Catalytically Enhanced Hydrogen Storage Systems

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Rationale

$NaAlH_4 \Leftrightarrow 1/3\ Na_3AlH_6 + 2/3\ Al + H_2\uparrow$ (3.73 wt %)

$Na_3AlH_6 \Leftrightarrow 3\ NaH + Al + 1.5\ H_2\uparrow$ (1.87 wt %)

Ashby and Koberts *Inorg. Chem.* **1966**, *5*, 1615 and references therein.
Dymova, Eliseeva, and Bakum Dok. *Akad. Nauk USSR* **1974**, 215,1369.

Bogdanovic Breakthrough - 1997 The dehydrogenation process is rapid and reversible under **unprecedented**, moderate conditions upon treatment with a few mole % of selected dopant precursors.

Can doped complex hydrides be developed as hydrogen storage materials that are compatible with the Freedom CAR hydrogen storage system targets (Key parameters: cost, specific energy, and energy density).

Objectives

I. Determination of the chemical nature of the titanium species responsible for the enhanced kinetics of Ti doped $NaAlH_4$.

II. Determination of the mechanism of action of the dopants in the dehydrogenation and re-hydrogenation processes (i.e. H-H bond activation, Al-H bond activation, long-range Al atom transport?).

III. Apply fundamental insights to produce hydrides with improved hydrogen storage properties that are compatible with the Freedom CAR hydrogen storage system targets. Key parameters: cost, specific energy, and energy density.

Approach

Electron paramagnetic resonance (EPR) studies Detection of site isolated Ti^{3+}.

Magnetic susceptibility studies Quantification of the amount(s) of Ti^{3+} and Ti^{4+} present in Ti doped hydride.

X-ray diffraction Structural information (Na, Al, Ti).

Neutron diffraction Structural information (H atoms).

