

# Fundamental Studies of Advanced High-Capacity, Reversible Metal Hydrides

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5/17/06

STP 6

# Overview

## Timeline

- Start date: 3/01/05
- End date: 2/26/10
- Percent complete: 20%

## Budget

- Total project funding \$1,041,220
  - DOE share \$823,605
  - Contractor share \$217,615
  - Funding received in FY05 \$225,000
- Funding for FY06 \$255,000

## Barriers

1. Lack of understanding of hydrogen chemisorption and physisorption
2. Hydrogen capacity and reversibility
3. Thermal management

## Collaborators

- Prof. Ian Robertson - U. Illinois
- Prof. Shin-ichi Orimo, Dr. Yuko Nakamori - Tokoku U.
- Dr. Hendrik Brinks, Prof. Bjorn Hauback - Institute for Energy Technology, Norway
- Dr. Lee Sefanakos, Dr. Sesha Srinivasan - U. South Florida
- Dr. James Rielly, Dr. Jason Graetz - BNL
- Dr. Robert Bowman - Jet Propulsion Laboratory
- Prof. Rosario Cantelli - U. Rome
- Dr. Etsuo Akiba, Katsu Sakaki - AIST, Tskuba, Japan
- Dr. Rysuke Kuboto\_KEK, Tskuba, Japan
- Dr. Terry Udovic - NIST
- Dr. John Vajo, Dr. Greg Olsen - HRL
- Prof. Dhanesh Chandra - University of Nevada

# Objectives

- I. Characterization of the active titanium species in Ti-doped  $\text{NaAlH}_4$ .
- II. Development of a model of the mechanism of action of dopants in the dehydrogenation and re-hydrogenation of  $\text{NaAlH}_4$  and related capacity hydrogen storage materials.
- III. Determine the enthalpy of dehydrogenation of high capacity hydrogen storage materials.
- IV. Develop catalysts to improve the hydrogen cycling kinetics of “thermodynamically tuned” binary hydrides with potential to meet the DOE 2010 system gravimetric storage capacity target.

# Approach

## Task 1. Characterization of the active species in doped complex hydrides

All candidate alanates, amides, and borohydride hydrogen storage materials have unacceptable dehydrogenation-rehydrogenation kinetics. Elucidation of the species responsible for the enhanced kinetics that arises upon doping of some of these materials would be a great aid in effort to develop methods of improving the kinetics.

The majority of the Ti in cycled, Ti-doped  $\text{NaAlH}_4$  has been found by electron paramagnetic resonance spectroscopy, Synchrotron X-ray diffraction, X-ray absorption fine structure, and tunnelling electron microscopy to be an Al-Ti alloy that is catalytically inactive. This implies the enhanced hydrogen cycling kinetics are due to a minority Ti species. Thus our efforts are currently focus on the characterization the active, minority Ti species through tunneling electron microscopy studies (collaboration with University of Illinois).

# Approach

## Task 2. Elucidation of Mechanism of Action in Dopants

A second key aid to improving the kinetics of the reversible dehydrogenation of complex hydrides would be a fundamental understanding development of a model of the mechanism of action of the dopants in the dehydrogenation and re-hydrogenation processes in  $\text{NaAlH}_4$  and related materials.

- FY05 studies of Ti- doped  $\text{NaAlH}_4$  by anelastic spectroscopy (collaboration with the University of Rome) revealed that highly mobile point-defects arise upon thermal treatment of the hydride.

### FY06 efforts

- 1) Confirm of the presence of hydrogen vacancies in the defects through observation of isotope effect.
- 2) Conduct analogous anelastic spectroscopy studies on Group I and II amides.
- 3) Conduct complimentary studies of the defects in the doped materials by positron annihilation studies (collaboration with AIST, Tskuba, Japan) and muon spin resonance studies (collaboration with KEK, Tskuba, Japan).
- 4) Continue studies of the anomalous, highly mobile population of hydrogen in  $\text{NaAlH}_4$  by  $^1\text{H}$  and  $^2\text{H}$  nuclear magnetic resonances (NMR) studies.

