

# Metal Borohydrides, Ammines, and Aluminum Hydrides as Hydrogen Storage Materials

**Gilbert M. Brown, PI**

Other participants:

Douglas A. Knight, Daniel A. Hillesheim,  
Jianming Bai, Antonio F. Moreira dos Santos,  
and Claudia J. Rawn

**Oak Ridge National Laboratory  
Oak Ridge, Tennessee**

**June 7-11, 2010**

**Project ID # ST068**

# Overview

## Timeline

- Start: March 1, 2005
- End: Sept 30, 2010
- 91% complete

## Barriers Addressed

- B. Weight and volume
- M. Hydrogen capacity and reversibility
- N. Lack of understanding of hydrogen chemisorption and physisorption

## Budget

- Total project funding to date - \$2470K (DOE 100%)
- Funding for FY09 - \$700K
- Planned Funding for FY10 - \$300K

## Partners/Collaborators

- Participant in the MHCoe
- Ohio State University
- JPL and Cal Tech (NMR)
- Brookhaven National Lab (AlH<sub>3</sub> chemistry)

# Relevance/Program Objectives

---

The program objective is to develop the chemistry for a *reversible Hydrogen* storage system based on **Boron, Nitrogen** (ammine/amide/imide) and **Aluminum**. ORNL focuses on high hydrogen content materials (>10 wt %).

Focus of research during the review period was the preparation, structural determination, and hydrogen desorption reactions of ammine aluminum borohydrides, formed by the reaction of  $\text{NH}_3$  with  $\text{Al}(\text{BH}_4)_3$ . A greater understanding of desorption reactions will help overcome the reversibility barriers in select  $\text{H}_2$  storage materials.

## Materials Investigated by ORNL during review period

Compound	Formula Weight	Theory % hydrogen
$\text{Al}(\text{BH}_4)_3$	71.508	16.92%
$\text{Al}(\text{BH}_4)_3 \cdot 2\text{NH}_3$	105.570	17.19%
$\text{Al}(\text{BH}_4)_3 \cdot 3\text{NH}_3$	122.601	17.26%

# Approach

---

Research at ORNL takes advantage of expertise in handling oxygen and moisture sensitive reagents, knowledge of reaction pathways in solution, and insight into mechanisms of reactions and catalytic pathways. Collaborations provide structural characterization of new materials by XRD or solid MAS-NMR

Quantity of hydrogen evolved from aluminum amine borohydrides confirms that ammonia protons contribute to hydrogen evolution. This begins to **address weight and volume technical barriers**. Identification of reaction intermediates has contributed to an **increased understanding of the hydrogen desorption process**.

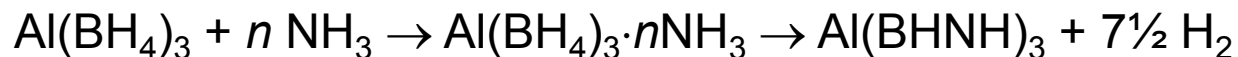
## Main Milestones for FY10 and Progress

- Investigate ammine metal borohydrides as hydrogen storage materials – good progress, on schedule
- Determine structure of aluminum amine borohydride reaction intermediate – structure completed

# Technical Accomplishments and Progress

## Overview of Important Results for the Review Period

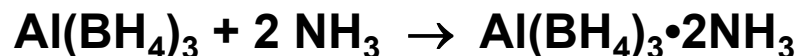
- $\text{NH}_3$  adducts of  $\text{Al}(\text{BH}_4)_3$  are formed in both in solution and under solvent-free conditions
- Products depend on reaction conditions (solvent/solvent-free)
- Product formed in toluene solvent,  $\text{Al}(\text{BH}_4)_3 \cdot 3\text{NH}_3$ , evolves as much hydrogen as a function of temperature as ammonia borane,  $\text{NH}_3\text{BH}_3$
- Structure of product formed during reaction of  $\text{Al}(\text{BH}_4)_3$  with  $\text{NH}_3$  in diethyl ether gives insight into the reaction mechanism for hydrogen desorption
- Quantity of hydrogen desorbed from aluminum ammine borohydrides indicates both  $\text{NH}_3$  and  $\text{BH}_4^-$  contribute to hydrogen evolution reaction
- Use of deuterated ammonia ( $\text{ND}_3$ ) shows first hydrogen evolved is HD (indicating equal contributions from from  $\text{ND}_3$  and  $\text{BH}_4^-$ )
- Solid state MAS-NMR spectroscopy of the hydrogen desorption reaction products
  - Al metal is **not** a product
  - Boron-nitride polymer **is** formed



# Formation of Ammine Aluminum Borohydrides

---

A rapid, solvent-free reaction occurs between  $\text{Al}(\text{BH}_4)_3$  and  $\text{NH}_3$



The structure of the product is not known with certainty but it is thought to be a trigonal bipyramid with axial  $\text{NH}_3$  ligands and equatorial  $\text{BH}_4^-$  ligands

Formation of a 2:1  $\text{NH}_3:\text{Al}(\text{BH}_4)_3$  adduct in agreement with literature

Bird and Wallbridge, *J. Chem. Soc. A*, **1967**, 664

XRD shows structure different from previously reported and structurally characterized ammonia adducts of aluminum borohydride:

- $[\text{Al}(\text{NH}_3)_6](\text{BH}_4)_3$  - octahedral aluminum, ionic borohydride

Semenenko, *et al*, *Izv. AN SSSR, Ser. Khim.*, **1974**, 1455-1460.

