Discovery of Novel Complex Metal Hydrides for Hydrogen Storage through Molecular Modeling and Combinatorial Methods

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J.W. Adriaan Sachtler

UOP LLC

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Project ID # ST5

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Overview

Timeline

- Start date: 5/1/2004
- End date: 4/30/2007
- % Complete: 33

Budget

- Total project funding
  - DOE: $2,000,000
  - UOP: $2,910,618
  - Ford: $ 75,000
- FY04 DOE: $553,807
- FY05 DOE: $550,000

Barriers

- Barriers addressed (DOE-2010)
- Useable H_2 Density
  - 2.0 kWh/kg & 1.5 kWh/L
- H_2 Delivery Temperature Range
  - -30 to 100˚C
- Cycle Life
  - 1000 Cycles
- Refueling Time
  - < 5 Minutes

Partners

- Hawaii Hydrogen Carriers
- UCLA
- Ford
- Striatus

Project Objectives

- **Overall Program:**
  - **Discovery of a complex metal hydride through Molecular Modeling and Combinatorial Methods which will enable a hydrogen storage system that meets DOE 2010 goals**
  - **Project completion in three years**
  - **Deliverables:**
    - **One kilogram of optimized material**
    - **Potential manufacturing process**
    - **Design for a hydrogen storage system**
    - **Documentation**
- **Program Year #1:**
  - **Milestones**
    - **Hydride/Catalyst > state-of-the-art [Reversible %H, Temp.]**
  - **Downselects**
    - **Downselect from Na, Li, Mg/AlH_4**
  - **Go/No-Go Points**
    - **Validation and Demonstration of VHTS (Molecular Modeling)**
    - **Validation and Demonstration of Medium Throughput Combinatorial Tools**

Approach

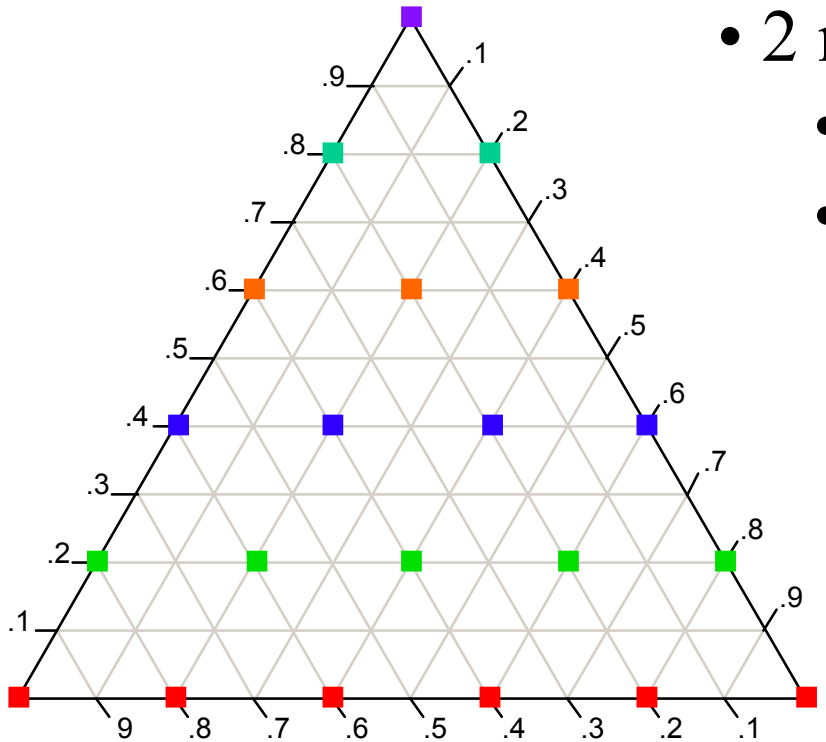
- **Virtual High Throughput Screening**
  - **Molecular Mechanics VHTS (~1000 compositions/month)**
  - **DFT to refine leads, predict thermodynamics**

  >>Guide experiments to find optimal system faster
- **Combi Synthesis & Screening**
  - **Medium Throughput (8x), then High Throughput (48x)**
  - ***Representative sample preparations – powders by ball-milling***

  >>Feedback to theoretical efforts to refine models
- **Follow up on Leads:**
  - **Additional testing, characterization & modeling for increased understanding**
  - **Intermediate scale-up & multi-cycle testing**
- **Material Meeting Targets:**
  - **Optimization & scale-up to 1 kg**
  - **Identify commercial manufacturing routes**
  - **Design storage system & develop cost estimate**

Na–Li–Mg/AlH_4 Phase Diagram: Experimental Design

$NaAlH_4$, 5.6%



$LiAlH_4$, 8.0%

0.5 $Mg(AlH_4)_2$, 7.0%

21 Design Points

- 2 mole % $Ti(iOPr)_4$ dopant
  - Synthesis by Ball Milling
  - XRD on fresh & spent
    - H_2 capacity in 8-Rx apparatus

3 Phase Diagrams

- Two types of milling
- Reverse Reaction

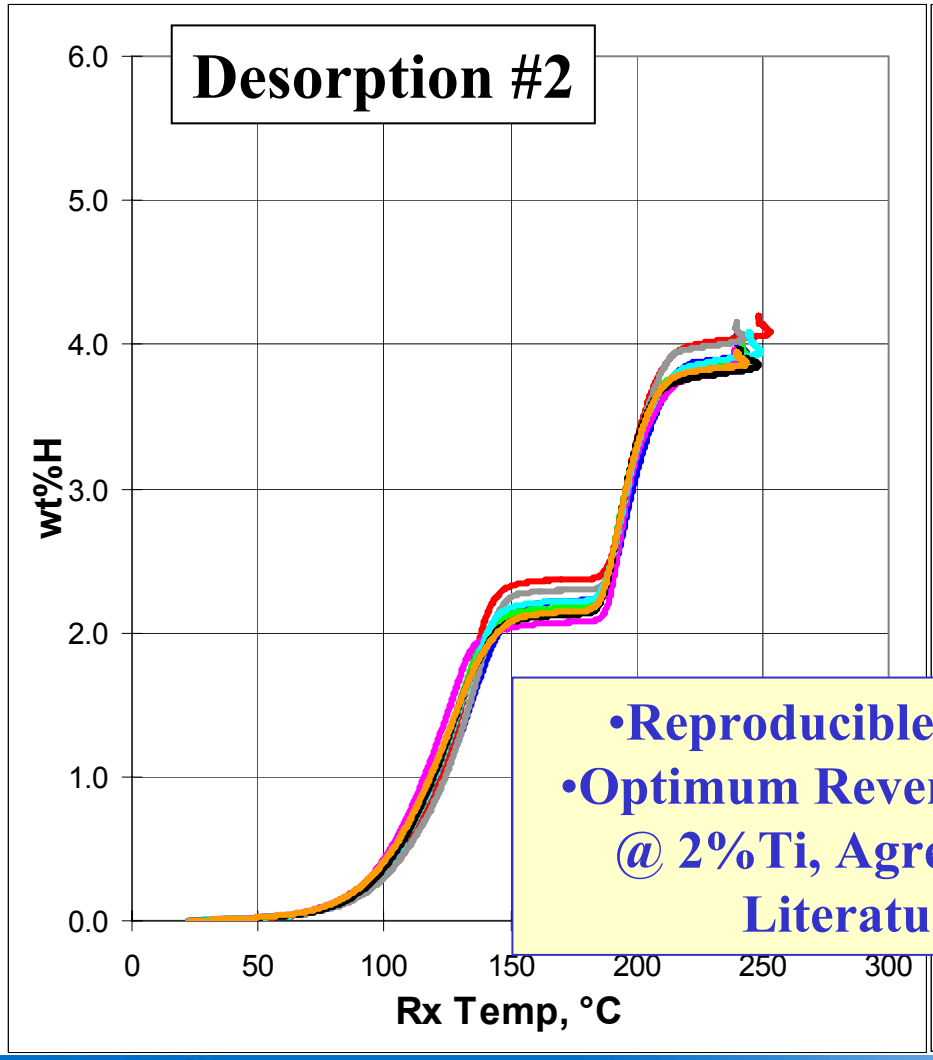
Screen for new mixed metal alanate phase