# Approach

## Task 3. Determination of the Thermodynamic Properties of Complex Hydrides

- Determine if the thermodynamics of the reversible dehydrogenation of alanates are altered upon doping through the determination of enthalpies of dehydrogenation through differential scanning calorimetry (collaboration with University of South Florida).
- Determination of the enthalpy of the various phases of  $\text{AlH}_3$  (collaboration with Tohoku University).

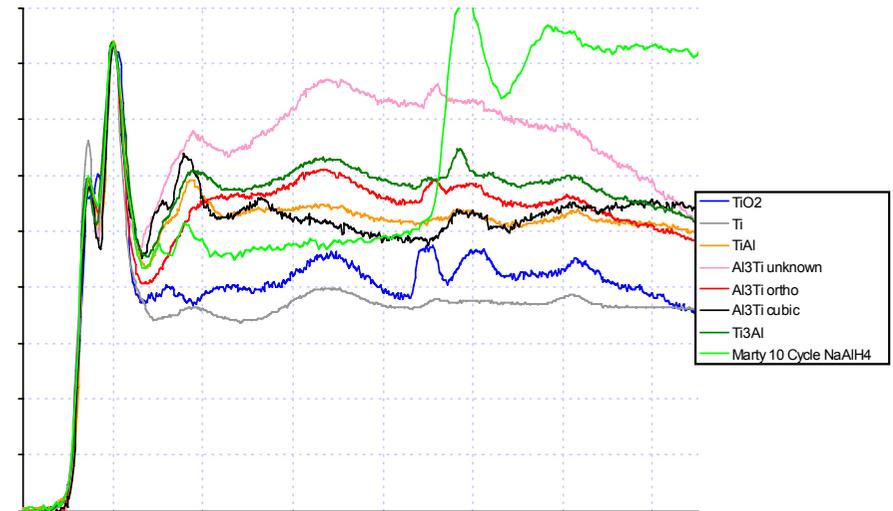
## Task 4. Kinetically Enhancement of “Thermodynamically Tuned” Binary Hydrides and Other Novel, High Capacity Hydrogen Storage Materials

- Studies of the effects of doping and ball milling on the hydrogen cycling kinetics of “thermodynamically tuned binary hydrides developed by HRL. Efforts are in progress to quantify the kinetic enhancement of the reversible dehydrogenation of  $\text{LiBH}_4/\text{MgH}_2$  that is achieved with Ti-dopants. We are also exploring the conversion of  $\text{Mg}_2\text{Si}$  to  $\text{MgH}_2/\text{Si}$  through ball low temperature balling milling under hydrogen pressure.
- Studies of the dehydrogenation and rehydrogenation kinetics of novel hydrides that have been developed Hawaii Hydrogen Carriers as part of the UOP US DOE EERE hydrogen storage project.

# Progress/Results

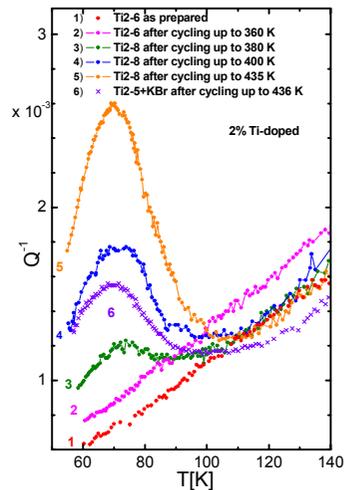
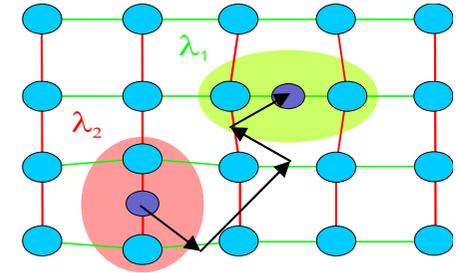
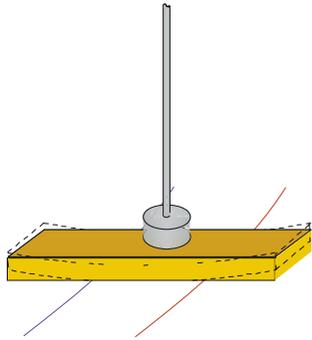
## Characterization of Ti species in doped and cycled $\text{NaAlH}_4$ through EELS spectroscopy (collaboration with U. Illinois)