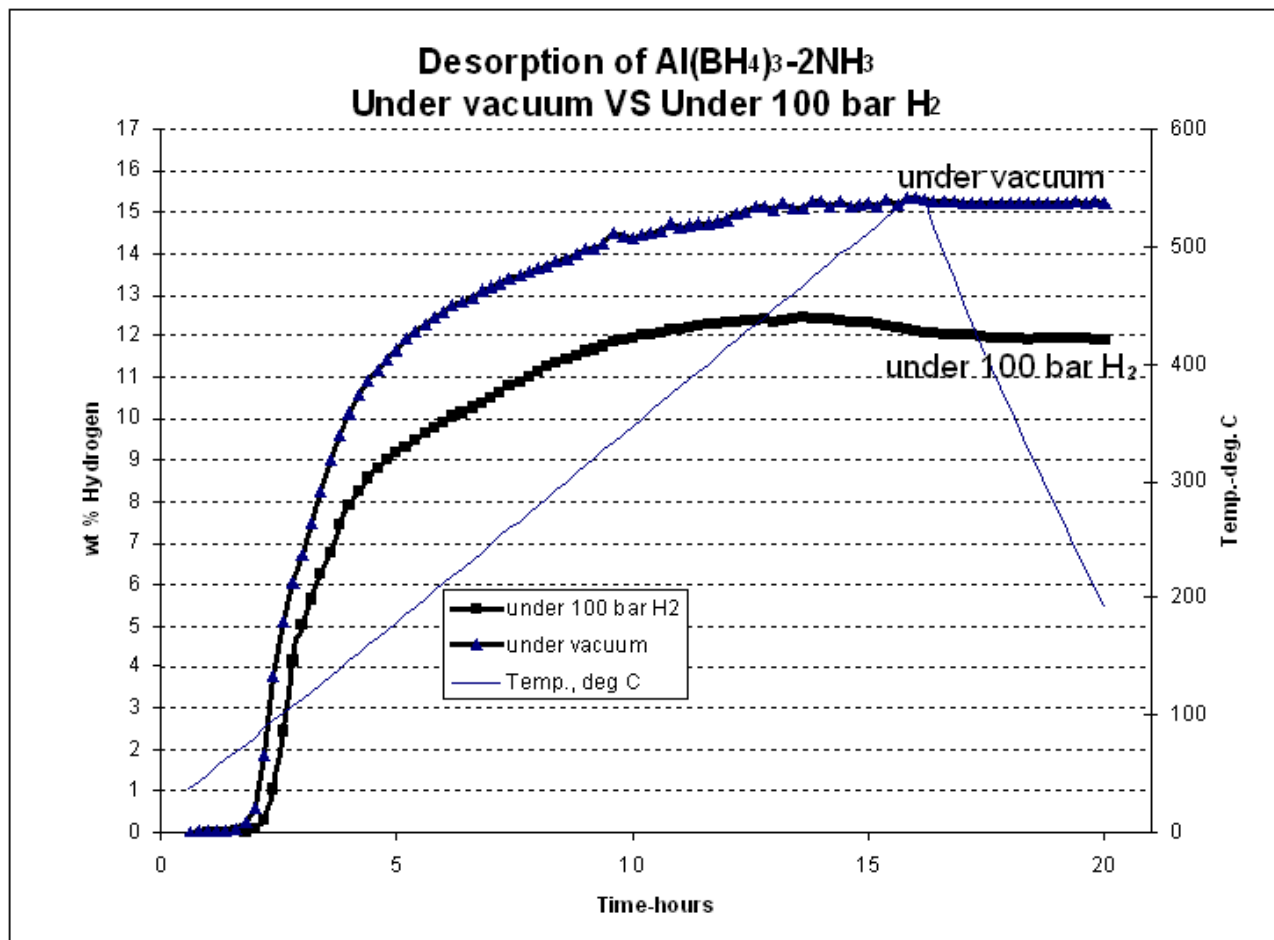
- $\text{Al}(\text{BH}_4)_3\text{NH}_3$  - tetrahedral aluminum

Lobkovskii, *et al*, *Zh. Strukt. Khim.*, **1974**, 15, 70-73.

