CHARACTERIZATION OF ALUMINUM HYDRIDE POLYMORPHS (α-, β-, γ-
AlH₃): A POTENTIAL HYDROGEN STORAGE MATERIAL FOR USE WITH
HYDROGEN FUEL CELLS

A THESIS SUBMITTED TO THE GRADUATE DIVISION OF THE
UNIVERSITY OF HAWAII IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF

MASTER OF SCIENCE

IN

CHEMISTRY

MAY 2006

By
Caleb M. Brown

Thesis Committee:
Craig Jensen, Ph.D., Chairperson
Satoshi Takara, Ph.D.
John Head, Ph.D.
We certify that we have read this thesis and that in our opinion, it is satisfactory in scope and quality as a thesis for the degree of Master of Science in Chemistry.
ACKNOWLEDGEMENTS

I would like to give thanks to the following people: Dr. Jensen for allowing me to work in his lab and for offering his guidance and support; Dr. Takara and Dr. Head for being apart of my thesis committee; the entire Jensen group, especially Walker Langley and Todd Dalton, for sharing their knowledge and friendship as I pursued my graduate degree here at the University of Hawaii; the Chemistry department for their financial support; and finally the Orimo group at Tohoku University for allowing me to visit their research institute in Japan and utilize their analytical equipment.
ABSTRACT

The α-, β-, and γ-polymorphs of AlH₃ have been successfully synthesized and the intrinsic and mechanically modified thermal stabilities of each polymorph have been experimentally determined. The thermogravimetric profiles of the α- and γ-phases exhibit dehydriding reactions in the temperature range of 370-450 K. The profile of the β-phase shows the continuous dehydriding reactions, which differs from the other two phases. The values of the enthalpy of dehydriding reactions $\Delta H_{\text{dehyd}}$ are determined to be $6.0 \pm 1.5$, -3 to approximately -5, and $1.0 \pm 0.5$ kJ/mol H₂ for the α-, β-, and γ-phases, respectively. The milling-time dependences of the powder X-ray diffraction measurement and thermal analyses indicate the occurrence of the dehydriding reactions both in the α- and γ-phases during milling, but there is no drastic change in the β-phase. The temperature at which dehydrogenation occurs for the α- and γ-phase is drastically reduced by approximately 50 K upon milling, results that are similar to doping. Infrared spectroscopy was used in order to develop a convenient, low-cost alternative to X-ray diffraction for differentiating between the various polymorphs of AlH₃. The spectroscopy data also indicates that γ-AlH₃ may have a combination of bridging and terminal hydrogens, and β-AlH₃ may lack any long-range ordering of the crystalline structure. The dehydrogenation reaction for each phase was found to be nearly 9 mass %. The β- and γ-phases have improved kinetics relative to the α-phase, results that are similar to doping. Titanium dopants did not appear to improve the dehydrogenation reaction in this study, nor did they allow for the rehydrogenation of AlH₃ or metallic aluminum. Preliminary results from Raman and neutron vibrational spectroscopy, in addition to powder neutron diffraction data are also presented.
TABLE OF CONTENTS

Acknowledgements .......................................................................................... iii
Abstract ............................................................................................................ iv
List of Tables ..................................................................................................... viii
List of Figures .................................................................................................... ix
List of Equations ............................................................................................... xi
List of Abbreviations ........................................................................................ xii
Chapter 1: Introduction .................................................................................... 1
  1.1 Fossil Fuel Economy ............................................................................. 1
  1.2 Hydrogen Economy ............................................................................. 3
  1.3 Hydrogen Fuel Cells .......................................................................... 5
  1.4 Technological Barriers ........................................................................ 8
  1.5 Hydrogen Storage ............................................................................... 10
  1.6 Aluminum Hydride, AlH₃ .................................................................. 11
  1.7 Scope of Thesis .................................................................................... 13
Chapter 2: Synthesis of Aluminum Hydride Polymorphs (α-, β-, γ-AlH₃) ... 14
  2.1 Introduction ......................................................................................... 14
  2.2 Experimental ....................................................................................... 15
  2.3 Results and Discussion ...................................................................... 18
  2.4 Conclusion .......................................................................................... 20
Chapter 3: Intrinsic and Mechanically Modified Thermal Stabilities of Aluminum Hydride Polymorphs .......................................................... 22
  3.1 Introduction ......................................................................................... 22
3.2 Experimental ....................................................... 23
3.3 Results and Discussion ............................................ 23
   Intrinsic Thermal Stability ........................................ 23
   Mechanical Modification of Thermal Stability ................. 28
3.4 Conclusion .......................................................... 31

Chapter 4: Infrared Spectroscopy of Aluminum Hydride Polymorphs .... 33
4.1 Introduction ....................................................... 33
4.2 Experimental ....................................................... 33
4.3 Results and Discussion ............................................ 33
4.4 Conclusion ......................................................... 40

Chapter 5: Dehydrogenation and Rehydrogenation of AlH₃ Polymorphs..... 41
5.1 Introduction ......................................................... 41
5.2 Experimental ....................................................... 41
5.3 Results and Discussion ........................................... 42
   Dehydrogenation ................................................... 42
   Rehydrogenation .................................................. 43
5.4 Conclusion ......................................................... 43

Chapter 6: Future Studies ........................................................ 45

Appendix A: Crystal Structures of Aluminum Deuteride Polymorphs...... 46
A.1 Introduction ......................................................... 46
A.2 Experimental ....................................................... 47
A.3 Results and Discussion ........................................... 48
A.4 Conclusion ......................................................... 49
Appendix B: Raman and Neutron Vibrational Spectroscopy of Aluminum Hydride Polymorphs

B.1 Introduction .......................................................... 50
B.2 Experimental .......................................................... 50
B.3 Results and Discussion ............................................. 50
    Raman Spectroscopy .................................................. 50
    Neutron Vibrational Spectroscopy ................................. 53
B.4 Conclusion ........................................................... 55
References ...................................................................... 56
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Summary</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Summary of the Differences Between Procedures For Making α-, β-, and γ-AlH₃</td>
<td>16</td>
</tr>
<tr>
<td>1.2</td>
<td>Summary of Reactions Run in an Attempt to make α-, β-, and γ-AlH₃</td>
<td>17</td>
</tr>
<tr>
<td>4.1</td>
<td>Summary of Infrared Spectroscopy Results for AlH₃ Polymorphs</td>
<td>37</td>
</tr>
<tr>
<td>B.1</td>
<td>Summary of Raman and Neutron Vibrational Spectroscopy Results for AlH₃ Polymorphs</td>
<td>53</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>Global Production of Oil Estimates Based on the Hubbert Curve.</td>
<td>3</td>
</tr>
<tr>
<td>1.2</td>
<td>Renewable H₂ Energy Cycle.</td>
<td>5</td>
</tr>
<tr>
<td>1.3</td>
<td>Fuel Cell Stack Used to Power a Motor Vehicle.</td>
<td>7</td>
</tr>
<tr>
<td>1.4</td>
<td>Proton Exchange Membrane Fuel Cell (PEMFC) Diagram.</td>
<td>8</td>
</tr>
<tr>
<td>1.5</td>
<td>Storage Density of Hydrogen in Compressed Gas, Liquid, Adsorbed Monolayer, and Selected Chemical Compounds.</td>
<td>11</td>
</tr>
<tr>
<td>2.1</td>
<td>Powder X-ray Diffraction (XRD) Profiles of α-, β-, and γ-AlH₃.</td>
<td>19</td>
</tr>
<tr>
<td>2.2</td>
<td>Powder X-ray Diffraction (XRD) Profiles of β/α- and Etherated AlH₃.</td>
<td>20</td>
</tr>
<tr>
<td>3.1</td>
<td>Thermogravimetry and Differential Thermal Analysis (TG-DTA) Results for α-, β-, and γ-AlH₃.</td>
<td>25</td>
</tr>
<tr>
<td>3.2</td>
<td>Powder X-ray diffraction (XRD) Profiles of α-, β-, and γ-AlH₃ after TG-DTA.</td>
<td>25</td>
</tr>
<tr>
<td>3.3</td>
<td>Mass Spectroscopy Results for α-, β-, and γ-AlH₃ After TG-DTA Analysis.</td>
<td>26</td>
</tr>
<tr>
<td>3.4</td>
<td>Differential Scanning Calorimetry (DSC) Results for α- and γ-AlH₃.</td>
<td>27</td>
</tr>
<tr>
<td>3.5</td>
<td>Thermal Stability Diagram for α-, β-, and γ-AlH₃.</td>
<td>28</td>
</tr>
<tr>
<td>3.6</td>
<td>Powder X-ray Diffraction (XRD) Profiles of α-, β-, and γ-AlH₃ Before and After Mechanical Milling.</td>
<td>29</td>
</tr>
<tr>
<td>3.7</td>
<td>Thermogravimetry and Differential Thermal Analysis (TG-DTA) Results for α-, β-, and γ-AlH₃ Before and After Mechanically Milling.</td>
<td>30</td>
</tr>
<tr>
<td>4.1</td>
<td>Infrared Spectrum of α-AlH₃.</td>
<td>37</td>
</tr>
<tr>
<td>4.2</td>
<td>Infrared Spectrum of Mixed Phase β/α-AlH₃.</td>
<td>38</td>
</tr>
</tbody>
</table>
4.3 Infrared Spectrum of β-AlD₃ ............................................. 38
4.4 Infrared Spectrum of γ-AlH₃ ............................................. 39
4.5 Infrared spectrum of γ-AlD₃ ............................................. 39
4.6 Infrared Spectrum of Etherated AlH₃ (AlH₃·[(C₂H₅)₂O])³⁻ ...... 40
5.1 Isothermal Decomposition Profile of α-, β-, and γ-AlH₃ ...... 43
A.1 The Six Al···H···Al Bridges Formed by the Aluminum Atom in the Rhombohedral Unit Cell of α-AlH₃ ....................... 47
B.1 Raman Spectra of Etherated, α-, γ-, and β/α-AlH₃ .......... 52
B.2 Neutron Vibrational Spectra of α- and γ-AlH₃ .......... 54
## LIST OF EQUATIONS

