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

DOE Annual Merit Review

June 10, 2015

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Lawrence Livermore National Laboratory

LLNL-PRES-669450

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Project ID# ST118

Overview

Timeline

Project start date: 06/30/2014
Project end date: 06/30/2017

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)
Total funds spent (as of 3/15): $275K

Team

Project Lead:
Lawrence Livermore National Laboratory

Funded Partners:
Sandia National Laboratories
University of Michigan

Relevance

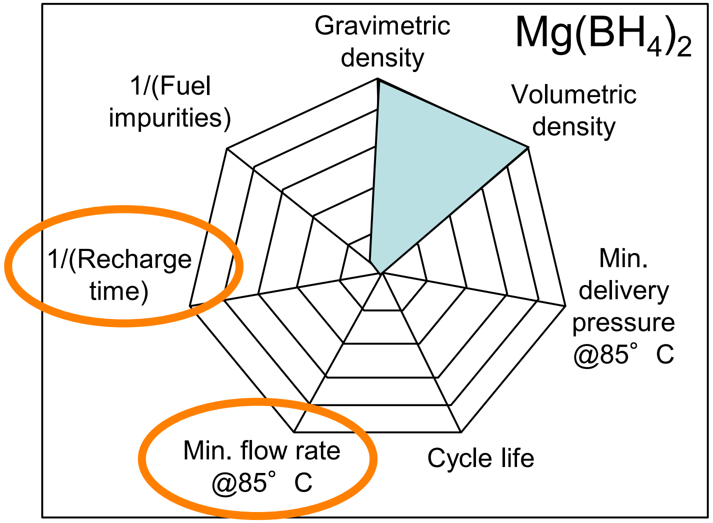
Light-metal hydrides such as $Mg(BH_4)_2$ are attractive candidates for compact, lightweight, and safe hydrogen storage tanks for fuel cell vehicles, but they absorb and release hydrogen **too slowly**

Project objectives:

- Combine **theory, synthesis, and characterization** techniques at **multiple length/time scales** to understand kinetic limitations and possible improvement strategies in $Mg(BH_4)_2$ with relevance to light-metal hydrides
- Deliver a **flexible, validated, multiscale theoretical model** of (de)hydrogenation kinetics in "real" Mg-B-H materials, and use predictions to develop a **practical material** that satisfies 2020 onboard H_2 storage targets

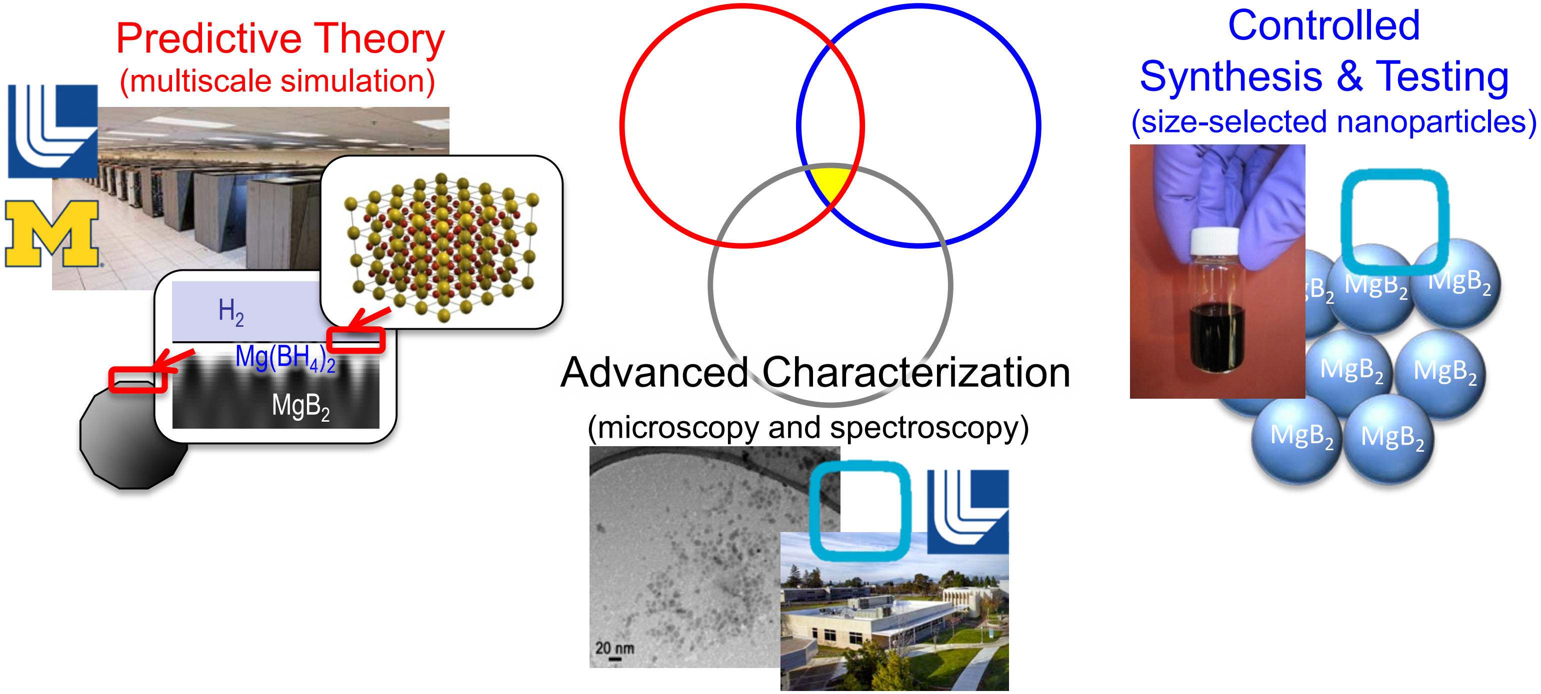
Current project year objectives:

- Synthesize & characterize high-purity MgB_2 and $Mg(BH_4)_2$ materials
- Measure hydrogenation kinetics of bulk MgB_2
- Establish & calibrate initial modeling framework, and test computational feasibility



adapted from: L.E. Klebanoff and J.O. Keller, IJHE **38** (2013) 4533-4576

Approach: Integrated multiscale experiment-theory framework



Predictive Theory
(multiscale simulation)

Controlled Synthesis & Testing
(size-selected nanoparticles)

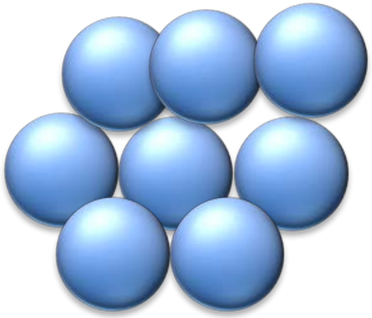
Advanced Characterization
(microscopy and spectroscopy)

- Tightly integrated **theory-synthesis-characterization** effort focuses on scalable, cost-effective optimization by reducing particle size or using metal additives
- **Multiscale modeling** of diverse chemical processes during hydrogen uptake and release in $Mg(BH_4)_2$ particles using state-of-the-art supercomputing facilities at LLNL
- Novel **synthesis & characterization** approach for directly informing, vallidating, and verifying predictions using advanced experimental capabilities at Sandia and LBNL
- Addresses challenges of **"real" materials** beyond idealized theoretical descriptions

Approach: Controlled synthetic routes to kinetic improvement

Dehydrogenation kinetics are poor, but there are consistent reports of pathways to improvement via **chemical** and **structural** changes in metal hydrides. We focus on two routes:

Nanosizing



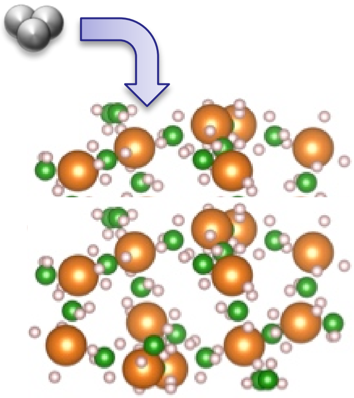
$Mg(BH_4)_2$: M. Fichtner et al., *Nanotechnology* **20**, 204029 (2009)

$NaAlH_4$: T. Mueller and G. Ceder, *ACS Nano* **4**, 5647 (2010) ; V. Stavila et al., *ACS Nano* **6**, 9807 (2012)

$LiNH_2$: N. Poonyayant et al., manuscript in preparation

$LiBH_4$: X. Liu et al., *J. Phys. Chem. C* **114**, 14036 (2010)

Catalytic Doping



$Mg(BH_4)_2$: Newhouse et al., *J. Phys. Chem. C* **114**, 3224 (2010)

$NaAlH_4$: Bogdanovic & Schwickardi., *J. Alloys Compd.* **253**, 1 (1997)

$NaBH_4$. D. Hua et *al., Int. J. Hydrogen Energy* **28,** 1095 (2003)

