may be even higher

Accomplishment: Understanding phase nucleation

Computed nucleation barriers for key reaction phases to assess role of phase nucleation in (de)hydrogenation rate

Stress-free nucleation barriers

Phase	Barriers in meV (elemental reference)	Barriers in meV at heterogeneous interface
γ-$Mg(BH_4)_2$	0.6	0.1
β-$Mg(BH_4)_2$	7.0−54.7	1.0−8.0
$MgB_{12}H_{12}$	0.02	0.03
MgB_2	624.3−961.7	–
MgH_2	115.2−154.8	0.2

Based on Wulff construction; ranges are Mg/B rich limits

Volume expansion suggests internal stress will play significant role

Reaction			Volume expansion (%)
MgB_2 + x H_2	→	γ-$Mg(BH_4)_2$	+469%
MgB_2 + x H_2	→	β-$Mg(BH_4)_2$	+334%
MgB_2 + x H_2	→	1/6 $MgB_{12}H_{12}$ + 5/6 MgH_2	+160%
1/6 $MgB_{12}H_{12}$ + 5/6 MgH_2	→	γ-$Mg(BH_4)_2$	+119%
1/6 $MgB_{12}H_{12}$ + 5/6 MgH_2	→	β-$Mg(BH_4)_2$	+67%

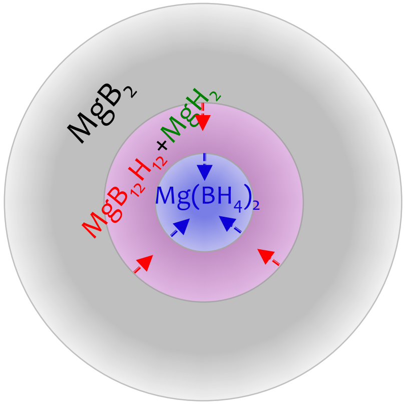
Working to include stress and interfacial penalties to predict microstructure by integrating into phase-field model and comparing against uptake kinetics in nanoparticles

Accomplishment: Phase fraction predictions of Mg-B-H

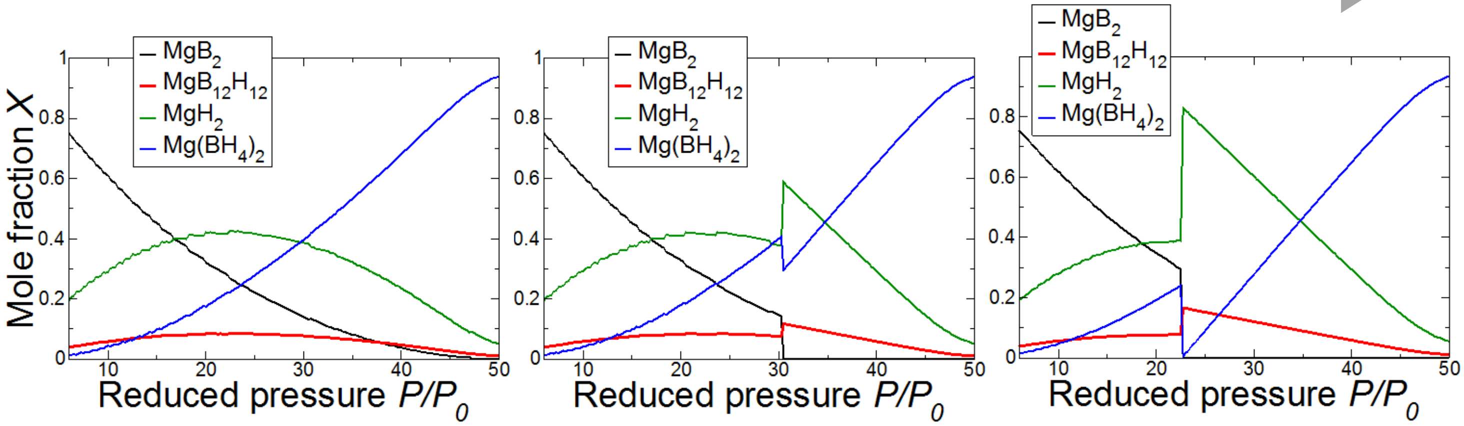
As proof-of-concept, tested size-dependent phase fraction predictions for $MgB_2/MgB_{12}H_{12}/Mg(BH_4)_2$ three-phase system using model core-shell microstructure (no entropy yet)