Ti species will be identified on the basis of comparison to standards of known Ti species. As a test of this approach, we have obtained the EELS spectrum of the major Ti species in a doped and cycled sample of  $\text{NaAlH}_4$ . Synchrotron X-ray and EXAFS studies have previously identified this material either cubic  $\text{Al}_3\text{Ti}$  or a solid solution of  $\text{Al}_{0.93}\text{Ti}_{0.07}$ . Although an excellent fit was observed between our spectra of the major Ti species and cubic  $\text{Al}_3\text{Ti}$ , it was not distinguishable from orthorhombic  $\text{Al}_3\text{Ti}$ . It should, however, be possible to obtain better spectra and/or deconvolution of the data such that the cubic and orthorhombic phases can be differentiated. Once the majority Ti species can be unambiguously identified, we will examine the minor Ti species in the grain boundary regions that are not associated with the segregated alloy crystallites.



# Progress/Results

## Anelastic Spectroscopy



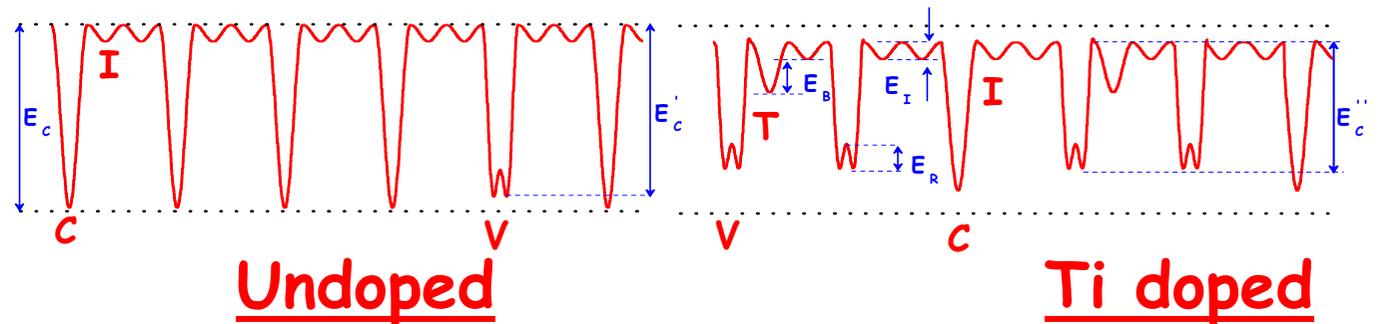
Anelastic Spectroscopy (collaboration with University of Rome) has revealed that highly mobile point defects ( $5 \times 10^3$  jumps/s at 70 K) arise in Ti-doped hydride  $\text{NaAlH}_4$  through a thermally activated process.

Our recent observation of a deuterium isotope effect in the low temperature spectra shows that a mobilized population of hydrogen (defect hydride complexes) plays a fundamental role in the reversible dehydrogenation of  $\text{NaAlH}_4$ .

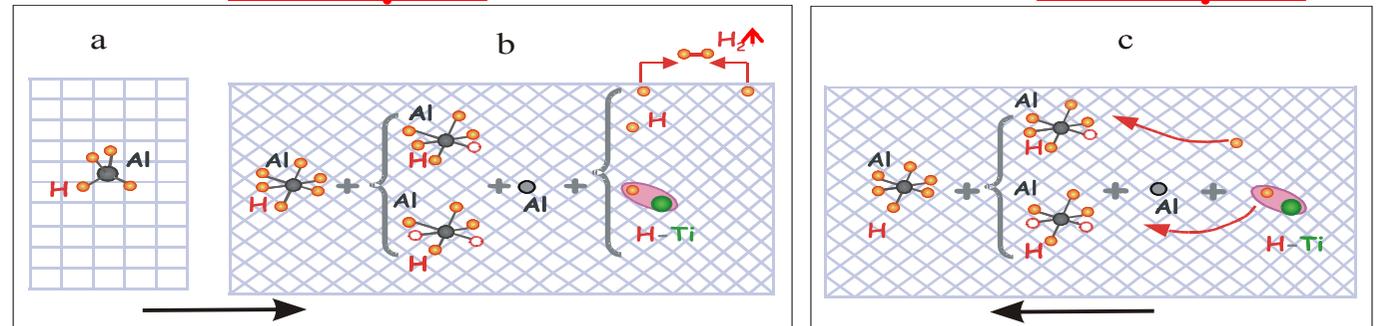
# Progress/Results

Anelastic spectroscopy has provided insight into the mechanism of the reversible dehydrogenation of Ti-doped  $\text{NaAlH}_4$ .

