Reversible Hydrogen Storage Materials – Structure, Chemistry and Electronic Structure

Ian Robertson and Duane Johnson
University of Illinois, Urbana-Champaign

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Project ID # ST32

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Overview

Timeline

- Project start date
  - March 2005
- Project end date
  - February 2010
- Percent complete 60%

Barriers

- Issues addressed
  - A: Understanding chemical response to hydrogen
  - B: Understanding system weight and particle packing
  - C: Theory support to address critical issues blocking experimental progress.

Budget

- Total project funding
  - $1 250 000 committed, no contractor share
- FY07: $195K (received)
- FY08: $260K (just received 5/8/08)

Partners

- Project lead: Sandia National Laboratory & MHCoE
- HRL Laboratory, NIST
- Brookhaven National Laboratory
- Pittsburg and Georgia Tech

Objectives

- The main focus of UIUC within the Metal Hydride Center of Excellence is
  - Advance the understanding of the microstructural and modeling characteristics of complex hydrides.
  - Provide feedback and knowledge to partners within MHCoE framework.
  - Provide more reliable theoretical methods to assess hydrogen-storage materials, including key issues affecting materials under study.
  - Help achievement of specific targets and milestones.

Plan & Approach

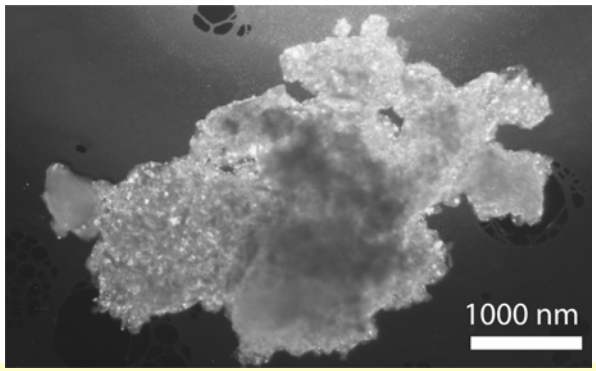
70 % complete

- Task 1: Experimental investigation of MHCoE partner materials
  - Investigate and model microstructural and chemical changes in hydrogen storage materials

60 % complete

- Task 2: Incorporation and development of new models
  - Development of new theoretical models and incorporation into MHCoE work

$Ca(BH_4)_2$ and intermediate phase



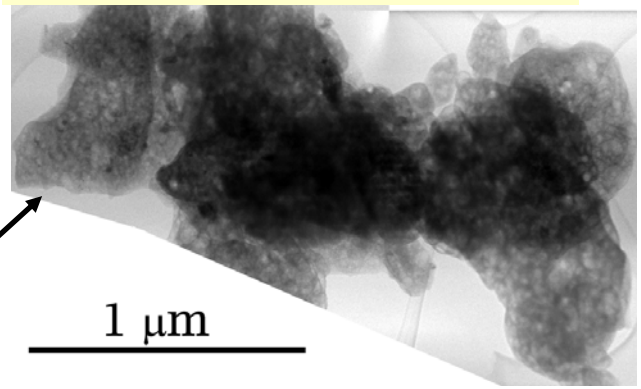
Starting from CaB_6 + CaH_2

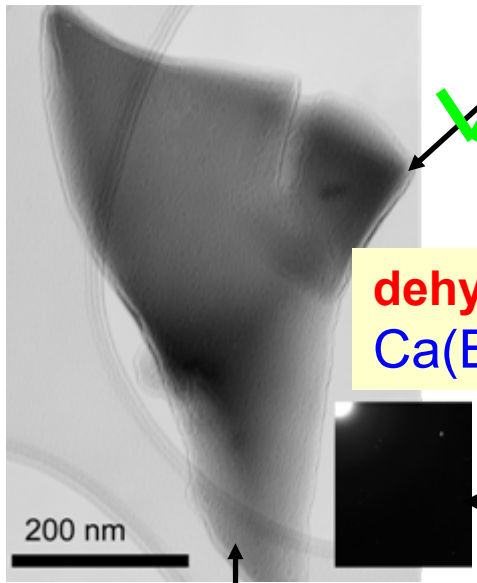
No storage (previously reported)

- **attempts to hydride failed**

Start point matters!