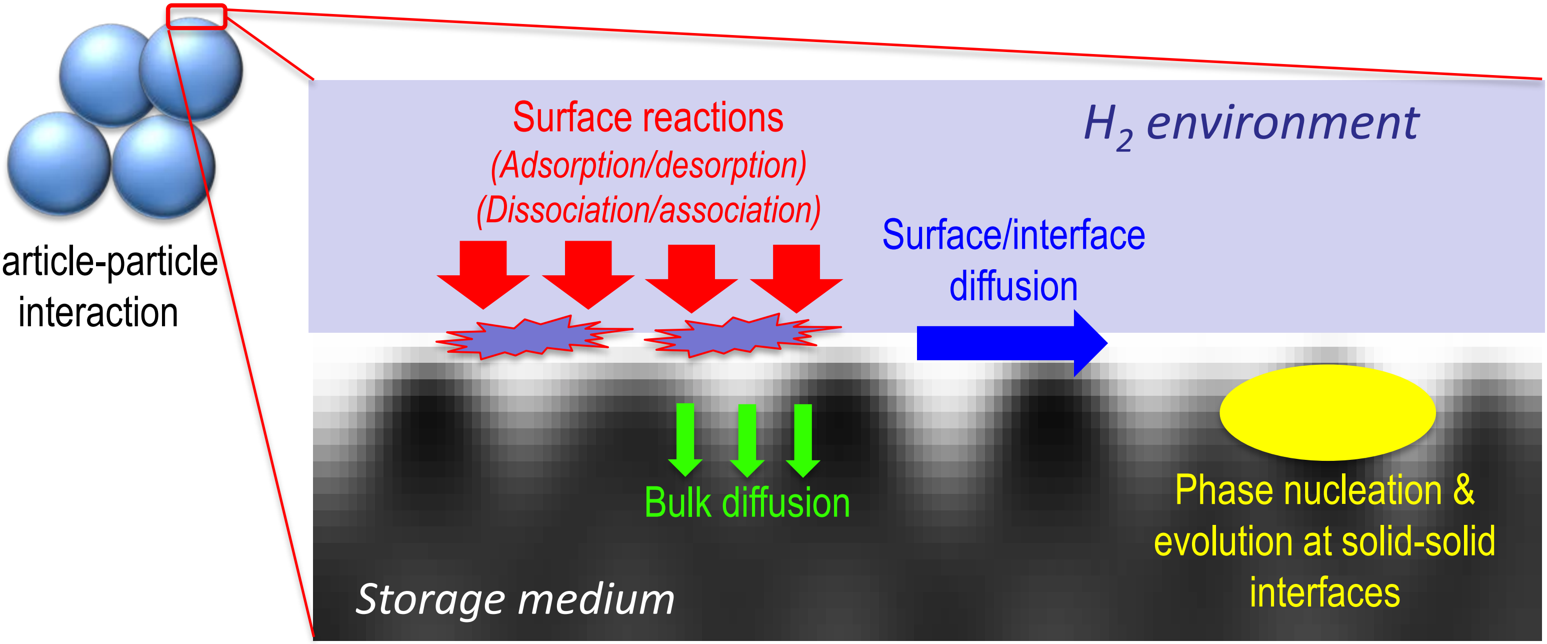
H_3NBH_3: T. He et al., *Chem. Mater.* **21**, 2315 (2009)

$LiNH_2$. T. Ichikawa et *al., J. Alloys Compd.* **365**, 271 (2004)

Our project is built around understanding and leveraging these strategies for improvement: how, why, and when can they help?

Approach: Model diverse H_2 storage physical processes

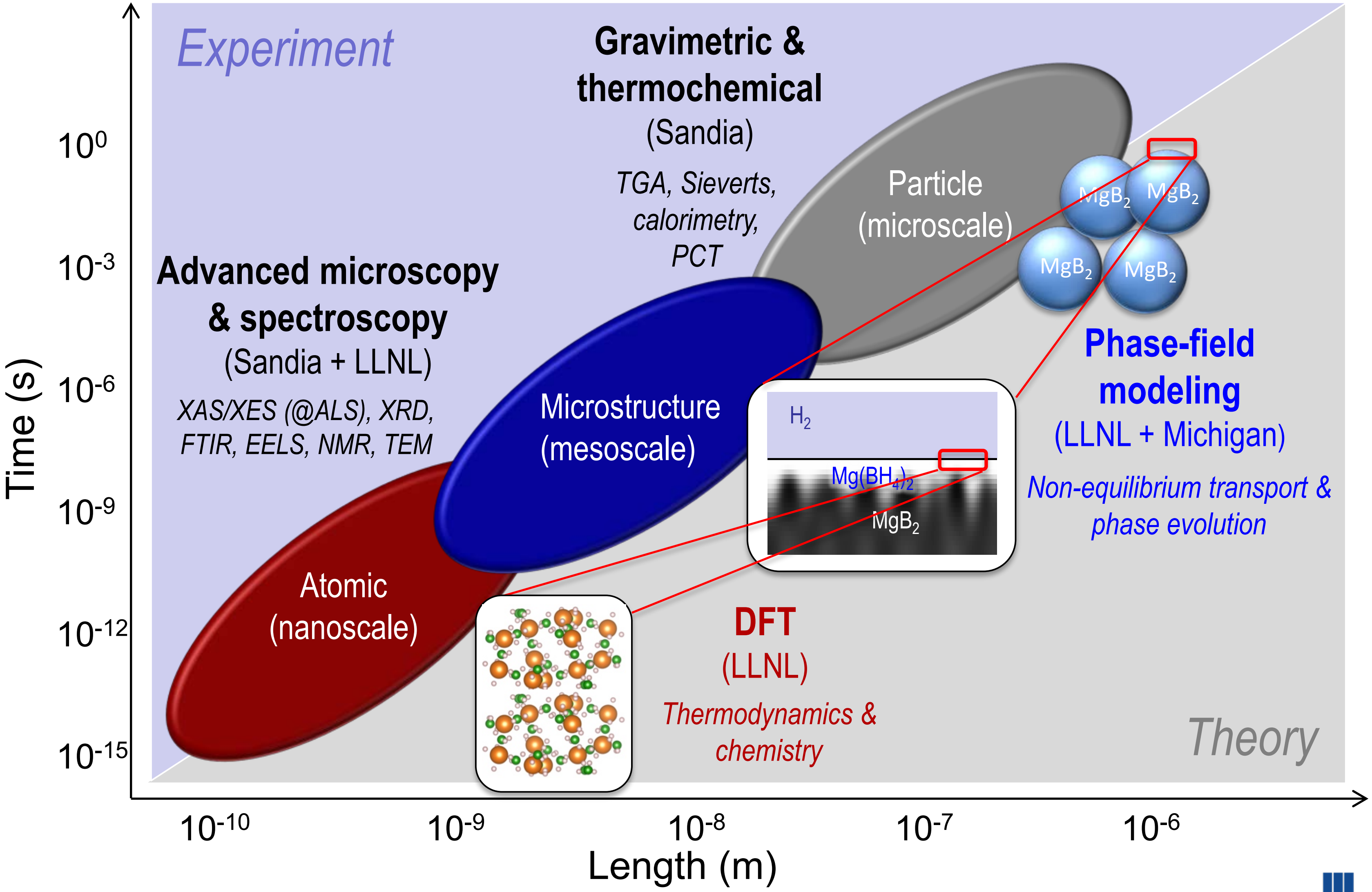
Combined DFT (nanoscale) + phase-field (mesoscale) modeling framework goes beyond bulk thermodynamic properties to include surface and interface effects under non-equilibrium (de)hydrogenation conditions



Leverages prior LLNL LDRD investment in optimized mesoscale methodologies and codes developed for leadership-class supercomputers

Approach: Multiscale characterization and modeling

Understanding **chemical**, **transport**, and **phase** behavior



Experiment

Gravimetric & thermochemical
(Sandia)

TGA, Sieverts, calorimetry, PCT

Advanced microscopy & spectroscopy
(Sandia + LLNL)

XAS/XES (@ALS), XRD, FTIR, EELS, NMR, TEM

Particle (microscale)

Microstructure (mesoscale)

Atomic (nanoscale)

Phase-field modeling
(LLNL + Michigan)

Non-equilibrium transport & phase evolution

DFT
(LLNL)

Thermodynamics & chemistry

Theory

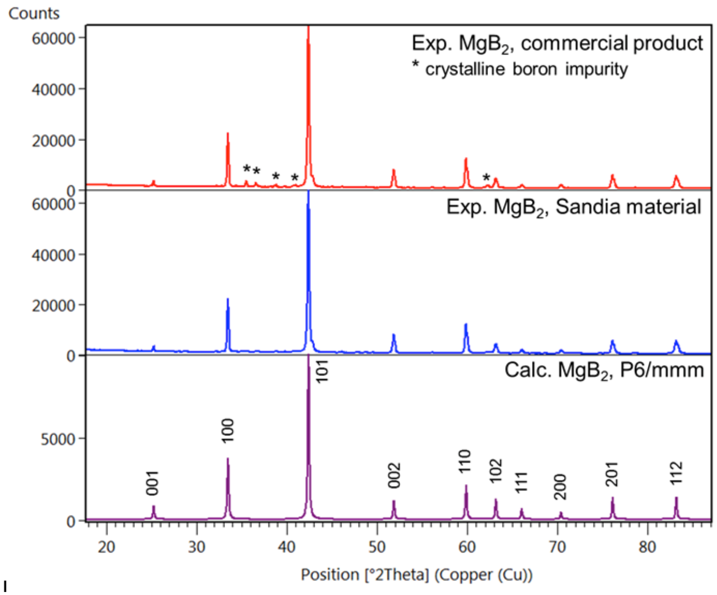
Y1 milestones and key technical accomplishments