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

Model microstructure for dehydrogenation



Decreasing particle size (@ fixed temperature)



Tests show reaction pathways can be altered by controlling particle sizes

Future work will focus on alternative microstructures with interfacial transport pathways, as well as incorporating fully anharmonic entropy

Accomplishment: Initial phase-field kinetics simulation

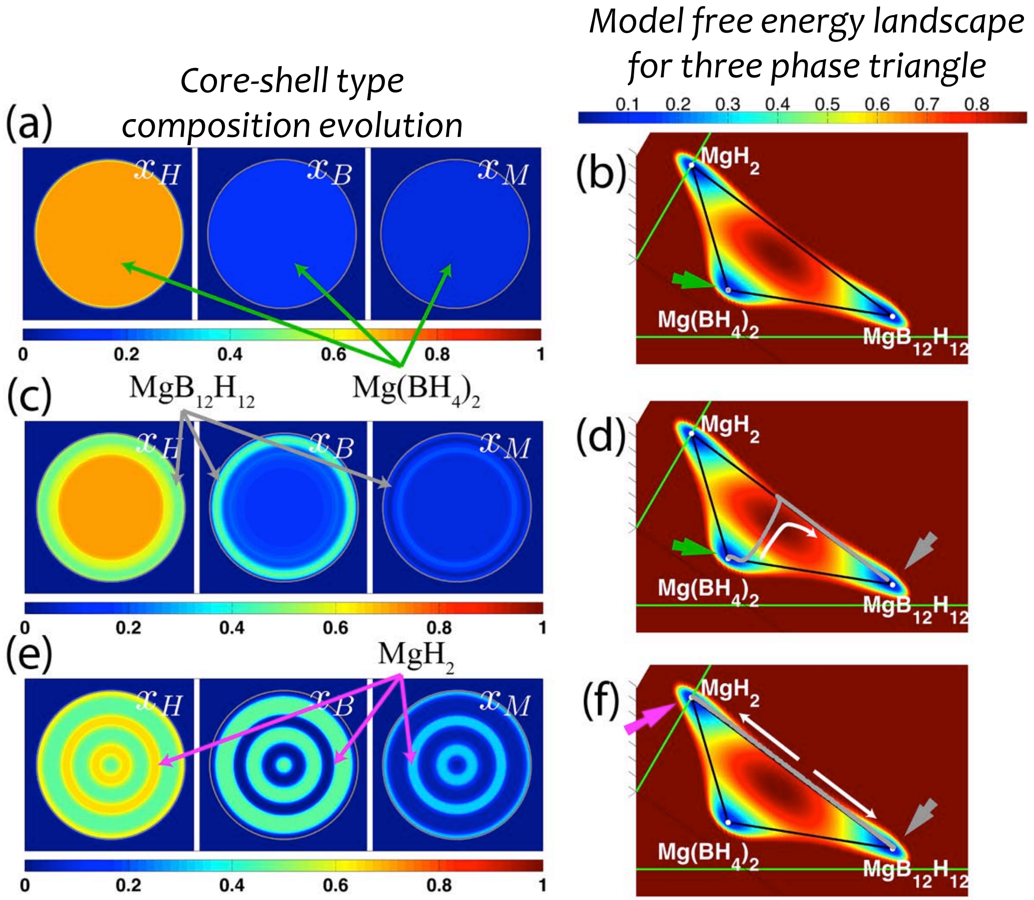
Demonstrated feasibility of phase-field kinetics simulation based on assumed free energy surface and three-phase model (MgH_2, $Mg(BH_4)_2$, $MgB_{12}H_{12}$)

