

Structural and Thermogravimetric Studies of Group I and II 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 whilst a student of the Inorganic Chemistry Laboratory, University of Oxford from 2006 to 2010, under the supervision of Professor P. P. Edwards and Professor W. I. F. David. All of the work is my own unless otherwise stated and has not been previously submitted for any other degree at this or any other university.

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Borohydrides

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Abstract

This thesis investigates the structure and thermal behaviour of LiBH_4 , NaBH_4 , KBH_4 , $\text{LiK}(\text{BH}_4)_2$, $\text{Ca}(\text{BH}_4)_2$ and $\text{Sr}(\text{BH}_4)_2$. $\text{LiK}(\text{BH}_4)_2$ is the first mixed alkali metal borohydride and was synthesised and characterised during this work.

The crystal structures of these borohydrides were studied using variable temperature neutron and synchrotron X-ray diffraction. The synthesis of isotopically enriched samples of $^7\text{Li}^{11}\text{BD}_4$, $\text{Li}^{11}\text{BD}_4$, $\text{Na}^{11}\text{BD}_4$ and K^{11}BD_4 allowed high quality neutron diffraction data to be collected. Particular attention was paid to the exact geometry of the borohydride ions which were generally found to be perfect tetrahedra but with orientational disorder. New structures of $\text{Ca}(\text{BH}_4)_2$ were identified and the first crystal structure of $\text{Sr}(\text{BH}_4)_2$ was determined from synchrotron X-ray diffraction data. Solid state ^{11}B NMR and Raman spectroscopy provided further information about the structure of these borohydrides.

The thermal behaviour of the borohydrides was investigated using thermogravimetric analysis with mass spectrometry of the decomposition gas products. Hydrogen is the main decomposition gas product from all of these compounds but small amounts of B_2H_6 and BH_3 were also detected during decomposition. Thermogravimetric analyses of $\text{Na}^{11}\text{BD}_4$ and K^{11}BD_4 were completed whilst collecting *in-situ* neutron diffraction data allowing information about structural changes and mass losses to be combined in order to better understand the decomposition process.

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1 Introduction

1.1 A Hydrogen economy

In the future, our energy needs may be met by a hydrogen economy rather than by fossil fuels. A hydrogen economy would be based around the use of hydrogen as an energy vector. Energy would be used to produce hydrogen which would then be treated as an energy vector which could be stored and transported. When the energy was needed, hydrogen would be oxidised either electrochemically or burnt in order to release the energy. A hydrogen economy could potentially have the advantages of sustainability and security of energy supply with low carbon emissions. However, there are considerable technological barriers to overcome in our ability to produce, store and use hydrogen effectively in a sustainable manner, consequently, the technology required for a hydrogen economy has recently become the focus of significant research.^[1-5] The potential options for the storage of hydrogen will be discussed here.

1.2 Hydrogen storage

Hydrogen can be used relatively efficiently to produce energy via a hydrogen fuel cell (hydrogen fuel cell efficiency 50 % to 60 % compared to 25 % for an internal combustion engine^[3]). Hydrogen gas has a high gravimetric energy density but a low volumetric energy density when compared to hydrocarbon fuels, therefore, if hydrogen is stored as a gas, larger storage tanks are needed than for hydrocarbon fuels in order to store the same amount of energy. In order to use a fuel cell to power a vehicle, an on-board supply of hydrogen is required and although large storage tanks

of gaseous hydrogen can be used for stationary storage, the volume and mass of these tanks makes them impractical for mobile applications. An average modern car currently has a range of approximately 400 km. An electric car powered by a fuel cell would need about 4 kg hydrogen in order to achieve this range. If this amount of hydrogen was stored as a compressed gas at 200 bar, a 225 litre tank would be required.^[3]

In order for hydrogen to be used within fuel cells to provide energy for transport, a storage method must be found which can store a high gravimetric and volumetric density of hydrogen and be capable of rapid charge and discharge of hydrogen at a reasonable temperature.^[1, 4] In 2003, the U.S. Department of Energy (Energy Efficiency and Renewable Energy), DOE, issued the “Grand Challenge” for hydrogen storage.^[6] This project set targets for the volumetric and gravimetric capacities of complete hydrogen storage systems along with other requirements necessary to make the system compatible with a fuel cell and acceptable to a user who is currently accustomed to a petrol internal combustion engine. Initially the target for a complete hydrogen storage system was a hydrogen content of 6 weight percent, (wt%) in 2010 with a higher target of 9 wt% for 2015. These targets have recently been revised to a 2015 target of 5.5 wt% and $0.04 \text{ kg H}_2 \text{ L}(\text{system volume})^{-1}$ with an eventual target of 7.5 wt% and $0.07 \text{ kg H}_2 \text{ L}^{-1}$. The hydrogen must be supplied at temperatures between -40°C and 85°C with the system operating in ambient conditions of -40°C to 60°C . By 2015, the system should be capable of being recharged with hydrogen in 3.3 min and be capable of cycling between a quarter-full and full 1500 times. The target cost to the end user at the fuel pump is US\$2 to US\$3 for the equivalent to a gallon of gasoline.^[6] There are several hydrogen storage options which may have the potential to meet these requirements. Figure 1.1 shows the theoretical volumetric and

gravimetric hydrogen capacities of complete hydrogen storage systems using compressed or liquid hydrogen, hydrogen bound to a solid by physisorption (cryogenic sorbents) and hydrogen chemically bound within a solid as a chemical or complex hydride.

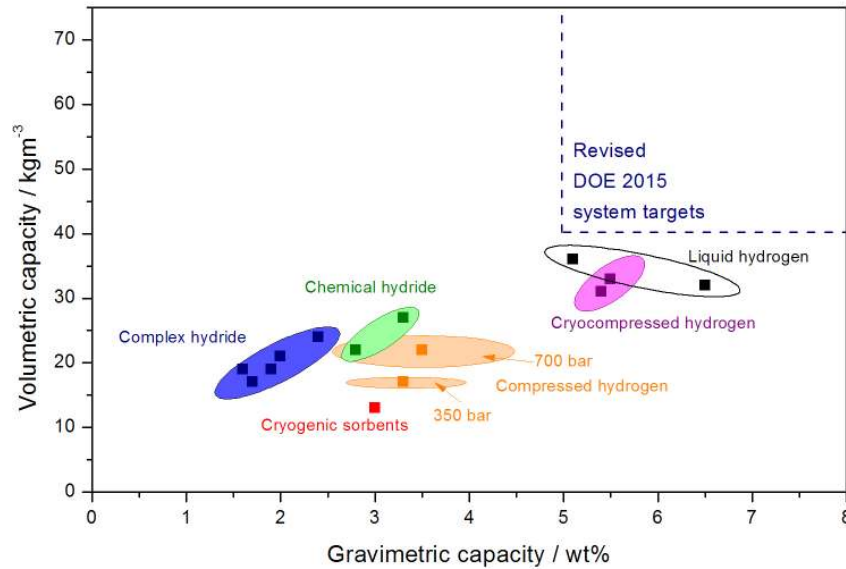


Figure 1.1 The theoretical capacities of hydrogen storage systems based on current knowledge in comparison to the targets for 2015^[6]

1.2.1 Liquid hydrogen

Condensing hydrogen to a liquid or solid would consume a significant portion of the energy contained in the hydrogen. A medium sized liquefaction plant produces 182 kg of liquid hydrogen per hour using 54 MJ per kilogram of liquid hydrogen, larger plants can reduce this energy consumption to 36 MJ per kilogram of liquid hydrogen, which corresponds to approximately 30 % of the energy contained within the hydrogen. On top of this, liquid hydrogen is stored in open systems to avoid over-pressurisation and 3 % to 4 % of the stored liquid hydrogen could be expected to boil off each day.^[7]

1.2.2 Physisorption

Hydrogen could be stored by being weakly bound to a surface or within a porous solid by physisorption. The hydrogen molecules remain intact and are held on to the surface by van der Waals forces. Physisorption of hydrogen to metal organic frameworks (MOFs), zeolites, activated carbon, carbon nanostructures and polymers has been investigated.^[5, 8]

Zeolites and MOFs both consist of interconnected frameworks which form structures containing an ordered network of pores and channels. Various molecules including hydrogen can diffuse into and out of these structures. The potential of MOFs for hydrogen storage was first reported in 2003 by Yaghi *et al.*. MOF-5 which has the composition $\text{Zn}_4\text{O}(\text{BDC})_3$, (BDC=1,4-benzenedicarboxylate), absorbed 4.5 wt% H_2 at -195°C and 1 wt% H_2 at room temperature under a pressure of 20 bar. Further research showed that the hydrogen absorption enthalpy of MOFs could be controlled by modifying the pore size within the structure and the amount of hydrogen absorbed increased linearly with the surface area of the material. This knowledge led to the synthesis of MOFs which could absorb 6.7 - 7.5 wt% H_2 at -196°C under pressures of 70 - 80 bar. The small enthalpy change associated with the absorption of hydrogen onto MOFs results in fast, reversible hydrogen uptake.^[5]

Activated carbon is a form of carbon which has been modified to produce a very high surface area and is often derived from charcoal. An activated carbon at -196°C and 5 bar can store hydrogen with a density equivalent to approximately 40 % of the density of liquid hydrogen at -253°C . The heat of absorption of hydrogen onto activated carbons is approximately 6 kJ mol^{-1} , this means that controlling heat flow during hydrogen desorption and absorption is less of a concern than it would be in a system where the hydrogen was more strongly bound. The powdered activated

carbon, AX-21, has a surface area of $2800 \text{ m}^2 \text{ g}^{-1}$ and a density of 0.3 g ml^{-1} . The excess absorbed density of a material is defined by the difference between the amount of gas stored by interaction with the material surface and the amount which could be contained within the pores of the material without any interaction with the material. Under 10 bar hydrogen, the excess absorbed density for AX-21 was 45 mol kg^{-1} at -243°C , decreasing to 22 mol kg^{-1} at -196°C and 2 mol kg^{-1} at -60°C . Clearly, the problem with storing hydrogen in this way is that a significant amount of hydrogen can only be stored below -196°C .^[8]

Carbon nanostructures include nanostructured graphite and carbon nanotubes. A study of carbon nanofibres between 0.1 bar and 105 bar and -196°C and 22°C stored a maximum of 0.7 wt% H_2 at 105 bar suggesting that carbon nanofibres do not have any significant potential for hydrogen storage.^[8]

Other reports have stated that nanostructured graphite with a surface area of $1000 \text{ m}^2 \text{ g}^{-1}$ adsorbed 1.5 wt% hydrogen at -196°C . The uptake of 7.4 wt% hydrogen was reported in a sample of nanostructured graphite produced by mechanically milling the graphite for 80 hours under 10 bar hydrogen, however, 80 % of this hydrogen could not be removed without heating above 300°C .^[3]

Initial experimental results for hydrogen physisorption onto carbon nanotubes varied between 0 wt% and 10 wt%, probably due to the small samples available for experiments. More recent results suggest that at room temperature, carbon nanotubes can absorb less than 1 wt% H_2 . Typical hydrogen capacities under cryogenic conditions range from 1 wt% to 2.4 wt%, however some research groups have reported higher capacities of up to 8 wt% using bundles of single walled carbon nanotubes at -193°C under 40 bar hydrogen.^[8]

1.3 Solid state chemical hydrogen stores

The chemical storage of hydrogen involves hydrogen being chemically bound within a solid in the form of a chemical hydride. During hydrogen absorption, the hydrogen molecules are chemisorbed to the material surface before being absorbed into the bulk material.^[5] The classes of chemical hydrides which could potentially be used in solid state hydrogen storage systems are interstitial hydrides, covalent hydrides, ionic hydrides including complex hydrides and molecular hydrides. In order to achieve the necessary high weight percentage of hydrogen, a compound consisting of light elements is required.

1.3.1 Interstitial hydrides

Interstitial metal hydrides are formed by a metal (or metal alloy) absorbing hydrogen atoms which then occupy spaces between the metal atomic sites (interstitial sites) within the metal crystal structure. These hydrides are often non-stoichiometric, for example $\text{TiH}_{1.7}$ and are most common amongst the transition metals. At low hydrogen content, the crystal structure of the metal is often retained but the lattice may be expanded to accommodate the hydrogen atoms.^[9]

In order to form a metal hydride which will reversibly absorb hydrogen, alloys containing a strongly hydriding metal and a weakly hydriding metal have been used. Lanthanum which forms LaH_2 with a formation enthalpy, ΔH_f , of $-208 \text{ kJ (mol H}_2\text{)}^{-1}$ and a dehydriding plateau pressure, P_d , at 25°C of $3 \times 10^{-29} \text{ bar}$ is combined with nickel which forms NiH , ΔH_f , $-8.8 \text{ kJ (mol H}_2\text{)}^{-1}$ and P_d , 3445 bar, to form the AB_5 alloy, LaNi_5 which hydrides to $\text{LaNi}_5\text{H}_{6+}$, P_d 1.6 bar, ΔH_f , $-30.9 \text{ kJ (mol H}_2\text{)}^{-1}$.^[10]

AB_2 alloys such as ZrMn_2 , AB alloys such as TiFe and A_2B alloys, for example Mg_2Ni are also known. AB_2 alloys often have lower raw materials costs than AB_5

alloys and along with AB alloys have comparable reversible hydrogen capacities to AB_5 alloys; however the activation energy to absorb hydrogen is higher. The A_2B alloy hydride, Mg_2NiH_4 , has been researched for many years because it can reversibly store 3.3 wt% hydrogen but this hydrogen is not released until 255 °C.^[10]

In general, interstitial hydrides only store a small amount of hydrogen but reversibly release it at a low temperature. $LaNi_5$ for example, quickly absorbs hydrogen at 2 bar to reversibly form $LaNi_5H_{6.5}$ but cannot store more than 2 wt% hydrogen.^[3]

1.3.2 Covalent hydrides

The transition group metals and the more electronegative group II metals can also form covalent hydrides. In these compounds the hydrogen atoms are bonded to one or more metal atoms forming continuous structures containing stoichiometric amounts of hydrogen.

The reaction between the metal and hydrogen to form a covalent hydride consists of multiple steps. In the case of MgH_2 , for example, hydrogen is physisorbed onto the metal surface, the H-H bond dissociated, the hydrogen atoms are then chemisorbed onto the metal surface before they diffuse into the metal structure to form the hydride. When hydrogen is released, the magnesium atoms nucleate and the hydrogen atoms diffuse to the metal surface where they recombine into hydrogen molecules.^[11]

MgH_2 contains 7.7 wt% hydrogen and reversibly releases hydrogen but not until 300 °C and then only relatively slowly.^[12] Research into improving the hydrogen storage properties of MgH_2 has focussed on improving the kinetics of the rate limiting steps within these processes, usually by reducing the particle size by mechanical milling or introducing additives by alloying or doping. These additives have included carbon, transition metals, oxides and halides. Mechanically milled Ni-doped MgH_2 contains 6.5 wt% hydrogen which is released between 150 °C and 250 °C. MgH_2

doped with 1 mol% Nb_2O_5 releases hydrogen at 160 °C with good desorption kinetics.^[5]

Alloying MgH_2 with copper in order to chemically destabilise MgH_2 dates back to the 1960s. MgCu_2 was hydrogenated to form MgH_2 and Mg_2Cu at 240 °C under 1 bar hydrogen. More recently silicon has been used to destabilise MgH_2 causing Mg_2Si to form on dehydrogenation, however the kinetics of the hydrogenation / dehydrogenation reactions are still slow at 150 °C.^[5]

The properties of MgH_2 combined with other hydrides have also been investigated. In particular, MgH_2 combined with LiBH_4 , NaBH_4 or $\text{Ca}(\text{BH}_4)_2$ forms a reactive hydride composite. The two compounds react exothermically during hydrogen desorption to form MgB_2 . MgB_2 can be reversibly hydrogenated, thus providing the possibility of a reversible hydrogen store. MgB_2 has also been used to reversibly hydrogenate borohydrides in the gas phase, providing an alternative synthesis route to the borohydrides.^[11]

1.3.3 Molecular hydrides

The solid state structure of a molecular hydride consists of discrete molecules. Ammonia borane, NH_3BH_3 , is a covalently bonded compound which forms a colourless solid that is stable at room temperature. NH_3BH_3 has one of the highest hydrogen contents (19.6 wt% H_2) of the compounds currently being investigated for hydrogen storage. The compound is interesting because it contains hydrogen in both the hydridic form and the protonic form in the B-H and N-H bonds respectively, these hydrogen atoms can combine to form H_2 during decomposition, (research into the other hydrides discussed here, has included introducing a second compound so that both hydridic and protonic hydrogen atoms are present). Hydrogen is released from NH_3BH_3 by thermal decomposition below 100 °C. During decomposition under most

conditions, the presence of the B-N bond is thought to prevent the release of borane or ammonia before hydrogen is released (impurity gases could be problematic during hydrogen use). The thermal decomposition route varies depending on the experimental conditions (*e.g.* temperature ramping rate) and consequently different intermediates including polyaminoborane, $(\text{NH}_2\text{BH}_2)_n$, polyiminoborane, $(\text{NHBH})_n$, and borazine, $(\text{N}_3\text{B}_3\text{H}_6)$ have been observed. The decomposition reaction usually begins very slowly with a negligible amount of hydrogen being produced within the first three hours; the use of ionic solvents has been found to improve the kinetics of decomposition.^[5]

An important recent development in molecular hydride research has been the discovery of alkali metal amidoboranes such as LiNH_2BH_3 (10.9 wt% H_2) and NaNH_2BH_3 (7.5 wt% H_2). These compounds release hydrogen at 90 °C, do not produce borazine and have improved hydrogen release kinetics compared to NH_3BH_3 . Unfortunately, despite the many advantages of amidoboranes, the dehydrogenation reaction is still not easily reversible.^[5, 13]

1.3.4 Ionic hydrides

Group I and heavier group II metals quickly form ionic hydrides when they are heated in the presence of hydrogen. The group I hydrides crystallize with a rock salt type lattice and the group II hydrides crystallize with a barium chloride type lattice. Hydrogen within the ionic hydride structure is generally in the form of H^- ions. Ionic hydrides react with water and so can only be used in moisture-free conditions. The reactivity of group I metal hydrides increases with increasing atomic number.^[9] The ionic metal hydrides are white, high melting temperature solids which generally decompose at temperatures which are too high to be useful for hydrogen storage. For example, LiH contains 12.5 wt% hydrogen, melts at 680 °C and desorbs hydrogen at

910 °C with an equilibrium pressure of 1 bar. The dehydrogenation enthalpy is $190 \text{ kJ (mol H}_2\text{)}^{-1}$.^[9, 14] As with other hydrides, the destabilising effect of adding additives to binary hydrides in order to form alloys on dehydrogenation has been investigated. The dehydrogenation / rehydrogenation cycle is then between the hydride and the alloy instead of the elemental metal. For this reason, the effect of adding silicon to LiH and CaH₂ has been investigated. LiH forms a range of lithium-silicon alloys, for example LiSi, Li₁₂Si₇, Li₇Si₃, Li₁₃Si₄, and Li₂₂Si₅, with the result that the dehydrogenation enthalpy is lowered to $120 \text{ kJ (mol H}_2\text{)}^{-1}$ and hydrogen is desorbed at 470 °C. However, the gravimetric hydrogen density of the system is also reduced to between 2.8 wt% and 7 wt%.^[14]

Another method for potentially reducing the dehydrogenation enthalpy is to reduce the particle size. Mechanical milling can be used to produce metal hydride nanoparticles but a broad particle size distribution is normally produced and the smallest particles at ~100 nm are still too large to make a significant difference to the dehydrogenation enthalpy.^[14] Alternatively metal hydrides have been integrated into nanoporous scaffolds producing particle sizes down to 2 nm. Interactions between the metal hydride and the scaffold and defects created due to the enforced nanostructure lower the dehydrogenation enthalpy.^[14]

The ionic hydrides also include complex hydrides such as metal amides, NH₂⁻; alanates, AlH₄⁻ and borohydrides, BH₄⁻. In a complex hydride, the hydrogen atoms are covalently bonded to another element to form a complex ion and if this element is more electronegative than hydrogen, the hydrogen will adopt a positive charge, for example in the NH₂⁻ ion. In general, complex hydrides can be found that contain a high weight percentage of hydrogen but it is released at too high a temperature and hydrogen release is not reversible (the hydrogen storage system could not be simply

recharged by exposing it to a hydrogen pressure). Lithium amide, LiNH_2 , reversibly releases 6.5 wt% hydrogen at 255 °C according to Equation 1.1.^[15]



Lithium alanate, LiAlH_4 , irreversibly releases 8 wt% hydrogen at 200 °C. The hydrogen is released in two stages via Equation 1.2 and Equation 1.3. The first stage occurs between 190 °C and 220 °C and the second stage between 230 °C and 280 °C.^[16]



NaAlH_4 is thought to release hydrogen at 210 °C but melts at 183 °C, potentially making the system difficult to handle. NaAlH_4 is prepared commercially using a solution of NaH and activated aluminium in THF solution under hydrogen; thus demonstrating that rehydrogenation from NaH is possible, however the hydrogen capacity of the material decreases after a few dehydrogenation / rehydrogenation cycles.^[16]

In general, borohydrides contain more hydrogen than alanates and amides (Figure 1.2) and are relatively inexpensive.^[17] LiBH_4 for example, contains 18.5 wt% hydrogen, but needs to be heated to around 400 °C in order to release the hydrogen by thermal decomposition. The reaction is only expected to be reversible under extreme conditions (using either a high hydrogen pressure or heating above 400 °C under 1 bar hydrogen).^[18]

Much work has been carried out investigating the effects of adding impurities such as metal oxides, halides and hydrides to complex hydrides in an attempt to destabilise the compounds or catalyse decomposition so that hydrogen is released at a lower temperature.^[3, 15] Züttel *et al.* found that when SiO_2 powder was mixed with LiBH_4 ,

hydrogen desorption began at lower temperatures with 9 wt% hydrogen released below 400 °C^[19]. Vajo *et al.* found that adding MgH₂ to LiBH₄ lowered the enthalpy of dehydrogenation and hydrogenation by 25 kJ (mol H₂)⁻¹ making the process more reversible^[18]. Binary combinations of ionic hydrides such as LiBH₄/LiNH₂ and Mg(NH₂)₂/LiH have also been investigated as methods to destabilise the hydrides, usually via the formation of stable dehydrogenation products.^[14]

An alternative method for accelerating hydrogen release is to improve the mobility of the H⁺ and H⁻ ions within the hydrides, for example by combining CaH₂ and LiNH₂. On heating, the H⁻ ions in CaH₂ become highly mobile due to a small number of dehydrogenation vacancies and rapidly combine with H⁺ ions from LiNH₂ to release H₂. This also prevents the H⁺ ions filling Li⁺ vacancies left by the mobile Li⁺ ions.^[14]

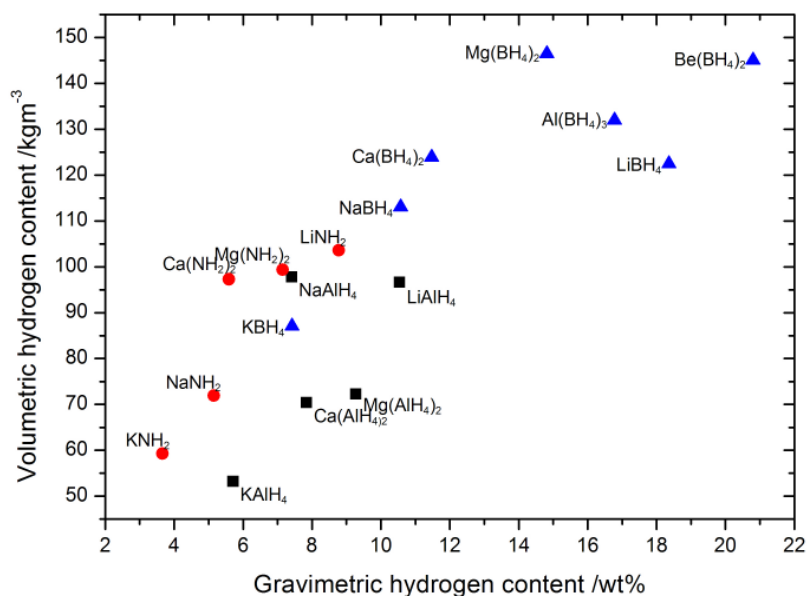


Figure 1.2 A comparison of hydrogen contents for amides, alanates and borohydrides

1.4 Borohydrides

1.4.1 Overview of the borohydrides

1.4.1.1 General properties

Borohydrides, alternatively known as tetrahydroborates or tetrahydridoborates are classically thought to consist of a positive metal cation M^+ and a negative tetrahedral BH_4^- anion. The alkali (group I) metal borohydrides are ionic in character compared to group III and transition metal borohydrides which are covalent, the alkali earth (group II) metal borohydrides are intermediate, they are still ionic but have more covalent character than the alkali metal compounds.^[20]

The co-ordination number of the metal cation within a borohydride varies with its ionic radius suggesting that the borohydride ion does not exhibit a strong preference for co-ordination number. Small ions such as beryllium and aluminium co-ordinate to three borohydride ions, lithium and magnesium to four ions, sodium, potassium and calcium can co-ordinate to six borohydride ions.^[21]

The first significant research into the borohydrides was completed by Schlesinger *et al.* during the 1940s under contract to the United States National Defense Research Committee, initially focusing on uranium compounds. This work included the syntheses of lithium, sodium, potassium and uranium borohydrides.^[22] Further borohydride research was carried out in the USSR during the Cold War era, including early syntheses of calcium and strontium borohydride.^[23-27]

In vibrational spectroscopy, borohydrides typically show signals at around 2300 cm^{-1} for B-H bond stretching and 1100 cm^{-1} for B-H bond bending. Solution state ^1H NMR shows a quartet of peaks at 1 ppm to 2 ppm due to the coupling of the protons to

boron-11 ($I = 3/2$).^[28] ^{11}B NMR resonances from borohydrides are observed in the range -26 ppm to -45 ppm.^[29]

The alkali and alkali earth metal borohydrides are white, crystalline solids. Borohydrides are sensitive to moisture in the atmosphere, being slowly hydrolysed to borates. Borohydrides are not sensitive to oxygen but for applications and experiments where a high purity is necessary, they should be handled using inert atmosphere techniques to prevent exposure to moist air.

1.4.1.2 Hydrogen release

Hydrogen is released from the borohydrides by thermal decomposition via a variety of routes shown by Equation 1.4 to Equation 1.7. The route is dependent on factors such as pressure and decomposition temperature. Borohydride decomposition temperatures are in the range of 85 °C ($\text{Zn}(\text{BH}_4)_2$ ^[30]) to 500 °C (KBH_4 ^[19]).



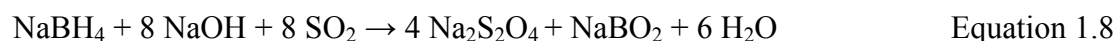
Compared to the interstitial metal hydrides where the structure does not change significantly with the removal or addition of hydrogen, in the borohydrides, hydrogen is only released by decomposition creating a new compound.^[20] The thermal behaviour of each of the borohydrides investigated in this thesis is discussed in the individual introductions (sections 1.5.1 to 1.6.3).

Hydrogen can also be released from borohydrides by hydrolysis, their reaction with water. Research on hydrolysis has particularly focused on NaBH_4 ; the hydrolysis of NaBH_4 was used commercially by Millenium Cell (see section 1.5.2).^[31]

1.4.1.3 Other applications

Apart from being potential hydrogen storage materials, the main modern interest in borohydrides comes from their use as organic reducing agents. This is particularly the case with sodium borohydride, NaBH_4 . NaBH_4 is used to reduce aldehydes and ketones to alcohols but will not reduce esters, amides or carboxylic acids.^[32]

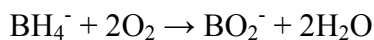
NaBH_4 can be used in the bleaching of wood pulp. Carbonyl groups such as aldehydes and ketones are involved in the process which makes paper turn yellow as it ages. NaBH_4 is used to reduce these groups, preventing this aging process.^[33] Alternatively, NaBH_4 is used to produce sodium hydrosulfite, according to Equation 1.8, which is also used in the wood pulp bleaching process.^[34]



Borohydrides can be used in redox reactions to fuel direct borohydride fuel cells. The equilibrium voltage of a direct borohydride fuel cell is about 1.6 V per mole of borohydride ions compared to approximately 1.24 V per two moles hydrogen (one mole borohydride ions) for a hydrogen fuel cell.^[35] Therefore it is possible that more energy could be produced from a direct borohydride fuel cell than from a hydrogen fuel cell fuelled with hydrogen produced from borohydrides.^[36]

Although borohydrides are rapidly hydrolysed in acid or neutral conditions, they are stable in alkaline solutions as used in a direct borohydride fuel cell.^[35] The borohydride oxidation reaction occurs at the anode according to Equation 1.9. The cathode reaction occurs according to Equation 1.10 with the overall reaction given by Equation 1.11. Borate is considered to be an environmentally acceptable by-product and could potentially be converted back to the borohydride.^[35]





Equation 1.11

1.5 Group I borohydrides

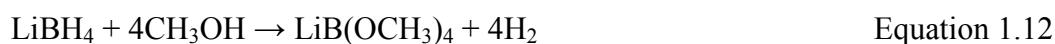
Until recently, the majority of borohydride research has focused on the group I borohydrides.

1.5.1 Introduction to lithium borohydride

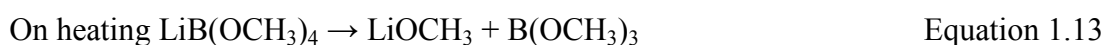
Lithium borohydride, LiBH_4 is the lightest metal borohydride and contains the greatest gravimetric density of hydrogen, 18.5 wt% (121 kg m^{-3}). Consequently, LiBH_4 has been the focus of much hydrogen storage research ^[17-19, 37, 38] and is the logical starting point for a study of alkali and alkali earth metal borohydrides.

1.5.1.1 Synthesis

The first reported synthesis of an alkali metal borohydride was LiBH_4 in 1940 by Schlesinger and Brown from ethyllithium ($\text{CH}_3\text{CH}_2\text{Li}$) and diborane (B_2H_6).^[39] This work was carried out as an extension to the synthesis of $\text{Be}(\text{BH}_4)_2$ and $\text{Al}(\text{BH}_4)_3$. Measured volumes of diborane were added to a reaction flask containing ethyllithium at two hourly intervals. The reaction occurred at room temperature producing a variety of ethyl derivatives of diborane but LiBH_4 was distinct because it was still stable at 240°C . LiBH_4 was identified by its reaction with methanol (Equation 1.12 and Equation 1.13) and also by comparison of the composition of the other more volatile products with those of the starting materials.^[39]



Equation 1.12



Equation 1.13

The reaction between ethyl lithium and diborane had many disadvantages; ethyllithium was difficult to prepare, the reaction was slow and a large excess of diborane was required. Consequently, Schlesinger *et al.* developed a new synthesis route where diborane was reacted with lithium hydride dissolved in ether, (no reaction occurs without the use of solvent). The reaction occurs at room temperature and atmospheric pressure according to Equation 1.14. The lithium borohydride solvent adduct is soluble in ether but the by-products of the reaction are insoluble, making purification simple. The solvent adduct is easily removed by heating under vacuum to between 70 °C and 100 °C. This reaction provides a synthetic route to a clean source of LiBH₄ in reasonable quantities; the reactions were carried out in 1g batches.^[22, 40]



Further work by Schlesinger *et al.* showed that LiBH₄ could also be produced by a metathesis reaction between NaBH₄ and a slight excess of LiCl refluxed in either ethylamine, methylamine or isopropylamine. NaCl formed a precipitate so the solution could be filtered and then LiBH₄ extracted using ether. The yield of LiBH₄ was 90-95 % with a purity of 97-98 %.^[41]

Synthesis of LiBH₄ from NaBH₄ and lithium halides (Equation 1.15) attracted commercial interest due to the relatively low cost of NaBH₄; this led to further investigation of these reactions. The reactivity of the lithium halides towards the reaction decreased in the order LiBr > LiI > LiCl. The reaction was found to proceed most easily in isopropylamine but desolvating the product was difficult. Ether was much easier to remove from the product but neither NaBH₄ or LiCl are soluble in ether, hindering the reaction. The reaction was very effective if LiBr or LiI were used. Reactions could be carried out either at room temperature or under reflux. For scaled

up reactions where a mechanical stirrer was used instead of a magnetic stirrer, glass beads were used to reproduce the abrasive effect of the magnetic stirrer.^[42]

Now LiBH_4 is synthesised commercially by a metathesis reaction in either ether or isopropyl amine solution from NaBH_4 and a lithium halide, LiX , (Equation 1.15).^[43]



1.5.1.1.1 Synthesis from the elements

In 2005, Orimo *et al.* reported the rehydrogenation of a dehydrided sample of LiBH_4 . LiBH_4 was dehydrided under 10 bar hydrogen at 600 °C for five minutes. The dehydrogenated sample contained LiH identified by X-ray diffraction and was assumed to contain amorphous boron. The sample was then rehydrided under 350 bar hydrogen at 600 °C for 12 hours. After rehydrogenation, only small Bragg peaks relating to LiBH_4 were observed by X-ray diffraction, suggesting that LiBH_4 may have become amorphous. However the Raman spectrum of the sample was consistent with LiBH_4 .^[44]

In 2008, Friedrichs *et al.* reported the synthesis of LiBH_4 and LiBD_4 directly from the elements according to Equation 1.16. Crystalline boron powder was mechanically milled and then manually ground together with lithium using a pestle and mortar within an argon filled glove box. The molar $\text{Li}:\text{B}$ ratio was 8:5. The mixture was heated for 60 hours to 330 °C under an argon atmosphere to form LiB_3 with excess lithium. Next, the mixture was heated for a further 60 hours to 450 °C to form Li_7B_6 with excess lithium. Samples of lithium, the unheated Li-B mixture, LiB_3 and Li_7B_6 were then heated to 700 °C in a sealed system with a room temperature starting pressure of 150 bar hydrogen. The level of hydrogen absorption was monitored throughout the experiments. Lithium did not absorb hydrogen until 150 °C, when a small amount of hydrogen was absorbed, this continued until 670 °C when sufficient

hydrogen was rapidly absorbed to form LiH. The Li-B mixture showed similar behaviour but also slowly absorbed hydrogen at room temperature and continued to absorb enough hydrogen to form LiBH₄ and LiH from the excess lithium. This pattern of hydrogen absorption was thought to be the result of a layer of LiH forming on the surface of the material, blocking further hydrogen absorption. At 670 °C, this layer melted so further hydrogen absorption could rapidly occur. The LiB₃ and Li₇B₆ samples showed an increase in the rate of hydrogen absorption at 550 °C but there was no abrupt hydrogen absorption due to the absence of elemental lithium in the samples. LiB₃ absorbed more hydrogen, faster, at lower temperatures than Li₇B₆ producing more LiBH₄ relative to the amount of LiH, possibly suggesting two different reaction mechanisms. LiBD₄ was prepared using the same method. This direct synthesis method from the elements provides a solvent-free synthesis route eliminating the possibility of solvate formation and may also be used to produce isotopically enriched compound. The absence of by-products and solvates dramatically simplifies the procedure to purify the product.^[43]



Remhof *et al.* (2008) carried out an in-situ neutron diffraction study of the formation of LiBD₄ from the elements. This suggested that the reaction occurred in a series of stages characterised by increased rates of deuterium absorption and also changes in the neutron diffraction data. First, the LiB intermediate reacted with deuterium to form LiD at 200 °C (this is also close to the melting temperature of lithium), releasing boron which was then in a completely amorphous state. At 350 °C, the boron and LiD began to combine to form LiBD₄ whilst at the same time more LiD was formed.^[45] Boron has been shown to catalyse the decomposition of LiBH₄ so that the reaction ends around 350 °C instead of 500 °C, this is thought to occur by stabilising the

intermediate decomposition products which may form such as $\text{Li}_2\text{B}_{12}\text{H}_{12}$, possibly by providing a nucleation seed.^[46]

Züttel *et al.* proposed two reaction pathways for the formation of LiBH_4 from LiH , boron and hydrogen. Either LiH reacts with boron to form an intermediate which is then further hydrogenated or boron and hydrogen react to form diborane which is known to react with LiH to produce LiBH_4 . The formation of diborane is unlikely because the reaction is endothermic and would require higher temperatures and pressures than have been observed. Also boron is generally kinetically inert. Consequently, hydrogenation of a Li-B-H intermediate is the most likely reaction pathway.^[20]

Çakanyildirim and Gürü reported the synthesis of LiBH_4 in 2008 by mechanically milling lithium and boron together and then exposing the mixture to 60 bar hydrogen. Milling lithium and boron together was thought to produce LiB . The pressure vessel was charged and evacuated with 60 bar hydrogen three times to compensate for hydrogen adsorption onto the walls of the vessel and possible leakage. A molar ratio of $\text{B/Li} = 0.214$ produced the highest yield of LiBH_4 determined by FTIR and hydrogen desorption.^[47]

In 2009, Agresti and Khandelwal reported the synthesis of LiBH_4 by mechanically milling LiH and boron under 10.1 bar hydrogen for 138 hours. The hydrogen pressure was periodically topped up. The yield determined by hydrogen desorption from the sample was 27 wt%.^[48]

Recently, Haiping *et al.* have reported the synthesis of thin films of LiBH_4 by pulsed laser deposition. A LiB source was used with a molar ratio $\text{B/Li} = 0.25$. Different hydrogen pressures between 0.05 and 0.7 mbar were used. At 0.7 mbar and room temperature, the yield of LiBH_4 was 74.4 wt%. $\text{Li}_2\text{B}_{12}\text{H}_{12}$ and LiB were identified

during the film formation process. The films were analysed by Raman, FTIR and X-ray diffraction.^[49]

1.5.1.2 Structure

Harris *et al.* (1947) first investigated the crystal structure of LiBH₄ by X-ray diffraction using Cu K_α radiation, as a result of communication with Schlesinger. They determined the structure to be orthorhombic (space group *Pcmn*, $a = 6.81$ Å, $b = 4.43$ Å, $c = 7.17$ Å). Knowing the density of LiBH₄ to be 0.66 gcm⁻³, four formula units were expected within the unit cell. Atomic positions were not refined and co-ordinates were not published but the boron atoms were found to be in a distorted tetrahedron around the lithium atom with two Li-B distances of 2.47 Å and two at 2.56 Å; the B-Li-B angles ranged from 97° to 116°. The hydrogen atoms were thought to be arranged so that the lithium atom was surrounded by four hydrogen atoms, one from each borohydride ion.^[50]

In 1971, Semenenko *et al.* published indexed unit cells for both a room temperature ($a = 6.80$ Å, $b = 4.44(1)$ Å, $c = 7.26$ Å, $V = 219.2$ Å³ at 20 °C) and a high temperature structure of LiBH₄ using diffraction patterns from a 86 mm diameter MGU high-temperature X-ray camera. The high temperature structure was thought to be tetragonal ($a = 4.93$ Å, $c = 11.32(1)$ Å, $V = 275.1$ Å³ at 150 °C). The phase transformation was stated to be at 108 °C and was reversible. If the sample was cooled below the transition temperature the room temperature phase reformed.^[23]

In 2002, Soulié *et al.* published refined structures of both phases of LiBH₄ determined from powder synchrotron X-ray diffraction. The room temperature structure of LiBH₄ was determined to be orthorhombic with the space group, *Pnma* ($a = 7.17858(4)$ Å, $b = 4.43686(2)$ Å, $c = 6.80321(4)$ Å and $V = 216.685(3)$ Å³ at 20 °C) (Figure 1.3). The lithium cations and borohydride anions were both surrounded tetrahedrally by

four ions of the opposite charge. The point symmetry of the borohydride ions was m and the borohydride ion shape was found to be strongly distorted with B-H bond lengths varying from 1.04(2) Å to 1.28(1) Å and H-B-H angles varying from 85° to 120°.^[51]

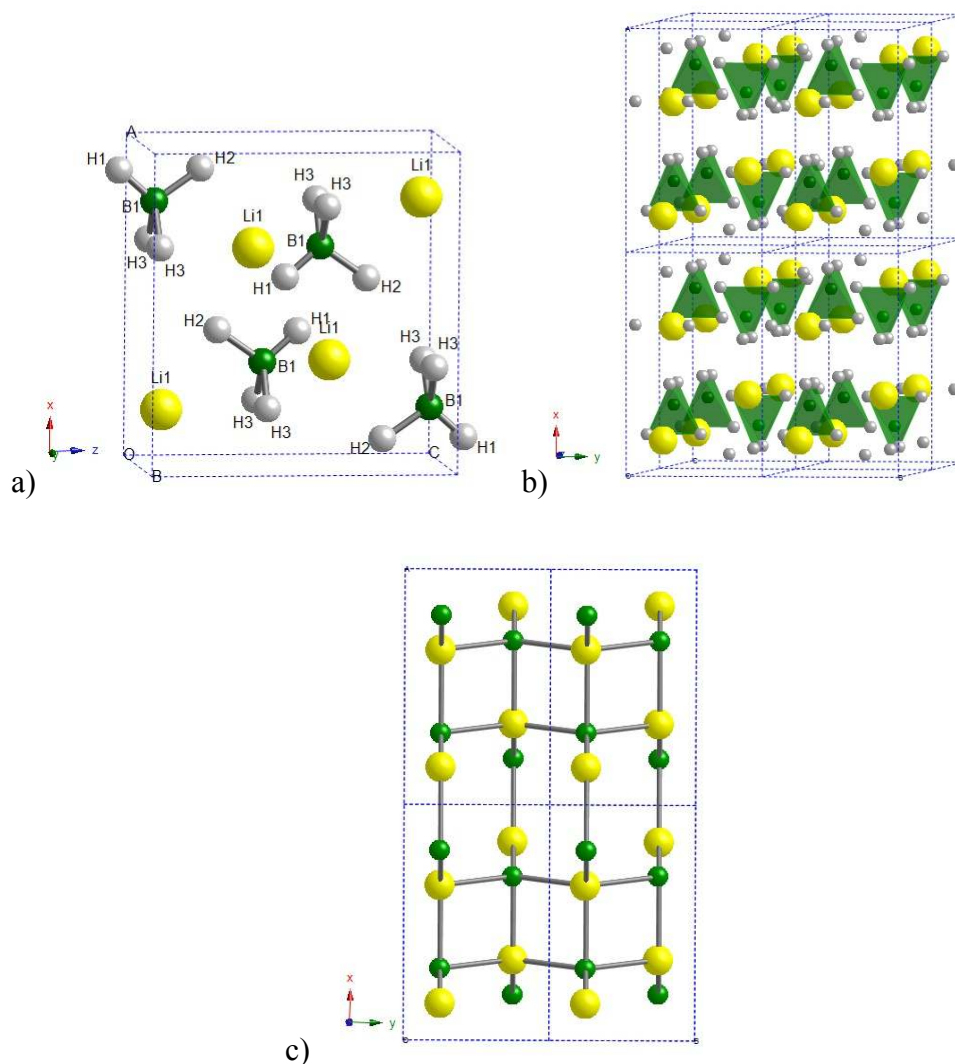


Figure 1.3 The structure of room temperature orthorhombic LiBH_4 ^[51] (Li yellow, B green, H grey) a) showing the composition of the unit cell (two hydrogen atoms are located on a mirror plane at $y = 0.25$, the other two hydrogen atoms are mirror images and so can be generated from a single atomic position), b) showing the orientation of borohydride ion tetrahedra and c) showing the arrangement of lithium ions and boron atoms within the lattice.

Soulié *et al.* refined the atomic positions for the high temperature phase within the hexagonal space group $P6_3mc$ with cell parameters, $a = 4.27631(5) \text{ \AA}$, $c = 6.94844(8) \text{ \AA}$ and $V = 110.041(4) \text{ \AA}^3$ (Figure 1.4). The unit cell contains two formula units; each ion is surrounded by three equatorial and two axial ions of the opposite charge. The borohydride units were thought to be more symmetrical in the high temperature phase with point symmetry $3m$; B-H bond lengths were found to be in the range $1.27 \text{ \AA}$ to $1.29 \text{ \AA}$ and H-B-H angles in the range 106° to 112° . The phase transformation is first-order and involves a contraction along the orthorhombic a (hexagonal c) axis and an expansion in the orthorhombic bc (hexagonal basal) plane.^[51]

Hartman *et al.* carried out the first neutron powder diffraction study of $^7\text{Li}^{11}\text{BD}_4$ and also collected neutron vibrational spectroscopy data from a sample of $^7\text{Li}^{11}\text{BH}_4$. At -269.5°C , the borohydride ions were closer to ideal tetrahedra than was observed by Soulié *et al.*. The D-B-D bond angles ranged from $107.2(3)^\circ$ to $111.7(4)^\circ$. At 87°C , the sample was still in the $Pnma$ space group but the atomic displacement ellipsoids within the borohydride ions were much larger than at -269.5°C . At 127°C the diffraction data were refined within the $P6_3mc$ space group. The hydrogen atoms had large atomic displacement ellipsoids suggesting that the borohydride units may be disordered. The neutron vibrational spectroscopy data shows two internal vibrational modes for the borohydride ions.^[52]

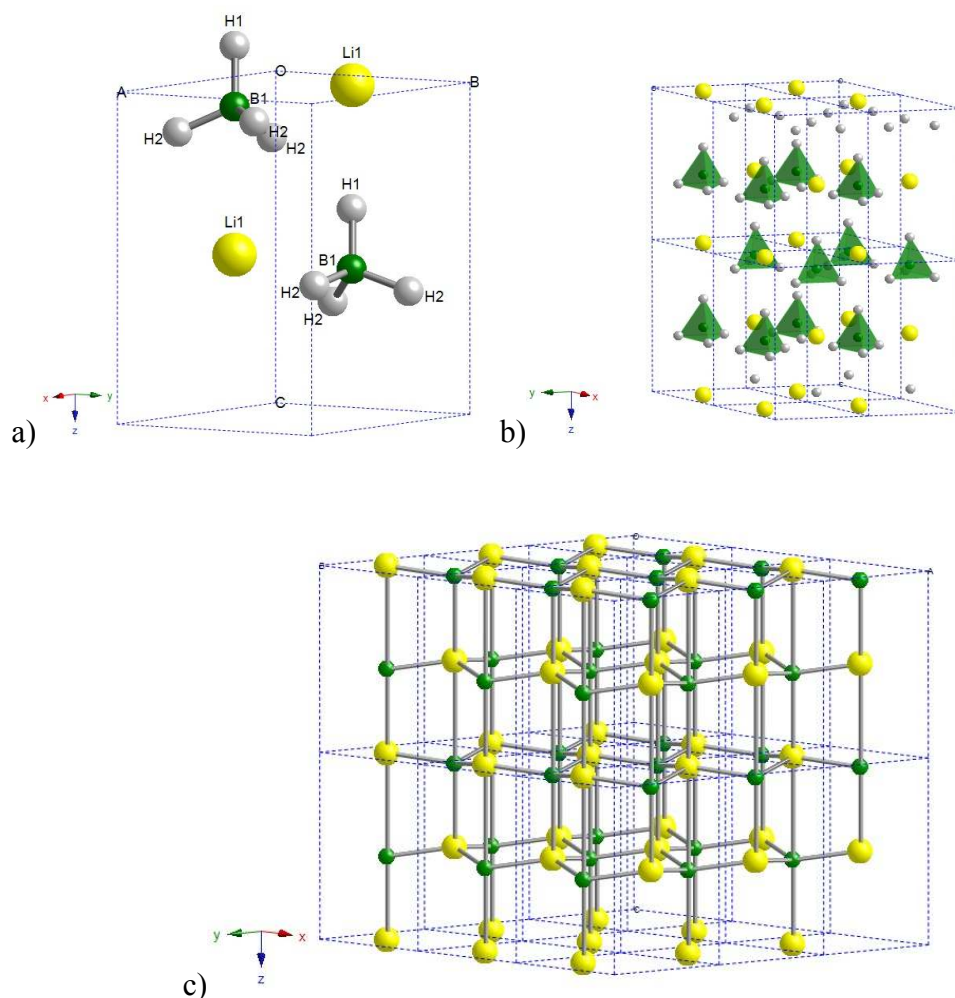


Figure 1.4 The structure of hexagonal high temperature LiBH_4 , (Li yellow, B green, H grey)^[51] a) showing the composition of the unit cell (one hydrogen atom is located on a three-fold rotational axis, the other three hydrogen atoms are generated from a single atomic position by rotation around this axis), b) showing the orientation of borohydride ion tetrahedra and c) showing the arrangement of lithium ions and boron atoms within the lattice.

A theoretical study in 2004 found the $P6_3mc$ phase to be unstable and suggested that the space group of the high temperature phase should be Cc .^[53]

In 2008 a neutron powder diffraction study by Buchter *et al.* using LiBD_4 (natural abundance of boron) at -263°C and 29°C showed the borohydride ions to be nearly ideal tetrahedra with a variation in B-D length of less than 4 %.^[54]

Also in 2008, Filinchuk *et al.* reported the first single crystal synchrotron study of the high temperature phase of LiBH_4 at 262 °C combined with a new single crystal study of the low temperature phase at -48 °C, and a powder diffraction study across the temperature range -193 °C to 227 °C. More information can be extracted from a single crystal study than from powder diffraction where Bragg reflections can overlap but in order to obtain the high temperature structure, the crystal had to be grown above the phase transition temperature. Consequently this study was able to confirm the $P6_3mc$ space group of the high temperature phase. The single crystal studies showed nearly ideal tetrahedra for the borohydride ions in both phases but the high temperature phase had large atomic displacement ellipsoids perpendicular to the B-H bonds showing that the borohydride ions were disordered but also rotated as rigid bodies. The *in-situ* powder diffraction study showed a decrease in the volume per asymmetric unit at the phase change which was observed to occur at 108 °C. Although the high temperature phase shows relatively linear increases in the cell parameters with increasing temperature, the low temperature phase shows non-linear and anisotropic expansion with the b parameter decreasing with increasing temperature.^[55]

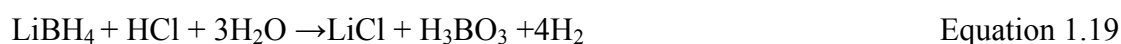
1.5.1.3 Thermodynamics

The standard enthalpy of formation of LiBH_4 (Equation 1.17) and the standard enthalpy of reaction (Equation 1.18) have been reported by several groups as discussed below. The values are summarised in Table 1.1.



In 1949, Davis *et al.* determined the enthalpy of formation of LiBH_4 by measuring the enthalpy of the reaction of LiBH_4 with HCl within a bomb calorimeter, using the

known formation enthalpies of all of the other compounds involved (Equation 1.19). The formation enthalpy was determined to be $-184.7 \text{ kJ mol}^{-1}$.^[56] Later, in 1963, Smith *et al.* recalculated the formation enthalpy to be $-194.0 \text{ kJ mol}^{-1}$ from the same experiment and combined with the formation enthalpy of LiH ($-90.7 \text{ kJ mol}^{-1}$) determined the standard enthalpy of reaction to be $68.9 \text{ kJ (mol H}_2\text{)}^{-1}$ ($\Delta S_r^0 = 100.3 \text{ J K}^{-1} \text{ (mol H}_2\text{)}^{-1}$).^[57]



The US National Institute of Standards and Technology states the formation enthalpy of LiBH₄ to be $-190.46 \text{ kJ mol}^{-1}$, the entropy to be $75.88 \text{ J K}^{-1} \text{ mol}^{-1}$ and based on the values for LiH the reaction enthalpy and entropy to be $66.6 \text{ kJ (mol H}_2\text{)}^{-1}$ and $97.4 \text{ J K}^{-1} \text{ (mol H}_2\text{)}^{-1}$ respectively.^[58]

More recently, Miwa *et al.* estimated the enthalpy of formation including zero point energies from first principles to be -160 kJ mol^{-1} . Combined with the enthalpy of formation of LiH, the enthalpy of reaction was calculated to be $56 \text{ kJ (mol H}_2\text{)}^{-1}$.^[59]

Nakamori *et al.* established a correlation between the Pauling electronegativity, χ_P of the cation and the formation enthalpy of the borohydride with the linear relationship $\Delta H_{\text{boro}} = 248.7\chi_P - 390.8$ with the units $\text{kJ (mol BH}_4\text{)}^{-1}$, this results in a value of $-147.1 \text{ kJ mol}^{-1}$ for LiBH₄ using a value of 0.98 for the electronegativity of lithium.^[60]

Mauron *et al.* determined the reaction enthalpy of LiBH₄ using pcT (pressure, concentration and temperature) measurements. This involved pressurising an autoclave containing a sample of LiBH₄ with hydrogen to the required pressure (e.g. 20 bar), heating to the required temperature (temperature intervals between 410 °C and 520 °C) and then releasing the pressure at a variety of hydrogen flow rates whilst monitoring the pressure. Plateaus in the pressure indicate an equilibrium between hydrogen being desorbed from the sample and released from the autoclave.

The enthalpy and entropy of the reaction can be calculated from the van't Hoff equation (Equation 1.20). The values determined in this way were $\Delta H_r = 74 \text{ kJ (mol H}_2\text{)}^{-1}$ and $\Delta S_r = 115 \text{ JK}^{-1} \text{ (mol H}_2\text{)}^{-1}$, these values may be higher than other published values because the uncatalysed dehydrogenation reaction is very slow and so the equilibrium may not always have been reached.^[58]

$$\ln\left(\frac{p_{eq}}{p_0}\right) = \frac{\Delta_r H}{R} \bullet \frac{1}{T} - \frac{\Delta_r S}{R} \quad \text{Equation 1.20}$$

Table 1.1 Standard enthalpies of formation and reaction for LiBH₄

$\Delta H_f^0 / \text{kJ mol}^{-1}$	$\Delta H_r^0 / \text{kJ mol}^{-1}$
-184.7 ^[56]	
-194.0 ^[57]	68.9 ^[57]
-190.46 ^[58]	66.6 ^[58]
-160 ^[59]	56 ^[59]
-147.1 ^[60]	74 ^[58]

1.5.1.4 Thermal behaviour

On heating, LiBH₄ first undergoes an orthorhombic to hexagonal phase transformation at 108 °C^[55] which is accompanied by the release of a small amount (0.3 wt%) of hydrogen gas.^[19] The phase change is slightly endothermic (4.18 kJ mol⁻¹).^[20]

LiBH₄ melts around 270 °C but no hydrogen loss has been observed at this temperature.^[19]

Based on pcT measurements, Mauron *et al.* calculated that under 1 bar H₂, LiBH₄ is expected to decompose to LiH and boron, releasing hydrogen according to Equation 1.21 at 370 °C.^[58]



Züttel *et al.* conducted desorption studies of LiBH_4 under a flowing inert gas. Most of the hydrogen was released in two stages, the first beginning at 320 °C and the second stage between 400 °C and 500 °C. A total of 9 wt% hydrogen was reported to be released,^[37] which is equivalent to half of the total hydrogen content of LiBH_4 .

Orimo *et al.* investigated the decomposition of LiBH_4 and found that an intermediate was formed at 427 °C when 11 wt% mass was lost. The Raman spectrum was consistent with a theoretical monoclinic structure of $\text{Li}_2\text{B}_{12}\text{H}_{12}$.^[61]

Work has been carried out investigating the effects of catalysts on the decomposition temperature of LiBH_4 ,^[17, 62] however this is outside of the scope of this thesis.

1.5.2 Introduction to sodium borohydride

Sodium borohydride, NaBH_4 , contains 10.6 wt% hydrogen. Although substantial, this is less than LiBH_4 . However NaBH_4 is much less expensive than LiBH_4 .^[63]

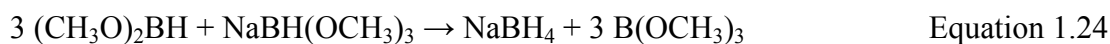
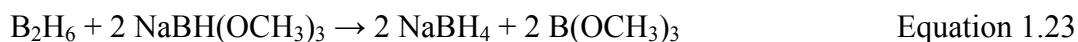
NaBH_4 has already been used commercially as a hydrogen source by Millenium Cell via its hydrolysis reaction.^[31] When NaBH_4 is dissolved in water in the presence of a ruthenium catalyst, it decomposes releasing hydrogen (Equation 1.22). This reaction has the advantage of occurring at room temperature whereas the thermal decomposition reaction temperature is too high for use with a fuel cell. Also, the hydrolysis reaction does not release any B_xH_y type by-products which would poison the PEM fuel cell catalyst and damage the membrane. Half of the hydrogen released comes from water but excess water is necessary to keep NaBH_4 in solution so a typical system contains 20 wt% NaBH_4 and 1 wt% NaOH to stabilise the solution resulting in a hydrogen storage capacity for the system of 4 wt%.^[64]



1.5.2.1 Synthesis

The first, reported synthesis of NaBH₄ was in 1949 by Kasper *et al.*^[65] However, the first crystal structure was published in 1947 by Soldate without stating how the sample was made.^[66] Kasper *et al.* reported the synthesis of NaBH₄ by shaking sodium amalgam in the presence of diborane gas for several days. The product was initially thought to be Na₂B₂H₆ but too much diborane had been absorbed and the Cu K_α X-ray diffraction pattern was consistent with that of Soldate.^[65, 66]

The synthesis of NaBH₄ was later reported in 1953 by Schlesinger *et al.* according to Equation 1.23. The reaction between diborane and sodium trimethoxyborohydride was very rapid, to the extent, that sodium trimethoxyborohydride could absorb nearly all the diborane from a stream of gas flowing over the sample. Equation 1.24, Equation 1.25 and Equation 1.26 are variations on the reaction which were also found to be successful. In contrast to LiBH₄, there was no reaction between NaH and B₂H₆ in ether.^[40]



However, NaBH₄ can be synthesised via the reaction of sodium hydride with diborane in diglyme (Equation 1.27)^[28].



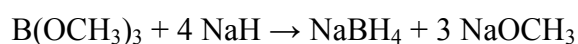
NaBH₄ can also be made from sodium hydride and a trialkyl borate (Equation 1.28).^[28]



NaBH_4 is commercially produced via the Schlesinger Process (Equation 1.29). This is a multi step process including the reduction of trialkylborate with sodium hydride (Equation 1.30). Sodium metal is produced by electrolysis of NaCl . Some of the reaction steps are exothermic so the overall reaction process could be made more energy efficient if the energy released was used elsewhere in the process.^[67]



Equation 1.29



Equation 1.30

1.5.2.2 Structure

Like all of the alkali metal borohydrides apart from LiBH_4 , NaBH_4 adopts a rock salt, face-centred-cubic structure at room temperature. At low temperatures, NaBH_4 distorts to a tetragonal structure. The space group of the high temperature structure has been debated and is dependent on the orientational disorder within the borohydride anions. All of the structures discussed here have octahedral co-ordination between the sodium and borohydride ions.^[21]

An order-disorder phase transition of NaBH_4 occurs around -83°C from a low temperature tetragonal phase to the room (high) temperature structure. The high temperature space group has been described as either $Fm-3m$ or $F-43m$. The $Fm-3m$ space group has the boron atoms situated on centres of inversion so each boron atom is co-ordinated to eight half occupancy hydrogen atoms, causing the structure to be intrinsically disordered. In the $F-43m$ space group the inversion centre is not present leaving four hydrogen atoms tetrahedrally co-ordinated around the boron atom, however the hydrogen atoms can still be disordered across two sites giving the same result as the $Fm-3m$ space group.^[68, 69]

A crystal structure of NaBH₄ was first reported by Soldate in 1947 determined by X-ray powder diffraction using Cu K_α radiation. The unit cell was identified as face centred cubic with $a = 6.151(9)$ Å containing four NaBH₄ molecules. The density was calculated to be 1.074 gcm⁻³. Based on intensity calculations from the sodium and boron atoms, two possible structures were proposed. The first structure located the boron atoms on octahedral sites meaning that the hydrogen atoms would be disordered over two sites, the second located the boron atoms on tetrahedral sites so that the borohydride ions were ordered. It was not possible to determine which the correct structure was; however the boron and sodium atoms were thought to be sufficiently separated to allow for free borohydride ion rotation. [66]

In 1954, Abrahams and Kalnajs completed an X-ray diffraction study of NaBH₄. The room temperature crystal structure was found to be in agreement with that proposed by Soldate with $a = 6.1635$ Å. Below -83 °C, the structure was identified to have a face-centred tetragonal unit cell which was converted to the conventional body centred unit cell by a 45° rotation around the c axis. The lattice parameters were $a = 4.354(5)$ Å and $c = 5.907(5)$ Å. [70]

Peterson suggested that room temperature NaBH₄ had the space group $Fm-3m$ based on single crystal neutron diffraction in 1965. The borohydride B-H lengths were 1.260 Å and the H-B-H angles were 109.5°. [69]

The room temperature structure of NaBD₄ was investigated by neutron powder diffraction by Davis and Kennard in 1985. It was concluded that the structure was disordered $F-43m$ where the borohydride ions had two different orientations but with the boron atoms on tetrahedral sites rather than $Fm-3m$ where the boron atoms are located on octahedral sites. The lattice parameter was 6.137(7) Å, the B-D distances were 1.160(7) Å and the D-B-D bond angles were 109.5(2)° at 22 °C. Details of the

structure are shown in Table 1.2.^[69] The structures of NaBH₄ in the space groups *Fm-3m* and *F-43m* are shown in Figure 1.5.

Table 1.2 The atomic co-ordinates of room temperature NaBD₄ in space group *F-43m*^[69]

Site	x/a	y/b	z/c	occ
Na	0	0	0	1.0
B	0.5	0.5	0.5	1.0
D1	0.3901(6)	0.3901(6)	0.3901(6)	0.5
D2	0.6099(6)	0.6099(6)	0.6099(6)	0.5

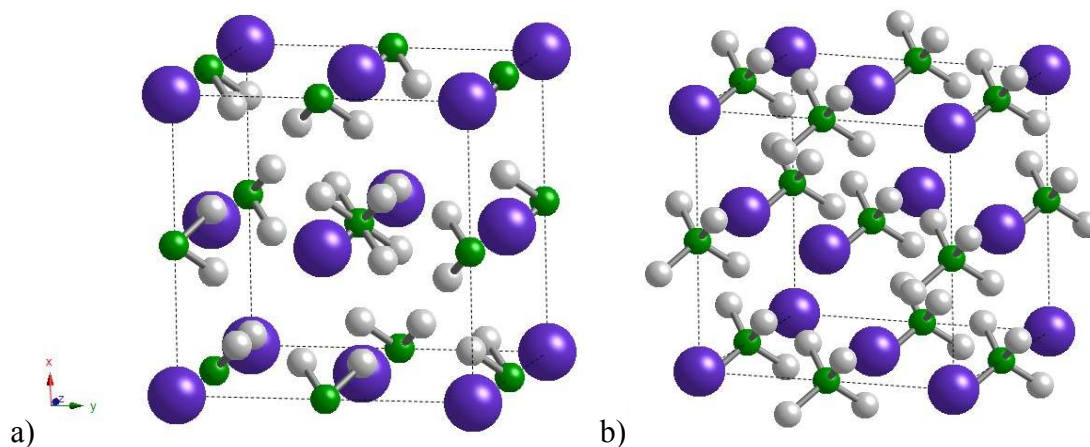


Figure 1.5 a) The *Fm-3m*^[68] and b) *F-43m*^[69] fully ordered structure of NaBH₄, showing sodium (blue), boron (green) and hydrogen (grey)

In 2001, Fischer and Züttel, proposed the space group *P-42₁c* for the low temperature phase of NaBD₄ from a neutron powder diffraction using natural abundance boron.^[71]

This work was continued in 2004 by Fischer *et al.* At -263 °C, NaBD₄ was identified in a tetragonal structure with lattice parameters of $a = 4.332(1)$ Å and $c = 5.869(1)$ Å.

$h+k+l = 2n$ peaks were observed in the diffraction pattern showing that the structure was not body centred but primitive (these peaks are systematically absent from body centred structures) and consequently the space group *P4₂/nmc* was assigned. The

borohydride units were ordered with the boron atoms located on tetrahedral sites. B-D separations were 1.220(1) Å. The atomic co-ordinates are give in Table 1.3.^[72]

Table 1.3 The atomic co-ordinates in the low temperature structure of NaBD₄ with the space group $P4_2/nmc$ (Origin choice 2)^[72]

Site	x/a	y/b	z/c	occ
Na	0.75	0.25	0.75	1.0
B	0.75	0.25	0.25	1.0
D	0.25	-0.0193(2)	-0.1308(1)	0.5

At 22 °C, NaBD₄ was identified to be in a cubic space group with lattice parameter $a = 6.148(1)$ Å. The B-D separations were 1.178(2) Å. The space group $Fm-3m$ was assigned which is a supergroup of $P4_2/nmc$.^[72]

In 2008, Ugrnani *et al.* modelled the room temperature structure of NaBH₄ using *ab initio* calculations. The lattice parameter was calculated to be 6.1440 Å and the distance between the boron and hydrogen atoms was 1.2182 Å.^[73]

Also in 2008, Filinchuk and Hagemann completed a synchrotron X-ray single crystal diffraction study of NaBH₄. The space group was identified as $Fm-3m$ with the lattice parameter $a = 6.13080(10)$ Å.^[68]

Table 1.4 The atomic co-ordinates of room temperature NaBH₄ in the space group $Fm-3m$ ^[68]

Site	x/a	y/b	z/c
Na	0	0	0
B	0	0.5	0
H	-0.103(2)	-0.397(2)	0.103(2)

Recently, Babanova *et al.* have completed a variable temperature synchrotron X-ray diffraction study of NaBH₄. The study confirms that the low temperature structure has the space group $P4_2/nmc$ by analysis of the $hk0$ reflections where $h + k = 2n$. The borohydride groups in this structure are fully ordered. The phase transformation to the cubic $Fm-3m$ structure was observed at -86 °C and was accompanied by a 0.4 % increase in volume and a 25 % increase in the volumetric expansion coefficient. The volume of the cubic unit cell increased linearly with increasing temperature. The phase transition was thought to be caused by a reduction in the number of repulsive H-H interactions. The number of these interactions is also reduced by the high temperature phase adopting the disordered $Fm-3m$ structure instead of the ordered $F-43m$ structure.^[74]

Density functional theory (DFT) calculations were completed for the structures of NaBH₄ by Kim and Sholl. The optimised unit cell of the high temperature structure had the lattice parameter $a = 6.02$ Å, which is 6.19 % smaller than the experimentally determined structure. DFT cannot calculate partially occupied sites so half the hydrogen sites were treated as occupied and the other half unoccupied. It was possible to rearrange the hydrogen atoms within the unit cell without changing the total energy of the material. The optimised unit cell of the low temperature structure was 2.52 % smaller than determined by experiment with lattice parameters of $a = 4.31$ Å and $c = 5.82$ Å.^[75]

At ambient temperatures with pressures between 6.3×10^4 bar and 7.1×10^4 bar, NaBH₄ has a tetragonal $P-42_1c$ structure ($a = 4.0864$ Å, $c = 5.5967$ Å) and above 8.9×10^4 bar there is an orthorhombic $Pnma$ structure ($a = 7.389$ Å, $b = 4.166$ Å, and $c = 5.633$ Å), this is the same space group as room temperature LiBH₄.^[76] However high pressure phases are beyond the scope of this thesis.

1.5.2.3 Thermodynamics

Urgnani *et al.* completed *ab initio* calculations based on the *Fm-3m* structure of NaBH₄. The formation of NaBH₄ from BH₃ and NaH according to Equation 1.31 was studied. BH₃ and NaH were also treated with the same DFT functional and basis sets in an attempt to reduce the effects of any systematic errors within the models. The total electronic energy, zero point energy, thermal effects on the zero point energy and the entropy were calculated for all three compounds (the latter two values at 27 °C). Using these values, estimates for ΔH and ΔG were calculated to be -188 kJ mol⁻¹ and -152 kJ mol⁻¹ respectively for the formation reaction in Equation 1.31. The standard enthalpy of formation (according to Equation 1.32) for NaBH₄ was calculated to be -192 kJ mol⁻¹. Combined with calculated values for NaH and BH₃ in a Hess thermodynamic cycle, ΔH for Equation 1.31 was also calculated from the standard formation enthalpy to be -224 kJ mol⁻¹. This value was thought to be in good agreement with the value of -188 kJ mol⁻¹ calculated from the electronic energy.^[73]



The CRC Handbook of Chemistry and Physics reports the thermodynamic values $\Delta H_f^0 = -188.6 \text{ J mol}^{-1}$, $\Delta G_f^0 = -123.9 \text{ kJ mol}^{-1}$, $S^0 = 101.3 \text{ J mol}^{-1} \text{ K}^{-1}$ and $C_p = 86.8 \text{ J mol}^{-1} \text{ K}^{-1}$.^[77]

Züttel *et al.* reported $\Delta H_f^0 = -191 \text{ kJ mol}^{-1}$ for NaBH₄.^[20] Nakamori *et al.* calculated the formation enthalpy to be -182 kJ mol⁻¹ based on the differences in total energy between the two sides of Equation 1.32.^[60]

Recently, Martelli *et al.* used pressure concentration isotherms of NaBH₄ between 600 °C and 700 °C to determine the enthalpy and entropy of the hydrogen desorption

reaction. The values determined were $\Delta H = -108 \pm 3 \text{ kJ mol}^{-1}$ of H_2 and $\Delta S = 133 \pm 3 \text{ J K}^{-1} \text{ mol}^{-1}$ of H_2 .^[78]

1.5.2.4 Thermal behaviour

An order-disorder phase transition associated with the re-ordering of borohydride tetrahedra occurs at -83°C in NaBH_4 from the low temperature tetragonal structure to the high temperature cubic structure.^[72]

In 1968, Stasinevich and Egorenko reported the melting temperature of NaBH_4 to be 505°C under pressures of hydrogen between 1 bar and 10 bar. This was thought to be a lower temperature than the decomposition reaction.^[73] A DSC measurement of NaBH_4 under 1 bar hydrogen, heating at $10^\circ\text{C min}^{-1}$ by Orimo *et al.* showed the melting temperature to be 497°C .^[79]

NaBH_4 is thought to decompose by a combination of Equation 1.33 and Equation 1.34.^[73]



Urgnani *et al.* heated NaBH_4 under vacuum with the apparatus connected to a mass spectrometer. Hydrogen was observed to be released in several stages, the first hydrogen release was at 150°C and a larger amount of hydrogen was released from 470°C , peaking above 500°C after the material had melted. Further hydrogen release was observed around 580°C .^[73]

A second sample of NaBH_4 was heated gradually under an inert atmosphere from room temperature to 475°C (below the melting temperature of NaBH_4). Hydrogen was released starting at 150°C , peaking at 240°C . The bulk of the hydrogen was released from 440°C continuing at 475°C . 10.4 wt% hydrogen was released which is the entire amount contained in NaBH_4 . B_2H_6 release was not observed. X-ray

diffraction of a sample taken after the first hydrogen release beginning at 150 °C only showed diffraction peaks related to NaBH₄. X-ray diffraction of the sample after decomposition only showed diffraction peaks relating to sodium, boron may also have been present but was not expected to result in diffraction peaks.^[73]

From their determination of the enthalpy and entropy of desorption (Section 1.5.2.3), Martelli *et al.* calculated the decomposition temperature of NaBH₄ to be $\Delta H/\Delta S = 534 \pm 10$ °C. The desorbed product consisted of a “soft, grey metallic material and a black powder”. The ratio of the weights of the two phases was consistent with a 1:1 ratio of Na:B. The identity of the sodium phase was confirmed by X-ray diffraction but the identity of the “boron” phase could not be confirmed. Unlike with LiBH₄, NaH was not expected as a decomposition product due to its lower thermodynamic stability relative to NaBH₄.^[78]

1.5.3 Introduction to potassium borohydride

Potassium borohydride, KBH₄ contains 7.4 wt% H₂. In addition to being investigated as a potential hydrogen storage material, KBH₄ is used as a reducing reagent in organic synthesis and in the synthesis of vitamin A^[80].

KBH₄ has also been investigated for use in organic light-emitting diodes. KBH₄ is thermally decomposed releasing metallic potassium which could be used as an electron injection material for the LED.^[81]

KBH₄ only hydrolyses slowly in air, the proportion of borohydride in a sample exposed to air decreased from 98.4 % to 96.7 % in 48 days. KBH₄ is soluble in liquid ammonia, water and ethanol but not in isopropylamine, ether, tetrahydrofuran and acetonitrile. The density of KBH₄ is 1.17 gcm⁻³.^[28]

1.5.3.1 Synthesis

The first reported synthesis of KBH_4 was by Schlesinger *et al.* in 1953. KBH_4 was made from diborane and potassium tetramethoxyborate at $-80\text{ }^\circ\text{C}$ according to Equation 1.35. Unlike the synthesis of NaBH_4 , potassium methoxide did not react with diborane.^[40]



KBH_4 forms as a precipitate when potassium hydroxide is added to an aqueous solution of NaBH_4 ^[28]. Alternatively, a methanol or ethanol solution of NaBH_4 can be mixed with a similar solution of potassium hydroxide at room temperature. Depending on the solvent used, potassium hydroxide can be replaced with potassium methoxide or another alkoxide, potassium iodide, bromide or acetate. The washed product is dried under vacuum at temperatures ranging from $70\text{ }^\circ\text{C}$ to $130\text{ }^\circ\text{C}$.^[82] This synthesis is also used commercially with a 85 % to 90 % yield.^[83]



Synthesis of KBH_4 from potassium hydride in the same way as NaBH_4 is not convenient due to the high reactivity of potassium hydride.^[82] In 1950, Goubeau *et al.* found that there was no reaction between potassium hydride and diborane between $-185\text{ }^\circ\text{C}$ and $200\text{ }^\circ\text{C}$ at pressures between 0.2 bar and 0.9 bar.^[28] However in 1962, Chamberlain patented the reaction in diglyme and other ethers under a nitrogen atmosphere at room temperature according to Equation 1.37.^[84]



More recently, the synthesis of KBH_4 has also been reported by mechanically grinding KBO_2 with excess MgH_2 . MgO is formed as a by-product according to Equation 1.38. The mixture was milled at 490 rpm for 120 minutes. KBH_4 was extracted by washing the milled mixture in anhydrous ethylenediamine. KBH_4 was

identified by solid state ^{11}B NMR and X-ray powder diffraction. A 35 % excess of MgH_2 was required for the KBH_4 yield to reach 100 %. If NaH and CaH_2 were used instead of MgH_2 , the yield was only about 1 %.^[80]



1.5.3.2 Structure

KBH_4 , like NaBH_4 has a cubic face centred rock salt structure. Unlike NaBH_4 , the structure of KBH_4 has not been published with a $F-43m$ space group.

The crystal structure of KBH_4 was first reported in 1954 by Abrahams and Kalnajs as face-centred-cubic with the lattice parameter 6.7272 Å at 25 °C. The structure was determined by single crystal $\text{Cu K}\alpha$ X-ray diffraction.^[70]

In 1999, Luck and Schelter published the crystal structure of KBH_4 in the space group $Fm-3m$ determined from single crystal $\text{Mo K}\alpha$ X-ray diffraction. At 20 °C the lattice parameters were $a = 6.7280(8)$ Å, $b = 6.7280(19)$ Å and $c = 6.7280(13)$ Å. Due to the symmetry of the boron site, there were eight half occupancy hydrogen atoms around the boron atom so the borohydride ions were intrinsically disordered. The B-H distance was 1.09(1) Å. The room temperature structure of KBH_4 is shown in Figure 1.6.^[85]

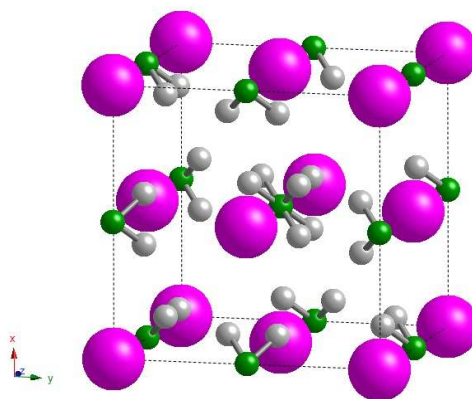


Figure 1.6 The room temperature and pressure structure of KBH_4 (K crimson, B green, H grey)^[85]

In 2004, Renaudin *et al.* reported an X-ray and neutron powder diffraction study of KBH_4 and a neutron powder diffraction study of KBD_4 . From the X-ray diffraction study, the structure of KBH_4 at 22 °C was identified in the $Fm-3m$ space group with the lattice parameter $a = 6.7306(1) \text{ \AA}$ and volume $304.90(1) \text{ \AA}^3$. There were four formula units per unit cell. A phase transition occurred between -208 °C and -203 °C. At -263 °C, KBH_4 was in the tetragonal $P4_2/nmc$ space group with lattice parameters $a = 4.7004(2) \text{ \AA}$ and $c = 6.5979(3) \text{ \AA}$ and volume $145.78(1) \text{ \AA}^3$. There were two formula units per unit cell. For KBD_4 , the lattice parameter at 22 °C was $6.7074(1) \text{ \AA}$ and at -263 °C the parameters were $a = 4.6836(1) \text{ \AA}$ and $c = 6.5707(2) \text{ \AA}$. For the neutron diffraction study, the lattice parameters were maintained at the values determined from the X-ray diffraction study. The atomic positions of the room temperature structure are shown in Table 1.5 and of the structure at -271.5 °C in Table 1.6. The B-D distances at -271.5 °C were $1.205(3) \text{ \AA}$ and $1.196(3) \text{ \AA}$ at 22 °C.^[86]

Table 1.5 The atomic positions within the $Fm-3m$ structure of KBD_4 ^[86]

Site	x/a	y/b	z/c	occ
K	0	0	0	1
B	0.5	0.5	0.5	1
D	0.6029(4)	0.6029(4)	0.6029(4)	0.5

Table 1.6 The atomic positions within the $P4_2/nmc$ structure of KBD_4 ^[86]

Site	x/a	y/b	z/c	occ
K	0.75	0.25	0.25	1
B	0.75	0.25	0.75	1
D	0.25	0.5400(6)	0.1440(5)	1

Recently, Kim and Sholl investigated the structures of KBH_4 by density functional theory (DFT) calculations. DFT cannot calculate partially occupied sites so half the hydrogen sites were treated as occupied and the other half unoccupied. The low temperature structure was calculated to have a unit cell that was 1.81 % larger than that determined from experimental data with lattice parameters of $a = 4.71 \text{ \AA}$ and $c = 6.61 \text{ \AA}$. The optimised room temperature unit cell was 0.93 % smaller than the experimentally determined structure with the lattice parameter $a = 6.69 \text{ \AA}$.^[75]

At a pressure of $3.8 \times 10^4 \text{ bar}$, the KBH_4 structure transforms to a tetragonal $P-42_1c$ space group ($a = 4.4754(2) \text{ \AA}$, $c = 6.363(2) \text{ \AA}$). At $7 \times 10^4 \text{ bar}$, the diffraction peaks relating to the tetragonal phase begin to split and by $11 \times 10^4 \text{ bar}$ the structure has converted to an orthorhombic $Pnma$ space group ($a = 6.976(6) \text{ \AA}$, $b = 4.933(4) \text{ \AA}$, $c = 5.111(3) \text{ \AA}$). This is the same sequence of structures with increasing pressure as is observed with NaBH_4 .^[87] However, high pressure phases are beyond the scope of this thesis.

1.5.3.3 Thermodynamics

The CRC Handbook of Chemistry and Physics reports the following thermodynamic values for KBH_4 , $\Delta H_f^0 = -227.4 \text{ kJ mol}^{-1}$, $\Delta G_f^0 = -160.3 \text{ kJ mol}^{-1}$, $S^0 = 106.3 \text{ J mol}^{-1} \text{ K}^{-1}$ and $C_p = 96.1 \text{ J mol}^{-1} \text{ K}^{-1}$.^[77]

Züttel *et al.* report the standard formation enthalpy of KBH_4 to be -229 kJ mol^{-1} .^[20]

Nakamori *et al.* calculated the enthalpy of formation of KBH_4 from the differences in energy of the two sides of Equation 1.39 to be -228 kJ mol^{-1} .^[60]

Xiao *et al.* calculated the formation enthalpy according to Equation 1.39 to be $-241.6 \text{ kJ mol}^{-1}$ from first principles calculations using the Vienna *ab initio* simulation package (VASP) code. The enthalpy of dehydrogenation for the reaction of Equation 1.39 in reverse was calculated to be $120.8 \text{ kJ mol}^{-1} \text{ H}_2$.^[88]

Zapol'skii *et al.* calculated the activation energy for thermal decomposition according to the reverse of Equation 1.39 to be 308 kJ mol^{-1} by measuring the rate of decomposition at different temperatures.^[89] Liu *et al.* calculated the Gibbs free energy for the same reaction to be -154 kJ mol^{-1} .^[81]



1.5.3.4 Thermal behaviour

Züttel *et al.* report that KBH_4 melts at 585°C but decomposes at 500°C .^[19] Orimo *et al.* report KBH_4 to melt at 607°C and decompose at 584°C .^[79] Xiao *et al.* report KBH_4 to decompose at 500°C according to Equation 1.40.^[88]

Liu *et al.* report the decomposition of KBH_4 to occur according to Equation 1.40 at 347°C and $1 \times 10^{-8} \text{ bar}$.^[81]



In 1967, Zapol'skii *et al.* reported KBH_4 to be completely stable up to 600°C . KBH_4 melted at 620°C and some hydrogen was released between 600°C and 620°C . A heating curve of KBH_4 was observed to show endothermic effects at 620°C and 695°C . The first effect was related to the melting of KBH_4 and the second to the start of the rapid decomposition of KBH_4 releasing hydrogen. Significant hydrogen release was observed from 640°C .^[90]

In 1968, Stasinevich and Egorenko completed a thermographic investigation of KBH_4 under a range of pressures. Two endothermic effects were observed. The temperature of the first effect was affected by the pressure and was not associated with hydrogen release. The second effect was associated with hydrogen release and its temperature was dependent on the pressure of the system. Therefore the first effect was thought to be the melting of KBH_4 occurring between 592°C and 625°C . The second effect was

suggested to be decomposition which at a pressure of 1 bar hydrogen was observed to begin at 680 °C. The decomposition temperature (in °C) was suggested to vary with pressure according to Equation 1.41.^[91]

$$\log(p_{atm}) = -\frac{4975}{T} + 5.19 \quad \text{Equation 1.41}$$

In 1970, Zapol'skii *et al.* further investigated the decomposition of KBH₄ by heating a sample in a furnace and recording the volume of gas released. Some decomposition was observed to occur between 557 °C and 600 °C according to Equation 1.40. At 557 °C, 10 % of the sample of KBH₄ had decomposed after 10 to 15 minutes, at 599 °C, 20 % of the sample had decomposed.^[89]

Interestingly, the more recent studies report KBH₄ to begin decomposition before melting^[19, 79, 88], whilst earlier studies suggest the opposite^[89-91].

1.6 Group II borohydrides

1.6.1 General synthesis routes

Alkali earth metal borohydrides can be prepared using similar synthetic routes to those discussed for the alkali metal borohydrides above, however the most common method is a metathetic reaction between a metal chloride and either LiBH₄ or NaBH₄ (Equation 1.42) in a variety of solvents such as tetrahydrofuran, ether, pyridine or dimethylformamide.^[24, 25, 27]



There is some evidence that group II⁺ borohydrides may be prepared by mechanical milling using either LiBH₄ or NaBH₄ and the appropriate metal chloride.^[60, 92, 93]

These metathesis reactions were found to proceed more easily if the ionic radii of the

cations being exchanged were similar.^[92] Mechanical milling can sometimes produce samples with low crystallinity and small particle sizes, therefore reactions may be deemed to occur by the appearance of LiCl or NaCl peaks in the X-ray powder diffraction data rather than peaks relating to the new borohydride.^[92]

1.6.2 Introduction to calcium borohydride

Calcium borohydride, $\text{Ca}(\text{BH}_4)_2$ is of considerable interest as a potential solid state hydrogen store because of its high hydrogen content per formula unit (11.5 wt%) and its direct reversibility under hydrogen pressure^[94, 95].