Medium-Throughput Testing Methodology

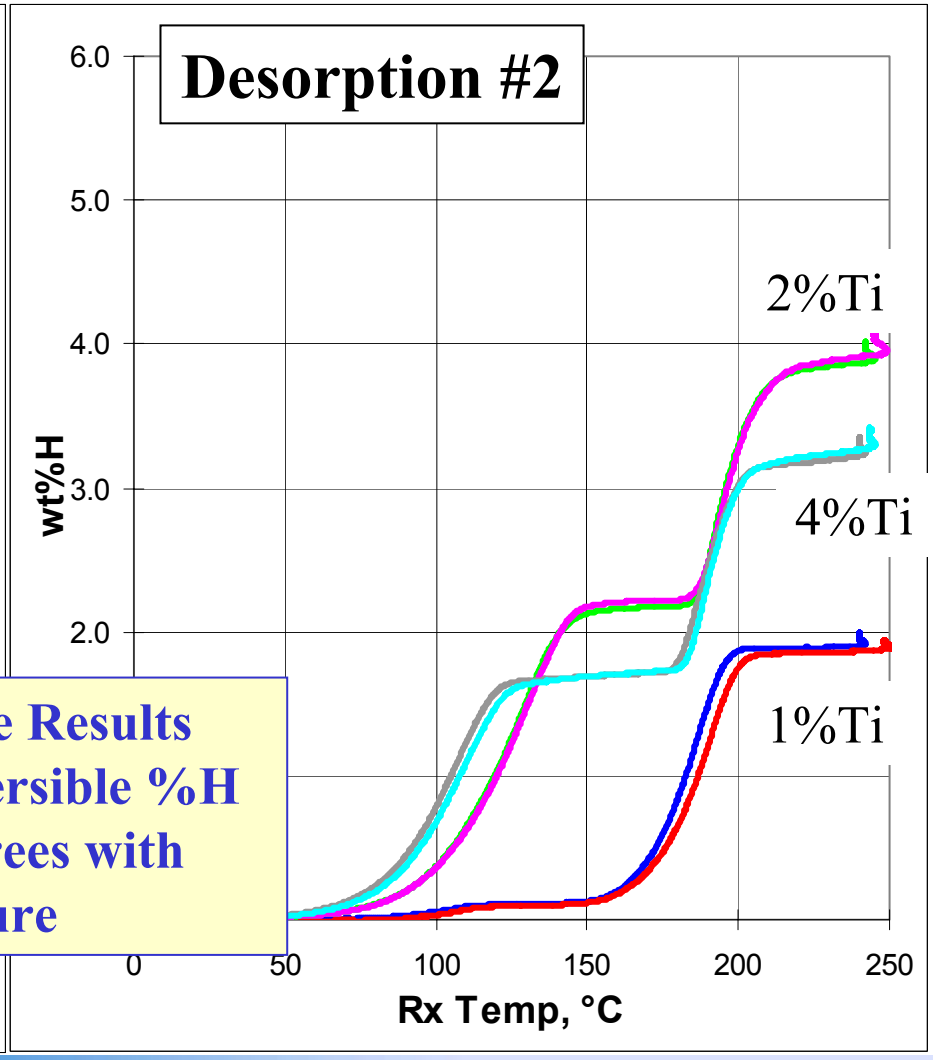
- **Temperature Programmed Desorption**
  - **Ramp to 220°C @ 2°C/min**
  - **Hold at 220°C, 1 hour**
  - **Closed cell, wt-%H from pressure measurement**
  - **8 Reactors in parallel (simultaneous)**
- **Rehydriding**
  - **125°C, 1250 psig (87 bar), 12 hours**
- **Cycles**
  - **Two cycles is standard for screening**
  - **Cycle #2 → reversible wt-%H**
  - **Original protocol ended after 2nd desorption; recently added a final rehydriding for characterization**
- **Optional Pretreatment**
  - **Perform hydriding step before first desorption**

Medium Throughput Validation: Synthesis & Testing

8 Samples of 2%Ti/$NaAlH_4$



Variable %Ti Study on $NaAlH_4$

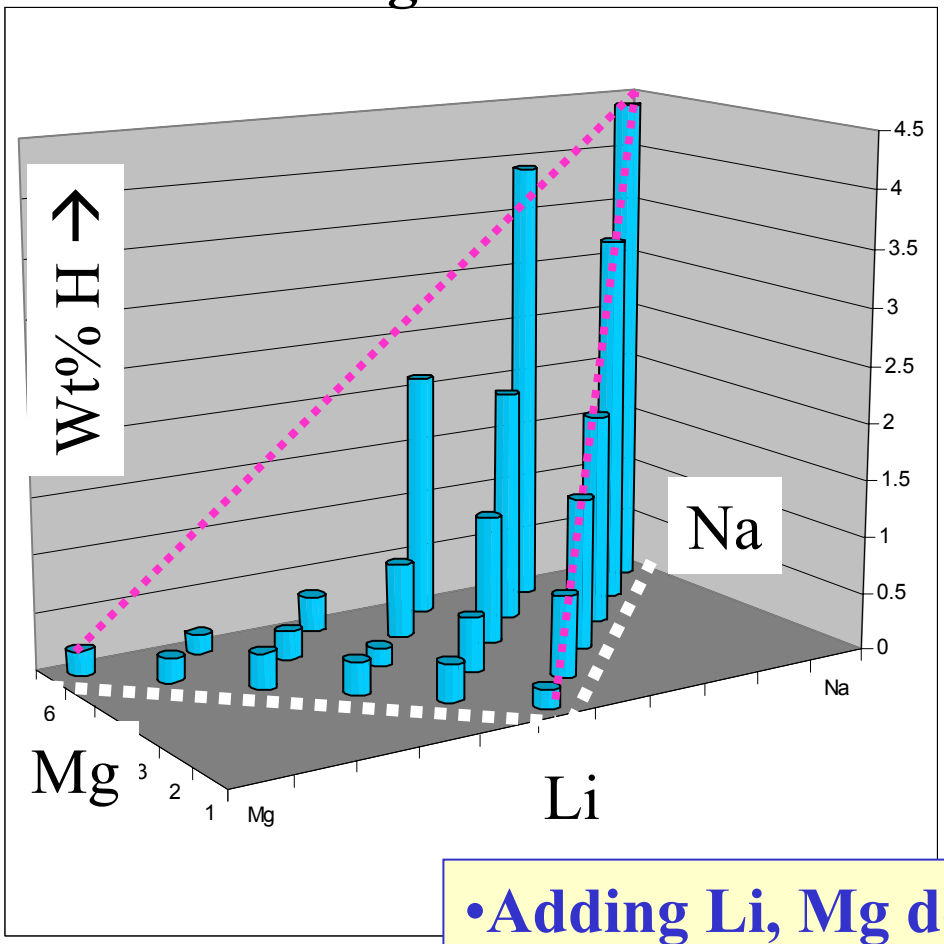


- **Reproducible Results**
- **Optimum Reversible %H @ 2%Ti, Agrees with Literature**