Starting from $Ca(BH_4)_2$
reversible, ~6 wt% H_2





dehydrided
$Ca(BH_4)_2$

Featureless TEM diffraction pattern

What is the intermediate phase?

-- with Ewa Rönnebro

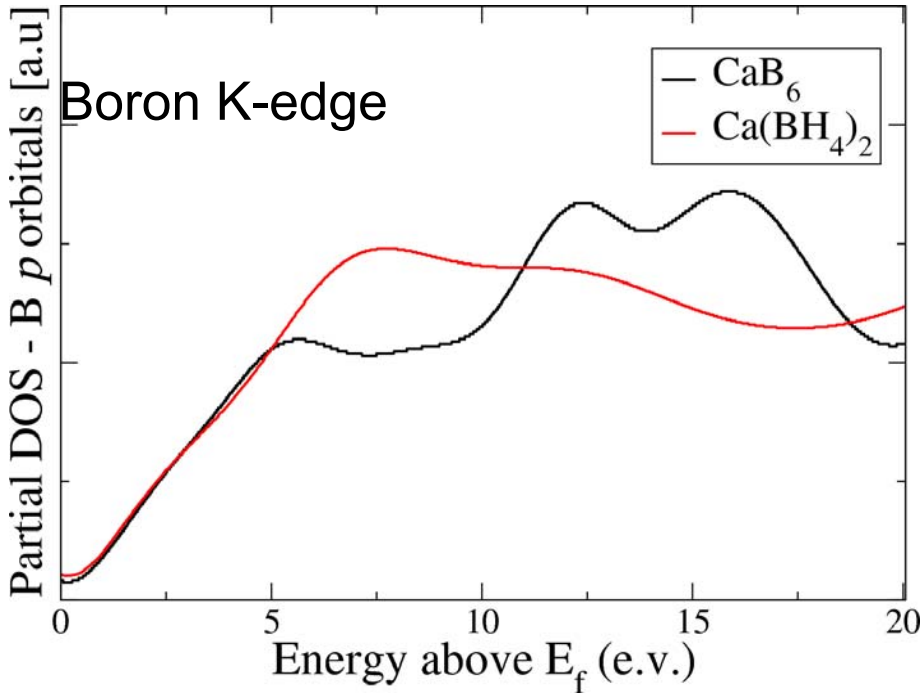
Sandia National Laboratories

Featureless (possibly amorphous) in low-dose TEM diffraction (connects with "CaB_6 + amorphous" XRD)

Can EELS identify intermediate Boron phase?

DFT-calculated empty *p*-states for CaB_6 and $Ca(BH_4)_2$.

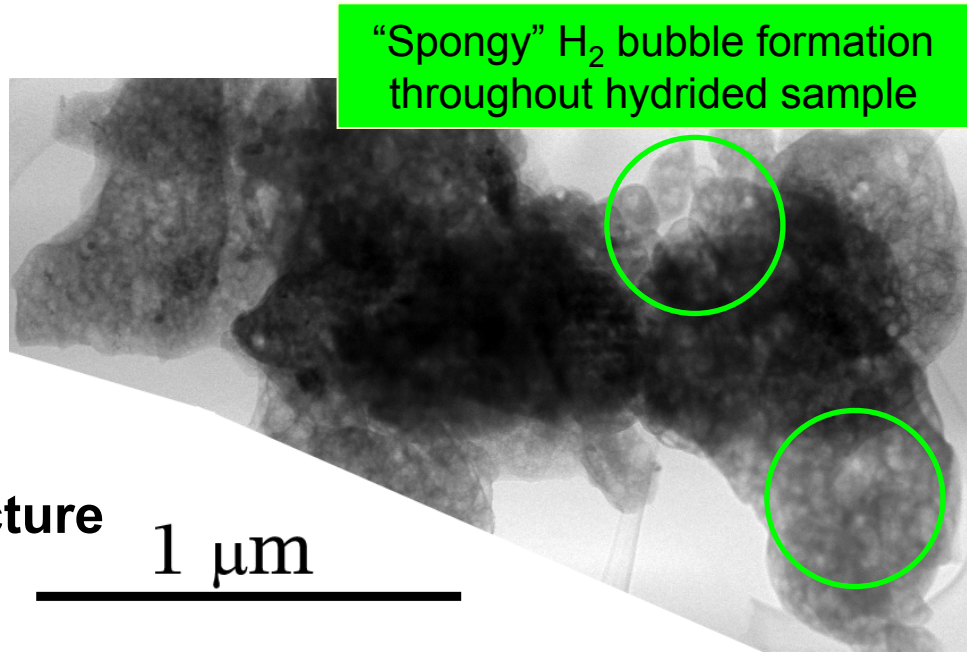
- calculated with 1 eV Gaussian smear (EELS resolution).