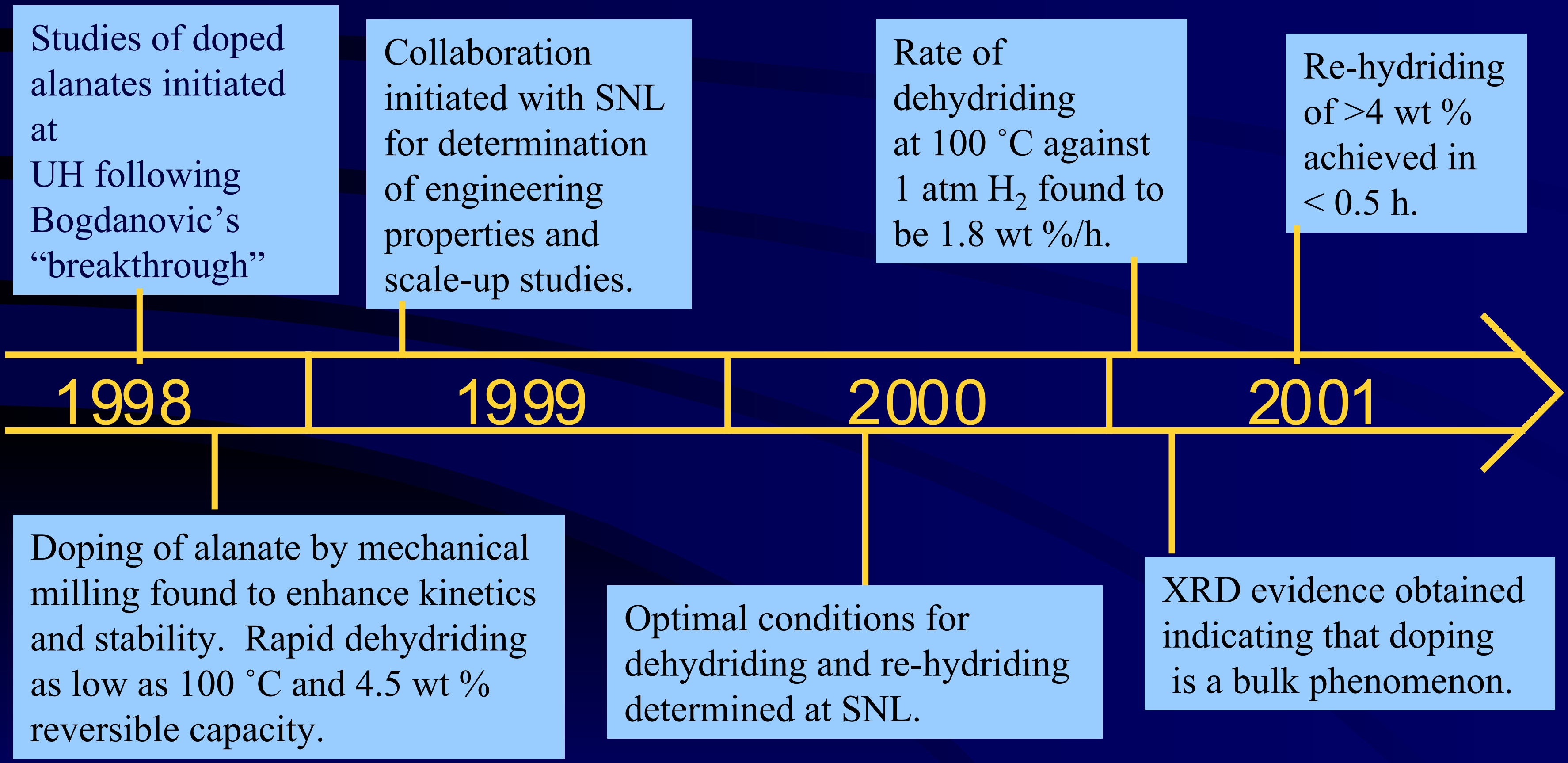
Approach

Solid State nuclear magnetic resonance (NMR) spectroscopy and inelastic neutron scattering (INS) Motions of the $[AlH_4]^-$ anion.

Infrared spectroscopy - Al-H bond vibrations.

Synthesis and testing of advanced alanates or other complex hydrides that are brought to light by the fundamental studies.

Timeline of Doped $NaAlH_4$ R&D Activities