- Synthesized high-purity MgB_2 and $Mg(BH_4)_2$ materials
- Performed first measurements of bulk MgB_2 hydrogenation kinetics
- Preliminary spectroscopy of pristine and partially hydrogenated bulk MgB_2
- Established initial modeling framework to predict phase fractions, accounting for:
  - Thermodynamics of interfaces, surfaces, and bulk
  - Elastic effects and mechanical stress/strain
  - Phase nucleation/evolution and nonequilbrium (de)hydrogenation
- Established platform for simple integration of first-principles thermodynamic data into phase-fraction code
- Initial calculations of equilibrium thermodynamic parameters for bulk MgB_2-$Mg(BH_4)_2$
- Tested computational feasibility of codes on LLNL supercomputers
- Tested theoretical predictive capability using Li-N-H system; successfully explained observed changes in reaction pathways with nanoconfinement
- **Met all key milestones for Y1**

Accomplishment: Synthesized high-purity MgB_2 and $Mg(BH_4)_2$

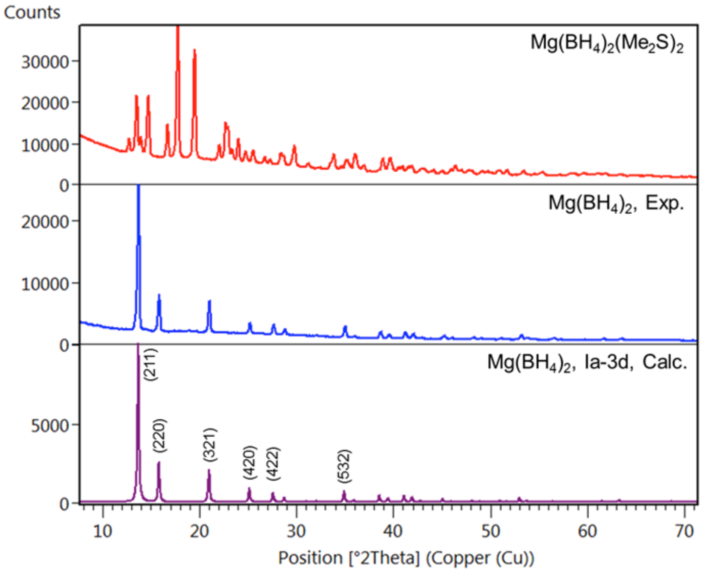
Very pure samples of $Mg(BH_4)_2$ and MgB_2 are needed for the experiments

MgB_2



We developed a synthetic approach utilizing the reaction of excess Mg with boron to isolate phase-pure MgB_2 with no impurities

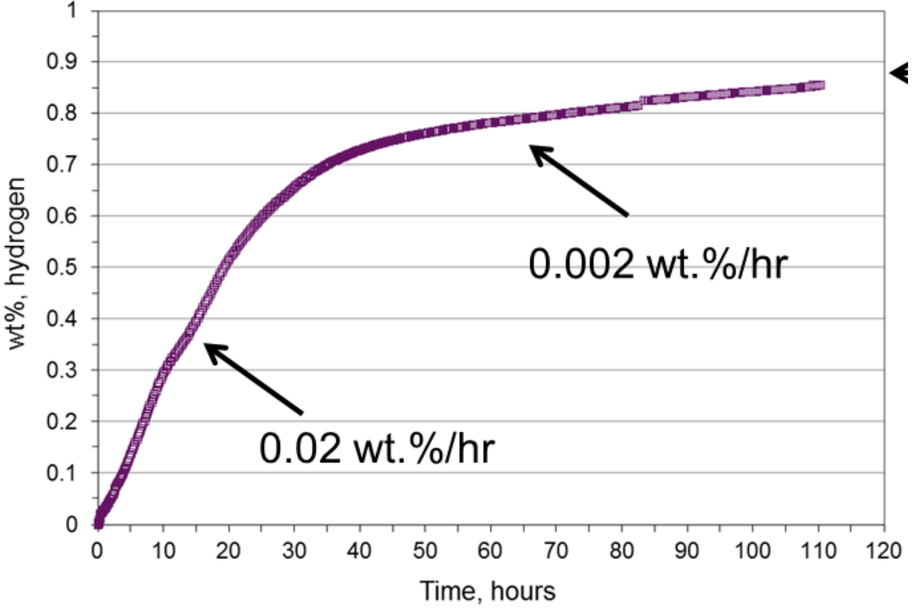
$Mg(BH_4)_2$



Pure α-$Mg(BH_4)_2$ was synthesized using reaction of $MgBt_2$ with BH_3-SMe_2 in heptane, followed by mild heating in vacuum

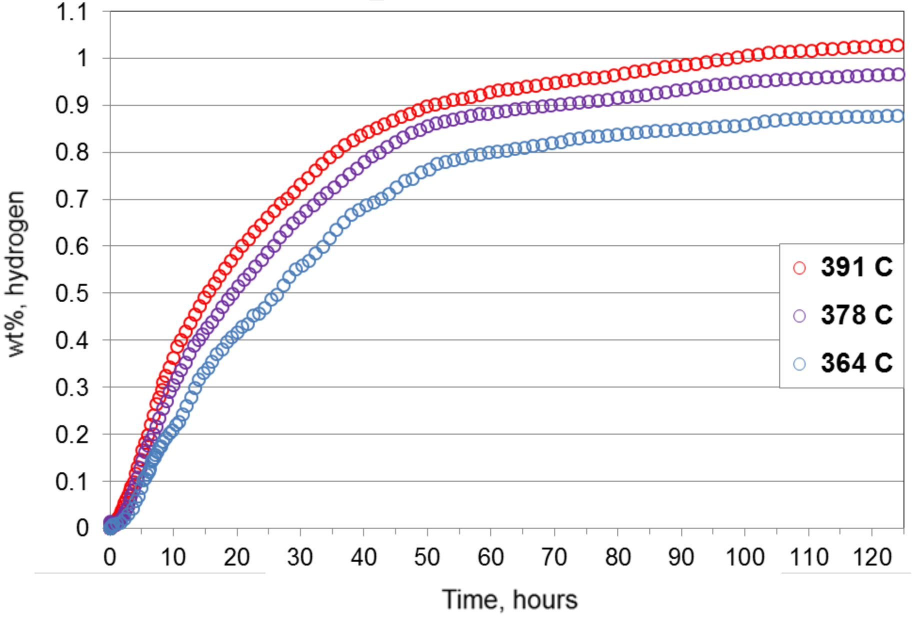
Accomplishment: Measured initial bulk MgB_2 hydrogenation rate

105 bar H_2, 380 °C



~ 39 mole % of MgB_2 sample has reacted to form MgB_2-H, identification of products in progress

145 bar H_2, 364, 378 and 391 °C



Temperature-dependent hydrogenation studies will allow for extraction of activation energies, for comparison with theory

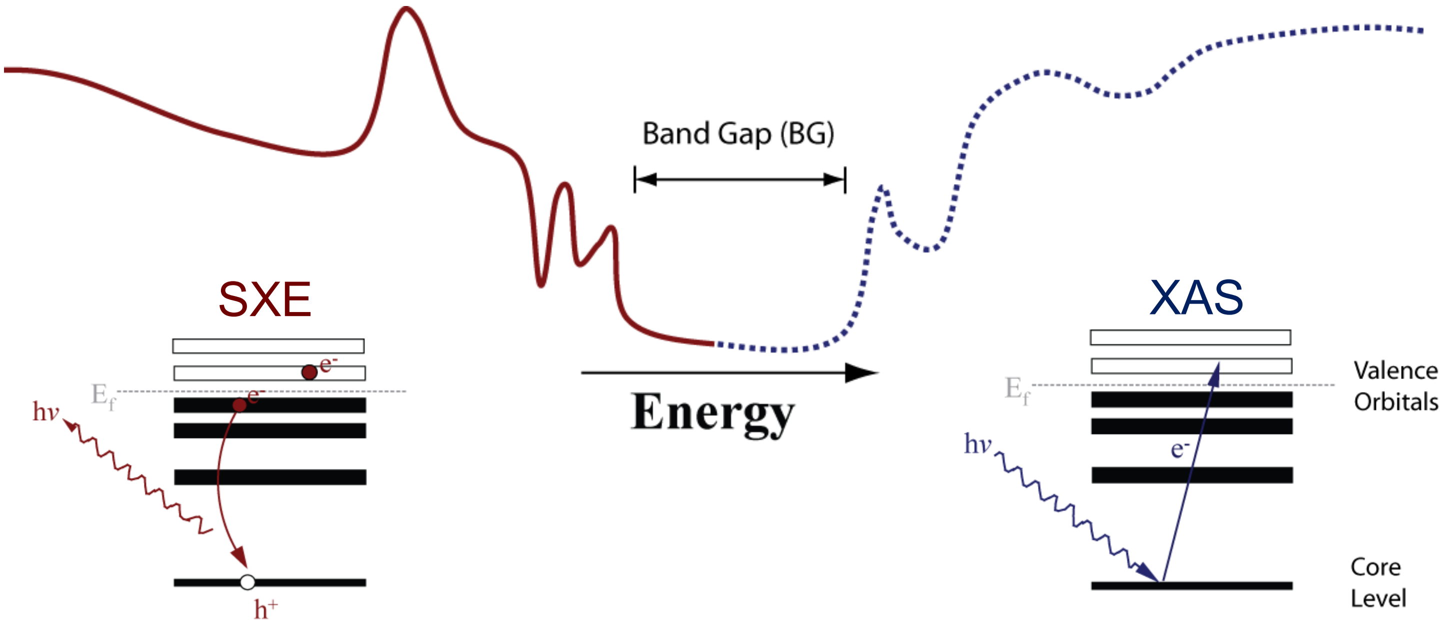
- Initial bulk hydrogenation rate ~ 0.02 wt.%/hr, followed by a slower ~ 0.002 wt.%/hr., suggestive of multiple-barrier processes
- Determination of initial bulk MgB_2 hydrogenation activation energies is in progress