<table>
<thead>
<tr>
<th>Equation</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1</td>
<td>$\text{H}_2 + 1/2\text{O}_2 \rightarrow \text{H}_2\text{O}$</td>
</tr>
<tr>
<td>1.2</td>
<td>$\text{H}_2 \rightarrow 2\text{H}^+ + 2\text{e}^-$</td>
</tr>
<tr>
<td>1.3</td>
<td>$1/2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O}$</td>
</tr>
<tr>
<td>1.4</td>
<td>$\text{AlH}_3 \rightarrow \text{Al} + 3/2\text{H}_2$</td>
</tr>
<tr>
<td>2.1</td>
<td>$3\text{LiAlH}_4 + \text{AlCl}_3 \rightarrow 4\text{AlH}_3 + 3\text{LiCl}$</td>
</tr>
<tr>
<td>4.1</td>
<td>$v_{\text{Al-H}}/v_{\text{Al-D}} = [1/2\pi(k/\mu_{\text{Al-H}})^{1/2}]/[1/2\pi(k/\mu_{\text{Al-D}})^{1/2}]$</td>
</tr>
<tr>
<td>5.1</td>
<td>$\text{NaAlH}_4 \leftrightarrow 1/3\text{Na}_3\text{AlH}_6 + 2/3\text{Al} + \text{H}_2 \leftrightarrow \text{NaH} + \text{Al} + 3/2\text{H}_2$</td>
</tr>
<tr>
<td>A.1</td>
<td>$3\text{LiAlD}_4 + \text{AlCl}_3 \rightarrow 4\text{AlD}_3 + 3\text{LiCl}$</td>
</tr>
</tbody>
</table>
**LIST OF ABBREVIATIONS**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>Aluminum</td>
</tr>
<tr>
<td>B</td>
<td>Boron</td>
</tr>
<tr>
<td>C</td>
<td>Celsius</td>
</tr>
<tr>
<td>Cl</td>
<td>Chlorine</td>
</tr>
<tr>
<td>cm</td>
<td>Centimeters</td>
</tr>
<tr>
<td>cm⁻¹</td>
<td>Wavenumbers (Reciprocal Centimeters)</td>
</tr>
<tr>
<td>D</td>
<td>Deuterium</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential Scanning Calorimetry</td>
</tr>
<tr>
<td>e⁻</td>
<td>Electron</td>
</tr>
<tr>
<td>Eq.</td>
<td>Equation</td>
</tr>
<tr>
<td>GPa</td>
<td>Gigapascal</td>
</tr>
<tr>
<td>H⁺</td>
<td>Proton</td>
</tr>
<tr>
<td>H₂</td>
<td>Hydrogen</td>
</tr>
<tr>
<td>Li</td>
<td>Lithium</td>
</tr>
<tr>
<td>M</td>
<td>Molarity (mole/L)</td>
</tr>
<tr>
<td>m</td>
<td>Mass</td>
</tr>
<tr>
<td>meV</td>
<td>Milielectron-Volts</td>
</tr>
<tr>
<td>mg</td>
<td>Milligram</td>
</tr>
<tr>
<td>ml</td>
<td>Milliliter</td>
</tr>
<tr>
<td>n</td>
<td>Number of Moles</td>
</tr>
<tr>
<td>O₂</td>
<td>Oxygen</td>
</tr>
<tr>
<td>Na</td>
<td>Sodium</td>
</tr>
<tr>
<td>Symbol</td>
<td>Definition</td>
</tr>
<tr>
<td>--------</td>
<td>------------</td>
</tr>
<tr>
<td>P</td>
<td>Pressure</td>
</tr>
<tr>
<td>PND</td>
<td>Powder Neutron Diffraction</td>
</tr>
<tr>
<td>PCT</td>
<td>Pressure-Composition-Temperature Analysis</td>
</tr>
<tr>
<td>R</td>
<td>Gas Constant (8.31451 J/Kmol)</td>
</tr>
<tr>
<td>T</td>
<td>Temperature</td>
</tr>
<tr>
<td>TG-DTA</td>
<td>Thermogravimetric and Differential Thermal Analysis</td>
</tr>
<tr>
<td>V</td>
<td>Volume</td>
</tr>
<tr>
<td>XRD</td>
<td>X-Ray Diffraction</td>
</tr>
<tr>
<td>μ</td>
<td>Reduced Mass ([\frac{(m_1m_2)}{(m_1+m_2)}])</td>
</tr>
<tr>
<td>ν</td>
<td>Frequency</td>
</tr>
<tr>
<td>o</td>
<td>Degree</td>
</tr>
<tr>
<td>%</td>
<td>Percent</td>
</tr>
</tbody>
</table>
CHAPTER 1

Introduction

1.1 Fossil Fuel Economy

Since the beginning of the industrial revolution in the 18th century, fossil fuels have been the primary source of power that has driven our society. Fossil fuels, in the form of coal, oil, and natural gas produce electricity for our appliances, power our automobiles, and heat our homes. In addition, petrochemicals, which are made from oil, are used in making plastics. It is estimated that fossil fuels currently provide more than 85% of the energy consumed in the United States. Although relatively inexpensive, fossil fuels create numerous health, environmental, and political problems that come at a high cost.

When cars burn gasoline, for example, they ideally create nothing but carbon dioxide and water in their exhaust. Unfortunately, the internal combustion engine is not perfect. In the process of burning gasoline, carbon monoxide (a poisonous gas), nitrogen oxides (the main source of urban smog), and unburned hydrocarbons (the main source of urban ozone) are produced. Furthermore, air pollution from automobiles is a major cause of illness in urban areas and is harmful to the health of our environment.

Yet, even an ideal gasoline engine emits carbon dioxide, a greenhouse gas that is slowly raising the temperature of the planet. The ultimate effects are unknown, but it is a strong possibility that, eventually, there will be drastic climate changes that will affect everyone on the planet. For example, if the polar ice caps were to melt due to a rise in global temperature, sea levels would rise significantly, flooding and destroying all coastal cities in existence today. Severe changes in normal weather patterns may occur as well.
For example, it is speculated that the severity of hurricane Katrina may be attributed to the rise in global temperature.³

The process of transporting and storing oil has major impacts on the environment as well. For example, pipeline explosions, well fires, and oil spills can create huge environmental disasters. Many recall the oil spill caused by the Exxon Valdez oil tanker when 11 million gallons of crude oil was emptied into Prince William Sound, the largest spill in U.S. history.⁴ Although such major spills are rare, minor spills constantly occur, endangering marine life and their environments.⁵

There exists an additional problem due to the localized source of fossil fuels. The United States, in addition to most countries, cannot produce enough oil to meet demand. Therefore, it must be imported from oil-rich countries, which creates an economic dependence. When Middle East oil producers—where 2/3 of the oil reserves are currently located—decide to raise the price of oil, the rest of the world has little choice but to pay the higher price.⁶ Furthermore, it is the belief of Michael Renner—in addition to numerous others—as written in Foreign Policy in Focus, that “Washington's war on Iraq is the lynchpin to controlling Persian gulf oil.”⁷

The world's demand for energy is projected to double by 2050 in response to population growth and the industrialization of developing countries.⁸ However, it is unlikely the world’s fossil fuel supply will be able to keep up with this demand. Figure 1:1 displays oil production trends and future estimates. This predication is based on the Hubbert model, which assumes that if oil production is unrestrained in a very large producing region, it will follow a bell-shaped curve with peak production occurring when approximately one-half of the ultimately recoverable amount of oil is extracted.⁹ Figure
1.1 predicts that the global production of oil already peaked around the year 2005, and will continue to decrease over the next 60 years until the reserves are eventually exhausted.\textsuperscript{10}

As a result, alternative sources of energy are urgently needed in order to prepare for the inevitable shortage of fossil fuels. Renewable energy sources—solar, wind, hydroelectric, hydrogen, etc.—are the best alternatives, as they reduce the amount of damage to our health and environment.

1.2 Hydrogen Economy

Molecular hydrogen (H\textsubscript{2}) has a high potential in becoming the primary energy source of the future. When used in combustion engines similar to the ones currently used to power motor vehicles, hydrogen reacts with oxygen to produce an exothermic reaction that powers the car’s pistons. However, it is most likely that hydrogen will be used in conjunction with fuel cells due to the increased operational safety and energy-
effectiveness relative to combustion engines. For example, a car powered by a fuel cell uses no energy while at a standstill, whereas a combustion engine continues to consume energy. Even at low speeds combustion engines are very inefficient, unlike their fuel cell counterparts.

When hydrogen and oxygen react in a fuel cell the only byproduct is water, unlike gasoline powered combustion engines which produce greenhouse gas emissions and air pollution. Furthermore, if the electrolysis of water—splitting water into molecular hydrogen and oxygen via an electric current—becomes an efficient means of producing hydrogen gas, hydrogen fuel cells have the potential to become the second-half of a renewable, sustainable energy cycle, as illustrated in Figure 1.2.

Hydrogen is also the most abundant element in the universe and is generously distributed throughout the world without regard for national boundaries. Using it to create a hydrogen economy—a future energy system based on hydrogen and electricity—only requires technology, not political access. This could greatly reduce our dependency on oil from foreign countries.
Figure 1.2 Renewable H\textsubscript{2} energy cycle in which sunlight is being used to produce an electric current via a photoelectric cell which splits water to produce O\textsubscript{2} and H\textsubscript{2} gas. The H\textsubscript{2} gas then reacts with O\textsubscript{2} inside a hydrogen fuel cell onboard an automobile, which produces H\textsubscript{2}O, heat, and an electric current to power the vehicle. Note that all materials are recyclable.

1.3 Hydrogen Fuel Cells

There are several different types of fuel cells, each using a different type of chemistry. Most fuel cells in use today, however, use molecular hydrogen and oxygen as chemicals. Similar to a standard electrochemical battery, a fuel cell produces an electric current to power devices. However, chemicals are constantly flowing into a fuel cell in
order to recharge, in contrast to a battery where a set amount of chemicals are stored inside, this causing the battery to eventually run dead.\textsuperscript{13}

The proton exchange membrane fuel cell (PEMFC) is one of the most promising full cell technologies and, therefore, is most likely to end up powering our cars, buses and possibly even individual homes.\textsuperscript{14} A PEMFC converts molecular hydrogen and oxygen into water while producing heat and an electric current according to Equation 1.1. It is the electric current, not the heat that will be used to power motor vehicles, although it is likely that this excess heat will be used in some form, such as maintaining the internal cabin temperature.

$$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$$ \textit{(Eq. 1.1)}

As the name suggests, the proton exchange membrane fuel cell is made up of a central proton exchange membrane (PEM)—also known as a polymer electrolyte membrane—sandwiched between a cathode and an anode, which is then sandwiched between a hydrogen flow field and an oxygen flow field, as illustrated in Figure 1.4. The PEM allows only positively charged ions ($H^+$) to pass through to the cathode. A PEMFC also contains a catalyst, usually made of platinum powder thinly coated onto carbon paper or cloth. The catalyst is rough and porous so that the maximum surface area of the platinum can be exposed to the hydrogen or oxygen. The platinum-coated side of the catalyst faces the PEM.\textsuperscript{15}

As hydrogen gas enters the anode-side of the fuel cell via the hydrogen flow field, molecular hydrogen is split into two moles of hydrogen ions ($H^+$) and two moles of electrons ($e^{-}$) via the platinum catalyst, according to Equation 1.2. The negatively charged electrons cannot pass through the PEM and, therefore, must pass through an
external circuit before returning to the cathode-side of the fuel cell. In the process, an electrical current is produced in the circuit capable of producing work.

$$\text{H}_2 \rightarrow 2\text{H}^+ + 2e^- \quad (\text{Eq. 1.2})$$

As oxygen in the atmosphere enters the cathode-side of the fuel cell via the oxygen flow field, a half-mole of molecular oxygen reacts with two moles of electrons from the external circuit and is split into a mole of negatively charged oxygen ions ($\text{O}^{2-}$) via the platinum catalyst. Each negatively charged oxygen ion attracts two $\text{H}^+$ ions through the PEM to the cathode, where the ions combine to form water according to Equation 1.3.

$$\frac{1}{2}\text{O}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{H}_2\text{O} \quad (\text{Eq. 1.3})$$

Most fuel cells produce less than 1.16 volts of electricity, far from enough to power a vehicle. Therefore, multiple cells must be assembled into a fuel cell stack, as shown in Figure 1.3. The potential power generated by a fuel cell stack depends on the number and size of the individual fuel cells that comprise the stack and the surface area of the PEM.\textsuperscript{15}

![Figure 1.3 Fuel Cell Stack Used to Power a Motor Vehicle\textsuperscript{14}](image)
Hydrogen fuel is channeled through field flow plates to the anode on one side of the fuel cell, while oxygen from the air is channeled to the cathode on the other side of the cell.