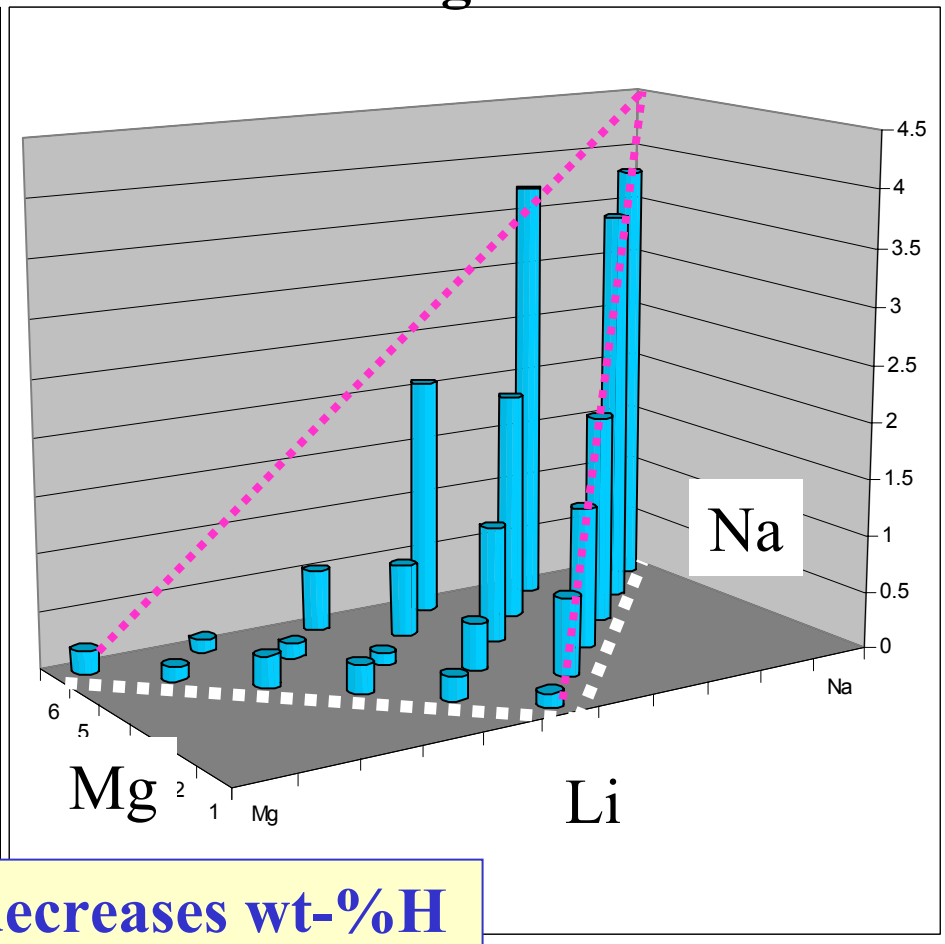
$NaAlH_4$+$LiAlH_4$+$Mg(AlH_4)_2$ Phase Diagram

Reversible wt-%H (2nd Cycle)

