Reversible Hydrogen Storage Materials – Structure, Chemistry and Electronic Structure

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A Participant in the DOE Metal Hydride Center of Excellence

DOE 2006. Hydrogen Program Annual Review, Washington, D.C., 2006

This presentation does not contain any proprietary or confidential information

Project ID: ST18

Overview

Timeline

Start date: FY 05

End Date: FY 09

Percent Complete: 15%

Budget

- **Total project funding**
  - $1,566,746
  - DOE Share: $1,253,396
  - UIUC Share: $ 313,350

Funding for FY05: $150,000

Funding for FY 06: $175,000

Barriers addressed

Optimization of absorption /desorption kinetics of solid-state storage systems.

Theoretical modeling to guide material development

Improve understanding of fundamental processes impacting alloy development that surpass targets.

Partners

Participants in the ***DOE Metal Hydride Center of Excellence, specifically Sandia National Laboratory, HRL, University of Hawaii, University of Pittsburgh, General Electric.***

Objectives

Overall	**Support and guide development of complex metal hydrides to meet systems requirements by** **• provide center partners with structural and chemical insight of candidate systems.** **• provide experimentally based and validated theoretical modeling.**
2006	**• to determine degradation during transfer to analytical instruments and conduct structural and chemical analysis of systems of interest to partners.** **• developed structural database for information sharing with partners.**
2007	**• to provide theoretical modeling to guide materials development.** **• to provide understanding of role of catalysts and to determine nature, state and effect of surface contaminants on uptake and release.**

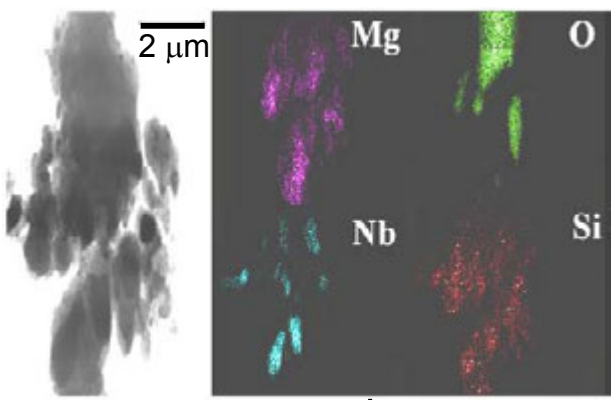
Approach overview

Our approach combines use of advanced characterization capabilities with first principles electronic and thermodynamic calculations.

Structural/chemical information

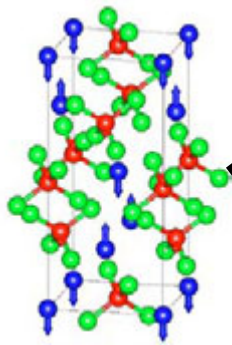
TEM structure
And crystallography

EDS and EELS
Chemical and bonding information

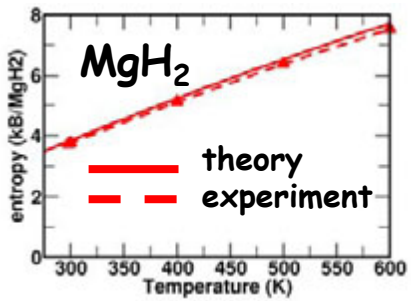


Provides Needed information

First principles calculations of thermodynamic properties



+ **PHONON code**



Aids interpretation

X-ray diffraction – Clemens, Stanford University
Neutron diffraction – Udovic, NIST

DFT ---------- K. Johnson, U. Pitt.
Monte Carlo Mojzoub – SNL
DFT----- Sholl - CMU

Outcome: Provides guidance for new alloys with improved properties

The structural database. Data sharing

The Structural Database

Home | Structures | Lattices | Symbols | Elements | Methods | Authors | Comments

All VASP structures (xyx), energies (ΔH), … are stored into electronic Structural Database (http://data.mse.uiuc.edu)

Logon:
Username:
Password:
Logon

Search results by:
Keyword:
Case insenitive

Lattice:
AND: OR:

Method:
AND: OR:

Structures

: Recently added : Other

First found 2 structures, displaying 1 through 15

	Name	Energy (eV/atom)	FE (eV/atom)	Error (eV/atom)	Pressure (kbars)	Stoichiometry	Composition	# Atoms	# Types	Author
☐	LiBH4-hex	-4.190185	null	.01	-.67	2:8:2	B H Li	12	3	Nikolai Zarkevich
☐	LiBH4-ort	-4.22446	null	.01	-.82	4:16:4	B H Li	24	3	Nikolai Zarkevich

Check All Uncheck All

e.g. "click" name, structure appears via JMOL© with xyz coordinates, etc.