1.6.2.1 Synthesis

$\text{Ca}(\text{BH}_4)_2$ was first prepared in 1954 by Kollonitsch in an alcoholic solution between -50°C and -20°C from NaBH_4 and CaCl_2 according to Equation 1.43.^[96]



The interest in $\text{Ca}(\text{BH}_4)_2$ at this time was due to its ability to reduce aldehydes and ketones to alcohols. Alcoholic solutions of $\text{Ca}(\text{BH}_4)_2$ could not be used at temperatures higher than -10°C in order to avoid the decomposition of $\text{Ca}(\text{BH}_4)_2$. A solution of $\text{Ca}(\text{BH}_4)_2$ in tetrahydrofuran (THF) could also be used and the synthesis of $\text{Ca}(\text{BH}_4)_2$ by stirring in THF for 4 to 8 hours was reported. The sodium chloride by-product was separated using a centrifuge. Evaporating the THF solvent left the product in the form of a THF solvent adduct. The alkaline earth metal borohydrides were thought to be more effective reducing agents than the alkali metal borohydrides.^[97]

In 1964, Mikheeva and Titov reported the synthesis of $\text{Ca}(\text{BH}_4)_2$ according to Equation 1.43 in pyridine. The product was washed in THF and consequently formed

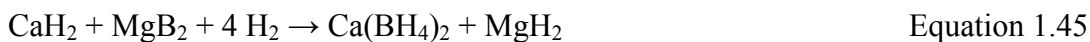
a solvent adduct which was thought to initially be $\text{Ca}(\text{BH}_4)_2 \cdot 4\text{THF}$. This could be converted to $\text{Ca}(\text{BH}_4)_2 \cdot 2\text{THF}$ by drying under vacuum and to $\text{Ca}(\text{BH}_4)_2$ by heating under vacuum to 190°C . The product was identified by independently analysing for calcium and borohydride ions. $\text{Ca}(\text{BH}_4)_2$ was found to be a white powder with a density of 1.13 gcm^{-3} which was stable in dry air. $\text{Ca}(\text{BH}_4)_2$ was found to be soluble in water and THF, insoluble in ether and dioxin and sparingly soluble in pyridine. Dissolving $\text{Ca}(\text{BH}_4)_2$ in water or THF is very exothermic and dissolving coarse samples in water can sometimes cause ignition. Solutions of $\text{Ca}(\text{BH}_4)_2$ in water were relatively stable at room temperature and more stable at 0°C . Although $\text{Ca}(\text{BH}_4)_2$ could be dissolved in water without evolving hydrogen, contact with wet organic solvents caused rapid decomposition.^[24] In 1968, Titov extended this work by establishing that when producing $\text{Ca}(\text{BH}_4)_2$ according to Equation 1.43, a 50% excess of NaBH_4 was necessary to limit the formation of $\text{CaCl}(\text{BH}_4)$ as a by-product, thus producing $\text{Ca}(\text{BH}_4)_2$ in a 98% yield. The product was identified by elemental analysis.^[98]

$\text{Ca}(\text{BH}_4)_2$ did not receive any significant further attention in the literature until it recently began to be investigated as a potential hydrogen storage material. The first work of this type was by Miwa *et al.* in 2006.^[99] By this time $\text{Ca}(\text{BH}_4)_2 \cdot 2\text{THF}$ was available commercially from Sigma Aldrich^[63] thus allowing $\text{Ca}(\text{BH}_4)_2$ to be produced by simply heating $\text{Ca}(\text{BH}_4)_2 \cdot 2\text{THF}$ under dynamic vacuum for 1 hour at 160°C .^[99]

In 2007, Rönnebro and Majzoub reported the synthesis of $\text{Ca}(\text{BH}_4)_2$ according to Equation 1.44. A mechanically milled mixture of CaB_6 and CaH_2 in a 1:2 molar ratio was heated to a temperature between 400°C and 440°C for 48 hours under 700 bar H_2 . $\text{Ca}(\text{BH}_4)_2$ was only produced if 4 to 8 wt % of a catalyst such as TiCl_3 was present.^[94]



In 2008, Barkhordarian *et al.* reported the synthesis of $\text{Ca}(\text{BH}_4)_2$ from CaH_2 and MgB_2 at 350°C under 300 bar H_2 according to Equation 1.45. The CaH_2 and MgB_2 powders were mechanically milled together before heating. $\text{Ca}(\text{BH}_4)_2$ initially formed with a new structure which was labelled the β -phase. On cooling to room temperature, $\text{Ca}(\text{BH}_4)_2$ converted to the previously known structure, now labelled the α -phase. If the α -phase was heated above 130°C , it converted to the β -phase but returned to the α -phase on cooling.^[100]



Synthesis of $\text{Ca}(\text{BH}_4)_2$ from CaH_2 and boron using the same method was not possible. This is thought to be because it is much harder to remove boron atoms from the icosahedron unit of elemental boron than from an sp^2 bonded layer of boron atoms within MgB_2 .^[100]

Also in 2008, Buchter *et al.* reported the synthesis of $\text{Ca}(\text{BH}_4)_2$ from the solution state reaction between CaH_2 and triethylamine borane complex, BH_3NEt_3 according to Equation 1.46. BH_3NEt_3 is a liquid and so also acts as a solvent for the reaction. This synthesis route produced $\text{Ca}(\text{BH}_4)_2$ in the β -phase and also a new γ - phase.^[101] This synthesis was based on the analogous synthesis of $\text{Mg}(\text{BH}_4)_2$ by Chłopek *et al.*. The solution is stirred under reflux for one hour at 100°C followed by six hours at 145°C . After cooling to room temperature, hexane was added and the suspension was stirred for eight hours before being filtered, washed in hexane and dried under vacuum. The solid product is the triethylamine complex which in the case of $\text{Mg}(\text{BH}_4)_2$ was dried by heating under dynamic vacuum for 17 hours at temperatures up to 170°C .^[102]



Buchter *et al.* also made $\text{Ca}(\text{BH}_4)_2$ using the method of Barkhordarian *et al.* according to Equation 1.45. The sample contained the α -phase and also a small amount of the γ -phase.^[101]

Recently, Kim *et al.* have reported the synthesis of $\text{Ca}(\text{BH}_4)_2$ from a mixture of CaH_2 , CaB_6 and Mg which had been produced by the dehydrogenation of $\text{Ca}(\text{BH}_4)_2 + \text{MgH}_2$. The mixture was hydrogenated under 90 bar hydrogen at 350 °C for 24 hours. First the magnesium was hydrogenated to MgH_2 which then reacted with CaH_2 to form $\text{Ca}_4\text{Mg}_3\text{H}_{14}$. $\text{Ca}(\text{BH}_4)_2$ began to form after three hours from the reaction between $\text{Ca}_4\text{Mg}_3\text{H}_{14}$ and CaB_6 according to Equation 1.47. Hydrogenation of a mixture of fresh CaH_2 , CaB_6 and Mg which had not been produced by dehydrogenation of $\text{Ca}(\text{BH}_4)_2$ did not produce $\text{Ca}(\text{BH}_4)_2$. This was thought to be an effect of the particle size of CaB_6 .^[103]



The phases present in a sample of $\text{Ca}(\text{BH}_4)_2$ are dependent on the synthetic route used. Samples produced from $\text{Ca}(\text{BH}_4)_2 \cdot 2\text{THF}$ produce mainly α - $\text{Ca}(\text{BH}_4)_2$ or the β -phase if the sample is heated to a higher temperature or for a longer time. Samples produced from CaH_2 and $\text{Et}_3\text{N} \cdot \text{BH}_3$ or CaH_2 and MgB_2 may also contain the γ -phase.^[104]

1.6.2.2 Structure

In 2006, Miwa *et al.* prepared a sample of $\text{Ca}(\text{BH}_4)_2$ by heating commercial $\text{Ca}(\text{BH}_4)_2 \cdot 2\text{THF}$ under vacuum to 160°C for one hour. Powder X-ray diffraction data from the $\text{Ca}(\text{BH}_4)_2$ sample were recorded using Cu K_α radiation. A crystal structure of $\text{Ca}(\text{BH}_4)_2$ was solved with an *Fddd* space group with lattice parameters of $a = 8.791(1) \text{ \AA}$, $b = 13.137(1) \text{ \AA}$ and $c = 7.500(1) \text{ \AA}$. The B-H bond lengths were between 1.11 Å and 1.13 Å and the H-B-H bond angles were between 102° and 119°.

The atomic positions are shown in Table 1.7. A density functional theory optimisation of the experimental structure resulted in very similar unit cell parameters, $a = 8.802 \text{ \AA}$, $b = 13.244 \text{ \AA}$ and $c = 7.473 \text{ \AA}$.^[99]

Table 1.7 The atomic positions of $Fddd \text{ Ca(BH}_4)_2$ ^[99]

Site	x/a	y/b	z/c
Ca	0	0	0
B	0	0.227(4)	0
H1	-0.102(16)	0.274(9)	0.037(23)
H2	0.009(21)	0.176(7)	0.117(16)

Around the same time that the first crystal structure of $\text{Ca(BH}_4)_2$ was experimentally determined, the structure was correctly predicted by Vajeeston *et al.* by optimising 28 potential structure types and searching for the structure with the lowest energy. The space group was predicted to be $Fddd$ with lattice parameters, $a = 13.1491 \text{ \AA}$, $b = 8.8052 \text{ \AA}$ and $c = 7.4799 \text{ \AA}$. The B-H distances were predicted to be between $1.22 \text{ \AA}$ and $1.23 \text{ \AA}$ and the H-B-H bond angles between 106° and 113° . The predicted B-H distances are longer than those determined from the X-ray diffraction study which makes B-H distances appear artificially short due to the displacement of electron density into the B-H bond.^[105]

In 2008, Aoki *et al.* prepared $\text{Ca(BH}_4)_2$ from $\text{Ca(BH}_4)_2 \cdot 2\text{THF}$. A low temperature sample was prepared by heating $\text{Ca(BH}_4)_2 \cdot 2\text{THF}$ to 160°C for 10 hours under vacuum and a high temperature sample was prepared by heating $\text{Ca(BH}_4)_2 \cdot 2\text{THF}$ to 250°C for 80 hours under vacuum. Room temperature, laboratory powder X-ray diffraction patterns of the low temperature sample were indexed to an orthorhombic unit cell with lattice parameters $a = 8.791(1) \text{ \AA}$, $b = 13.137(1) \text{ \AA}$ and $c = 7.500(1) \text{ \AA}$ in agreement with the structure determined by Miwa *et al.*^[99]. Room temperature X-ray powder

diffraction patterns of the high temperature sample were indexed to a tetragonal unit cell with lattice parameters $a = 6.951(1) \text{ \AA}$ and $c = 4.369(1) \text{ \AA}$. Room temperature X-ray powder diffraction patterns of the high temperature sample after it had been stored for a week contained diffraction peaks relating to both the orthorhombic and tetragonal phases suggesting that the orthorhombic phase is stable compared to the tetragonal phase. X-ray powder diffraction patterns recorded after decomposition of the sample showed evidence of a decomposition intermediate phase which was indexed to a unit cell with lattice parameters $a = 4.0082(3) \text{ \AA}$, $b = 3.8974(2) \text{ \AA}$ and $c = 12.812(1) \text{ \AA}$.^[106]

Two more crystal structures of $\text{Ca}(\text{BH}_4)_2$ were identified by Buchter *et al.* in 2008. Samples of $\text{Ca}(\text{BH}_4)_2$ and $\text{Ca}(\text{BD}_4)_2$ were investigated by variable temperature neutron and synchrotron powder X-ray diffraction. The first sample was prepared from MgB_2 and CaD_2 at 400°C under 350 bar D_2 according to Equation 1.45, using the method of Barkordarian *et al.*^[100] This sample contained the by-product MgD_2 . In addition to the previously identified α - $\text{Ca}(\text{BH}_4)_2$ structure (space group, $Fddd$), this sample was found to contain two more polymorphs of $\text{Ca}(\text{BH}_4)_2$, β - and γ - $\text{Ca}(\text{BH}_4)_2$. At room temperature, the majority of the sample was α - $\text{Ca}(\text{BH}_4)_2$ but above 127°C the sample was predominantly β - $\text{Ca}(\text{BH}_4)_2$, allowing the structure of this polymorph to be solved. β - $\text{Ca}(\text{BH}_4)_2$ was identified as having a tetragonal unit cell with the space group, $P4_2/m$, at 207°C the lattice parameters were $a = 6.9468(1) \text{ \AA}$ and $c = 4.3661(1) \text{ \AA}$. The atomic co-ordinates are displayed in Table 1.8. The borohydride units were reported as slightly distorted with B-D lengths of $1.02(3) \text{ \AA}$ to $1.16(3) \text{ \AA}$. The structure was expected to show disorder above 207°C . Details of α - $\text{Ca}(\text{BH}_4)_2$ were refined from this first sample at room temperature, refinements led to a variation in the B-D lengths of between $1.164(11) \text{ \AA}$ and $1.174(11) \text{ \AA}$.^[101]

Table 1.8 The atomic co-ordinates in β -Ca(BH₄)₂ ($P4_2/m$)^[101]

Site	x/a	y/b	z/c
Ca	0.5	0	0.5
B	0.302(4)	0.200(5)	0
D1	0.295(8)	0.347(9)	0
D2	0.468(7)	0.185(5)	0
D3	0.226(5)	0.161(5)	0.800(6)

The second sample was prepared by solution state synthesis from CaH₂ and Et₃N·BH₃.^[102] This sample was found to contain a significant amount of γ -Ca(BH₄)₂ which has an orthorhombic unit cell and the space group $Pbca$. The lattice parameters were $a = 13.0582(3)$ Å, $b = 8.3882(5)$ Å and $c = 7.5108(4)$ Å.^[101]

The structure of γ -Ca(BH₄)₂ was later solved by Buchter *et al.*. At 27°C, the lattice parameters were $a = 13.0584(8)$ Å, $b = 8.3881(4)$ Å and $c = 7.5107(4)$ Å. The atomic co-ordinates are given in Table 1.9. The atomic displacement parameters were all less than $B_{\text{iso}} = 5$ Å² suggesting that this structure does not contain any significant disorder, particularly when compared with LiBH₄. The B-D bond lengths for the two borohydride ions vary from 1.06(3) Å to 1.24(3) Å and 1.17(3) Å to 1.33(3) Å.^[104] This is likely to be an artefact of the refinement.

Table 1.9 The atomic co-ordinates of *Pbca* γ -Ca(BH₄)₂^[104]

Site	x/a	y/b	z/c
Ca	0.6276(7)	0.379(1)	0.366(1)
B1	0.255(4)	0.410(6)	0.480(5)
D11	0.264(7)	0.344(10)	0.348(12)
D12	0.265(6)	0.347(12)	0.596(12)
D13	0.237(6)	0.535(9)	0.473(13)
D14	0.136(7)	0.368(10)	0.480(10)
B2	0.503(3)	0.842(5)	0.817(6)
D21	0.524(6)	0.688(9)	0.798(11)
D22	0.409(6)	0.867(13)	0.814(12)
D23	0.542(6)	0.862(10)	0.956(12)
D24	0.542(7)	0.921(10)	0.708(12)

The α -, β - and γ - structures of Ca(BH₄)₂ are all made up of octahedra consisting of six borohydride groups arranged around a calcium ion. The octahedra of the α - and γ -phases are more distorted than in the β - phase. The difference between the longest and shortest B-B distance in the β - phase is 11% compared to 14% and 17% for the α - and γ - phases. At 27°C the densities of the α -, β - and γ - phases are 1.2060(1)gcm⁻³, 1.2523(1) gcm⁻³ and 1.2565(2) gcm⁻³, the densities of the β - and γ - phases are very similar.^[104]

Lee *et al.* agreed with Miwa and Buchter finding that the α - and β -phases have the space groups *Fddd* and *P4₂/m* respectively using laboratory X-ray powder diffraction. The sample of Ca(BH₄)₂ was made by desolvating Ca(BH₄)₂.2THF.^[107]

Raman and IR spectra were recorded for Ca(BH₄)₂ by Fichtner *et al.*. α - Ca(BH₄)₂ was obtained by desolvating Ca(BH₄)₂.2THF under vacuum at 160°C for one hour. β -Ca(BH₄)₂ was produced by annealing α - Ca(BH₄)₂ at 200°C for 16 hours and then quenching or annealing at 250°C for 90 minutes and then quenching. Mixed samples

of β - and γ - $\text{Ca}(\text{BH}_4)_2$ were synthesised in solution from CaH_2 and BH_3NEt_3 ^[102]. Peaks in the spectra of β - $\text{Ca}(\text{BH}_4)_2$ were broader than in α - $\text{Ca}(\text{BH}_4)_2$ suggesting some disorder in the β -phase. Variable temperature Raman spectra show that the transition from the α - to β - phase was continuous and occurred around 180°C.^[108]

In 2009, Majzoub and Rönnebro investigated the structures of $\text{Ca}(\text{BH}_4)_2$ theoretically using PEGS (prototype electrostatic ground states), Vienna Ab Initio Simulation Package (VASP) and by optimising AB_2X_8 structures from the Inorganic Crystal Structure Database, (ICSD). In addition to the BaMnO_4 *Fddd* type structure previously identified, the ICSD search and PEGS also suggested a HfMo_2O_8 type structure with the space group *C2/c* with the same energy. This could be an alternative ground state structure for the α -phase. A structure with the space group *P-4* was identified as a possible alternative for β - $\text{Ca}(\text{BH}_4)_2$. The γ -phase *Pbca* structure was also identified. A structure with the space group *I-42d* was not thought to be a candidate for a real structure.^[109]

Majzoub and Rönnebro also prepared a sample of $\text{Ca}(\text{BH}_4)_2$ by desolvating $\text{Ca}(\text{BH}_4)_2 \cdot 2\text{THF}$. The sample was then mechanically milled with a catalyst, dehydrogenated at 330°C under vacuum and then rehydrogenated under 120 bar hydrogen at 330°C. Using powder Cu X-ray diffraction, the original sample was determined to contain α - and β - $\text{Ca}(\text{BH}_4)_2$ in a 93:7 ratio, after milling with the catalyst, the ratio was 50:50. After rehydrogenation, the $\text{Ca}(\text{BH}_4)_2$ formed in the sample was mainly in the β -phase, the sample also contained 10 % CaH_2 and an unidentified phase. The β -phase had lattice parameters of $a = 6.892(2)$ Å and $c = 4.336(2)$ Å, the best fit to the data was found with the space group *P-4* rather than *P4₂/m*. The B-H bond lengths were between 1.166 Å and 1.173 Å, the H-B-H bond angles had an average of 109.5°.^[109]

Table 1.10 Atomic co-ordinates of β - $\text{Ca}(\text{BH}_4)_2$ in space group $P-4$ ^[109]

Site	x/a	y/b	z/c
Ca	0.5	0	0.259(7)
B	0.779(2)	0.680(2)	0.269(2)
H1	0.614(2)	0.683(3)	0.211(5)
H2	0.805(3)	0.746(3)	0.514(3)
H3	0.835(3)	0.520(2)	0.263(5)
H4	0.864(3)	0.773(3)	0.088(4)

In 2009, Filinchuk *et al.* conducted variable temperature, powder synchrotron X-ray diffraction studies of a sample of $\text{Ca}(\text{BH}_4)_2$ prepared by heating $\text{Ca}(\text{BH}_4)_2 \cdot 2\text{THF}$ to 155 °C under vacuum for 2 to 3 days. The room temperature sample contained 87% α - and 13 % β -phase. The best fit to the data for the α -phase was obtained with the space group $F2dd$ rather than $Fddd$. At -182 °C, the lattice parameters were $a = 8.7795(3)$ Å, $b = 13.0234(4)$ Å and $c = 7.4132(2)$ Å. The atomic co-ordinates are shown in Table 1.11. In the $F2dd$ space group, the borohydride ions were closer to an ideal tetrahedral shape than in the $Fddd$ space group. On heating, the a lattice parameter of the α -phase increased and the c lattice parameter decreased until at 222 °C, the phase transformed to a tetragonal α' -structure. With the α -phase taking the $F2dd$ space group, the α' -phase has to be a minimal supergroup of $F2dd$, these are $I4_1md$, $I4_1cd$ and $I-42d$. The best fit to the data was obtained with the space group $I-42d$ with lattice parameters of $a = 5.8446(3)$ Å and $c = 13.2279(11)$ Å. The atomic co-ordinates for the α' -phase with the space group $I-42d$ are shown in Table 1.12. For the β -phase, the best fit to the data and the most reasonable interatomic distances were obtained with the space group $P-4$ (lattice parameters $a = 6.91894(11)$ Å and $c = 4.34711(12)$ Å).^[110]

Table 1.11 Atomic co-ordinates of α - $\text{Ca}(\text{BH}_4)_2$ in the space group $F2dd^{[110]}$

Site	x/a	y/b	z/c
Ca	0	0	0
B	0.0056(9)	0.2243(2)	0.0081(11)
H1	0.0190(19)	0.1648(10)	0.1272(16)
H2	0.0345(19)	0.1817(11)	-0.1256(14)
H3	-0.1180(10)	0.2553(12)	0.012(2)
H4	0.0910(15)	0.2922(9)	0.028(2)

Table 1.12 Atomic co-ordinates of α' - $\text{Ca}(\text{BH}_4)_2$ in the space group $I-42d^{[110]}$

Site	x/a	y/b	z/c
Ca	0	0	0
B	0	0	0.2250(6)
H1	-0.1608(16)	-0.035(3)	0.1762(10)
H2	0.032(3)	-0.1613(16)	0.2752(10)

Riktor *et al.* observed an intermediate decomposition phase of $\text{Ca}(\text{BH}_4)_2$ present between 370 °C and 400 °C. The intermediate phase was suggested to be CaB_2H_2 and a structure was suggested by a combination of the analysis of synchrotron X-ray diffraction patterns and theoretical calculations. The atomic co-ordinates are shown in Table 1.13. The B H bond lengths within the structure are in the range 1.07 Å to 1.23 Å.^[111]

Table 1.13 Atomic co-ordinates for the proposed CaB_2H_2 structure, $Pnma$, $a = 12.8105(8) \text{ \AA}$, $b = 4.0825(2) \text{ \AA}$, $c = 3.9034(2) \text{ \AA}$ ^[111]

Site	x/a	y/b	z/c
Ca	0.8419(2)	0.75	-0.007(7)
B	0.02(2)	0.75	0.45(2)
B	0.238(1)	0.75	-0.04(1)
H	0.5	0	0
H	0.026	0.75	0.141

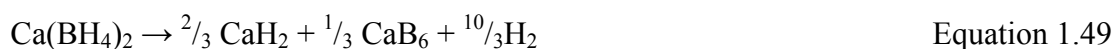
In addition to the α - and β -phases, Noritake *et al.* identified $\text{Ca}(\text{BH}_4)_2 \cdot \text{H}_2\text{O}$ by room temperature synchrotron X-ray powder diffraction within a sample of $\text{Ca}(\text{BH}_4)_2$ prepared from $\text{Ca}(\text{BH}_4)_2 \cdot 2\text{THF}$. This solvate has the space group $Pnma$ and lattice parameters $a = 8.200(1) \text{ \AA}$, $b = 5.8366(7) \text{ \AA}$ and $c = 11.851(2) \text{ \AA}$. The centrosymmetric space group $Fddd$ was used for α - $\text{Ca}(\text{BH}_4)_2$ rather than the noncentrosymmetric space group $F2dd$, because there was no significant improvement in the quality of the fit to the data or the structure itself from using space group $F2dd$. At 160°C , X-ray powder diffraction showed that the majority of the sample had transformed to the β -phase and $\text{Ca}(\text{BH}_4)_2 \cdot \text{H}_2\text{O}$ is thought to have transformed to γ - $\text{Ca}(\text{BH}_4)_2$. The structure of the β -phase was refined with the space group $P4_2/m$ and the borohydride ions were expected to be disordered at high temperature. The structure of the γ -phase was solved with the space group $Pbca$ with a structure analogous to that of brookite TiO_2 (lattice parameters $a = 7.525(1) \text{ \AA}$, $b = 13.109(2) \text{ \AA}$ and $c = 8.403(1) \text{ \AA}$). The structures of α -, β - and γ - $\text{Ca}(\text{BH}_4)_2$ all consist of octahedra built of six boron atoms surrounding a calcium ion, the difference between the phases is the combination of sharing of vertexes and edges.^[112]

Noritake *et al.* also analysed the charge density distribution in α -Ca(BH₄)₂. The bonding between the Ca²⁺ and BH₄⁻ ions was found to be ionic with no indication of metallic bonding. The radius of the Ca²⁺ cation was found to be 1.34 Å.^[112]

1.6.2.3 Thermodynamics

A review by Konoplev *et al.* in 1992 stated that the calculated formation enthalpy, ΔH_f^0 of Ca(BH₄)₂ was -351 kJ mol⁻¹. The calculated Gibbs free energy of formation, ΔG_f^0 was -226 kJ mol⁻¹ and the calculated enthalpy, ΔH_{dec}^0 and Gibbs free energy, ΔG_{dec}^0 of decomposition were 191 kJ mol⁻¹ and 159 kJ mol⁻¹ respectively.^[113]

In 2006, Miwa *et al.* predicted the heat of formation of Ca(BH₄)₂ according to Equation 1.48 to be -151 kJ mol⁻¹ and Ca(BH₄)₂ was predicted to decompose according to Equation 1.49.^[99]



In 2009, the structures of the α -, β - and γ -phases of Ca(BH₄)₂ were modelled and investigated using density functional theory by Buchter *et al.*. The calculated difference in free energy at room temperature between the α - and β -phase was 0.13 eV f.u.⁻¹ (eV per formula unit, or 12.5 kJ mol⁻¹). At room temperature the α -phase had the lowest free energy, consequently, the α - phase is thought to be the ground state of Ca(BH₄)₂. The γ -phase had a free energy that was ~0.08 eV f.u.⁻¹ (7.7 kJ mol⁻¹) higher than the α -phase at room temperature so the γ -phase is more stable than the β -phase. With increasing temperature, the β -phase became more stable with respect to the α -phase but the γ -phase became less stable, consequently the γ -phase is always metastable. Expected disorder in the borohydride units of the β -phase may further stabilise this phase with increasing temperature. This means that the β -phase may eventually become more stable than the α -phase, thus explaining the phase transition.

The β -phase may also become more stable than the γ -phase, preventing conversion back to the γ -phase from the β -phase.^[104]

Lee *et al.* calculated the entropy difference at room temperature between the α - and β -phases to be $16 \text{ J K}^{-1} \text{ mol}^{-1}$ and the energy difference at -273°C , (0 K, no vibrations) to be 10.9 kJ mol^{-1} using density functional theory.^[107]

Wang *et al.* have shown that a partial decomposition of $\text{Ca}(\text{BH}_4)_2$ to a $\text{CaB}_{12}\text{H}_{12}$ intermediate according to Equation 1.50 is reversible under 14 MPa H_2 at 400°C using a catalyst such as TiCl_3 . Several polymorphs of $\text{CaB}_{12}\text{H}_{12}$ were thought to exist and evidence of their existence was produced from electron-energy-loss spectroscopy, X-ray diffraction and energy-dispersive spectroscopy. Wang *et al.* also calculated the reaction enthalpies for a range of decomposition routes for $\text{Ca}(\text{BH}_4)_2$ and showed that decomposition to CaB_6 or $\text{CaB}_{12}\text{H}_{12}$ are the most favourable.^[114] The existence of $\text{CaB}_{12}\text{H}_{12} \cdot 8\text{H}_2\text{O}$ has been previously reported.^[115]

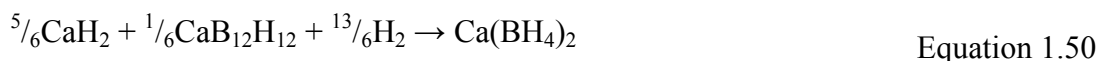


Table 1.14 Decomposition enthalpies and mass losses of $\text{Ca}(\text{BH}_4)_2$ by various routes (the range in enthalpy for decomposition to $\text{CaB}_{12}\text{H}_{12}$ is due to the range of polymorphs thought to exist)^[114]

Decomposition route	$\Delta H / \text{kJ (mol H}_2\text{)}^{-1}$	Mass loss / wt%
$\text{Ca}(\text{BH}_4)_2 \rightarrow \text{Ca} + 2\text{B} + 4\text{H}_2$	83.3	11.6
$\text{Ca}(\text{BH}_4)_2 \rightarrow \text{CaH}_2 + 2\text{B} + 3\text{H}_2$	56.1	8.7
$\text{Ca}(\text{BH}_4)_2 \rightarrow \frac{2}{3}\text{CaH}_2 + \frac{1}{3}\text{CaB}_6 + \frac{10}{3}\text{H}_2$	37.9	9.6
$\text{Ca}(\text{BH}_4)_2 \rightarrow \frac{5}{6}\text{CaH}_2 + \frac{1}{6}\text{CaB}_{12}\text{H}_{12} + \frac{13}{6}\text{H}_2$	35.8-39.1	6.3

1.6.2.4 Thermal behaviour

The thermal behaviour of $\text{Ca}(\text{BH}_4)_2$ was first investigated in 1964 by Mikheeva and Titov. On heating, they found that the thermal decomposition of $\text{Ca}(\text{BH}_4)_2$ began at 245 °C and was vigorous by 350 °C. Hydrogen was evolved but the sample did not melt.^[24]

In 2007, an analysis of $\text{Ca}(\text{BH}_4)_2$ by DSC and TGA by Rönnebro and Majzoub found two endothermic peaks at 140 °C and 350 °C and mass loss between 350 °C and 390 °C. The mass loss was thought to be due to hydrogen evolution during decomposition. The decomposition products were found to be CaB_6 and CaH_2 by X-ray diffraction, which are also the starting materials for the synthesis of this $\text{Ca}(\text{BH}_4)_2$ sample showing that the dehydrogenation reaction is at least partially reversible.^[94]

DSC analysis coupled with mass spectrometry was carried out on a sample of $\text{Ca}(\text{BH}_4)_2$ by J.-H. Kim *et al.*. The sample had been prepared by heating $\text{Ca}(\text{BH}_4)_2 \cdot 2\text{THF}$ under vacuum to 200 °C for one hour. A small endothermic peak was observed at 167 °C without any gas evolution. A large endothermic peak was observed at 397 °C and a broad endothermic peak was observed between 397 °C and 497 °C. Both of these peaks were accompanied by hydrogen evolution. TGA analysis showed a slight mass loss before 327 °C but otherwise the mass loss was in agreement with the DSC and mass spectrometry, the total mass loss was 9 wt%. This mass loss is more than is possible by Equation 1.51 (8.7 wt%) but not as much as would be expected by the predicted decomposition according to Equation 1.49^[99] (9.6 wt%). The endothermic peak at 167°C was shown to be a phase change by variable temperature X-ray powder diffraction. X-ray diffraction patterns at 390 °C showed Bragg peaks relating to CaH_2 and another unidentified phase which is thought to be a

decomposition intermediate. At 480 °C, only CaH₂ Bragg peaks are observed, CaB₆ or elemental boron were thought to be amorphous.^[116]



Aoki *et al.* carried out TGA, DSC and mass spectrometry on a sample of Ca(BH₄)₂ prepared by heating Ca(BH₄)₂.2THF under vacuum to 250 °C for 80 hours. The sample lost 9.4 % of its mass during heating to 527 °C. The DSC showed two endothermic peaks at 367 °C and 447 °C, suggesting that the sample decomposed in two stages. The only gas detected by mass spectrometry was hydrogen. The endothermic peak observed by Kim *et al.*^[116] at 167 °C was not seen in this sample, which as it only contained β-Ca(BH₄)₂ suggests that this peak related to the α- to β-phase transition. A p-c isotherm measurement of the sample only containing β-Ca(BH₄)₂ at 320 °C had a plateau at 0.6 MPa. The sample lost 5.9 wt% mass which agreed with the DSC study. X-ray powder diffraction patterns recorded after the decomposition showed diffraction peaks relating to an unidentified decomposition intermediate phase.^[106]

A DSC study of a mixture of Ca(BH₄)₂ and MgH₂ was completed by Barkhordarian *et al.* under 3 bar hydrogen, heating at 2 °C/min between 25 °C and 500 °C. In order to identify the origins of the endothermic DSC peaks, the results were compared to the diffraction patterns from an *in-situ* variable temperature synchrotron X-ray powder diffraction experiment with a heating rate of 3 °C/min. An endothermic DSC peak was observed at 130 °C corresponding to the α to β phase transition. A second DSC peak at 360 °C corresponded to the decomposition of β-Ca(BH₄)₂ to Ca₄Mg₃H₁₄, CaH₂, Mg, B, and H₂. A third DSC peak at 420 °C is related to the decomposition of Ca₄Mg₃H₁₄.^[100]

When Buchter *et al.*'s samples of $\text{Ca}(\text{BD}_4)_2$ and $\text{Ca}(\text{BD}_4)_2 + \text{MgD}_2$ were heated, the α -phase began to transform to the β - phase before the γ -phase began to transform. After heating to 217 °C, the proportion of α -phase in the sample had decreased but the proportion of γ -phase was unchanged. When heated below 200 °C the α -phase transformed to the β -phase reversibly, returning to the α -phase on cooling to room temperature. When heated above 200 °C, the β -phase became metastable and only part of the phase converted back to the α -phase. The whole sample was converted to the β -phase above 260 °C to 320 °C.^[104]

Riktor *et al.* heated a sample containing β - and γ - $\text{Ca}(\text{BH}_4)_2$ synthesised in solution from CaH_2 and BH_3NEt_3 to 500 °C at 2 °C/min. A large gas desorption peak was observed between 335 °C and 400 °C and a smaller, broader peak between 420 °C and 500 °C. X-ray diffraction patterns of a sample heated to 330 °C showed only the β -phase to be present. A sample heated between 370 °C and 400 °C contained CaH_2 , CaO and an unidentified phase. Above 400 °C, the unidentified phase was not present and no other boron-containing phases were identified suggesting that the boron decomposition product must be amorphous.^[111]

Using variable temperature synchrotron X-ray diffraction, Filinchuk *et al.* found that the β -phase decomposed between 382 °C and 387 °C forming some new unidentified crystalline phases. The weight fraction of the β -phase remained constant below 180 °C, then increased rapidly until after the α - to α' -phase transition at 220 °C when the increase in weight fraction slowed down again until 278 °C. At this point, the weight fraction increased quickly until the entire sample was in the β - phase at 300°C. This suggests a connection between the α to α' transition and the α/α' to β transition.^[110]

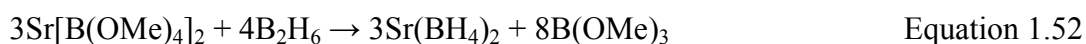
Y. Kim *et al.* investigated the decomposition of $\text{Ca}(\text{BH}_4)_2$ using TGA and DSC. Decomposition was found to begin at 320 °C with 9 wt% mass loss by 550 °C. Two separate samples were dehydrogenated at 330 °C and 480 °C in order to identify the partial and complete decomposition products. Decomposition did not occur immediately at 330 °C but 5.6 wt% hydrogen was released over two hours. Raman peaks relating to CaB_6 were detected in both samples along with X-ray diffraction peaks from CaH_2 .^[117]

The effects of catalysing the decomposition of $\text{Ca}(\text{BH}_4)_2$ have been investigated but are outside of the scope of this thesis.^[95, 118]

1.6.3 Introduction to strontium borohydride

1.6.3.1 Synthesis

The synthesis of strontium borohydride, $\text{Sr}(\text{BH}_4)_2$, from strontium tetramethoxyborate and diborane in ether, THF or without solvent according to Equation 1.52 was reported in 1955 by Wiberg *et al.*. After 2.5 hours without solvent at 75 °C the yield was 50 % to 75 %. Using ether as a solvent did not appreciably increase the yield because of the insolubility of $\text{Sr}(\text{BH}_4)_2$ in ether. In THF, the reaction proceeded to completion.^[119]



This reaction was extended to strontium methoxide and ethoxide. Without solvent, the reaction was incomplete up to 100 °C. In ether, the reaction produced a mixture of $\text{Sr}(\text{OR})_2$ and $\text{Sr}(\text{BH}_4)_2$. In THF, $\text{Sr}(\text{BH}_4)_2 \cdot 2\text{THF}$ was produced. Strontium ethoxide was more effective than strontium methoxide, reacting according to Equation 1.53.^[120]



The final reaction in this series was between SrH_2 and diborane in THF to produce $\text{Sr}(\text{BH}_4)_2 \cdot 2\text{THF}$ according to Equation 1.54.^[121]



Another synthesis of $\text{Sr}(\text{BH}_4)_2$ was reported in 1973 by Mikheeva and Tolmacheva. $\text{Sr}(\text{BH}_4)_2$ was produced from the reaction between SrCl_2 and NaBH_4 in tetrahydrofuran (THF) according to Equation 1.55. The solution was stirred for 7 to 12 hours at temperatures between 20 °C and 40 °C. An excess of NaBH_4 was used, with molar ratios between 2.6:1 and 5:1 $\text{NaBH}_4\text{:SrCl}_2$. The solution was then filtered to remove insoluble remaining starting materials and reaction by-products and then the THF was removed by distillation to produce $\text{Sr}(\text{BH}_4)_2 \cdot 2\text{THF}$. After drying between 180 °C and 190 °C for one to six hours, the product contained 88 % to 93 % strontium, boron and hydrogen in a ratio close to 1:2:8. The optimum yield was obtained with a starting ratio of $\text{NaBH}_4\text{:SrCl}_2$ of 3:1, stirred at 40 °C for 7 hours in a large excess of THF. The density of the material was found to be 1.76 gcm^{-3} .^[25]



Mikheeva and Sizareva extended this work in 1977. It had been found that the solubility of $\text{Sr}(\text{BH}_4)_2$ in THF was improved by the presence of LiBH_4 . The poor solubility of $\text{Sr}(\text{BH}_4)_2$ in THF was limiting the effectiveness of the reaction in Equation 1.55 in THF. Consequently, the reaction was repeated with LiBH_4 in addition to NaBH_4 and SrCl_2 . The starting materials were stirred in THF as before and then filtered to remove NaCl . $\text{Sr}(\text{BH}_4)_2$ was precipitated out of the THF solution by the addition of an excess of diethyl ether at 2 °C to 4 °C.^[122]

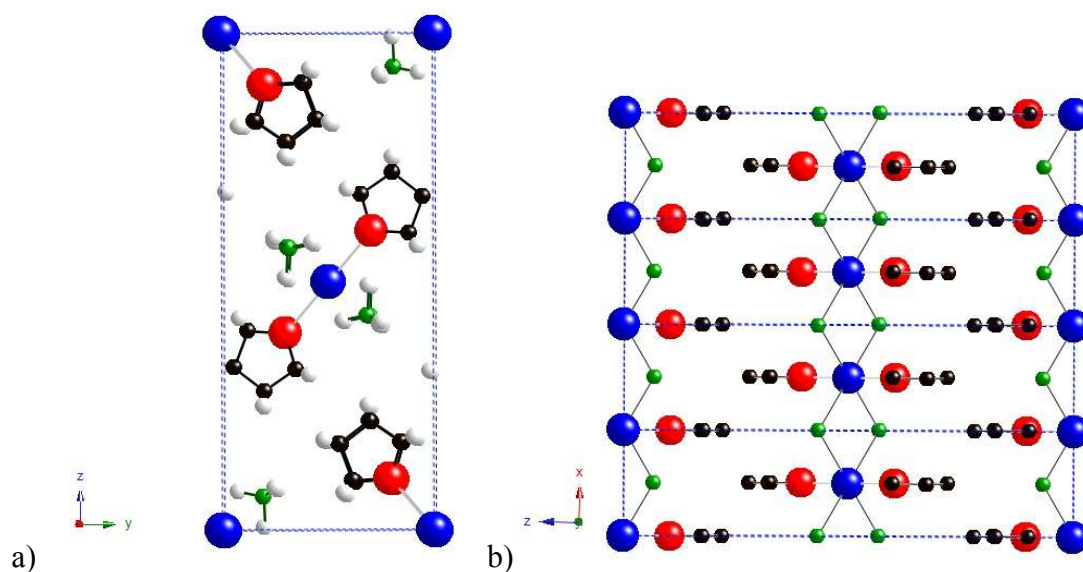
Bremer *et al.* reported the synthesis of $\text{Sr}(\text{BH}_4)_2 \cdot 18\text{-crown-6}$ and $\text{Sr}(\text{BH}_4)_2 \cdot 2$ diglyme by adding diglyme or 18-crown-6 to a solution of $\text{Sr}(\text{BH}_4)_2 \cdot 2\text{THF}$ in THF.^[123]

1.6.3.2 Structure

Bremer *et al.* reported the ^{11}B NMR chemical shifts in DMSO for the THF, diglyme and 18-crown-6 complexes of $\text{Sr}(\text{BH}_4)_2$ to be -36.4 ppm, -35.2 ppm and -34.9 ppm respectively. The IR spectrum of $\text{Sr}(\text{BH}_4)_2 \cdot 2\text{-diglyme}$ showed signals at 2347 cm^{-1} , 2247 cm^{-1} and 2166 cm^{-1} . Crystal structures of these solvent adducts were determined using X-ray diffraction at -100°C . Both $\text{Sr}(\text{BH}_4)_2 \cdot 2\text{THF}$ and $\text{Sr}(\text{BH}_4)_2 \cdot 2\text{-diglyme}$ crystallised in the space group $P2_1/n$; the 18-crown-6 adduct has the space group $R-3$. The lattice parameters for the three complexes are given in Table 1.15. Within $\text{Sr}(\text{BH}_4)_2 \cdot 2\text{THF}$, the metal atoms are situated on centres of inversion within the structure. The structure consists of infinite chains of strontium and borohydride ions with THF branches. The Sr-B distance is $2.960\text{ \AA}$ and the B-H distances are in the range $0.95(6)\text{ \AA}$ to $1.15(5)\text{ \AA}$. Two of the hydrogen atoms in each borohydride ion are in contact with two strontium ions whilst the other two hydrogen atoms are only linked to one strontium ion. The O-Sr-O angle is 180° so the THF molecules are located trans to each other. The structure of $\text{Sr}(\text{BH}_4)_2 \cdot 2\text{THF}$ is displayed in Figure 1.7.^[123]

Table 1.15 The lattice parameters of $\text{Sr}(\text{BH}_4)_2 \cdot 2\text{THF}$, $\text{Sr}(\text{BH}_4)_2 \cdot 2$ diglyme and $\text{Sr}(\text{BH}_4)_2 \cdot 18\text{-crown-6}$ ^[123]

	$\text{Sr}(\text{BH}_4)_2 \cdot 2\text{THF}$	$\text{Sr}(\text{BH}_4)_2 \cdot 2$ diglyme	$\text{Sr}(\text{BH}_4)_2 \cdot 18\text{-crown-6}$
$a / \text{\AA}$	4.405(1)	9.7992(2)	11.850(3)
$b / \text{\AA}$	7.997(2)	9.789(2)	11.850(3)
$c / \text{\AA}$	18.826(5)	12.247(3)	11.969(4)
$\alpha / ^\circ$	90	90	90
$\beta / ^\circ$	90.00(2)	102.56(2)	90
$\gamma / ^\circ$	90	90	120
$V / \text{\AA}^3$	663.2(3)	1029.6(4)	1457.6(8)
Z	2	2	3

**Figure 1.7** The crystal structure of $\text{Sr}(\text{BH}_4)_2 \cdot 2\text{THF}$ showing a) the unit cell and b) the strontium and borohydride ion chain (with hydrogen atoms removed for clarity). Strontium ions are shown as blue spheres, boron in green, hydrogen in grey, oxygen in red and carbon as black spheres.

1.6.3.3 Thermodynamics and thermal behaviour

Wiberg *et al.* suggested that the decomposition temperature of $\text{Sr}(\text{BH}_4)_2$ was 350 °C to 400 °C probably to SrH_2 , B and H_2 .^[119]

The thermal analysis of $\text{Sr}(\text{BH}_4)_2 \cdot 2\text{THF}$ reported by Mikheeva and Tolmacheva, showed endothermic events between 130 °C and 148 °C and between 178 °C and 195 °C associated with the removal of solvent. Further events were noted at 410 °C to 430 °C and at about 475 °C which were thought to be the decomposition of $\text{Sr}(\text{BH}_4)_2$. Finally an event was observed between 740 °C and 750 °C which was thought to be associated with metallic strontium and strontium hydride. A small amount of gas was released during the supposed removal of solvent with more gas being released during the decomposition stages. Thermal analysis results of desolvated $\text{Sr}(\text{BH}_4)_2$ were the same as for the solvated compound except that the events associated with loss of solvent were not observed. $\text{Sr}(\text{BH}_4)_2$ was found to decompose when dissolved in water and was much less soluble in THF than $\text{Ca}(\text{BH}_4)_2$.^[25]

A review by Konoplev *et al.* in 1992 stated that the formation enthalpy, ΔH_f^0 of $\text{Sr}(\text{BH}_4)_2$ was -364 kJ mol^{-1} . The Gibbs free energy of formation, ΔG_f^0 was reported to be -238 kJ mol^{-1} and the enthalpy, ΔH_{dec}^0 and Gibbs free energy, ΔG_{dec}^0 of decomposition were 215 kJ mol^{-1} and 186 kJ mol^{-1} respectively.^[113]

1.7 Other borohydrides

1.7.1 Groups I and II

The borohydrides of the heavier group I elements have similar structures to NaBH_4 and KBH_4 and will not be discussed further in this thesis. $\text{Ca}(\text{BH}_4)_2$ and $\text{Sr}(\text{BH}_4)_2$ are the only group II borohydrides discussed in detail in this thesis, discussion of a greater number of compounds would be detrimental to the depth of this study. $\text{Be}(\text{BH}_4)_2$ has a covalent structure consisting of polymeric chains of beryllium atoms and borohydride units and decomposes at approximately $123\text{ }^\circ\text{C}$.^[20, 124] $\text{Mg}(\text{BH}_4)_2$ has a complex room temperature crystal structure in the space group P6_1 and decomposes at approximately $300\text{ }^\circ\text{C}$.^[125] The heavier group II borohydrides are not widely known.

1.7.2 Transition elements

Borohydrides of many transition metals including zinc, scandium, titanium and vanadium have been synthesised by mechanically milling the required metal chloride with either LiBH_4 or NaBH_4 but most have not been fully characterised.^[92] These borohydrides tend to be more covalent and much less stable than those of groups I and II.^[28] Recently, $\text{Mn}(\text{BH}_4)_2$ was the first transition metal borohydride to be crystallographically characterised.^[126] The crystal structure of $\text{Al}(\text{BH}_4)_3$ has also been determined.^[127, 128] $\text{Al}(\text{BH}_4)_3$ is a liquid at room temperature, (melting temperature $-64.5\text{ }^\circ\text{C}$, boiling temperature $44.5\text{ }^\circ\text{C}$) and is a covalent compound. The aluminium atoms of $\text{Al}(\text{BH}_4)_3$ are connected to three boron atoms via two hydrogen bridge bonds to each boron atom. These hydrogen bridging bonds are similar to those found in diborane and both compounds begin to decompose at approximately $150\text{ }^\circ\text{C}$.^[28, 129]

1.8 Stability and decomposition temperature

1.8.1 Effect of cation electronegativity

The stability of the group I and II borohydrides is affected by the degree of charge transfer between the cation and anion.^[60] One measure of the expected degree of charge transfer is the electronegativity of the cation. More electronegative cations attract electron density back from the borohydride ion, reducing the electron density in the B-H bonds, thus destabilising the borohydride ion.^[60]

This effect has been investigated by Nakamori *et al.*, who in 2004, proposed that substituting smaller sized or higher valence cations with higher electronegativities into lithium based complex hydrides would lower the hydrogen desorption temperature of the complex hydride.^[130]

Nakamori *et al.* extended this work in 2006 when a positive correlation was proposed between the electronegativity of the metal cation in a borohydride complex and its formation enthalpy (Equation 1.56) based on first-principles density functional theory calculations. The linear relationship between the cation electronegativity and the borohydride formation enthalpy has the form $\Delta H_{\text{boro}} = 248.7\chi_p - 390.8$ where the units of enthalpy are kJ (mol BH₄)⁻¹.^[60]



A correlation was also experimentally determined between the cation electronegativity and the temperature of the first observed hydrogen desorption, T_d . The hydrogen desorption reactions of the borohydrides, where M = Li, Na, K, Mg, Zn, Sc, Zr, and Hf, were investigated experimentally. The borohydrides, M(BH₄)_n where M = Mg, Zn, Sc, Zr, and Hf, were synthesised by mechanically milling together the metal chloride, MCl_n with LiBH₄ according to Equation 1.57.^[60]



The synthesis of the borohydride was confirmed by the loss of X-ray powder diffraction peaks from the starting materials and the appearance of X-ray diffraction peaks from LiCl. Diffraction peaks were not observed for the product borohydrides which were thought to be disordered but the presence of B-H bonds was determined by IR spectroscopy.^[60]

The decomposition temperature of the borohydrides decreases with increasing electronegativity of the cation (Figure 1.8). Borohydrides with more electronegative cations than boron (Pauling electronegativity 2.0) are either unstable or do not exist, synthesis attempts usually result in the formation of the hydride, *e.g.* SiH_4 and PH_3 . This could suggest that the cation competes with boron to bond to the hydride ion.^[28]

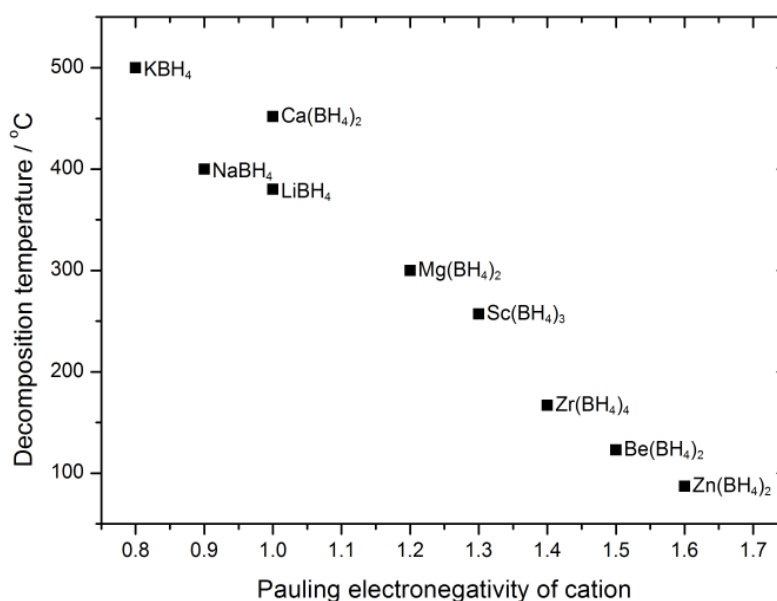


Figure 1.8 The correlation between decomposition temperature and Pauling electronegativity of the metal borohydrides ^[19, 25, 30, 92, 125]

Nakamori *et al.* also completed theoretical calculations for the hydrogen desorption reaction. Apart from $\text{Zn}(\text{BH}_4)_2$ which was shown to desorb some diborane, the borohydrides were assumed to decompose according to Equation 1.58.^[60]



The enthalpy, ΔH_{des} for this reaction was calculated from the predicted formation enthalpy of the borohydride and the experimentally determined formation enthalpies of the metal hydrides, MH . A positive correlation was determined between the desorption temperature, T_{d} and the desorption enthalpy ΔH_{des} , higher desorption temperatures corresponded to higher desorption enthalpies.^[60]

1.8.2 Comparison to the binary hydrides, MH_n

The stability of a borohydride species may be estimated from a Born-Haber cycle, where the interplay of the lattice, atomisation and ionisation enthalpies give an indication of compound stability. However, the Born-Haber cycle does not give the full picture because the borohydride ion contains covalent, not ionic B-H bonds and therefore, more charge transfer to the anion will result in stronger B-H bonds within the borohydride unit, stabilising the anion.^[60] Additionally, using a Born-Haber cycle to estimate the stability of a borohydride assumes that the borohydride decomposes to the metal, boron and hydrogen, (the reverse of the formation enthalpy) which is not necessarily the case. On the other hand clear trends can be observed in the stability of the borohydrides regardless of their decomposition products suggesting some conclusions about the factors affecting borohydride stability can still be made. A modified Born-Haber cycle for the formation of metal borohydrides is shown in Figure 1.9.

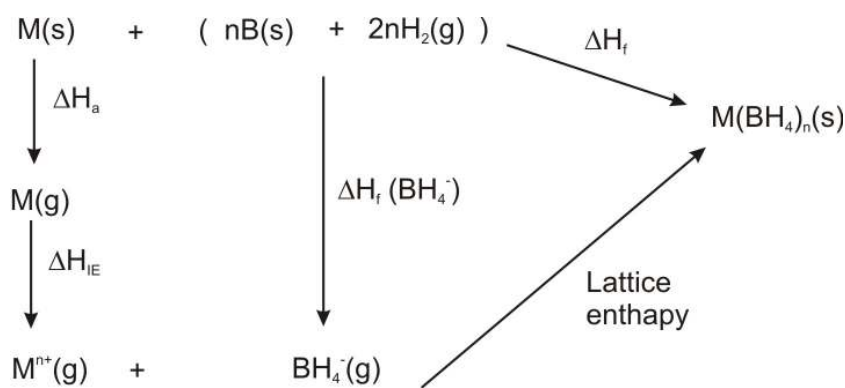


Figure 1.9 A modified Born-Haber cycle for the formation of metal borohydrides

On descending groups I and II of the periodic table, the ionic radii increase which has the effect of reducing the lattice enthalpy (less negative on forming the lattice from the ions) as shown by the Kapustinskii equation (Equation 1.59, assuming that $\Delta U (-273\text{ }^{\circ}\text{C}, 0\text{K}) \approx \Delta H (25\text{ }^{\circ}\text{C}, 298\text{K})$ ^[9]) destabilising the borohydride. However, the atomisation and ionisation enthalpies of the metals also decrease on descending groups I and II, contributing to more stable borohydrides and outweighing the effect of the reduced lattice enthalpy. The electronegativity of the cations also decreases on descending groups I and which will leave a higher electron density on the borohydride ion, increasing the anion stability.

$$\Delta U(0\text{K}) = \frac{(1.07 \times 10^5) \nu |z_+| |z_-|}{r_+ + r_-} \quad \text{Equation 1.59}$$

where ν is the number of ions in the empirical formula,
 z_+ and z_- are the charges of the cation and anion respectively and
 r_+ and r_- are the ionic radii of the cation and anion respectively.^[9]

The stability of the group I and II borohydrides increases on descending groups I and II of the periodic table as shown in Figure 1.10. The effective ionic radius of the borohydride anion has been reported to be $2.03\text{ \AA}$, this is similar to the bromide ion

(1.96 Å).^[60] The stability of the metal borohydrides are shown to increase as the ionic radii of the cation and anion become similar.

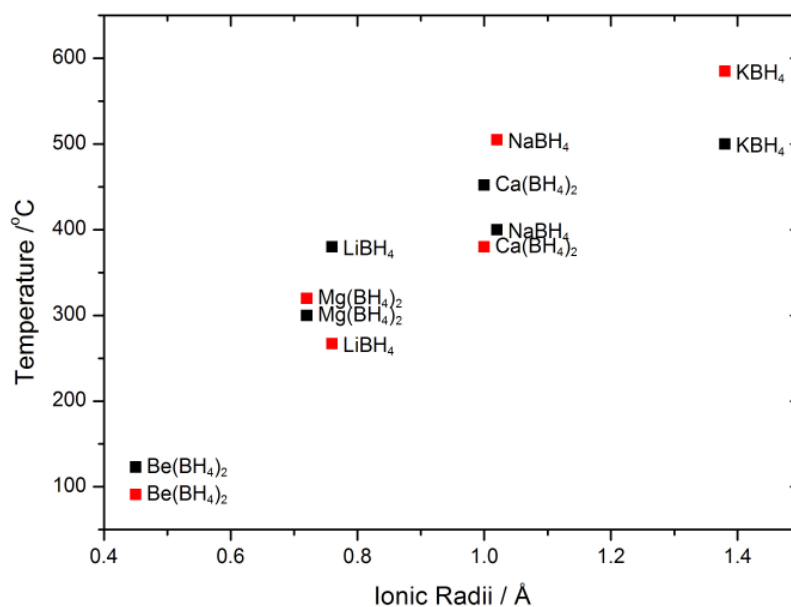


Figure 1.10 Melting (red) and decomposition (black) temperature of the borohydrides of group I and II shown as a function of cation ionic radius

A comparison with the metal hydrides shows a similar trend for the group II hydrides, which become more stable on descending the periodic table, however the opposite trend occurs for the group I metal hydrides.

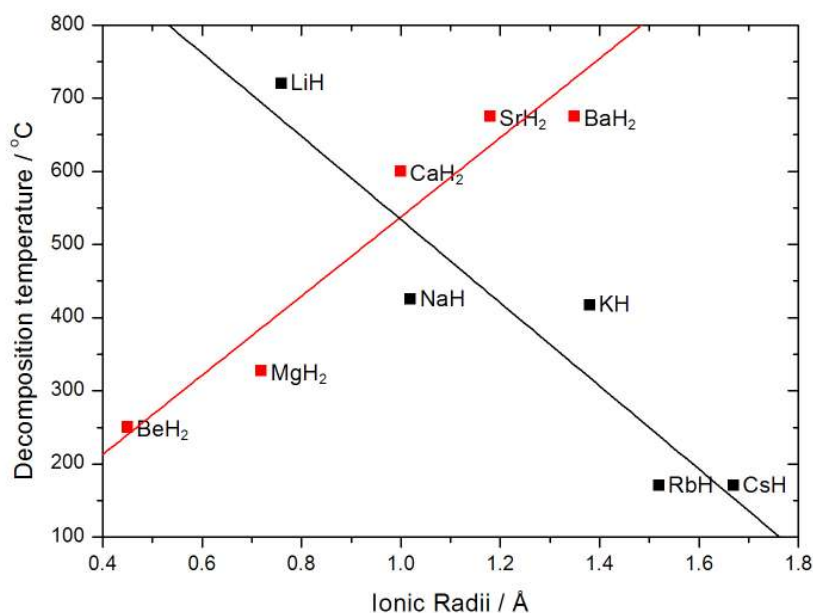


Figure 1.11 Decomposition temperature of the hydrides of group I and II shown as a function of ionic radius

The Born-Haber cycle for the formation of a metal hydride is shown in Figure 1.12. The atomisation and ionisation enthalpies of the group I and II metals and the lattice enthalpies of their respective metal hydrides (calculated using the Kapustinskii equation) are shown in Figure 1.13. The stabilisation of the group I hydrides is due to hybridisation between the cation and anion orbitals^[131] and the decrease in lattice enthalpy on descending the group outweighs the effect of the decreases in atomisation and ionisation enthalpies, destabilising the group I hydrides.

The low stability of BeH₂ is due to the high stability of the metal (indicated by the high atomisation enthalpy of beryllium in Figure 1.13).^[131] The trend for the rest of the group II metal hydrides is less well understood^[131] but is thought likely to be due to the rapid decrease in ionisation enthalpy (Figure 1.13), outweighing the decrease in lattice enthalpy on descending the group.

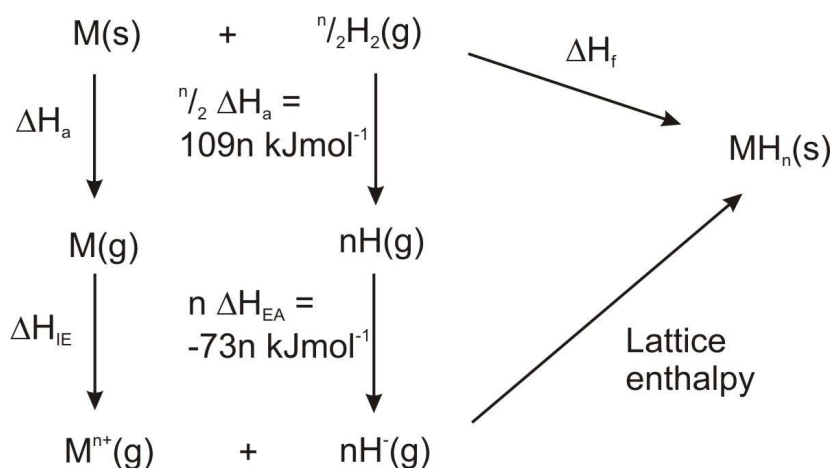


Figure 1.12 The Born-Haber cycle for the formation of metal hydrides

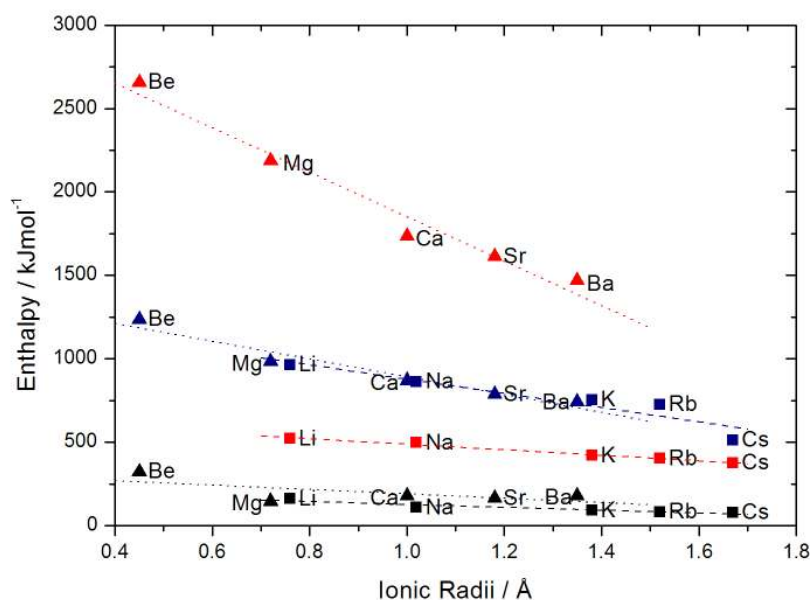


Figure 1.13 The atomisation enthalpy (black), ionisation enthalpy to form the most stable cation (red) of the group I and II metals and the lattice enthalpies of the metal hydrides (blue).

In summary, for the group I metal hydrides, the effect of decreasing lattice enthalpy outweighs the effect of decreasing atomisation enthalpy on descending the group. The opposite occurs for the group II hydrides. For the borohydrides, the decreasing atomic ionisation enthalpy is more important even in group I because of the requirement to also stabilise the covalent B-H bonds.

1.9 Mixed metal cation systems

1.9.1 Rationale for mixed metal cation systems

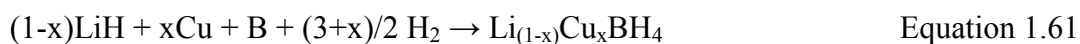
Although light metal borohydrides are considered as potential hydrogen storage materials due to their high proportion of hydrogen by weight, as already discussed, the alkali and alkaline earth metal borohydrides are thermodynamically stable and require high temperatures in order to release hydrogen by thermal decomposition. Some modification of these borohydrides is therefore required in order to create a hydrogen storage system capable of releasing hydrogen at lower temperatures.^[4, 16, 17] Various studies have been carried out investigating the effects of adding impurities to LiBH_4 in an attempt to destabilise the compound and hence lower the decomposition temperature.^{[18],[19]} For example, Au and Jurgensen found that mechanically milling LiBH_4 with 25% TiO_2 , TiCl_3 , ZrO_2 , V_2O_3 or SnO_2 reduced the decomposition temperature and increased the rate of hydrogen evolution compared to LiBH_4 alone. LiBH_4 mixed with TiO_2 released hydrogen at 200°C compared to 325°C for milled LiBH_4 .^[17]

The trend of decreasing borohydride decomposition temperature with increasing electronegativity would suggest that the decomposition temperature of borohydrides could be controlled by changing the electronegativity of the cation. Although it is not possible to modify the electronegativity of a particular cation, the average electronegativity of a mixed cation species could be modified.

1.9.2 Examples of mixed-metal cation systems

In 2005, Miwa *et al.* published a first principles study investigating the possibility of substituting copper into orthorhombic LiBH_4 to form $\text{Li}_{(1-x)}\text{Cu}_x\text{BH}_4$. The Cu^+ and Li^+ ions have similar ionic radii ($0.60 \text{ \AA}$ and $0.59 \text{ \AA}$ respectively) but copper is much

more electronegative than lithium, (Pauling electronegativity for Cu and Li are 1.9 and 1.0 respectively). The enthalpy of formation from the elements (Equation 1.60) was found to increase linearly with increasing copper content, becoming positive when $x \approx 0.8$. When formation from LiH, Cu, B and H₂ was considered (Equation 1.61) which is more relevant to the decomposition process, the enthalpy became positive at $x \approx 0.7$. The optimum composition was thought to be $x = 0.3$, when the formation enthalpy from the elements (Equation 1.60) was -121 kJ mol^{-1} and from LiH (Equation 1.61) was -39 kJ mol^{-1} . This compound contained 8.6 wt% H₂.^[132]



In 2007, Li *et al.* investigated the synthesis and thermal desorption properties of $\text{ZnLi}(\text{BH}_4)_3$, $\text{AlLi}(\text{BH}_4)_4$ and $\text{ZrLi}_{m-4}(\text{BH}_4)_m$ ($m = 5$ and 6) by mechanically milling LiBH_4 and a metal chloride. On heating $\text{ZnLi}(\text{BH}_4)_3$ and $\text{AlLi}(\text{BH}_4)_4$ were found to disproportionate into LiBH_4 and $\text{Zn}(\text{BH}_4)_2$ or $\text{Al}(\text{BH}_4)_3$, the $\text{ZrLi}_{m-4}(\text{BH}_4)_m$ ($m = 5$ and 6) complexes however, were stable and their decomposition temperatures were inversely proportional to the average electronegativities of their cations. The decomposition temperatures were 167°C for $\text{Zr}(\text{BH}_4)_4$, 322°C for $\text{ZrLi}(\text{BH}_4)_5$ and 377°C for $\text{ZrLi}_2(\text{BH}_4)_6$.^[30]

In 2008, Hagemann *et al.* synthesised $\text{LiSc}(\text{BH}_4)_4$ by mechanically milling LiBH_4 with ScCl_3 . High resolution synchrotron X-ray diffraction indicated a tetragonal unit cell, (space group $P-42c$, $a = 6.076 \text{ \AA}$ and $c = 12.034 \text{ \AA}$). The complex consists of Li^+ and $\text{Sc}(\text{BH}_4)_4^-$ ions. Hagemann *et al.* believe that this is the same compound which was synthesised by Nakamori *et al.*^[60] which was thought to be $\text{Sc}(\text{BH}_4)_3$. $\text{LiSc}(\text{BH}_4)_4$ released hydrogen between 177°C and 256°C .^[133] This work was extended by the

synthesis of $\text{NaSc}(\text{BH}_4)_4$ using a similar method, but unlike the lithium analogue, this synthesis also results in a new chloride, Na_3ScCl_6 . The $\text{NaSc}(\text{BH}_4)_4$ - Na_3ScCl_6 sample loses mass in two steps between $189\text{ }^\circ\text{C} - 223\text{ }^\circ\text{C}$ and $225\text{ }^\circ\text{C} - 292\text{ }^\circ\text{C}$, suggesting that decomposition is a complex process potentially involving an interaction between the two compounds. X-ray diffraction peaks for $\text{NaSc}(\text{BH}_4)_4$ were observed to disappear at $137\text{ }^\circ\text{C}$ suggesting that $\text{NaSc}(\text{BH}_4)_4$ melts before decomposing. Like $\text{LiSc}(\text{BH}_4)_4$, the crystal structure of $\text{NaSc}(\text{BH}_4)_4$ contains discrete $\text{Sc}(\text{BH}_4)_4^-$ ions with four borohydride units co-ordinated tetrahedrally to a scandium ion. The sodium ions are co-ordinated to six borohydride ions.^[134]

Recently, Ravnsbæk *et al.* synthesised a series of mixed alkali metal (Li or Na) - zinc borohydrides by mechanically milling the alkali metal borohydride with zinc chloride, ZnCl_2 . The LiBH_4 - ZnCl_2 combination produced $\text{LiZn}_2(\text{BH}_4)_5$ and the reaction went to completion when the appropriate molar ratio ($\text{LiBH}_4:\text{ZnCl}_2$ 2.5:1) was used. However the NaBH_4 - ZnCl_2 combination produced both $\text{NaZn}_2(\text{BH}_4)_5$ and $\text{NaZn}(\text{BH}_4)_3$ depending on the starting $\text{NaBH}_4:\text{ZnCl}_2$ ratio. NaZnCl_4 was also produced by ZnCl_2 -rich mixtures. The structures were identified by synchrotron X-ray powder diffraction and are not analogous to any previously known inorganic structures. The $\text{MZn}_2(\text{BH}_4)_5$ compounds have the space groups *Cmca* and $P2_1/c$ for $M = \text{Li}$ and Na respectively. The structure of $\text{NaZn}_2(\text{BH}_4)_5$ is a monoclinic distortion of the structure of $\text{LiZn}_2(\text{BH}_4)_5$. In $\text{MZn}_2(\text{BH}_4)_5$ the co-ordination numbers are 3, 4 and 2 for Zn, M and BH_4^- respectively. $\text{NaZn}(\text{BH}_4)_3$ also adopts the space group $P2_1/c$ but here the zinc ions are also coordinated to four borohydride units whilst the borohydride units have a combination of linear and trigonal planar co-ordination. ^{11}B magic angle spinning NMR spectroscopy showed a small shift in the ^{11}B frequency due to coordination to the zinc ions ($\delta(^{11}\text{B}) \approx -42\text{ ppm}$ to -46 ppm compared with

$\delta(^{11}\text{B}) = -41.2$ ppm for LiBH_4 and $\delta(^{11}\text{B}) = -42.0$ ppm for NaBH_4). There were two ^{11}B resonances in the ratio 1:2, showing that two of the boron sites are very similar. All of the compounds decompose to the alkali metal borohydride and zinc releasing diborane in the temperature range 95°C to 130°C . Decomposition also occurs after a week at room temperature. The ability of zinc to form covalent bonds to borohydride units was thought to stabilise these complexes.^[135]

$\text{NaK}(\text{BH}_4)_2$ has also recently been synthesised by Seballos *et al.* by mechanically milling NaBH_4 and KBH_4 . $\text{NaK}(\text{BH}_4)_2$ was thought to adopt a rhombohedral space group, most likely $R\bar{3}$ with lattice parameters of $a = 4.615(2)$ Å and $c = 22.39(2)$ Å. However the complex only has a lifetime of approximately 14 hours.^[136]

A density functional theory study of $\text{M}_1\text{M}_2(\text{BH}_4)_{2-5}$ was completed in 2009, where M_1 is either Li, Na or K and M_2 is an alkali, alkaline earth or a 3d/4d transition metal atom. The metal atoms were allowed to be either tetrahedrally or octahedrally coordinated by boron atoms apart from in the case of $\text{M}_1\text{M}_2(\text{BH}_4)_3$ where M_2 was allowed to be coordinated to three boron atoms. The alloying (Equation 1.62) and decomposition (Equation 1.63) enthalpies were calculated.^[137]

$$\Delta E_{\text{alloy}} = E_{\text{M}_1\text{M}_2(\text{BH}_4)_{2-5}} - (E_{\text{M}_1(\text{BH}_4)_n} + E_{\text{M}_2(\text{BH}_4)_n}) \quad \text{Equation 1.62}$$

$$\Delta E_{\text{decomp}} = E_{\text{M}_1\text{M}_2(\text{BH}_4)_{2-5}} - (E_{\text{M}_1\text{H}} + E_{\text{M}_2(\text{H})} + E_{\text{B}} + E_{n\text{H}_2}) \quad \text{Equation 1.63}$$

The alloying enthalpy determines if the compound is stable with respect to its parent compounds. The decomposition routes of these borohydrides are undetermined so decomposition was assumed to be to the alkali and alkaline earth metal hydride, transition metal, boron and hydrogen. The target stability range was $\Delta E_{\text{alloy}} \leq 0.0 \text{ eV f.u.}^{-1}$ so that the compound would not separate into its parent compounds and $\Delta E_{\text{decomp}} = -0.5 - 0.0 \text{ eV H}_2^{-1}$ so that the compound would be stable at

room temperature but the decomposition temperature would not be too high. Most of the compounds investigated were found to be stable with respect to decomposition but not with respect to separation into their parent compounds. The experimentally observed stable or metastable compounds $\text{LiSc}(\text{BH}_4)_4$, $\text{KNa}(\text{BH}_4)_2$ and $\text{Li}_2\text{Cd}(\text{BH}_4)_4$ were found to have potential to be stable but have a slight possibility of separating into the parent compounds. $\text{LiK}(\text{BH}_4)_2$ and $\text{LiNi}(\text{BH}_4)_3$ were not found within the target ranges. $\text{LiMn}(\text{BH}_4)_3$ and $\text{NaMn}(\text{BH}_4)_3$ were found within the target ranges and are known experimentally to decompose between 100°C and 110°C . $\text{LiZn}(\text{BH}_4)_3$ and $\text{LiAl}(\text{BH}_4)_4$ were also within the target ranges and but are known experimentally to disproportionate at approximately 130°C . The $\text{M}_1(\text{Al/Mn/Fe})(\text{BH}_4)_4$, $(\text{Li/Na})\text{Zn}(\text{BH}_4)_3$ and $(\text{Na/K})(\text{Ni/Co})(\text{BH}_4)_3$ compounds were found to be the most promising.^[137]

A mixed lithium-magnesium borohydride, $\text{Li}_{1-x}\text{Mg}_{1-y}(\text{BH}_4)_{3-x-2y}$ is thought to have been synthesised by Fang *et al.*. The compound was produced by mechanically milling LiBH_4 with $\text{Mg}(\text{BH}_4)_2$. The mixed sample was found to release hydrogen at 240°C which is lower than both LiBH_4 and $\text{Mg}(\text{BH}_4)_2$. X-ray diffraction showed only weak peaks for the starting materials and a series of unidentified peaks suggesting that a new compound had been formed from the starting materials.^[138]

The combination of two metal borohydrides does not necessarily need to form a new compound in order to have an effect. Lee *et al.* have published a study of the mixed metal borohydride system $x \text{LiBH}_4 + (1-x) \text{Ca}(\text{BH}_4)_2$ which was synthesised by mechanical milling. X-ray diffraction showed that the mixture did not react to form a new product but formed a eutectic mixture which melted at 200°C compared to 280°C for LiBH_4 . This was confirmed by differential scanning calorimetry which showed that the orthorhombic to hexagonal phase transition of LiBH_4 still occurred at 110°C and endothermic peaks related to $\text{Ca}(\text{BH}_4)_2$ at 150°C were still present,

however new endothermic peaks were observed at 200 °C coinciding with the loss of the peak at 280 °C which corresponded to the melting of LiBH_4 . The decomposition of the system was also affected by the mixture although mixtures which were rich in either $\text{Ca}(\text{BH}_4)_2$ or LiBH_4 showed evidence of decomposition above 400 °C, suggesting that excesses of one compound were unaffected by the other compound. Intermediate mixtures showed different decomposition characteristics, for $x = 0.4$, the decomposition was complete by 370 °C. X-ray diffraction showed evidence of a $\text{Ca}(\text{BH}_4)_2$ decomposition intermediate appearing at 230 °C, 100 °C lower than would otherwise be expected. Mixtures with $x = 0.4$ or 0.6 released 10 wt% hydrogen below 400°C.^[139]

Mixed alkali metal cation complexes have been observed in other complex hydrides for example the amides (2008), where $\text{Li}_3\text{Na}(\text{NH}_2)_4$ and $\text{LiNa}_2(\text{NH}_2)_3$ have been synthesised by manually grinding LiNH_2 and NaNH_2 together and heating to 200°C. $\text{Li}_3\text{Na}(\text{NH}_2)_4$ is non stoichiometric within the range of $\text{Li}_{4-y}\text{Na}_y(\text{NH}_2)_4$ where $0 \leq y \leq 1.0$.^[140] The mixed metal alanate (1999), $\text{Na}_2\text{LiAlH}_6$ has also been observed and was synthesised by mechanically milling NaH , LiH and NaAlH_4 for 40 hours, the synthesis was confirmed by X-ray diffraction.^[141]

Mixtures of LiBH_4 with NaBH_4 and KBH_4 with NaBH_4 form solid solutions in the same way as the corresponding chloride mixtures, LiCl with NaCl and KCl with NaCl . However a mixture of LiCl with KCl is eutectic and likewise a mixture of LiBH_4 with KBH_4 is eutectic with 53 mole% KBH_4 , melting at 103°C.^[23]

The existence of this LiBH_4 - KBH_4 eutectic composition initiated further research into the interaction between LiBH_4 and KBH_4 leading to the first ever synthesis and crystal structure determination of a mixed alkali metal borohydride, $\text{LiK}(\text{BH}_4)_2$ in 2008,^[142]

which is discussed in Chapter 7. Importantly, in this new material the observed decomposition temperature lies intermediate between that of the constituent phases.

Xiao *et al.* published a first-principles study of $\text{LiK}(\text{BH}_4)_2$. The material was found to be insulating. Enthalpy calculations suggested that the most favourable synthesis route was from the elements and that the decomposition temperature should be between that of LiBH_4 and KBH_4 .^[88] Kim and Sholl have also carried out first-principles calculations on the crystal structure and thermodynamics of $\text{LiK}(\text{BH}_4)_2$. $\text{LiK}(\text{BH}_4)_2$ was found to be unstable with respect to decomposition into LiBH_4 and KBH_4 at most temperatures including room temperature.^[75]

1.10 Decomposition products

There is a level of uncertainty over the decomposition products of borohydrides. Most are thought to release hydrogen on decomposition. However, many have not yet been determined. There is evidence that borohydrides with a cation Pauling electronegativity which is less than 1.5 only release hydrogen whereas other borohydrides such as Mn, Zn and Al release diborane as well.^[92] There may also be a connection between the decomposition temperature and the observed decomposition products. Significant decomposition of diborane begins above 150°C ^[129] making it less likely to be observed as a decomposition product for decompositions occurring far above this temperature, both because decomposition to hydrogen will be more favourable and because any diborane that is released may decompose before it is detected. The decomposition temperatures of $\text{Mn}(\text{BH}_4)_2$ and $\text{Zn}(\text{BH}_4)_2$ are 169°C and 160°C respectively. $\text{Al}(\text{BH}_4)_3$ vapour begins to decompose above 60°C and rapid decomposition begins at approximately 150°C . These temperatures are either below the decomposition temperature of diborane or in a temperature range where diborane

decomposition has only just begun and therefore, there is a higher probability of observing diborane as a borohydride decomposition product than for borohydrides with higher decomposition temperatures.^[28, 92]

1.11 Borohydride ion geometry

There is dispute as to the level of symmetry of the borohydride ion, is it perfectly tetrahedral or distorted and is the distortion significant?^[51, 55, 88, 143] A perfectly tetrahedral ion would have internal H-B-H angles of 109.5° and all the B-H bond lengths equal. A borohydride ion is not particularly amenable to study by X-ray diffraction due to the low electron density of hydrogen. There are problems with neutron diffraction studies of borohydrides due to neutron absorption by boron-10 (a 20 % isotope of boron) and the incoherent scattering of hydrogen. Early synchrotron X-ray powder diffraction studies of LiBH_4 reported the BH_4^- tetrahedra to be distorted (B-H lengths 1.04(2) Å to 1.28(1) Å, H-B-H bond angles 85° to 120° ^[51]). However, later X-ray diffraction data and neutron diffraction data from LiBH_4 show the borohydride ion to be closer to the ideal tetrahedral shape. B-H bond lengths of 1.104(11) Å to 1.131(15) Å and H-B-H angles of $108.8(9)^\circ$ to $109.9(7)^\circ$ were determined by X-ray diffraction^[55] and B-H lengths of 1.186(7) Å to 1.217(15) Å and H-B-H bond lengths of $105.4(9)^\circ$ to $111.8(8)^\circ$ ^[52] were determined by neutron diffraction. B-D lengths in LiBD_4 have been reported to be between 1.18(2) Å and 1.20(2) Å as determined by neutron diffraction.^[54]

It has been suggested that borohydride ions with a reduced anionic charge are destabilised and distorted.^[143] The reduced negative charge is a result of highly electronegative cations or cations with a high ionisation enthalpy. $\text{Al}(\text{BH}_4)_3$ which has

a strongly polarising cation with a Pauling electronegativity of 1.5^[77] has been reported to have distorted borohydride ion tetrahedra.^[21]

1.12 Project aims

The scope of this thesis is focused on many of the issues discussed in this chapter, in particular the structure of the alkali and alkali earth metal borohydrides, including the geometry of the borohydride ions, their thermal behaviour and decomposition routes.

Consequently the aims of this project are to

- improve the knowledge of the structures of the known alkali and alkali-earth borohydrides including the shapes of the borohydride ions as a function of temperature
- synthesise and solve the structures of alkali and alkali-earth metal borohydrides without a known structure
- synthesise and analyse new mixed metal borohydrides in an attempt to modify their properties relative to the parent compounds
- investigate the decomposition temperatures and routes of the above borohydrides

This will lead to a greater understanding of the potential of borohydrides as hydrogen storage materials and how their properties can be manipulated. The main focus of this project is on LiBH_4 , NaBH_4 , KBH_4 , $\text{LiK}(\text{BH}_4)_2$, $\text{Ca}(\text{BH}_4)_2$, and $\text{Sr}(\text{BH}_4)_2$.

1.12.1 Group I borohydrides

Isotopically enriched $\text{Li}^{11}\text{BD}_4$, $^7\text{Li}^{11}\text{BD}_4$, $\text{Na}^{11}\text{BD}_4$ and K^{11}BD_4 were synthesised using a high pressure solid-gas reaction. Variable temperature and X-ray diffraction studies of these isotopically enriched products have been completed focusing on the changes in lattice parameters, the phase change of $\text{Li}^{11}\text{BD}_4$ and the geometries of the

borohydride ions. Thermogravimetric analysis with mass spectrometry has investigated the temperatures and stages of decomposition and the decomposition products.

1.12.2 LiK(BH₄)₂

Lithium-potassium borohydride, LiK(BH₄)₂, the first mixed alkali metal borohydride has been synthesised as a part of this project. The structure was solved by synchrotron X-ray diffraction revealing that the space group is *Pnma* which is the same space group as LiBH₄. The thermal behaviour of LiK(BH₄)₂ was investigated by variable temperature synchrotron X-ray diffraction and by thermogravimetric analysis with mass spectrometry.

1.12.3 Ca(BH₄)₂

A variable temperature synchrotron X-ray diffraction study of Ca(BH₄)₂ was completed, enabling the elucidation of new Ca(BH₄)₂ phases. The decomposition of Ca(BH₄)₂ was investigated by thermogravimetric analysis with mass spectrometry. The effects of the phase changes on the boron environments were investigated by variable temperature solid state ¹¹B NMR.

1.12.4 Sr(BH₄)₂

Strontium borohydride was synthesised via a solution state synthesis route. Its structure was solved using variable temperature synchrotron X-ray diffraction. The unit cells of polymorphs and solvates were also indexed. The decomposition of Sr(BH₄)₂ was investigated by thermogravimetric analysis with mass spectrometry.

2 Experimental techniques

2.1 Synthesis techniques

2.1.1 *Glove box*

All of the samples discussed in this thesis are sensitive to moisture in the atmosphere. Consequently, the majority of sample manipulation was carried out within an MBraun Unilab glove box operating with an argon atmosphere ($O_2 < 20$ ppm).

2.1.2 *Sealed evacuated tubes*

The syntheses of most of the samples of $LiK(BH_4)_2$ (Chapter 7) were carried out in a sealed evacuated tube within a Carbolite muffle furnace. This process involves grinding the samples by hand using an agate pestle and mortar in an argon atmosphere glove box. The sample is placed into an alumina crucible which is placed inside a quartz tube which has already been sealed at one end. The open end of the tube is then sealed with a Young's tap *via* an Ultra-Torr fitting and removed from the glove box. The tube is evacuated to 10^{-6} mbar using a high vacuum line and then sealed by melting the tube close to the Young's tap and thus separating the top of the tube and Young's tap from the sealed portion containing the crucible. The sealed evacuated tube is then heated inside a muffle furnace. Examples of a sealed evacuated tube and the muffle furnace are shown in Figure 2.1.