Milling Method#1

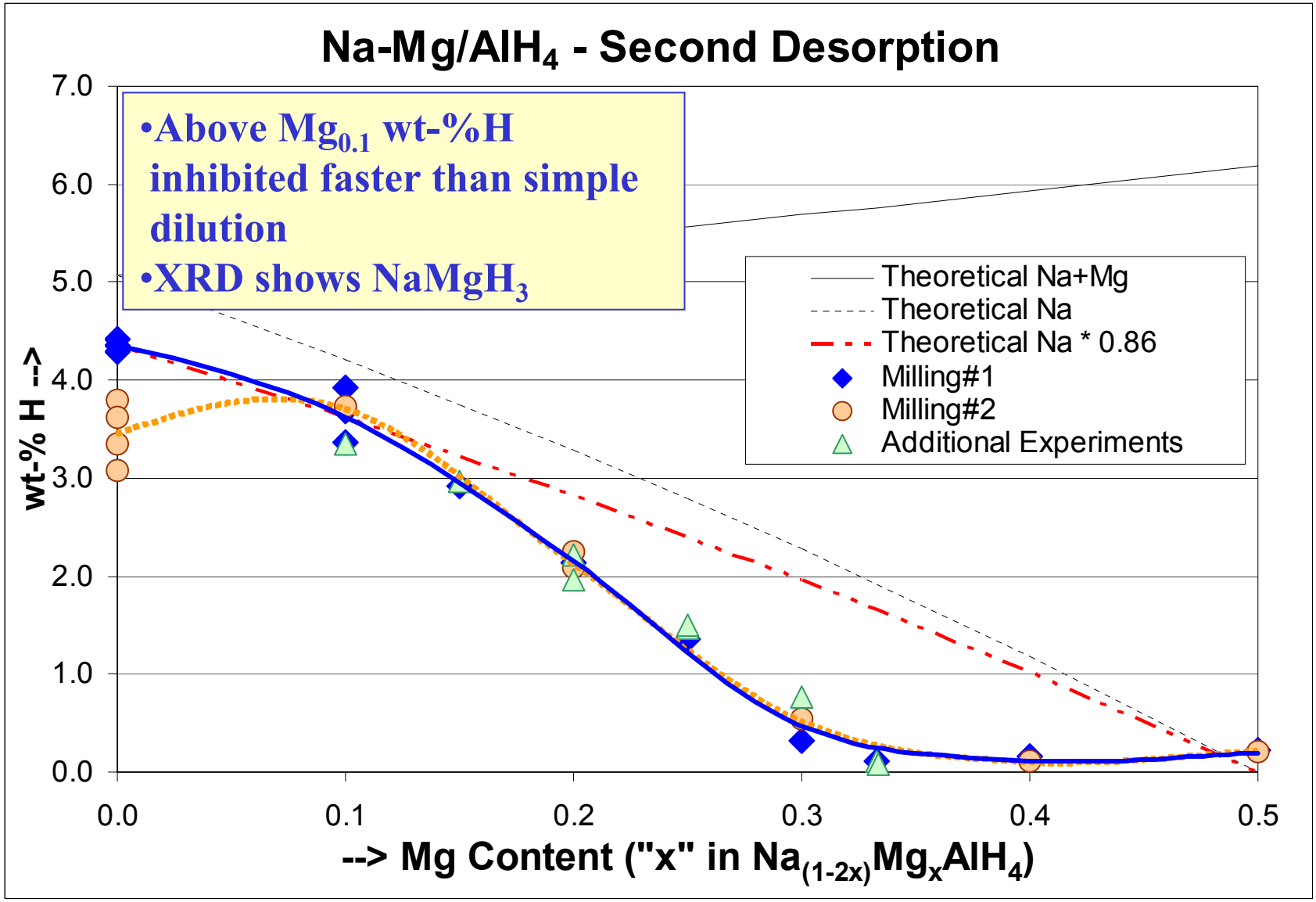


Milling Method#2

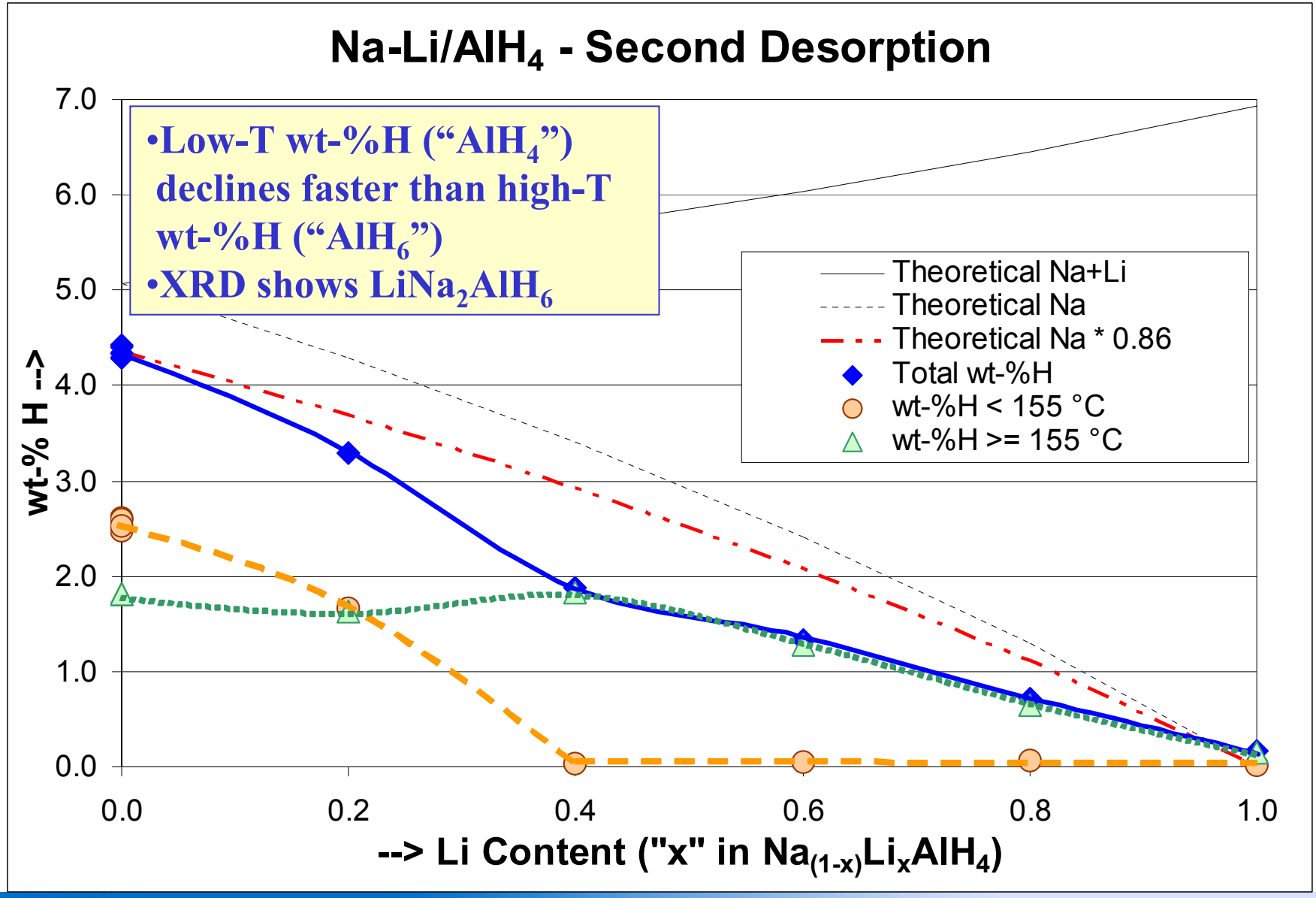


- **Adding Li, Mg decreases wt-%H**
- **Mg effect is non-linear**

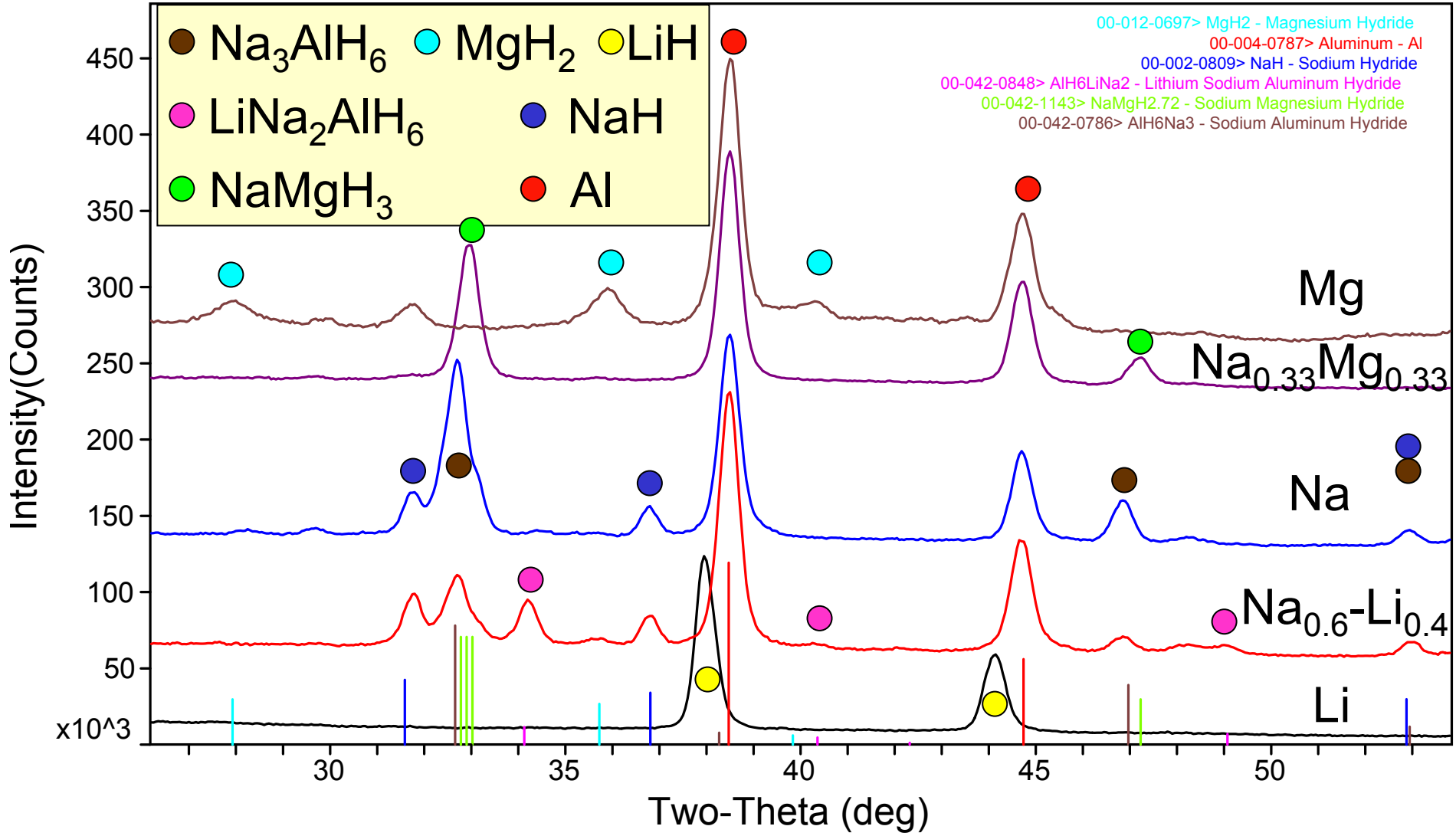
Na-Mg/AlH$_4$ Binary Sub-System



Na-Li/AlH_4 Binary Sub-System



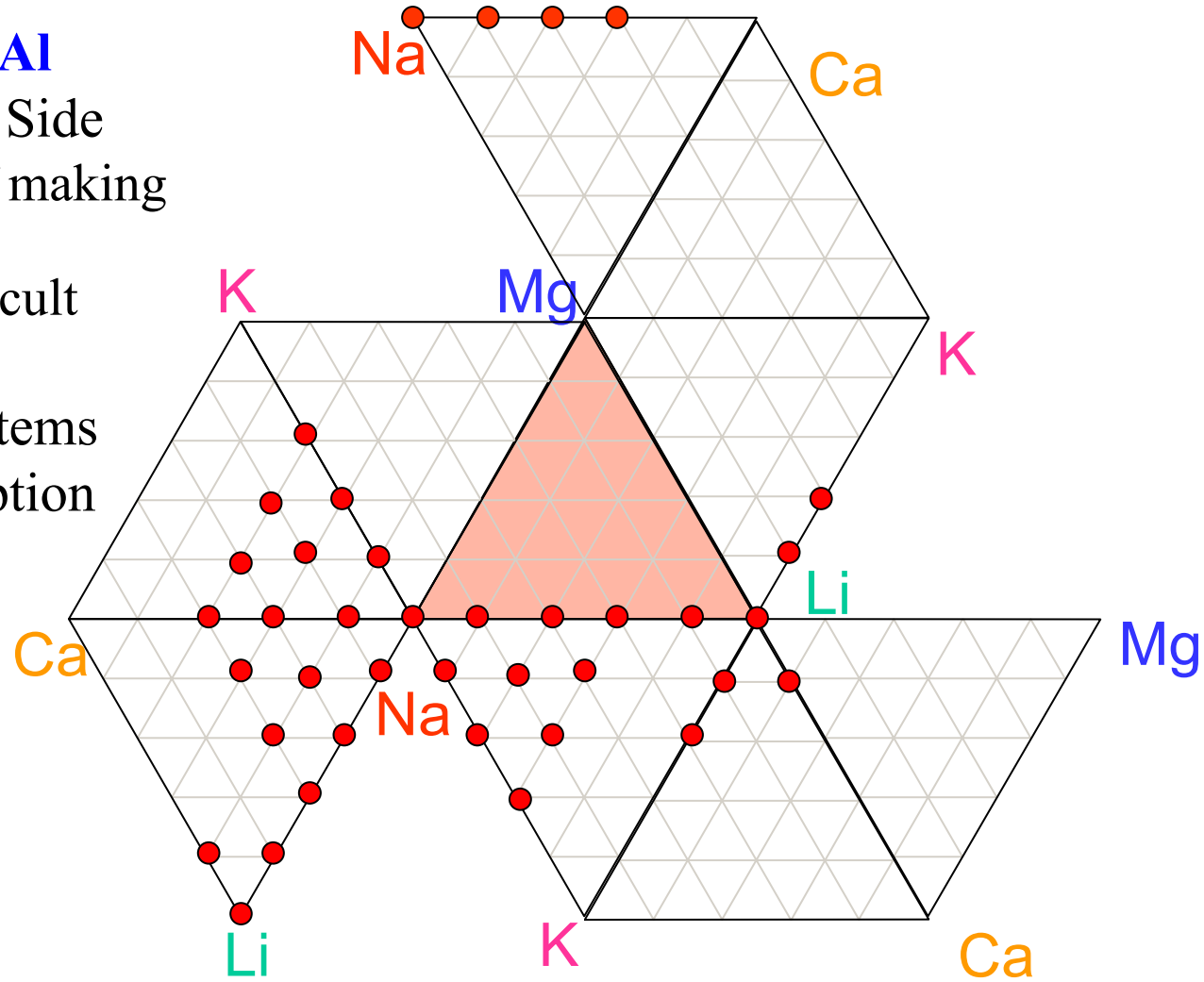
Phases Observed In Li-Na-Mg/AlH_4 System: Samples After Testing