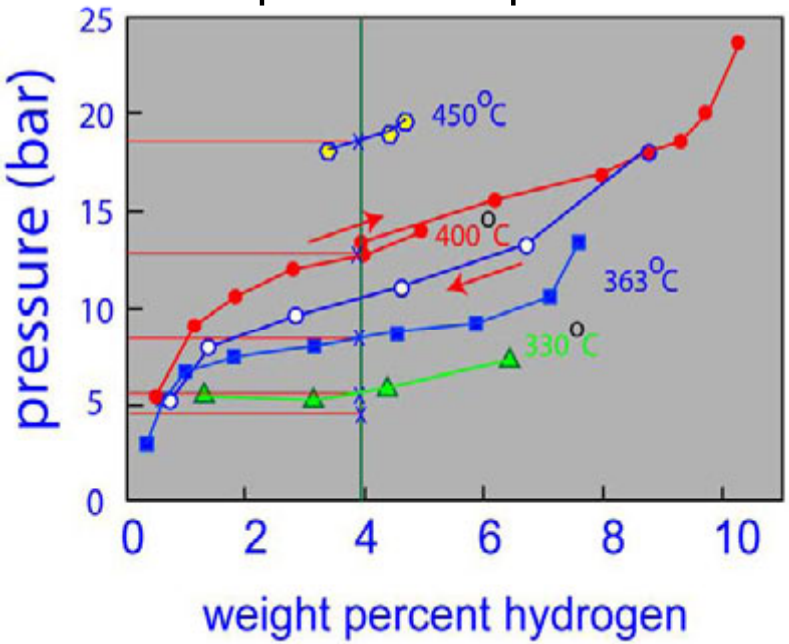
N. Zarkevich and D.D. Johnson (2005)

ORACLE® type database.

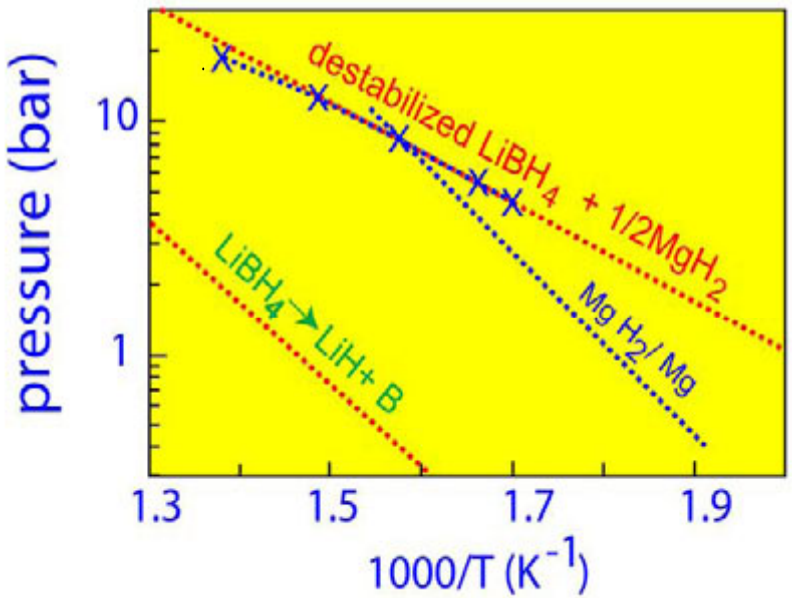
All MHCoE collaborators (and others) access, download, and contribute by upload via scripts. No unnecessary repetition!

Absorption/desorption isotherms and Van't Hoff plot for Destabilized $LiBH_4$

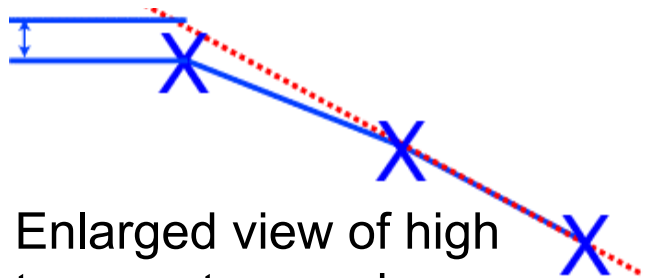
Absorption/desorption isotherm



Van't Hoff Plot



This deviation is simply due to melting and should not be included in the analysis.



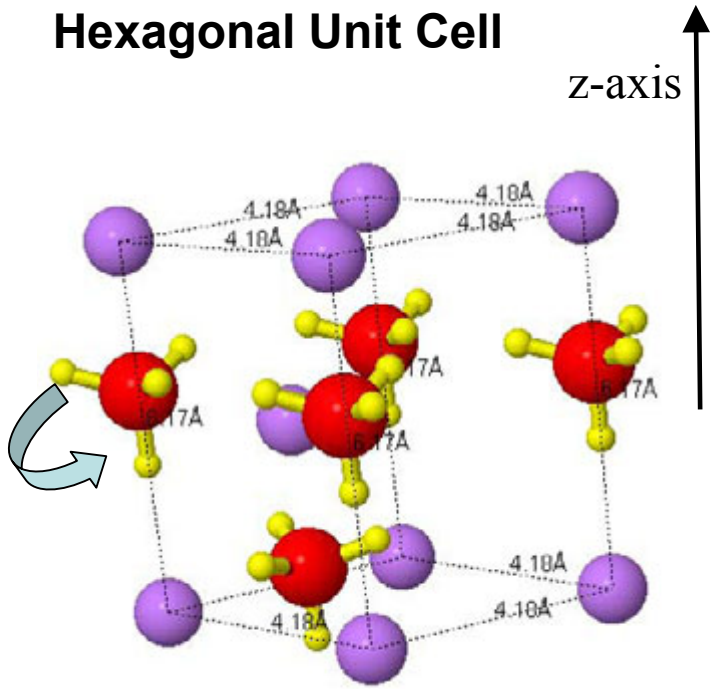
Enlarged view of high temperature region