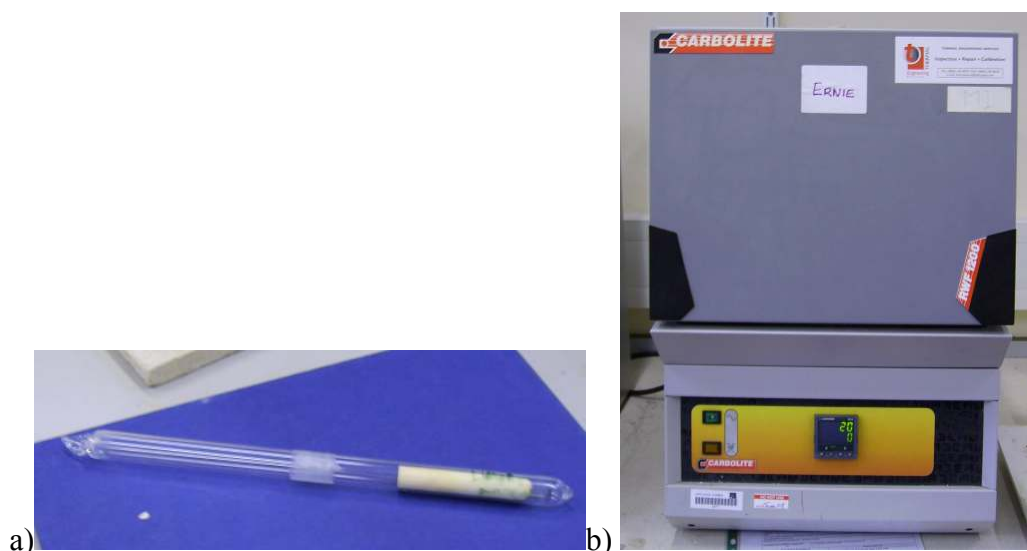


Figure 2.1 An example of a) a sealed evacuated tube and b) the muffle furnace

2.1.3 Tube furnace with dynamic vacuum or flowing gas

$\text{LiK}(\text{BH}_4)_2$ (Chapter 7) was also prepared by heating a ground mixture with a molar ratio of 2:1 $\text{LiBH}_4\text{:KBH}_4$ to 125 °C for 12 hours under flowing nitrogen within a tube furnace. $\text{Ca}(\text{BH}_4)_2$ (Chapter 8) was prepared by heating $\text{Ca}(\text{BH}_4)_2 \cdot 2\text{THF}$ to 160 °C under dynamic vacuum for one hour.

When a tube furnace is used, the ground sample is placed inside an alumina crucible within a quartz tube which is sealed at one end; the open end is sealed via a Young's tap. The end of the tube containing the sample is heated in a Carbolite tube furnace. For a dynamic vacuum, the tube is connected directly to a vacuum pump or to a high vacuum line via the Young's tap allowing the sample to be heated under dynamic vacuum. This achieves a better level of vacuum and easier temperature control than using an oil bath and a Schlenk line as detailed below. Alternatively the tube can be fitted with three Young's taps allowing either nitrogen or argon to be flowed in and out through the taps via gas bubblers providing a gas flow across the end of the tube containing the sample as shown in Figure 2.2.

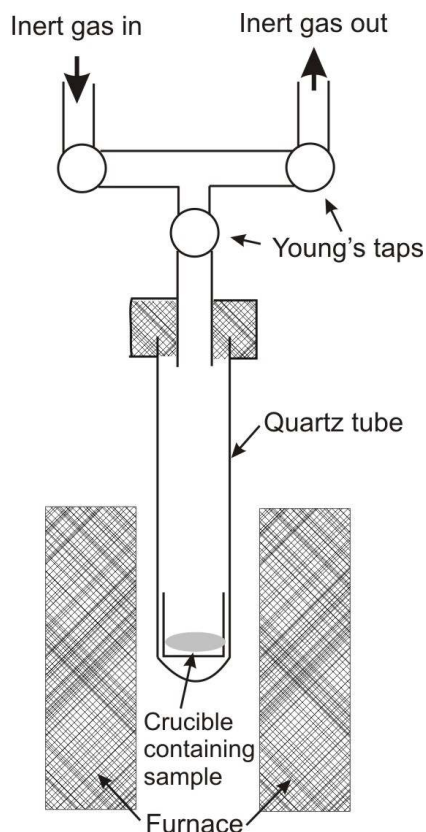


Figure 2.2 The experimental set up for using a tube furnace with inert gas flowing over the sample

2.1.4 Schlenk line

Isotopically enriched samples (Chapter 3) were washed in anhydrous solvent using a Schlenk line. A synthesis of $\text{LiK}(\text{BH}_4)_2$ (Chapter 7) from LiBH_4 and KBH_4 in ether was attempted using a Schlenk line. $\text{Sr}(\text{BH}_4)_2$ (Chapter 9) was prepared from LiBH_4 , NaBH_4 and SrCl_2 in THF using a Schlenk line. The Schlenk line assembly is shown diagrammatically in Figure 2.3.

A Schlenk line consists of combined vacuum and inert gas (normally nitrogen) lines connected via double oblique taps. Schlenk reaction vessels are connected to the line via flexible tubing and the double oblique taps select whether the vessel is under nitrogen or vacuum. A Schlenk line allows solution based reactions to be carried out on air-sensitive compounds under a protective nitrogen atmosphere. The nitrogen pressure can be used to transfer liquids via cannulae between vessels (Figure 2.4). The

tap on the solvent Schlenk flask and the bung on the reaction flask are replaced by rubber septa and a cannula is used to connect the flasks. The tap to the nitrogen supply on the reaction flask is closed and an exit needle put into the rubber septum on the reaction flask. Solvent is pushed along the cannula into the reaction flask by the nitrogen pressure. Cannulae fitted with filters can be used for filtration. Reactions can be stirred in a flask under a nitrogen atmosphere at room temperature or for a heated, reflux reaction, the nitrogen supply is connected to the top of the reflux condenser to prevent evaporated solvent escaping via the nitrogen supply. After a reaction, solvent can be evaporated under reduced vacuum via the vacuum section of the Schlenk line. For a typical reaction, solid reagents were loaded into a Schlenk flask within an argon atmosphere glove box. If necessary a condenser is fitted and then the flask is sealed, removed from the glove box and connected to the Schlenk line via the flexible tubing. A solvent Schlenk flask is also connected. The tubing is purged with nitrogen three times before the taps to the flasks are opened. Solvent is added to the flask via a cannula and rubber septa. The reaction is stirred under nitrogen at room temperature or whilst refluxing. When the reaction time is complete and the solution is cooled, the solution is filtered to separate precipitates which can be washed with more solvent if necessary and then dried under reduced pressure. Further drying with heating is sometimes necessary.

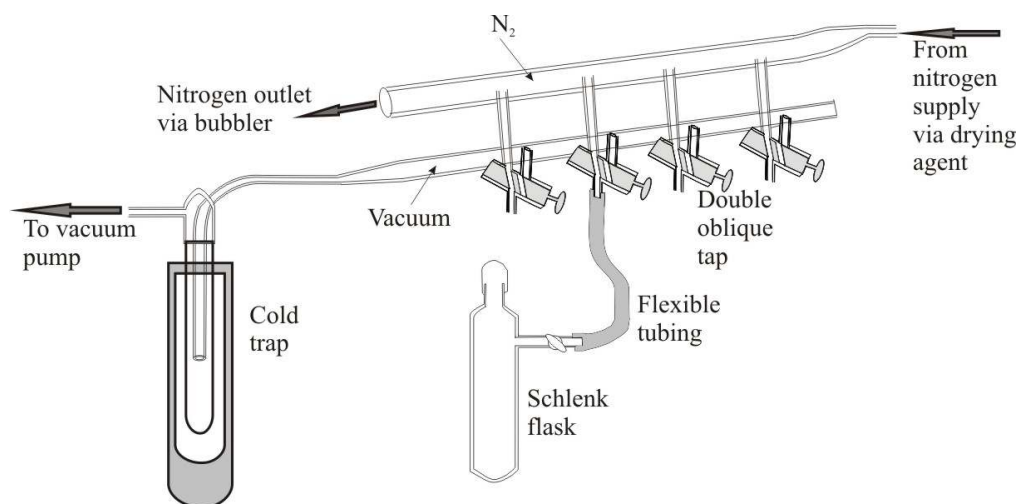


Figure 2.3 A diagram of a Schlenk line assembly

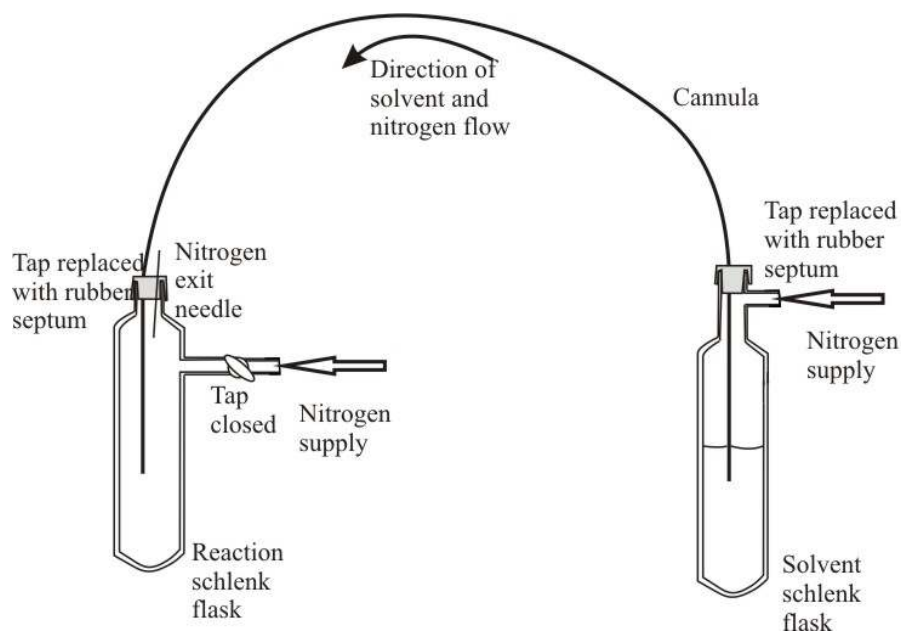


Figure 2.4 The method of transferring solvent via a cannula using nitrogen pressure

2.1.5 High pressure furnace

Isotopically enriched ${}^7\text{Li}^{11}\text{BD}_4$ and $\text{Li}^{11}\text{BD}_4$ (Chapter 4), $\text{Na}^{11}\text{BD}_4$ (Chapter 5) and K^{11}BD_4 (Chapter 6) were prepared using a high pressure furnace (Chapter 3).

The high pressure furnace consists of a pressure vessel which is inserted into a separate heater assembly once it is loaded. The pressure vessel is a 73 ml custom

made reactor from Parr made from Haynes Alloy 230. This is a nickel, chromium and tungsten alloy which can withstand high temperatures and pressures (limits 700 °C and 200 bar) and is also resistant to H₂ embrittlement. The vessel is sealed with a screw cap containing six screws to exert a sealing force onto a flat flexible graphite gasket. A Gage Block Assembly attached to the top of the vessel connects a pressure gauge, a safety rupture disc, a gas inlet/outlet and a tap to seal the vessel. A thermocouple is inserted into the bottom of the vessel.

The pressure vessel is loaded with the solid reactants within an argon filled glovebox before being sealed and taken out of the glove box. The vessel is connected to gas supply tubing via the gas inlet/outlet. This connects the vessel to a vacuum pump and a reactant gas supply. The vessel is evacuated and then charged with the required gas pressure and sealed. The supply tubing is removed, the heater assembly and thermocouple brought into place and heating is commenced. At the end of the heating cycle, the vessel can be evacuated again via the supply tubing.

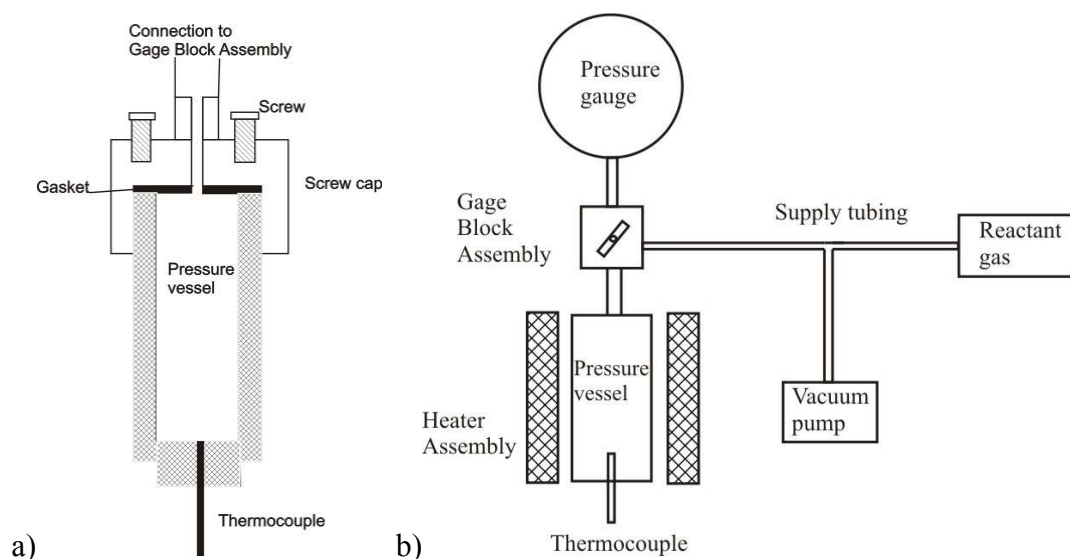


Figure 2.5 a) The pressure vessel and b) the complete set up for of the High Pressure Furnace

2.1.6 Ball mill

For the synthesis of the isotopically enriched compounds (Chapter 3), the ^{11}B powder was mechanically milled to increase the surface area, prior to use.

Mechanical milling was carried out using a planetary (rotating) ball mill (Retsch PM100) under an argon atmosphere. Milling was carried out in a 125 ml milling jar with six 20 mm milling balls so that the mass ratio of balls to powder was approximately 35:1. Both the milling jar and balls (Figure 2.6) are made of tungsten carbide (WC). The sample and milling balls were loaded into the milling jar within an argon filled glove box, the jar was then sealed closed with a tungsten carbide lid via a rubber O-ring seal. The sealed jar was removed from the glove box and secured within the ball mill. Milling was carried out at 400 rpm with one hour pauses every hour. Pauses are necessary to minimise increases in temperature due to friction caused during the milling process. The direction of milling was reversed after each pause. After milling, the jar was returned to the glove box to remove the sample.



Figure 2.6 The milling jar and balls

2.2 Sample analysis

2.2.1 Crystallography^[144]

Crystals are solids containing a periodic arrangement of atoms and consequently have long range order. The arrangement of atoms within the crystal, the crystal structure, can be classified depending on which one of seven sets of reference axes, crystal systems, can be used to describe the crystal structure. Crystal systems are defined by the relative magnitude of the reference axes and the angles between them. The unit cell is the smallest volume unit with the highest symmetry which can be translated in all directions to construct a 3D lattice. The shape of the unit cell is generally determined by the reference axes of the crystal system; the dimensions of the unit cell faces are a , b and c and the angles between them are α (between b and c), β (between a and c) and γ (between a and b) (Figure 2.7). Z is defined as the number of times that the molecular formula occurs within the unit cell.

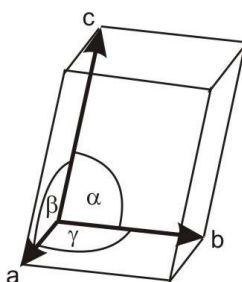


Figure 2.7 A diagram of a unit cell showing a , b , c , α , β and γ and also the reference axes

The unit cell is constructed from the asymmetric unit which is the arrangement of atoms which are moved around the unit cell by different symmetry operations; reflections, rotations, screw axes (rotation and translation) and glide planes (reflection and translation). The number of formula units within the asymmetric unit is Z' , this

may be less than one if a molecule is positioned on a centre of symmetry. Atomic positions within the unit cell are expressed as fractions of the unit cell dimension, for example the centre of the unit cell is ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$).

A Bravais lattice simplifies the crystal into an array of equivalent points with each point being represented as a lattice point. Lattice point arrangements can be:

- primitive, *P*, where lattice points only occur on the corners of the unit cell,
- body centred, *I*, where lattice points occur on the corners and in the centre of each unit cell,
- side centred, *C*, where lattice points occur on the corners of the unit cell and in the centres of a pair of opposite faces, usually designated to be perpendicular to the *c* axis,
- face centred, *F*, where lattice points occur on the corners and in the centre of all the faces of the unit cell.

The combination of seven crystal systems and four different arrangements of lattice points results in 14 possible Bravais Lattices (Table 2.1). The trigonal crystal system contains a 3 fold rotational axis and can be displayed using two different sets of axes. Planes of lattice points can be defined, these are the planes which are traditionally used to explain diffraction points. Miller Indices (*hkl*) are used to define planes which cross the unit cell axes at intervals of a/h , b/k , c/l .

The symmetry of crystal structures is described by their space group, which gives the type of Bravais lattice and the combination of symmetry elements which are required to construct the unit cell from the asymmetric unit.

Table 2.1 The seven crystal systems, their parameters and possible Bravais Lattices

Crystal System	Parameters	Bravais Lattices
Cubic	$a = b = c, \alpha = \beta = \gamma = 90^\circ$	P, I, F
Tetragonal	$a = b \neq c, \alpha = \beta = \gamma = 90^\circ$	P, I
Orthorhombic	$a \neq b \neq c, \alpha = \beta = \gamma = 90^\circ$	P, C, I, F
Trigonal –		P
<i>Rhombohedral or</i>	$a = b = c, \alpha = \beta = \gamma \neq 90^\circ$	
<i>Hexagonal setting</i>	$a' = b' \neq c', \alpha' = \beta' = 90^\circ, \gamma' = 120^\circ$	
Hexagonal	$a = b \neq c, \alpha = \beta = 90^\circ, \gamma = 120^\circ$	P
Monoclinic	$a \neq b \neq c, \alpha = \gamma = 90^\circ, \beta \neq 90^\circ$	P, C
Trigonal	$a \neq b \neq c, \alpha \neq 90^\circ, \beta \neq 90^\circ, \gamma \neq 90^\circ$	P

2.2.2 Diffraction theory

2.2.2.1 Diffraction

Waves can be diffracted when they interact with objects of a similar size to their wavelength, (or objects with a similar separation to their wavelength). The wavelengths of X-rays and thermal neutrons are similar to the separation of atoms within a solid. Crystalline materials contain regularly spaced atoms in a repeating lattice so that the same interaction with radiation occurs many times creating a measurable difference between the incident and diffracted radiation. This difference can be in the phase or direction of the waves and can be used to determine structural information about a solid. Elastic scattering, where there is no energy exchange between the radiation and the sample is used to determine structural information and will be discussed here. Inelastic scattering is also possible and can be used to gather spectroscopic information about a sample but is outside of the scope of this thesis.

2.2.2.2 Bragg's Law

Bragg's Law (Equation 2.1) gives a simple explanation of when radiation diffracted by a crystalline sample will combine constructively so that the diffracted beam can be detected. Figure 2.8 shows monochromatic waves from a coherent source being diffracted from planes of lattice points with separation d . The angles of the incident and diffracted beam will be equal. In order for the diffracted waves to superimpose constructively, the difference in the path lengths of the waves must be equal to a whole number of wavelengths. In practice the equation is often simplified by treating n as equal to one. If n was equal to a larger number, for a given angle of incidence, θ , the plane separation, d would be larger, however diffraction from this larger plane separation could also be observed by changing the angle of incidence of the radiation.

$$n\lambda = 2d \sin\theta$$

Equation 2.1

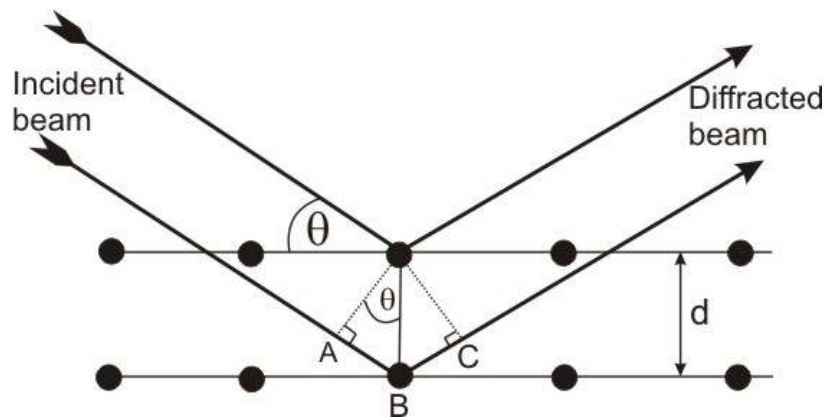


Figure 2.8 A graphical demonstration of Bragg's Law

2.2.2.3 Reciprocal space

When radiation interacts with a three dimensional sample, diffraction information can only be collected on the surface of a sphere surrounding the sample. This surface is two dimensional, hence one dimension of information is lost. Diffraction theory deals with this by the use of reciprocal space, where sets of parallel planes of lattice points in real (direct) space are represented by reciprocal lattice points in reciprocal space, *i.e.* diffraction patterns occur in reciprocal space. Sets of planes with a common h , k or l value produce a line of spots (Figure 2.9).

The unit cell vectors for the reciprocal lattice, a^* , b^* and c^* are perpendicular to the end faces of the unit cell in the direct (real space) lattice, this also means that for example, a^* is perpendicular to the bc plane. The lengths of the vectors are the inverse of the perpendicular distances of the unit cell faces from the origin, so $a^* = 1/d_{100}$. The origins for both the direct and reciprocal lattice occur at the same place. In the same way, the reciprocal lattice is constructed from the normals to the sets of Miller planes in direct space. Lattice points are located on these normals at a distance of $1/d$ from the lattice origin where d is the separation of the planes in direct space. The units of reciprocal space are $\text{\AA}^{-1}$. Small spaces in reciprocal space equate to large spaces in direct space. Vertical patterns in the sample in direct space result in horizontal patterns in the diffraction pattern in reciprocal space. This situation is seen in the equation for Bragg's Law because $\sin \theta$ is inversely proportional to d .^[144]

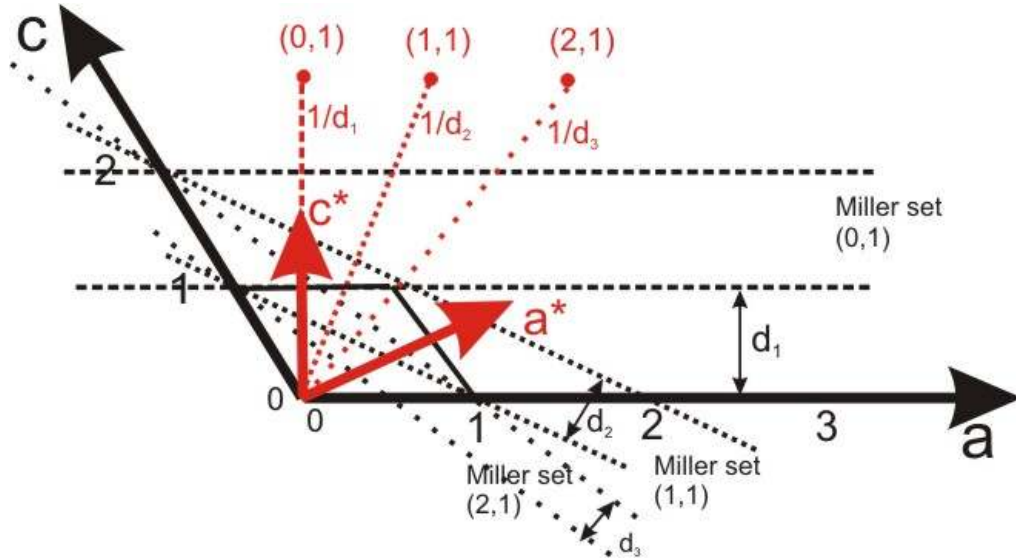


Figure 2.9 The direct and reciprocal lattice showing the direct space unit cell vectors a and c and the reciprocal vectors a^* and c^* . (The direct space axes x and z are along the same direction as the unit cell vectors a and c .)

2.2.2.4 Ewald sphere

The Ewald Sphere is used to determine which sets of planes of lattice points will diffract radiation of a given wavelength, λ . Bragg's Law can be rearranged to Equation 2.2. In reciprocal space, Equation 2.3 applies which can be rewritten as Equation 2.4.

$$\sin \theta = \lambda \frac{1}{2d} \quad \text{Equation 2.2}$$

$$\sin \theta = \frac{1}{2d} \frac{1}{\lambda} \quad \text{Equation 2.3}$$

$$2 \sin \theta = \frac{1}{d} \frac{1}{\lambda} \quad \text{Equation 2.4}$$

So for diffraction to occur, this condition (Equation 2.4) must be met and is represented graphically by the surface of the Ewald sphere. Only reciprocal lattice points occurring on the surface of a sphere with radius $1/\lambda$ will be seen using radiation

of wavelength, λ . The sphere is located so that its circumference passes through the origin of the reciprocal lattice. The incident radiation is placed along a radius of the sphere passing through the origin of the reciprocal lattice (Figure 2.10). Rotating the crystalline sample relative to the incident radiation has the effect of rotating the sphere around the origin so different reciprocal lattice points are on the surface.

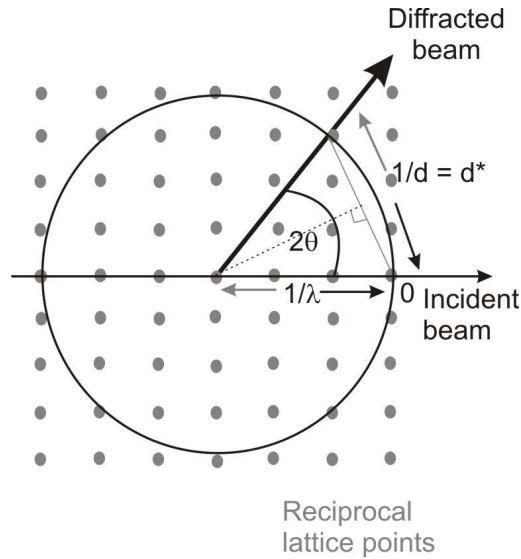


Figure 2.10 The Ewald Sphere

$$\text{If } 2\theta = 180^\circ, (1/d)/(1/\lambda) = \lambda/d = 2 \sin 90^\circ = 2 \text{ so } \lambda = 2d \text{ or } 1/d = d^* = 2/\lambda$$

Equation 2.5

$$\text{If } 2\theta = \text{very small}, \lambda/d = \text{very small}, \lambda > d_{\max}$$

Equation 2.6

For diffraction to occur, the reciprocal lattice spacing must be less than $2/\lambda$ (Equation 2.5). Equally, the wavelength must be larger than the maximum d spacing in direct space (Equation 2.6).^[144, 145]

2.2.2.5 Laue Conditions

Although Bragg's Law provides a simple explanation for when diffraction will be observed, it relies on radiation being diffracted by planes of lattice points. The Laue Conditions give a more complex but complete description of when diffraction will be observed and is summarised here.

Figure 2.11 shows radiation being diffracted by a one dimensional sample. For the diffracted beam to be observed, the difference in path length between the diffracted waves ($BC-AB$) must be an integer number of wavelengths. Unlike in Bragg's Law where diffraction is treated like reflection and the angle of incidence is equal to the diffracted angle, if the wave is diffracted through a material the angles may be different. The relationship between the wavelength, λ , and the object separation, a , is given by Equation 2.8 where h is an integer.

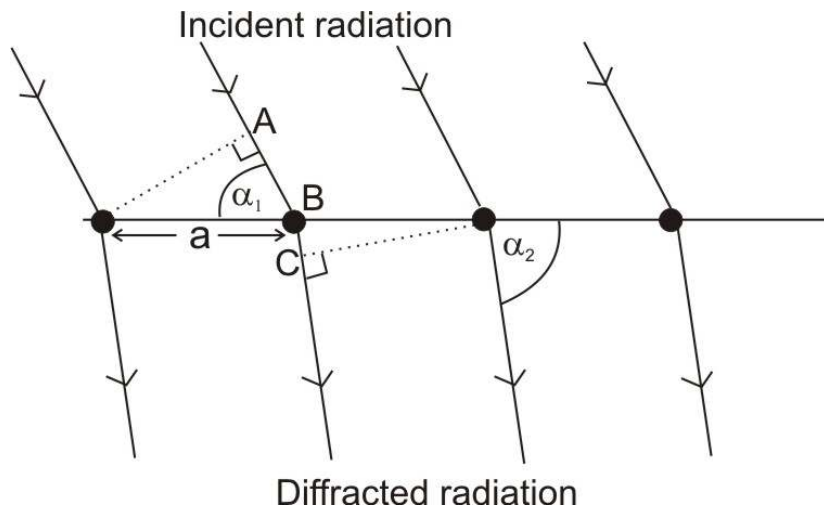


Figure 2.11 Diffraction in one dimension

$$AB = a \cos \alpha_1 \quad BC = a \cos \alpha_2 \quad \text{Equation 2.7}$$

$$h\lambda = BC - AB = a (\cos \alpha_2 - \cos \alpha_1) \quad \text{Equation 2.8}$$

If the one dimensional object in Equation 2.13 was the a axis of a three dimensional unit cell, in order for diffraction to be observed, this equation must also be obeyed in the other two dimensions (Equation 2.9 and Equation 2.10). In three dimensions, each required angle results in a cone around the unit cell axis and diffraction will only occur where the cones around each axis intersect. These are the Laue conditions.^[146]

$$k\lambda = b (\cos \beta_2 - \cos \beta_1) \quad \text{Equation 2.9}$$

$$l\lambda = c (\cos \gamma_2 - \cos \gamma_1) \quad \text{Equation 2.10}$$

2.2.2.6 Intensities of peaks

The symmetry of the unit cell determines the locations of diffraction peaks but the intensities of these peaks are determined by the atomic positions within the unit cell. This is a result of the addition of different waves being diffracted by different atoms within the sample. The diffracted waves have different phase angles causing constructive and destructive interference resulting in different intensities. The intensities are equal to the square of the structure factor, F , after corrections have been applied (Equation 2.11). These corrections are for Lorentz polarization relating to the proportion of time that a particular diffraction point fulfils the conditions for diffraction, polarization because the X-ray beam may become partially polarized by reflection and absorption because some atoms absorb X-rays as well as scattering them. There are similar correction factors for neutron diffraction experiments taking into account the ways that neutrons are treated prior to hitting the sample. The structure factor contains contributions from the atomic scattering factor, f_j , of all the atoms within the sample (Equation 2.12). For X-rays, at low Bragg angles, the atomic scattering factor is proportional to the square of the atom's electron density but it decreases at higher angles. This is because the electron cloud is larger than the X-ray wavelength so scattering from different parts of the electron cloud may be out of

phase. Neutron scattering factors vary randomly across the periodic table but they have a smaller variance than those for X-rays. Neutron scattering factors or cross sections do not decrease with $\sin \theta/\lambda$ because the nucleus is much smaller than the electron cloud however they are affected by resonance scattering where a nucleus absorbs a neutron and releases it later. Equation 2.12 is a Fourier series and can also be expressed as an exponential function (Equation 2.13). The electron density within the crystal (Equation 2.14) is the Fourier transform of the structure factor and *vice versa*.^[147] The structure factor is determined from the square root of the intensity which means it is not possible to determine the phase angle (positive or negative) of the diffracted wave, this makes structure solution more complicated and is known as the phase problem.^[144]

$$I_{hkl}^{corr} = (F_{hkl}^{obs})^2 \quad \text{Equation 2.11}$$

$$F_{hkl} = \sum_{j=1}^{j=n} f_j \cos 2\pi(hx_j + ky_j + lz_j) + i \sum_{j=1}^{j=n} f_j \sin 2\pi(hx_j + ky_j + lz_j) \quad \text{Equation 2.12}$$

$$F_{hkl} = \sum_j f_j e^{2\pi i(hx_j + ky_j + lz_j)} \quad \text{Equation 2.13}$$

$$\rho(x, y, z) = \frac{1}{V} \sum_h \sum_k \sum_l F_{hkl} e^{-2\pi i(hx + ky + lz)} \quad \text{Equation 2.14}$$

2.2.2.7 Powder diffraction

A single crystal has long range order in all three dimensions and the results of a diffraction experiment are diffraction spots positioned all around the sample. In a crystalline powder, there are many crystallites with random orientations. Each crystallite will produce its own set of diffraction spots according to its orientation. The combination of all these spots will form diffraction rings which are observed in powder diffraction. Data is collected at a range of two theta values in order to

intersect these rings, producing a powder diffraction pattern showing peaks as a function of two theta. Diffraction spots from different planes which would be expected in different places within a single crystal are condensed into a single ring or diffraction peak, the number of planes which can contribute to a single peak is known as the multiplicity and must be taken into account when analysing peak intensities (Figure 2.12).^[144]

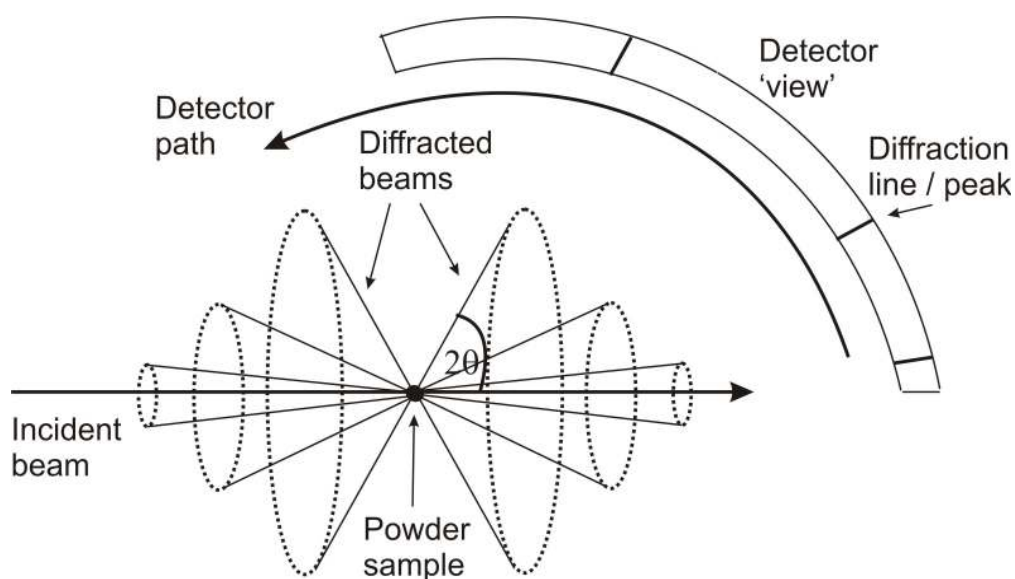


Figure 2.12 The rings of diffracted beam from a powder sample

2.2.3 Laboratory X-ray diffraction

Preliminary X-ray diffraction patterns of all samples were recorded using a Philips PANalytical X'Pert diffractometer operating at 45 kV and 40 mA. This diffractometer was used to assess the proportions of LiBH_4 , KBH_4 and $\text{LiK}(\text{BH}_4)_2$ in the mixed $\text{LiK}(\text{BH}_4)_2$ samples (Chapter 7) and the effect of different synthesis methods of $\text{Ca}(\text{BH}_4)_2$ (Chapter 8). Cu $K\alpha$ radiation ($\alpha_1 = 1.540598 \text{ \AA}$) was used with a Ge (111) crystal monochromator to select the α_1 radiation. The diffractometer operates in Bragg-Brentano geometry (the incident beam is divergent from a single point rather than a

series of parallel waves) with a fixed X-ray source and the detector set on the two theta axis.

Samples were finely ground within an argon filled glovebox and mounted on either a greased glass slide or within an indentation on an aluminium slide which was contained within an air-tight sample holder. Measurements were carried out at two theta angles between 10° and 70° using a step-size of 0.008° .

2.2.4 Synchrotron X-ray diffraction

High resolution X-ray powder diffraction data were collected at either the ID31 beamline at the European Synchrotron Radiation Facility in Grenoble, the I11 beamline at Diamond in the United Kingdom or the MS X04SA beam line at the Swiss Light Source in Villigen.

2.2.4.1 Source

Electrons from an electron gun are accelerated by a linear accelerator and then in a booster synchrotron ring until they approach the speed of light before being released into the storage ring (Figure 2.13).

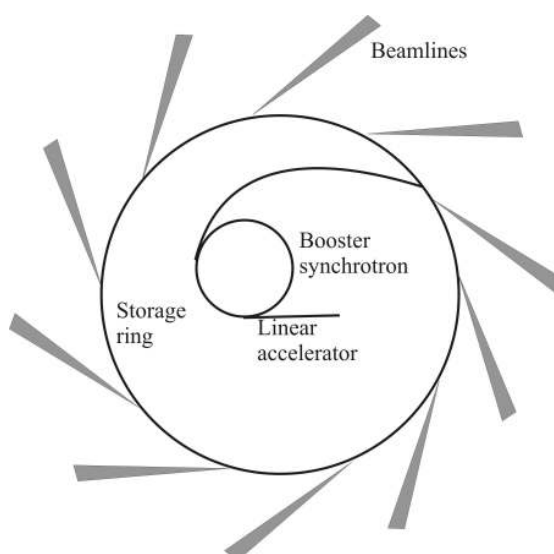


Figure 2.13 The layout of a synchrotron

The storage ring is a series of straight sections interspersed with bending magnets. When the electron path is bent by a bending magnet, Brehmstrahlung radiation is emitted, the combination of the electron energy and the strength of magnetic field of the bending magnet causes the Brehmstrahlung radiation to be mainly in the form of X-rays (Equation 2.15). The X-ray radiation is produced in a tight cone and can be further collimated using magnets.

$$E_c = 0.665BE^2 \quad \text{Equation 2.15}$$

where E_c is the energy of the X-ray photon in keV

E is the energy of the electron in GeV

and B is the strength of the magnetic field in T^[148]

X-rays are also produced from the straight sections of the storage ring using insertion devices, either multipole wigglers or undulators. These consist of a series of opposing magnets which “wobble” the electron beam creating a series of X-ray sources.

2.2.4.2 ID31 beamline

The X-rays for ID31 are produced using three undulators which provide an energy range of 5 keV to 60 keV which is equivalent to wavelengths of 2.48 Å to 0.21 Å. The X-ray beam is monochromated by a double crystal monochromator (Si (111)) which is cryogenically cooled.

The diffractometer at ID31 consists of 9 crystal-analyser detectors rotating vertically to collect intensity data over a range of two theta values. Each detector has a Si (111) crystal to ensure precision in the two theta angle measurement. The crystals for the detectors are all mounted on the same rotation stage so that only one adjustment is needed when the wavelength is changed. Samples are contained in spinning borosilicate-glass capillaries to remove the majority of the effects of preferred

orientation. The sample holder is mounted on a translation stage which allows different parts of the sample within the capillary to be moved into the beam. The flux at the sample is of the order of 6.1×10^{12} photons $\text{mm}^{-2}\text{s}^{-1}$ at a wavelength of 0.85 Å. The high intensity means that diffraction patterns can be collected quickly; data suitable for structure refinement can be collected in 15 minutes with peak intensities in the order of thousands of counts but radiation damage to samples can also be an issue.^[149]

The beamline has a sample changing robot capable of automatically loading 50 samples thus enabling a high throughput approach to data collection.

2.2.4.3 I11 beamline

The I11 beamline is very similar to ID31 with X-ray energies of 5 keV to 30 keV. The typical flux at the sample is 10^{14} photons s^{-1} $0.1\%bw^{-1}$ at 10 keV. There are 45 crystal-analyser detectors (five banks of nine detectors) and the sample changing robot is designed to handle 200 samples.^[150]

2.2.4.4 MS X04SA beamline

The MS X04SA beam line at the Swiss Light Source uses X-rays produced from a wiggler with an energy range of 5 keV to 40 keV.

In addition to five crystal-analyser detectors, the MS X04SA diffractometer is fitted with a second generation microstrip detector (PSD), Mythen 2 which was used for the experiment within this thesis. This detector consists of 15360 Si-detector elements covering a 60° range in two theta. The microstrip detector has a lower angular resolution than the crystal-analyser detectors (0.02° compared to 0.005°) but can collect data more quickly, reducing the chance of radiation damage to the sample.

The typical flux at the sample is 10^{13} photons s^{-1} $0.1\% \text{bw}^{-1}$ at 13 keV and 2×10^{12} photons s^{-1} $0.1\% \text{bw}^{-1}$ at 20 keV. The sample is contained in a spinning borosilicate-glass capillary as with ID31 and I11.^[151, 152]

2.2.4.5 Experiments

Synchrotron X-ray diffraction data were collected using ID31 at the ESRF for KBH_4 (Chapter 6), $\text{LiK}(\text{BH}_4)_2$ (Chapter 7), $\text{Ca}(\text{BH}_4)_2$ (Chapter 8) and $\text{Sr}(\text{BH}_4)_2$ (Chapter 9). Beamline I11 at Diamond was used for $\text{Li}^{11}\text{BD}_4$ (Chapter 4) and $\text{LiK}(^{11}\text{BD}_4)_2$ (Chapter 7). Beamline MS X04SA at the Swiss Light Source was used for an additional experiment on $\text{Sr}(\text{BH}_4)_2$ (Chapter 9).

Finely ground samples are loaded into borosilicate-glass capillaries, (usually 1 mm diameter for ID31, where the sample is held in place within the capillary using a borosilicate-glass rod and 0.7 mm diameter for I11 and MS X04SA), within a nitrogen filled glovebag. The capillaries are temporarily sealed with vacuum grease before being removed from the glove bag and flame sealed. The capillaries are mounted on magnetic sample holders which can be loaded onto the diffractometer or the robot sample rack. Diffraction data are collected at room temperature and also during *in-situ* heating experiments where the sample is heated either by an Oxford Cryosystems cryostream cold-nitrogen-gas blower (-193 - 227°C) or a Cyberstar hot-air blower (up to 950°C). The wavelengths used were in the region of $0.8 \text{ \AA}$ with a step size of 0.003° , (the exact parameters for specific experiments are given in the results chapters).

2.2.5 Neutron diffraction

Neutron powder diffraction data was collected on the GEM and HRPD beamlines at ISIS.

2.2.5.1 Comparison to X-ray diffraction

Neutron powder diffraction is a complimentary technique to using X-rays. X-rays are diffracted by the electrons of the atoms in a sample; neutrons are diffracted by the atomic nuclei. Consequently neutron diffraction will give more accurate atomic positions because it is unaffected by electron density being concentrated into interatomic bonds, this effect is particularly significant for hydrogen atoms and bonds to hydrogen often appear too short when determined by X-ray diffraction. On the other hand neutrons have less energy than X-rays resulting in weaker scattering so larger samples are needed.

The scattering cross section of isotopes varies randomly as a function of their position in the Periodic Table and consists of coherent scattering (which is used to gain structural information from diffraction patterns using elastic neutron scattering) and incoherent scattering (which is used to gain spectroscopic data using inelastic neutron scattering). The distribution of scattering cross sections allows electronically similar elements and light elements to be distinguished. Neutron scattering factors do not vary significantly with $\sin \theta / \lambda$, meaning that more information can be extracted from a powder pattern at high theta angles. However, some isotopes such as ^{10}B strongly absorb neutrons making data collection very difficult.

Neutrons possess spin and so have a magnetic moment, this means that neutrons can be scattered magnetically allowing the level of magnetic ordering within a sample to be investigated, which is not possible with X-rays. Neutrons are not charged so the interaction with the sample is weak, so a large sample is needed, (neutron diffraction

samples are typically contained in 8mm diameter vanadium cans compared to 0.8 mm glass capillaries for synchrotron X-ray diffraction). This also means that neutrons are very penetrating so more complicated sample environments (*e.g.* furnaces) can be used without blocking the incident radiation.

Neutrons are expensive to produce and are only available at specialist facilities around the world such as ISIS (UK) and ILL (Grenoble); neutron diffraction experiments cannot be carried out within university laboratories.

2.2.5.2 Theory and time of flight

Neutrons can be treated as waves as well as particles. The wavelength of a neutron is determined by the De Broglie relationship from its momentum, (Equation 2.16, Equation 2.17).

$$\lambda = \frac{h}{p} \quad \text{Equation 2.16}$$

$$p = m.v \quad \text{Equation 2.17}$$

During a neutron experiment, the momentum transfer, Q , is measured (Equation 2.19) which is the change in the wavevector, k , of the neutron (Equation 2.18).

$$|k| = \frac{2\pi}{\lambda} \quad p = \hbar.k \quad \text{Equation 2.18}$$

$$Q = k_f - k_i \quad \text{Equation 2.19}$$

For elastic neutron scattering there is no energy transfer between the neutron and the sample so the amplitude of the wavevector does not change, $|k_i| = |k_f|$. The direction of the wavevector does change so intensities of neutron diffraction peaks can be collected as a function of Q by only using neutrons of a specific energy or collecting data at a specific angle (Equation 2.20).

$$Q = 2k_f \sin(\theta) = \frac{4\pi \sin(\theta)}{\lambda} = \frac{2\pi}{d} \quad \text{Equation 2.20}$$

Using a pulsed neutron source, it is possible to use the entire neutron beam and collect data as a function of the time taken for a neutron to reach the sample from the target; this is time-of-flight (tof). From the time-of-flight and path length from the target to the sample it is possible to calculate the speed and hence energy of the neutron. Combining Bragg's Law (Equation 2.21), the De Broglie relationship (Equation 2.16) and $v = L/t$, the relationship between the d spacing and time-of-flight is given by Equation 2.22.^[153]

$$\lambda = 2d \sin \theta \quad \text{Equation 2.21}$$

$$d = \frac{ht}{2mL \sin \theta} \quad \text{Equation 2.22}$$

2.2.5.3 Source

Neutrons can be generated either by nuclear fission reactions in a nuclear reactor or, alternatively using a spallation source. ISIS uses a spallation neutron source which produces a pulsed beam of neutrons. The process begins with H^- ions being produced by an electric discharge. These ions are initially accelerated using a Radio Frequency Quadrupole accelerator which also divides the ions into bunches. Bunches of ions are further accelerated to 37 % of the speed of light in a linear accelerator. Next the ions enter a synchrotron via an alumina foil which removes the electrons, leaving protons, (H^+ ions). Once enough protons have collected in the synchrotron they are accelerated to 86 % of the speed of light by ten radio frequency electric field cavities. When the protons reach the required speed they are extracted by kicker magnets towards the targets. The protons are extracted in paired pulses and the whole process is repeated 50 times a second with four-fifths of the protons going to Target Station One and the

remaining fifth to Target Station Two. The total mean current delivered to the two targets is $200\ \mu\text{A}$.^[154]

The extracted protons hit the metal target (tungsten in the case of Target Station One) causing neutrons to be ejected. Moderators are used to slow down the neutrons to the speeds required for experiments. The neutrons from Target Station One pass through one of four moderators. Two of these moderators use room temperature water, one contains methane at $-173\ ^\circ\text{C}$ and the other contains liquid hydrogen at $-253\ ^\circ\text{C}$. The moderators are about 0.5 L in volume and are surrounded by water-cooled beryllium reflectors which scatter divergent neutrons back into the moderator, this increases the flux of neutrons leaving the moderator and moving towards the individual beam lines and experiments.^[154]

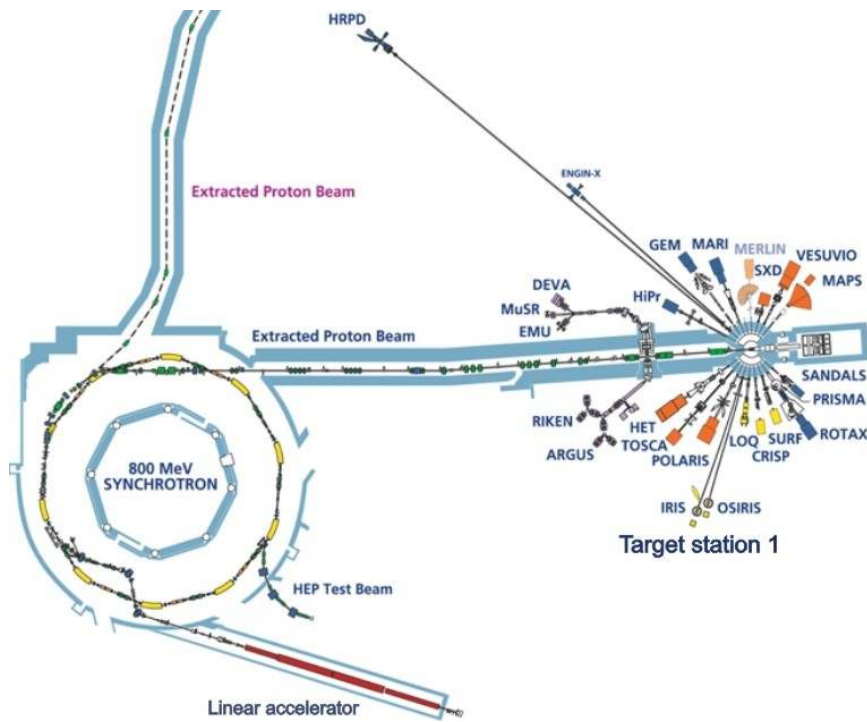


Figure 2.14 The layout of ISIS showing the linear accelerator, synchrotron and neutron beamlines around Target Station One.^[154]

2.2.5.4 Instrument

For a neutron diffraction experiment, detectors are arranged in banks all around the sample. Back scattering banks at high angles of two theta give high resolution whilst banks at lower angles give lower resolution but allow higher d -spacings to be observed. Resolution is increased by increasing the distances between the neutron source and the sample and the sample to the detectors so that neutrons of different energies (and speeds) within a pulse become more widely spaced.

2.2.5.4.1 GEM- General Materials diffractometer

GEM is designed to perform high intensity, high resolution structural experiments on disordered materials and crystalline powders. The neutrons used by the GEM diffractometer have passed through the methane moderator. The length of the flight path from the moderator to the sample is 17 m, this long flight path increases the resolution of the instrument. Spread over this path there are two disc choppers which are used to control the wavelength range and a nimonic chopper to remove high energy neutrons which increase the background signal. There are also five apertures for beam collimation which are remotely controlled and within the sample tank there is a beam-scraper. The beam-scraper is the last aperture that the beam passes through before hitting the sample and is computer controlled to precisely define the dimensions of the beam which is incident on the sample. The detectors are ZnS / ^6Li scintillators and cover a very wide angle range from 1.2° to 171.4° . Neutrons hitting the scintillators cause flashes of light which are then transmitted to photomultiplier tubes.^[154, 155]

2.2.5.5 Experiments

Neutron diffraction data were collected from ${}^7\text{Li}^{11}\text{BD}_4$ and $\text{Li}^{11}\text{BD}_4$ (Chapter 4), $\text{Na}^{11}\text{BD}_4$ (Chapter 5), K^{11}BD_4 (Chapter 6) and $\text{LiK}({}^{11}\text{BD}_4)_2$ (Chapter 7).

Room temperature diffraction experiments were carried out with the samples contained in either a 6 mm or 8 mm vanadium can sealed with indium wire. Variable temperature experiments used a vanadium can sealed with a copper gasket and inserted into either a furnace (8 mm vanadium can) or a block heater (6 mm vanadium can). Other variable temperature experiments were carried out using the IGAⁿ (see section 2.2.7.2) where the sample is contained in a bucket within a reaction vessel rather than being sealed into a vanadium can.

Vanadium does not interact with neutrons particularly strongly and scatters neutrons almost completely incoherently, therefore Bragg peaks relating to vanadium are not observed in the diffraction patterns. The contribution to the background of the diffraction patterns from vanadium can be measured by recording a diffraction data from an empty vanadium can which can then be subtracted from the experimental diffraction data.

2.2.6 Thermogravimetric analysis

Thermogravimetric analyses of KBH_4 (Chapter 6) and $\text{LiK}(\text{BH}_4)_2$ (Chapter 7) were completed using a Perkin Elmer STA 6000 Simultaneous Thermal Analyzer. This instrument normally allows simultaneous thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) however the DSC aspect of the equipment was not active.

The entire instrument was contained within an argon filled glove bag to allow samples to be loaded under an inert atmosphere. The glove bag was purged for 30 minutes

before the sample was loaded. Samples of approximately 10 mg were heated in a pre-weighed 180 μ l alumina sample pan at a rate of 5 $^{\circ}$ C/min. The sample chamber was continuously purged with flowing argon at 1 bar pressure flowing at 30 ml/min as controlled by the TGA software. The TGA can heat to 1000 $^{\circ}$ C which is a higher temperature than the IGA (Section 2.2.7). Changes in the sample mass during heating were recorded by a balance with a resolution of 0.1 μ g. The balance can measure up to 1500 mg but small samples were used due to the low sample density.

2.2.7 Intelligent Gravimetric Analysis

Intelligent gravimetric analysis allows the completion of thermogravimetric analysis with greater choice and control of the gas atmosphere and pressure around the sample. Two modifications of the Hiden Intelligent Gravimetric Analyser (IGA) were used. These allow the sample mass to be monitored whilst the temperature and pressure are changed; the sample can be heated under dynamic vacuum, in a sealed system at a set pressure or under a flowing gas. The IGA can be used alone, with the exit gas connected to a mass spectrometer or in the case of the IGAⁿ in conjunction with neutron diffraction.

2.2.7.1 Intelligent Gravimetric Analysis with mass spectrometry

The Intelligent Gravimetric Analyser (IGA) consists of a balance housed within an ultra high vacuum stainless steel reactor vessel with vacuum and gas pressure control, heated by an external furnace. The reactor vessel can be used at pressures from 10^{-6} mbar to 20 bar and temperatures up to 1000 $^{\circ}$ C, the control system can automatically adjust for changes in pressure as a result of temperature changes. The balance has a capacity of up to 1 g or 5 g depending on the setting with a resolution of 0.1 μ g. The sample is contained in a pre-weighed stainless steel mesh bucket with a

mass between 0.07 g and 0.1 g which can withstand temperatures up to 500 °C. This is connected to the balance via a gold chain and tungsten wire. A dry loader can be attached to the IGA and purged with nitrogen to allow sample loading within an inert atmosphere. The IGA was used with an external furnace which heats up to 500 °C.

Gravimetric analysis can be carried out either in a sealed system (at a set pressure of gas or a vacuum) or under flowing helium gas. When flowing gas is used, a small proportion of the exhaust gas can be fed via a 10 bar capillary tube, directly to a dynamic sampling mass spectrometer, model HAL201, type 124100, with a dual Faraday/Electron Multiplier. The atomic mass range for this mass spectrometer is 200 amu (atomic mass units) with a detection limit range of 0.1 to 1 ppm, subject to spectral interference. The mass spectrometer was configured to record the partial pressures of up to six gases with different mass to charge ratios every 12.5 seconds.

Samples (typically 50 – 70 mg) were loaded into the bucket within an argon filled glove box and then the bucket was sealed within a transportation pod to be taken to the IGA equipment. The sample bucket was transferred to the balance under an inert atmosphere using the dry loader equipment which was purged for 30 minutes with nitrogen before sample loading. The steel reactor vessel was sealed with a copper gasket. Samples were typically heated to 500°C at 2 °C/min under flowing helium gas with the mass spectrometer configured to detect H₂ (2 amu), BH₃ (14 amu) and B₂H₆ (28 amu). All of the data recorded was updated every 20 seconds.

All of the compounds discussed in this thesis were analysed using the IGA.

2.2.7.2 Intelligent Gravimetric Analysis with neutrons – IGAⁿ

The IGAⁿ is a custom made IGA instrument developed through a collaboration between ISIS and Hiden, taking advantage of the high penetration of neutrons which allows them to pass through bulky sample environments. This instrument is designed

to be used on the GEM and HRPD neutron beamlines at ISIS allowing simultaneous collection of thermogravimetric and neutron diffraction data enabling correlation between changes in the crystallinity of a sample with mass changes under a variety of conditions.

The IGAⁿ is similar to the IGA but there is no mass spectrometer connected to the IGAⁿ. The sample container for the IGAⁿ is a quartz bucket (0.6 – 1.2 g) and for inert sample loading, the IGAⁿ is lowered into the top of a custom made argon-filled glove box rather than using the dry loader. The IGAⁿ is fitted with a Tomkinson flange which allows it to be fitted into the GEM and HRPD beamlines as well as the glove box and the connections to the control unit and gas supplies are much longer allowing the reactor vessel unit to be craned into the beamline without moving the control unit (Figure 2.15). Rather than inserting the reactor vessel into an external furnace, the IGAⁿ is heated via two heater bands which are positioned above and below the sample and the neutron beam to avoid interference with the neutron beam.

Samples (572 mg Na¹¹BD₄ Chapter 5, 795 mg K¹¹BD₄, Chapter 6) were loaded into the quartz bucket within an argon filled glove box before being transferred to the IGAⁿ glove box in an air tight container. Once the IGAⁿ was located in the top of the glove box, the glove box was purged for 30 minutes before the sample was loaded and the reactor vessel sealed. The IGAⁿ was craned into the neutron diffractometer. Experiments were typically carried out under dynamic vacuum (10^{-6} mbar) so that the presence of decomposition gases would not slow decomposition. Heating rates were between 2 and 5 °C/min with the final temperature adjusted depending on the expected reaction but typically 450°C for a decomposition reaction. Thermogravimetric data was recorded every 10 seconds and a neutron diffraction pattern every 3.5 minutes. Mass measurements are accurate to ± 0.0001 mg,

temperature measurements to ± 0.001 °C and pressure measurements are accurate to ± 0.01 mbar.

The IGAⁿ was also used for the thermogravimetric analysis under dynamic vacuum without neutron diffraction of LiBH₄ (Chapter 4), KBH₄ (discussed in Chapter 7) and LiK(BH₄)₂ (Chapter 7).

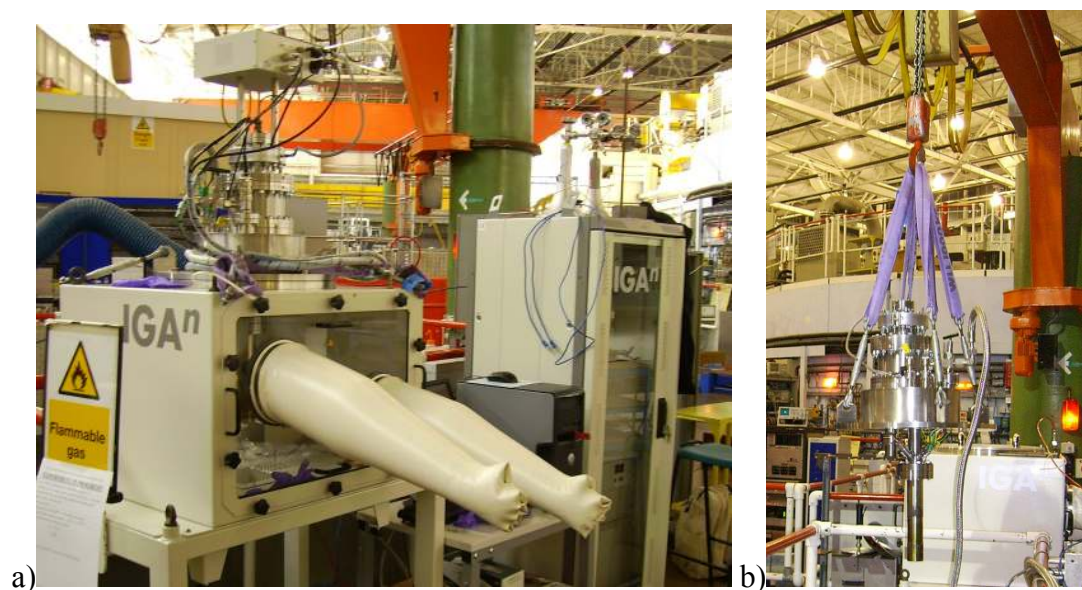


Figure 2.15 The IGAⁿ a) inserted into the custom-made glove box next to the control unit and b) being craned into the diffractometer

2.2.8 Raman spectroscopy

Raman spectroscopy involves irradiating a sample with a coherent light source. The majority of the light is scattered elastically so there is no net energy exchange with the sample, this is known as Rayleigh scattering. A small amount of the light (about 1×10^{-7}) will be scattered inelastically, this is Raman scattering. Scattered light with frequencies below the incident light frequency (lost energy to the sample) are known as Stokes frequencies, frequencies above the incident light frequency (gained energy from the sample) are anti-Stokes frequencies. Rayleigh scattering will result in the highest intensity and must be filtered out before the detector. Stokes frequencies have

higher intensities than anti-Stokes because Stokes frequencies involve the vibration moving to an excited state and statistically with a Boltzmann distribution of energy level occupations, more molecules will be in the ground state. Therefore it is Stokes frequencies which are recorded. The exchange of energy occurs when the vibrating molecule interacts with the oscillating electric field of the incident radiation, the extra energy causes the vibration to be excited to a virtual state followed by immediate decay, in the case of Stokes frequencies, back to a higher energy state than the original (Figure 2.16).

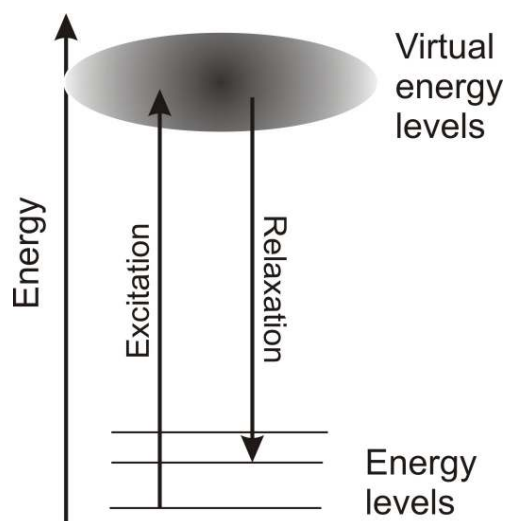


Figure 2.16 The excitation of vibrational states to a virtual energy level and decay back to a different energy level

Raman spectra show the change in frequency of the detected radiation relative to the incident radiation so they are independent of the incident radiation frequency that was used.

Vibrational Raman scattering only occurs in molecules where the bond vibration results in a change of polarizability for the molecule. For a mode to be Raman active, its symmetry species must have a quadratic form designated by the character table for the molecule's point group. In a molecule with a centre of symmetry, no vibration

modes can be both infrared and Raman active. For a non-linear molecule there are $3N-6$ independent modes of vibration where N is the number of atoms within the molecule.

Room temperature Raman spectra for all the compounds discussed in this thesis were recorded on a Jobin Yvon Dilor Labram 300 confocal spectrometer, fitted with an Olympus microscope using the 10-fold magnification objective. A 20 mW He–Ne laser (633 nm) was used. The spectrometer is fitted with a 1800 L/mm (lines per mm) grating which gives a resolution ranging from 1.0 cm^{-1} at 200 cm^{-1} to 0.5 cm^{-1} at 3600 cm^{-1} . The spectrometer was calibrated with a silicon standard, and the sharp Raman shifts are accurate to $\pm 2\text{ cm}^{-1}$.

Samples were contained inside melting point tubes which were loaded within an argon filled glove box and temporarily sealed with vacuum grease before being removed from the glove box and flame sealed.

2.2.8.1 Raman spectroscopy of borohydride ions

A tetrahedral molecule such as a free borohydride ion has a total of $3N-6 = 9$ vibrational modes (where N is the number of atoms in the molecule). They are the ν_1 symmetric stretch (singly degenerate, symmetry A_1), ν_2 symmetric bend (doubly degenerate, symmetry E), ν_3 asymmetric stretch (triply degenerate, symmetry T_2) and ν_4 asymmetric bend (triply degenerate, symmetry T_2). These vibrational modes are shown in Figure 2.17.^[9] Within crystal structures, the symmetry of the borohydride ion is dependent on its point group which is determined by the symmetry elements that the ion is located on. The point group of the borohydride ion will determine the specific symmetry of each bond vibration.

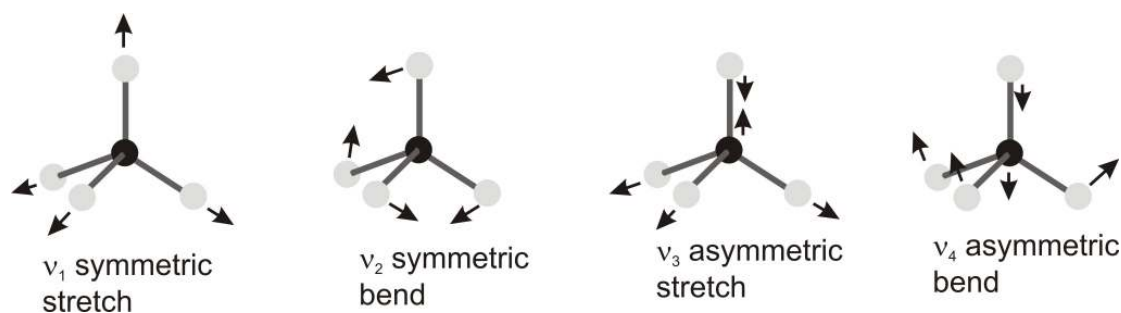


Figure 2.17 The vibrational modes of a tetrahedral molecule^[9]

For example, in LiBH_4 , the borohydride ions are located on a mirror plane and hence have the point group C_s . The symmetries of the vibrational modes can be calculated by first determining the representation of the total translational, rotational and vibrational modes for the ion, Γ_{3N} . The reducible representation of Γ_{3N} is first determined by assigning x , y and z vectors to each atom within the borohydride ion. A matrix is constructed showing how the vectors are affected by the symmetry operations for point group C_s which are E (identity) and σ_h (mirror plane); 1 indicates that the vector is unaffected, -1 that the vector is reversed and 0 that the atom has moved. The character of the matrix (the sum of the diagonal) is used for the reducible representation. This calculation can be simplified by counting the number of unshifted atoms within the ion and multiplying by the character of a 3×3 matrix showing the effect of the symmetry elements on three general vectors, x , y and z . For a borohydride ion, for E , there are five unshifted atoms and the 3×3 matrix character is 3, for σ_h , there are three unshifted atoms and the 3×3 matrix character is 1 (Table 2.2). The reducible representation of Γ_{3N} is $15E + 3\sigma_h$.

Table 2.2 The 3 x 3 matrices for E and σ_h

$$\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

3 x 3 matrix for E

$$\begin{bmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

3 x 3 matrix for σ_h

The irreducible representation of Γ_{3N} is calculated from Equation 2.23, where a_i is the number of times that the irreducible representation appears in the reducible representation, g is the total number of symmetry operations, n_R is the number of operations in a class, ζ_R is the character in the reducible representation and ζ_{IR} is the character in the irreducible representation (from the character table for that point group, Table 2.3).

$$a_i = \frac{1}{g} \sum n_R \zeta_R \zeta_{IR} \quad \text{Equation 2.23}$$

Table 2.3 The character table for point group $C_s^{[9]}$

C_s	E	σ_h		
A'	1	1	x, y, R_z	x^2, y^2, z^2, xy
A''	1	-1	z, R_x, R_y	yz, xz

Thus for a borohydride ion in point group C_s the irreducible representation of Γ_{3N} is

$$\begin{aligned} A' &= \frac{1}{2} [(1 \times 15 \times 1) + (1 \times 3 \times 1)] = 9A' \\ A'' &= \frac{1}{2} [(1 \times 15 \times 1) + (1 \times 3 \times -1)] = 6A'' \end{aligned}$$

$$\Gamma_{3N} = 9A' + 6A''$$

From the character table, the translational and rotational modes are $\Gamma_{t+r} = 3A' + 3A''$ (shown as x, y, z, R_x, R_y, R_z) so the vibrational modes are $\Gamma_{\text{vib}} = 6A' + 3A''$. Modes with the symmetry A'' are changed by a reflection in the mirror plane whilst those with symmetry A' are not. All of these modes are Raman active (indicated by the presence of quadratic terms, $x^2, y^2, z^2, xy, yz, xz$ in the character table). A' Raman signals will be polarised and A'' Raman signals will be depolarised. The symmetries of the vibrational modes of a borohydride ion with point group C_s are $\nu_1 = A', \nu_2 = A' + A'', \nu_3 = 2A' + A'', \nu_4 = 2A' + A''$.^[156]

2.2.8.2 Effect of isotopic substitution

In the Raman spectra of isotopically enriched borohydrides, $M^{11}\text{BD}_4$, the frequencies of the B-D bonds are shifted to lower frequencies compared to the un-enriched B-H bonds. This is because atomic bonds act as harmonic oscillators; when an atom is displaced it experiences a restoring force equal to its displacement. Bonds containing heavier atoms vibrate at lower frequencies because the restoring force will not move a heavier atom as quickly.

The substitution of natural abundance boron for boron-11 will have little effect on the bond vibration frequencies due to the small percentage difference in mass and the high natural abundance of boron-11. In the majority of cases, the B-H vibrations which are strong enough to be observed will involve boron-11. However, deuterium has twice the mass of hydrogen and a very low natural abundance and consequently has a significant effect on the frequencies of the bond vibrations. The ratio of the bond vibrations, $\nu_{\text{B-H}} / \nu_{\text{B-D}}$ depends on the symmetry of the vibrational mode; vibrations with the same symmetry (including external lattice vibrations) will interact. In a molecule with tetrahedral symmetry, in the case of ν_1 and ν_2 , there is only one internal vibration with that symmetry (A and E) so there are no interactions with other B-H

bond vibrations and the bond can be treated as a simple harmonic oscillator (Equation 2.24). Only the hydrogen atoms are moving, so the mass of the boron atom does not need to be considered. The mass of the hydrogen or deuterium atom can be substituted for μ (instead of using Equation 2.25 if both atoms were moving) and the ratio $\nu_{\text{B-H}} / \nu_{\text{B-D}}$ is expected to be $\sqrt{2} = 1.41$.

Alternatively, if the boron and hydrogen atom are involved in a bond vibration, as shown in Equation 2.26, the B-D bond vibrations in free borohydride ions could be expected to have frequencies which are closer to a factor of $\sqrt{1.85} = 1.36$ lower than the B-H frequency.^[157, 158]

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad \text{Equation 2.24}$$

$$\mu = \frac{m_A m_B}{m_A + m_B} \quad \text{Equation 2.25}$$

$$\frac{\nu_{^{11}\text{B-H}}}{\nu_{^{11}\text{B-D}}} = \sqrt{\frac{\frac{11 \times 2}{11 + 2}}{\frac{11 \times 1}{11 + 1}}} = 1.36 \quad \text{Equation 2.26}$$

where ν is the vibration frequency, k is the force constant, μ is the reduced mass and m_A and m_B are the masses of the atoms

The situation for ν_3 and ν_4 is more complicated because the hydrogen atoms are not all moving in the same direction relative to the boron atom which will affect the motion of the boron atom within an individual bond vibration. Also both vibrations have the same symmetry (T_2) and will interact. The expected ratios for the bond vibration frequencies for the B-D and B-H bonds for ν_3 and ν_4 can be determined using the Teller-Redlich product rule (Equation 2.27).^[159] The superscript i denotes the isotopically enriched atom, m is the mass of the atom representing a set of atoms that are transformed into each other by a symmetry operator, α and β are the number

of individual vibrations that the set of atoms contributes to the molecular vibration, M is the mass of the molecule, t is the number of translations with the same symmetry type as the molecular vibration, I is the moment of inertia about the x , y and z axes and δ_x , δ_y and δ_z , are 1 if there is a rotation present about that axis for the symmetry of the molecular vibration and 0 otherwise. For ν_3 and ν_4 in the tetrahedral molecule, the hydrogen atoms are transformed into each other by rotation around the 3 fold axis, there is one translation with symmetry T_2 so $t=1$, there are no rotations with symmetry T_2 so δ_x , δ_y and $\delta_z = 0$ and the equation simplifies to Equation 2.28. Equation 2.26 is also a simplification of Equation 2.27.^[159]

$$\frac{\nu_1^i \nu_2^i}{\nu_1 \nu_2} \dots \frac{\nu_f^i}{\nu_f} = \sqrt{\left(\frac{m_1}{m_1^i}\right)^\alpha \left(\frac{m_2}{m_2^i}\right)^\beta \dots \left(\frac{M^i}{M}\right)^t \left(\frac{I_x^i}{I_x}\right)^{\delta_x} \left(\frac{I_y^i}{I_y}\right)^{\delta_y} \left(\frac{I_z^i}{I_z}\right)^{\delta_z}} \quad \text{Equation 2.27}$$

$$\frac{\nu_3^D \nu_4^D}{\nu_3 \nu_4} = \sqrt{\left(\frac{11}{11}\right)^1 \left(\frac{1}{2}\right)^2 \left(\frac{19}{15}\right)^1} = 0.563 \quad \text{Equation 2.28}$$

2.2.9 Nuclear magnetic resonance spectroscopy - NMR

NMR spectroscopy measures the interaction of the nuclear spin of an atomic nucleus with an applied magnetic field and the nuclear spin of surrounding nuclei. NMR spectra can be collected from nuclei which have a nuclear spin, I , which is greater than zero. The nuclear spin of ^1H is $\frac{1}{2}$ and for ^{11}B it is $\frac{3}{2}$. The nuclear spin of an atomic nucleus has an associated magnetic moment which is responsible for the interaction with the magnetic field. Nuclei with a spin larger than $\frac{1}{2}$ also have a quadrupole moment which interacts with the magnetic moment leading to rapid relaxation of the nucleus which can cause broad lines in the NMR spectra.

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 , is applied the energy levels move apart, this

is known as Zeeman splitting.^[160] NMR spectroscopy measures the transition between adjacent energy levels. Radio frequency radiation is applied to the sample to provide the nuclei with energy to make the transition between energy levels. Either the magnetic field or the radio frequency is varied in order to collect data from a range of transitions and the radio frequency emission from the sample is monitored. Alternatively in a Fourier Transform spectrometer, a pulse containing many frequencies is used and the results are extracted by Fourier transform.^[160]

When an atom is within a molecule, the magnetic field which it experiences is modified by the chemical environment around the nucleus so the same nucleus in different environments will exhibit different chemical shifts, this effect is known as shielding.

The frequency, ν , at which the transition between spin states occurs (the chemical shift) is given by Equation 2.29, it is proportional to the external magnetic field, B_0 , and the gyromagnetic ratio of the isotope, γ . The energy of the chemical shift is recorded as a frequency but the chemical shift varies as a function of the frequency that the spectrometer is operating at, so chemical shifts are recorded in parts per million (ppm) of the spectrometer frequency. Chemical shifts are also referenced to a known chemical shift which is set at zero, for ^1H NMR this is tetramethylsilane, for ^{11}B , $\text{BF}_3 \cdot \text{Et}_2\text{O}$ is used. Chemical shift is positive when it is at a higher frequency than the standard (or lower magnetic field). Alternatively known peaks within the solvent can be used to reference the spectrum. Therefore the chemical shift of a signal is given by Equation 2.30.

$$\nu = \frac{\gamma B_0}{2\pi} \quad \text{Equation 2.29}$$

$$\delta(ppm) = \frac{\nu_{signal}(Hz) - \nu_{reference}(Hz)}{spectrometer\ frequency(Hz)} \times 10^6 \quad \text{Equation 2.30}$$

Electrons within the NMR sample also have a charge and will move in response to a magnetic field in an attempt to generate an opposing field. This means that nuclei with more electrons are partially shielded from the magnetic field, so the energy level transition will occur at a higher applied magnetic field or lower radio frequency (lower ppm).^[160]

If an NMR active nucleus is chemically bonded to other NMR active nuclei which are in different environments, the magnetic field generated by the electrons associated with these nuclei will cause the nucleus in question to experience a range of magnetic fields. This range of magnetic fields will result in an additional range of energy levels being available to the nucleus causing multiple peaks to be present in the spectrum. Each interacting nuclei will split the signal into $2I+1$ peaks, this is known as coupling, the separation between the peaks is the coupling constant, J , which represents the strength of the interaction between the nuclei.^[160]

Interactions between nuclei will also occur directly through space and are known as dipole-dipole interactions. In solution, where the molecules can tumble and rotate freely, these dipole-dipole reactions may be averaged to zero. However, within a solid, the interactions between the dipoles of nearby nuclei can cause broad peaks in the spectra. Also in a solid, the time taken for the nuclei to react to a magnetic field and relax afterwards is much longer. NMR spectrometers can be adapted to overcome these problems. Pulses of radiation must be less frequent to allow the sample to relax after a pulse and also stronger to cause an effect. At the magic-angle of 54.74° to the direction of the magnetic field, the dipole-dipole interactions average to zero. Solid

state NMR spectrometers spin the sample at this angle to produce higher resolution data.^[160]

Solution state ^1H NMR studies of LiBH_4 and $^7\text{Li}^{11}\text{BD}_4$ (Chapter 4) were carried out using a Varian Mercury 300 MHz spectrometer. The samples were loaded into NMR tubes within an argon atmosphere glove box and then dissolved in $\text{d}_8\text{-THF}$ within a nitrogen filled glove bag, the NMR tubes were sealed with parafilm.

Solid state ^{11}B MAS-NMR studies of LiBH_4 (Chapter 4), KBH_4 (Chapter 6), $\text{LiK}(\text{BH}_4)_2$ (Chapter 7) and $\text{Ca}(\text{BH}_4)_2$ (Chapter 8) were carried out by the NMR staff within the Chemistry Department at the University of Oxford. The spectra were obtained at 64.2 MHz (4.7 T) on a Varian/Chemagnetics Infinity spectrometer, using a 7.5 mm double resonance probe and a sample rotation rate of 5 kHz. The ^{11}B spectra were referenced to BPO_3 (the resonance was taken to be at $\delta = -3.60$ ppm^[161] on a scale where $\delta(\text{BF}_3\cdot\text{Et}_2\text{O}) = 0$) was a secondary reference.

Studies of $\text{Li}^{11}\text{BD}_4$ (Chapter 4), NaBH_4 (Chapter 5) and $\text{Sr}(\text{BH}_4)_2$ (Chapter 9) 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 sample spinning rate was approximately 14 kHz (see individual chapters). The samples were packed into the rotors under inert gas.

2.2.10 Elemental analysis

Elemental analyses of samples of $\text{Ca}(\text{BH}_4)_2$ (Chapter 8) for carbon and hydrogen were performed by the Elemental Analysis service at London Metropolitan University.

2.3 Diffraction data analysis

The primary aim of diffraction data analysis is usually to obtain a detailed crystal structure of the sample. This process involves two steps. The first step is determine the basic details of the structure (space group, unit cell parameters, atomic positions) either by comparison of the data with known structures or by solving a new structure. The second step is to refine that structure to obtain as much accurate information as possible about the particular sample being studied.

Traditionally X-ray diffraction is preferred for initial structure determination. X-ray diffraction data is mainly influenced by heavier atoms, allowing a simpler structure based only on the heavier atoms to be determined as a step towards the full structure solution. Then neutron diffraction is used to refine the structure in order to accurately determine the atomic positions and atomic displacement parameters of all of the atoms present within a structure. However both X-ray and neutron diffraction can be used for both stages of the structure determination process.

2.3.1 *Structure solution from powder diffraction*^[144, 162, 163]

Powder diffraction can be used to determine the structure of an unknown crystalline phase. One of the main problems when working with powder diffraction data instead of single crystal data is that the three dimensional information from a single crystal is condensed onto a single two theta axis so diffraction peaks may be located on top of each other making them harder to distinguish. The first stage in the process is to collect data of the highest possible quality (*e.g.* high intensity, sharp diffraction peaks relative to the background from a pure, homogeneous crystalline sample) so that as much information as possible can be extracted from it. High quality data makes it

easier to identify the presence of peaks and their positions; higher resolution data reduces the degree of diffraction peak overlap.

2.3.1.1 Indexing

Once data has been collected, the peak positions are identified and indexed in order to determine the unit cell parameters. Indexing diffraction peaks involves their assignment to the planes of lattice points responsible for their diffraction. It is important that peak positions are determined accurately as well as precisely, an internal standard might be used to reduce the chances of systematic errors. Time-of-flight neutron data can be advantageous for determining peak positions because the zero error is very small due to there being no wavelength selection. During peak indexing it is necessary to be aware of weaker peaks which are either broader or sharper suggesting that an impurity may be present in the sample. Peaks that are split or asymmetric may suggest a distorted unit cell or that the composition of the sample is inhomogeneous.

Indexing of diffraction peaks is usually carried out using an auto indexing program. For indexing of powder diffraction data, the function Q_{hkl} is often used. Q_{hkl} can be defined as equal to $1/d_{hkl}^2$ or $10^4/d_{hkl}^2$. $1/d$ is also equal to the reciprocal lattice vector, r^* . Using the dot product of a reciprocal lattice vector with itself, Q can also be determined to be equal to Equation 2.31, where the parameters a_{ij} are related to the reciprocal and hence direct lattice parameters.

$$Q_{hkl} = h^2 a_{11} + k^2 a_{22} + l^2 a_{33} + hka_{12} + kla_{23} + hla_{13} \quad \text{Equation 2.31}$$

Equation 2.31 can be simplified for each of the crystal systems. The structure is indexed by assigning different crystallographic indices to each value of Q observed.

Caution is needed with auto indexing because it is possible to incorrectly index a very large cubic unit cell to most data sets or to index a hexagonal unit cell as

orthorhombic with lattice parameters $a/2$, $a\sqrt{3}/2$, c , where a and c are the hexagonal lattice parameters. Alternatively a superlattice with twice the correct volume or a sublattice with half the volume may be indexed. Problems can occur if the unit cell has one very short axis so that very few peaks relating to this axis will be present within the data range. Figures of merit are needed to assess the reliability of indexing; these compare the number of indexed peaks, the number of Q values and the difference between calculated and observed values. It is also important to check the pattern for peaks which have not been indexed which may be the result of an impurity or may suggest an error in the indexing. Peaks at low angles of two theta are expected to have small hkl values, so large values should cause concern. Overlapping diffraction peaks can cause problems because it can be difficult to determine how many peaks are responsible for the overall shape observed and hence how to index the combination of peaks.

2.3.1.2 Determination of space group

After the diffraction peaks have been indexed, the next stage is to determine the space group. Patterns of absent diffraction peaks are used to do this. General absences occur across the entire data set and indicate the unit cell centring, for a body centred unit cell, the sum of $h+k+l$ must be even for a peak to be present. Systematic absences affect only parts of the data set and indicate translational symmetry elements: *e.g.* a 2_1 screw axis along the a axis is indicated by an absence of peaks when h is odd for peaks within the $h00$ set. The absences of peaks indicate extinction symbols which may have more than one possible space group. For example the extinction symbol $P-2_1-$ could indicate the space groups $P2_1$ or $P2_1/m$. Space group determination can be carried out computationally. However, it is often difficult to decide whether a weak peak is actually present so space groups are also determined visually; this has the

disadvantage that only a few peaks may be considered. Again there is the problem of overlapping peaks which may disguise an absent or present peak. Space groups with fewer symmetry elements have fewer extinction rules for systematic absences so an incorrect lower symmetry space group may provide a better fit to the data than the correct higher symmetry space group.

The space group determination is tested by either a Pawley or Le Bail refinement of the peak intensities to the unit cell size, shape and space group. A Pawley refinement is a least squares refinement method meaning that variables are adjusted in order to reduce the value of the sum of the differences between the squares of the observed and calculated intensities. The values of the peak areas themselves are used instead of variables relating to peak areas in a Rietveld refinement (see section 2.3.2). The drawback of a Pawley refinement is that it can produce negative peak intensities so a parameter is needed to ensure that peak intensities remain positive, for example by refining the magnitudes of structure factors instead of peak intensities. A Le Bail refinement is an iterative process where the calculation of the area of the diffraction peaks in each step is based on the area from the previous step.

For a Pawley or Le Bail refinement, a single peak shape is used across the whole diffraction pattern. If the fit to the data is poor then either an impurity is present or there is a problem with the space group determination. If the agreement factors for the final Rietveld refinement at the end of the structure refinement process are worse than at this stage, it is likely that an error has been made later in the structure solution process.

2.3.1.3 Atomic positions

Atoms and their positions within the unit cell can be identified using a variety of methods. The Patterson synthesis and Direct Methods approaches both involve methods to extract peak intensities from the diffraction pattern using a Pawley or Le Bail refinement. Alternatively, structure solution can be attempted using a simulated annealing or Monte Carlo approach where information about the connectivity of atoms within a molecule is used to generate a trial structural model which can then be refined and improved.

The Patterson method uses the intensities of diffraction peaks to develop a Patterson map which is similar to an electron density map. However rather than showing electron density, the peaks on a Patterson map correspond to interatomic vectors with the heights of the peaks corresponding to the product of the scattering factors of the two atoms involved. This method does not use the phases of the diffracted beams, instead the squares of the structure factors are used which can be determined from the intensities of the diffraction peaks.

Direct Methods uses statistical relationships between amplitudes and phases of strong reflections to develop algorithms which allow crystal structures to be derived directly from the position, intensity and *hkl* index of the diffraction peaks. The problem of determining the phases of the structure factor is dealt with by processing the phases within reciprocal space and effectively initially estimating the phases based on the calculations.