- DFT suggests Boron K-edge EELS has structure and we could differentiate on nm-scale between boride and borohydride.

H_2 bubble formation in $Ca(BH_4)_2$

- **Want to know intermediate phase**
  - Need non-diffraction method of identification
- **EELS can identify electronic structure**
  - However, electron beam damages hydrided sample rapidly.

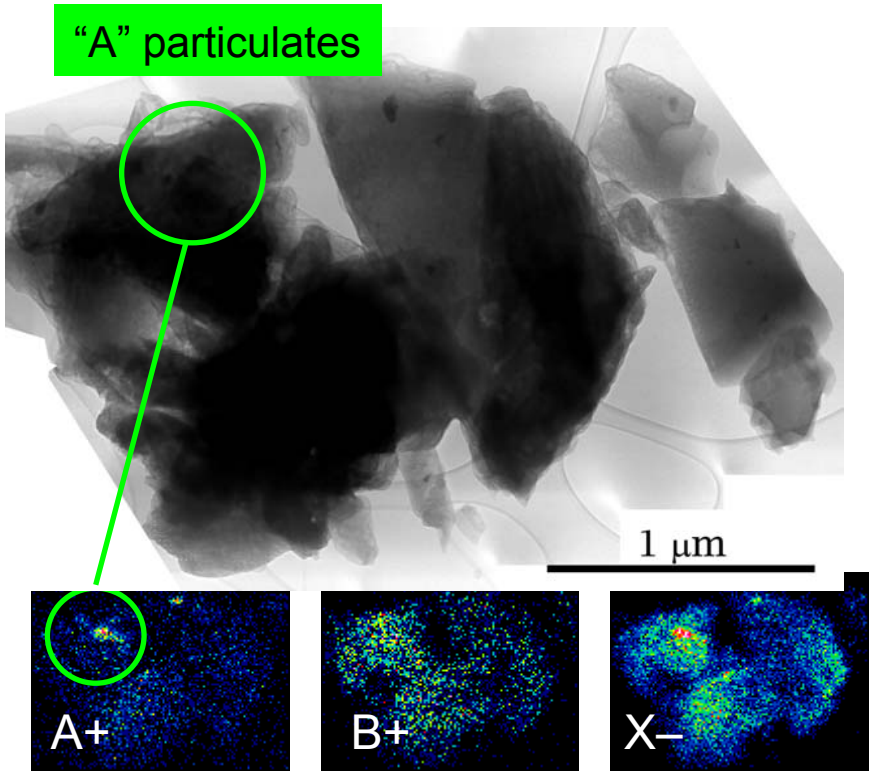


$Ca(BH_4)_2$ + 3 wt % "A" + 3 wt % "B", after 1st cycle, in hydrided state

∴ Beam damage in "low-dose" STEM mode may preclude distinguishing boride/borohydride using EELS.

∴ EELS is not viable to distinguish phase, regardless of DFT findings.