Using the correct physics we can construct van't Hoff plot!

Can calculate the enthalpy change or latent heat and Gibbs Free Energy by including Electronic + vibrational (harmonic) + librational energies.

Debate about stable high temperature phase – get wrong answer if you do not include rotational energies

Hexagonal Unit Cell



Important missing term

Librational mode is approximated by a free rotation and we obtain Free Energy per LiBH4 *analytically*

$$F_r = -k_B T\left(\frac{\ln T}{2} + \ln\frac{\sqrt{2\pi k_B I_3}}{3\hbar}\right)$$

***All other vibrational modes are obtained via VASP/PHONON code, but no imaginary frequency. Therefore, the hexagonal phase is not inherently unstable as predicted in previous models.**

H atoms undistinguishable after 2π/3 rotation
5± 5kJ barrier

van't Hoff plot
DFT Theory and Experiment

Experimental Data (HRL)

Vajo, Skeith, and Mertens,
J. Phys. Chem. B 109, 3719 (2005).

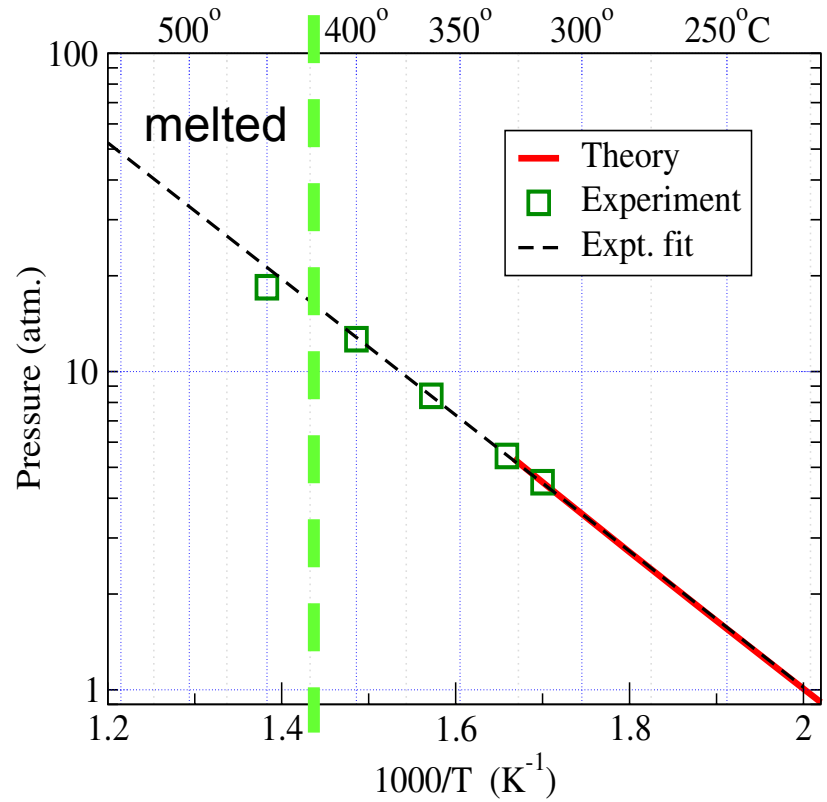
Theory using DFT*

$$\ln P = -\frac{\Delta G_{elec} + \Delta G_{vibr}}{k_B T} + \left(\frac{7}{2} - \frac{1}{4}\right)\ln T + E$$

This has the proper well-known general form of

$$\ln P = \frac{A}{T} + B\ln T + CT + DT^2 + E$$

*** DFT was shifted by a constant ΔE arising from nuclear degrees of freedom, which is not included**



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

How do we compare Latent Heat determined from theory and measured experimentally?