$6Mg(BH_4)_2 \rightarrow MgB_{12}H_{12}+5MgH_2+13H_2$

Considered two (de)hydrogenation stages:

- *Mg-MgH_2 (interstitial hydride model[1])*
- *$Mg(BH_4)_2$-$MgB_{12}H_{12}$-MgH_2 (multiphase conversion model[2])*

Decomposition of $Mg(BH_4)_2$ into $MgB_{12}H_{12}$ and MgH_2 within phase-field simulations



Core-shell type composition evolution

Model free energy landscape for three phase triangle

Will parameterize with accurate free energy surface generated by combining first-principles DFT with experimental uptake curves

---

[1] T. G. Voskuilen *et al.*, *Int. J. Hydrogen Energy*, 38, 7363 (2013)

[2] H.-C. Yu *et al.*, *J. Phase Equilib. Diff.* (2015)

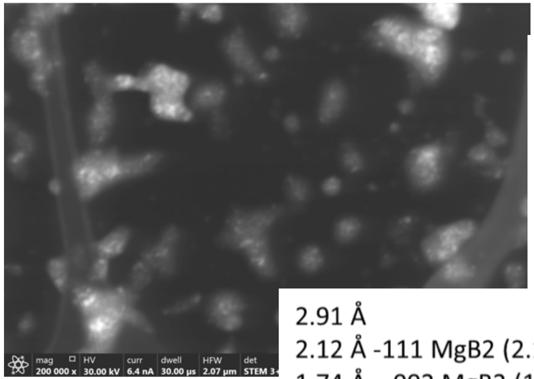
Accomplishment: Nanoparticle synthesis

Demonstrated synthesis of MgB_2 nanoparticles with small diameter (< 10 nm)

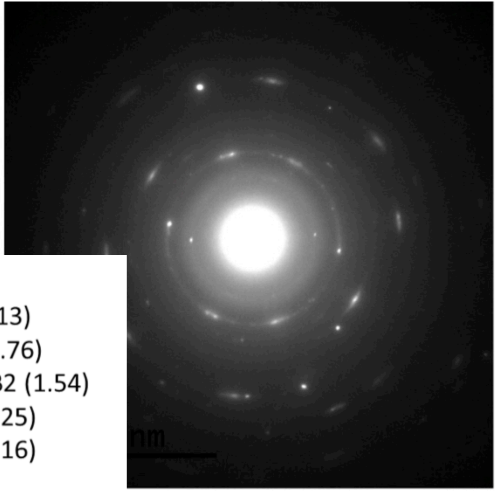
Size-selective nanoparticles are key to validating and informing models and proposed mechanisms and necessary for progressing to Phases II and III of the project

- *Our approach uses **surfactant-assisted ball milling** combined with Stavila Stripping Method for surfactant removal and solvent dispersion to separate out size fractions*

STEM of the very small particle fraction from an early trial

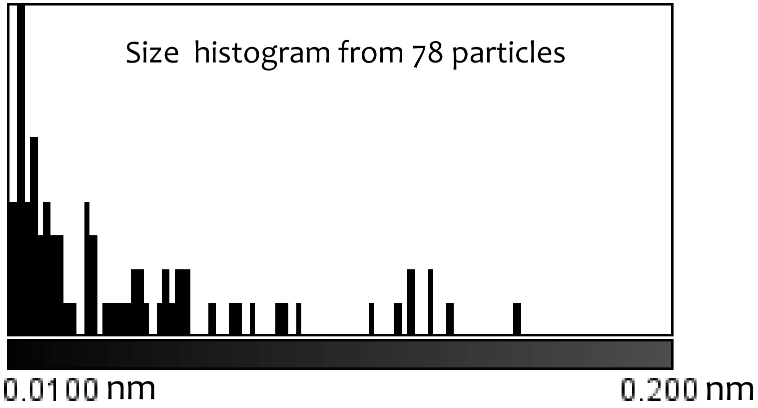


STEM Electron Diffraction shows crystalline MgB_2 with some impurities



2.91 Å
2.12 Å -111 MgB2 (2.13)
1.74 Å – 002 MgB2 (1.76)
1.52Å – 110/120 MgB2 (1.54)
1.24Å – 021 MgB2 (1.25)
1.14Å – 210 MgB2 (1.16)
0.954Å