Studies of doped alanates initiated at UH following Bogdanovic's "breakthrough"

Doping of alanate by mechanical milling found to enhance kinetics and stability. Rapid dehydriding as low as 100 ˚C and 4.5 wt % reversible capacity.

Collaboration initiated with SNL for determination of engineering properties and scale-up studies.

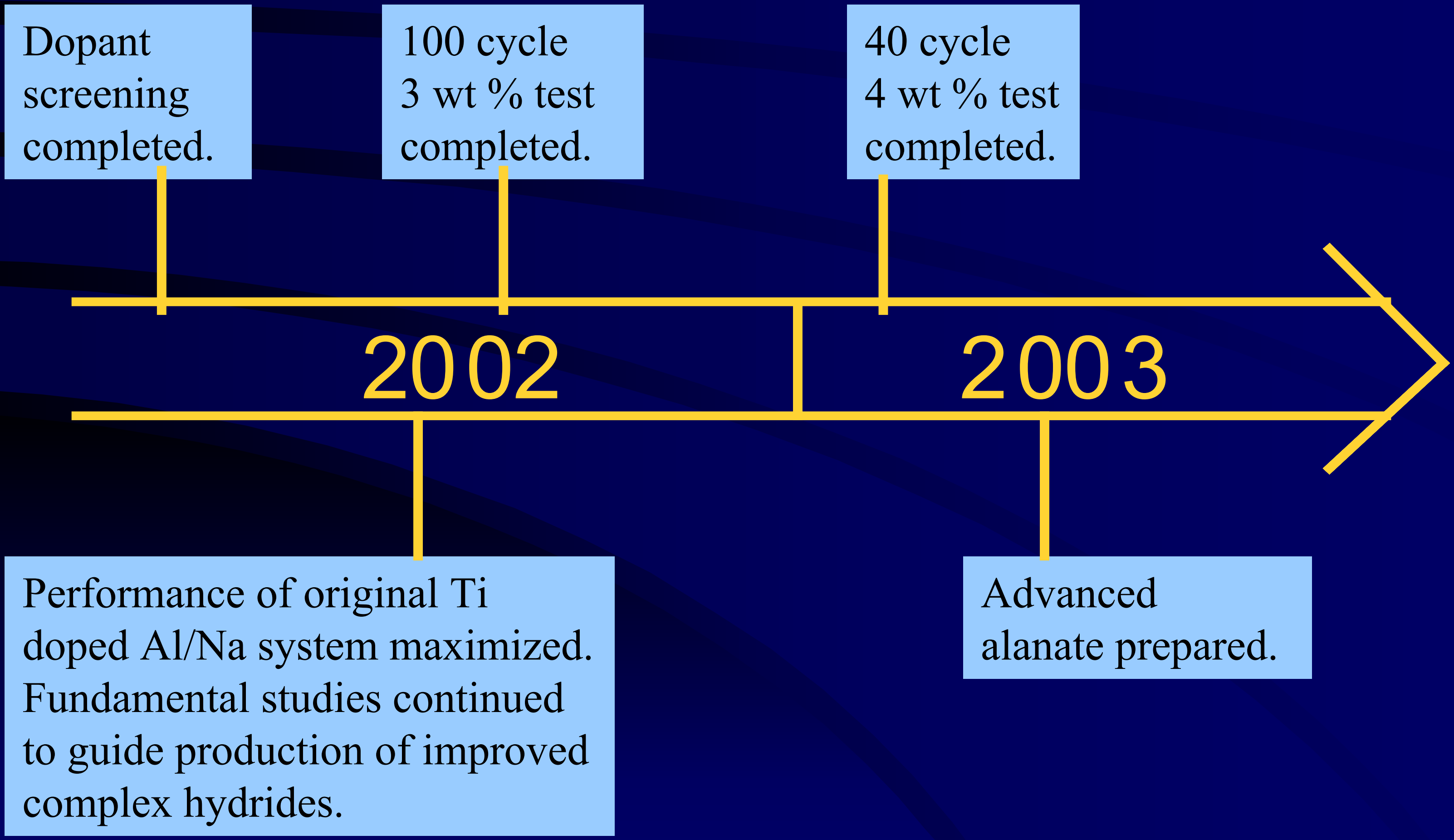
Optimal conditions for dehydriding and re-hydriding determined at SNL.