Phase Diagram From Dehydrided Side, Including Year#2 Phase Diagrams

[Na-Li-K-Mg-Ca]H_x + Al

- Start on De-Hydrided Side
  - Increase chance of making new compounds
  - Alternative to difficult $MAlH_4$ synthesis
- Screen ternary subsystems
- Hydride before desorption
- *Solid dots done (24)*
- So far, no improvement over NaH+Al



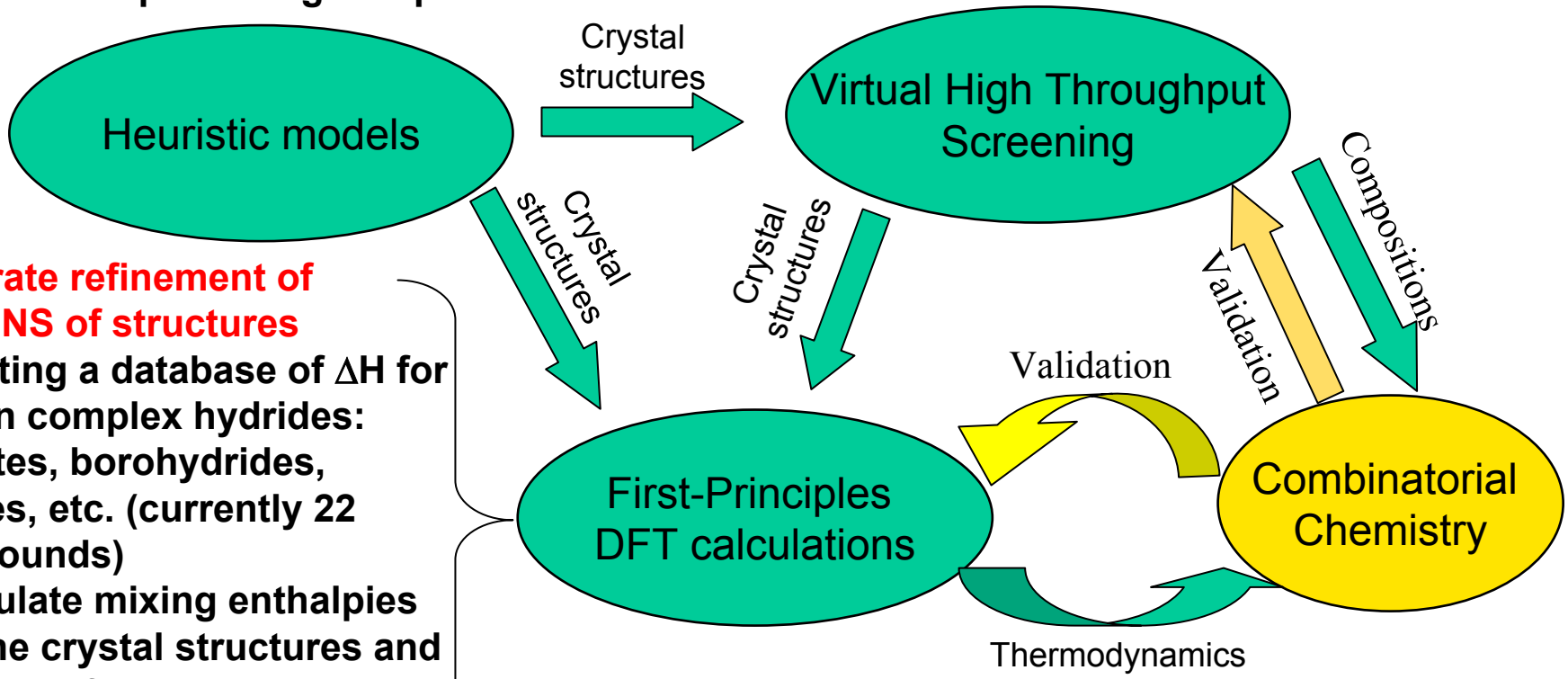
Molecular Modeling

Select Regions of Phase Space

- **Gravimetric Density**
- **Published Thermodynamic Data and Chemistry**
- **Electrostatics and Alloy Theory**
- **Pauling's Rules**
- **Predict promising compositions**

Screen THOUSANDS of phases with Molecular Mechanics

- **Optimize crystal structures**
- **Search for stable compounds**
- **Estimate Thermodynamics**
- **Predict Promising Compositions**



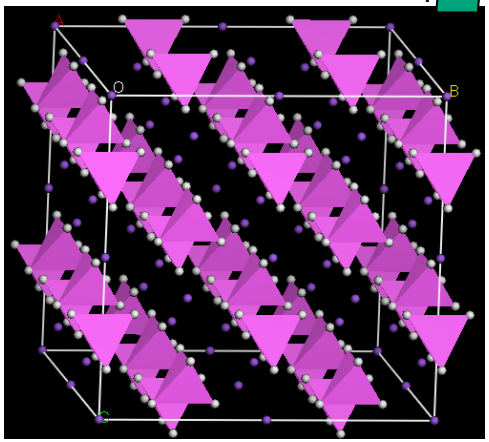
Accurate refinement of DOZENS of structures

- **Creating a database of ΔH for known complex hydrides: alanates, borohydrides, amides, etc. (currently 22 compounds)**
- **Calculate mixing enthalpies**
- **Refine crystal structures and obtain ΔH for predicted compounds**