Mostly small (< 10 nm dia.) particles are being made but there is a distribution



Working to narrow size distribution and improve purity of synthesized NPs by altering milling parmeters and solvent dispersion steps

Collaborations

Collaborations are crucial for realizing theory/characterization/synthesis partnership

Ab initio modeling/multiscale integration

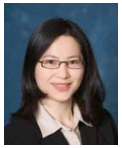
Dr. Brandon Wood (PI, LLNL)*

Dr. Keith Ray (LLNL)*

Dr. ShinYoung Kang (LLNL)*

Mesoscale phase-field modeling

Prof. Katsuyo Thornton (Univ. Michigan)**



Dr. Tae Wook Heo (LLNL)*

Nanoparticle synthesis & testing

Dr. Vitalie Stavila (Sandia)**

Characterization

Dr. Lennie Klebanoff (Sandia)**

Dr. Jonathan Lee (LLNL)*

Additional collaborations

- Neutron diffraction/spectroscopy: T. Udovic (NIST; within DOE Hydrogen Program)
- Borohydride chemistry and NMR: T. Autrey and M. Bowden (PNNL; H_2 storage characterization group)
- Kinetic Monte-Carlo for solid-state diffusion: H. Kreuzer (Dalhousie U.)
- HyMARC collaborations: XAS/XES and computational spectroscopy (LBNL); free energy analysis (LLNL); phase fraction prediction/phase-field codes (LLNL); high-pressure hydrogenation (SNL); nanoconfining carbons (LLNL)
- Ultra-high-pressure synthesis of Mg-B-H materials (D. Novella, LLNL)

*prime **subcontract

Remaining challenges/barriers & mitigation strategies

- **Nanoparticle agglomeration may make size-dependent assessment difficult**
  - *Will compare nanoparticle results against the more traditional nanoconfinement approach using nanoconfining media provided through HyMARC*
- **Slow hydrogenation kinetics limits data collection**
  - *Take advantage of slow kinetics to inform models with ex situ characterization of samples with arrested (de)hydrogenation*
- **Need techniques to bridge time scales associated with kinetic processes**
  - *Leveraging HyMARC capabilities to apply multiscale transport formalism*
- **Phase diagram for the Mg-B-H system is highly complex**
  - *Developing multi-phase framework that can handle multiple intermediates*
  - *Short-lived intermediates may safely be neglected*
- **Free energy surface may depend on temperature**
  - *Ab initio molecular dynamics at various temperatures will help elucidate key thermal effects and anharmonic processes*
  - *Models are flexible enough to accept direct experimental inputs from rate analysis*
- **No direct knowledge of interfacial structure**
  - *Will continue to engage HyMARC in an attempt to image nanoparticle interfaces without sample damage*
  - *Adapting HyMARC statistical models that examine consequences of interface energy assumptions on overall predicted phase pathway*

Remaining FY16/FY17 milestones and proposed completion

Milestone	Description	Proposed completion
1	Compute thermodynamics of surfaces and interfaces of nanoscale $MgB_2/Mg(BH_4)_2$ and measure desorption/absorption rate*	Q3 FY16
2	Establish modeling framework for surface chemical reactions and calculate surface-dependent thermodynamics, migration, and dissociation	Q4 FY16
G/NG #2	G/NG for Phase II: Demonstrate 75% agreement between model predictions and observations of bulk phase fractions and demonstrate scalable synthesis of $MgB_2/Mg(BH_4)_2$ nanoparticles in 50 g quantities	Q1 FY17
3	Identify rate-limiting process in (de)hydrogenation of nanoscale $Mg(BH_4)_2/MgB_2$	Q2 FY17
4	Compute kinetic improvement upon nanosizing/catalyzing Mg-B-H, and deliver three-phase kinetic model that shows 50% agreement with experimental (de)hydrogenation rates	Q3 FY17

