

THE CRYSTAL CHEMISTRY AND HYDROGEN STORAGE PROPERTIES OF LIGHT METAL BOROHYDRIDES

A thesis submitted to the University of Oxford for the degree of
Doctor of Philosophy

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The work described in this thesis was carried out in the Inorganic Chemistry Laboratory, University of Oxford from October 2009 until May 2013, under the supervision of Professor Bill David and Professor Peter P. Edwards. All of the work is my own unless otherwise stated, and has not been previously submitted for an degree at this or any other university.

Scott D. Culligan

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To my parents,



who taught me the most important lessons
not by telling, but by showing.

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The Crystal Chemistry and Hydrogen Storage Properties of Light Metal Borohydrides

Scott D. Culligan

Submitted for the degree of Doctor of Philosophy

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Abstract

This work examines various light metal borohydrides, particularly those formed from group II metals, with the aim of understanding their fundamental physical properties and improving their hydrogen storage ability. The structure of a new phase (γ) of $\text{Mg}(\text{BH}_4)_2$ is reported and the decomposition is fully characterized in a combination of diffraction and thermogravimetric studies. The bulk properties of $\gamma\text{-Mg}(\text{BH}_4)_2$ are compared to those of an SiO_2 isostructure and probed by various neutron scattering techniques. Negative thermal expansion is observed at low temperatures and the material absorbs up to 1.5 moles of hydrogen gas to form one of the most gravimetrically hydrogen-dense materials ever reported. The structural evolution of $\text{Ca}(\text{BH}_4)_2$ under different synthetic conditions and external influences (e.g. temperature) is studied up until the material decomposes. The effects of various additives on group II metal borohydrides are also examined and the influence of each is justified by observing subtle structural changes in the mixed system via *in situ* synchrotron X-ray powder diffraction and ^{11}B NMR measurements.

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Extended Abstract

Chapter 1 provides a general introduction to the hydrogen economy and outlines the key technological barriers that currently inhibit widespread adoption of hydrogen energy stores. The pros and cons of various hydrogen storage systems are discussed and a review of metal borohydrides, which are the focus of this thesis, is presented.

In Chapter 2, the synthetic and characterization techniques used in this thesis are discussed. Details of the instrumentation and conditions used in all syntheses and experiments are provided. Background theory of analytical techniques (such as diffraction and vibrational spectroscopy) is also discussed where relevant.

A new phase (γ) of $\text{Mg}(\text{BH}_4)_2$ is reported in Chapter 3 and characterized using synchrotron X-ray powder diffraction by direct comparison with an SiO_2 isostructure. The structure of $\gamma\text{-Mg}(\text{BH}_4)_2$ is unlike any other borohydride previously observed and contains large pores along the $[\text{h},\text{k},\text{l}] = [\pm 1, \pm 1, \pm 1]$ directions. The structural evolution of the material with temperature is examined in a combination of *in* and *ex situ* variable temperature X-ray diffraction studies through decomposition (up to 750 K). The short and long range order in $\gamma\text{-Mg}(\text{BH}_4)_2$ are studied using Pair Distribution Function analysis and

compared to that of known phases. Solution and solid state ^{11}B NMR measurements reveal the formation of polyborane species upon decomposition and a mechanism for hydrogen release is hypothesized based on correlation to the thermogravimetric profile of the material.

Various neutron scattering techniques are utilized to study the properties of $\gamma\text{-Mg}(\text{BH}_4)_2$ resembling those of SiO_2 on a fundamental physical level. The crystal structure of the material is refined from high resolution powder neutron diffraction on $\gamma\text{-Mg}(^{11}\text{BD}_4)_2$ at 4 K and isotropic negative thermal expansion is observed in the material up until 190 K. The unit cell behaviour is simulated using a Debye-Einstein model of the phonon density of states and an excellent fit to the experimental data is produced. The vibrations of both $\gamma\text{-Mg}(^{11}\text{BH}_4)_2$ and $\gamma\text{-Mg}(^{11}\text{BD}_4)_2$ are probed directly using Inelastic Neutron Spectroscopy and compared to DFT calculations of the full phonon density of states. An excellent match between the two is achieved and a rigid unit mode responsible for negative thermal expansion in the material is observed near the energy predicted by the Debye-Einstein model of the variable temperature diffraction data.

The ability of $\gamma\text{-Mg}(^{11}\text{BD}_4)_2$ to adsorb hydrogen into its pores is examined in both neutron spectroscopic and diffraction studies. The material reversibly takes up to nearly 1.5 moles of hydrogen gas below about 50 K and a small amount still remains even near room temperature. $\text{Mg}(\text{BH}_4)_2 \cdot 1.5\text{H}_2$ is one of the most hydrogen-dense solid state stores ever reported, with 19.5 wt. % contained in the material (about 5% of which is physisorbed). The quantum dynamics of hydrogen adsorbed into the system are studied by comparing INS spectra of the material with different spin states of H_2 and HD adsorbed. The studies reveal that the potential of the hydrogen site lies between that of a harmonic and flat potential well. Diffraction studies reveal that adsorbed hydrogen occupies the 32e symmetry site and forms long chains along the pore channels of the

γ -Mg(BH₄)₂ framework.

In Chapter 5, Ca(BH₄)₂ that has been synthesized both in house and by Sigma Aldrich is structurally characterized in a series of measurements. The phase composition of Ca(BH₄)₂ is found to be very sensitive to the synthetic and experimental conditions used when preparing the material. A second order ferroelastic transition of the α -phase is observed as the sample is heated and a first order transition to the β -polymorph is reported just below 500 K. *In situ* NMR, X-ray diffraction and thermogravimetric analyses allow the sample to be characterized up until melting and decomposition. The polymorphism in Ca(BH₄)₂ is compared to that of TiO₂ and stability of the individual phases is rationalized based on Pauling's 3rd rule.

Lithium and sodium borohydride are characterized in Chapter 6 and their effects on Ca(BH₄)₂ are studied. The superionic transition in LiBH₄ causes the transition to a metastable Ca(BH₄)₂ phase and a eutectic melting is observed at a lower temperature than that of either parent compound. A explanation is provided based on a Li ion insertion mechanism into the Ca(BH₄)₂ framework by analogy with Li insertion into TiO₂. Further evidence of a mixed phase is provided by *in situ* ¹¹B NMR measurements. The low temperature order-disorder transition in NaBH₄ is characterized by high resolution neutron powder diffraction on the isotropically enriched compound. The high stability of the high temperature phase means that it does not appear to interact with Ca(BH₄)₂ when the two are milled together and heated. It is reported that the addition of LiNH₂ to either Mg(BH₄)₂ or Ca(BH₄)₂ lowers the decomposition temperature and increases the amount of gas released, but also causes large amount of ammonia to be formed.

Finally, in Chapter 7, the key findings presented in this thesis are summarized. The impacts of this research are discussed in the context of potential for

hydrogen storage application in industry. Suggestions for further experiments are given and the scope of the technological hurdles that remain for borohydrides as hydrogen stores is addressed.

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Chapter 1

Introduction

1.1 The Energy Economy Outlook

Over the past several decades, the global energy economy has existed in a state of flux. Increased threats of oil insecurity, rising fossil fuel prices, and growing concerns about their effects on earth's climate have led to the emergence of a new energy economy. The shift from traditional energy sources such as oil and coal toward renewable sources such as wind, solar, and geothermal is happening at an ever-increasing pace. In the 2012 BP Energy Outlook 2030[1], it is predicted that renewable energy production will continue to grow indefinitely, and will make up over 5% of global energy production by 2030 (see Fig. 1.1.1).

As wind and solar photovoltaic (PV) energies become more widespread, a new technological hurdle has developed. Unlike other forms of primary energy, the supply generated by wind and solar PV is intermittent. The oscillatory nature of these technologies makes their integration into a power grid challenging and complexifies the widespread adoption of wind and solar PV as primary energy sources. At present, the most viable solution to the problems posed by

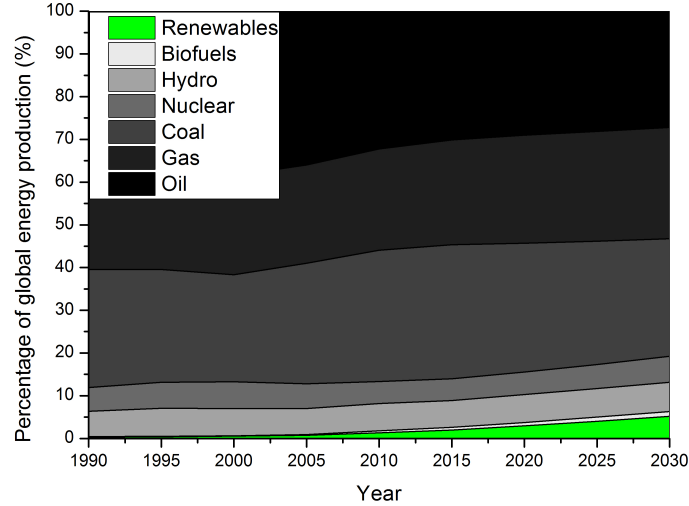


Figure 1.1.1: Global energy output mix projections from the 2012 BP Energy Outlook 2030 report. Renewable energy sources are expected to grow continually over the next few decades.

this intermittency is a credible form of energy storage. Until a safe, efficient and affordable energy store is found, fluctuating renewables will struggle to become viable players in the move toward CO₂-free energy sources[2].

Despite considerable efforts, no clear storage solution has emerged from the research community. A recent analysis[3] of the business case for various storage applications suggests that a mix of various technologies will be required. Of the various technologies identified in the study, stationary batteries are believed to be the most promising and will become increasingly important due to their flexibility, particularly in decentralized applications. Hydrogen storage is especially considered to be a key technology in the future storage economy due to its potential to store large amounts of energy and increased operational efficiency. It is projected that hydrogen storage may begin replacing more traditional methods, such as compressed-air energy storage and pumped hydro, as

early as 2020[3].

1.1.1 The Hydrogen Economy

At a glance, hydrogen appears to be an ideal alternative to fossil fuels. The use of hydrogen as a vector to store and transport energy could potentially lower dependence on foreign oil, reduce air pollution, and slow the build-up of greenhouse gases. Hydrogen is the most abundant element on earth and, as a constituent of water, is found all around the earth. Hydrogen is also an extremely clean burning fuel. When oxidized in a fuel cell, it emits no harmful pollution and, pound for pound, releases more energy than any other fuel. As a result, both industry and governments across the globe have invested billions of dollars in an attempt to realize a hydrogen economy[4].

The success of stationary batteries, and hydrogen storage in particular, on an economic scale will rely heavily on the development of affordable technologies. Current energy infrastructure is so vast, that substantially more investment is needed if hydrogen technology is to compete with fossil fuels. However, as Robert Service pointed out in *Science* [5], despite substantial political and economic difficulties, the most glaring problems remain technical.

1.2 Hydrogen Production

Firstly, we currently do not have a cheap and sustainable way to source hydrogen. While hydrogen remains the most common element on earth, most of it exists chemically bonded to other elements. As such, hydrogen must be split off these molecules to generate dihydrogen (H_2) gas, which is then combined with oxygen in a fuel cell to liberate electricity and form water in the process. However, each time fuel is converted from one source to another, energy input

Criterion	Units	2010	2015	Ultimate
Gravimetric Capacity	wt. % usable H ₂	4.5	5.5	7.5
Volumetric Capacity	kg usable H ₂ L ⁻¹	0.028	0.04	0.07
Max/Min Operating Temp	°C	50/-30	60/-40	60/-40
System Filling Time (5 kg H ₂)	Minutes	4.2	3.3	2.5
Purity	% H ₂	99.97	99.97	99.97

Table 1.1: Revised U.S. Department of Energy criteria for a viable hydrogen storage technology[7]

(and therefore money) is required. Currently, a large majority of hydrogen is produced from dry methane reformation, in which natural gas is split into H₂ and CO₂. As renewable energy sources become cheaper and more efficient, electrochemically splitting water, using solar or wind energy for example, may become a more attractive option to produce H₂ without the greenhouses gas emissions.

1.3 Hydrogen Storage

Secondly, and of particular importance to the automotive industry, is the challenge of how to best store hydrogen. It is generally believed that consumers will not accept lower performance hydrogen cars compared to their fossil fuel equivalents. In 2003, the U.S. Department of Energy (DOE) examined current performance levels to develop a set of criteria that need to be met for hydrogen storage to be considered as a replacement[6]. The targets were revised in 2009[7], and are the generally accepted set of goals for driving range, time to refuel, durability, affordability and safety that need to all be realized by a single technology to viably replace fossil fuels (see Table 1.1).

Many different systems have been studied in an attempt to solve the hydrogen storage problem and the field is vast. Broadly, there are three categories of research, which are each discussed in more detail below: physical containment, physisorption, and chemical bonding.

1.3.1 Physical Containment

Physical containment of hydrogen simply involves the liquification or compression of hydrogen gas. The advantage to this form of storage is that hydrogen fuel is immediately available to be consumed in a fuel cell. DOE prototype cars have used hydrogen stored in gas cylinders at up to 700 bar however, the low energy content by volume means that this form of storage will be unable to meet the DOE's ultimate targets, even when the mass of the containment system is ignored[8]. Liquifaction, on the other hand, is able to meet volumetric DOE targets (ignoring the size of the container). However, this requires cooling H_2 to 20K which, in turn, requires a substantial energy investment (about 30% of the fuel's energy is consumed in this process)[9]. Most recently, cryo-compression has been viewed as a potential alternative. The technology involves fueling with either liquid hydrogen or compressed H_2 gas at low temperatures, allowing for increased flexibility on the user end. While promising, volumetric capacities are still below DOE targets and the cost of liquefying H_2 and the tanks themselves is still too high[10].

1.3.2 Physisorption

Physisorption involves storing hydrogen by weakly binding it to a surface or on the inside of a solid. In this case, the H_2 molecules remain intact and are held in place by weak van der Waals forces. As the systems required for this type of interaction are highly porous, the most widely investigated systems have been metal-organic frameworks (MOFs), zeolites, activated carbon, carbon nanostructures and tailored organic polymers[11, 12].

Both zeolites and MOFs are made up of a series of interconnected frameworks that form an overall structure containing ordered networks of pores and channels. Gas molecules can diffuse into and out of the empty space present in the structure, which can often be controlled by varying temperature and/or

pressure[13]. The use of these materials as gas stores is by no means limited to hydrogen and they have also been shown to adsorb an array of molecules such as CO_2 and CH_4 [14].

Carbon hosts, such as nanostructured graphite and carbon nanotubes, initially were reported to produce widely varying and often irreproducible hydrogen storage capacities[15]. Initial experimental results varied between 0 wt % and 10 wt%, likely due to the small sample sizes used and concomitant adsorption of other species such as water. Today, typical reported capacities range between 1 wt% to 2.4 wt% at cryogenic temperatures, however bundling single walled nanotubes has produced up to 8 wt% storage potential under 40 bar hydrogen at 80 K. A large study of carbon nanofibres between 0.1 bar and 105 bar and 77 K and 295 K found a maximum potential of 0.7 wt% H_2 at 105 bar, suggesting that carbon nanofibres are an unlikely solution to the hydrogen storage challenge[12].

As the enthalpy change associated with the physisorption of such gases is relatively small (4-10 kJ mol^{-1}), adsorption of host molecules into these systems is typically fast and reversible. However, the entropy contribution of H_2 at room temperature is much higher (nearly 40 kJ mol^{-1}), so these systems are generally impractical because they need to either be cooled to approximately 77 K or stored at high pressures to overcome this entropy barrier.[16] To increase adsorption temperature and/or hydrogen capacity, attempts to increase the enthalpy of adsorption have been made by introducing groups into the host that have a higher affinity for H_2 . For example, by doping boron into nanoporous carbon or introducing lithium into MOFs, higher storage capacities have been achieved[17]. However, this can often involve H_2 dissociating into hydrogen atoms, moving these types of physisorbed systems more into the third broad category of hydrogen storage research discussed here (chemisorption).

Other attempts to blur the boundaries between physisorption and chemisorption have also been made. A 2011 study[18] attempted to bond various cationic species to the pore wall of a range of anionic MOFs. These cations then acted as a gate to control hydrogen and nitrogen flow into and out of the host species, thereby combining physisorption and chemisorption processes. Yet, despite considerable advancements in this field, no physisorption systems currently meet the targets set out by the DOE[19].

1.3.3 Chemically Bound Hydrogen Stores

Chemically storing hydrogen involves forming a chemical hydride by binding hydrogen in a solid. During the absorption process, hydrogen is chemisorbed to the material surface and then absorbed into the bulk material[11]. The problems that plague physisorbed systems tend to be different than the challenges faced in chemisorbed systems. Firstly, solid state hydrogen stores typically have the highest gravimetric densities, with many compounds falling within DOE targets. However, the scope for tailoring these materials is limited to rather light elements. Simple atomic-mass-based considerations limit chemists to only low atomic number elements if DOE criteria are to be met. Heavier elements may be included in small, catalytic amounts but, generally speaking, only approximately the first 20 elements of the periodic table can make up the majority of a good hydrogen storage material. The toxicity and/or unfavourable chemical properties of certain light elemental hydrides (e.g. Be, P, etc.) impose additional constraints on the components of a feasible hydrogen storage material[20].

Secondly, reversibility of chemical stores can often pose a large problem. It is necessary that hydrogen be released from a given store without too much difficulty however, this often comes at the price of difficult re-fueling[6]. Most hydrides are in fact either too stable, such that absorption is easy but desorption requires high temperatures, or too unstable, requiring high hydrogen pressures

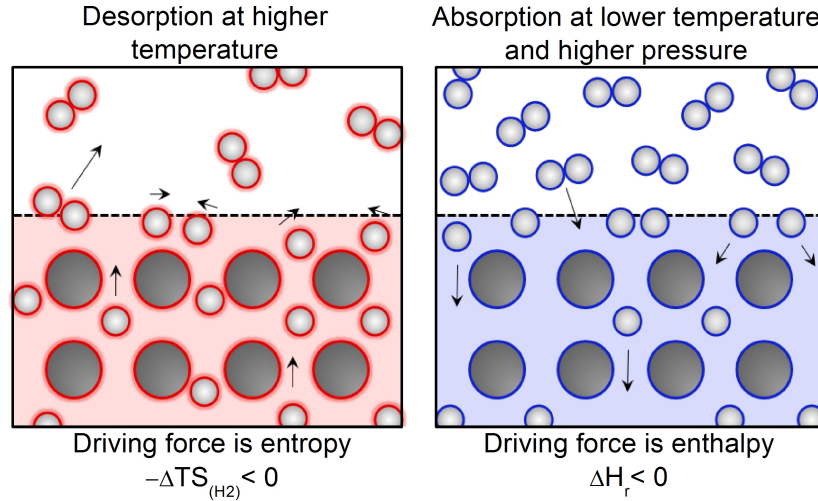


Figure 1.3.1: Ideal hydrogen desorption and absorption in chemical hydrides. Entropy drives H_2 desorption at high temperatures (left), while at lower temperatures and higher pressures, hydrogen absorption is driven by enthalpy (right).

for absorption but desorbing readily at or below ambient temperature[20].

Furthermore, while exposing many solid state stores to moisture and/or oxygen often liberates large amounts of hydrogen, the reaction products (e.g. oxides, hydroxides, borates, etc.) are very thermodynamically stable. Converting these compounds back to their parents hydrides is complicated and, consequently, too energy/cost intensive. The system is governed by the equation for Gibb's Free Energy:

$$\Delta G = \Delta H - T\Delta S \quad (1.3.1)$$

As a result, the widespread approach has been to heat a given store to release hydrogen, a reaction which is driven by entropic contributions. Attempts to balance the thermodynamics are then made such that, At lower temperatures and higher pressures, enthalpy then drives the hydrogen re-absorption, thus producing a reversible system (see Fig. 1.3.1). Despite decades of research, even the most attractive stores have a decomposition temperature that is too

high or absorption temperatures and pressures that are outside of the DOE criteria[6].

In general, there are four broad classes of solid state chemical hydrides; interstitial hydrides, covalent hydrides, molecular hydrides and ionic/complex hydrides.

1.3.3.1 Interstitial Hydrides

An interstitial metal hydride is formed when hydrogen atoms are absorbed into a metal (or metal alloy) and occupy the interstitial sites in the metal crystal structure. The crystal structure of the metal is often retained, though it may expand to accommodate the extra hydrogen atoms. Single metal interstitial hydrides are found most commonly amongst the transition metals and are often non-stoichiometric (e.g. $\text{TiH}_{1.7}$).

Metal alloy interstitial hydrides became popular due to their favourable reversibility[9]. By combining a weakly hydriding metal (e.g. Ni) with a strongly hydriding metal (e.g. La), an alloy is formed that will easily store hydrogen and release it at a relatively low temperature. For example, LaNi_5 absorbs hydrogen at a pressure of less than 2 bar to form $\text{LaNi}_5\text{H}_{6.5}$ and desorbs at around room temperature. The drawback to most interstitial hydrides is that, since they contain heavier metal elements, gravimetric hydrogen capacities tend to be less than 2%, far below what is required to meet DOE targets[21].

1.3.3.2 Covalent Hydrides

Certain transition metals and group II metals with high electronegativity are able to form covalent hydrides. These are continuous structures, containing stoichiometric amounts of hydrogen bonded to one or more metal atoms. The sorption processes in these materials typically occur in multiple steps. For example, absorption in MgH_2 occurs when hydrogen is physisorbed on the metal surface, where it dissociates into hydrogen atoms. The atoms are then chemisorbed onto

the surface before diffusing into the bulk to form a hydride. For desorption, the reverse of this process takes place[22]. The problem with covalent hydrides is that they tend to desorb hydrogen at relatively high temperatures and the kinetics of the process are relatively sluggish (though ongoing research attempts to find catalysts/additives to improve this)[23, 24].

1.3.3.3 Molecular Hydrides

A compound may be classified as a molecular hydride when its solid state structure is built from discrete molecules. The most widely studied material in this class is ammonia borane (NH_3BH_3), which has received a considerable amount of attention in recent years due to its extremely high gravimetric hydrogen content (19.6 wt% H_2) and relatively low decomposition temperature (*ca.* 100 °C)[25]. In the solid state, the compound is made up of a 3D network of acidic N-H and protic B-H groups, which are stabilized by N-H...H-B proton-hydride interactions. These interactions dominate the physical and chemical properties of the compound and were historically believed to play a key role in the mechanism and thermodynamics of hydrogen evolution. The decomposition route in the material is complex, and intermediates such as polyaminoborane ($(\text{NH}_2\text{BH}_2)_n$), polyiminoborane ($(\text{NH}_2\text{BH}_2)_n$), and borazine ($(\text{N}_3\text{B}_3\text{H}_6)$) have all been observed. Most recently, it was reported that decomposition proceeds via disruption of the proton-hydride bonding during an induction period which then leads to the formation of a mobile phase and subsequently converts to the diammoniate of diborane ($[\text{NH}_3\text{BH}_2\text{NH}_3]^+[\text{BH}_4]^-$). This ionic material then reacts with NH_3BH_3 to liberate H_2 in a bimolecular process[26].

Research to suppress the formation of borazine and improve decomposition kinetics of ammonia borane has led to the development of alkali metal amidoboranes such as LiNH_2BH_3 (10.9 wt% H_2) and NaNH_2BH_3 (7.5 wt% H_2). While these materials release hydrogen at 90 °C, the dehydrogenation reaction is still

not readily reversible[27]. While it was long believed that protic-hydridic interaction were responsible for hydrogen evolution in these systems, recent research suggests that homopolar $\text{B-H}^{\delta-}\cdots\delta^-\text{H-B}$ may play an important role in decomposition and that $\text{N-H}^{\delta+}\cdots\delta^+\text{H-N}$ interactions contribute to the overall stability of the crystalline structure in both ammonia borane[28] and alkali metal amidoboranes [29].

1.3.3.4 Ionic & Complex Hydrides

When heated in the presence of hydrogen, group I and less electronegative group II metals form ionic hydrides, where hydrogen within the structure exists as H^- . Ionic hydrides react readily with water and may only be used in moisture-free conditions. Ionic metal hydrides may possess high hydrogen densities, but generally have melting temperatures that are much too high to be of practical use as a hydrogen store. As with other hydrides, most current research efforts attempt to destabilize the decomposition process by reducing particle size (through mechanochemical milling or integration into nanoporous scaffolds), or mixing with additives to form binary hydrides and other alloys[30].

A second class of ionic hydrides are formed by the group I and II salts of $[\text{AlH}_4]^-$, $[\text{NH}_2]^-$, and $[\text{BH}_4]^-$, called alanates, amides, and borohydrides, respectively. These materials are commonly referred to as “complex hydrides”, though only alanates truly contain anionic metal complexes. The origin of the terminology in amines and borohydrides derives from hydrogen being covalently bonded to central atoms in “complex” anions[31]. One attractive aspect of complex hydrides is that many are already used in industry, making them readily available. Many complex hydrides also fall well above the DOE targets for gravimetric capacity though many of these systems are plagued by high desorption temperatures (defined as the first peak observed in the thermal desorption profile of a given borohydride[32]) and/or kinetic barriers to rehydrogenation in the solid

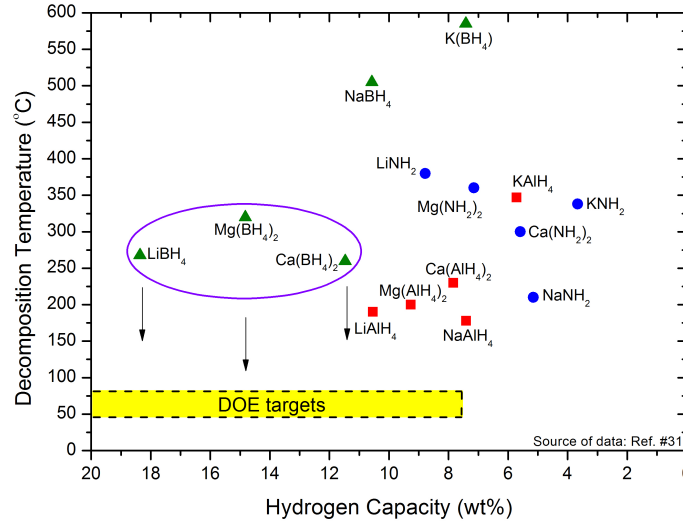


Figure 1.3.2: The material properties of group I and group II complex hydrides (data used was obtained from: Ref[31]). This thesis focuses particularly on high hydrogen capacity metal borohydrides (those circled in purple). Attempts are made to destabilize such borohydrides, thereby lowering their decomposition temperature to meet DOE targets (as indicated by the arrows above).

state (see 1.3.2).

Until the late 90's, these systems were considered impractical as rechargeable hydrogen carriers, though were considered as viable 'one shot' stores. At that time, it was reported that doping alanates with titanium based compounds could enhance the kinetics of dehydrogenation and make the reaction reversible under mild conditions[33]. Since then, complex hydrides are widely viewed as one of the most promising solutions to the hydrogen storage problem[31, 34]. While both amides and alanates may prove to be useful as solid state hydrogen stores, this thesis will focus primarily on the high hydrogen density metal borohydrides. Bear in mind that, in order for a system to be feasible, the gravimetric density of the material and containment system combined must be above the DOE target

(the capacities shown in Figure 1.3 are for the materials alone). Therefore, the highest possible hydrogen density materials are preferred. The development of these materials for commercial use requires a working knowledge of their fundamental chemical and structural properties, which will be the focus of this work.

1.4 Metal Borohydrides

1.4.1 General Properties and History

Metal borohydrides (also known as tetrahydroborates¹ or tetrahydridoborates) are compounds with a general formula $M(BH_4)_n$, consisting of metal cations M^{n+} and tetrahydroborate anions BH_4^- [35]. It is generally well known that boron forms unstable polymeric hydrides (e.g. $(BH_3)_x$). The BH_3 monomer is a Lewis acid that achieves electronic saturation by dimerizing to form diborane (B_2H_6)[36]. However, boron is also able to form a complex hydride $[BH_4]^-$ through additional charge localization on the boron atom, achieved by charge transfer from a metal. Borohydrides have been formed with alkali and alkaline-earth elements, which are more ionic in character, and also with various transition metals and aluminum, which possess more covalent character.

Group I and group II metal borohydrides are white, crystalline solids that are sensitive to moisture. To prevent borohydrides from being hydrolyzed to borates, they are usually handled under an inert atmosphere to avoid exposure to any moisture present in the air. In general, the number of BH_4 groups per metal atom reflects the valency of the cation. The borohydride ion ideally exists as a tetrahedron (with the B coordinated in the centre to 4 Hs located on the corners) though it may be strongly distorted from a perfectly tetrahedral shape (e.g. $H-B-H = 85.1(9)-120.1(9)^\circ$ for room temperature $LiBH_4$)[31]. It

¹While IUPAC has recommended the name tetrahydroborate to designate $[BH_4]^-$, they are commonly referred to as borohydrides for traditional reasons.

does not seem to exhibit a strong preference for co-ordination number, which generally seems to vary from 3-6, depending on the size of the coordinating cation[37].

The first study on borohydrides was completed in the 1939 by Schlesinger et al., who were contracted by the United States National Defense Research Committee. The work initially focused on uranium borohydride, but also produced borohydrides of several group I metals[38, 39]. Further work throughout the 60s and 70s, particularly by researchers in Russia, produced a variety of other metal borohydrides[40, 41, 42, 43, 44].

For a long time, the interest in alkali metal borohydrides was driven by their use as reducing agents in organic chemistry[38]. Since its application in carbonyl reduction[45], NaBH_4 in particular has been commonly used as a cheap, mild reducing agent of carbonyls and related compounds. Suitable substrates include conjugated carbonyl compounds, alkoxysulfonium salts, nitro compounds, carboxylic acids, esters, alkyl halides, nitriles, and amides[46].

Interest in borohydrides was rejuvenated early in the last decade as research in hydrogen storage matured (see 1.4.1). While many metal borohydrides had been known for 50 years, very little was known about their decomposition or fundamental properties. Much of the current research on borohydrides is dedicated to understanding various physical properties (e.g. structure) as well as the kinetics, thermodynamics, and mechanisms of hydrogen sorption.

1.4.2 Stability and Desorption Mechanics

The stability of metal borohydrides is of utmost importance as it defines the operational temperature of the storage material. Several different models have been used to describe borohydride stability, but it is generally discussed in the context of ionic character[47, 20], though the effects of sterics have also been discussed[48]. The cation Pauling electronegativity, χ_p , is most commonly used

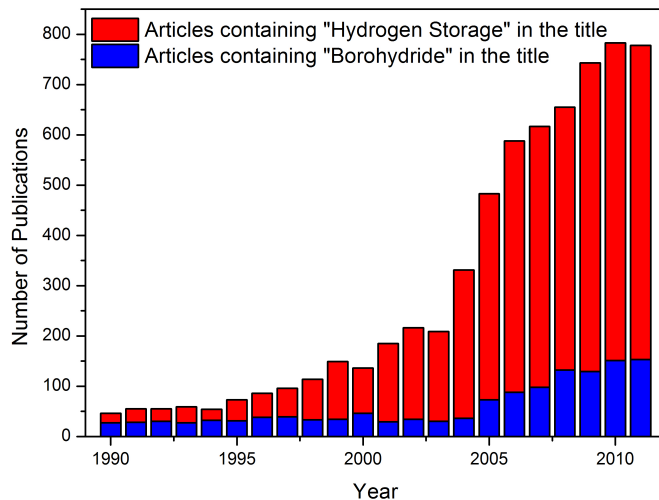


Figure 1.4.1: An increase in the field of hydrogen storage has fueled an increased interest in borohydrides over the past 10 years. Source: Scopus.com

to describe the amount of charge transfer (and hence ionic character) between a metal, M , and a borohydride anion. This relationship was first described in 2004 by Nakamori and Orimo, who suggested substituting smaller or higher valence metal cations with higher electronegativities into lithium based complex hydrides to lower the hydrogen desorption temperature[49]. The rationale behind this argument is that more electronegative cations withdraw electron density from the B-H bonds, thereby destabilizing the borohydride ion. Borohydrides with less ionic character than diborane, the simplest “electron deficient” molecule, are therefore expected to be unstable[35].

The authors followed this work two years later by using first principles density functional theory calculations to suggest a relationship between the formation enthalpy of a borohydride and the Pauling electronegativity of the cation (Eq.1.4.1)[50].

$$\Delta H_f(MBH_4) = 248.7\chi_{p(M)} - 390.8kJmol^{-1}BH_4 \quad (1.4.1)$$

Experimentally, the decomposition temperature of the borohydrides has been found to decrease with increasing electronegativity of the cation and those containing cations more electronegative than boron (Pauling electronegativity 2.0) are either unstable or do not exist. While the studies by Nakamori prompted scientists to examine the large differences in decomposition temperatures/pressures of various borohydrides, more recent work has attempted to rationalize the observed differences in their mechanism of decomposition[51].

One of the most widely studied features of the decomposition of borohydrides is the formation of diborane; while some borohydrides release significant amounts of B_2H_6 during decomposition, others do not[52]. As B_2H_6 is a pyrophoric and toxic gas, it is an extremely undesirable side product of decomposition and many attempts have been made to understand its formation in borohydride decomposition. A recent study by Callini *et. al*[53] presented a model for the formation of B_2H_6 based on asymmetric assembly on the surface of tetrahydroborates. It has been theoretically predicted[54] and experimentally confirmed[55] that when a metal withdraws electron density from the BH_4 units, they distort from their ideal tetrahedral shape. Callini *et. al* proposed that this distortion (which they measured using vibrational spectroscopy) in unstable borohydrides lowers the thermodynamic constraints to the formation of $[BH_2]^+$ units, which then combine with $[BH_4]^-$ units to form B_2H_6 . This offers a new perspective on the suppression of diborane formation and links it directly to an observable feature (the difference in B-H bond lengths in the BH_4 unit) in borohydrides .

Recent work by Jones [56] examined the published data on a range of metal tetrahydroborates to understand the thermodynamics of their decomposition by

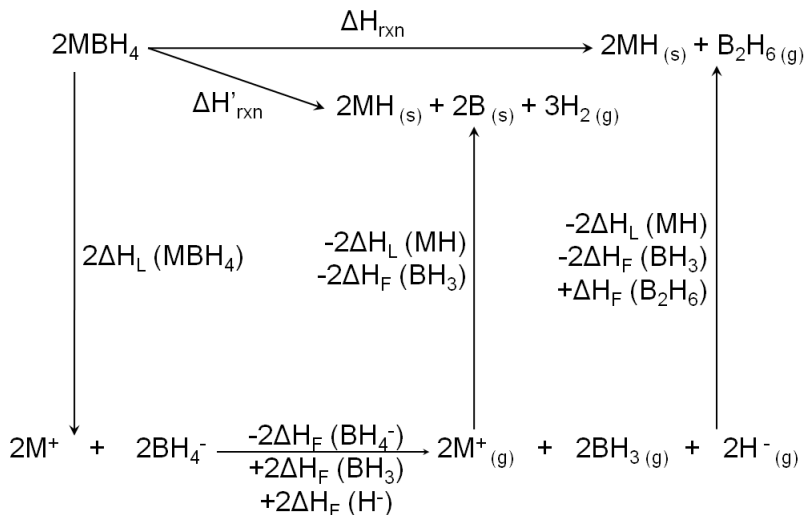


Figure 1.4.2: Hess cycle for two different decomposition routes of a metal tetrahydroborate

comparing two different composition routes through the Hess cycle shown in Fig. 1.4.2. Summing the energies and taking the difference between the two reaction pathways, it may be seen that the pathway ΔH_{rxn} is larger than $\Delta H'_{\text{rxn}}$ by the enthalpy of formation of diborane, $\Delta H_{\text{F}}(\text{B}_2\text{H}_6)$, and so we expect the pathway $\Delta H'_{\text{rxn}}$ to dominate. However, for two different metals, both $\Delta H_{\text{F}}(\text{B}_2\text{H}_6)$ and $\Delta H_{\text{F}}([\text{BH}_4]^-)$ are constant and so the difference in their decomposition temperature will be given by the relative stabilities of the MBH_4 and MH species. This helps explain the dependence of decomposition temperature on the ionic radius of the metal cation since the lattice enthalpy of MH will be increasingly larger than the corresponding MBH_4 species as the cation radius decreases. We would therefore expect that borohydrides with larger metal cations will have higher decomposition temperatures, which is validated experimentally[57]. At a certain temperature (and corresponding cationic radius), the decomposition of the metal borohydride surpasses that of diborane (*ca.* 575K[58]) and B_2H_6 is

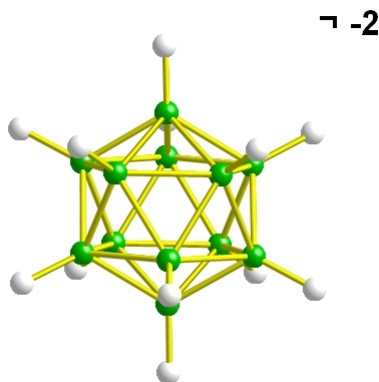


Figure 1.4.3: The hypercloso dodecaborane anion

no longer observed as it dissociates to hydrogen and boron. It is worth noting, however, that the suppression of diborane may actually only be a kinetic issue rather than a thermodynamic one.

The hydrogen desorption of borohydrides often occurs in a multiple step process. For example, the dehydrogenation process of LiBH_4 at a slow heating rate is found to exhibit three distinct stages[35]. This was first attributed to the formation $\text{Li}_2(\text{B}_{12}\text{H}_{12})$, which had been theoretically predicted and experimentally observed by Raman spectroscopy and solid state NMR[59]. While the mechanisms are still not fully understood, the dodecaborane species (1.4.3) has been observed in many (e.g. Li, Mg) metal borohydride species.

The $[\text{B}_{12}\text{H}_{12}]^{2-}$ anion is very stable and, as such, it remains at relatively high temperatures. This makes it an unfavourable thermodynamic sink and, when formed as a decomposition product, limits the potential reversibility of these systems. Although it has been predicted in the decomposition of several other borohydrides (e.g. Ca), it has yet to be found experimentally for all metal tetrahydroborates[60]. Other polyborane species have also been observed as intermediates in the decomposition of metal borohydrides. Chong *et. al* recently

proposed a mechanism for the decomposition of $\text{Mg}(\text{BH}_4)_2$ based on a metal ion-assisted B-H condensation pathway, which involved the formation of several polyborane species as intermediates. The work went on to show that by stopping the reaction after forming $\text{Mg}(\text{B}_3\text{H}_8)_2$ and before reaching the end product of $\text{Mg}(\text{B}_{12}\text{H}_{12})$, the system was reversible under moderate conditions[61]. While this offers promising insight into the reversibility of magnesium borohydride, it has yet to be observed in any other system and more mechanistic studies on the decomposition of tetrahydroborates are needed.

1.4.3 Synthesis

Numerous synthetic routes have been investigated for the more industrially relevant borohydrides. For instance, there are over 100 documented methods to produce NaBH_4 [57]. Direct synthesis of borohydrides has been reported by reacting the metal with elemental boron under a pressure of 30-150 bar H_2 at elevated temperatures as in Eq. 1.4.2[62].



Although this synthesis route is generally applicable to group I and II metals, it is not possible to form all borohydrides in this way. The more commonly used synthetic routes to produce other metal borohydrides are generally divided into two categories: wet (solvent-mediated) and mechanochemical (ball milling). While wet synthesis generally affords the synthesis of much purer products, mechanochemical synthesis is frequently used due to its convenience and a number of borohydrides have only been synthesized using this technique[57].

1.4.3.1 Solvent-mediated Synthesis

As previously mentioned, the earliest reports on borohydrides were done by Schlesinger *et. al* in the late 1930s and 40s[63, 64]. The materials were

synthesized by directly reacting the metal with diborane in ethereal solvents:



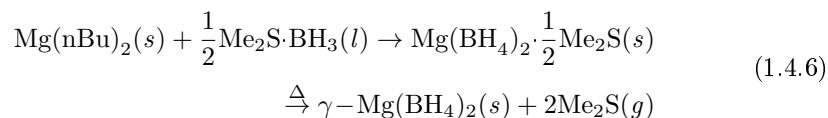
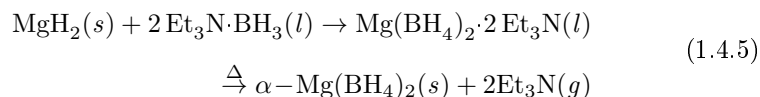
Due to safety issues surrounding the use of diborane, a variety of other synthetic techniques have been explored (for instance, the synthesis described in Eq 1.4.3 can also be achieved in a ball mill in the absence of a solvent). When the syntheses described in Eqns. 1.4.2 or 1.4.3 are not used, the most common way to produce borohydrides is by substituting $[\text{BH}_4]^-$ units for the anion of a corresponding metal halide[31]. For example, the synthesis of magnesium borohydride may be achieved via 1.4.4.



The above metathesis is extremely versatile and widely used to form even LiBH_4 using lithium chloride and sodium borohydride in isopropylamine[38]. In fact, the metathesis of metal halides with an excess of an alkali metal borohydride has been achieved for a variety of transition metals, lanthanides, and actinides, though it is often accompanied by a corresponding reduction in the oxidation state of the metal ion[31]. The process is generally completed by extraction using an ethereal solvent and removal of said solvent under vacuum to yield the pure borohydride. Furthermore, certain borohydrides are stable in a basic environment. For example, potassium borohydride may be produced by combining NaBH_4 and KOH [65].

Many recent synthetic efforts are geared toward producing phase pure, solvent-free samples. For example, the first phase pure sample of magnesium borohydride was first reported in 1950 by Wiberg and Bauer who produced the alpha

polymorph from diethylmagnesium (MgEt_2) and B_2H_6 in ether[57]. More recent work has attempted to refine the production of $\alpha\text{-Mg}(\text{BH}_4)_2$ to reduce the amount of the beta phase present (the transition from α - to $\beta\text{-Mg}(\text{BH}_4)_2$ is irreversible). The reaction between MgH_2 and triethylamineborane complex (1.4.5[66]) at elevated temperatures is known to produce the pure $\alpha\text{-Mg}(\text{BH}_4)_2$ when the complexing solvent is removed at low temperatures. Later work at the University of Aarhus developed a method for the production of a new porous gamma phase by reacting dibutylmagnesium and a dimethylsulfide borane complex (Eq. 1.4.6[67]).

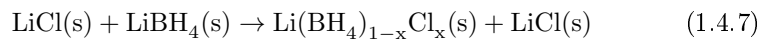


1.4.3.2 Mechanochemical Synthesis

Mechanochemistry is a well-established technique to synthesize compounds and promote properties that help facilitate hydrogen sorption (small particle size, even catalysis distribution, etc.). Although debated, the conditions produced when ball milling are often not well understood. Studies have found that the temperatures produced during milling are moderate (below 60 °C) and seem to suggest the reactivity observed is a result of the collisions between the balls, vial and powder[68]. Such collisions produce a high pressure environment and may introduce deformations (caused by sheer stress, for example)[69]. Short milling intervals, separated by pauses, in alternating rotation directions are typically used to help reduce and distribute the amount of heat developed from friction in the vial.

The solid state metathesis reaction between an alkali metal borohydride and a metal halide in an inert gas atmosphere has been observed to form a number of metal borohydrides (e.g. $\text{Y}(\text{BH}_4)_3$, $\text{Dy}(\text{BH}_4)_3$, $\text{Gd}(\text{BH}_4)_3$, etc.[70]). However, a major setback of mechanochemical synthesis is that side ionic products are often formed and the borohydrides produced are rarely pure.

Mechanochemical synthesis has perhaps been found most useful in producing bimetallic borohydrides (which are discussed in more detail later in this chapter) and solid solution borohydrides. For example, work by Ravnsbaek et al.[71] showed that a series of mixed alkali metal-zinc borohydrides could be formed using mechanochemical synthesis. By changing the composition of their reactants, the study found they could produce significantly different reaction products, many of which have not yet been synthesized in solution. Earlier work from the same group[72] found that by milling lithium borohydride with lithium chloride, they were able to form the solid solution $\text{Li}(\text{BH}_4)_{1-x}\text{Cl}_x$:



Currently, the drawbacks associated with mechanochemical synthesis (inability to produce phase-pure products) make it less widely investigated than wet chemical synthesis. Furthermore, industrial scale-up of mechanochemical borohydride production would be extremely energy intensive. However, the cost of solvent and low solubility of many borohydrides make mechanochemical synthesis an increasingly important technique in borohydride chemistry.

1.4.4 Structure

In the last decade, the field of structural borohydride science has seen rapid evolution as the search for better hydrogen storage materials was hampered by the lack of fundamental crystallographic knowledge. Nearly all borohydrides exist as crystalline solids at SATP but it was not until approximately 10 years

ago that the first detailed study on their structural properties emerged (the first study was on LiBH_4 [73]). As mentioned previously, one of the key difficulties in studying metal borohydrides is that they often exist as fine powders in a synthesis product that contains several different compounds. As synthetic chemistry on this class of compounds has matured in combination with increasingly advanced *ab-initio* structure determination methods, there has been concomitant growth in the number of structural studies of metal borohydrides, as evidenced by a number of recent reviews on the subject (e.g. [74, 37]).

Powder diffraction techniques (which are discussed in more detail in chapter 2) are considered to be one of the most useful tools in the study of borohydride materials; they enable scientists to not only determine detailed structural information about metal borohydrides, but also to screen for reaction products and intermediates. The hydrogen sorption processes in metal tetrahydroborates generally occur with significant changes in composition and structure[75]. Many of the reaction intermediates are often well crystalline phases and so are well suited to the use of X-ray, neutron, and electron diffraction (more recently used to study submicrometer particles [76]). In the best examples, the accuracy obtained from powder diffraction is comparable to that obtained by single crystal diffraction. However, the biggest advantage of powder diffraction comes from obtaining data at variable temperature; the behaviour of a sample may be tracked from differences in the diffraction peaks resulting from decomposition, phase changes, or other chemical reactions.

Many borohydrides have been found to exist as a number of different polymorphs, indicating a complex potential energy profile. Although each compound will be discussed in more detail in later chapters, a summary of borohydrides relevant to this thesis is given in Table 1.2. Even the seemingly simple LiBH_4 system exhibits a number of different phase transitions, depending on the con-

Table 1.2: A summary of the structures of group I and II borohydrides relevant to this report. SATP is assumed unless otherwise stated.

Compound	Space Group	Conditions	References
LiBH₄	<i>Pnma</i>		[73, 78, 77]
	<i>P6₃mc</i>	400 K	[73, 78, 77]
	<i>Ama2</i>	2.4 GPa	[79]
	<i>Fm$\bar{3}$m</i>	18.1 GPa	[79]
NaBH₄	<i>Fm$\bar{3}$m</i> or <i>F$\bar{4}$3m</i>		[80]
	<i>P$\bar{4}$₂1c</i> or <i>P4₂nmc</i>	10 K	[81]
	<i>Pnma</i>	11.2 GPa	[82]
KBH₄	<i>Fm$\bar{3}$m</i>		[83, 55]
Mg(BH₄)₂	<i>P6₁</i> or <i>P6₁22</i>		[84] or [85]
	<i>Fddd</i>		[86]
	<i>Ia$\bar{3}$d</i>		[87, 67]
	<i>P4₂nm</i>	2.1 GPa	[67]
Ca(BH₄)₂	<i>Fddd</i> or <i>F2dd</i>		[88] or [89]
	<i>P4₂/m</i> or <i>P$\bar{4}$</i> or <i>P4₂nm</i>	480 K	[90] or [89]
	<i>I$\bar{4}$2d</i> or <i>I4₁/amd</i>	495 K	[89]
	<i>Pbca</i>	300 K	[91]

ditions applied to it[77].

While the structures adopted by various metal borohydrides differ greatly, a common feature observed in many tetrahydroborates is a similarity to analogous oxides[92]. For example, calcium borohydride has been experimentally found in three different phases (α/α' , β , and γ) which all correspond to different phases of titanium dioxide (rutile, anatase, and brookite, respectively). A theoretical basis for this observation was first provided by Aeberhard *et al.* [93] who noticed four similarities between $\text{Ca}(\text{BH}_4)_2$ and TiO_2 . First, both are essentially ionic crystals; $\text{Ca}(\text{BH}_4)_2$ is formed of Ca^{2+} and $[\text{BH}_4]^-$ ions and is isoelectronic to TiO_2 , which is composed of Ti^{4+} and O^{2-} ions. Second, the ratio between the ionic radius of the cation and that of the anion is similar in both compounds, although the average Ca-B distance is about 1.5 times larger than the Ti-O bond

length. This is manifested as a difference between the unit cell parameters of the two structures, which are 1.5 times longer in $\text{Ca}(\text{BH}_4)_2$ than in corresponding TiO_2 phases. Third, the electronic density of states of the two compounds are qualitatively comparable; both cations have the [Ar] electronic configuration and may accept electron density into their vacant d orbitals ($\text{Mg}(\text{BH}_4)_2$, for example, does not possess the same d-character). While this alone does not indicate a causation, it is interesting to note that only borohydrides formed with metals in a d^0 , d^5 , or d^{10} configuration have been obtained so far. This suggests that electronic configuration plays an important role in the stability of a borohydride[57]. Lastly, the cation-anion binding potentials (calculated using DFT) possess a very similar shape around their respective equilibrium distances. When scaled to account for the difference in bond lengths, a remarkable overlap in the shape of the curves is obtained. This is not the case when other cations or anions are substituted, indicating that the cation and anion must share similar properties.