Accomplishment: XES/XAS at the Advanced Light Source (LBNL)

X-ray Emission Spectroscopy (XES) and X-ray Absorption Spectroscopy (XAS) enable element-specific tracking of the course of hydrogen storage reactions

Soft X-ray Emission (SXE) spectroscopy

X-ray Absorption Spectroscopy (XAS)

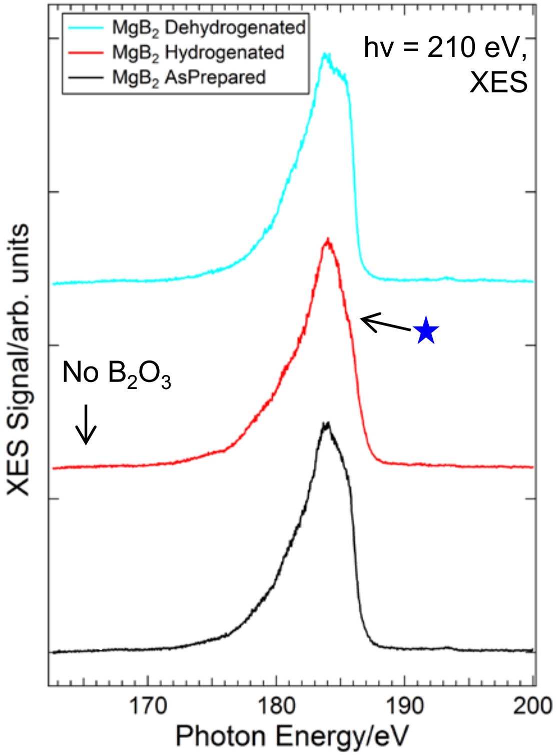


- Measurement of the occupied DOS
- Resolve structure of filled electronic density of states states

- Element-specific technique
- Angular momentum-resolved probe of the unoccupied electronic DOS

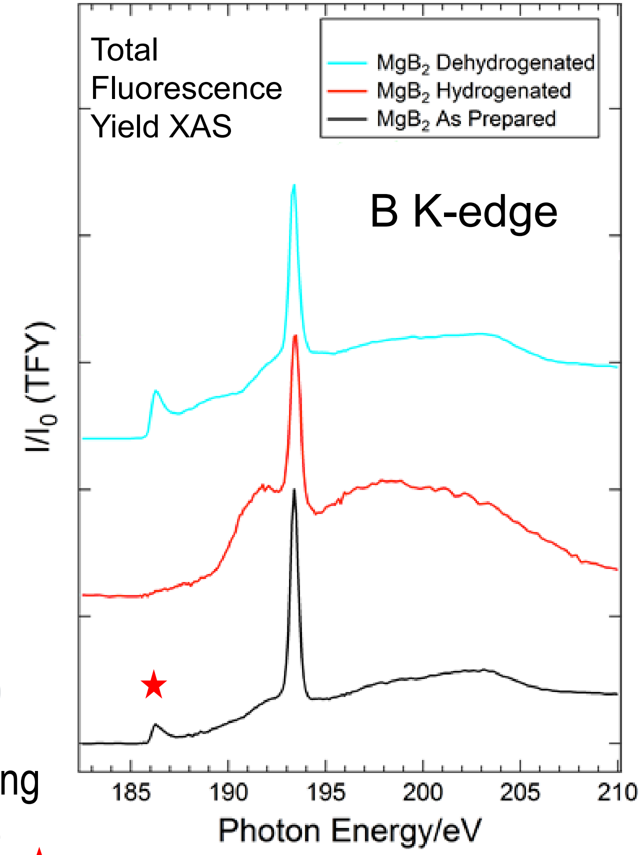
Accomplishment: X-ray spectroscopy of MgB_2-H

Spectroscopy shows that wholesale changes to the MgB_2 electronic structure at the B site are being made with H addition ***throughout the sample***

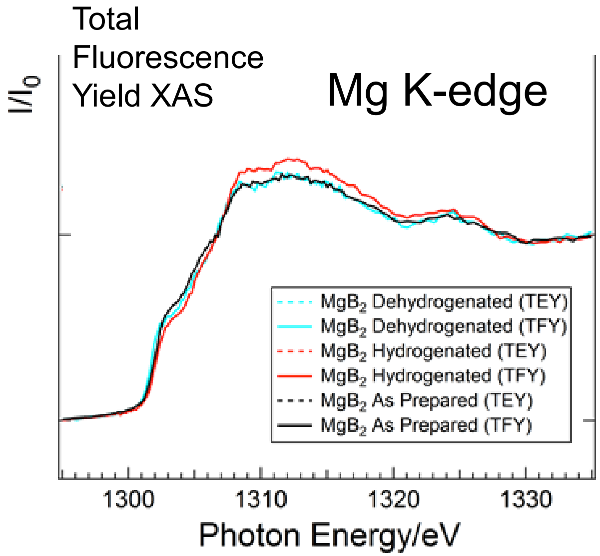


XES shows that sample processing (handling, adsorption/desorption) produces undetectable oxidation

★ B $2p_{xy}$ states just below E_F changed by H absorption



★ B $2p_z$, other states above E_F **strongly modified** by H absorption



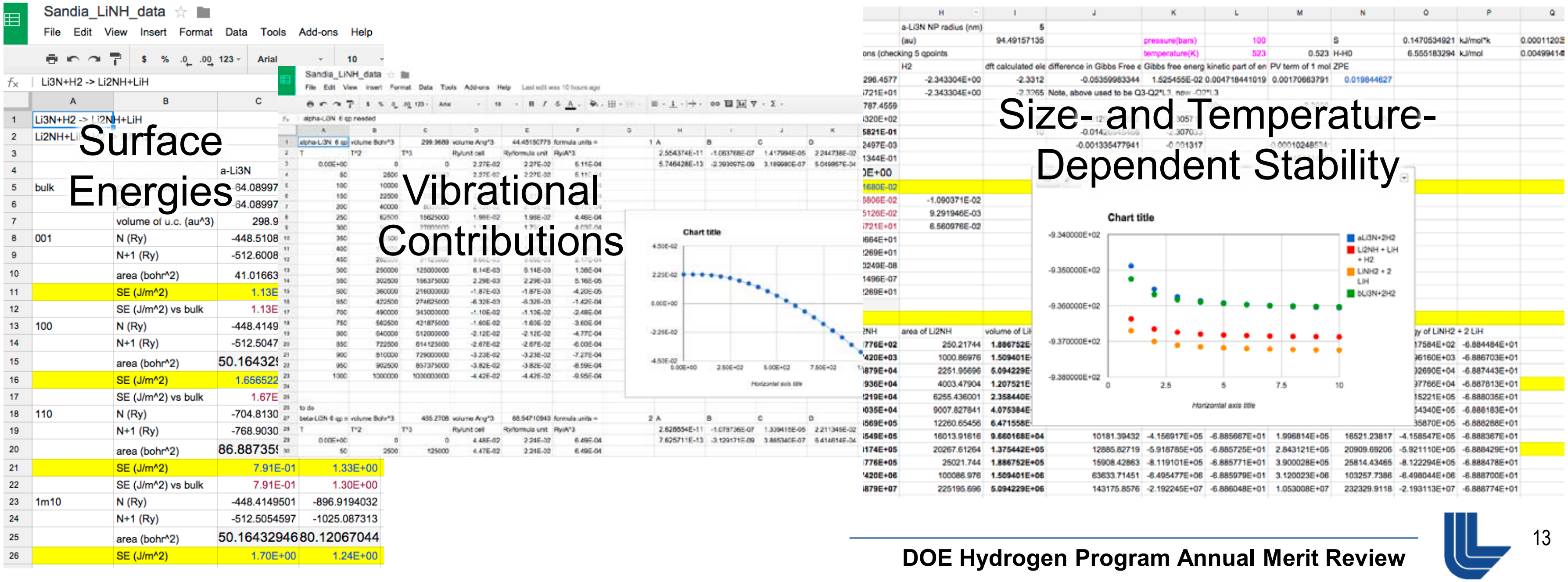
Little change occurring at at Mg with H addition