$\text{NH}_3$  adduct of  $\text{Al}(\text{BH}_4)_3$  desorbs  $\text{H}_2$  at a lower temperature than parent compound

# Thermal Desorption of $\text{H}_2$ from $\text{Al}(\text{BH}_4)_3 \cdot 2(\text{NH}_3)$

Quantity of  $\text{H}_2$  released indicates  $\text{NH}_3$  is decomposing as well as  $\text{BH}_4^-$



Catalysts ( $\text{RuCl}_3$  and  $\text{TiCl}_3$ ) have no influence on desorption temperature; consistent with forming  $\text{Al-H}$  and  $\text{BH}_3$  in rate determining step

Decreased  $\text{H}_2$  evolution under 100 bar hydrogen pressure indicates potential reversibility

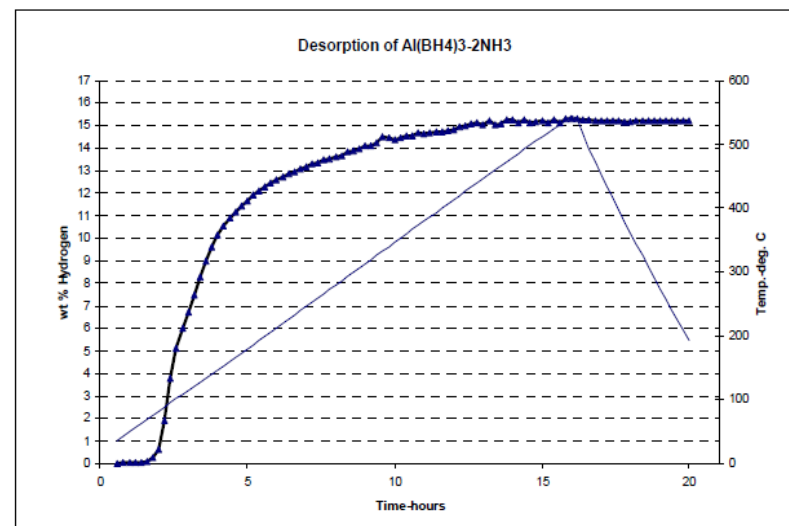
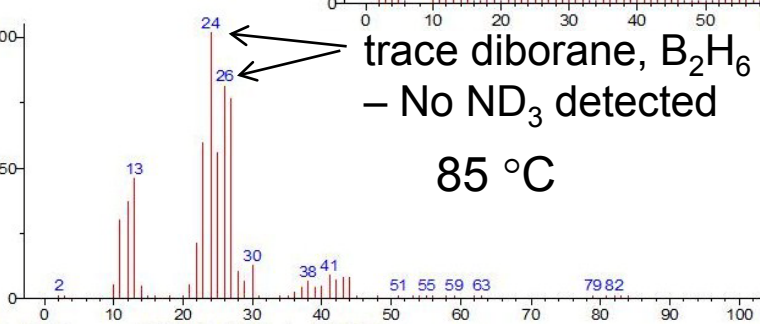
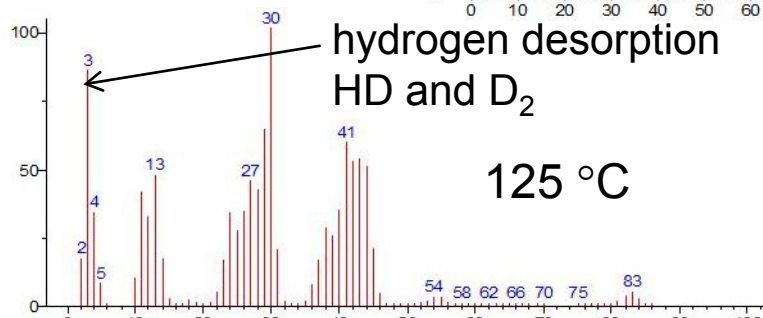
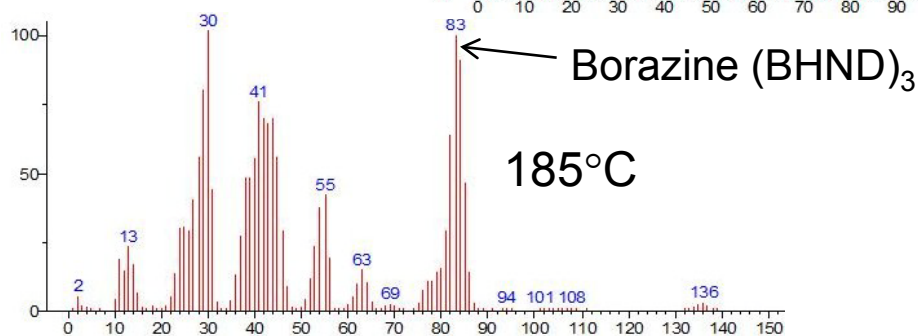
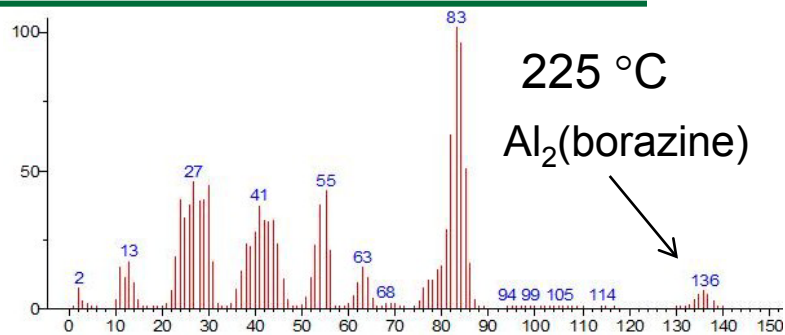
# Deuterium Labeled Mechanistic Study

Prepared  $\text{Al}(\text{BH}_4)_3 \cdot 2(\text{ND}_3)$  in a solvent free reaction using  $\text{ND}_3$  ammonia

Determined mass spectra of evolved gas as a function of temperature

Detection of HD indicates source of hydrogen is both  $\text{BH}_4^-$  and  $\text{ND}_3$ .