Rate of dehydriding at 100 ˚C against 1 atm H_2 found to be 1.8 wt %/h.

XRD evidence obtained indicating that doping is a bulk phenomenon.

Re-hydriding of >4 wt % achieved in < 0.5 h.

Timeline of Doped NaAlH$_4$ R&D Activities



Dopant screening completed.

100 cycle 3 wt % test completed.

40 cycle 4 wt % test completed.

2002

2003

Performance of original Ti doped Al/Na system maximized. Fundamental studies continued to guide production of improved complex hydrides.

Advanced alanate prepared.

Suitable Properties of Doped $NaAlH_4$ for Practical Onboard Storage of Hydrogen

- $NaAlH_4$/Na_3AlH_6 equilibrium plateau pressure: ~8 atm at 80 ˚C.
- Rate of dehydrogenation of 2 mol % Ti doped $NaAlH_4$ to Na_3AlH_6: 1.8 wt % per hour at 100 ˚C (adequate to meet the demands of an onboard PEM fuel cell).
- Rehydriding kinetics: > 4.0 wt % absorbed in 1 h (100 ˚C under 100 atm H_2).
- Stable cycling capacity for >100 cycles at 120 ˚C.

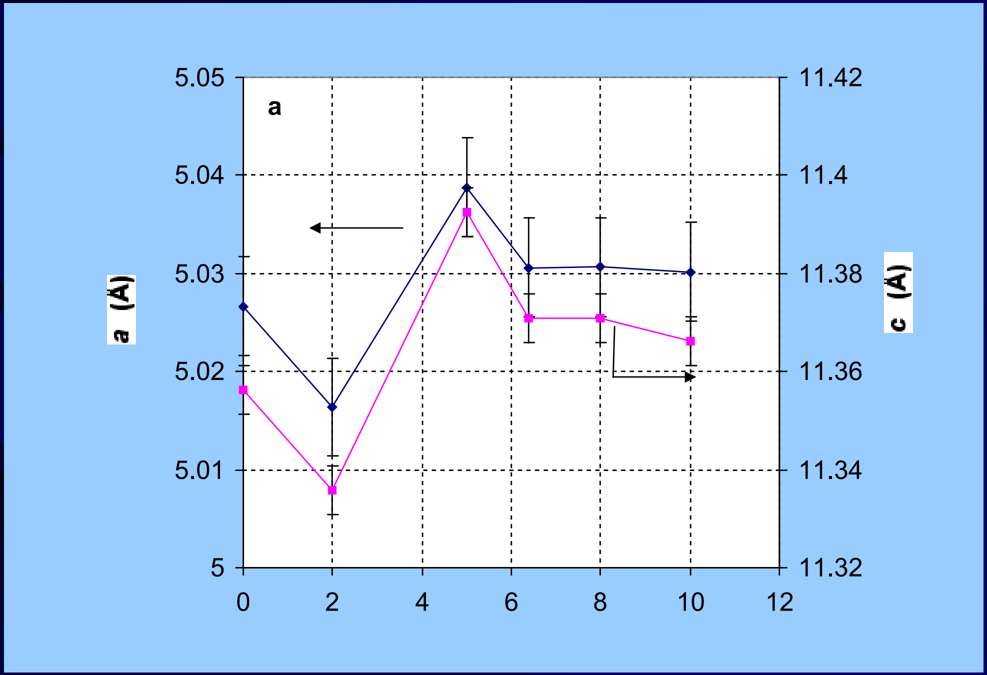
Barriers to Practicality

- Plateau pressure of the Na_3AlH_6/NaH equilibrium is less than 1 atm below 100 ˚C.
- Rate of dehydrogention of Na_3AlH_6 to NaH + Al is too slow even at 150 ˚C.
- Practical cycling capacity is (3.0 wt % at 120 ˚C and 4.0 wt % 150 ˚C) is too low.
- Search for improved dopants is exhausted.
- Dehydridng of other alanates (ie $LiAlH_4$ and $Mg(AlH_4)_2$, and alkali borohydrides (ie $NaBH_4$) irreversible under H_2 pressure.

Key question: Can the hydrogen storage properties of doped alanates or other complex hydrides be improved beyond those of the “original recipe, Ti doped Na/Al system????

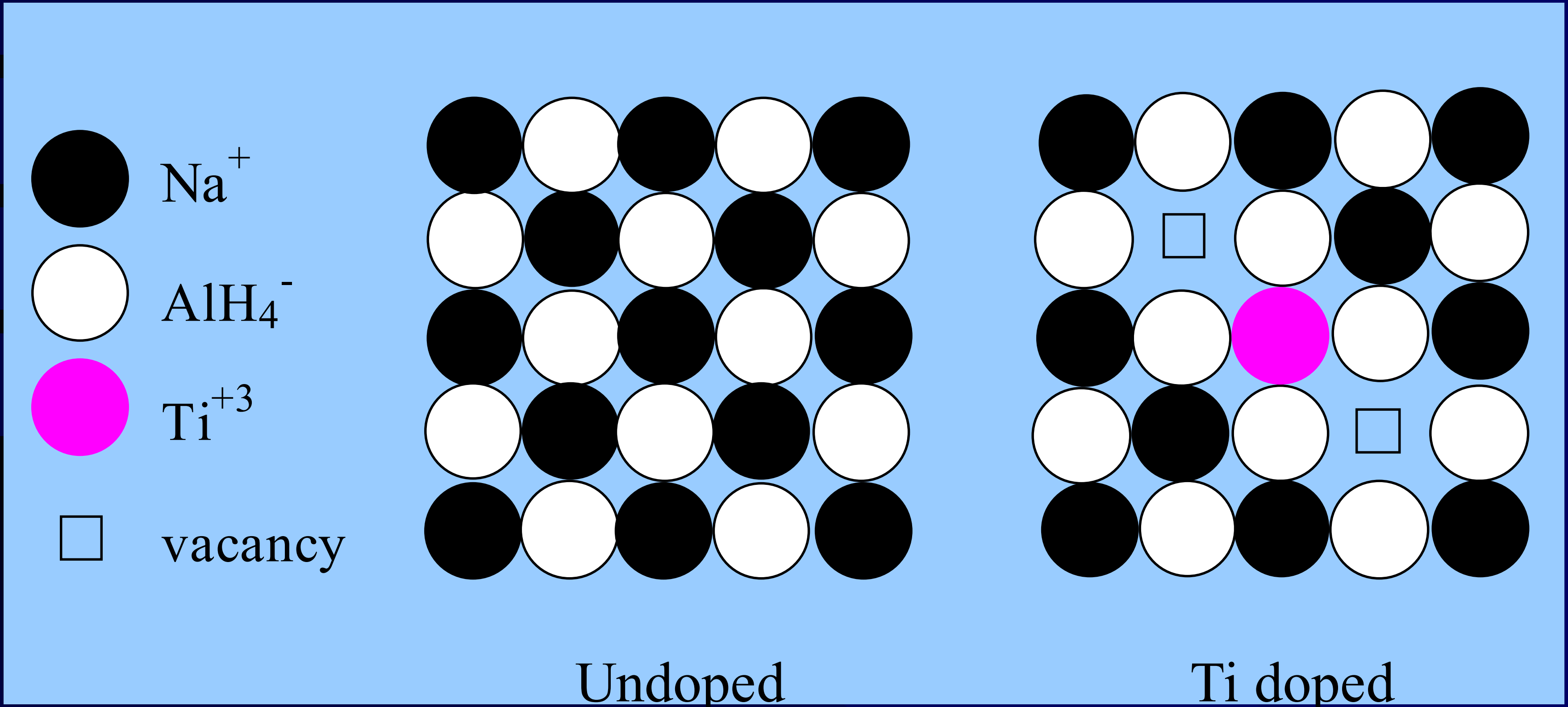
X-ray Diffraction Studies

Collaboration with the National Institute for Advanced Industrial Science and Technology, Osaka.