DFT simulations of XES, XAS data will determine unique signatures of B-H_x

Accomplishment: Collaboration, data management, and data sharing

Established platform for collaboration, data management, and data sharing using online and open-source tools

- Created online repository for data and literature compilation using Google tools
- Developed subroutines for DFT calculation of **surface/bulk energetics, zero-point energies, bulk/surface vibrational entropies**, and **elastic moduli** with a high level of automation
- DFT-derived thermodynamic data is collected into **shared, interactive Google spreadsheet** that automatically fits & extracts thermodynamic parameters for any **temperature**, **pressure**, and **particle size** to efficiently inform mesoscale simulations



Surface Energies

Vibrational Contributions

Size- and Temperature-Dependent Stability

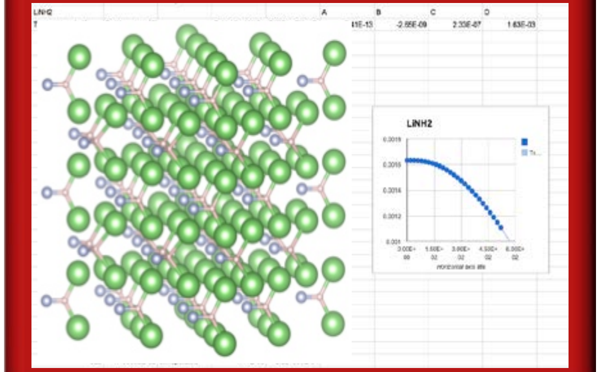
fx Li3N+H2 -> Li2NH+LiH

	A	B	C	
1	Li3N+H2 -> Li2NH+LiH			
2	Li2NH+Li			
3				
4			a-Li3N	
5	bulk		-64.08997	
6			-64.08997	
7		volume of u.c. (au^3)	298.9	
8	001	N (Ry)	-448.5108	
9		N+1 (Ry)	-512.6008	
10		area (bohr^2)	41.01663	
11		SE (J/m^2)	1.13E	
12		SE (J/m^2) vs bulk	1.13E	
13	100	N (Ry)	-448.4149	
14		N+1 (Ry)	-512.5047	
15		area (bohr^2)	50.16432	
16		SE (J/m^2)	1.656522	
17		SE (J/m^2) vs bulk	1.67E	
18	110	N (Ry)	-704.8130	
19		N+1 (Ry)	-768.9030	
20		area (bohr^2)	86.88735	
21		SE (J/m^2)	7.91E-01	1.33E+00
22		SE (J/m^2) vs bulk	7.91E-01	1.30E+00
23	1m10	N (Ry)	-448.4149501	-896.9194032
24		N+1 (Ry)	-512.5054597	-1025.087313
25		area (bohr^2)	50.16432946	80.12067044
26		SE (J/m^2)	1.70E+00	1.24E+00

Accomplishment: Framework for phase-fraction prediction

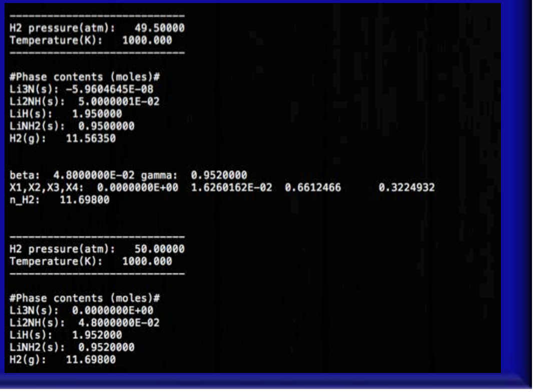
Established theoretical framework for predicting equilibrium phase fractions from DFT thermodynamics as function of temperature, pressure, and particle size

DFT thermodynamics



Bulk, surface, and interfacial free energies

Phase fraction code



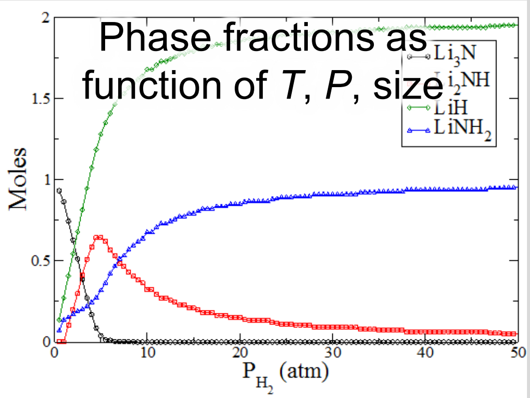
```
-----------------------------
H2 pressure(atm):   49.50000
Temperature(K):   1000.000
-----------------------------

#Phase contents (moles)#
Li3N(s): -5.9604645E-08
Li2NH(s):  5.0000001E-02
LiH(s):   1.950000
LiNH2(s):  0.9500000
H2(g):   11.56350


beta:  4.8000000E-02 gamma:  0.9520000
X1,X2,X3,X4:  0.0000000E+00  1.6260162E-02  0.6612466      0.3224932
n_H2:   11.69800


-----------------------------
H2 pressure(atm):   50.00000
Temperature(K):   1000.000
-----------------------------

#Phase contents (moles)#
Li3N(s):  0.0000000E+00
Li2NH(s):  4.8000000E-02
LiH(s):   1.952000
LiNH2(s):  0.9520000
H2(g):   11.69800
```



Phase fractions as function of *T*, *P*, size

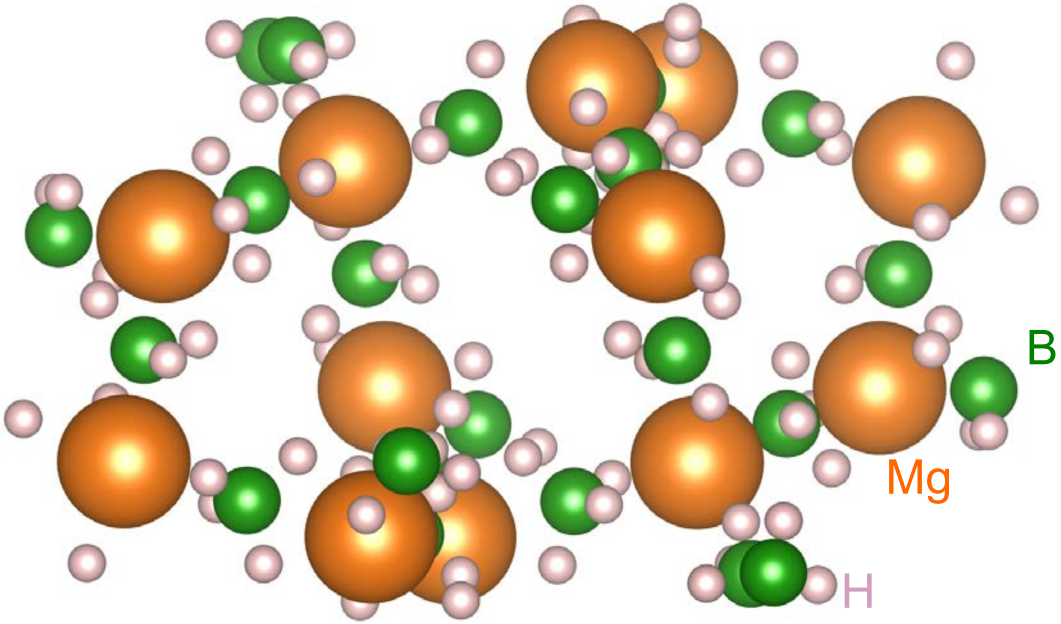
- New theoretical methodology for phase-fraction prediction incorporates bulk, surface, and interfacial DFT thermodynamics (obtained from the interactive spreadsheet), plus thermodynamics of mixing

Accomplishment: Thermodynamic parameters for $Mg(BH_4)_2/MgB_2$

Calculations of DFT thermodynamic parameters for $Mg(BH_4)_2/MgB_2$ (in progress)

- Working on DFT calculations of thermodynamic parameters ("standard" parameters, plus surface energy/entropy and elastic moduli)
- Benchmarking against available values obtained by Wolverton and Ozolins*

α-$Mg(BH_4)_2$



Key challenges are surmountable, but carry high computational cost:

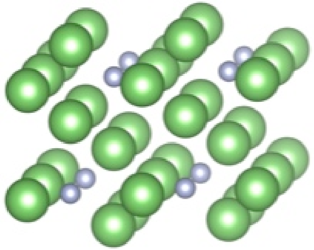
- Multiple possible intermediates and surfaces to examine
- Large unit cells with many internal degrees of freedom

*see 2013 & 2014 Annual Reports for DOE Hydrogen Program Annual Merit Review

Accomplishment: Early learning/feedback for modeling framework

Tested models and obtained key insights by studying Li-N-H system

- What determines kinetic improvement with nanosizing?
- What is the role of surfaces and interfaces in determining H_2 storage reaction pathways and kinetics?