Presence of  $\text{D}_3$ -borazine is evidence of reaction between  $\text{BH}_3$  and  $\text{ND}_3$ .





# Multinuclear MAS NMR Characterization of Ammine Aluminum Borohydrides

---

## Summary of results and conclusions collaboration with JPL/CalTech

- Determined  $^{27}\text{Al}$ ,  $^{11}\text{B}$ ,  $^1\text{H}$ , and  $^{15}\text{N}$  NMR spectra of  $\text{Al}(\text{BH}_4)_3 \cdot 2(\text{NH}_3)$  prepared by solvent free reaction
- Determined spectra of hydrogen desorption products
- Used samples prepared from normal isotopic composition ammonia and  $^{15}\text{N}$ -ammonia
- $^{11}\text{B}$  and  $^{27}\text{Al}$  spectra of as prepared materials indicate nuclei are in two different sites (8:1 ratio), one having asymmetry – from preparative route we can speculate that  $[\text{Al}(\text{NH}_3)_6](\text{BH}_4)_3$  may be present in minor amount

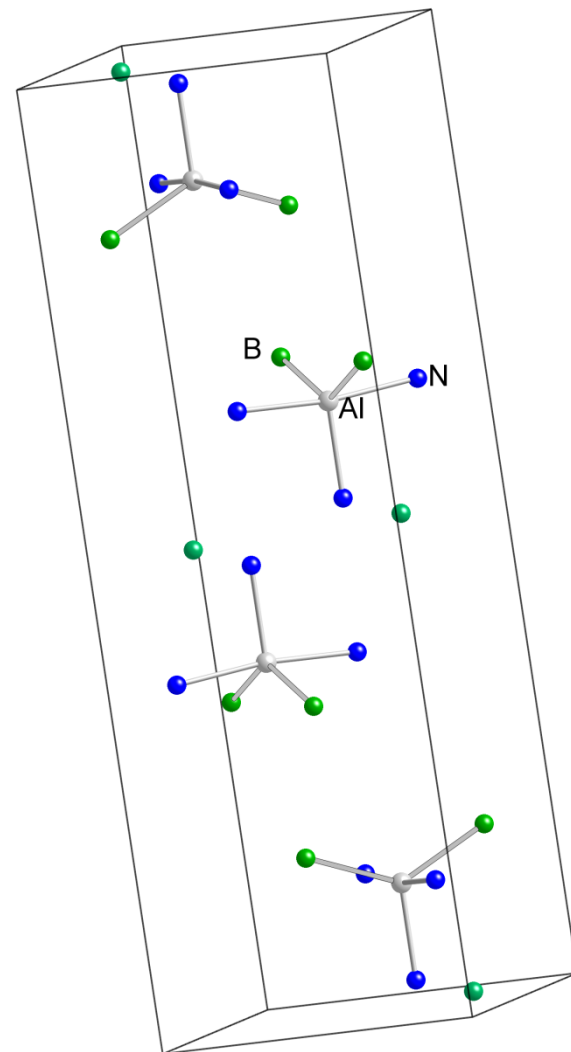
# More Multinuclear MAS NMR

---

- $^{27}\text{Al}$  NMR of material desorbed at 135 °C or 200 °C shows overlap of broad resonance, one disappearing upon desorption at 500 °C – chemical shift indicates coordination number of Al has decreased at higher T – spectra clearly show that Al metal is not a product
- $^{11}\text{B}$  NMR of material desorbed at 100 °C, 135 °C, 200 °C, and 500 °C show progression from boron hydride species to a **boron nitride polymer as the chemical form of the hydrogen desorption species**
- $^1\text{H}$  NMR of material desorbed at 200 °C and recharged with 100 bar hydrogen shows **no evidence of hydrogen uptake**
- $^{15}\text{N}$  NMR of desorption products inconclusive