*surfactant-assisted ball milled MgB_2 will be compared with nanoconfined using frameworks from HyMARC

Future work focuses on nanoparticle measurements and kinetic modeling

Technology transfer activities

- Viktor Balema (Sigma-Aldrich) is kept informed of our research progress, which will foster commercialization of viable new materials

Summary

Key Concepts:

- Integrated **theory/synthesis/characterization** framework aims to understand and improve $Mg(BH_4)_2$ by comparing bulk properties with effects of **nanostructuring** and **doping**
- Unraveling kinetics and reaction pathways for bulk and nanoparticle $Mg(BH_4)_2 \leftrightarrow MgB_2 + 4H_2$ interconversions relies on understanding both **local chemistry** and **solid-state phase transformation** mechanisms at multiple scales
- Knowledge gained demonstrates the relevance of chemical and transport processes at **interfaces**, suggesting the possibility of **morphology/microstructure engineering** as a viable improvement strategy
- Complete **synthesis & characterization** approach directly informs and validates theoretical models with respect to reaction pathways, intermediates, kinetics

Impact:

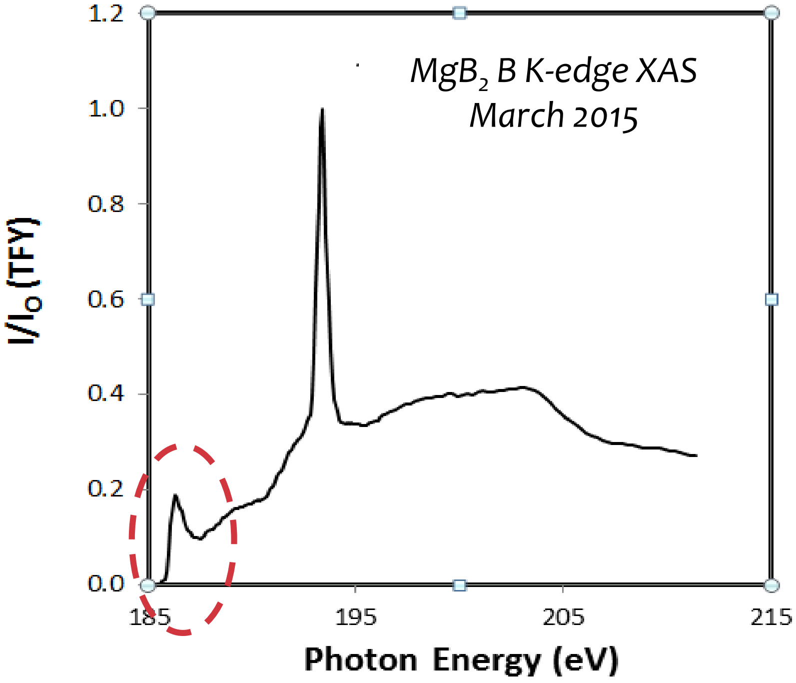
- Focuses on material with potential to meet **ultimate DOE hydrogen storage targets**
- Goes beyond ideal thermodynamic modeling to directly target **kinetics in a comprehensive way** and address challenges of **"real" materials**
- Understanding limitations & sensitivities could lead to $Mg(BH_4)_2$ particles with **optimized morphology and composition** for favorable kinetics
- **Knowledge gained** can be applied to other complex hydride candidates