Lattice parameters (bulk structure) of $NaAlH_4$ vary as a function of dopant concentration.

Ti^{3+}/Na^{+} substitution model of Ti doped $NaAlH_4$



● Na^{+}

○ AlH_4^{-}

🟣 Ti^{+3}

□ vacancy

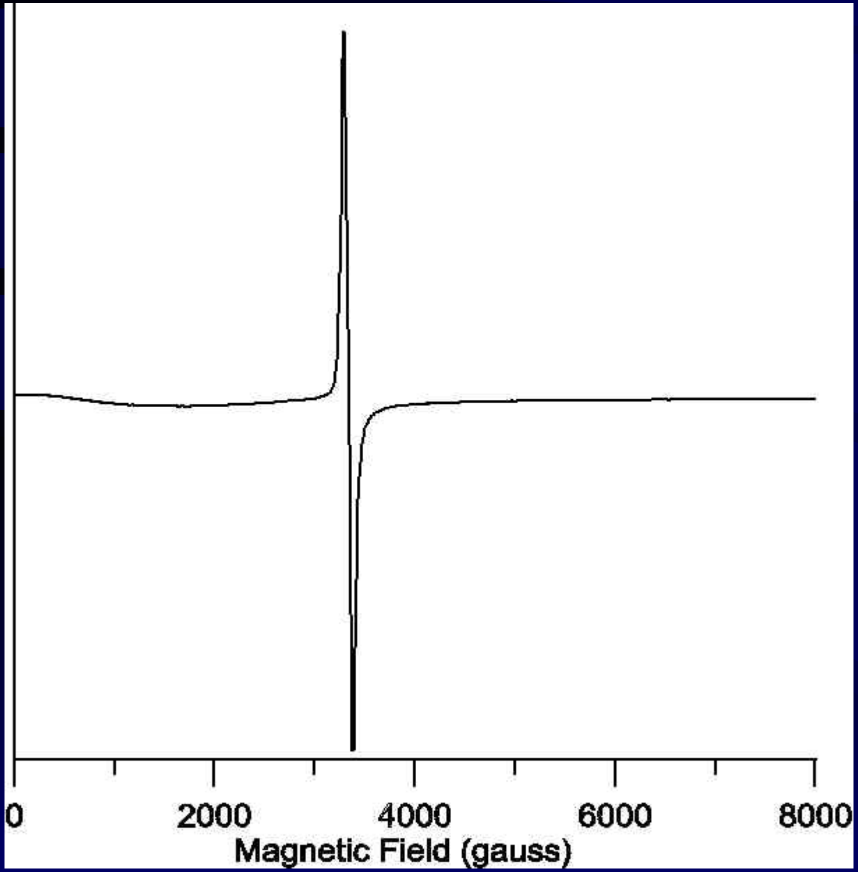
Undoped

Ti doped

D. Sun, T. Kiyobayashi, H. Takeshita, N. Kuriyama, and C. M. Jensen; *J. Alloys Compd.* **2002**, *337*, 8.

02-03 Results: EPR Studies

Collaboration with the University of Denver and Sandia National Laboratories



The EPR spectrum of $NaAlH_4$ doped with 1.5 mol % of $Ti(OBu)_4$ is dominated by a signal that is characteristic of spin isolated Ti(III). This finding is consistent with our model of the doped hydride in which Na^+ sites are substituted by Ti^{3+}.

02-03 Results
Magnetic Susceptibility

- Quantification of the amount of Ti(III) in Ti doped hydrides can be accomplished by comparison to standard curve of χ vs. moles Ti(III) loaded in inert material.