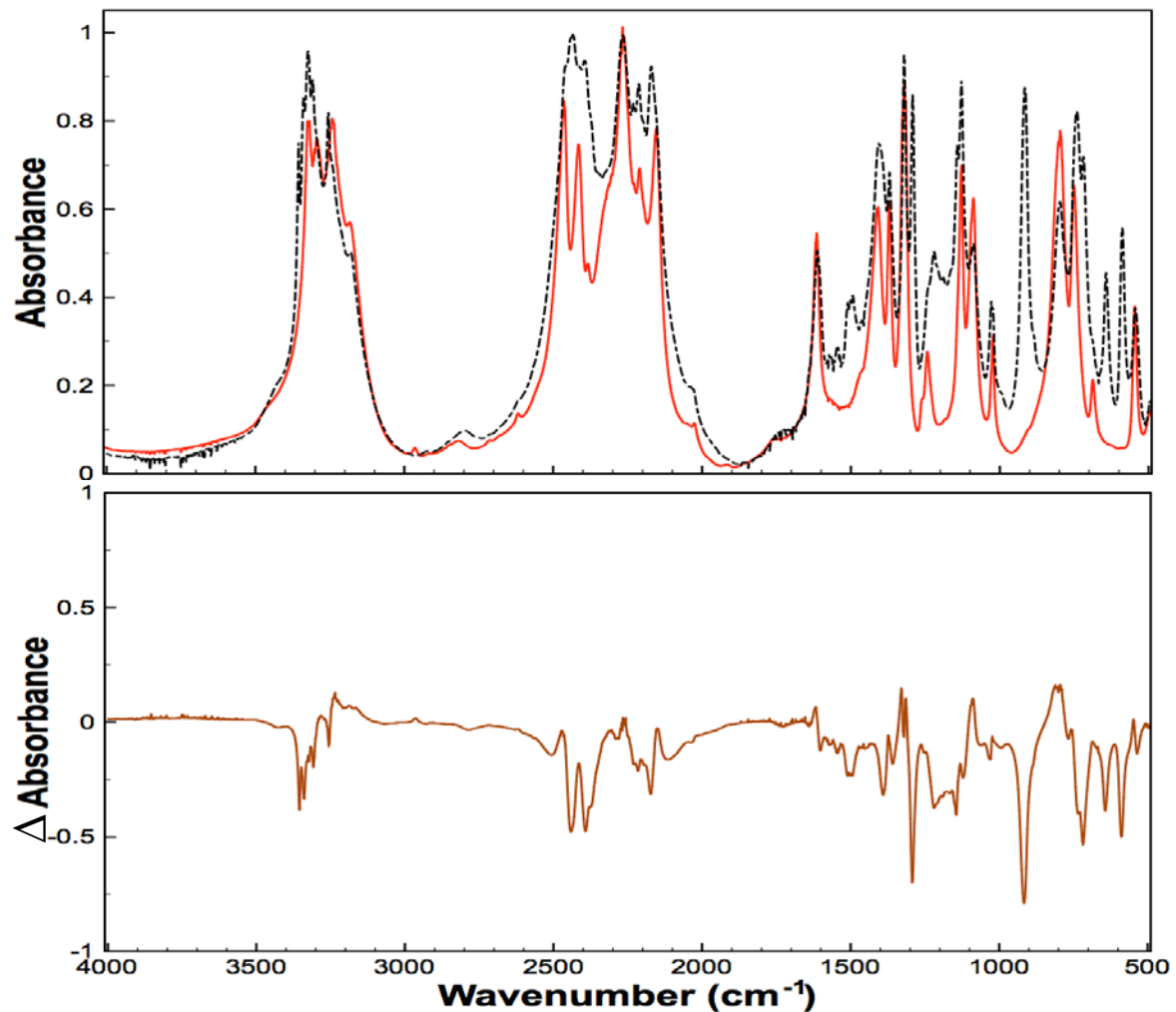
# Reaction of $\text{Al}(\text{BH}_4)_3$ with $\text{NH}_3$ in Toluene

- The reaction of  $\text{Al}(\text{BH}_4)_3$  with  $\text{NH}_3$  in toluene gives a product which has an XRD pattern different from the ammonia adduct in the solvent free reaction; the elemental analysis of the product suggest the composition is  $\text{Al}(\text{BH}_4)_3 \cdot 3\text{NH}_3$
- Bird and Wallbridge (*J. Chem. Soc. A*, **1967**, 664) indicate two moles of  $\text{NH}_3$  react with the stoichiometric ratio but the species  $[\text{Al}(\text{NH}_3)_6](\text{BH}_4)_3$  is formed with excess ammonia – the FTIR spectrum and the XRD pattern of our product shows the hexamine is not formed
- High resolution XRD obtained at NSLS. Preliminary structure which was reported at the AMR last year (shown to right) is now believed to be in error; work is in progress to resolve structure