Direct vs Assessed from van't Hoff Plot

Latent Heat

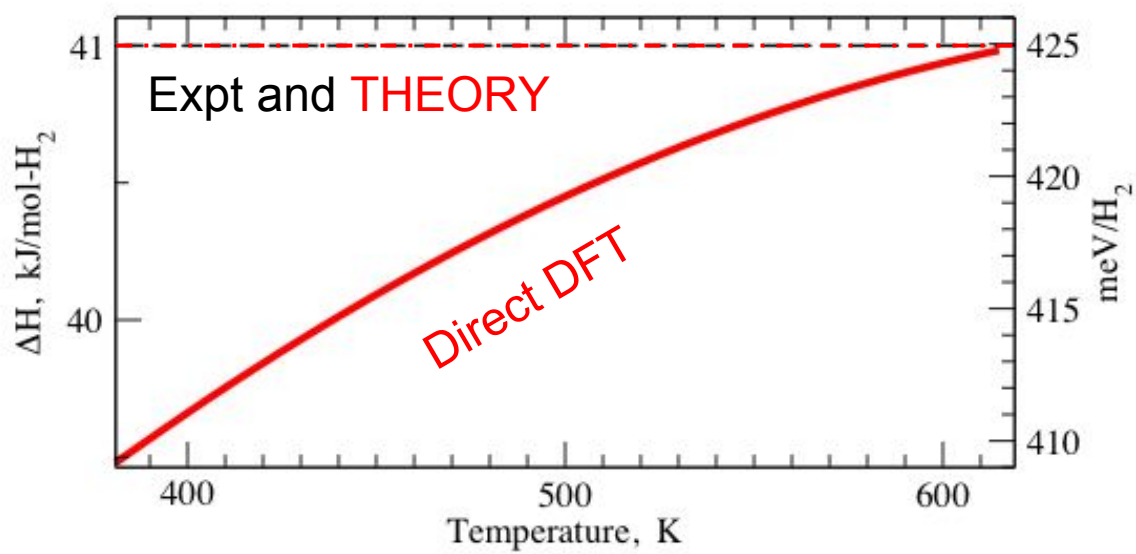
$$\Delta H(T) = -Nk_B \frac{d(\ln P)}{d(1/T)}$$

But, experimentally, $\Delta H(T)$ is extracted assuming

$$\ln P \approx A/T + E$$

that is van't Hoff slope is a constant $\Delta H \sim A$

Comparison of DFT $\Delta H(T)$, $\Delta H \approx A$, and ΔH from experiment.

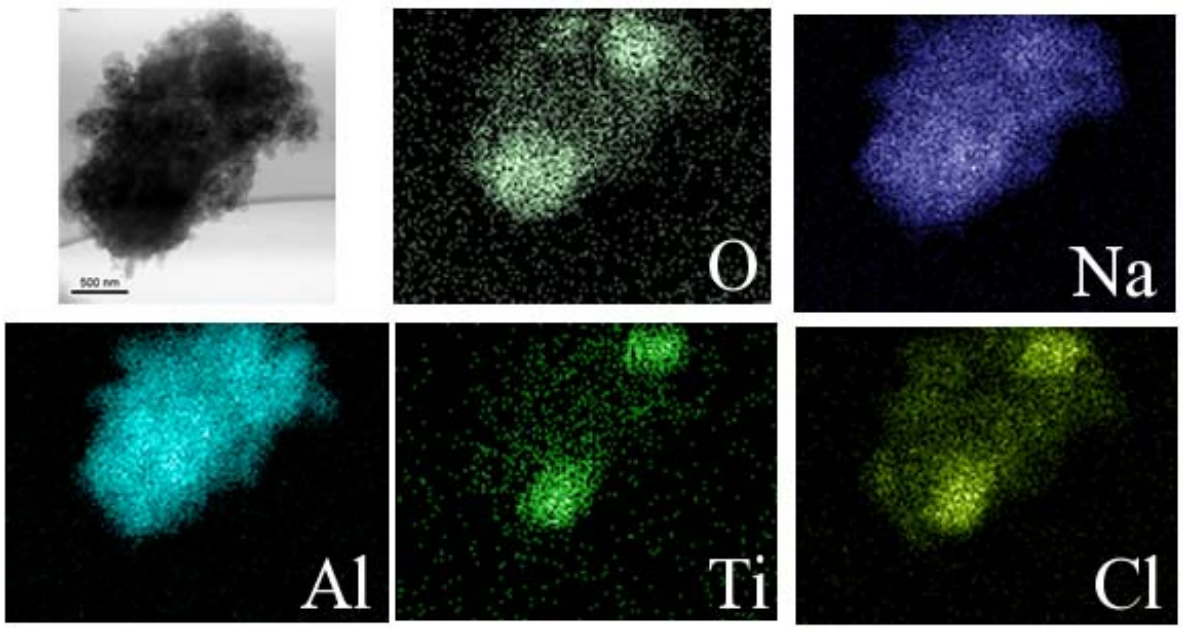


✓ **Excellent agreement between theory and experiment when assessed from van't Hoff plot using a constant slope.**