The above is an example based on only calcium borohydride however, the oxide analogy has proven true for various others as well[74]. In fact, this observation has even recently made structural solution of new borohydrides possible by comparing directly to an oxide isostructure[87].

1.4.4.1 Borohydride Ion Geometry

In borohydrides, B and H are covalently bonded in a tetrahedral structure. There are several difficulties associated with studying this using diffraction methods. Hydrogen is not amenable to being studied by X-ray diffraction due to its low electron density and therefore weak scattering cross section. Studying borohydride ions using neutron diffraction is complicated by the fact that boron-10 is a strong absorber of neutrons and that hydrogen has a particularly high incoherent scattering cross section. Furthermore, there is a discrepancy between

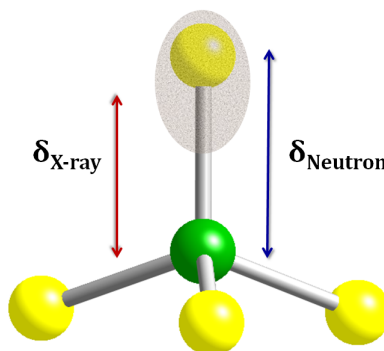


Figure 1.4.4: Representation of the difference in measured bond lengths using X-ray vs. neutron diffraction. In the former, the measured distances are between electron cloud centres, which are often displaced from the average nuclear positions.

the results obtained by the two methods. As neutrons are scattered by nuclei and X-rays are scattered by electrons, use of the latter often leads to shorter bond lengths as the electron cloud of hydrogen is displaced toward the boron atom (see 1.4.4). By its nature, this difference is temperature independent.

Conflicting reports on LiBH_4 lead to some debate over the degree to which $[\text{BH}_4]$ tetrahedra are distorted from uniform bond lengths and angles. The earliest of these studies[73, 94] found B-H lengths from 1.04(2) Å to 1.28(1) Å and H-B-H bond angles between 85° and 120°, suggesting that the degree of distortion was significant in this material. This prompted scientists to consider whether the strongly polarizing Li^+ cation can cause deformations in the tetrahedral $[\text{BH}_4]^-$ anion, which was previously presumed rigid due to its covalent nature. However, later single crystal X-ray[77] and powder neutron diffraction (of isotopically substituted $^7\text{Li}^{11}\text{BD}_4$ [78]) measurements found that the H-B-H bond angles were nearly all identical and that three B-H bonds were approximately the same length. This showed that the distortions of the borohydride

ion initially observed by Soulie *et al.*[73] were simply due to the nature of the interaction between X-rays and the light hydrogen atoms.

It has been suggested that highly electronegative cations (or those with a high ionization enthalpy) withdraw electron density from the $[\text{BH}_4]$ unit. Based on first principles calculations, it is believed that this reduced anionic charge caused a destabilization and resulting distortion of the borohydride anion[54, 95]. This is indeed observed experimentally. For example, the Pauling electronegativities of potassium and aluminum are 0.82 and 1.61, respectively[96]. The bond angles and bond lengths in KBH_4 are found to be all identical (109.5° and $1.196\text{\AA}$)[55], while in $\text{Al}(\text{BH}_4)_3$ there is considerable distortion, with the bond angles ranging from 103° to 121° and the lengths from $0.99\text{\AA}$ to $1.14\text{\AA}$ [97].

1.5 Routes to Improved Borohydrides

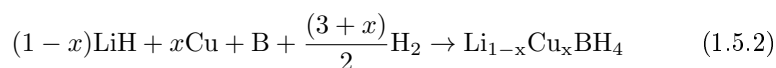
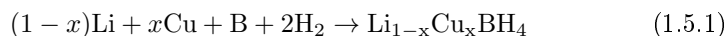
Although the high hydrogen content of light metal borohydrides makes them attractive as hydrogen storage materials, their thermodynamic stability (and therefore high decomposition temperatures) and/or slow kinetics of hydrogen sorption currently prevent their widespread practical utilization. As a result, a great deal of effort has focused on tailoring the properties of borohydrides. The field is vast and a number of techniques exist to improve the thermodynamics and kinetics of hydrogen sorption. The focus of this section will be to give a brief outline of the key approaches that have been developed.

1.5.1 Mixed-Metal Borohydrides

The trend of decreasing borohydride decomposition temperature with increasing electronegativity of the cation motivated researchers to consider how one might alter the electronegativity of a metal. While it is not possible to alter the electronegativity of a particular metal, it is possible to form a system with multiple cations that possesses a lower average electronegativity than a parent

metal.

The first published work on mixed metal borohydrides was a first principles study that investigated the substitution of copper into LiBH_4 via 1.5.1 and 1.5.2 (the second being more relevant to the decomposition process)[98].



Both Li^+ and Cu^+ possess similar atomic radii, but the electronegativity of the latter is significantly higher. The ideal composition of $x = 0.3$ (giving a formation enthalpy of -39kJ/mol^{-1} from LiH) was predicted, however synthesis of this compound has not yet been possible.

The first pure bimetallic borohydride, $\text{LiK}(\text{BH}_4)_2$, was reported by Nickels *et al.* in 2008[99]. The decomposition temperature of this compound was not lower than that of both constituent borohydrides but rather an intermediate between the two. A number of studies producing various mixed metal borohydrides followed (e.g. $\text{LiSc}(\text{BH}_4)_4$ [100] and $\text{NaSc}(\text{BH}_4)_4$ [101]), though generally the hydrogen desorption temperatures of these compounds are high, but may be reduced when more electronegative elements are incorporated.

In a study of a series of mixed cation borohydrides[71], it was noted that mixed metal borohydrides containing more electronegative elements (e.g. Sc, Zn) have the ability to form partly covalent, complex anions ($[\text{Zn}_2(\text{BH}_4)_5]^-$, $[\text{Sc}(\text{BH}_4)_4]^-$). These complex anions then combine with alkali metal cations to form, for example $\text{Li}[\text{Sc}(\text{BH}_4)_4]$ or $(\text{Li}[\text{Zn}_2(\text{BH}_4)_5])$, in the solid state. Neither Sc nor Zn borohydride have yet been synthesized and their instability may contribute to the lower decomposition temperatures of the Sc- and Zn- (or more recently Cd-[102])based bimetallic borohydrides. The use of mixed-metal systems thus offers

great promise for tuning the properties of group I and II borohydrides.

1.5.2 The Addition of Impurities (or Catalysts)

The field of catalysis in borohydrides first stemmed from a pioneering discovery in the late 90s by Schwickardi and Bogdanovic, who found that titanium-doped alanate systems showed dramatically improved kinetics and reversibility of hydrogen uptake[33]. This sparked interest in doping hydrogen storage systems with transition metals and, to date, a large number of different additives have been investigated across most classes of hydrogen stores[103, 104, 105, 106, 107]. The principle challenge at the heart of catalysis and indeed hydrogen storage is developing an understanding of the exact mechanism by which the metals act as a catalyst. Although a number of studies have attempted to find the best catalyst for hydrogen storage by screening large numbers of compounds through trial and error, few offer an explanation as to the role of the additive during in hydrogen sorption[6].

Often, the addition of transition metal halides will alter the decomposition products observed, meaning that the additive is not functioning as a catalyst (as it is consumed during the reaction). For example, the best known catalyst for the $\text{Ca}(\text{BH}_4)_2$ system is NbF_5 , though it is found that the main dehydrogenation product is a $\text{CaH}_{2-x}\text{F}_x$ solid solution[108]. This indicates that NbF_5 is consumed during the reaction and is therefore not a true catalyst. Understanding catalysis in such systems is often further complicated by the use of ball milling, which is used in order to evenly disperse the additive throughout the sample. It is well known that the kinetics of hydrogen storage are improved by decreasing particle size[31]. Therefore, when mechanochemical techniques are employed to distribute a catalyst, the properties of the parent system may be adversely affected, making it increasingly difficult to understand the precise effect of the additive.

Commercially viable system will undoubtedly contain additives to improve their functional properties. This further imposes the restriction that a given additive must be relatively inexpensive. There is a great amount of work remaining to be done in the field, and future studies should focus on understanding the mechanistic role of the additive.

1.5.3 Other Techniques

1.5.3.1 Reactive Composites

The formation of reactive composites, either by employing mixed anions (e.g. borohydride-amides) or by combining a borohydride with another borohydride or metal hydride[109] is a common way to influence stability and improve hydrogen storage properties[22, 110, 111]. The mixed anion system $\text{LiBH}_4\text{--LiNH}_2$, for example, has been extensively studied and shows improved hydrogen storage properties over the parent compounds[112, 113, 51]. More recently, there have been reports of a number of mixed borohydride-amide (e.g. $\text{Li}_4(\text{BH}_4)(\text{NH}_2)_3$ [114, 115] or $\text{Li}_2(\text{BH}_4)(\text{NH}_2)$ [116]) species, which possess an extremely high capacity of hydrogen.

1.5.3.2 Anion Substitution and Modification

Modification of the $[\text{BH}_4]$ group or partial substitution of the entire anion, usually by halides, has also been examined to help tune stability of borohydrides. A number of mixed-cation, mixed-anion borohydrides (e.g. $\text{KZn}(\text{BH}_4)\text{Cl}_2$ [117]) have recently been reported in a series of studies by Ravnsbaek *et al.*[92]. Many exhibit a lower decomposition temperature than the parent compounds and may even have applications in battery technologies[118]. The non-stoichiometric $\text{LiBH}_4 + \text{LiX}$ system (where X is a halide) has also been investigated for its potential application as a fast lithium ion conductor[119, 120]. The $[\text{BH}_4]$ groups are gradually replaced by the halide ion as temperature is increased and the fast

ion conducting high temperature phase of LiBH_4 becomes stabilized at lower temperatures, particularly when larger halides are used[121].

Modification of the hydrogens in the anionic group has been achieved in alanates and, to a degree, also in borohydrides. Fluorine-substituted sodium alanate ($\text{Na}_3\text{AlH}_{6-x}\text{F}_x$) was found to be less stable than the parent sodium alanate. Modifying the rather covalent $[\text{BH}_4]$ group is more difficult. Metal amidoboranes, containing the general formula $\text{M}(\text{BH}_3\text{NH}_2)$, have received a great deal of attention recently due to their incredibly high gravimetric content of hydrogen[122]. In a sense, these may be viewed as modified borohydrides, where one of the hydrogen atoms has been substituted for an $[\text{NH}_2]$ group. However, these materials are currently obtained from ammonia borane, which already contains the B-N bond, rather than from modifying borohydrides.

1.5.3.3 Nanoconfinement

As mentioned earlier, nanoparticles often have properties that facilitate the release and uptake of hydrogen. This is due to a combination of increased surface area, smaller diffusion distances, an increased number of atoms in the grain boundaries, and more intimate contact between different compounds within a system[123]. Therefore, another technique that is rapidly developing in the field of hydrogen storage is the use of nanoporous materials as scaffolds for preparing and confining nanosized metal hydrides[124]. For example, it has been reported that $\text{Mg}(\text{BH}_4)_2$ shows improved desorption properties when infiltrated into an activated carbon scaffold[125, 126, 127]. In certain cases, improved thermodynamics of the nanoconfined system have even been reported and the development of novel nanomaterials is expected to have a tremendous impact on the development of commercially viable energy storage technologies[57, 12, 6, 22, 128].

1.5.3.4 Spillover

Another phenomenon known as hydrogen spillover, which is arguably a form of catalysis in itself, has existed for several years (see the 1995 review [129]) but has only recently emerged as a trend in hydrogen storage[130]. Spillover is the dissociation of hydrogen molecules into atoms by transition metals, followed by subsequent diffusion of these atoms into a host material. The hydrogen atoms can then hydrogenate unsaturated C-C bonds. The rate limiting step in this process is the barrier for migration to the host material by the hydrogen atoms and many current efforts in the field attempt to minimize this energy barrier[131]. As spillover is a relatively immature field of hydrogen storage, it is still widely disputed due to conflicting reports on the same materials[132]. Nevertheless, it is a rapidly developing field that may influence the future of borohydride chemistry, particularly when systems contain nanostructured additives[133].

1.5.3.5 Combining Chemi- and Physisorption

At the 2011 Faraday Discussion on hydrogen storage materials, Yang *et al.* presented an attempt to bridge the gap between chemisorption and physisorption of hydrogen[18]. Their paper presented a method for storing hydrogen in metal organic frameworks whereby organic cations are incorporate into the host materials by binding to the pore wall. These cations then essentially act as a gate to controlling the flow of H₂ (or N₂) gas into and out of the pore. Using post-synthetic ion exchange, they were able to achieve a loss of hysteric adsorption. Although this system does not posses a gravimetric hydrogen capacity that is considered commercially applicable, it opens an interesting area of hydrogen storage that may become increasingly relevant in the area of borohydrides as more and more framework structures have recently been discovered (e.g. Y(BH₄)₃[70]).

1.6 Project Aims

The principle goal of this thesis is to further the understanding of the fundamental physical properties of various borohydrides and relate said properties to hydrogen storage behaviour in the materials. To achieve this goal, this project will attempt to do the following:

- Understand the synthetic route to producing borohydrides and the role it plays in determining the phase composition of a given borohydride.
- Develop precise structural models for both new and known borohydrides using advanced diffraction techniques and understand the physical relationship between different polymorphs of the same compound. This includes determining borohydride ion geometry and understanding order/disorder in the materials, where appropriate.
- Characterize the structural transformations of borohydrides with temperature. In doing so, develop a mechanism for the evolution of each material, from room temperature through decomposition.
- Where possible, provide analogy between borohydride and oxide chemistry. When new materials are developed (e.g. those analogous to SiO_2), attempt to explore and understand avenues of chemistry not previously possible in borohydride systems (e.g. gas physisorption).
- Examine the influence of additives on borohydride decomposition. Attempt to rationalize the effects from detailed structural analyses and provide a mechanism for observed changes in the mixed system.

The two principle materials studied in this thesis are $\text{Mg}(\text{BH}_4)_2$ and $\text{Ca}(\text{BH}_4)_2$. LiBH_4 , NaBH_4 , and LiNH_2 are also examined in the context of additives to group II borohydrides.

Chapter 2

Theory and Experimental Techniques

Borohydrides have not been found to be sensitive to oxygen, though they are slowly hydrolyzed to borates from moisture present in the atmosphere[134]. Consequently, all samples were stored and handled inside an MBraun Unilab argon-filled gloved box ($O_2 < 20$ ppm, $H_2O < 5$ ppm), thereby preventing exposure to moist air.

2.1 Synthesis Techniques

2.1.1 Tube Furnace with dynamic vacuum or flowing gas

Ground samples were placed inside an alumina crucible, which was then placed inside a quartz tube that had been sealed at one end. The open end of the tube was sealed under argon using a custom made dual Young's tap and fitted adapter. The tube was removed from the glove box and the Young's tap was connected directly to a vacuum pump or high vacuum line (via a cold

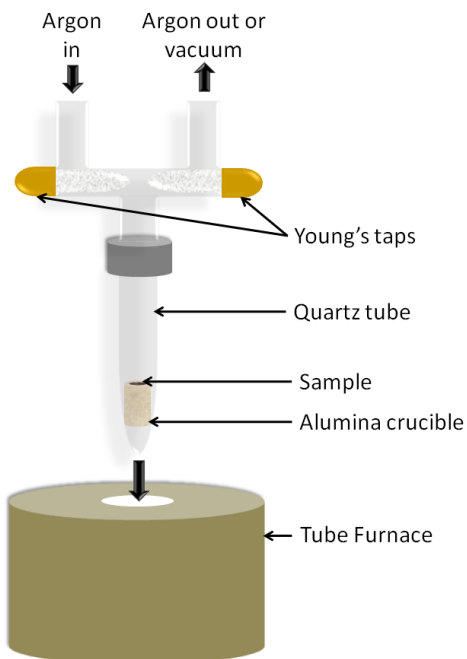


Figure 2.1.1: Lab setup for tube furnace with dynamic vacuum or flowing argon.

trap). Alternatively, the first Young's tap was connected to an argon line and the second to an oil bubbler. The end of the tube containing the sample was lowered into a Carbolite tube furnace, allowing it to be heated under dynamic vacuum or gas flow. This setup is display in Fig.2.1.1.

2.1.2 Schlenk Line

Schlenk reaction vessels were attached by flexible tubing to a combined vacuum and nitrogen gas line (the lines are connected via double oblique taps). In-house nitrogen provides enough pressure to transfer liquids between Schlenk tubes via cannulae and a rubber septa seal. In this way, solvent may be added or the cannulae may be fitted with filters to perform a filtration. Solvent can be removed from completed reactions by evaporating it under the vacuum at-

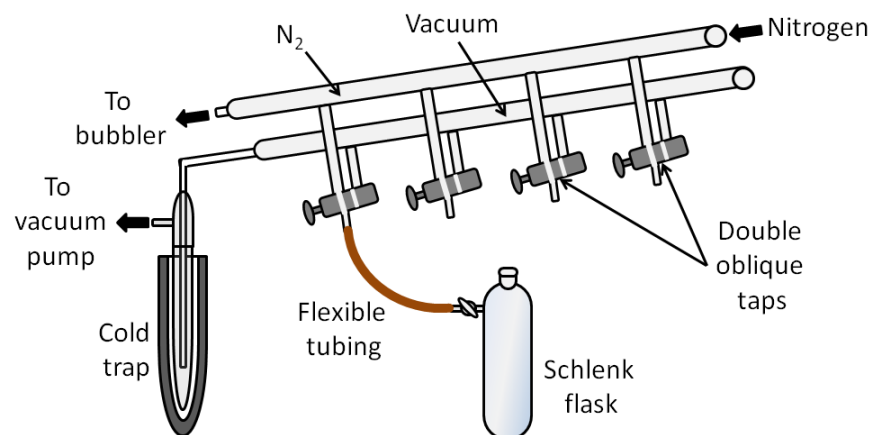


Figure 2.1.2: Schlenk line assembly

tachment of the Schlenk line and condensing it in a cold trap. When heating is required, an oil bath is placed under the vessel and a reflux condenser is attached to the top of the Schlenk tube to prevent solvent from escaping through the nitrogen supply.

For reactions using the Schlenk line, solid reagents were loaded into a flask within a glove box, which was then sealed and connected to the Schlenk line tubing. A flask containing the desired solvent is connected and the line is purged with nitrogen at least three times before the flasks are opened. Solvent is added to the flask through a cannula and rubber stopper. When the reaction is complete, the solution is cooled and filtered. The precipitates are then washed or dried under reduced pressure.

2.1.3 High Pressure Furnace

Isotopically enriched samples were synthesized in custom-built high pressure

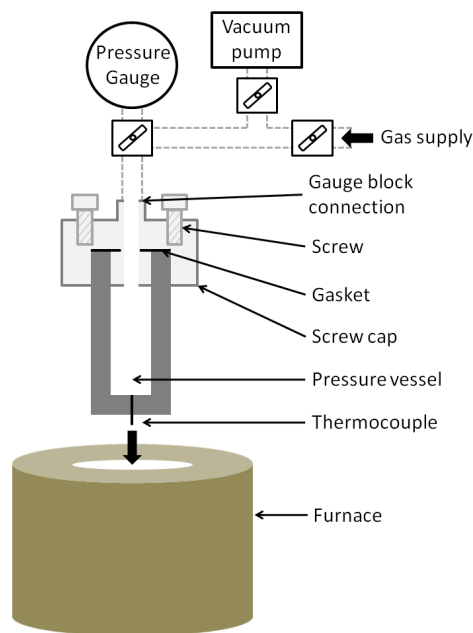


Figure 2.1.3: High pressure furnace setup

73mL Parr reactor vessel, made from a nickel-chromium-tungsten (Haynes 230) Alloy. The reactor can withstand temperatures up to 700 °C, pressures of 200 bar, and is resistant to H₂ embrittlement. Solid reactants are loaded in an argon filled glovebox and the vessel is sealed with six screws and a flexible graphite gasket. A pressure gauge fitted with a gas inlet/outlet and safety rupture disc for immediate venting is connected to the top of the vessel and a thermocouple is attached to the bottom. The loaded assembly is inserted into a separate furnace, which can be adjusted using a Parr control box. The chamber in the vessel is first evacuated and then filled to the desired gas pressure, sealed, and then heated.

2.1.4 Mechanochemical Milling

Certain samples were milled together under an argon atmosphere to ensure intimate mixing of the materials or increased surface area of the boron when



Figure 2.1.4: Mechanochemical mill vessel and balls

synthesizing isotopically enriched compounds. A Retsch PM100 planetary ball mill equipped with a 125mL jar (sealed with an O-ring), containing six 20mm milling balls was used. Both the jar and milling balls are made from tungsten carbide and enough sample was added such that the ball to powder weight ratio was approximately 35 to 1. Milling was done at 400 rpm in one hour intervals, pausing for one hour and reversing direction of milling after each hour (to minimize the temperature increase arising from the milling process).

2.2 Crystallography

Crystallography is the study of the arrangement of atoms in solids. The constituent atoms, molecules or ions in crystalline materials are periodically arranged in all spatial dimensions and are said to have long range order (>1000 Å). The full description of a crystal structure requires both a lattice and a basis. A lattice is a purely mathematical construct and represents an array of points repeating periodically in three dimensions. A basis is the smallest repeating unit of atoms, ions or molecules whose symmetry is described by one of the 32 crystallographic point groups. To generate the overall structure, the basis is placed on each lattice point.

Crystal structures are typically described by their unit cell. This can be

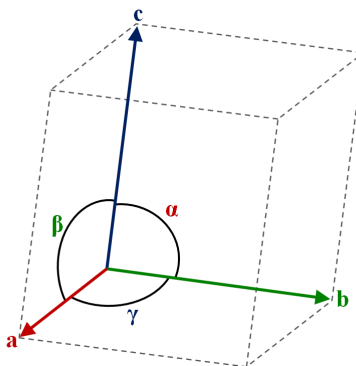


Figure 2.2.1: Schematic of the unit cell showing the lattice parameters (a, b, c) and the angles between them (α, β, γ) .

thought of as the smallest three dimensional collection of atoms or molecules that, when stacked together, reproduces the bulk arrangement of atoms in the crystal structure. A unit cell is described by its lattice parameters (a, b, c) , which are the lengths of the unit cell edges, and the angles between them (α, β, γ) . Atomic positions inside the unit cell are described by the set of numbers (x_i, y_i, z_i) measured from a lattice point (written as a fraction of the unit cell). Inside the unit cell is the asymmetric unit. This is the smallest unit the crystal can be divided into using symmetry operations of the space group.

Crystals are described by one of seven different crystal systems, which are sets of reference axes containing distinct axial relationships. In other words, all crystal systems are described by one of seven different combinations of a, b, c, α, β , and γ [135]. In addition to the seven different basic unit cell shapes, a crystal can possess one of 5 different types of centering:

1. Primitive, P , in which lattice points are located only on the corners of the unit cell.
2. Body centered, I , in which lattice points are located on the corners and in the centre of the unit cell.

Table 2.1: The seven crystal systems and their possible Bravais lattices

Crystal System	Axial Relationships	Bravais Lattice
Triclinic	$a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90^\circ$	P
Monoclinic	$a \neq b \neq c, \alpha = \beta = 90^\circ \gamma \neq 90^\circ$	P, C
Trigonal		
Hexagonal or	$a = b \neq c, \alpha = \beta = 90^\circ \gamma = 120^\circ$ or	P
Rhombohedral	$a = b = c, \alpha = \beta = \gamma \neq 90^\circ$	R
Hexagonal	$a = b \neq c, \alpha = \beta = 90^\circ \gamma = 120^\circ$	P
Orthorhombic	$a \neq b \neq c, \alpha = \beta = \gamma = 90^\circ$	P, C, F, I
Tetragonal	$a = b \neq c, \alpha = \beta = \gamma = 90^\circ$	P, I
Cubic	$a = b = c, \alpha = \beta = \gamma = 90^\circ$	P, F, I

3. Face centered, *F*, in which lattice points are located on the corners and in the centre of all faces of the unit cell.

4. Side centered, *C*, in which lattice points are located on the corners and in the centres of a pair of opposite faces. This may be the *a* or *b* axes but, is usually designated as the *c* axis.

5. Rhombohedral, *R*, in which lattice points are located on the corners of a rhombohedral cell.

When the 7 crystal systems are combined with the 5 types of centering, a total of 14 different arrangements, called Bravais lattices, are possible (see Table 2.1). It should be noted that the trigonal crystal system can be displayed using two different sets of axes (rhombohedral or hexagonal). When additional translational symmetry (e.g. glide planes, screw axes) are taken with the symmetry of the 14 Bravais lattices and 32 point groups, a total of 230 space groups are formed. These describe all possible symmetry relations within a structure. Space groups are denoted using Hermann–Mauguin (or international) notation, which includes up to four symbols. The first represents the Bravais lattice and the following three describe the most prominent symmetry operations along one

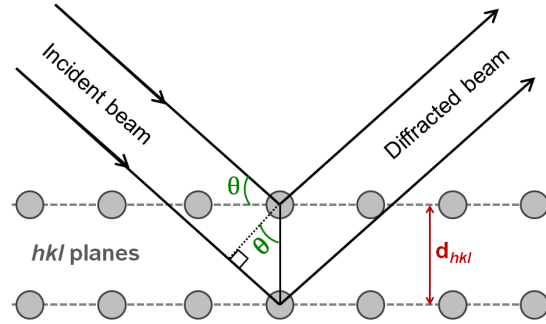


Figure 2.2.2: Illustrated Bragg condition for coherent scattering.

of the high symmetry directions in the crystal.

Diffraction

When a wave comes into contact with an obstacle that is on the order of magnitude of (or larger than) its wavelength, it will diffract. When diffraction occurs from a periodic arrangement in three dimensions, it is called Bragg scattering. In a crystal structure, Bragg diffraction occurs from the interaction of waves with the planes of repeating atoms. These are designated by Miller indices, (h, k, l) , which define planes that cross the unit cell axes at $(\frac{a}{h}, \frac{b}{k}, \frac{c}{l})$.

The distance between the Miller planes, d , may be probed using light of very short wavelength, such as X-rays, or matter waves, such as neutrons, whose wavelength is on the order (or smaller) than the spacing being observed. As an array of atoms is irradiated, it acts as a diffraction grating, causing the incident beam to be scattered. Each atom acts as a source of diffracted beam, causing the emanating waves to interfere with each other. This results in regions of both coherent and incoherent scattering in the diffracted waves.

The condition for constructive interference, known as Bragg's law, is illustrated in Fig. 2.2.2 and given by

$$n\lambda = 2d \sin(\theta), \quad (2.2.1)$$

where n is an integer, λ is the wavelength of the incoming beam, and θ is the angle of the diffracted beam. This equation states that, in order for the diffracted waves to superimpose constructively, the difference in the length of the path taken must be equal to an integer number of wavelengths.

A diffraction pattern is collected by monitoring the intensity of the diffracted beam as a function of scattering angle. At angles when the Bragg condition is met, the signal will be most intense and a Bragg peak will be observed. A material that is well crystalline will have many atomic planes interacting with the incoming radiation producing very sharp peaks surrounded by mostly destructive interference[136].

Reciprocal Space

Diffraction data is collected on the surface of a sphere surrounding a sample. As this surface contains only two dimensions of information, a third dimension of information is lost. This is dealt with by the introduction of a reciprocal space. Here, sets of parallel planes of lattice points in real space, d_{hkl} , are converted to reciprocal lattice points at a distance of d_{hkl}^* from the origin, where

$$d_{hkl}^* = \frac{1}{d_{hkl}} \quad (2.2.2)$$

and has units of $\text{\AA}^{-1}$. The axes for the reciprocal lattice (a^*, b^*, c^*) are now defined as vectors perpendicular to the faces of the real space unit cell (e.g. a^* is perpendicular to the bc plane) whose lengths are given by the inverse of the distance of the perpendicular unit cell face from the origin (e.g. $a^* = \frac{1}{d_{100}}$). The reciprocal space angles are given by 180° - the real space angles. This formulation allows real space Miller planes to be expressed as vectors in reciprocal space:

$$d_{hkl}^* = ha^* + kb^* + lc^* \quad (2.2.3)$$

Laue Conditions

Von Laue developed a set of equations to describe the conditions necessary for diffraction to be observed. He started by considering the wave vector, $\vec{k}$, whose magnitude is given by

$$|\vec{k}| = \frac{2\pi}{\lambda} \quad (2.2.4)$$

In diffraction, the collision of radiation with a sample is assumed to be perfectly elastic, i.e. there is no transfer of energy. In such a case, an incident wave with wavevector, k_i , will be equal in magnitude to the outgoing wavevector, k_o and the difference between the two vectors is called the scattering vector, Δk .

$$\Delta k = k_o - k_i \quad (2.2.5)$$

In order for diffraction to be observed, the difference in path length between diffracted waves must be an integer number of wavelengths. If this condition is satisfied in all directions, then one obtains the following 3 relationships from simple geometry:

$$a \bullet \Delta k = 2\pi h \quad (2.2.6)$$

$$b \bullet \Delta k = 2\pi k \quad (2.2.7)$$

$$c \bullet \Delta k = 2\pi l \quad (2.2.8)$$

Each of these equations says that Δk must lie on a cone around a , b , or c . To satisfy all of these conditions Δk must therefore lie on the intersection of 3 cones: one around each base vectors.

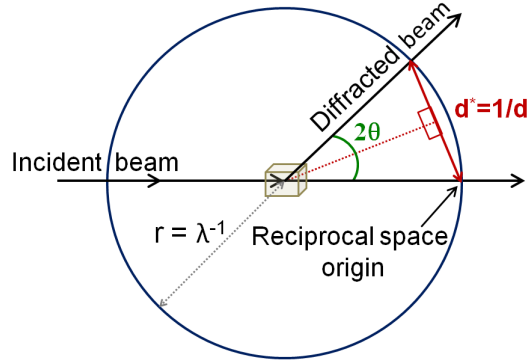


Figure 2.2.3: Illustration of an Ewald sphere

Ewald's Sphere

An Ewald sphere is a geometric construct that demonstrates the relationship between the incident wavevector, the diffraction angle, and reciprocal space. Sets of planes with a common h , k or l value are observed to produce a line of spots in a diffractogram. In reciprocal space, Bragg's law may be written as

$$2 \sin \theta = \frac{1}{d\lambda} \quad (2.2.9)$$

When this equation is satisfied with incident radiation of wavelength λ , the reciprocal lattice point will lie exactly on a sphere of radius $\frac{1}{\lambda}$, whose circumference passes through the origin of the reciprocal lattice (Fig. 2.2.3). So rotating the crystal in real space will cause the reciprocal lattice points to intersect the Ewald sphere. This can be arrived at equivalently from the Laue conditions.

If $2\theta = 180^\circ$, then

$$\frac{\lambda}{d} = 2 \sin 90 = 2, \text{ so } \frac{1}{d} = d^* = \frac{2}{\lambda} \quad (2.2.10)$$

So for diffraction to occur, then the reciprocal lattice spacing must be less

than $\frac{2}{\lambda}$ [136].

Peak Intensities

While location of diffracted peaks depends on the geometry of the crystal, the intensities of the Bragg peaks are derived from the atoms and their positions within the unit cell. Like the incoming radiation, each atom has an oscillating electromagnetic field that interacts with the incident beam. Different atoms will possess different scattering powers that will contribute to the amplitude of the reflection; each peak contains the summed scattering from all atoms in the unit cell. The beams also may take different paths through the crystal and will have different phases, resulting in constructive/destructive interference and affecting the intensities.

The complex structure factor, F_{hkl} , is used to represent both the magnitude (cosine part) and the phase (sine part) of a wave diffracted from a structure with N atoms:

$$F_{hkl} = \sum_{j=1}^N f_j e^{2\pi i(hx_j + ky_j + lz_j)} \quad (2.2.11)$$

where (x_j, y_j, z_j) are the atomic coordinates of the j^{th} element and f_j is the atomic scattering factor. When X-rays are used, the scattering power is proportional to the number of electrons in an atom at low 2θ . At higher angles, the electron cloud becomes larger than the X-ray wavelength and scattering from different parts of the cloud become out of phase. The ability of elements to scatter neutrons varies randomly across the periodic table. As the neutrons are diffracted by the much smaller nucleus, there is no angle dependence of scattering power, however scattering ability may be affected by resonance scattering, where a nucleus absorbs a neutron and emits it later.

X-ray diffraction is further limited due to the dependence of the atomic scattering factor on the atomic number, Z . Of utmost relevance to this thesis is

the drawback that, due to only having one electron, hydrogen atoms are difficult, if not impossible, to observe with X-rays. Furthermore, if there are light atoms in the vicinity of much heavier ones, the signal will be entirely dominated by the large Z atom. Lastly, if two elements are near each other on the periodic table, it can be very difficult to distinguish between them using X-ray diffraction.

The intensities of Bragg peaks are found by taking the square modulus of a corrected structure factor, $|F_{hkl}^{corr}|^2$. The corrections applied are dependent on the sample used and diffractometer geometry. They include:

1. Absorption correction to account for the fact that some atoms will absorb radiation as well as scatter it.
2. Lorentz geometric correction that accounts for the amount of time that a moving crystal spends in the diffracting position for a scattered beam.
3. Polarization correction to account for the fact that, as the beam is monochromatized upon reflection from a crystal, it will be partially polarized resulting in the two parts of the beam having unequal intensities.

The electron density in a crystal is a continuous function given by the Fourier transform of the structure factor. Since a crystal is periodic, the electron density at a point (x, y, z) may be written as a Fourier series summation:

$$\rho(x, y, z) = \frac{1}{V} \sum_h \sum_k \sum_l |F_{hkl}| \cos 2\pi(hx + ky + lz - \phi_{hkl}), \quad (2.2.12)$$

where ϕ_{hkl} is the phase angle of reflection hkl . Practically, the structure factor is calculated from the square root of the measured peak intensities. This means that it is not possible to determine the phase angle and direct re-construction of the electron density map is not possible from beam intensities alone. This dilemma is known as the *phase problem* and requires that other techniques be used to deduce information not included in the Bragg peak intensities.

The two most common solutions to the phase problem are Direct Methods

and Patterson Mapping (or more recently, charge flipping). The former statistically analyzes the intensity distribution and generates a set of equations to give a probability to the value of the phases. In the latter technique, a Patterson function is used to generate a map of interatomic vectors. The function gives a large value in positions which correspond to heavier atoms so their location can be determined directly[136].

2.2.1 Powder X-ray Diffraction (PXD)

The diffraction theory formulated above was developed to analyze single crystals that possess enough long range order in all three dimensions to produce diffraction spots all around the sample. However, it is not always possible to grow crystals of sufficient size and often scientists are forced to work with a powder that possesses a large number of small, randomly orientated crystallites. As a result, each small crystallite will produce its own set of diffraction spots and, on average, every hkl plane will be simultaneously irradiated for all incident angles of the beam. The scattering vector is on rings of radius d_{hkl}^* rather than on individual lattice points and the 3D space of a single crystal is reduced to a 2D space. The combination of spots from individual crystallites create a ring of diffraction that propagates out at a given angle from the incident beam, leading to what are called Debye-Scherrer cones. The cones are intersected at a range of 2θ values by a detector to produce a set powder diffraction peaks (See Fig. 2.2.4).

Collapsing the data into two dimensions has implications on data analysis, particularly when trying to assign intensities to individual reflections. Lattice planes with different hkl values that have the same d spacing will appear at the same place on a powder diffractogram. A factor called multiplicity, which takes into account the number of planes which contribute to a single peak, is therefore used when assigning intensities. Further complications may arise when peaks

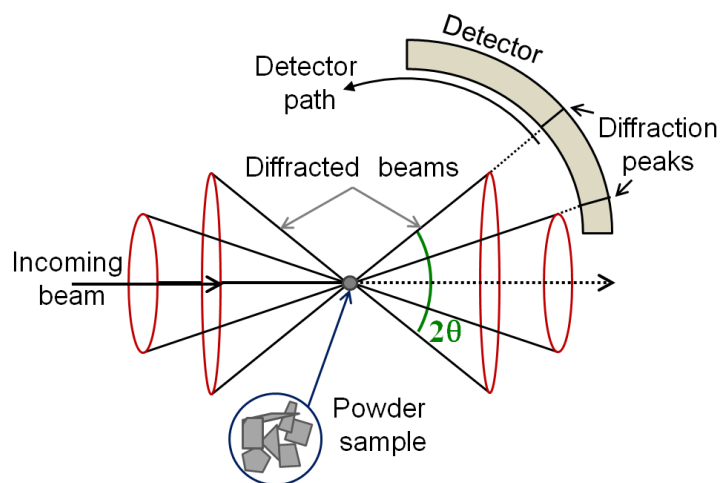


Figure 2.2.4: Experimental setup for a powder X-ray diffraction measurement showing the Debye-Scherrer cones generated when a sample is irradiated.

with similar (but not equal) scattering angles overlap due to their finite width.

2.2.1.1 Laboratory X-ray Diffraction

X-ray diffraction patterns were collected in Oxford on a Philips PANalytical X'Pert diffractometer operating at 45 kV and 40 mA. Samples were mounted on a greased glass slide and placed in an air-tight sample holder within an argon filled glove box. Cu K_α radiation was used with a Ge (111) crystal monochromator to select α_1 (1.540598 Å) radiation. Measurements were carried out using a 2θ step size of 0.008° from 10° to 70°.

2.2.1.2 Synchrotron X-ray Diffraction

The best X-ray diffraction data typically comes from a synchrotron, where the intensity of the incoming radiation is many orders of magnitude larger than that achieved in most laboratory instruments. In a synchrotron, electrons are initially produced from an electron gun and then sped up by passing them through a linear accelerator (LINAC). They are then ejected into a 'booster

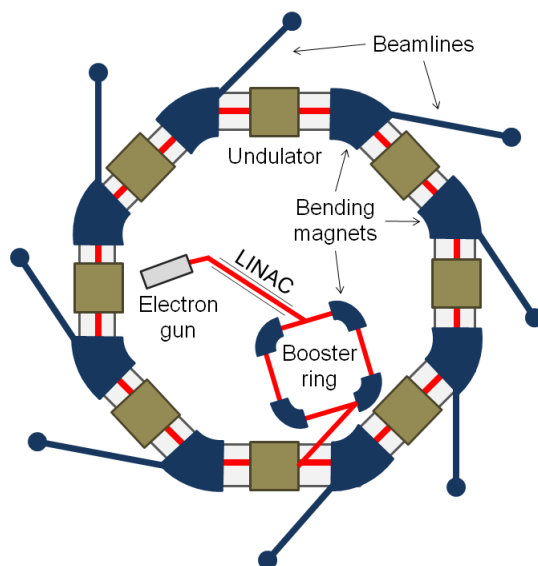


Figure 2.2.5: A simplified synchrotron design

ring', where they are accelerated until they approach the speed of light. They are then released into a storage ring, which contains straight sections joined together by several bending magnets. At these bends, the fast traveling electrons emit Bremsstrahlung radiation in a direction tangent to their path. This radiation is mostly in the form of X-rays and is emitted in a small collimated cone, which is then passed to the beamlines for further collimation. Undulators, which consist of a series of opposing magnets that cause the electron beam to undergo oscillations and produce additional X-rays in the straight regions of the synchrotron.

Sample Preparation

Samples were loaded into borosilicate capillaries (approximately 0.8mm in diameter) in an inert atmosphere and temporarily sealed using vacuum grease. Once removed from the glove bag or glove box, they were permanently sealed by melting the end shut. To ensure good powder averaging, the capillaries were

mounted into a brass spinner and spun in the beam during data collection.

X-ray Diffraction at the Diamond Light Source: Beamline I11

The I11 beamline at the Diamond Light Source is a high resolution powder diffraction instrument that was used to study many of the samples in this thesis. The high angular resolution, high count rates, and diversity of environmental conditions on I11 make it possible to perform structural studies of powder samples at variable temperature and pressure. The beamline has a resolution of $\frac{\Delta d}{d} \approx 10^{-3} - 10^{-4}$ Å and can detect rapid changes ($\Delta t \approx \text{ms-s}$) under non-ambient conditions. X-rays produced on I11 have energies of 5 keV to 30 keV and the optics hutch houses several slits systems, beam diagnostics, a monochromator and harmonic rejection mirrors.

High resolution measurements were performed using 5 multiple analyzing crystal (MAC) devices, which are each comprised of 9 crystals and detectors that scan positive 2θ angles (above the beam). A robotic arm exists which allows for high sample throughput (up to 200 capillaries). For variable temperature measurements, a hot air blower (RT-1000°C) was used to heat the sample. For time-resolved work, a wide-angle position sensitive detector (PSD), which is mounted below the sample, was used. The PSD can perform fast data collection (on the order of milliseconds) with a 90° aperture, an angular resolution of 0.01° , and is based on Mythen-2 modules. A custom-built high pressure gas cell and sapphire capillaries were used for hydrogen absorption measurements[137].

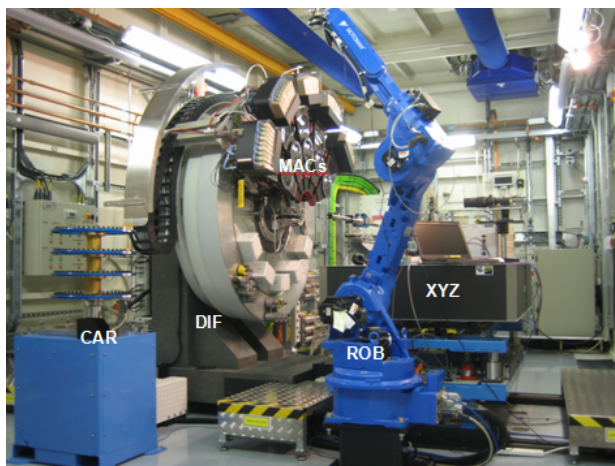


Figure 2.2.6: The experimental hutch on I11 showing the diffractometer (DIF), 5 arms for multi-analyzing crystal-detectors (MACs), robot for high throughput screening (ROB), carousel with 200 sample positions (CAR), and robotically controlled table (XYZ). The Position Sensitive Detector (PSD) is located on the underside of the diffractometer (opposite the MACs).

X-ray Diffraction at the Swiss Light Source (SLS): Beamline MS X04SA

Beams produced at the SLS have more flexible energy and intensities as it is a third-generation synchrotron facility. The MS X04SA beamline uses the hardest X-rays (5-40 keV), which are generated from an undulator. This beamline is also equipped with both 5 crystal-analyzer detectors and a wide-angle silicon microstrip detector (PSD) for fast data acquisition (though at the cost of angular resolution). Typical photon fluxes are on the order of 10^{13} photons s^{-1} at 13 keV and 2×10^{12} photons s^{-1} at 20 keV[138].

X-ray Diffraction at the European Synchrotron Radiation Facility (ESRF): Beamline ID31

The ID31 at the ESRF is a dedicated High Resolution Powder Diffraction beamline. Three separate undulators produce X-rays over an energy range of 5keV to 60keV that have typical fluxes of $1.5 * 10^{12}$ photons $\text{mm}^{-2}\text{s}^{-1}$ at 29 keV and $6.1 * 10^{12}$ photons $\text{mm}^{-2}\text{s}^{-1}$ at 15 keV. The X-ray beam is monochromated by cryogenically cooled Si (111) crystals, but it is not collimated to allow improved powder averaging. ID31 also has a robotic arm capable of handling up to 50 samples for high throughput screening. The beamline uses 9 crystal-analyzer detectors, each with its own Si (111) crystal, that rotate vertically to collect data over the range of 2θ [139].

2.3 Neutron Scattering

Neutrons are uncharged constituents of atoms that have the ability to penetrate a variety of materials. It is therefore possible to probe atomic location and motion in a non-destructive way by scattering neutrons from the nuclei of atoms. Neutron diffraction is still a relatively young technique; there are only approximately 20 neutron sources in the world, though others are being developed (e.g. the China Spallation Neutron Source).

Modern neutron research facilities produce neutrons in one of two ways. In the first, neutrons are produced as a by-product of nuclear fission in a nuclear reactor. The Institut Laue-Langevin source in Grenoble, and the High Flux Isotope Reactor at the Oak Ridge National Laboratory are examples of large facilities that use this method of neutron generation. Although reactor neutron sources produce very large quantities of neutrons, they also produce nuclear

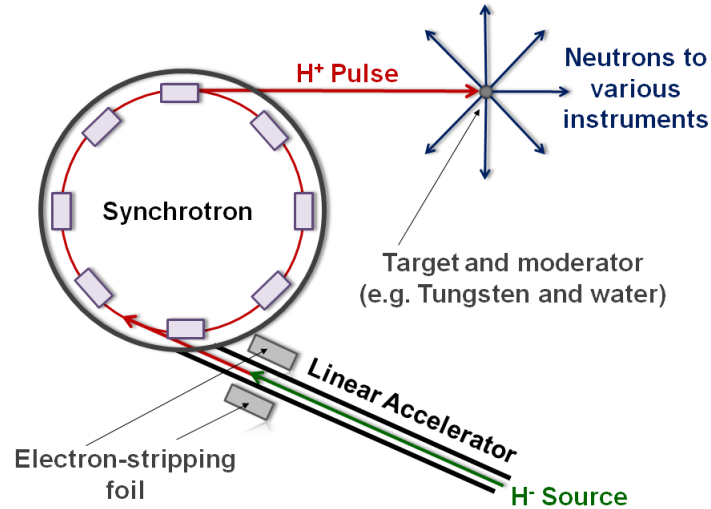


Figure 2.3.1: Simplified schematic of a spallation neutron source

waste and require highly-enriched uranium fuel. As such, newer sources typically favour the second method of generation, known as spallation (see Fig 2.3.1).

Spallation begins with an ion source that produces negatively charged hydrogen ions. The ions are accelerated to very high energies through a linear particle accelerator and passed through a foil that strips them of their electrons. The remaining protons are then passed into a ring-shaped structure (synchrotron), where they circle at high speeds and accumulate in clusters. Each bunch of protons is extracted from the synchrotron and then strikes a target (e.g. liquid mercury, tungsten). The high-energy pulses of protons drive neutrons away from the nuclei of the target atoms (this is the process of spallation), producing a very intense pulse of neutrons.

The neutrons are then slowed down to speeds useful for condensed matter research by guiding them through one or more moderators. They are then directed to a variety of different instruments (or beamlines), whose geometry and

detector banks have been optimized for a variety of specific research purposes. A majority of neutron sources operate via spallation, including the ISIS facility in the UK. All neutron experiments presented in this thesis have been conducted there. At ISIS, the process of extracting paired proton pulses occurs 50 times per second. Four-fifths of the extracted pulses are sent to the first set of beamlines (Target Station One, TS1) and the remaining are sent to a second set (Target Station Two, TS2).

Like all particles, neutrons exhibit wave-particle duality and their wavelength is given by the DeBroglie relationship:

$$p = h\lambda, \quad (2.3.1)$$

where h is Planck's constant, λ is the wavelength and p is the momentum, given by

$$p = mv, \quad (2.3.2)$$

where m is the mass and v is the velocity. In a neutron scattering experiment, the moment transfer (Q) is measured, which is the difference between the final and initial wave vector (k) of the neutron.

$$Q = k_f - k_i \quad (2.3.3)$$

and

$$|k| = \frac{2\pi}{\lambda}; \quad p = \hbar k \quad (2.3.4)$$

Broadly, the interaction of neutrons with nuclei can be categorized in one of three ways:

1. Elastic scattering, in which no energy transfer takes place. This is the

type of scattering harnessed for diffraction studies.

2. Inelastic scattering, in which the energy transfer occurs between the neutron wave and the sample. This is the type of scattering harnessed for spectroscopic studies.