β-Li_3N

- Examined recent SNL data* on Li-N-H system [Li_3N/($LiNH_2$+2LiH)] confined in 3.2 nm nanoporous carbon (npC) to quickly build needed capability and validate modeling framework. [Li_3N/($LiNH_2$+2LiH)] @ npC:
  - Exhibits **new reaction pathway** and kinetic improvement with nanosizing
  - Well-characterized system (XRD, Sieverts, NVE [collaboration w/ T. Udovic, NIST]) with demonstrated reversibility

Bulk:

$\alpha\text{-}Li_3N + H_2 \rightarrow Li_2NH + LiH$

$Li_2NH + LiH + H_2 \rightarrow LiNH_2 + 2LiH$

Multi-step

➡

Nanoconfined (3.2 nm):

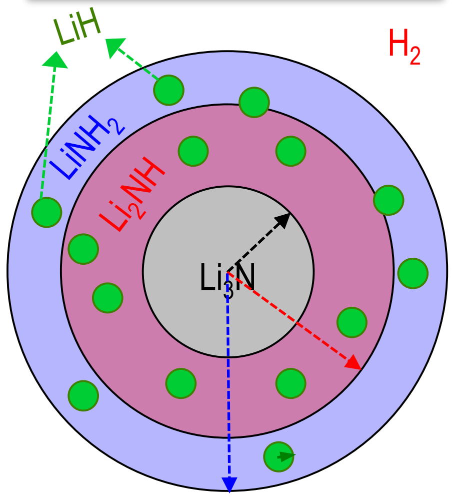
$\beta\text{-}Li_3N + 2H_2 \rightarrow LiNH_2 + 2LiH$

One-step

*Performed under Sandia/Boeing CRADA; with J. Breit (Boeing) and N. Poonyayant, N. Angboonpong and P. Pakawatpanurut (Mahidol University, Thailand). Manuscripts in preparation.

Accomplishment: Predict & explain different phase pathways in nano-Li_3N

Possible internal phase configurations in a particle



Models show interfacial effects drive single-stage hydrogenation of nano-Li_3N

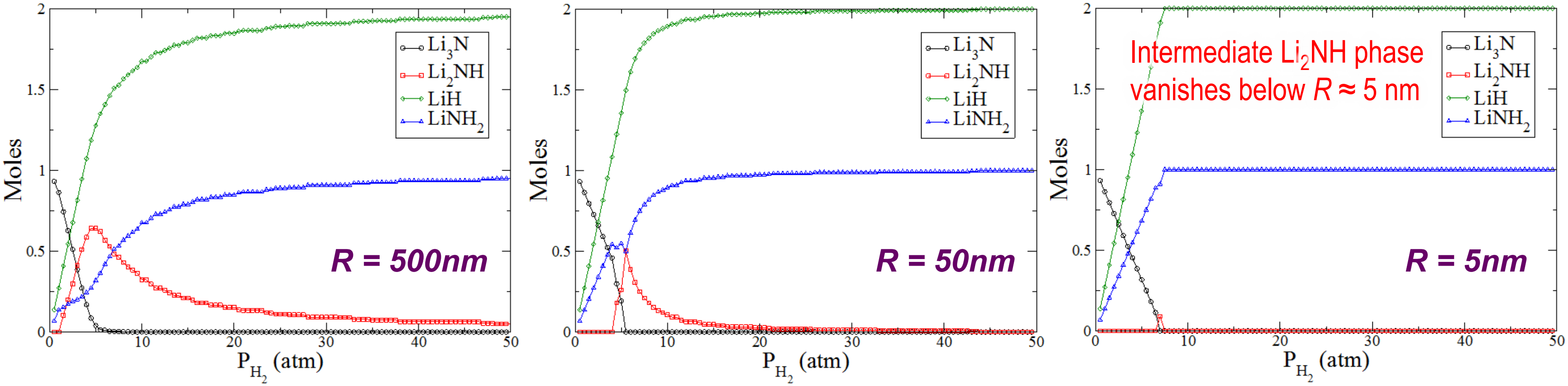
Reaction

2 step: $Li_3N+2H_2 \leftrightarrow Li_2NH+LiH+H_2 \leftrightarrow LiNH_2+2LiH$

1 step: $Li_3N+2H_2 \longleftrightarrow LiNH_2+2LiH$

Opens the door to possibility of optimizing reaction pathways through particle **morphology** and **microstructure**

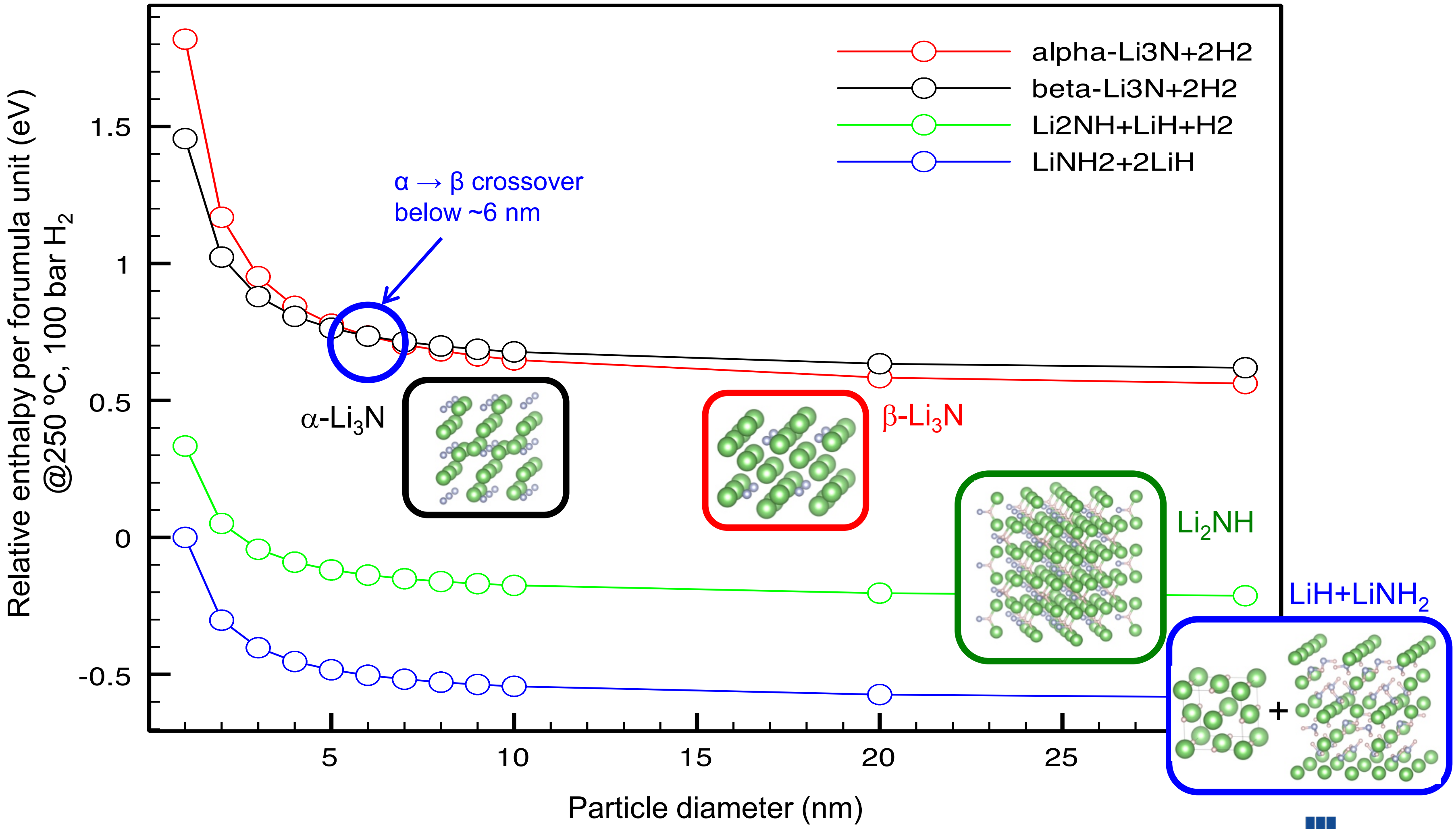
Decreasing particle size (@ fixed temperature)



Intermediate Li_2NH phase vanishes below $R \approx 5$ nm

Accomplishment: Predict & explain different phase pathways in nano-Li_3N

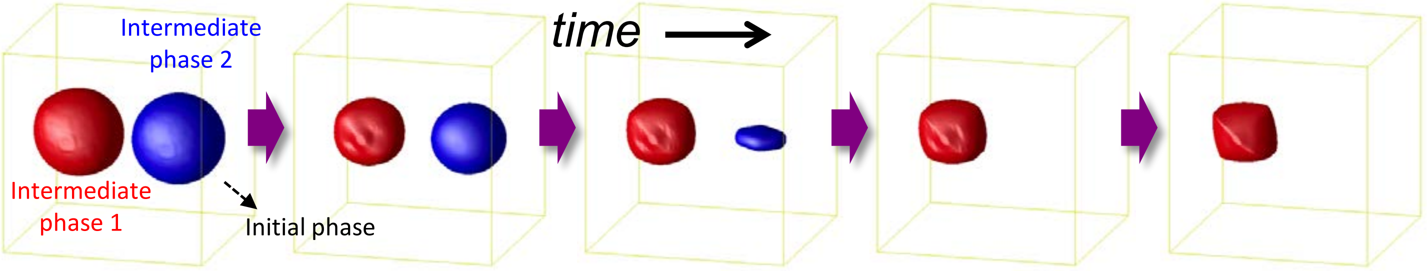
Models also successfully predict α → β conversion for nano-Li_3N, which is primarily driven by surface energy differences