The Monte Carlo or simulated annealing techniques operate in direct space. A trial structural model is constructed based on known information about the connectivity of the molecule. Initially this structural model may only include atoms which diffract more strongly, (heavier atoms in the case of X-ray diffraction). The calculated

diffraction pattern from the model is compared to the experimental data. The quality of the fit of the calculated pattern to the experimental pattern is determined using the same methods as for the Rietveld method discussed in section 2.3.2. The structural model is then adjusted randomly and the calculated diffraction pattern is again compared to the experimental data. The change in the structural model may be accepted or rejected depending on criteria defined by the user; the change might be rejected if it does not improve the fit of the structural model to the data or some decrease in the quality of the fit may be accepted in order to thoroughly explore potential structural models. A structural model is adjusted until the quality of the fit to the data is no longer improved; a minimum has been found in the difference between the calculated and experimental structure. Structure calculations are started from several different structural models to ensure that the minimum identified is the global not a local minimum. This technique can be particularly useful for ionic structures where the connectivity within the composite ions is already known. The process used to solve structures within this thesis is based on this method (see section 2.3.3).

2.3.2 *Structure refinement -Rietveld Refinement*^[144, 162, 164]

Once a crystal structure has been determined, it is refined by further comparison to the diffraction pattern to make it as accurate as possible. The Rietveld Refinement is one of the most popular methods particularly for powder diffraction patterns.

The Rietveld method was developed by Rietveld taking advantage of the recently available computing power in the 1960s to fully exploit all of the information contained in a powder diffraction pattern. This work was published in two papers in 1967^[165] and 1969^[166] and the computer program was also made widely available. The Rietveld refinement has made powder diffraction data much more useful.

In a Rietveld refinement, the entire diffraction pattern is modelled as a whole because every part of the pattern contains information even if it is the absence of a diffraction peak. The shape of each peak is calculated from the existing model and compared to the experimental data and adjustments are made until the peak shapes match; consequently peak shape modelling is an important part of the Rietveld method.

The Rietveld refinement method was originally developed for neutron diffraction patterns because of the simpler peak shapes attributed to this technique. The refinement method was later extended to X-ray diffraction data by using alternative peak shape models and later to time-of-flight neutron data and synchrotron X-ray diffraction data. Various methods are available to model the peak shape, the pseudo-Voigt function is used which contains a combination of Gaussian and Lorentzian contributions. Other, more advanced models are derived directly from experimental conditions or by modelling the size and strain of the sample particles (an indication of particle size and strain can be gained from the peak shape).

Apart from the more complex peak shapes, X-ray diffraction data can be more prone to systematic errors than neutron diffraction data. If the sample particles are large and the sample is small then the diffracting particles may not represent a good average of the sample. If the shape of the crystallites causes them to adopt a preferred orientation within the sample then this can affect the intensity of some of the diffraction peaks. In a neutron diffraction experiment where the sample is larger, preferred orientation is less of a problem because a smaller proportion of the sample is packed against the sides of the container. Also absorption of the X-rays may cause a problem which may be indicated by negative thermal parameters.

The Rietveld refinement method works by expressing the diffraction pattern in terms of the observed intensity, $y(obs)$ as a function of two theta (or time-of-flight or

another more suitable parameter). The values of $y(obs)$ are then compared to values which have been calculated from the existing structural model, $y(calc)$ for each value of two theta. $y(calc)$ is calculated by summing the background intensity and the intensities of expected diffraction peaks which are thought to be in a range where they could contribute to the intensity at a particular value of two theta, this is done using Equation 2.32. A least squares method is used to adjust structural parameters such as the unit cell dimensions, atomic co-ordinates, thermal displacement parameters, and instrument and experiment parameters to minimise the difference between $y(obs)$ and $y(calc)$ over the whole pattern. This minimises S_y in Equation 2.33.

$$y_{calc} = s \sum_K L_K |F_K|^2 \phi(2\theta_i - 2\theta_K) P_K A + y_{back} \quad \text{Equation 2.32}$$

$$S_y = \sum_i w_{obs} (y(obs) - y(calc))^2 \quad \text{Equation 2.33}$$

where

s = the scale factor

K = the Miller indices, hkl for a diffraction peak

L_K = the Lorentz polarization and multiplicity factors

ϕ = the reflection profile function (approximates the effect of the instrument and sample features on the peak shape)

P_K = the preferred orientation function

A = the absorption factor

F_K = the structure factor of the K th Bragg reflection

$w_{obs} = 1/y_{obs}$

$y(obs)$ = the observed intensity at the i th step

$y(calc)$ = the calculated intensity at the i th step

y_{back} = the background intensity at the i th step

The Rietveld method is unique because there is a feedback between improving the crystal structure and improving the assignment of peak intensity where peaks overlap. Other methods assign the peak intensities separately and independently. However the

relationship between the peak intensities and some of the adjustable parameters in a structure are non-linear. This means that if the starting model is not good enough then the refinement may diverge or find a false minimum.

At the beginning of a Rietveld refinement the shape of the background to the data should be refined. Next the scale parameter, zero point error and the sample height should be refined until the peak positions are correct. After this, parameters which describe the peak shape should be refined until the observed and calculated peak shapes agree. Lattice parameters are determined from peak positions but in order to specify a value for a peak position, the peak shape must first be modelled. Finally, parameters which affect the peak intensities such as atomic co-ordinates and thermal displacement parameters can be refined.

The quality of the refinement can be assessed by using agreement factors such as R_{wp} (Equation 2.34) and R_{Bragg} (Equation 2.35). R_{wp} is a useful value because it is directly related to the difference between $y(obs)$ and $y(calc)$, however data with a large background will give a misleadingly low value so it is better to use background-subtracted R_{wp} factors. R_{wp} can be biased if the intensities of overlapping peaks were fixed before the refinement. The goodness-of-fit (GOF or χ^2 , Equation 2.37) which compares R_{wp} to the statistically expected value, R_{exp} (Equation 2.36) is used to assess the quality of the fit allowing for the quality of the data. This value also gives an indication of the reliability of the fit; χ^2 should not be less than unity. It is important to visually inspect a graphical representation of the quality of the fit to the data in case there are other errors which are not immediately obvious from the agreement factors.

$$R_{wp} = \sqrt{\frac{\sum_i w_i [y_i(obs) - y_i(calc)]^2}{\sum_i w_i [y_i(obs)]^2}} \quad \text{Equation 2.34}$$

$$R_{Bragg} = \frac{\sum_{hkl} [y_{hkl}(obs) - y_{hkl}(calc)]}{\sum_{hkl} y_{hkl}(obs)} \quad \text{Equation 2.35}$$

$$R_{exp} = \sqrt{\frac{(n-p)}{\sum_{i=1}^n w_i y_i(obs)^2}} \quad \text{Equation 2.36}$$

$$(GOF)^2 = \chi^2 = \left(\frac{R_{wp}}{R_{exp}} \right)^2 \quad \text{Equation 2.37}$$

where n = number of observations, p = number of parameters and w_i = weighting factor

Estimated standard deviations (esd) generated by the Rietveld refinement process are the minimum possible errors due to random errors, not the experimental probable error. Random errors do not include background effects, preferred orientation, the zero error or graininess (large particle size causing poor powder averaging).

Powder diffraction patterns are collected from samples containing crystallites in a variety of unknown relative orientations, therefore the relative orientation of the reciprocal lattice is not known for any of the diffraction peaks. Compared to single crystal diffraction, an entire dimension of information is lost and there are fewer data points or observations in a powder diffraction study. There are unlikely to be ten observations made for each refined parameter as would be expected for a single crystal study. As a result, it is possible to force an incorrect structure to give a good fit to the data and it is important to be aware that because many parameters are inter-related they should not be refined together. Rietveld refinements carried out on diffraction patterns from powder samples are more likely to diverge or find false minima than other refinements of single crystal diffraction data.

2.3.3 *TOPAS Academic*

The structure determinations of $\text{LiK}(\text{BH}_4)_2$ (Chapter 7), $\text{Ca}(\text{BH}_4)_2$ (Chapter 8) and $\text{Sr}(\text{BH}_4)_2$ (Chapter 9) and the structure refinements of all of the structures within this thesis were performed using the profile refinement program, TOPAS Academic^[167]. DASH^[168] was also used to determine extinction symbols.

The first stage in analysing a diffraction data set was to refine a model to fit to the background. Next, data sets were checked for the presence of known phases using crystallographic information files (cif) from the Inorganic Crystal Structure Database (ICSD). If known structures were present, the zero error and lattice parameters were refined. The positions, peak shapes and intensities of unidentified peaks were identified, refined and then indexed in order to determine the unit cell parameters and potential space groups of unidentified phases within the sample. In addition to gaining information about how a structure changes as a function of temperature, variable temperature experiments were sometimes used to distinguish diffraction peaks relating to phases with different melting temperatures.

Once a space group had been determined, the unit cell parameters and peak positions and shapes were refined within the space group using a Pawley refinement. The ICSD was searched for potential similar crystal structures. Using knowledge of the expected molecular formula of an unidentified phase and the crystal structures of related compounds, the heaviest atom was inserted into the unit cell at a random position. The atomic site occupancy was fixed to unity and the atom was allowed to move freely around the unit cell using a series of Rietveld refinements from different starting positions, similar to a simulated annealing process. The best atomic position was identified based on the level of agreement between the calculated and experimental diffraction patterns. In the majority of metal borohydride structures, both the metal

and borohydride ions are located on a special position. Consequently, the site occupancies of atoms fixed onto special positions were also refined to investigate if an atom was present on a particular site. All of the non-hydrogen atoms were gradually added to the unit cell in this way whilst also assuring that the interatomic distances remained reasonable. Once all of the expected non-hydrogen atoms had been added to the structure, hydrogen atoms were added. Initially the hydrogen atom positions were constrained to form tetrahedral borohydride ions using a rigid-body model. The rigid bodies were allowed to rotate around the boron atoms subject to any symmetry constraints within the unit cell and the single B-H bond length to all of the hydrogen atoms within particular tetrahedra was refined. The effect of allowing the hydrogen atomic positions to refine independently using an unconstrained model was also investigated; a distorted but recognisable tetrahedral co-ordination of hydrogen atoms around a boron atom justifies using a tetrahedral rigid body model. The results of the constrained and unconstrained refinements were compared.

Hydrogen positions within borohydride ions can only be refined from X-ray diffraction data with great caution due to the potential orientational disorder of the borohydride ions. In a standard diffraction experiment, the atomic positions observed are the average positions across the sample. The B-H bonds are in a range of different orientations throughout the sample so the hydrogen positions are disordered. In an attempt to fit the highest proportion of electron density, the modelled B-H bond, $B-H_m$, will be shorter than the real B-H bond, $B-H_r$, as shown in Figure 2.18.

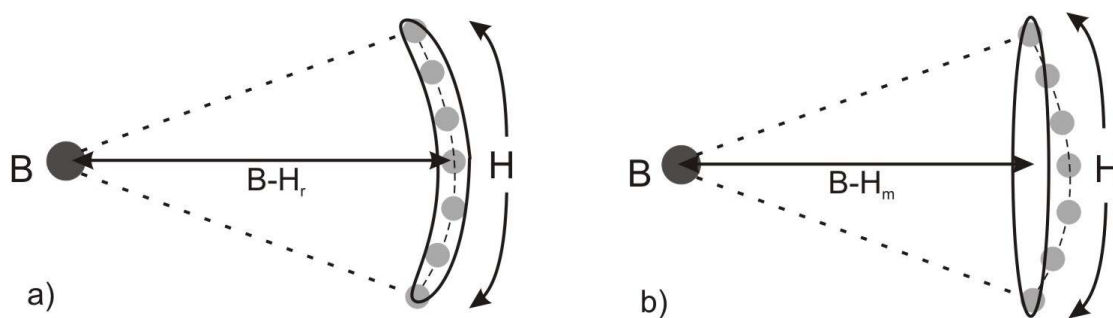


Figure 2.18 a) The B-H bond length within the structure, $B-H_r$ which occurs at a range of orientations throughout the sample and b) the B-H bond length determined from the average electron density, $B-H_m$

When the basic details of new structures had been determined, or were already known, scale parameters and peak shapes could be refined further followed by thermal parameters and site occupancies if appropriate. The quality of the fit to the data was assessed visually and by monitoring the agreement factors.

In the case of variable temperature experiments where high numbers of diffraction patterns were collected with only small changes between them, batch refinements were performed within TOPAS Academic^[167]. This allows a series of diffraction profiles to be refined automatically with the starting point for each refinement being the result of the previous refinement. The first diffraction profile is refined manually using the usual process and is then used as a seed for successive refinements. If there is a significant change in the profile, a new seed must be manually created and a new batch process started. Batch processes can be used to quickly collect a large amount of crystallographic information but this information must be critically assessed before further use because there was no user interaction during the refinement process.

3 Synthesis of ^{11}B enriched compounds

3.1 Determining accurate structural information about hydrogen

Neutron diffraction is the technique of choice for determining reliable structural information about hydrogen positions and atomic displacement parameters (adps) in crystal structures. The scattering lengths for hydrogen and its heavier isotope, deuterium, are similar to many heavier elements and contribute significantly to any hydride neutron diffraction pattern.

Unfortunately, there are problems with using neutron diffraction to study borohydrides. Figure 3.1 shows the coherent and incoherent neutron scattering cross sections of the elements involved with the light alkali metal borohydrides. Figure 3.2 shows the absorbance cross section of these elements. Hydrogen is a strong incoherent scatterer which results in a large background in neutron diffraction studies making structure determination more difficult. Boron-10 absorbs neutrons very strongly reducing the intensity of the diffracted beam. Therefore in order to gain high quality neutron diffraction data of borohydrides it is necessary to doubly isotopically enrich the compounds with boron-11 and deuterium. Furthermore, in the case of LiBH_4 , lithium-6 also significantly absorbs neutrons and therefore the quality of neutron diffraction data from LiBH_4 can be further improved by isotopically enriching with lithium-7. Doubly or triply enriched borohydrides are either extremely expensive (£10 000/g) or unavailable commercially so it was necessary to synthesise the compounds as a part of this project.

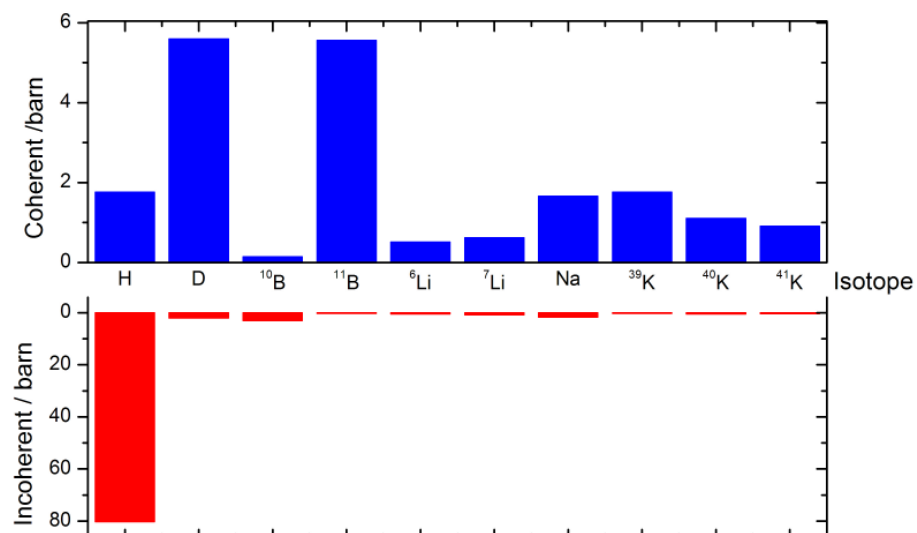


Figure 3.1 The coherent and incoherent neutron scattering cross section of the elements concerned with alkali metal borohydrides ^[169]

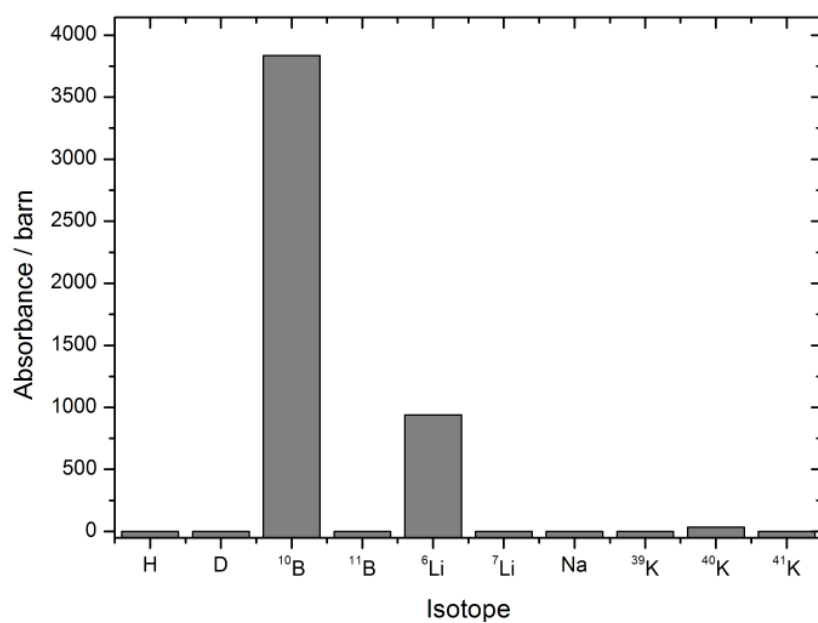


Figure 3.2 The absorption cross section of the elements concerned with alkali metal borohydrides ^[169]

3.2 Experimental and observations

$^7\text{Li}^{11}\text{BD}_4$, $\text{Li}^{11}\text{BD}_4$, $\text{Na}^{11}\text{BD}_4$, K^{11}BD_4 and $\text{LiK}(^{11}\text{BD}_4)_2$ were synthesised using a Parr High Pressure Reactor Furnace (see Experimental, Chapter 2) based on the method of Friedrichs *et al.*^[43] according to Equation 3.1. To make $\text{Li}^{11}\text{BD}_4$, crystalline boron-11 (Alfa Aesar) was ball milled for five hours at 300 rpm under 1 bar argon to reduce the particle size. The milling jar was loaded and sealed within an argon glove box, removed from the glove box for the milling process and then returned to the glove box to be emptied (see Chapter 2). Excess lithium (Sigma Alrich) was ground together with the boron as much as possible by hand within the argon filled glove box. The mixture was sealed into the pressure vessel under 1 bar argon and heated to 330 °C for 16 hours. The vessel was then cooled and evacuated before being charged with 55 bar deuterium and heated to 700 °C for 48 hours. After the vessel had cooled, it was evacuated and then returned to the glove box to remove the reaction mixture. The reaction mixture was found to be very hard and firmly attached to the inside of the pressure vessel; it could only be removed by the application of significant physical force.



The pressure, 55 bar was chosen because according to the ideal gas equation (Equation 3.2), if there was no absorption, this pressure would increase to just below 200 bar at 700 °C which was the limit of the equipment. During the reaction the pressure did not exceed 120 bar, this may be due to deuterium uptake as the reaction progresses, physisorption to the walls of the reaction vessel or because hydrogen does not act as an ideal gas and Equation 3.3 would be more appropriate than the ideal gas equation. For hydrogen, the constants are $A_0 = 0.1975$, $a = -0.00506$, $B_0 = 0.02096$, $b = -0.04359$, $c = 0.0504 \times 10^4$ $R = 0.08206$ with pressures in atmospheres, volumes in

litres per mole and temperatures in degrees Kelvin.^[170] This equation predicts the pressure at 700 °C to be 170 bar.

$$pV = nRT \quad \text{Equation 3.2}$$

$$p = \frac{RT(1-\varepsilon)}{V^2}(V+B) - \frac{A}{V^2} \quad \text{[170] Equation 3.3}$$

$$A = A_0(1/a/V), B = B_0(1-b/V), \varepsilon = c/VT^3$$

The dark-coloured reaction mixture which was removed from the pressure vessel was washed in dry ether using a Schlenk line to separate white $\text{Li}^{11}\text{BD}_4$ from LiD and amorphous boron (see Experimental, Chapter 2). The yield for the first reaction was about 15 %. The remaining LiD and boron were reused in further reactions which produced higher yields due to the previous heating and mixing processes. It was later found that $\text{Li}^{11}\text{BD}_4$ could be produced by heating lithium, boron and 55 bar deuterium to 700 °C for 12 hours without preheating under argon.

$\text{Na}^{11}\text{BD}_4$ and K^{11}BD_4 were made using a similar method except the mixture was not heated under argon before adding the deuterium, the reaction mixture was only heated for 12 hours and it was not possible to wash the K^{11}BD_4 product in ether because of its low solubility. Washing of $\text{Na}^{11}\text{BD}_4$ was not attempted. The yields of $\text{Na}^{11}\text{BD}_4$ and K^{11}BD_4 were much higher at around 50 % with 50 % binary deuterides also present. The yields reported here are, of course, very likely limited by the difficulty of extracting the product from the pressure vessel. The deuteride separated from the borodeuteride during synthesis forming a white fluffy layer in the furnace above the hard dark borodeuteride. No crystalline boron was observed in the products, but the dark colouration of the borodeuteride phase suggests the presence of amorphous or nanoparticulate boron.

The synthesis of $\text{Ca}(\text{BD}_4)_2$ and $\text{Mg}(\text{BD}_4)_2$ were attempted using the same technique but only resulted in the formation of CaD_2 and MgD_2 .

An attempted synthesis of $\text{LiK}(\text{BD}_4)_2$ from Li, K, B and D_2 formed approximately 50 wt% $\text{LiK}(\text{BD}_4)_2$ with the rest of the mixture being LiBD_4 , KBD_4 , LiD and KD .

3.3 Rationalisation

In the synthesis of $\text{Na}^{11}\text{BD}_4$ and K^{11}BD_4 , it was observed that a layer of white deuteride formed at the top of the furnace above the dark borodeuteride. This could be because the potassium and sodium boiled within the pressure vessel, the gas rose to the top of the pressure vessel and reacted with the deuterium but the boron powder remained at the bottom of the pressure vessel so only deuteride formed at the top. The deuteride is white because it is not contaminated with elemental boron. This would suggest that the boiling temperature of the metal is significant to the success of the synthesis. The boiling temperatures of sodium and potassium (Table 3.1) are above the 700°C of the furnace but close enough for a significant vapour pressure to form over a period of 12 hours. This white layer of deuteride is not observed in the synthesis of LiBD_4 which is unsurprising given the higher boiling temperature of lithium.

Table 3.1 The melting and boiling temperatures of the elements concerned with the synthesis^[77]

Element	Melting temperature / $^\circ\text{C}$	Boiling temperature / $^\circ\text{C}$
Lithium	180	1342
Sodium	97.8	883
Potassium	63.5	759
Magnesium	650	1090
Calcium	842	1484
Boron	2076	3927

The LiBD_4 synthesis is thought to occur via a variety of Li-B intermediates which form before reacting with deuterium. Friedrichs *et al.* suggested the formation of LiB_3 and Li_7B_6 .^[43] M_xB_y compounds with a M:B ratio less than or equal to three which could act as reaction intermediates are not known for sodium and potassium so it is possible that there is more than one synthesis pathway for the formation of borohydrides directly from the elements. A very small amount of what is likely to be a K-B phase was observed in the sample of K^{11}BD_4 (see Chapter 6) suggesting that the formation of K-B compounds may be possible but did not occur to any significant extent.

The synthesis of LiBH_4 is thought to be delayed until above the melting temperature of LiH which forms a layer on the surface of the elemental lithium.^[43] This would be less of a problem for sodium and potassium which are thought to react in the gas phase. The melting temperatures of LiH , MgH_2 and CaH_2 are shown in Table 3.2. MgH_2 melts at 327°C so should not significantly affect the formation of $\text{Mg}(\text{BH}_4)_2$ but CaH_2 does not melt until 1000°C and hence may prevent the formation of $\text{Ca}(\text{BH}_4)_2$.

Table 3.2 Melting temperatures of selected hydrides^[77]

Hydride	Melting temperature $^\circ\text{C}$
LiH	689
MgH_2	327
CaH_2	1000

An alternative indication of the likelihood of a successful synthesis may be the formation enthalpies of the borohydrides and the related hydrides (Table 3.3). The enthalpies of formation of $\text{Mg}(\text{BH}_4)_2$ and $\text{Ca}(\text{BH}_4)_2$ are less negative than the alkali

metal borohydrides so the syntheses direct from the elements might be expected to be unsuccessful. Also, the formation enthalpy of CaH_2 is more favourable than $\text{Ca}(\text{BH}_4)_2$ which is not the case for the other borohydrides under investigation. This would suggest that CaH_2 could be formed in preference to $\text{Ca}(\text{BH}_4)_2$.

Table 3.3 Formation enthalpies for the borohydrides and hydrides

	Borohydride $\Delta H_f / \text{kJ mol}^{-1}$	Hydride ^[77] $\Delta H_f / \text{kJ mol}^{-1}$
Lithium	-194.2 ^[43]	-90.5
Sodium	-191 ^[20]	-56.3
Potassium	-229 ^[20]	-57.7
Magnesium	-152.8 ^[113]	-75.3
Calcium	-151 ^[99]	-181.5

One of the more significant barriers to overcome in the synthesis of the borohydrides from the elements is removing boron atoms from elemental boron.^[100] This is illustrated by the Born-Haber cycle in Figure 3.3. The atomisation and ionisation enthalpies for the alkali and alkaline earth metals are shown in Table 3.4. The lattice energies could be estimated from the Kapustinskii equation (Equation 3.4) and then used within the Born-Haber cycle to estimate the formation enthalpies. However the values estimated will be very different to the experimental values because both the Born-Haber cycle and the Kapustinskii equation are assuming that the borohydride is completely ionic whilst the B-H bonds within the borohydride ion are covalent. It is probably inaccurate to treat boron as a B^{3+} ion but the value of 6888 kJ mol^{-1} for the sum of the first three ionization energies of boron gives an indication of the energies involved. Also the atomisation enthalpy of boron (582 kJ mol^{-1}) is much larger than for the alkali and alkali earth metals.

In order to synthesise an alkaline earth borohydride directly from the elements, the second ionisation enthalpy of the metal has to be overcome providing an increased barrier to the success of the reaction. Consequently, the syntheses of $\text{Ca}(\text{BH}_4)_2$ and $\text{Mg}(\text{BH}_4)_2$ from $\text{CaH}_2 + \text{MgB}_2$,^[100] $\text{CaH}_2 + \text{CaB}_6 + \text{Mg}$ ^[103] or $\text{MgB}_2 + \text{H}_2$ ^[171] have recently been investigated.

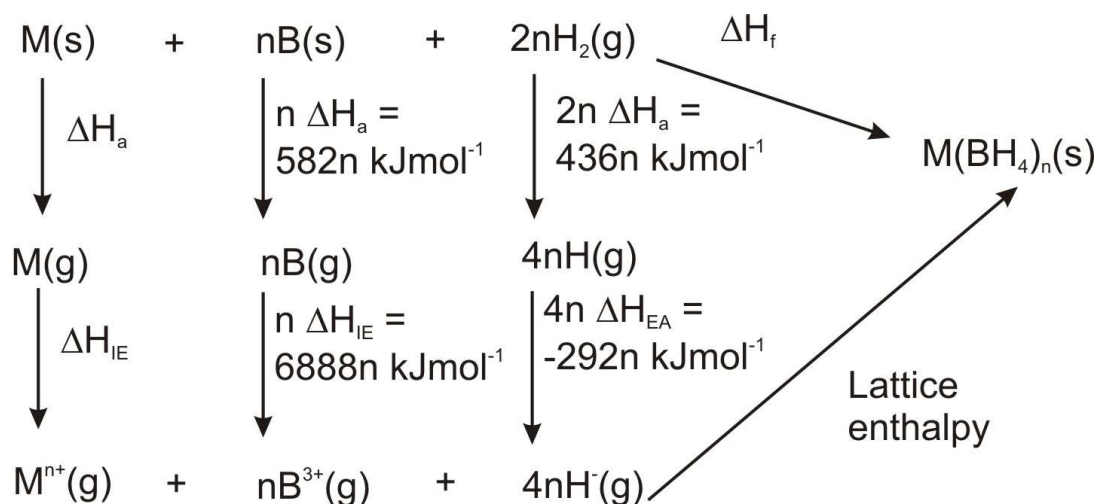


Figure 3.3 A Born-Haber cycle for the synthesis of borohydrides, ΔH_a = atomisation enthalpy, ΔH_{IE} = ionisation enthalpy, ΔH_{EA} = electron affinity, ΔH_f = formation enthalpy^[9]

$$\Delta U(0K) = \frac{(1.07 \times 10^5) \nu |z_+||z_-|}{r_+ + r_-} \quad \text{Equation 3.4}$$

where ν is the number of ions in the empirical formula,
 z_+ and z_- are the charges of the cation and anion respectively and
 r_+ and r_- are the ionic radii of the cation and anion respectively.^[9]

Table 3.4 Atomisation and ionisation enthalpies for the alkali and alkaline earth metals^[9]

Element	$\Delta H_a / \text{kJ mol}^{-1}$	$\Delta H_{\text{IE}} / \text{kJ mol}^{-1}$
Li	161	520
Na	108	496
K	90	419
Mg	146	$738 + 1451 = 2189$
Ca	178	$590 + 1145 = 1735$

3.4 Effects of deuteration

Although hydrogen and deuterium are chemically equivalent, deuterium has twice the mass of hydrogen and this can result in differences between hydrogenated and deuterated compounds. This effect could be particularly significant in light compounds where the change in mass is a significant portion of the molar mass.

The unit cell volumes of borodeuterides are smaller than borohydrides. In the case of KBH_4 , RbBH_4 and CsBH_4 , the difference decreases as the radius of the alkali metal cation increases.^[86]

Raman spectra show that there are significant differences in the vibration frequencies of B-H and B-D bonds within borohydrides and borodeuterides. To a first approximation, treating the bonds as harmonic oscillators, the frequencies of B-D bond vibrations are a factor of $\sqrt{2}$ smaller than B-H vibrations due to the increased mass; this is explained by Equation 3.5 where ν is the vibration frequency, k is the force constant and μ is the reduced mass.^[86] The differences in vibration frequencies between B-H and B-D bonds are discussed in more detail in the Experimental, Chapter 2 and the relevant chapters for the compounds involved. The change in bond vibration frequency could be expected to affect the reactivity of deuterated compounds.

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad \text{Equation 3.5}$$

3.5 Conclusions

$^7\text{Li}^{11}\text{BD}_4$, $\text{Li}^{11}\text{BD}_4$, $\text{Na}^{11}\text{BD}_4$, K^{11}BD_4 and $\text{LiK}(^{11}\text{BD}_4)_2$ were successfully synthesised directly from the elements at 700 °C under 55 bar deuterium at room temperature. The syntheses of $\text{Mg}(\text{BD}_4)_2$ and $\text{Ca}(\text{BD}_4)_2$ were also attempted but were unsuccessful.

LiBD_4 is thought to be formed via a Li-B intermediate, the formation of LiBD_4 is delayed until after the melting temperature of LiD . NaBD_4 and KBD_4 do not form via an intermediate but the lower boiling temperature of sodium and potassium and their lower ionisation enthalpies make the reactions possible. The reactions would not be affected by the melting temperatures of the hydrides because sodium and potassium react in the gas phase.

Syntheses of the alkaline earth metal borohydrides from the elements are thought to be less favourable due to the higher boiling points of the metals and the second ionisation enthalpies which must be overcome. In the case of calcium, formation of $\text{Ca}(\text{BH}_4)_2$ may be prevented by a surface layer of CaH_2 which does not melt until 1000 °C and the formation enthalpy of CaH_2 is more favourable than that of $\text{Ca}(\text{BH}_4)_2$.

B-D bonds have a lower vibration frequency than B-H bonds which may affect the properties of the deuterated compounds.

4 Lithium borohydride

4.1 Chapter focus

The focus of this chapter is the first detailed variable temperature neutron and synchrotron X-ray diffraction study of isotopically enriched $\text{Li}^{11}\text{BD}_4$. A neutron diffraction study of triply isotopically enriched $^7\text{Li}^{11}\text{BD}_4$ is also discussed. Thermogravimetric, Raman and NMR studies of LiBH_4 and $\text{Li}^{11}\text{BD}_4$ are compared. Unless stated otherwise, LiBH_4 was used as received from Sigma Aldrich.

4.2 Structure of lithium borohydride at -223 °C

$^7\text{Li}^{11}\text{BD}_4$ was synthesised from the elements using the high pressure furnace as discussed in Chapter 3.

Neutron diffraction data for $^7\text{Li}^{11}\text{BD}_4$ were collected in a 6 mm vanadium can within a cryostat on the GEM beamline at ISIS at -223 °C for 3 hours (464 μA). The sample was found to consist only of $^7\text{Li}^{11}\text{BD}_4$ with no impurity phases. A model based on the orthorhombic structure proposed by Soulié *et al.*^[51] was fitted to the data and χ^2 , R_{wp} and R_{exp} values of 13.0, 1.86 % and 0.52 % respectively were obtained. A typical fit to the data is shown in Figure 4.1 and refined parameters are shown in Table 4.1 and Table 4.2. The shapes of the thermal ellipsoids are shown in Figure 4.2.

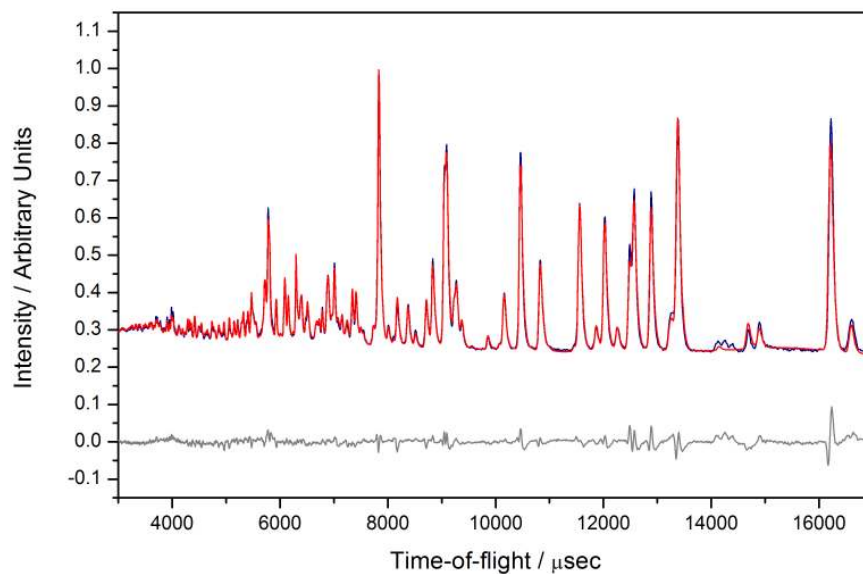


Figure 4.1 A typical fit to the data for a neutron diffraction pattern of ${}^7\text{Li}{}^{11}\text{BD}_4$ at $-223\text{ }^\circ\text{C}$ showing the observed data (blue), the calculated fit (red) and the difference (grey).

Table 4.1 Lattice parameters and atomic positions for ${}^7\text{Li}{}^{11}\text{BD}_4$ at $-223\text{ }^\circ\text{C}$ in space group $Pnma$

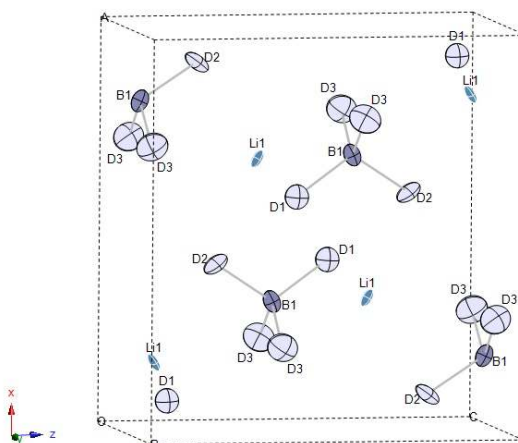
$a = 7.11395(14)\text{ \AA}$, $b = 4.40666(8)\text{ \AA}$, $c = 6.67133(12)\text{ \AA}$, $V = 209.138(6)\text{ \AA}^3$			
Site	x/a	y/b	z/c
${}^7\text{Li}$	0.1586(4)	0.25	0.1130(4)
${}^{11}\text{B}$	0.30547(13)	0.25	0.4296(2)
D1	0.90752(16)	0.25	0.9224(3)
D2	0.39921(19)	0.25	0.27748(18)
D3	0.20398(12)	0.02849(14)	0.42727(16)
$R_{wp} = 1.86\%$, $R_{exp} = 0.52\%$, $\chi^2 = 13.0$			

Table 4.2 Atomic displacement parameters / $\text{\AA}^2$ for $^7\text{Li}^{11}\text{BD}_4$ at $-223\text{ }^\circ\text{C}$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
^7Li	0.0190(41)	0.0121(20)	0.0072(30)	0	-0.0059(15)	0
^{11}B	0.0160(11)	0.0111(10)	0.0103(10)	0	-0.0018(9)	0
D1	0.0238(10)	0.0295(11)	0.0175(13)	0	-0.0002(15)	0
D2	0.0125(16)	0.0461(17)	0.0164(15)	0	0.0049(9)	0
D3	0.0265(10)	0.0195(8)	0.0311(9)	-0.0074(6)	-0.0067(10)	0.0021(8)

Table 4.3 Bond lengths and angles within the borohydride ion in $^7\text{Li}^{11}\text{BD}_4$ at $-223\text{ }^\circ\text{C}$

Bond lengths / $\text{\AA}$		Bond angles / $^\circ$	
B-D1	1.2252(20)	D1-B-D2	110.33(12)
B-D2	1.2147(18)	D1-B-D3	111.25(9)
B-D3	1.2140(9)	D2-B-D3	108.44(10)
		D3-B-D3	107.02(10)

**Figure 4.2** The structure of LiBH_4 at $-223\text{ }^\circ\text{C}$ showing the thermal ellipsoids at 50 % probability

The borohydride ions are close to ideal tetrahedra with a very small range in B-D bond lengths ($0.011\text{ \AA}$, 0.9% , average bond length $1.217\text{ \AA}$) and a variation in D-B-D bond angle of 4.23° across the three independent B-D bonds. The anisotropic displacement parameters for all of the atoms are small, those for the deuterium atoms

are largest (maximum $0.0461(17) \text{ \AA}^2$ for atom D2) due to rotation of the borohydride ions. The data is comparable to that collected by Hartman *et al.* at a lower temperature, $-269.5 \text{ }^\circ\text{C}$ where the average B-D bond length was $1.214(5) \text{ \AA}$ with a variation of $0.017 \text{ \AA}$, (1.4 %) and the maximum anisotropic displacement parameter for a deuterium atom was $0.0308 \text{ \AA}^2$ ^[52].

4.3 Structure of lithium borohydride at room temperature

In addition to the sample of $^7\text{Li}^{11}\text{BD}_4$ discussed in Section 4.2, a sample of $\text{Li}^{11}\text{BD}_4$ was also synthesised from the elements using a high pressure synthesis route.

At room temperature, neutron diffraction data for the $\text{Li}^{11}\text{BD}_4$ sample were collected in an 8 mm vanadium can within a furnace on the GEM beamline at ISIS for 2.5 hours ($400 \text{ }\mu\text{A}$). High resolution X-ray diffraction data were also collected on the sample in a rotating 0.7 mm borosilicate-glass capillary on the I11 beamline at Diamond for 30 minutes.

Neutron diffraction data for $^7\text{Li}^{11}\text{BD}_4$ were collected in a 6 mm vanadium can with a block heater on the GEM beamline at ISIS at room temperature for 5 hours ($800 \text{ }\mu\text{A}$).

All of the room temperature diffraction data were modelled independently starting from the orthorhombic structure proposed by Soulié *et al.* ^[51] as in Section 4.2. Neither sample was found to contain impurity phases. Graphical representations of typical refinements are shown in Figure 4.3 and Figure 4.4.

The refined lattice parameters are compared to previously published data in Table 4.4.

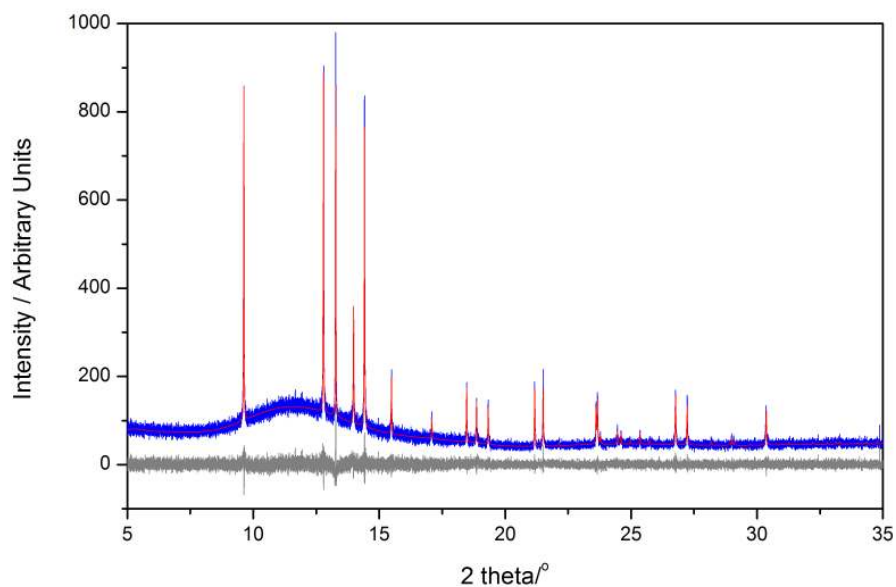


Figure 4.3 A typical fit to the data for an X-ray diffraction pattern of $\text{Li}^{11}\text{BD}_4$ at room temperature (20 °C) showing the observed data (blue), the calculated fit to the data (red) and the difference ($Y_{\text{obs}} - Y_{\text{calc}}$, grey).

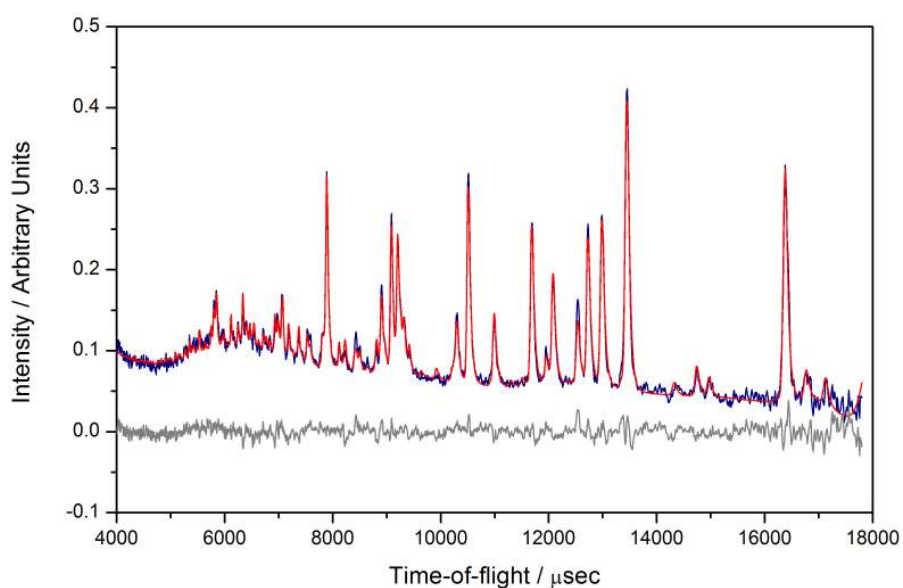


Figure 4.4 A graphical representation of a typical refinement, showing the observed (blue), calculated (red) and difference ($Y_{\text{obs}} - Y_{\text{calc}}$, grey) plots for room temperature (20 °C) neutron diffraction data of $\text{Li}^{11}\text{BD}_4$

Table 4.4 The experimentally observed lattice parameters for room temperature ($\sim 20^\circ\text{C}$) orthorhombic LiBD_4 with comparison to published values

	Study	$a / \text{\AA}$	$b / \text{\AA}$	$c / \text{\AA}$	$V / \text{\AA}^3$
This study	Neutron	7.1517(7)	4.4295(3)	6.7854(5)	214.95(3)
	$\text{Li}^{11}\text{BD}_4$				
	Neutron	7.1478(7)	4.4246(3)	6.7842(5)	214.56(3)
	$^7\text{Li}^{11}\text{BD}_4$				
	X-ray	7.13764(7)	4.42120(4)	6.77664(8)	213.850(4)
	$\text{Li}^{11}\text{BD}_4$				
Previously reported	Neutron	7.1526(6)	4.4278(4)	6.7933(6)	215.15(4)
	LiBD_4				
	29°C ^[54]				
	X-ray	7.17858(4)	4.43686(2)	6.80321(4)	216.685(3)
	LiBH_4 ^[51]				
	X-ray	7.1900(7)	4.4447(4)	6.8135(7)	217.74(4)
	LiBH_4				
	20°C ^[55]				

The experimentally determined room temperature, orthorhombic structure of LiBD_4 is in agreement with previously published data. The observed lattice parameters from both X-ray and neutron diffraction data (Table 4.4) are smaller than those previously published although the atomic positions obtained from both the X-ray and neutron diffraction data (Table 4.5) are comparable, ($B_{\text{eq}} = 8 \pi^2 U_{\text{eq}}$).

The B-D bond lengths of 1.11(4) $\text{\AA}$ to 1.20(4) $\text{\AA}$ obtained from X-ray diffraction data (Table 4.6) are comparable to those published by Filinchuk *et al.* (1.118(7) $\text{\AA}$ to 1.151(11) $\text{\AA}$) but a narrower range of D-B-D bond angles is observed (10° in this work and 14.3° observed by Filinchuk *et al.*).^[55] The longest and shortest B-D bonds are reported to D2 and D1 respectively in both cases. There is a very strong similarity between the work reported here and that by Filinchuk *et al.* for the length of the

shortest bond, B-D1.^[55] The B-D bond lengths obtained from neutron diffraction from $\text{Li}^{11}\text{BD}_4$ (1.195(5) Å to 1.203(10) Å) and $^7\text{Li}^{11}\text{BD}_4$ (1.178(4) to 1.223(6) Å) are comparable to those obtained by Buchter *et al.* (1.18(2) Å to 1.20(2) Å).^[54] The difference in bond lengths determined from the neutron and X-ray powder diffraction studies is due to the electron density from deuterium being drawn into the B-D bond, making the bond appear shorter by X-ray diffraction. The fact that this effect appears greater for the shorter B-D bonds may be due to experimental effects.

Wu *et al.* reported the B-H bond length in lithium amidoborane (LiNH_2BH_3) to be 1.249 Å by X-ray diffraction.^[172] Yang *et al.* reported the B-D bond length in ND_3BD_3 to be 1.204 Å at 22 °C by neutron powder diffraction.^[173] The length of the terminal B-H bonds in diborane (B_2H_6) were reported as 1.16 Å determined by X-ray diffraction at -179 °C by Hübschle *et al.*^[174] So the B-D bond lengths observed here for LiBD_4 are closer to those for diborane and ammonia borane than for lithium amidoborane but again this may be a result of experimental uncertainties.

It has been observed that when thermal parameters for the deuterium atoms of $\text{Ca}(\text{BH}_4)_2$ at room temperature are allowed to refine independently, the borohydride ion appears to more closely approach the shape of an ideal tetrahedron.^[107] The same effect has been observed in this work, the range of B-D bond lengths and D-B-D bond angles is narrower if the thermal parameters of the deuterium atoms are allowed to refine independently.

Structural refinements using rigid body tetrahedral borohydride units were also attempted using the room temperature diffraction data. It was not possible to achieve a reasonable fit to the neutron diffraction data for either $\text{Li}^{11}\text{BD}_4$ or $^7\text{Li}^{11}\text{BD}_4$. However a structure was refined from the synchrotron X-ray diffraction data from $\text{Li}^{11}\text{BD}_4$ with χ^2 , R_{wp} and R_{exp} values of 1.0, 9.40 % and 9.21 % respectively. These values are

nearly identical to the values obtained for the unconstrained model. The B-D bond length was 1.143(10) Å. The difficulty in refining a structural model from the neutron diffraction data is more likely to be due to the orientational disorder of the borohydride ions than any distortion in their shape.

The structures refined from both the room temperature neutron and X-ray diffraction data are very similar.

Table 4.5 Atomic positions for LiBD₄ by neutron and X-ray diffraction at room temperature

Neutron Li ¹¹ BD ₄	x/a	y/b	z/c	B _{eq} / Å ²
Li	0.168(2)	0.25	0.1211(19)	3.3(3)
¹¹ B	0.2959(5)	0.25	0.4349(7)	2.40(18)
D1	0.9005(6)	0.25	0.9280(10)	3.52(14)
D2	0.4015(10)	0.25	0.2970(9)	3.52(14)
D3	0.19933(5)	0.0331(7)	0.4175(6)	3.52(14)
$R_{wp} = 5.97\%$, $R_{exp} = 4.09\%$, $\chi^2 = 2.1$				
Neutron ⁷ Li ¹¹ BD ₄	x/a	y/b	z/c	B _{eq} / Å ²
⁷ Li	0.1752(15)	0.25	0.1133(15)	2.6(2)
¹¹ B	0.2968(4)	0.25	0.4325(6)	2.19(10)
D1	0.9016(5)	0.25	0.9248(8)	3.98(10)
D2	0.4004(6)	0.25	0.2952(6)	3.98(10)
D3	0.2009(3)	0.0347(5)	0.4184(4)	3.98(10)
$R_{wp} = 2.07\%$, $R_{exp} = 0.46\%$, $\chi^2 = 19.9$				
X-ray Li ¹¹ BD ₄	x/a	y/b	z/c	B _{eq} / Å ²
Li	0.1613(8)	0.25	0.1115(10)	5.0(3)
¹¹ B	0.3029(8)	0.25	0.4265(10)	3.4(2)
D1	0.891(4)	0.25	0.939(6)	1
D2	0.392(6)	0.25	0.277(5)	1
D3	0.201(4)	0.044(5)	0.424(3)	1
$R_{wp} = 9.39\%$, $R_{exp} = 9.21\%$, $\chi^2 = 1.0$				

Table 4.6 Observed B-H bond lengths and angles by X-ray and neutron powder diffraction in comparison to previously published values

<i>X-ray powder diffraction</i>	This work $\text{Li}^{11}\text{BD}_4$ 20 °C	Filinchuk <i>et al.</i> LiBH_4 20 °C ^[55]	Soulié <i>et al.</i> LiBH_4 RT ^[51]
B-D lengths / Å	1.11(4)-1.20(4)	1.118(7)-1.151(11)	1.04(2)-1.28(1)
Angles /°	103(3)-113(3)	98.7(9)-113(1)	85.1(9)-120.1(9)

<i>Neutron powder diffraction</i>	This work $\text{Li}^{11}\text{BD}_4$ 20 °C	This work $^7\text{Li}^{11}\text{BD}_4$ 20 °C	Buchter <i>et al.</i> LiBD_4 29 °C ^[54]
B-D lengths / Å	1.195(5)-1.203(10)	1.178(4)-1.223(6)	1.18(2)–1.20(2)
Angles /°	103.4(7)-115.5(4)	103.8(4)-114.9(3)	

<i>Refining individual B_{eq} for D, neutron diffraction</i>	This work $\text{Li}^{11}\text{BD}_4$ 20 °C	This work $^7\text{Li}^{11}\text{BD}_4$ 20 °C
B-D lengths / Å	1.197(5)-1.202(9)	1.186(7)-1.206(8)
Angles /°	105.3(6)-114.7(4)	106.7(4) -115.1(3)

4.4 Variable temperature diffraction

Variable temperature neutron powder diffraction data were collected for both $^7\text{Li}^{11}\text{BD}_4$ and $\text{Li}^{11}\text{BD}_4$ using the GEM diffractometer at ISIS in order to investigate the orthorhombic to hexagonal phase transition. Variable temperature synchrotron X-ray powder diffraction data were also collected for $\text{Li}^{11}\text{BD}_4$ using the I11 beamline at Diamond.

A sample of $\text{Li}^{11}\text{BD}_4$ was loaded into an 8 mm vanadium can which was positioned within a furnace inside the diffractometer. Data were collected for 2.5 hours (400 μA) at 90 °C, for four minutes (10 μA) at 2 °C intervals from 92 °C to 148 °C and then 6.5 hours (1040 μA) at 150 °C.

Neutron diffraction data for ${}^7\text{Li}{}^{11}\text{BD}_4$ were collected in a 6 mm vanadium can fitted with a block heater for 6 hours (960 μA) at 100 $^\circ\text{C}$. Data were also collected for 9 hours (1440 μA) each at 150 $^\circ\text{C}$, 200 $^\circ\text{C}$ and 250 $^\circ\text{C}$.

High resolution X-ray diffraction data were collected on a sample of $\text{Li}{}^{11}\text{BD}_4$ in a rotating 0.7 mm borosilicate-glass capillary. Data were collected between 5° and 80° two theta using a wavelength of 0.8250 $\text{\AA}$ for five minutes at 10 $^\circ\text{C}$ intervals from 26 $^\circ\text{C}$ to 226 $^\circ\text{C}$. The sample temperature was controlled using a cryostream.

Portions of the diffraction data as a function of temperature are shown in Figure 4.5 and Figure 4.6. The figures show a representation of how a surface plot of the diffraction patterns as a function of temperature would appear if viewed from above. The coloured lines show the positions of the diffraction peaks as a function of temperature. The width of the lines shows the width of the peaks and the intensities of the colours indicate the relative intensities of the peaks. Models based on the orthorhombic and hexagonal structures proposed by Soulié *et al.* were refined independently to the diffraction data from each sample. The neutron diffraction patterns have lower intensity after the phase change due to disorder within the hexagonal structure.

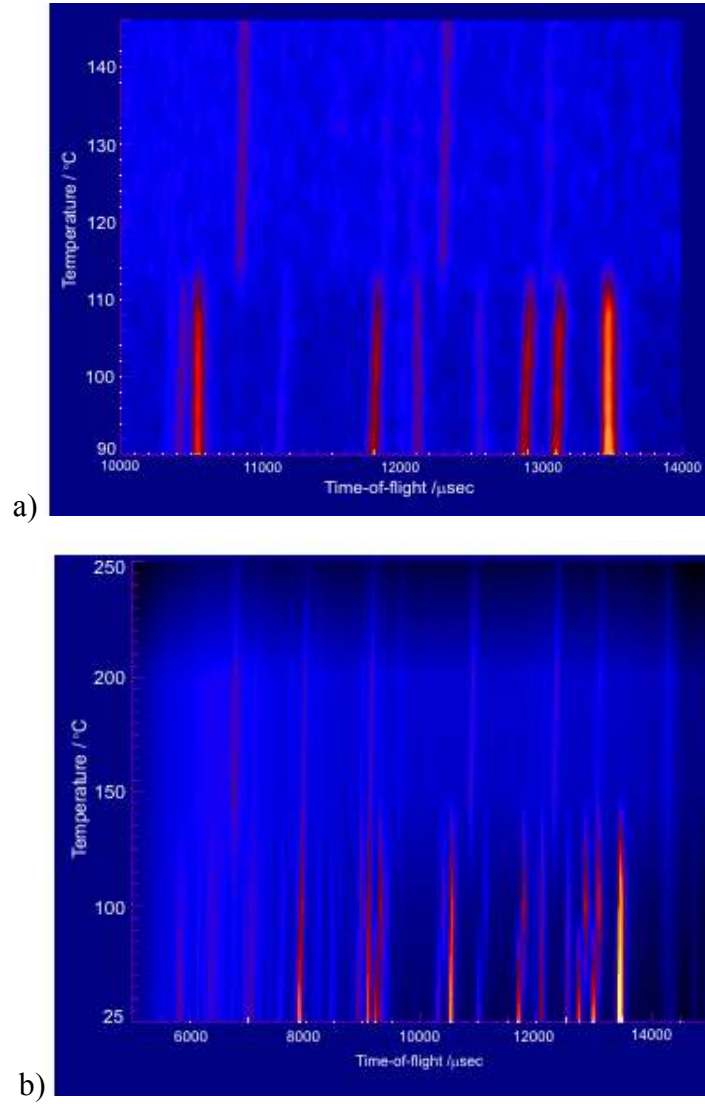


Figure 4.5 Neutron diffraction patterns as a function of temperature for a) $\text{Li}^{11}\text{BD}_4$ (2 °C steps) and b) $^7\text{Li}^{11}\text{BD}_4$ (at 25 °C, 100 °C, 150 °C, 200 °C, 250 °C). The patterns show how a surface plot of the diffraction patterns as a function of temperature would appear if viewed from above. The coloured lines show the time-of-flight positions of diffraction peaks as a function of temperature. The width of the lines shows the width of the peaks and the intensities of the colours indicate the relative intensities of the peaks.

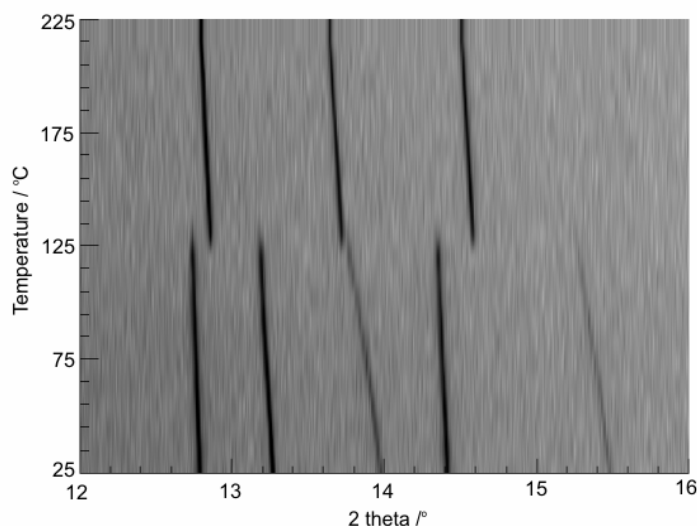


Figure 4.6 X-ray diffraction patterns for $\text{Li}^{11}\text{BD}_4$ as a function of temperature. The pattern is a representation of how a surface plot of the diffraction patterns as a function of temperature would appear if viewed from above. The lines show the two theta positions of the diffraction peaks as a function of temperature. The width of the lines shows the width of the peaks and the intensities of the lines indicate the relative intensities of the peaks.

4.4.1 *Orthorhombic structure*

The lattice parameters of the orthorhombic phase were determined from variable temperature neutron and X-ray diffraction studies. The lattice parameters obtained from the separate diffraction experiments are compared as a function of temperature in Figure 4.7 and Figure 4.8. The difference in the lattice parameters refined from the neutron and X-ray diffraction data may be a result of the different peak shapes resulting from the two techniques or a difference in how deuterium atoms are modelled when refining neutron and X-ray diffraction data. The radiation may also have caused damage to the sample, distorting the lattice parameters.

All of the atomic positions in the orthorhombic phase were refined from the neutron diffraction data of $\text{Li}^{11}\text{BD}_4$ but no significant changes from the room temperature

positions were observed. The thermal parameters were refined with the parameters for lithium and boron fixed to be equivalent and all of the deuterium atoms fixed to be equivalent, again no significant changes were observed.

For the neutron diffraction data of $^7\text{Li}^{11}\text{BD}_4$, all of the atomic positions were refined, but no significant changes from the room temperature positions were observed. The thermal parameters were refined but the deuterium atoms were fixed to be equivalent.

For the variable temperature X-ray diffraction data, the atomic positions of lithium and boron were refined but the deuterium positions were fixed. The lithium and boron thermal parameters were refined individually, the deuterium thermal parameters were not refined.

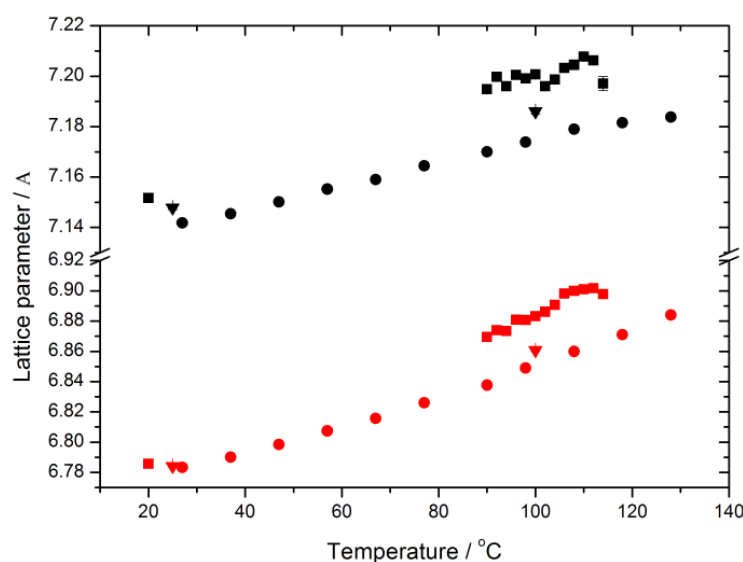


Figure 4.7 The a (black) and c (red) lattice parameters from neutron diffraction of $\text{Li}^{11}\text{BD}_4$ (squares) and $^7\text{Li}^{11}\text{BD}_4$ (triangles) and X-ray diffraction of $\text{Li}^{11}\text{BD}_4$ (circles) for the orthorhombic phase as a function of temperature. Where error bars are not shown, they are smaller than the data symbols.

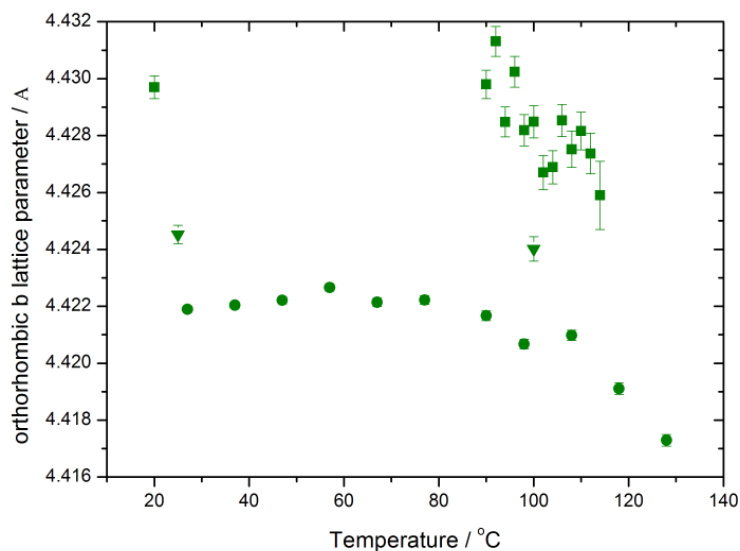


Figure 4.8 The b lattice parameter from neutron diffraction of $\text{Li}^{11}\text{BD}_4$ (squares) and $^7\text{Li}^{11}\text{BD}_4$ (triangles) and X-ray diffraction of $\text{Li}^{11}\text{BD}_4$ (circles) for the orthorhombic phase as a function of temperature. When error bars are not shown, they are smaller than the data symbols.

The thermal expansion of orthorhombic $\text{Li}^{11}\text{BD}_4$ is anisotropic. As the temperature increases, the a and c lattice parameters of the orthorhombic unit cell increase (Figure 4.7) whilst the b parameter is observed to decrease (Figure 4.8).

The X-ray diffraction data show that the rate of increase of the a lattice parameter decreases above 108 °C and the rate of increase of the c lattice parameter increases above 80 °C. Across the temperature range of the orthorhombic phase, the X-ray diffraction study shows that the c lattice parameter increases from 6.7833(2) Å at 26 °C to 6.8840(4) Å at 128 °C (1.5 % increase) while the a lattice parameter only increases from 7.1417(2) Å to 7.1837(4) Å in the same temperature range (0.6 % increase). The b lattice parameter shows an approximate plateau from room temperature until 78 °C before beginning to decrease; according to the X-ray diffraction study, the b lattice parameter is 4.42190(11) Å at 26 °C, very similar at 4.42222(15) Å at 78 °C and then decreases to 4.4173(2) Å at 128 °C. Despite previous

work suggesting that the orthorhombic to hexagonal phase change occurs at 108 °C^[55], Bragg peaks relating to the orthorhombic phase were observed up to 128 °C in the X-ray diffraction data. This may be due to the faster heating rate used in this experiment, 2 °C/min compared to 20 °C/hr used by Filinchuk *et al.*.

4.4.2 Phase transition

The neutron diffraction data for Li¹¹BD₄ (2 °C steps, Figure 4.5) shows the orthorhombic to hexagonal phase transition at 116 °C. The neutron diffraction data for ⁷Li¹¹BD₄ shows that the transition occurred between data collected at 100 °C and 150 °C. The X-ray diffraction data for Li¹¹BD₄ (10 °C steps) shows the transition between 128 °C and 138 °C but the delayed transition may be an effect of the increased heating rate.

At the phase transition, the volume per formula unit decreases as previously observed by Filinchuk *et al.*^[55]. According to the neutron diffraction data this is from 55.05(2) Å³ at 112 °C to 54.52(7) Å³ at 118 °C (Figure 4.9). This decrease in volume results in an increase in the density of the structure, making the structure more stable.

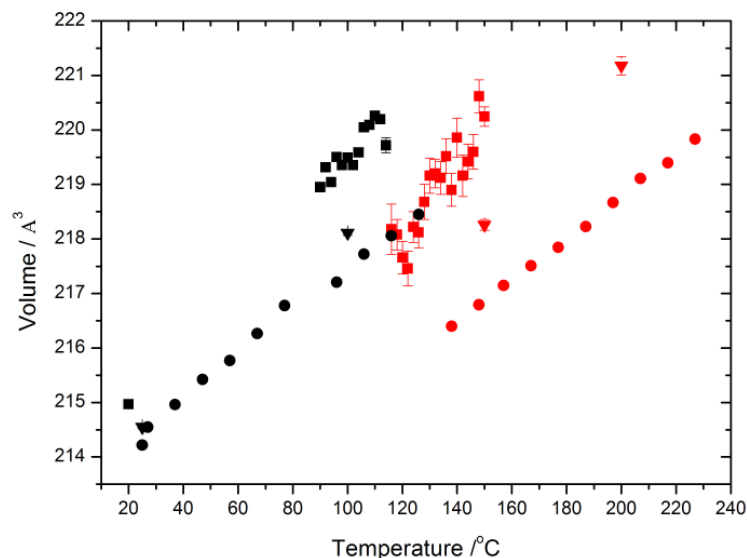


Figure 4.9 The volume of LiBD_4 (per four formula units) as a function of temperature for the orthorhombic low temperature phase (black) and hexagonal high temperature phase (red). The data are from X-ray diffraction of $\text{Li}^{11}\text{BD}_4$ (circles), neutron diffraction of $\text{Li}^{11}\text{BD}_4$ (squares) and neutron diffraction of $^7\text{Li}^{11}\text{BD}_4$ (triangles)

The c lattice parameter of the orthorhombic phase has a similar magnitude to the c lattice parameter of the hexagonal phase, however there is no simple relationship between the structures along these two directions. Both the orthorhombic and hexagonal phases contain layers with a hexagonal framework of lithium and boron atoms. In the orthorhombic phase the layers are buckled and in the bc plane; in the hexagonal phase the layers are flatter and are in the ab plane (Figure 4.10)^[175]. Consequently, a relationship is expected between the a lattice parameter of the orthorhombic phase and the c lattice parameter of the hexagonal phase (the separation of the layers), the b lattice parameter of the orthorhombic phase and the a lattice parameter of the hexagonal phase and finally, half the c lattice parameter of the orthorhombic phase and the a lattice parameter of the hexagonal phase multiplied by $\cos 30^\circ$ (or the c lattice parameter of the orthorhombic phase and the a lattice parameter of the hexagonal phase multiplied by $\sqrt{3}$; $2\cos 30^\circ = \sqrt{3}$).

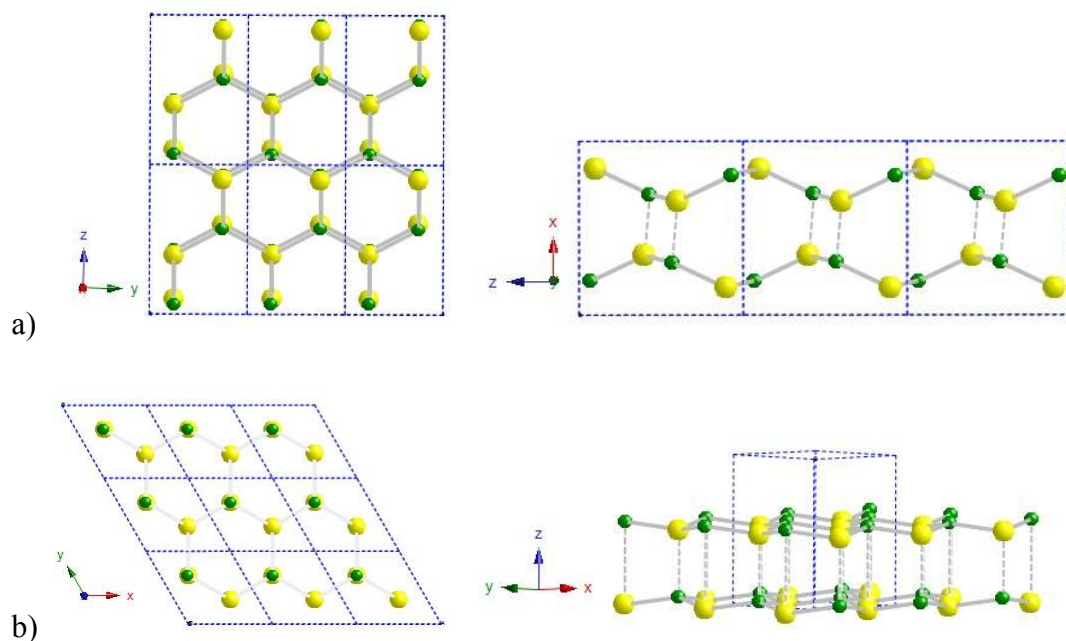


Figure 4.10 The hexagonal framework of the layers and the stacking of the layers of Li (yellow) and B (green) atoms in a) orthorhombic LiBH_4 and b) hexagonal LiBH_4 ^[175]

The c lattice parameter of the hexagonal phase is smaller than the a lattice parameter of the orthorhombic phase because the flatter layers in the hexagonal phase can pack together more tightly. The orthorhombic b lattice parameter is similar to but larger than the hexagonal a lattice parameter. In the direction of the orthorhombic c lattice parameter, the hexagonal phase is expanded compared to the orthorhombic phase because the layers have unfolded in this direction. According to the neutron diffraction data of $\text{Li}^{11}\text{BD}_4$, the orthorhombic a lattice parameter is 7.2062(17) Å at 112 °C and the c lattice parameter of the hexagonal phase is 6.9250(41) Å; the orthorhombic b lattice parameter is 4.4274(7) Å and the hexagonal a lattice parameter is 4.426(2) Å at the same temperatures.

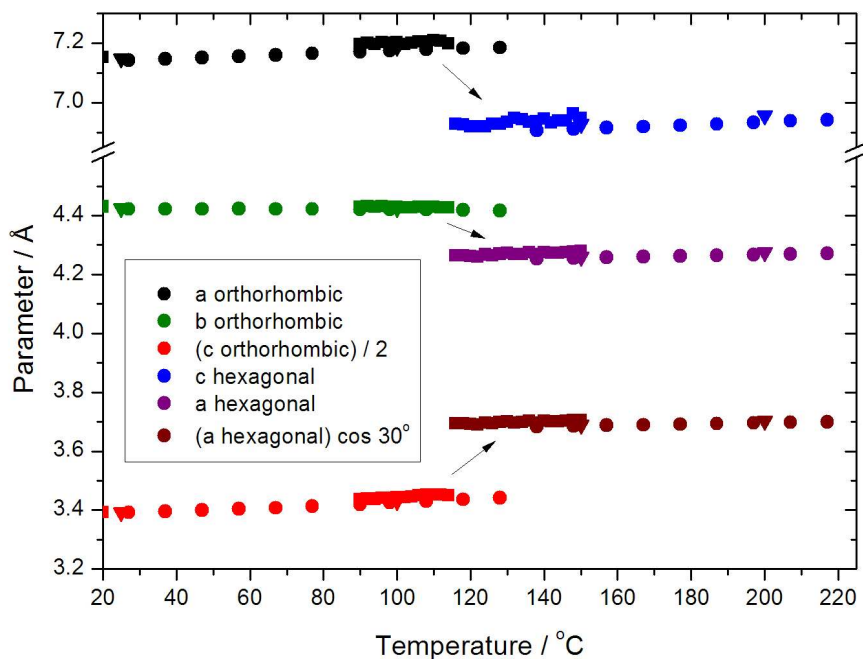


Figure 4.11 The relationship between the unit cell parameters of the orthorhombic and hexagonal phases of LiBD_4 . The data are from X-ray diffraction of $\text{Li}^{11}\text{BD}_4$ (circles), neutron diffraction of $\text{Li}^{11}\text{BD}_4$ (squares) and neutron diffraction of $^7\text{Li}^{11}\text{BD}_4$ (triangles)

4.4.3 Hexagonal phase

Diffraction peaks due to the high temperature $P6_3mc$ structure of $\text{Li}^{11}\text{BD}_4$ are observed in the diffraction patterns after the phase change in agreement with previously published data.^[51, 55] The variation of the lattice parameters with temperature are shown in Figure 4.12 and Figure 4.13.

Above the phase change, the z parameters of the atomic positions for the boron and deuterium atoms were refined from the neutron diffraction data of both $\text{Li}^{11}\text{BD}_4$ and $^7\text{Li}^{11}\text{BD}_4$, the other atomic position parameters are on special positions. The thermal parameters were refined for all the atoms but the deuterium atoms were fixed to be equivalent.

Only the z parameter of the boron atomic position and the thermal parameters were refined from the synchrotron X-ray diffraction data. Again the deuterium thermal parameters were refined to be equivalent.

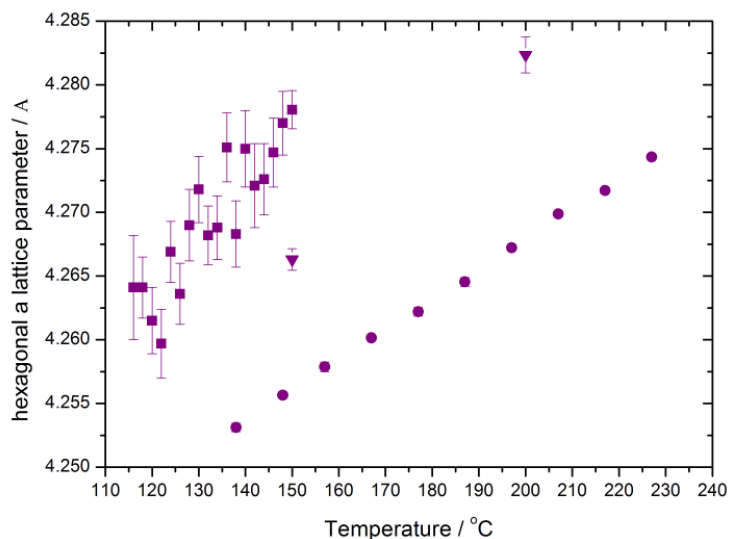


Figure 4.12 The a lattice parameter of the high temperature hexagonal phase as a function of temperature. Values refined from $\text{Li}^{11}\text{BD}_4$ neutron diffraction (squares), $^7\text{Li}^{11}\text{BD}_4$ neutron diffraction (triangles) and $\text{Li}^{11}\text{BD}_4$ synchrotron X-ray diffraction (circles). Where error bars are not shown they are smaller than the data symbols.

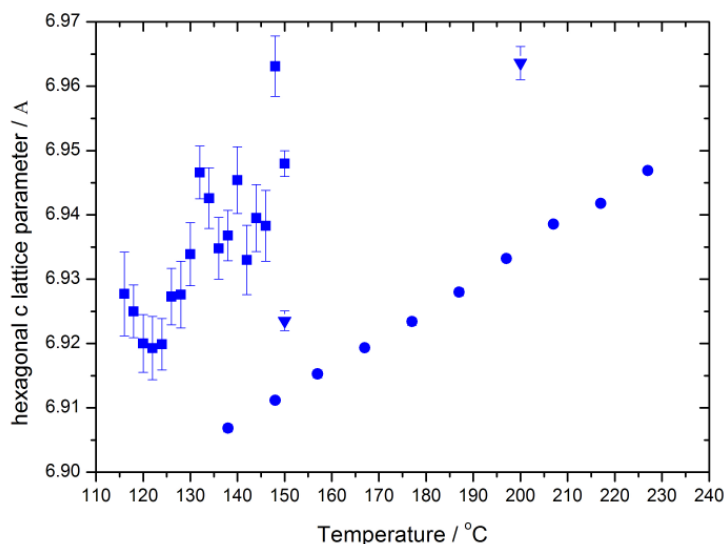


Figure 4.13 The c lattice parameter of the high temperature hexagonal phase as a function of temperature. Values refined from $\text{Li}^{11}\text{BD}_4$ neutron diffraction (squares), $^7\text{Li}^{11}\text{BD}_4$ neutron diffraction (triangles) and $\text{Li}^{11}\text{BD}_4$ synchrotron X-ray diffraction (circles). Where error bars are not shown they are smaller than the data symbols.

Both the a and c lattice parameters of the hexagonal phase increase uniformly with temperature. The X-ray diffraction study shows an increase from 4.2531(3) Å at 138 °C to 4.2743(2) Å at 226 °C for the a parameter and from 6.9069(6) Å to 6.9569(3) Å for the c parameter in the same temperature range. The neutron diffraction study suggests a faster increase in lattice parameters. The a lattice parameter increases from 4.2615(26) Å to 4.2781(15) Å and the c parameter from 6.9200(45) Å to 6.9480(20) Å between 120 °C and 150 °C. The neutron diffraction study also shows a larger, faster increase in the ratio c/a (from 1.622 at 124 °C to 1.628 at 148 °C) than the X-ray diffraction study where the ratio remains at approximately 1.624. The ratio c/a in the X-ray diffraction study reported by Filinchuk *et al.*^[55] has similar values and shows a similar trend to the X-ray diffraction study reported here. The differences between the lattice parameters determined from the neutron and X-ray diffraction studies suggest that at least one of the samples may have been damaged by the radiation.

The structure of $^7\text{Li}^{11}\text{BD}_4$ at 150°C was refined from the neutron diffraction data using two separate models. In the first model, the atomic positions were only constrained in order to obey the symmetry of the unit cell, in the second model, the borohydride ions were also constrained as tetrahedral rigid bodies. The lattice parameters and atomic positions for the unconstrained and constrained models are shown in Table 4.7 and Table 4.8 respectively. Anisotropic atomic displacement parameters, B-D bond lengths and D-B-D bond angles within the borohydride units for the unconstrained model are shown in Table 4.9 and Table 4.10. The structure is shown in Figure 4.14. The anisotropic displacement parameters are particularly large for the deuterium atoms reflecting the rotational disorder of the borohydride ions and the vibrations of

the B-D bonds at this temperature. For atom D2, five of the six displacement parameters are above or around $1 \text{ \AA}^2$ whereas at $-223 \text{ }^\circ\text{C}$ the maximum parameter was $0.0461(17) \text{ \AA}^2$ for atom D2. Hartman *et al.* also observed large anisotropic displacement parameters, particularly for the deuterium atoms. The values determined in this work are greater than those determined by Hartman *et al.* reflecting the higher temperature of the sample ($150 \text{ }^\circ\text{C}$ in this work, $127 \text{ }^\circ\text{C}$ by Hartman *et al.*)^[52]. The orientational disorder of the borohydride ions results in large variations in the apparent B-D bond lengths and D-B-D bond angles within the borohydride units. In the unconstrained model, the bond lengths vary from $0.73(8) \text{ \AA}$ to $1.227(18) \text{ \AA}$ and the bond angles from $89.966(4)^\circ$ to $114(3)^\circ$, compared to $1.2140(9) \text{ \AA}$ to $1.225(2) \text{ \AA}$ and $107.02(10)^\circ$ to $111.25(9)^\circ$ in the orthorhombic structure at $-223 \text{ }^\circ\text{C}$. In the constrained model, the B-D bond length refined to $1.26(4) \text{ \AA}$. The problem with anisotropic displacement parameters being modelled as ellipsoids is that this shape does not curve around the edge of the borohydride ion. The distance from the boron atom to the end of the ellipsoid is greater than the distance from the boron atom to the centre of the ellipsoid. This problem becomes more significant with larger displacement parameters. Clearly, the B-D distance is not expected to change as the borohydride ion rotates or the B-D-B bond angle deforms. A more accurate representation would model the ellipsoids curved around the borohydride ion in a crescent or banana shape, however this model is more complex and has not been attempted here. Figure 4.14 gives an impression of the relative size of the displacement parameters but not the actual shape of the area likely to contain the deuterium atom.

Table 4.7 Lattice parameters and atomic positions refined from the neutron diffraction data from ${}^7\text{Li}{}^{11}\text{BD}_4$ at 150°C using an unconstrained borohydride ion geometry

$a = 4.2670(8) \text{ \AA}, c = 6.9293(15) \text{ \AA}, V = 109.26(5) \text{ \AA}^3$			
Site	x/a	y/b	z/c
${}^7\text{Li}$	0.3333	0.6667	0
${}^{11}\text{B}$	0.3333	0.6667	0.604(8)
D1	0.3333	0.6667	0.499(7)
D2	0.172	0.3446	0.647(7)
$R_{wp} = 0.94 \%, R_{exp} = 0.35 \%, \chi^2 = 7.2$			

Table 4.8 Lattice parameters and atomic positions refined from the neutron diffraction data from ${}^7\text{Li}{}^{11}\text{BD}_4$ at 150 °C with the borohydride ion refined as a rigid tetrahedron

$a = 4.2656(8) \text{ \AA}, c = 6.9280(13) \text{ \AA}, V = 109.17(5) \text{ \AA}^3$			
Site	x/a	y/b	z/c
${}^7\text{Li}$	0.3333	0.6667	0
${}^{11}\text{B}$	0.3333	0.6667	0.574(2)
D1	0.3333	0.6667	0.756(2)
D2	0.173(2)	0.3456(2)	0.513(2)
$R_{wp} = 0.70 \%, R_{exp} = 0.30 \%, \chi^2 = 5.4$			

Table 4.9 Atomic displacement parameters for ${}^7\text{Li}{}^{11}\text{BD}_4$ at 150 °C refined from the neutron diffraction study / $\text{\AA}^2$

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
${}^7\text{Li}$	0.71(17)	1.3(2)	0.19(5)	0.99(19)	0	0
${}^{11}\text{B}$	0.97(10)	0.97(12)	0.084(16)	0.98(11)	0	0
D1	0.9(24)	1.2(31)	0.06(2)	0.5(48)	0	0
D2	0.88(9)	1.07(11)	1.49(14)	0.96(10)	1.14(11)	1.14(12)

Table 4.10 B-D bond lengths and D-B-D bond angles within the borohydride units of ${}^7\text{Li}^{11}\text{BD}_4$ at 150 °C refined from the neutron diffraction study

Bond lengths / Å		Bond angles / °	
B-D1	0.73(8)	D1-B-D1	89.966(4)
B-D2	1.227(18)	D1-B-D2	104(3)
		D2-B-D2	114(3)

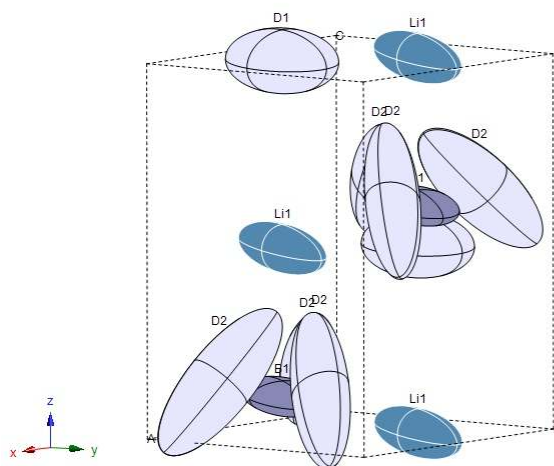


Figure 4.14 The structure of ${}^7\text{Li}^{11}\text{BD}_4$ at 150 °C showing anisotropic atomic displacement parameters

4.4.4 Atomic Pair Distribution Function analysis

Atomic Pair Distribution Function (PDF) analysis was completed on the neutron diffraction data from ${}^7\text{Li}{}^{11}\text{BD}_4$ by the Rutherford Appleton Laboratory.^[176] In this method, it is possible to obtain information about the distances between atoms within the structure by Fourier transforming the data and accounting for all the experimental parameters. The PDF plots show the total radial distribution function, $G(r)$ as a function of atomic separation, r as defined by Keen.^[177] The PDF plots calculated from the fully ordered crystal structures show $r(G(r)-1)$ instead of $G(r)$; $r(G(r)-1)$ emphasises the peaks at larger values of r . Figure 4.15a shows a PDF plot calculated from a fully ordered crystal structure refined from the data at 20 °C. Figure 4.15b shows the PDF plot calculated from the actual room temperature diffraction pattern. Data is not shown for separations of less than 1 Å because it is not possible for atoms to be this close together. The majority of the observed peaks are broader than those obtained in the calculated Pair Distribution Function analysis due to the disorder present in the experimental sample. This disorder arises from the orientational disorder of the borohydride units at 20 °C. The sharp peak at 1.21 Å relates to the B-D bond length and indicates that all of the B-D bonds within the structure have the same length. The peak at 1.95 Å relates to the D...D separation, indicating that the D...D distances are all the same so the borohydride ions have ideal tetrahedral geometry. These sharp peaks have similar widths in both the predicted and experimental plots; these peak widths are as a result of the variation in bond length due to thermal libration.