3. Absorption, in which the incident neutron is incorporated into nuclei in the sample.

In the case of an elastic collision, the amplitude of the wavevector remains the same (i.e. , $|k_i| = |k_f|$) but the direction is changed. This means that diffraction peaks may be collected as a function of Q by using only neutrons with a specific wavelength, or by collecting data at a single angle. Combining the above equations, we obtain Eq. 2.3.5 for elastic scattering.

$$Q = 2k_f \sin\theta = \frac{4\pi \sin\theta}{\lambda} = \frac{2\pi}{d} \quad (2.3.5)$$

When a beam of neutrons is produced, it contains a variety of different wavelengths and only a particular wavelength of the neutrons is often desired to study a given material. As such, neutrons are either passed through a monochromator, or a “Time of Flight” (TOF) setup is used. In a TOF configuration, choppers slice the neutrons into phases. The initial velocity and position of a pulse is known while the final position and time after the pulse is measured, making it possible to determine the speed and hence energy of the neutrons. Using the DeBroglie equation, Bragg’s Law, and the relationship $v = L/t$, it is possible to establish a correlation between d spacing and time of flight (Eq. 2.3.6).

$$d = \frac{ht}{2mL \sin\theta} \quad (2.3.6)$$

In a diffraction experiment, detectors surround the sample in a number of banks. Those positioned at high angles (2θ) are called back scattering detectors

and provide the highest resolution. Banks at lower angles have a lower resolution but allow larger d-spacings to be observed. It is also possible to increase resolution by increasing the distance between the neutron source and the sample, or the sample and the detectors. This causes there to be a wider separation in the time taken for neutrons that have different speeds (energies) within a pulse to reach the detector. The resolution for a TOF diffractometer may be approximated by Eq. 2.3.7.

$$\frac{\Delta d}{d} = \left(\left(\frac{\Delta t}{t} \right)^2 + \left(\frac{\Delta L}{L} \right)^2 + (\Delta \theta \cot \theta)^2 \right)^{\frac{1}{2}} \quad (2.3.7)$$

The $\frac{\Delta t}{t}$ term is dependent on the moderator used, and is roughly constant for a given moderator. The second relates to uncertainties in the flight path; increasing the path will increase the resolution of the instrument (though typically at the cost of lower flux). The last term dominates at low angles and is an angular dispersion term that arises due to the widths of the detectors and sample. This means that a range of wavelengths satisfy the Bragg condition for each reflection[140].

2.3.1 Neutron Scattering and Borohydrides

As previously mentioned, the nature of X-ray diffraction means that studying light atoms, or atoms with similar Z, is extremely difficult using this technique. For neutron diffraction, the coherent elastic scattering cross section, σ , is calculated via Eq. 2.3.8.

$$\sigma = 4\pi b^2, \quad (2.3.8)$$

where b is the coherent scattering length, which is different for all atoms and isotopes. The principle benefit of neutron scattering is that scattering cross

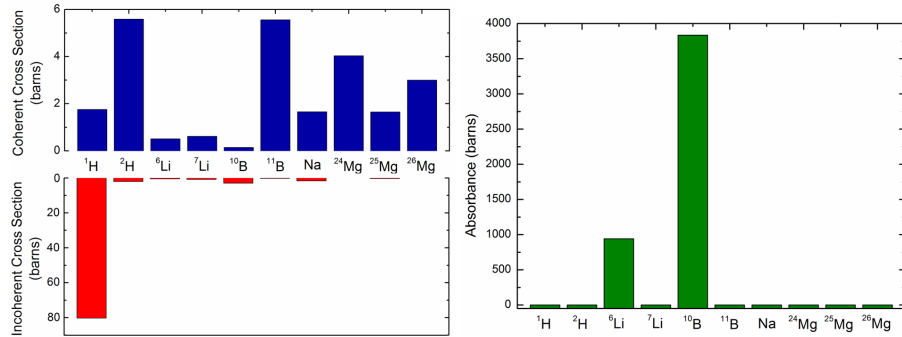


Figure 2.3.2: Coherent/incoherent (left) and absorption neutron scattering cross sections (right) for isotopes relevant to this thesis (Source:[141]).

sections vary by isotope and randomly across the periodic table, making it possible to observe both light and heavy atoms simultaneously.

There are however a number of problems associated with using neutrons to study metal borohydrides. The first problem arises from the difference in the coherent and incoherent scattering lengths of various elements and isotopes (see Fig. 2.3.2). For example, hydrogen has a very large incoherent scattering cross section. When diffraction measurements are performed, this means that a very large background will be seen in the data, making structure determination more difficult.

Secondly, certain isotopes will absorb large amounts of neutrons (Fig. 2.3.2). Boron-10 and lithium-6 are examples of elements that possess high absorption cross sections. When these isotopes are present in a sample, they significantly reduce the intensity of the diffracted beam. This means that unfeasibly long collection times will be needed to obtain data of sufficient quality.

As a result of these difficulties, it is typically necessary to isotopically enrich borohydride samples that are to be studied using neutrons. Doubly enriched boron-10, deuterium compounds are needed for diffraction measurements, while singly enriched boron-10 samples are preferred for inelastic neutron spectroscopy

measurements. Such isotopically enriched compounds can be extremely expensive ($>£10,000/\text{g}$) and so those used in this thesis were either made in house using a High Pressure reactor or were synthesized in collaboration with Torben Jensen's group at the University of Aarhus.

Although hydrogen and deuterium are chemically equivalent, the mass difference between the two isotopes can give rise to differences in the enriched compounds. The unit cell volumes are smaller for borodeuterides than for borohydrides and in some instances (e.g. alkali metal borohydrides) the difference may decrease as the radius of the metal increases (since the change in mass represents a smaller proportion of the overall mass)[55]. There are also marked differences in the vibrational frequencies observed between borodeuterides and borohydrides. A given B-H or B-D vibration will occur at:

$$v = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad (2.3.9)$$

where v is the vibration frequency, k is the force constant and μ is the reduced mass. Therefore, we expect that the B-D bond vibrations will occur at $\frac{1}{\sqrt{2}}$ of the frequency of an equivalent B-H vibrations due to its doubled mass. It is possible that a change in bond vibration frequency could affect the reactivity of deuterated compounds.

2.3.2 Diffraction at the ISIS Spallation Source

The beamlines that have been used for diffraction in this thesis include GEM, HRPD and WISH. All experiments were conducted with the sample in 6mm – 8mm vanadium cans unless otherwise stated.

2.3.2.1 General Materials Diffractometer (GEM)

GEM is a diffractometer in TS1 at ISIS that can be used to perform high resolution, high intensity experiments on disordered materials and crystalline

powders[142]. Neutrons pass through a methane moderator and travel 17m to the sample. This relatively long flight path allows high resolution measurements to be achieved. Two disc choppers control the range of wavelengths and one ni-monic chopper stops the very fast neutrons. There are several apertures along the beam path, the last of which is remotely controlled to define the dimensions of the beam that will hit the sample. Neutrons are detected by ZnS/⁶Li scintillators placed over the range of 1.1° to 169.3°[143].

2.3.2.2 High Resolution Powder Diffractometer (HRPD)

HRPD is the highest resolution neutron powder diffractometer of its kind in the world and is particularly useful for studying subtle changes in structure[140]. At short d-spacing, there is often a large number of nearly overlapping peaks that are often indistinguishable. In these cases, flux alone is not enough to sufficiently extract all information and high-resolution cold-neutron diffraction is best. The flight path at HRPD is extremely long; it is located nearly 100m from the ISIS target at the end of the neutron guide. This allows for a backscattering resolution of $\frac{\Delta d}{d} \approx 4 \times 10^{-4}$ to be achieved over a d-spacing range of 0.6 Å to 5 Å. Incident neutrons are moderated by liquid methane. They have a maximum wavelength of approximately 10-12 Å and a peak flux just over 2 Å, corresponding to a d-spacing of around 1 Å when observed through backscattering geometry. ZnS scintillator detectors at low angles and 90° allow a measurable d-spacing range of over 20 Å (though at the cost of lower resolution). Choppers at 6m and 9m after the moderator serve to select the wavelength and prevent frame overlap, respectively[144].

2.3.2.3 Long-Wavelength Diffractometer (WISH)

Unlike the previous two beamlines, WISH is located in the 2nd target station at ISIS (TS2)[145]. It has been designed principally to investigate powders at long d-spacings in magnetic and other large unit cell systems (though it has

the capabilities to perform single crystal measurements as well). The neutrons at WISH pass through a decoupled solid methane moderator and have a thermalized flux peaking around 4 Å. The very long flight path of 50m allows high resolution data to be collected over a d-spacing range of 0.7 to 17 Å with a single frame bandwidth of 8 Å. Wish uses pixellated ^3He detectors that cover scattering angles between 10° and 175° . There are 2 double and 1 single disc choppers and 5 slits for tuning beam divergence[146]. Wish can run in event mode, in which data is continuously collected while other controls (e.g. temperature using a cryofurnace) are changed. The data is then processed into useable slices using standard Mantid routines available at ISIS.

2.4 Diffraction Data Analysis

Crystallographic information is obtained from diffraction data by first determining the structural details of a given phase (e.g. unit cell, atomic positions, etc.) and then refining that structure to obtain information with the highest possible accuracy. If the structures present in a sample are known, they are compared to published data and refined using current experimental conditions. If the structure is unknown, it may be solved for the first time from diffraction data. A single crystal diffraction data set will contain information in all three dimensions. When powder diffraction is used, this information is condensed onto a single 2θ axis. This often causes peaks to overlap, making it difficult to extract accurate intensities and positions. As such, high quality data (such as that from a synchrotron source) is often necessary to obtain sufficiently sharp peaks on a low background[136].

2.4.1 Unit Cell Determination

The first step in solving a structure is to determine peak positions and index them to assign unit cell parameters. The term indexing refers to the process

of assigning the planes of lattice points responsible for a particular diffraction peak. It is possible to do this manually for the simplest systems though an auto-indexing program is used for more complicated structures. Caution is still needed when using such programs, as it is possible to incorrectly index many systems that may still reproduce the diffraction pattern. For example, it is possible to index a superlattice that has twice the volume of the correct lattice. Auto-indexing routines typically include several figures of merit in their output, which compare the differences between calculated and observed values of the functions used to index the pattern.

A by-product of indexing is to determine the space group (i.e. symmetry) of the crystal. This is often accomplished by examining the missing peaks in a diffraction pattern; if two elements occupy positions in the unit cell that cause them to reflect X-rays completely out-of-phase with one another, no reflection will be observed. Absences across an entire data set indicate the type of unit cell centering (e.g. h, k, l are all odd or all even for F centering) and systematic absences indicate translational symmetry (e.g. h may be even for a glide plane). From this, the Laue class may be determined and the final space group determination is carried out computationally.

Once a space group has been found, the size, shape, and symmetry are tested using a Pawley refinement. A Pawley refinement adjusts variables to minimize the sum of the differences between the squares of the measured and calculated intensities (least squares method) using a single peak shape across the entire diffraction pattern. If a good fit cannot be achieved, then either the space group used is incorrect or there is an impurity present in the sample[136].

2.4.2 Atomic positions Determination

There are several different ways that have been developed to locate the atoms of an unknown structure. The Patterson method examines the intensities of the

diffraction peaks to develop a map similar to an electron density map. However, instead of electron density, the map shows peaks corresponding to interatomic vectors, with the intensities relating to the product of the scattering functions of the elements involved. This method does not include phases, but rather uses the squares of the structure factors, which are obtained from peak intensities. Another technique, called Direct Methods, incorporates phases of the structure factor by processing in reciprocal space and making initial guesses at the phases based on calculations[136].

A method more often used in this thesis is a Monte Carlo or simulated annealing technique. This method operates in direct space and requires some initial information about connectivity in the sample. A simple structural model is given initially and the calculated diffraction pattern from this model is compared to the experimental pattern using the same metrics for quality of fit as in a Rietveld refinement (see Sect. 2.4.3). The model is adjusted randomly, the quality of fit is recalculated, and the new model is accepted or rejected based on criteria set by the user. The process is repeated until the fit is no longer significantly improved[147].

2.4.3 Rietveld Refinement

A Rietveld refinement is one of the most common ways to refine a crystal structure to best match diffraction data. The method was developed in the late 60s[148, 149] and made use of computers to exploit all available information in a diffractogram. The entire pattern is modeled as a whole to be able to determine where absences are located. Unlike Pawley refinements, the peak shape is modeled and refined against the experimental data. The method was originally developed for neutron diffraction patterns because of the simple peak shapes, but was later extended X-ray and TOF diffraction data sets as more sophisticated models for peak shape emerged. A common model for peak shape is a

pseudo-Voigt function, which is built from Gaussian and Lorentzian functions, but more sophisticated functions model the experimental conditions or particle size and strain directly (these are related to the peak shape).

In a Rietveld refinement, the background intensity, y_{obs} , is expressed as a function of 2θ (or TOF). The existing structural model is used to calculate theoretical intensities at each point, y_{calc} . This is achieved through Eq. 2.4.1, where the background intensity is summed with the intensities of expected diffraction peaks.

$$y_{calc} = s \sum_k L_k |F_k|^2 \phi(2\theta_i - 2\theta_k) P_k A + y_{obs}, \quad (2.4.1)$$

where s is the scale factor; k is the miller indices for a Bragg reflection; L_k includes the Lorentz polarization and multiplicity factors; F_k is the structure factor for the k^{th} Bragg reflection; $\phi(2\theta_i - 2\theta_k)$ is a function which approximates the effect of the instrument and peak shape (called the reflection profile function); P_k corrects for preferred orientation; A is an absorption factor[147].

A least squares method (Eq. 2.4.2) is then used to minimize the difference between y_{obs} and y_{calc} by adjusting structural parameters (e.g. size of unit cell, atom positions, thermal displacement parameters, etc.) and experimental parameters over the entire data set.

$$M = \sum_i \frac{(y_{obs} - y_{calc})^2}{y_{obs}} \quad (2.4.2)$$

Unlike other methods, which assign peak intensities independently, the Rietveld method provides a feedback mechanism between the crystal structure and peak intensity in the regions where peaks overlap. The relationship between peak intensities and the adjustable parameters in a Rietveld refinement are not always linear and, as such, if the starting model is poor, the fit may

diverge or reach a false minimum. It is therefore best to proceed with the refinement in a step-wise fashion:

1. Refine the shape of the background to the data
2. Refine the scale parameter, zero point error, unit cell parameters, and sample height until the correct peak positions are achieved.
3. Refine parameters relating to peak shape using an appropriate model.
4. Refine parameters relating to peak intensities, such as atomic positions and thermal displacement parameters.

The factor R_{wp} (Eq. 2.4.3) is a useful metric to determine the quality of agreement between the calculated fit and the experimental data[150].

$$R_{wp} = \sqrt{\frac{\sum w_i (y_{obs} - y_{calc})^2}{\sum w_i (y_{obs})^2}}, \text{ where } w_i = \frac{1}{y_{obs}} \quad (2.4.3)$$

R_{wp} is directly related to the difference between y_{obs} and y_{calc} , however data with a larger background will produce a lower value, so it is best to consider background-subtracted R_{wp} factors. Another parameter worth considering is the goodness-of-fit (GOF) or χ^2 .

$$\chi^2 = \left(\frac{R_{wp}}{R_{exp}} \right)^2 \text{ where } R_{exp} = \sqrt{\frac{(n - p)}{\sum w_i (y_{obs})^2}} \quad (2.4.4)$$

The GOF compares R_{wp} to a statistically expected value, R_{exp} and may be used to assess the quality of the fit independent of the quality of the data ($\chi^2 \geq 1$). Here, n is the number of observations and p is the number of parameters. When performing a Rietveld refinement, estimated standard deviations (esd) are generated for each of the refined parameters. Esds are errors due to random errors and do not include diffractometer alignment or particle size/direction effects.

X-ray diffraction is more prone to systematic errors in refinement than neu-

tron diffraction due to increased complexity of peak shape and poor crystal averaging, particularly if the particles are large and the sample is small. Crystallites may also adopt a preferred orientation, which may affect the intensities of the diffraction peaks (this is less of a problem in a neutron diffraction experiment as the sample is larger and less is packed against the container walls).

For powder diffraction, the relative orientation of the reciprocal lattice is unknown and there are far fewer observations made per refined parameter than for single crystal diffraction. Therefore, it may be possible to force an incorrect structure to give a relatively good fit and caution must be exercised when refining inter-related parameters together[147].

2.4.4 Topas Academic

All structure determinations and refinements in this thesis have been carried out using the program TOPAS Academic[151]. Known phases were refined using the crystallographic information files (cif) from the Inorganic Crystal Structure Database (ICSD).

If an unknown structure was present, the program DASH[152] was used to determine the extinction symbols. Unit cell parameters were then refined using a Pawley refinement. With a fixed occupancy of one, the heaviest atom was placed randomly in the structure, and then allowed to move freely. Several Rietveld refinements from various starting positions were carried out in a simulated annealing process. When the best atomic position had been identified, the occupancies were examined (as the metal and borohydride atom often are located on special positions). The remaining atoms were gradually added to the structure, ensuring that interatomic distances were physically feasible. Any hydrogen atoms added were initially constrained as tetrahedra surrounding the boron atom. As mentioned previously, the use of neutron vs. X-ray diffraction has implications on the degree of certainty to which hydrogen positions in a

BH₄ tetrahedron may be refined.

When variable temperature experiments were performed, large numbers of diffraction patterns close in temperature were collected. As there was little difference between two consecutive patterns, batch refinements were performed. In this process, the lowest temperature data set was refined manually. The output of the refinement was used as the starting point for the next temperature step and the process was continued until a significant change in the profile was seen (e.g. phase change). At this point, another manual refinement was made and the batch file refinements were continued.

2.5 Pair Distribution Function Analysis

In a powder diffractogram, there is a great deal of information located in the Bragg peaks about long range order, but there is also significant information about the short range order given in the diffuse scattering. Pair distribution function analysis allows both the Bragg and diffuse scattering to be analyzed simultaneously, revealing information about both long and short range order. While the technique has been developed to study liquids and glasses, it can also provide a great deal of insight into the short range order of crystalline materials[153].

The pair distribution function (PDF) itself is a mathematical equation that describes the probability of finding two atoms separated by a certain distance in a material. It is typically written as $G(r)$ and is given by:

$$G(r) = 4\pi r (\rho(r) - \rho_o) \quad (2.5.1)$$

where ρ_o is the average atomic number density, $\rho(r)$ is the atomic pair-density and r is a radial distance. This function gives information about the number of atoms in a spherical shell at a distance r from a reference atom

and peaks at characteristic distances separating pairs of atoms. $G(r)$ is an experimentally accessible function through a Fourier transform of X-ray (or neutron) powder diffraction data. Mathematically;

$$G(r) = \frac{2}{\pi} \int_{Q=0}^{Q_{max}} Q (S(Q) - 1) \sin(Qr) dQ, \quad (2.5.2)$$

where $S(Q)$ is the total scattering structure function given by

$$S(Q) = \frac{I^{coh}(Q) - \sum c_i |f_i(Q)|^2}{|\sum c_i f_i(Q)|^2} + 1, \quad (2.5.3)$$

where $I^{coh}(Q)$ is the corrected scattering intensity from a sample, c_i is the atomic concentration, and f_i is the X-ray atomic form factor for atom i (in the case of neutron experiments, the f s are replaced by neutron scattering lengths). To achieve a correct $I^{coh}(Q)$, the measured intensity must be background corrected and normalized by both the flux and number of atoms in the sample. Corrections are needed for various experimental effects such as sample absorption, multiple scattering, etc., and the data are normalized to get the structure function $S(Q)$. This process is typically carried out in a software package[154].

While the PDF is not particularly susceptible to data processing errors, imperfect corrections result in distortions to $S(Q)$ and it is important to exercise caution when interpreting data at low r values. However, since the PDF does still include information contained in the Bragg peaks as well as the diffuse scattering, it can provide useful structural data out to very long r values.

X-ray measurements were collected on the dedicated PDF 11-ID-B beamline at the Advanced Photon Source at the Argonne National Laboratory, which operates at fixed energies of 58 and 90 keV[155]. Data were normalized, corrected, and Fourier transformed to give the radial distribution function using the GudrunGui2 software package.

2.6 Vibrational Spectroscopy

All molecules possess some vibrational motion; the atoms possess a form of periodic motion as the whole molecule translates or rotates. A molecule with N atoms has $3N - 6$ normal modes of vibration, unless it is linear, in which case it will have $3N - 5$ modes (rotation about its molecular axis cannot be observed). The different types of molecular vibrations may be subdivided depending on whether or not they are in or out of plane (see Fig. 2.6.1). In plane vibrations include:

1. Stretching, which results in a change in bond length. Stretches can be either symmetric or asymmetric.
2. Bending, in which the angle between the bonds involved changes.
3. Rocking, in which the angle between a group of atoms and the rest of the molecule is changed.

Out of plane vibrations are:

1. Twisting, where the angle of the plane formed by a group of atoms is changed.
2. Wagging, in which the angle between the plane of a group of atoms and a plane bisecting the rest of the molecule is changed.

When a molecule absorbs a quantum of energy, E , a molecular vibration of frequency ν will be excited according to the relation:

$$E = h\nu \quad (2.6.1)$$

The absorption of a single quantum of energy from the ground state is called the fundamental vibration, while the absorption of multiple quanta is called an overtone. To a first approximation, these vibrational modes may be treated as a simple quantum harmonic oscillator with associated energy E_v (Eq. 2.6.2).

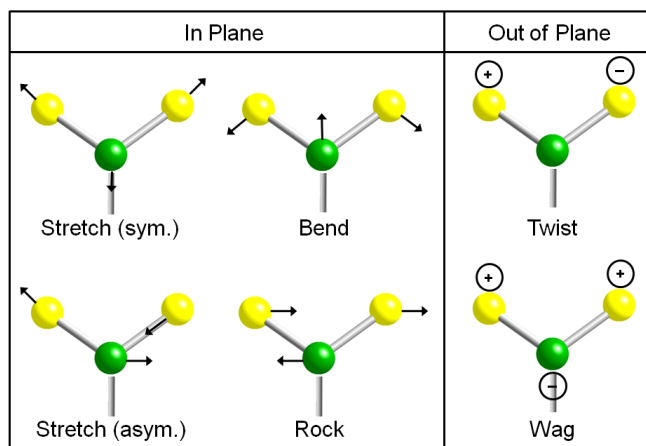


Figure 2.6.1: Vibrations of a simple AB_2 group. Arrows represent the direction of motion of atoms in the plane of the group, while the $+$ and $-$ signs represent motion above and below the plane, respectively.

$$E_v = hv \left(v + \frac{1}{2} \right), \quad (2.6.2)$$

where v is the vibrational quantum number. Here, the vibrational energy is a quadratic function with respect to the atomic displacements and the first overtone has a frequency that is double that of the fundamental.

While this may be a good approximation for the bottom of a potential energy well (lowest energy vibrations), in reality, vibrations behave like anharmonic oscillators and excitation of higher energy overtones eventually leads to complete dissociation of the molecule. Here, the restoring force is no longer directly proportional to the displacement from equilibrium and each progressive overtone has an energy that becomes increasingly closer to that of the previous one. The discrete energies of each level, E_v , are modeled well using a Morse potential (Eq. 2.6.3).

$$E_v = \omega_e \left(v + \frac{1}{2} \right) - x_e \omega_e \left(v + \frac{1}{2} \right)^2, \quad (2.6.3)$$

where ω_e is the vibrational wavenumber (the harmonic vibrational frequency expressed in units of cm^{-1}), and x_e is a correctional term. While the energy levels of a harmonic oscillator were evenly spaced by an amount ω_e , those of an anharmonic oscillator grow increasingly closer together as v increases until they form a continuum. The energy at which this occurs is the dissociation energy and corresponds to the point at which the potential energy function reaches zero. As such, there is a maximum possible value of v that occurs when the derivative of the energy with respect to the vibrational quantum number is zero.

$$\frac{dE}{dv} = 0 = \omega_e - 2x_e \omega_e \left(v_{max} + \frac{1}{2} \right) \quad (2.6.4)$$

so,

$$v_{max} = \frac{\omega_e}{2x_e \omega_e} - \frac{1}{2} \quad (2.6.5)$$

The vibrational states in a molecule can be probed in a number of ways. Most commonly, infrared spectroscopy (IR) is used as vibrational transitions often correspond to an amount of energy found in the infrared region of the frequency spectrum. Although IR spectroscopy was not performed in this thesis, two other spectroscopic techniques (Raman and Inelastic Neutron Scattering) have been used[156, 157, 158].

2.6.1 Raman Spectroscopy

When monochromatic light from a laser in the visible, near IR, or near UV range of the spectrum hits a sample, most is scattered elastically. The incident light interacts with excitations in the sample and the scattered photons are shifted up or down in energy. When there is no net change of energy in the incident and outgoing beam, this is known as Rayleigh scattering. Raman scattering

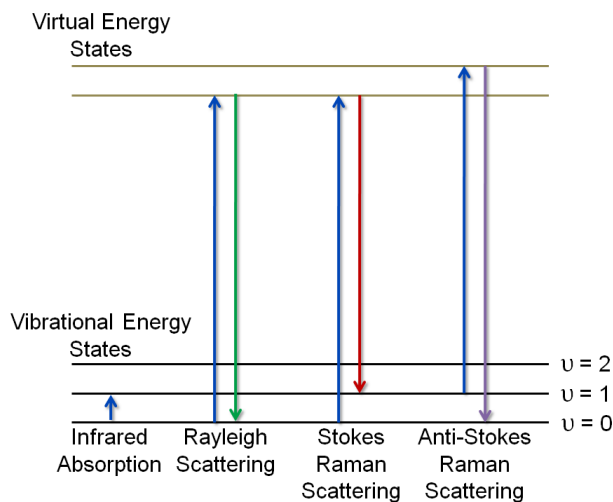


Figure 2.6.2: The excitation of vibrational states showing those used in Raman scattering.

takes advantage of the small percentage of light that is inelastically scattered from a sample, where the energy of the scattered laser photons is shifted up or down and gives information about the molecular vibrations, phonons and other excitations in the system[157].

When the oscillating electric field of the incident laser lights interacts with a sample, it is excited to a 'virtual state'. This occurs since the electron cloud becomes polarized and only vibrations that change the polarizability of the molecule are Raman active (the symmetry of the vibration must have a quadratic form in character table of the molecule's point group). Following excitation, the sample decays immediately back to a lower energy state. In a Raman experiment, the intense Rayleigh scattering (relaxation back to the ground state, close to the elastic laser line) is filtered out and the photons with different outgoing energy are analyzed. Scattered photons that are red-shifted (lower in energy) produce what is known as Stokes scattering and those that are blue-

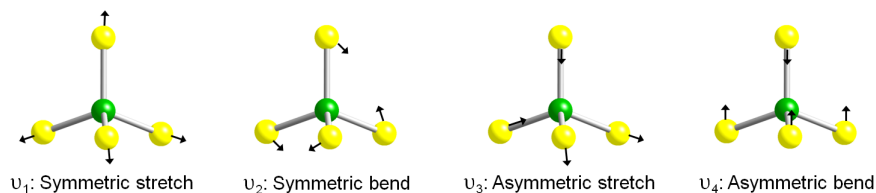


Figure 2.6.3: The four different types of possible vibrations a free $[\text{BH}_4]^-$ ion.

shifted (higher in energy) produce Anti-Stokes scattering (Fig. [fig:Raman]).

In order for energy to be conserved, the vibrational quantum number must also change by ± 1 . Population of the energy levels follows a Boltzmann distribution and a majority of the molecules will be in the ground state. As a result, the Stokes scattering is much more intense than the Anti-Stokes scattering and it is the Stokes frequencies that are recorded. A Raman spectrum shows the frequency of the outgoing radiation relative to that of the incident beam.

A tetrahedral molecule has a total of 9 vibrational modes (Fig. 2.6.3):

1. A singly degenerate (A) symmetric stretch, v_1 .
2. A doubly degenerate (E) symmetric bend, v_2 .
3. A triply degenerate (T_2) asymmetric stretch, v_3 .
4. A triply degenerate (T_2) asymmetric bend, v_4 .

Within a crystal, a borohydride ion may occupy a variety of sites with different symmetries. Since the symmetry of a given vibration is determined by the point group of the borohydride ion, the vibrational symmetries are dependent on the symmetry elements present on the borohydride ion site in a crystal structure[158].

Raman spectra were collected on a Renishaw InVia reflex Raman microscope at the University of Birmingham. A 488 nm laser was focused onto the sample using a 20x objective with a spot diameter of approximately 50 μm and beam power of 20 mW. In an argon filled glove box, roughly 10 mg of sample was

loaded in an aluminum crucible and placed in an Instec HCS621V sample cell with a fused silica window. Samples were heated at 2° C/min under an argon gas flowing of 100 ml/min.

2.6.2 Inelastic Neutron Spectroscopy (INS)

As mentioned previously, INS exploits the change in momentum that may occur when neutrons interact with nuclei (recall Eq. 2.3.3). We define the energy transfer experienced by the sample as $\hbar\omega$

$$\hbar\omega = \Delta E = E_i - E_f = \frac{\hbar^2 (k_i^2 - k_f^2)}{2m_n} \quad (2.6.6)$$

defined so that a loss of energy by the neutron gives a positive value of $\hbar\omega$.

For inelastic scattering, it is important to take into account the energy dependence of the scattered neutrons. An INS spectrometer scans the energy spectrum of a sample while recording the flux of the incident and scattered neutrons. The response of the sample is a function of both energy and the solid angle, at which the neutrons are scattered. Therefore, in INS the partial differential cross section, $\frac{d^2\sigma}{d\Omega dE_f}$, is measured. This describes a fraction of neutrons that may be scattered in a solid angle of $d\Omega$ within an energy range $E_f + dE_f$.

The results of an INS experiment are reported using the dynamic structure factor, $S(Q, \omega)$, which is related to the amplitude and cross section weighted density of states. For a molecule containing N atoms (l), it is given by:

$$S(Q, \omega)_{total} = y \sum_{l=1}^N S(Q, \omega)_l \sigma_l = 4\pi \frac{k_i}{k_f} \left(\frac{d^2\sigma}{d\Omega dE_f} \right)_{observed} \quad (2.6.7)$$

$S(Q, \omega)_{total}$ is reported in scaled units of (energy)¹, which is related to the correct units (barns, (cm⁻¹)⁻¹) by the linear scale factor y . When hydrogen

atoms are present, INS spectra are dominated by their large cross section, which (along with the number of atoms in the neutron beam) is subsumed into the scale factor. As such, spectra are compared in terms of relative intensities. For a given mode (v) the relative intensity for the atom l at momentum transfer Q and energy transfer ω_v is related to the atomic displacement $^v u$ by the Eq. 2.6.8.

$$S(Q, \omega_v)_l^n = y\sigma_l \frac{[(Q \cdot ^v u_l)^2]^n}{n!} \exp \left[- \left(Q \cdot \sum_v ^v u_l \right)^2 \right] \quad (2.6.8)$$

which, when averaged over an entire powder, becomes

$$S(Q, \omega)_{\text{powder}} = \frac{1}{4\pi} \int S(Q, \omega) dQ. \quad (2.6.9)$$

The expression on the right of Eq. 2.6.8 may be divided into two major terms; a pre-exponential term, related to $Q^2 u^2$, and an exponential term, $e^{-Q^2 u^2}$. The former increases as momentum transfer or scattering atom displacement increases. Since Q is fixed by the spectrometer, measuring $S(Q, \omega)$ allows the atomic displacements (eigenvectors of the vibration) to be determined. The second, exponential term is known as the Debye-Waller factor. It always increases faster than the pre-exponential term increases and has significant temperature dependence (through the atomic displacement). As such, INS measurements are typically carried out at cryogenic temperatures to achieve the highest possible signal intensity.

What the above formulation tells us is that INS gives direct access to both the eigenvectors and eigenvalues of a vibration. The position of transitions (eigenvalues) are a function of molecular structure and intramolecular forces, which correspond to energy loss from incident neutrons. The strength of a particular transition (eigenvectors) is a function of the atomic displacement

(determined by molecular structure/intramolecular forces) and momentum lost by incident neutrons (determined by the spectrometer)[159].

Although conceptually similar to Raman spectroscopy, there are several advantages to INS. The light used in Raman scattering corresponds to wavelengths that are thousands of Angstroms long, while neutron energies correspond to wavelengths that are similar or smaller than atomic spacings. As a result, INS is not limited to the centre of the Brillouin zone (i.e. measurements are over a range of Q) and there are no “selection rules” as there are for optical spectroscopy. The spectral range also tends to be much larger for INS (typically 0-4000 cm^{-1}) than for Raman. INS can also be modeled as the intensity of a band is proportional to the concentration of elements in the sample and their cross sections. Calculating the associated displacement of the scattering atom and its vibrational energy from ab initio methods is relatively straightforward.

Finally, and of particular interest to studying borohydrides, INS is very sensitive to hydrogen atoms. The intensity of an INS band is proportional to the incoherent scattering cross section, where as Raman is more sensitive to heavier elements. As was seen earlier, this is considerably larger for hydrogen than for any other element[160].

2.6.2.1 TOSCA

TOSCA is a high resolution, inverted geometry, time-of-flight spectrometer with a range of 0-4000 cm^{-1} located at the ISIS spallation neutron source at the Rutherford Appleton Laboratory.

At TOSCA, a pulsed polychromatic neutron beam hits the sample, located 17 m from the neutron source. The neutrons are then backscattered through an angle of 45° or 135° and hit a graphite crystal. As the angle and distance are fixed, only a single energy (32 cm^{-1}) is Bragg scattered and passed on to a ^3He detector bank and the others are absorbed by a beryllium filter. TOSCA

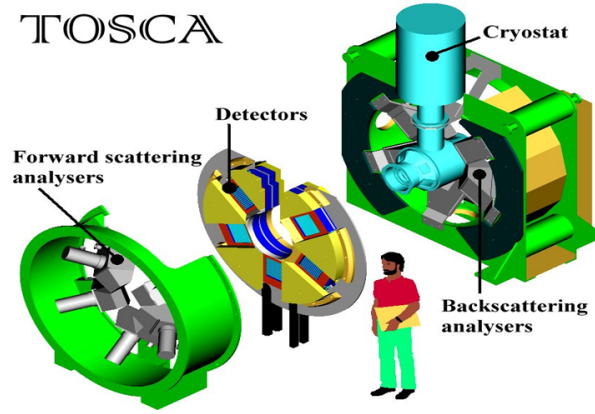


Figure 2.6.4: Schematic of the setup at TOSCA, showing the detectors, analysers and, cryostat (where the sample is located).

covers an extended energy transfer range ($-2.5 \text{ meV} < E < 1000 \text{ meV}$), and has a resolution $\frac{\Delta E}{E} \sim 1[160]$.

Approximately 1g of ^{11}B enriched samples (to avoid the high absorption cross section of ^{10}B) were loaded in a glove box into either a vanadium can or an aluminum foil sachet, which was then placed into a flat back sample can using indium wire as a sealant. Measurements are undertaken in neutron energy loss mode at cryogenic temperatures, unless otherwise stated. The signal of the empty sample holder and a flat background were subtracted from the signal. The raw data was corrected for the polarization and Debye-Waller factors to obtain $S(Q, \omega)$ using standard routines in the software suite MantidPlot available at ISIS.

2.6.2.2 MARI

MARI is also a time-of-flight inelastic neutron scattering spectrometer at ISIS. The beamline utilizes Fermi choppers, which is a set of five choppers that allow the incident radiation to be tuned to optimize resolution in different

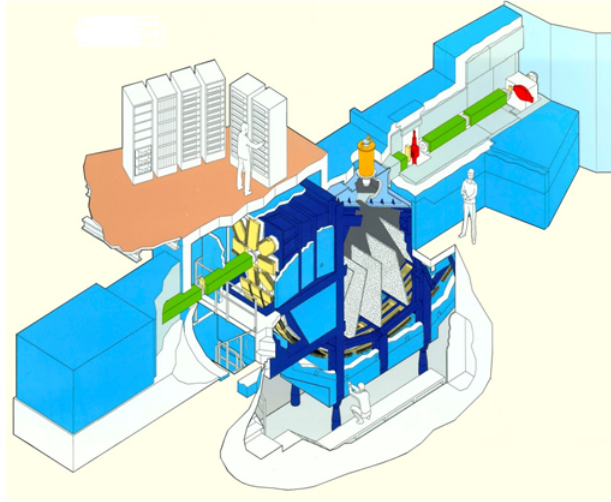


Figure 2.6.5: Schematic of the MARI setup

energy ranges. Depending on the range used, a resolution of $\frac{\Delta E}{E} \sim 1 - 2\%$ can be achieved. The primary flight path (from the source to the sample) is 11.739 m long and the Fermi chopper is located at 10.050 m from the source. The secondary flight path (from the sample to the detectors) is 4.020 m. Mari has continuous ^3He detector bank coverage from 3° to 134° , with a low angle bank covering from 3° to 13° , and high angle bank covering from 12° to 135° [161].

Samples were packed in aluminum foil and loaded into an Al can following the same procedure as the TOSCA experiments. To obtain good statistics data was collected for 12 hours at 5 K using incident energy ranges of 9-150 meV and 9-250 meV.

2.7 Nuclear Magnetic Resonance Spectroscopy

Nuclear Magnetic Resonance is a physical phenomenon whereby certain solids absorb and re-emit electromagnetic radiation. Fundamentally, NMR is applicable to atoms which possess a non-zero spin, I (a non-classical form of angular momentum); if a given atom has non-zero spin, it will also possess a

non-zero magnetic moment. A nuclear spin has $2I + 1$ possible energy states. In a free atom, these spin states are degenerate but when a magnetic field, B_0 , they separate in energy in a process called Zeeman splitting. When a particle with a non-zero magnetic moment is placed in an external magnetic field, two different energy states arise: one in which the magnetic moment and the external field are parallel (α state) and one in which they are anti-parallel (β state). The difference in energy, E , between the α state and the β state is given by

$$E = \gamma h B_0 \quad (2.7.1)$$

where γ is the gyromagnetic ratio of the given atom and h is Planck's constant. If the net magnetization is placed in a plane that is not parallel with the B_0 field, it will rotate about the axis along the direction of B_0 at a frequency equal to that of a photon which would cause a transition between the two energy levels of the spin. This frequency is known as the Larmor frequency. It is this resonance condition that is detected by NMR (transitions are promoted via a second, oscillating magnetic field)[157].

If we define the z-axis to lie along the direction of the applied external magnetic, at equilibrium, the net magnetization is oriented in the z-direction. As mentioned above, it is possible to change the orientation of the net magnetization by exposing the nuclear spin system to a photon equal to the energy between the two states. If the spin is aligned along the z-axis, it will gradually return to its equilibrium position. The time constant that governs the recovery of the z component of the nuclear spin magnetization, towards its equilibrium value, is known as spin-lattice relaxation time, T_1 .

Furthermore, since the magnetization is rotating at its own Larmor frequency, it will begin to dephase as each of the individual spins experience slightly different magnetic fields. The time constant that governs the recovery of the

transverse (i.e. XY plane) magnetization is known as the spin-spin relaxation time, T_2 . T_1 is always greater or equal to T_2 . If this were not the case, then the transverse magnetization would have not dephased by the time the sample had returned to equilibrium. This is physically impossible, as once the sample has returned to equilibrium, there remains no transverse magnetization. Hence, T_1 must be greater than or equal to T_2 . In practice, T_2 defines the lifetime of the observed NMR signal (i.e. in a Fourier transform, T_2 relates to the width of the NMR signal).

Hydrogen and boron have spins of $\frac{1}{2}$ and $\frac{3}{2}$, respectively. Nuclei that have a spin larger than $\frac{1}{2}$ also have a quadrupole moment. This interacts with the magnetic moment causing a more rapid relaxation to the ground state and therefore, broadening of the lines in the NMR spectra[162].

When placed in a magnetic field, the electrons of an atom circulate about the direction of the applied magnetic field, causing a small magnetic field at the nucleus that opposes the external field (this is termed shielding). Therefore, the magnetic field experienced at the nucleus of an atom is generally less than that of the applied field, causing atoms in different environments (of different electron densities) to resonate at different frequencies. Both this frequency shift and the fundamental resonant frequency are directly proportional to the strength of the B_0 field. The deviation in frequency is converted to a value called the chemical shift, δ , which is independent of the B_0 field used. The chemical shift of a nucleus is the difference between the resonance frequency of the nucleus and that of a standard, reported in ppm (Eq. 2.7.2).

$$\delta = \frac{\nu - \nu_{ref}}{\nu_{ref}} * 10^6 \quad (2.7.2)$$

The standards used for ^1H and ^{11}B NMR are tetramethylsilane (TMS), $\text{Si}(\text{CH}_3)_4$, and $\text{BF}_3 \cdot \text{Et}_2\text{O}$, respectively. Chemical shift is positive when reso-

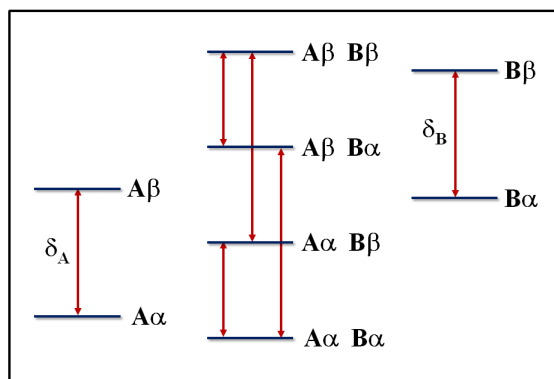


Figure 2.7.1: Four configurations arising from the interaction of two nearby nuclei

nance occurs at a higher frequency (or lower magnetic field) than the standard.

Nuclei that experience different chemical environments are said to be non-equivalent. When two non-equivalent nuclei are near one another (generally, near refers to less than four bond lengths away), they can affect each other's effective magnetic field. This effect is known as spin-spin coupling. As coupling arises through chemical bonding in a molecule, it can provide an insight into the connectivity of atoms. Consider the interaction of the two nearby nuclei, A and B. Both nuclei can be either aligned parallel (α) or anti-parallel (β) to the external magnetic field, leading to four possible different configurations. In Fig. 2.7.1 the allowed transitions (those in which the spin of one nucleus changes) have been indicated.

As Fig. 2.7.1 suggests, the NMR signals of nuclei A and B have each been split into two lines each centered at δ_A and δ_B , respectively. The distance between each of the lines is termed the coupling constant, J , and is a measure of the interaction between the two nuclei. The multiplicity (number of peaks observed) in this case is a doublet. Following a similar argument, the multiplicities and intensity ratios for an atom in the vicinity of multiple others can be

determined. Interactions between nuclei that occur directly through space are termed dipole-dipole interactions. In solution, the molecules are able to tumble and rotate freely, causing the dipole-dipole interactions to be averaged to zero. Furthermore, in a solid, it takes longer for nuclei to react to an external magnetic field and relax back to their ground state. As a result, spectra obtained from solution NMR are typically much sharper than those obtained from solid state NMR. Solid state NMR machines are consequently modified slightly to compensate for these issues and produce higher resolution data. Firstly, radiation pulses are more infrequent to allow adequate time for the sample to relax. Secondly, a technique known as magic-angle spinning (MAS) is used. At an angle of 54.74° to the direction of the magnetic field, dipole-dipole interactions in a solid are averaged to zero.

Solution state NMR studies were carried out in the Chemistry Department at the University of Oxford using a Varian Mercury 300 MHz spectrometer. The samples were loaded into NMR tubes within an argon atmosphere glove box. They were then taken to an argon-filled glove bag, dissolved in THF and sealed with parafilm.

Solid state MAS-NMR measurements were completed by the Durham University Solid State NMR Research Service using a Varian Unity Inova spectrometer with a 4 mm magic angle spinning probe operating at 96.19 MHz for ^{11}B (300 MHz for ^1H). The samples were packed into the rotors under inert gas and the spinning rate was approximately 14 kHz.

2.8 Thermogravimetric Characterization Techniques

2.8.1 Differential Thermal Analysis (DTA)

Differential Scanning Calorimetry (DSC) is an analysis technique in which the difference in the amount of heat required to raise the temperature of a sam-

ple and a reference is recorded as a function of temperature. The sample and the reference are kept at the same temperature using two different power supplies and the difference in the power supplied to the sample is recorded as a function of temperature. Thermal events (e.g. a phase change) are recorded as deviations from the baseline and may be endothermic or exothermic, depending on whether more or less power was supplied to the sample relative to the reference. Thermogravimetric analysis (TGA) is a technique in which the sample mass is monitored as a function of time as the external temperature is changed[157].

Both DSC and TGA measurements were performed simultaneously using a Perkin Elmer STA 6000 Thermal Analyzer. Samples of approximately 10-20 mg were loaded into a pre-weighed alumina crucible and heated at a rate of 5 °C/min. The mass of each sample was recorded with increasing temperature every eighth of a second on a balance with a resolution of 0.1 µg. The entire instrument was contained within an argon filled glove bag and the sample chamber was continuously purged by flowing argon at a rate of 30ml/min to allow samples to be loaded and contained in an inert atmosphere.

2.8.2 Intelligent Gravimetric Analysis (IGA) with Mass Spectrometry

Intelligent gravimetric analysis is similar to TGA but allows improved control over the sample environment (though it also requires more sample per measurement). Furthermore, a mass spectrometer connected to the system allows any gases evolved during decomposition to be analyzed. Approximately 100 mg of sample is placed in a pre-weighed stainless steel mesh bucket that can withstand temperatures up to 500 °C. A dry loader is connected to the IGA and purged with nitrogen to allow the sample to be loaded under inert atmosphere. The mesh bucket is then connected to a balance in the IGA using a gold chain and tungsten wire. The system is then covered with a stainless steel reactor vessel



Figure 2.8.1: *Left:* The entire IGAⁿ unit. *Upper right:* Inside the reaction vessel, showing the balance and sample bucket. *Lower right:* A loaded sample being craned into a diffractometer.

that is capable of withstanding pressures from 10^{-9} to 20 bar and temperatures up to 1000 °C. The system is sealed with a copper gasket and an external furnace is attached. The system may then be heated up to 500 °C as the mass on the balance inside is monitored. As the sample is heated, a control system automatically adjusts for changes in pressure that result from temperature increase. Gravimetric analysis can be carried out in either a sealed system, under vacuum, or flowing gas. When using flowing gas, a portion of the exhaust is fed directly into a model HAL201, type 124100 dynamic sampling mass spectrometer (MS) with dual Faraday/Electron multiplier. The detection limit of the MS is approximately 0.1 to 1 ppm, depending on spectral interference, and the atomic mass range is 200 amu. The MS was configured to record the partial pressures of various gasses every 12.5 seconds.

2.8.3 IGA with neutrons (IGAⁿ)

Neutrons possess the ability to penetrate a number of bulky sample environ-

ments. As a result, Hiden (in collaboration with ISIS) developed a custom built instrument called IGAn, which is designed for use on the GEM, WISH, and HRPD neutron beamlines at ISIS. This allows simultaneous collection of neutron diffraction and thermogravimetric data. The IGAn is functionally similar to the IGA, however it lacks a mass spectrometer. At low temperatures, approximately 1g of sample is loaded into a quartz bucket and a stainless steel bucket is used for higher temperature measurements. While quartz does not diffract neutrons, steel does. This results in steel peaks being visible in high temperature IGAn data. Two heating coils, positioned above and below the sample, replace an external furnace. The IGAn is fitted with a Tomkinson flange, allowing it to be fitted to and craned between the beamlines and a custom-built argon glove box (for sample loading). Mass, temperature, and pressure measurements are accurate to within $\pm 0.1 \mu\text{g}$, $\pm 0.001 \text{ }^\circ\text{C}$ and $\pm 0.01 \text{ mbar}$, respectively.

Chapter 3

A New Phase of Magnesium Borohydride

3.1 Introduction to Magnesium Borohydride and Chapter Outline

The earliest structural report of magnesium borohydride dates back to a 1971 paper by Konoplev and Bakulina[163, 42]. At the time the paper was published, much of the information available in the literature on $\text{Mg}(\text{BH}_4)_2$ was conflicting and incomplete. In their work, they synthesized a 99% pure sample of $\text{Mg}(\text{BH}_4)_2$ by an exchange reaction of sodium borohydride and magnesium chloride in diethyl ether. In doing so, they identified two crystalline phases of $\text{Mg}(\text{BH}_4)_2$: a room temperature tetragonal lattice ($a = 13.59 \text{ \AA}$, $c = 16.51 \text{ \AA}$) and a cubic face-centered lattice ($a = 15.5 \text{ \AA}$), which they designated as α and β , respectively. They identified the temperature of the polymorphic transition between the two phases as 460 K. The work went on to examine the decomposition

of the compound and assigned three later thermal events to MgH_2 formation, metallic Mg formation and metallic Mg melting.

It was not until the resurgence of interest in borohydrides of the 2000s that another report of pure $\text{Mg}(\text{BH}_4)_2$ emerged from Chopek *et al.*[66], in which $\text{Mg}(\text{BH}_4)_2$ was synthesized from the reaction of MgH_2 with aminoboranes. The report found two different phases of $\text{Mg}(\text{BH}_4)_2$, which they also designated as α and β . They observed a transition temperature of 465 K between the two polymorphs but did not provide full structural solutions to the phases they had identified.