Catalyst additions in $Ca(BH_4)_2$



$Ca(BH_4)_2$ + 3 wt % "A" + 3 wt % "B", after 2nd cycle, dehydrided state – Ru region ~ 100 nm

- $Ca(BH_4)_2$ shown reversible by SNL.
  - Catalyst 3 wt% each "A" and "B".
- "A" may have catalytic action but is not dispersed
  - Not present in 50% of dehydrided $Ca(BH_4)_2$ particles.
  - Results for hydrided material similar.
  - **"B" is well dispersed** and present in all particles

-- with E. Rönnebro, SNL

- "A" additions in $Ca(BH_4)_2$ do not mix effectively.
- "A" may be catalytic but is not dispersed, while "B" is well dispersed.

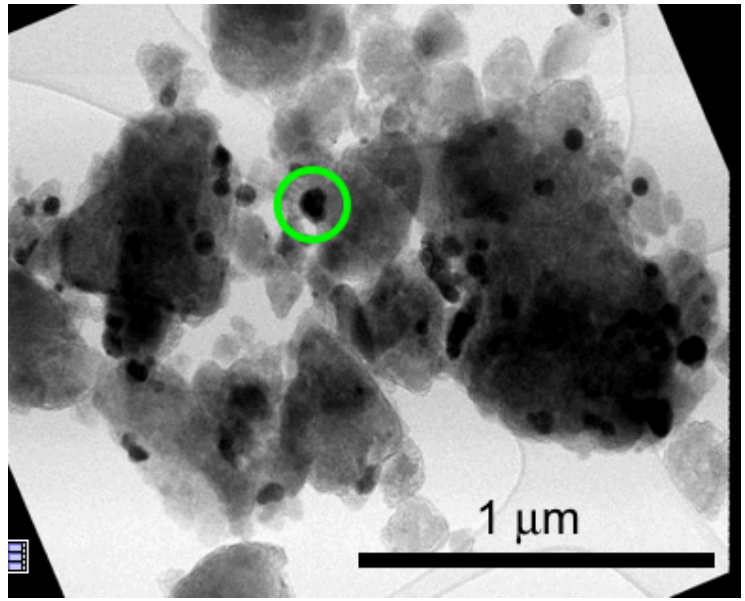
Determining Catalyst Distributions

Ex: Ni dispersion in MgH_2/Si

Although down selected this system shows differing generic behavior of catalytic particles interacting with primary material.

- **Ball milling used to reduce size and disperse Ni catalyst.**
- **Surface is not preferred by Ni.**
  - Large fraction of Ni particles are embedded in the Mg matrix as viewed in *movie of* reconstruction.
  - Ni is like "A" in $Ca(BH_4)_2$ – particles NOT homogeneously distributed.
  - EELS → no atomic Ni elsewhere.
- **Similar size distribution found (~30 nm) for 1 & 5 hr milling**.

Tilt movie, showing Ni nodule orientation



MgH_2 + 1/2 Si + 0.05 Ni, as milled for 1 hr

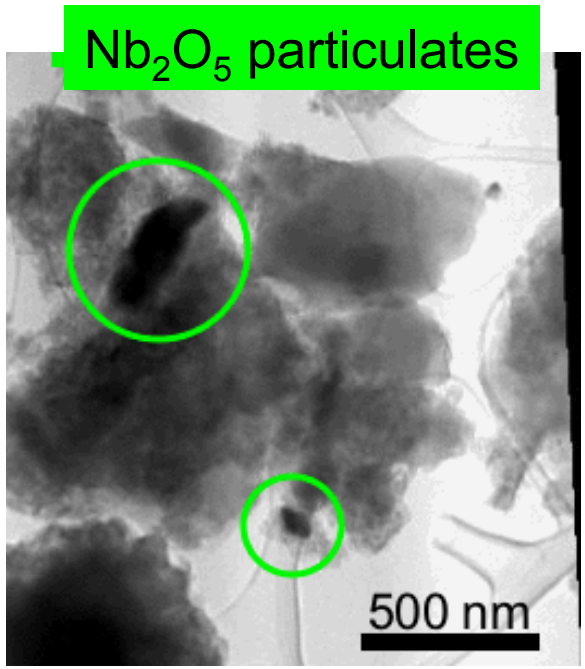
- Milling beyond 1 hr (30 nm) *not effective* for Ni reduction.
- Generally, must verify if catalytic material is dissolved.
- Tomography (CAT scan) permits 3D imaging and reconstructions.