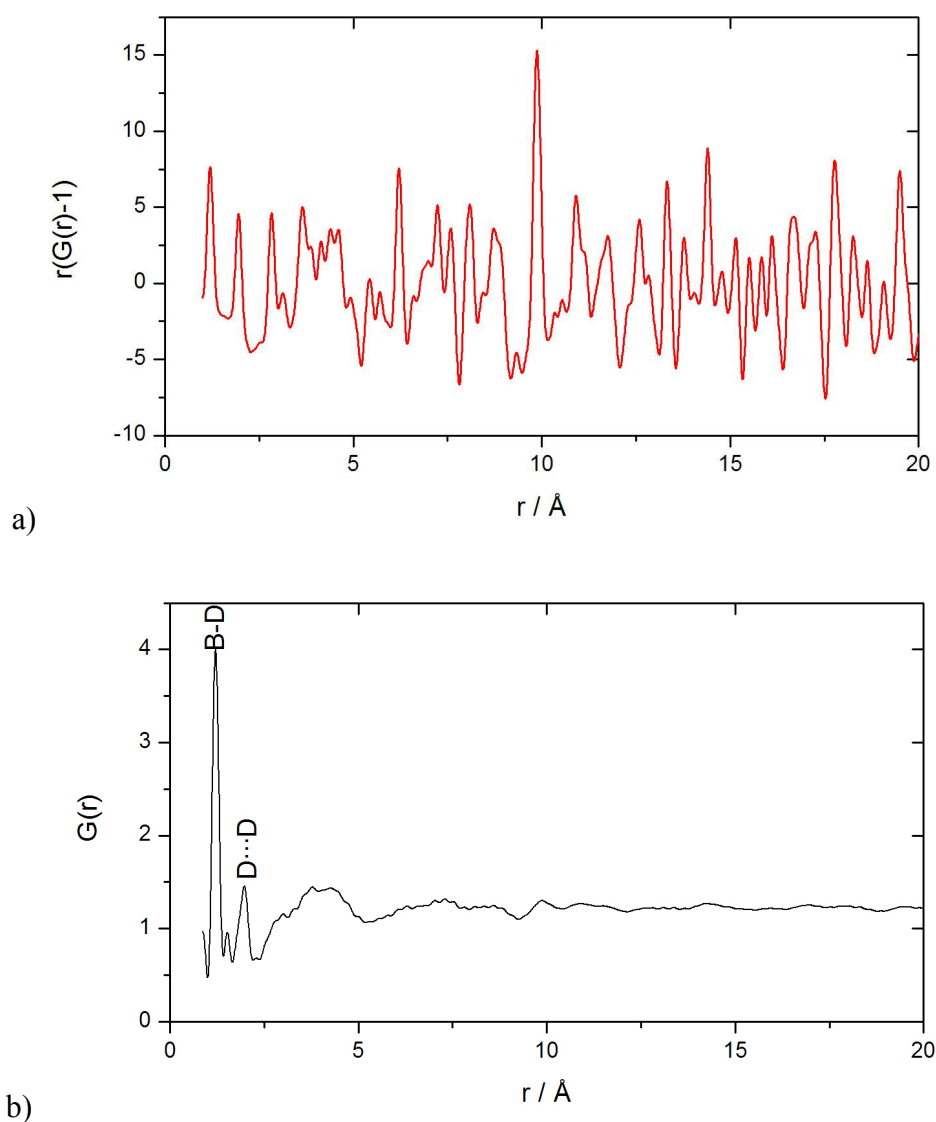


Figure 4.15 a) Predicted and b) experimental PDF plots of total radial distribution function, $G(r)$ as a function of atomic separation, r for ${}^7\text{Li}^{11}\text{BD}_4$ at 20 °C

Figure 4.16a shows the predicted PDF plot calculated from a fully ordered crystal structure of ${}^7\text{Li}^{11}\text{BD}_4$ refined from the diffraction data at 200 °C. Figure 4.16b shows the PDF plot determined directly from the diffraction pattern at 200 °C. The absence of sharp peaks beyond 3 Å illustrates the high level of disorder within this structure. The data in these plots was calculated with a resolution of 0.01 Å, at this resolution, a difference between the bond lengths at 20 °C and 200 °C could not be detected.

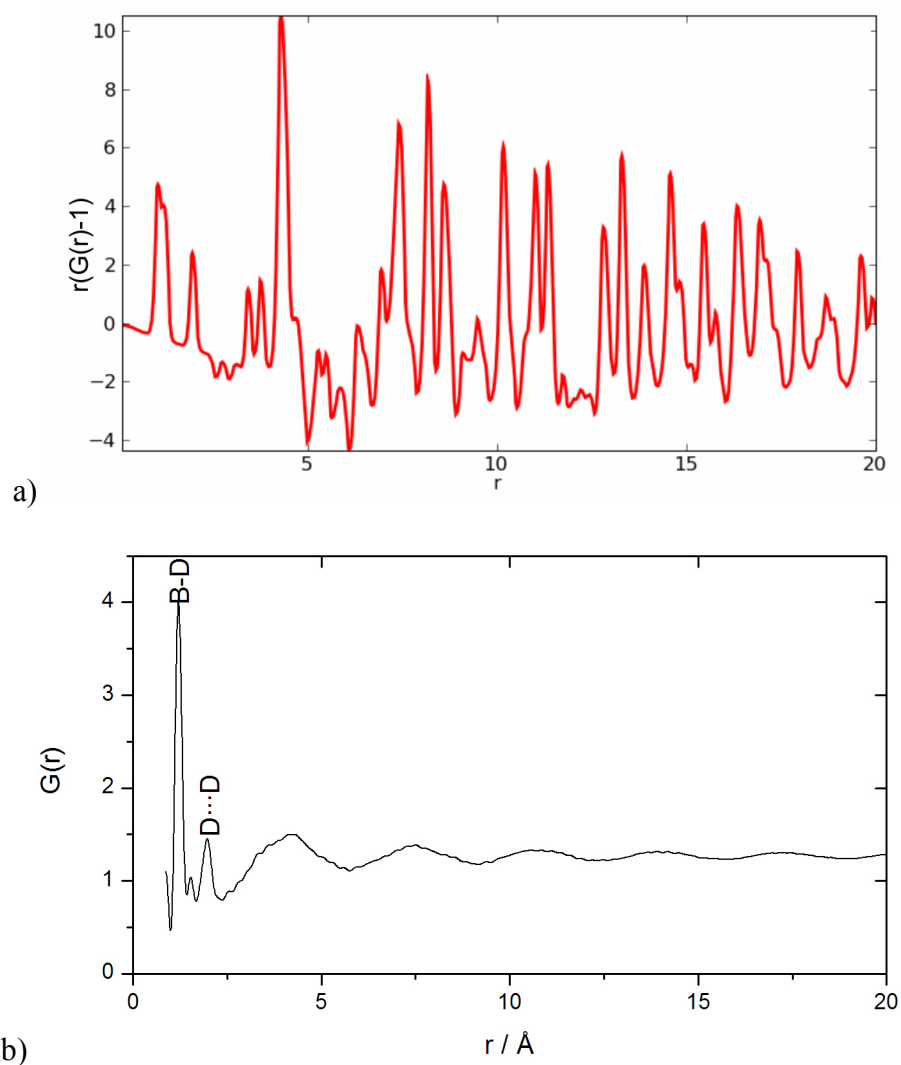


Figure 4.16 a) Theoretical and b) experimental PDF plots of total radial distribution function, $G(r)$ as a function of atomic separation, r for ${}^7\text{Li}{}^{11}\text{BD}_4$ at 200°C

4.5 Raman spectroscopy

Raman spectroscopy was performed at room temperature using a Dilor Labram 300 spectrometer with the sample contained in a sealed glass capillary.

The Raman spectrum of LiBH_4 between 500 cm^{-1} and 3000 cm^{-1} (Figure 4.17) shows the internal bending (below 1750 cm^{-1}) and stretching modes of the B-H bonds in the borohydride ion. The external modes which are movements between the lithium and borohydride ions where the borohydride ion acts as a rigid body^[178] occur at wavenumbers below 500 cm^{-1} .

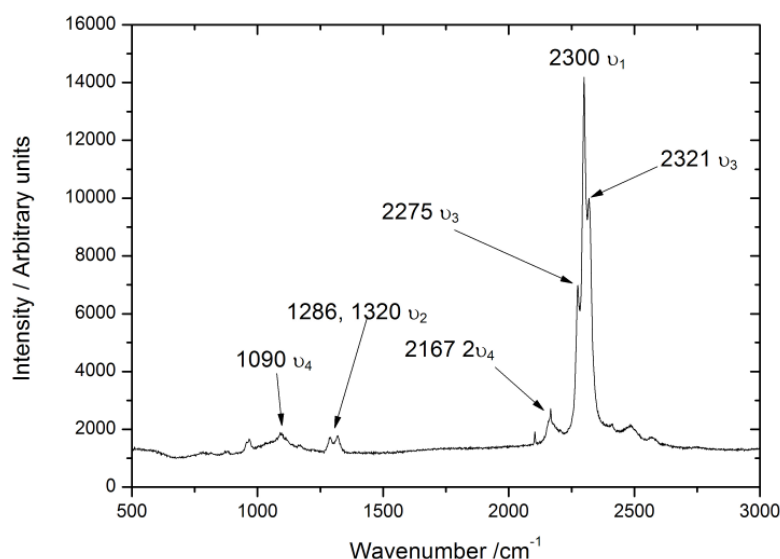


Figure 4.17 The Raman spectrum of LiBH_4 at room temperature with the principle B-H bond vibrations labelled.

In the room temperature orthorhombic phase of LiBH_4 , the borohydride ion is located on a mirror plane within the unit cell and so has the point group C_s . (A perfectly tetrahedral borohydride ion on its own would have the point group T_d). The symmetries of the vibrational modes of a borohydride ion with point group C_s are $\nu_1 = A'$, $\nu_2 = A' + A''$, $\nu_3 = 2A' + A''$, $\nu_4 = 2A' + A''$ (See example in Experimental Chapter 2).^[156]

The strongest signal in the Raman spectrum of LiBH_4 is the symmetric B-H bond stretch, ν_1 at 2300 cm^{-1} . The symmetric B-H bond bending modes, ν_2 are observed at 1286 cm^{-1} and 1320 cm^{-1} . The asymmetric B-H bond stretches, ν_3 are observed in the LiBH_4 spectrum as shoulders either side of the ν_1 signal at 2275 cm^{-1} and 2321 cm^{-1} . The asymmetric B-H bond bending mode, ν_4 signals are indistinguishable from each other around 1090 cm^{-1} .^[156]

Figure 4.18 and Table 4.11 show a comparison of the Raman spectra of LiBH_4 and $\text{Li}^{11}\text{BD}_4$. In $\text{Li}^{11}\text{BD}_4$, the B-D stretches are shifted to lower frequency compared to the B-H stretches in LiBH_4 . This is the effect of the isotopic substitution as discussed in Chapter 2, the approximate ratio of $\nu_{\text{B-H}}/\nu_{\text{B-D}}$ is expected to be close to 1.41 if only the hydrogen / deuterium atom is moving significantly in the bond vibration and closer to 1.36 if the boron atom is also moving in the bond vibration.

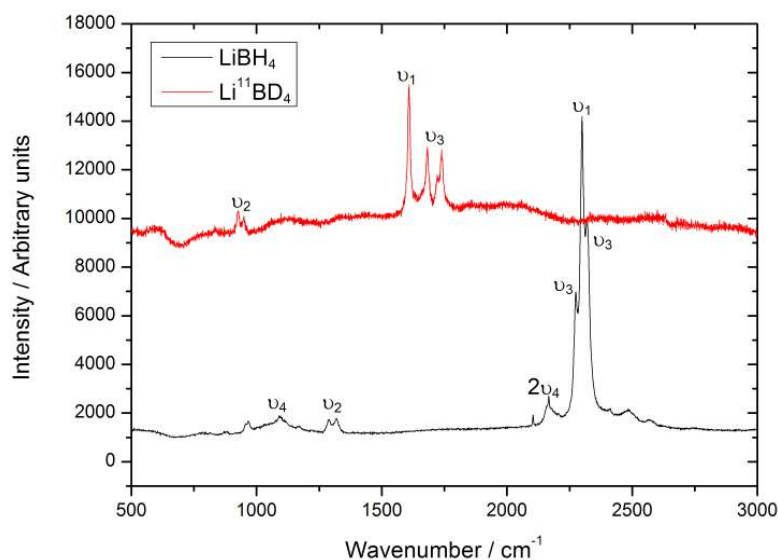


Figure 4.18 Raman spectra for LiBH_4 and $\text{Li}^{11}\text{BD}_4$ at room temperature

Table 4.11 Raman frequencies of LiBH_4 and $\text{Li}^{11}\text{BD}_4$ at room temperature

Assignment	LiBH_4	$\text{Li}^{11}\text{BD}_4$	Ratio $\text{LiBH}_4/\text{Li}^{11}\text{BD}_4$	Theoretical ratio $\text{LiBH}_4/\text{Li}^{11}\text{BD}_4$ [179]
ν_4	1090			
ν_2	1286	927	1.39	1.40
ν_2	1320	951	1.39	1.39
$2\nu_4$	2167			
ν_3	2275	1682	1.35	1.32
ν_1	2300	1609	1.43	1.43
ν_3	2321	1739	1.33	1.34

The Raman spectrum of $\text{Li}^{11}\text{BD}_4$ has lower intensities and more noise than that of LiBH_4 because the LiBH_4 sample was more crystalline, making it easier to obtain a spectrum. The ratio $\nu_{\text{B-H}} / \nu_{\text{B-D}}$ decreases in the order $\nu_1 > \nu_2 > \nu_3$, this has been observed in other alkali metal borohydrides by Renaudin *et al.*^[86] For ν_1 and ν_2 the ratio $\nu_{\text{B-H}} / \nu_{\text{B-D}}$ is close to 1.41 suggesting that it is mainly the hydrogen / deuterium atom which is moving in each individual vibration. The $\nu_{\text{B-H}} / \nu_{\text{B-D}}$ ratio for ν_3 is lower suggesting that the boron atom is also moving significantly in the vibration as would be expected. The $\nu_{\text{B-H}} / \nu_{\text{B-D}}$ ratio is lower than 1.36 suggesting that the internal ν_3 vibration may also be affected by resonances with other internal or external vibrations. A signal for ν_4 was not observed in the spectrum of $\text{Li}^{11}\text{BD}_4$ so the $\nu_{\text{B-H}} / \nu_{\text{B-D}}$ ratio for ν_4 cannot be determined.

4.6 NMR spectroscopy

4.6.1 Solution state ^1H NMR

Solution state NMR samples were prepared in a nitrogen glove bag by dissolving the sample in anhydrous d_8 -THF within the NMR tube. Spectra were collected using a Varian Mercury 300 MHz spectrometer.

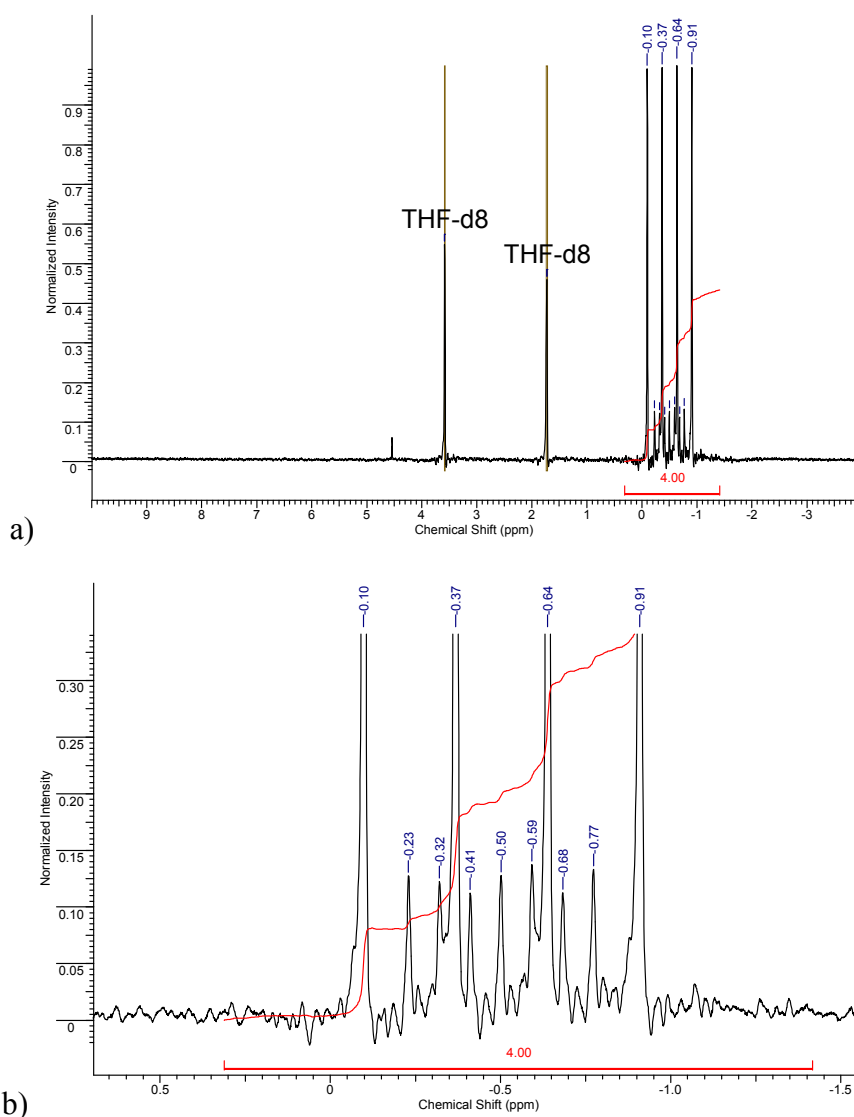


Figure 4.19 ^1H NMR spectra of LiBH_4 in d_8 -THF showing a) the full spectrum from 10 to -4 ppm with the solvent peaks labelled and b) zoomed in on the small septet.

The ^1H NMR spectrum of LiBH_4 (Figure 4.19a) contains peaks due to the solvent (THF) at 3.59 ppm and 1.74 ppm. There is a quartet centred around -0.50 ppm (± 0.05 ppm) due to ^1H - ^{11}B coupling (^{11}B , $I = 3/2$), the coupling constant, J , is 81 Hz. At the same chemical shift there is also a septet due to ^1H - ^{10}B coupling (^{10}B , $I = 3$) with $J = 27$ Hz, the intensity of the septet is much lower due to the lower abundance of ^{10}B (Abundances ^{11}B 80.4%, ^{10}B 19.6%). These chemical shift and coupling values are in agreement with previously published values of -0.48 ppm and $J(^{11}\text{B}\text{-}^1\text{H}) = 81.1$ Hz.^[180]

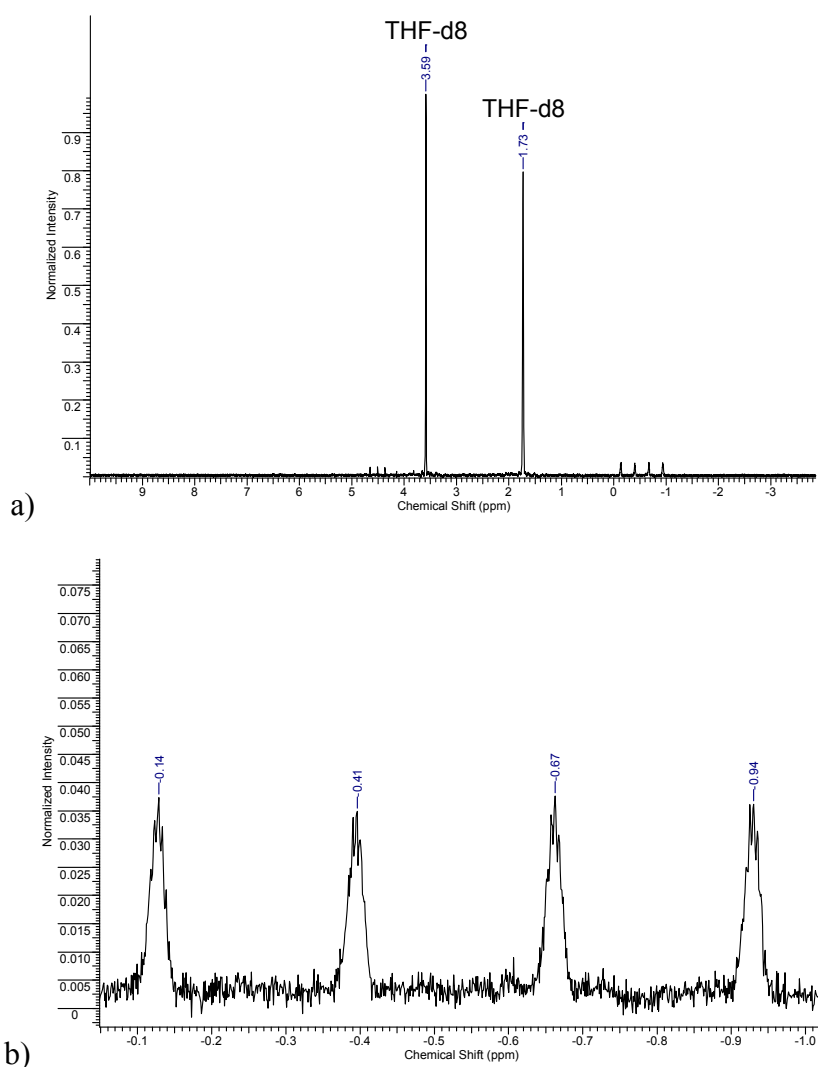


Figure 4.20 ^1H NMR spectra of $^7\text{Li}^{11}\text{BD}_4$ in $\text{d}_8\text{-THF}$ showing a) the full spectrum from 10 to -4 ppm with the solvent peaks labelled and b) zoomed in on the small quartet.

The ^1H NMR spectrum of $^7\text{Li}^{11}\text{BD}_4$ (Figure 4.20) also contains peaks due to the solvent (THF) at 3.59 ppm and 1.74 ppm. There is a very small quartet centred around -0.54 ppm (± 0.05 ppm) with a coupling constant of 81 Hz. This is the same chemical shift and coupling constant as in the ^1H - ^{11}B quartet in the LiBH_4 spectrum suggesting that this quartet is also due to ^1H - ^{11}B coupling. H-D exchange is known to occur within LiBH_4 dissolved in THF ^[180]. The origin of this very small number of protons could be the d_8 -THF (99.5% D) solvent or from the deuterium gas used during the synthesis (99.8% D).

4.6.2 Solid state ^{11}B NMR

Solid state ^{11}B NMR spectroscopy was carried out on a sample of LiBH_4 at room temperature by NMR staff within the Chemistry Department at the University of Oxford. A Varian/Chemagnetics Infinity spectrometer was used, fitted with a 7.5 mm double resonance probe.

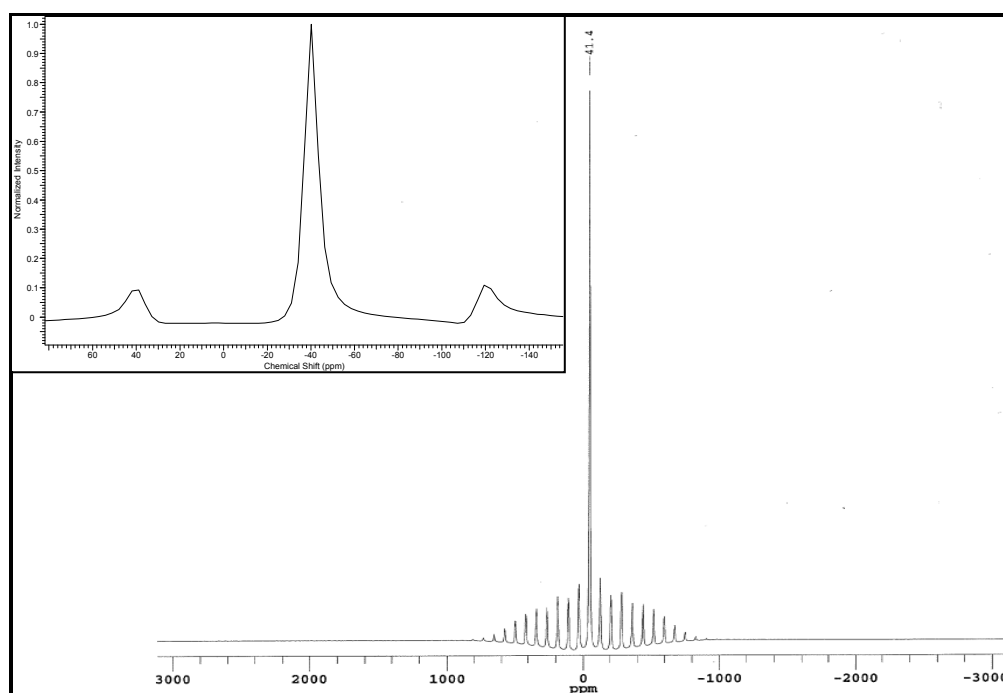


Figure 4.21 The room temperature solid state ^{11}B NMR spectrum of LiBH_4 , the inset shows an expansion of the spectrum around the principal peak.

The room temperature solid state ^{11}B NMR spectrum of LiBH_4 has a single peak (with spinning side bands) with a chemical shift of -41.4 ppm ($\pm 0.2 \text{ ppm}$) indicating a single boron environment within the structure. This is consistent with previously reported values of -41.0 ppm ($\pm 0.5 \text{ ppm}$)^[181] and -41.5 ppm ($\pm 0.1 \text{ ppm}$)^[182]. The ^{11}B NMR chemical shift of ammonia borane (NH_3BH_3) is -27 ppm ^[183].

Solid state ^{11}B NMR spectra were collected for a sample of $\text{Li}^{11}\text{BD}_4$ at room temperature 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 sample spinning rate was 14090 Hz.

The main peak in the solid state ^{11}B NMR spectrum of $\text{Li}^{11}\text{BD}_4$ is at -42.0 ppm ($\pm 0.2 \text{ ppm}$) which is very similar to the chemical shift of LiBH_4 suggesting very little change in the crystal structure due to isotopic substitution. The peak at 0 ppm ($\pm 0.2 \text{ ppm}$) is thought to be due to an impurity and was also observed by Hartman *et al.*^[52]

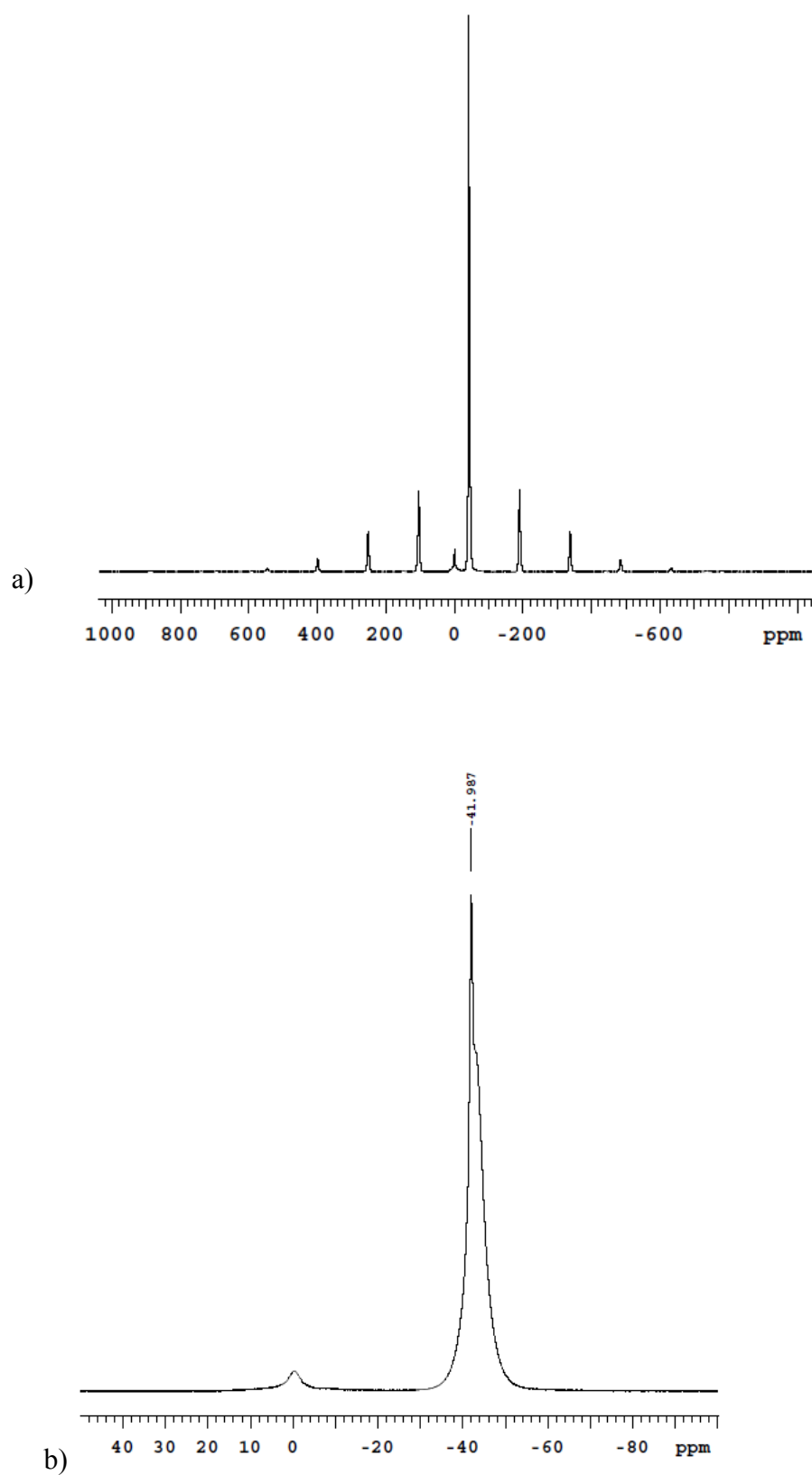


Figure 4.22 Solid state ^{11}B NMR spectrum of $\text{Li}^{11}\text{BD}_4$ showing a) the full spectrum and b) zoomed in onto the main peak

4.7 Thermogravimetric analysis

4.7.1 Thermogravimetric analysis with mass spectrometry

Thermogravimetric analysis was carried out using a Hiden Isochema Intelligent Gravimetric Analyser (IGA) connected to a mass spectrometer. A 70 mg sample of LiBH_4 was heated to $450\text{ }^\circ\text{C}$ at a rate of $2\text{ }^\circ\text{C}/\text{min}$ under 1 bar of flowing helium. A small proportion of the exhaust helium along with gas released from the sample was fed, via a capillary tube, to a mass spectrometer set to detect B_2H_6 ($m/z = 28$), BH_3 ($m/z = 14$) and H_2 ($m/z = 2$).

The mass spectrometer first detected hydrogen evolution at $115\text{ }^\circ\text{C}$, which is approximately the temperature of the phase change. Only a small amount of hydrogen was released and this is best shown by Figure 4.23, which shows the first derivative of the partial pressure of hydrogen evolved as a function of temperature. The first derivative contains a peak at $80\text{ }^\circ\text{C}$ and a trough at $150\text{ }^\circ\text{C}$ indicating a hydrogen evolution peak at $115\text{ }^\circ\text{C}$.

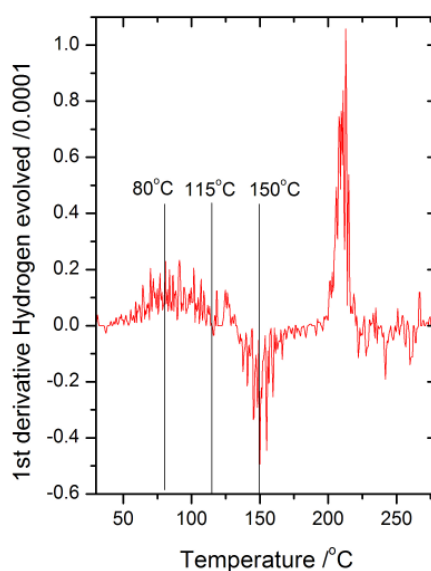


Figure 4.23 The 1st derivative of the partial pressure of hydrogen evolved between room temperature and $280\text{ }^\circ\text{C}$

Figure 4.24 shows the mass and temperature of the sample as a function of time. Figure 4.25 shows the sample mass loss and hydrogen evolution as a function of temperature. LiBH_4 was observed to lose 10.5 mg, 14 % of its mass which is equivalent to three moles of hydrogen atoms, or 1.5 molar equivalents of H_2 . This mass loss corresponds to a decomposition to lithium hydride and boron. Mass loss was first observed at 285 °C, 180 minutes into the experiment, when 0.5 mg mass was lost, this is a similar temperature to the melting point of LiBH_4 (170 °C^[19]). The rate of mass loss changed at 300 °C (188 minutes into the experiment) and coincided with the first significant hydrogen release. The hydrogen evolution peak was sharp and the sample mass decreased by approximately 0.5 mg at this time. Further hydrogen evolution gradually increasing in rate was observed from around 380 °C (233 minutes into the experiment). The area under this hydrogen evolution peak is approximately four times the area under the peak at 300 °C. A very small amount of B_2H_6 and BH_3 were detected by the mass spectrometer 287 minutes into the experiment which was just after the experiment reached 450 °C (Figure 4.26), by this time there was rapid mass loss and hydrogen evolution. The partial pressures of B_2H_6 and BH_3 were of the order of a thousand times less than the partial pressure of hydrogen and are likely to be the result of the rapid decomposition at this stage of the experiment.

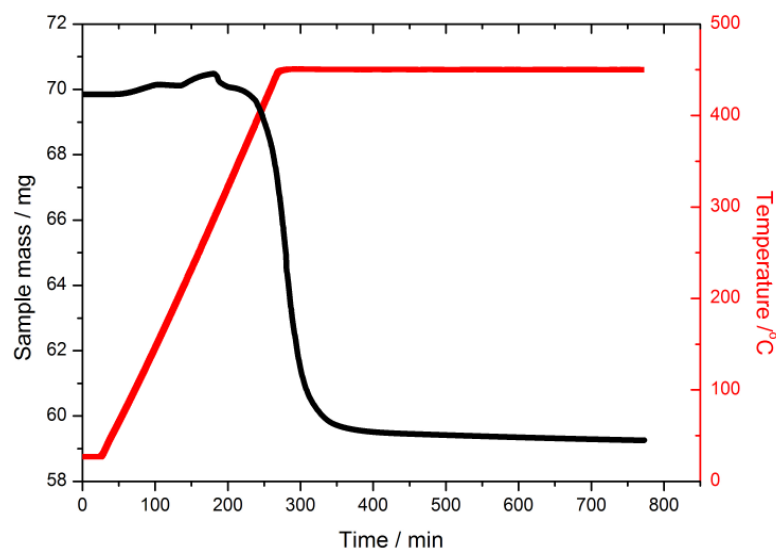


Figure 4.24 Graph showing sample mass (black, left vertical axis) and increasing sample temperature (red, right vertical axis) as a function of time for LiBH_4

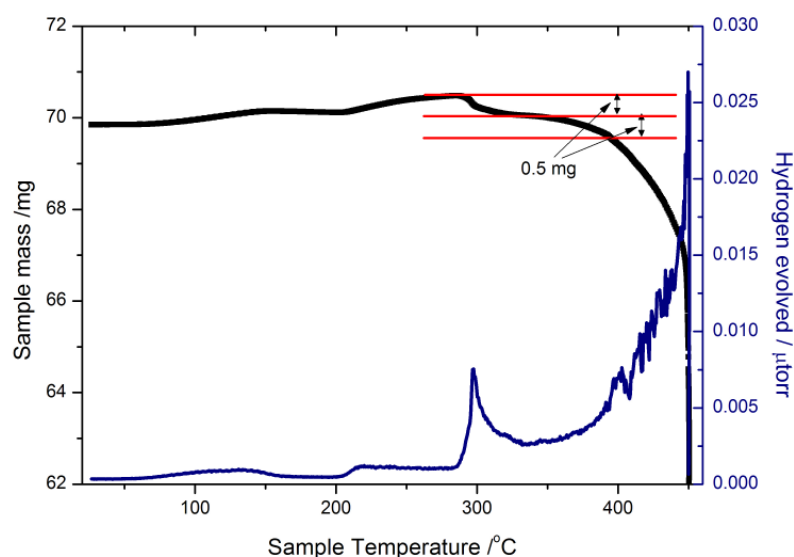


Figure 4.25 The sample mass loss (black, left vertical axis) and hydrogen evolution (blue, right vertical axis) as a function of temperature for LiBH_4 . The mass loss accompanying the hydrogen evolution at 300 °C is labelled.

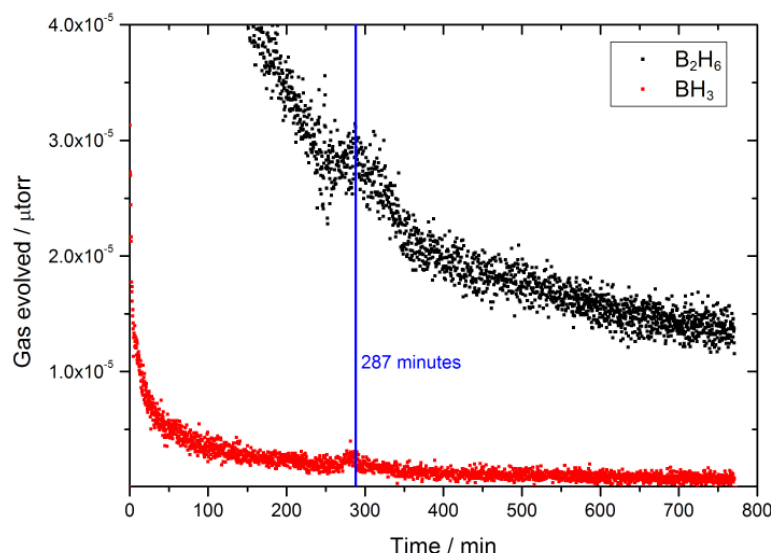


Figure 4.26 B_2H_6 (black) and BH_3 (red) evolved during the decomposition of $LiBH_4$

Figure 4.27 shows the first derivative of the difference between the temperature of the IGA furnace and the temperature of the sample itself. There are peaks at 122 °C and 298 °C. The peak at 122 °C is likely to relate to the endothermic phase change, although this would be expected slightly earlier at 108 °C^[55] and the hydrogen evolution suggests that in this experiment the phase change may have occurred at 115 °C. There may be a delay between the endothermic event and the effect on the sample temperature. The second endothermic event expected for $LiBH_4$ is melting which is expected around 270 °C^[19], the mass loss and hydrogen evolution suggest that melting may have occurred at 285 °C in this case, so again there is a delay between the endothermic event and the effect on the sample temperature.

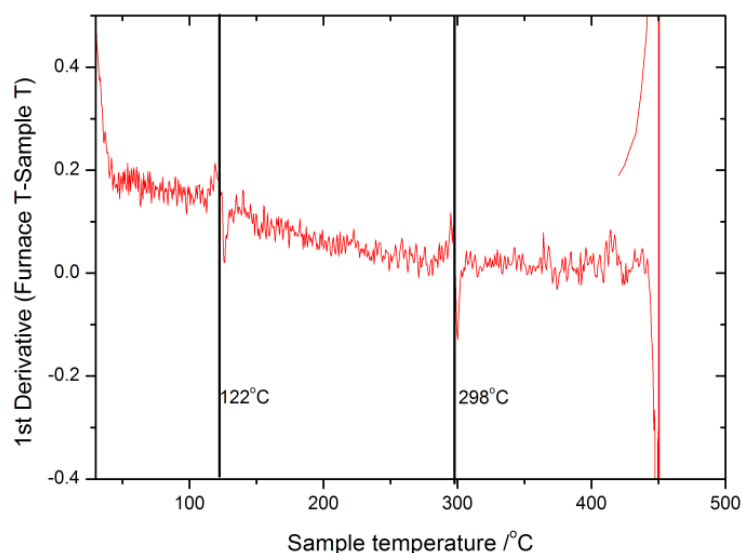


Figure 4.27 The 1st derivative of the difference between the furnace and sample temperature as a function of sample temperature

The pattern of mass loss and hydrogen evolution suggest that LiBH_4 melted at 285°C and decomposed in two stages at 300°C and 380°C . This hydrogen evolution pattern is in agreement with published literature where a slight hydrogen evolution is observed between 100°C and 200°C associated with the phase change and the main hydrogen loss occurs in two stages, one beginning at 320°C and the second at 400°C .^[37]

4.7.2 Thermogravimetric analysis under dynamic vacuum

Thermogravimetric analysis was carried out using a Hiden Isochema Intelligent Gravimetric Analyser. A 103 mg sample of LiBH_4 was heated to 400°C at a rate of $2^\circ\text{C}/\text{min}$ under dynamic vacuum (base pressure 10^{-6}mbar). The sample mass and temperature as a function of time are shown in Figure 4.28. The temperature was held constant at 30°C for the first 100 minutes in order to ensure that the sample mass was stable.

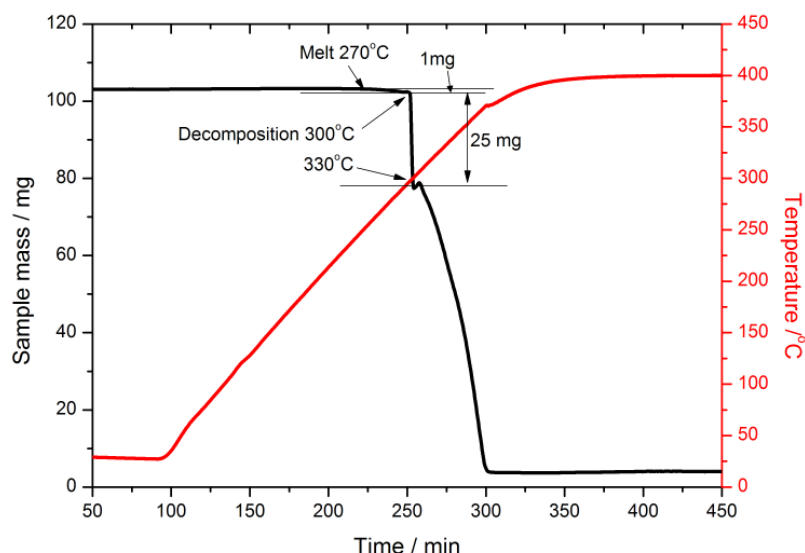


Figure 4.28 Sample mass and temperature for a sample of LiBH₄ under dynamic vacuum

The sample mass remains constant until 235 minutes into the experiment at 270 °C where the sample loses 1 mg over 15 minutes, corresponding to the sample melting. Significant mass loss begins 250 minutes into the experiment at 300 °C when the sample suddenly loses 25 mg mass and corresponds to the first stage of decomposition. At 330 °C, 273 minutes into the experiment, the rate of mass loss decreased as the second phase of decomposition occurred. The final sample mass was only 2 mg, this is a greater mass loss than is possible by decomposition of LiBH₄ by any combination of loss of H₂ and B₂H₆ (Equation 4.1 to Equation 4.3). This suggests that the majority of the decomposed sample also boiled-off under vacuum. Lithium melts at 180 °C, and so would be expected to be liquid at the experiment temperature, LiH does not normally melt until 689°C but may also be affected by the vacuum.^[77]



4.8 Conclusions

$^7\text{Li}^{11}\text{BD}_4$ and $\text{Li}^{11}\text{BD}_4$ were synthesised directly from the elements and the samples were not found to have any impurities.

Neutron diffraction data of $^7\text{Li}^{11}\text{BD}_4$ were collected at $-223\text{ }^\circ\text{C}$. The crystal structure of $^7\text{Li}^{11}\text{BD}_4$ was found to be consistent with the structure originally proposed by Soulié *et al.*^[51] The space group is *Pnma* and the lattice parameters were found to be $a = 7.11395(14)\text{ \AA}$, $b = 4.40666(8)\text{ \AA}$, $c = 6.67133(12)\text{ \AA}$ and $V = 209.138(6)\text{ \AA}^3$. At $-223\text{ }^\circ\text{C}$ it was possible to refine anisotropic atomic displacement parameters which were small, the largest parameter being $0.0461(17)\text{ \AA}^2$. The borohydride units were found to be nearly perfectly tetrahedral in shape with B-D bond lengths between $1.2140(9)\text{ \AA}$ and $1.225(2)\text{ \AA}$ and D-B-D bond angles between $107.02(10)^\circ$ and $111.25(9)^\circ$.

X-ray and neutron diffraction data were collected at room temperature for both $^7\text{Li}^{11}\text{BD}_4$ and $\text{Li}^{11}\text{BD}_4$. The crystal lattice has expanded compared to the structure at $-223\text{ }^\circ\text{C}$. The neutron diffraction study of $^7\text{Li}^{11}\text{BD}_4$ showed the lattice parameters to be $a = 7.1478(7)\text{ \AA}$, $b = 4.4246(3)\text{ \AA}$, $c = 6.7842(5)\text{ \AA}$ and $V = 214.56(3)\text{ \AA}^3$. The crystal structure showed the borohydride units to be more distorted away from an ideal tetrahedral shape than they were at $-223\text{ }^\circ\text{C}$. The range of B-D bond lengths was greatest ($1.11(4)\text{ \AA}$ to $1.20(4)\text{ \AA}$) when determined from the X-ray diffraction study and smallest when determined from the neutron diffraction study of $^7\text{Li}^{11}\text{BD}_4$ ($1.178(4)\text{ \AA}$ to $1.216(8)\text{ \AA}$). The range of D-B-D bond angles was observed to be approximately 103° to 115° in all of the studies. In addition to the unconstrained models, it was also possible to refine a constrained structure with rigid body tetrahedral borohydride units to the synchrotron X-ray diffraction data. The quality of fit was nearly identical to that of the unconstrained model. A constrained structure

could not be fitted to the neutron diffraction data, the fit was particularly bad for large time-of-flights.

Variable temperature diffraction studies were made using both X-ray and neutron radiation. Orthorhombic $\text{Li}^{11}\text{BD}_4$ shows anisotropic thermal expansion behaviour. The a and c lattice parameters increase with increasing temperature but the b lattice parameter initially remains constant before beginning to decrease above 80 °C.

The variable temperature neutron diffraction study of $\text{Li}^{11}\text{BD}_4$ had the smallest increments in temperature. This study shows the orthorhombic to hexagonal phase change to occur at 116 °C which is higher than the previously reported temperature of 108 °C.^[55] This may be an effect of the isotopic substitution within the sample. At the phase change there is a decrease in the volume per formula unit. According to the neutron diffraction data this is from 55.05(2) Å³ at 112 °C to 54.52(7) Å³ at 118 °C. This decrease in volume results in an increase in the density of the structure making the structure more stable.

Above the phase change $\text{Li}^{11}\text{BD}_4$ is observed to have a hexagonal structure with a $P6_3mc$ space group consistent with that reported by Soulié *et al*^[51]. The lattice parameters increase approximately linearly with increasing temperature. Large anisotropic atomic displacement parameters were determined for the $\text{Li}^{11}\text{BD}_4$ structure at 150 °C. The parameters relating to the deuterium atoms were particularly large due to the disorder caused by the flexing and rotation of the borohydride ions. This disorder makes the shape of the borohydride ions appear much more distorted away from the ideal tetrahedral shape with B-D bond lengths varying from 0.73(8) Å to 1.227(18) Å and D-B-D bond angles varying from 89.966(4)° to 114(3)°.

PDF analysis of the $^7\text{Li}^{11}\text{BD}_4$ neutron diffraction data shows broad peaks at large separations even in the room temperature data indicating that some disorder is already

present at room temperature. At 200 °C the PDF plots do not contain any sharp peaks at separations greater than 3 Å showing a high level of disorder within the hexagonal structure with a complete lack of long range order. However, the plots of $G(r)$ for both room temperature and 200 °C do show a sharp peak at 1.21 Å corresponding to the B-D bond length and a peak at 1.95 Å corresponding to the D...D separation. This shows that all of the short range B-D bond lengths and D...D distances within the structure are equivalent meaning that the borohydride ions must have ideal tetrahedral geometry. The crystal structure from the same room temperature neutron diffraction data showed distorted tetrahedra because it is modelling the orientation of the borohydride ions as well as their geometry averaged across the structure. The borohydride ions have orientational disorder causing them to appear distorted in the crystal structures.

Thermogravimetric analysis carried out under flowing helium gas, showed LiBH_4 to lose mass equivalent to 3 moles of hydrogen during heating to 450 °C. A small amount of hydrogen evolution was detected at 115 °C which is around the temperature where the phase change would be expected. A small mass loss associated with melting was observed at 285 °C. Further hydrogen evolution associated with decomposition was observed in two stages, the first at 300 °C with the main hydrogen evolution occurring with increasing rate from 380 °C. A very small amount of BH_3 and B_2H_6 were detected at 450 °C when the rate of hydrogen evolution was very high. Significant decomposition of B_2H_6 begins at approximately 150 °C^[129] so it is possible that more B_2H_6 is released than is observed due to its rapid decomposition at 450 °C.

Thermogravimetric analysis under dynamic vacuum showed the sample to melt at 270 °C and decompose in two stages beginning at 300 °C and 330 °C. Nearly the

entire mass of the sample was lost indicating that liquid sample evaporated under vacuum.

The room temperature Raman spectrum of LiBH_4 shows B-H stretching and bending frequencies consistent with the expected symmetry of the borohydride ion. The B-D vibration frequencies in the Raman spectrum of $\text{Li}^{11}\text{BD}_4$ are shifted by a factor of approximately $\sqrt{2}$ compared to LiBH_4 due to the increased mass of deuterium compared to hydrogen.

The ^1H NMR spectrum of LiBH_4 shows both ^1H - ^{11}B and ^1H - ^{10}B coupling whilst the spectrum of $^7\text{Li}^{11}\text{BD}_4$ shows hardly any protons related to the sample. Protons which are present may be a result of hydrogen-deuterium substitution with the solvent. The solid state ^{11}B NMR spectra of LiBH_4 and $\text{Li}^{11}\text{BD}_4$ are very similar and are consistent with previously reported data.

In conclusion, the phase change, melting and decomposition of LiBH_4 and $\text{Li}^{11}\text{BD}_4$ have been observed. Substituting hydrogen for deuterium significantly affects the B-H bond vibrations and consequently is likely to affect the reactivity of LiBH_4 and may also affect the temperatures of thermal events. At low temperatures, the borohydride units can be observed to be nearly ideally tetrahedral. By room temperature there is evidence of disorder within the structure and the disorder becomes significant at higher temperatures. This disorder includes orientational disorder of the borohydride ions making it difficult to determine the exact geometry of the borohydride ion from the crystal structure alone; however PDF analysis indicates that all of the B-H bond lengths are equivalent.

5 Sodium borohydride

5.1 Chapter focus

The focus of this chapter is a detailed variable temperature neutron diffraction study of $\text{Na}^{11}\text{BD}_4$ with *in-situ* thermogravimetric analysis under dynamic vacuum. A thermogravimetric analysis of NaBH_4 with mass spectrometry under 1 bar flowing helium was also completed.

Unless stated otherwise, NaBH_4 was used as received from Sigma Aldrich.

5.2 Room temperature structure

$\text{Na}^{11}\text{BD}_4$ was synthesised from its elements using a high pressure furnace as previously discussed (See Chapter 3).

Neutron diffraction data were collected on the GEM beamline at ISIS at room temperature in a 8 mm vanadium can for two hours (312 μA). The diffraction data were analysed and structural models refined using the Rietveld method within the profile refinement program TOPAS-Academic^[167] starting from the structure proposed by Soldate.^[66] A representation of a typical fit to the data is shown in Figure 5.1.

$\text{Na}^{11}\text{BD}_4$ was identified as having the cubic high temperature structure. Originally, the structure was refined using the space group $F-43m$ with the deuterium atoms disordered over two sites and the total occupancy of the deuterium sites was set to unity. The resulting R_{wp} value was 3.77 %. The occupancies and isotropic thermal displacement parameters of the two deuterium sites were very similar, (occupancies, 0.42(5) and 0.58(5); isotropic thermal displacement parameters, 6.8(13) $\text{\AA}^2$ and

7.0(8) Å²). The B-D bond lengths were also similar at 1.17(2) Å and 1.18(3) Å. The similarities between the two sites indicate that as far as can be determined from powder diffraction data, the deuterium sites are equivalent and the structure should be refined within the space group *Fm-3m*. Details of the structure in the space group *Fm-3m* are given in Table 5.1. The B-D bond length refined to 1.176(2) Å. This bond length is slightly smaller than those observed in Li¹¹BD₄ (1.195(5) Å to 1.203(10) Å, see Chapter 4) and similar to those observed by Fischer *et al.* (1.178(2) Å)^[72].

Some small peaks relating to a largely amorphous phase were identified in the diffraction pattern, and are labelled X in Figure 5.1. This phase is likely to be a Na-B phase, analogous to the K-B phase discussed in Chapter 6. A small amount of NaD impurity was also present in the sample.

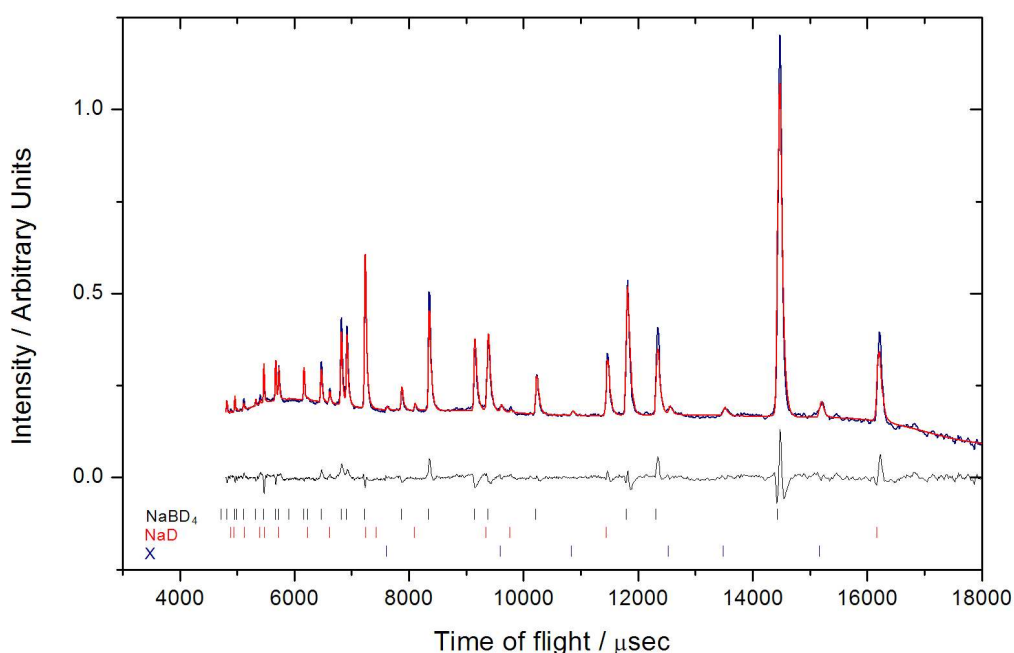


Figure 5.1 A representation of a typical refinement, showing the observed (blue), calculated (red) and difference ($Y_{obs}-Y_{calc}$, grey) plots for room temperature (20 °C) neutron diffraction data of Na¹¹BD₄. The positions of the Bragg peaks for Na¹¹BD₄ (black), NaD (red) and the amorphous phase, X, (blue) are shown.

Table 5.1 Details of the room temperature (20 °C) structure of Na¹¹BD₄

<i>Fm-3m</i> , <i>a</i> = 6.1539(3) Å, <i>V</i> = 233.05(3) Å ³					
Atom	x/a	y/b	z/c	occ	B _{eq} / Å ²
Na	0	0	0	1	4.32(11)
¹¹ B	0.5	0.5	0.5	1	2.58(10)
D	-0.1103(2)	-0.3897(2)	0.1103(2)	0.5	7.16(10)
<i>R</i> _{wp} = 3.84 %, <i>R</i> _{exp} = 0.92 %, χ^2 = 17.4, B-D bond length 1.176(2) Å					

5.3 Variable temperature neutron diffraction with thermogravimetric analysis

Neutron diffraction data were collected using the GEM diffractometer at ISIS whilst heating a sample of Na¹¹BD₄ within the IGAⁿ (Hiden Isochema Intelligent Gravimetric Analyser with neutrons, see Chapter 2). This allows the mass of the sample to be recorded and the pressure of the sample environment to be controlled whilst neutron diffraction data are also being collected. The 572 mg sample was heated to 450 °C at a rate of 3 °C/min under dynamic vacuum (base pressure 10⁻⁶ mbar). The sample was then cooled to 400 °C and held at this temperature before cooling to 110 °C. Neutron diffraction data were collected continuously with data being collected for three minutes for each pattern.

Figure 5.2 shows a representation of how a surface plot of the neutron diffraction patterns as a function of time would appear if viewed from above, alongside the sample temperature and mass, also as a function of time. The coloured lines show the time-of-flight positions of diffraction peaks as a function of time. The width of the lines shows the width of the peaks and the intensities of the colours indicate the relative intensities of the peaks. Neutron diffraction patterns recorded for samples within the IGAⁿ show diffraction peaks from the IGAⁿ itself in the form of iron,

throughout the experiment. At room temperature, peaks for NaD and $\text{Na}^{11}\text{BD}_4$ were present; the starting composition of the sample was 12 wt% NaD and 88 wt% $\text{Na}^{11}\text{BD}_4$. The peaks relating to NaD disappeared at 350 °C. Sample mass loss also began at 350 °C and continued over the course of the experiment at a relatively even rate, until the sample was cooled to 400 °C, suggesting that mass loss would have continued if the sample had been heated for a longer time. A total of 44 wt% of the sample mass was lost during the experiment. Once the sample had reached 450 °C, the Bragg peaks for $\text{Na}^{11}\text{BD}_4$ noticeably began to weaken and became very faint after 90 minutes at 450 °C. No Bragg peaks returned when the sample was cooled to 110 °C. The possible decomposition routes of $\text{Na}^{11}\text{BD}_4$ and the respective mass losses are shown in Table 5.2. The observed mass loss is greater than would be expected from any of these routes, particularly when the NaD present in the sample, which will only lose 8 wt% mass decomposing to sodium is taken into account. It is therefore likely that the entire sample melted and was evaporating as a result of the dynamic vacuum. It is not possible to tell if NaD was formed as a decomposition production from the neutron diffraction pattern because the existing NaD peaks disappeared before the $\text{Na}^{11}\text{BD}_4$ peaks began to weaken. NaH melts and decomposes at 425 °C.^[77] If the Bragg peaks relating to NaD disappeared due to the decomposition rather than melting of NaD, then it is unlikely that NaD would form as a decomposition product of $\text{Na}^{11}\text{BD}_4$, any NaD that did form would immediately decompose.

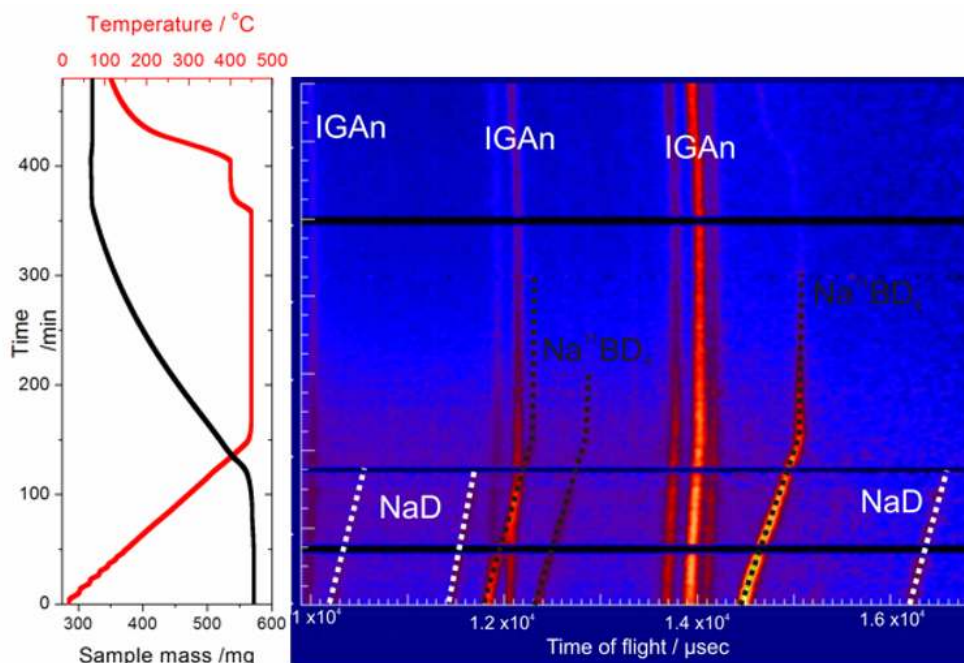


Figure 5.2 A surface plot of the neutron diffraction patterns for $\text{Na}^{11}\text{BD}_4$ as a function of time, the intensities of the diffraction peaks are shown by the intensities of the colours. Bragg peaks relating to $\text{Na}^{11}\text{BD}_4$ and NaD are indicated. The black areas are when there was no neutron radiation available. The sample temperature and mass are also shown.

Table 5.2 Possible decomposition routes and their respective mass losses for $\text{Na}^{11}\text{BD}_4$

Decomposition route	Mass loss / wt%
$\text{Na}^{11}\text{BD}_4 (\text{s}) \rightarrow \text{NaD} (\text{s}) + {}^{11}\text{B} (\text{s}) + 1.5\text{D}_2 (\text{g})$	14.3
$2\text{Na}^{11}\text{BD}_4 (\text{s}) \rightarrow 2\text{NaD} (\text{s}) + {}^{11}\text{B}_2\text{D}_6 (\text{g})$	40.5
$\text{Na}^{11}\text{BD}_4 (\text{s}) \rightarrow \text{Na} (\text{s}) + {}^{11}\text{B} (\text{s}) + 2\text{D}_2 (\text{g})$	19.0

Compounds shown as solids may have melted during the experiment

The lattice parameter of $\text{Na}^{11}\text{BD}_4$ is shown as a function of temperature in Figure 5.3. As the temperature increased, the unit cell parameter of $\text{Na}^{11}\text{BD}_4$ expanded in a linear fashion at a rate of $5.96(4) \times 10^{-4} \text{ \AA}^\circ\text{C}^{-1}$. No phase changes were expected or observed within this temperature range. The details of the structure at 300°C are shown in Table 5.3.

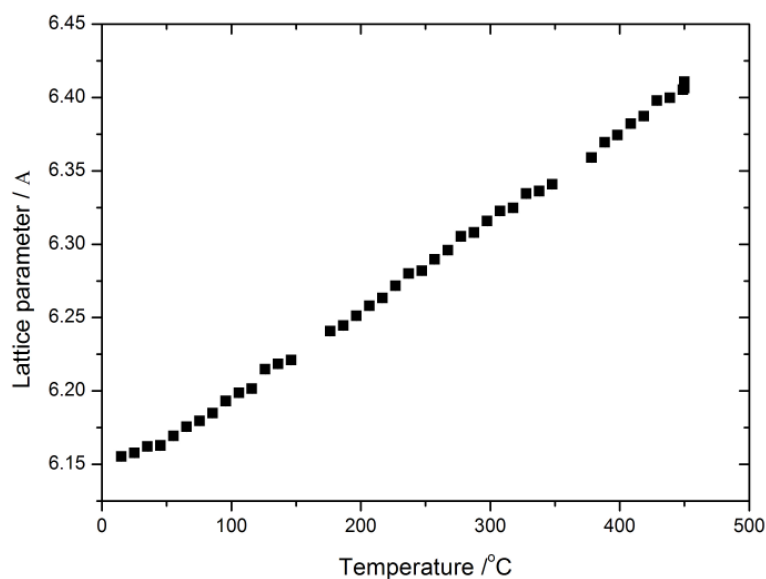


Figure 5.3 The a lattice parameter of $\text{Na}^{11}\text{BD}_4$ as a function of temperature. The uncertainties in the lattice parameters are smaller than the data points.

Table 5.3 Details of the structure of $\text{Na}^{11}\text{BD}_4$ at 300 °C

$Fm-3m$, $a = 6.3174(19) \text{ \AA}$, $V = 252.1(2) \text{ \AA}^3$					
Atom	x/a	y/b	z/c	occ	$B_{\text{eq}} / \text{\AA}^2$
Na	0	0	0	1	2.6(16)
^{11}B	0.5	0.5	0.5	1	1.6(15)
D	-0.112(3)	-0.388(3)	0.112(3)	0.5	7.5(14)
$R_{\text{wp}} = 5.62 \%$, $R_{\text{exp}} = 5.10 \%$, $\chi^2 = 1.2$, B-D bond length $1.23(3) \text{ \AA}$					

5.4 Raman spectroscopy

Raman spectroscopy was performed at room temperature using a Dilor Labram 300 spectrometer with the sample contained in a sealed glass capillary. Raman spectra were collected for NaBH_4 and $\text{Na}^{11}\text{BD}_4$.

In either the $F4-3m$ or $Fm-3m$ structure of NaBH_4 (and $\text{Na}^{11}\text{BD}_4$) the borohydride ions have tetrahedral symmetry. Consequently the symmetry of the internal vibrational modes ν_1 , ν_2 , ν_3 and ν_4 are A , E , T_2 and T_2 respectively (see Chapter 2).

Figure 5.4 shows the room temperature Raman spectra of NaBH_4 and $\text{Na}^{11}\text{BD}_4$. Table 5.4 shows the frequencies of the Raman active vibrations, their assignments based on the work of Renaudin *et al.*^[86] and the ratio $\nu_{\text{B-H}} / \nu_{\text{B-D}}$.

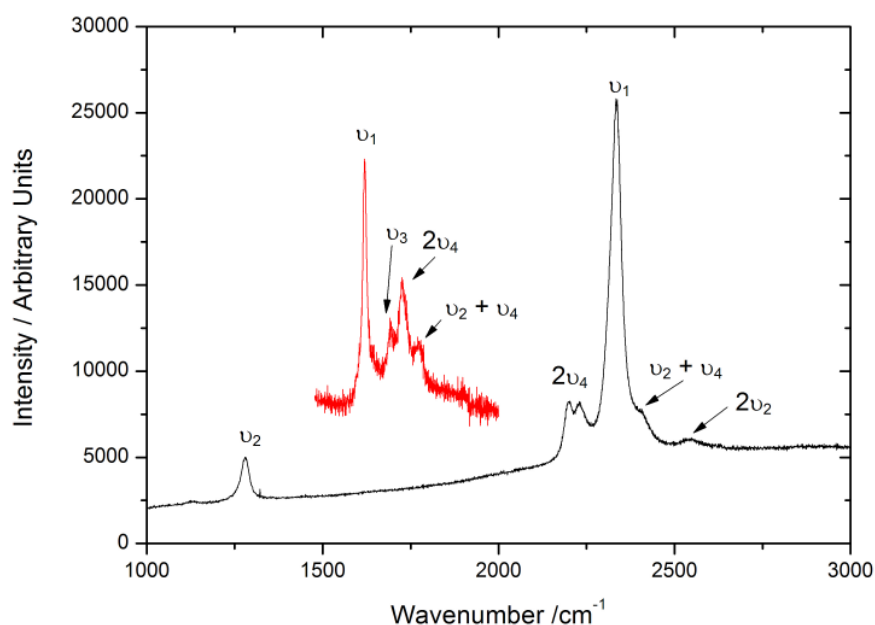


Figure 5.4 The room temperature Raman Spectra of NaBH_4 and $\text{Na}^{11}\text{BD}_4$

Table 5.4 Raman frequencies / cm^{-1} for NaBH_4 and $\text{Na}^{11}\text{BD}_4$, their assignments and the ratio $\text{NaBH}_4 / \text{Na}^{11}\text{BD}_4$

Assignment [86]	$\text{NaBH}_4 / \text{cm}^{-1}$	$\text{Na}^{11}\text{BD}_4 / \text{cm}^{-1}$	$\nu_{\text{B-H}} / \nu_{\text{B-D}}$	$\nu_{\text{B-H}} / \nu_{\text{B-D}}$ Renaudin <i>et al.</i> [86]
ν_2	1280	$(\nu_2 + \nu_4) - (\nu_4) =$ $1779 - 863 = 916$	1.40	1.40
$2 \nu_4$	2200, 2230 (average 2215), $\nu_4 = 2215 / 2 = 1108$	$1725 (\nu_4 = 1725/2$ $= 863)$	1.28	1.28
ν_1	2336	1618	1.44	1.45
ν_3		1694		1.38
$\nu_2 + \nu_4$	2410	1779	1.35	1.37
$2 \nu_2$	2544			

The Raman spectrum of NaBH_4 contains the ν_1 symmetric B-H stretching vibration (the largest peak) at 2336 cm^{-1} and the ν_2 symmetric B-H bending vibration at 1280 cm^{-1} . The ν_3 asymmetric B-H stretch was not observed, the ν_4 asymmetric B-H bending frequency can be estimated to be around 1108 cm^{-1} by taking half the average frequency of the overtones.

As previously discussed (see Chapter 2), the vibration frequencies of $\text{Na}^{11}\text{BD}_4$ are expected to be lower than those of NaBH_4 . The ν_1 symmetric B-D stretch in $\text{Na}^{11}\text{BD}_4$ is observed at 1618 cm^{-1} , the ν_2 asymmetric B-D stretch can be estimated to be at 916 cm^{-1} from the overtones, the ν_3 symmetric B-D bend was at 1694 cm^{-1} and the ν_4 asymmetric B-D bend is estimated to be at 863 cm^{-1} from the overtones. The $\nu_{\text{B-H}} / \nu_{\text{B-D}}$ ratios for ν_1 and ν_2 are close to $\sqrt{2} = 1.41$ suggesting that only the hydrogen / deuterium atom is moving significantly in the bond vibration. The ratio is higher for ν_1 suggesting that the vibration may have resonances with external lattice vibrations. For ν_4 , the $\nu_{\text{B-H}} / \nu_{\text{B-D}}$ ratio is lower, this is due to resonances between the ν_3 and ν_4

vibrations. These resonances mean that there is not a simple relationship between $\nu_{\text{B-H}}$ and $\nu_{\text{B-D}}$, for the ν_3 and ν_4 vibrations, however the ratio $\nu_3^{\text{D}}\nu_4^{\text{D}} / \nu_3^{\text{H}}\nu_4^{\text{H}}$ is expected to be 0.563 (see Chapter 2). The vibration frequencies for ν_3 were not identified in NaBH_4 , however the ratios observed in this work are similar to those reported by Renaudin *et al.*^[86] where a value close to 0.563 was obtained.

5.5 Solid state ^{11}B NMR

A room temperature solid state ^{11}B NMR spectrum of NaBH_4 was obtained by the Durham 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 sample spinning rate was 14120 Hz. Figure 5.5 shows the spectrum which was collected.

The chemical shift of boron in NaBH_4 is -43.3 ppm (± 0.2 ppm). This is a smaller chemical shift than has previously been observed, (-42.0 ppm (solid state) Ravnsbæk *et al.*^[135], -41.2 ppm (aqueous solution) Bremer *et al.*^[123], -41.6 ppm (alkaline aqueous solution) Guella *et al.*^[184]).

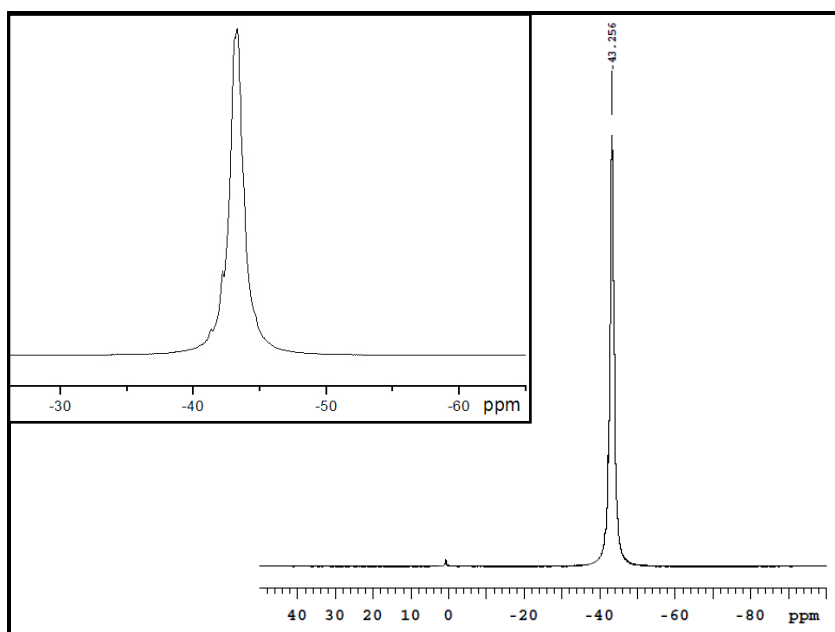


Figure 5.5 The room temperature solid state ^{11}B NMR spectrum of NaBH_4 , the inset shows an expansion of the spectrum around the principal peak, the possible shoulder towards larger chemical shift is likely due to a slight LiBH_4 impurity.

The ^{11}B chemical shift of NaBH_4 is smaller than that of LiBH_4 (-41.4 ppm (± 0.2 ppm), see Chapter 4). There are two possible explanations for this observation. The smaller chemical shift may be an effect of the increased shielding provided by the electron density donated by six sodium atoms around the boron atoms in NaBH_4 compared to four lithium ions in LiBH_4 . Alternatively, the increased number of cations in NaBH_4 may be attracting the electron density from the hydrogen atoms of the borohydride ion. This would weaken the B-H bonds causing the boron electrons in the B-H bonds to return closer to the boron atom, thus improving the shielding of the boron atom from the magnetic field.

There is only one signal in the spectrum indicating that only one boron environment is present within the sample. The absence of sidebands compared to the spectrum of LiBH_4 suggests that the boron environment has a high degree of symmetry, higher than in LiBH_4 .

5.6 Thermogravimetric analysis with mass spectrometry

Thermogravimetric analysis was carried out using a Hiden Isochema Intelligent Gravimetric Analyser (IGA) connected to a mass spectrometer (see Chapter 2). A 60 mg sample of NaBH_4 was heated to $500\text{ }^\circ\text{C}$ at a rate of $2\text{ }^\circ\text{C}/\text{min}$ under 1 bar of flowing helium. A small proportion of the exhaust helium along with gas released from the sample was fed, via a capillary tube, to a mass spectrometer set to detect B_2H_6 ($m/z = 28$), BH_3 ($m/z = 14$) and H_2 ($m/z = 2$). Figure 5.6 shows the sample mass and temperature and the partial pressure of hydrogen detected by the mass spectrometer as a function of time.

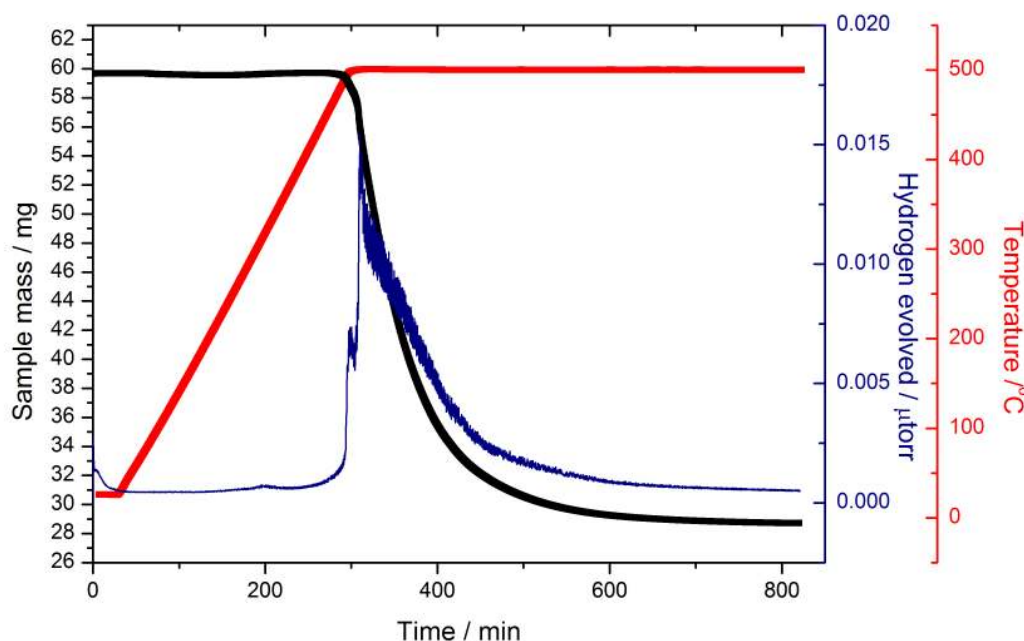


Figure 5.6 Mass (black) and temperature (red) of NaBH_4 and hydrogen evolved (blue) as a function of time

The sample mass remained constant whilst heating to $500\text{ }^\circ\text{C}$. At $500\text{ }^\circ\text{C}$ the sample lost 31 mg (52 wt%) over 520 minutes. The start of mass loss coincided with hydrogen first being detected by the mass spectrometer. There was a small hydrogen peak 300 minutes into the experiment just as the sample reached $500\text{ }^\circ\text{C}$. The majority

of the hydrogen loss began 310 minutes into the experiment and continued throughout mass loss which was 99 % complete after 250 minutes (550 minutes into the experiment). A small amount of B_2H_6 is also detected by the mass spectrometer peaking at 310 minutes, 500 °C (Figure 5.7). No BH_3 was detected. The partial pressure of hydrogen at the peak of hydrogen evolution is 500 times higher than that of B_2H_6 .

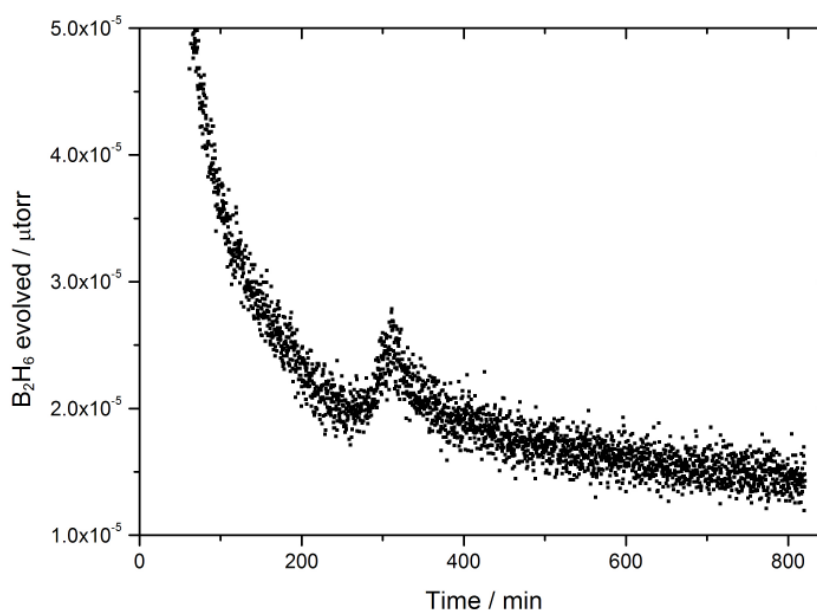


Figure 5.7. B_2H_6 evolution from $NaBH_4$ as a function of time

There is also a very slight hydrogen evolution around 320 °C (200 minutes into the experiment) accompanied by a temporary loss in mass beginning at 100 °C (Figure 5.8). $NaBH_4$ is not expected to melt until 505 °C^[73] and there are no phase changes expected in this temperature range. This slight loss of hydrogen is likely to relate to an impurity or water within the sample or the equipment. In particular the sample is known to contain ~0.5 % magnesium carbonate as an anti-caking agent.^[63]

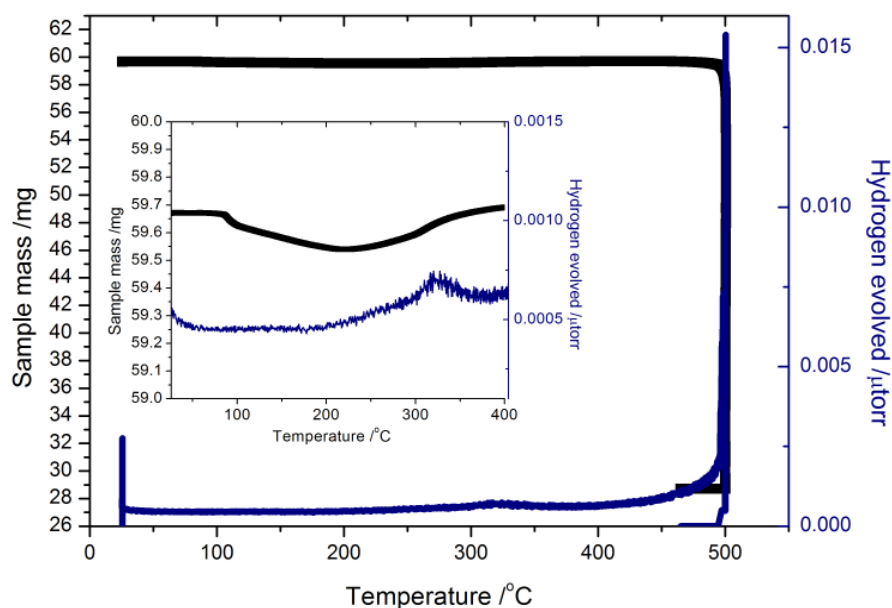


Figure 5.8 Mass loss and hydrogen evolution as a function of temperature for NaBH_4

Urgnani *et al.* observed a small amount of hydrogen to be released, peaking around 240 °C before the main hydrogen desorption which began at 440 °C.^[73] This behaviour is not dissimilar to that observed here.

Table 5.5 shows possible decomposition routes for NaBH_4 and their respective mass losses. The observed 52 wt% mass loss is larger than all of the expected mass losses. Sodium accounts for 60 wt% of the mass of the sample, so the mass loss is not consistent with losing all of the boron and hydrogen from the sample. This mass loss suggests that there is boil-off from the liquid sample although sodium does not boil until 883 °C^[77].

Table 5.5 Possible decomposition routes and their respective mass losses for NaBH_4

Decomposition route	Mass loss / wt%
$\text{NaBH}_4 (\text{s}) \rightarrow \text{NaH} (\text{s}) + \text{B} (\text{s}) + 1.5\text{H}_2 (\text{g})$	8.0
$2\text{NaBH}_4 (\text{s}) \rightarrow 2\text{NaH} (\text{s}) + \text{B}_2\text{H}_6 (\text{g})$	36.6
$\text{NaBH}_4 (\text{s}) \rightarrow \text{Na} (\text{s}) + \text{B} (\text{s}) + 2\text{H}_2 (\text{g})$	10.7

Compounds shown as solids may have melted during the experiment

Mass loss occurs at a higher temperature in this experiment than in the IGAⁿ during the neutron diffraction experiment because this experiment was run at ambient pressure instead of under dynamic vacuum in the neutron experiment. The 52 wt% mass loss observed here is also consistent with the continuing mass loss observed in the neutron experiment.

5.7 Conclusions

Na¹¹BD₄ was synthesised directly from the elements allowing a detailed variable temperature neutron diffraction study with *in situ* thermogravimetric analysis to be completed.

At room temperature, a structural model of Na¹¹BD₄ in the space group *F-43m* with the deuterium atoms disordered over two sites was originally refined to the neutron diffraction data. The occupancies, isotropic thermal parameters and B-D bond lengths to the two deuterium sites were very similar suggesting that the structure should have the space group *Fm-3m*. Within the space group *Fm-3m*, the lattice parameter was 6.1539(3) Å and the volume was 233.05(3) Å³. Due to the space group symmetry, the deuterium atoms are intrinsically disordered over two sites resulting in octahedral co-ordination of the deuterium atoms to the boron atoms. The B-D length was 1.176(2) Å.