Soon after this work, two groups (Černý *et al.*[84] & Her *et al.*[86]) independently solved the structure of the two phases, revealing that the α phase produced by Chopek *et al.* was inconsistent with that reported in 1971. The room temperature phase was found to adopt a complex hexagonal framework ($a = 10.3414 \text{ \AA}$, $c = 37.086 \text{ \AA}$), with several unoccupied voids in the structure. The structure was solved using synchrotron X-ray and neutron powder diffraction and was assigned a space group of $P6_1$ (although it was later shown that the orientation of some of the BH_4 tetrahedra was incorrect in this model). A 2008 paper by Dai *et al.*[164] used density functional theory to geometrically optimize this structure and suggested that the true symmetry may actually be $P6_122$. Later work by Filinchuk *et al.*[85] used single crystal X-ray diffraction to revise the structure at 100 K and confirm the true symmetry as $P6_122$. While Kono-plev and Bakulina were indeed the first to assign the ' α ' label to their structure, modern literature has adopted α to designate the hexagonal $P6_122$ phase of $\text{Mg}(\text{BH}_4)_2$ and this report will remain consistent with that nomenclature.

By approximately 500 K, all of the α phase is converted irreversibly to the β phase, which was also solved by Her *et al.* in their 2007 paper. The structure is a less dense, face-centered orthorhombic structure that may be described by a

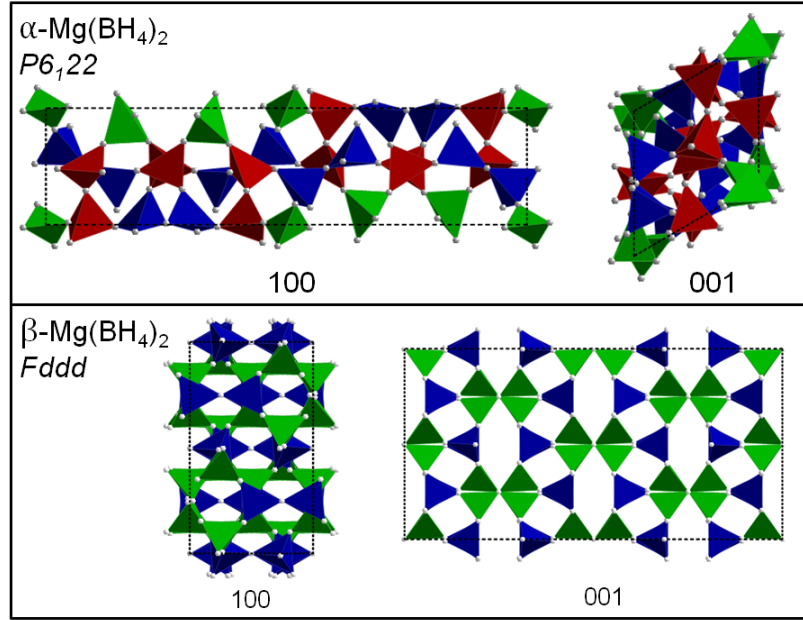


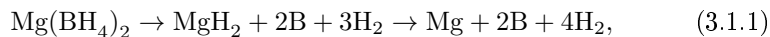
Figure 3.1.1: A view of the MgB_2 sub lattice in α - and β - $\text{Mg}(\text{BH}_4)_2$ viewed along the $[100]$ and $[001]$ directions. Symmetry independent Mg atom sites are shown as different colours.

relatively simple $Immm$ structure. However, β - $\text{Mg}(\text{BH}_4)_2$ exhibits strong anti-site disorder in the a lattice direction, and the $Immm$ model only represent an average structure. Her *et al.* therefore used a supercell 8 times the size, with $Fddd$ symmetry to obtain the currently accepted model of β - $\text{Mg}(\text{BH}_4)_2$ ($a = 37.072 \text{ \AA}$, $b = 18.6476 \text{ \AA}$, $c = 10.9123 \text{ \AA}$)[86].

Both the α and β phases consist of a complex corner-sharing 3D network of heavily distorted tetrahedra, which are built from a central Mg atom and four $[\text{BH}_4]$ units. The hexagonal structure contains three different Mg^{2+} symmetry sites and six different $[\text{BH}_4]^-$ sites, while the orthorhombic structure has two symmetry independent Mg^{2+} sites and five symmetry independent $[\text{BH}_4]^-$ sites (see Fig 3.1.1). The transition between the two phases is reconstructive and therefore irreversible.

Konoplev and Bakulina originally pointed out that, based on IR spectra and covalency arguments, $\text{Mg}(\text{BH}_4)_2$ finds itself between LiBH_4 and $\text{Be}(\text{BH}_4)_2$ [42]. This turns out to also be the case on a local structural level, with respect to metal-hydrogen bond lengths and coordination geometry around the metal. In $\text{Be}(\text{BH}_4)_2$, Be^{2+} is coordinated by three $[\text{BH}_4]^-$ anions in a flat trigonal formation while Li^+ is coordinated by four $[\text{BH}_4]^-$ anions in a nearly ideal tetrahedral formation in LiBH_4 . This indicates that covalency and the cation-to-anion radius ratio may be responsible for the structural complexity and rich crystal chemistry of $\text{Mg}(\text{BH}_4)_2$ that is unprecedented for this class of compounds. More recently, it was shown that charge transfer in metal borohydrides explains the structural diversity of these compounds and, since they are ionic systems, they fall into the classification of Linus Pauling[165].

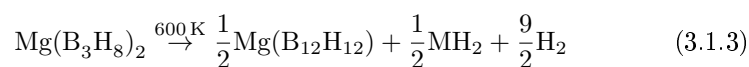
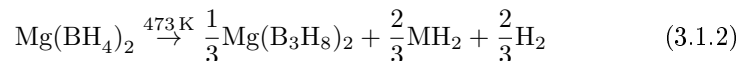
The basic decomposition route of $\text{Mg}(\text{BH}_4)_2$ [42] was first reported as



although various studies have identified the products shown in Eq. 3.1.1[66, 166], the reaction products are not definitively observed until around 600 K, while gas is evolved below this temperature[167]. Later work suggests that dehydrogenation occurs in several more steps and that the actual mechanism of decomposition in the solid state may be more complex[168]. The first reaction intermediate that was identified as a significant product of reaction was the dodecaborane species, $[\text{B}_{12}\text{H}_{12}]^{2-}$ [169], which has been previously observed as an “intermediate” in the decomposition of several other borohydrides[170]. The decomposition of $\text{Mg}(\text{BH}_4)_2$ to $\text{Mg}(\text{B}_{12}\text{H}_{12})$ and ultimately MgB_2 via several polyboranes was suggested by Soloveichik *et al.*[167], who examined earlier work by Stasinevich and Egorenko[171]. The high kinetic barrier to the hydrogenation of $\text{Mg}(\text{B}_{12}\text{H}_{12})$ was suggested as the reason why the system was not fully

reversible.

A recent paper by Chong *et al.*[61] suggested a more complex decomposition mechanism based on the formation of several polyborane species. The work found that dehydrogenation at 473 K *en vacuo* for 5 weeks resulted in the highly selective formation of $\text{Mg}(\text{B}_3\text{H}_8)_2$, which was identified using solution NMR. $[\text{B}_{10}\text{H}_{10}]^{2-}$, $[\text{B}_{12}\text{H}_{12}]^{2-}$, and other borate species were also observed as decomposition products/intermediates when higher temperatures were used. The authors then postulated that decomposition proceeds via a metal-ion-assisted B-H condensation pathway, in which B_nH_{n+x} species are built from B-H insertion into a growing polyborane with simultaneous formation of hydrogen and a corresponding metal hydride. Therefore, decomposition of $\text{Mg}(\text{BH}_4)_2$ is currently believed to proceed via Eqs. 3.1.2 & 3.1.3, where Eq. 3.1.3 proceeds via the formation of several other polyborane species.



MgH_2 then goes on to decompose to H_2 and Mg metal, which then combines with $\text{Mg}(\text{B}_{12}\text{H}_{12})$ to form MgB_2 and H_2 .

The discovery that $\text{Mg}(\text{BH}_4)_2$ decomposes via polyborane species has certain implications for the reversibility of such systems. By stopping the reaction at the stage of $\text{Mg}(\text{B}_3\text{H}_8)_2$ formation, Chong *et al.* were able to reform $\text{Mg}(\text{BH}_4)_2$ by re-hydrogenation under 120 atm of H_2 at 523 K for 48 hours. Previously, reversibility of the MgB_2 - $\text{Mg}(\text{BH}_4)_2$ system had been achieved by Severa *et al.*[172], though much more draconian conditions were needed to achieve hydrogenation of milled MgB_2 (950 bar H_2 at 673K for 108 hours). Although both

the kinetics of hydrogen sorption and gravimetric capacities in this system are far too sluggish to be of practical use, this is the first time reversibility has been achieved in $\text{Mg}(\text{BH}_4)_2$ using such mild conditions. Quenching polyborane reactions thus offers promise for further tuning borohydride materials if other aspects of the reactions may be improved.

This chapter presents a new phase of $\text{Mg}(\text{BH}_4)_2$ that was determined from synchrotron X-ray diffraction. The structure is the first of its kind ever seen in borohydrides and it is compared to the other known polymorphs of $\text{Mg}(\text{BH}_4)_2$ using X-ray diffraction and Pair Distribution Function Analysis. The decomposition pathway of the new phase is examined using *in situ* PXD, NMR, DTA, MS, and Raman measurements as well as *ex situ* PXD, NMR and Raman. Much of the work in this chapter was reported in Ref. [87] and the new phase was independently discovered at the same time and reported by another group in Ref. [67].

3.2 Room Temperature X-ray Measurements

Samples of 95% pure $\text{Mg}(\text{BH}_4)_2$ were purchased from Sigma Aldrich in 1g batches. These were originally purchased to study the effects of $\text{LiBH}_4/\text{LiNH}_2$ addition on the decomposition behaviour of the pure borohydride. However, while performing a series of measurements on beamline I11 at Diamond, it was noticed that X-ray diffraction measurements of pure $\text{Mg}(\text{BH}_4)_2$ did not match the pattern of the published phases. Far fewer peaks were seen in the Sigma Aldrich samples, which suggested that the compound possessed a structure higher in symmetry than either the α or β polymorphs. The data was sent to Prof. Bill David who quickly solved the structure by first determining the space group using TOPAS academic/DASH and then looking for structural analogues of the corresponding oxide (SiO_2) in the Inorganic Crystal Structure Database

(the relationship to between the two compounds is discussed in more detail in Chapter 4). Keeping in line with modern convention, this new polymorph of $\text{Mg}(\text{BH}_4)_2$ is designated with the Greek letter γ .

The author later independently used TOPAS/DASH to determine the space group of the compound to be $Ia\bar{3}d$. A Pawley refinement of the data found that the cubic structure had a lattice cell parameter of $a = 15.7395(3)$ Å. The ICSD was then searched for a cubic polymorph of SiO_2 that crystallizes in the space group $Ia\bar{3}d$. Three matches were found in a theoretical study of uninodal zeolites published by Foster *et al.* in 2004[173]. However, of the three matches, only one possessed a unit cell smaller than that found for $\gamma\text{-Mg}(\text{BH}_4)_2$. As discussed in Section 1.4.4, it is expected that unit cell parameters are approximately 1.5 times longer for borohydrides than their corresponding oxide. Therefore, the structure with a lattice cell parameter of 10.03799 Å (PDF # 01-073-3462) was used as a basis for the $\gamma\text{-Mg}(\text{BH}_4)_2$ structural solution.

The positions of the Mg and B atoms were first introduced to the structure by placing them respectively on the equivalent Si and O atom positions in the SiO_2 isostructure. The lattice cell parameter and boron atom positions were refined using a Rietveld refinement before hydrogen atoms were introduced.

As X-ray diffraction is not very sensitive to light elements, when hydrogen atoms were added, they were constrained around the B atoms in a rigid tetrahedron using a Z matrix. This is an internal coordinate representation of an atomic system that is added into the structural refinement in TOPAS. The atoms are described by their atomic number, bond length, bond angle, and dihedral angle. These are converted to Cartesian coordinates and back in TOPAS, allowing rigid bodies to be defined in terms of bond lengths/angles during a Rietveld refinement. These rigid bodies can be translated or rotated. In the case of $\gamma\text{-Mg}(\text{BH}_4)_2$, the tetrahedron was centered on the boron atom and allowed

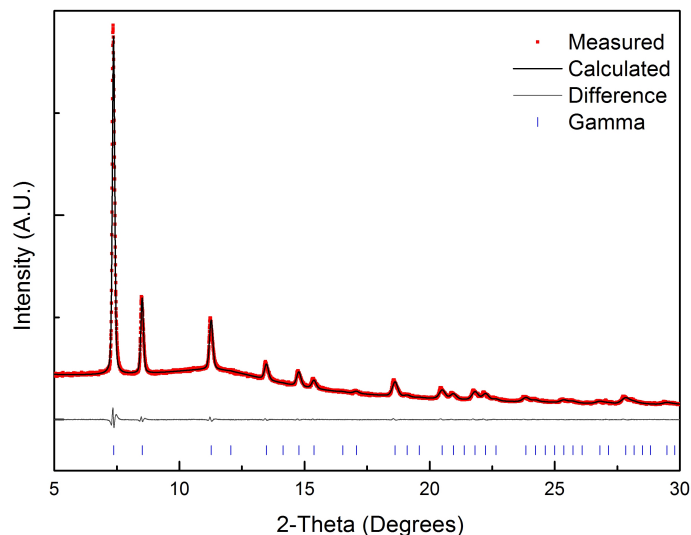


Figure 3.2.1: Graphical representation of the Rietveld refinement obtained from synchrotron X-ray diffraction data of $\text{Mg}(\text{BH}_4)_2$, showing the measured (red) and calculated (black) plots as well as the difference (Yobs-Ycalc) between them (gray). Expected peak positions are shown below as blue ticks.

to translate with it or rotate around it. Nearly ideal tetrahedra are expected so the bond angle was restricted to 109.5° . The bond length was allowed to refine between 1.05 and 1.20 Å.

Using this approach (and constraining the thermal parameters to be positive), a good overall fit to the data was achieved, with an R_{wp} of 4.103% (see Fig. 3.2.1). The final B-H bond length determined was 1.08(2) Å. Though this is rather short, B-H bond lengths on the order of 1.08 Å have been previously reported in other phases of $\text{Mg}(\text{BH}_4)_2$ [37]. It is likely that the electron density of the boron atom dominates in the signal and the refinement converges when density is added nearer the centre of the tetrahedron. The atomic positions from the final refinement are given in Table 3.1.

Recent DFT geometry optimizations of α -, β -, and γ - $\text{Mg}(\text{BH}_4)_2$ were performed by Mulliner in a direct comparison with SiO_2 [174]. The results showed

Table 3.1: Atomic positions of γ -Mg(BH₄)₂ from synchrotron X-ray diffraction at room temperature. H atoms were constrained to tetrahedra around the B atoms.

γ -Mg(BH ₄) ₂ $Ia\bar{3}d$ $a = 15.7395(3)$ Å				
Site	x/a	y/b	z/c	Wyckoff site
Mg	$\frac{1}{2}$	$\frac{3}{4}$	$\frac{7}{8}$	24d
B	0.3093	0.0593	$\frac{3}{8}$	48g
H1	0.2772	0.0371	0.3186	96h
H2	0.3754	0.0411	0.3724	96h
$\chi^2 = 2.103$ $R_{wp} = 4.103\%$ $R_{exp} = 1.950\%$				

that the structure obtained from X-ray diffraction is in close agreement with the energy minimized structure, although the structure determined by DFT was calculated at 0 K. The most notable difference between the two structural models was that bond lengths are considerably longer for the energy minimized structure (1.228 Å), although this is likely the result of the insensitivity of X-ray diffraction to hydrogen. When dispersion forces were ignored, the γ phase was predicted to be more stable than the α phase, although the order was reversed as these were included.

The short range order found in γ -Mg(BH₄)₂ is similar to that of previously known phases. The Mg atoms are surrounded by four BH₄ groups to form a heavily distorted tetrahedral environment ($\angle_{B-Mg-B} = 100-129^\circ$). Each boron atom is nearly linearly coordinated by two Mg atoms ($\angle_{Mg-B-Mg} = 177^\circ$), as is the case for β -Mg(BH₄)₂. The Mg-B distance in the new cubic phase is 2.41 Å, which is close to the range previously observed in both the hexagonal (2.39-2.45 Å [85]) and orthorhombic (2.34-2.47 Å [86]) phases.

It is the long range order of γ -Mg(BH₄)₂ that makes it a particularly fascinating material. It adopts a metal inorganic framework structure unlike any

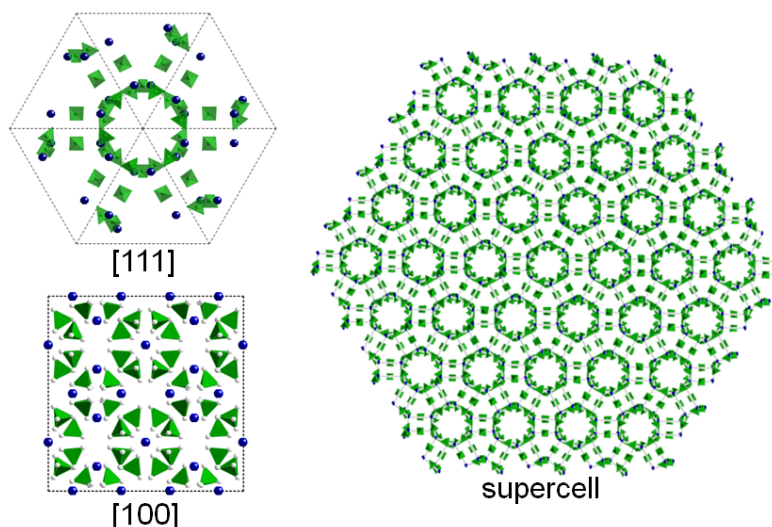


Figure 3.2.2: The structure of $\gamma\text{-Mg}(\text{BH}_4)_2$ as viewed along the $[111]$ and $[100]$ directions. On the left, a supercell shows the many the many porous channels of the γ phase structure.

other previously observed in metal borohydrides. The most striking feature of the framework is that it contains a 3D network of interpenetrating channels of void space, approximately 8 Å in diameter each (see Fig.3.2.2). This means that over 30% of the unit cell is made up of empty space and the bulk material has a remarkably low density of $\rho = 0.55 \text{ g cm}^{-3}$.

Porous and low density structures of $\text{Mg}(\text{BH}_4)_2$, such as the tetragonal $I\bar{4}m2$ ($\rho = 0.547 \text{ g cm}^{-3}$ [175]) and orthorhombic $F222$ phases ($\rho = 0.54 \text{ g cm}^{-3}$ [176]), have previously been predicted but have yet to be synthesized. This may be due to the ability of solvent molecules to promote nucleation and facilitate the growth of solution-grown phases. The identification of $\gamma\text{-Mg}(\text{BH}_4)_2$ is the first experimental observation of such a high degree of porosity in metal borohydrides and allows for new areas of exploration in borohydrides (e.g. gas physisorption), which are explored in more detail in Chapter 4.

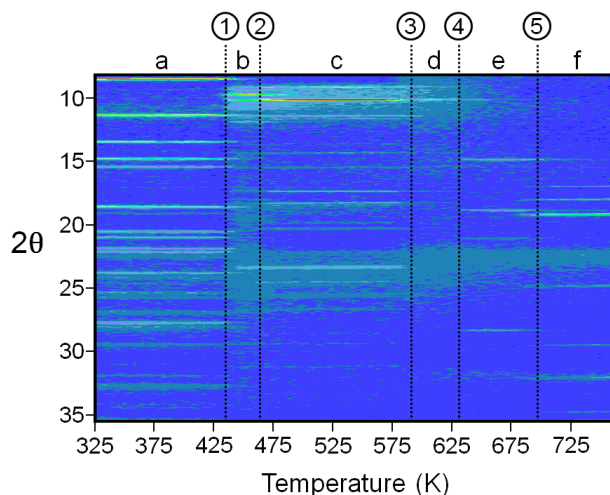


Figure 3.3.1: Surface plot of variable temperature synchrotron X-ray diffraction measurements of γ -Mg(BH₄)₂. Various regions are labeled at the top of the graph and major phase changes are numbered.

3.3 Variable Temperature X-ray Diffraction

To understand the decomposition of γ -Mg(BH₄)₂, several variable temperature X-ray diffraction studies were performed on samples that were heated directly in the beam. Furthermore, to understand the stability of the phases produced, a series of samples that were heated externally (and then quenched) were also studied.

3.3.1 *In Situ* Measurements

γ -Mg(BH₄)₂ was heated from room temperature to approximately 775 K at a rate of 10°K/min while diffraction data was simultaneously collected on beam-line I11 at Diamond. The position sensitive detector was used and 1 second scans were collected every 5 K. A surface plot of the complete data set, in which the colour is proportional to peak intensity, is shown in Fig. 3.3.1.

Referring to Fig. 3.3.1, the sole phase present in region **a** is the γ polymorph.

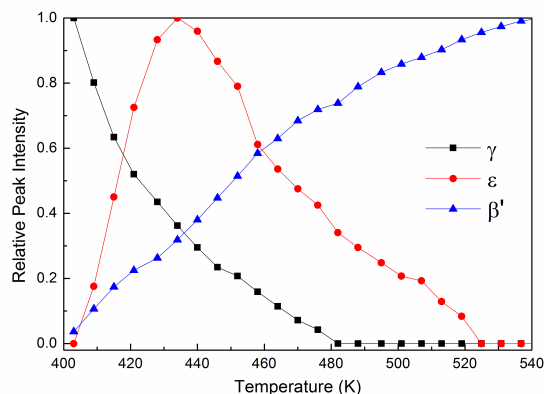


Figure 3.3.2: Peak intensities of the γ , β , and ϵ phases of $\text{Mg}(\text{BH}_4)_2$ as a function of temperature, taken from synchrotron X-ray diffraction measurements.

Unlike the *ex situ* measurements discussed in the next subsection, the α phase was not observed at the heating rate used. A similar observation was recently reported by Paskevicius *et al.*[177], who found that the proportion of α phase present did not increase before a phase change was observed, though it was formed upon quenching. At around 440 K (1), the spectrum becomes rather complicated as the γ polymorph begins to disappear and the β phase appears. Amid this change, a third phase appears to form, although 3 overlapping phases in a narrow region of the spectrum meant that it was only possible to assign fewer than 5 peaks to the third phase. Attempts to index the structure (henceforth called the ϵ phase) from these data were unsuccessful.

However, by following the intensity of a peak corresponding to each phase, it is possible to assess the different temperatures at which $\text{Mg}(\text{BH}_4)_2$ transforms between polymorphs. This data, extracted from peak fitting in TOPAS is shown in Fig. 3.3.2. Although peak intensities do not directly give phase fractions, it can be seen that the maximum amount of ϵ - $\text{Mg}(\text{BH}_4)_2$ is observed at around 435 K and the transition to the β phase is complete by around 520 K.

The assignment of peaks in this region is further complicated by the anti-site

disorder present in the β phase. As the phase transition occurs, nearly all of the peaks in the full β cell are present. As temperature increases, so do the number of stacking faults present, leading to a broadening and decrease in intensity of the odd-odd-odd hkl peaks of the full structure. As pointed out by Her *et al.*[86], the remaining peaks can be modeled by an $Immm$ cell that is half of the full $Fddd$ structure in each direction. To help distinguish between the pure β phase and the structure that contains strong anti-site disorder, the latter will be herein designated as β' when it appears.

As the β' phase disappears, all Bragg peaks disappear in the diffractogram. Through region **d**, there is a significant amount of amorphous material present in the spectrum, evidenced by broad, diffuse scattering in the $2\theta = 8-11^\circ$ and $22-25^\circ$ regions. An amorphous phase (δ) of $\text{Mg}(\text{BH}_4)_2$ has previously been observed by Filinchuk *et al.*[67], though it was only achieved at high pressures. It is possible that the amorphous phase is either $\delta\text{-Mg}(\text{BH}_4)_2$ or, more likely, that it is an intermediate decomposition product (such as a polyborane species). Later results show that gas evolution begins around this temperature at this particular heating rate.

The amorphous phase disappears at around 630 K as the peaks attributed to MgH_2 appear (event 4). These, in turn, disappear as Mg metal appears in the spectrum at temperatures above 700 K. While this remains the only crystalline phase at high temperatures, there is still a larger amount of diffuse scattering than in the low temperature samples, suggesting that other amorphous phases are present. To determine if the origin of the amorphous peaks was MgO, formed from reaction with the borosilicate capillary sample holder, the *in situ* experiment was repeated using a sapphire capillary but the diffuse scattering was still observed. This does not rule out the possibility of MgO formation (from reaction with outside oxygen contamination) but allows for the possibility that

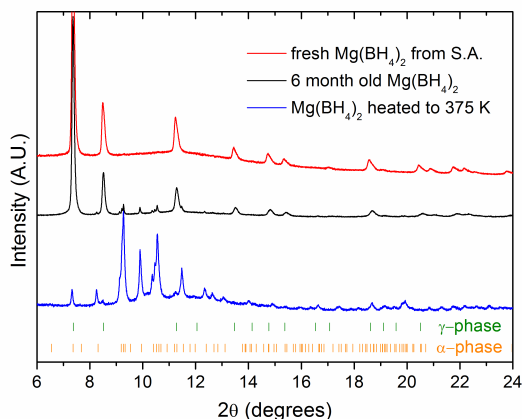


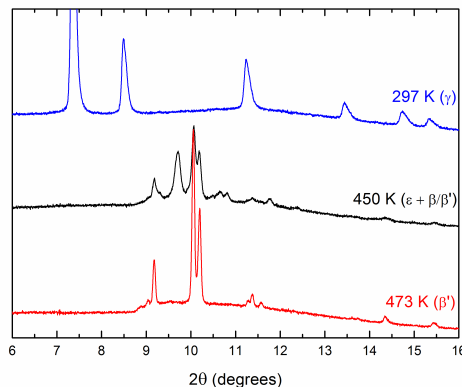
Figure 3.3.3: Synchrotron X-ray diffraction measurements of γ - $\text{Mg}(\text{BH}_4)_2$ fresh from Sigma Aldrich, 6 months old, and heated to 375 K for 12 hours. Conversion to the α phase occurs relatively slowly but is quantitative when held at temperatures around 350 K and below the transition to the β' phase.

other amorphous phases may be responsible for the broad peaks. Both MgB_2 and $\text{Mg}(\text{B}_{12}\text{H}_{12})$ have been suggested or previously observed as decomposition products of $\text{Mg}(\text{BH}_4)_2$.

3.3.2 *Ex Situ* Measurements

Samples of γ - $\text{Mg}(\text{BH}_4)_2$ were heated in 1 g batches for 12 hours under a very light flow of argon (approximately $1 \text{ cm}^3\text{s}^{-1}$ at various temperatures (approximately every 10 degrees from 370 to 600 K).

A marked difference between the *in situ* and *ex situ* measurements is that samples heated to around 350 K or higher transformed entirely from the γ to the α phase. This suggests that the latter is more stable than the former at temperatures far below the decomposition point. Indeed, if the samples from Sigma Aldrich were opened and left in a glove box they began converting slowly to the α phase after a period of a few months (see Fig. 3.3.3). This confirms



2

Figure 3.3.4: Samples of γ - $\text{Mg}(\text{BH}_4)_2$ at room temperature, and heated to 450 and 473 K, showing that it was not possible to form the pure ϵ phase.

that the α phase is more stable than the γ phase and that the kinetics of the transformation are sped up by supplying heat to the sample. However, the α phase was never observed during in situ measurements, suggesting that the rate of γ to α conversion is relatively slow. It is worth noting that the samples of γ - $\text{Mg}(\text{BH}_4)_2$ heated to temperatures above 350 K and below the phase change to the β' polymorph formed α - $\text{Mg}(\text{BH}_4)_2$ without any impurities (within the detection limit of the synchrotron X-ray diffraction that was used to characterize it). Conversion from the γ phase may prove to be the best synthetic route to producing pure α - $\text{Mg}(\text{BH}_4)_2$.

The results of the ex situ measurements generally matched those of the in situ experiments. Quenching the reaction to produce the pure ϵ phase was not possible; when heated to temperatures below 473 K, it was only observed to form in combination with the β/β' polymorph (Fig. 3.3.4). At temperatures above this, the pure β' phase was formed until the sample began decomposing.

From 543 K, the β' phase is no longer observed and MgH_2 is formed. Mg metal is the only crystalline phase formed above temperatures of 563 K. After the

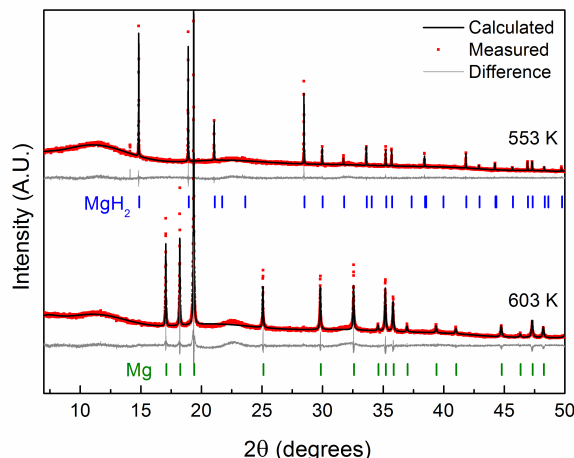


Figure 3.3.5: High temperature *ex situ* diffraction data including a Rietveld refinements of MgH_2 and Mg . At each temperature, these are the only crystalline phases present in the sample, the amorphous component of the spectrum appears to also grow as temperature increases.

disappearance of the β' phase there is a noticeably larger amorphous component to the diffraction patterns with broad peaks appearing around $2\theta = 12^\circ$ and 23° . As previously discussed, this is possibly due to the formation of $\text{Mg}(\text{B}_{12}\text{H}_{12})$, MgB_2 , or even possibly MgO (from outside contamination).

It should finally be noted that certain quenching experiments reproducibly gave entirely amorphous materials at temperatures well below the decomposition point. This was particularly common in the 450-475 K temperature range and several attempts were necessary to produce crystalline phases in that region. In private communication with other research groups working on $\gamma\text{-Mg}(\text{BH}_4)_2$ (such as the authors from Ref. [67] and [177]) it was confirmed this, along with other anomalous unexpected phase changes, has been observed in other experiments. This is indicative of a very complex potential energy profile and offers great possibility for further structural exploration of $\text{Mg}(\text{BH}_4)_2$.

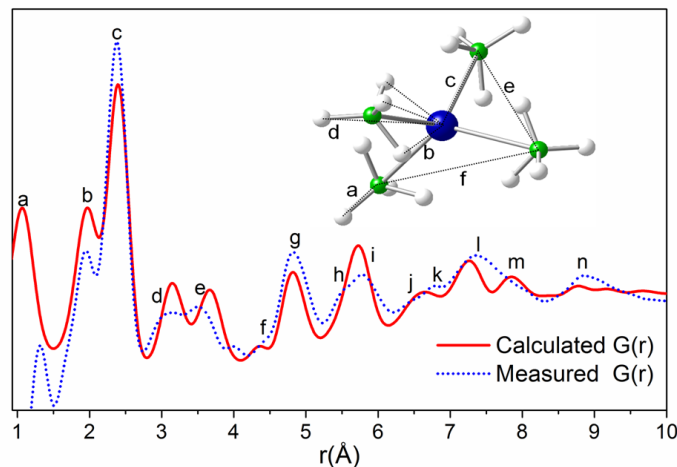


Figure 3.4.1: Measured and calculated (from the structural model in Section 3.2) Pair Distribution Functions for γ -Mg(BH₄)₂. Measured peak positions below approximately 1.5 Å are unreliable. The inset shows the physical distances in a distorted Mg(BH₄)₄ tetrahedron (the inner coordination sphere of Mg), to which the individual peaks correspond.

3.4 Pair Distribution Function

The Pair Distribution Function of Mg(BH₄)₂ allows information about both the short and long range order to be extracted. The PDF of room temperature γ -Mg(BH₄)₂ (from Sigma Aldrich) is shown in Fig. 3.4.1 from 0.9 to 10 Å. Also shown in Fig. 3.4.1 is a calculated PDF of γ -Mg(BH₄)₂ that was generated from the refined structural model obtained in Section 3.2 using the PDFgui software package[178]. Data below 0.9 Å are not shown, as it does not make physical sense to have atoms that close together.

Each of the peaks of the PDF were fit using a Pseudo-Voigt function in TOPAS, allowing their positions to be extracted. By comparing the distances given in the .cif file with those measured in the PDF, it is possible to assign each peak to a particular interaction; this information is summarized in Table 3.2.

As synchrotron X-rays were used to obtain the data, the intensity of each peak in the PDF is proportional not only to the number of interactions at a given distance, but also the electron density of the atoms involved. As a result, it is not likely that interactions involving hydrogen will appear in the PDF unless there are several occurring at a single distance (e.g. B-H in the BH_4 group) or the interaction is with the heaviest atom (Mg-H). Furthermore, determination of the B-H bond length will not be very reliable, as only the two lightest elements are involved in the interaction and it is difficult to precisely measure their locations (especially if the hydrogens are in motion). The use of X-rays also means that peaks assigned to Mg-Mg interactions are most visible, even at relatively long separations (a majority of peaks appearing beyond the data shown in Fig. 3.4.1 can be attributed to Mg-Mg interactions).

The measured distances in the PDF match those determined from X-ray diffraction in Section 3.2 very well and are similar to distances observed in other phases of $\text{Mg}(\text{BH}_4)_2$. The Mg-B distance within the first Mg co-ordination sphere is very close to the Mg-B distance found in the α and β phases (2.34-2.47 Å). The variation in boron-boron distances within this sphere confirms that the MgB_4 tetrahedra are severely deformed, as they are in both other phases. This distortion is even more pronounced in the PDF than in the PXD data and the difference between measured and calculated distances tends to increase when smaller atoms are involved.

PDF measurements were also collected for all samples that were heated *ex situ*. Before decomposition, the short range order in all phases of $\text{Mg}(\text{BH}_4)_2$ is very similar (see Fig. 3.4.2). However, as interaction distance increases beyond *ca.* 10 Å, the $G(r)$ of the α and γ phases still shows several features while the PDF of the β' phase flattens out and provides very little information. This occurs since stacking faults present in the β' polymorph cause separations at

Table 3.2: Assignment of the peaks in the pair distribution function of γ - $\text{Mg}(\text{BH}_4)_2$ by comparison with the refined structural model from Section 3.2.

Peak Label	Measured Separation [$\text{\AA}$]	Interacting Pair	Calculated Separation [$\text{\AA}$]
a	1.30	B-H	1.09
b	1.97	Mg-H	1.96-2.03
c	2.37	Mg-B	2.41
d	3.12	Mg-H	3.11-3.20
e	3.52	B-B	3.71
f	4.40	B-B	4.36
g	4.83	Mg-Mg	4.82
h	5.52	Mg-B	5.72
i	5.78	Mg-B	5.79
j	6.46	Mg-B	6.42
k	6.78	Mg-B	6.65
l	7.37	Mg-Mg	7.36
m	7.86	Mg-B	7.77
n	8.86	Mg-Mg	8.80

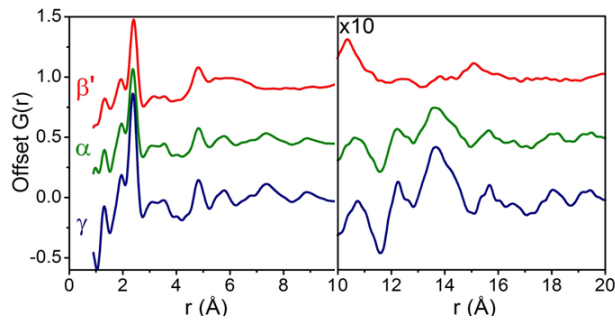


Figure 3.4.2: The PDFs of the α , β' , and γ phases of $\text{Mg}(\text{BH}_4)_2$. On the right, the intensity has been scaled by a factor of 10 to show the lack of long range ordering in the β' structure.

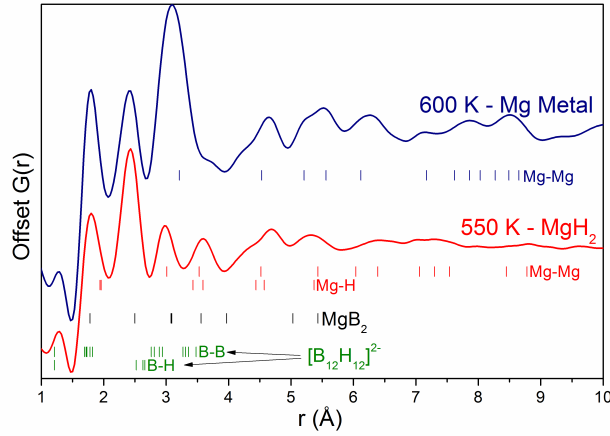


Figure 3.4.3: PDFs of samples heated to 550 and 600 K under argon for 12 hours. Ticks below indicate expected interaction distances for Mg metal, MgH_2 , MgB_2 , and $[\text{B}_{12}\text{H}_{12}]^{2-}$ from known crystal structures found in the ICSD.

high r to be averaged out over the bulk material, while the local order around the individual atoms is retained. The interaction distances within the first coordination shell of each atom measured in the PDFs are consistent with those that have been previously reported from X-ray diffraction measurements[86, 85].

Upon decomposition, the PDFs begin to take a very different shape. In Fig. 3.4.3, the PDFs of samples heated to 550 and 600 K under argon for 12 hours are shown. Also shown are the expected interaction distances of the dominant phases in each PDF (MgH_2 and Mg metal) taken from known structures found in the ICSD. While it is clear that both MgH_2 and Mg metal are formed in large amounts, there remain several peaks at interaction distances below those found in either of these two compounds. It is possible that an amorphous phase of $\text{Mg}(\text{BH}_4)_2$ is present (as no other crystalline phases are observed in the X-ray diffraction data) though it is unlikely to be stable at such a high temperature. Another possibility is the presence of $\text{Mg}(\text{B}_{12}\text{H}_{12})$, which has B-B and B-H interaction distances on the order of 1.2-3.5 Å, and has previously been observed

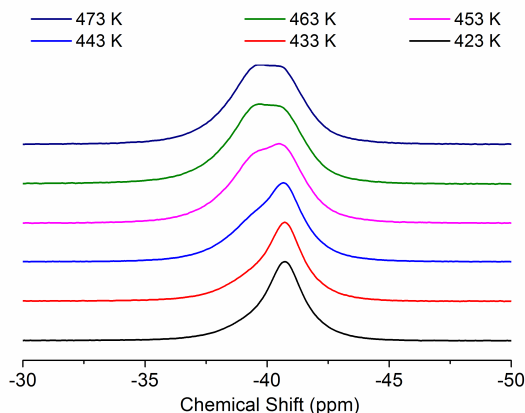


Figure 3.5.1: Variable temperature solid state 11-boron NMR measurements showing a partial γ to β' phase transition.

to persist at temperatures in this regime. $\text{Ca}(\text{B}_{12}\text{H}_{12})$ from Ref. [179] was used to obtain the expected B-B and B-H separations in the $[\text{B}_{12}\text{H}_{12}]^{2-}$ anion that are shown in Fig. 3.4.3. The formation of MgB_2 may also be possible, which has also been previously observed as a decomposition product[177].

3.5 NMR

In situ variable temperature solid state 11-boron NMR measurements indicate that a single boron environment ($\delta = -41$ ppm) exists until approximately 443 K. At this point, a second peak starts to grow at *ca.* -40 ppm while the first decreases in intensity (Fig. 3.5.1). Both environments are typical of the $[\text{BH}_4]^-$ anion, which has a characteristic chemical shift of around -40ppm. This data therefore corresponds to the γ to β' phase transition in $\gamma\text{-Mg}(\text{BH}_4)_2$.

The solid state 11-boron NMR spectrum of a sample heated to 610 K is shown in Fig. 3.5.2. This spectrum shows that, even when heated to this temperature, the decomposed material still contains characteristic peaks in the $[\text{BH}_4]^-$

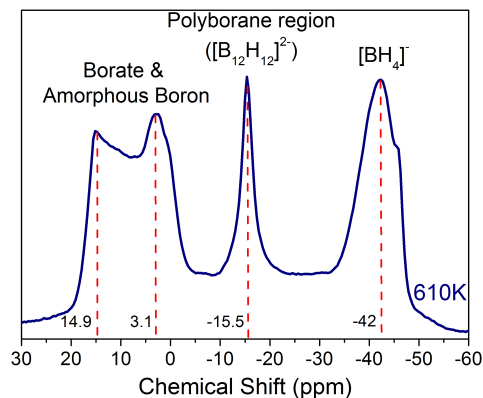


Figure 3.5.2: Solid state 11-boron NMR measurement of γ - $\text{Mg}(\text{BH}_4)_2$ heated to 610 K for 12 hours under argon.

region, presumably attributed to unreacted $\text{Mg}(\text{BH}_4)_2$. The dominant peak in this spectrum however occurs exactly at the chemical shift where the $[\text{B}_{12}\text{H}_{12}]^{-2}$ is expected (*ca.* -15 ppm). Furthermore, the region associated with polyborane species (-10 to -35 ppm) contains no discernible individual peaks (apart from that of $[\text{B}_{12}\text{H}_{12}]^{-2}$) but it does contain a significantly higher background. This may be due to the formation of several polyborane species during decomposition (as suggested in the mechanism proposed by Chong et al.) that remain in the material at this temperature. The last region of the spectrum with discernible features is from around 0 to 15 ppm, which is typically associated with amorphous boron and B-O compounds. If the sample was contaminated with even small amounts of oxygen it is likely that stable boron-oxygen compounds would be formed at 610 K. As mentioned in Section 3.3.2, the diffraction pattern of the same sample shows the only crystalline compound in this sample is Mg metal. Therefore, despite the rich boron NMR spectrum, it is difficult to definitively conclude much about the structure of each boron containing compound in the material at this temperature.

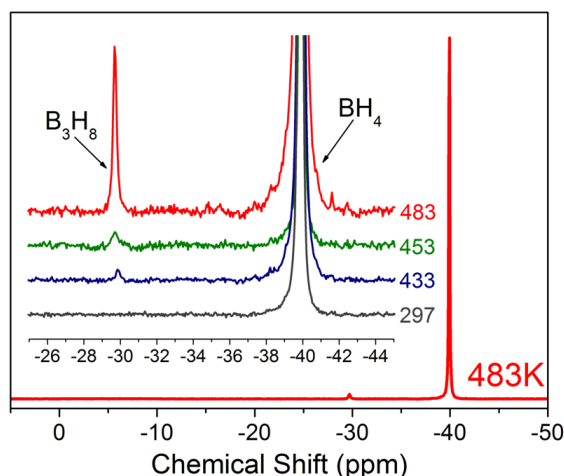


Figure 3.5.3: Solution NMR spectrum of γ - $\text{Mg}(\text{BH}_4)_2$ heated to 483K and dissolved in THF. The inset shows a zoomed-in view of the spectra of samples heated to various temperatures.

To better understand the potential for reversibility in γ - $\text{Mg}(\text{BH}_4)_2$, the ability to decompose via the $[\text{B}_3\text{H}_8]^-$ anion was investigated by dissolving the samples in THF and performing solution NMR measurements. This offers much better resolution compared to solid state NMR and the soluble $[\text{B}_3\text{H}_8]^-$ anion has a characteristic chemical shift at around -30 ppm, making it easy to observe. As can be seen in the inset of Fig. 3.5.3, $[\text{B}_3\text{H}_8]^-$ was seen in samples heated to as low as 433 K, with a noticeable amount formed around 483 K. To the authors knowledge, this is the lowest reported uncatalyzed decomposition temperature in borohydrides. The kinetics of this process are rather slow however, and the amount of $[\text{B}_3\text{H}_8]^-$ formed relative to unreacted $[\text{BH}_4]^-$ remaining in the samples is almost negligible (see the full spectrum of the sample at 433 K in Fig. 3.5.3). Regardless, these results indicate that if the kinetics of this process may be improved, $\text{Mg}(\text{BH}_4)_2$ offers great potential as a reversible, low temperature hydrogen storage material.

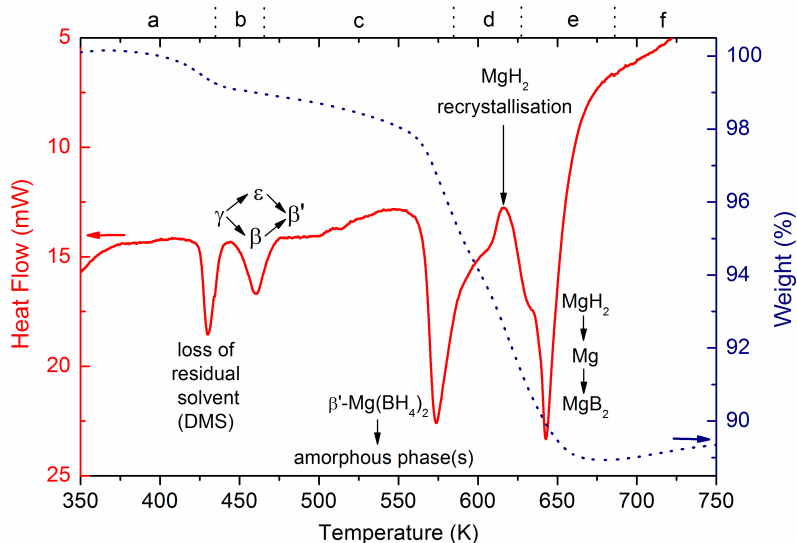


Figure 3.6.1: Combined DSC/TGA scan for γ - $\text{Mg}(\text{BH}_4)_2$. For direct comparison with, Fig. 3.3.1, the same regions have been indicated above the plot. Each corresponding thermal event observed in the DSC trace has been labeled.

3.6 Differential Thermal Analysis

Combined DSC-TGA measurements were performed on a sample of γ - $\text{Mg}(\text{BH}_4)_2$ purchased from Sigma Aldrich up to around 750K (Fig. 3.6.1). The first thermal event begins at around 425 K and is accompanied by a weight loss of about 1%. Mass spectrometry measurements (not shown) of gas evolved at this temperature indicate that a large amount of a compound with $m/z = 62.02$ g/mol is produced. This is a result of the evolution of residual solvent remaining in the sample. Dimethyl sulfide (DMS), $(\text{CH}_3)_2\text{S}$, has a molar mass of 62.13 g/mol and was used to synthesize the γ - $\text{Mg}(\text{BH}_4)_2$ used in these experiments.

Following the loss of DMS, the sample undergoes the phase changes observed in the variable temperature diffraction data. It is interesting that this change occurs immediately following the loss of solvent and may indicate that the solvent

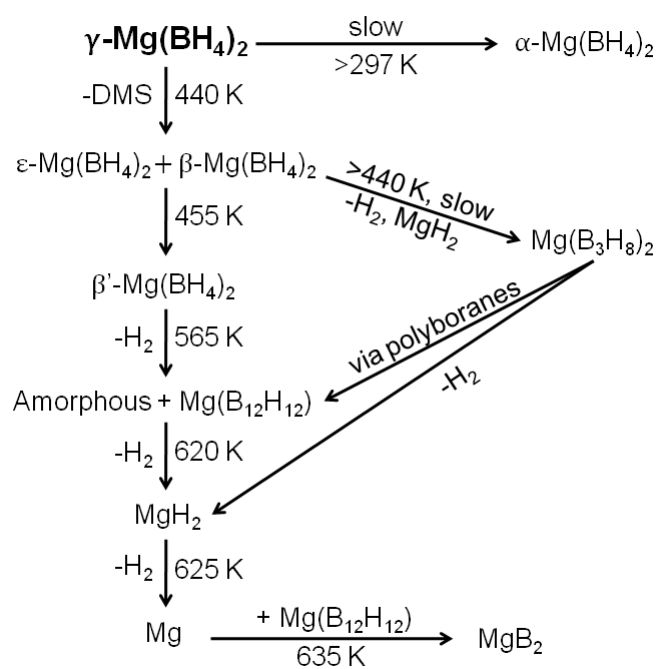
has a stabilizing effect on the γ phase. During and following the phase change to the β' phase, the sample begins gradually losing more weight. As $[\text{B}_3\text{H}_8]$ is observed to begin forming at around this temperature (Fig. 3.5.3), a competing side decomposition reaction via polyborane species also starts to take place once the residual solvent is lost. However, it has been shown that the kinetics of this reaction are sluggish, resulting in the very slow weight loss observed up until the faster decomposition at 565 K. At this point, the sample is formed of totally amorphous decomposition intermediates, including $\text{Mg}(\text{B}_{12}\text{H}_{12})$. The exothermic peak at 620 K corresponds to the formation of MgH_2 , which crystallizes out of the amorphous sample and then decomposes to Mg metal and MgB_2 . In agreement with the decomposition mechanism proposed by Chong *et al.*, this appears to occur in two separate steps as the DSC trace contains two overlapping consecutive peaks and the weight loss occurs at two distinct rates (as seen in the derivative of the TGA trace). After 675 K, the TGA trace shows that the sample begins to gain weight. This is likely due to the formation of borates and/or magnesium oxide, which give rise to the broad diffraction peaks observed at this temperatures.