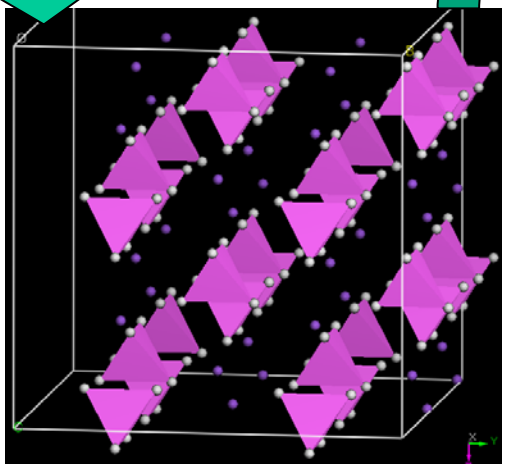
Virtual High Throughput Screening

Structure Prediction

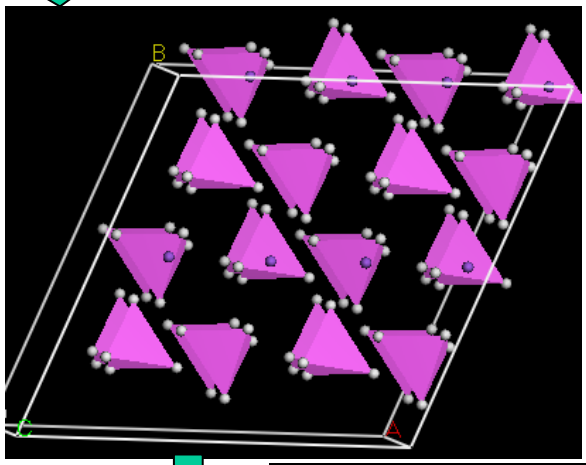
Initial Guess – $NaAlH_4$



After 200K MD

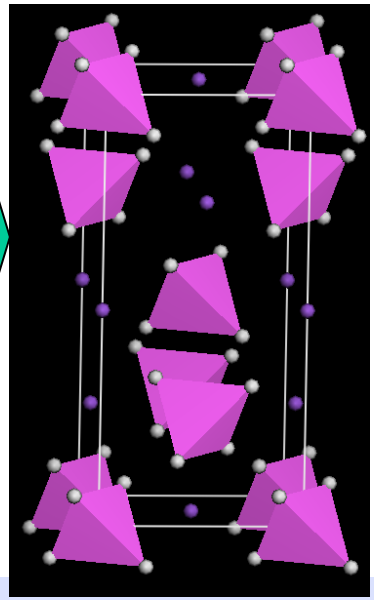


After 500K MD



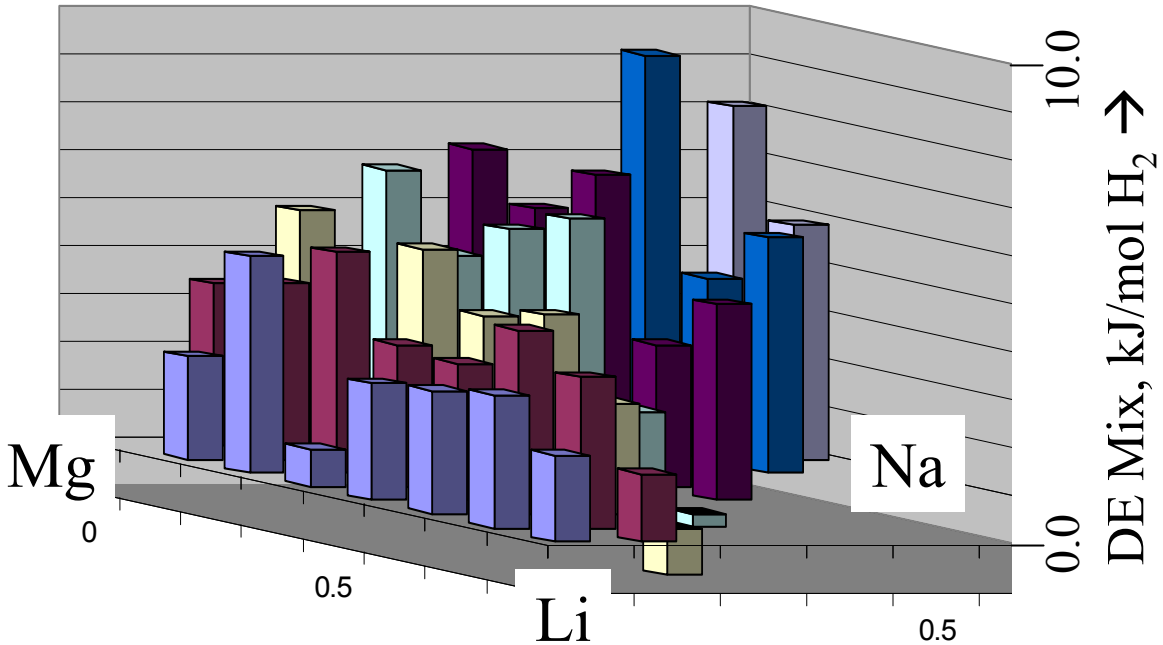
- Molecular Mechanics/Molecular Dynamics to predict structure
  - Simulated Annealing
- Unit Cell contains 180 to 200 atoms.
- Predicted structures are close in energy ($\Delta E<0.03$ eV/AlH_4) to the experimental structures for $NaAlH_4$, $LiAlH_4$ and $Mg(AlH_4)_2$

Symmetrize "NaAlH4" structure



Virtual High Throughput Screening

- **35 points in the Na-Li-Mg Phase Diagram**



•Found two phases with Negative Heats of Mixing.

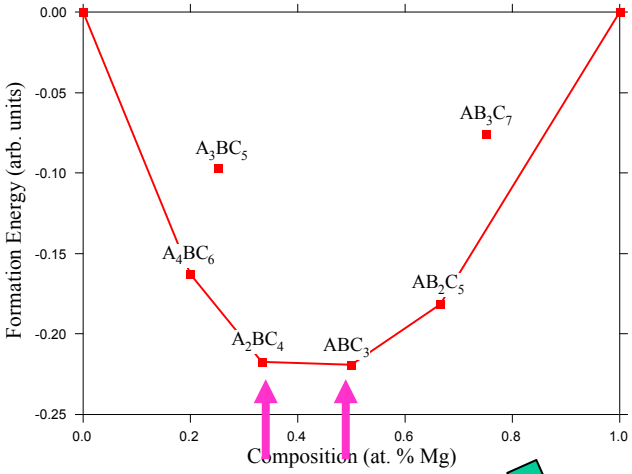
•Not stable with respect to loss of hydrogen.

•Each Estimate of Energy of Mixing takes ~ 3 hours CPU.

•Can estimate heats of mixing of 1000 phases/month.

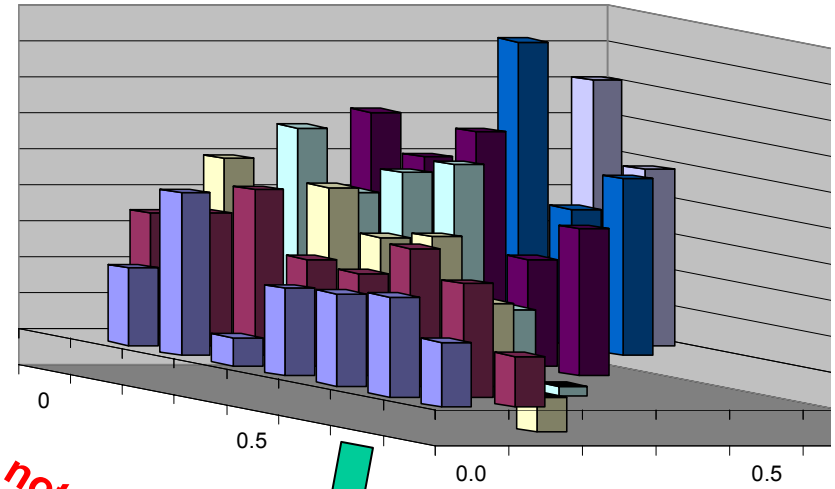
Application of Models to Na-Mg-Li alanates

Electrostatic lattice model



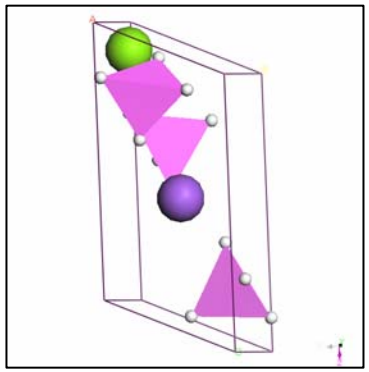
Crystal structures of $NaMg(AlH_4)_3$ and $Na_2Mg(AlH_4)_4$

Molecular Mechanics



Enthalpies $\Delta H>0$

Compounds not found, refine heuristics



DFT calculations

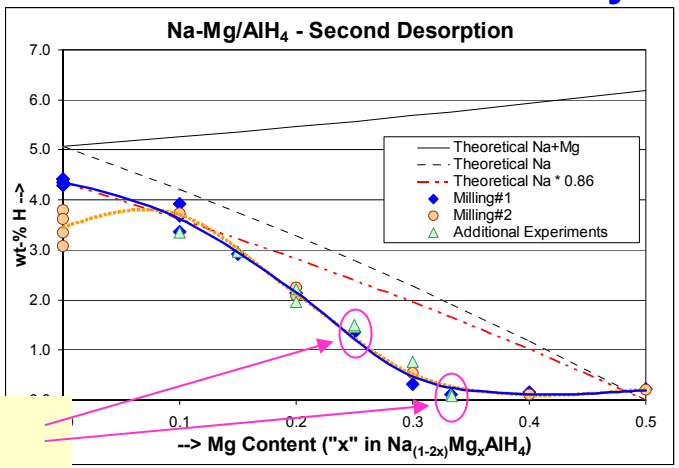
Structure refinement & formation enthalpy:

$$Mg(AlH_4)_2 + NaAlH_4 \rightarrow MgNa(AlH_4)_3$$

$\Delta H = +2$ kJ/mol H_2 **- will not form**

Enthalpies of Na-Mg-Li alanates

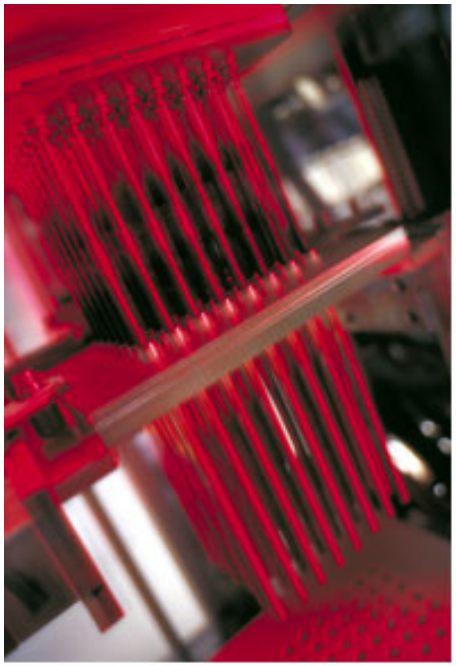
Combi Chemistry



Predicted compositions

High-Throughput Combi System

- **Synthesis**
  - **Capability**
    - **Automated solution and powder dispensing**
    - **MT Vacuum, filtration, sample washing and drying**
    - **Sample agitation, sample heating to 250°C**
  - **HT Milling (successful POP completed)**
- **Characterization**
  - **HT XRD fully operational**
- **Testing**
  - **Using TPD, against atmospheric pressure**
  - **Higher T,P capability than 8-Rx: 350°C, 120 bar**
- **Details are confidential**
- **System builds on UOP's extensive Combi expertise**
  - **Material synthesis, catalyst preparation & testing, DOE, informatics**
- **Timing: start screening early 4Q2005, as planned**



UOP Combi Catalyst Test System

Summary

- **Medium Throughput Synthesis & Testing** ***(Yr#1 Go/No-Go)***
  - **Results match literature data**
  - **Used in production mode**
- **Na-Li-Mg/AlH_4 Phase Diagram Downselect** ***(Yr#1 Milestone)***
  - **Experiments + MM Modeling + DFT Modeling => no promising new compositions in this system**
- **Modeling**
  - **Three-Tier approach demonstrated for Na-Li-Mg/AlH_4**
  - **VHTS demonstrated and checked against experiment** ***(Yr#1 Go/No-Go)***
  - **Ready to start screening new systems**
- **Extension to other elements**
  - **K, Ca phase diagrams started** ***(Yr#2 Downselects)***
- **High-Throughput system construction on schedule**

Time-line, Yr#2 milestones + downselects + Go/No-Go's in supplemental slides

Responses to 2004 Reviewers' Comments

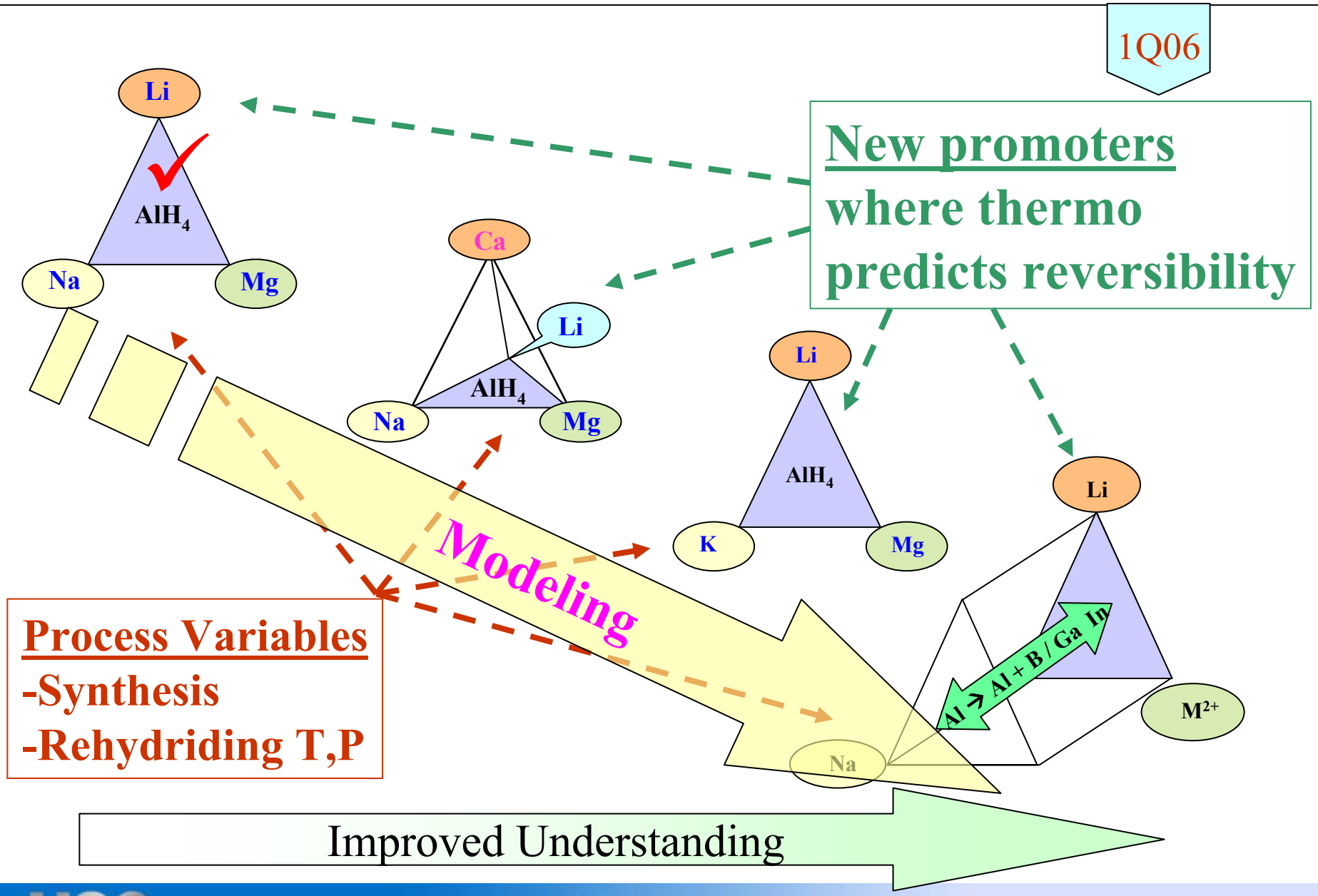
- **1) Comments asking about the combinatorial work:**
  - **"better definition of how they will analyze at high rates", "more info on screens", "will combinatorial approach be used for synthesis and screening, or just screening?", "more details on the high-throughput combinatorial screening technique are needed", "high throughput preparation and couple it to the human interface. This can be and often is the downfall to many discovery science activities and it was not clearly defined"**
- ***Both synthesis and testing will be done combinatorially.***
- ***Details of the high-throughput system are confidential, however, the system builds on UOP's extensive expertise in Combi materials synthesis, catalyst preparation & testing, design of experiments and informatics. Two of the team members have been part of the Combi development at UOP.***

- **2) Comments about not being explicit about the materials to be studied:**
  - **"vague on the materials to be studied", "this reviewer finds the future (especially materials) rather vague", "future plans lacking in detail for such a large project", "come to FY2005 review with clearly laid out plans for FY2006 and beyond".**
- ***A more detailed plan is being presented today. However, full disclosure is limited by IP issues.***

Response to comments from Tech Team meeting & DOE

- **Demonstrate how modeling is impacting the experimental efforts and the discovery aspect of this project**
- ***Validation:***
  - ***We have tested two theoretical predictions experimentally, providing feedback to the modeling (MM=DFT=OK, Heuristics=Refine)***
  - ***DFT, VHTS/MM, Experiment agree for Na-Li-Mg/AlH_4***
- ***Modeling directing experimental efforts:***
  - ***Modeling indicates that we are not "missing" any promising compositions in the Na-Li-Mg/AlH_4 phase space → this information helps move experimental work to other systems.***
  - ***Modeling is ready to start predicting new phases***
  - ***Modeling will predict whether compounds are thermodynamically reversible → may direct experiments to new promoters, alternate test conditions***