At the anode, a platinum catalyst causes the hydrogen to split into positive hydrogen ions (protons) and negatively charged electrons.

The Polymer Electrolyte Membrane (PEM) allows only the positively charged ions to pass through it to the cathode. The negatively charged electrons must travel along an external circuit to the cathode, creating an electrical current.

At the cathode, the electrons and positively charged hydrogen ions combine with oxygen to form water, which flows out of the cell.

Figure 1.4. Proton exchange membrane fuel cell (PEMFC) diagram outlining the process by which hydrogen reacts with oxygen to produce water, heat, and an electric current.

1.4 Technological Barriers

The technological barriers that prevent the widespread use of hydrogen fuel cells have little to do with the fuel cell itself. In fact, hydrogen-powered vehicles have already been created and currently are being tested by numerous auto manufacturers, although they are not expected to reach the mass market any time soon. The reason being is we
have yet to create an environmentally friendly, energy-efficient means of generating hydrogen in addition to a safe, effective way to store the gas.

At present, most of the world's hydrogen is produced from natural gas by a process called steam reforming. However, producing hydrogen from fossil fuels defeats the main purpose of creating a hydrogen economy: to reduce the use of fossil fuels. Thus, to achieve the benefits of a hydrogen economy we must ultimately produce hydrogen from a non-fossil resource, such as water, using a renewable energy source, such as the sun. For example, using electricity it is easy to split water molecules to create pure hydrogen and oxygen. Creating enough electricity to separate hydrogen from water, and generating that electricity without using fossil fuels, will be the greatest challenge in creating a hydrogen economy.

The hydrogen storage problem also hinders the mainstream use of hydrogen fuel cells. Due to the fact that hydrogen is the simplest element, it will leak from any container, no matter how strong or how well insulated. And while hydrogen contains more energy per weight than any other energy carrier, it also contains much less energy by volume. This makes it difficult to store a large amount of hydrogen in a small space, such as an automobile's gas tank. Compressing or liquefying the gas reduces the volume, but requires a substantial amount of energy. Moreover, a compressed hydrogen tank would be at risk of developing pressure leaks, possibly resulting in explosions. Yet, despite the problems with hydrogen storage, current research is advancing and potential solutions are emerging.
1.5 Metal Hydrides

Metal hydrides are a commonly proposed solution for the problem with hydrogen storage. In this approach, hydrogen combines with a pure or alloyed metal to produce a metal hydride, such as NaAlH$_4$, LiBH$_4$, MgH$_2$, or AlH$_3$. Ideally, a metal hydride would be permanently placed inside a vehicle’s hydrogen tank. When hydrogen fuel is needed the metal hydride would be heated, which releases the gas from the metal hydride for the fuel cell to use. The metal, now free of hydrogen, remains in the vehicle’s hydrogen storage tank, which will later be reused to absorb additional hydrogen once the driver refills the vehicle with hydrogen fuel.

Studies have shown that these systems can store hydrogen at densities higher than simple compression, as shown in Figure 1.5. The challenge remains, though, to identify a metal hydride that will adhere to the requirements put forth by the Department of Energy. For example, the storage material must be safe, non-toxic, and relatively inexpensive. In addition, it must contain at least 6.4 weight % hydrogen and have a volumetric density of 65g/L to allow for a range of 300 miles. The material must also be reversible up to 1500 cycles and desorb hydrogen from 60 to 120 °C. Finally, the onboard refueling time must also not exceed three minutes.

This final requirement can be circumvented by using a system based on off-board recharging. In this approach, the free metal would be removed from the vehicle’s hydrogen storage tank and replaced with a metal hydride that was recharged in a different location. Although this approach is attractive, the on-board refueling method is preferred as it is more efficient and economical.
1.6 Aluminum Hydride, AlH₃

Aluminum hydride (AlH₃, also known as alane) has recently attracted attention for its potential as a hydrogen storage material for low-temperature fuel cells. Alane has a volumetric hydrogen capacity of 148 g/L, which is much higher than that of liquid hydrogen (45 g/L) and of most metal hydrides, thus suggesting its application as a possible hydrogen storage material. In addition, AlH₃ contains approximately 10 weight % hydrogen, and desorbs according to Equation 1.4.

\[
\text{AlH}_3 \rightarrow \text{Al} + \frac{3}{2}\text{H}_2 \quad (\text{Eq. 1.4})
\]

The decomposition reaction of AlH₃ produces elemental aluminum, a non-toxic, commonly available, and recycled material which could be an acceptable component of a future sustainable society. However, due to the large increase in entropy Equation 1.4...
is not easily reversed under ambient temperature and hydrogen-pressure conditions. \(^2\) Furthermore, theoretical calculations performed by Ke et al. \(^3\) indicate that hydrogenation of aluminum does not take place even under conditions of high pressure (up to 10 GPa) and low temperature (down to 0 K), conclusions that are consistent with previous experimental results. \(^4\) To date, only high-pressure \(^2\) and electrochemical \(^5\) processes have been studied as a means of (re)hydrogenating metallic aluminum.

Despite the high favorability for AlH\(_3\) to decompose according to Equation 1.4, the metal hydride is relatively stable at room temperature. This stability is generally attributed to a surface oxide layer, which acts as a kinetic barrier to decomposition. \(^6\) As a result of the high-activation barrier and the overall slow desorption kinetics, AlH\(_3\) was long thought to be unsuitable for low-temperature systems. However, recent studies by Sandrok et al. \(^7\) demonstrated that a dopant introduced by ball milling can alter the surface barrier of alane (here, \(\alpha\)-AlH\(_3\)) and lead to decomposition kinetics at 100 °C that are adequate for use in hydrogen powered vehicles. An additional study by Graetz and Reilly \(^8\) showed that a specific polymorph of alane (\(\gamma\)-AlH\(_3\)) shows similar increased kinetics as the doped, \(\alpha\)-AlH\(_3\) used in the studies by Sandrok et al.

Although these studies prompted further investigation into aluminum hydride’s potential as a hydrogen storage material, the real issue lies not in the forward reaction according to Equation 1.4, but in the ability for this decomposition reaction to be reversed and reabsorb hydrogen under suitable conditions. Until additional studies are conducted that focus on the rehydrogenation of AlH\(_3\), aluminum hydride cannot be used as a hydrogen storage material for use with hydrogen fuel cells onboard motor vehicles.
1.7 Scope of Thesis

In order to determine aluminum hydride's potential of becoming a hydrogen storage material for automobiles, this thesis attempts to accomplish the following objectives: i) determine a reliable means of synthesizing the α-, β-, and γ-phase polymorphs of AlH$_3$; ii) determine the intrinsic and mechanically modified thermal stabilities of the AlH$_3$ polymorphs; iii) use infrared spectroscopy to determine a convenient, low-cost alternative to X-ray diffraction for differentiating between the different phases of AlH$_3$, while providing additional structural information of β- and γ-AlH$_3$; iv) explore the possibility of rehydrogenating AlH$_3$ and metallic aluminum; v) determine the crystal structures of the β- and γ-AlH$_3$; and vi) use Raman and neutron vibrational spectroscopy to provide two additional alternatives to X-ray diffraction for differentiating between the different phases of AlH$_3$. 
CHAPTER 2

Synthesis of Aluminum Hydride Polymorphs ($\alpha$-, $\beta$-, $\gamma$-AlH$_3$)

2.1 Introduction

A convenient synthesis of aluminum hydride was first developed by Finholt et al. in 1947. This involves the ethereal reaction of lithium aluminum hydride (LiAlH$_4$) with aluminum chloride according to Equation 2.1. Due to the ease of decomposition of AlH$_3$ at low temperatures, the complete removal of the diethyl ether solvent could not be achieved. As a result, solid AlH$_3$ existed as a diethyl etherate, AlH$_3$·0.3[(C$_2$H$_5$)$_2$O].

3LiAlH$_4$ + AlCl$_3$ → 4AlH$_3$ + 3LiCl (Eq. 2.1)

However, in 1975 Brower et al. at the Dow Chemical Company found that excess LiAlH$_4$ could be used to prevent AlH$_3$ decomposition while removing the diethyl ether under heat. Apparently, the excess LiAlH$_4$ bonds to the AlH$_3$, which displaces the diethyl ether and stabilizes the alane while heating. The insoluble AlH$_3$ can then be washed with ether to remove the excess LiAlH$_4$, leaving an ether-free AlH$_3$ product. The use of LiBH$_4$ in conjunction with LiAlH$_4$ lowers the temperature at which desolvation can occur to an even greater extent. However, LiBH$_4$ used in the absence of LiAlH$_4$ does not protect AlH$_3$ from decomposition.

In the process of synthesizing unetherated AlH$_3$, Brower et al. identified seven polymorphs of AlH$_3$ via X-ray diffraction (XRD) experiments, which they named $\alpha$-, $\alpha'$-, $\beta$-, $\gamma$-, $\delta$-, $\epsilon$-, and $\zeta$-AlH$_3$. Each polymorph was synthesized in a similar manner, with minor variations used to isolate a specific phase (see Chapter 2.2). However, only a detailed description of the synthesis of $\alpha$-, $\alpha'$-, and $\gamma$-phase AlH$_3$ were reported. At no time were Brower et al. able to prepare a sample that contained pure $\beta$-AlH$_3$. 
Furthermore, reproducing their results to obtain a specific polymorph was difficult. Brower et al. even noted that repeated attempts to prepare single-phase samples of $\gamma$- or $\alpha$-$\text{AlH}_3$ were unsuccessful. Since then, there have been numerous publications on the synthesis of unetherated $\text{AlH}_3$ (i.e. Matzek$^{31}$ and Graetz$^{28}$) all of which vary slightly in the procedure.

2.2 Experimental

In this work, the $\alpha$-, $\beta$-, and $\gamma$-polymorphs of $\text{AlH}_3$ were selected to be synthesized and studied. The publications written by Brower,$^{30}$ Matzek,$^{31}$ and Graetz$^{28}$ were used as references for the synthesis. Each procedure involved the reaction of $\text{AlCl}_3$ with an excess of $\text{LiAlH}_4$ in diethyl ether, which were then immediately filtered to remove the $\text{LiCl}$ precipitate. The diethyl ether was removed under vacuum, leaving a white solid precipitate of $\text{AlH}_3$ etherate and excess $\text{LiAlH}_4$. The powder was ground with a mortar and pestle, and heated to approximately 65 °C under vacuum to produce the unetherated $\text{AlH}_3$. The final product was then washed with diethyl ether to remove the excess $\text{LiAlH}_4$. However, each procedure varied in the molar concentration of reactants, number of equivalents used, whether or not $\text{LiBH}_4$ was added, and the temperature and time of heating. The variables between each procedure are summarized in Table 1.1. In addition, a reliable method for synthesizing each polymorph based on the procedures in Table 1.1 was systematically attempted, with the variables and results summarized in Table 1.2.