At the point decomposition is finished, the sample has lost about 10% of its original weight (excluding the 1% weight lost due to residual solvent). This equates to slightly fewer than 3 moles of H_2 . IGA-MS measurements (not shown) indicate that diborane is not evolved at any point and the entire weight loss is attributed to H_2 evolution. The remaining hydrogen likely exists as the $[\text{B}_{12}\text{H}_{12}]^{2-}$ anion (if 3 entire moles of H_2 were released, the remaining amount of boron and hydrogen would be exactly equal). *In situ* variable temperature Raman measurements during decomposition (also not shown) support this; a Raman peak associated with $[\text{B}_{12}\text{H}_{12}]^{2-}$ begins growing at around 590 K and remains beyond 750 K.

3.7 Conclusions

A new phase (designated γ) of $\text{Mg}(\text{BH}_4)_2$ has been reported. The crystal structure was solved using high resolution synchrotron X-ray powder diffraction. The polymorph crystallizes in the cubic $Ia\bar{3}d$ space group, with a lattice parameter of $a = 15.7395(3)$ Å. The structure was solved by direct comparison with an SiO_2 isostructure that is roughly 1.5 times smaller. $\gamma\text{-Mg}(\text{BH}_4)_2$ is one of the first known borohydrides with a large, porous framework structure and has a remarkably low density of $\rho = 0.55$ g cm⁻³. Pair distribution function analysis shows that the short range order of the γ polymorph is similar to that of the β -phase, but that the two differ at long r due to stacking faults present in the β phase. The new structure is stabilized at room temperature by a small amount of residual solvent, but transforms to the α phase slowly over time.

The phase changes and decomposition of $\gamma\text{-Mg}(\text{BH}_4)_2$ were examined using variable temperature X-ray diffraction, solid state and solution NMR, Pair Distribution Function analysis, Differential Thermal Calorimetry, IGA-MS and Raman Spectroscopy. A step by step mechanism for the thermal evolution of $\gamma\text{-Mg}(\text{BH}_4)_2$ has been suggested and is summarized in Fig. 3.7.1. Before decomposition, the γ phase transforms to the β' phase via the β phase and an unknown intermediate phase. At temperatures above this transition, the material very slowly decomposes to $\text{Mg}(\text{B}_3\text{H}_8)_2$, which suggests the potential for reversibility if kinetics may be improved. Decomposition and H_2 evolution at higher temperatures proceeds via several steps, beginning around 565 K. The thermodynamically stable polyborane $[\text{B}_{12}\text{H}_{12}]^{2-}$ is produced during decomposition and persists at temperatures above 750 K. Overall, the sample loses 10 wt. % hydrogen below 675 K, although impractical conditions would be needed to reversibly form $\text{Mg}(\text{BH}_4)_2$ from the reaction products (primarily Mg, MgB_2 and $\text{Mg}(\text{B}_{12}\text{H}_{12})$) at this temperature.

Figure 3.7.1: The decomposition of $\gamma\text{-Mg(BH}_4)_2$

Chapter 4

γ -Mg(BH₄)₂ Studied by Neutron Scattering

4.1 Introduction and Chapter Outline

The novel structure of γ -Mg(BH₄)₂ and its resemblance to SiO₂ opens many new avenues of exploration that have not been previously possible in borohydride chemistry. If the crystal structure of γ -Mg(BH₄)₂ resembles that of a metal organic framework, then it is possible that some of the bulk properties of the material may also display similar chemical behaviour. This chapter will examine some of these similarities and attempt to rationalize their existence in γ -Mg(BH₄)₂.

It has been known since the early 1960s that certain phases of SiO₂ exhibit anomalous unit cell behaviour at low temperatures[180]. For example, a negative thermal expansion (NTE) coefficient is observed in quartz at temperatures below 12 K. Anomalous unit cell behaviour in the α and β phases of Mg(BH₄)₂ has previously been observed by Filinchuk *et al.* at low temperatures[85]. However,

neither of these phases exhibit strictly isotropic negative thermal expansion. The reports found that the α phase shrinks as heated in the a and b directions in the range 100-170 K (temperatures below this were not studied) but expands in the c direction over the same temperature range. Above 170 K, the phase expands in all directions. As a result, the total unit cell volume remains roughly constant in the 100-170 K range and then expands at temperatures above this. The thermal expansion of the β phase is highly anisotropic and each lattice parameter behaves differently. The a lattice parameter decreases slowly in the 100-200 K region and then increases roughly linearly from 250 K onward. In the b direction, the cell expands relatively quickly until approximately 240 K when it begins to contract slowly and then begins expanding again above 350 K. The c lattice parameter shrinks up until about 440 K and then begins to contract. However, the combination of all these effects means that the overall volume in β -Mg(BH₄)₂ expands linearly with temperature.

A general survey of SiO₂ and related MXO₄ materials (M = Al, Ge, Fe; X = P, As) found that the effects of pressure and temperature on crystal structure distortions in these materials were similar[181]. It was observed that the induced distortions in the crystal structure and bulk physical properties (e.g. piezoelectric coupling constant) of the various materials could be predicted and rationalized only in terms of the M-O-X bond angle.

Anomalous unit cell behaviour is often explained by examining the phonon density of states in a particular material. There are a number of physical processes that can cause contraction with increasing temperature such as transverse vibrational modes, rigid body modes, and phase transitions. For instance, the principle affect of temperature on quartz from 78 to 296 K is a nearly rigid unit rotation of SiO₄ tetrahedra. At lower temperatures, this effect is reduced due as the tetrahedral rotation turns to distortion, giving rise to anomalously small

thermal expansion[182]. In the late 1990s, various models were developed and tested to accurately describe negative thermal expansion in materials that had large coefficients of negative thermal expansion over long ranges[183, 184, 185]. Recently, more fundamental criteria have been suggested; it has been shown that the NTE phenomenon originates from the existence of high pressure, small volume phases with higher entropy[186].

Much of the interest in porous framework materials is their potential for application in a wide variety of chemical processes. The unique structure of MOFs, particularly the presence of empty space within a unit cell, has prompted wide-exploration of MOFs as gas stores[14]. The porous structure of γ -Mg(BH₄)₂ suggests that it may have added application in gas adsorption, while previous studies of borohydrides looked solely at the chemical absorption of hydrogen. Indeed, Filinchuk *et al.* found that, at high pressures, they were able to introduce CH₂Cl₂, H₂, and N₂ gas into the pores[67].

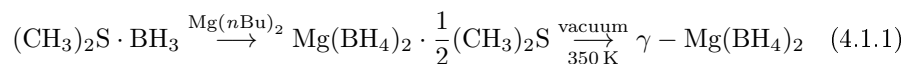
In this chapter, the properties of γ -Mg(BH₄)₂ resembling those of framework materials are explored, primarily using neutron scattering techniques on isotopically enriched compounds. Accurate structure determination, including precise determination of all hydrogen atom locations, is first accomplished using high resolution neutron powder diffraction (PND). The thermal evolution of the structure from base temperature through decomposition is then investigated using *in situ* PND, revealing isotropic NTE at low temperatures. Data are fit using a Debye-Einstein model for the density of states and the phenomena is rationalized based on rigid body movement of the BH₄ tetrahedra. The phonon density of states is directly probed using INS and Raman spectroscopy and then compared to theoretical calculations generated by collaborators Phillippe Aeberhard and Alex Mulliner.

The adsorption of H₂ into the pores of γ -Mg(BH₄)₂ is also examined. INS

measurements reveal that the adsorbed gas molecules are bound, resulting in one of the highest hydrogen density materials ever formed at relatively low pressure. PND measurements of samples with H₂ and D₂ adsorbed show that they fill γ -Mg(BH₄)₂ in long chains at the centre of its pores and cause anomalous unit cell behaviour to be observed in the host material. In certain instances, the H₂ molecules remain in the pores at temperatures upwards of 200 K, indicating the potential for combined physi-/chemi-sorbed hydrogen storage materials.

4.1.1 Synthesis of γ -Mg(BH₄)₂

γ -Mg(BH₄)₂ was first synthesized by Mr. Bo Richter, who was working in the group of Prof. Torben Jensen at Aarhus University. At the time the new structure was discovered, the details of its synthesis were not publicly known and the process was pending patent approval. As such, it was not possible to synthesize the new polymorph in house at the University of Oxford, but rather a collaboration was developed with Prof. Jensen's group. A majority of the techniques used in this chapter involve a neutron source and, as such, required isotopic enrichment of the boron and/or hydrogen atoms. All chemicals used in this chapter were prepared by Mr. Richter at Aarhus University via the general Eq. 4.1.1, where the reactants were isotopically enriched to produce γ -Mg(¹¹BD₄)₂ and γ -Mg(¹¹BH₄)₂ where appropriate.



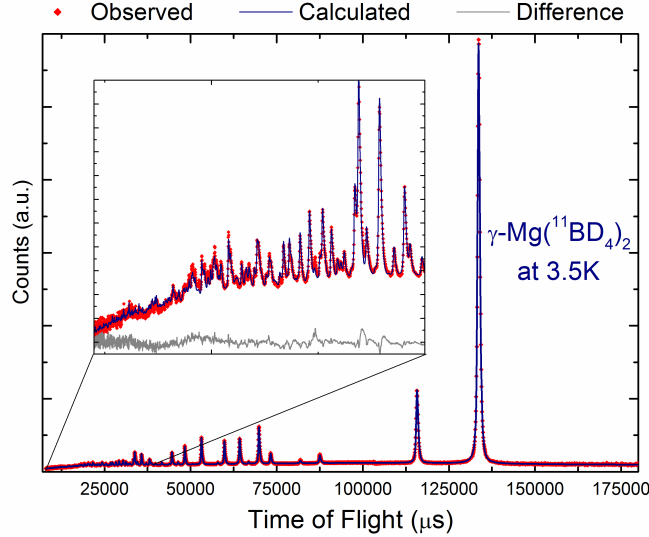


Figure 4.2.1: Rietveld refinement of γ -Mg(¹¹BD₄)₂ from PND at 3.5 K.

4.2 Crystal Structure of γ -Mg(BD₄)₂ From Low Temperature Neutron Diffraction

PND diffraction measurements of γ -Mg(¹¹BD₄)₂ were collected on the WISH beamline at the ISIS facility. The temperature was maintained as low as possible for the duration of the measurement (*ca.* 3.5 K), allowing very accurate determination of all atomic positions. The structural model from chapter 3 was used as a basis for Rietveld refinement and no impurity phases were detected. Values of $\chi^2 = 2.84\%$, $R_{wp} = 2.46\%$, and $R_{exp} = 0.87\%$ were obtained at base temperature and the fit is shown in Fig. 4.2.1.

As PND is much more sensitive to deuterium atoms than XRD, the deuterium atoms were allowed to move freely during the refinement (provided they remain on the correct symmetry site) and anisotropic displacement parameters (adps) were used rather than b_{eq} . The newly determined atomic positions are

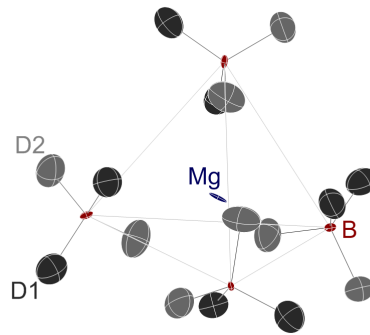
Table 4.1: Atomic positions of γ -Mg(¹¹BD₄)₂ from powder neutron diffraction at 3.5 K.
$$\gamma\text{-Mg}(\text{}^{11}\text{BD}_4)_2 \text{ } Ia\bar{3}d \text{ } a = 15.75897(8) \text{ \AA}$$

Site	x/a	y/b	z/c	Distance From Boron
Mg/24d	$\frac{1}{2}$	$\frac{3}{4}$	$\frac{7}{8}$	2.4126 Å
¹¹ B/48g	0.3120	0.0620	$\frac{3}{8}$	—
D1/96h	0.3014	0.1371	0.3821	1.2010 Å
D2/96h	0.2893	0.0204	0.4352	1.2075 Å

$\chi^2 = 2.840$ $R_{wp} = 2.459\%$ $R_{exp} = 0.866\%$

Table 4.2: Atomic displacement parameters (Å⁻²) for γ -Mg(¹¹BD₄)₂ from PND at 3.5 K. The thermal ellipsoids of a distorted Mg(¹¹BD₄)₄ tetrahedron are shown below.

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mg	0.0103	0.00390	0.0002	0	0	0
¹¹ B	0.0033	0.0033	0.0042	-0.0004	-0.0019	0.0020
D1	0.0295	0.0332	0.0299	-0.0037	0.0029	0.0061
D2	0.0498	0.0274	0.0267	-0.0083	0.0047	0.0024



given in Table 4.1, and the shapes of the thermal ellipsoids are tabulated and shown in Table 4.2.

The borodeuteride ions are much nearer to ideal tetrahedral shape than was found from PXD in Chapter 3. The average B-D distance refines to a value of 1.2043 Å and very little deviation is seen between the different bond lengths (0.0065 Å $\approx$ 0.5%). The value of the B-D bond length is larger than that determined from X-ray diffraction (as expected) but it is remarkably close to what has been observed in other borodeuterides when PND is used to determine the structure[78, 40]. The bond angles of the refined structure show that the borodeuteride ions are slightly distorted from perfect tetrahedral shape; three D-B-D angles are similar (106.5°-107.1°) while one is much larger (114.9°). Again, this type of distortion was seen by Hartman *et al.*[78] in LiBD₄ (107.2°-111.7°) studied by NPD at 3.5K, however the effect is larger in γ -Mg(¹¹BD₄)₂. The distortion of D-B-D angles is even more pronounced in Be(BH₄)₂ (104°-127°) than it is in Mg(BH₄)₂. Therefore, as Konoplev and Bakulina suggested based on the IR spectra and covalency arguments[42], borohydride ion geometry in Mg(BH₄)₂ lies between that of LiBH₄ and Be(BH₄)₂.

The Mg(BD₄)₄ tetrahedra are heavily distorted ($\angle_{B-Mg-B} = 100^\circ - 131^\circ$) while each boron atom is exactly linearly coordinated by two Mg atoms ($\angle_{Mg-B-Mg} = 180^\circ$). The anisotropic displacement parameters for all of the atoms, particularly the heavier ones, are quite small. The largest adps are seen for deuterium atoms which is a result of borohydride ion rotation that still occurs at this temperature. Again, this is comparable to what has been previously reported at for borodeuterides at this temperature.

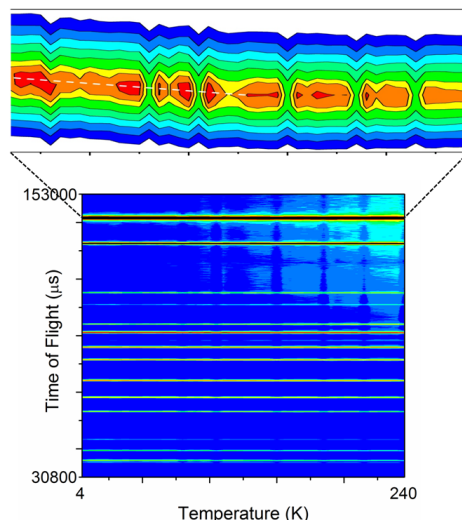


Figure 4.3.1: Surface plot of γ -Mg(¹¹BD₄)₂ heated from 4 K to 250 K. No phase changes were observed and close inspection of the peaks shows that the movement toward lower TOF as the sample is heated.

4.3 Negative Thermal Expansion From Variable Temperature Neutron Diffraction

A 0.8g sample of γ -Mg(11BD₄)₂ was heated from 4 K to 310 K at a rate of 0.5 K/min while neutron powder diffraction data was simultaneously collected on WISH in event mode. Data were typically saved in files containing 1 hour (or 30 K) worth of information. Approximately every 6 hours, the sample was held at a single temperature as the methane moderator was regenerated. There were also a few small temperature ranges (e.g. 90 - 100 K) during which the beam at ISIS failed and no data was collected. It can be seen from the surface plot of diffraction data (Fig. 4.3.1) that no phase changes occur throughout the entire heating range. While it would appear from Fig. 4.3.1 that very little change takes place, close inspection of the Bragg peaks shows a uniform shift of all peaks toward lower ToF until nearly 200 K. This is indicative that the unit

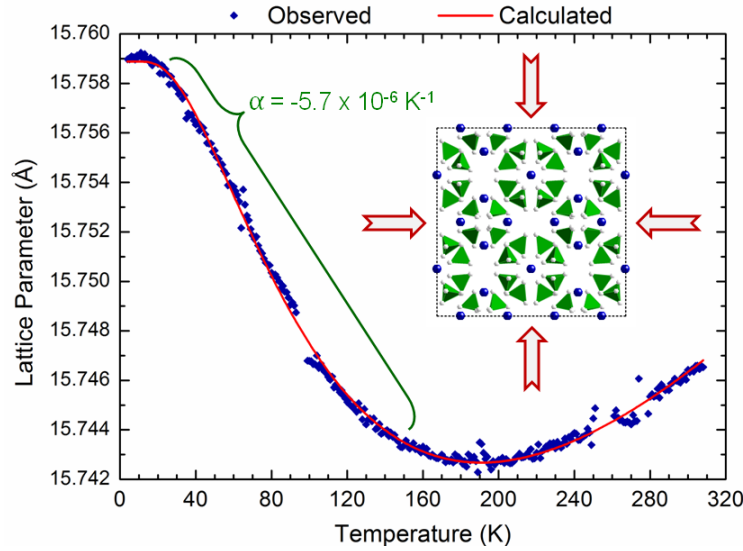


Figure 4.3.2: The lattice parameter of γ - $\text{Mg}(\text{BH}_4)_2$ at low temperatures showing negative thermal expansion in the region 20 - 190 K. The data was fit using a Debye-Einstein model for the density of states and the coefficient of negative thermal expansion is provided.

cell is shrinking in all directions as the sample is heated.

The data were then processed into 2 minute slices, to produce a diffraction pattern at each 1 K step. The structure was refined at each temperature step and the cubic cell lattice parameter has been plotted in Fig. 4.3.2. An incorrigible error in the data collecting/processing routines at WISH lead to incorrect slicing of the data. As a result, the data sets include extra measurements outside the true temperature range. This manifests as jumps in the lattice parameter that can be seen in Fig. 4.3.2 approximately every 30 K (e.g. at 40 K, 70 K, etc.).

Overall, however, the unit cell behaviour at low temperature is consistent with the ToF shift observed in the surface plot. Following expansion at temperatures below 15 K, an isotropic contraction of the lattice is seen between *ca.* 15 - 190 K. The linear coefficient of thermal expansion (CTE), α_l , was calculated in this range by Eq. 4.3.1:

$$\alpha_l = \frac{1}{a_0} \left(\frac{a_T - a_0}{T - T_0} \right), \quad (4.3.1)$$

where a_0 is the lattice parameter at temperature T_0 , when the cell begins contracting and a_T is the lattice parameter at temperature T , when the contraction stops. A value of $\alpha_l = -5.7 \times 10^{-6} \text{K}^{-1}$ was obtained, which is remarkably high for a material of this type. While a select number of zeolites have been found to possess a similar CTE, most typically fall into the “very low expansion group[187]” ($-2 \times 10^{-6} \text{K}^{-1} \leq \alpha_l \leq 2 \times 10^{-6} \text{K}^{-1}$), and often have a CTE that is 1-2 orders of magnitude lower than that observed in γ -Mg(¹¹BD₄)₂. While it does not match the exceptionally large CTEs that have been observed in cyanide-bridged framework materials discovered in recent years[188], the CTE of γ -Mg(¹¹BD₄)₂ is comparable to several zirconium and tungsten oxide-based materials that have been extensively investigated in the past[189].

In general, positive thermal expansion occurs as a material is heated since the population of vibrational modes results in an increase in inter-atomic distances. It is possible, however, for transverse vibrational modes to have the opposite effect and lead to negative thermal expansion. Consider a [BH₄] tetrahedron, in which the boron is linearly coordinated by magnesium atoms. At low energies, rigid body movement of the tetrahedron in the direction transverse to the Mg-B-Mg should not affect the Mg-B distance. The result is concomitant movement of the Mg atoms towards one another and overall contraction of the unit cell (see the inset in Fig. 4.3.3). As a result, NTE is often observed as a result of the presence of such low energy rigid unit modes (RUMs) that have a negative Gruneisen parameter. Here, polyhedra in a molecule undergo coupled movement in such a way that volume of the cell is reduced, without any distortion of intrapolyhedral bond distances and angles (hence they are low energy phonons)[189].

Variable temperature lattice parameter (as well as specific heat) data are often modeled to give an indication of the phonons that contribute to lattice contraction or expansion in a material[185]. The phonon density of states can be modeled in several different ways such as Debye and/or Einstein models of thermal expansion or by reconstructing the Gruneisen parameter weighted phonon density of states using maximum entropy analysis[184]. The calculated data shown in Fig. 4.3.2 were generated using the FORTRAN program 'Fitter' developed by Prof. David, which employs a polynomial function that combines both Debye and Einstein model of thermal expansion (it has been shown previously by David *et al.*[190] that the use of both in conjunction produces an improved fit over the use of a pure Debye or Einstein model). The Einstein term is represented by a single phonon frequency that has an associated weighting and characteristic energy, ω_E :

$$\frac{(a - a(T=0))}{T} = \frac{(\omega_E/T)}{e^{(\omega_E/T)} - 1} \quad (4.3.2)$$

In this model, this is the sole phonon that is responsible for negative thermal expansion in the material (designated by a negative sign in its weighting). The Debye model is built of a distribution of phonon frequencies given by:

$$\frac{(a - a(T=0))}{T} = \left[\frac{\pi^4}{5(\omega_D/T)^3} - \sum_{n=1}^{\infty} \left(3 + \frac{9}{(n\omega_D/T)} + \frac{18}{(n\omega_D/T)^2} + \frac{18}{(n\omega_D/T)^3} \right) \frac{e^{(n\omega_D/T)}}{n} \right] \quad (4.3.3)$$

The Debye temperature represents the point above which most vibrational modes of the crystal are excited.

As can be seen in Fig. 4.3.2, an excellent fit to the experimental data was obtained using the combined Debye Einstein model. The fit that was obtained

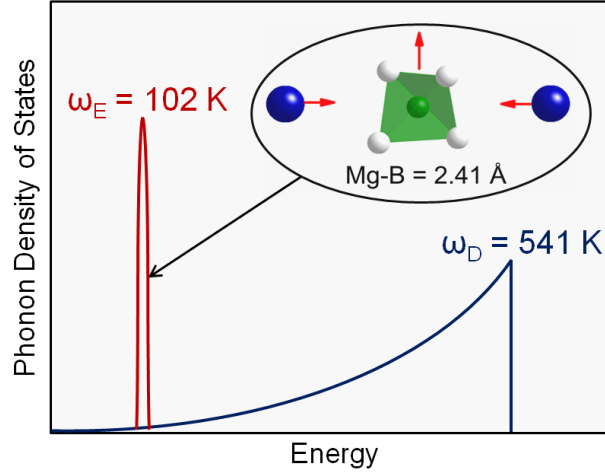


Figure 4.3.3: Schematic of the Debye-Einstein model of the phonon density of states used to fit the lattice parameter of γ -Mg(¹¹BH₄)₂. The inset shows rigid body motion of the [BH₄] tetrahedron that is believed to be responsible for negative thermal expansion observed in the material.

is given by the formula:

$$\begin{aligned}
 a(T) = & 5.7589 + [-2.6081 \times 10^{-4} \times a_E(101.5136/T)] \\
 & + [3.6935 \times 10^{-4} \times a_D(541.3191/T)]
 \end{aligned}
 \quad (4.3.4)$$

The derived Debye and Einstein temperatures are therefore 102 K (71 cm⁻¹) and 541 K (376 cm⁻¹), respectively.

A schematic of the combined phonon density of states is shown in figure 4.3.3. At low energies, the first states to be populated are the ω_D states, which produce the expansion seen at very low temperatures in Fig. 4.3.2. When there is enough thermal energy present to populate the transverse ω_E phonon mode, the cell then begins to shrink. As the temperature is further increased, more ω_D states are populated and the material begins to display the positive

thermal expansion again.

4.4 Inelastic Neutron Scattering of Enriched Samples

4.4.1 Mg(¹¹BH₄)₂

To further investigate the phonon density of states in this material, low temperature INS measurements were performed on a sample of γ -Mg(¹¹BH₄)₂ on the MARI spectrometer at ISIS using incident energies of 150 and 250 meV. The data were collected over a wide range of momentum transfer and integrated from $Q = 1\text{--}8 \text{ \AA}^{-1}$ to produce the INS spectra shown in Fig. 4.4.1 & 4.4.2.

To assign the spectrum, density functional theory (DFT) calculations were performed by Alex Mulliner and Philippe Aeberhard using the *ab initio* plane-wave pseudopotential total energy package 'CASTEP'[191, 192, 193]. Phonon frequency calculations were determined with a finite displacement/supercell calculation performed on a geometry optimized structure. The density of states was generated in CASTEP by performing a Gaussian broadening with a full width at half maximum of 10 cm^{-1} . Fig. 4.4.1 shows an excellent qualitative agreement between the calculated and measured spectra. To visualize the motions responsible for each mode, the program Jmol was used. A full list of phonon frequencies in γ -Mg(¹¹BH₄)₂ and their assignments is given in Appendix A.

The phonon calculations include frequencies beyond those measured on MARI. To experimentally access data in the B-H stretching region ($>2000 \text{ cm}^{-1}$), room temperature Raman measurements were collected on γ -Mg(BH₄)₂ at the University of Birmingham. The Raman peaks were fit with pseudo-Voigt functions and their frequencies were extracted. This data has been plotted in Fig. 4.4.2 along with the INS data from MARI and the calculated phonon density of states.

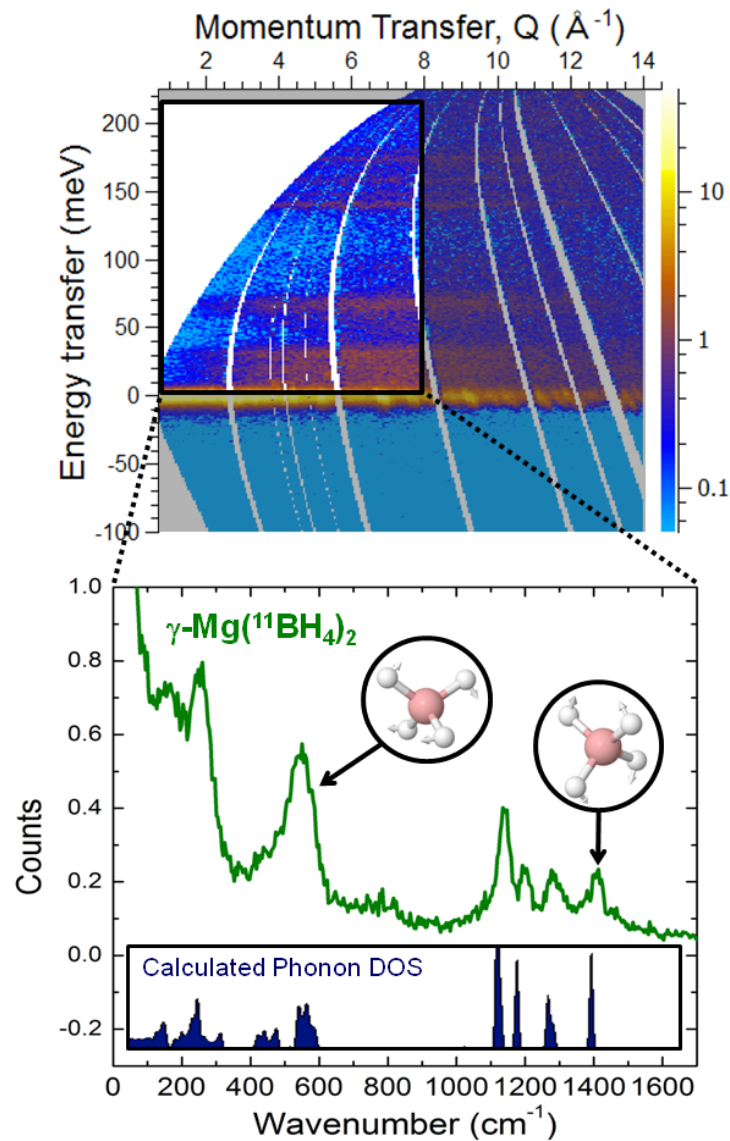


Figure 4.4.1: Above: Surface plot of the full INS spectrum collected for γ -Mg(¹¹BH₄)₂ on MARI. Below: Data were integrated from $Q = 1$ -8 Å⁻¹ and energies were converted to wavenumber for comparison with the calculated phonon density of states (generated using CASTEP). Examples of rocking and bending modes are indicated on the spectrum.

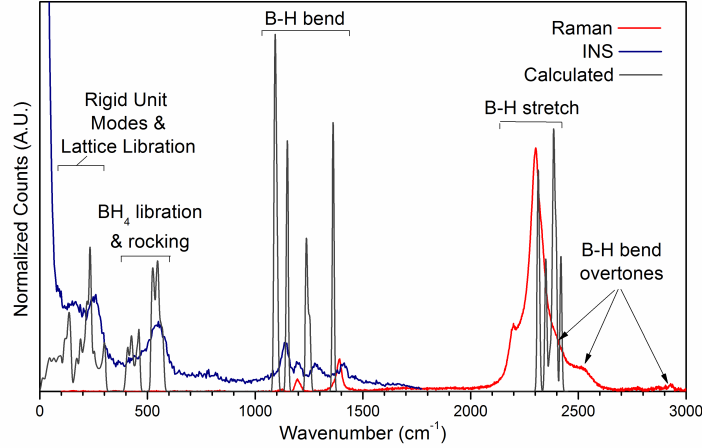


Figure 4.4.2: INS, Raman, and DFT spectroscopic data for γ - $\text{Mg}(\text{}^{11}\text{BH}_4)_2$ compared over the same range. Full assignment of all modes is provided in Appendix A.

The excellent match between the calculated and experimental spectra allowed the various peaks to be unambiguously assigned. Frequencies above 1000 cm^{-1} correspond to internal borohydride bending and stretching modes, while those below are due to movement of larger bodies, lattice distortions, or translations. The spectroscopic data may be classified into five different regions with distinct characteristics:

- $< 200 \text{ cm}^{-1}$: At very low energies, modes close to the elastic line are seen. These are typically librations of the lattice as a whole. However, two modes corresponding to BH_4 motion in the direction transverse to the Mg-B-Mg plane are seen in the calculations at approximately 77 and 102 cm^{-1} . It is possible that these modes are responsible for the negative thermal expansion observed in the material at low temperatures.

- 200-500 cm^{-1} : Phonons in this energy region correspond to libration of the borohydride ion as a whole. A single mode corresponding to BH_4 movement in

the direction longitudinal to the Mg-B-Mg plane is also seen in the calculations at 396 cm⁻¹. Given the instrumental resolution at these energies, it is not possible to assign specific INS peaks at energies below 500 cm⁻¹, but a good qualitative agreement between in the shape of the calculated and experimental phonon density of states is seen.

- 500-600 cm⁻¹: A broad feature in the INS spectrum centered at around 550 cm⁻¹ is due to various rocking motions of the borohydride ions about its lattice.

- 1000-1500 cm⁻¹: This region contains four distinct features in the INS spectrum which correspond to the doubly degenerate symmetric (ν_2) and triply degenerate asymmetric (ν_4) bending modes of the borohydride ion (although degeneracy as been lifted for the ion on the 48g site). Raman spectroscopy requires a change in polarizability of the molecule and thus only the non-polar symmetric bending motions are observed in the Raman spectrum.

- 2000-3000 cm⁻¹: The frequencies in this region were generally overestimated by calculations since the energy minimized structure at 0 K was used to generate theoretical phonon energies. As measurements were taken at room temperature, the hydrogen atoms spend on average more time further from the nucleus, resulting in longer B-H distances and lower vibrational energies. The singly degenerate symmetric stretch (ν_1) is seen at as a shoulder on the band due to the triply degenerate asymmetric stretch (ν_3). Fitting of the shoulders on the high energy end of the Raman spectrum found peaks centered at 2395 and 2531 cm⁻¹, which correspond to the first overtone ($2 * 1198 = 2396$) and combination band ($1198 + 1388 = 2586$) of the bending modes, respectively.

Finally, the DFT calculations revealed two imaginary modes at -17.27 and -0.07 cm⁻¹. Imaginary phonon modes indicate a degree of instability and are associated with a lowering of symmetry[194]. It is possible that these are ob-

served since the structure of γ -Mg(¹¹BD₄)₂ is stabilized by a small amount of residual solvent. The presence of negative frequency modes also supports the observation that Mg(BH₄)₂ converts from the γ to α phase over time.

4.4.2 Mg(¹¹BD₄)₂

For direct comparison with the sample used for diffraction at low temperatures, the INS spectra of γ -Mg(¹¹BD₄)₂ was collected at 4 K on the TOSCA spectrometer at ISIS for 12 hours. Phonon calculations were performed by Alex Mulliner using the same process described in the previous section. The INS spectrum along with the calculated phonon density of states is shown in Fig. 4.4.3.

Although the INS spectrum of γ -Mg(¹¹BD₄)₂ reveals some interesting information about the material, the relatively small incoherent cross section of the elements in this material meant that a long collection time was necessary before any features became visible in the spectrum. Even after collecting data for 12 hours, many of the peaks in the spectrum were extremely weak.

An excellent match of the the calculated phonon density of states to the experimental data was achieved and a full assignment of all modes is provided in Appendix B. By rescaling the x-axis by a factor of $\sqrt{2}$ (from ratio of the reduced masses when hydrogen is involved) the spectrum may be directly compared to that of Mg(¹¹BH₄)₂. Many of the same features of the INS spectrum observed for Mg(¹¹BH₄)₂ are also present in Mg(¹¹BD₄)₂ and the match in shape between the scaled spectra was very good (for example, the ratio of the measured ν_2 frequencies between the two is $\frac{1412}{1010} = 1.40$).

At low energies, lattice deformations and rigid body modes are seen while the region between 700 and 1100 cm⁻¹ corresponds to B-D bending in the borohydride ion. The experimental stretches are at higher energies than those that have been calculated, which are likely due to the longer B-D bond length of the

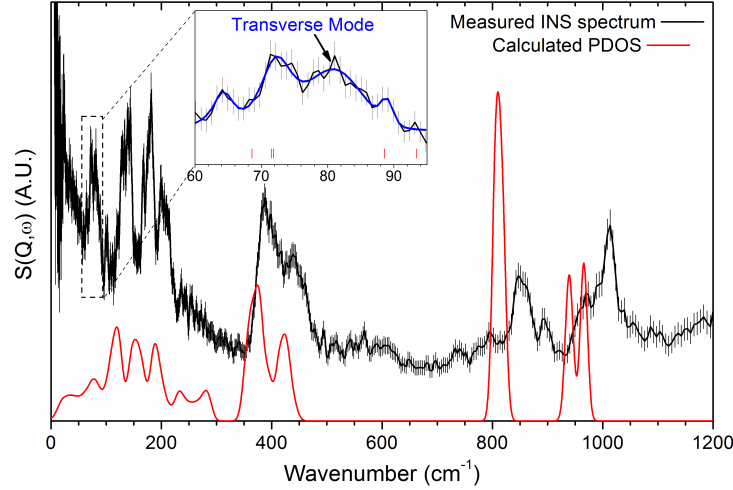


Figure 4.4.3: INS spectrum (from TOSCA) and calculated phonon density of states for γ -Mg(¹¹BD₄)₂. The inset shows the fit achieved from fitting with Voigt functions to extract a temperature for the transverse BD₄ mode.

energy minimized structure (1.228 Å) than of the experimentally determined value at this temperature (1.204 Å). Theoretical values of B-D stretching frequencies are also provided in Appendix B, however, no peaks were seen in the INS spectrum due to the poor resolution of the instrument in this energy range.

The lowest energy transverse mode (believed to be responsible for negative thermal expansion) is observed in the spectrum at approximately 81 cm⁻¹. However, several other modes exist around this energy, which broaden the peak and make it difficult to extract an exact frequency. The Debye-Einstein model of the unit cell parameter predicted the mode to have an energy of 71 cm⁻¹, which is a relatively close match to the observed value, given the weak intensity (due to small incoherent cross section of ¹¹BD₄), spectral resolution of the spectrum, and errors in the diffraction data.

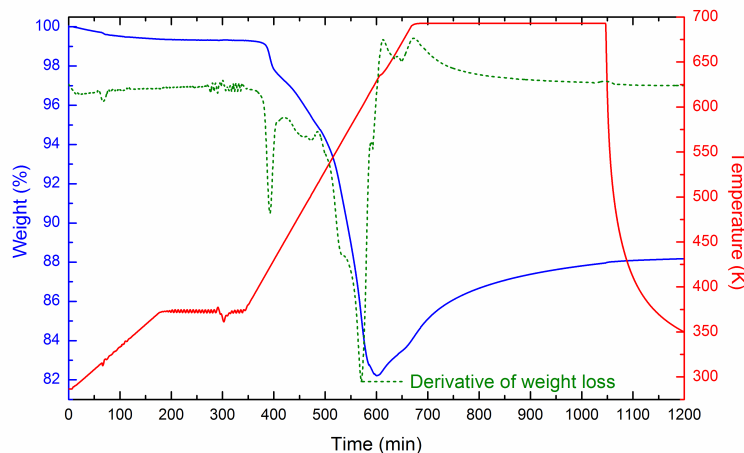


Figure 4.5.1: Full temperature and weight loss profile of γ -Mg(¹¹BD₄)₂ measured on the IGAⁿ.

4.5 *In Situ* Decomposition Using the IGAⁿ

A fresh 1g sample of γ -Mg(¹¹BD₄)₂ was loaded into the IGAⁿ, which was then craned into the WISH beamline. The sample was heated from around 290 K to 373 K at 0.5 K/min and then held at this temperature while the methane was regenerated in the moderator (no diffraction data was collected during this time). The sample was then heated to just under 700 K at 1 K/min and allowed to cool back to room temperature. The full temperature profile, along with the mass loss and its derivative, is shown in Fig. 4.5.1.

The IGAⁿ data reveals an extremely complex weight loss profile. The only crystalline phase observed in the diffraction data up until approximately 425 K is γ -Mg(¹¹BD₄)₂, apart from the strong Bragg peaks from the steel container, which were present in all measurements (Fig. 4.5.2). Interestingly, the lattice parameter of this phase grows as temperature increases up until about 335 K, at which point it remains constant and then ultimately begins shrinking (See

Fig. 4.5.3). A small amount of weight loss is observed over this temperature range and so it is possible that a small amount of solvent is released even at these low temperatures. As it is believed that the solvent stabilizes the overall structure, loss of solvent may explain the slow conversion to the α phase that is observed at such low temperatures. The rapid decrease in volume observed just below 400 K is accompanied by a very fast gravimetric loss of about 2 wt. % and occurs simultaneously with the disappearance of the γ phase. As has been previously observed, this corresponds to the complete destruction of the γ phase and release of all remaining solvent in the structure.

It was originally believed that high resolution neutron data might help resolve the structural evolution in the 420 - 460 K range. However, even with such high quality data, the spectrum becomes very complex due to the presence of multiple, rapidly changing phases. Firstly, the β phase appears; the odd-odd-odd hkl peaks become increasingly broad and weak (see the spectrum at 470 K in Fig. 4.5.2) and the structure ultimately ends up as the β' phase. However, as γ phase disappears, there is at least one other phase present that has only a few peaks, most of which overlap with the β phase. As such, it was still not possible to index the new (ϵ) phase.

As was observed in the DTA, gradual weight loss occurs from the point at which the β/ϵ phases first appear. The amount of β' present is constant until approximately 520 K (and the phase is stable upon quenching). This observation supports the mechanism proposed in Chapter 3 and suggests that the weight loss from *ca.* 400-520 K must be due to a side reaction. Furthermore, the derivative of the weight loss curve appears to contain more than one minimum, suggesting that the weight loss is a series of decompositions, each with a different rate of reaction (and therefore slope of weight loss curve). It is possible that the extra Bragg peaks seen between 435 and 460 K are the result of an intermediate in

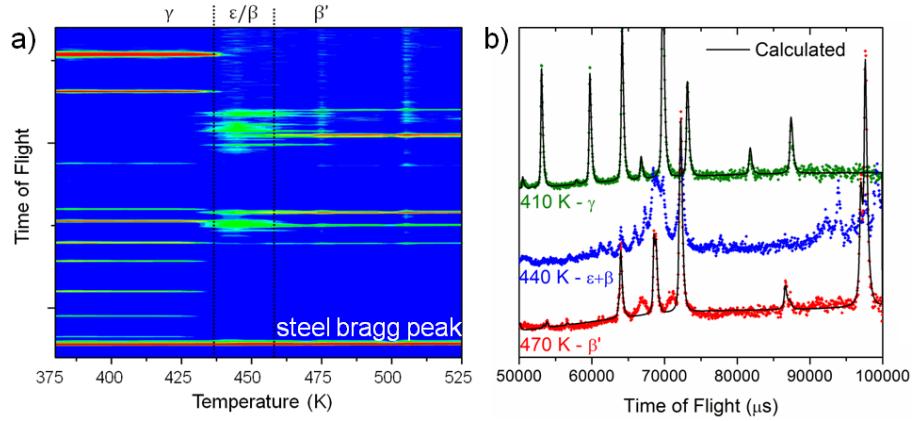


Figure 4.5.2: a) Surface plot of variable temperature neutron diffraction measurements collected in the IGAⁿ at WISH. A phase change from γ to β' - $\text{Mg}({}^{11}\text{BD}_4)_2$ is indicated b) Slices of the data at three different temperatures. A fit to the data is shown at 410 K (γ phase) and 470 K (β' phase). At least one other phase is clearly visible at 440 K

the multi-step decomposition to the $[\text{B}_3\text{H}_8]^-$ species previously reported. Hence, the “ ϵ phase” is only observed over a small range of temperatures.

The lattice parameters of the β' phase were extracted from a Pawley refinement of an $Immm$ cell half the size of the true $Fddd$ structure of the β phase, as was suggested by Her *et al*[86]. Although the β phase is clearly present at temperatures above 435 K, a reliable refinement was not possible below 465 K due to the large number of overlapping peaks present. It was seen that the a and b axes (and overall volume) expand as temperature increases, while the c axis remains roughly constant over the entire temperature range. Anisotropic unit cell behaviour has been previously reported for β - $\text{Mg}(\text{BH}_4)_2$ by Filinchuk *et al.*[85]. In this work, the authors were able to fit a third order polynomial to the c unit cell data over a range of approximately 100 - 475 K. However, the model (a third-order polynomial) suggested that at temperatures above 450 K, the c axis should expand. It appears that the unit cell behaviour of this phase is more complicated than previously believed and future work should attempt

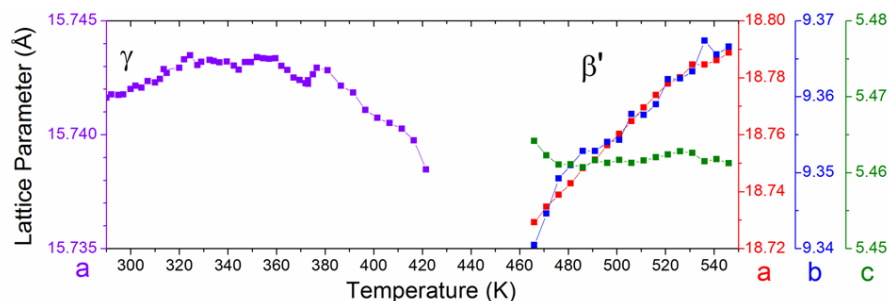


Figure 4.5.3: The lattice parameters of the γ and β' phases over the range of temperatures they are observed

to rationalize this behaviour in terms of the phonon density of states.

The neutron diffraction data during decomposition (not shown) matched that of the variable temperature X-ray diffraction data in chapter 3. The only major difference was that transitions were observed at lower temperatures than in the PXD measurements, likely due to the slower heating rates used on WISH. The β' phase is seen to begin disappearing around 520 K and is completely gone by 550 K, at which point no more crystalline peaks are observed in the data. At 595 K, MgD_2 appears and begins transforming at 520 K to Mg metal, which is the only remaining crystalline species as the sample was cooled (though background intensity increased). Again, the derivative of weight loss curve reveals details about the kinetics of this decomposition; three distinct minima align exactly with the changes in the diffraction data and are observed at 560, 600, and 620 K. From the relative position of the minima, it is also possible to conclude that transition from the amorphous phase to MgD_2 occurs very quickly, while the conversion to Mg metal happens much more slowly (the diffraction data shows that MgD_2 persists for about 50 K). Overall, the sample loses over 16 wt. % during decomposition, corresponding to around 2.5 moles of D_2 .

Following decomposition, the sample begins gaining weight. As suggested in Chapter 3, this is likely due to the formation of various amorphous oxide

species. However, there are at least three different rates of reaction observed in the weight gain section of the curve, indicating conversion to oxides may occur at different rates and/or temperatures for the remaining phases in the sample.

4.6 Hydrogen Adsorption and Desorption Studies Using INS

As mentioned previously, large pores in the structure of γ -Mg(BH₄)₂ prompted a study on the adsorption of gas molecules into the framework[67]. However, these measurements were carried out at high pressures and little is known about how the adsorbed gas is released from the material. The INS instrument TOSCA at ISIS is optimized to study hydrogen and, due to its large incoherent scattering cross section, any H₂ gas molecules adsorbed into a compound containing no hydrogen will dominate an INS spectrum.

4.6.1 Parahydrogen Adsorbed Into γ -Mg(¹¹BD₄)₂

Molecular hydrogen typically exists as a mixture of two different species; ortho-hydrogen, where J is odd and spin = 1, and para-hydrogen (p-H₂), where J is even and spin = 0. To achieve molecular hydrogen in the ground state, p-H₂ was prepared by exposing molecular H₂ to a paramagnetic catalyst at very low temperatures. The sample of γ -Mg(¹¹BD₄)₂ was then heated to 50K and attached to a gas manifold containing p-H₂ at 4 K. The p-H₂ was heated and allowed to enter a chamber of known volume, where the vapour pressure was monitored. Once the chamber had been filled, the source was closed off and the amount of hydrogen present in the chamber was calculated. The valve connecting the warmed p-H₂ to the sample of (cold) γ -Mg(¹¹BD₄)₂ was then opened and the hydrogen was absorbed into the structure. The process was

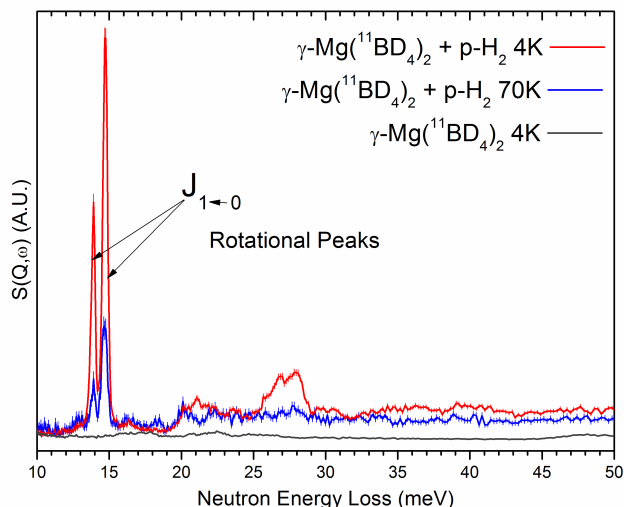


Figure 4.6.1: INS spectra of γ -Mg(¹¹BD₄)₂ a) at 4 K b) with 403 mL adsorbed p-H₂ at 4 K and c) with adsorbed p-H₂ remaining at 70 K. Rotational transitions of the H₂ molecule are indicated.

repeated until no more p-H₂ would enter the structure. The sample was then cooled to 4 K and the INS spectrum was collected. The sample was then heated to 70 K as the over pressure was monitored (it was not allowed to exceed 1 bar).

Fig. 4.6.1 shows the INS spectrum of a sample containing 403 mL of p-H₂ at 4 and 70 K (the background spectrum of pure γ -Mg(¹¹BD₄)₂ is also shown for reference). As the cross section of the adsorbed hydrogen is much larger than any constituents of the host framework, the spectra are completely dominated by the signal from p-H₂. The total amount of scattering observed is therefore a good indicator of the amount of hydrogen present in the framework. From this, it is evident that a significant amount of hydrogen remains in the framework at 70 K.