The formation of defect complex anions in concert with  $\text{Na}_3\text{AlH}_6$  and takes place at much lower temperatures upon Ti doping of the hydride.



$\Rightarrow$  Ti atoms decrease the energy barrier to breaking the Al-H bond, thus enhancing the kinetics of the dehydrogenation processes.



# Progress/Results

## Studies of the Mobile Population of Hydrogen in $\text{NaAlH}_4$ by $^1\text{H}$ and $^2\text{H}$ Nuclear Magnetic Resonance Spectroscopy

The  $^1\text{H}$  NMR spectrum  $\text{NaAlH}_4$  consists of an expected broad component with a very long, 2000 sec,  $T_1$  relaxation time and an anomalous sharp component with a short, 240 ms relaxation time indicating that it corresponds to highly mobile population of hydrogen. The sharp component is often ascribed to residual solvent BUT.....

The  $^2\text{H}$  NMR spectrum of  $\text{NaAlD}_4$  that is prepared in protio-solvents also contains a sharp component.

We have also eliminated the possibility that the sharp component is free  $\text{H}_2$  gas as its spectrum consists of a resonance that is much narrower and has a  $T_1$  of 13 msec.

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# Progress/Results

Determination of the intrinsic and mechanically modified thermal stabilities of  $\alpha$ ,  $\beta$ , and  $\gamma$  alane (collaboration with Tohoku University)

X-ray diffraction

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are needed to see this picture.

(TG-DTA)

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Enthalpies of dehydrating reactions  $\Delta H_{\text{dehyd.}}$  of the three phases of  $\text{AlH}_3$ .

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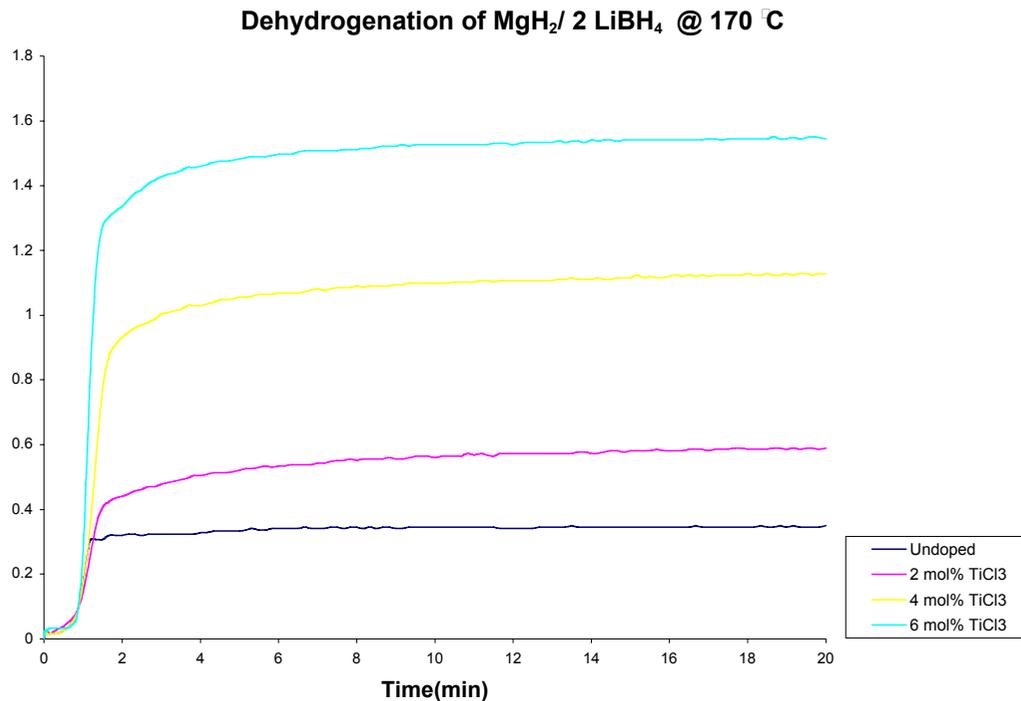
Profiles of the three phases of  $\text{AlH}_3$  before and after mechanical milling.