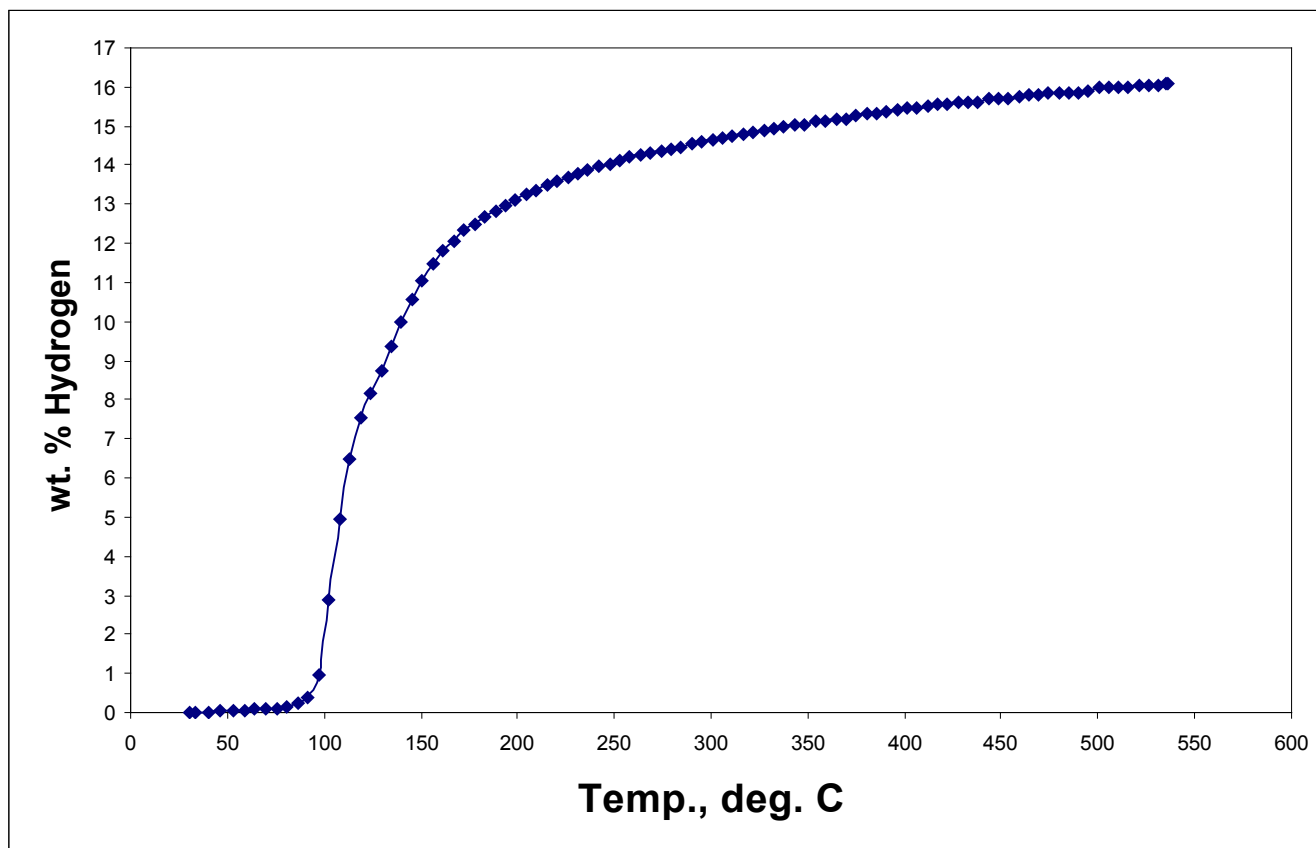
Hydrogen atoms were not refined

# FTIR Spectra of Ammine Aluminum Borohydrides



- **Top:** The FTIR spectra of the solvent free preparation ( - - ) and the synthesis from toluene ( - ) are shown (KBr pellets, protected from air)
- **Bottom:** Calculated difference spectrum. Both figures share a common x axis.
- Spectra are very close in N-H, Al-H, and B-H stretching vibration regions
- Hydrogen desorption reactions differ mainly in quantity of H<sub>2</sub> evolved

# Hydrogen TPD of $\text{Al}(\text{BH}_4)_3 \cdot 3\text{NH}_3$



MS analysis of evolved gas indicates that less diborane is evolved by the three ammonia adduct compared to the two ammonia adduct

Hydrogen desorption takes place in three stages, beginning at  $< 100\text{ }^\circ\text{C}$

Objective of further research is to make first two stages of reaction reversible

# Aluminum Amine Borohydrides Release Large Amounts of H<sub>2</sub>

Compound	Formula Weight	% hydrogen (calc)	% hydrogen (500 C)
Al(BH <sub>4</sub> ) <sub>3</sub>	71.508	16.92%	12.7%
Al(BH <sub>4</sub> ) <sub>3</sub> ·2NH <sub>3</sub>	105.570	17.19%	15.1%
Al(BH <sub>4</sub> ) <sub>3</sub> ·3NH <sub>3</sub>	122.601	17.26%	15.9%
NH <sub>3</sub> BH <sub>3</sub>	30.865	19.59%	~12%*

Both the diammonia and the triammonia compounds release such a large amount of H<sub>2</sub> that ammonia must be losing hydrogen as well as borohydride

We don't know the exact composition of the product after the second stage (~150 °C), but the amount of hydrogen is consistent with the reaction



MAS NMR indicates a BN polymer is the thermal decomposition product

Ammonia borane (potential 19.6% hydrogen) going to (BHNH)<sub>n</sub> is 13.06%

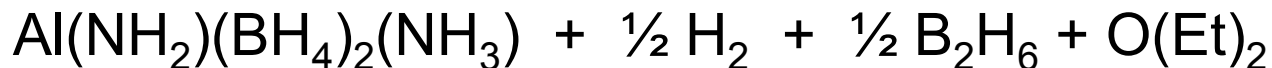
Quantity of H<sub>2</sub> evolved from Al(BH<sub>4</sub>)<sub>3</sub>·3NH<sub>3</sub> is competitive with that evolved from ammonia borane at the same temperature.