Plans - I: Alanates



Plans - II: Other Systems

- **Since our proposal was written, several new interesting approaches have been published:**
  - **Amides**
    - **$2\ Li(NH_2) + MgH_2 \leftrightarrow Li_2Mg(NH)_2 + 2H_2$**
    - ***Y. Nakamori and S. Orimo J. Alloys Compd. 370, 2004, 271.***
    - ***S. Orimo, Y. Nakamori, G. Kitahara, K. Miwa, N. Ohba, T. Noritake, and S. Towata Appl. Phys. A 2004, 79, 1765.***
    - ***W. Luo J. Alloys Compd. 381, 2004, 284.***
  - **Destabilization of Hydrides**
    - $4LiH + Si \leftrightarrow SiLi_4 + 2\ H_2$
    - $2LiBH_4 + MgH_2 \leftrightarrow 2LiH + MgB_2 + 4H_2$
    - ***J.J.Vajo, et al. J.Phys.Chem. B 108(2004)13977; 104(2005)3719***
- **After completing the alanate systems –*if needed*- we plan to pursue approaches building on or extending concepts like this, or other idea's.**

The Team

DOE Project Manager

UOP
Dave Lesch – Project Manager
Adriaan Sachtler – Team Leader, Testing
John Low – Modeling
Greg Lewis – Synthesis
Syed Faheem – Synthesis
Lisa Knight – Combi Synthesis
Paul Dosek – Combi Testing
Doug Galloway – Characterization
Leon Halloran – Characterization

Ford
Chris Wolverton
Modeling

UCLA
Vidvuds Ozolins
Modeling

H_2C
Craig Jensen
Char/Testing

Striatus
Laurel Harmon
Informatics

Supplemental Slides

The following three slides are for the purposes of the reviewers only – they are not to be presented as part of your oral or poster presentation. They will be included in the hardcopies of your presentation that might be made for review purposes.

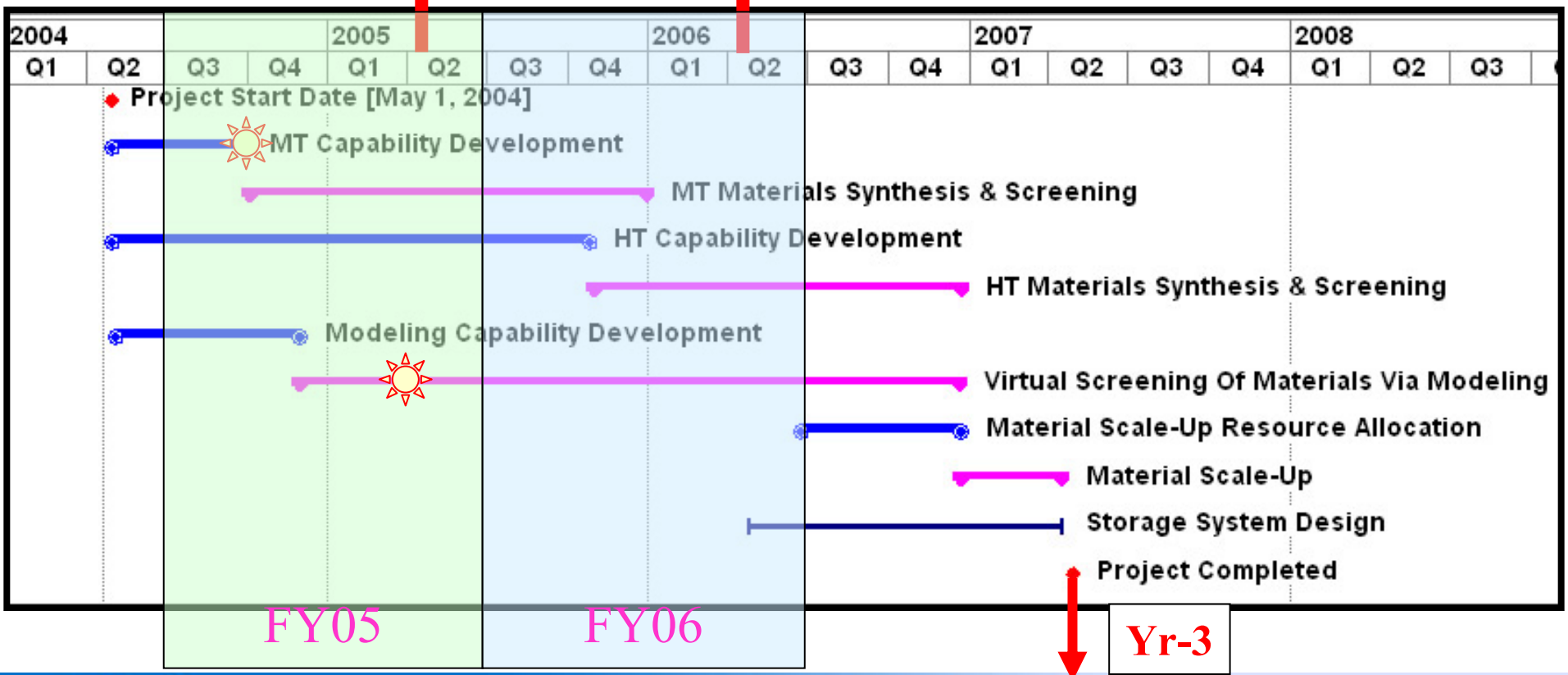
FY05,06 Plans, Milestones, Down Selects

Hydride/Catalyst > state-of-the-art [Reversible Capacity, Temperature], Downselect Na, Li, Mg-Alanates

Hydride/Catalyst approaching DOE system targets, Downselect Ca, B, Ga, and In hydrides

Yr-1

Yr-2



Yr-3

1 kg Hydride/Catalyst @ DOE system targets

Yr#1 Milestones, Downselects & Go/No-Go Points

- **Milestones:**
  - **Hydride/Catalyst > state-of-the-art**
    - **[Reversible Capacity, Temperature]**
  - ***Not met: no promising compounds found in Na-Li-Mg/AlH_4 system***
- **Downselects:**
  - **Downselect Na, Li, Mg/AlH_4**
  - ***Completed downselect: no winners found, by combination of experimentation and modeling***
  - ***Started work on Year#2 systems***
- **Go/No-Go**
  - **Validation and Demonstration of VHTS (Molecular Modeling)**
  - ***VHTS demonstrated for Na-Li-Mg/AlH_4, consistent with experiments, ready to start predicting new phases.***
  - **Validation and Demonstration of Medium Throughput Combinatorial Tools**
  - ***Tools demonstrated, consistent with literature, producing data***

Year #2 Milestones, Downselects & Go/No-Go's

- **Downselects:**
  - **Downselect Ca, B, Ga, and In hydrides**
- **Go/No-Go Points**
  - **Demonstration of High Throughput Combinatorial Tools**
  - **Identification of New Materials Approaching DOE Targets**

	Milestone	Outcome
Q 2	High throughput synthesis and testing implemented	HT synthesis and screening (48 in parallel) operational and validated using known materials
Q 4	Modeling extended to catalysts	Model descriptors have been identified that correlate with reaction rates over catalyzed materials. Models have been validated using known catalyst systems and are ready to search for new systems.
Q 4	Phase II hydride/catalyst screening completed	At least one hydride/catalyst combination that approaches DOE targets. This material has been validated at Univ. Hawaii
Q 4	Improved mechanistic understanding	Fundamental studies at the Univ. Hawaii have increased the understanding of hydride and catalysts.

Publications and Presentations

Presentations:

3/18/2004: Freedom CAR/Tech Team Review

1/20/2005: Freedom CAR/Tech Team Review

Planned:

IPHE International Hydrogen Storage Technology Conference, Italy, June 19 - 22, 2005

IX International Conference "Hydrogen Materials Science & Chemistry of Carbon Nanomaterials“ Sevastopol, Crimea, Ukraine, September 5 - 11, 2005

Hydrogen Safety

The most significant hydrogen hazard associated with this project is:

- **Potential Explosion of the ball mill**
  - **Vigorous mixing during milling can lead to hydride decomposition**
  - **Potential for the release of hydrogen into the milling chamber causing explosive mixture, during milling or un-clamping after run**

Hydrogen Safety

Our approach to deal with this hazard is:

- **Installation of blow-out panels on ball mills**
  - **Safely dissipate energy in case of hydrogen-air reaction inside milling chamber during run**
- **Use N_2 purged enclosure over mixing bowls when releasing clamp from the mill**
  - **Prevent fire if the seal of the bowl is compromised when loosening the clamp**

Acknowledgement

- **Acknowledgement is made to the US Department of Energy for sponsorship under contract number DE-FC36-04G014013.**