$\text{AlH}_3$ etherate was synthesized by the reaction of a stoichiometric amount of $\text{LiAlH}_4$ and $\text{AlCl}_3$ in diethyl ether according to Equation 2.1, followed by ether removal.
under vacuum without heat (Table 1.2 Reaction 19). The resulting white powder was then washed with diethyl ether to ensure the product was free of any excess LiAlH₄.

Verification of each sample was examined by powder X-ray diffraction measurements (XRD, PANalytical X'PERT-Pro with Cu Kα radiation and a semiconductor detector for high-speed measurements within 3 minutes). All samples were handled inside glove boxes circulating with nitrogen, helium, or argon atmospheres.

<table>
<thead>
<tr>
<th>Brower³⁰</th>
<th>[AlCl₃], (eq)</th>
<th>[LiAlH₄], (eq)</th>
<th>[LiBH₄], (eq)</th>
<th>Temp (°C)</th>
<th>Time (hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>alpha</td>
<td>1.0M (1)</td>
<td>1.0M (4)</td>
<td>1.0M (1)</td>
<td>65</td>
<td>6.5</td>
</tr>
<tr>
<td>beta</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>gamma</td>
<td>1.0M (1)</td>
<td>1.0M (4)</td>
<td>0</td>
<td>60</td>
<td>4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Matzek³¹</th>
<th>[AlCl₃], (eq)</th>
<th>[LiAlH₄], (eq)</th>
<th>[LiBH₄], (eq)</th>
<th>Temp (°C)</th>
<th>Time (hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>alpha</td>
<td>Not reported</td>
<td>Not reported</td>
<td>0</td>
<td>65</td>
<td>15</td>
</tr>
<tr>
<td>beta</td>
<td>Not reported</td>
<td>Not reported</td>
<td>Not reported</td>
<td>65</td>
<td>2</td>
</tr>
<tr>
<td>gamma</td>
<td>Not reported</td>
<td>Not reported</td>
<td>0</td>
<td>65</td>
<td>1</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Graetz²⁸</th>
<th>[AlCl₃], (eq)</th>
<th>[LiAlH₄], (eq)</th>
<th>[LiBH₄], (eq)</th>
<th>Temp (°C)</th>
<th>Time (hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>alpha</td>
<td>0.8M (1)</td>
<td>0.8M (4)</td>
<td>0.6M (2.1)</td>
<td>65</td>
<td>3</td>
</tr>
<tr>
<td>beta</td>
<td>0.8M (1)</td>
<td>0.8M (4)</td>
<td>0.6M (2.1)</td>
<td>65</td>
<td>0.75</td>
</tr>
<tr>
<td>gamma</td>
<td>0.8M (1)</td>
<td>0.8M (8)</td>
<td>0</td>
<td>60</td>
<td>2 to 4</td>
</tr>
</tbody>
</table>

Table 1.1 Summary of the differences in the literature procedures for making α-, β-, and γ-AlH₃, listing concentration and equivalents of reactants, and temperature and length of time of heating. Note that Brower et al. did not report a procedure for making the β-phase, and Matzek et al. did not provide information regarding quantities used.
<table>
<thead>
<tr>
<th>Reaction</th>
<th>[AlCl₃] (eq)</th>
<th>[LiAlH₄] (eq)</th>
<th>[LiBH₄] (eq)</th>
<th>Temp (°C)</th>
<th>Time (hr)</th>
<th>Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.0M (1)</td>
<td>1.0M (4)</td>
<td>0</td>
<td>-65</td>
<td>1</td>
<td>α/γ</td>
</tr>
<tr>
<td>2</td>
<td>1.0M (1)</td>
<td>1.0M (4)</td>
<td>0</td>
<td>-65</td>
<td>4</td>
<td>α</td>
</tr>
<tr>
<td>3a</td>
<td>1.0M (1)</td>
<td>1.0M (4)</td>
<td>0</td>
<td>-65</td>
<td>15</td>
<td>γ</td>
</tr>
<tr>
<td>3b</td>
<td>1.0M (1)</td>
<td>1.0M (4)</td>
<td>0</td>
<td>-65</td>
<td>15</td>
<td>α/γ</td>
</tr>
<tr>
<td>3c</td>
<td>1.0M (1)</td>
<td>1.0M (4)</td>
<td>0</td>
<td>-65</td>
<td>15</td>
<td>α</td>
</tr>
<tr>
<td>4</td>
<td>1.0M (1)</td>
<td>1.0M (8)</td>
<td>0</td>
<td>-65</td>
<td>1</td>
<td>amorph</td>
</tr>
<tr>
<td>5</td>
<td>1.0M (1)</td>
<td>1.0M (8)</td>
<td>0</td>
<td>-65</td>
<td>4</td>
<td>α</td>
</tr>
<tr>
<td>6</td>
<td>1.0M (1)</td>
<td>1.0M (8)</td>
<td>0</td>
<td>-65</td>
<td>15</td>
<td>α/γ</td>
</tr>
<tr>
<td>7a</td>
<td>0.8M (1)</td>
<td>0.8M (4)</td>
<td>0</td>
<td>-65</td>
<td>1</td>
<td>β</td>
</tr>
<tr>
<td>7b</td>
<td>0.8M (1)</td>
<td>0.8M (4)</td>
<td>0</td>
<td>-65</td>
<td>1</td>
<td>α</td>
</tr>
<tr>
<td>7c</td>
<td>0.8M (1)</td>
<td>0.8M (4)</td>
<td>0</td>
<td>-65</td>
<td>1</td>
<td>α</td>
</tr>
<tr>
<td>8</td>
<td>0.8M (1)</td>
<td>0.8M (4)</td>
<td>0</td>
<td>-65</td>
<td>4</td>
<td>α/γ</td>
</tr>
<tr>
<td>9</td>
<td>0.8M (1)</td>
<td>0.8M (4)</td>
<td>0</td>
<td>-65</td>
<td>15</td>
<td>amorph</td>
</tr>
<tr>
<td>10</td>
<td>1.0M (1)</td>
<td>1.0M (4)</td>
<td>1.0M (4)</td>
<td>-65</td>
<td>1</td>
<td>γ</td>
</tr>
<tr>
<td>11a</td>
<td>1.0M (1)</td>
<td>1.0M (4)</td>
<td>1.0M (4)</td>
<td>-65</td>
<td>4</td>
<td>α</td>
</tr>
<tr>
<td>11b</td>
<td>1.0M (1)</td>
<td>1.0M (4)</td>
<td>1.0M (4)</td>
<td>-65</td>
<td>4</td>
<td>α/γ</td>
</tr>
<tr>
<td>12</td>
<td>1.0M (1)</td>
<td>1.0M (4)</td>
<td>1.0M (4)</td>
<td>-65</td>
<td>15</td>
<td>α/γ</td>
</tr>
<tr>
<td>13</td>
<td>1.0M (1)</td>
<td>1.0M (8)</td>
<td>1.0M (8)</td>
<td>-65</td>
<td>1</td>
<td>amorph</td>
</tr>
<tr>
<td>14</td>
<td>1.0M (1)</td>
<td>1.0M (8)</td>
<td>1.0M (8)</td>
<td>-65</td>
<td>4</td>
<td>α/γ</td>
</tr>
<tr>
<td>15</td>
<td>1.0M (1)</td>
<td>1.0M (8)</td>
<td>1.0M (8)</td>
<td>-65</td>
<td>15</td>
<td>β/α</td>
</tr>
<tr>
<td>16a</td>
<td>0.8M (1)</td>
<td>0.6M (4)</td>
<td>0.8M (4)</td>
<td>-65</td>
<td>1</td>
<td>α</td>
</tr>
<tr>
<td>16b</td>
<td>0.8M (1)</td>
<td>0.8M (4)</td>
<td>0.8M (4)</td>
<td>-65</td>
<td>1</td>
<td>α/γ</td>
</tr>
<tr>
<td>17</td>
<td>0.8M (1)</td>
<td>0.8M (4)</td>
<td>0.8M (4)</td>
<td>-65</td>
<td>4</td>
<td>γ</td>
</tr>
<tr>
<td>18</td>
<td>0.8M (1)</td>
<td>0.8M (4)</td>
<td>0.8M (4)</td>
<td>-65</td>
<td>15</td>
<td>amorph</td>
</tr>
<tr>
<td>19</td>
<td>1.0M (1)</td>
<td>1.0M (3)</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>etherate</td>
</tr>
</tbody>
</table>

Table 1.2 Summary of reactions run in attempt to make α-, β-, and γ-AlH₃, listing reaction number, concentration and equivalents of reactants, temperature and length of time of heating, and primary resulting phase as verified via XRD (small amounts of other phases may be present, but not significant). Note that numerous reactions produced a mixed phase (almost equal amounts of two phases), and others produced an unknown amorphous phase (possibly AlH₃ etherate) indicated by the amorphous XRD pattern. Note also that some procedures were repeated, as indicated by the letter following the reaction number.
2.3 Results and Discussion

Following the procedures in the literature\textsuperscript{30,31,28} did not reliably yield the results as described. For example, when attempting to synthesize a specific polymorph, either a completely different phase was isolated, or a mix-phase of AlH\textsubscript{3} resulted. At the time of this study, other research groups were also attempting to reproduce the results reported by Brower,\textsuperscript{30} but to no avail. \(\beta\)-AlH\textsubscript{3} appears to be the most difficult to isolate, followed by \(\gamma\)-AlH\textsubscript{3}, and finally \(\alpha\)-AlH\textsubscript{3}. This could account for the reason why \(\alpha\)-AlH\textsubscript{3} has been the most extensively studied polymorph.\textsuperscript{28}

An attempt to develop a reliable method for synthesizing the various polymorphs was unsuccessful. For example, Table 1.2 Reaction 3 was repeated multiple times, each resulting in a different phase. It is possible that small impurities or inconsistent heating methods may affect the resulting phase. This suggests the polymorphs may have similar stabilities.

Although synthesized through an unreliable method, all three polymorphs were eventually isolated. The XRD profiles of \(\alpha\)-, \(\beta\)-, and \(\gamma\)-AlH\textsubscript{3} as prepared by Table 1.2 Reactions 5, 7, and 3, respectively, are shown in Figure 2.1. The profiles are well defined and identified to be the \(\alpha\)-, \(\beta\)-, and \(\gamma\)-phases, although a small amount of the \(\gamma\)-phase is coexisting in the \(\alpha\)-phase. The weak diffraction peaks of the \(\beta\)-phase might indicate the lack of long-range ordering of the crystalline structure. To the best of our knowledge, no other research group at the time of this study had been successful in making pure beta or gamma alane.

The XRD profiles of the mixed \(\beta/\alpha\)-AlH\textsubscript{3} as prepared by Table 1.2 Reaction 15, and etherated alane AlH\textsubscript{3}([(C\textsubscript{2}H\textsubscript{5})\textsubscript{2}O]) as prepared by Table 1.2 Reaction 19, are shown in
Figure 2.2. The XRD profile for the mixed phase clearly shows distinct peaks corresponding to both beta and alpha. However, the XRD of the etherated AlH$_3$ exhibits a few broad amorphous peaks but shows no indication of any crystalline phase, results that are consistent with the literature.$^{28}$

![XRD Profile](image)

Figure 2.1. Powder X-ray diffraction (XRD) profiles of the three phases of AlH$_3$. A small amount of the $\gamma$-phase is detected in the $\alpha$-phase. The broad hill in the 10-30 degree range is due to the glass plate used in the measurement.
Figure 2.2 Powder X-ray diffraction (XRD) profile for $\beta/\alpha$-AlH$_3$ on top (circles corresponding to beta and squares corresponding to alpha), and XRD for etherated AlH$_3$ (AlH$_3$·[(C$_2$H$_5$)$_2$O]) shown below. The broad hill in the 10-30 degree range is due to the glass plate used in the measurement.