The most notable feature of the spectrum is the two large peaks centered around 14.5 meV. For a hydrogen molecule that interacts only with itself (e.g.

in solid H₂) the rotational term of the Schrodinger equation can be separated out and the energy of the levels are given by:

$$E_J = J(J+1)B_{rot} = J(J+1)\frac{\hbar^2}{2I} \quad (4.6.1)$$

where B_{rot} is the rotational constant for H₂ (7.35 meV) and I is the moment of inertia. The above energy levels are degenerate in the quantum number M ($= 0, \pm 1, \pm 2, \dots, \pm J$) when the H₂ is in an isotropic potential. However, when the molecule experiences an asymmetric potential, the degeneracy may be lifted. The intense split peaks at around $2B_{rot}$ in Fig. 4.6.1 are therefore likely to correspond to the $J_{1\leftarrow 0}$ rotational transition of an H₂ molecule experiencing an anisotropic environment within the γ -Mg(¹¹BD₄)₂ framework.

The second visible feature in the spectrum at 4 K is a weaker band centered at around 27.5 meV. The origin of this band is difficult to assess from the spectra in Fig. 4.6.1 alone. The $J_{2\leftarrow 1}$ transition is expected at $4B_{rot} = 29.40$ meV. Although an anisotropic potential will have the effect of decreasing the distance between successive energy levels, the observed peaks are several meV lower than predicted. Furthermore, a majority of the H₂ is in the ground state and it is not expected that transitions from the excited $J=1$ state would be observed at such a large intensity. The origin of this band is discussed further in the next section. The remainder of the transitions in p-H₂ experience recoil and therefore, are not observed in the spectra of Fig. 4.6.1[159].

4.6.2 Molecular Hydrogen Rattling

The double differential cross section (ignoring the coherent part) is proportional to the self-part of the structure factor ($S_{self}(Q, \omega)$) for the center of mass (c.o.m.) motion convoluted with a Dirac function δ centered at the energies of

the rotational transition $\hbar\omega_{JJ'}$.

$$\frac{d^2\sigma}{d\Omega d\omega} = \frac{k_f}{k_i} S_{self}(Q, \omega) \otimes \sum_{JJ'} \delta(\omega - \omega_{JJ'}) v(J, J', Q), \quad (4.6.2)$$

where $v(J, J', Q)$ is an intensity factor that depends on the rotational $J \rightarrow J'$ transitions of a molecule and the momentum transfer. As INS is not subject to selection rules, all transitions to rotational and c.o.m. vibrational states are allowed. Spectra therefore consist of c.o.m. excitations repeated at an energy shift equal to that of any possible rotational excitations in the molecule[195].

In p-H₂, only the J=0 rotational state is populated and the elastic $J_{0 \leftarrow 0}$ transition does not contribute appreciably to the spectrum as it is weighted only by the coherent scattering length[196]. Therefore, to fully understand molecular hydrogen c.o.m. rattling in this system, gas containing ortho hydrogen must be used. In this case, the elastic $J_{1 \leftarrow 1}$ rotational transition combines with the rattling transition of the c.o.m. motion to produce a rattling fundamental[197]. Two additional adsorption experiments were performed using 250mL of normal (a mixture of para- and ortho-) hydrogen (n-H₂) and 250mL of hydrogen deuteride (which will also be a mixture of the two different spin isomers). In each case, spectra were collected at 4 K. The peaks in the low energy region (8-20 meV) of each data set were fit using two or more pseudo-Voigt functions. The fit to the data is shown in Fig. 4.6.2 and the results are presented in Table 4.3.

Assignment of the $J_{1 \leftarrow 0}$ rotational lines is unambiguous from the spectrum of p-H₂. The same two lines are observed in both n-H₂ and HD and a comparison of their energies can provide information about the potential. The ratio of the average HD rotational energy (11.64 meV) to that of H₂ in both the para- and normal samples is 0.814. For a free rotor, the ratio of their energies is given by

$$\frac{E_{HD}}{E_{H_2}} = \frac{B_{HD}}{B_{H_2}} = \frac{\mu_{H_2}}{\mu_{HD}} = \left(\frac{1 \cdot 1}{1 + 1} \right) \left(\frac{1 + 2}{1 \cdot 2} \right) = 0.75 \quad (4.6.3)$$

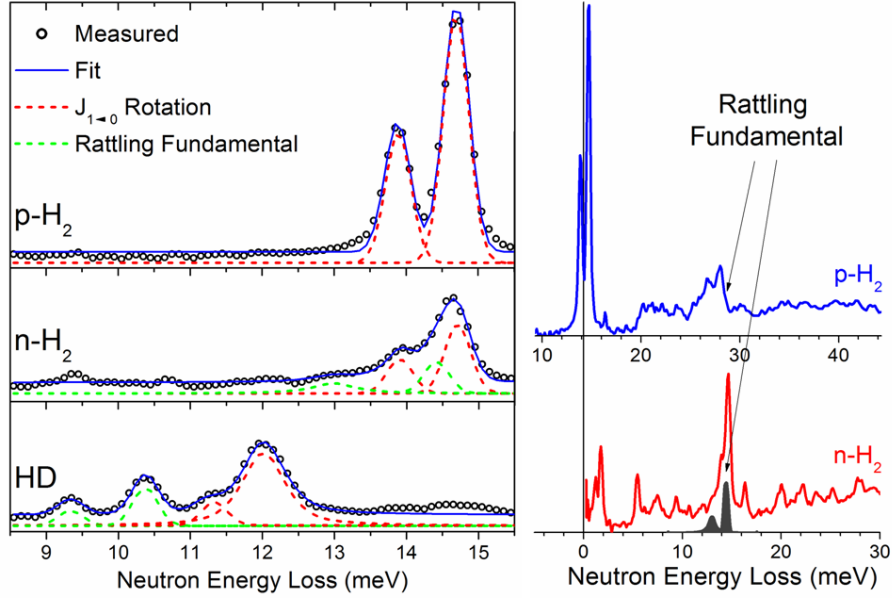


Figure 4.6.2: Left: Deconvoluted pseudo-Voigt functions used to fit the $J_{1\leftarrow 0}$ rotational lines (red) and fundamental rattling peaks (green) for 250mL of n-H₂, p-H₂, and HD adsorbed into γ -Mg(¹¹BD₄)₂. Right: Spectrum of p-H₂ (blue) shifted by -14.3meV to show the coincidence in frequency and shape of the first overtone with the rattling fundamental observed in n-H₂ (red). The component of the spectrum representing the rattling fundamental is shown below in grey.

Table 4.3: Energies (in meV) of the $J_{1\leftarrow 0}$ rotational transitions and rattling fundamental in HD, p-H₂, and n-H₂.

Rotational Peak	HD	p-H ₂	Ratio	n-H ₂	Ratio
I	11.26	13.88	0.811	13.89	0.810
II	12.02	14.70	0.818	14.71	0.817
Average	11.64	14.29	0.814	14.30	0.814

Rattling Fundamental	n-H ₂	HD	Ratio
I	12.99	9.34	1.391
II	14.41	10.37	1.389
Average	13.70	9.85	1.390

Deviations from this value are caused by an anisotropic potential that, in addition to removing degeneracy, can also affect the average value of the rotational energy. The deviation we have observed is very close that reported for dihydrogen adsorbed into clathrate hydrates (0.80 meV [197]).

By rescaling the p-H₂ spectrum and subtracting it from the n-H₂ data, it is possible to obtain an approximate spectrum of ortho-H₂. While at first there did not appear to be any rattling transitions in the spectrum of n-H₂, this process revealed that a significant amount of intensity exists in between the two lines assigned to the $J_{1\leftarrow 0}$ rotational transition. Two extra peaks were found in the n-H₂ data that had originally been masked by the rotational lines of p-H₂. These have been assigned as split rattling fundamental centered at an energy of 13.70 meV (again, the splitting suggests a degree of anisotropy of to the H₂ environment). This assignment is supported by the HD adsorption data, where two additional peaks are observed at energies slightly below those of the $J_{1\leftarrow 0}$ rotational transitions. The ratio of the rattling frequencies measured for H₂ and HD is to be compared with the harmonic value ($\sqrt{m_{HD}/m_{H_2}} = \sqrt{3/2} = 1.225$) and that expected for a square well potential ($m_{HD}/m_{H_2} = 3/2 = 1.5$). The experimental result of is 1.390 is an intermediate value, indicating that the environment is slightly closer to a flat potential than a harmonic one.

Further evidence for the assignment is provided in the right panel of Fig. 4.6.2. Here, the spectrum of p-H₂ has been shifted by the average value of the rotational transition (-14.3 meV) and plotted with the spectrum of n-H₂. As the p-H₂ contains the pure rotational transition in combination with the c.o.m. transitions, an excellent match in energy and shape to the component of rattling in n-H₂ is obtained.

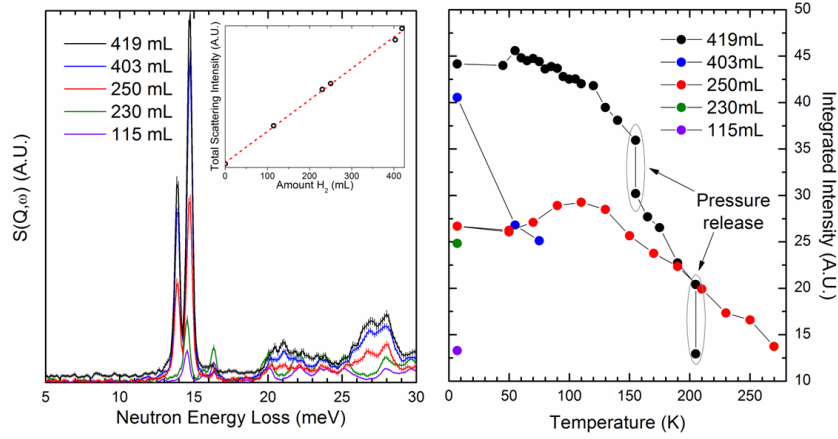


Figure 4.6.3: Left: The INS spectra of various amounts of p-H₂ adsorbed into γ -Mg(¹¹BD₄)₂ at 4K. The inset shows the linear relation between total scattering and volume of adsorbed H₂. Right: Integrated total scattering intensities for each loading at various temperatures. As the signal is dominated by hydrogen, this is directly related to the amount of hydrogen present in the sample.

4.6.3 Variable Temperature Measurements

Another series of experiments were performed to investigate the potential of γ -Mg(¹¹BD₄)₂ for hydrogen storage at more ambient conditions. In the previous experiment, the sample was heated rather rapidly from 4 to 70 K, which may have caused the hydrogen to leave the framework more quickly at a lower temperature. As such, hydrogen was adsorbed in various quantities and spectra were measured at base temperature. For loadings of 419mL and 250mL of p-H₂, the sample was heated in 5 or 10 K steps up to nearly room temperature and data were collected for 2 hours at each step. The spectrum of pure γ -Mg(¹¹BD₄)₂ was subtracted from each run and the spectra were then integrated to give the total scattering intensity. The INS spectra of each loading at base temperature and the integrated scattering intensity with at various temperatures are plotted in Fig. 4.6.3.

An interesting observation is that the spectrum at low loadings (<230 mL

H₂) is different than that at higher loadings. In the low-H₂ spectra, the rotational line is not split, indicating that the hydrogen may first adopt a site that is more isotropic than its final position when enough hydrogen is forced into the structure. A feature at around 16meV is present at higher loadings but is much stronger when less hydrogen is adsorbed. The origin of this peak is unknown and it would be interesting to perform further studies to examine the mechanism by which hydrogen loads into γ -Mg(¹¹BD₄)₂.

The sample of γ -Mg(¹¹BD₄)₂ was able to adsorb up to a maximum of 419mL (at SATP) H₂ into its framework at 4K. Assuming ideal gas behaviour, this corresponds to 1.5 moles of H₂ per mole of γ -Mg(¹¹BD₄)₂. The related borohydride, Mg(BH₄)₂·1.5H₂, is one of the most hydrogen-rich materials ever reported, with a gravimetric content of 19.5 wt %. The adsorbed hydrogen represents about 5 wt. % which, despite being a relatively small amount, could be commercially useful if the thermodynamics and kinetics of release/uptake were favourable.

As INS spectra are dominated by hydrogen, it is possible to directly probe the amount of adsorbed H₂ remaining at higher temperatures by examining the total integrated scattering intensity. As shown in Fig. 4.6.3, a good linear fit between the volume of p-H₂ exposed to the sample and integral of total intensity is achieved. It is evident from both variable temperature studies that the amount of adsorbed hydrogen remains relatively constant until around 110 K. Measurements taken before and after cooling the sample from 50 K to 4 K indicate that no extra hydrogen is adsorbed into the structure upon cooling. While 50K was used in this particular experiment, further work is needed to determine the highest temperature at which hydrogen is adsorbed into γ -Mg(¹¹BD₄)₂ and to understand reversibility of this system.

Above 110 K, hydrogen begins leaving the structure very slowly (recall that each data point represents a 2 hour measurement). A slight over pressure was

noted at this point, which grew at each temperature step. Note that for the run in which 419mL of hydrogen was adsorbed, the over pressure grew too large and the sample was opened up to a larger manifold at 160 K. For the 250 mL H₂ sample, the larger manifold was connected from the beginning of the run and no pressure evacuation was needed. It should also be noted that at higher temperatures, the spectra are much more noisy due to the Debye-Waller factor. As a result, total integration is less reliable however the J_{1←0} rotational peak is still visible at temperatures as high as 270 K, confirming that some hydrogen remains in the structure even near room temperature.

4.7 Adsorbed Hydrogen Location and Anomalous Unit Cell Behaviour From In Situ Neutron Diffraction

To further understand the behaviour of the adsorbed gas molecules, adsorption experiments were repeated on the WISH beamline. Due to the small coherent cross section of hydrogen, both H₂ and D₂ were used to ensure that data were of sufficient quality. Four different experiments were performed, in which 300mL and 312mL of D₂, and 60mL and 250mL of H₂ were adsorbed into the sample at 50 K. The sample was then cooled to 4K and scans were collected for 15 minutes.

Figure 4.7.1 (a) shows a Rietveld refinement to the diffraction data for the material at 4K with 300mL of D₂ and 250mL of H₂ adsorbed. The first evidence that hydrogen has been adsorbed into the structure is seen in the H₂ samples as an increase in background intensity below *ca.* ToF = 25000μs due to the large incoherent scattering length at low ToF. To determine the exact location of the adsorbed molecules, the spectra were first fit using the structural model

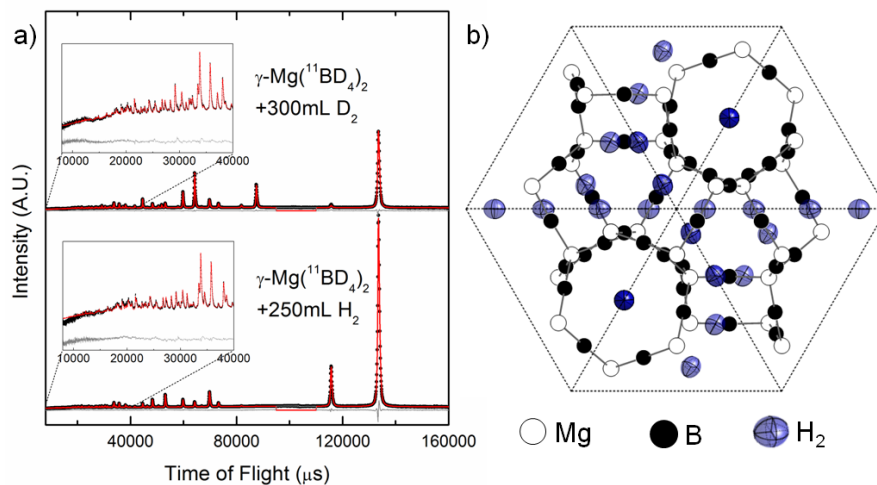


Figure 4.7.1: a) Neutron ToF diffraction spectra of 300mL D₂ (top) and 250 mL H₂ (bottom) adsorbed into γ -Mg(¹¹BD₄)₂. Observed data are shown as black dots, while the calculated data from the structural model obtain from a Rietveld refinement are shown in red. b) Refined structure of γ -Mg(¹¹BD₄)₂ (only the MgB₂ sublattice is shown for clarity) containing H₂ molecules in long chains along the centre of the pores in the [111] directions.

determined earlier in this chapter. Then, Patterson maps of the electron density were generated using TOPAS. In samples with H₂ adsorbed, negative scattering intensity was seen in the centre of the pores, while extra scattering intensity was seen for the D₂ adsorbed samples. As the adsorbed gas will likely exist as a diatomic molecule inside the framework, a single additional atom site was introduced into the structure and its position, occupancy and atomic displacement parameters were allowed to refine.

The additional site refines to the 32e Wyckoff position $\frac{x}{a} = \frac{y}{b} = \frac{z}{c} = 0.43323(9)$ and a very good fit was achieved for all measurements (typical values of $\chi^2 = 2.8$ $R_{wp} = 2.7\%$ $R_{exp} = 0.98\%$). In Fig. 4.7.1, the thermal ellipsoid of the additional site is shown adsorbed into the MgB₂ sublattice (additional deuteriums omitted for clarity). The ADPS provide an indication that the molecules are stretched as rods along the insides of the pores. Lengthening in this way is

indicative of a relatively flat potential along the rod. The adsorbed gas site sits at several different distances from other D (3.036-4.098 Å), B (4.123-4.166 Å), and Mg (4.323 Å) neighbours, confirming that there is a degree of anisotropy to the potential that causes the splitting of rotational and rattling peaks in the INS spectra. Separations on this order of magnitude are indicative of Van der Waals type interactions.

Full occupation of the 32e symmetry site by hydrogen would give 1.5 moles of H₂ per mole of γ -Mg(¹¹BD₄)₂, which is exactly what was achieved for maximum loadings on TOSCA. Curiously, no more than 312mL D₂ and 250mL of H₂ would adsorb into the framework on WISH (this corresponds to 0.86 moles of H₂ and 1.08 moles of D₂ per mole of γ -Mg(¹¹BD₄)₂). The reason why the sample did not adsorb as much as it did on TOSCA is still unknown; the exact same sample/vanadium can and hydrogen dosing system were used. However, even upon repeating the measurements on WISH, no more hydrogen would adsorb into the structure. The experiment in which 60mL of H₂ was introduced into the framework was used to check if the adsorbed molecules occupy a different location in at lower vs. higher loadings (therefore explaining the differences in the INS spectra). However, the adsorbed molecules were found to occupy the same position at low loadings as they did when larger amounts were added.

For each different loading, the sample was heated in the beam at approximately 1 K per minute, while stopping every 10 K to collect a spectrum for 15 minutes. The lattice parameter of the γ -Mg(¹¹BD₄)₂ framework and the adsorbed gas site occupancy as a function of temperature are compared with that of pure γ -Mg(¹¹BD₄)₂ in Fig. 4.7.2. An interesting effect of the adsorbed gas is observed in all experiments; when added to the structure, the gas causes the lattice parameter to 'lock' into a given value. Below the temperature of about 50 K, the lattice parameter shows no variation when gas is adsorbed and

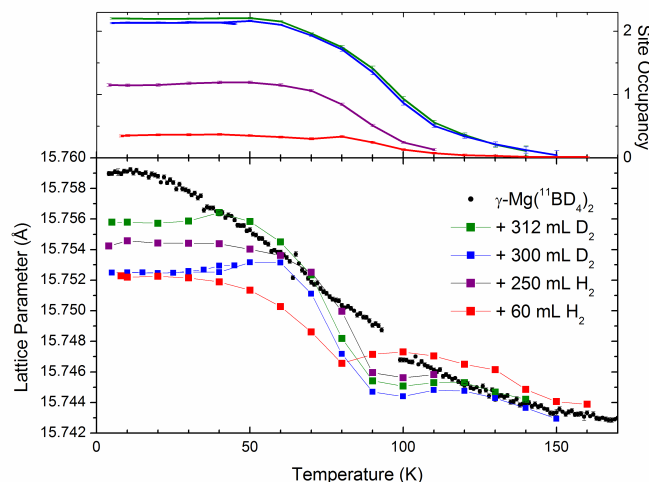


Figure 4.7.2: Lattice parameter of the γ -Mg($^{11}\text{BD}_4$)₂ framework with different amounts of hydrogen/deuterium adsorbed as a function of temperature. The affect of the adsorbed gas is to 'lock' the lattice parameter at temperatures below 50 K. The occupancy of the adsorbed gas site with temperature is shown above.

the negative thermal expansion observed in the pure compound is no longer present. While this phenomenon has been noted in other framework structures when hydrogen (or another gas) is adsorbed[198], its origin remains unknown. In the case of γ -Mg($^{11}\text{BD}_4$)₂, it is possible that the Van der Waals interaction of the adsorbed molecule with the BD₄ tetrahedra partially stifles the transverse rigid unit phonon mode, resulting in a constant lattice parameter over the low energy range. As the gas begins to exit the framework around 60 K, a very rapid shrinking of the lattice parameter is seen. The lattice parameter reaches a minimum around 100 K and then increases to match that of the pure γ -Mg($^{11}\text{BD}_4$)₂.

The desorbed gas could be reversibly added to the sample by simply cooling it down. After heating the sample containing 300mL of D₂, an overpressure of desorbed gas was monitored. As the system was cooled, that pressure began to

drop (around 60 K) as the hydrogen re-entered the pores of γ -Mg(¹¹BD₄)₂.

Inexplicably, the results of hydrogen desorption, though self consistent, do not match those obtained on TOSCA. On WISH, the adsorbed gas began leaving the structure at around 60 K and was completely gone by 150 K, while on TOSCA it persisted until nearly room temperature. The reason for this discrepancy as well as the apparent difference in gas capacities is not well understood and merits further investigation.

4.8 Conclusions

γ -Mg(BH₄)₂ and its ability to adsorb hydrogen has been studied in a series of neutron scattering experiments.

The structural model has been refined using high resolution neutron powder diffraction on γ -Mg(¹¹BD₄)₂ at 4 K, allowing a more precise determination of deuterium atom locations. The borodeuteride ion possesses nearly ideal tetrahedral geometry, with little deviation in the average B-D distance of 1.2043 Å. Three D-B-D bond angles are around 106.8° while one is larger 114.9°. *Ab initio* DFT energy minimization calculations support this observation and suggest an even larger spread of the bond angles.

Variable temperature diffraction measurements have shown that γ -Mg(¹¹BD₄)₂ is the only phase present upon heating from 4 K to room temperature. As it warms, γ -Mg(¹¹BD₄)₂ undergoes negative thermal expansion from approximately 15 to 190 K. The coefficient of expansion $\alpha_l = -5.7 \times 10^{-6} \text{K}^{-1}$ over this range, which is comparable to zirconium tungsten oxides. The lattice parameter as a function of temperature was fit using a Debye-Einstein model for the phonon density of states and an excellent fit to the experimental data was achieved with Debye and Einstein temperatures of 102 K (71 cm⁻¹) and 541 K (376 cm⁻¹), respectively. This represents the first report of isotropic negative

thermal expansion in this class compounds and is another interesting property that invites comparison to SiO₂.

The phonon density of states of γ -Mg(¹¹HD₄)₂ and γ -Mg(¹¹BD₄)₂ were investigated using inelastic neutron and Raman spectroscopy. The experimental spectra were compared with theoretical values generated from *ab initio* DFT calculations and an excellent match between the two were seen. Each mode has been assigned and compared to theoretical values where possible (see Appendices A & B). A low energy rigid unit mode in which the borohydride ion moves in a direction transverse to the Mg-B-Mg bond was observed at approximately 81 cm⁻¹ and is believed to be responsible for negative thermal expansion in the material.

γ -Mg(¹¹BD₄)₂ was decomposed while obtaining simultaneous thermogravimetric and neutron powder diffraction data using the IGAⁿ. The mechanism proposed in Chapter 3 was validated and the unsolved ϵ phase was observed as the γ phase changed to the β' phase. Overall, the sample gives off 16 wt. % (or about 2.5 moles) of D₂ by 625 K in three distinct chemical processes. Following desorption, the sample undergoes gains a significant amount of weight gain (6 wt. %), which has negative implications on the reversibility of the fully desorbed system.

Molecular para-hydrogen was adsorbed into the framework of γ -Mg(¹¹BD₄)₂ and studied using INS. A splitting of the rotational line suggests an anisotropic potential at the hydrogen site. By adsorbing HD as well as a mixture of para- and ortho- hydrogen, the quantum dynamics of the system have been probed. A transition corresponding to molecular hydrogen rattling within the framework has been characterized and assigned an energy of 13.70 meV for H₂. Coupling between the J_{1←0} rotational transition and centre of mass rattling is observed, causing an overtone to be present in the spectrum of parahydrogen. The ratio

of rattling frequencies between hydrogen and hydrogen deuteride suggests an environment closer to a flat potential than a harmonic one.

Overall, the framework adsorbed up to 1.5 moles of hydrogen per mole of Mg(BD₄)₂ (or 19.5 wt % for the corresponding borohydride). This is one of the most gravimetrically hydrogen-rich materials ever reported, with a total capacity similar to that of ammonia borane. Upon heating, the hydrogen remains in the structure until about 110 K, when it slowly begins to desorb. Even at nearly room temperature, a small amount of adsorbed hydrogen remains in the structure.

The sample with adsorbed hydrogen and deuterium was studied using high resolution neutron powder diffraction. It was observed that the adsorbed species organizes itself in a long chain along the centre of the pores, occupying the 32e Wyckoff position of the host framework. The adsorption site is found at multiple distances from various other atoms and elongation of the ADPS along the centre of the pores confirms the flatness of the potential observed in the INS measurements. The adsorbed gas also has the effect of 'locking' the lattice parameter of the host material, which may be due to Van der Waals interactions stifling phonon modes responsible for thermal expansion. While the results on both instruments were reproducible, lower loadings and desorption temperatures were achieved on WISH relative to TOSCA. The discrepancy is not well understood and future work should attempt to rationalize the loss of adsorbed hydrogen in this material.

The discovery of porous Mg(BH₄)₂ opened a new area borohydride chemistry in which direct comparison with metal organic frameworks is possible. In this chapter, a variety of the functional properties displayed by MOFs have been applied to γ -Mg(¹¹BH₄)₂ and studied using neutron scattering. Most remarkable is the ability of the material to reversibly adsorb considerable quantities of

hydrogen at relatively ambient conditions. If the thermodynamic properties of this system may be tuned by increasing the affinity of H₂ for the host framework and catalyzing its release, it offers great potential as a future storage material.

Chapter 5

Crystallographic Studies of $\text{Ca}(\text{BH}_4)_2$

5.1 Introduction to Calcium Borohydride and Chapter Outline

Calcium borohydride was first prepared as an alcoholic solution by Kollonitsch *et al.*, who formed it by metathesis of sodium borohydride with calcium chloride[39]. Like NaBH_4 , the main interest in the compound at the time was application as a reducing agent in organic syntheses. As an alcoholic solution, $\text{Ca}(\text{BH}_4)_2$ decomposes at temperatures above -10°C and so the same group reported a year later that a more stable solution of $\text{Ca}(\text{BH}_4)_2$ is formed by dissolving it in tetrahydrofuran (THF). Other work in the 1950s reported that $\text{Ca}(\text{BH}_4)_2$ was formed by reacting calcium hydride or alkoxides with diborane[199, 200]. Mikheeva and Titov first prepared the solid solvated adduct $\text{Ca}(\text{BH}_4)_2 \cdot 2\text{THF}$ in 1964 by metathesis in pyridine followed by washing with THF and drying under

vacuum. When the adduct was heated under vacuum to 190 °C, pure $\text{Ca}(\text{BH}_4)_2$ was produced as a white powder[201]. Later work by the same authors showed that formation of the mixed anion $\text{CaCl}(\text{BH}_4)$ as a byproduct was likely unless an excess of NaBH_4 was used[202].

As with most borohydrides, $\text{Ca}(\text{BH}_4)_2$ did not attract much more attention until the development of interest in materials for hydrogen storage. $\text{Ca}(\text{BH}_4)_2$ has a high gravimetric hydrogen capacity (11.5 wt%) and, in an attempt to tune hydrogen storage behaviour, recent research has focused on understanding the physical properties of the material. The first study of this kind was done by Miwa *et al.* in 2006[88] who characterized $\text{Ca}(\text{BH}_4)_2$ formed from removing solvent from the adduct at 433 K under vacuum for one hour. The study used powder X-ray diffraction (Cu K_α radiation) to determine that $\text{Ca}(\text{BH}_4)_2$ crystallizes in the orthorhombic $Fddd$ space group, which is now designated as the ' α ' phase. Around the same time, the $Fddd$ structure was independently predicted for $\alpha\text{-Ca}(\text{BH}_4)_2$ from DFT calculations in a separate work by Vajeeston *et al.*[203]. Both studies found similar lattice parameters for the compound, although DFT calculations predicted longer B-H distances than those observed using PXD. Soon after, Rönnebro and Majzoub reported that synthesis of this phase is possible by mechanically milling a 1:2 mixture of CaB_6 and CaH_2 and heating at 673 K for 2 days under 700 bar H_2 . While these are relatively harsh conditions, they demonstrate the potential for reversibility of $\text{Ca}(\text{BH}_4)_2$ by direct hydrogenation of likely decomposition products.

Work by Filinchuk *et al.* in 2009 found that diffraction data of $\alpha\text{-Ca}(\text{BH}_4)_2$ was better modeled by noncentrosymmetric subgroups of $Fddd$ (either $F2dd$ or $Fdd2$). This suggested that the symmetry of the true orthorhombic structure was lower than originally believed. The paper also reported a second order transition to a tetragonal phase, where the a and c axes of the α phase continually

approach one another and eventually merge at around 495 K. The “merged axis” phase was modeled in the $I\bar{4}2d$ subgroup of $F2dd$ and is designated as the α' -phase.

In 2007, Riktor *et al.* reported the existence of several different $\text{Ca}(\text{BH}_4)_2$ phases at different temperatures but structural details were not given[204]. Aoki *et al.* reported that $\alpha\text{-Ca}(\text{BH}_4)_2$ undergoes a phase transformation to a new tetragonal modification between 433K and 523 K[205]. The crystal structure of this polymorph (now called the β -phase) was solved by Buchter *et al.* later the same year by variable temperature neutron and synchrotron powder X-ray diffraction measurements. The study found that conversion from the α to β phase occurred around 400 K. $\beta\text{-Ca}(\text{BH}_4)_2$ crystallizes in the $P42/m$ space group and the borohydride units were found to be slightly distorted (B-D length = 1.02-1.16 Å)[90]. A solid state synthesis was used to produce $\beta\text{-Ca}(\text{BH}_4)_2$, in which milled MgB_2 and CaH_2 are heated at 723 K under 300 bar H_2 [206]. Later work found that a Rietveld refinement of the structure in the P-4 space group also gave an excellent fit to experimental diffraction data[89]. However, the fit was only possible since the true structure possesses intrinsic disorder of the BH_4 and the correct symmetry of $\beta\text{-Ca}(\text{BH}_4)_2$ is $P4_2nm$ [37]. Raman studies found that the signal of $\beta\text{-Ca}(\text{BH}_4)_2$ was broader than that of the α -phase, indicating that disorder may indeed be present. Most studies have reported that the β -polymorph is stable upon cooling to room temperature, however Fichtner *et al.* found that it is meta-stable at room temperature and transforms slowly into the α phase[207].

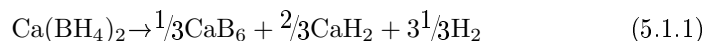
Both papers by Riktor [204] and Buchter[91] also identified a third (γ) phase that crystallizes in the orthorhombic $Pbca$ space group when a wet chemical synthesis ($\text{CaH}_2 + \text{Et}_3\text{N}\cdot\text{BH}_3$ in n-hexane) is used. A later paper from the same group provided a more detailed structural analysis of $\gamma\text{-Ca}(\text{BH}_4)_2$ and

found that it is metastable at all temperatures and irreversibly transforms into the β -phase at around 590K[91].

The phases present in a given sample of $\text{Ca}(\text{BH}_4)_2$ depend heavily on the synthetic route used. Samples produced by heating $\text{Ca}(\text{BH}_4)_2 \cdot 2\text{THF}$ primarily give α - and β - $\text{Ca}(\text{BH}_4)_2$ (depending on the conditions used), while those formed by milling in the solid state or by combining CaH_2 and $\text{Et}_3\text{N} \cdot \text{BH}_3$ in solution may also contain the γ -phase. A more recent study by Borgschulte *et al.* used combined DFT calculations and INS measurements to show that librational modes are a key determinant of stability for individual $\text{Ca}(\text{BH}_4)_2$ phases[208].

Each of the four $\text{Ca}(\text{BH}_4)_2$ polymorphs are made up of calcium cations octahedrally coordinated by six borohydride groups. The octahedra may be slightly distorted and the Ca-B distance of all phases is within a similar range ($2.90 \pm 0.08\text{\AA}$). The densities of the β - and γ - phases are similar ($\sim 1.25 \text{ gcm}^{-3}$), while that of the α -phase is slightly smaller ($\sim 1.21 \text{ gcm}^{-3}$).

Hydrogen desorption generally begins as early as 600 K in $\text{Ca}(\text{BH}_4)_2$ and MS measurements show that it is the only gas evolved. It was first reported that the compound decomposes by releasing $3^{1/3}$ molar equivalents of hydrogen according to Eq. 5.1.1[88].



However, careful analysis of $\text{Ca}(\text{BH}_4)_2$ decomposition suggests that it may be more complex than originally believed. While these reactions products have been observed, they are not always reproducible and their appearance relies on the experimental conditions used. Several reports suggested that decomposition is a two step process[103, 108, 209] however the only decomposition products identified were CaB_6 and CaH_2 [210]. Another paper found a large amorphous component in the diffraction data of the partially decomposed material and iden-

tified a third “ δ ” phase of $\text{Ca}(\text{BH}_4)_2$ [204]. Later work found that the reported δ -phase was actually a borohydride borate, $\text{Ca}_3(\text{BH}_4)_3(\text{BO}_3)$, formed from oxidation of the borohydride. The crystal structure of the compound was reported, though its formation is still not well understood[211]. The same authors were able to isolate a reaction intermediate which was assigned as CaB_2H_x ($x \approx 2$)[212]. However, DFT studies[213, 214] have found that CaB_2H_2 and CaB_2H_4 are unstable with respect to $\text{CaB}_{12}\text{H}_{12}$ and are therefore unlikely to play a role in the decomposition of $\text{Ca}(\text{BH}_4)_2$. It was further suggested that CaB_2H_6 forms a low energy intermediate and may be involved. A recent study found that decomposition temperature and complexity depends on the phase composition of a given $\text{Ca}(\text{BH}_4)_2$ sample, however CaB_2H_x and $\text{Ca}_3(\text{BH}_4)_3(\text{BO}_3)$ formation are not related to polymorphic fraction content[215].

This chapter presents a study of the various phases of $\text{Ca}(\text{BH}_4)_2$ and how they are affected by temperature. Synchrotron powder X-ray diffraction is used to characterize individual polymorphs at room temperature. *In situ* PXD measurements provide insight into the phase changes of the material. The α - to α' -phase transition is modeled as a 2nd order ferroelastic and assigned a transition temperature of 498K. *In situ* solid state NMR and Differential Scanning Calorimetry measurements support the PXD data and reveal that the compound only loses about 5 wt% below 750 K.

Much of the work in this chapter was presented in a talk at the 2010 International Symposium on Metal Hydrogen Systems and some was included in Ref [216]. As the field has seen rapid advancement, many similar studies have now been published by other groups. Where possible, comparison of the results in this chapter to other works in literature will be made. The work in this chapter also forms a basis for many of the borohydride destabilization studies performed in the following chapter.

5.2 Synthesis

Unless otherwise stated, all samples of calcium borohydride were synthesized by heating calcium borohydride bistetrahydrofuran powder ($\text{Ca}(\text{BH}_4)_2 \cdot 2\text{THF}$), which was purchased from Sigma Aldrich, in a vertical tube furnace at 160 °C under dynamic vacuum (base pressure 10^{-6} mbar) for one hour. As the coordinating solvent THF was removed, an increase in pressure was observed and the reaction was deemed complete when the vacuum returned to the base pressure of 10^{-6} mbar.

A separate sample of $\text{Ca}(\text{BH}_4)_2 \cdot 2\text{THF}$ was synthesized at Oxford based on the method suggested in Ref [202]. CaCl_2 and NaBH_4 were added together in a 1:1 mole ratio in a round bottom flask and sealed under argon. Approximately 75mL of THF was added and the sample was stirred for 72 hours. The solid contents were separated from the mixture by a filtration and dried under vacuum. $\text{Ca}(\text{BH}_4)_2 \cdot 2\text{THF}$ then remained as white powder (60% yield), which was later heated under vacuum using the same conditions described above. The filtered liquid from the reaction was also exposed to vacuum until only a solid remained. Diffraction analysis showed that this contained NaCl and well as unreacted CaCl_2 and NaBH_4 .

5.3 Room Temperature X-ray Measurements

Room temperature synchrotron X-ray diffraction measurements were collected on beamline I11 at Diamond. All samples prepared from Sigma Aldrich $\text{Ca}(\text{BH}_4)_2 \cdot 2\text{THF}$ were observed to contain α - and β - $\text{Ca}(\text{BH}_4)_2$ only. X-ray data collected on a Philips X-Pert diffractometer has shown that varying the preparation of $\text{Ca}(\text{BH}_4)_2$ has a significant effect on the polymorphs observed. When removing the solvent from $\text{Ca}(\text{BH}_4)_2 \cdot 2\text{THF}$, heating at higher temperatures or for longer

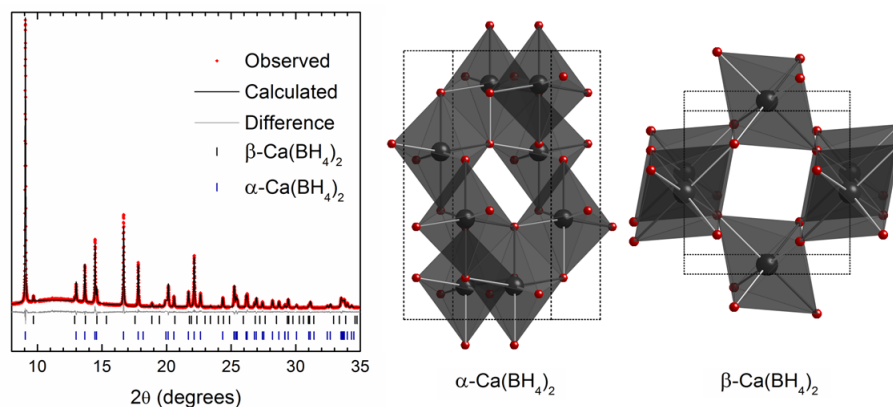


Figure 5.3.1: Left: Rietveld refine of a typical $\text{Ca}(\text{BH}_4)_2$ sample, which contains the α polymorph and a small amount of the β phase. Right: structures of both polymorphs, showing the CaB_6 octahedra (hydrogens omitted for clarity), which are much more distorted in the α phase.

times increased the relative amount of $\beta\text{-Ca}(\text{BH}_4)_2$ present upon cooling to room temperature. For example, samples prepared by 12 hours of heating contained an α to β ratio of 1:4, compared with a ratio of roughly 10:1 observed in samples heated for one hour.

Structural refinement from high resolution X-ray data using the Rietveld method allowed the complete elucidation of the structure of orthorhombic $\alpha\text{-Ca}(\text{BH}_4)_2$, which was indexed according to the unit cell proposed by Buchter[90]. An excellent fit to the data was achieved ($\chi^2 = 1.477$ $R_{\text{exp}} = 3.349$ $R_{\text{wp}} = 4.948$), which was made worse by attempting to restrain the hydrogen atoms around boron using a Z matrix ($\chi^2 = 1.498$ when this was attempted). The thermal parameters of the hydrogen atoms were however restrained to be the same as that of the boron atom. The Rietveld refinement of a typical sample, which contains predominantly the α phase, is shown in Fig. 5.3.1. Cell parameters refined to values of $a = 8.7842(2)$ Å, $b = 13.1335(2)$ Å, and $c = 7.4967(1)$ Å, which agree well with those determined by Buchter at 300K ($a = 8.7461(8)$ Å, $b = 13.0942(9)$ Å, $c = 7.4660(7)$ Å). The structure of $\alpha\text{-Ca}(\text{BH}_4)_2$ can be

Table 5.1: Atomic positions and thermal parameters of $\alpha\text{-Ca}(\text{BH}_4)_2$ from synchrotron X-ray diffraction at room temperature.

$\alpha\text{-Ca}(\text{BH}_4)_2$ - <i>Fddd</i>				
a = 8.7842(2) Å, b = 13.1335(2) Å, c = 7.4967(1) Å				
Site	x/a	y/b	z/c	b_{eq}
Ca	$\frac{1}{8}$	$\frac{1}{8}$	$\frac{1}{8}$	1.47(2)
B	$\frac{1}{8}$	0.345	$\frac{1}{8}$	1.68(5)
H1	0.018	0.399	0.113	1.68(5)
H2	0.126	0.298	0.257	1.68(5)
$\chi^2 = 1.477$ $R_{wp} = 4.946\%$ $R_{exp} = 3.349\%$				

described as a face centered arrangement of calcium cations, with four further calcium ions occupying half of the tetrahedral holes. Each of the calcium cations is octahedrally coordinated by six $[\text{BH}_4]^-$, with two hydrogen atoms pointing approximately towards the cation. These octahedra are heavily distorted, as seen by a large variation in Ca-B distances. Each octahedron shares edges with four other octahedra, and also shares corners with four further octahedra.

Work by Filinchuk et al.[89] has suggested that the true symmetry of the α is lower and a better fit to their data was obtained using the *F2dd* space group. However, when this structural model was used on the data from Diamond, the fit to the data was slightly worse ($\chi^2 = 1.482$ $R_{wp} = 4.961\%$). As the data in Ref. [89] were collected at the ESRF on a more intense X-ray beam, it is possible that their sample was subject to beam damage causing the structure to tend toward lower symmetry. The effects of beam damage were pronounced in the measurements taken at Diamond as well (it is for this reason that the position sensitive detector was used). Fig. 5.3.2 shows the diffraction pattern of $\alpha\text{-Ca}(\text{BH}_4)_2$ taken before and after 1000s of beam exposure. The overall effect of beam exposure was the same in using either the *Fddd* or *F2dd* structural model; a non-uniform increase in strain is observed in which the lattice contracts in

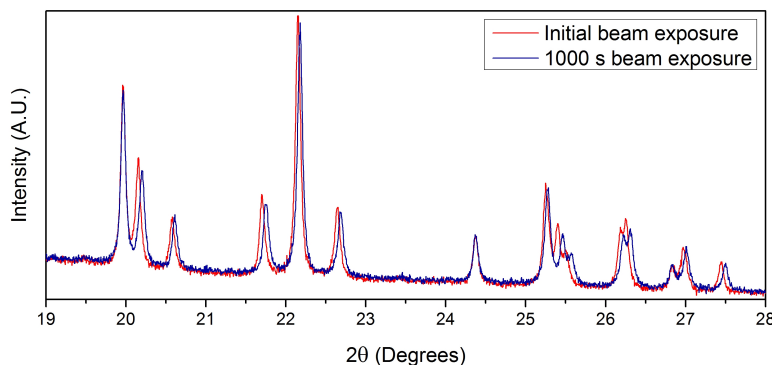


Figure 5.3.2: Spectrum of $\alpha\text{-Ca}(\text{BH}_4)_2$ before and after 1000 s of beam exposure, showing non-uniform peak movement.

along the a and c axes and expands along the b axis (thermal parameters are also increased). While, no noticeable improvement on the quality of fit was observed before and after beam exposure using either structural model, the strain resulting from the incident radiation may be the reason a better fit was achieved using the lower symmetry structural model on data collected at the ESRF.

Room temperature tetragonal $\beta\text{-Ca}(\text{BH}_4)_2$ was indexed based on the tetragonal unit cell proposed by Buchter[90], and cell parameters $a = 6.9196(4) \text{ \AA}$, $c = 4.3478(5) \text{ \AA}$ obtained, which agree well with those that were published ($a = 6.9468(1) \text{ \AA}$ and $c = 4.3661(1) \text{ \AA}$). The structure of $\beta\text{-Ca}(\text{BH}_4)_2$ may be described as a body centered arrangement of calcium cations with six $[\text{BH}_4]^-$ groups arranged nearly octahedrally around each Ca^{2+} . Four of the coordinating $[\text{BH}_4]^-$ units are closer to the calcium cation (Ca-B $2.91087(9) \text{ \AA}$) and each has two hydrogen atoms pointing towards the Ca^{2+} , while the two next nearest $[\text{BH}_4]^-$ units (Ca-B $= 2.9328(1) \text{ \AA}$) have three hydrogen atoms pointing towards the cation. This range in Ca-B distances is smaller than that observed in $\alpha\text{-Ca}(\text{BH}_4)_2$ and the local environment around the Ca atom is much more symmetrical in the β phase. The octahedra share edges with two other octa-

Table 5.2: Atomic positions and thermal parameters of $\beta\text{-Ca}(\text{BH}_4)_2$ from synchrotron X-ray diffraction at room temperature.

$\beta\text{-Ca}(\text{BH}_4)_2$ - $P42/m$				
a = 6.9196(4) Å, c = 4.3478(5) Å				
Site	x/a	y/b	z/c	b_{eq}
Ca	$\frac{1}{2}$	0	$\frac{1}{2}$	1.0(4)
B	0.302	0.200	0	7.9(2)
H1	0.295	0.347	0	7.9(2)
H2	0.468	0.185	0	7.9(2)
H3	0.226	0.161	0.800	7.9(2)
$\chi^2 = 1.477$ $R_{\text{wp}} = 4.946\%$ $R_{\text{exp}} = 3.349\%$				

hedra and corners with a further six octahedra, forming chains of edge-sharing octahedra, corner linked to other chains of octahedra. Each boron atom is co-ordinated to eleven other boron atoms and three calcium ions (ignoring the hydrogen atoms). The CaB_6 sublattice of both the α and β structures are shown in Fig. 5.3.1.

$\gamma\text{-Ca}(\text{BH}_4)_2$ was typically not observed in samples prepared from $\text{Ca}(\text{BH}_4)_2 \cdot 2\text{THF}$ purchased from Sigma Aldrich and studied using the diffractometer at Oxford or at Diamond. However, when the samples were studied on beamline MS X04SA at the SLS, a very small amount of the γ phase was observed. Another way to form the γ polymorph is by mechanochemically milling samples $\text{Ca}(\text{BH}_4)_2$. Diffraction data from $\alpha\text{-Ca}(\text{BH}_4)_2$ milled at 400 rpm for 4 hours shows that all of the α phase is converted into the β and γ polymorphs in a roughly 1:2 β to γ ratio. However, the small particles sizes formed from milling means that the Bragg peaks are very broad and a large amorphous component to the diffraction pattern is seen. Perhaps most interesting is that when the solvent was removed from $\text{Ca}(\text{BH}_4)_2 \cdot 2\text{THF}$ prepared at Oxford, over half of the sample crystallized as the γ polymorph and the remainder was a mix of both the α and β phases.

Table 5.3: Atomic positions and thermal parameters of $\gamma\text{-Ca}(\text{BH}_4)_2$ from synchrotron X-ray diffraction of $\text{Ca}(\text{BH}_4)_2$ prepared in Oxford at room temperature.

γ -Ca(BH ₄) ₂ - <i>Pbca</i>					
a = 13.1017(2) Å, b = 8.3967(1) Å, c = 7.5229(1) Å					
Site	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	b _{eq}	Structure
Ca	0.6276	0.379	0.366	1.61(3)	
B1	0.225	0.410	0.480	0.4(1)	
H1	0.264	0.344	0.348	0.4(1)	
H2	0.265	0.347	0.596	0.4(1)	
H3	0.237	0.535	0.473	0.4(1)	
H4	0.136	0.368	0.480	0.4(1)	
B2	0.503	0.842	0.817	0.3(1)	
H5	0.524	0.688	0.798	0.3(1)	
H6	0.409	0.867	0.814	0.3(1)	
H7	0.542	0.862	0.956	0.3(1)	
H8	0.542	0.921	0.708	0.3(1)	
$\chi^2 = 6.697$ $R_{wp} = 2.941\%$ $R_{exp} = 0.439\%$					

It is possible that the long reaction time used (72 hours) is responsible for the formation of the metastable γ -phase.