In the variable temperature neutron diffraction study, Bragg peaks relating to Na¹¹BD₄ remained present up to 450 °C. At this temperature, the peaks began to weaken in intensity and disappeared after 90 minutes at 450 °C. The sample lost 44 wt% mass; the mass loss began at 350 °C when Bragg peaks relating to NaD disappeared from the diffraction patterns. No Bragg peaks returned when the sample was cooled to 110 °C. This mass loss (44 wt%), is more than is expected for the decomposition of Na¹¹BD₄

by any route suggesting that the sample melted and then began to evaporate under dynamic vacuum. Bragg peaks relating to NaD disappeared before those of $\text{Na}^{11}\text{BD}_4$ so it was not possible to determine if NaD is a decomposition product of $\text{Na}^{11}\text{BD}_4$.

Thermogravimetric analysis of NaBH_4 under 1 bar flowing helium showed the sample to begin losing mass at 500°C . The sample lost 52 wt% mass over 520 minutes. This mass loss coincided with the mass spectrometer detecting hydrogen. In addition to the hydrogen evolution, a small amount of B_2H_6 was detected at the beginning of decomposition. The evolution of B_2H_6 may be an effect of rapid decomposition. Again, mass loss was larger than would be expected due to decomposition, suggesting that there was some sample evaporation. A small amount of hydrogen was also released peaking at 320°C . Ugrnani *et al* also observed a small amount of hydrogen to be released from NaBH_4 well before decomposition but did not offer an explanation.^[73]

Raman spectra of NaBH_4 and $\text{Na}^{11}\text{BD}_4$ were consistent with ionic borohydrides and showed the effect of the increased mass of deuterium on the B-D bond vibration. No B-D bond vibrations were observed in $\text{Na}^{11}\text{BD}_4$ after the variable temperature neutron diffraction with thermogravimetric analysis experiment.

Solid state ^{11}B NMR spectroscopy showed that the boron environment in NaBH_4 is more shielded from the magnetic field than in LiBH_4 . This is the result of the borohydride ions being co-ordinated to six sodium ions instead of four lithium ions. More electron density may be being transferred to the borohydride ions by the increased number of cations, increasing the shielding of the boron atom. Alternatively, the hydrogen electron density is being attracted by the cations, weakening the B-H bonds causing the boron electron density to return closer to the boron nucleus, increasing the shielding. The boron environment in NaBH_4 also has

higher symmetry than in LiBH_4 which is consistent with the cubic space group with an octahedral arrangement of hydrogen atoms around the boron atom.

$\text{Na}^{11}\text{BD}_4$ was synthesised directly from the elements and found to decompose at $450\text{ }^\circ\text{C}$ under dynamic vacuum. NaBH_4 did not decompose until $500\text{ }^\circ\text{C}$ under flowing helium. A structural model of $\text{Na}^{11}\text{BD}_4$ was refined in the $Fm-3m$ space group and solid state ^{11}B NMR showed boron to be in a highly symmetrical environment within NaBH_4 .

6 Potassium borohydride

6.1 Chapter focus

The focus of this chapter is a detailed variable temperature neutron diffraction study of K^{11}BD_4 with *in situ* gravimetric analysis. Thermogravimetric analysis of KBH_4 with mass spectrometry was also completed. K^{11}BD_4 was synthesised directly from the elements as previously discussed in Chapter 3. KBH_4 was used as received from Sigma Aldrich.

6.2 Room temperature structure

K^{11}BD_4 was synthesised from its elements using a high pressure furnace as discussed in Chapter 3.

Room temperature neutron diffraction data were collected for 30 minutes (72.5 μA) from K^{11}BD_4 using the GEM diffractometer at ISIS in a 8mm vanadium can.

High-resolution room temperature X-ray diffraction data of KBH_4 were collected on the ID31 diffractometer, ESRF, Grenoble at a wavelength and step size of 0.79953 Å and 0.003°, respectively.

The diffraction data were analysed and structural models were refined independently for each study using the Rietveld method within the profile refinement program TOPAS-Academic^[167]. Refinements were started from the KBH_4 structure proposed by Luck and Schelter^[85] in the space group $Fm-3m$. Representations of typical fits to the data are shown in Figure 6.1 for the neutron diffraction study and Figure 6.2 for the synchrotron X-ray diffraction study.

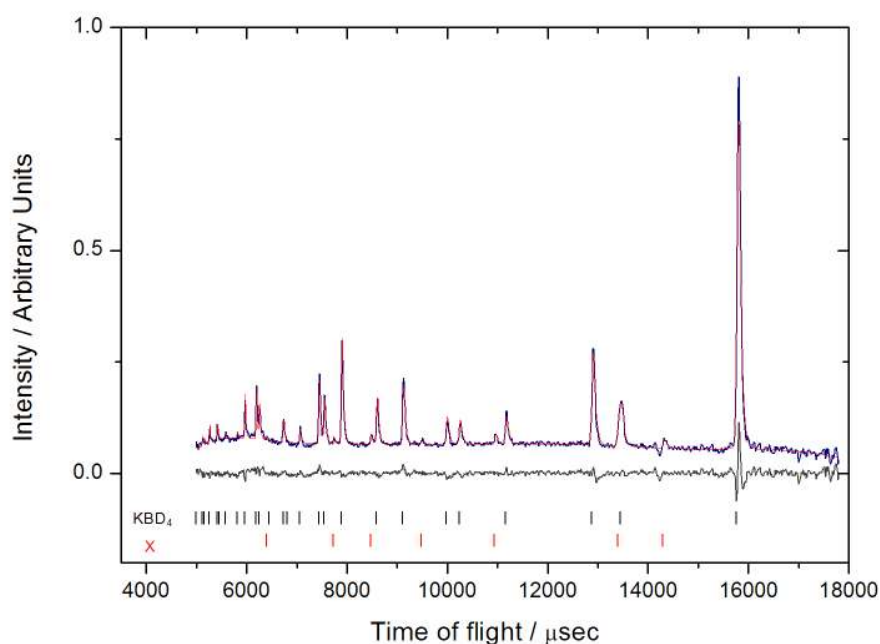


Figure 6.1 A representation of a typical refinement, showing the observed (blue), calculated (red) and difference ($Y_{obs}-Y_{calc}$, grey) plots for room temperature (20 °C) neutron diffraction data of $K^{11}BD_4$. The positions of the Bragg peaks for $K^{11}BD_4$ (black) and the minority impurity phase (red) are shown.

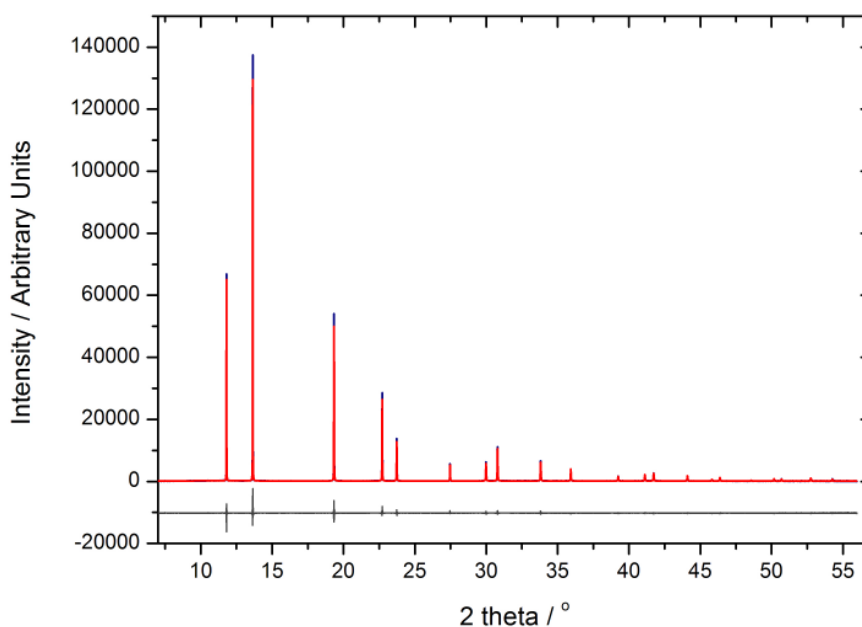


Figure 6.2 A representation of a typical refinement, showing the observed (blue), calculated (red) and difference ($Y_{obs}-Y_{calc}$, grey) plots for room temperature (20 °C) synchrotron X-ray diffraction data of $K^{11}BD_4$.

Details of the room temperature structure of K^{11}BD_4 determined from the neutron diffraction study are shown in Table 6.1 and details from the room temperature structure of KBH_4 determined from the synchrotron X-ray diffraction study are shown in Table 6.2. Both studies showed K^{11}BD_4 to have a cubic face centred structure in the space group $Fm-3m$. No impurities were observed in the KBH_4 X-ray diffraction sample. A minor impurity phase was observed in the K^{11}BD_4 sample, the positions of the Bragg peaks relating to this phase are labelled X in Figure 6.1. These peaks can be indexed to a tetragonal unit cell with parameters $a = 5.7(3) \text{ \AA}$ and $c = 4.0(3) \text{ \AA}$. These parameters are similar to those of KB_6 (cubic, $Pm-3m$, $a = 4.22185(10) \text{ \AA}$ ^[185]), suggesting that this minor impurity is a K-B phase. Crystalline KD was not observed to be present in the sample.

The synchrotron X-ray diffraction data shows that the unit cell of KBH_4 has a larger volume than K^{11}BD_4 , ($305.4142(17) \text{ \AA}^3$ and $302.58(4) \text{ \AA}^3$ for KBH_4 and K^{11}BD_4 respectively), this has previously been observed and is due to the larger vibration amplitudes (and zero point energies) for B-H bonds than B-D bonds.^[86] These volumes are similar to those reported by Renaudin *et al.* ($304.90(1) \text{ \AA}^3$ for KBH_4 and $301.77(1) \text{ \AA}^3$ for K^{11}BD_4).^[86] The errors in the lattice parameters from the synchrotron X-ray diffraction data are smaller than from the neutron diffraction data reflecting the higher resolution of this particular diffractometer.

The position of the deuterium/hydrogen atom is very similar in the two structures. The thermal displacement parameter for this site is larger in K^{11}BD_4 than KBH_4 . The B-H/D bond length appears longer in K^{11}BD_4 than in KBH_4 ($1.192(2) \text{ \AA}$ and $1.114(5) \text{ \AA}$ for K^{11}BD_4 and KBH_4 respectively) as would be expected for a neutron and X-ray diffraction study. The values are similar to the room temperature B-D length of $1.196(3) \text{ \AA}$ reported by Renaudin *et al.*^[86]

Table 6.1 Details of the room temperature (20 °C) structure of K¹¹BD₄ from neutron diffraction data

<i>Fm-3m</i> , $a = 6.7184(2) \text{ \AA}$, $V = 302.58(4) \text{ \AA}^3$					
Site	x/a	y/b	z/c	occ	B _{eq} / $\text{\AA}^2$
K	0	0	0	1	2.64(8)
¹¹ B	0.5	0.5	0.5	1	1.16(5)
D	0.60245(16)	0.60245(16)	0.60245(16)	0.5	4.94(5)
$R_{wp} = 8.34 \%$, $R_{exp} = 3.95 \%$, $\chi^2 = 4.5$, Bond lengths B-D 1.192(2) $\text{\AA}$					

Table 6.2 The room temperature (20 °C) structure of KBH₄ from synchrotron X-ray diffraction data

<i>Fm-3m</i> , $a = 6.73436(1) \text{ \AA}$, $V = 305.4142(17) \text{ \AA}^3$					
Site	x/a	y/b	z/c	occ	B _{eq} / $\text{\AA}^2$
K	0	0	0	1	2.656(12)
B	0.5	0.5	0.5	1	2.92(4)
H	0.5955(4)	0.5955(4)	0.5955(4)	0.5	0.8(3)
$R_{wp} = 8.76 \%$, $R_{exp} = 4.69 \%$, $\chi^2 = 3.5$, Bond lengths B-H 1.114(5) $\text{\AA}$					

6.3 Variable temperature neutron diffraction with gravimetric analysis

Variable temperature neutron diffraction data from K^{11}BD_4 were collected on the GEM beamline at ISIS. The 795 mg sample was heated to 450 °C at a rate of 5 °C/min under dynamic vacuum within the IGAⁿ (Hiden Isochema Intelligent Gravimetric Analyser with neutrons, see Chapter 2). This allows the mass of the sample to be recorded and the pressure of the sample environment to be controlled whilst neutron diffraction data is also being collected. The sample was held at 450 °C for 250 minutes and was then allowed to cool to room temperature. The IGAⁿ was switched off when the sample cooled to 185 °C so there are no sample temperature and mass data after this point.

The diffraction data were analysed and a structural model was refined using the Rietveld method within the profile refinement program TOPAS-Academic^[167] starting from the model refined from the room temperature structure. Figure 6.3 shows a representation of how a surface plot of the diffraction patterns as a function of time would appear if viewed from above. The coloured lines show the time-of-flight positions of diffraction peaks as a function of time. The width of the lines shows the width of the peaks and the intensities of the colours indicate the relative intensities of the peaks.

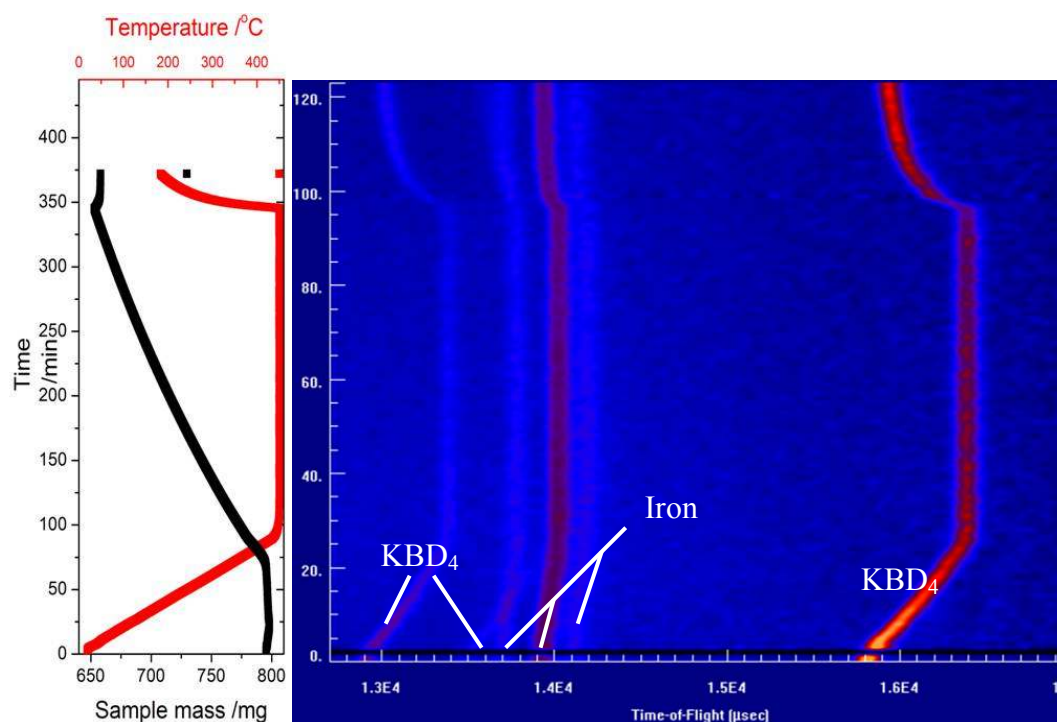


Figure 6.3 Right - A surface plot of the neutron diffraction patterns. The coloured lines show the time-of-flight positions of peaks as a function of time (y-axis) with the intensities of the peaks represented by the intensities of the colours. The width of the lines indicates the width of the peaks. The positions of Bragg peaks relating to $K^{11}BD_4$ and the IGAⁿ (iron) are shown.

Left - The sample temperature and mass as a function of the same time scale.

The diffraction patterns recorded from $K^{11}BD_4$ within the IGAⁿ show peaks relating to the IGAⁿ in the form of iron in addition to $K^{11}BD_4$. The Bragg peaks from $K^{11}BD_4$ began to weaken in intensity around 400 °C when mass loss began but the peaks remained present throughout the experiment and became stronger again on cooling. The sample lost 137.4 mg or 17.3 wt% mass during the heating experiment. Mass loss occurred at a constant rate throughout the time at 450 °C suggesting that if heating had continued, mass loss would also have continued.

Table 6.3 shows the possible decomposition routes for $K^{11}BD_4$ and their respective mass losses. The observed 17.3 wt% mass loss is greater than the 13.8 wt% mass loss

expected if K^{11}BD_4 decomposed to potassium and boron releasing all of its deuterium as gas. Therefore either some diborane was released or the sample melted and then began to evaporate as a result of the dynamic vacuum. The weakening and then return of the K^{11}BD_4 Bragg peaks could suggest that the sample partially melted, part of the melted sample was then lost under dynamic vacuum causing the mass loss but the rest of the sample recrystallised when the temperature decreased.

Table 6.3 Possible decomposition routes and their mass losses for K^{11}BD_4

Decomposition route	Mass loss / wt%
$\text{K}^{11}\text{BD}_4 (\text{s}) \rightarrow \text{KD} (\text{s}) + {}^{11}\text{B} (\text{s}) + 1.5\text{D}_2 (\text{g})$	10.3
$2\text{K}^{11}\text{BD}_4 (\text{s}) \rightarrow 2\text{KD} (\text{s}) + {}^{11}\text{B}_2\text{D}_6 (\text{g})$	29.3
$\text{K}^{11}\text{BD}_4 (\text{s}) \rightarrow \text{K} (\text{s}) + {}^{11}\text{B} (\text{s}) + 2\text{D}_2 (\text{g})$	13.8

Compounds shown as solids may have melted during the experiment

Figure 6.4 shows the lattice parameter of K^{11}BD_4 as a function of temperature when the sample was heated and then cooled. The lattice parameter for the K^{11}BD_4 unit cell increases relatively linearly with increasing temperature at a rate of $5.7 \times 10^{-4} \text{ \AA}$ per every 1°C temperature increase. When the sample was cooled, there was some hysteresis in the unit cell size. Figure 6.5 shows a Bragg peak from two diffraction patterns recorded at 245°C , one whilst the sample is being heated, the other during cooling. The peak from the diffraction pattern collected during cooling is shifted to the right as a function of time-of-flight compared to the sample collected during heating. The hysteresis is equivalent to a temperature lag of approximately 40°C .

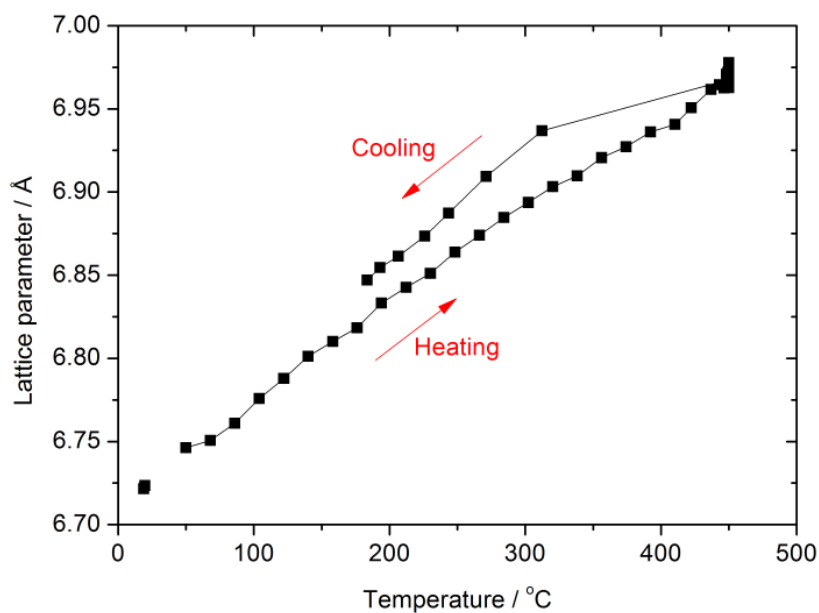


Figure 6.4 The lattice parameter for the KBD_4 unit cell as a function of temperature, heating from room temperature to 450 °C and then cooling to 185 °C. Errors are smaller than the data symbols.

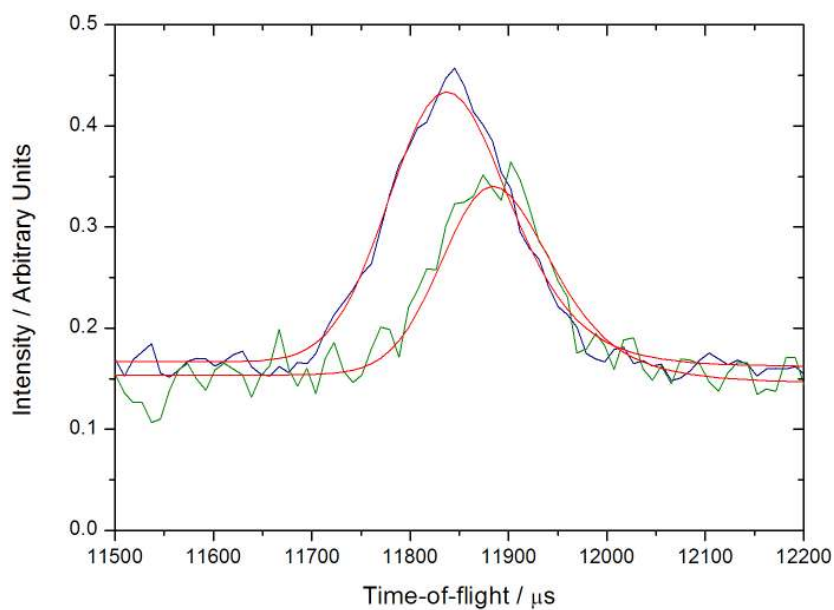


Figure 6.5 A K^{11}BD_4 Bragg peak during heating (blue) and cooling (green) at 245 °C. The fit to both peaks is shown in red.

Table 6.4 shows the details of the structure of $K^{11}BD_4$ when the sample was being heated, Table 6.5 shows the details of the structure at the same temperature during sample cooling. The diffraction patterns from the sample during cooling show broader peaks, this is reflected in the increased atomic displacement parameters and deuterium atomic position errors in the structure refinement data.

Table 6.4 The structure of $K^{11}BD_4$ at 245°C during sample heating

<i>Fm-3m</i> , $a = 6.8491(8) \text{ \AA}$, $V = 321.29(11) \text{ \AA}^3$					
Site	x/a	y/b	z/c	occ	$B_{eq} / \text{\AA}^2$
Na	0	0	0	1	2.5(5)
^{11}B	0.5	0.5	0.5	1	2.2(5)
D1	0.5995(14)	0.5995(14)	0.5995(14)	0.5	6.6(4)
$R_{wp} = 6.72 \%$, $R_{exp} = 5.18 \%$, $\chi^2 = 1.7$					

Table 6.5 The structure of $K^{11}BD_4$ at 245°C during sample cooling

<i>Fm-3m</i> , $a = 6.8734(19) \text{ \AA}$, $V = 324.72(11) \text{ \AA}^3$					
Site	x/a	y/b	z/c	occ	$B_{eq} / \text{\AA}^2$
Na	0	0	0	1	3.9(18)
^{11}B	0.5	0.5	0.5	1	3.6(16)
D1	0.598(4)	0.598(4)	0.598(4)	0.5	6.9(13)
$R_{wp} = 13.12 \%$, $R_{exp} = 12.76 \%$, $\chi^2 = 1.1$					

6.4 Raman spectroscopy

Raman spectroscopy was performed at room temperature using a Dilor Labram 300 spectrometer with the sample contained in a sealed glass capillary (see Chapter 2).

Raman spectra were collected for KBH_4 and K^{11}BD_4 .

In the $Fm-3m$ structure of KBH_4 (and K^{11}BD_4) the borohydride ions have tetrahedral symmetry. Consequently the symmetry of the internal vibrational modes ν_1 , ν_2 , ν_3 and ν_4 are A , E , T_2 and T_2 respectively (see Chapter 2).

Figure 6.6 shows the Raman spectra of KBH_4 and K^{11}BD_4 between 500 cm^{-1} and 3000 cm^{-1} . This is the region where the B-H and B-D bond stretching and bending vibrations within the borohydride ions are observed. Table 6.6 shows the frequencies of the Raman active vibrations, their assignments based on the work of Renaudin *et al.*^[86] and the ratios $\nu_{\text{B-H}}/\nu_{\text{B-D}}$.

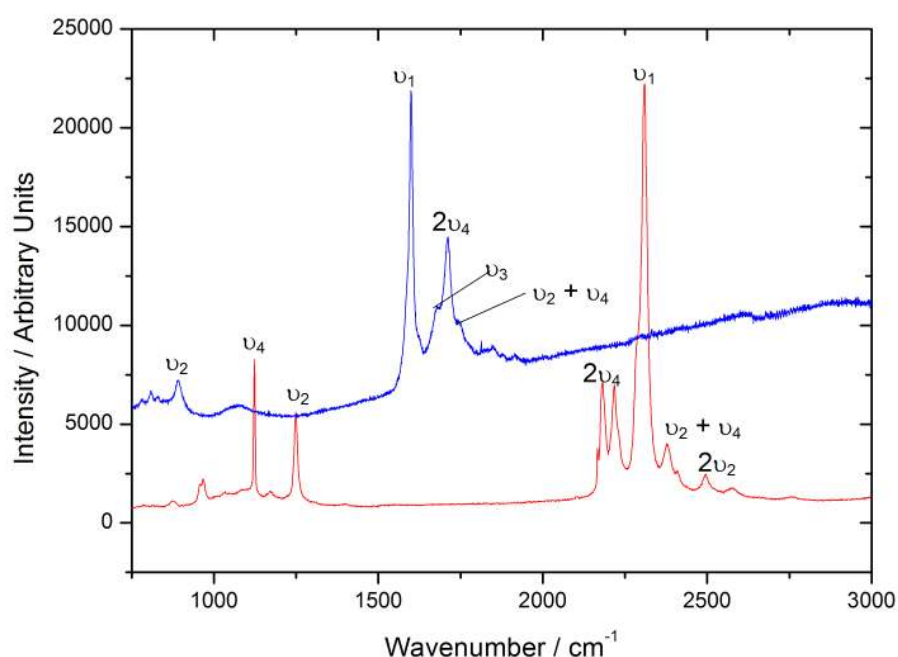


Figure 6.6 Room temperature Raman spectra of KBH_4 (red) and K^{11}BD_4 (blue)

Table 6.6 Raman frequencies / cm^{-1} for KBH_4 and K^{11}BD_4 , their assignments and the ratio $\nu_{\text{B-H}} / \nu_{\text{B-D}}$

Assignment ^[86]	KBH_4 / cm^{-1}	K^{11}BD_4 / cm^{-1}	$\nu_{\text{B-H}} / \nu_{\text{B-D}}$	$\nu_{\text{B-H}} / \nu_{\text{B-D}}$ Renaudin <i>et al.</i> ^[86]
ν_4	1123			1.31
ν_2	1249	892	1.40	1.40
$2 \nu_4$	2182	1712	1.27	1.28
$2 \nu_4$	2219			
ν_3		1679		1.37
ν_1	2308	1599	1.44	1.45
$\nu_2 + \nu_4$	2376	1741	1.36	1.36
$2 \nu_2$	2494			1.41

In the Raman spectrum of KBH_4 , the ν_1 symmetric B-H bond stretch was observed at 2308 cm^{-1} , the ν_2 symmetric B-H bond bending mode was observed at 1249 cm^{-1} and the ν_4 asymmetric B-H bending mode was observed at 1123 cm^{-1} . The ν_3 asymmetric B-H bond stretching mode could not be identified. The bond bending vibrations occur at approximately half the frequency of the stretching vibrations, consequently overtones and combinations of the bending vibrations occur in the bond stretching region.^[86]

The B-D bond vibrations are expected to be at a lower frequency than the B-H vibrations due to the increased mass of deuterium compared to hydrogen (see Chapter 2). For the symmetric ν_1 and ν_2 modes, the ratio $\nu_{\text{B-H}} / \nu_{\text{B-D}}$ of the Raman frequencies is expected to be approximately $\sqrt{2} = 1.41$ because only the hydrogen / deuterium atom moves during the vibration. The ratio for ν_1 is greater than this due to interactions with the external lattice vibrations; ν_2 is close to the expected value. For the asymmetric modes, the ratio $\nu_{\text{B-H}} / \nu_{\text{B-D}}$ is lower because the movement of the boron atom is more significant, a value closer to 1.36 might be expected. The

$\nu_{\text{B-H}} / \nu_{\text{B-D}}$ ratio is particularly low for ν_4 which was also the case for NaBH_4 (see Chapter 5). The asymmetric vibrations ν_3 and ν_4 interact because they have the same symmetry which affects the vibration frequencies. Consequently there is not a simple relationship between $\nu_{\text{B-H}}$ and $\nu_{\text{B-D}}$, however the ratio $\nu_3^{\text{D}}\nu_4^{\text{D}} / \nu_3^{\text{H}}\nu_4^{\text{H}}$ is expected to be 0.563 (see Chapter 2). The vibration frequencies for ν_3 and ν_4 were not identified in both KBH_4 and K^{11}BD_4 , however the ratios observed in this work are similar to those reported by Renaudin *et al.*^[86] where a value close to 0.563 was obtained.

6.5 Solid state ^{11}B NMR spectroscopy

Solid state ^{11}B MAS-NMR spectroscopy was carried out on a sample of KBH_4 at room temperature by NMR staff within the Chemistry Department at the University of Oxford. The spectrum was collected using a Varian/Chemagnetics Infinity spectrometer, with a 7.5 mm double resonance probe. The spectrum is shown in Figure 6.7.

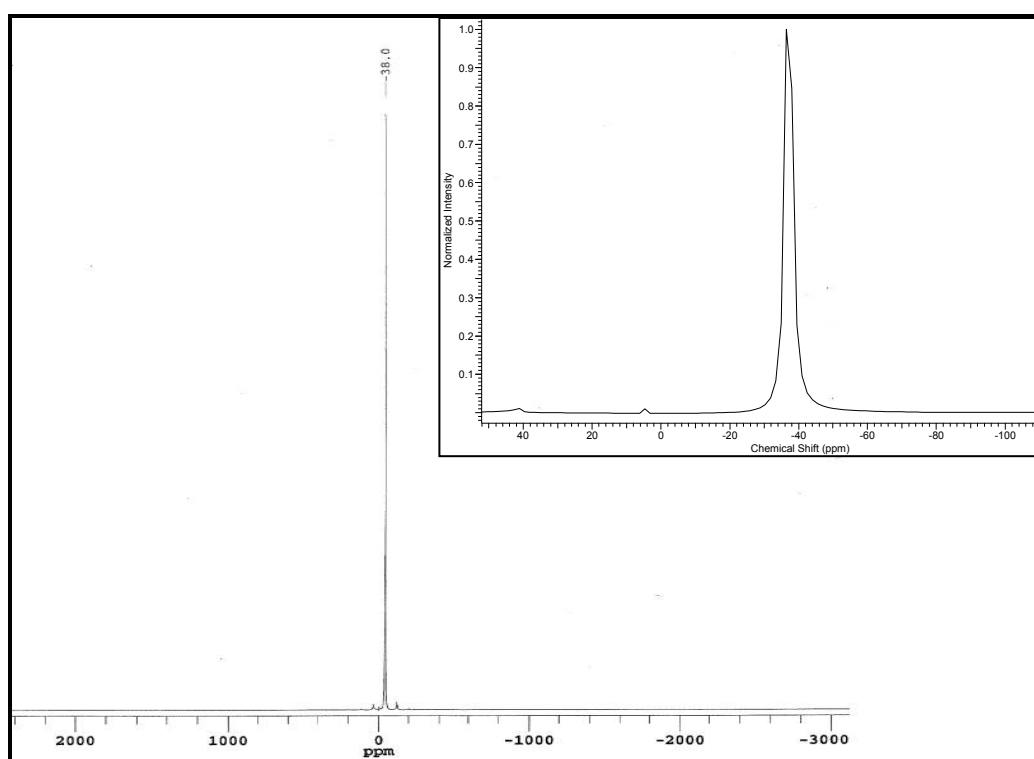


Figure 6.7 The room temperature solid state ^{11}B NMR spectrum of KBH_4 , the inset shows an expansion of the spectrum around the principal peak.

The chemical shift of boron in KBH_4 was observed to be $-38.0 \text{ ppm} (\pm 0.2 \text{ ppm})$. This is the same value that was reported by Li *et al.*^[80] The boron chemical shift in KBH_4 is larger than in NaBH_4 ($-43.3 \text{ ppm} (\pm 0.2 \text{ ppm})$, see Chapter 5) which has a similar crystal structure. This means that the boron atoms in KBH_4 are less shielded from the

magnetic field than in NaBH_4 . Potassium is less electronegative (Pauling electronegativities K 0.8, Na 0.9^[77]) and has a smaller ionisation potential than sodium (K 419 kJ mol⁻¹, Na 496 kJ mol⁻¹^[77]). If the potassium cation is attracting the electrons from the hydrogen atoms more weakly than a sodium cation, the hydrogen electrons will be able to interact with the boron electrons more effectively, creating a stronger B-H bond. If the boron electrons are pulled into the B-H bond, they will be further from the boron nuclei giving less shielding from the magnetic field.

As with NaBH_4 , the absence of spinning sidebands indicates that the boron nuclei within KBH_4 are in an environment with a high degree of symmetry.

6.6 Thermogravimetric analysis with mass spectrometry

Thermogravimetric analysis of KBH_4 was carried out using a Hiden Isochema Intelligent Gravimetric Analyser (IGA) connected to a mass spectrometer (see Chapter 2). A 66 mg sample of KBH_4 was heated to 500 °C at a rate of 2 °C/min under 1 bar of flowing helium. A small proportion of the exhaust helium along with gas released from the sample was fed, via a capillary tube, to a mass spectrometer set to detect B_2H_6 ($m/z = 28$), BH_3 ($m/z = 14$) and H_2 ($m/z = 2$). Figure 6.8 shows the sample mass and temperature and the partial pressure of hydrogen detected by the mass spectrometer as a function of time.

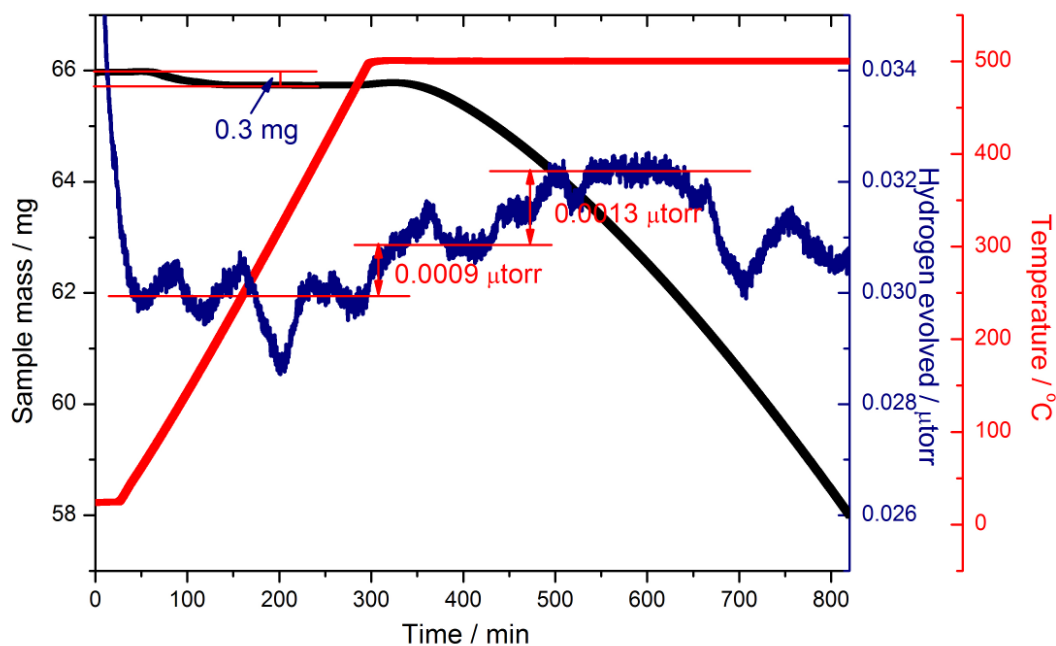


Figure 6.8 The temperature (red), mass (black) and hydrogen evolution (blue) for a sample of KBH_4 as a function of time

The first mass loss from the sample of KBH_4 occurred 60 minutes into the experiment when the sample reached 76°C . The sample lost 0.3 mg or 0.4 wt% mass. This mass loss is likely to be due to the decomposition of some solvent or impurity from the sample or equipment.

The main mass loss began approximately 30 minutes after the temperature reached 500°C . 12 mg or 17.1 wt% of the sample mass was lost during the experiment (including 500 minutes at 500°C). The rate of mass loss did not decrease before the end of the experiment which suggests that mass loss would have continued if the temperature had been maintained for a longer time. There is a general increase in the partial pressure of hydrogen detected by the mass spectrometer which coincided with the onset of mass loss, however the partial pressure of hydrogen showed small variations throughout the experiment and there were no large hydrogen evolution peaks as observed for LiBH_4 and NaBH_4 (see Chapters 4 and 5). On average, the

partial pressure of hydrogen detected by the mass spectrometer increased by 0.009 μtorr at the start of mass loss and increased by a further 0.0013 μtorr after 170 minutes at 500 $^{\circ}\text{C}$. There was a slight increase in the rate of mass loss at the same time as the second increase in the partial pressure of hydrogen. A small amount of B_2H_6 (Figure 6.9) was also detected by the mass spectrometer 330 minutes into the experiment which coincided with the onset of mass loss. The partial pressure of B_2H_6 was three orders of magnitude lower than the partial pressure of hydrogen.

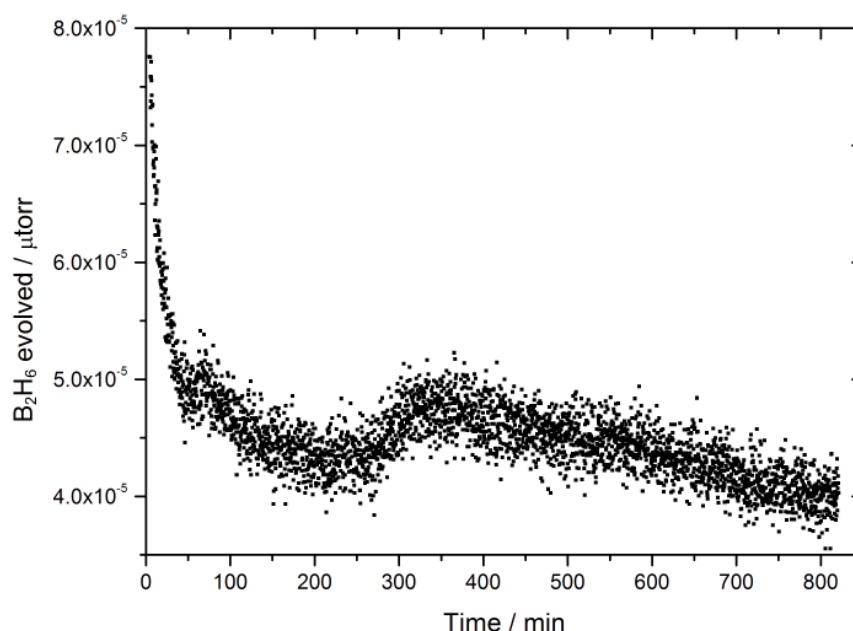


Figure 6.9 The partial pressure of B_2H_6 evolved from a sample of KBH_4 as detected by the mass spectrometer

The mass loss observed in this sample (17.1 wt% in 500 minutes) is slower than for the deuterated sample (which lost 17.3 wt% of its mass in 275 minutes) and occurs at a higher temperature. This is to be expected because this sample was analysed under 1 bar of flowing helium instead of dynamic vacuum.

Table 6.7 shows possible decomposition routes of KBH_4 and their expected mass losses. The 17.1 wt% mass loss is more than would be expected due to loss of hydrogen during decomposition to either potassium or KH. Only a small amount of diborane was detected but diborane decomposes rapidly above 150 °C so it is possible that more diborane was released and immediately decomposed to hydrogen and other B_xH_y compounds.^[129] KH melts and decomposes at 417 °C so KH is unlikely to be observed as a decomposition product of KBH_4 .^[77] Therefore it is possible that KBH_4 decomposes to potassium releasing diborane (which then decomposes further) and hydrogen with an eventual weight loss of 27.7 wt%.

Table 6.7 Decomposition routes for KBH_4 and their respective mass losses

Decomposition route	Mass loss / wt%
$\text{KBH}_4 (\text{s}) \rightarrow \text{KH} (\text{s}) + \text{B} (\text{s}) + 1.5\text{H}_2 (\text{g})$	5.6
$2\text{KBH}_4 (\text{s}) \rightarrow 2\text{KH} (\text{s}) + \text{B}_2\text{H}_6 (\text{g})$	25.6
$\text{KBH}_4 (\text{s}) \rightarrow \text{K} (\text{s}) + \text{B} (\text{s}) + 2\text{H}_2 (\text{g})$	7.5
$2\text{KBH}_4 (\text{s}) \rightarrow 2\text{K} (\text{s}) + \text{B}_2\text{H}_6 (\text{g}) + \text{H}_2 (\text{g})$	27.7

Compounds shown as solids may have melted during the experiment

6.7 Thermogravimetric analysis to higher temperature

A thermogravimetric analysis (TGA) study of KBH_4 was also completed up to 700 °C. A 9 mg sample of KBH_4 was analysed using the TGA aspect of a Perkin Elmer STA6000 simultaneous thermogravimetric analyser and differential scanning calorimeter (see Chapter 2) under 1 bar flowing argon, heating from 30 °C to 700 °C at 5 °C/min. The sample mass as a function of temperature is shown in Figure 6.10.

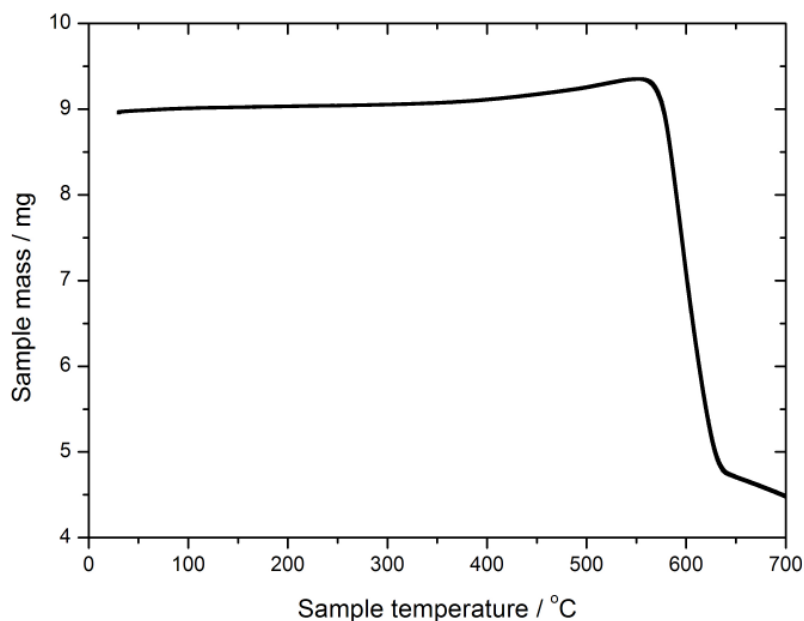


Figure 6.10 The mass of a sample of KBH_4 as a function of temperature

Mass loss from the sample of KBH_4 began at 560°C . When the sample reached 638°C , it had lost 4.56 mg or 49 wt% mass. The rate of mass loss decreased significantly above 638°C . Potassium accounts for 72 wt% of the mass of KBH_4 so this mass loss is not solely due to decomposition. Potassium metal boils at 759°C ^[77] however with boron present as an impurity some evaporation may occur at lower temperatures.

6.8 Conclusions

K^{11}BD_4 was synthesised directly from the elements using a high pressure synthesis route. The structure of K^{11}BD_4 was investigated by neutron powder diffraction and the structure of KBH_4 was analysed by synchrotron X-ray powder diffraction. K^{11}BD_4 and KBH_4 were identified to have the same face-centred-cubic structure at room temperature in the space group $Fm-3m$. The room temperature lattice parameter of

K^{11}BD_4 was 6.7184(2) Å and the room temperature lattice parameter of KBH_4 was 6.73436(1) Å.

A variable temperature neutron diffraction study of K^{11}BD_4 with gravimetric analysis was also completed. The lattice parameter of K^{11}BD_4 increased linearly with increasing temperature from 20 °C to 450 °C. The intensities of the K^{11}BD_4 Bragg diffraction peaks decreased above 400 °C, the peak intensities increased when the sample was cooled but not to their original level. Mass loss from the sample of K^{11}BD_4 also began at 400 °C and the sample lost 17.3 wt% during the study. The rate of mass loss did not decrease towards the end of the study suggesting that mass loss would have continued if the sample was held at 450 °C for longer than 250 minutes. However the mass loss was already greater than would be expected if only deuterium gas was released. Either some diborane was released or alternatively the sample partially melted and evaporated as a result of the dynamic vacuum, the remaining sample would have recrystallised when the sample cooled.

A thermogravimetric analysis with mass spectrometry study of KBH_4 was completed. KBH_4 was heated to 500 °C under 1 bar flowing helium. Significant mass loss began after the sample had been held at 500 °C for 30 minutes and the sample lost 17.1 wt% mass during 500 minutes at 500 °C. As with the K^{11}BD_4 study, the rate of mass loss did not decrease towards the end of the study suggesting that mass loss would have continued and the mass loss was greater than would be expected just from loss of hydrogen. The mass spectrometer detected hydrogen and a small amount of diborane. The extent of diborane release may have been masked by its rapid decomposition at 500 °C. Under 1 bar flowing helium, the sample is less likely to have evaporated than under dynamic vacuum so the total mass loss might be attributed to the evolution of diborane and hydrogen.

In a second thermogravimetric analysis study of KBH_4 under 1 bar flowing argon, with a larger temperature range, mass loss began at 560°C . The rate of mass loss decreased significantly after 638°C .

The chemical shift of KBH_4 in solid state ^{11}B NMR spectroscopy was determined to be -38.0 ppm ($\pm 0.2\text{ ppm}$). This suggests that boron is in a less shielded environment within KBH_4 than in NaBH_4 . The ^{11}B NMR spectrum of KBH_4 does not have any significant side bands suggesting that the boron environment has a high level of symmetry consistent with the proposed crystal structure in the space group $Fm-3m$.

The room temperature Raman spectrum of KBH_4 is consistent with an ionic borohydride.

KBH_4 and K^{11}BD_4 both have the same ionic borohydride face centred cubic structure in the space group $Fm-3m$. This structure has a high degree of symmetry. Melting and decomposition will occur over time if KBH_4 or K^{11}BD_4 are heated to 450°C under vacuum or 500°C at 1 bar, however, if the sample temperature is continually increased, significant decomposition does not occur until 560°C . Züttel *et al.* reported KBH_4 to begin decomposition at 500°C and melt at 585°C which would be expected to increase the rate of decomposition. These temperatures are in a similar range to those reported here.

7 Lithium potassium borohydride

7.1 Chapter focus

The focus of this chapter is the synthesis and characterisation of lithium-potassium borohydride, $\text{LiK}(\text{BH}_4)_2$. This is the first mixed alkali metal borohydride. $\text{LiK}(\text{BH}_4)_2$ has been characterised by synchrotron X-ray and neutron powder diffraction, Raman and solid state NMR spectroscopy and by thermogravimetric analysis.

7.2 Synthesis

Thirteen samples of general composition $n\text{LiBH}_4:(12-n)\text{KBH}_4$ ($n=0, 1, 2, \dots, 12$) were prepared in an identical fashion. Appropriate molar quantities of LiBH_4 and KBH_4 (Sigma-Aldrich) were ground together by hand using a pestle and mortar under an inert argon atmosphere within a glove box. The samples were packed into alumina crucibles (approximately 350 mg per crucible) and placed inside quartz tubes. The tubes were initially capped with a Young's tap and then evacuated to 10^{-6} mbar. Once evacuated the tubes were sealed by melting the quartz using a gas torch. After sealing, all of the samples were heated to 125 °C at 1 °C/min and remained at this temperature for 12 hours within a muffle furnace. The maximum proportion of $\text{LiK}(\text{BH}_4)_2$ produced using this sealed evacuated tube method was 66 wt%, and was obtained for a precursor ratio of 2:1 $\text{LiBH}_4:\text{KBH}_4$. This result appears anomalous as a 1:1 ratio of precursors would be expected to produce single phase $\text{LiK}(\text{BH}_4)_2$.

Various attempts have been made to increase the yield of $\text{LiK}(\text{BH}_4)_2$ by varying the conditions of the solid state reaction. Heating the ground mixture of 2:1 $\text{LiBH}_4:\text{KBH}_4$ under flowing nitrogen, or heating a sealed evacuated tube at the reduced rate of

0.1 °C/min both increased the yield to 70 wt%. A variety of other methods to increase the yield were attempted including quenching the reaction tubes, varying the reaction temperature and annealing the reaction mixture but all were unsuccessful. During the quenching of reaction tubes it was observed that the sample was molten when it was removed from the furnace.

A solution state reaction between LiBH_4 and KBH_4 refluxed in ether overnight was attempted but did not produce any $\text{LiK}(\text{BH}_4)_2$, only LiBH_4 and KBH_4 were detected by X-ray diffraction.

$\text{LiK}({}^{11}\text{BD}_4)_2$ was synthesised using a Parr High Pressure Reactor Furnace. Metallic lithium (0.4 g), potassium (1.4 g) and ${}^{11}\text{B}$ (0.8 g) were mixed together within an argon filled glove box and then placed inside the reactor vessel. The vessel was evacuated and then charged with 55 bar D_2 and sealed before heating to 700 °C for 48 hours. Here, the yield was 50 wt%.

$\text{LiK}({}^{11}\text{BD}_4)_2$ was also synthesised from $\text{Li}{}^{11}\text{BD}_4$ and $\text{K}{}^{11}\text{BD}_4$ by manually grinding together the starting materials and then heating in sealed evacuated tubes within a muffle furnace in the same way as for $\text{LiK}(\text{BH}_4)_2$, excepting that heating to 200 °C was required in order for a reaction to occur. The reaction at 200 °C gave a 17 wt% yield.

Due to the similarity of the solubility of LiBH_4 and KBH_4 in solvents and the likelihood that $\text{LiK}(\text{BH}_4)_2$ will have intermediate solubilities, it has not been possible to purify the product by washing in solvent.

An attempt was made to purify the product by melting the product mixture and filtering, thus taking advantage of the reduced melting point of $\text{LiK}(\text{BH}_4)_2$. Unfortunately it was not possible to melt $\text{LiK}(\text{BH}_4)_2$ sufficiently to flow through a filter without melting the other components or decomposing the product.

7.3 Room temperature X-ray diffraction

High-resolution X-ray diffraction data were collected from the thirteen samples of general composition $n\text{LiBH}_4:(12-n)\text{KBH}_4$ ($n=0, 1, 2, \dots, 12$) whose synthesis is discussed in Section 7.2. The diffraction data were collected using the ID31 diffractometer (ESRF, Grenoble) at a wavelength and step size of 0.79953 Å and 0.003° respectively. The X-ray data from all of the samples consisted of sharp Bragg peaks indicating a high degree of crystallinity.

Detailed structural modelling of these diffraction data was performed using the profile refinement program TOPAS.^[167] LiBH_4 and KBH_4 Bragg peaks were observed across the full composition range of $n\text{LiBH}_4:(12-n)\text{KBH}_4$ ($n=0, 1, 2, \dots, 12$), together with a number of prominent additional peaks, which were indexed to a single extra phase with an orthorhombic structure and lattice parameters of $a = 7.91(1)$ Å, $b = 4.49(1)$ Å and $c = 13.84(3)$ Å. Assessment of the extinction symbol associated with the space group of the new phase using DASH^[168] indicated the most probable to be $Pn-a$, which corresponds to space groups $Pn2_1a$ and $Pnma$. This further strengthened the likelihood of structural similarity between the new phase and LiBH_4 , which adopts the space group $Pnma$. A probable composition of the new phase was surmised from a comparison of the lattice volumes of the precursors, LiBH_4 and KBH_4 , which have volumes per formula unit of 54.2 Å³ and 76.1 Å³ respectively. The new phase had a volume per formula unit of 123.0 Å³, (assuming four formula units per unit cell which is consistent with the extinction symbol $Pn-a$) which is approximately the sum of the values for LiBH_4 and KBH_4 (130.3 Å³), this suggested that the new phase may possess a $\text{LiK}(\text{BH}_4)_2$ stoichiometry.

While it was probable that the space group of this new phase was $Pnma$, given the precedent of LiBH_4 , it was found to be more straightforward to work initially within

the $Pn2_1a$ space group, which has no special positions and this makes structure solution by global optimisation more straightforward. Simulated annealing studies whereby one potassium and two boron atoms (which dominate the scattering) were allowed to move within the asymmetric unit of $Pn2_1a$ were performed. At the end of the structure solution process, all three atoms were located on positions consistent with the special position of $(x, \frac{1}{4}, z)$ in $Pnma$. Subsequent optimisation of the fit to the diffraction data was thus performed in this centrosymmetric space group, with these three atoms and the Li atom restricted to the $(x, \frac{1}{4}, z)$ plane. Although lithium is a relatively weak scatterer, multiple simulated annealing analyses consistently returned the same lithium coordinates, with the observed Li-B distances consistent with those in LiBH_4 (see Table 7.3). Finally, two rigid-body constrained borohydride groups were allowed to rotate around the independent B positions. Two H atoms were found to lie on the $(x, \frac{1}{4}, z)$ plane with the two other hydrogen atoms related to one another by the mirror plane along $(x, \frac{1}{4}, z)$ for both borohydride ion tetrahedra. This arrangement of H atoms is identical to the orientation of the borohydride groups in orthorhombic LiBH_4 . In the final refinement, the quality of the data was sufficient to allow the coordinates of all hydrogen atoms to be refined unconstrained. A typical final fit to the data is shown in Figure 7.1. The refinement details and structural coordinates of the structure of $\text{LiK}(\text{BH}_4)_2$ with the borohydride ions constrained as rigid bodies are listed in Table 7.1. The refinement details and structural co-ordinates for the structure with the hydrogen atomic positions refined unconstrained are listed in Table 7.2. A schematic diagram representing the crystal structure of the new phase, together with that for orthorhombic LiBH_4 , is shown in Figure 7.2. The new phase, $\text{LiK}(\text{BH}_4)_2$, is present across the full range of the reaction series, and lattice constants for $\text{LiK}(\text{BH}_4)_2$ remain constant to one decimal place for all precursor ratios.

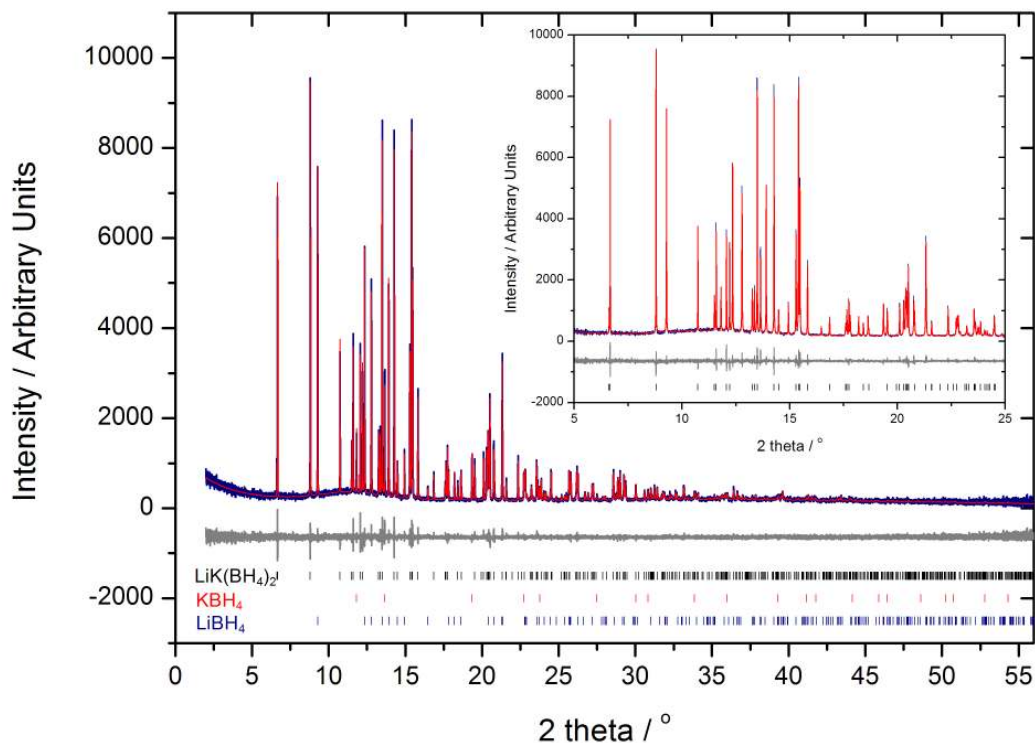


Figure 7.1. The observed (blue), calculated (red) and difference ($Y_{\text{obs}} - Y_{\text{calc}}$, grey) diffraction patterns for the structure refinement of $\text{LiK}(\text{BH}_4)_2$ from X-ray synchrotron diffraction data at 20 °C. The Bragg peak positions for LiBH_4 , KBH_4 and $\text{LiK}(\text{BH}_4)_2$ are indicated by the vertical tick marks. The inset shows an expansion of the 5 to 25 degrees two-theta range with the Bragg peak positions for $\text{LiK}(\text{BH}_4)_2$ indicated.

Table 7.1 Refined crystallographic data for LiK(BH₄)₂ with the borohydride ions constrained as rigid tetrahedra

Site	x/a	y/b	z/c	B _{eq} /Å ²
K	0.33704(14)	¼	0.86935(8)	3.27(3)
Li	0.1894(10)	¼	0.1297(7)	3.27(3)
B1	0.2488(5)	¼	0.5456(3)	2.34(11)
H1	0.261(2)	0.465(2)	0.594(2)	2.34(11)
H2	0.357(2)	¼	0.487(2)	2.34(11)
H3	0.116(2)	¼	0.507(2)	2.34(11)
B2	0.9277(6)	¼	0.2393(4)	2.34(11)
H4	0.980(2)	0.465(2)	0.278(2)	2.34(11)
H5	0.779(2)	¼	0.243(2)	2.34(11)
H6	0.972(2)	¼	0.158(2)	2.34(11)
$a = 7.91327(4) \text{ \AA}, b = 4.49061(2) \text{ \AA}, c = 13.84313(7) \text{ \AA}, V = 491.921(4) \text{ \AA}^3$				
$R_{wp} = 10.89 \%, R_{exp} = 6.27 \%, \chi^2 = 3.0$				

Table 7.2 Refined crystallographic data for LiK(BH₄)₂ with the hydrogen atoms refined unconstrained

Site	x/a	y/b	z/c	B _{eq} /Å ²
K	0.33814(12)	¼	0.86851(7)	3.42(2)
Li	0.1885(9)	¼	0.1349(6)	3.42(2)
B1	0.2508(7)	¼	0.5460(4)	2.38(6)
H1	0.324(2)	0.456(4)	0.5288(13)	2.38(6)
H2	0.206(4)	¼	0.614(2)	2.38(6)
H3	0.140(4)	¼	0.498(2)	2.38(6)
B2	0.9292(7)	¼	0.2397(4)	2.38(6)
H4	0.976(2)	0.452(4)	0.2057(15)	2.38(6)
H5	0.789(4)	¼	0.218(2)	2.38(6)
H6	0.960(4)	¼	0.316(2)	2.38(6)
$a = 7.91337(5) \text{ \AA}, b = 4.49067(3) \text{ \AA}, c = 13.84396(11) \text{ \AA}, V = 491.964(10) \text{ \AA}^3$				
$R_{wp} = 10.34 \%, R_{exp} = 6.47 \%, \chi^2 = 2.6$				

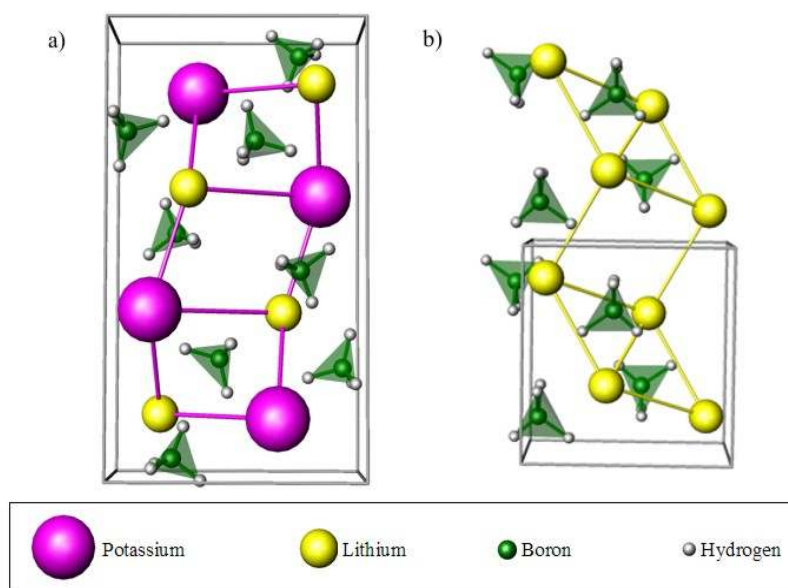


Figure 7.2 A schematic diagram of (a) the proposed $\text{LiK}(\text{BH}_4)_2$ structure and (b) that of orthorhombic LiBH_4 .

There is very little difference in the quality of the fit to the data between the model where the hydrogen atoms are unconstrained and the borohydride ions are distorted and a model with rigid body tetrahedral borohydride ions. The R_{wp} values for the constrained and unconstrained models are 10.89 % and 10.34 % respectively. It is preferable to use a simpler structural model if the quality of the fit to the data is not compromised so in this case the focus will be on the constrained model.

The b -axis lattice parameter of $\text{LiK}(\text{BH}_4)_2$ (4.49061(2) Å) is very similar to that of orthorhombic LiBH_4 (4.43686(2) Å^[51]). Given the common $Pnma$ space group, this suggests a degree of structural similarity between the phases.

The borohydride units in $\text{LiK}(\text{BH}_4)_2$ form an approximately tetrahedral coordination around Li^+ , similar to that found in orthorhombic LiBH_4 (Figure 7.3). The Li-B bond distances are greater in $\text{LiK}(\text{BH}_4)_2$ than those reported in LiBH_4 ^[51] but with a narrower range of angles (Table 7.3). The larger Li-B separations observed in the new phase may be considered to originate from the presence of potassium cations in the

structure, which are considerably larger than their lithium counterparts (Li^+ ionic radius 0.59 Å, K^+ ionic radius 1.38 Å in tetrahedral coordination).^[77]

Table 7.3 Comparison of Li-B distances and B-Li-B angles in $\text{LiK}(\text{BH}_4)_2$ and LiBH_4

	$\text{LiK}(\text{BH}_4)_2$	LiBH_4 ^[51]
Li-B distances / Å	2.568(10)	2.475(4)
	2.576(5)	2.521(2)
	2.576(5)	2.521(2)
	2.616(10)	2.542(4)
B-Li-B angles / °	99.9(3)	94.1(2)
	100.2(2)	94.1(2)
	100.2(2)	111.7(2)
	114.9(2)	111.7(2)
	114.9(2)	120.2(2)
	121.3(4)	123.3(2)

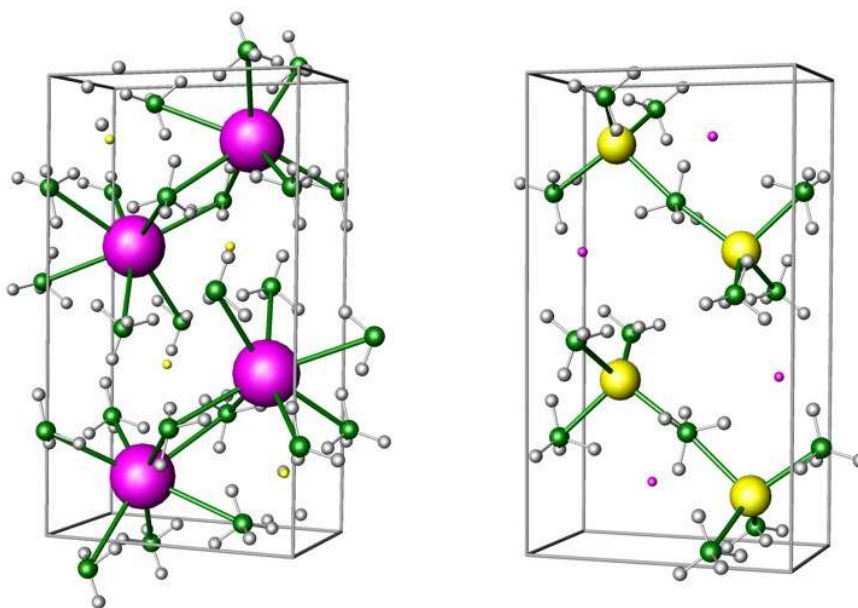


Figure 7.3 Schematic diagram depicting the environments of potassium in $\text{LiK}(\text{BH}_4)_2$ and of lithium in $\text{LiK}(\text{BH}_4)_2$.

Left The schematic structure of $\text{LiK}(\text{BH}_4)_2$ showing the 7-fold potassium coordination by boron. Potassium is represented by purple spheres, boron by green spheres and hydrogen by grey spheres. The lithium cations are represented by small yellow spheres.

Right The schematic structure of $\text{LiK}(\text{BH}_4)_2$ showing the 4-fold lithium coordination by boron. Lithium represented by yellow spheres, boron by green spheres and hydrogen by grey spheres. The potassium cations are represented by small purple spheres.

The arrangement of the borohydride units in $\text{LiK}(\text{BH}_4)_2$ and KBH_4 differs considerably. KBH_4 has an octahedral arrangement of borohydride units around the potassium ions, while those in $\text{LiK}(\text{BH}_4)_2$ might be best described as seven – co-ordinated mono-capped trigonal prisms (see Figure 7.3). All of the K-B distances in KBH_4 are reported as $3.3640 \text{ \AA}^{[85]}$, whereas in $\text{LiK}(\text{BH}_4)_2$ the distances are twice $3.384(3) \text{ \AA}$, twice $3.420(4) \text{ \AA}$, twice $3.427(4) \text{ \AA}$, and once $3.465(4) \text{ \AA}$. These larger

separations arise because of the greater number of borohydride units present around the potassium cation.

The two independent borohydride units have different co-ordination environments within $\text{LiK}(\text{BH}_4)_2$. If the hydrogen atoms are ignored, atom B1 has a five – co-ordinated square pyramidal co-ordination shape. The base of the square consists of two potassium (K-B distance 3.384(3) Å) and two lithium ions (Li-B distance 2.576(5) Å). A third potassium ion forms the apex (K-B distance 3.465(4) Å). Atom B2 has a distorted octahedral co-ordination to four equatorial potassium ions (K-B distances, 3.412(4) Å (twice) and 3.427(4) Å (twice)) and two axial lithium ions (Li-B distances 2.568(10) Å and 2.616(10) Å).

In the constrained borohydride ion model of $\text{LiK}(\text{BH}_4)_2$, the B-H length was 1.18(2) Å and the H-B-H bond angles were constrained to 109.5°. In the unconstrained model, the borohydride units appear to be distorted in a similar manner to those reported in the orthorhombic structure of LiBH_4 by Soulie *et al.*^[51] (see Table 7.4). $\text{LiK}(\text{BH}_4)_2$ appears to have a narrower range of B-H bond lengths than LiBH_4 (1.013(18) Å - 1.148(18) Å in $\text{LiK}(\text{BH}_4)_2$ compared with 1.04(2) Å – 1.28(1) Å in LiBH_4). This apparent distortion is likely to be an effect of some orientational disorder of the borohydride unit distorting the hydrogen electron cloud which is used to determine the atomic positions. If the borohydride ions are rotating, it is probable that the B-H bond lengths are all equivalent. The orientation of the borohydride ions in the constrained and unconstrained models are different suggesting that orientational disorder is indeed present in $\text{LiK}(\text{BH}_4)_2$.

Table 7.4. B-H distances in $\text{LiK}(\text{BH}_4)_2$, $\text{LiBH}_4^{[51]}$ and $\text{KBH}_4^{[85]}$. The H atom concerned is given in brackets for $\text{LiK}(\text{BH}_4)_2$

	$\text{LiK}(\text{BH}_4)_2$		$\text{LiBH}_4^{[51]}$	$\text{KBH}_4^{[85]}$
	B1	B2	B1	B1
B-H	1.013(18) (H2)	1.087(12) (H4)	1.04(2)	1.09(1)
distances / Å	1.101(18) (H3)	1.087(12) (H4)	1.25(1)	
	1.117(11) (H1)	1.091(18) (H6)	1.28(1)	
	1.117(11) (H1)	1.148(18) (H5)	1.28(1)	

7.4 Room temperature neutron diffraction

Neutron diffraction data were collected on a mixed sample of $\text{Li}^{11}\text{BD}_4$ (33 wt%), K^{11}BD_4 (28 wt%) and $\text{LiK}(\text{}^{11}\text{BD}_4)_2$ (39 wt%) for one hour (158 μA) at room temperature within an 8 mm vanadium can using the GEM diffractometer at ISIS, UK. Detailed structural modelling of the diffraction data was performed using the profile refinement program TOPAS^[167] starting from the models obtained from the X-ray diffraction study in Section 7.3. Two separate refinements were completed. In the first refinement, the borohydride ions of $\text{LiK}(\text{}^{11}\text{BD}_4)_2$ were constrained as tetrahedral rigid bodies. In the second refinement, the deuterium atoms were refined unconstrained. The positions of the lithium and boron atoms in $\text{Li}^{11}\text{BD}_4$ and the deuterium atoms in K^{11}BD_4 were also refined along with all of the thermal parameters for $\text{Li}^{11}\text{BD}_4$ and K^{11}BD_4 (the deuterium thermal parameters were maintained equal in the individual structures). A representation of a typical fit to the data is shown in Figure 7.4. The refined crystallographic data for the constrained model of $\text{LiK}(\text{}^{11}\text{BD}_4)_2$ are shown in Table 7.5 and for the unconstrained model in Table 7.6.

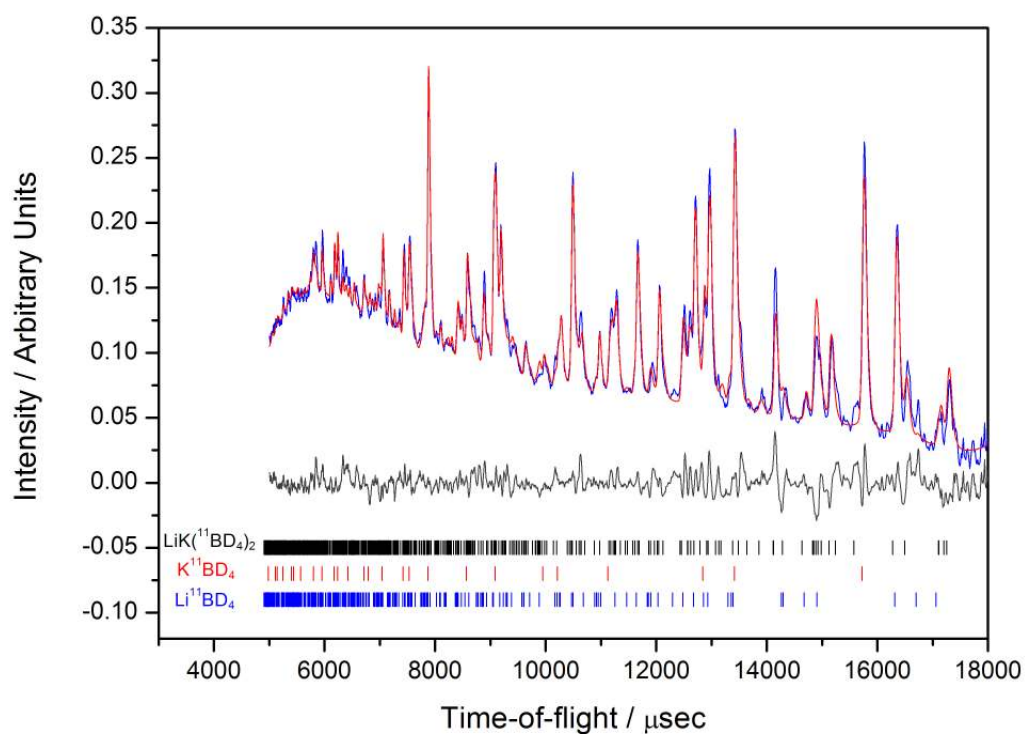


Figure 7.4 The observed (blue), calculated (red) and difference plots ($Y_{obs}-Y_{calc}$, grey) for the structure refinement of $\text{LiK}(^{11}\text{BD}_4)_2$ from neutron diffraction data at 20 °C. The Bragg peak positions for $\text{Li}^{11}\text{BD}_4$, K^{11}BD_4 and $\text{LiK}(^{11}\text{BD}_4)_2$ are all shown by the vertical tick marks.

Table 7.5 Refined crystallographic data for $\text{LiK}({}^{11}\text{BD}_4)_2$ with the borohydride ions constrained as tetrahedral rigid bodies.

Atom	x/a	y/b	z/c	$B_{\text{eq}}/\text{\AA}^2$
K	0.339(2)	$\frac{1}{4}$	0.845(5)	3.4(7)
Li	0.189(2)	$\frac{1}{4}$	0.122(11)	3.2(4)
B1	0.248(3)	$\frac{1}{4}$	0.5419(15)	3.7(8)
D1	0.18(3)	0.43(3)	0.56(3)	5.1(7)
D2	0.26(3)	$\frac{1}{4}$	0.47(3)	5.1(7)
D3	0.36(3)	$\frac{1}{4}$	0.56(3)	5.1(7)
B2	0.902(3)	$\frac{1}{4}$	0.226(2)	1.2(4)
D4	0.86(3)	0.44(2)	0.27(3)	5.4(7)
D5	0.03(3)	$\frac{1}{4}$	0.22(3)	5.4(7)
D6	0.85(3)	$\frac{1}{4}$	0.15(3)	5.4(7)
$a = 7.8874(19) \text{ \AA}, b = 4.4816(11) \text{ \AA}, c = 13.7400(13) \text{ \AA}, V = 485.68(17) \text{ \AA}^3$				
$R_{\text{wp}} = 6.48 \%, R_{\text{exp}} = 1.76 \%, \chi^2 = 13.6$				

Table 7.6 Refined crystallographic data for $\text{LiK}({}^{11}\text{BD}_4)_2$ with the hydrogen positions unconstrained.

Site	x/a	y/b	z/c	$B_{\text{eq}}/\text{\AA}^2$
K	0.330(5)	$\frac{1}{4}$	0.876(2)	2.8(7)
Li	0.202(8)	$\frac{1}{4}$	0.124(5)	2.0(7)
B1	0.266(6)	$\frac{1}{4}$	0.542(3)	7.8(10)
D1	0.327(3)	0.472(5)	0.5224(13)	3.6(5)
D2	0.245(3)	$\frac{1}{4}$	0.6367(18)	2.5(6)
D3	0.136(5)	$\frac{1}{4}$	0.473(5)	10.5(9)
B2	0.926(4)	$\frac{1}{4}$	0.243(2)	3.6(6)
D4	0.987(2)	0.478(4)	0.2036(14)	3.0(5)
D5	0.780(4)	$\frac{1}{4}$	0.219(2)	4.0(7)
D6	0.942(2)	$\frac{1}{4}$	0.3274(15)	1.5(5)
$a = 7.8846(7) \text{ \AA}, b = 4.4766(6) \text{ \AA}, c = 13.777(2) \text{ \AA}, V = 486.25(10) \text{ \AA}^3$				
$R_{\text{wp}} = 5.59 \%, R_{\text{exp}} = 1.75 \%, \chi^2 = 10.2$				

The quality of the fit to the data in the unconstrained models is slightly better than in the constrained model. However, as discussed previously in Section 7.3, a simpler model is generally preferable and if the borohydride ions are likely to rotate, the deuterium atoms would be expected to be equivalent, therefore the focus will be on the constrained model.

The lattice parameters determined for $\text{LiK}(^{11}\text{BD}_4)_2$ by neutron diffraction are smaller than for $\text{LiK}(\text{BH}_4)_2$ determined from synchrotron X-ray diffraction (unit cell volumes $485.68(17) \text{ \AA}^3$ and $491.921(4) \text{ \AA}^3$ for $\text{LiK}(^{11}\text{BD}_4)_2$ and $\text{LiK}(\text{BH}_4)_2$ respectively). This is to be expected due to the larger vibration amplitudes and zero point energies of B-H bonds compared to B-D bonds.^[86]

The atomic positions of Li, K and B in $\text{LiK}(^{11}\text{BD}_4)_2$ are similar to those determined from the X-ray study of the hydrogenated form. The hydrogen and deuterium positions vary. This suggests that the borohydride ions may be disordered in the same way as observed in the parent compound LiBD_4 (See Chapter 4).

In the constrained model the B-D distances in the borohydride ions refined to $1.056(25) \text{ \AA}$ and the B-D-B internal angle was constrained to 109.5° . The two borohydride ions are not equivalent, atom B1 is five - co-ordinated to three potassium ions and two lithium ions whilst atom B2 is six – co-ordinated to four potassium ions and two lithium ions.

Table 7.7 B-D distances in $\text{LiK}(\text{BD}_4)_2$

$\text{LiK}(\text{BD}_4)_2$		
	B1	B2
B-D distances / $\text{\AA}$	1.118(20) (D1)	1.354(19) (D4)
	1.118(20) (D1)	1.354(19) (D4)
	1.334(34) (D2)	1.157(34) (D5)
	1.397(43) (D3)	1.162(26) (D6)

In the unconstrained model, the B-D bond lengths are in the range 1.118(20) Å to 1.397(43) Å, with D-B-D bond angles between 100.9(19)° and 122(3)°. These variations are larger than those observed in the X-ray study of the hydrogenated form (variation in B-H lengths was 1.013(18) Å - 1.148(18) Å, range of H-B-H bond angles was 102.1 to 113.4). The thermal parameters for the deuterium atoms are all less than 4.0 Å² except for D3 which is significantly larger at 10.5(9) Å².

7.5 Variable temperature X-ray diffraction

Li¹¹BD₄ and K¹¹BD₄ were manually ground together using a pestle and mortar within a nitrogen filled glove bag. High-resolution X-ray diffraction data of the sample in a rotating 0.7 mm borosilicate-glass capillary were collected on the I11 diffractometer at Diamond, Rutherford Appleton Laboratory, UK. Data were collected between 5° and 80° two theta using a wavelength and step size of 0.82497 Å and 0.003° respectively. After an initial 10 minute room temperature run, further datasets were collected for 5 minutes at 5 °C intervals between 37 °C and 67 °C, 2 °C intervals from 67 °C to 97 °C and 5 °C intervals from 97 °C to 117 °C. 30 minutes later, data were collected for 5 minutes at 122 °C and then 177 °C. Finally, data were collected every minute whilst cooling freely to room temperature and for 10 minutes once the sample had cooled to room temperature. All X-ray data consisted of sharp Bragg peaks indicating a high degree of crystallinity.

The diffraction data were modelled using the profile refinement program TOPAS^[167] starting from the models obtained from the room temperature X-ray diffraction study detailed in Section 7.3. A typical fit to the data is shown in Figure 7.5.

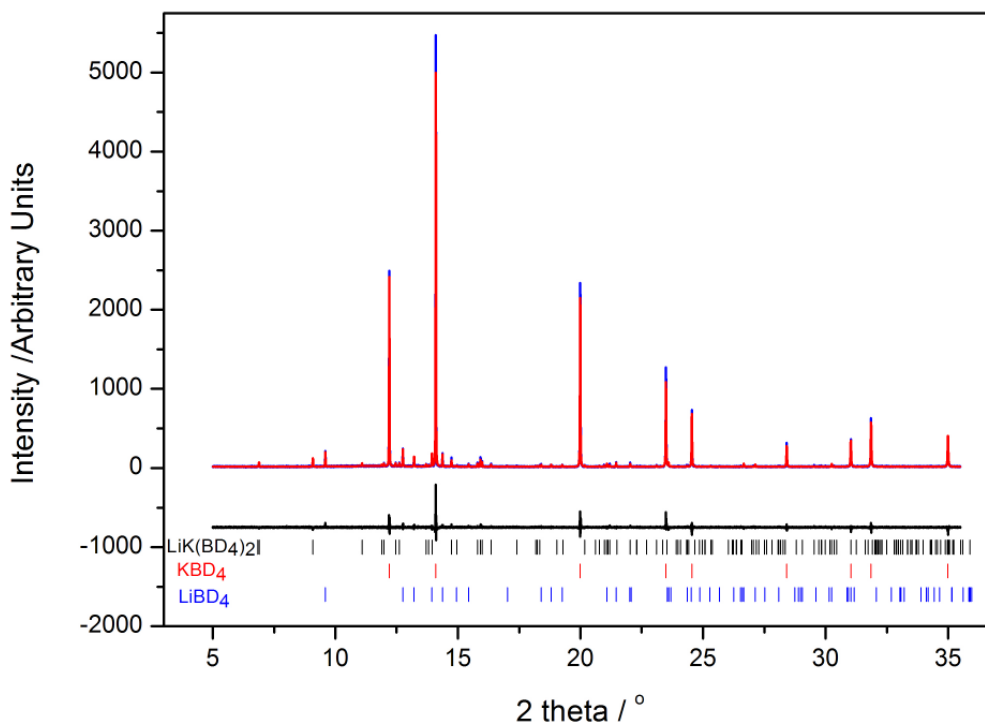


Figure 7.5 Observed (blue), calculated (red) and difference ($Y_{obs}-Y_{calc}$, grey) diffraction data from a mixed sample of $\text{Li}^{11}\text{BD}_4$, K^{11}BD_4 and $\text{LiK}(^{11}\text{BD}_4)_2$. The Bragg peak positions for $\text{Li}^{11}\text{BD}_4$, K^{11}BD_4 and $\text{LiK}(^{11}\text{BD}_4)_2$ are all shown by the vertical tick marks.

Figure 7.6 shows a representation of how a surface plot of the diffraction patterns as a function of temperature would appear if viewed from above. The lines show the two theta positions of diffraction peaks as a function of temperature. The width of the lines shows the width of the peaks and the intensities of the lines indicate the relative intensities of the peaks. At room temperature $\text{Li}^{11}\text{BD}_4$, K^{11}BD_4 , $\text{LiK}(^{11}\text{BD}_4)_2$ were all present in the proportions 30 wt%, 62 wt% and 8 wt% respectively. $\text{LiK}(^{11}\text{BD}_4)_2$ had formed just from the action of grinding together $\text{Li}^{11}\text{BD}_4$ and K^{11}BD_4 without any heating. Bragg peaks relating to $\text{LiK}(^{11}\text{BD}_4)_2$ were observed to disappear at 93 °C and Bragg peaks relating to $\text{Li}^{11}\text{BD}_4$ disappeared at 112 °C. Bragg peaks relating to K^{11}BD_4 were still present at 177 °C. During cooling to room temperature, Bragg peaks relating to $\text{Li}^{11}\text{BD}_4$ reappeared but peaks relating to $\text{LiK}(^{11}\text{BD}_4)_2$ did not reappear.