2.4 Conclusion

A new method for reliably synthesizing the various phases of AlH$_3$ was not achieved. However, the $\alpha$-, $\beta$-, and $\gamma$- phases of AlH$_3$ were successfully synthesized and identified via XRD. The $\beta$-phase appears to be the most difficult polymorph to synthesize cleanly, and as a result, attempts at synthesizing additional samples of pure beta have been unsuccessful. The $\gamma$-polymorph is also difficult to isolate, but less so than the beta. Additional attempts at synthesizing $\gamma$-AlH$_3$ have been successful. $\alpha$-AlH$_3$ is the most readily isolated polymorph, a testament to its relative stability among the polymorphs (see Chapter 3).
The α-, β-, γ-, mixed β/α-, and etherated AlH₃ synthesized will be used in this thesis for additional analysis (i.e. thermogravimetry and differential thermal analysis (TG-DTA), differential scanning calorimetry (DSC), infrared spectroscopy (IR), Raman spectroscopy, neutron vibrational spectroscopy (NVS), and pressure-composition-temperature (PCT) analysis), in order to gain insights in the potential for AlH₃ to be used as a hydrogen storage material for vehicles equipped with hydrogen fuel cells.
CHAPTER 3
Intrinsic and Mechanically Modified Thermal Stabilities of Aluminum Hydride Polymorphs

3.1 Introduction

The thermodynamic parameters of aluminum hydride are, of course, key issues in considering its reversibility. However, only the α-polymorph has been studied extensively and, therefore, little is known about the other polymorphs and their properties. The thermal stabilities of the beta and gamma phases of AlH₃ have yet to be systematically reported, and few thermodynamic studies have been performed on the alpha phase.

The originally reported value of the enthalpy of dehydriding reaction \( \Delta H_{\text{dehyd}} \) of the alpha phase was 7.6 kJ/mole H₂ according to Equation 1.4, and thus indicated the thermal dehydriding reaction to be endothermic. The absolute value of \( \Delta H_{\text{dehyd}} \) is, however, so small that it has been expected to become negative (exothermic dehydriding reaction) for a high purity sample without forming surface oxide layers and also with keeping in an equilibrium condition during the dehydriding reaction. Although the alpha phase is “chemically” stable at room temperature against decomposition most likely due to the surface oxide layers, it seems to have very low thermodynamic stabilities under ambient conditions.

It is also predicated that the thermal stabilities might be affected by mechanical milling of AlH₃ due to modifications of the crystalline structures. Therefore, the intrinsic and mechanically modified thermal stabilities of the different phases of AlH₃ have been studied and will be described in this Chapter. This report provides fundamental
information that is required to determine the appropriate phases for the reversible dehydrogenation and rehydrogenation of AlH₃ under ambient conditions.

3.2 Experimental

Separate samples (100 mg) of α-, β-, and γ-AlH₃ and 20 steel balls were placed in separate steel vials. The vials were then mechanically milled by a planetary ball mill apparatus (Fritsch P7) at 400 rpm for 5 and 60 minutes.

The samples before and after mechanical milling were then examined by powder X-ray diffraction measurements (XRD, PANalytical X'PERT-Pro with Cu Kα radiation and a semiconductor detector for high-speed measurements within 3 minutes), thermogravimetric and differential thermal analysis (TG-DTA, Rigaku TG8120, heating rate with 5 K/min under a high purity-helium (>99.9999%) combined with a quadrupole mass spectrometer (Anelva M-QA200TS, with emission current at 1.0 mA and secondary electron multiplier at 1000V), and differential scanning calorimetry (DSC, Brucker-AXS PDSC 3100S, heating rate with 5 K/min under a high purity argon (99.9999%). All samples were handled inside glove boxes circulating with nitrogen, helium, or argon atmospheres.

3.3 Results and Discussion

Intrinsic Thermal Stability

Figure 3.1 presents the results of the TG-DTA under a helium flow of 150 cc/min. The TG profile of the α-phase indicates that the dehydriding reaction starts around 400 K and the dehydriding amount is found to be nearly 9 mass %, corresponding to 90% of the
ideal amount of 10.1 mass %. The TG profile of the γ-phase is similar to that of the α-phase. The β-phase, however, has a different TG profile showing a continuous dehydriding reaction starting at about 370 K. In the DTA profile of the α-phase, a single and large endothermic peak is observed at 420 to 450 K, following a small exothermic peak due to the transformation of the γ-phase (the second phases as indicated in Figure 3.1) into the α-phases. Some series of small endothermic peaks are detected at 380 to 440 K for the β-phase. Also, there are three steps for the dehydriding reaction in the γ-phase: i) the broad exothermic reaction at 380 to 425 K; ii) the sharp exothermic reaction at 430 K; iii) the successive endothermic reaction at 440 K. Judging from the rapid weight loss in the TG profile, the dehydriding reaction proceeds mainly during steps ii) and iii).

The XRD profiles obtained after the TG-DTA measurements are shown in Figure 3.2, and only metallic Al was detected in each phase. The mass spectrometer results performed after the TG-DTA measurements are shown in Figure 3.3. The data suggest that only H₂ is released in the α- and γ-phases during dehydrogenation (large peak corresponding to H₂ molecular ion of mass 2 atomic units, and minor peak corresponding to H⁺ fragment ion of mass 1 atomic unit). However, the mass spectrometer data of the β-phase indicates other impurities are evolved as well, one with a mass of 18 atomic units and another of 28 atomic units. These impurities possibly correspond to H₂O and N₂, respectively. It is unclear how these impurities arose in the β-phase. It is also unclear whether ether is contained in each phase (74 atomic units), as the mass spectrometer only analyzed up to 50 atomic units. However, the fragment ions of mass 45 and 29 atomic units expected from ether are absent.
Figure 3.1 Results of thermogravimetry and differential thermal analysis (TG-DTA) of the three phases of AlH₃: α-phase (solid line), β-phase (dotted line), and γ-phase (dashed line).

Figure 3.2 Powder X-ray diffraction (XRD) profiles of three phases of AlH₃ after TG-DTA shown in Figure 3.1. All phases change into metallic aluminum.
Figure 3.3 Mass spectrometry results of the gasses evolved from the three phases of AlH$_3$ after TG-DTA analysis shown in Figure 3.1. The $\alpha$- and $\gamma$-phases shown are unmilled. For the $\beta$-phase the solid lines, dotted lines, and broken lines correspond to unmilled, milled for 5 mins, and milled for 60 mins, respectively.
One of the important issues is to quantitatively determine the values of the enthalpies of dehydriding reactions $\Delta H_{\text{dehyd}}$ according to Equation 1.4. Figure 3.4 presents the results of the DSC under an argon flow of 500 cc/min. The reference used was the dehydriding reaction of Mg$_2$NiH$_4$ in which the hydrogen concentration was also precisely determined by the TG. The known $\Delta H_{\text{dehyd}}$ of Mg$_2$NiH$_4$ (64 kJ/mol H$_2$) was related to the area of the peak for Mg$_2$NiH$_4$ in Figure 3.4. This was then used to determine the values of the $\Delta H_{\text{dehyd}}$ for the $\alpha$- and $\gamma$-AlH$_3$. These values are summarized in Figure 3.5. Note that the value for the $\beta$-phase is an estimate based on the TG-DTA results. At the time of the study, there was an insufficient amount of $\beta$-AlH$_3$ for DSC analysis and repeated attempts at synthesizing pure beta were unsuccessful.

![Figure 3.4 Results of differential scanning calorimetry (DSC) of the two phases of AlH$_3$: $\alpha$-phase (solid line) and $\gamma$-phase (dashed line). The dehydriding reaction of Mg$_2$NiH$_4$ was used as a reference.](image)

Figure 3.4 Results of differential scanning calorimetry (DSC) of the two phases of AlH$_3$: $\alpha$-phase (solid line) and $\gamma$-phase (dashed line). The dehydriding reaction of Mg$_2$NiH$_4$ was used as a reference.
The α-phase shows an endothermic dehydriding reaction with $6.0 \pm 1.5 \text{ kJ/mol H}_2$. This value is consistent with the reported value of $7.6 \text{ kJ/mol H}_2$. In the case of the γ-phase, the value is only $1.0 \pm 0.5 \text{ kJ/mol H}_2$. Therefore, the γ-phase changes first into the α-phase by heating (possibly corresponding to the steps i) and/or ii), as seen in the DTA profile displayed in Figure 3.1), followed by the formation of metallic Al (step iii)). The value of $\Delta H_{\text{dehyd}}$ for the β-phase is roughly estimated from Figure 3.1 to be $-3 \sim -5 \text{ kJ/mol H}_2$, indicating the direct formation of metallic Al by heating.

**Mechanical Modification of Thermal Stability**

The milling-time dependent XRD profiles are shown in Figure 3.6. The dehydriding reaction of the α-phase is observed during mechanical milling, and only
metallic Al was detected after 60 minutes of milling. The dehydriding reaction was also observed for the γ-phase but the α-phase still remains after 60 minutes of milling. There is almost no change in the β-phase even after 60 minutes of milling.

![Figure 3.6 Powder X-ray diffraction (XRD) profiles of the three phases of AlH₃ before and after mechanical milling; α-phase (squares), β-phase (crosses), and metallic aluminum (circles). All other major peaks are due to the gamma-phase. The mechanical milling time is indicated on the figures.](image)

Figure 3.7 present the results of the milling-time dependences of the TG-DTA under a helium flow of 150 cc/min. For the α-phase, the start of the dehydriding temperature is drastically lowered from 400 K down to 350 K after 5 minutes of milling, and the corresponding endothermic reaction was detected in the DTA profiles. After 60 minutes of milling, neither weight loss nor thermal reaction was detected, due to the fact that metallic Al was already formed during milling. The similar tendency was observed in the γ-phase, although the α-phase that is derived form the γ-phase still remains after 60 minutes of milling. This indicates the simple act of milling, not doping introduced by milling as previously described by Sandrok et al., improves the decomposition kinetics of AlH₃. For the β-phase there is no drastic change in the TG-DTA results upon milling, results that are consistent with the XRD profile in Figure 3.6. However, the TG data in
Figure 3.7 indicates that milling reduces the weight % of H2 given off during dehydrogenation for all three phases.

The mass spectrometry data for the β-phase shown in Figure 3.3 also indicates that milling reduces the weight % of H2 released during dehydrogenation (note differences in solid lines, dotted lines, and broken lines for M2 which correspond to unmilled, milled for 5 mins, and milled for 60 mins, respectively). However, milling does not reduce the amount of impurities in the β-phase, as can be seen in the similarities in the unmilled and milled plots for M18 in Figure 3.2.