More Catalyst Dispersal

- $MgB_2 + 2MgH_2 + 2B$ + catalyst *not reversible*
  - $Mg(BH_4)_2$ is *not reversible*
    (some literature claims otherwise)
  - Chemical similarity to $Ca(BH_4)_2$ suggests intermediate can't be crossed, limiting storage.

- Difficult to predict efficacy of ball-milling in dispersing catalysts
  - $Ca(BH_4)_2$
    - "B"disperses.
    - "A" does not disperse!
  - MgH_2 / MgB_2
    - Nb_2O_5 and Ni do not disperse.
    - But, both Nb_2O_5 and Ni works.

tomographic movie, showing



$MgH_2 + MgB_2 + 2\ B + 0.02\ Nb_2O_5$, bright-field, after 1x hydrogen cycle.

Electron tomography indicates entire thickness of structure is ~200 nm

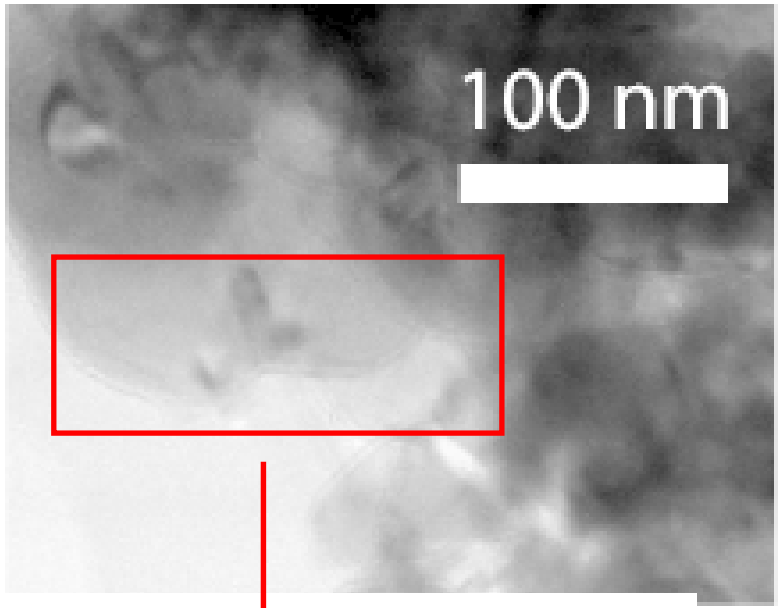
Big Nb_2O_5 particle ~ 300x300x60 nm

- Except for $TiCl_3$, milling *not effective* for dispersing catalysts.
- Reversibility affected by material, limited by intermediate phase.

Alane precursor

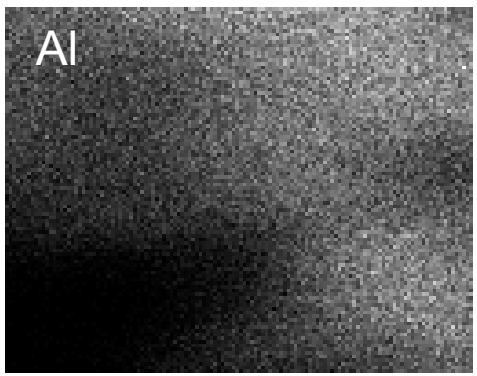
with BNL, J. Reilly

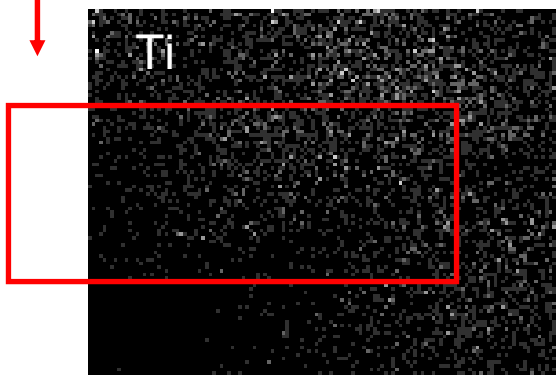
Al*
(Ti Catalyzed)



No enhancement of local Ti conc. at edge of Al particle.