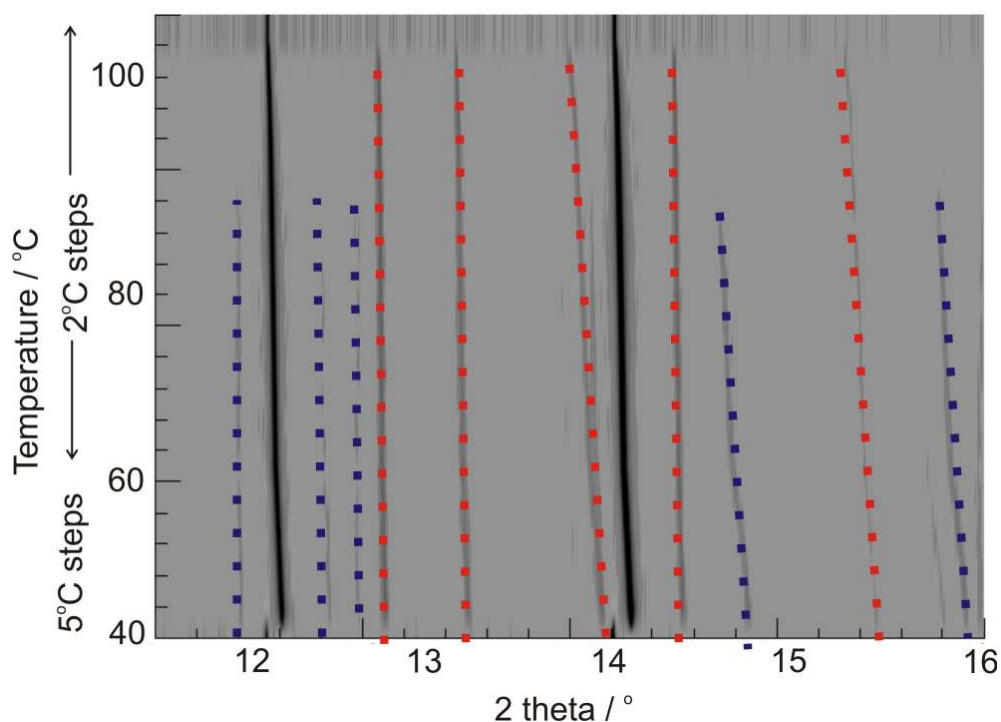


Figure 7.6 A surface plot of the synchrotron X-ray diffraction patterns for $\text{Li}^{11}\text{BD}_4$, K^{11}BD_4 and $\text{LiK}^{(11}\text{BD}_4)_2$. The lines show the two theta positions of diffraction peaks as a function of temperature. The width of the lines shows the width of the peaks and the intensities of the lines indicates the relative intensities of the peaks. Bragg peaks for $\text{LiK}^{(11}\text{BD}_4)_2$ (blue) and $\text{Li}^{11}\text{BD}_4$ (red) are labelled with dashed lines. The two very intense peaks relate to K^{11}BD_4 .

The lattice parameters of $\text{LiK}^{(11}\text{BD}_4)_2$ were investigated as a function of temperature between 20 °C and 93 °C when Bragg peaks were no longer observed. The a and b lattice parameters only show very small variations within this temperature range. The a lattice parameter of the unit cell of $\text{LiK}^{(11}\text{BD}_4)_2$ increased by 0.2 % from 7.90676(14) Å at room temperature to 7.9221(3) Å at 67°C (Figure 7.7). Above 67 °C, the a lattice parameter plateaued, remaining at 7.92 Å to two decimal places.

The b lattice parameter of the unit cell of $\text{LiK}^{(11}\text{BD}_4)_2$ decreased from 4.48621(8) Å at room temperature to 4.4746(6) Å at 91 °C (Figure 7.8). This is a 0.3 % decrease and occurred mainly above 57 °C. This is analogous to the decrease in the similarly sized b

lattice parameter of $\text{Li}^{11}\text{BD}_4$ which decreased from $4.42266(13) \text{ \AA}$ at 57°C to $4.4173(2) \text{ \AA}$ at 127°C (See Chapter 4).

The c lattice parameter of the unit cell of $\text{LiK}(^{11}\text{BD}_4)_2$ varied more as a function of temperature than the a and b parameters. The c lattice parameter increased by 2.9 % from $13.8348(3) \text{ \AA}$ at room temperature to $14.233(2) \text{ \AA}$ at 91°C (Figure 7.9).

The unit cell volume of $\text{LiK}(^{11}\text{BD}_4)_2$ was observed to increase by 2.8 % from $490.7 \text{ \AA}^3$ at room temperature to $504.6 \text{ \AA}^3$ at 91°C (Figure 7.10). The increase of the c lattice parameter is responsible for the majority of the volume increase with the effects of the increasing a and decreasing b lattice parameters effectively cancelling each other out.

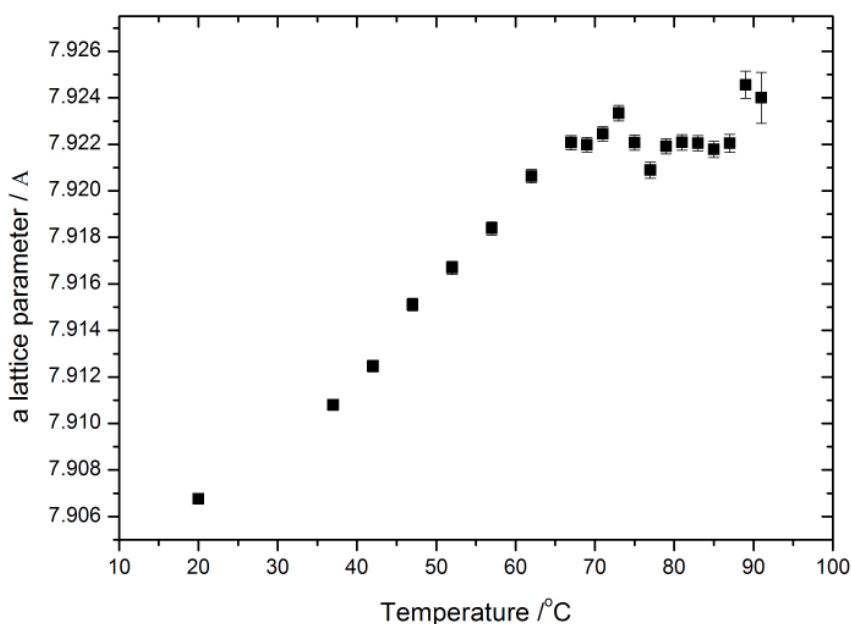


Figure 7.7 The magnitude of the a lattice parameter of the unit cell of $\text{LiK}(^{11}\text{BD}_4)_2$ as a function of temperature. Where errors are not shown they are smaller than the data points.

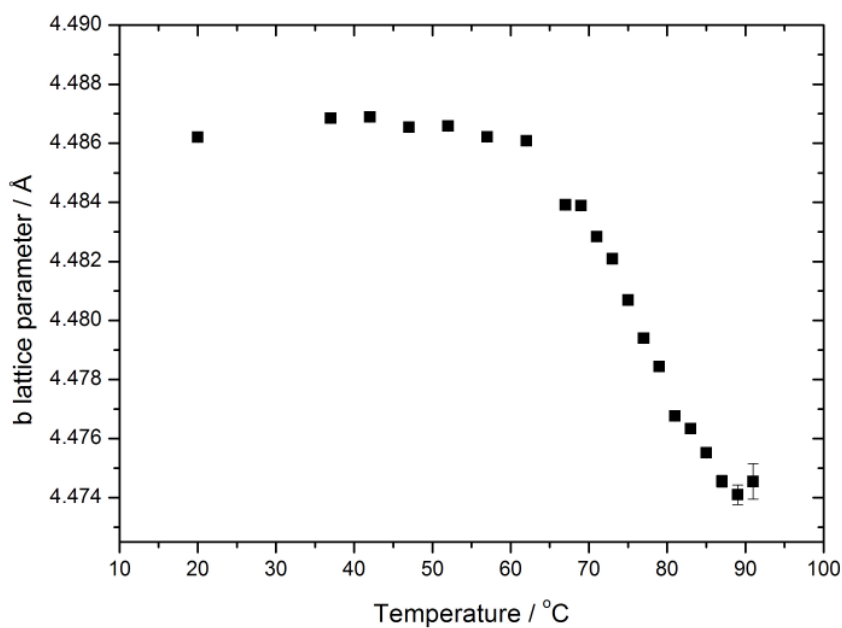


Figure 7.8 The magnitude of the b lattice parameter of the unit cell of $\text{LiK}({}^{11}\text{BD}_4)_2$ as a function of temperature. When errors are not shown they are smaller than the data symbols.

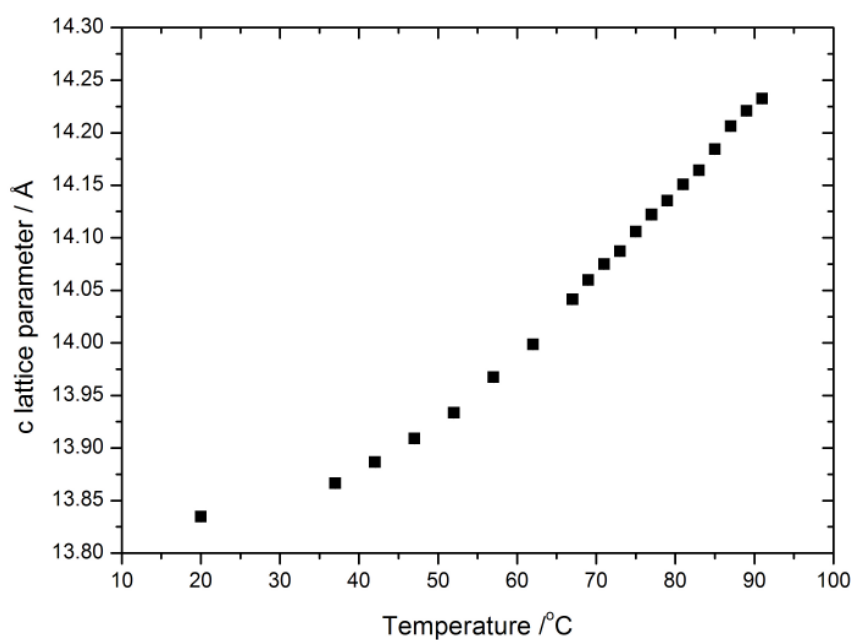


Figure 7.9 The magnitude of the c lattice parameter of the unit cell of $\text{LiK}({}^{11}\text{BD}_4)_2$ as a function of temperature. Errors are smaller than the data symbols.

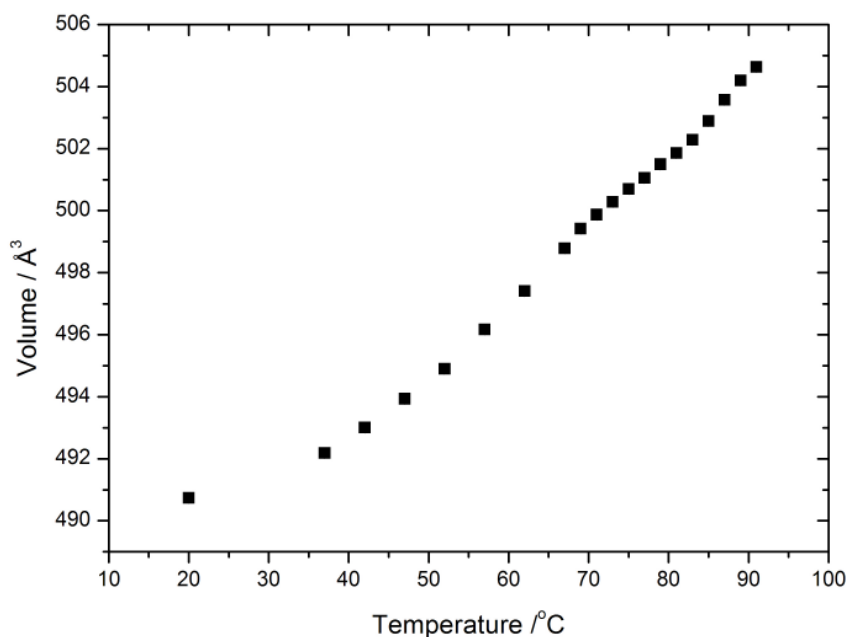


Figure 7.10 The volume of the unit cell of $\text{LiK}(\text{}^{11}\text{BD}_4)_2$ as a function of temperature. Errors are smaller than the data symbols.

Within the mixture of $\text{Li}^{11}\text{BD}_4$, K^{11}BD_4 and $\text{LiK}(\text{}^{11}\text{BD}_4)_2$, the $\text{Li}^{11}\text{BD}_4$ lattice parameters were expanded with respect to a sample of pure $\text{Li}^{11}\text{BD}_4$ when the data was collected under the same conditions using the same diffractometer (Figure 7.11 to Figure 7.13). This may suggest a degree of insertion of K^{11}BD_4 into the $\text{Li}^{11}\text{BD}_4$ lattice *en route* to the formation of $\text{LiK}(\text{}^{11}\text{BD}_4)_2$. At 37 °C, the $\text{Li}^{11}\text{BD}_4$ crystal lattice was expanded to $a = 7.17639(8) \text{ \AA}$, $b = 4.43194(4) \text{ \AA}$ and $c = 6.79806(7) \text{ \AA}$ in the mixture compared to $a = 7.14545(19) \text{ \AA}$, $b = 4.42190(11) \text{ \AA}$ and $c = 6.7833(2) \text{ \AA}$ in the pure sample. This is an increase of 0.4 %, 1.0 % and 0.2 % in the a , b and c lattice parameters respectively. The higher percentage increase in the b lattice parameter of $\text{Li}^{11}\text{BD}_4$ compared to the other lattice parameters of $\text{Li}^{11}\text{BD}_4$ may be a result of the similarity in magnitude of the b lattice parameters in $\text{Li}^{11}\text{BD}_4$ and $\text{LiK}(\text{}^{11}\text{BD}_4)_2$ which itself suggests some structural similarity between the two phases. If $\text{Li}^{11}\text{BD}_4$ was beginning to react to form $\text{LiK}(\text{}^{11}\text{BD}_4)_2$ and the two structures are similar along the

direction of the y axis, then the b lattice parameter of $\text{Li}^{11}\text{BD}_4$ may be the first parameter to show the effect of this transformation.

The lattice parameter of KBD_4 increased linearly with temperature up to 177°C (Figure 7.14).

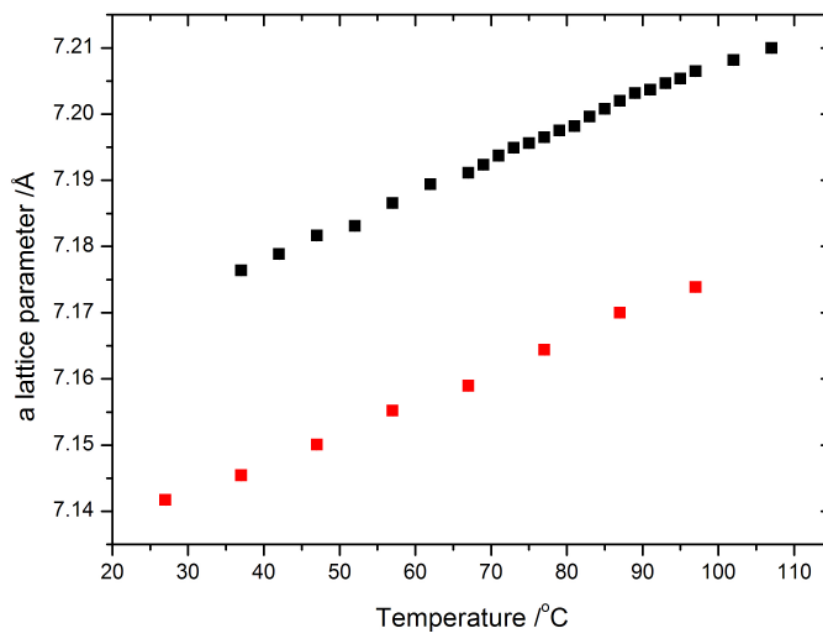


Figure 7.11 A comparison of the a lattice parameter of $\text{Li}^{11}\text{BD}_4$ as a function of temperature in pure $\text{Li}^{11}\text{BD}_4$ (red) with $\text{Li}^{11}\text{BD}_4$ in a mixture with $\text{LiK}(\text{}^{11}\text{BD}_4)_2$ and K^{11}BD_4 (black). Errors are smaller than the data symbols.

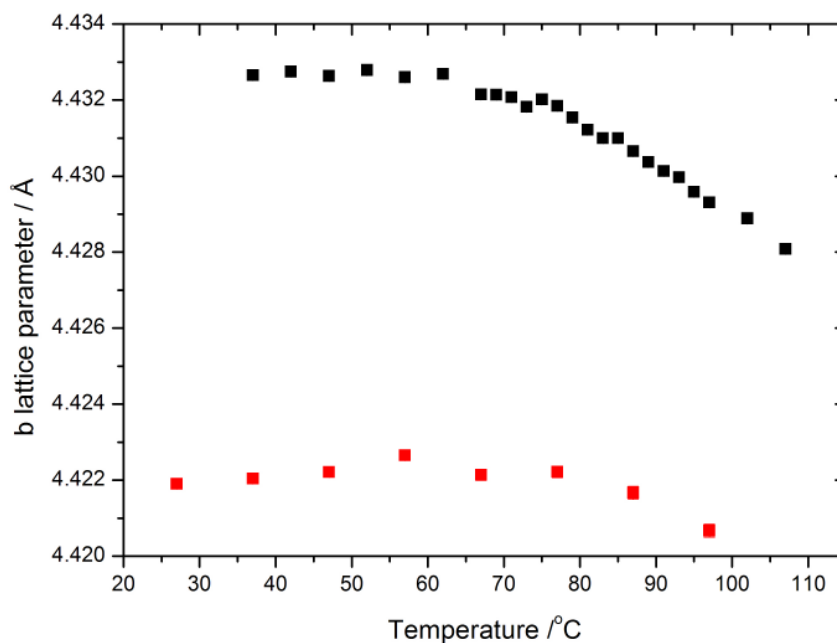


Figure 7.12 A comparison of the b lattice parameter of $\text{Li}^{11}\text{BD}_4$ as a function of temperature in pure $\text{Li}^{11}\text{BD}_4$ (red) with $\text{Li}^{11}\text{BD}_4$ in a mixture with $\text{LiK}(\text{}^{11}\text{BD}_4)_2$ and K^{11}BD_4 (black). Errors are smaller than the data symbols.

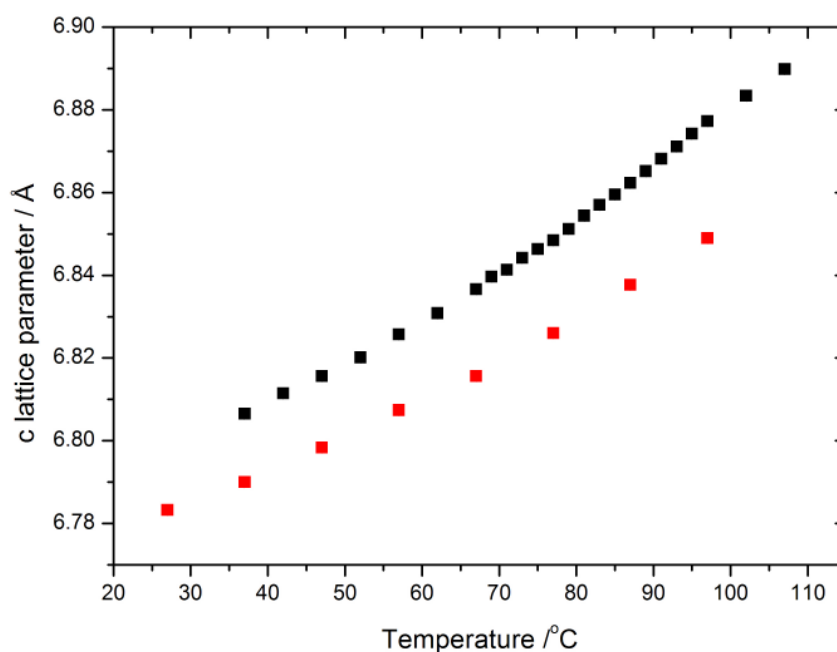


Figure 7.13 A comparison of the c lattice parameter of $\text{Li}^{11}\text{BD}_4$ as a function of temperature in pure $\text{Li}^{11}\text{BD}_4$ (red) with $\text{Li}^{11}\text{BD}_4$ in a mixture with $\text{LiK}(\text{}^{11}\text{BD}_4)_2$ and K^{11}BD_4 (black). Errors are smaller than the data symbols.

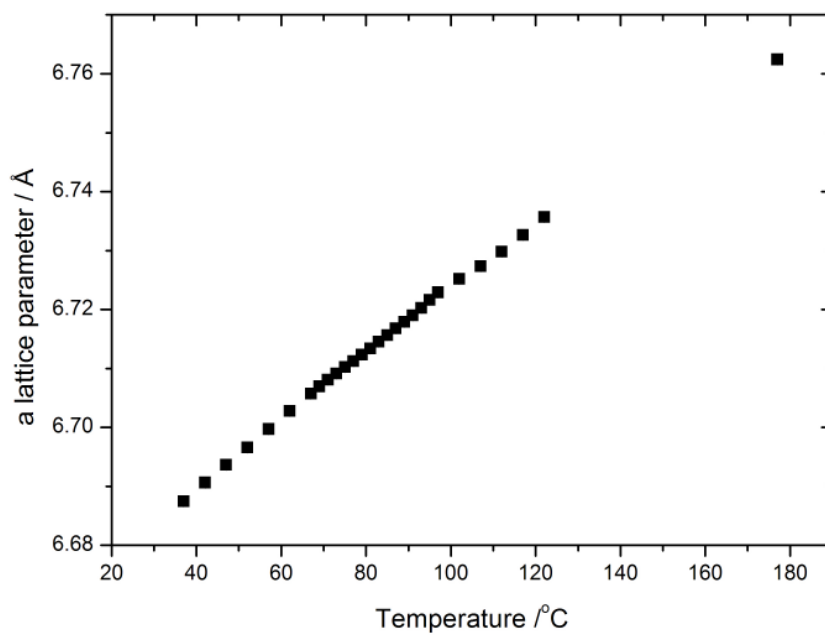


Figure 7.14 The lattice parameter of K¹¹BD₄ as a function of temperature within the mixture with Li¹¹BD₄ and LiK(¹¹BD₄)₂.

7.6 Raman spectroscopy

Raman spectroscopy was performed at room temperature using a Dilor Labram 300 spectrometer with the sample contained in a sealed glass capillary (see Chapter 2). An annotated spectrum of $\text{LiK}(\text{BH}_4)_2$ is shown in Figure 7.15. Peaks marked with * relate to impurity LiBH_4 within the sample.

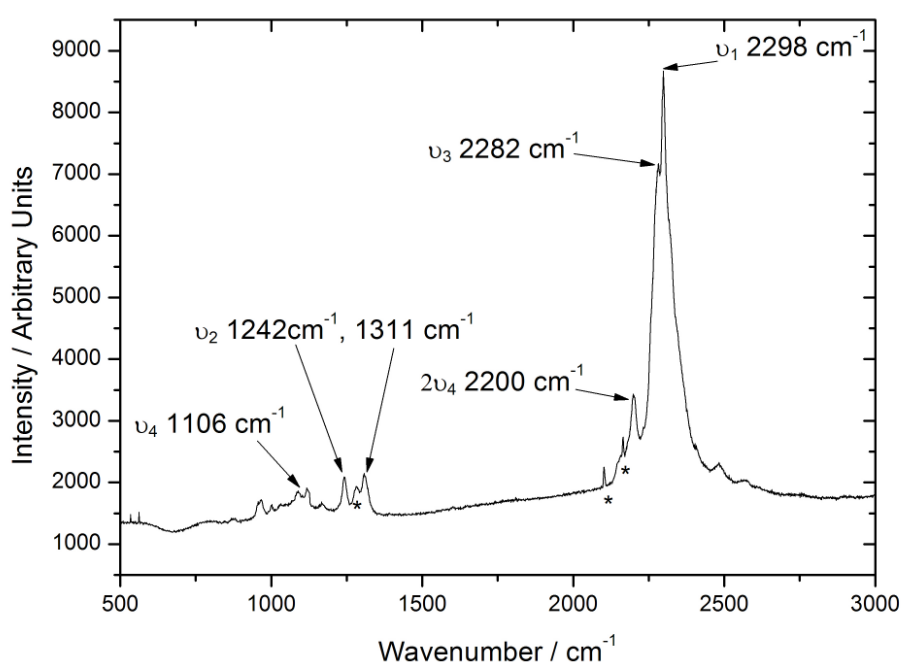


Figure 7.15 The Raman spectrum of $\text{LiK}(\text{BH}_4)_2$ with the principal vibrations labelled

Although the two borohydride ions in $\text{LiK}(\text{BH}_4)_2$ have different co-ordination environments (five co-ordinate and six co-ordinate), they are both located on a mirror plane and consequently have the symmetry C_s identical to those in LiBH_4 . The symmetries of the vibrational modes are consequently $\nu_1 = A'$, $\nu_2 = A' + A''$, $\nu_3 = 2A' + A''$, $\nu_4 = 2A' + A''$ which are all Raman active (See Raman example in Chapter 2).^[156]

Any signal splitting due to the different borohydride environments in $\text{LiK}(\text{BH}_4)_2$ is unlikely to be visible at this resolution. Five of the Raman active modes were identified in the Raman spectrum of $\text{LiK}(\text{BH}_4)_2$. The symmetric stretch, ν_1 , is observed at 2298 cm^{-1} . The symmetric bending modes, ν_2 , are observed at 1242 cm^{-1} and 1311 cm^{-1} . An asymmetric stretching mode, ν_3 , is observed at 2282 cm^{-1} , this frequency is very low for a ν_1 stretch so is not thought to be a second ν_1 stretch related to the second borohydride ion environment. The asymmetric bending modes, ν_4 , are observed around 1106 cm^{-1} . The A' and A'' modes cannot be distinguished without using a polarising filter with the Raman spectrometer.

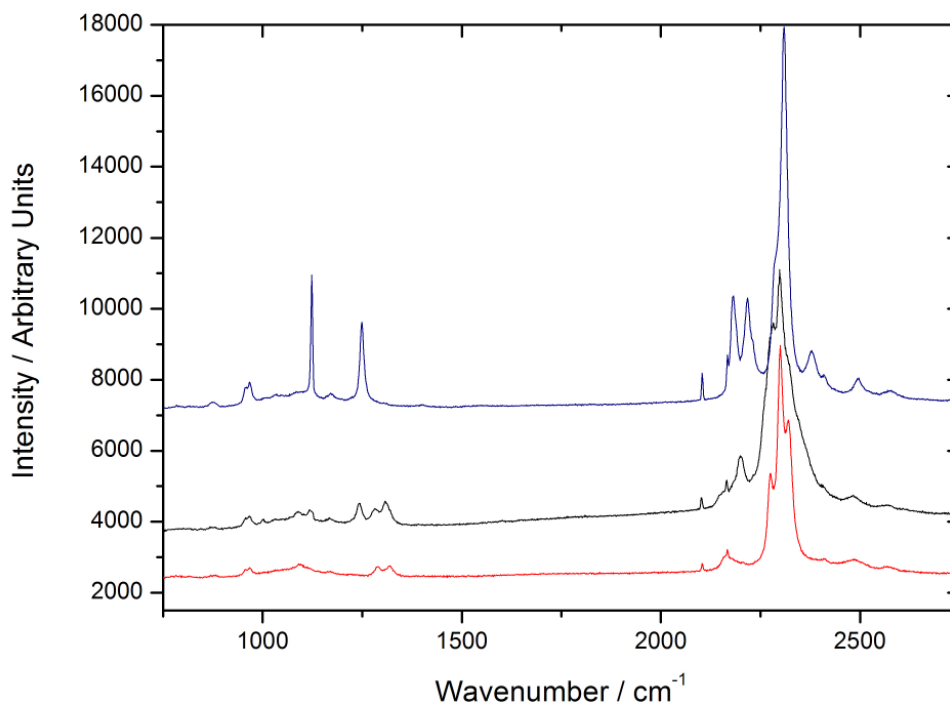
The borohydride ions in KBH_4 have the point group T_d . The different crystal structures and point groups of LiBH_4 and $\text{LiK}(\text{BH}_4)_2$ compared to KBH_4 make comparison of the Raman spectra more complex, particularly in the case of ν_1 .^[79]

The Raman spectra of $\text{LiK}(\text{BH}_4)_2$, LiBH_4 and KBH_4 are shown in Figure 7.16 and the frequencies of the Raman active modes are listed in Table 7.8. The frequency of the symmetric B-H stretch, ν_1 , in $\text{LiK}(\text{BH}_4)_2$ is similar to that in LiBH_4 reflecting the identical space group of the two structures. The symmetric bend, ν_2 , of $\text{LiK}(\text{BH}_4)_2$ is closer to that of KBH_4 reflecting the similarity in co-ordination environment of the borohydride ions within the two structures. The frequencies of the asymmetric modes of $\text{LiK}(\text{BH}_4)_2$, ν_3 and ν_4 , are intermediate to those of LiBH_4 and KBH_4 .

Table 7.8 A comparison of the Raman modes of LiBH_4 , $\text{LiK}(\text{BH}_4)_2$ and KBH_4

Assignment	$\text{LiBH}_4 / \text{cm}^{-1} *$	$\text{LiK}(\text{BH}_4)_2 / \text{cm}^{-1}$	$\text{KBH}_4 / \text{cm}^{-1} *$
ν_4 asym. bend	1090	1106	1123
ν_2 sym. bend	1286	1242	1249
ν_2' sym. bend	1320	1311	
$2\nu_4$ asym. bend	2167	2200	
ν_3 asym. stretch	2275	2282	2300 [†]
ν_1 sym. stretch	2300	2298	2308
ν_3' asym. stretch	2321		

* See Chapters 4 and 6, [†] calculated from the expected ratio of $\text{KBH}_4/\text{K}^{11}\text{BD}_4$

**Figure 7.16** The Raman spectra of $\text{LiK}(\text{BH}_4)_2$ (black), LiBH_4 (red) and KBH_4 (blue) displayed on the same axes

7.7 Solid state ^{11}B NMR Spectroscopy

Solid state ^{11}B MAS-NMR spectroscopy was carried out on a sample of $\text{LiK}(\text{BH}_4)_2$ at room temperature by NMR staff within the Chemistry Department at the University of Oxford. A Varian/Chemagnetics Infinity spectrometer with a 7.5 mm double resonance probe was used (See Chapter 2).

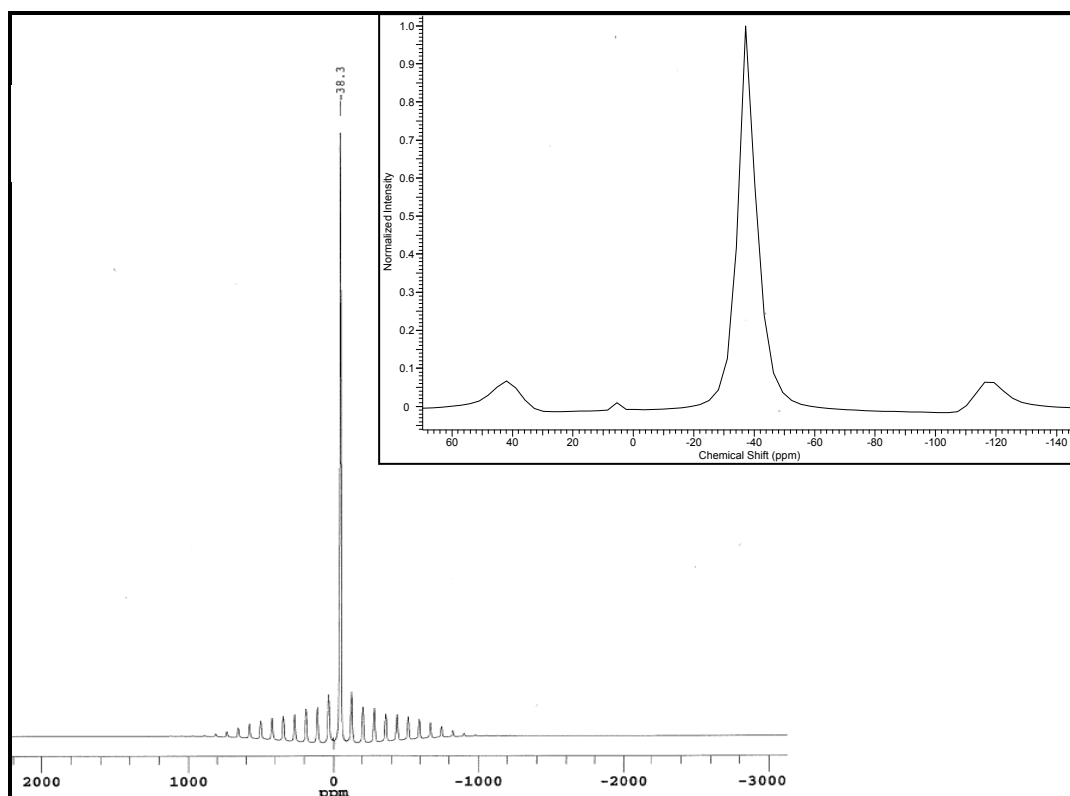


Figure 7.17 Solid state room temperature ^{11}B NMR spectrum of $\text{LiK}(\text{BH}_4)_2$

The ^{11}B NMR spectrum of $\text{LiK}(\text{BH}_4)_2$ shows a single peak. This suggests that the different co-ordination environments of the two borohydride units in $\text{LiK}(\text{BH}_4)_2$ have similar levels of shielding from the magnetic field. The chemical shift for $\text{LiK}(\text{BH}_4)_2$ is -38.3 ppm (± 0.2 ppm) compared to -41.4 ppm (± 0.2 ppm) for LiBH_4 and -38.0 ppm (± 0.2 ppm) for KBH_4 . This suggests that there is a similar level of electron density providing shielding from the magnetic field in the borohydride units of $\text{LiK}(\text{BH}_4)_2$ as in KBH_4 and a lower electron density than found in LiBH_4 . The ^{11}B

chemical shift is influenced by the number of cations co-ordinated to the boron atom. In LiBH_4 , the boron atom is surrounded by four lithium ions, in KBH_4 , the boron atom is octahedrally co-ordinated to six potassium ions. The boron atoms in $\text{LiK}(\text{BH}_4)_2$ have either a slightly distorted octahedral co-ordination to four equatorial potassium and two axial lithium ions or square pyramidal co-ordination to three potassium and two lithium ions. The total co-ordination number is therefore either five or six which is similar to KBH_4 , which explains the similarity in ^{11}B chemical shift between KBH_4 and $\text{LiK}(\text{BH}_4)_2$.

7.8 Thermogravimetric analysis

7.8.1 *Under dynamic vacuum*

Thermogravimetric analysis was carried out using a Hiden Isochema Intelligent Gravimetric Analyser (see Chapter 2). A 50 mg sample containing a majority of $\text{LiK}(\text{BH}_4)_2$ with minority LiBH_4 and KBH_4 impurities (70 wt% $\text{LiK}(\text{BH}_4)_2$), as determined by X-ray powder diffraction using a Philips PANalytical X'Pert diffractometer (see Experimental Chapter 2), was heated to 400 °C at a rate of 2 °C/min under dynamic vacuum (base pressure 10^{-6} mbar). The change in mass and temperature as a function of time are shown in Figure 7.18. Mass loss was observed from 225 °C with a mass loss of 23.5 mg (47 %) by 380 °C. At 380 °C the rate of mass loss was noted to decrease and a further 20.5 mg (41 %) was subsequently lost.

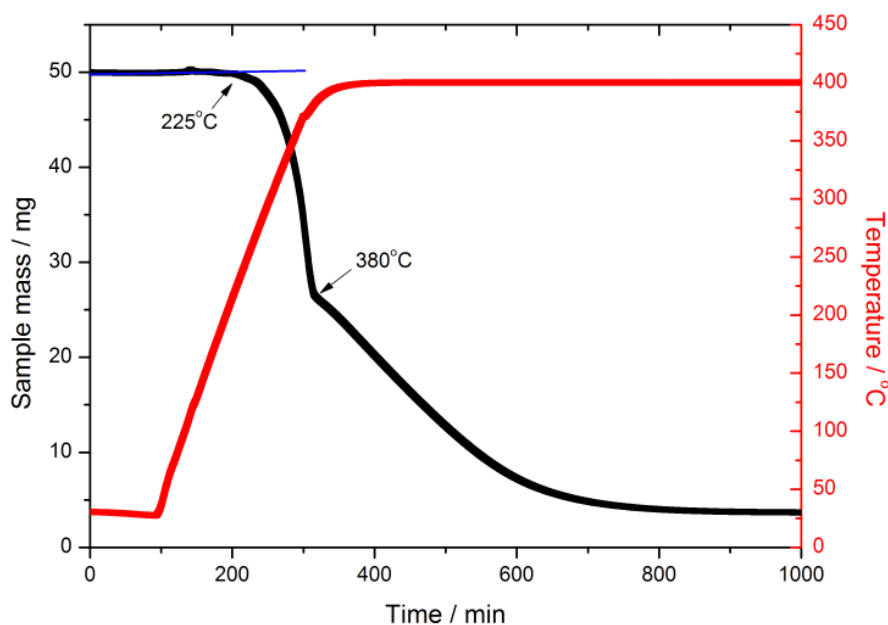


Figure 7.18 The mass (black) and temperature (red) shown as a function of time for a sample of majority $\text{LiK}(\text{BH}_4)_2$ under dynamic vacuum

7.8.2 Under flowing helium with mass spectrometry

Thermogravimetric analysis was carried out using a Hiden Isochema Intelligent Gravimetric Analyser fitted with a mass spectrometer set to detect B_2H_6 ($m/z = 28$), BH_3 ($m/z = 14$) and H_2 ($m/z = 2$) (see Chapter 2). A 37 mg sample containing a majority of $\text{LiK}(\text{BH}_4)_2$ with minority LiBH_4 and KBH_4 impurities (70.2 wt% $\text{LiK}(\text{BH}_4)_2$, 2.7 wt% LiBH_4 and 26.4 wt% KBH_4) as determined by X-ray powder diffraction using a Philips PANalytical X'Pert diffractometer (see Chapter 2), was heated to 450 °C at a rate of 2 °C/min under 1 bar flowing helium. A small proportion of the helium along with any gas released from the sample was directed to the mass spectrometer via a 10 bar capillary tube. The change in mass and temperature of the sample as a function of time are shown in Figure 7.19.

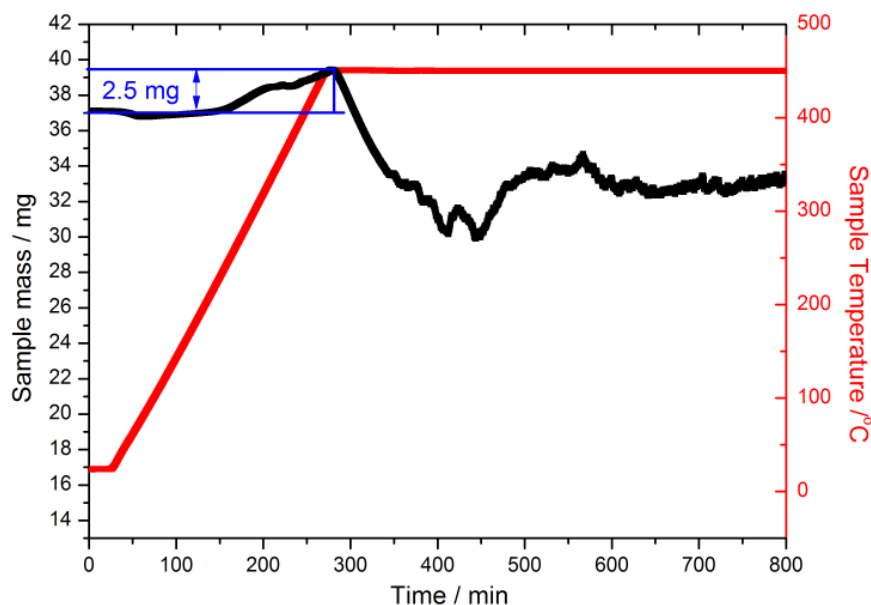


Figure 7.19 The temperature (red) and mass (black) of a sample of majority $\text{LiK}(\text{BH}_4)_2$ as a function of time

An increase in mass of the sample was observed during sample heating (to 450 °C). This mass gain of approximately 2.5 mg (6.7 wt%) was most likely due to instrumental buoyancy corrections relating to heating within a flowing gas system, in particular changes in density of the flow gas and the sample and is not thought to be associated with any mass uptake by the sample. This phenomenon has also been observed elsewhere with other borohydrides^[94] and unfortunately complicates data interpretation. Comparison of the observed mass loss data with the $m/z = 2$ mass spectrum (Figure 7.20) indicates where we may expect mass loss due to sample decomposition and hence evolution of hydrogen. However, the small masses involved and the buoyancy of the sample mean that we do not always observe a decrease in mass.

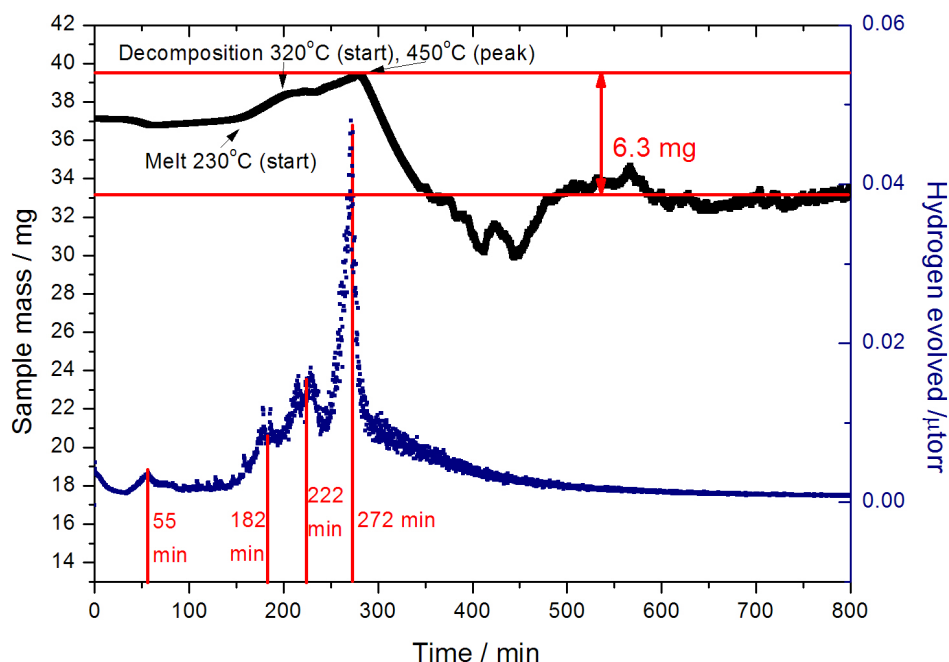


Figure 7.20 Mass loss (black) and hydrogen evolved (blue) as a function of time from the sample of majority $\text{LiK}(\text{BH}_4)_2$. Hydrogen evolution peaks are labelled in addition to the mass loss and the proposed melting and decomposition temperatures.

Figure 7.20 shows that the mass spectrometer detected hydrogen evolutions peaking at 70 °C (55 minutes), 285 °C (182 minutes), 358 °C (222 minutes) and 450 °C (270 minutes). The first hydrogen evolution (70 °C) was small and coincided with a small mass loss (0.33 mg, 0.9 %) which is made evident by looking at the first derivative of the sample mass as a function of temperature (Figure 7.21).

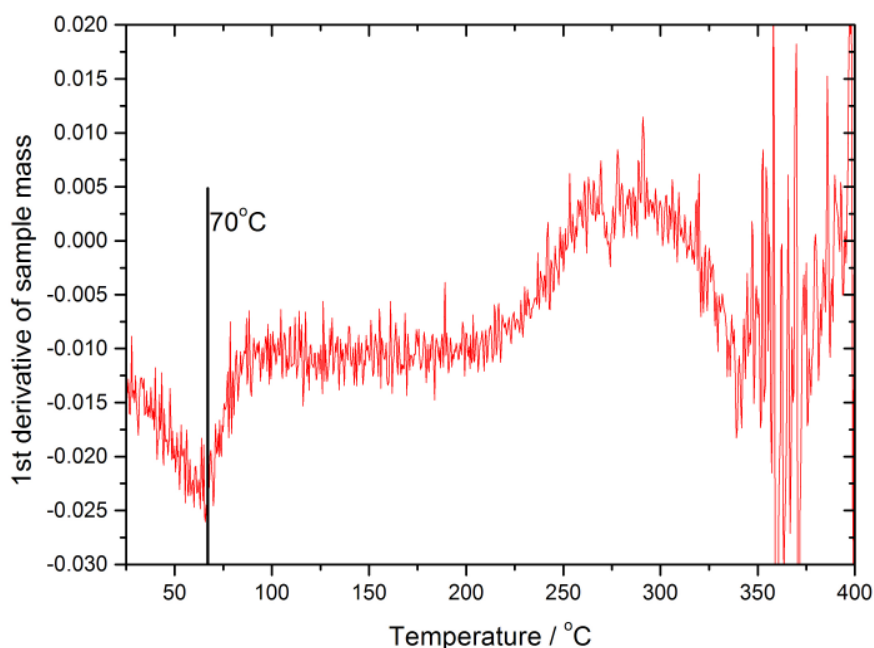


Figure 7.21 The first derviative of the sample mass as a function of temperature whilst heating the sample from room temperature to 400 °C

The following two hydrogen releases (between 230 °C and 320 °C and between 320 °C and 400 °C), occurred in two stages. The first hydrogen release was centred around 182 minutes, 285 °C and coincided with an increase in the rate of mass increase. The second hydrogen release was centred around 222 minutes, 358 °C and coincided with a plateau in the sample mass. These mass changes are shown in a larger scale plot of the sample mass and hydrogen evolution from 100 to 300 minutes into the experiment (Figure 7.22). A small amount of BH_3 was released beginning at 200 minutes (Figure 7.23).

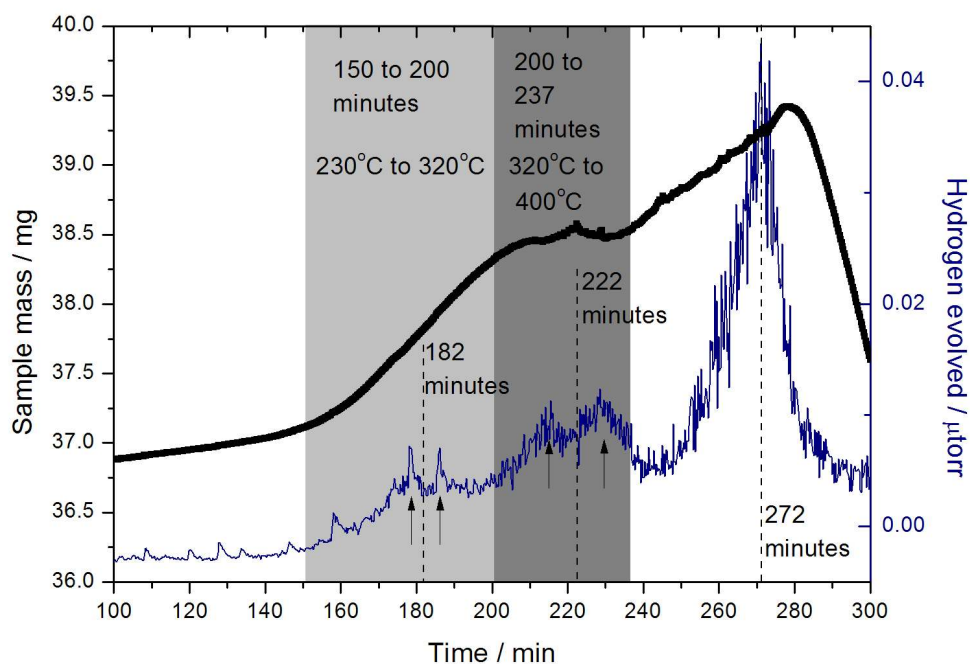


Figure 7.22 Larger scale plot of the mass (black) and hydrogen evolved (blue) from a sample of majority $\text{LiK}(\text{BH}_4)_2$ between 100 and 300 minutes into the experiment showing the correlation between hydrogen evolutions and changes in sample mass behaviour.

The peak of the largest hydrogen evolution and the onset of mass loss were observed at 272 minutes just as the sample temperature reached 450°C . A small amount of B_2H_6 was also evolved around this time (Figure 7.23). The mass loss at this stage was 6.3 mg (16 %). Further mass gain was observed between 400 and 600 minutes into the experiment when the temperature was constant.

By normalising the area under the B_2H_6 peak between 260 and 310 minutes in Figure 7.23 to 1, the approximate areas under the gas evolution peaks can be compared, as shown in Table 7.9. The area under the main hydrogen evolution peak beginning at 240 minutes is nearly 10^4 times larger than the area under the B_2H_6 peak.

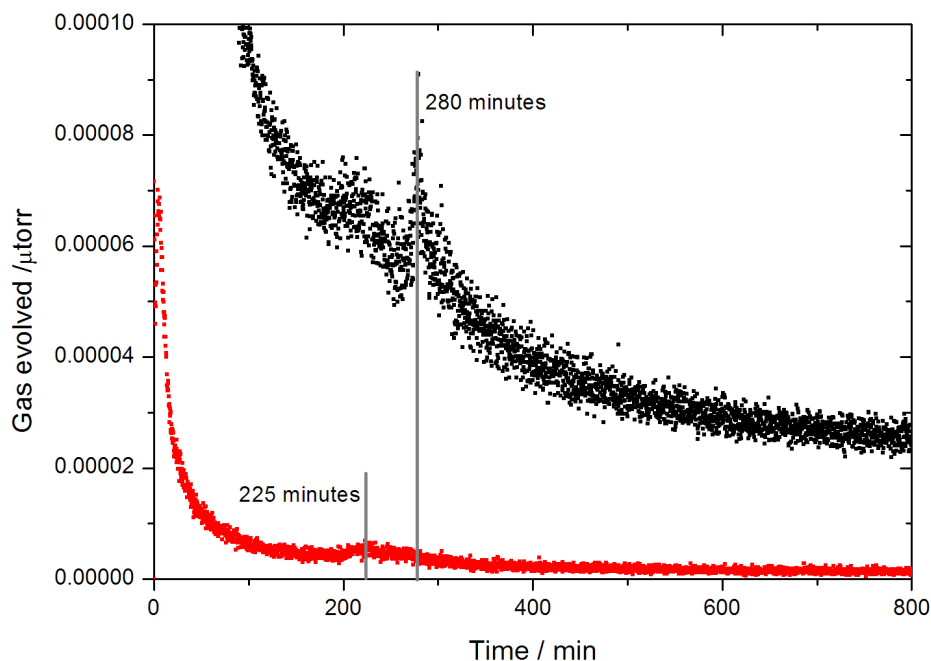


Figure 7.23 Evolution of B_2H_6 (black) and BH_3 (red) from the sample of majority $LiK(BH_4)_2$ as a function of time

Table 7.9 Normalised areas under gas evolution curves

Gas	Time peak start / min	Time peak at maximum/ min	Time peak end / min	Peak area normalised to B_2H_6
BH_3	200	225	270	0.6
B_2H_6	260	280	310	1
H_2	33	55	91	240
H_2	144	182	200	2430
H_2	200	222	237	4200
H_2	240	272	300	9600
H_2 (shoulder of peak)	300		800	3700

7.8.3 Thermogravimetric analysis under flowing argon

A thermogravimetric analysis (TGA) study of $\text{LiK}(\text{BH}_4)_2$ was also completed under flowing argon using a 8.4 mg sample of majority $\text{LiK}(\text{BH}_4)_2$ with minority LiBH_4 and KBH_4 impurities (70.2 wt% $\text{LiK}(\text{BH}_4)_2$, 2.7 wt% LiBH_4 and 26.4 wt% KBH_4) as determined by X-ray powder diffraction (from the same sample as was used in Section 7.8.2). The sample was analysed using the TGA aspect of a Perkin Elmer STA6000 simultaneous thermogravimetric analyser and differential scanning calorimeter (see Chapter 2) under 1 bar flowing argon, heating from 30 °C to 650 °C at 5 °C/min. The sample mass as a function of temperature is shown in Figure 7.24.

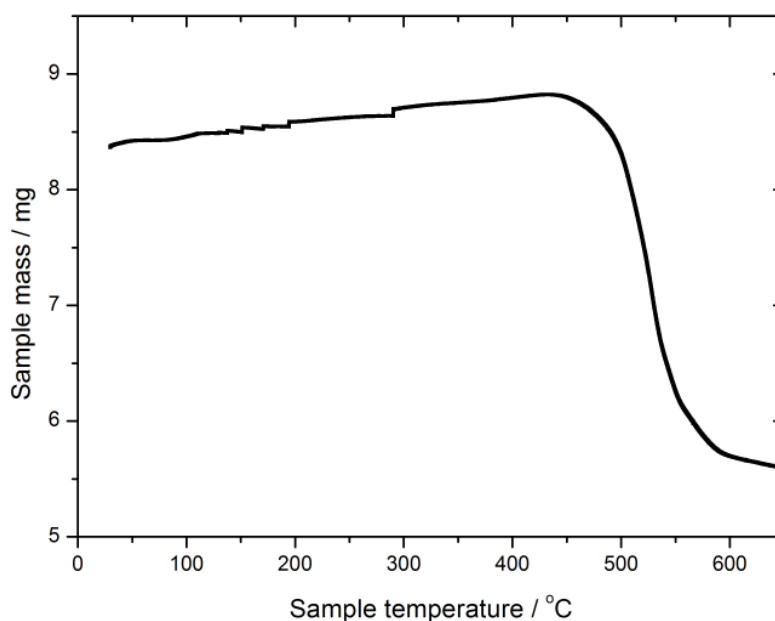
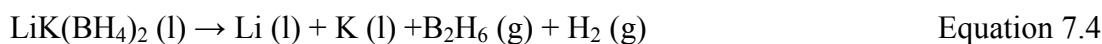
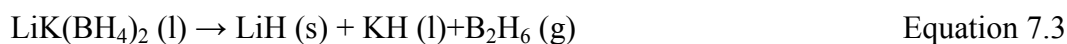
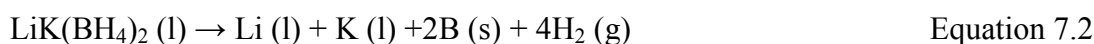
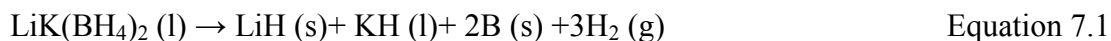


Figure 7.24 The mass of a sample of majority $\text{LiK}(\text{BH}_4)_2$ as a function of temperature during a TGA experiment under flowing argon.

Mass loss began at 440 °C. The sample lost 3.1 mg, 35 wt% by 595 °C when the rate of mass loss decreased. The step in the sample mass at 290 °C is likely to be associated with decomposition of the LiBH_4 impurity.

7.8.4 Thermogravimetric analysis conclusion

Alkali metal borohydrides are generally thought to release hydrogen on decomposition forming either the metal hydride or metal.^[19] Zinc, manganese and aluminium borohydrides, on the other hand, release B₂H₆ on decomposition.^[92, 93] LiK(BH₄)₂ can be imagined to decompose by four distinct mechanisms to either LiH and KH or elemental lithium and potassium releasing either B₂H₆ or H₂. Alternatively, LiK(BH₄)₂ could decompose to LiBH₄ and KBH₄ which then decompose individually resulting in the same total mass loss as for direct decomposition.



If LiK(BH₄)₂ decomposed to the metal hydrides and boron, releasing hydrogen according to Equation 7.1, the expected mass loss would be 8 wt%. Decomposition to the elements according to Equation 7.2 would result in an expected mass loss of 10.6 wt%. Decomposition of LiK(BH₄)₂ releasing B₂H₆ according to Equation 7.3 would result in 36.5 % of the mass being lost. If hydrogen and B₂H₆ were released according to Equation 7.4, the mass loss would be 39 wt%.

Elemental lithium and potassium are both liquid by 400 °C (melting temperatures are 180.5 °C and 63.4 °C respectively^[77]) so there is potential for evaporation from liquid samples after decomposition, particularly when under dynamic vacuum. LiH does not melt until 689 °C but KH melts and decomposes at 417 °C.^[77]

Under dynamic vacuum, the majority LiK(BH₄)₂ sample lost mass in two nearly equal stages beginning at 225 °C (47 wt%) and 380 °C (41 wt%). At the end of the

experiment, only 12 wt% of the starting mass of the sample remained. $\text{LiK}(\text{BH}_4)_2$ contains 10.6 wt% H_2 so this mass loss is not only due to hydrogen evolution suggesting that the sample may have melted and then evaporated under the dynamic vacuum.

Under flowing helium, there were hydrogen gas evolutions at 70 °C, 230 °C to 320 °C, 320 °C to 400 °C and 400 °C to 450 °C. The first three hydrogen evolutions corresponded to a small mass loss at 70 °C (0.33 mg, 0.9 wt%), an increase in the rate of mass increase at 230 °C and a plateau in the sample mass at 320 °C. BH_3 was also detected by the mass spectrometer beginning at 318 °C. The final hydrogen evolution peaked at 450 °C when the main mass loss of 6.3 mg (16 wt%) began. A small quantity of B_2H_6 was also detected by the mass spectrometer. The observation of the release of a small amount of BH_3 and B_2H_6 suggests a combination of decomposition routes account for the mass loss observed. The 16 wt% mass loss is greater than is possible due only to hydrogen release but the majority of the evolved gas is still hydrogen. Significant decomposition of B_2H_6 begins at approximately 150 °C to BH_3 and other B_xH_y compounds^[129] so it is possible that more B_2H_6 was released than was observed due to its rapid decomposition at 450 °C.

Under flowing argon, the sample of majority $\text{LiK}(\text{BH}_4)_2$ lost 35 wt% beginning at 440 °C. This is close to the mass loss of 36.5 wt% expected if the sample decomposed according to Equation 7.3.

A possible order of events could be as follows, the key thermal events and their observed temperatures under the different experimental conditions are summarised in Table 7.10.

Under dynamic vacuum, $\text{LiK}(\text{BH}_4)_2$ melted at 225 °C, resulting in significant evaporation and weight loss of sample and then decomposed from 380 °C.

Under flowing helium, a small amount (0.9 %) of residual solvent (potentially tetrahydrofuran) was lost at 70 °C. $\text{LiK}(\text{BH}_4)_2$ began to melt under flowing helium at 230 °C, the increase in density associated with melting combined with the instrumental buoyancy effects to create an apparent mass increase. Hydrogen evolution associated with melting peaked at 285 °C. Under flowing helium, decomposition occurred in two stages, the first stage between 320 °C and 400 °C, peaking at 358 °C resulted in hydrogen and BH_3 ($\text{H}_2:\text{BH}_3$ 4200:0.6) evolution. The mass loss due to decomposition combined with the apparent mass gain due to instrumental effects to create a plateau in the sample mass. A second, faster stage of decomposition then began from 400 °C, peaking at 450 °C where B_2H_6 was released in addition to hydrogen. This is analogous to the decomposition of LiBH_4 which decomposes in two stages at 300 °C and 380 °C (see Chapter 4).^[37]

Under flowing argon decomposition occurred at 440 °C which is higher than observed under flowing helium due to the increased sample heating rate.

It is possible that the decomposition of $\text{LiK}(\text{BH}_4)_2$ occurs in multiple stages under all of the experimental conditions but the individual stages can only be identified by the detection of gas evolution by the mass spectrometer. Alternatively, the different environmental conditions may result in slightly different decomposition routes of $\text{LiK}(\text{BH}_4)_2$, (occurring in a single stage under vacuum and two stages under helium pressure). Different decomposition routes under different environmental conditions have previously been observed for NaNH_2 which decomposes to sodium or sodium hydride depending on whether the system pressure is above or below the decomposition temperature of NaH .^[186]

Table 7.10 The temperature / °C when various thermal events were observed to begin under different experimental conditions

Event	Experimental conditions, (atmosphere, heating rate)		
	Dynamic vacuum, 2 °C/min	Flowing helium, 2 °C/min	Flowing argon, 5 °C /min
Solvent loss		70	
Melting	225	230	
Decomposition 1		320	
Decomposition 2	380	400	440

$\text{LiK}(\text{BH}_4)_2$ is observed to melt before it decomposes forming a liquid composed of lithium, potassium and borohydride ions. This melting could occur congruently to directly form the liquid or incongruently so that LiBH_4 melts out of the compound leaving KBH_4 to dissolve into the liquid LiBH_4 before KBH_4 also melts. It is not possible to determine from this experiment if melting was congruent or incongruent. $\text{LiK}(\text{BH}_4)_2$ could only decompose by division into LiBH_4 and KBH_4 with subsequent independent decomposition of the two phases, if melting occurred incongruently and the LiBH_4 part of the sample decomposed before the remaining KBH_4 melted.

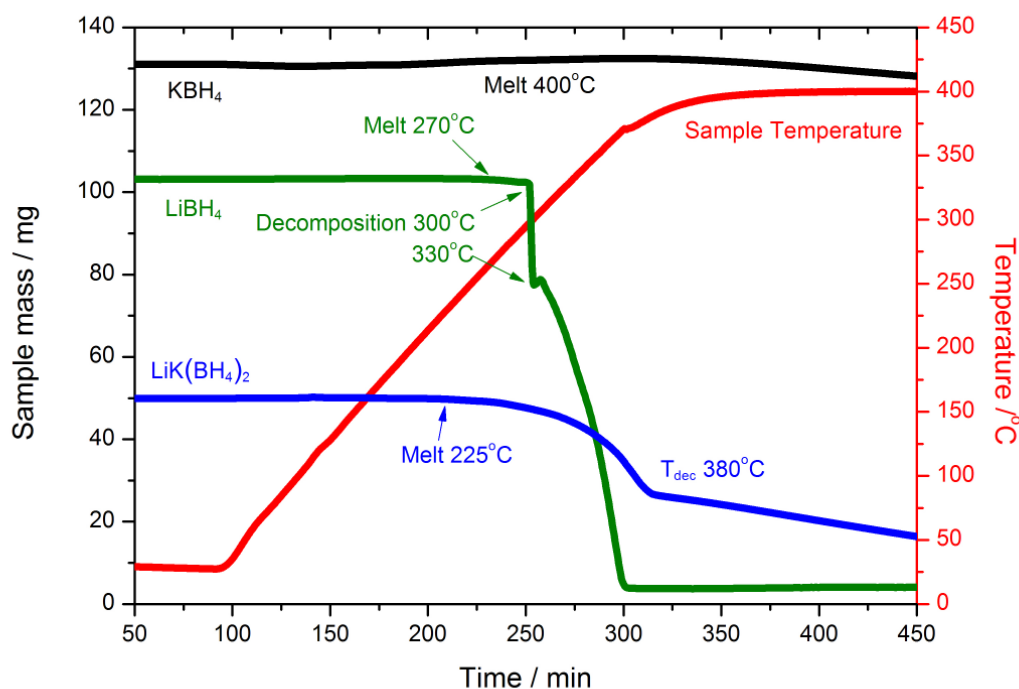


Figure 7.25 Thermogravimetric data and sample temperature plotted as a function of time for LiBH₄ (green), KBH₄ (black) and majority LiK(BH₄)₂ (blue) for experiments carried out under dynamic vacuum.

Figure 7.25 shows the mass loss for LiBH₄, KBH₄ and LiK(BH₄)₂ as a function of time under the same conditions (heating to 400 °C at 2 °C/min under dynamic vacuum). LiK(BH₄)₂ appears to have a reduced melting point (225 °C) compared to LiBH₄ and an intermediate decomposition temperature (380 °C) compared to its parent compounds, LiBH₄ (melts 270 °C and decomposes 300 °C and 330 °C) and KBH₄ (melts 400 °C), however ideally, this should be further investigated. The mass changes in the LiBH₄ and KBH₄ samples do not appear to have corresponding mass changes in the majority LiK(BH₄)₂ sample, however the presence of LiBH₄ and KBH₄ impurities may affect the temperatures at which thermal events for LiK(BH₄)₂ are observed.

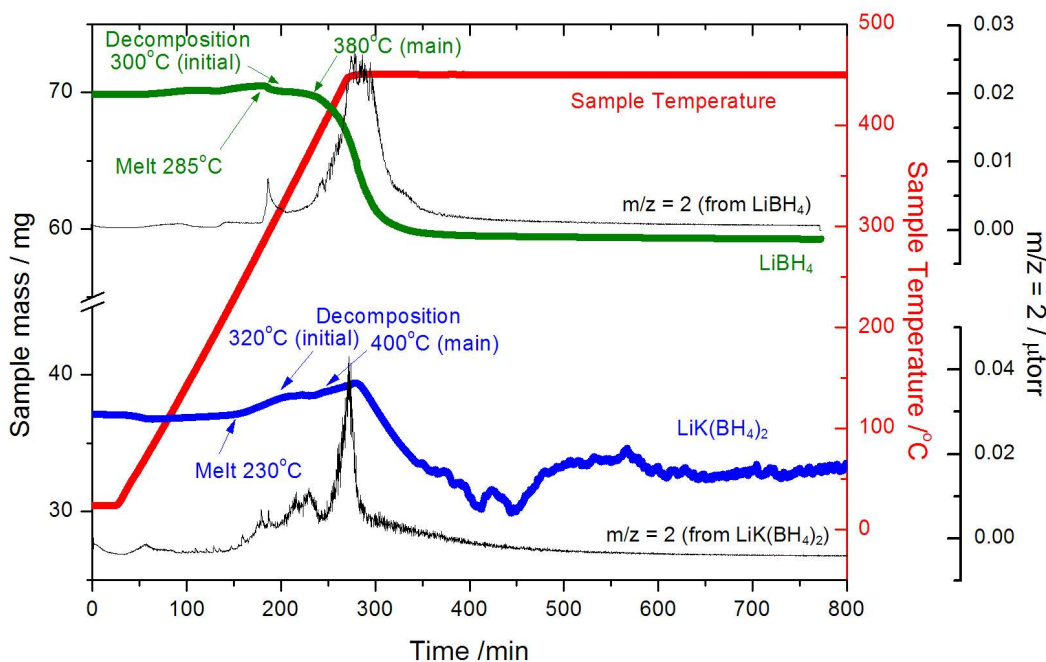


Figure 7.26 Sample mass (green /blue), temperature (red) and hydrogen evolution (black) plotted as a function of time for LiBH_4 and majority $\text{LiK}(\text{BH}_4)_2$ for an experiment carried out under flowing helium.

Figure 7.26 shows a comparison of the mass loss of LiBH_4 and $\text{LiK}(\text{BH}_4)_2$ as a function of time under the same conditions (flowing helium, heating to 450 °C at 2 °C/min). The events from the LiBH_4 experiment do not appear to have corresponding events in the $\text{LiK}(\text{BH}_4)_2$ experiment although the decomposition temperatures are similar. KBH_4 does not decompose until higher temperatures than were possible in this experiment. However, the presence of LiBH_4 and KBH_4 impurities may still affect the temperatures at which thermal events for $\text{LiK}(\text{BH}_4)_2$ are observed. LiBH_4 melts at 285 °C and then loses mass and evolves hydrogen in two stages, the first beginning at 300 °C and the second main step begins at 380 °C. $\text{LiK}(\text{BH}_4)_2$ also loses mass and evolves hydrogen in two stages the first between 320 °C and 400 °C and the second larger step begins at 400 °C and peaks at 450 °C. There is no clear evidence of $\text{LiK}(\text{BH}_4)_2$ decomposing to LiBH_4 and KBH_4 .

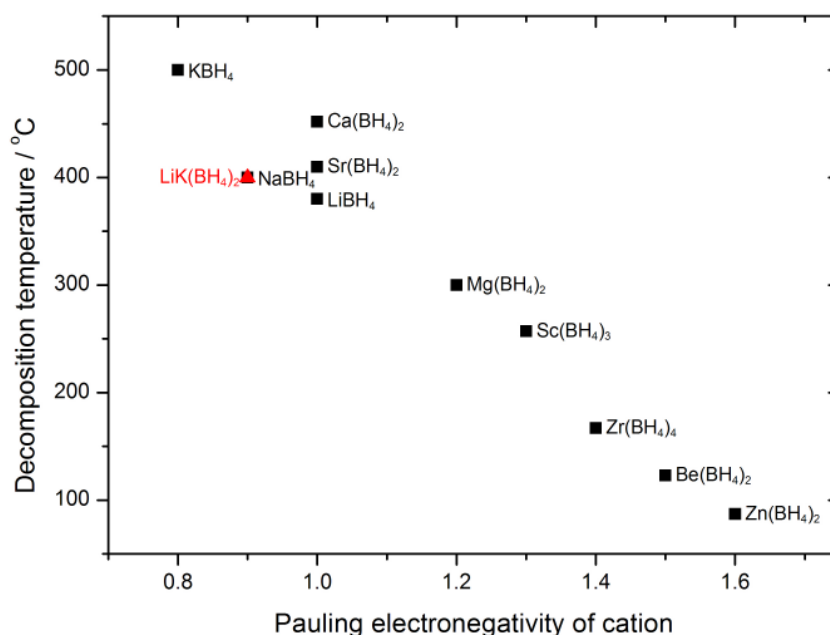


Figure 7.27. A plot of thermal decomposition temperature at 1 bar vs. Pauling electronegativity for a number of borohydrides including $\text{LiK}(\text{BH}_4)_2$

Based on the work of Nakamori *et al.* which established a correlation between the Pauling electronegativity of the cation of a borohydride and both its formation enthalpy and decomposition temperature,^[60] $\text{LiK}(\text{BH}_4)_2$ was compared to other borohydrides. Figure 7.27 shows a comparison of the thermal decomposition temperature with the Pauling electronegativity for $\text{LiK}(\text{BH}_4)_2$ and a number of other common borohydride materials using decomposition temperatures from the literature.^[19, 25, 30, 92, 125] The trend using values from this thesis is shown in Chapter 10. The average electronegativity of lithium and potassium was used for $\text{LiK}(\text{BH}_4)_2$. It can be seen that the data for $\text{LiK}(\text{BH}_4)_2$ fit well with the correlation identified by Nakamori *et al.*, in between that for lithium and potassium and directly on top of NaBH_4 .

Decomposition of borohydride compounds generally involves breaking B-H bonds. The stability of a borohydride compound is dependent on the stability of the borohydride ion within its structure and the stability of the borohydride ion is related to the strength of the B-H bonds within the borohydride ion. The negative charge on the borohydride ion is necessary in order to stabilise the four B-H bonds (boron only having three valence electrons). The amount of negative charge on the borohydride ion will be influenced by the electronegativity of the cation, a more electronegative cation will reduce the negative charge on the borohydride ion, destabilising the B-H bonds and consequently the entire complex.^[143]

In a series of borohydrides, as the electronegativity of the metal cation increases, its increasing affinity to an electron results in an increasing affinity to a hydrogen atom; the metal becomes more basic. If the metal is too basic, it will force boron to act as an acid, releasing a hydrogen atom. The metal will form a hydride and consequently the borohydride will have decomposed.

7.9 Conclusions

$\text{LiK}(\text{BH}_4)_2$ has been synthesised from LiBH_4 and KBH_4 . The structure of $\text{LiK}(\text{BH}_4)_2$ is orthorhombic with a $Pnma$ space group. At room temperature from synchrotron X-ray powder diffraction, the unit cell parameters were determined to be $a = 7.91327(4) \text{ \AA}$, $b = 4.49061(2) \text{ \AA}$, $c = 13.84313(7) \text{ \AA}$ and $V = 491.921(4) \text{ \AA}^3$. $\text{LiK}({}^{11}\text{BD}_4)_2$ was also synthesised at room temperature, from neutron diffraction data, the unit cell parameters were determined to be $a = 7.8874(19) \text{ \AA}$, $b = 4.4816(11) \text{ \AA}$, $c = 13.7400(13) \text{ \AA}$ and $V = 485.68(17) \text{ \AA}^3$. Theoretical calculations by Kim and Scholl found the optimised lattice parameters to be $a = 7.78 \text{ \AA}$, $b = 4.43 \text{ \AA}$, $c = 13.72 \text{ \AA}$ and $V = 473.4 \text{ \AA}^3$ ^[75]. The volume reported by Kim and Scholl is 96 % of the volume determined by synchrotron X-ray diffraction. Similarly, Xiao *et al.* calculated the lattice parameters to be $a = 7.8240 \text{ \AA}$, $b = 4.4263 \text{ \AA}$ and $c = 13.6950 \text{ \AA}$ ^[88], resulting in a volume of $474.28 \text{ \AA}^3$. These differences in volume between the experimental and DFT-optimised structures have also been seen in other borohydrides.^[75]

LiBH_4 and $\text{LiK}(\text{BH}_4)_2$ both have the space group $Pnma$. The size of the b lattice parameter is very similar in the crystal structure of the two compounds ($4.49061(2) \text{ \AA}$ and $4.43686(2) \text{ \AA}$ ^[51] for $\text{LiK}(\text{BH}_4)_2$ and LiBH_4 respectively). The b lattice parameters also show similar behaviour with varying temperature, both decreasing with increasing temperature above approximately 50°C . Interestingly, the space group and b lattice parameter are also shared by $\text{LiBH}_4\cdot\text{NH}_3$ ($Pnma$, $a = 5.96910(3) \text{ \AA}$, $b = 4.46355(2) \text{ \AA}$, $c = 14.34199(8) \text{ \AA}$, $V = 382.119(2) \text{ \AA}^3$). In this compound the b lattice parameter increases with increasing temperature from room temperature to 40°C but then remains constant until 50°C when the measurement was stopped^[187]. It seems that when the LiBH_4 structure is expanded to accommodate other ions, it has a

tendency to keep the b lattice parameter relatively constant and also retains the anisotropic thermal expansion behaviour relating to the b axis. The size of the b axis in both LiBH_4 and $\text{LiK}(\text{BH}_4)_2$ is determined by the diameter of two borohydride ions, in $\text{LiBH}_4 \cdot \text{NH}_3$ the size of the b axis is determined by the diameter of a borohydride ion and an ammonia molecule.

Unlike LiBH_4 , $\text{LiK}(\text{BH}_4)_2$ does not undergo an orthorhombic to hexagonal phase transition. In LiBH_4 , this transition is a result of the unfolding of layers of hexagonal frameworks of lithium and boron atoms in the ab plane, resulting in a higher density structure (see Chapter 4). In $\text{LiK}(\text{BH}_4)_2$, the rearrangement of ions due to the insertion of potassium ions has made these layers less well defined. Metal - boron bond lengths are not longer between the layers than between layers. The increased co-ordination number of the borohydride ions from four in LiBH_4 to five and six in $\text{LiK}(\text{BH}_4)_2$ strengthens the connections between the layers and stabilises the observed orthorhombic structure compared to a possible hexagonal structure.

Xiao *et al.* found the borohydride ions in $\text{LiK}(\text{BH}_4)_2$ to be much closer to an ideal tetrahedral shape than the experimental studies with bond lengths and angles ranging from 1.2237 Å to 1.2272 Å and 105.85° to 111.66°.^[88] The unconstrained model determined from the synchrotron X-ray powder diffraction study had B-H bond lengths in the range of 1.013(18) Å to 1.148(18) Å and H-B-H angles in the range 102.1(14)° to 113(2)°. In the constrained model the B-H bond length was 1.18(2) Å and the H-B-H bond angles were constrained to 109.5°. However, it is likely that the borohydride ions are disordered making it difficult to determine reliable measurements.

The highest proportion of $\text{LiK}(\text{BH}_4)_2$ obtained in a reaction was 70 wt% achieved by heating a mixture with a starting ratio of 2:1 LiBH_4 : KBH_4 to 125 °C. If the starting

ratio is 2:1 LiBH_4 : KBH_4 , it is not possible to produce more than 78 wt% $\text{LiK}(\text{BH}_4)_2$ due to the excess LiBH_4 in the starting mixture. Therefore, the effective yield of $\text{LiK}(\text{BH}_4)_2$ was 90 %. In the case of $\text{LiK}(^{11}\text{BD}_4)_2$ the reaction mixture had to be heated to 200 °C in order for $\text{Li}^{11}\text{BD}_4$ and K^{11}BD_4 to react. The higher reaction temperature required for the deuterated compounds may be the result of the effect of the isotopic substitution on the B-H/D bond vibrations. Raman studies of LiBH_4 and KBH_4 (see Chapters 4 and 6) show that the vibration frequency of the $^{11}\text{B-D}$ bond is approximately a factor of $\sqrt{2}$ lower than that of a B-H bond due to the increased mass of deuterium compared to hydrogen (see Chapter 2). This may affect the effective size and mobility of the borohydride ion and also the mobility of cations past the borohydride ion.

It was also possible to synthesise $\text{LiK}(^{11}\text{BD}_4)_2$ directly from the elements as predicted by Xiao *et al.*^[88] Xiao *et al.* calculated that the enthalpy of reaction for the formation of $\text{LiK}(\text{BH}_4)_2$ from the elements (Equation 7.5) is $-449.8 \text{ kJ mol}^{-1}$, whereas the enthalpy for formation from LiBH_4 and KBH_4 (Equation 7.6) is only about -0.6 kJ mol^{-1} . This suggests that formation from the elements should be the easiest synthetic route but does not include any kinetic considerations.^[88]



The preference for a 2:1 LiBH_4 : KBH_4 starting ratio may be due to LiBH_4 acting as a solvent as well as a reagent. (At 125 °C the sample was observed to be liquid.) However, if LiBH_4 was only acting as a solvent, only an excess of LiBH_4 would be required rather than the precise 2:1 ratio observed. Alternatively, all of the borohydride ions for $\text{LiK}(\text{BH}_4)_2$ may be coming from LiBH_4 with KBH_4 only supplying the potassium ions. The variable temperature X-ray diffraction study of a

mixture of $\text{LiK}({}^{11}\text{BD}_4)_2$, $\text{Li}^{11}\text{BD}_4$ and K^{11}BD_4 showed the $\text{Li}^{11}\text{BD}_4$ lattice parameters to be expanded compared to a pure sample. In general, expanded lattice parameters suggest the insertion of a new ion into a crystal structure. In this case, potassium ions could be inserted into the LiBH_4 structure. The precise 2:1 LiBH_4 : KBH_4 ratio is more consistent with all of the borohydride ions coming from LiBH_4 and potassium ions moving into the expanding structure. In future, this hypothesis could be tested by attempting the synthesis of $\text{LiK}(\text{BH}_4)_2$ from LiBH_4 and either metallic potassium or a compound containing potassium ions such as a potassium halide.

Under dynamic vacuum, $\text{LiK}(\text{BH}_4)_2$ was observed to have a reduced melting point ($225\text{ }^\circ\text{C}$) compared to LiBH_4 and an intermediate decomposition temperature ($380\text{ }^\circ\text{C}$) compared to its parent compounds; LiBH_4 melted at $270\text{ }^\circ\text{C}$ and decomposed in two stages at $300\text{ }^\circ\text{C}$ and $330\text{ }^\circ\text{C}$ and KBH_4 melted at $400\text{ }^\circ\text{C}$. Under flowing helium, $\text{LiK}(\text{BH}_4)_2$ began to melt at $230\text{ }^\circ\text{C}$ (LiBH_4 melted at $285\text{ }^\circ\text{C}$) and decomposition occurred in two stages, the first between $320\text{ }^\circ\text{C}$ and $400\text{ }^\circ\text{C}$, peaking at $358\text{ }^\circ\text{C}$ and the main decomposition step occurred from $400\text{ }^\circ\text{C}$, peaking at $450\text{ }^\circ\text{C}$. (LiBH_4 decomposed in two stages at $300\text{ }^\circ\text{C}$ and at $380\text{ }^\circ\text{C}$.) A small amount of B_2H_6 and BH_3 were evolved but the majority of the gas released was hydrogen. Under flowing argon, mass loss was not observed until $440\text{ }^\circ\text{C}$ but the delay in decomposition is likely due to the increased heating rate. After decomposition, no crystalline products were detected by X-ray diffraction. The melting of $\text{LiK}(\text{BH}_4)_2$ may have been congruent or incongruent. If $\text{LiK}(\text{BH}_4)_2$ forms by potassium ions inserting into liquid LiBH_4 then an incongruent melting would seem likely.

During the variable temperature X-ray diffraction experiment, Bragg peaks relating to $\text{LiK}({}^{11}\text{BD}_4)_2$ were observed to disappear at $93\text{ }^\circ\text{C}$ and Bragg peaks relating to $\text{Li}^{11}\text{BD}_4$ disappeared at $112\text{ }^\circ\text{C}$. These temperatures are much lower than observed in the

thermogravimetric analysis of $\text{LiK}(\text{BH}_4)_2$ and LiBH_4 . This may be an effect of isotopic substitution in the samples or due to the much larger proportions of $\text{Li}^{11}\text{BD}_4$ and K^{11}BD_4 present in the sample.

The decomposition temperature of $\text{LiK}(\text{BH}_4)_2$ is intermediate to those of LiBH_4 and KBH_4 which is consistent with its intermediate “average electronegativity” and the correlation between Pauling electronegativity and decomposition temperature established by Nakamori *et al.*^[60] It was not possible to purify $\text{LiK}(\text{BH}_4)_2$ so all of the samples discussed contain LiBH_4 and KBH_4 which may have affected the temperatures at which thermal events are observed to occur.

Kim and Sholl’s calculations suggested that $\text{LiK}(\text{BH}_4)_2$ is unstable towards decomposition into LiBH_4 and KBH_4 at nearly all temperatures. Consequently they predict that the decomposition route will be to the parent compounds which will then decompose independently.^[75] However, given that $\text{LiK}(\text{BH}_4)_2$ is known to melt before decomposition, decomposition to LiBH_4 and KBH_4 would only be possible if $\text{LiK}(\text{BH}_4)_2$ melted incongruently. The decomposition temperature of $\text{LiK}(\text{BH}_4)_2$ is intermediate to those of LiBH_4 and KBH_4 , so there is no clear evidence of decomposition to LiBH_4 and KBH_4 .

The thermodynamics of a decomposition reaction can be described by $\Delta G = \Delta H - T\Delta S$, when a material decomposes, $\Delta G = 0$ so $\Delta H = T\Delta S$. The entropy changes during the decomposition of $\text{LiK}(\text{BH}_4)_2$, LiBH_4 and KBH_4 are mainly related to hydrogen release so the values will all be similar and are estimated by Xiao *et al.* to be in the range of $95 \leq \Delta S \leq 140 \text{ J K}^{-1} \text{ mol}^{-1}$. Consequently, the decomposition temperature will be approximately proportional to the enthalpy change of decomposition. Xiao *et al.* calculated the enthalpies of decomposition to the elements to be $112.5 \text{ kJ (mol H}_2\text{)}^{-1}$, $103.6 \text{ kJ (mol H}_2\text{)}^{-1}$ and $120.8 \text{ kJ (mol H}_2\text{)}^{-1}$ for $\text{LiK}(\text{BH}_4)_2$, LiBH_4 and KBH_4

respectively. Therefore, the decomposition temperature of $\text{LiK}(\text{BH}_4)_2$ is expected to be in between that of LiBH_4 and KBH_4 .^[88]

In general, the properties of $\text{LiK}(\text{BH}_4)_2$ are similar to LiBH_4 rather than KBH_4 . Essentially $\text{LiK}(\text{BH}_4)_2$ acts like an expanded form of LiBH_4 which contains potassium ions. LiBH_4 and $\text{LiK}(\text{BH}_4)_2$ share the same space group and have a very similar *b* lattice parameter. Both compounds show anisotropic thermal expansion with their *b* lattice parameters decreasing with increasing temperature and both compounds decompose in two stages. However, unlike LiBH_4 , $\text{LiK}(\text{BH}_4)_2$ does not have an orthorhombic to hexagonal phase transition. Solid state ^{11}B NMR is the only analysis which has shown $\text{LiK}(\text{BH}_4)_2$ to be similar to KBH_4 because the boron atoms in both compounds are surrounded by a similar number of metal cations.

The first mixed alkali metal borohydride, $\text{LiK}(\text{BH}_4)_2$, has been synthesised and has a structure closely related to that of orthorhombic LiBH_4 and a decomposition temperature that is intermediate between those of the congener compounds. This approach illustrates a viable general route to the chemical control of the desorption temperatures of complex hydrides.

8 Calcium borohydride

8.1 Chapter focus

The focus of this chapter is a new, temperature-resolved high-resolution X-ray diffraction study of the polymorphs and phase transformations of calcium borohydride, $\text{Ca}(\text{BH}_4)_2$, including structure solutions for the α -, α' - and β - $\text{Ca}(\text{BH}_4)_2$ polymorphs. Thermogravimetric analyses of $\text{Ca}(\text{BH}_4)_2$ both under dynamic vacuum and under flowing helium coupled to a mass spectrometer were also conducted.

8.2 Synthesis

Calcium borohydride was synthesised by heating calcium borohydride bistetrahydrofuran powder, $\text{Ca}(\text{BH}_4)_2 \cdot 2\text{THF}$ (Sigma Aldrich) to 160 °C in a vertical tube furnace, under dynamic vacuum (base pressure 10^{-6} mbar) for one hour. An increase in pressure was observed during the heating as the coordinating solvent, tetrahydrofuran, was evolved. The reaction was deemed complete when a vacuum of 10^{-6} mbar had been re-established.