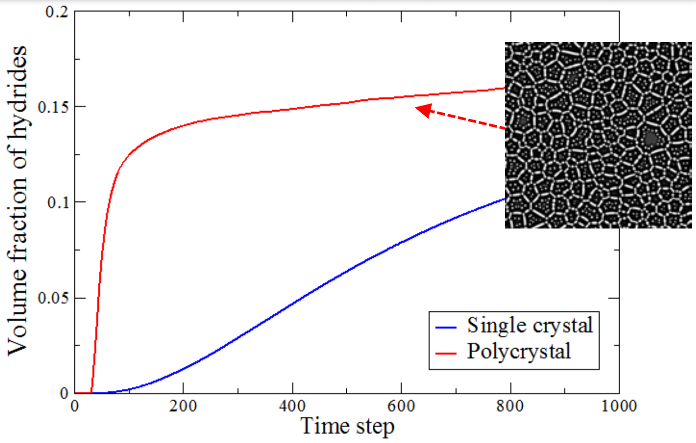
Accomplishment: Implementation of additional kinetic driving forces in code

Developing and implementing formalism for elastic (mechanical), phase nucleation/polycrystallinity, and nonequilbrium (de)hydrogenation in mesoscale kinetics code (in progress)

Elastic effects (stress/strain)

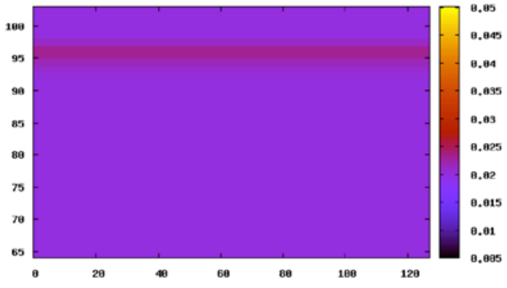


Phase nucleation/polycrstallinity

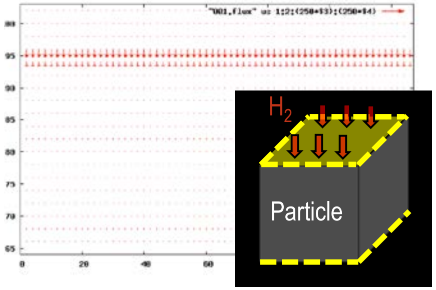


Nonequilibrium (de)hydrogenation

<H composition near a surface>



<H Flux>



Collaborations

Collaborations are crucial for realizing theory/characterization/synthesis partnership

Ab initio **modeling/multiscale integration**

Dr. Brandon Wood
(PI, LLNL)*

Dr. Keith Ray
(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)*

External & ongoing collaborations

- Neutron diffraction/spectroscopy: T. Udovic (NIST; within DOE Hydrogen Program)
- XAS/XES spectroscopy & modeling: D. Prendergast, Jinghua Guo (LBNL; DOE User Facility)
- Li-N-H system: J. Breit (Boeing); N. Poonyayant, N. Angboonpong, and P. Pakawatpanurut (Mahidol University, Thailand)
- Kinetic Monte-Carlo for solid-state diffusion: H. Kreuzer (Dalhousie U.), S. Bonev (LLNL)

*prime **subcontract

Remaining challenges/barriers & proposed mitigation strategies

- **Need better understanding of intermediate phases and local chemistry to inform models**
  - *Increased proposed characterization activity in FY15 & FY16, including new tasks for theoretical simulation and interpretation of spectra*
- **Limited beamtime at ALS and NIST characterization facilities**
  - *Planning schedule and preparing samples to coincide with beamtime*
  - *Plan to submit user facility proposal to ALS in Fall 2015*
- **Slow hydrogenation kinetics limits data collection**
  - *Inform models with existing data and on other materials in the meantime (e.g., Li_3N)*
- **Need techniques to bridge time scales associated with kinetic processes (e.g., diffusion)**
  - *Leveraging internal LLNL LDRD funding and existing external collaborations to develop new methods and techniques, including grain boundary/amorphous transport*
- **Need to adapt modeling formalism to address surface reactions (dissocation/association and adsorption/desorption)**
  - *Added task to test new ideas; currently working on implementation and testing*
- **Phase transformation pathway for $Mg(BH_4)_2$ may be very complex**
  - *Developing multi-phase framework; may require careful identification of rate-limiting intermediates*

Proposed future work: FY15 & FY16

Milestone	Description	Proposed completion
1	Refine size-selective synthesis of $MgB_2/Mg(BH_4)_2$ nanoparticles	Q3 FY15
2	Complete study of Li-N-H and submit manuscripts for publication	Q3 FY15
3	Complete experimental H_2 uptake/release kinetics measurements for bulk $MgB_2/Mg(BH_4)_2$ as function of temperature and pressure	Q4 FY15
4	Complete XAS/XES spectrscopy for $MgB_2/Mg(BH_4)_2$ and perform first-principles simulations of B/Mg-edge XAS/XES spectra for interpretation	Q4 FY15
5	Establish modeling framework for surface chemical reactions (dissociation/association and desorption/adsorption of H_2)	Q1 FY16
6	Compute DFT thermodynamic parameters for $MgB_2/Mg(BH_4)_2/MgB_{12}H_{12}$, including surfaces and interfaces	Q2 FY16
7	Use models to predict bulk and nanoscale phase pathways (neglecting transport) and compare kinetics with available experimental data	Q3 FY16
8	Transport calculations (bulk, surface, intermediates, defects)	Q4 FY16

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 kinetics of $Mg(BH_4)_2$ and related metal hydrides by exploring **nanostructuring** and **doping**
- **Understanding** kinetic limitations & enhancement mechanisms could lead to $Mg(BH_4)_2$ particles with **optimized geometry and composition**
- Early learning on Li-N-H system demonstrates the need to consider **interfaces**, and suggests the possibility of **morphology/microstructure engineering** as a viable strategy for kinetic improvement

Technology summary:

- **Multiscale modeling** of kinetics and reaction pathways for bulk and nanoparticle $Mg(BH_4)_2 \leftrightarrow MgB_2 + 4H_2$ interconversions, including interfacial, surface, and bulk energy/entropy contributions
- Complete **synthesis & characterization** approach directly informs and validates theoretical models with respect to reaction pathways, intermediates, kinetics

Impact:

- Goes beyond thermodynamics to directly target **kinetics in a comprehensive way** and address challenges of "real" materials
- Focuses on material with potential to meet **2020 DOE hydrogen storage targets**
- **Flexible modeling and synthesis** frameworks can be easily applied to other candidates, ties into Presidential Materials Genome Initiative for accelerated materials discovery & design

Technical backup slide: Laboratory upgrades at Sandia

Sandia Does Not Provide Cost Share, But…….

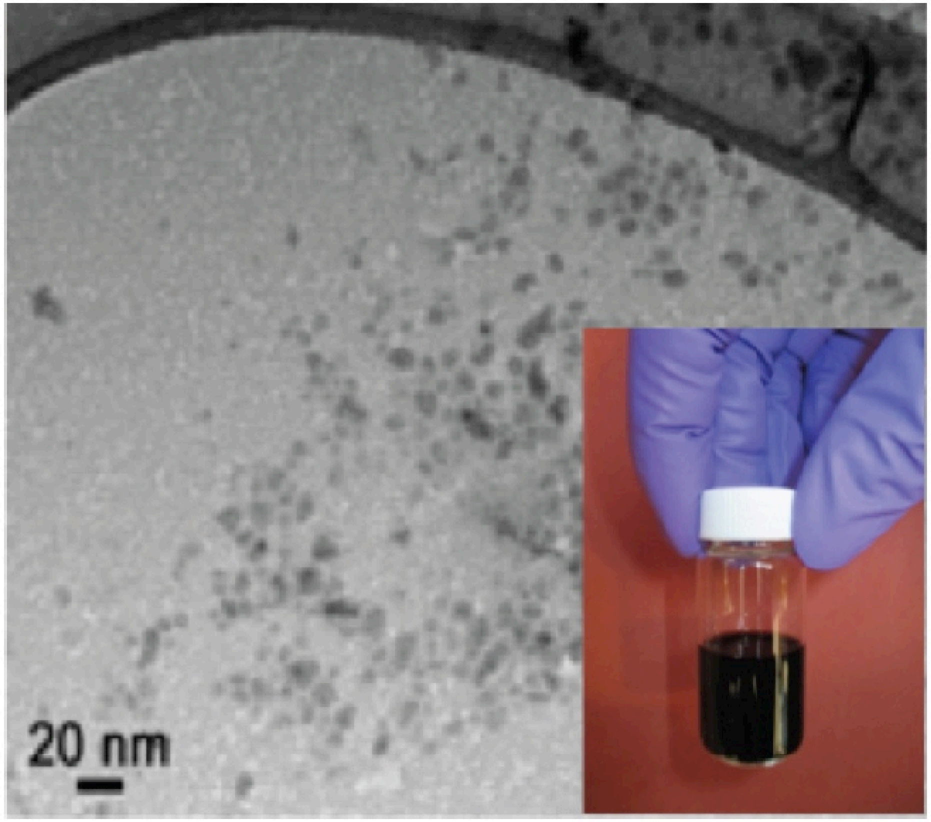
Sandia began the project by installing significant laboratory upgrades, without expenditure of project funds, courtesy of other Sandia mission areas:

1. New Ar Glovebox with exceptionally low (0.5 ppm) oxygen, which will be dedicated to this work.

2. New FTIR instrument installed in the Glovebox and used for characterizing intermediates in the hydrogen storage reactions of the Mg-B-H system.