Thermogravimetry and differential thermal analysis of the three phases of  $\text{AlH}_3$  before and after mechanical milling.

S. Orimo, Y. Nakamori, T. Kato, C. Brown, C.M. Jensen Applied Physics **2006** 117, 27.

# Progress/Results

## Determination of Ti-dopants on the kinetic enhancement of the dehydrogenation of $\text{MgH}_2/2 \text{LiBH}_4$



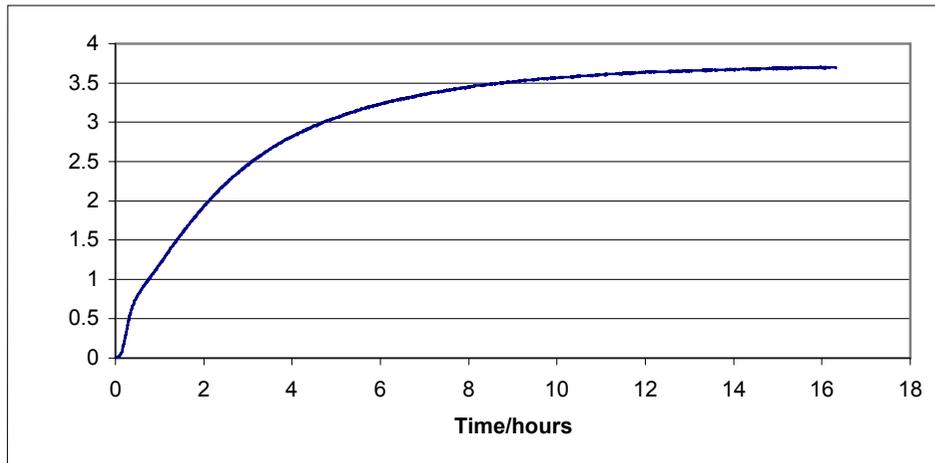
- $\text{TiCl}_3$  has a pronounced effect on the kinetics of the dehydrogenation of  $\text{MgH}_2/2 \text{LiBH}_4$ .
- No enhancement is observed during second cycle following rehydrogenation.
- Amount of rapidly released hydrogen has a linear relationship with amount of  $\text{TiCl}_3$  added.
- Similar effects have been found with upon addition of  $\text{TiCl}_3$  to  $\text{LiBH}_4$  M. Au and A. Jurgensen J Phys. Chem. **2006**, *110*, 7062.

⇒ Kinetic effect is due to **stoichiometric** reaction between  $\text{LiBH}_4$  and  $\text{TiCl}_3$ .

# Progress/Results

Effects of dopants with novel hydrides developed by Hawaii Hydrogen Carriers as part of UOP led project are under investigation.

Initial composition was found to undergo rapid dehydrogenation at 120 °C.



Advanced composition shows more promising dehydrogenation behavior

- **Complete dehydrogenation of >11 wt %**
- **Reversible?**

# Future Work

## FY06 only

- Complete fundamental studies of alanates.
  - Characterize the minority Ti species in Ti-doped  $\text{NaAlH}_4$  in the grain boundary regions that are not associated with the segregated  $\text{Al}_3\text{Ti}$  crystallites by EELS (collaboration with U. Illinois).
  - Carry out positron annihilation (collaboration with AIST, Tskuba) and muon spin resonance studies (collaboration with KEK, Tskuba) to further characterize point defects in Ti-doped  $\text{NaAlH}_4$ .