$\gamma\text{-Ca}(\text{BH}_4)_2$ was indexed according to the orthorhombic cell proposed by Buchter[91]. Cell parameters of $a = 13.1016(2) \text{ \AA}$, $b = 8.3967(1) \text{ \AA}$, and $c = 7.5229(1) \text{ \AA}$ were obtained at room temperature, which are very close to those given in the literature at 300K ($a = 13.0584(8) \text{ \AA}$, $b = 8.3881(4) \text{ \AA}$, $c = 7.5107(4) \text{ \AA}$). The results of the refinement and the structure of $\gamma\text{-Ca}(\text{BH}_4)_2$ are shown in Table 5.3. The CaB_6 octahedra share 3 edges and 6 corners, and resemble those of the α phase as they are heavily distorted.

The exact conditions needed to form $\gamma\text{-Ca}(\text{BH}_4)_2$ are still not well understood and these studies suggest that both synthetic conditions and experimental

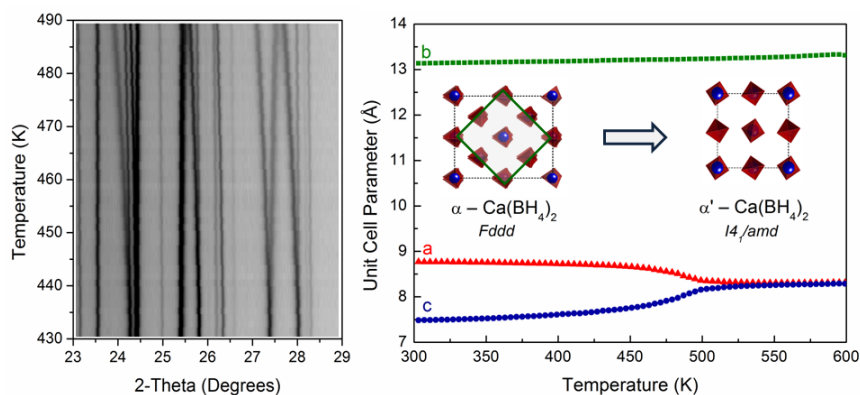


Figure 5.4.1: Left: Surface plot of diffraction data from 430-490 K showing diffraction peaks merging. Right: Lattice parameters of $\alpha\text{-Ca}(\text{BH}_4)_2$ with temperature extracted from Rietveld refinements every 4 K. The a and c axes eventually merge around 500 K and the structure may then be described using the tetragonal $I4_1/amd$ space group.

probes can have a dramatic effect on the phase composition of $\text{Ca}(\text{BH}_4)_2$.

5.4 Variable Temperature X-ray Diffraction

In situ variable temperature synchrotron X-ray diffraction measurements were collected at Diamond from 300 to 770 K and at the SLS from 200 to 480 K. Data in the overlapping temperature range was identical between the two experiments and the results from the Diamond experiment are discussed here.

5.4.1 A Ferroelastic Phase Transition

As $\alpha\text{-Ca}(\text{BH}_4)_2$ was heated, a Rietveld refinement of the diffraction data was performed every 4 K, the lattice parameters were extracted and are plotted in Fig. 5.4.1. As temperature increases, several of the Bragg reflections (e.g. 220, 311) from $\alpha\text{-Ca}(\text{BH}_4)_2$ begin to merge, corresponding to a decrease in the a/c ratio. The rate of change of both lattice parameters increases with temperature

until the two merge at approximately 500K ($a = c \approx 8.3 \text{ \AA}$). Such a change in the lattice parameter without a sudden volume change is indicative of a second order phase transition. The rectangular a - c plane of the orthorhombic α phase is un-distorted to a square, producing a face-centered tetrahedral phase (α' - $\text{Ca}(\text{BH}_4)_2$) that can be described by the $F4_1/ddm$ space group. By rotating 45° through the cell axes the space group $I4_1/amd$ is obtained, which is conventionally used to describe this structure. The structural model is effectively disordered as it contains eight different hydrogen sites with an occupancy of $\frac{1}{2}$. At 523 K, unit cell parameters of $a = 5.8481(5) \text{ \AA}$ and $c = 13.2547(13) \text{ \AA}$ were determined, which agree well with those published ($a = 5.8446(3) \text{ \AA}$ and $c = 13.2279(11) \text{ \AA}$ at 495 K). However, as previously discuss, published work on α' - $\text{Ca}(\text{BH}_4)_2$ achieved a better fit to the α -phase using the $F2dd$ structural model and therefore required that the α' -phase be described by the minimal order subgroup of $F2dd$. As a result, the literature suggests the fully ordered $I\bar{4}2d$ structure for α' - $\text{Ca}(\text{BH}_4)_2$ [89].

As the α - to α' -phase transition progresses, a broadening of certain Bragg peaks is observed. This suggests that the structure may display ferroelastic behaviour arising from the interchange of two orthogonal orthorhombic structures via the tetragonal one. When the phase change is complete, the peaks of α' - $\text{Ca}(\text{BH}_4)_2$ are sharp and the sample is non-ferroelastic.

For an orthorhombic crystal structure with lattice parameters a , b , and c , strain (ε) is given by:

$$\varepsilon = \frac{(a - c)}{(a + c)} \quad (5.4.1)$$

The Gibbs free energy of a system experiencing strain as a function of temper-

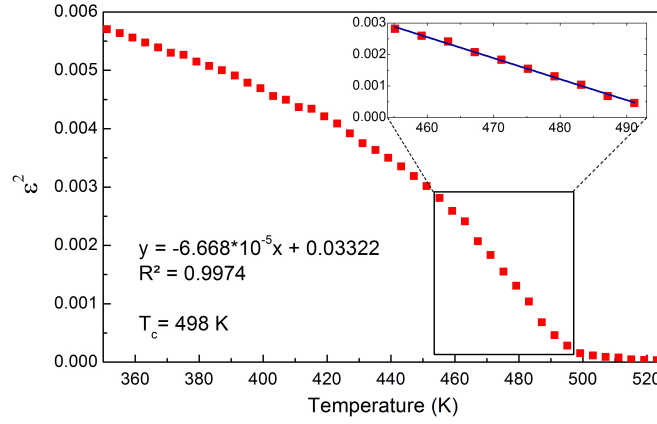


Figure 5.4.2: Assignment of a transition temperature to the 2nd order ferroelastic α to α' phase transition in $\text{Ca}(\text{BH}_4)_2$. The plot shows the square of the strain as a function of temperature, while the inset displays the linear fit to the region in which ferroelasticity is observed.

ature may be expanded as a Taylor series:

$$\Delta G(T) = \Delta G_0(T) + \frac{1}{2}x_1(T - T_c)\varepsilon^2 + \frac{1}{4}x_2\varepsilon^4, \quad (5.4.2)$$

where $\Delta G_0(T)$ is the zero-point free energy, x_1 and x_2 are constants, T is the temperature of the system, T_c is the temperature of the ferroelastic transition. For stability, change in free energy will be minimized with respect to strain, i.e. the derivative of $\Delta G(T)$ with respect to ε will be zero:

$$\frac{\delta(\Delta G(T))}{\delta\varepsilon} = 0 = x_1(T - T_c)\varepsilon + x_2\varepsilon^3 \quad (5.4.3)$$

This gives two solutions for ε :

$$\varepsilon^2 = 0 \text{ and } \varepsilon^2 = \frac{x_1(T - T_c)}{x_2} = \varphi(T - T_c) \quad (5.4.4)$$

The first corresponds to a tetragonal unit cell, i.e. $a = c$ (or the α' poly-

morph in the case of $\text{Ca}(\text{BH}_4)_2$). The second describes strain as a function of temperature for the transition from orthorhombic to tetragonal (the α to α' phase transition in the case of $\text{Ca}(\text{BH}_4)_2$). Therefore, by performing a linear fit of temperature vs. ε^2 in the region of the transition (where the Bragg peaks begin to broaden), a temperature of 498K can assigned to the α to α' phase change in $\text{Ca}(\text{BH}_4)_2$ (Fig. 5.4.2).

5.4.2 α to β Phase Change and Melting

At approximately 460K, intensity of the weak Bragg peaks arising from β - $\text{Ca}(\text{BH}_4)_2$ begins growing as those of α' - $\text{Ca}(\text{BH}_4)_2$ begin abruptly disappearing (Fig. 5.4.3a). The transition is complete by approximately 490K, which is consistent with what was observed by Buchter *et al.*[217]. Fig. 5.4.3b shows the linear increase of the β - $\text{Ca}(\text{BH}_4)_2$ lattice parameters with temperature over the entire range it is observed. At approximately 660K, the Bragg reflections of β - $\text{Ca}(\text{BH}_4)_2$ begin disappearing (lattice parameters shown at the highest temperatures in Fig. 5.4.3b are less reliable as very little β - $\text{Ca}(\text{BH}_4)_2$ is left). At this point, no increase in the background is seen and no new Bragg peaks appear, suggesting that $\text{Ca}(\text{BH}_4)_2$ decomposes or melts at this temperature.

It should also be noted that, in certain experiments, some intensity is lost from the Bragg peaks of β - $\text{Ca}(\text{BH}_4)_2$ as a new phase appears. This phase has been observed in a number of other studies and was originally believed to be a new phase, δ - $\text{Ca}(\text{BH}_4)_2$, although no solution of its structure was ever reported. Recent work has shown that this phase arises from oxygen impurity in the system and the Bragg peaks correspond to $\text{Ca}(\text{BO}_3)(\text{BH}_4)_3$ [211]. Unfortunately, no Bragg peaks were observed in the diffraction pattern above 700 K, making it difficult to assess decomposition products and elucidate a mechanism of reaction using diffraction.

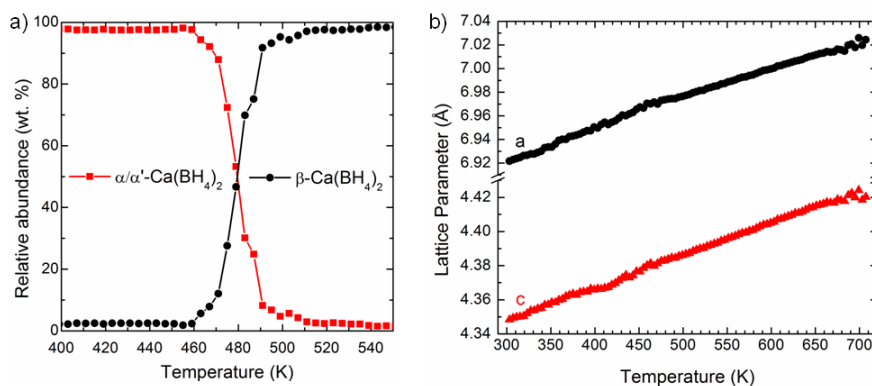


Figure 5.4.3: a) Relative abundance of α and β - $\text{Ca}(\text{BH}_4)_2$ with temperature b) Lattice parameters of β - $\text{Ca}(\text{BH}_4)_2$ with temperature. Data is taken from Rietveld refinements of synchrotron X-ray diffraction measurements every 4 K.

5.5 In-Situ NMR

Variable temperature solid state 11-boron NMR measurements support the observations made from diffraction measurements. At room temperature, two boron environments are observed at around -30.2 and -32.8 ppm, corresponding to the α - and β -phases, respectively. In $\text{Mg}(\text{BH}_4)_2$, typical boron shifts were found about 10 ppm lower than those observed in $\text{Ca}(\text{BH}_4)_2$. This indicates that more electron density shields the boron atoms in $\text{Mg}(\text{BH}_4)_2$ compared to $\text{Ca}(\text{BH}_4)_2$. Based on the electronegativity of each metal, this result is unexpected since the more withdrawing magnesium atoms should pull more electron density from the borohydride ion than calcium. However, in $\text{Mg}(\text{BH}_4)_2$, boron atoms are coordinated to two magnesium atoms while three calciums surround each boron in $\text{Ca}(\text{BH}_4)_2$. The downfield shift in $\text{Ca}(\text{BH}_4)_2$ is therefore reflective of a larger coordination number for each boron.

As the sample is heated, the peak at -32.8 ppm begins to grow while the other shrinks, corresponding to the α - to β -phase transition. This is first noticeable at around 453 K and the transition is complete by about 493 K (the maximum

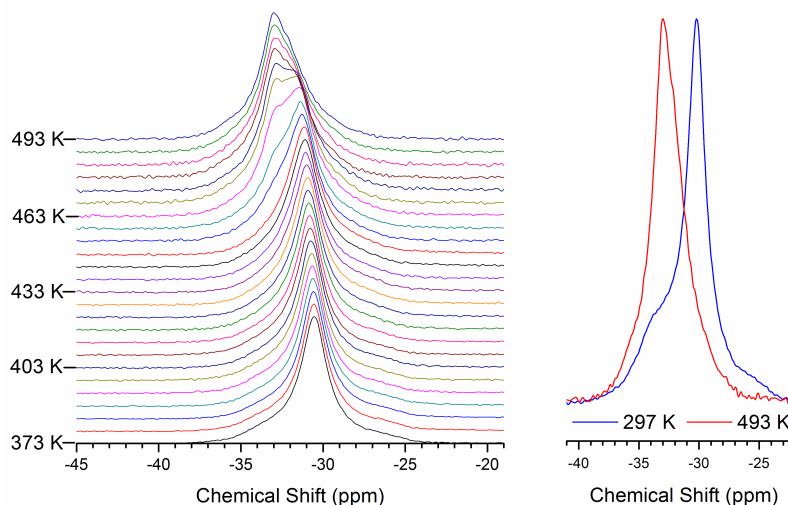


Figure 5.5.1: Left: Evolution of the ^{11}B NMR signal of $\text{Ca}(\text{BH}_4)_2$ with temperature. Right: NMR spectrum taken before and after heating to 493 K, showing spectra dominated by α - to β -phase, respectively.

allowable temperature on the NMR machine used). Upon cooling, the β -phase is stable at room temperature, which is exactly what has been observed in *ex situ* diffraction measurements.

5.6 Differential Thermal Analysis

Combined DSC/TGA measurements are shown for $\text{Ca}(\text{BH}_4)_2$ in Fig. 5.6.1. Weight increase is seen in the sample up until a thermal event corresponding to the α - to β -phase change is observed at approximately 450 K. The origin of weight increase at such low temperatures is unknown but is likely due to the formation of $\text{Ca}(\text{BO}_3)(\text{BH}_4)_3$. After the phase change, a slow weight loss is observed as the DSC baseline becomes more and more exothermic. As a very slow melting was observed in the diffraction measurements, it is likely that melting, followed by very slow or partial decomposition, is occurring over

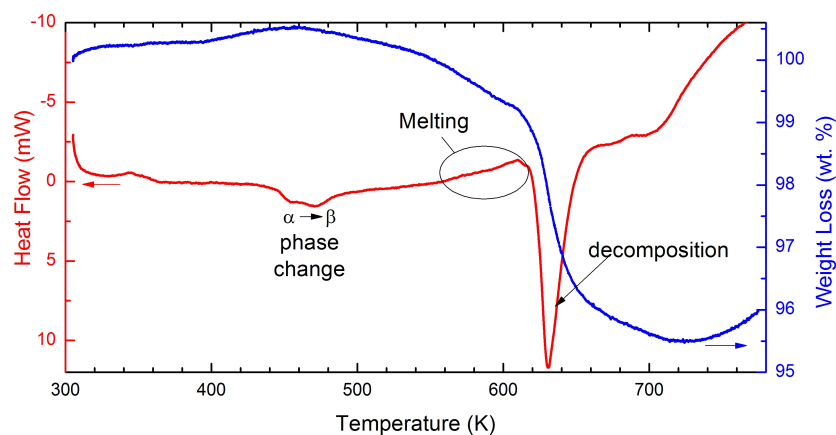


Figure 5.6.1: Combined DSC/TGA scan for $\text{Ca}(\text{BH}_4)_2$. Thermal events in the DSC trace corresponding to the α - to β -phase, melting and decomposition have been labeled.

this temperature range. At around 630 K, a much faster weight loss and a large exothermic event corresponding to the sample decomposition are observed. Following decomposition, the sample continues to gain weight.

The temperatures observed in the DTA traces are, in general, slightly lower than those observed on Diamond. It is likely that the DTA temperatures are more reliable than those of the hot air blower on Diamond. Previous measurements have shown that calibration of the temperature control at Diamond is not always reliable, particularly at higher temperatures, since heat is not always evenly distributed by the blower.

Overall, the sample loses just under 5 wt%, however this value is misleading. A gradual weight gain from oxide/borate formation is observed early on in the spectrum and undoubtedly continues throughout decomposition. As a result, the weight loss from hydrogen release is masked by that from oxygen uptake and the true amount of gas evolved is difficult to assess. For comparison, the decomposition mechanism given in Eq. 5.1.1 predicts a weight loss of 9.6 wt%.

5.7 Conclusions

$\text{Ca}(\text{BH}_4)_2$ has been prepared by heating $\text{Ca}(\text{BH}_4)_2 \cdot 2\text{THF}$ purchased from Sigma Aldrich. High resolution synchrotron X-ray diffraction shows the sample exists primarily as the α polymorph ($Fddd$), though a small amount of the β -phase ($P42/m$) is also often observed. The structure of each was refined using the structural model suggested by Buchter *et al.* in references [90] and [91]. No improvement to the fit of the α -phase was observed using the lower symmetry $F2dd$ space group that has been suggested as the true space group. A sample of $\text{Ca}(\text{BH}_4)_2 \cdot 2\text{THF}$ was also prepared in Oxford and, when heated under vacuum, was seen to contain mostly metastable γ -phase $\text{Ca}(\text{BH}_4)_2$ ($Pbca$), with smaller amounts of the α and β polymorphs present. Milling samples of α - $\text{Ca}(\text{BH}_4)_2$ or exposing them to higher radiation was also seen to produce the γ -phase.

Variable temperature synchrotron X-ray diffraction measurements showed that orthorhombic α - $\text{Ca}(\text{BH}_4)_2$ undergoes a second order ferroelastic transition to α' - $\text{Ca}(\text{BH}_4)_2$ ($I4_1/amd$). By performing a linear fit of temperature vs. strain squared in the region of the transition a temperature of 498K was assigned to the transition. α' - $\text{Ca}(\text{BH}_4)_2$ then converts to β - $\text{Ca}(\text{BH}_4)_2$ over the temperature range of 460-490 K. In situ solid state 11-boron NMR measurements support this and reveal that chemical shifts are approximately 10 ppm higher in $\text{Ca}(\text{BH}_4)_2$ than $\text{Mg}(\text{BH}_4)_2$ due to a higher coordination number of the boron in the former. Lattice parameters of the β -phase undergo a monotonic increase with temperature until the sample melts just below 700 K. Bragg peaks assigned to $\text{Ca}(\text{BO}_3)(\text{BH}_4)_3$ are also observed to grow as the sample is heated. DTA measurements support this, showing a consistent weight gain in the sample at temperatures above *ca.* 400 K and decomposition above 620 K.

The polymorphism observed in $\text{Ca}(\text{BH}_4)_2$ resembles that of TiO_2 and is derived from the ability of $\text{Ca}[\text{BH}_4]_6$ octahedra present in each crystal structure

Table 5.4: Summary of edge and corner sharing by $\text{Ca}[\text{BH}_4]_6$ octahedra in the various polymorphs of $\text{Ca}(\text{BH}_4)_2$.

$\text{Ca}(\text{BH}_4)_2$ Polymorph	TiO_2 Equivalent	Edges Shared	Corners Shared
α/α'	Anatase ($I4_1/amd$)	4	4
γ	Brookite ($Pbca$)	3	6
β	Rutile ($P42/m$)	2	8

to distort and reorganize. The trends in edge and corner sharing between various $\text{Ca}(\text{BH}_4)_2$ and corresponding TiO_2 phases are summarized in Table 5.4.

Based on Pauling's 3rd rule, it is expected that the polymorph with the fewest edge/face sharing octahedra would be most stable. Both α - and α' - $\text{Ca}(\text{BH}_4)_2$ contain distorted octahedra that share 4 corners and 4 edges. Reorganization from one to another therefore requires little change in free energy and is observed at a relatively low temperature. However, Pauling noted that the effects are most pronounced for high valence, large cations, with low coordination number. In $\text{Ca}(\text{BH}_4)_2$, valency is low and octahedra distort from ideal geometry to stabilize the α and γ phases. Therefore, the energy gain conferred by reduced edge sharing in $\text{Ca}(\text{BH}_4)_2$ is small and the polymorphic stability is more complicated and shows temperature dependence. Recent work has shown that the energy differences from vibrational entropy are relatively small, but not negligible[208]. Free energy differences between the various phases are small and, as such, phase composition of a given sample is highly dependent on the synthetic route and, in some cases, the experimental probes used.

Chapter 6

Understanding Borohydride Destabilization

6.1 Introduction and Chapter Outline

Although Group I and II metal borohydrides possess some of the highest gravimetric hydrogen densities known today, the largest barrier to their practical application is typically a high decomposition temperature, sluggish kinetics, and limited reversibility. To change the reaction pathway and improve both thermodynamic and kinetic hydrogen storage properties, several recent reports have examined large numbers of metal borohydrides in combination with other materials. Although many studies on the fundamental physical properties of individual borohydrides have emerged in recent years, there is still a great deal unknown about mixed systems and how two individual borohydrides interact when combined.

This chapter will investigate a few different combined systems with the aim of understanding the interaction between the two materials. Firstly, the effect

of adding group I borohydrides to $\text{Ca}(\text{BH}_4)_2$ will be investigated. In order to fully understand the effects of the additives (LiBH_4 and NaBH_4), each of the alkali metal borohydrides will first be characterized by a variety of techniques. Then the mixed system will be studied by variable temperature diffraction and the decomposition investigated by thermogravimetric techniques. Lastly, the effects of an amide additive (LiNH_2) on $\text{Ca}(\text{BH}_4)_2$ and $\text{Mg}(\text{BH}_4)_2$ will be briefly investigated.

Some of the work in this chapter was presented in a talk at the 2010 International Symposium on Metal Hydrides and in a poster at the Faraday Discussion 151: Hydrogen Storage Materials. However, as some of the work (particularly in the last few sections of this chapter) did not produce improved hydrogen storage materials, it has not been presented or published and represents work carried out during the author's D.Phil that will not be pursued further.

6.2 Lithium Borohydride

As the lightest metal borohydride, LiBH_4 contains the greatest gravimetric density of hydrogen (18.5 wt%). It was first synthesized by Schlesinger and Brown[64], however the crystal structure was not investigated until several years later in a study by Harris and Meibohm[218], who found that it adopted an orthorhombic structure at room temperature. In 1971, the cell was indexed and a high temperature phase was reported by Semenenko *et al*[219]. The structures were refined by Soulie *et al.* in 2002 and the currently accepted space groups of orthorhombic $Pnma$ and hexagonal $P6_3mc$ were reported for the low and high temperature phases, respectively[73]. The borohydride ion was initially believed to be heavily distorted in the room temperature phase and more symmetrical in the higher temperature phase, however later neutron powder diffraction[78, 220] and single crystal studies[77] have shown that the true

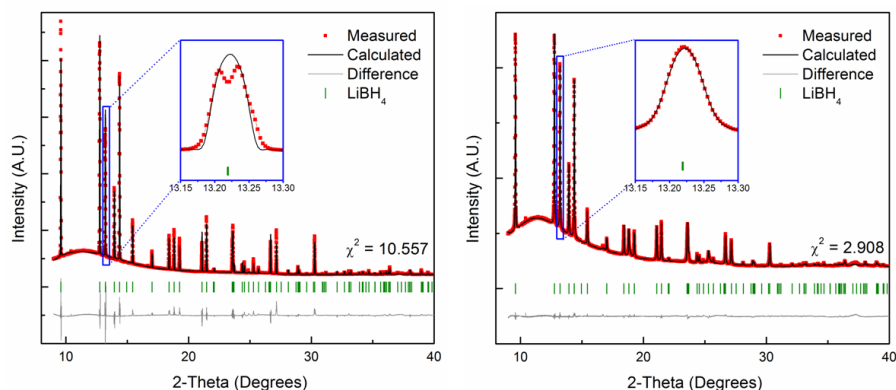


Figure 6.2.1: Rietveld refinements of LiBH_4 purchased from Sigma Aldrich (Left) and post milling (Right). The insets show the difference in peak shapes between the two samples due to crystallite size effects.

geometry of the BH_4 tetrahedra is very nearly ideal in both phases. The single crystal study showed that the atomic displacement ellipsoids were large in the direction perpendicular to the B-H bond, suggesting that the BH_4 ions are disordered and rotate as rigid bodies. An analysis of the Pair Distribution Function of LiBD_4 at different temperatures confirmed that the BD_4 anions possess nearly perfect tetrahedral geometry and are highly orientationally disordered in the high temperature phase (disorder was also observed in the low temperature phase at room temperature)[221]. Two high pressure polymorphs of LiBH_4 have also been reported[79], but were not observed under the conditions used in this thesis.

Room temperature synchrotron X-ray diffraction measurements were collected on beamline I11 at Diamond on a sample of LiBH_4 that was purchased from Sigma Aldrich both before and after milling. A Rietveld refinement was then performed using the structural model from Ref. [77] as an input. However, an improved fit to the data was obtained by allowing the position of the lithium atom site to refine (although changing the BH_4 ions did not dramatically affect

Table 6.1: Atomic positions and thermal parameters of milled LiBH_4 at room temperature from synchrotron X-ray diffraction at room temperature.

o-LiBH₄- <i>Pnma</i>				
a = 7.18036(5) Å, b = 4.43825(3)Å, c = 6.80631(5) Å				
Site	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	b_{eq}
Li	0.1617(1)	$\frac{1}{4}$	0.1060(1)	5.04(4)
B	0.3008	$\frac{1}{4}$	0.4282	2.87(3)
H1	0.8917	$\frac{1}{4}$	0.9370	2.87(3)
H2	0.3945	$\frac{1}{4}$	0.2912	2.87(3)
H3	0.1995	0.0592	0.4302	2.87(3)
$\chi^2 = 2.908$ $R_{wp} = 1.462\%$ $R_{exp} = 0.444\%$				

the fit). A plot of the fit for each sample is shown in Fig. 6.2.1 and the results of the refinement of the milled sample are given in Table 6.1.

As the position sensitive detector was used to collect data over all 2-theta for only a small period of time, the effects of particle size are particularly apparent. By examining the inset in the left of Fig. 6.2.1, it may be seen that an anomalous asymmetric peak shape is observed in the Sigma Aldrich sample due to poor powder averaging. The effects of milling are shown in the inset on the right. Here, each of the Bragg reflections are much more broad and symmetric as a result of the small and uniform particle size that results from the milling process.

The DTA trace of LiBH_4 is shown in the left of Fig. 6.2.2. At temperatures above *ca.* 380 K, the orthorhombic phase (o- LiBH_4) transforms into the hexagonal polymorph (h- LiBH_4) and a corresponding endothermic event is observed. The latent heat absorbed by the system at this temperature is indicative of the first-order nature of the phase transformation. This agrees well with work published by Soulie *et al.*, who reported that the transition occurs at temperature of 381 K by reorientation of the BH_4 tetrahedra. The resulting effect is a contraction along the orthorhombic *a* (hexagonal *c*) axis and an expanding in

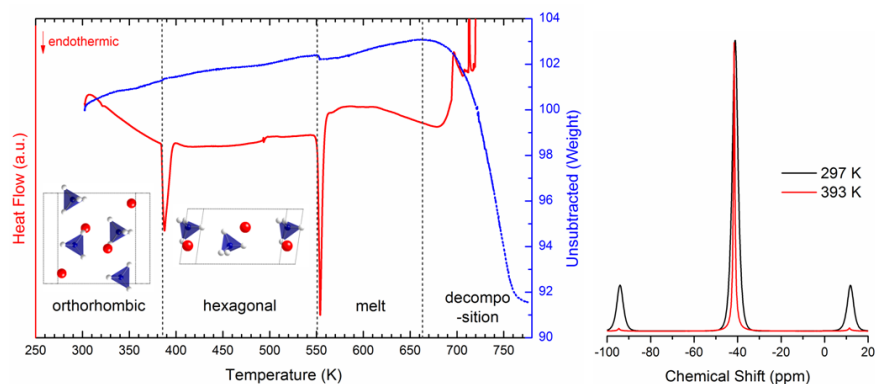


Figure 6.2.2: Left: DTA trace of LiBH_4 showing the phase evolution of the compound. Right: Solid state ^{11}B NMR signal of LiBH_4 at 297 K and 393 K. Decreased spinning side bands and a narrow line shape at high temperatures are indicative of a more averaged boron environment.

the orthorhombic bc (hexagonal ab) plane.

The high temperature phase of LiBH_4 has attracted a great deal of attention in recent years due to its high lithium ion conductivity[222]. At temperatures above 440 K, a conductivity greater than 10^{-2} Scm^{-1} is achieved in h- LiBH_4 (typically a conductivity greater than 10^{-3} Scm^{-1} is considered for application in solid-state batteries and supercapacitors). It was recently reported that the h- LiBH_4 could be stabilized at room temperature by combination with lithium iodide, LiI [119, 121, 120]. To investigate the effect of LiI on LiBH_4 , a sample of $^7\text{Li}^{11}\text{BD}_4 + ^7\text{LiI}$ was prepared by grinding together the two individual powders that were prepared in a high pressure furnace at Oxford. However, at the temperatures used on the GEM neutron diffraction beamline at ISIS, only the orthorhombic phase was observed.

Above 550 K, the sample melts and a corresponding large endothermic event is observed in the DSC trace. At approximately 670 K, the sample begins losing weight as it decomposes from the liquid phase and a series of sharp up and down peaks are seen in the DSC trace (due to the sample bubbling as gas is released).

Overall, the sample loses nearly 13 wt. % by 760 K (ignoring the baseline drift in the gravimetric trace). The results correlate well with previous reports, where LiBH_4 was observed to release 13.5 wt % (the remaining hydrogen exists as LiH) in two distinct processes over the temperature range 653 - 773 K[94, 223, 224].

The solid state 11-boron NMR spectra of LiBH_4 at room temperature and 393K are shown in the right of Fig. 6.2.2. The signal from the high temperature phase is much sharper than that of o- LiBH_4 and the spinning sidebands are much more pronounced in the latter. Both the large amount of hydrogen disorder and motional averaging of the lithium atoms in LiBH_4 at elevated temperatures contribute to a more uniform boron environment in h- LiBH_4 that produces the sharp NMR signal observed in Fig. 6.2.2.

6.3 Calcium Borohydride + Lithium Borohydride

Lee *et al.*[225] have found that various milled stoichiometric mixtures of LiBH_4 and $\text{Ca}(\text{BH}_4)_2$ produced a composite with a eutectic melting point and a decomposition temperature lower than that of either parent compound. In this study, new unidentified decomposition products were observed and partial rehydrogenation of the system (post decomposition) was achieved by the incorporation of a catalyst. However, little is known about the structure of the intermediate phases, product phases or the mechanism by which the mixed Li-Ca tetrahydroborate system releases and absorbs hydrogen. Fang *et al.*[226] have previously reported the formation of a dual-cation tetrahydroborate when LiBH_4 was mixed with $\text{Mg}(\text{BH}_4)_2$ and found that this new compound exhibited a lower onset dehydrogenation temperature compared with the constituent tetrahydroborates. Furthermore, the authors were able to use TG/DSC data combined with XRD measurements to postulate the desorption mechanism, which differs from that observed in either of the parent compounds. However, no direct observa-

tions of the decomposition process(es) were made and the intermediate phase was not characterized. Both of the aforementioned studies display the potential for tailoring the decomposition temperature of a tetrahydroborate by forming ternary systems composed of group 1 and group 2 metals.

A more recent study of the $\text{LiBH}_4/\text{Ca}(\text{BH}_4)_2$ system by Fang *et al.*[227] reported significantly different experimental findings; milling the mixture generated a new dual-cation (Li, Ca) borohydride, $\text{Li}_{0.9}\text{Ca}(\text{BH}_4)_{2.9}$, which further transformed to $\text{LiCa}(\text{BH}_4)_3$ at elevated temperatures. However, the authors in this study based these conclusions solely on the fact that new diffraction peaks were seen in the XRD spectrum of the milled sample that could not match that of either $\alpha\text{-LiBH}_4$ or $\alpha/\beta\text{-Ca}(\text{BH}_4)_2$. The structures were not indexed nor were other phases of the parent compounds considered. The study also found that, in comparison with the component phases, $\text{LiCa}(\text{BH}_4)_3$ exhibited improved dehydrogenation properties and a different decomposition pathway.

6.3.1 Variable temperature X-ray Diffraction

Samples of $n\alpha\text{-Ca}(\text{BH}_4)_2 + (12-n)\text{LiBH}_4$ were milled in various ratios ($n = 1-11$) at 400 rpm for 4 hours. Variable temperature high resolution synchrotron powder X-ray diffraction measurements were collected on beamline I11 at Diamond. Lee *et al.* found that the best hydrogen sorption characteristics for the milled system $x\text{LiBH}_4 + (1-x)\alpha\text{-Ca}(\text{BH}_4)_2$ were observed between $x = 0.6$ and 0.7 (however, they did not test the stoichiometric ratio $x = \frac{2}{3}$). As a result, this section will focus on understanding the $n = 4$ system, i.e. $\alpha\text{-Ca}(\text{BH}_4)_2 + 2\text{LiBH}_4$.

Despite the report from Fang *et al.* that a new phase was observed upon milling, a Rietveld refinement of milled $\alpha\text{-Ca}(\text{BH}_4)_2 + 2\text{LiBH}_4$ showed that all Bragg reflections may be assigned to $\alpha\text{-Ca}(\text{BH}_4)_2$, $\gamma\text{-Ca}(\text{BH}_4)_2$ or LiBH_4 and

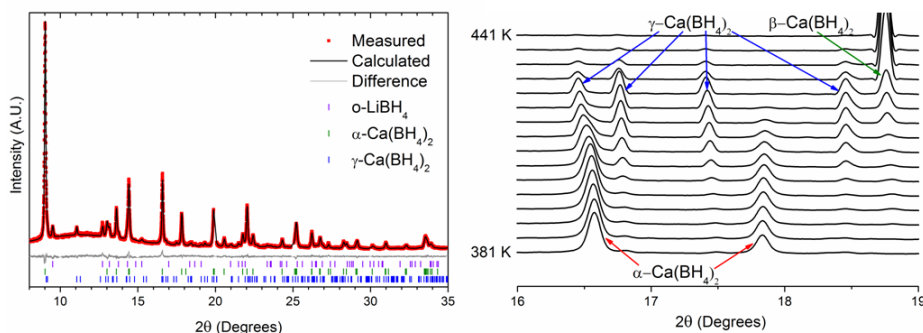


Figure 6.3.1: Left: Rietveld refinement of milled α - $\text{Ca}(\text{BH}_4)_2 + 2\text{LiBH}_4$ at room temperature. All Bragg reflections may be assigned to α - $\text{Ca}(\text{BH}_4)_2$, γ - $\text{Ca}(\text{BH}_4)_2$ or LiBH_4 . Right: Evolution of $\text{Ca}(\text{BH}_4)_2$ with temperature. Peaks assigned to the γ -phase begin to grow in intensity before transition to the β -polymorph.

that no other phases are present (Fig.6.3.1). As was shown in the previous chapter, milling often causes the formation of a small amount of γ - $\text{Ca}(\text{BH}_4)_2$, which remains present at room temperature. This is likely the source of the “new” Bragg reflections in Ref. [227], as the dominant peak was observed just below that of β - $\text{Ca}(\text{BH}_4)_2$ (exactly where that of γ - $\text{Ca}(\text{BH}_4)_2$ occurs).

$\text{Ca}(\text{BH}_4)_2$ displayed significantly different behaviour when mixed with LiBH_4 then when studied on its own. As shown in Fig. 6.3.1, the intensity of the peaks assigned to γ - $\text{Ca}(\text{BH}_4)_2$ grows before transition to β - $\text{Ca}(\text{BH}_4)_2$. Close inspection of the variable temperature data shows that this coincides with the transition of orthorhombic to hexagonal LiBH_4 , which is observed at *ca.* 389 K, as expected (transition a, Fig. 6.3.2). As this transition occurs, the Bragg reflections of the α -phase begin disappearing, while those of γ - $\text{Ca}(\text{BH}_4)_2$ grow in intensity (transition b, Fig.6.3.2). The γ -polymorph quickly becomes the dominant phase of $\text{Ca}(\text{BH}_4)_2$ present in the temperature range 400 - 435 K, when a phase change to β - $\text{Ca}(\text{BH}_4)_2$ is observed (transition c, Fig.6.3.2). This is about 40 degrees lower than the α - β transition observed in pure $\text{Ca}(\text{BH}_4)_2$. At *ca.* 475K, the Bragg peaks from both β - $\text{Ca}(\text{BH}_4)_2$ and hexagonal LiBH_4 begin

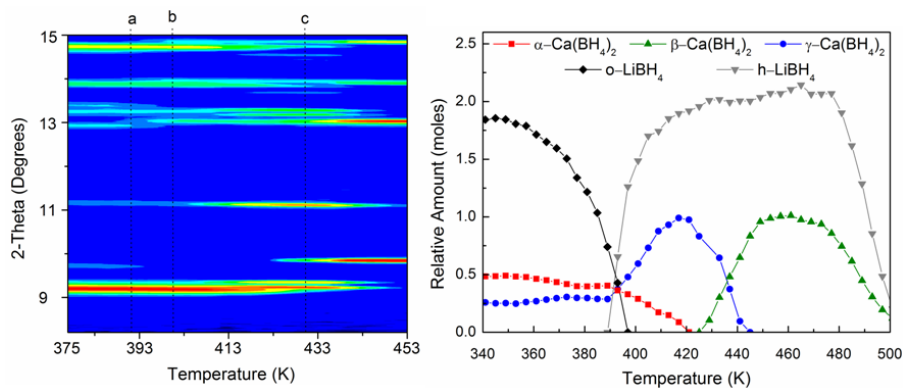


Figure 6.3.2: Left: Surface plot of variable temperature synchrotron PXD data. Right: Relative molar amount of each phase present in the sample taken from Rietveld refinements every 4 K.

to decrease in intensity, while no new crystalline phases appear. As no mass loss is observed in the TGA trace of the material at this temperature (Fig. 6.3.4), the disappearance of both phases is due to the formation of a eutectic mixture of Ca(BH₄)₂ and LiBH₄, which occurs at a lower temperature than the melting of either parent compound.

The origin of the observed phase transformations in the combined LiBH₄/Ca(BH₄)₂ system is unknown, but may possibly be a result of the high lithium ion conductivity present in hexagonal LiBH₄. This ionic conductivity may facilitate lithium insertion into the lattice of Ca(BH₄)₂ thereby destabilizing the α phase and promoting a transition to the γ phase. Some evidence for this is provided by examining the lattice parameters of α -Ca(BH₄)₂ as a function of temperature in both the pure and mixed material. While there is little difference in the thermal variation of the *a* and *c* axes between the two materials, the *b* axis differs in behaviour between the two (Fig. 6.3.3). Before the phase transition in LiBH₄, the value for the *b* lattice parameter in Ca(BH₄)₂ is similar between the mixture and the pure compound; both display typical thermal expansion. Following the phase change of LiBH₄, the *b* lattice parameter of Ca(BH₄)₂ in

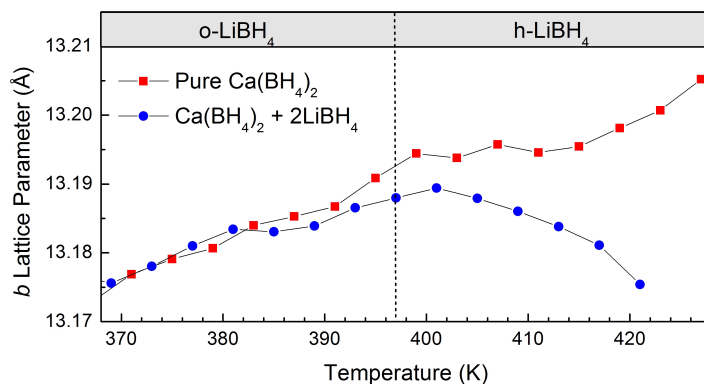


Figure 6.3.3: The b lattice parameter of $\alpha\text{-Ca(BH}_4)_2$ with temperature in a pure sample and when milled with LiBH_4 . The orthorhombic to hexagonal LiBH_4 transition is indicated by a dashed line.

the mixed sample is seen to begin decreasing with increasing temperature, while that of the pure compound continues to expand.

As previously discussed, the polymorphism of $\text{Ca(BH}_4)_2$ is analogous to that of TiO_2 , where Ca^{2+} ions replace Ti^{4+} and BH_4^- tetrahedra replace O^{2-} atoms. In 1999, a theoretical study found that Li insertion in anatase resulted in a change in Ti stacking of the a-b layers, causing a decrease in the unique c axis[228]. In much the same way, a decrease has been observed in the unique axis of the analogous $\alpha/\alpha'\text{-Ca(BH}_4)_2$ polymorph upon combination with h-LiBH_4 in this study. In Ref. [228], it was suggested that the decrease in the c lattice parameter is the result of the movement of Ti atoms off of their symmetry site in order to fit closer together. If allowed to refine, the occupancy of the Ca site decreases upon the o- to h-LiBH_4 and continues to decrease as the sample is heated. The means reduced scattering is observed from Ca site, thereby supporting the mechanism of stacking change/Li insertion proposed by Ebina *et al.* [228].

As the phase transformations in $\text{Ca(BH}_4)_2$ originate from the librational modes present in the material, the inclusion of lithium into the crystal lattice

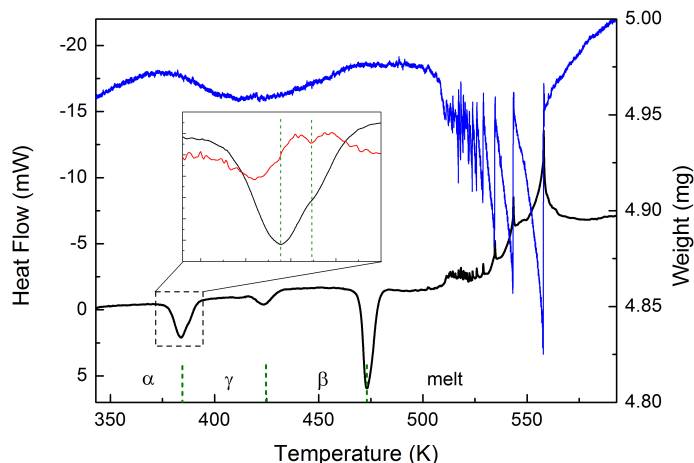


Figure 6.3.4: DSC (black) and TGA (blue) traces of milled α - $\text{Ca}(\text{BH}_4)_2 + 2\text{LiBH}_4$. The dominant $\text{Ca}(\text{BH}_4)_2$ is shown along the bottom. The inset shows that the derivative of the DSC trace (red) contains two distinct values, indicating that two different processes occur over this temperature range.

may affect the orientation of the BH_4^- units, thereby on the affecting the energy of vibrations and inducing a phase change to metastable γ - $\text{Ca}(\text{BH}_4)_2$. Although the exact positions of the Li^+ ions are not yet known, this study demonstrates the potential to alter the thermal behaviour of compounds and offers a plausible mechanism for the observed change.

6.3.2 Thermogravimetric Measurements

Combined DSC/TGA measurements, shown in Fig. 6.3.4, supported the PXD observations. The first endothermic event beginning around 380 K has been appropriately identified by both Lee *et al.*[225] and Fang *et al.*[227] as the orthorhombic to hexagonal phase transformation of LiBH_4 . However, close examination reveals that the peak is actually made up of two events; two separate peaks centered at 384 K and 389 K appear in the DSC trace. This explains

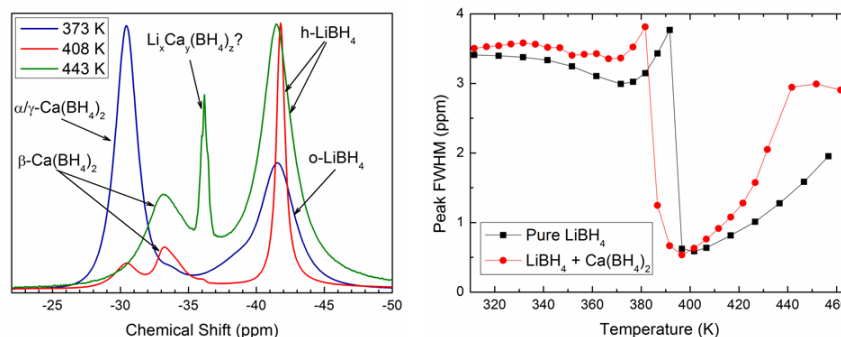


Figure 6.3.5: Left: Solid state ^{11}B NMR measurements of milled $\text{Ca}(\text{BH}_4)_2 + 2\text{LiBH}_4$ taken *in situ* at 373, 408, and 443 K. Right: Line width of the signal from LiBH_4 as temperature is increased.

the broad nature of the peak that was reported in each of the previous studies (in some compositions studied by Lee et al., two distinct peaks were actually seen). The second event corresponds to the transition from the α to γ phase of $\text{Ca}(\text{BH}_4)_2$. Further events with onset temperatures of 420 K and 465 K may be assigned to the γ to β $\text{Ca}(\text{BH}_4)_2$ phase transition and the eutectic melting of $\text{Ca}(\text{BH}_4)_2/\text{LiBH}_4$, respectively. Around 510 K, the melt begins decomposing, which is over 100 K lower than the decomposition temperature observed in either parent compound. However, the total amount of hydrogen released is difficult to assess as bubbling of the melt causes several anomalous fluctuations of the TGA trace.

6.3.3 In Situ Solid State ^{11}B NMR

Three different solid-state ^{11}B NMR spectra collected *in situ* on milled $\text{Ca}(\text{BH}_4)_2 + 2\text{LiBH}_4$ are shown in Fig. 6.3.5. As discussed in the previous chapter, local atom arrangement in the α - and γ - $\text{Ca}(\text{BH}_4)_2$ phases is similar. As such, it would be expected that the chemical shift of the NMR signal would be similar in the two compounds. Indeed at 373 K, only two distinct boron environments are visible at ca. -41 ppm and -30 ppm, corresponding to orthorhombic LiBH_4 and

α/γ - $\text{Ca}(\text{BH}_4)_2$, respectively. From 388 K to 393 K, the peak corresponding to LiBH_4 is seen to abruptly narrow and shifts slightly upfield, as LiBH_4 undergoes a transition to the superionic hexagonal phase. The peak corresponding to α/γ - $\text{Ca}(\text{BH}_4)_2$ then decreases in intensity as that of the β -phase grows.

Concomitant with this transition, there is some evidence of a mixed Ca/Li phase; a new resonance appears in the NMR spectrum exactly half way between that of $\text{Ca}(\text{BH}_4)_2$ and LiBH_4 , at *ca.* -36 ppm. No new Bragg peaks were seen in the diffraction data nor was a thermodynamic event observed to indicate crystallization of a new mixed phase. As such, either the resonance at -36 ppm is due to the second order (as it involved no latent heat) formation of an amorphous mixed phase or it is the resulting chemical shift of a Li-doped $\text{Ca}(\text{BH}_4)_2$ that has been previously suggested based on diffraction data. If lithium were indeed entering into the lattice of $\text{Ca}(\text{BH}_4)_2$, loss of motional averaging from the Li ions that contributes to the sharp resonance of the high temperature phase would be expected and the peak would broaden. In support of this hypothesis, it can be seen in the right of Fig. 6.3.5 that the resonance from h- LiBH_4 broadens much more quickly when mixed with $\text{Ca}(\text{BH}_4)_2$ than it does in the pure compound.

6.4 Sodium Borohydride

Although sodium borohydride only contains a moderate gravimetric hydrogen content (10.7 wt%), it is still extensively explored as it is more widely available commercially (due to its use as a reducing agent) and is therefore much less expensive than some of the other borohydrides explored in this thesis. Furthermore, NaBH_4 dissolved in water in the presence of a ruthenium catalyst will decompose to release pure hydrogen at ambient temperature, whereas decomposition proceeds at much higher temperatures for most borohydrides[229].

Like all of the group I metal borohydrides (except LiBH_4), NaBH_4 adopts a

face-centered rock salt structure at room temperature, which was first reported in 1947[230]. A structural model using either the $Fm\bar{3}m$ or $F\bar{4}3m$ space group can reproduce the diffraction pattern of the material (the two differ only by the center of inversion present in $Fm\bar{3}m$). In the centrosymmetric structure, boron atoms lie on the centres of inversion and are coordinated to eight half-occupied hydrogen sites. As a result, the $Fm\bar{3}m$ structure is intrinsically disordered, while the borohydride anion in the $F\bar{4}3m$ space group is fully or partially ordered (hydrogens may be disordered across two different sites)[37]. Several structural studies of cubic NaBH_4 exist; most recently it has been characterized by neutron powder diffraction on NaBD_4 at 293K[231] and by synchrotron diffraction on a NaBH_4 single crystal at 200K[80]. Both of the most recent reports used a disordered structural model, as the enthalpy of a transition occurring at 190 K is indicative of a first-order order to disorder phase transition[232].