Technical backup slides

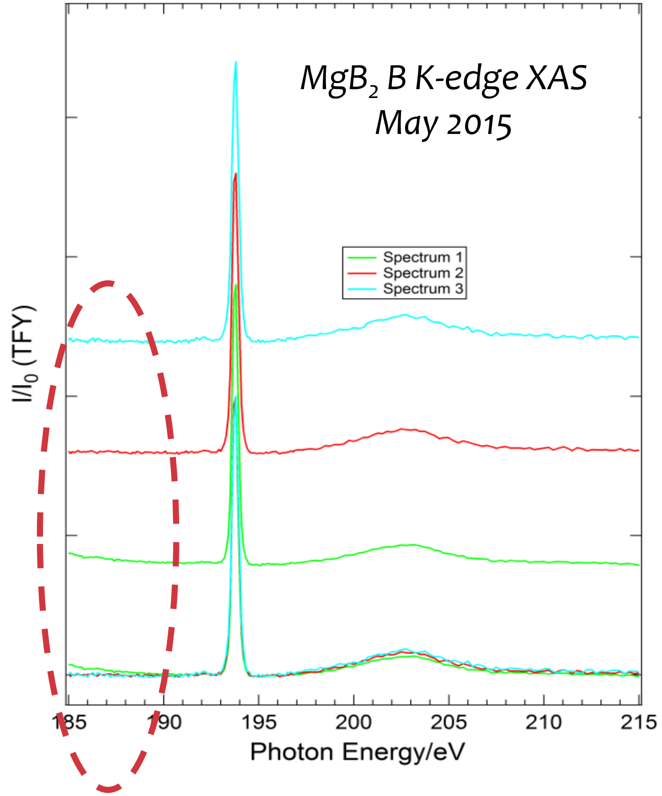
Accomplishment: Spectroscopy to probe local chemistry

Oxidation was found to be an issue, which may explain heterogeneous surface kinetics

XAS total fluorescence yield, ~300 nm penetration



MgB_2 B K-edge XAS
March 2015



MgB_2 B K-edge XAS
May 2015

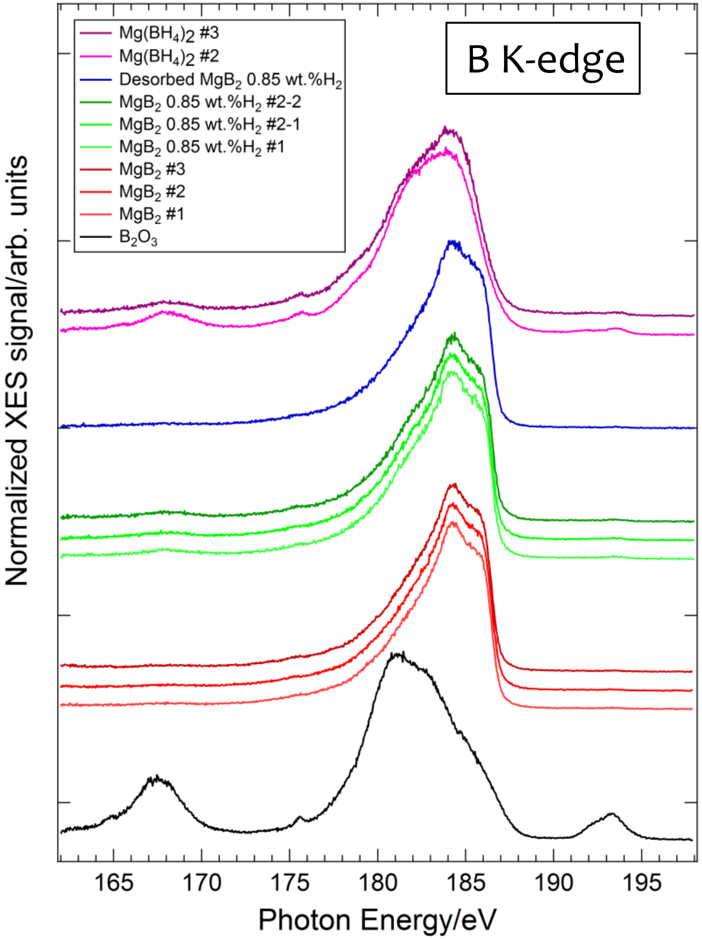
- *Oxidation increases with time*
- *Established protocols to minimize oxidation by using fresh samples and proper handling*
- *Surface oxidation cannot be entirely eliminated*

Care must be taken to minimize oxidation, and its effects must be considered

Backup slide: New protocols for largely minimizing oxidation

XES and XAS measurements (both TEY and TFY) show that one can get meaningful spectra with high surface sensitivity using these protocols with manageable levels of surface oxide

X-Ray Emission Spectra (XES)



(1) Use freshly (< 1 week) prepared samples if possible.