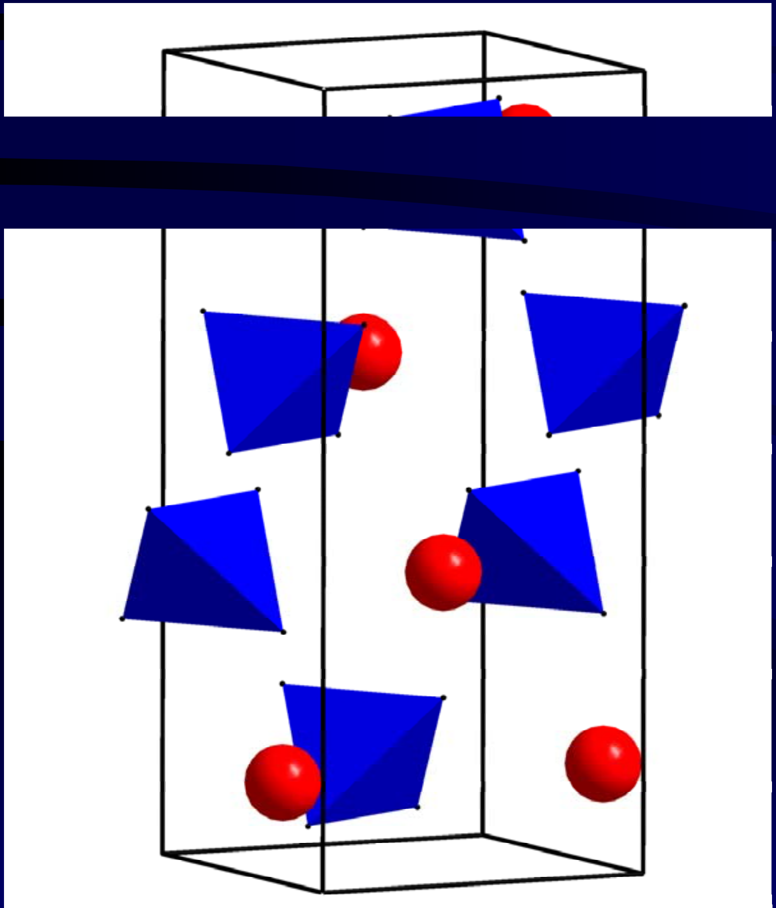
- Amount of Ti(IV) in doped hydrides can be determined by Ti_{total} - Ti(III).

- Standard curve has been generated.

Does kinetic enhancement track level of Ti(III), Ti(IV) or both?

02-03 Results
Neutron Diffraction

Collaboration with the Institute for Energy Technology, Norway



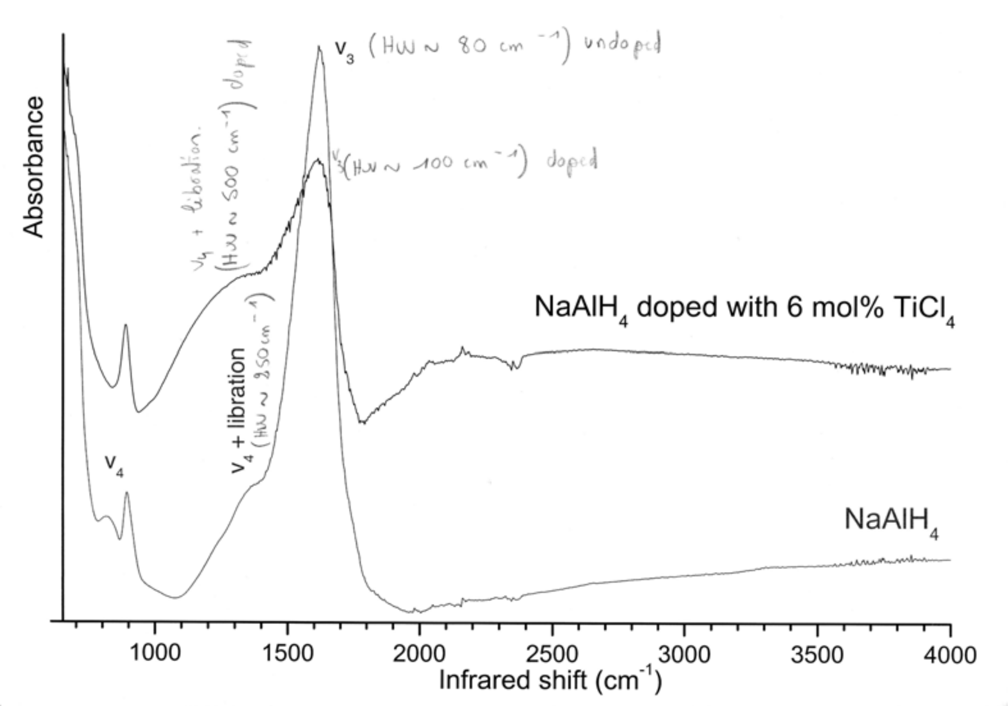
- Method developed for the synthesis of high purity $NaAlD_4$ (key to high quality neutron structure). Al-D 1.627(2), 1.626(2) Å; D-Al-D 107.30(1), 113.90(1)°.