\*G. Wolf, et. al., *Thermochimica Acta*, **445**, 2, 121-125.  
Technical Accomplishments and Progress

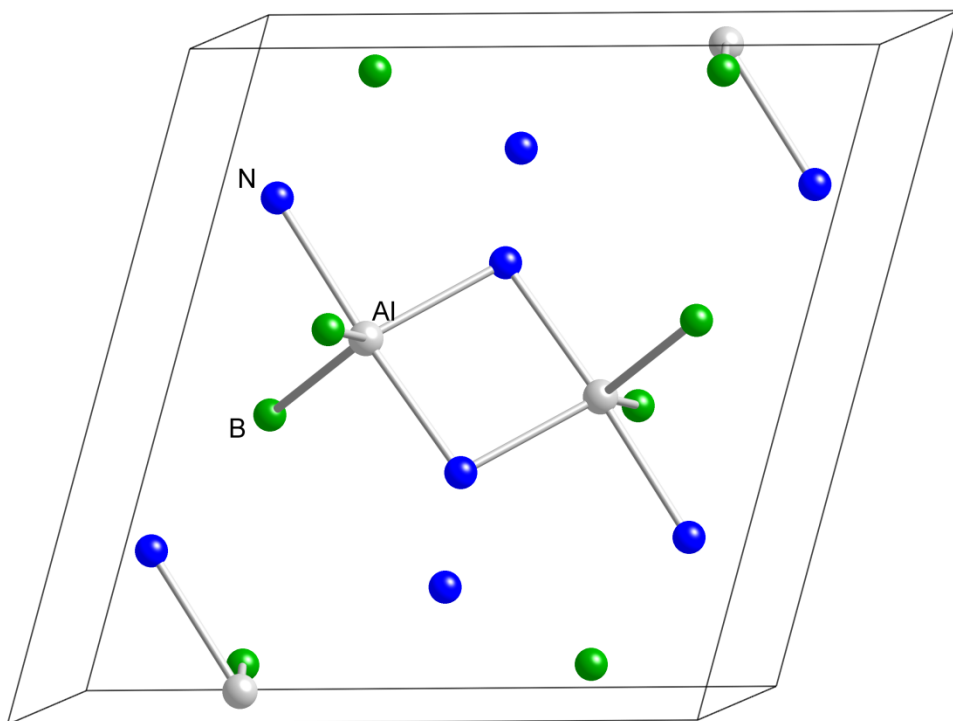
# Aluminum Borohydride-Ammonia in Ether

---

- Reaction of aluminum borohydride with ammonia was studied in diethyl ether solvent. This solvent forms a 1:1 adduct with aluminum borohydride having roughly tetrahedral geometry around the Al center.
- Gases ( $B_2H_6$  and  $H_2$ ) evolved during the reaction – products will be quantified in future work.
- XRD pattern and FTIR spectra distinctly different from solvent free reaction and reaction in toluene
- Chemical analysis shows Al:B ratio is 1:2, a loss of one borohydride from starting  $Al(BH_4)_3$
- $Al(BH_4)_3 \cdot O(Et)_2 + 2 NH_3 \rightarrow$