(2) Store samples in glove box < 0.5 ppm H_2O

(3) Transport samples under Ar in hermetically sealed double envelopes

(4) Load into the spectrometer vacuum system under a UHP argon environment in a glove bag with humidity meter (can detect 25 ppm water), or in a portable load lock.

(5) Minimize transfer time to spectrometer load lock to 15 mins or less.

(5) Pump down (from argon) to <10^{-7} Torr in < 1 hr.

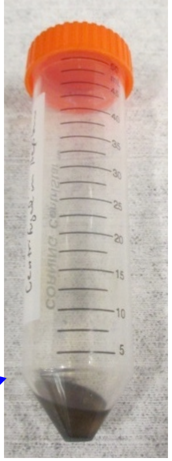
(6) Conduct XES/XAS measurements at ~ 10^{-9} Torr

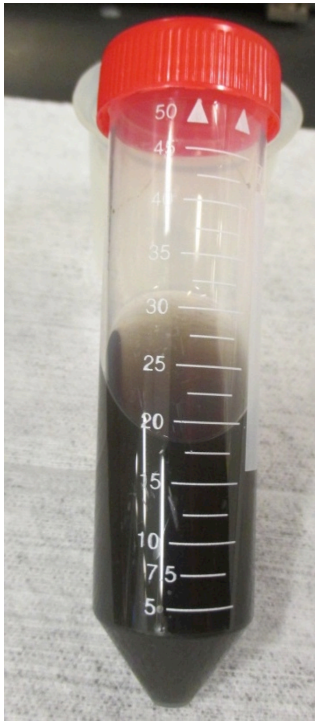
Backup slide: Procedure for making MgB_2 nanoparticles

Surfactant –assisted Ball Milling: *Y. Wang et al. Nanotechnology* ***18****, 465701 (2007).*

Typical Procedure:

1. Combine high-purity MgB_2 with heptane, oleic acid and oleyl amine.
2. Use a ZrO_2 or WC milling pot.
3. Ball mill for 5 - 20 hours.
4. Disperse product in heptane, filter out insolubles (bulk particles).
5. Centrifuge at 5000 rpm for 25 minutes, producing deposit and remaining solution.
6. Remove material that deposits (medium size NPs (> 10 nm) coated with surfactant)
7. Recover material that remains in solution (NPs < 10 nm dia. coated with surfactant) with EtOH wash, collect depositing NPs (<10 nm).