Finding the location of the elusive catalyst particles

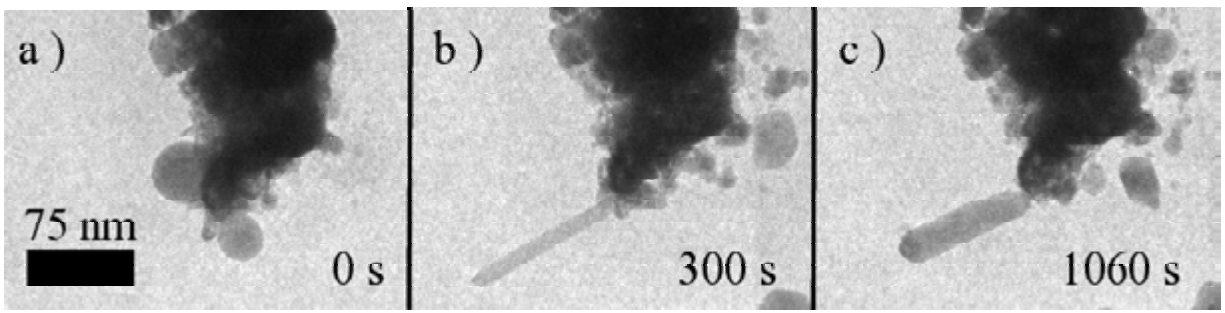
(Univ. of Hawaii)

Chemical map of 2 mol % $TiCl_3$ doped $NaAlH_4$, 10x cycle



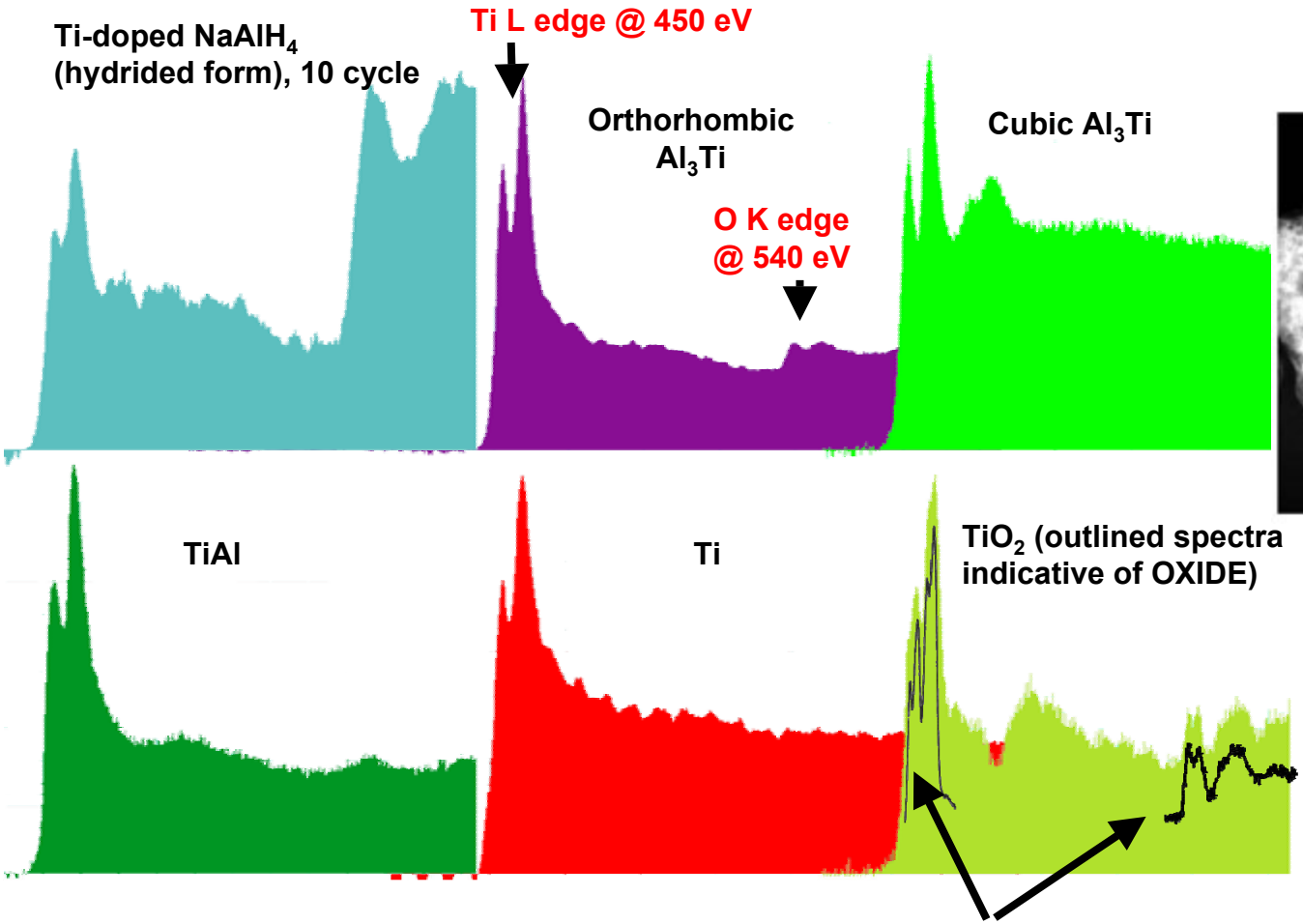
- Acquisition of Gatan transfer stage prevents excess oxidation during transfer.
- EDS elemental maps show distribution after ten cycles – Ti still highly localized and associated with Cl.
- Growth of Na-bearing crystals may alter composition of storage material
  - Both heat and electron beam stimulated growth