# Structure of Aluminum Borohydride-Ammonia Synthesized in Ether

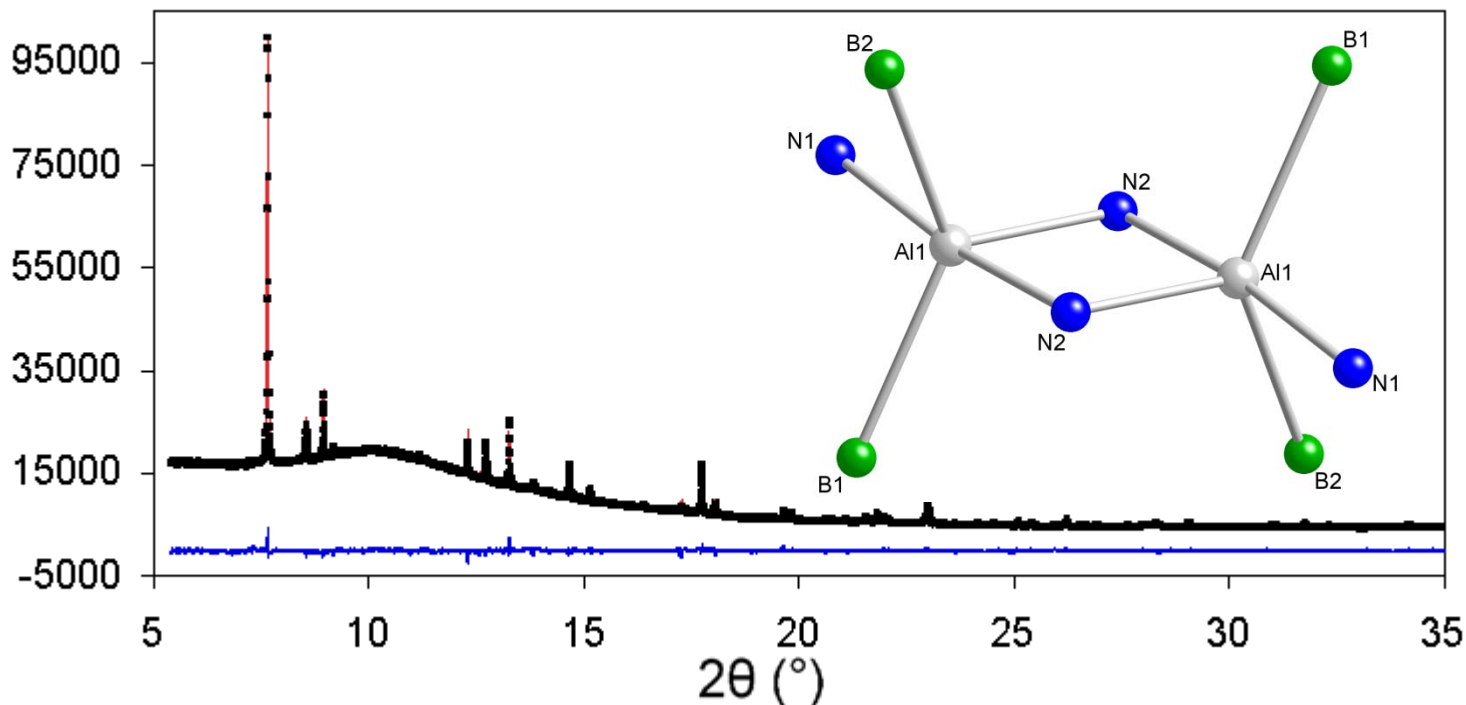


Hydrogen atoms were not refined

- Structure of the product of the reaction of aluminum borohydride with ammonia in diethyl ether was determined by high resolution XRD data taken at the NSLS
- Product is an amide ( $\text{NH}_2^-$ ) bridged dimer with terminal ammonia and borohydride groups
- Structure offers insight into mechanism of hydrogen desorption from amine-borohydride complexes
- First step is reaction of  $\text{Al-BH}_4$  to form  $\text{Al-H}$  and  $\text{BH}_3$
- Second step is reaction of coordinated ammonia with  $\text{Al-H}$  to evolve  $\text{H}_2$  and make  $\text{Al-NH}_2$
- Consistent with  $\text{ND}_3$  labeling results



# High Resolution XRD and Refinement Results



Rietveld refinement (48 variables)

$$\chi^2 = 17.52$$

$$wRp = 4.74\%$$

$$R_{exp} = 1.14\%$$

Bond	Length (Å)
Al – B1	2.307(6) Å
Al – B2	2.282(6) Å
Al – N1	2.017(7) Å
Al – N2	1.997(4), 2.014(7) Å

# Technical Accomplishments and Progress

---

- We have identified a high yield synthesis of  $\text{HAl}(\text{BH}_4)_2$
- This compound will react with diborane in part to reform  $\text{Al}(\text{BH}_4)_3$
- Literature results indicate another product formed which is insoluble in hydrocarbon solvent
- Work is in progress to investigate reaction of diborane with  $\text{HAl}(\text{BH}_4)_2$  at elevated diborane pressure; objective is to obtain a more readily characterized aluminoborane product

Collaboration with J.-C. Zhao at Ohio State University to investigate the chemistry of aluminoboranes such as  $\text{AlB}_4\text{H}_{11}$  continues

# Collaborations

---

## MHCoE Partners

- J.-C. Zhao, Ohio State University – Development of aluminoboranes such as  $\text{AlB}_4\text{H}_{11}$  as hydrogen storage materials and chemistry of ammine borohydrides
- Cal Tech and JPL – Structural characterization of materials by MAS NMR
- BNL – Chemistry of alane and Ti – catalyzed activated Al metal

## Other Collaborators

- Claudia J. Rawn, MSTD, ORNL – Heated Stage X-ray diffraction (XRD); synchrotron based XRD for structural determination
- Jianming Bai and Antonio F. Moreira dos Santos, structure determination by synchrotron based XRD

# Future Plans

---

- Refine the elemental analysis of the aluminum ammine borohydrides and precisely determine the amounts of gaseous products in the reaction of ammonia with aluminum borohydride in solvents (toluene and ether)
- Multinuclear solution and solid MAS-NMR of aluminum ammine borohydrides will be used to identify intermediates in desorption reactions
- TGA with evolved gas analysis by MS will be implemented to follow reactions of ammine metal borohydrides and identify intermediates
- Continue study of aluminoboranes in collaboration with J.-C. Zhao, Ohio State Univ.
- Investigate chemistry of alane amines ( $\text{AlH}_3 \cdot n\text{NH}_3$ )

# Summary Slide

---

Relevance/Program Objectives: ORNL is developing the chemistry for a reversible hydrogen storage system based on high hydrogen content (>10 wt %) materials

Plan and Approach: ORNL has expertise in handling oxygen and moisture sensitive reagents, knowledge of reaction pathways in solution, and insight into mechanisms of reactions and catalytic pathways which it uses in materials development.

Technical Accomplishments and Progress:

- Reaction of ammonia with aluminum borohydride give materials with high hydrogen content.
- Deuterium labeling experiments demonstrate that the first hydrogen evolved comes equally from the ammonia and the borohydride components.
- The reaction of ammonia with aluminum borohydride in ether yields a product that gives insight into the reaction mechanism of evolution from this class of materials.

Collaborations: Ohio State University, CalTech/JPL, BNL

Proposed Future Research: We will continue aluminum ammine borohydride studies with an emphasis on identifying BN product and making hydrogen desorption reversible, aluminoborane research will continue, and chemistry of  $\text{AlH}_3$  with ammonia will be initiated if funding is available.