- **suggests bulk alloying, not surface**



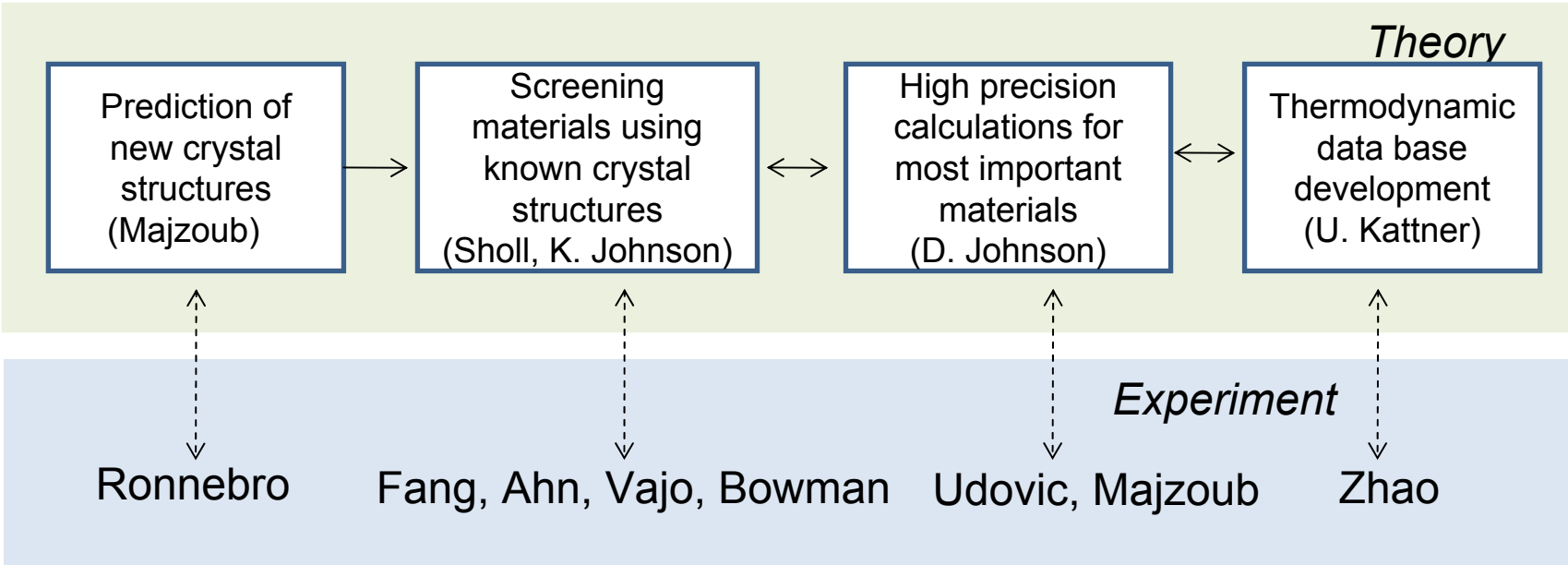


- Precursor material (before organic conversion to reversible material).
- EDS image suggests homogeneous alloy-like distribution.
  - –Surface distribution would show as enhanced distribution at particle edges
  - –Grain size ~ 160 nm

- Alane precursor material appears as Al/Ti alloy before TEDA conversion.

Theory Drives MHCoE Materials Work

(A) Materials Discovery (structure, energetics, mechanisms)



Only interactions with MHCOE experiments shown; links to multiple other groups are also active

(B) Role of Contamination on Reaction Kinetics (Allendorf, Sholl, Johnsons)

-- Reported in ST33 (Pitt/GeorgiaTech)

(C) Improving AlH_3 Regeneration Approaches (Allendorf)

-- reported in ST36 (SNL)

(D) Scaffold-nanoparticle interactions (Opalka)

-- reported in STP16 (UTRC)

Accurate Reaction Enthalpies in Molecular Solids

Zarkevich and Johnson, Phys Rev. Lett. 100, 040602-4 (2008)

What was known before?