Below 190 K or at pressures above 6 GPa at room temperature[233, 234], NaBH_4 distorts to a tetragonal structure that was first reported in 1954[81]. Structural reports in the literature are conflicting; the $P\bar{4}2_1c$ space group was originally reported for the tetragonal phase[231], although the higher symmetry $P4_2/nmc$ was later suggested[235]. A third (orthorhombic) phase, has also been reported at higher pressures ($>9\text{GPa}$)[233, 82], but will not be studied in this report.

6.4.1 Structure of Low Temperature Phase

Isotopically enriched sodium borodeuteride was prepared by heating 2g of sodium metal and 0.8g of milled 11-boron powder under 55 bar of deuterium at 973 K for 12 hours. A yield of approximately 50% was achieved. High resolution synchrotron powder diffraction measurements were then collected on HRPD at ISIS at 12.5 K.

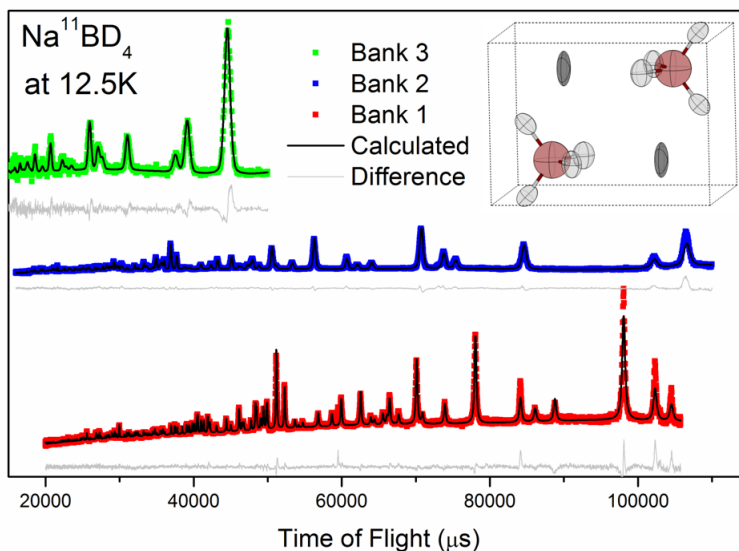


Figure 6.4.1: Rietveld refinements of $\text{Na}^{11}\text{BD}_4$ at 12.5 K performed simultaneously on three different banks on HRPD. The inset shows the structure and thermal ellipsoids at this temperature.

A Rietveld refinement of the structure was attempted using both the $P\bar{4}2_1c$ and $P4_2/nmc$ space groups. The quality of fit achieved was nearly identical using each structural model. As pointed out by Babanova *et al.*[235], the two space groups differ in the presence of $hk0$ reflections. Those with an odd value of $h + k$ should be observed in $P\bar{4}2_1c$, while they are systematically absent in $P4_2/nmc$. Inspection of the diffraction data shows that, even though many reflections (e.g. 210, 320, 410) are well separated in TOF from other peaks, they are indeed absent in the pattern. This confirms that the true symmetry of the low temperature phase is the higher symmetry $P4_2/nmc$, and not $P\bar{4}2_1c$ as was originally reported.

The results of a Rietveld refinement performed simultaneously on data from all three detector banks are given in Table 6.2 and shown graphically in Fig. 6.4.1. Deuterium positions and ADPS were allowed to refine and lattice param-

Table 6.2: Atomic positions of Na¹¹BD₄ from synchrotron neutron powder diffraction at 12.5 K.

Na ¹¹ BD ₄ $P4_2/nmc$ $a = 4.32808(5)$ Å $c = 5.8697(1)$									
Site	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Na	$\frac{3}{4}$	$\frac{1}{4}$	$\frac{3}{4}$	0.013	0.013	0.068	0	0	0
B	$\frac{3}{4}$	$\frac{1}{4}$	$\frac{1}{4}$	0.006	0.006	0.001	0	0	0
D	$\frac{3}{4}$	0.0188(3)	0.1327(4)	0.036	0.026	0.032	0	0	0.097
$\chi^2 = 1.866$ $R_{wp} = 3.147\%$ $R_{exp} = 1.687\%$									

eters of $a = 4.32808(5)$ Å $c = 5.8697(1)$ Å were found for the material at 12.5 K. As with all known phases of NaBH₄, both the Na atoms and the BH₄ units are exactly octahedrally coordinated in the structure ($\angle_{Na-B-Na} = 180^\circ$) and the two nearest Na-B distances are 2.935 Å and 3.060 Å. The borohydride ions of the refined structure are almost perfectly tetrahedral in shape; the B-H bond length refined to 1.179 Å and less than a 1% deviation was seen in the bond angles (108.8-109.8°). Babanova *et al.*[235] found that the material possessed a B-H bond length of 1.152 Å and observed a greater variation in the H-B-H bond angles (107.3-113.9°) at 100 K. X-ray diffraction has the propensity to displace electron density toward the boron atom and the discrepancy is likely due to due to the inability to precisely determine hydrogen atom locations using this technique. Due to the larger electron density surrounding the atoms, the Na-B distances found using X-ray diffraction at 180 K (2.976-3.091 Å) were much closer to those observed in this study. Energy minimization calculations[236] on the lower symmetry $P\bar{4}2_1c$ structure give a B-H length and bond angles much closer to what has been observed here (1.187 Å and *ca.* 109.47°, respectively), while Fischer and Zuttel found a bond length of 1.22 Å from neutron powder diffraction on NaBD₄ using this structural model[231].

The structure was checked for disorder by introducing a second deuterium atom site via rotation about the 4_2 axis and refining the occupancy of each site, beginning from $\frac{1}{2}$. The occupancy of the new site refined to nearly zero while that shown in Table 6.2 refined to nearly 1. Alternatively, if the occupancies were fixed at $\frac{1}{2}$ and the positions allowed to refined, the (x, y, z) coordinated of each site converged to those shown in Table 6.2. These results confirm that the low temperature phase of sodium borohydride is indeed fully ordered in the higher symmetry $P4_2/nmc$ space group.

6.4.2 Low Temperature Phase Change

The sample of $\text{Na}^{11}\text{BD}_4$ was heated from 12.5 to 300 K in approximately 3 K intervals while PND data was simultaneously collected on HRPD. At each temperature step, data was collected for approximately 10 minutes. When the sample reached *ca.* 90 K, a beam failure meant that the experiment was stopped. That sample was cooled back to 50 K and, when the beam came back on, the experiment was resumed (hence there are twice as many data points in the 50 - 90 K temperature range). For each data set, the structure was refined and the lattice parameters extracted. The results of the entire run are displayed in Fig. 6.4.2.

As the sample is heated, the peaks from the disordered cubic high temperature phase of $\text{Na}^{11}\text{BD}_4$ become visible in the diffraction pattern at 188 K and the phase transition is complete by about 194 K. At 191 K, the volume of the high temperature phase is slightly larger (0.35 %) than the equivalent pseudocubic tetragonal phase ($\sqrt{2}a \times \sqrt{2}a \times c$). The lattice parameters of the low temperature phase display anisotropic thermal expansion over the range they are observed, particularly at temperatures approaching the phase transition. This is seen most obviously by considering the c/a ratio of the pseudocubic low

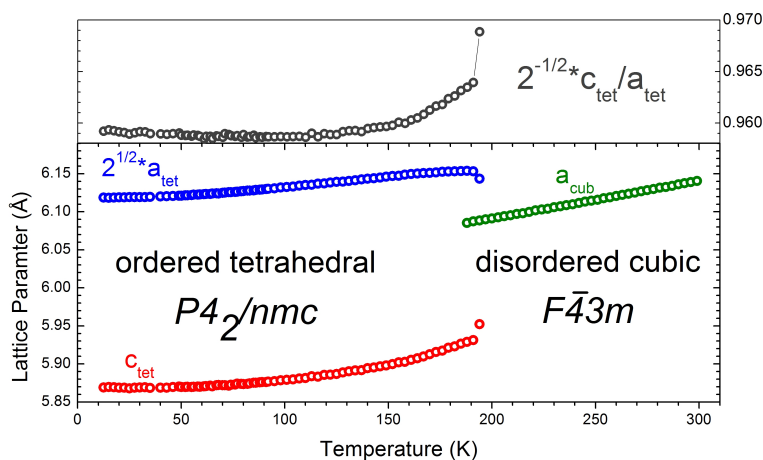


Figure 6.4.2: Lattice parameters for Na¹¹BD₄ from 12.5 to 300 K, showing the ordered tetragonal to disordered cubic phase change over the 188-194 K temperature range. The c/a ratio is plotted above, showing a large disjoint at the phase change.

temperature phase. As the material approaches the phase transition, the rate of the c/a increase grows and there is a large jump from about 0.965 to 1 (for the cubic phase) at the phase transition. The change in volume and c/a ratio are all indicative of the first order nature of the order to disorder phase transition in Na¹¹BD₄.

A dramatically improved fit to the high temperature data was achieved using a the disordered non-centrosymmetric $F\bar{4}3m$ structure rather than the intrinsically disordered $Fm\bar{3}m$ model ($\chi^2 = 1.028$ vs. 1.264). The deuteriums in $F\bar{4}3m$ were allowed to refine in two different sites, each with an occupancy of $\frac{1}{2}$. At 200 K, the a lattice parameter of the cubic cell refined to a value of 6.09133(17) Å, which is nearly exactly to what has been previously observed in the borohydride at the same temperature[80]. The results of the refinement are given in Table 6.3.

Upon heating to higher temperatures, DSC/TGA measurements (not shown) indicate that cubic NaBH₄ is stable up until approximately 773 K and that

Table 6.3: Atomic positions of disordered $\text{Na}^{11}\text{BD}_4$ from synchrotron neutron powder diffraction at 200 K.

$\text{Na}^{11}\text{BD}_4$ $F\bar{4}3m$ $a = 6.09133(17)$ Å				
Site	$x/a=y/b=z/c$	occ	$U_{11}=U_{22}=U_{33}$	$U_{12}=U_{13}=U_{23}$
Na	0	1	0.018(3)	0
B	$\frac{1}{2}$	1	0	0
D1	0.398(1)	0.5	0.055(4)	0.0046(7)
D2	0.623(1)	0.5	0.031(4)	-0.014(5)
$\chi^2 = 1.028$ $R_{wp} = 3.544\%$ $R_{exp} = 3.447\%$				

decomposition is complete by 873 K. Previous reports have found a similar decomposition temperature and suggested that hydrogen release happens in two different steps, centered around 773 and 853 K[237, 238].

6.5 Calcium Borohydride + Sodium Borohydride

Calcium borohydride was milled with sodium borohydride in various ratios, similar to what was done with LiBH_4 . A sample of $\text{Ca}(\text{BH}_4)_2 + 0.1\text{NaBH}_4$ was then heated from 297 K to 673 K while high resolution powder X-ray diffraction data was collected on beamline I11 at Diamond. Data were collected every 4 K and a Rietveld refinement was performed at each temperature step.

At room temperature, $\text{Ca}(\text{BH}_4)_2$ exists primarily in the α -phase, although the β - and γ -polymorphs are also present in small amounts (around 10 and 5%, respectively). As before, the appearance of β - and γ - $\text{Ca}(\text{BH}_4)_2$ is a result of milling, and not influence from NaBH_4 . The only other phase present in the sample is cubic NaBH_4 . As with LiBH_4 , the affect of milling on NaBH_4 is to produce a more symmetrical peak shape (due to a more uniform particle size).

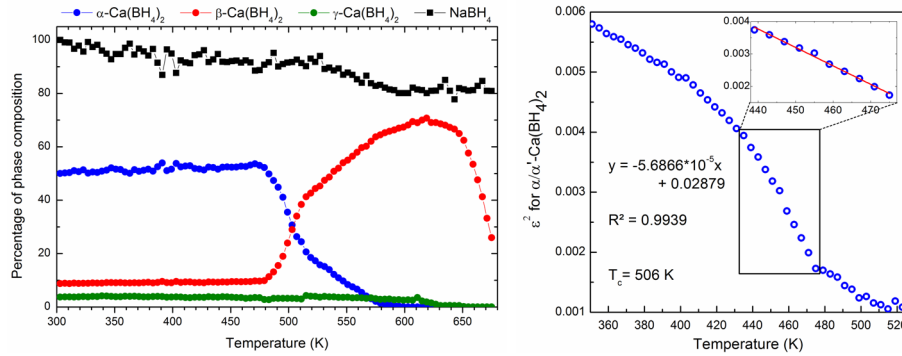


Figure 6.5.1: Left: Phase composition of milled Ca(BH₄)₂ and NaBH₄ as a function of temperature, taken from Rietveld refinements of *in situ* variable temperature synchrotron X-ray diffraction measurements. Right: Strain squared plotted with temperature for α -Ca(BH₄)₂, showing linear behaviour in the region of the second order ferroelastic transition.

The results of Rietveld refinements at each temperature step are shown in Fig. 6.5.1. As the sodium borohydride exists in the stable rock salt structure, it has very little effect on Ca(BH₄)₂. As in the pure compound, the lattice parameters of the α -phase are seen to merge below 500 K as the material distorts to the α' -phase. The right of Fig. 6.5.1 shows that square of the strain is linear with respect to temperature in the region of the transition, providing evidence for the second order nature of the ferroelastic transition. The α - to β -phase transformation is observed around 470-500 K and the sample begins melting/decomposing at around 650 K (as evidenced by the disappearance of all peaks assigned to Ca(BH₄)₂). The Bragg peaks from NaBH₄ remain throughout the entire temperature range and, unlike when milled with LiBH₄, a eutectic melt was not observed. This indicates that NaBH₄ is insoluble in melted Ca(BH₄)₂ and the high thermodynamic stability of NaBH₄ means that the two compounds interact very little with each other even when intimately mixed via milling. A slight decrease in the amount of NaBH₄ present was observed at higher temperatures, but may be due to increased background intensity from Debye Waller effects

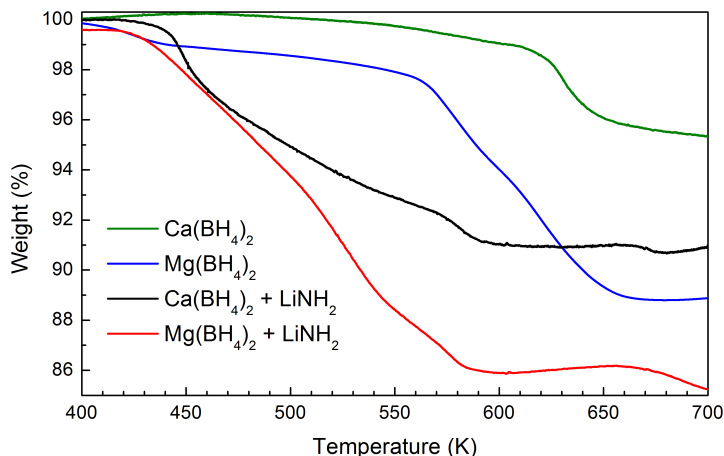


Figure 6.6.1: Thermogravimetric profiles of the $\text{Ca}(\text{BH}_4)_2/\text{Mg}(\text{BH}_4)_2 + 2\text{LiNH}_2$ composite systems compared to those of the pure group II borohydrides.

and the melted $\text{Ca}(\text{BH}_4)_2$.

6.6 Magnesium/Calcium Borohydride + Lithium Amine

In 2005, a report by Aoki *et al.* suggested that significant destabilization of LiBH_4 was possible by combining it with the LiNH_2 [239]. A higher gas pressure was observed for the combined material than that of either parent compound upon decomposition. It was believed that the material decomposes to Li_3BN_2 , while releasing 4 moles of hydrogen gas. Since then, a large number of combination studies, which seek to destabilize borohydride decomposition, have been reported and are summarized in Ref. [60].

LiNH_2 was ground with samples of $\text{Ca}(\text{BH}_4)_2$ and $\text{Mg}(\text{BH}_4)_2$ in a 2:1 mole ratio. The rationale behind this combination is that the protic-hydridic interac-

tions between $\text{N-H}^{\delta+}$ and $\text{B-H}^{\delta-}$ will lower the activation energy of H_2 formation and cause the mixed sample to decompose at a lower temperature than either constituent compound. The TGA trace of each composite is compared to that of the pure borohydride in Fig. 6.6.1. The addition of LiNH_2 to the group II borohydrides has a significant effect on the thermogravimetric profile of each material. In each case, weight loss is observed at a much lower temperature than that of either parent compound, beginning as low as 425 K (decomposition in LiNH_2 begins around 550K). Furthermore, the amount of gas released in each case is dramatically larger than that of the parent compounds. Preliminary IGA measurements indicate that this is due to a combined loss of ammonia and hydrogen. As this thesis is concerned primarily with compounds acting as pure hydrogen sources, the composite systems were not investigated further. Shortly after these studies were performed, several papers emerged on the group II borohydride-lithium amide systems[240, 241, 242, 243]. The general consensus from these reports is that, although the dehydrogenation temperature is lowered, the impurity of the gas released (ammonia was also found in all studies) and the thermodynamic stability of the decomposition products (typically Li_3BN_2 or $\text{LiM}_4(\text{BN}_2)_3$, $\text{M} = \text{Mg/Ca}$) means that much more work is needed before these systems can possibly be used as reversible hydrogen stores.

6.7 Conclusions

Lithium borohydride has been characterized by synchrotron powder X-ray diffraction, solid state $^{11}\text{-boron}$ NMR and differential thermal analysis. Milling the material results in a smaller, more uniform particle size that creates more symmetrical diffraction peaks. At 380 K, the material undergoes an orthorhombic to hexagonal phase transformation. The high temperature phase is a fast lithium ion conductor and a sharp NMR signal is observed from motional averaging in

the material. The material melts above 550 K and begins decomposing at 670 K, losing nearly 13 wt. % by 760 K.

When milled with $\text{Ca}(\text{BH}_4)_2$, the mixture exhibits significantly different behaviour than either of the parent compounds. Concomitant with the superionic phase transformation in LiBH_4 , $\alpha\text{-Ca}(\text{BH}_4)_2$ undergoes a transformation to the metastable γ -phase, before transforming to the β -polymorph at 420 K (about 60 K lower than in the pure compound). The reason for the lower phase change is explained in terms of lithium ion doping in the $\text{Ca}(\text{BH}_4)_2$ lattice, and experimental results match those observed in the analogous Li-doped TiO_2 compound. A eutectic melting point is observed at 465 K and the liquid begins decomposing around 510 K, which is over 100 K lower than the decomposition temperature of either constituent borohydride. *In situ* ^{11}B NMR measurements suggest that a mixed phase lithium-calcium borohydride may be present around 443 K, although no diffraction peaks are observed for the mixed species.

The structure of $\text{Na}^{11}\text{BD}_4$ was refined at low temperature using neutron powder diffraction. Precise determination of deuterium atom locations was possible and the borohydride ions are very nearly perfect tetrahedra. The material exists in the fully ordered higher symmetry $P4_2/nmc$ phase at 12.5 K rather than the $P\bar{4}2_1c$ structure that was originally reported. In situ NPD measurements allowed the ordered tetragonal to disordered cubic structural transition in $\text{Na}^{11}\text{BD}_4$ to be fully characterized. A sudden change in volume and disjoint in c/a ratio of the pseudocubic low temperature phase indicate that the transition is first order in nature. The high temperature phase is best fit using the $F\bar{4}3m$ structure with the hydrogen atoms fully disordered across two different sites and a lattice parameter $a = 6.09133(17)$ Å at 200 K.

When NaBH_4 was milled with $\text{Ca}(\text{BH}_4)_2$, neither borohydride appeared to have any effect on the other. $\text{Ca}(\text{BH}_4)_2$ underwent the second-order ferroelastic

transition, α - to β -phase change and decomposition at nearly identical temperatures to the pure compound. The stability of NaBH_4 in the rock salt structure means that it has little effect on other borohydrides and the absence of a eutectic melting suggests it is insoluble in other borohydride melts.

Finally, LiNH_2 was combined with $\text{Mg}(\text{BH}_4)_2$ and $\text{Ca}(\text{BH}_4)_2$ in an attempt to exploit protic-hydridic interactions and lower decomposition temperature. While a large amount of weight loss proceeded at a lower temperature than the decomposition of either constituent, analysis of the gas released suggested that it was due largely to the formation of ammonia.

All of these studies demonstrate the potential to tune the hydrogen storage properties of group II borohydrides. Furthermore, they illustrate the point that careful inspection of the thermal behaviour of both parent compounds is necessary to understand behaviour of the mixed system. A commercially useful system involving borohydrides will undoubtedly require some combination of catalysts and future studies should attempt to understand the influence of such additives from a fundamental physical point of view.

Chapter 7

Conclusions and Future Work

7.1 Thesis Summary

In summary, this thesis has primarily examined light group I and II metal borohydrides with the aim of understanding their physical properties and potential for use as hydrogen stores. Various combinations of X-ray/neutron scattering, NMR, and thermogravimetric techniques have been used to characterize compounds synthesized either in house or by collaborators at the University of Aarhus. The key findings from each chapter are summarized here:

- The structure of a new, porous phase of magnesium borohydride (γ - $\text{Mg}(\text{BH}_4)_2$) has been solved and studied by direct comparison with SiO_2 . The borohydride ion is nearly perfectly tetrahedral with an average B-D distance of 1.2043 Å. The material transforms to the β' -phase above 440 K, which lacks long range order due to stacking faults present in the structure. The material decomposes via various polyborane species, which suggests reversibility may be possible under ambient conditions. At higher temperatures, the sample loses 10 wt. % hydrogen below 675 K although more draconian conditions are needed

to reform $\text{Mg}(\text{BH}_4)_2$ from the decomposition products (950 bar H_2 at 673 K for 108 hours).

- The new phase of $\text{Mg}(\text{BH}_4)$ undergoes negative thermal expansion from approximately 15 to 190 K, which is due to a low energy rigid unit mode in which the borohydride ion moves transverse to the Mg-B-Mg bond. The energy was predicted using a Debye-Einstein model of the lattice parameter behaviour and observed directly using Inelastic Neutron Spectroscopy. Below 50 K, the framework structure physisorbs up to 1.5 moles of hydrogen (about 5 wt. %) per mole of $\text{Mg}(\text{BH}_4)_2$ to form one of the most gravimetrically hydrogen-rich solid state materials ever reported (at 19.5 wt % H_2). The potential at the hydrogen site is relatively flat and the molecules form long chains along the pores of the γ - $\text{Mg}(\text{BH}_4)_2$ framework.

- The α -, β - and γ -phases of $\text{Ca}(\text{BH}_4)_2$ have been studied and the polymorphic content of a given sample has been found to rely heavily on synthetic/experimental conditions. A second order ferroelastic α - to α' -phase transition and a first order α - to β -polymorphic transition have been characterized and found to occur just below 500 K. Comparison with polymorphism in TiO_2 helps rationalize the stability of the individual $\text{Ca}(\text{BH}_4)_2$ phases.

- The superionic transition in LiBH_4 has been studied and, when milled with $\text{Ca}(\text{BH}_4)_2$, coincides with the formation of metastable γ - $\text{Ca}(\text{BH}_4)_2$. Eutectic melting and decomposition occur at a lower temperatures than in either constituent, which is believed to be a result of lithium insertion into the $\text{Ca}(\text{BH}_4)_2$ lattice. A chemical shift exactly halfway between that of LiBH_4 and $\text{Ca}(\text{BH}_4)_2$ is observed below melting in the NMR spectrum of the mixed species, although no new Bragg peaks are observed in the diffraction pattern. The order-disorder transition in NaBH_4 at approximately 194 K has been characterized. When NaBH_4 is milled with $\text{Ca}(\text{BH}_4)_2$, no interaction between the two compounds is

observed. Adding LiNH_2 to either $\text{Mg}(\text{BH}_4)_2$ or $\text{Ca}(\text{BH}_4)_2$ improves desorption kinetics and thermodynamics at the cost of forming ammonia, thereby decreasing the purity of the gas. These studies demonstrate the potential to tune the hydrogen storage behaviour of group II borohydrides using additives and illustrate that knowledge of the fundamental physical properties of each constituent is required to understand and ultimately tailor the mixed system.

7.2 Future Work

While this thesis reports a great deal of new information, it also presents a number of unanswered questions and further work is needed to fully understand the systems studied here. As such, several suggestions for experiments continuing on from the work done here are given in this section.

One of the first things that requires more research is the γ - to β' -phase change in $\text{Mg}(\text{BH}_4)_2$, particularly understanding the apparent competing side reaction to the unknown ε -phase that occurs. Perhaps if very slow heating rates were used, it could be possible to form a sample composed predominantly of the ε -phase. Alternatively, if the ε -phase is in fact an intermediate in the decomposition rather than a new polymorph of $\text{Mg}(\text{BH}_4)_2$, it may be possible to catalyze its formation. However, to develop a suitable catalyst, it would help to first acquire knowledge of the ε -phase composition. It may be helpful in the future to carefully track the sample by elemental analysis across the transition to see if the weight loss observed is indeed due to decomposition of $\text{Mg}(\text{BH}_4)_2$ at this temperature.

As $\text{Mg}(\text{BH}_4)_2$ is heated and weight loss is first observed, it transforms to a completely amorphous state in the region before MgH_2 formation. To understand the decomposition as best as possible, it would be helpful to fully characterize this amorphous state. The *ex situ* PDF measurements carried out

here provide some indication that polyborane species exist at this temperature, but do not definitively tell us which ones or where they appear. Again, elemental analysis could help determine the stoichiometry of the remaining material and *in situ* Raman measurements could provide insight into the nature of the B-H bond (assuming sufficient resolution to resolve the different polyborane species, which may be difficult at elevated temperatures).

While it has been shown previously that $\text{Mg}(\text{BH}_4)_2$ can be reformed under ambient conditions from material that has partially decomposed to $\text{Mg}(\text{B}_3\text{H}_8)_2$, the conditions surrounding this reversibility have not been studied[61]. Furthermore, the phase of the reformed material has not been reported. Wet synthesis of $\text{Mg}(\text{B}_3\text{H}_8)_2$ should be possible and, if made pure, reversibility of this system could be studied much more easily. If a definitive reaction mechanism could be developed and conversion between the two catalyzed, the system offers great potential as a reversible storage material (assuming the formation of $\text{Mg}(\text{B}_{12}\text{H}_{12})$ can be prevented).

The neutron diffraction data on which negative thermal expansion in $\gamma\text{-Mg}(\text{BH}_4)_2$ was modeled suffered from beam failure and incorrect processing routines on WISH. As such, more beam time has been allocated to the author and the low temperature neutron diffraction measurements will be repeated on the HRPD beamline and the data will be re-fit using the same Debye-Einstein model. This will hopefully yield a closer match between the observed and calculated energy of the rigid unit mode that contributes to negative thermal expansion in the material.

While the anomalous lattice parameter behaviour of $\gamma\text{-Mg}(\text{BH}_4)_2$ has been well characterized here, there are several other phases of $\text{Mg}(\text{BH}_4)_2$ and $\text{Ca}(\text{BH}_4)_2$ that display anisotropic unit cell behaviour with temperature. These have previously been fit using various order polynomials, however, correlating the

existence of anomalous lattice parameter behaviour to the structure and phonon density of states (as has been done here for γ -Mg(BH₄)₂) could be useful for the other phases of Mg(BH₄)₂ and Ca(BH₄)₂ as well. Being able to more broadly correlate such behaviour to structural features across all phases would provide a basis for designing borohydrides with tailored expansive and contractive properties.

There remains a great deal of work to be done in understanding hydrogen adsorption into and out of γ -Mg(BH₄)₂. The discrepancies between measurements performed on TOSCA and WISH are puzzling, particularly since the results on each beam were reproducible and the exact same equipment and conditions were used between the two instruments. The conditions surrounding loading hydrogen into the structure are open to much more investigation. The difference in INS spectra between low and high loadings suggests that hydrogen may first occupy a different site as it enters the structure, although more work is needed to confirm this. Furthermore, the effects of loading temperature and pressure have yet to be investigated and future work should try to understand how uptake and release may be tuned using these controls.

The locking of the framework unit cell parameter when hydrogen is loaded is also a curious phenomenon that has been observed in other gas-adsorbed MOF systems. It was hypothesized that this effect is due to Van der Waals interactions stiffening phonon modes responsible for negative thermal expansion (therefore affecting the oscillator strength in the Debye-Einstein model). It would be interesting to check this by performing an INS experiment of D₂ adsorbed into γ -Mg(¹¹BH₄)₂. The signal would be dominated by the large incoherent cross section of the framework and very little signal would be seen from the adsorbed gas. By comparing INS spectra of γ -Mg(¹¹BH₄)₂ with and without adsorbed D₂, it would be possible to see exactly which phonon modes are affected. It

would then be useful to compare INS spectra of the adsorbed system with the DFT-generated phonon density of states for $\gamma\text{-Mg}({}^{11}\text{BH}_4)_2 \cdot 1.5\text{D}_2$ and produce rattling frequency DFT calculations for comparison with the systems studied in Chapter 4.

Although some evidence is provided in the NMR spectrum for a mixed Li-Ca-BH₄ system, it would be interesting to attempt to determine more about this mixed phase. It may be possible to observe lithium insertion by isotopically enriching Li, B and H in the parent compounds and performing a diffraction study, but the low coherent cross section of ${}^7\text{Li}$ might still make it difficult to observe. If lithium insertion is indeed a result of the high ion mobility in hexagonal LiBH₄, it should be possible to extend this phenomenon to other mixed systems and various eutectic melts may be possible by combination with the material. Furthermore, as a great deal of interest in LiBH₄ stems from application as a battery electrode, it would be interesting to perform studies to see if conductivity of the mixed Li-Ca material (or perhaps other mixed lithium systems) is improved over the parent borohydride.

7.3 General Outlook on Borohydride Chemistry and Hydrogen Storage

None of the borohydrides studied here come close to meeting all of the criteria set out by the D.O.E. and there is still a great deal of work to be done before borohydrides are viable as commercial hydrogen stores. Most generally, they are plagued by high desorption temperatures, poor reversibility, and safety concerns resulting from their reactivity with moisture. Breakthroughs are needed in each of these areas and ongoing research worldwide will attempt to overcome these barriers. Simultaneously, researchers should explore other applications for

borohydrides, much in the way they have been considered as electrode materials in recent years. While lithium reserves continue to be discovered, diversifying energy reliance as much as possible can avoid issues associated with supplier oligopolies and a fast sodium or magnesium ion conductor would serve the market well.

The studies performed in this thesis, particularly those demonstrating the comparison between γ - $\text{Mg}(\text{BH}_4)_2$ and SiO_2 , open up many new avenues for exploration that were not previously possible in borohydride chemistry. Some of those have been explored here, but there are several others that remain. The challenge lies perhaps most with the skilled synthetic and structural chemist. If the analogy with SiO_2 stands, synthesis of a vast number of $\text{Mg}(\text{BH}_4)_2$ polymorphs should be possible. Most researchers in the world that currently have experience working on the compound agree that they have often formed amorphous and/or new crystalline phases of $\text{Mg}(\text{BH}_4)_2$, and that it is very sensitive to the conditions used to produce it. It is quite possible that controlling the connectivity of vertices in the material could be achieved much in the same way that it has been done in MOFs. Sophisticated synthetic chemistry should allow frameworks of many different shapes and sizes to be formed by, for example, techniques such as templating. Tailoring the structure of the material is one of the best steps toward improving gas storage in the material (both for chemi- and physi-sorbed hydrogen). Furthermore, if the structure is readily tuned, it is possible to envisage further application of borohydrides in heterogeneous catalysis or as a more selective reducing agent than NaBH_4 . Obviously a great amount of work is needed before such a system is ever realized, but the work here provides an indication of the breadth of possibilities that remain within borohydride chemistry.

The $\text{Mg}(\text{BH}_4)_2 \cdot 1.5\text{H}_2$ system is one of the first ever reported materials in

which physisorption has been directly combined with chemisorption. As the physisorbed hydrogen is readily added/removed from the framework, in practice this could form a battery that reversibly stores a small amount of energy when a single control (in this case temperature) is used (though it should be noted that 5 wt. % is a pretty modest amount for physisorbed systems). However, the system has additional functionality in that, if ever required, the material can generate even more energy by increasing the temperature further, at the cost of reversibility. In essence, the material operates as a typical reversible battery at low temperatures but also has a large additional capacity that could be generated as a one-shot if required. It is possible to imagine many scenarios in which this type of battery would be useful. The key challenge now remains raising the temperature at which the physisorbed hydrogen is released and lowering the temperature/improving reversibility of chemisorption. If such a system may be properly tuned, combining physi- and chemi-sorption may one day prove to be extremely valuable from a commercial point of view.

The problems posed by the hydrogen economy are large in scale. From a technological standpoint, many different types of work are still needed. Combinatorial studies are required to test the vast different combinations of materials and catalysts possible. The fundamental physical properties of many compounds still need to be probed in order to understand and tailor their functionality. Work attempting to scale up and implement storage technologies needs to take place in order to bring the most promising scientific developments to the consumer. Perhaps most important is the need for ongoing public and private sector investment to ensure that such work continues to be carried out in universities and research institutions. Collaboration is needed on all fronts; physicists, economists, engineers, chemists, politicians, and industry must all work together if any alternative fuel economy is to ever be realized.

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Appendix A - INS and
Raman Mode Assignments for
 γ -Mg($^{11}\text{B}\text{H}_4$)₂

DFT (cm⁻¹)	INS (cm⁻¹)	Raman (cm⁻¹)	Assignment
-17.27			Anharmonic lattice deformation
-0.07			Translation
25.31			Lattice libration
27.40			Lattice libration
28.23			Lattice libration
47.17			Lattice libration
71.97			Lattice libration
76.76			Transverse BH ₄ libration
86.13			Lattice libration
94.76			Lattice libration
97.89			Lattice libration
101.72			Transverse BH ₄ libration
101.95			Lattice libration
113.54			Lattice libration
121.50			Lattice libration
131.84			Lattice libration
137.89			Lattice libration
138.00			Lattice libration
138.281			Lattice libration
145.61			Lattice libration
149.94			Lattice libration
171.97			Lattice libration
188.20			Lattice libration
189.92			Lattice libration
195.38			Lattice libration
195.38			Lattice libration

DFT (cm ⁻¹)	INS (cm ⁻¹)	Raman (cm ⁻¹)	Assignment
208.30			BH ₄ libration
212.08			BH ₄ libration
212.36			BH ₄ libration
221.09			BH ₄ libration
223.05			BH ₄ libration
225.35			BH ₄ libration
229.49			BH ₄ libration
232.46			BH ₄ libration
234.37			BH ₄ libration
239.86			BH ₄ libration
241.26			BH ₄ libration
244.73			BH ₄ libration
246.26			BH ₄ libration
253.67			BH ₄ libration
254.89			BH ₄ libration
262.32			BH ₄ libration
268.13			BH ₄ libration
302.37			BH ₄ libration
308.32			BH ₄ libration
395.78			Longitudinal BH ₄ libration
412.76			BH ₄ libration
413.18			BH ₄ libration
419.29			BH ₄ libration
428.46			BH ₄ libration
429.30			BH ₄ libration
448.27			BH ₄ libration

DFT (cm ⁻¹)	INS (cm ⁻¹)	Raman (cm ⁻¹)	Assignment
460.46			BH ₄ libration
462.23			BH ₄ libration
463.18			BH ₄ libration
518.70			BH ₄ rocking
519.31			BH ₄ rocking
526.97			BH ₄ rocking
527.10			BH ₄ rocking
530.46			BH ₄ rocking
530.73			BH ₄ rocking
530.78			BH ₄ rocking
534.54			BH ₄ rocking
538.55			BH ₄ rocking
543.60			BH ₄ rocking
545.02			BH ₄ rocking
548.03			BH ₄ rocking
551.61			BH ₄ rocking
551.62			BH ₄ rocking
551.82			BH ₄ rocking
558.45			BH ₄ rocking
566.29			BH ₄ rocking
568.05			BH ₄ rocking
570.27			BH ₄ rocking
579.83			BH ₄ rocking
1089.31			Asymmetric BH ₄ bend
1089.46	1140		Asymmetric BH ₄ bend
1090.02			Asymmetric BH ₄ bend

DFT (cm^{-1})	INS (cm^{-1})	Raman (cm^{-1})	Assignment
1090.77	1140		Asymmetric BH_4 bend
1092.06			Asymmetric BH_4 bend
1092.63			Asymmetric BH_4 bend
1093.35			Asymmetric BH_4 bend
1093.71			Asymmetric BH_4 bend
1093.91			Asymmetric BH_4 bend
1094.44			Asymmetric BH_4 bend
1094.76			Asymmetric BH_4 bend
1096.02			Asymmetric BH_4 bend
1096.07			Asymmetric BH_4 bend
1096.38			Asymmetric BH_4 bend
1102.01			Asymmetric BH_4 bend
1102.91			Asymmetric BH_4 bend
1103.02			Asymmetric BH_4 bend
1103.59			Asymmetric BH_4 bend
1104.22			Asymmetric BH_4 bend
1104.89			Asymmetric BH_4 bend
1145.13	1200	1198	Symmetric BH_4 bend
1146.54			Symmetric BH_4 bend
1147.76			Symmetric BH_4 bend
1147.77			Symmetric BH_4 bend
1149.67			Symmetric BH_4 bend
1150.32			Symmetric BH_4 bend
1150.48			Symmetric BH_4 bend
1151.16			Symmetric BH_4 bend
1151.32			Symmetric BH_4 bend

DFT (cm ⁻¹)	INS (cm ⁻¹)	Raman (cm ⁻¹)	Assignment
1152.52	1200	1198	Symmetric BH ₄ bend
1234.12	1280		Asymmetric BH ₄ bend
1236.16			Asymmetric BH ₄ bend
1237.20			Asymmetric BH ₄ bend
1238.60			Asymmetric BH ₄ bend
1239.33			Asymmetric BH ₄ bend
1241.34			Asymmetric BH ₄ bend
1250.55			Asymmetric BH ₄ bend
1251.71			Asymmetric BH ₄ bend
1254.29			Asymmetric BH ₄ bend
1259.52			Asymmetric BH ₄ bend
1361.12	1410	1388	Symmetric BH ₄ bend
1361.94			Symmetric BH ₄ bend
1362.17			Symmetric BH ₄ bend
1362.69			Symmetric BH ₄ bend
1362.73			Symmetric BH ₄ bend
1363.05			Symmetric BH ₄ bend
1363.24			Symmetric BH ₄ bend
1363.28			Symmetric BH ₄ bend
1363.96			Symmetric BH ₄ bend
2311.82		2200	Symmetric BH ₄ stretch
2311.95			Symmetric BH ₄ stretch
2312.76			Symmetric BH ₄ stretch
2313.06			Symmetric BH ₄ stretch
2316.11			Symmetric BH ₄ stretch
2316.16			Symmetric BH ₄ stretch

DFT (cm^{-1})	INS (cm^{-1})	Raman (cm^{-1})	Assignment
2317.88		2200	Symmetric BH_4 stretch
2320.58			Symmetric BH_4 stretch
2321.03			Symmetric BH_4 stretch
2321.35			Symmetric BH_4 stretch
2347.21		2278	Asymmetric BH_4 stretch
2347.52			Asymmetric BH_4 stretch
2350.28			Asymmetric BH_4 stretch
2350.52			Asymmetric BH_4 stretch
2352.63			Asymmetric BH_4 stretch
2371.38		2302	Asymmetric BH_4 stretch
2375.41			Asymmetric BH_4 stretch
2376.17			Asymmetric BH_4 stretch
2381.82			Asymmetric BH_4 stretch
2383.19			Asymmetric BH_4 stretch
2383.94			Asymmetric BH_4 stretch
2384.94			Asymmetric BH_4 stretch
2386.62			Asymmetric BH_4 stretch
2388.32			Asymmetric BH_4 stretch
2388.42			Asymmetric BH_4 stretch
2389.23			Asymmetric BH_4 stretch
2389.46			Asymmetric BH_4 stretch
2390.23			Asymmetric BH_4 stretch
2396.87			Asymmetric BH_4 stretch
2397.01			Asymmetric BH_4 stretch
2397.58			Asymmetric BH_4 stretch
2398.18			Asymmetric BH_4 stretch

DFT (cm ⁻¹)	INS (cm ⁻¹)	Raman (cm ⁻¹)	Assignment
2398.34		2302	Asymmetric BH ₄ stretch
2398.57			Asymmetric BH ₄ stretch
2418.56		2321	Asymmetric BH ₄ stretch
2418.92			Asymmetric BH ₄ stretch
2419.72			Asymmetric BH ₄ stretch
2419.86			Asymmetric BH ₄ stretch
2420.76			Asymmetric BH ₄ stretch
2421.23			Asymmetric BH ₄ stretch

Appendix B - INS Mode
Assignments for
 γ -Mg($^{11}\text{BD}_4$)₂

DFT (cm⁻¹)	INS (cm⁻¹)	Assignment
-0.06 0.31		Anharmonic Translation Translation
46.08 46.65	46	Lattice deformation Lattice deformation
52.12	54	Lattice libration
59.50	59	Lattice libration
68.59	64	Lattice libration
71.55 71.82	72	Lattice libration Lattice libration
88.56	81	Transverse BD ₄ libration
93.42 93.44	89	Lattice libration Lattice libration
100.06	101	Lattice libration
104.79	102.5	Anharmonic Translation
107.70	107.5	Lattice libration
115.30 117.76 117.81 120.27 123.00 123.06 123.09 123.97 132.09 134.17	115-150	Transverse BD ₄ libration Lattice libration Lattice libration Lattice libration Lattice libration Lattice libration Lattice libration Lattice libration Lattice libration Lattice libration
142.53	162-190	BD ₄ libration

DFT (cm^{-1})	INS (cm^{-1})	Assignment
144.80	162-190	BD_4 libration
152.57		BD_4 libration
152.75		BD_4 libration
155.84		BD_4 libration
161.08		BD_4 libration
167.61		BD_4 libration
169.27		BD_4 libration
170.80		BD_4 libration
180.89	199-220	Lattice libration
183.98		Lattice libration
184.00		Lattice libration
184.27		Lattice libration
194.20		Lattice libration
197.26		Lattice libration
203.32		Lattice libration
209.83	230-300	Lattice libration
211.00		Lattice libration
220.07		Lattice libration
227.51		Lattice libration
230.80		Lattice libration
242.42		Lattice libration
245.85		Lattice libration
247.47		Lattice libration
285.87		Lattice libration
291.30		Lattice libration
348.99	360-490	BD_4 libration

DFT (cm^{-1})	INS (cm^{-1})	Assignment
355.18	360-490	BD_4 rocking
355.26		BD_4 rocking
356.97		BD_4 rocking
358.82		BD_4 rocking
359.35		BD_4 rocking
362.18		BD_4 rocking
362.82		BD_4 rocking
370.12		BD_4 rocking
371.54		BD_4 rocking
371.56		BD_4 rocking
371.79		BD_4 rocking
372.65		BD_4 rocking
373.35		BD_4 rocking
376.16		BD_4 rocking
378.10		BD_4 rocking
378.30		BD_4 rocking
382.37		BD_4 rocking
384.86		BD_4 rocking
395.02		BD_4 rocking
395.38		BD_4 rocking
397.08		BD_4 rocking
402.48		BD_4 rocking
405.75		BD_4 rocking
408.56		BD_4 rocking
412.84		BD_4 libration
418.33		BD_4 rocking

DFT (cm^{-1})	INS (cm^{-1})	Assignment
420.04	360-490	Longitudinal BD_4 libration
424.72		BD_4 libration
425.33		BD_4 rocking
426.89		BD_4 rocking
427.56		BD_4 rocking
430.70		Lattice libration
434.29		Lattice libration
451.77		Lattice libration
803.85	820-915	Asymmetric BD_4 bend
804.32		Asymmetric BD_4 bend
804.43		Asymmetric BD_4 bend
804.45		Asymmetric BD_4 bend
805.40		Asymmetric BD_4 bend
805.51		Asymmetric BD_4 bend
806.37		Asymmetric BD_4 bend
806.89		Asymmetric BD_4 bend
807.03		Asymmetric BD_4 bend
807.28		Asymmetric BD_4 bend
807.31		Asymmetric BD_4 bend
807.92		Asymmetric BD_4 bend
808.01		Symmetric BD_4 bend
808.86		Asymmetric BD_4 bend
809.34		Asymmetric BD_4 bend
809.49		Asymmetric BD_4 bend
809.50		Asymmetric BD_4 bend
810.72		Asymmetric BD_4 bend

DFT (cm^{-1})	INS (cm^{-1})	Assignment
812.52	810-915	Asymmetric BD_4 bend
812.67		Asymmetric BD_4 bend
815.69		Asymmetric BD_4 bend
817.06		Symmetric BD_4 bend
817.79		Symmetric BD_4 bend
817.93		Asymmetric BD_4 bend
818.28		Symmetric BD_4 bend
818.45		Symmetric BD_4 bend
818.57		Symmetric BD_4 bend
819.29		Symmetric BD_4 bend
820.29		Asymmetric BD_4 bend
820.91		Asymmetric BD_4 bend
820.92		Asymmetric BD_4 bend
821.02		Asymmetric BD_4 bend
823.15		Asymmetric BD_4 bend
934.62	950-990	Asymmetric BD_4 bend
936.63		Asymmetric BD_4 bend
937.13		Asymmetric BD_4 bend
937.28		Asymmetric BD_4 bend
937.67		Asymmetric BD_4 bend
938.96		Asymmetric BD_4 bend
939.00		Asymmetric BD_4 bend
940.89		Asymmetric BD_4 bend
942.38		Asymmetric BD_4 bend
943.03		Asymmetric BD_4 bend
943.63		Asymmetric BD_4 bend

DFT (cm^{-1})	INS (cm^{-1})	Assignment
945.05	950-990	Asymmetric BD_4 bend
964.31	990-1050	Symmetric BD_4 bend
965.21		Symmetric BD_4 bend
965.26		Symmetric BD_4 bend
965.31		Symmetric BD_4 bend
965.32		Symmetric BD_4 bend
966.31		Symmetric BD_4 bend
966.39		Symmetric BD_4 bend
966.54		Symmetric BD_4 bend
966.75		Symmetric BD_4 bend
966.87		Symmetric BD_4 bend
972.08		Symmetric BD_4 bend
1675.67		Symmetric BD_4 stretch
1675.95		Symmetric BD_4 stretch
1678.33		Symmetric BD_4 stretch
1678.49		Symmetric BD_4 stretch
1679.27		Symmetric BD_4 stretch
1679.56		Symmetric BD_4 stretch
1680.40		Symmetric BD_4 stretch
1681.70		Symmetric BD_4 stretch
1682.08		Symmetric BD_4 stretch
1683.03		Symmetric BD_4 stretch
1778.31		Asymmetric BD_4 stretch
1778.34		Asymmetric BD_4 stretch
1779.34		Asymmetric BD_4 stretch
1779.59		Asymmetric BD_4 stretch

DFT (cm ⁻¹)	INS (cm ⁻¹)	Assignment
1779.73		Asymmetric BD ₄ stretch
1781.25		Asymmetric BD ₄ stretch
1788.69		Asymmetric BD ₄ stretch
1793.10		Asymmetric BD ₄ stretch
1797.34		Asymmetric BD ₄ stretch
1797.83		Asymmetric BD ₄ stretch
1802.56		Asymmetric BD ₄ stretch
1805.15		Asymmetric BD ₄ stretch
1825.84		Asymmetric BD ₄ stretch
1826.21		Asymmetric BD ₄ stretch
1826.55		Asymmetric BD ₄ stretch
1826.79		Asymmetric BD ₄ stretch
1826.84		Asymmetric BD ₄ stretch
1828.89		Asymmetric BD ₄ stretch
1829.18		Asymmetric BD ₄ stretch
1829.53		Asymmetric BD ₄ stretch
1829.81		Asymmetric BD ₄ stretch
1829.89		Asymmetric BD ₄ stretch
1823.78		Asymmetric BD ₄ stretch
1833.51		Asymmetric BD ₄ stretch
1833.57		Asymmetric BD ₄ stretch
1834.00		Asymmetric BD ₄ stretch
1834.21		Asymmetric BD ₄ stretch
1834.51		Asymmetric BD ₄ stretch
1850.21		Asymmetric BD ₄ stretch
1850.31		Asymmetric BD ₄ stretch

DFT (cm⁻¹)	INS (cm⁻¹)	Assignment
1850.32		Asymmetric BD ₄ stretch
1850.70		Asymmetric BD ₄ stretch
1851.81		Asymmetric BD ₄ stretch
1852.66		Asymmetric BD ₄ stretch
1853.40		Asymmetric BD ₄ stretch
1853.40		Asymmetric BD ₄ stretch