A schematic view of the mechanically modified thermal stabilities is seen in Figure 3.5, together with the values of the ΔHdehyd for the three phases of AlH3. The α-phase changes into metallic aluminum either upon heating or milling. The γ-phase is seen to initially undergo exothermic conversion to the stabilized α-phase either upon
heating or milling. The α-phase then undergoes endothermic dehydriding to metallic aluminum, as found for the original α-phase. The β-phase shows more specific behavior and undergoes exothermic dehydriding to metallic aluminum only upon heating, not upon milling. This implies that the β-phase is "chemically" stabilized by certain chemical species (possibly the impurities seen in Figure 3.3), and that these impurities are removed, not upon milling, but upon heating for the occurrence of the dehydriding reaction.

The systematic information on the thermodynamics of AlH₃ depending on both the intrinsic and mechanically modified crystalline structures is important to the search for phases that are suitable for the reversible dehydriding and rehydriding reactions of AlH₃ under ambient conditions.

3.4 Conclusion

The intrinsic and mechanically modified thermal stabilities of the three different phases of AlH₃ (α-, β- and γ-phases) have been experimentally determined. The TG profiles of the α- and γ-phases indicate that the dehydriding reaction starts around 400 and 370 K, respectively. The amount of hydrogen released was found to be nearly 9 mass %, corresponding to 90% of the ideal amount of 10.1 mass %. The β-phase, however, has a different TG profile showing the continuous dehydriding reaction, implying that the phase is "chemically" stabilized by impurities. The values of ΔH_{dehyd} are 6.0 ± 1.5, -3.5 and 1.0 ± 0.5 kJ/mol H₂ for the α-, β-, and γ-phases, respectively. The milling-time dependences of the powder XRD and TG-DTA indicate the occurrence of the dehydriding reaction of the α-phase (directly to the metallic Al) and γ-phase (first
forming the \( \alpha \)-phase, and then to metallic Al) during milling. The temperature at which dehydrogenation occurs for the \( \alpha \)- and \( \gamma \)-phase are drastically reduced by approximately 50 K upon milling, results that are similar to doping. There is no drastic change in the \( \beta \)-phase upon milling. This information about the dependence of the thermodynamics of AlH\(_3\) on both the intrinsic and mechanically modified crystalline structures should serve as an important guide for efforts to develop methods for the conversion of aluminum to AlH\(_3\).
CHAPTER 4
Infrared Spectroscopy of Aluminum Hydride Polymorphs

4.1 Introduction

A convenient, low-cost alternative to powder X-ray diffraction (XRD) for differentiating between the various polymorphs of AlH₃ is desired. Infrared (IR) spectroscopy has the potential to provide such an alternative. In addition, the spectroscopy data may assist in the structural determination of each polymorph.

4.2 Experimental

α-AlH₃ and γ-AlH₃ used in Chapter 3 (Table 1.2 Reactions 5 and 3, respectively) were examined in this study. β-AlH₃ used in Chapter 3 was exhausted, and therefore a mixed β/α-phase was used as a substitute (Table 1.2 Reaction 15). β- and γ-AlD₃ were synthesized with identical methods to Table 1.2 Reactions 11 and 2, respectively, with the exception of using LiAlD₄ instead of LiAlH₄ (see Appendix A). The AlH₃ etherate as prepared in Chapter 2 was also used. A small amount of each sample was ground with a mortar and pestle with KBr (previously heated to 120 °C for approximately 3 days to remove H₂O impurities) and pressed to form a KBr pellet for use with infrared (IR) spectroscopy (Nicolet, Nexus 470 FT-IR, ESP). All samples were handled inside glove boxes circulating with nitrogen, except during IR analysis.

4.3 Results and Discussion

Figure 4.1 presents the IR spectrum of α-AlH₃. The peak at 1735 cm⁻¹ is due to the Al—H stretch of the α-AlH₃. However, an additional peak appears at 1854 cm⁻¹. The
crystal structure of $\alpha$-AlH$_3$ contains only bridging hydrogens (see Appendix A) and, therefore, one would expect a single peak in this region. The peak at 1854 cm$^{-1}$ can be attributed to the Al–H stretch of AlH$_3$ etherate. This would indicate that the $\alpha$-AlH$_3$ used in this study is not entirely free of the diethyl ether solvent. Previous IR studies by Roszinski and Dautel came to similar conclusions.$^{37}$ The peak at 1854 cm$^{-1}$ also appears in the IR spectrum of AlH$_3$ etherate, AlH$_3\cdot[(C_2H_5)_2O]$ (Figure 4.6). Furthermore, the three peaks in Figure 4.1 around 2900 cm$^{-1}$ can be assigned to the C–H stretch of diethyl ether found in the AlH$_3$ etherate impurity, which is also found in the IR spectrum of AlH$_3$ etherate (Figure 4.6). The broad peak at 3421 cm$^{-1}$ in Figure 4.1 is due to the O–H stretch of H$_2$O found in the KBr pellet used in the IR analysis. Even though the amount of H$_2$O impurity was reduced by heating the KBr prior to making the pellet, a residual amount of water remained in the KBr. Additional peaks appear in the fingerprint region (889, 749, 669, and 458 cm$^{-1}$), which are unique and, therefore, can be used to discriminate between the phases.

Figure 4.2 presents the IR spectrum of $\alpha/\beta$-AlH$_3$. Although a large signal-to-noise ratio exists with little % transmittance, a better spectrum could not be obtained. A broad peak exists at 1680 cm$^{-1}$ likely due to the Al–H stretch of $\beta$-AlH$_3$, and an additional peak appears in the fingerprint region around 1075 cm$^{-1}$. The lack of clearly defined IR peaks for the $\beta$-phase indicates a lack of long-range ordering of the crystalline structure, similar to the XRD results in Chapter 2.3. Although no further structural information can be obtained from the data, the IR spectrum does appear different from the spectrum of the other polymorphs, which provides a useful means of differentiating between the phases.
Figure 4.3 presents the IR spectrum of $\beta$-AlD$_3$. The broad peak at 1191 cm$^{-1}$ can be assigned to the Al–D stretch of $\beta$-AlD$_3$. This is close to the expected value of 1208 cm$^{-1}$ based on the isotopic shift derived using Hooke's law, as shown in Equation 4.1, where $v$ is the frequency, $k$ is Hooke's law force constant, and $\mu$ is the reduced mass.

The broad peak at 3421 cm$^{-1}$ is due to the O–H stretch of H$_2$O found in the KBr pellet, and an additional peak is present in the fingerprint region at 679 cm$^{-1}$.

$$v_{\text{Al-H}}/v_{\text{Al-D}} = [1/2\pi(k/\mu_{\text{Al-H}})^{1/2}]/[1/2\pi(k/\mu_{\text{Al-D}})^{1/2}] \quad \text{(Eq. 4.1)}$$

$$v_{\text{Al-H}}/v_{\text{Al-D}} = [(\mu_{\text{Al-D}})^{1/2}]/[(\mu_{\text{Al-H}})^{1/2}]$$

$$\mu_{\text{Al-H}} = (m_{\text{Al}}m_{\text{H}})/(m_{\text{Al}}+m_{\text{H}}) = 0.964$$

$$\mu_{\text{Al-D}} = (m_{\text{Al}}m_{\text{D}})/(m_{\text{Al}}+m_{\text{D}}) = 1.862$$

$$v_{\text{Al-H}}/v_{\text{Al-D}} = [(1.862)^{1/2}]/[(0.964)^{1/2}] = 1.390$$

$$[v_{\text{Al-H}}]/[(v_{\text{Al-H}}/v_{\text{Al-D}})] = 1680 \text{ cm}^{-1}/1.390 = 1208 \text{ cm}^{-1}$$

Figure 4.4 presents the IR spectrum of $\gamma$-AlH$_3$. The strong peak at 1654 cm$^{-1}$ is due to the Al–H stretch of $\gamma$-AlH$_3$. The shoulder at approximately 1855 cm$^{-1}$ can be assigned to the Al–H stretch of AlH$_3$ etherate impurity similar to the spectrum of $\alpha$-AlH$_3$. However, an additional peak is present at 2064 cm$^{-1}$. This peak is most likely due to a higher energy Al–H stretch. This indicates that the structure of $\gamma$-AlH$_3$ may contain two types of hydrogens: bridging hydrogens similar to $\alpha$-AlH$_3$, which accounts for the lower energy stretch at 1654 cm$^{-1}$, and terminal hydrogens, which accounts for the higher energy stretch at 2064 cm$^{-1}$. The three peaks around 2900 cm$^{-1}$ are due to the C–H stretch of diethyl ether found in the AlH$_3$ etherate impurity. The broad peak at 3421 cm$^{-1}$ is due to the O–H stretch of H$_2$O found in the KBr pellet. The peaks in the fingerprint region of the spectrum for $\gamma$-AlH$_3$ (1388, 1218, 1015, 736, and 441 cm$^{-1}$) differ from the
fingerprint regions of the alpha, beta, and etherate. This may serve as an adequate means of discriminating among the polymorphs.

Figure 4.5 presents the results of the IR spectrum of $\gamma$-AlD$_3$. The peak at 1207 cm$^{-1}$ is likely due to the Al–D stretch of $\gamma$-AlD$_3$, in which the deuterium is bridging. This is close to the expected value of 1190 cm$^{-1}$ predicted by Equation 4.1. The additional Al–H stretch (terminal hydrogen) at 2064 cm$^{-1}$ in $\gamma$-AlH$_3$ (Figure 4.4) is expected to appear in the IR spectrum of the deuteride (Figure 4.5) around 1484 cm$^{-1}$ based on Equation 4.1. However, it appears the signal may have been lost due to background noise. A weak shoulder is present around 1325 cm$^{-1}$, which is likely due to the Al–D stretch of the AlD$_3$ etherate impurity. This is close to the expected value of 1333 cm$^{-1}$ predicted by Equation 4.1. The C–H stretch of diethyl ether is also present in the spectrum around 3000 cm$^{-1}$. The peaks in Figure 4.5 present at 1017 cm$^{-1}$ and 736 cm$^{-1}$ also appear in the IR spectrum of $\gamma$-AlH$_3$ (Figure 4.4), providing further evidence that the identity of the phase is gamma. An additional peak is present at 895 cm$^{-1}$, which is difficult to assign to any particular IR active mode. The broad peak at 3421 cm$^{-1}$ is due to the O–H stretch of H$_2$O found in the KBr pellet.