- No major structural differences found to arise upon doping.

B. Hauback, H. Brinks, C.M. Jensen, K. Murphy and A. Maeland; *J. Alloys Compd.* **2003,** in press.

02-03 Results
Infrared Spectroscopy

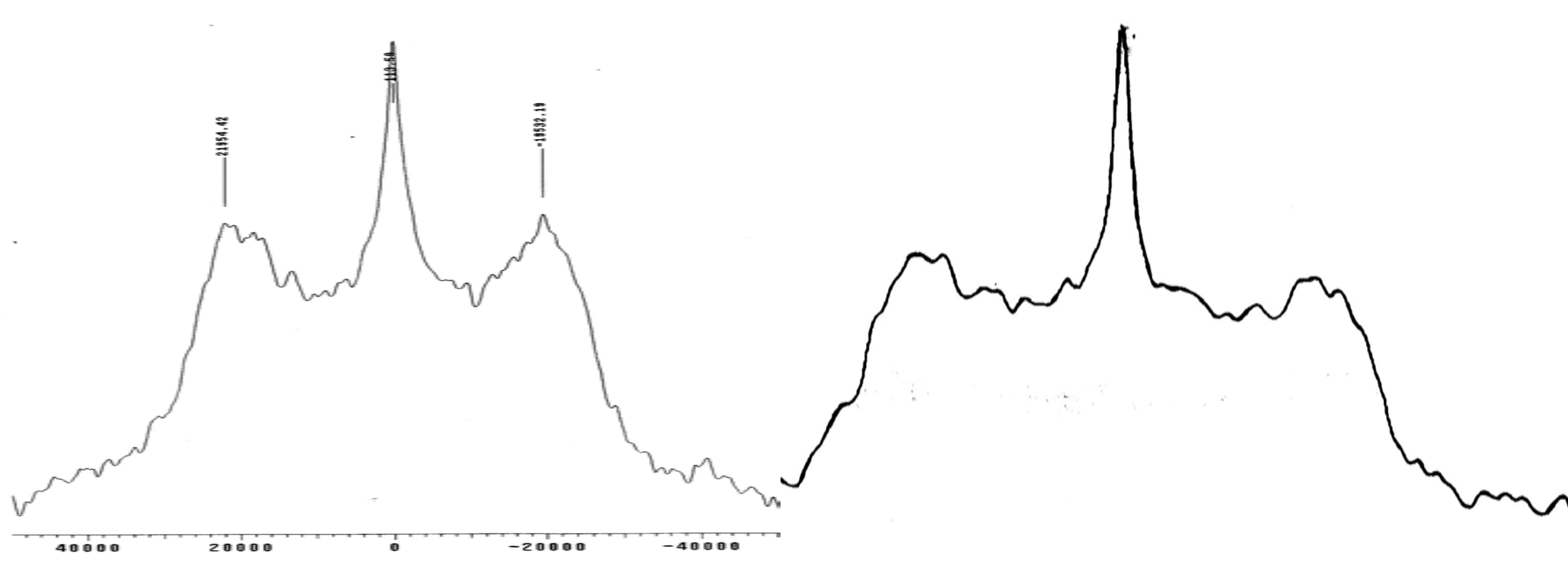
Collaboration with the University of Geneva



Broadening of Al-H upon Ti doping. ⇒ Increased distribution of Al-H vibrations.

02-03 Results: Nuclear Magnetic Resonance Spectroscopy

Collaboration with Washington University



^{2}H spectra show broadening dipolar doublet upon doping.

⇒ Deuterium in a wider range of environments.

02-03 Results: X-ray Diffraction and Inelastic Neutron Scattering

X-ray Diffraction

- “No broadening powder pattern lines upon doping”
  - University of Geneva
- “Broadening of one subset of lines upon doping”
  - IFE, Norway

Inelastic Neutron Scattering

- “Doped and undoped samples are very, very similar”
  - National Institute of Standards and Technology
- “Changes in relative intensities and widths of bands upon doping and new peaks in the low frequency region.”
  - Los Alamos National Laboratory

Advanced Alanates

Doping $NaAlH_4$ with $TiCl_3$ or $TiCl_4$ results in the production of segregated NaCl by-product. Verified by XRD - K. Gross, G. Sandrock, G. Thomas, *J. Alloys Compd.* 2002, *330*-332, 691.