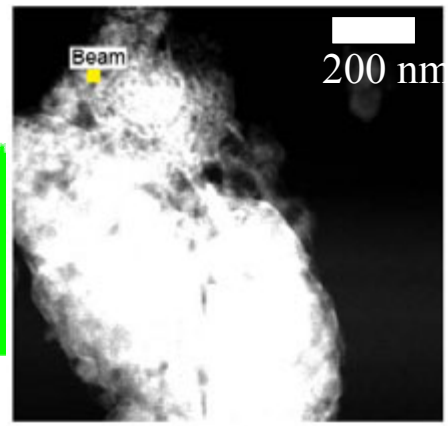
Na crystal growth in different crystal of Ti doped $NaAlH_4$, ~ 70 ^oC



No longer a Center material, presented to show capability as current effort not yet cleared for presentation

Location of the Ti.
Electron energy loss spectroscopy





Confirmed presence of Ti and peak shapes show it is NOT oxidized

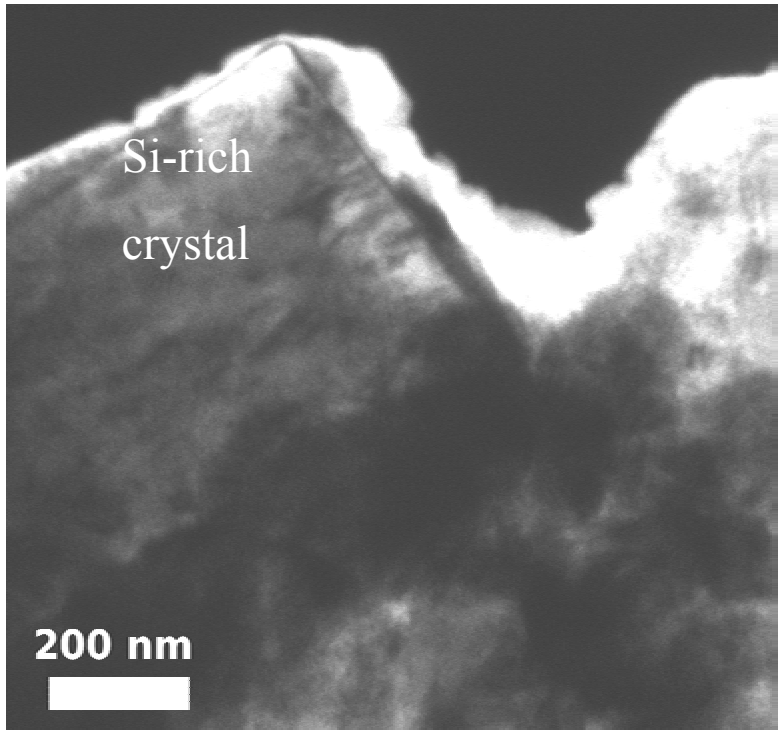
Post Ti shapes confirm **Al_3Ti** and possibly show orthorhombic form

From this can determine density of states – compare with theory.

MgH_2 + ½ Si – Oxidation

(collaboration with HRL)

- Direct imaging of oxide and its thickness using energy-filtered TEM
- **Oxide is present prior to microscopy**



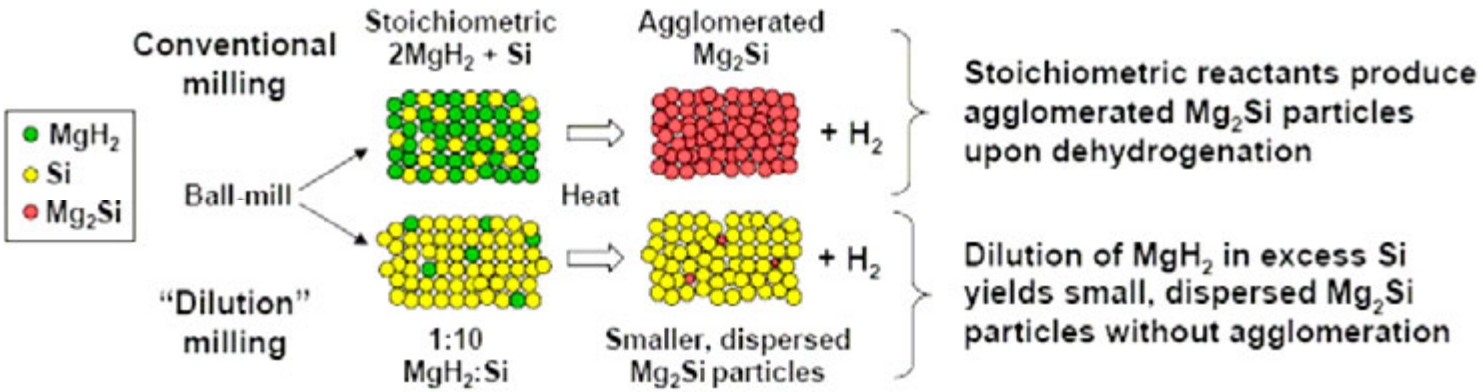
MgH_2 + ½ Si + 0.05 Nb_2O_5, previously dehydrided
EFTEM at 100 eV, 20 eV slit
Shows oxide on outside of Si particle.