Backup slide: Surface energies computed at 0 K

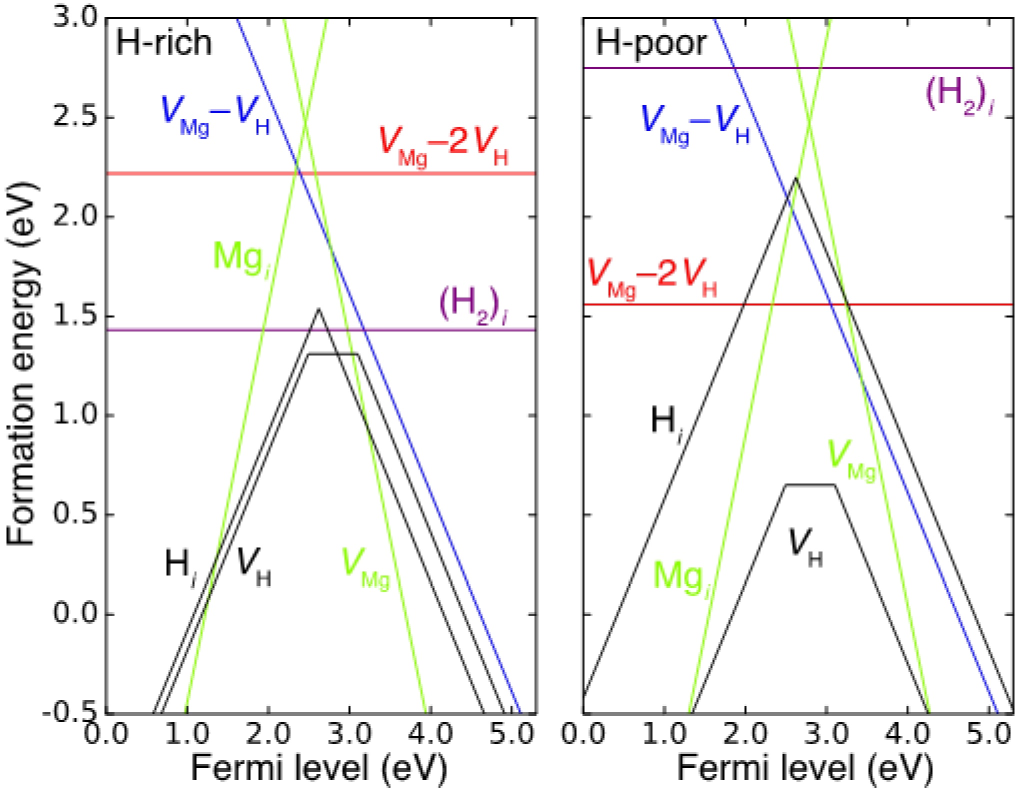
Phase	Surface	Surface energies w/o dipole correction (J/m²)	
		At Mg-rich limit	At Mg-poor limit
γ-Mg(BH$_4$)$_2$	{100} Mg rich	1.89	2.22
	{100} BH$_4$ rich	(in process)	(in process)
	{111} Mg rich	0.74	0.96
	{111} stoi.	0.22	0.22
	{111} BH$_4$ rich	−0.07	−0.30
	{110} stoi.	0.22	0.22
β-Mg(BH$_4$)$_2$	{100} Mg rich	0.46	0.64
	{100} BH$_4$ rich	0.11	−0.07
	{010} stoi.1	0.57	0.57
	{010} stoi.2	3.43	3.43
	{001} Mg rich	0.59	0.80
MgB$_{12}$H$_{12}$	{100} stoi.	0.13	0.13
	{010} stoi.	0.01	0.01
	{001} Mg full	1.44	2.45
	{001} Mg line	0.15	0.15
	{001} Mg para	0.12	0.12
	{001} BH full	−0.11	−1.10
	{001} BH line	0.65	0.65
	{001} BH zigzag	0.26	0.26

Phase	Surface	Surface energies w/o dipole correction (J/m²)	
		At Mg-rich limit	At Mg-poor limit
MgB$_2$	{1–100} Mg rich	1.60	1.91
	{1–100} B rich	2.98	2.68
	{1–100} stoi.	4.04	4.04
	{0001} Mg full	0.65	1.07
	{0001} Mg line	1.82	1.82
	{0001} Mg dia	1.82	1.82
	{0001} B full	3.17	2.76
	{0001} B line	5.18	5.18
	{0001} B dia	7.77	7.77
	{0001} B ziazag	2.18	2.18
	{11–20} stoi.	2.40	2.40
	{1–101} stoi.	1.80	1.80
MgH$_2$	{100} Mg rich	4.26	4.58
	{100} H rich	1.74	1.43
	{100} stoi.	0.94	0.94
	{001} full	0.84	0.84
	{001} Mg line	1.28	1.06
	{001} Mg square	0.82	0.61
	{001} B line	2.67	2.89
	{001} B square	4.10	4.31
	{001} B band	4.01	4.23

Backup slide: Defects in hydrogen-containing phases

Computed energies of H-related defects in parent phases to understand intermediate chemical reaction pathways in hydrogen-containing phases ($Mg(BH_4)_2$, MgH_2, $MgB_{12}H_{12}$)

Example: DFT-PBE defect formation energies for MgH_2



Differences between defect chemistries at H-poor and H-rich interfaces may be relevant for understanding hysteresis in reaction pathway