Key question: Can removal of “deadweight” NaCl lead to materials that meet program targets?

Advanced Alanates

Bogdanovic "Redox" model of doping predicts NO - Doping of $NaAlH_4$ with $TiCl_3$ thought to produce segregated AlTi alloy.

- No change in bulk thermodynamic properties
- One equivalent loss in hydrogen carrying Al
  - ⇒ 3 equivalent loss in hydrogen capacity
  - ⇒ Hydrogen capacity can not be improved over 5.60 wt % theoretical even upon removal of Na by-product.

Ti^{3+}/Na^{+} substitution model predicts YES - Doping results in bulk substitution.

- Changes in bulk thermodynamic properties.
- All Al remains available for hydrogen binding.
  - ⇒ Hydrogen capacity increases (and kinetics enhanced) upon increased doping if Na by-product is removed. Theoretical capacities of >6.00 wt %.

02-03 Results
Advanced Alanates

Effect of doping level on plateau pressure

Desorption plateau pressure of sodium aluminum hydride at 150 °C.

Dopants and Doping Level (mol. %)		Pressure (Mpa)
$Ti(OBu)_4$	1.3	3.0(±0.2)
	1.7	3.6(±0.2)
	2.0	4.7(±0.2)
$TiCl_4$	2.0	5.7(±0.1)
TiF_3	2.0	5.5(±0.3)

Thermodynamic properties effected ⇒ Doping is a bulk phenomenon

02-03 Results
Advanced Alanates

Collaboration with the University of Milan

Proprietary method has been developed for the removal of sodium by-product.

02-03 Highlight Summary

- EPR shows high levels of spin isolated Ti(III) are present after doping in accordance with Ti^{3+}/Na^{+} model. X-ray and neutron diffraction studies show only subtle structural changes occur upon doping.

- Spectroscopic studies (IR, NMR and INS) provide evidence of increases and changes in hydrogen motions throughout the bulk of the hydride upon doping.

- Predicted changes in plateau pressures upon doping have verified.

- Proprietary method has been developed for the removal of sodium by-product.

Collaborations and Technology Transfer

National Institute for Advanced Industrial Science and Technology, Osaka, Japan - XRD; Dr. Tetsu Kiyobayashi, Dr. Nobuhiro Kuriyama.

University of Denver - EPR; Prof. Sandra Eaton.

Sandia National Laboratories - EPR; Dr. Karl Gross, Dr. Eric Majzoub.

Institute for Energy Technology, Kjeller, Norway - Neutron diffraction and XRD; Dr. Hendrik Brinks, Dr. Bjorn Hauback.

University of Geneva - Infrared; Prof. Klaus Yvon, Dr. Sandrine Gomes

Washington University- NMR; Prof. Mark Conradi

Los Alamos National Laboratories - INS; Dr. Juergen Eckert.

National Institute of Standards and Technology - INS; Dr. Terry Udovic.

University of Milan - XRD; Prof. Alberto Albinati.

International Energy Agency Annex 17.

US patent 6,471,935 licensed by the University of Hawaii to Hawaii Hydrogen Technologies.

Future Directions

Continue characterization and quantification of titanium species in Ti doped hydrides by combination of EPR and magnetic susceptibility studies and establish if the kinetic enhancement is due to Ti(III), Ti(IV), or both.

Continue infrared, NMR, and INS spectroscopic studies and obtain Raman spectra to elucidate the influence of doping on the dynamics of the $[AlH_4]^-$ anion and the relationship of these motions to the mechanism of reversible dehydrogenation of the doped hydride.

Determine the hydrogen cycling properties of doped $NaAlH_4$ following removal of the sodium by-product. Test whether this approach can be extended to $\mathbf{Na_{0.4}Ti_{0.2}AlH_4}$ ⇒ 6.03 wt % available H and kinetic enhancement equal to 20 wt % Ti doping and its Li and Mg analogs (6.92 and 6.60 wt % available H respectively).

Response to 02 Reviewers

THANKS!

Question 8b "….benefit the Hydrogen Program in attainment
of the program goals…"
Reviewer: "will come close"

Key question: Can alanates meet the new, radically increased capacity targets or should we move on to other complex hydrides.

Response: 1) The practical improvement that can be achieved by the removal of sodium by-products needs to be determined.