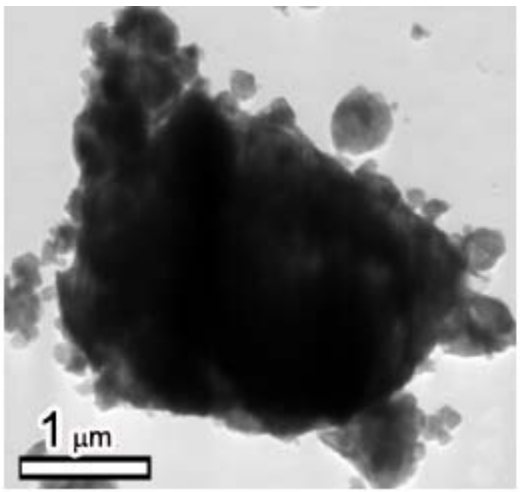
How much does oxide thickness on Mg and Si slow H penetration into lattice?

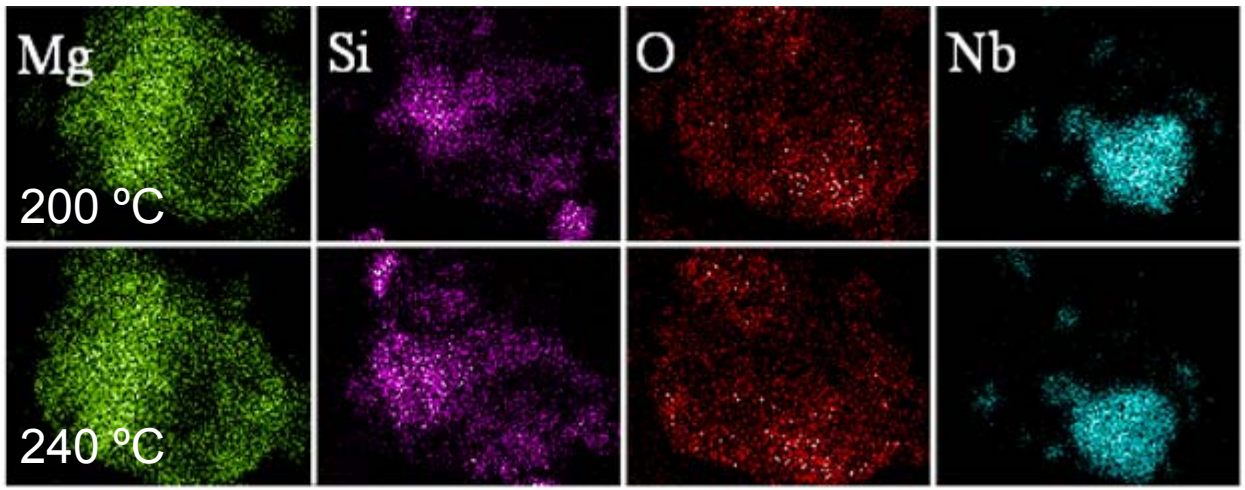
Does this affect H uptake?

Understanding Processing

(collaboration with HRL)







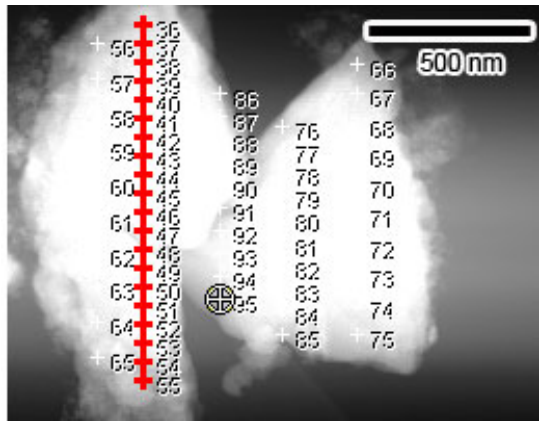
Dynamic studies not showing elemental segregation – need higher nominal temperatures
Nb not well distributed after ball milling . Need to verify effectiveness of "dilution milling."