Technical backup slide: Demonstrated MgB_2 nanoparticle synthesis

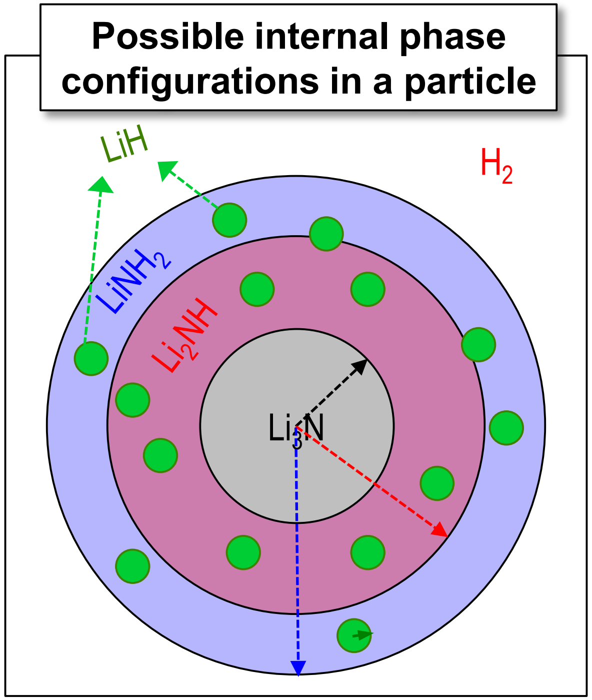
We have already demonstrated the feasibility of using surfactant-assisted ball milling* to produce nanoscale MgB_2. Producing variable size-selected nanoparticulate MgB_2 should be straightforward.



MgB_2 NPs (5- 10 nm) synthesized at Sandia: 86% yield, with 2 g suspended in 10 ml of heptane

*Y. Wang et al., *Nanotechnology* **18**, 465701 (2007)

Technical backup slide: Phase fraction calculation



Possible internal phase configurations in a particle

Reaction

$$(-\alpha)\cdot[\mathrm{Li_3N+2H_2}] \leftrightarrow \beta\cdot[\mathrm{Li_2NH+LiH+H_2}] \leftrightarrow \gamma\cdot[\mathrm{LiNH_2+2LiH}]$$

<Total Gibbs free energy of the system>

$$G=(n_1^0+\beta+2\gamma)\cdot g_S(\beta,\gamma,T)+(n_{H_2}^0-\beta-2\gamma)\cdot g_G(\beta,\gamma,P_{H_2},T)$$

We find the β and γ (phase fractions) that minimize the above expression for the free energy:

$$\boxed{G=\min(G)}$$

Molar Gibbs free energy of a solid phase (Ideal mixture of 4 components)

Surface/interface contribution

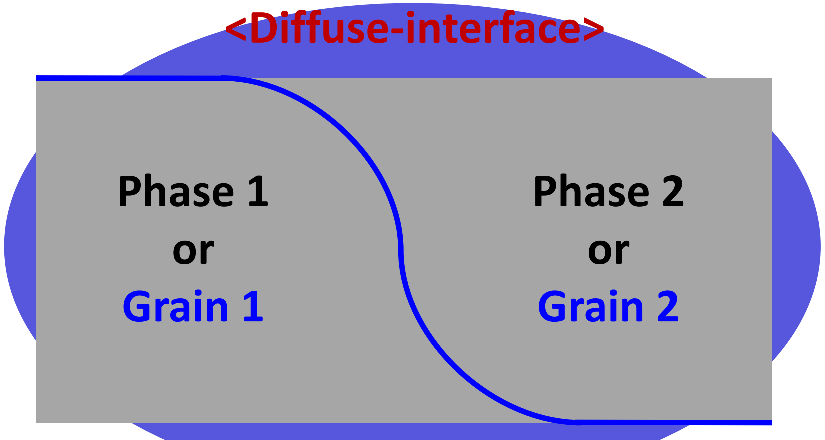
➡ $$g_S(X_i,T)=\sum_{i=1}^{4}X_i\cdot[g_i^0(T)+RT\cdot\ln X_i]+g_\gamma$$

Computed by DFT calculations

Molar Gibbs free energy of a gas phase (Pure ideal H_2 at pressure P_{H2})

➡ $$g_G(P_{H_2},T)=g_{H_2}^0(P_{H_2}=1\mathrm{atm},T)+RT\cdot\ln P_{H_2}$$

Technical backup slide: General framework of phase-field modeling



η, $X, \ldots$: "Phase-field" variables that describe continuous evolution of a given property across a solid-solid phase boundary (can represent non-conserved or conserved quantities)

Mathematical modeling

$$F = \int dV [f(\eta, X, \ldots) + \text{(gradient energy)} + \text{(long-range interactions)} + \ldots]$$

Numerically solving Governing equations

$$\frac{\partial \eta(\vec{r}, t)}{\partial t} = -L\left(\frac{\delta F}{\delta \eta}\right)$$

: Allen-Cahn equation

(*Non-conserved field*)

$$\frac{\partial X(\vec{r}, t)}{\partial t} = \vec{\nabla} \cdot \left[M\vec{\nabla}\left(\frac{\delta F}{\delta X}\right)\right]$$

: Cahn-Hilliard equation

(*Conserved field*)

Kinetic Phase Microstructure evolution

Technical backup slide: Surface energies & elastic moduli of Li-N-H system

Surface energies (J/m^2) and elastic moduli (GPa) for Li-N-H system were computed using DFT and used to estimate interface free energies

Surface energies of phases

Surface	α-Li_3N	β-Li_3N	Li_2NH	LiH	$LiNH_2$
(001)	1.13	**0.69**	--	--	1.02
(100)	1.66	1.24	0.59	**0.30**	0.97
(110)	**0.79**	1.33	**0.23**	0.71	1.64
(1-10)	1.70	1.24	--	--	--
(111)	--	--	0.62	1.85	**0.15**
(011)	--	--	--	--	0.82
(101)	1.80	1.74	--	--	--
(010)	1.66	1.24	--	--	--

Elastic moduli of phases

$$[C_{ij}^{\beta-Li_3N}]=\begin{pmatrix} 147.3 & 56.0 & 10.3 & 0 & 0 & 0 \\ & 147.3 & 10.3 & 0 & 0 & 0 \\ & & 201.0 & 0 & 0 & 0 \\ & & & 41.6 & 0 & 0 \\ & \text{Symmetric} & & & 41.6 & 0 \\ & & & & & 45.7 \end{pmatrix}$$

$$[C_{ij}^{\alpha-Li_3N}]=\begin{pmatrix} 139.3 & 39.3 & 8.5 & 0 & 0 & 0 \\ & 139.3 & 8.5 & 0 & 0 & 0 \\ & & 158.5 & 0 & 0 & 0 \\ & & & 17.9 & 0 & 0 \\ & \text{Symmetric} & & & 17.9 & 0 \\ & & & & & 50.0 \end{pmatrix}$$

$$[C_{ij}^{Li_2NH}]=\begin{pmatrix} 130.0 & 31.3 & 13.3 & 0 & 0 & 0 \\ & 138.8 & 13.0 & 0 & 0 & 0 \\ & & 149.8 & 0 & 0 & 0 \\ & & & 38.7 & 0 & 0 \\ & \text{Symmetric} & & & 37.0 & 0 \\ & & & & & 58.8 \end{pmatrix}$$

$$[C_{ij}^{LiNH_2}]=\begin{pmatrix} 43.2 & 12.0 & 12.0 & 0 & 0 & 0 \\ & 43.4 & 11.1 & 0 & 0 & 0 \\ & & 47.9 & 0 & 0 & 0 \\ & & & 13.2 & 0 & 0 \\ & \text{Symmetric} & & & 13.3 & 0 \\ & & & & & 20.5 \end{pmatrix}$$

$$[C_{ij}^{LiH}]=\begin{pmatrix} 91.0 & 14.8 & 14.8 & 0 & 0 & 0 \\ & 91.0 & 14.8 & 0 & 0 & 0 \\ & & 91.0 & 0 & 0 & 0 \\ & & & 51.7 & 0 & 0 \\ & \text{Symmetric} & & & 51.7 & 0 \\ & & & & & 51.7 \end{pmatrix}$$