- *Rehydriding* phase is "hexagonal" structure, where *dehydriding* phase is melt.
- Theory (DFT + Phonons) found all hexagonal $LiBH_4$ structures unstable.

✓Relevant high-T phase and/or anharmonic modes **were <u>not included</u>.**

DFT+ phonons + mode-counting results

Reaction in high-T melt phase

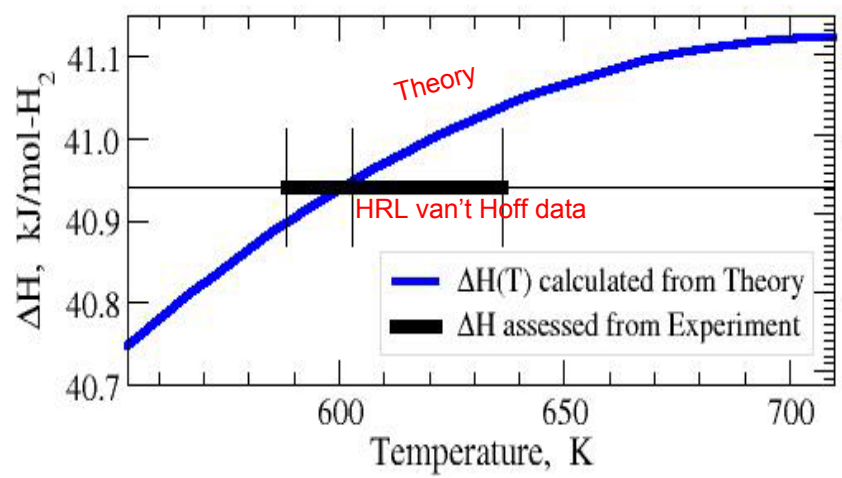
$2LiBH_4 + MgH_2 \leftrightarrow 2LiH + MgB_2 + 4H_2$

Theory: 41 kJ/mol-H_2 at 600 K

HRL data: 41 kJ/mol-H_2

Previous theory gave 30-100% error!

ΔH vs. T -- note expanded ΔH scale



- Provided accurate/general DFT-based method to predict enthalpies of destabilized reactions via mode counting of anharmonic modes.
  - ✓ Intramolecular harmonic modes always cancel in enthalpy differences!
  - ✓ Comparing predicted rehydriding phase with neutron data (with NIST, Udovic).
  - ✓ Not shown: XRD data for ortho and hex phases (with SNL, UMSL, Majzoub).