## FY06 and continuing in FY07

- Initiate studies of point defects in doped Group I and II amides by anelastic spectroscopy (collaboration with University of Rome and University of Nevada).
- Identify and optimize catalysts for HRL reversible borohydride based materials and novel HCC/UOP materials.

# Summary

- Our studies of alanates will conclude this year with an effort to identify minority Ti species in the grain boundary regions of Ti-doped  $\text{NaAlH}_4$  that is likely to be the species that is responsible for the enhanced kinetics.
- Anelastic spectroscopy has proven to be a powerful tool for the detection of the hydrogen containing point defects whose generation is greatly promoted in the Ti-doped  $\text{NaAlH}_4$  and thus they seem to be linked to the enhanced dehydrogenation kinetics. We are conducting further studies of the point defects with positron annihilation and muon spin resonance studies. We are also continuing our studies of the mobile population of hydrogen in the hydride by  $^1\text{H}$  and  $^2\text{H}$  NMR spectroscopy.
- Our study of point defects by anelastic spectroscopy is being extended Group I and II amides.
- Studies are underway to identify and optimize catalysts for HRL reversible borohydride based materials and novel HCC/UOP materials.
- The scope of work at UH has been extended to borohydrides, amides, and alane.

# Muon Spin Resonance Spectroscopy $\mu$ SR

Collaboration with R. Kadono - KEK-IMSS, Japan

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are needed to see this picture.

$$A_0(H) = A_{\text{dia}} + A_{\text{Mu}}(1 + 2x^2/2 + 2x^2) + c \cdot H$$

- Indicates that there is a fraction of implanted positive muons for which form a Mu state with a hyperfine parameter of  $\sim 420$  MHz) that substitutes for hydrogen.
- The recovery of  $A_0$  under a longitudinal field suggests that the origin of the relaxation is due to nuclear hyperfine interaction with surrounding nuclei.

# Responses to Previous Year Reviewers' Comments

- Current project was initiated in 3/05. However, it is largely a continuation of the previous UH project. Thus last year's reviewer's comments on the old project were highly relevant and taken into consideration.
- Main criticism: the work at UH is continuing to focus on doped sodium aluminum hydride.
- Response: Studies focused on borohydrides, alane, and amides are now underway.

# Publications

1. Effects of Milling, Doping and Cycling of NaAlH<sub>4</sub> Studied by Vibration Spectroscopy and X-ray Diffraction. S. Gomes, G. Renaudin, H. Hagemann, K. Yvon, M.P. Sulic, and C.M. Jensen, *J. Alloys Compd.* **2005** 390, 305.
2. Synthesis and Crystal Structure of Na<sub>2</sub>LiAlD<sub>6</sub>. H.W. Brinks, B.C. Hauback, C.M. Jensen, and R. Zidan; *J. Alloys Compd.* **2005** 392, 27.
3. Electron Microscopy Studies of NaAlH<sub>4</sub> Doped with TiF<sub>3</sub>: Hydrogen Cycling Effects. C.M. Andrei, J. Walmsley, H.W. Brinks, R. Homestad, C.M. Jensen, B.C. Hauback; *Appl. Phys. A.* **2005**, 80, 709.
4. Point Defect Dynamics and Evolution of Chemical Reactions in Alanates by Anelastic Spectroscopy. Oriele Palumbo, Rosario Cantelli, Annalisa Paolone, Sessa S. Srinivasan, and Craig M. Jensen; *J. Phys. Chem. B.* **2005**, 109, 1168.
5. Synchrotron X-ray Studies of Al<sub>1-y</sub>Ti<sub>y</sub> Formation and Re-hydriding Inhibition in Ti-enhanced NaAlH<sub>4</sub>. Hendrik W. Brinks, Bjørn C. Hauback, Sessa S. Srinivasan, and Craig M. Jensen; *J. Phys. Chem. B.* **2005** 109, 15780.
6. Characterization of Titanium Dopants in Sodium Alanate by Electron Paramagnetic Resonance Spectroscopy Meredith T. Kuba, Sandra S. Eaton, Christine Morales, and Craig M. Jensen; *J. Mater. Res.* **2005**, 20, 3265.