Figure 4.6 presents the IR spectrum of AlH$_3$ etherate, AlH$_3$[(C$_2$H$_5$)$_2$O]. The broad peak at 1841 cm$^{-1}$ is due to the Al–H stretch of the etherate. The three peaks around 2900 cm$^{-1}$ are due to the C–H stretch of diethyl ether found in the AlH$_3$ etherate. The broad peak at 3421 cm$^{-1}$ is due to the O–H stretch of H$_2$O found in the KBr pellet. Three additional peaks appear in the fingerprint region of the spectrum (1042, 900, and 506 cm$^{-1}$). The IR spectroscopy results are summarized in Table 4.1.
<table>
<thead>
<tr>
<th>Phase</th>
<th>( \alpha\text{-AlH}_3 )</th>
<th>( \beta/\alpha\text{-AlH}_3 )</th>
<th>( \beta\text{-AlD}_3 )</th>
<th>( \gamma\text{-AlH}_3 )</th>
<th>( \gamma\text{-AlD}_3 )</th>
<th>AIH (_3) Etherate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peaks (cm(^{-1}))</td>
<td>( 3421^K )</td>
<td>( 1680^\beta )</td>
<td>( 3444^K )</td>
<td>( 3421^K )</td>
<td>( 3421^K )</td>
<td>( 3421^K )</td>
</tr>
<tr>
<td></td>
<td>( 2925^E )</td>
<td>( 1075^\beta )</td>
<td>( 1191^\beta )</td>
<td>( 2924^E )</td>
<td>( 2924^E )</td>
<td>( 2977^E )</td>
</tr>
<tr>
<td></td>
<td>( 1854^E )</td>
<td>( 679^\beta )</td>
<td>( 2064^Y )</td>
<td>( 1207^Y )</td>
<td>( 2933^E )</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( 1735^a )</td>
<td>( 1854^E )</td>
<td>( 1017^Y )</td>
<td>( 2898^E )</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( 889^a )</td>
<td>( 1654^Y )</td>
<td>( 895^Y )</td>
<td>( 1841^E )</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( 749^a )</td>
<td>( 1388^Y )</td>
<td>( 736^Y )</td>
<td>( 1042^E )</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( 669^a )</td>
<td>( 1218^Y )</td>
<td>( 900^E )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( 458^a )</td>
<td>( 1015^Y )</td>
<td>( 506^E )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( 736^Y )</td>
<td>( 441^Y )</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 4.1 Summary of infrared spectroscopy results for the AlH\(_3\) polymorphs. The superscript indicates the likely origin of the peak (\( a \) for alpha, \( \beta \) for beta, \( \gamma \) for gamma, \( E \) for etherate, and \( K \) for KBr).

Figure 4.1 Infrared spectrum showing % transmittance versus wavenumbers (cm\(^{-1}\)) for \( \alpha\text{-AlH}_3\).
Figure 4.2 Infrared spectrum showing % transmittance versus wavenumbers (cm\(^{-1}\)) for mixed $\beta/\alpha$-AlH\(_3\).

Figure 4.3 Infrared spectrum showing % transmittance versus wavenumbers (cm\(^{-1}\)) for $\beta$-AlD\(_3\).
Figure 4.4 Infrared spectrum showing % transmittance versus wavenumbers (cm$^{-1}$) for $\gamma$-AlH$_3$.

Figure 4.5 Infrared spectrum showing % transmittance versus wavenumbers (cm$^{-1}$) for $\gamma$-AlD$_3$. 
4.4 Conclusion

The results of infrared spectroscopy have provided a convenient, low-cost means of differentiating between the AlH₃ polymorphs. By analyzing an unknown phase of AlH₃ by IR spectroscopy and comparing the collected data to Table 4.1, it is possible to determine the identity of the unknown. The agreement between the theoretical and experimental isotopic shifts for β-AlD₃ and γ-AlD₃ provides further support for the peak assignments for each.

The IR spectrum also indicates that γ-AlH₃ may contain bridging hydrogens, similar to α-AlH₃, but may also contain terminal hydrogens. Furthermore, the IR spectrum also indicates that β-AlH₃ may lack any long-range ordering of the crystalline structure, results that are consistent with XRD data.
 CHAPTER 5

Dehydrogenation and Rehydrogenation of Aluminum Hydride Polymorphs

5.1 Introduction

Although previous theoretical\textsuperscript{32} and experimental\textsuperscript{34} results indicate that AlH\textsubscript{3} cannot be rehydrogenated under ambient temperature and hydrogen-pressure conditions, these conclusions were based on the \textalpha\ polymorph and not the beta or gamma. As a result, this chapter attempts to determine whether the latter polymorphs can be rehydrogenated.

In 1997, Bogdanonic and Schwickardi reported that, upon doping with catalytic amounts of titanium, NaAlH\textsubscript{4} underwent a two-step reversible dehydrogenation reaction according to Equation 5.1 with markedly enhanced kinetics.\textsuperscript{33}

\begin{equation}
\text{NaAlH}_4 \leftrightarrow \frac{1}{3}\text{Na}_3\text{AlH}_6 + \frac{2}{3}\text{Al} + \text{H}_2 \leftrightarrow \text{NaH} + \text{Al} + \frac{3}{2}\text{H}_2 \quad \text{(Eq. 5.1)}
\end{equation}

The exact role that titanium plays in the reaction is unknown, yet it is currently under extensive investigation. The possibility that titanium dopants may affect the dehydrogenation and/or rehydrogenation of the AlH\textsubscript{3} polymorphs was also explored in this Chapter. In addition, the decomposition kinetics of \textalpha-, \textbeta-, and \textgamma-AlH\textsubscript{3} were compared.

5.2 Experimental

Separate samples (300 mg) of \textalpha-, \textbeta-, and \textgamma-AlH\textsubscript{3} synthesized from Table 1.2 Reactions 5, 7, and 3, respectively, were placed in specialized cylindrical reactors to be analyzed using a PCT (pressure-composition-temperature) automatic measuring system (PCT, SS-Type, Isuzu Seisakusho Co., LTD) at 393 K and approximately -0.069 MPa.
Dehydrogenation was followed by rehydrogenation at 10.22 MPa of H₂ at 298 K increased to 393 K. The procedure was then repeated with each polymorph doped with 2 mole % and 5 mole % titanium, mechanically milled with 7 steel balls in steel vials by a planetary ball mill apparatus (Fritsch P7) at 400 rpm for 20 minutes.

Pure metallic aluminum, aluminum doped with 2 mol % titanium, and aluminum doped with 5 mol % titanium were mechanically milled by a planetary ball mill apparatus at 400 rpm for 20 minutes, and run on the PCT at 10.35 MPa of H₂ at 298 K increased to 393 K. All samples were handled inside glove boxes circulating with nitrogen.

The PCT analysis measured either an increase or decrease in pressure versus time, corresponding to dehydrogenation and rehydrogenation. Solving for the number of moles of H₂ using the ideal gas law (PV=nRT) and the known values for pressure, volume, the gas constant R, and temperature, the weight % of H₂ released or absorbed versus time was determined.

5.3 Results and Discussion

Dehydrogenation

The results from the PCT data converted to weight % of H₂ are summarized in Figure 5.1. The dehydriding amount was found to be nearly 8.5 to 9 mass %, corresponding to 85 to 90% of the ideal amount of 10.1 mass % for α-, β-, and γ-AlH₃. This is in agreement with the TG data in Chapter 3.3. However, the amount of time required to achieve dehydrogenation varied. β- and γ-AlH₃ have similar dehydrogenation profiles. However, decomposition of the alpha phase was significantly slower than both beta and gamma. These results are consistent with the conclusions presented by Greatz.
and Reilly,\textsuperscript{28} which indicate that doping AlH\textsubscript{3} is unnecessary as previously describe by Sandrok et al.\textsuperscript{27} Addition of 2 and 5 mole \% titanium dopant had no effect on the dehydrogenation (Equation 1.4) for either \( \alpha \)-, \( \beta \)-, or \( \gamma \)-AlH\textsubscript{3}.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{isothermal_decomposition}
\caption{Isothermal decomposition profiles of \( \alpha \)-, \( \beta \)-, and \( \gamma \)-AlH\textsubscript{3} at 393 K plotted as weight loss of H\textsubscript{2} (mass \%) versus time (minutes).}
\label{fig:isothermal_decomposition}
\end{figure}

\textbf{Rehydrogenation}

Attempts at rehydrogenating \( \alpha \)-, \( \beta \)-, and \( \gamma \)-AlH\textsubscript{3} were unsuccessful, with and without titanium doping. Attempts at hydrogenating elemental aluminum were also unsuccessful.

\subsection*{5.4 Conclusion}

The dehydriding amount for \( \alpha \)-, \( \beta \)-, and \( \gamma \)-AlH\textsubscript{3} was found to be nearly 8.5 to 9 mass \%. The alpha phase appears to decompose the slowest, a testament to its relative stability among the polymorphs. Attempts at rehydrogenating \( \alpha \)-, \( \beta \)-, and \( \gamma \)-AlH\textsubscript{3}, and hydrogenating aluminum metal with and without titanium dopants were unsuccessful, results that are consistent with previous theoretical and experimental data.\textsuperscript{32,34}
Determining a means of rehydrogenating AlH₃ will be the greatest obstacle towards its use as a hydrogen storage material for use with hydrogen fuel cells onboard motor vehicles.
CHAPTER 6
Future Studies

The aluminum hydride polymorphs, α-, β-, and γ-AlH₃, have been characterized in this work. These results will enhance future studies in order to determine whether AlH₃ may be used as a hydrogen storage material for use with hydrogen fuel cells. However, the characterization of the remaining polymorphs (α', δ-, ε-, and ζ-AlH₃) will also be important in determining the usefulness of AlH₃. The structure determination of β- and γ-AlD₃ continues to be a focus of investigation, and it is likely that the structure determination of α', δ-, ε-, and ζ-AlH₃ will follow.

The greatest obstacle regarding AlH₃ will be identifying a means of hydrogenating aluminum in order to reform the hydride. Without such a reversible system, AlH₃ cannot be used as a hydrogen storage material onboard motor vehicles. However, AlH₃ may be used as a hydrogen source for low-powered devices where reversibility is not an issue, such as wrist watches. In fact, the Institute for Material Science Research at Tohoku University in Sendai, Japan is currently investigating AlH₃ for such use.
APPENDIX A

Crystal Structures of Aluminum Deuteride Polymorphs

A.1 Introduction

The crystal structure of $\alpha$-AlH$_3$ was first published in 1968 by Turley and Rinn. Powder X-ray (XRD) and neutron diffraction (PND) data for AlH$_3$ and AlD$_3$ were used to solve the structure. Both compounds crystallize in the trigonal space group R3c with six molecules in a hexagonal unit cell. Each aluminum is surrounded octahedrally by six hydrogens, three in the plane above and three in the plane below, and thereby participates in six three-center Al···H···Al bonds as shown in Figure A.1. Each aluminum-hydrogen bond is approximately 1.715 Å. Only bridging hydrogens are present.

The crystal structures of $\beta$- and $\gamma$-AlH$_3$ are presently unknown. In order to determine the structures of these polymorphs, $\beta$-AlD$_3$ and $\gamma$-AlD$_3$ must first be synthesized. X-ray diffraction cannot provide information of the location of the hydrogens due to the small size of the atom. Neutron diffraction, on the other hand, can give the locations, but only with the aluminum hydride isotope, AlD$_3$. 
Figure A.1 The six Al···H···Al bridges formed by the aluminum atom at $\frac{1}{2}, \frac{1}{2}, 0$, in the rhombohedral unit cell of $\alpha$-AlH$_3$. Numbers refer to twelfths of dimension $c$ of the hexagonal unit cell.