One New 2008 Theory Project

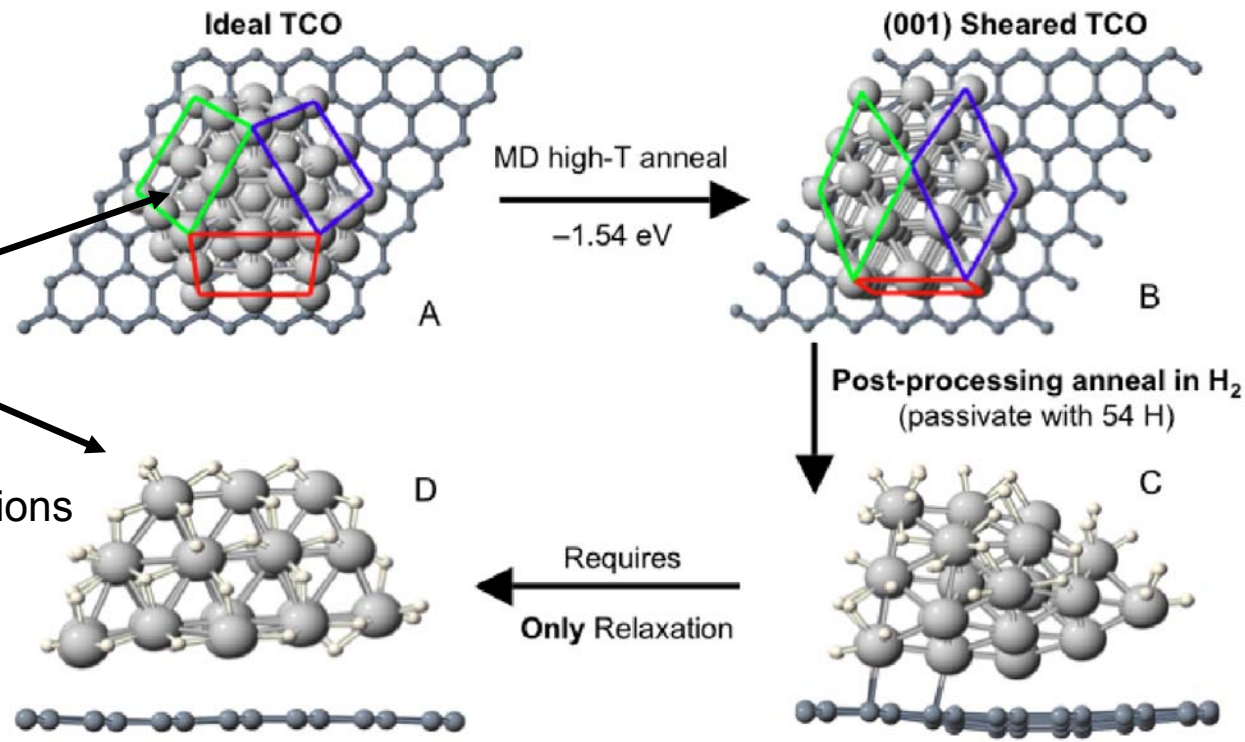
Effects of Nanosize and Scaffolds

Pt_{37}/C exhibit shear instabilities and topology changes that are removed after adsorption of H. Interactions with support are also reduced.

- TCO Pt_{37} unstable w/o H
- support interactions

TCO Pt_{37}

- TCO Pt_{37} stablized w/ H,
- Reduced support interactions



Wang and Johnson, J. Am. Chem. Soc., 129, 3658 (2007); ibid. 128, 131 (2006)

We are considering Mg and MgH_2 nanoparticles

- What is effect of size and C support on (de)adsorption properties?
- Can we elucidate MHCoE experimental finding?
- Do Mg particles rehydrogenate to stoichiometry, or something else?

Future Work

- For FY08-09 -

- **Explore nanostructure and nanoparticulate phases utilizing tomographic and spectroscopic analysis**
  - Full analysis of Ca-borohydride phases and catalysts (SNL)
  - Finish analysis of Si destabilization and Ni catalysis on MgH_2/B_2 systems (HRL, SNL).
  - Study alane complexed with amines, if helpful to MHCoE partners.

- **Modeling complex hydride systems**
  - Quantify size and confinement effects on Mg/MgH_2 supported nanoparticles and their adsorption properties (w/ SNL, HRL).
  - Apply reaction enthalpy prediction to systems of interest, and use these accurate predictions for van't Hoff plots (w/ GaTech).
  - Help understand intermediate phase and reversibility (w/ SNL)
  - Complete joint experiment and theory analysis on T-dependent XRD in $LiBH_4$. (w/ SNL, UMSL)

Project Summary

Relevance: We have demonstrated and used a framework for the microstructural analysis of complex hydrides

Approach: Characterization and theoretical tools are general and can be used with many materials above and beyond complex hydride materials.

Technical Accomplishments and Progress:

- Demonstrated ability to quantify efficacy of ball-milling and mixing for dispersion of catalyst.
- Detailed issues involving reversibility and starting phases – there appears to be intermediate phase that controls reversible reactions.
- Developed new theoretical method for accurate prediction of reaction enthalpies in molecular solids, eliminating limitations.

Technology Transfer/Collaborations: Active interfacing with MHCoE partners, presentations, publications.

- We address critical issues in hydrogen storage materials synthesis and characterization brought to us by MHCoE partners.