# Publications

7. Motion of Point Defects and Monitoring of Chemical Reactions in Sodium Aluminium Hydride. Oriele Palumbo, Rosario Cantelli, Annalisa Paolone, Craig M. Jensen, and Sesha S. Srinivasan; *J. Alloys Compd.* **2005**, 404-406, 748.
8. Intrinsic and Mechanically Modified thermal Stabilities of  $\alpha$ -,  $\beta$ - and  $\gamma$ -Aluminum Trihydride,  $\text{AlH}_3$ . S. Orimo, Y. Nakamori, T. Kato, C. Brown, C.M. Jensen; *Appl. Phys. A.* **2006**, 117, 27 .
9. Fast H-vacancy Dynamics During Alanate Decomposition by Anelastic Spectroscopy: Model for Ti-induced Defect Transport. Oriele Palumbo, Rosario Cantelli, Annalisa Paolone, Martin Sulic, and Craig M. Jensen; *Phys. Rev. B.* **2006**, in press.
10.  $\text{TiCl}_3$ -enhanced  $\text{NaAlH}_4$ ; Impact of Excess Al and Development of the  $\text{Al}_{1-y}\text{Ti}_y$  Phase During Cycling. Hendrik W. Brinks, Martin Sulic, Craig M. Jensen, and Bjørn C. Hauback; *J. Phys.Chem. B* **2006**, in press.

# Presentations

1. X-ray and Neutron Diffraction Studies of Ti-doped Sodium Aluminum Hydride, a Promising New Hydrogen Storage Material. American Crystallographic Association 2005 meeting, Orlando, Florida, May 31, 2005.
2. Doped Sodium Aluminum Hydride: Development and Fundamental Studies of a Promising New Hydrogen Storage Material. IPHE International Hydrogen Storage Technology Conference, Lucca, Italy; June 19, 2005.
3. Doped Sodium Aluminum Hydride: Development and Fundamental Studies of a Promising New Hydrogen Storage Material. Symposium on Research Challenges for the Hydrogen Economy, Hydrogen Storage, 230th American Chemical Society National Meeting, Washington D.C.; August 28, 2005.
4. Doped Sodium Aluminum Hydride: Development and Fundamental Studies of a Promising New Hydrogen Storage Material. Purdue University; October 17, 2005.
5. Doped Sodium Aluminum Hydride: Development and Fundamental Studies of a Promising New Hydrogen Storage Material. Department of Material Science and Engineering, University of Illinois at Urbana-Champaign; October 18, 2005.
6. Doped Sodium Aluminum Hydride: Development and Fundamental Studies of a Promising New Hydrogen Storage Material. Clean energy Research Center, University of South Florida; October 20, 2005.

# Presentations

7. Doped Sodium Aluminum Hydride: Development and Fundamental Studies of a Promising New Hydrogen Storage Materials WE-Heraeus-Seminar on Hydrogen Storage with Novel Nanomaterials, Bad Honnef, Germany; October 23, 2005
8. Doped Sodium Aluminum Hydride: Development and Fundamental Studies of a Promising New Hydrogen Storage Material. Nissan Research Center, Kanagawa, Japan; October 28, 2005.
9. Detection and Characterization of Point Defects in Doped Sodium Aluminium Hydride. Fall 2005 meeting of the Materials Research Society, Boston,MA; November, 2005.
10. Doped Sodium Aluminum Hydride: Development and Fundamental Studies of a Promising New Hydrogen Storage Material. Symposium on Metal Hydrides, Symposium on Metal Hydrides and Dihydrogen Complexes: Synthesis, Properties, and Applications in Catalysis and Hydrogen Storage, International Chemical Congress of the Pacific Basin Societies, Honolulu, Hawaii; December 19, 2005.
11. Doped Sodium Aluminum Hydride: Development and Fundamental Studies of a Promising New Hydrogen Storage Material. 7th International 21st Century Symposium on Integrated EcoChemistry, Honolulu, Hawaii; December 20, 2005.
12. Monitoring Point Defect Complexes Arising in the Dehydrogenation of Sodium Aluminum Hydride by Anelastic Spectroscopy. Symposium on Advanced Materials for Energy Conversion Iii, 2006 TMS Annual Meeting, San Antonio, Texas; March 21, 2006.