A.2 Experimental

AlD$_3$ was synthesized with similar methods as described in Chapter 2, with the exception of using LiAlD$_4$ instead of the hydride according to reaction A.1. Note, however, that an excess of LiAlD$_4$ was used, not a stoichiometric amount as Equation A.1 suggests.

$$3\text{LiAlD}_4 + \text{AlCl}_3 \rightarrow 4\text{AlD}_3 + 3\text{LiCl} \quad \text{(Eq. A.1)}$$

Each product was analyzed by powder X-ray diffraction and powder neutron diffraction (PUS diffractometer at the JEEP II reactor at Kjeller, Norway). All samples were handled inside glove boxes circulating with nitrogen, helium, or argon atmospheres.
A.3 Results and Discussion

Repeated attempts at synthesizing pure, unetherated AlD₃ polymorphs have been unsuccessful. The PND results indicate that a substantial amount of LiCl was present in the final product. It is possible that the metathesis reaction (Equation A.1) for the deuteride progresses at a slower rate than for the hydride. If this were true, the reaction may not have reached completion by the time the filtering took place. As a result, LiCl avoided filtration and was present in the final product. To circumvent this problem, a longer period of time (approximately 5 minutes) was allowed for LiAlD₄ and AlCl₃ to react to ensure the reaction had reached completion, and all of the LiCl had precipitated out before filtering. Additional PND results indicate that the amount of LiCl was greatly reduced.

However, an additional problem arose whenever LiBH₄ was used in the synthesis. (Note that it was unnecessary to substitute LiBD₄ for LiBH₄ as neither participates in the metathesis reaction (Equation A.1). The purpose is to stabilize the AlD₃ product while heating, and it is unlikely that hydride-deuteride transfer will occur.) The PND results identified boron atoms in the final product, which absorb neutrons and interferes with the analysis. As a result, the number of ether washes was increased in order to ensure the complete removal of LiBH₄. Additional PND results indicate the absent of LiBH₄ in the product.

Most recently, there have been difficulties with the complete removal of the solvent from the AlD₃ product. It is unclear why desolvation is more difficult with the deuteride, although the IR data (see Chapter 4.3) indicates that this may be occurring in the hydride as well. It is possible that the current heating method using a sand bath inside
the glove box is inadequate, and that heating with an oil bath outside the glove box may be necessary. It is also possible that during ether washes the etherate is reformed. This is difficult to correct due to the fact that the application of heat in an effort to remove the ether solvent will lead to AlD₃ decomposition, as excess LiAlD₄ is no longer present to stabilize the deuteride. A sample of AlD₃ was recently synthesized without washing and is currently awaiting PND analysis. In addition, the synthesis of additional AlD₃ polymorphs followed by PND analysis is currently underway with the hope that these AlD₃ samples will help determine the crystal structure of both β- and γ-AlD₃.

A.4 Conclusion

The crystal structures of β- and γ-AlD₃ have yet to be determined, although they are still under investigation. Based on the preliminary PND data, however, it is though that the structure of γ-AlD₃ may be Al(AlD₄)₃, although this conclusion has yet to be verified. It is hoped that the AlD₃ samples currently being analyzed via PND will verify the proposed structure. These crystal structures will aid the investigation of AlH₃ as a potential hydrogen storage material for use with hydrogen fuel cells.
APPENDIX B

Raman and Neutron Vibrational Spectroscopy of Aluminum Hydride Polymorphs

B.1 Introduction

In addition to infrared spectroscopy, Raman and neutron vibrational spectroscopy have the potential to provide a convenient, low-cost alternative to X-ray diffraction (XRD). The data in this Chapter offers two additional methods for differentiating between the various polymorphs of AlH₃.

B.2 Experimental

α-, mixed β/α-, γ-AlH₃, and etherated AlH₃ used in Chapter 5 were analyzed with Raman spectroscopy (Nicolet, Almega-HD, 532 nm-laser, 25mW, back scattering geometry), the spectrums being obtained by 5 readings at 10% power for 5 seconds. The α- and γ-phases were also analyzed with neutron vibrational spectroscopy (NVS, Filter-Analyzer Neutron Spectrometer using two monochromators, Cu(220) for energy transfers between 25 and 250 meV and pyrolytic graphite PG(002) for energy transfers between 4 and 45 meV. Two low-energy measurements were taken on the Fermi-Chopper Time-of-Flight Spectrometer using neutron energy gain with 6 Å (2.27 meV) incident neutrons).

B.3 Results and Discussion

Raman Spectroscopy

Figure B.1 presents the results of Raman spectroscopy for etherated AlH₃, α-AlH₃, γ-AlH₃, and β/α-AlH₃. For the etherate, the peaks at 3000 cm⁻¹ and 2920 cm⁻¹ likely correspond to the diethyl ether C—H stretches. In addition, the peaks at 1830 cm⁻¹
and 1710 cm\(^{-1}\) likely correspond to the Al—H stretch of the AlH\(_3\) etherate, the former being the same stretch that created the shoulder in the IR spectrum of \(\alpha\)- and \(\gamma\)-AlH\(_3\) (Figures 4.1 and 4.4, respectively) as discussed in Chapter 4. Additional peaks are present at 1450 cm\(^{-1}\) and 1080 cm\(^{-1}\), although it is difficult to assign these peaks to any particular Raman active mode.

The Raman spectrum of \(\gamma\)-AlH\(_3\) presented in Figure B.1 displays peaks at 2950, 1850, 1480, 1050, and 720 cm\(^{-1}\). The peak at 2950 cm\(^{-1}\) can be assigned to the diethyl ether C—H stretch in the AlH\(_3\) impurity. The peak at 1850 cm\(^{-1}\) is most likely due to the Al—H stretch of the AlH\(_3\) etherate impurity. The remaining peaks at 1480, 1050, and 720 cm\(^{-1}\) can be assigned to \(\gamma\)-AlH\(_3\), although it is difficult to assign these peaks to any particular Raman active mode.

The Raman peak assignment for \(\alpha\)-AlH\(_3\) is not as clear, due to the small impurity of \(\gamma\)-AlH\(_3\) as shown in Figure 2.1, the diethyl ether impurity, and the possibility that alpha and gamma share similar peaks. The Raman spectrum of \(\alpha\)-AlH\(_3\) (with \(\gamma\)-AlH\(_3\) impurity) presented in Figure B.1 displays peaks at 2100, 1850, 1480, 1050, 720, and 510 cm\(^{-1}\). Similar to the Raman spectrum of \(\gamma\)-AlH\(_3\), the peak at 1850 cm\(^{-1}\) is most likely due to the Al—H stretch of the AlH\(_3\) etherate impurity. The peaks at 1480 and 1050 cm\(^{-1}\) may be due to \(\alpha\)-AlH\(_3\) or the \(\gamma\)-AlH\(_3\) impurity. However, the strength of the signal at 720 cm\(^{-1}\) in the alpha spectrum, and the absence of peaks at 510 and 2100 cm\(^{-1}\) in the gamma spectrum imply that these peaks are due to pure \(\alpha\)-AlH\(_3\).

The Raman spectrum of the mixed phase \(\beta/\alpha\)-AlH\(_3\) presented in Figure B.1 displays peaks at 1850, 1480, 1120, 1050, 720, and 510 cm\(^{-1}\). By comparing the alpha spectrum to the mixed phase \(\beta/\alpha\)-AlH\(_3\) spectrum, it can be concluded that the peaks at
1480, 720, and 510 cm\(^{-1}\) are likely due to \(\alpha\)-AlH\(_3\). The peak at 1050 cm\(^{-1}\) may also be partially due to \(\alpha\)-AlH\(_3\). However, the strength of the signal at 1050 cm\(^{-1}\) implies that the peak is primarily due to \(\beta\)-AlH\(_3\). The absence of a peak at 1120 cm\(^{-1}\) in the alpha spectrum implies that this peak is due exclusively to \(\beta\)-AlH\(_3\). Again, the peak at 1850 cm\(^{-1}\) is most likely due to the Al–H stretch of the AlH\(_3\) etherate impurity. The Raman spectroscopy results are summarized in Table B.1.

![Raman spectra](image)

**Figure B.1** Raman spectra showing Raman intensity (arbitrary units) versus wavenumbers (cm\(^{-1}\)) for AlH\(_3\) etherate, \(\alpha\)-AlH\(_3\), \(\gamma\)-AlH\(_3\), and \(\beta\alpha\)-AlH\(_3\).
<table>
<thead>
<tr>
<th>Technique/Phase</th>
<th>α-AlH₃</th>
<th>β/α-AlH₃</th>
<th>γ-AlH₃</th>
<th>AlH₃ Etherate</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Raman peaks (cm⁻¹)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2100ἄ</td>
<td>1850Ե</td>
<td>2950Ե</td>
<td>3000Ե</td>
<td></td>
</tr>
<tr>
<td>1850Ե</td>
<td>1480፲</td>
<td>1850Ե</td>
<td>2920Ե</td>
<td></td>
</tr>
<tr>
<td>1480Svc or ṅ</td>
<td>1120Ѱ</td>
<td>1480Ѱ</td>
<td>1830Ե</td>
<td></td>
</tr>
<tr>
<td>1050_svc or ṅ</td>
<td>1050Ѱ</td>
<td>1050Ѱ</td>
<td>1710Ե</td>
<td></td>
</tr>
<tr>
<td>720ำ</td>
<td>720ำ</td>
<td>720Ѱ</td>
<td>1450Ե</td>
<td></td>
</tr>
<tr>
<td>510ำ</td>
<td>510ำ</td>
<td></td>
<td>1080Ե</td>
<td></td>
</tr>
<tr>
<td><strong>NVS peaks (cm⁻¹)</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1270</td>
<td>1077</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1170</td>
<td>1037</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1030</td>
<td>907</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>939</td>
<td>794</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>850</td>
<td>672</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>793</td>
<td>543</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>631</td>
<td>413</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>550</td>
<td>284</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>284</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table B.1 Summary of Raman and neutron vibrational spectroscopy results for AlH₃ polymorphs. The superscript indicates the origin of the peak (α for alpha, β for beta, γ for gamma, E for etherate, and K for KBr).

Neutron Vibrational Spectroscopy

Figure B.2 presents the preliminary results of the neutron vibrational spectroscopy (NVS) for α- and γ-AlH₃; additional NVS data collection is currently underway. At this time, no structural information can be deduced from the spectra. However, there is a significant difference between the alpha and gamma spectra, which can be used as a means of differentiating between the phases. α-AlH₃ displays peaks at 35, 68, 78, 98, 105, 116, 127, 145, and 157 meV corresponding to 284, 550, 631, 793, 850, 939, 1030, 1170, and 1270 cm⁻¹. γ-AlH₃ displays peaks at 35, 51, 67, 83, 98, 112, 128, and 133 meV.
corresponding to 284, 413, 543, 672, 794, 907, 1037, and 1077 cm\(^{-1}\). Theses results are summarized in Table B.1. Additional AlH\(_3\) samples are currently being analyzed.

![Graph showing neutron counts versus neutron energy loss (meV) for α- and γ-AlH\(_3\).](image)

**Figure B.2** Neutron vibrational spectroscopy (NVS) showing neutron counts versus neutron energy loss (meV) for α- and γ-AlH\(_3\).
B.4 Conclusion

Raman and neutron vibrational spectroscopy data has provided an additional convenient, low-cost means of differentiating between the AlH₃ polymorphs. By analyzing an unknown phase of AlH₃ by one of the above spectroscopy techniques, and comparing the collected data to Table B.1, it is possible to determine the identity of the unknown. Even though the lack of purity of the α- and β-phases did not allow for clear assignment of every peak, the data presented in this study provides a sufficient number of assignments, which will allow for an unambiguous identification of an unknown phase.
REFERENCES


27. Sandrock, G; Reilly, J; Graetz, J; Zhou, W; Johnson, J; Wegrzyn; J. Appl. Phys. A. 2005, 80, 687.