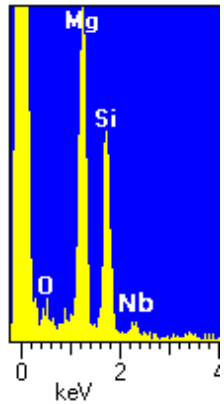
Element redistribution during discharge cycle

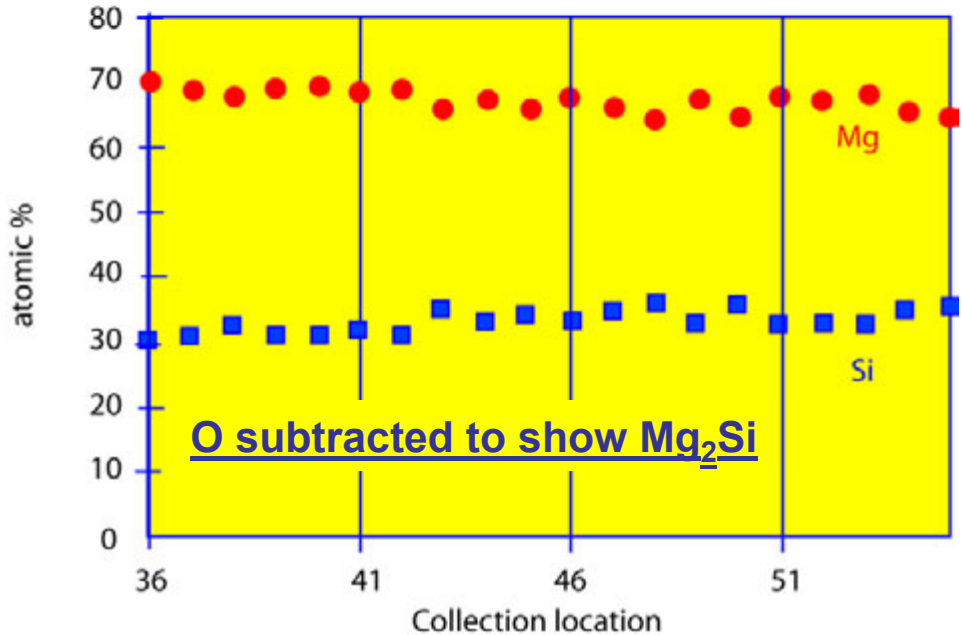
(Collaboration with HRL)

- Above 240 ˚C, Nb-doped Mg/Si does form the intermetallic (sub-grain size ~ 250 nm)
- Average composition over scan axis:
  - 10 at % O
  - 62 at % Mg
  - 29 at % Si
  - Nb near detector limit
- Removing O → 68 at % Mg, 35 at % Si (ideal 66/33)
- Very close to Mg_2Si as expected and reported via XRD

EDS spectra obtained at points







Future experiments and theory

Continued search and assessment of candidate metal-hydrides, as well as determining "best practice" for comparison to experiment and rapid design.

Focus efforts on most likely candidate systems with the goal of elucidating which defects and contaminants impact kinetics.

FY 06.

- Complete van't Hoff analysis for BH_4 systems. (with HRL, U.Pitt, CMU)
- Continue study of Ca $2CaH_2/CaB_6$ (with SNL)
- Continue to assess effectiveness of ball milling strategies for Li/Mg/destabilized systems (with SNL)
- Maintain database of candidate systems and reactions. Expand use, scope, and vetting reliability. (with all partners)

FY O7

- Determine chemical and structural change occur during (de)hydriding cycles? (with SNL, HRL, U Hawaii)
- Structure and energy of combined magnesium / boro-hydrides. (with GE)
- Complete study of CaH_2/CaB_6 (with SNL)
- Structure and chemistry of contaminant layers on (de)hydriding cycle (U. Nevada)

Talks, papers and Collaborations

Theory Tutorial to MHCoE: Capabilities and background of first-principles modeling to the experimentalists (*Aug. 17, 2005).*

– D.D. Johnson (UIUC) "Using DFT Methods: the good, bad and ugly"

Collaborative Visits/Talks*:*

– Duane Johnson (UIUC) talked at Pittsburgh (Nov. 16-17, 2005).

– S. Alapati (CMU) and R. Stumpf (SNLL): (Dec. 12-13, 2005)

– Craig Jensen 18-19 October 2005

– J.C. Zhao (GE) 18 April 2006.

– Christine Morales (U. Hawaii) Jan. 11-21 for modeling of defect barriers, and experiments with Lance Culnane (U. Hawaii). Feb. – Apr.2006

Papers.

– *Enthalpies of hydrogen storage complex-metal hydrides: calculated versus measured – submitted to Phys. Rev Lett.*

– Combining Electron Energy Loss Spectroscopy and Energy Dispersive Spectroscopy for Identification of Catalytic Species in Hydrogen Storage Materials – Hydrogen Meeting, Hawaii 2006

– Calculating enthalpies of hydrogen storage complex-metal hydrides - Hydrogen Meeting, Hawaii 2006

Summary

- Demonstrated how theory can interface with experiment and improve understanding of assessed properties.
- Used experiment to improve understanding of and to assess processing strategies and reliability.