Elemental analyses performed by Dr Stephen Boyer at the Elemental Analysis service at London Metropolitan University showed the sample to contain 1 % carbon suggesting that a minimal amount of solvent was retained within the powder.

8.3 Room temperature X-ray diffraction

Synchrotron X-ray powder diffraction data at room temperature were collected on the sample in a sealed capillary on the high-resolution ID31 diffractometer at the ESRF, Grenoble at a wavelength and step size of 0.79825 Å and 0.004° respectively. The diffraction data were analysed and structural models were refined by the Rietveld method using the profile refinement program TOPAS-Academic.^[167]

At room temperature, the data show the presence of two distinct structures which were identified as orthorhombic α -Ca(BH₄)₂, and tetragonal β -Ca(BH₄)₂. The structure of α -Ca(BH₄)₂ was refined starting from the structure proposed by Miwa *et al.*^[99] in the space group *Fddd*. The structure of β -Ca(BH₄)₂ was refined starting from the structure proposed by Buchter *et al.*^[101] in the space group *P4₂/m*. Both structures were refined using two different structural models. In one model, the positions of the hydrogen atoms were allowed to refine unconstrained, in the second model the hydrogen positions were constrained to form an ideal tetrahedral shape around the boron atom using a rigid body model. A typical plot of the refined data for α -Ca(BH₄)₂ and β -Ca(BH₄)₂ is shown in Figure 8.1. The refined crystallographic parameters using unconstrained atomic positions are presented in Table 8.1 and the refined crystallographic parameters using a constrained tetrahedral rigid body model for the borohydride ion are shown in Table 8.2.

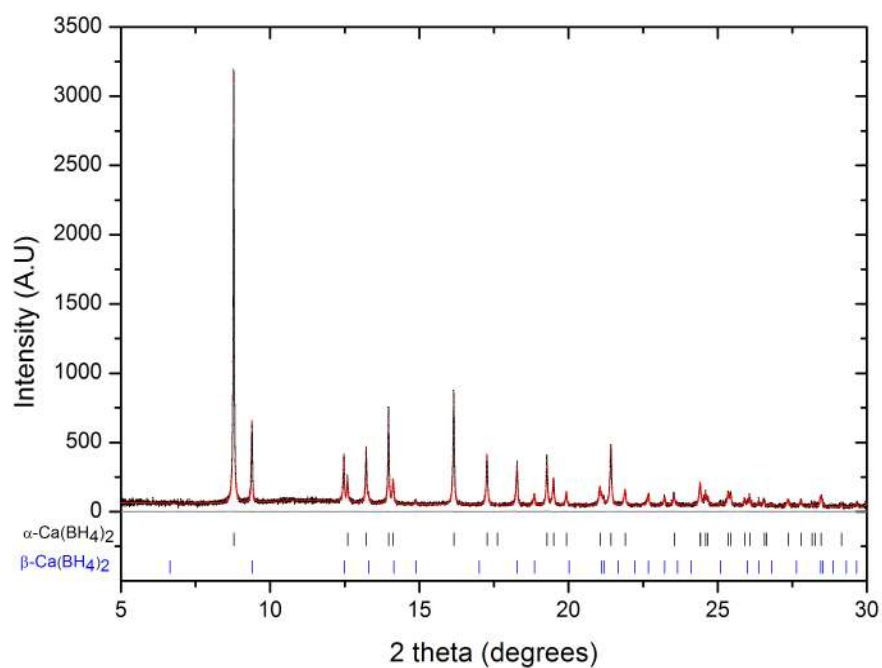


Figure 8.1 The observed (black), calculated (red) and difference plots ($Y_{obs} - Y_{calc}$, grey) for the structure refinement of $\alpha\text{-Ca(BH}_4)_2$ and $\beta\text{-Ca(BH}_4)_2$ from X-ray synchrotron diffraction data at 20 °C. The Bragg peak positions for both structures are indicated by the vertical tick marks.

Table 8.1 Refined crystallographic parameters for α -Ca(BH₄)₂ and β -Ca(BH₄)₂ at room temperature using unconstrained atomic positions

$R_{wp} = 7.95\%$, $R_{exp} = 5.90\%$, $\chi^2 = 1.8$

α -Ca(BH₄)₂ $Fddd$

$a = 8.77632(12) \text{ \AA}$, $b = 13.12747(15) \text{ \AA}$, $c = 7.48524(11) \text{ \AA}$, $V = 862.38(2) \text{ \AA}^3$

Site	x/a	y/b	z/b	B _{eq} / $\text{\AA}^2$
Ca	0	0	0	2.43(6)
B	0	0.2228(4)	0	3.41(19)
H1	0.0962(18)	0.2688(11)	0.003(3)	1
H2	0.006(3)	0.1775(10)	0.118(2)	1

β -Ca(BH₄)₂ $P4_2/m$

$a = 6.91226(10) \text{ \AA}$, $c = 4.34571(9) \text{ \AA}$, $V = 207.635(7) \text{ \AA}^3$

Site	x/a	y/b	z/c	B _{eq} / $\text{\AA}^2$
Ca	0.5	0	0.5	3.43(17)
B	0.283(7)	0.189(8)	0	3.5(9)
H1	0.32(2)	0.32(2)	0	4(3)
H2	0.45(2)	0.19(1)	0	4(3)
H3	0.22(2)	0.10(1)	0.74(2)	4(3)

Table 8.2 Refined crystallographic parameters for α -Ca(BH₄)₂ and β -Ca(BH₄)₂ at room temperature using a constrained tetrahedral rigid body model for the borohydride ion

$R_{wp} = 7.98\%$, $R_{exp} = 5.90\%$, $\chi^2 = 1.8$

α -Ca(BH₄)₂ $Fddd$

$a = 8.77627(12) \text{ \AA}$, $b = 13.12748(15) \text{ \AA}$, $c = 7.48527(11) \text{ \AA}$, $V = 862.38(2) \text{ \AA}^3$

Site	x/a	y/b	z/c	B _{eq} / $\text{\AA}^2$
Ca	0	0	0	2.38(6)
B	0	0.2233(4)	0	3.37(19)
H1	0.0967(18)	0.2693(11)	0.0005(3)	1
H2	0.0003(3)	0.1770(10)	0.1131(2)	1

β -Ca(BH₄)₂ $P4_2/m$

$a = 6.91225(10) \text{ \AA}$, $c = 4.34571(9) \text{ \AA}$, $V = 207.634(7) \text{ \AA}^3$

Site	x/a	y/b	z/c	B _{eq} / $\text{\AA}^2$
Ca	0.5	0	0.5	3.11(14)
B	0.299(5)	0.211(5)	0	4.9(6)
H1	0.42(2)	0.21(2)	0	18(3)
H2	0.26(2)	0.10(1)	0	18(3)
H3	0.26(2)	0.27(1)	0.15(2)	18(3)

The quality of the fit to the data is nearly identical if either the constrained or unconstrained model is used suggesting that the borohydride ions are ideally tetrahedral in shape. Unit cell parameters of $a = 8.77632(12) \text{ \AA}$, $b = 13.12747(15) \text{ \AA}$, $c = 7.48524(11) \text{ \AA}$ and $V = 862.38(2) \text{ \AA}^3$ were obtained for room temperature, orthorhombic α -Ca(BH₄)₂ using the unconstrained model. These agree well with those of Miwa *et al.*^[99] ($a = 8.791(1) \text{ \AA}$, $b = 13.137(1) \text{ \AA}$ and $c = 7.500(1) \text{ \AA}$). A structural model in the space group $F2dd$ did not fit the data as well as the structure in

the space group $Fddd$ and the hydrogen atoms were placed in unreasonable positions around the boron atoms.

The structure of $\alpha\text{-Ca}(\text{BH}_4)_2$ can be described as a face centred 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 borohydride ions, with two hydrogen atoms from each borohydride ion pointing towards the cation. These octahedra share edges with four other octahedra, and also share corners with four further octahedra. The octahedra are close to an ideal shape with equatorial Ca-B distances of $2.9057(6) \text{ \AA}$ and axial Ca-B distances of $2.925(5) \text{ \AA}$. In the unconstrained model, the borohydride ions are also close to ideally tetrahedral with B-H distances of $1.038(16) \text{ \AA}$ to $1.067(16) \text{ \AA}$ and H-B-H angles of $105.6(15)^\circ$ to $112.3(16)^\circ$. A schematic representation of the structure of $\alpha\text{-Ca}(\text{BH}_4)_2$ is shown in Figure 8.2 and the bond lengths and angles are displayed in Table 8.3. Using the constrained tetrahedral rigid body model for the borohydride ions, the B-H bond length refined to $1.042(10) \text{ \AA}$.

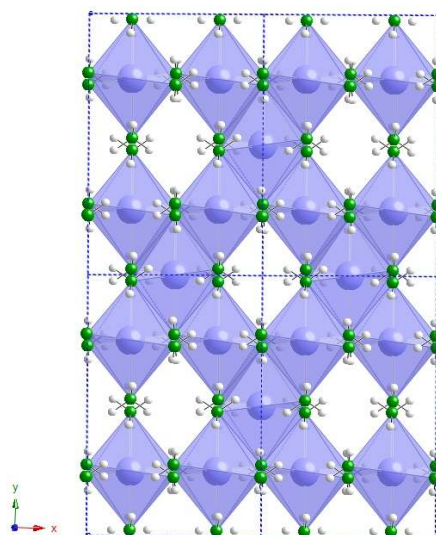


Figure 8.2 The structure of α -Ca(BH₄)₂ showing the octahedral co-ordination of boron atoms (green) around calcium ions (blue). Hydrogen atoms are shown in grey.

Table 8.3 Ca-B and B-H bond distances and H-B-H bond angles within α -Ca(BH₄)₂ using the unconstrained model.

Ca-B / Å	B-H / Å	H-B-H / °
2.9057(6)	1.038(16)	105.6(15)
2.9057(6)	1.038(16)	105.6(15)
2.9057(6)	1.067(16)	108.9(18)
2.9057(6)	1.067(16)	112.3(15)
2.925(5)		112.3(15)
2.925(5)		112.3(16)

Using the unconstrained model, unit cell parameters of $a = 6.91226(10)$ Å, $c = 4.34571(9)$ Å and $V = 207.635(7)$ Å³ were obtained for the room temperature, tetragonal β -Ca(BH₄)₂ phase, which agree well with those of Buchter *et al.*^[101] ($a = 6.9468(1)$ Å and $c = 4.3661(1)$ Å). The structure of β -Ca(BH₄)₂ may be described as a body centred arrangement of calcium cations with six borohydride ions arranged approximately octahedrally around each cation (Figure 8.3). Four of the coordinating

borohydride units are closer to the calcium cation with Ca-B distances of 2.91(6) Å, the other two axial borohydride units are 2.94(4) Å from the cation. The octahedra share edges with two other octahedra and corners with a further six octahedra, forming chains of edge-sharing octahedra, corner linked to other chains of octahedra. The co-ordination environment of the boron atoms (ignoring the hydrogen atoms) are eleven other boron atoms and three calcium ions. Using the unconstrained model, the borohydride ions in β -Ca(BH₄)₂ appear more distorted than in α -Ca(BH₄)₂ and also than the β -Ca(BH₄)₂ structure reported by Buchter *et al.*^[101]. The B-H distances range from 0.95(18) Å to 1.20(7) Å and the H-B-H angles from 72(10)° to 137(11)°. The bond distances and angles are displayed in Table 8.4. Using the constrained tetrahedral rigid body model for the borohydride ions, the B-H bond length refined to 0.81(7) Å with large atomic displacement parameters of 18(3) Å². The very short bond length in the constrained model and the very distorted geometry of the borohydride ion in the unconstrained model suggest a large degree of orientational disorder of the borohydride ion in the β -phase rather than unusually short bond lengths. The orientation of the borohydride ion in the constrained and unconstrained models is different; this also indicates orientational disorder in the borohydride ion. This disorder in the β -phase was predicted by Buchter *et al.*^[101] and Noritake *et al.*^[112]

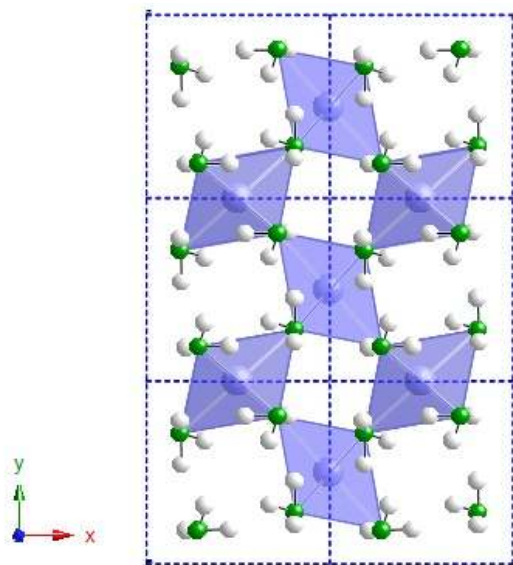


Figure 8.3 The structure of β -Ca(BH₄)₂ refined using the unconstrained model, showing the octahedral coordination of boron atoms (green) around calcium ions (blue). Hydrogen atoms are shown in grey.

Table 8.4 Ca-B and B-H bond distances and H-B-H bond angles within the unconstrained structural model of β -Ca(BH₄)₂

Ca-B / Å	B-H / Å	H-B-H / °
2.91(6)	0.95(18)	72(10)
2.91(6)	1.20(17)	97(6)
2.94(4)	1.20(7)	97(6)
2.94(4)	1.20(7)	112(6)
2.94(4)		112(6)
2.94(4)		137(11)

X-ray data collected on a Philips X-Pert diffractometer have shown that varying the preparation time of Ca(BH₄)₂ has a significant effect on the polymorphs observed in room temperature samples. Ca(BH₄)₂ prepared by 12 hours of heating contained an increased proportion of β -Ca(BH₄)₂, with a typical ratio of α : β 1:4 compared with a ratio of 4:1 observed for samples heated for one hour.

8.4 Variable temperature X-ray diffraction

High resolution synchrotron X-ray powder diffraction data at variable temperature were collected on a sample of $\text{Ca}(\text{BH}_4)_2$ contained in a sealed capillary on the high-resolution ID31 diffractometer at the ESRF, Grenoble at a wavelength and step size of 0.79825 Å and 0.004°, respectively. The sample was heated *in-situ* using a hot air blower, the temperature was increased in 2 °C steps from 26 °C to 410 °C, with data collected at each temperature for 2 minutes after thermal stabilization of the sample (30 seconds). The diffraction data were analysed and structural models refined by the Rietveld method using the profile refinement program TOPAS-Academic^[167] starting from the room temperature structures determined in Section 8.3. Figure 8.4 shows a representation of how a surface plot of the diffraction patterns as a function of temperature would appear if viewed from above. The coloured lines show the two theta positions of diffraction peaks as a function of temperature. The width of the lines shows the width of the peaks and the intensities of the colours indicate the relative intensities of the peaks.

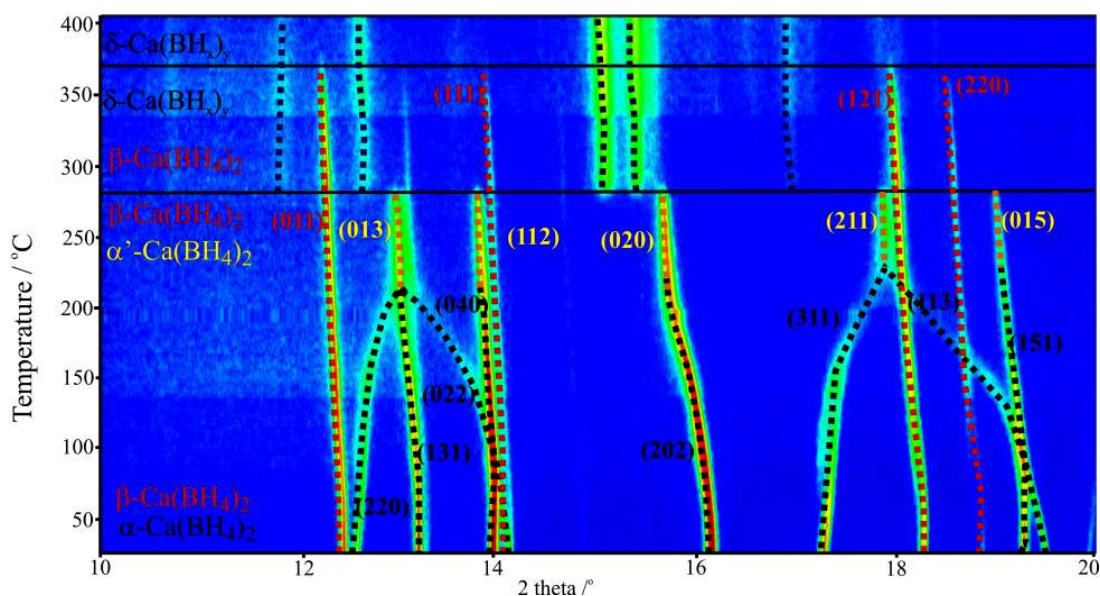


Figure 8.4 A surface plot of temperature resolved, high resolution X-ray diffraction data from $\text{Ca}(\text{BH}_4)_2$. The vertical lines correspond to various Bragg diffraction lines for $\alpha\text{-Ca}(\text{BH}_4)_2$, $\beta\text{-Ca}(\text{BH}_4)_2$, $\alpha'\text{-Ca}(\text{BH}_4)_2$ and $\delta\text{-Ca}(\text{BH}_x)_y$ with the intensity of each line represented by the intensity in colour. The phase transformation of $\alpha\text{-Ca}(\text{BH}_4)_2$ to $\alpha'\text{-Ca}(\text{BH}_4)_2$, the disappearance of $\alpha'\text{-Ca}(\text{BH}_4)_2$ (280 °C) and $\beta\text{-Ca}(\text{BH}_4)_2$ (380 °C) and the appearance of $\delta\text{-Ca}(\text{BH}_x)_y$ can all be clearly observed

At room temperature both $\alpha\text{-Ca}(\text{BH}_4)_2$ and $\beta\text{-Ca}(\text{BH}_4)_2$ were present within the sample. As the temperature was increased, between 70 °C and 170 °C, many of the Bragg peaks belonging to both the α - and $\beta\text{-Ca}(\text{BH}_4)_2$ polymorphs were seen to split. This is particularly noticeable in the $\alpha\text{-Ca}(\text{BH}_4)_2$ (311) and $\beta\text{-Ca}(\text{BH}_4)_2$ (121) and (220) peaks (Figure 8.5). As the entire sample was heated uniformly during the experiment it is not expected that this effect was due to differential thermal expansion. One possible explanation maybe that this peak splitting effect arises as a result of disorder in the borohydride ion orientation. If the borohydride ion rotates, the tetrahedral geometry of the borohydride ion may be simplified to a sphere, and the $P4_2/m$ space group of the $\beta\text{-Ca}(\text{BH}_4)_2$ simplified to $P4_2/mnm$, and that of $\alpha\text{-Ca}(\text{BH}_4)_2$

to $F4_1/ddm$. This modification of space group would naturally result in a slight change in the observed Bragg peaks and also in the rate of change of the cell parameters with increasing temperature, which may explain the complex peak structure observed in this temperature range. However, further work to investigate the cause of this peak structure is needed.

As the heating progressed, the 220 and 022, and the 311 and 113 Bragg reflections of α -Ca(BH₄)₂ were seen to merge (Figure 8.5), corresponding to a decrease in the a lattice parameter and an increase in the c lattice parameter, decreasing the a/c ratio. The rate of change of the a and c lattice parameters increased with increasing temperature, particularly above 125 °C until a/c became unity at approximately 230 °C ($a=c=8.2625(8)$ Å). The c lattice parameter increased more than the a lattice parameter decreased during this temperature range. The c lattice parameter increased by 0.7773 Å, 10.4 % from 7.48524(11) Å at room temperature whilst the a lattice parameter decreased by 0.5138 Å, 5.6 % from 8.77632(12) Å at room temperature. This gradual change in lattice parameter, with no sudden change in volume, suggests a second order phase transition (Figure 8.5), in which the orthorhombic structure un-distorted to form a tetragonal, face centred phase, which can also be described by the $F4_1/ddm$ space group. This space group may then be converted by a rotation through 45° of the cell axes around the b axis to obtain the conventional space group $I4_1/amd$, and a new polymorph of Ca(BH₄)₂, termed α' -Ca(BH₄)₂, with unit cell parameters of $a=5.8484(5)$ Å, $c=13.2546(13)$ Å and $V=453.35(9)$ Å³ (parameters quoted for the structure at 250 °C, see Table 8.5). The α' -Ca(BH₄)₂ structure contains borohydride units with eight hydrogen positions with an occupancy of one half so the borohydride units are effectively disordered analogous to the disorder within

NaBH_4 ^[68] and KBH_4 ^[85] within the $Fm-3m$ space group. A schematic representation of α' - $\text{Ca}(\text{BH}_4)_2$ is shown in Figure 8.6.

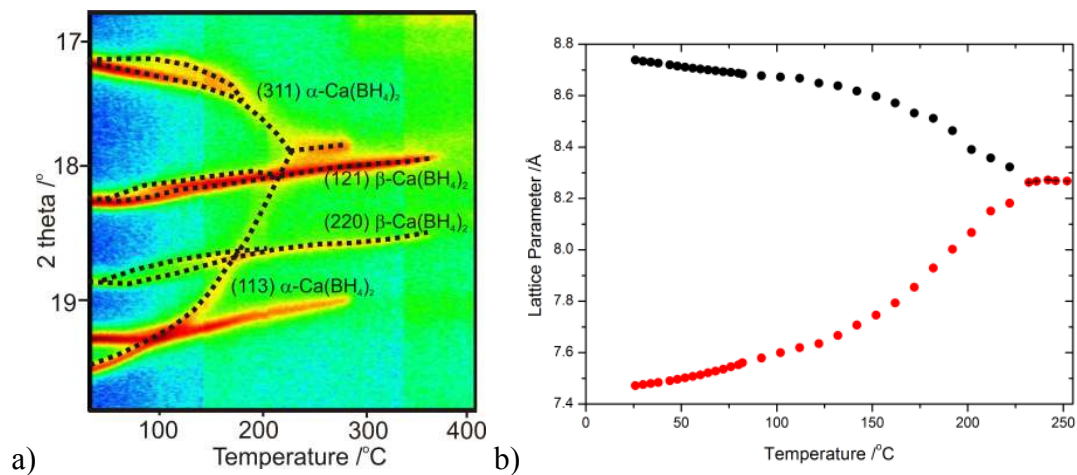


Figure 8.5 a) A portion of the surface plot of temperature resolved, high resolution X-ray diffraction data for $\text{Ca}(\text{BH}_4)_2$ showing the splitting of the α - $\text{Ca}(\text{BH}_4)_2$ (311) and β - $\text{Ca}(\text{BH}_4)_2$ (121) and (220) Bragg peaks, and the subsequent coalescence of the α - $\text{Ca}(\text{BH}_4)_2$ (311) and (113) Bragg peaks. b) the a (black) and c (red) lattice parameters of α - $\text{Ca}(\text{BH}_4)_2$ plotted as a function of temperature for the conversion of α - $\text{Ca}(\text{BH}_4)_2$ to α' - $\text{Ca}(\text{BH}_4)_2$. (Errors in the lattice parameters are smaller than the size of the data points).

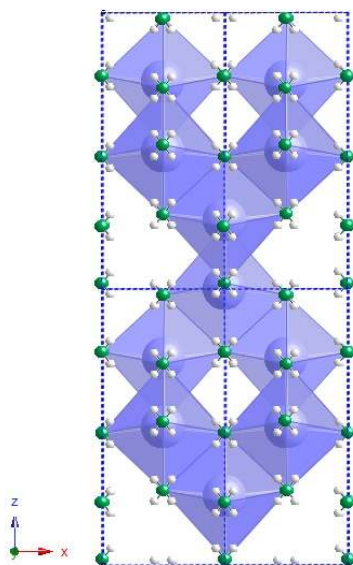


Figure 8.6 The structure of α' -Ca(BH₄)₂ showing the octahedral coordination of boron atoms (green) around calcium ions (blue). Hydrogen atoms are shown in grey.

Table 8.5 Refined crystallographic parameters for α' -Ca(BH₄)₂ and β -Ca(BH₄)₂ at 250 °C

 $R_{wp} = 12.42\%, R_{exp} = 10.21\%, \chi^2 = 1.5$

α' -Ca(BH₄)₂ $I4_1/amd$
 $a = 5.8484(5) \text{ \AA}, c = 13.2546(13) \text{ \AA}, V = 453.35(9) \text{ \AA}^3$

Site	x/a	y/b	z/c	B _{eq} / $\text{\AA}^2$
Ca	0	0	0	4.6(4)
B	0	0	0.2316(9)	10(4)
H1	0.070(16)	0.070(16)	0.263(8)	1
H2	-0.070(16)	0.070(16)	0.200(8)	1

β -Ca(BH₄)₂ $P4_2/m$
 $a = 6.9841(6) \text{ \AA}, c = 4.3938(4) \text{ \AA}, V = 214.32(4) \text{ \AA}^3$

Site	x/a	y/b	z/c	B _{eq} / $\text{\AA}^2$
Ca	0.5	0	0.5	6.4(6)
B	0.292(15)	0.197(16)	0	8.1(15)
H1	0.464(20)	0.197(20)	0	1
H2	0.235(20)	0.035(20)	0	1
H3	0.235(20)	0.278(20)	0.223(20)	1

Whilst the a and c lattice parameters of α -Ca(BH₄)₂ were converging, the b lattice parameter increased linearly above 100 °C with increasing temperature up to and across the phase change (Figure 8.6). However from room temperature to 60 °C, the b lattice parameter decreased from 13.12747(15) Å at room temperature to 12.1202(4) Å at 60°C. After 60°C, the lattice parameter increased with increasing rate towards 100°C.

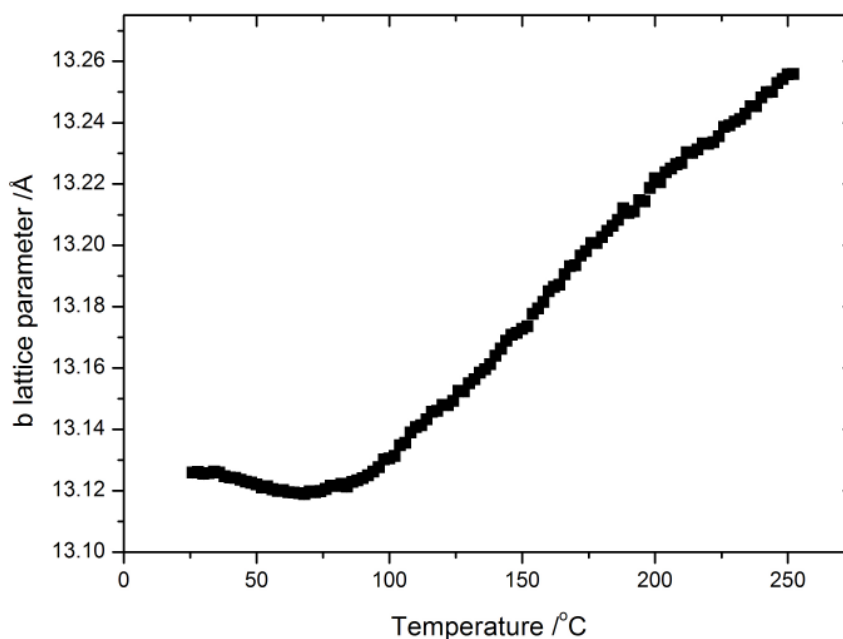


Figure 8.7 The b lattice parameter of $Fddd$ α - $\text{Ca}(\text{BH}_4)_2$ as a function of temperature from room temperature to 250 °C. (Errors in the lattice parameter data are smaller than the size of the data points).

As the α - to α' - $\text{Ca}(\text{BH}_4)_2$ phase transition progressed, the Bragg peaks of α - $\text{Ca}(\text{BH}_4)_2$ became broader and less well defined, suggesting that the structure may display ferroelastic behaviour arising from the interchanges between two equivalent orthorhombic structures orthogonal to each other, via the nearly tetragonal structure. Once the α to α' transition was complete, the Bragg peaks of the now α' - $\text{Ca}(\text{BH}_4)_2$ polymorph regained their sharpness as the sample became non-ferroelastic.

At 280 °C, the Bragg peaks from the α' - $\text{Ca}(\text{BH}_4)_2$ polymorph abruptly disappeared and a new phase appeared. This new phase has been indexed to an orthorhombic unit cell with lattice cell parameters of $a = 8.1763(8)$ Å, $b = 9.1532(9)$ Å, $c = 11.9307(9)$ Å, with a volume of $892.88(14)$ Å³ (parameters calculated from summed data sets between 380 °C and 410 °C), which is approximately double the volume of the α' - $\text{Ca}(\text{BH}_4)_2$ unit cell. The density of this phase, calculated from the

refined unit cell volume and assuming a stoichiometry of $\text{Ca}(\text{BH}_4)_2$, is intermediate to that of α - and α' - $\text{Ca}(\text{BH}_4)_2$. Therefore, it is possible that this phase represents a new polymorph of calcium borohydride or at least a structure with similar stoichiometry, termed $\delta\text{-Ca}(\text{BH}_x)_y$. The most probable space group of $\delta\text{-Ca}(\text{BH}_x)_y$ was identified as *Cmcm* (no. 63) using DASH^[168] and TOPAS-Academic^[167] routines, although attempts to further elucidate the structure of this high temperature phase have not been successful. When $\text{Ca}(\text{BH}_4)_2$ is synthesised from $\text{Ca}(\text{BH}_4)_2 \cdot 2\text{THF}$, neither increasing the reaction temperature or time has resulted in the observation of the $\delta\text{-Ca}(\text{BH}_x)_y$ phase.

The lattice parameters for $\beta\text{-Ca}(\text{BH}_4)_2$ generally increased monotonically (Figure 8.8) with temperature, from room temperature until 380 °C, at which point the Bragg diffraction lines for $\beta\text{-Ca}(\text{BH}_4)_2$ disappeared. The exception to this is below 100 °C, when the *a* lattice parameter of $\beta\text{-Ca}(\text{BH}_4)_2$ decreased from 6.91226(10) Å at room temperature to 6.8867(2) Å at 44 °C before increasing with increasing rate towards 100 °C. This is similar behaviour to that observed in the *b* lattice parameter of the α -phase. At 380 °C when the β -phase disappeared, there was no significant increase in the intensity of the background or of the $\delta\text{-Ca}(\text{BH}_x)_y$ Bragg peaks, and no new Bragg peaks appeared, suggesting that $\beta\text{-Ca}(\text{BH}_4)_2$ either decomposed or melted at this temperature.

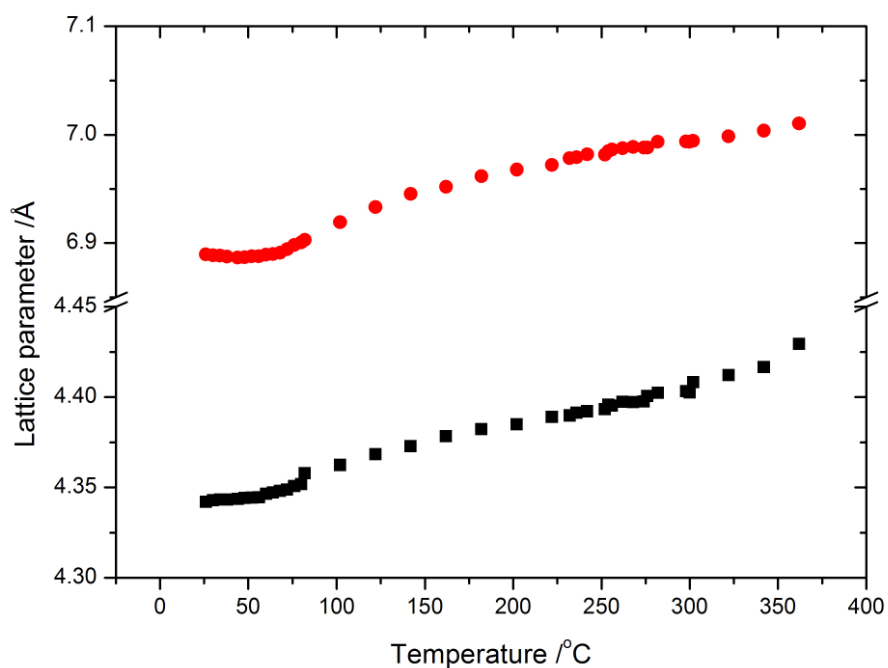


Figure 8.8 The a (red) and c (black) lattice parameters of β - $\text{Ca}(\text{BH}_4)_2$ as a function of temperature. (Errors in the lattice parameter data are smaller than the size of the data points).

The densities of the phases of $\text{Ca}(\text{BH}_4)_2$ as a function of temperature are shown in Figure 8.9 assuming that the stoichiometry of the δ -phase is $\text{Ca}(\text{BH}_4)_2$. The β -phase has the highest density so is expected to be the most stable phase.

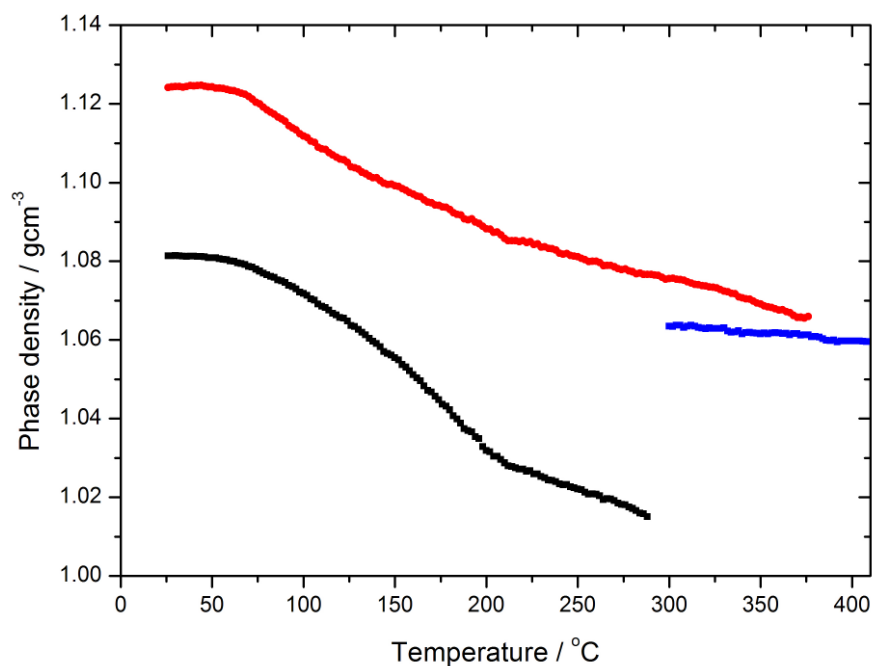


Figure 8.9 The density of the α / α' - (black), β - (red) and δ - (blue) phases of $\text{Ca}(\text{BH}_4)_2$ as a function of temperature. The stoichiometry of the δ - phase was assumed to be $\text{Ca}(\text{BH}_4)_2$ for the purposes of this calculation

8.5 Raman spectroscopy

Raman spectroscopy was performed at room temperature using a Dilor Labram 300 spectrometer with the sample contained in a sealed glass capillary (see Chapter 2). The room temperature Raman spectrum of $\text{Ca}(\text{BH}_4)_2$ between 1000 cm^{-1} and 3000 cm^{-1} is shown in Figure 8.10, the internal vibrations of the borohydride ion are expected within this region. This spectrum is in agreement with the room temperature spectrum of $\alpha\text{-Ca}(\text{BH}_4)_2$ reported by Fichtner *et al.*^[108] The observed Raman frequencies, their assignments and a comparison to the spectrum observed by Fichtner *et al.* are shown in Table 8.6. In common with other borohydrides,^[79, 156] the Raman spectrum is divided into the B-H stretching region between 2000 cm^{-1} and 3000 cm^{-1} and the B-H bending region between 1000 cm^{-1} and 2000 cm^{-1} .

Within the structure of $\alpha\text{-Ca}(\text{BH}_4)_2$, the borohydride ions are located on a two fold rotational axis and hence have the point group C_2 . With five atoms within the borohydride unit there are a total of $3N = 15$ degrees of freedom and $3N - 6 = 9$ vibrational modes. The symmetry of the modes can be determined as shown by the example in the Chapter 2. The 15 degrees of freedom have the symmetries $7A + 8B$ and the vibrational modes themselves are divided into $5A$ and $4B$ modes which were all observed in the Raman spectrum of $\alpha\text{-Ca}(\text{BH}_4)_2$ by Fichtner *et al.*^[108]. Modes with the symmetry A are symmetrical with respect to rotation around the C_2 axis, modes with the symmetry B are anti-symmetrical with respect to rotation around the C_2 axis.

In the Raman spectrum recorded here, the symmetric B-H stretch, ν_1 , which is generally the strongest signal in a borohydride Raman spectrum, is at 2273 cm^{-1} . This is a lower frequency than for the alkali metal borohydrides (ν_1 for LiBH_4 , NaBH_4 and KBH_4 occurs at 2300 cm^{-1} , 2336 cm^{-1} and 2308 cm^{-1} respectively; see respective chapters). On the other hand, the frequency of the ν_1 vibration is strongly influenced by the point group symmetry of the borohydride ion so this does not give an indication of the relative stability of the B-H bonds.^[79] The asymmetric B-H stretches, ν_3 are seen at 2331 cm^{-1} , 2357 cm^{-1} and 2416 cm^{-1} . The symmetric bending modes, ν_2 are seen at 1237 cm^{-1} and 1325 cm^{-1} and the asymmetric bending modes, ν_4 are seen at 1086 cm^{-1} and 1116 cm^{-1} . The asymmetric bending mode at 1204 cm^{-1} was not observed. The asymmetric bending modes in $\text{Ca}(\text{BH}_4)_2$ occur at similar frequencies to those of LiBH_4 (1090 cm^{-1}), the ν_4 bending frequency is less affected by the borohydride ion symmetry so this may indicate a similarity in B-H bond strength in LiBH_4 and $\text{Ca}(\text{BH}_4)_2$.

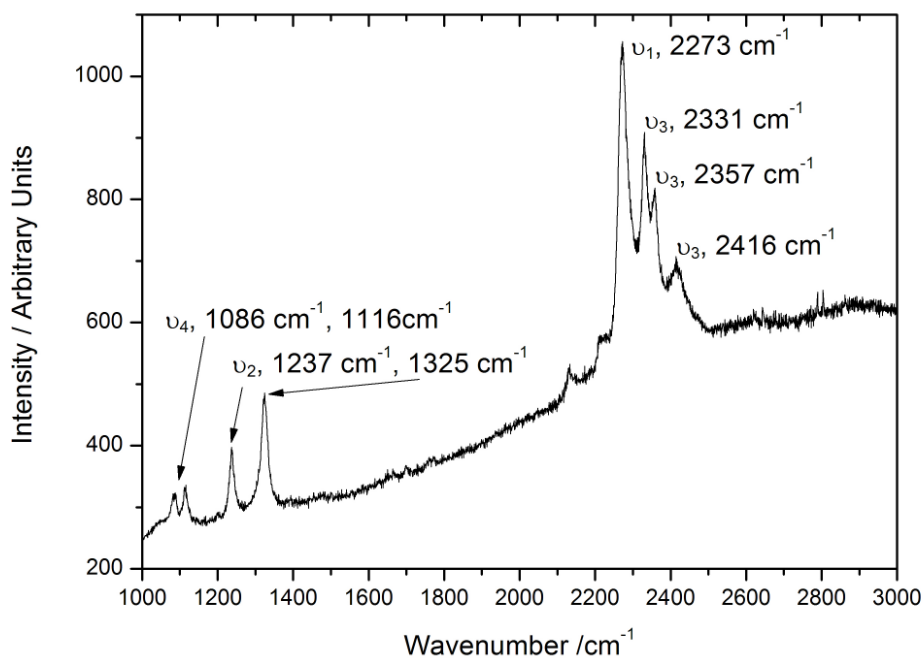


Figure 8.10 The room temperature Raman spectrum of Ca(BH₄)₂

Table 8.6 A comparison of the room temperature Raman frequencies of Ca(BH₄)₂ observed in this work and by Fichtner *et al.*

Assignment	C_2 symmetry	Ca(BH ₄) ₂ / cm ⁻¹ [108]	Ca(BH ₄) ₂ / cm ⁻¹ this work
ν ₄	<i>B</i>	1089	1086
ν ₄	<i>A</i>	1117	1116
ν ₄	<i>B</i>	1204	
ν ₂	<i>A</i>	1241	1237
ν ₂	<i>A</i>	1327	1325
ν ₁	<i>A</i>	2273	2273
ν ₃	<i>B</i>	2332	2331
ν ₃	<i>A</i>	2356	2357
ν ₃	<i>B</i>	2415	2416

8.6 Solid state ^{11}B NMR

Solid state ^{11}B MAS-NMR spectroscopy was carried out on a sample of $\text{Ca}(\text{BH}_4)_2$ at variable temperature by NMR staff within the Chemistry Department at the University of Oxford. The spectra were collected using a Varian/Chemagnetics Infinity spectrometer, with a 7.5 mm double resonance probe. The room temperature spectrum is shown in Figure 8.11. There is a single signal (with spinning side bands) with a chemical shift of -30.6 ppm ($\pm 0.2 \text{ ppm}$). The single signal suggests that all of the boron atoms within $\text{Ca}(\text{BH}_4)_2$ are in a similar environment. The ^{11}B NMR chemical shift of LiBH_4 is -41.4 ppm ($\pm 0.2 \text{ ppm}$), (See Chapter 4) suggesting that there is a larger electron density shielding the boron atoms from the magnetic field in LiBH_4 than in $\text{Ca}(\text{BH}_4)_2$. The electronegativity of both lithium and calcium is 1.0.^[77] Obviously, the calcium ion is carrying a 2+ charge compared to the 1+ charge of lithium and also has a higher ionisation potential, (1735 kJ mol^{-1} and 520 kJ mol^{-1} for calcium (sum of 1st and 2nd ionisation potentials) and lithium respectively).^[77] The boron atoms in $\text{Ca}(\text{BH}_4)_2$ are co-ordinated to three calcium ions (ignoring the boron atoms) whereas in LiBH_4 , there are four lithium ions surrounding a boron atom. The larger ^{11}B chemical shift of $\text{Ca}(\text{BH}_4)_2$ compared to LiBH_4 is a reflection of the smaller co-ordination number of the boron atoms. If the chemical shifts are divided by the boron atom co-ordination numbers for $\text{Ca}(\text{BH}_4)_2$ and LiBH_4 the values are very similar at -10.2 and -10.35 respectively.

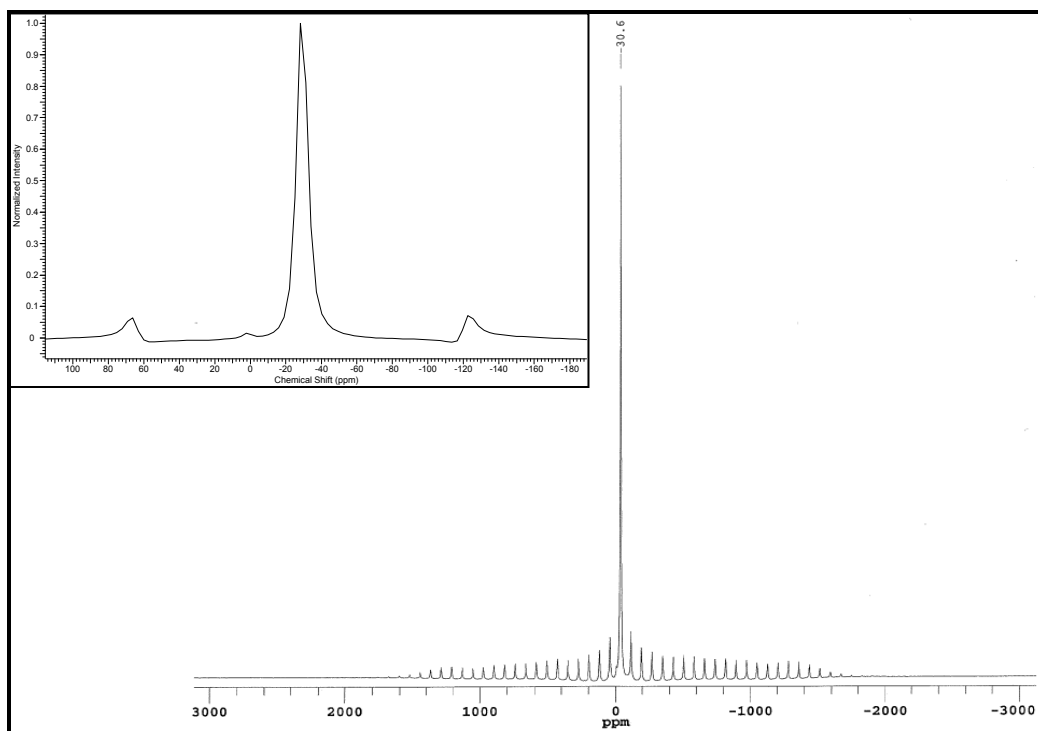
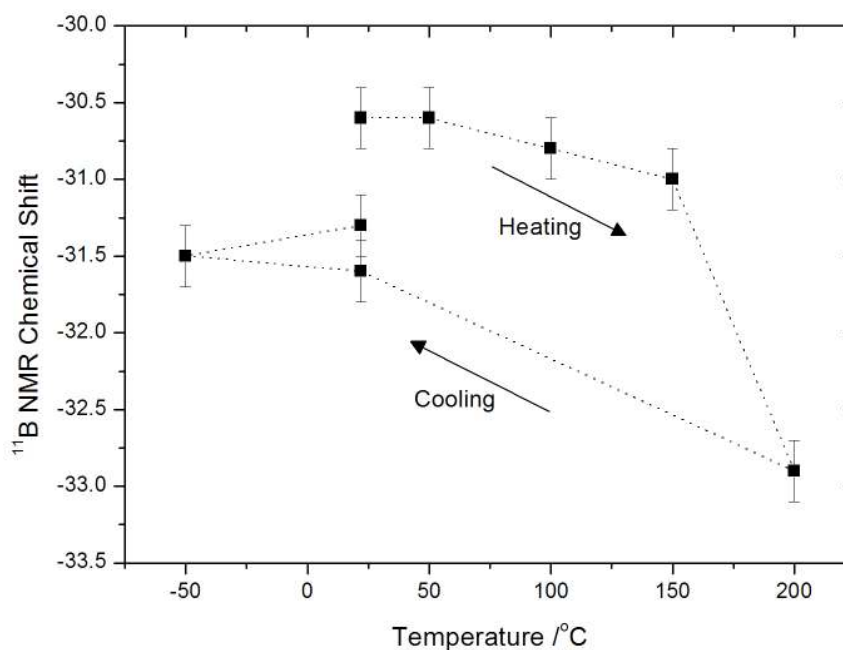


Figure 8.11 Room temperature solid state ^{11}B NMR spectrum of $\text{Ca}(\text{BH}_4)_2$, the inset shows an expansion of the spectrum around the principal peak.

After the initial room temperature ^{11}B NMR spectrum was recorded, further spectra were recorded at 50 °C, 100 °C, 150 °C and 200 °C before returning to room temperature, then cooling to -50 °C and finally returning to room temperature once again. The chemical shifts of the principal signal with varying temperature are listed in Table 8.7 and displayed graphically in Figure 8.12.

Table 8.7 The chemical shift of the principal signal in the ^{11}B NMR spectrum of $\text{Ca}(\text{BH}_4)_2$ at variable temperature

Temperature / $^{\circ}\text{C}$	^{11}B NMR Chemical shift (± 0.2 ppm)
RT	-30.6
50	-30.6
100	-30.8
150	-31.0
200	-32.9
RT	-31.6
-50	-31.5
RT	-31.3

**Figure 8.12** The chemical shift of the principal signal in the solid state ^{11}B NMR spectrum of $\text{Ca}(\text{BH}_4)_2$ as a function of temperature

On heating, the ^{11}B NMR chemical shift of $\text{Ca}(\text{BH}_4)_2$ decreases slightly between 50°C and 150°C but only within the range of the errors in the measurements. Between 150°C and 200°C there is a much larger decrease in the chemical shift, that is consistent with a change in the structure of $\text{Ca}(\text{BH}_4)_2$. When the sample is cooled,

the chemical shift does not return to the room temperature value, even when the sample is cooled to $-50\text{ }^{\circ}\text{C}$. This suggests that the modified structure remains present after cooling, possibly representing a metastable phase.

8.7 Thermogravimetric analysis

8.7.1 Thermogravimetric analysis under dynamic vacuum

Thermogravimetric analysis was carried out using a Hiden Isochema Intelligent Gravimetric Analyser (see Chapter 2). A 26 mg sample of $\text{Ca}(\text{BH}_4)_2$ was heated to $450\text{ }^{\circ}\text{C}$ at a rate of $2\text{ }^{\circ}\text{C}/\text{min}$ under dynamic vacuum (base pressure 10^{-6} mbar). The change in mass and temperature as a function of time are shown in Figure 8.13.

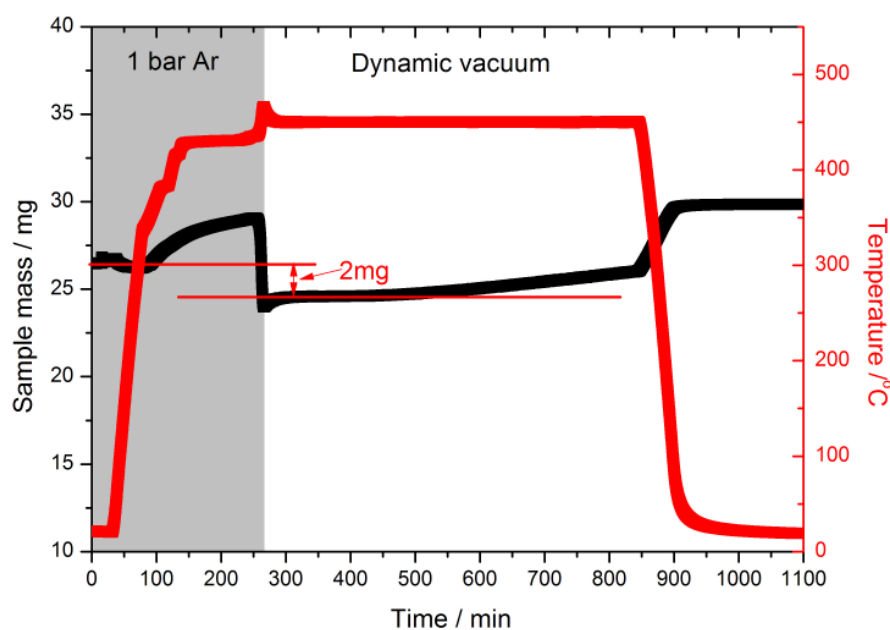


Figure 8.13 Sample mass (black) and temperature (red) plotted as a function of time for $\text{Ca}(\text{BH}_4)_2$.

Figure 8.13 does not show any large changes in mass whilst heating the sample of $\text{Ca}(\text{BH}_4)_2$ to 450°C . The majority of mass changes were due to changes in temperature or pressure, in particular the mass loss at 260 minutes and the mass increase at 870 minutes. However, there was a 2 mg mass loss between the mass of the sample at the start of the experiment and the mass after stabilization at 450°C under dynamic vacuum. This is a 7.5 wt% mass loss and may correspond to a partial decomposition of $\text{Ca}(\text{BH}_4)_2$. Table 8.8 shows that decomposition of $\text{Ca}(\text{BH}_4)_2$ to calcium hydride, boron and hydrogen would result in a 8.7 wt% loss.

Table 8.8 Decomposition routes and mass losses of $\text{Ca}(\text{BH}_4)_2$

Decomposition route	Mass loss / wt%
$\text{Ca}(\text{BH}_4)_2 (\text{s}) \rightarrow \text{Ca} (\text{s}) + 2\text{B} (\text{s}) + 4\text{H}_2 (\text{g})$	11.6
$\text{Ca}(\text{BH}_4)_2 (\text{s}) \rightarrow \text{CaH}_2 (\text{s}) + 2\text{B} (\text{s}) + 3\text{H}_2 (\text{g})$	8.7
$\text{Ca}(\text{BH}_4)_2 (\text{s}) \rightarrow \frac{2}{3} \text{CaH}_2 (\text{s}) + \frac{1}{3} \text{CaB}_6 (\text{s}) + \frac{10}{3} \text{H}_2 (\text{g})$	9.6

8.7.2 Thermogravimetric analysis with mass spectrometry

Thermogravimetric analysis was carried out using a Hiden Isochema Intelligent Gravimetric Analyser fitted with a mass spectrometer (see Chapter 2) set to detect B_2H_6 ($m/z = 28$), BH_3 ($m/z = 14$) and H_2 ($m/z = 2$). A 49 mg sample of $\text{Ca}(\text{BH}_4)_2$, was heated to 500°C at a rate of $2^\circ\text{C}/\text{min}$ under 1 bar flowing helium. A small proportion of the flowing helium along with any gas released from the sample was directed to the mass spectrometer via a 10 bar capillary tube. The change in mass and temperature of the sample and the hydrogen evolution detected from the mass spectrometer as a function of time are shown in Figure 8.14.

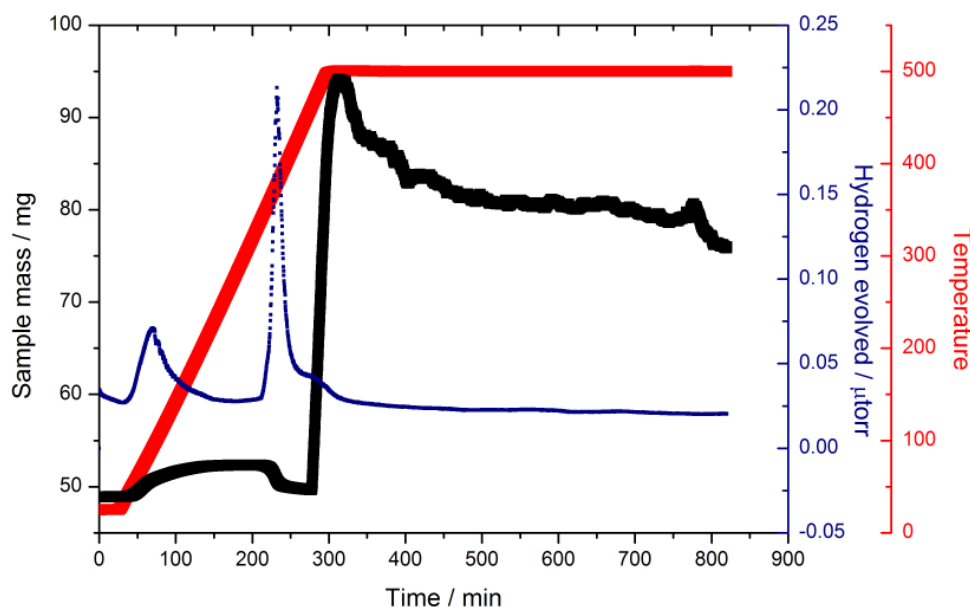


Figure 8.14 The change in temperature (red) and mass (black) of a sample of $\text{Ca}(\text{BH}_4)_2$ and hydrogen evolution (blue) as a function of time

The sample mass was constant until 50 °C, (42 minutes) when a slight increase in mass was observed to occur which continued until 190 °C (128 minutes). The mass increase was 3 mg (6 %). This coincided with hydrogen beginning to be detected by the mass spectrometer within the same temperature range. The mass then remained constant until 340 °C (212 minutes) when the mass decreased until 440 °C (266 minutes). The mass decrease was 2.6 mg (4.9 %) which is equal to 1.7 molar equivalents of hydrogen. The mass decrease also coincided with hydrogen evolution within the same temperature range which was larger than the first hydrogen release. The mass increase and loss below 450 °C are shown in Figure 8.15. At 460 °C (276 minutes) a large mass increase was observed which continued until the sample reached 500 °C (300 minutes). No hydrogen evolution was observed at this time and this mass increase is thought to be associated with instrumental effects. Once the sample reached 500 °C, there is a gradual weight loss continuing for the remaining time of the experiment. 17 mg (18 %) mass was lost over 500 minutes. The only

decomposition gas detected by the mass spectrometer was hydrogen; no BH_3 or B_2H_6 were observed.

The hydrogen evolution detected from 50 °C may be associated with co-ordinating solvent leaving the sample. The associated mass increase may be an effect of the way that the equipment handles the changing density of the sample. Apparent mass increases have been previously observed in $\text{Ca}(\text{BH}_4)_2$.^[94] The mass loss and hydrogen evolution between 340 °C and 440 °C could be expected to be the decomposition of $\text{Ca}(\text{BH}_4)_2$ in agreement with the observations of Rönnebro and Majzoub^[94]. Table 8.8 shows possible decomposition routes for $\text{Ca}(\text{BH}_4)_2$ with mass losses between 8.7 wt% and 11.6 wt%. These are all greater than the 4.9 wt% loss observed in this experiment. This is a similar mass loss to the 5.9 wt% loss observed at 330 °C by Kim *et al.*^[117] The mass loss could in reality be greater than the data suggests due to the instrumental mass increases. Alternatively, decomposition of $\text{Ca}(\text{BH}_4)_2$ could be occurring via an intermediate as suggested by Riktor *et al.*^[111] and Wang *et al.*^[114].

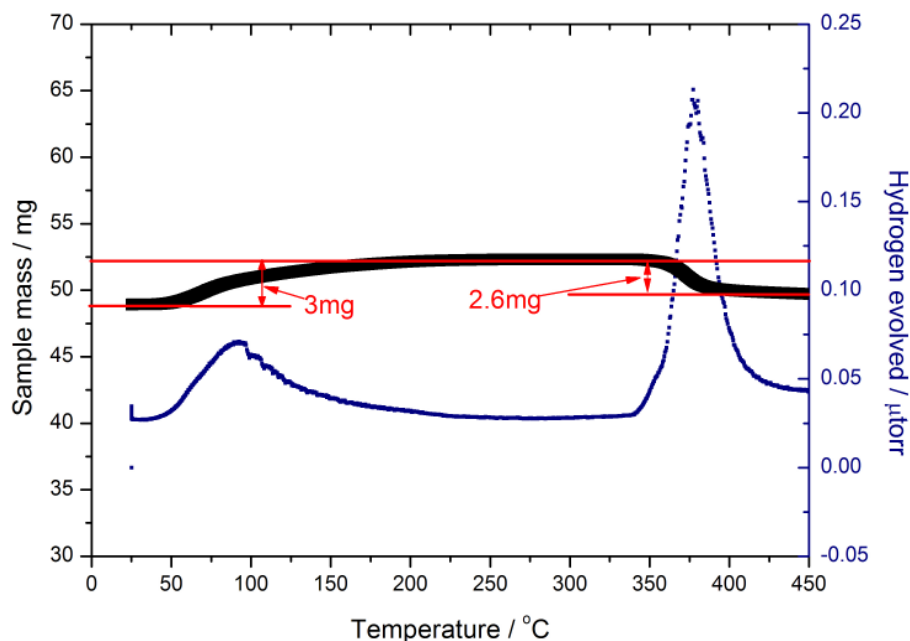


Figure 8.15 Mass loss (black) and hydrogen evolved (blue) as a function of time for a sample of $\text{Ca}(\text{BH}_4)_2$ showing the mass increase and loss below 450 °C.

8.8 Conclusions

A sample of $\text{Ca}(\text{BH}_4)_2$ was prepared by heating $\text{Ca}(\text{BH}_4)_2 \cdot 2\text{THF}$ under dynamic vacuum to 160 °C for one hour. High resolution synchrotron X-ray diffraction showed the sample to contain $\alpha\text{-Ca}(\text{BH}_4)_2$ (space group $Fddd$) and $\beta\text{-Ca}(\text{BH}_4)_2$ (space group $P4_2/m$). The lattice parameters at room temperature using a constrained tetrahedral rigid body model of the borohydride ions were $\alpha\text{-Ca}(\text{BH}_4)_2$; $a = 8.77627(12) \text{ \AA}$, $b = 13.12748(15) \text{ \AA}$, $c = 7.48527(11) \text{ \AA}$, $V = 862.38(2) \text{ \AA}^3$ and $\beta\text{-Ca}(\text{BH}_4)_2$; $a = 6.91225(10) \text{ \AA}$, $c = 4.34571(9) \text{ \AA}$, $V = 207.634(7) \text{ \AA}^3$. There was a similar quality of fit to the data for structural models using constrained and unconstrained hydrogen atomic positions suggesting that the borohydride ions are indeed tetrahedral. There is a high degree of orientational disorder of the borohydride ions in the β -phase. Variable temperature synchrotron X-ray diffraction showed that orthorhombic $\alpha\text{-Ca}(\text{BH}_4)_2$ undistorted to form $\alpha'\text{-Ca}(\text{BH}_4)_2$ by 230 °C. $\alpha'\text{-Ca}(\text{BH}_4)_2$ then converted to another phase at 280 °C which has been designated $\delta\text{-Ca}(\text{BH}_x)_y$. Bragg peaks relating to $\beta\text{-Ca}(\text{BH}_4)_2$ disappeared at 380 °C. Another polymorph of $\text{Ca}(\text{BH}_4)_2$, $\gamma\text{-Ca}(\text{BH}_4)_2$ was not observed in this study, this is unsurprising as $\gamma\text{-Ca}(\text{BH}_4)_2$ has been associated with solution state synthesis and is thought to be metastable.^[104]

Variable temperature, solid state ^{11}B NMR spectroscopy of a sample of $\text{Ca}(\text{BH}_4)_2$ showed a change in chemical shift between room temperature and 200 °C. This change did not revert when the sample was cooled.

A room temperature Raman spectrum was recorded and was found to be consistent with an ionic borohydride structure and with previously recorded spectra of $\text{Ca}(\text{BH}_4)_2$.^[108]

Thermogravimetric analysis under dynamic vacuum showed a 7.5 wt% mass loss to occur below 450 °C. Thermogravimetric analysis under 1 bar flowing helium showed a 4.9 wt% mass loss between 340 °C and 440 °C. Hydrogen was released during this mass loss and also between 50 °C and 190 °C. The lower temperature hydrogen release may be associated with loss of co-ordinating solvent.

Unlike previous work by Rönnebro and Majzoub^[94] and also Kim *et al.*^[116], a α -Ca(BH₄)₂ to β -Ca(BH₄)₂ phase change was not observed in the sample of Ca(BH₄)₂ around 140 °C to 170 °C. There was only a slight change in the ratio of α -Ca(BH₄)₂: β -Ca(BH₄)₂ from 76:24 at 100 °C to 75:25 at 150 °C to 70:30 at 200 °C.

The temporary decrease in the *a* lattice parameter of β -Ca(BH₄)₂ and the *b* lattice parameter of α -Ca(BH₄)₂ below 100 °C and the hydrogen release between 50 °C and 190 °C are likely to be associated with the loss of a small amount of residual solvent and the subsequent re-ordering of the crystal structures. This would result in improved packing efficiency, decreasing the volume of the unit cells until thermal expansion had a significant effect.

The splitting of Bragg peaks between 70 °C and 150 °C may be a consequence of the above re-ordering or of the borohydride ions gaining enough thermal energy to become disordered resulting in a choice of unit cell symmetry.

The change in chemical shift observed in the ¹¹B solid state NMR study is a result of the structure of α -Ca(BH₄)₂ un-distorting to form α' -Ca(BH₄)₂ by 230 °C.

The hydrogen release observed between 340 °C and 440 °C shows that the high temperature structure observed above 380 °C, designated δ -Ca(BH_x)_y must be at least a partial decomposition phase of Ca(BH₄)₂. Bragg peaks relating to δ -Ca(BH_x)_y did not appear in the diffraction patterns until 380 °C due to the increased pressure within the sealed capillary slightly delaying decomposition. The structure of CaB₂H₂

proposed by Riktor *et al.* does not appear to be the same as $\delta\text{-Ca}(\text{BH}_x)_y$.^[111] The shoulder on the hydrogen desorption peak suggests a second decomposition step occurring from 420 °C which is above the temperature range of the variable temperature X-ray diffraction study.

No hydrogen was released around 280 °C when the Bragg peaks relating to $\beta\text{-Ca}(\text{BH}_4)_2$ disappeared and the Bragg peaks relating to $\delta\text{-Ca}(\text{BH}_x)_y$ did not increase in intensity so it is likely that $\beta\text{-Ca}(\text{BH}_4)_2$ melted at 280 °C and then decomposed with the rest of the sample above 340 °C.

The sequence of $\alpha\text{-Ca}(\text{BH}_4)_2$ converting to $\alpha'\text{-Ca}(\text{BH}_4)_2$ rather than $\beta\text{-Ca}(\text{BH}_4)_2$ and then transforming to an unidentified $\delta\text{-Ca}(\text{BH}_x)_y$ phase is similar to that observed by Riktor *et al.*.^[111]

The various polymorphs and their transformations are summarized in Figure 8.16.

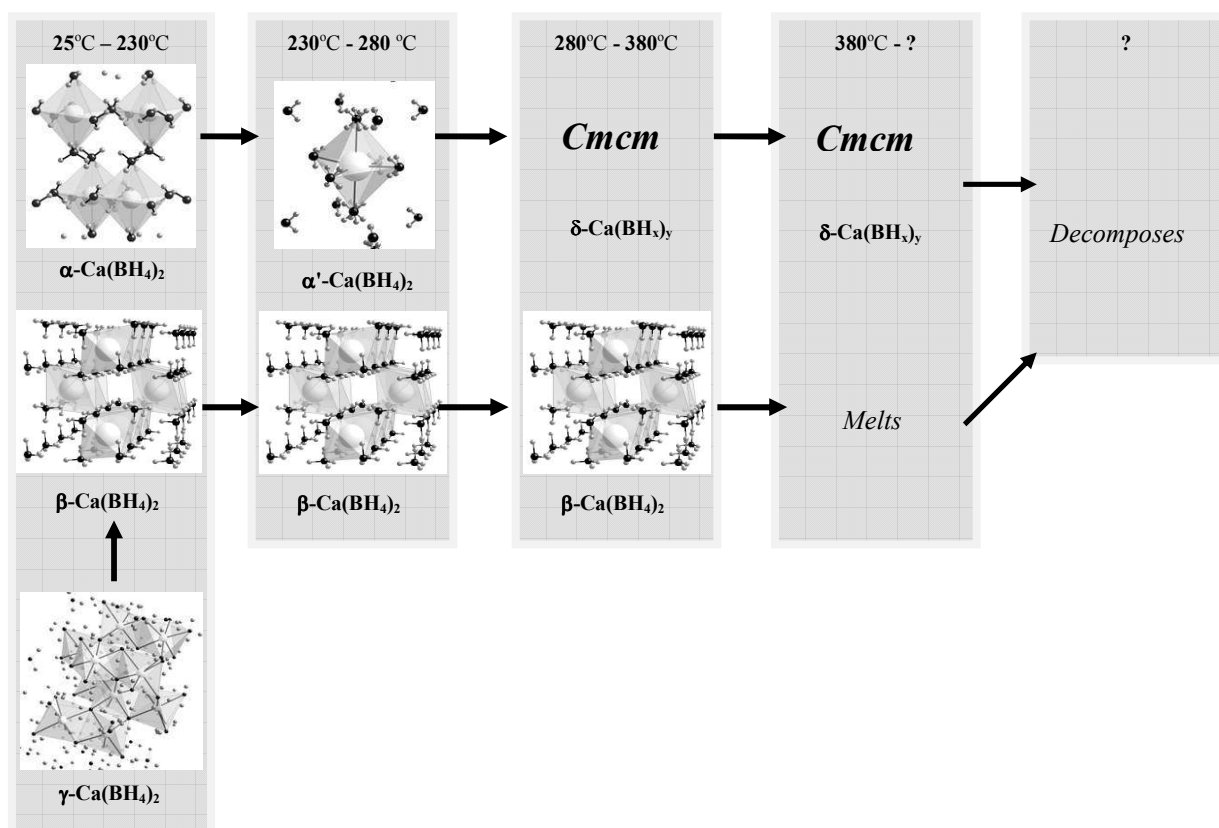


Figure 8.16 A summary of the temperature resolved phase transformations of $\text{Ca}(\text{BH}_4)_2$, showing a schematic diagram of the structure of $\alpha\text{-Ca}(\text{BH}_4)_2$, $\beta\text{-Ca}(\text{BH}_4)_2$ and $\alpha'\text{-Ca}(\text{BH}_4)_2$, with Ca represented by large dark grey spheres, B by small black spheres and H by small light grey spheres. The octahedra formed by $\text{Ca}[\text{BH}_4]_6$ are displayed.

The origin of the complex polymorphism in $\text{Ca}(\text{BH}_4)_2$ lies in the ability of the $\text{Ca}[\text{BH}_4]_6$ octahedra to reorganize their combination of corner and edge sharing relationships. Although Pauling's 3rd rule states that shared faces and to a lesser extent shared edges between co-ordination polyhedra destabilise a structure, this effect is not particularly large in $\text{Ca}(\text{BH}_4)_2$ where the cation has a relatively low valence and the radius ratio can be calculated to be well within the range for octahedral co-ordination.^[188] For $\text{Ca}(\text{BH}_4)_2$, the radius ratio may be estimated as 0.66 (Ca^{2+} radius 1.0 Å^[77], borohydride ion radius of 1.5 Å, calculated from boron-boron and

boron-hydrogen bond distances, $(\frac{1}{2}\text{B-B} + \text{B-H})/2$, from the model for $\beta\text{-Ca}(\text{BH}_4)_2$; the expected radius ratio range for octahedral coordination is 0.414 – 0.732.^[188] Furthermore, the $\text{Ca}[\text{BH}_4]_6$ octahedra are distorted which further reduces the effect of the number of shared edges. Consequently, the various phases of $\text{Ca}(\text{BH}_4)_2$ are similar in stability and can be observed to co-exist. Lee *et al.* calculated the difference in energy between the α - and β -phases to be 10.9 kJ mol^{-1} at -273°C , (0 K).^[107] Also, if the free energy barrier between the polymorphs is very small, it is reasonable to assume that barriers to polymorph transformation will be principally kinetic in nature. In such a case, we would expect the ratio of the polymorphs to vary with varying synthesis time. This is indeed what is observed, with the proportion of the most stable polymorph, $\beta\text{-Ca}(\text{BH}_4)_2$, increasing with increasing synthesis time.

The structures of $\alpha\text{-Ca}(\text{BH}_4)_2$ and $\alpha'\text{-Ca}(\text{BH}_4)_2$ consist of $\text{Ca}[\text{BH}_4]_6$ octahedra which share four corners and four edges with a total of eight octahedra (Figure 8.17a and b). The transformation of α - to $\alpha'\text{-Ca}(\text{BH}_4)_2$ would therefore involve very little change in free energy and thus the transformation occurs at a relatively low temperature (230°C). $\gamma\text{-Ca}(\text{BH}_4)_2$ has octahedra that share three edges and five corners with a total of nine octahedra (Figure 8.17c). $\gamma\text{-Ca}(\text{BH}_4)_2$ transforms to the β polymorph whose octahedra only share two edges and all six corners with a total of ten octahedra (Figure 8.17d). The change from three to two shared edges confers a small stabilization in free energy and this is confirmed by the gradual nature and broad temperature range (room temperature to 270°C)^[104] for this transformation. The stability of the β form with only two shared edges is demonstrated by the persistence of this phase to high temperature (380°C). Clearly from this analysis, the β polymorph is the most stable due to its low number of edge sharing octahedra.

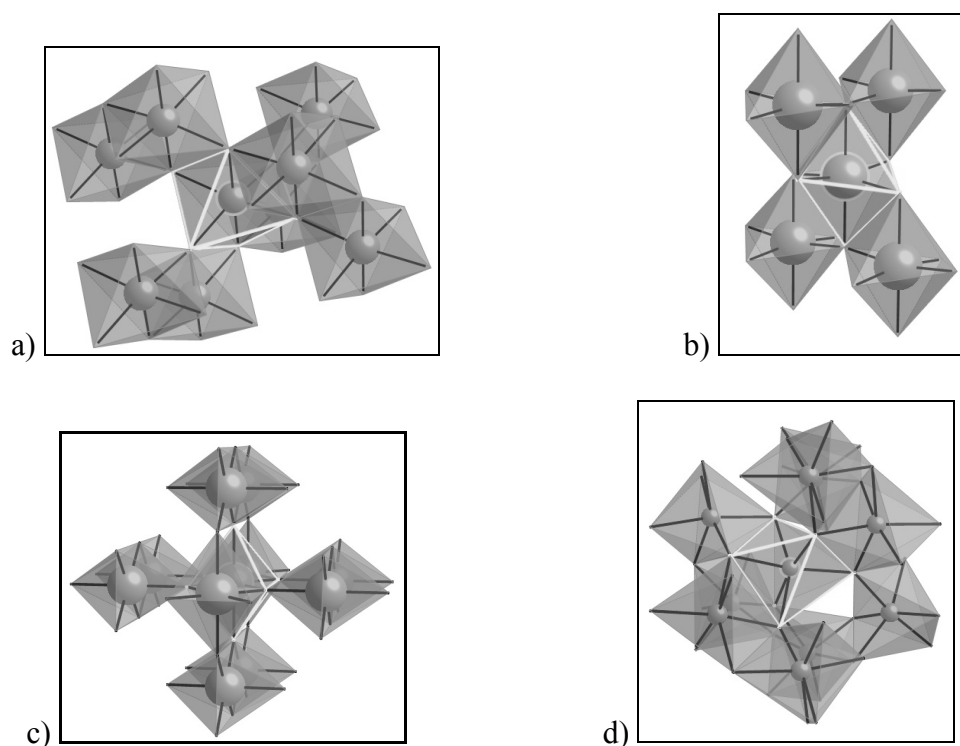


Figure 8.17 Schematic diagram of the structure of a) α - $\text{Ca}(\text{BH}_4)_2$ showing the 4 edge and 4 corner linking $\text{Ca}[\text{BH}_4]_6$ octahedra (central octahedra highlighted), b) α' - $\text{Ca}(\text{BH}_4)_2$ showing the 4 edge and 4 corner linking $\text{Ca}[\text{BH}_4]_6$ octahedra (central octahedra highlighted); c) β - $\text{Ca}(\text{BH}_4)_2$ showing the 2 edge and 8 corner linking $\text{Ca}[\text{BH}_4]_6$ octahedra (central octahedra highlighted). and d) γ - $\text{Ca}(\text{BH}_4)_2$ showing the 3 edge and 6 corner linking $\text{Ca}[\text{BH}_4]_6$ octahedra (central octahedra highlighted). The B and H atoms have been removed for simplicity from all the diagrams.

The β -phase of $\text{Ca}(\text{BH}_4)_2$ is expected to be the most stable due to its higher density compared to the other $\text{Ca}(\text{BH}_4)_2$ phases. Also, the TiO_2 analogue of the β -phase, rutile is more stable than the α -phase analogue, anatase.^[189] There is thought to be a critical size of particle above which rutile is more stable than anatase because the surface free energy of anatase is actually lower than that of rutile. Therefore different synthesis routes which produce different particle sizes produce different polymorphs of TiO_2 .^[190] This could also be the case for $\text{Ca}(\text{BH}_4)_2$ where different phases have been observed in samples produced in different ways, although further work will be needed to fully understand the complex polymorphism of $\text{Ca}(\text{BH}_4)_2$.

10 Conclusions and further work

10.1 Thesis summary

The work contained in this thesis has investigated the structures and thermal behaviour of a family of alkali and alkaline earth borohydrides consisting of LiBH_4 , NaBH_4 , KBH_4 , $\text{LiK}(\text{BH}_4)_2$, $\text{Ca}(\text{BH}_4)_2$ and $\text{Sr}(\text{BH}_4)_2$.

$^7\text{Li}^{11}\text{BD}_4$, $\text{Li}^{11}\text{BD}_4$, $\text{Na}^{11}\text{BD}_4$, K^{11}BD_4 and $\text{LiK}(^{11}\text{BD}_4)_2$ were synthesised directly from the elements using a high pressure furnace. Attempted syntheses of $\text{Mg}(^{11}\text{BD}_4)_2$ and $\text{Ca}(^{11}\text{BD}_4)_2$ were unsuccessful.

The structure of $^7\text{Li}^{11}\text{BD}_4$ and $\text{Li}^{11}\text{BD}_4$ was investigated at $-223\text{ }^\circ\text{C}$ and from room temperature up to $250\text{ }^\circ\text{C}$. Both the room temperature orthorhombic and hexagonal high temperature structures were observed. PDF analysis showed that the $\text{B}\cdots\text{D}$ and $\text{D}\cdots\text{D}$ separations are the same throughout the structure showing that the borohydride ions have ideal tetrahedral geometry, however, over longer range (greater than $3\text{ \AA}$), both the room temperature and high temperature structures are disordered.^[176] Thermogravimetric analysis showed LiBH_4 to decompose in two stages (at $300\text{ }^\circ\text{C}$ and $380\text{ }^\circ\text{C}$ under 1 bar flowing argon). The majority of the gas released during decomposition was hydrogen although a small amount of BH_3 and B_2H_6 were also released during the main (second) stage of decomposition.

Variable temperature neutron diffraction studies of $\text{Na}^{11}\text{BD}_4$ and K^{11}BD_4 from room temperature to $450\text{ }^\circ\text{C}$ showed linear expansions of the cubic-face-centred crystal structures. Thermogravimetric analysis of NaBH_4 and KBH_4 under both flowing gas and dynamic vacuum ($\text{Na}^{11}\text{BD}_4$ and K^{11}BD_4) revealed that the samples lost more mass than would be expected only from decomposition releasing hydrogen. Small

amounts of B_2H_6 were detected but the large mass loss is likely to be associated with evaporation or inadvertent loss of the molten samples from the mesh sample bucket.

$LiK(BH_4)_2$, the first mixed alkali metal borohydride, was synthesised during this project from $LiBH_4$ and KBH_4 .^[142] The crystal structure of $LiK(BH_4)_2$ shares the space group $Pnma$ with its parent compound $LiBH_4$ and also $LiBH_4.NH_3$.^[187] the b lattice parameter in all of these structures is approximately 4.5 Å. In $LiBH_4$ and $LiK(BH_4)_2$ this lattice parameter is determined by the diameter of two borohydride ions. As with $LiBH_4$, the b lattice parameter of $LiK(BH_4)_2$ decreases with increasing temperature. Decomposition of $LiK(BH_4)_2$ occurs in two stages; beginning at 320 °C and 400 °C under flowing gas, these temperatures are intermediate to the decomposition temperatures of the parent compounds.

$Ca(BH_4)_2$ was produced by desolvating $Ca(BH_4)_2.2THF$ under dynamic vacuum at 160 °C. At room temperature, the sample consisted of orthorhombic α - $Ca(BH_4)_2$ and tetragonal β - $Ca(BH_4)_2$. A variable temperature X-ray diffraction study showed that between room temperature and 230 °C, α - $Ca(BH_4)_2$ undistorted to form tetragonal α' - $Ca(BH_4)_2$. At 280 °C, α' - $Ca(BH_4)_2$ converted to a high temperature phase. At 380 °C, the Bragg peaks relating to β - $Ca(BH_4)_2$ also disappeared. γ - $Ca(BH_4)_2$ was not observed. Thermogravimetric analysis showed $Ca(BH_4)_2$ to lose mass beginning at 340 °C suggesting that the observed high temperature phase may be a decomposition intermediate, however the diffraction pattern is not consistent with the previously identified structure of CaB_2H_2 .^[111]

$Sr(BH_4)_2$ was synthesised from $LiBH_4$, $NaBH_4$ and $SrCl_2$ in THF. An orthorhombic crystal structure was determined from synchrotron X-ray diffraction data. The previously determined structure of $Sr(BH_4)_2.2THF$ was observed in addition to two unidentified phases which are thought to be polymorphs of $Sr(BH_4)_2$ and

$\text{Sr}(\text{BH}_4)_2 \cdot 2\text{THF}$. Both of the unidentified phases and the known THF solvate have one lattice parameter of approximately 4.5 Å in common with LiBH_4 and $\text{LiK}(\text{BH}_4)_2$.

10.2 Structure

10.2.1 The geometry of the borohydride ion

The geometry of the borohydride ion within metal borohydrides has been the subject of considerable debate.^[51, 55, 88, 143] For the structural refinements in this thesis, the structures of the borohydride ions were refined using both a tetrahedral rigid-body model and also, separately, a model where all of the atomic sites were allowed to refine independently. For the majority of structures the quality of fit was very similar in both cases, suggesting that the borohydride ions are actually tetrahedral. The B-H bond lengths from the rigid body refinements and also the B-H bond lengths from unconstrained structures which refined to tetrahedral ions are discussed here.

In $^7\text{Li}^{11}\text{BD}_4$ at -223 °C, the B-D bond lengths in an unconstrained model refined to be chemically identical with a range of 1.2140(9) Å to 1.225(2) Å. At room temperature the structures of both $^7\text{Li}^{11}\text{BD}_4$ and $\text{Li}^{11}\text{BD}_4$ from neutron diffraction showed distorted tetrahedra which would not fit a tetrahedral rigid body, the fit of the model to the data was particularly bad at longer time-of-flights (larger atomic separations). On the other hand, PDF analysis of the same neutron diffraction data from $^7\text{Li}^{11}\text{BD}_4$ showed that all of the short range B $\cdots$ D and D $\cdots$ D distances within the structure are the same and therefore the borohydride ions must be perfectly tetrahedral. PDF analysis also showed that the room temperature structure has disorder at longer range. The structural model contains information about the relative orientations of bonds in addition to the distances contained in the PDF analysis. It is disorder in the orientation

of the borohydride ions, not in the B-D lengths that prevented the structural model from fitting the data.

The synchrotron X-ray diffraction data of $\text{Li}^{11}\text{BD}_4$ fitted a tetrahedral rigid body with a B-D length of $1.143(10)$ Å, X-ray diffraction cannot determine the deuterium positions as accurately as neutron diffraction so the structural model could be fitted to the data despite the orientational disorder. At 150°C , in the high temperature structure, using tetrahedral rigid body borohydride ions, the B-D bond length in $^7\text{Li}^{11}\text{BD}_4$ refined to $1.26(4)$ Å. Importantly, PDF analysis of this structure also showed that the B $\cdots$ D and the D $\cdots$ D separations were all equivalent.

For $\text{LiK}(\text{BH}_4)_2$, the borohydride ions were found to be perfectly tetrahedral but again, structure refinement was hindered by orientational disorder of the borohydride ions. Using the rigid body borohydride ion model, X-ray diffraction from the hydrogenated compound indicated a B-H bond length of $1.18(2)$ Å and neutron diffraction from the deuterated compound showed a B-D bond length of $1.06(3)$ Å.

In the structures of $\text{Na}^{11}\text{BD}_4$ and K^{11}BD_4 in the space group $Fm-3m$, the borohydride ions are constrained to be perfectly tetrahedral by the symmetry of the space group.

Using a tetrahedral rigid body borohydride ion, synchrotron X-ray diffraction of $\text{Ca}(\text{BH}_4)_2$ showed the α -phase to have tetrahedral borohydride ions with a B-H length of $1.040(10)$ Å and in the β -phase the B-H length refined to $0.84(4)$ Å. If the atomic sites of the β -phase were allowed to refine freely, the borohydride ion appeared very distorted. This suggests a large amount of orientational disorder in the β -phase.

In $\text{Sr}(\text{BH}_4)_2$, it was not possible to identify the hydrogen atomic positions. The structure was modelled using constrained rigid body borohydride ions and the B-H lengths refined to the rather short distance of $0.99(3)$ Å. This may be a consequence of orientational disorder.

In conclusion, it is probable that all of the borohydride ions in these compounds are perfectly tetrahedral but also exhibit a large degree of orientational disorder. The B-H and B-D bond lengths are summarised in Table 10.1. The variation in observed bond lengths is due to the orientational disorder of the borohydride ion combined with the atomic thermal displacements of the atoms being modelled as either spheres or ellipsoids. Diffraction is an averaging technique so the B-H/D bond will be observed in different orientations across the sample. As the orientation of the borohydride ion changes, the hydrogen atoms move in an arc. As discussed in the Chapter 2 and shown here in Figure 10.1, in order to model the average atomic position within a structure, atomic sites are likely to be positioned to cover the ends of this arc rather than the centre, then the measured bond length will appear shorter than it actually is. The movement of the hydrogen atoms makes it particularly difficult to determine the geometry of the borohydride ion from X-ray diffraction data so it is usually necessary to use a tetrahedral rigid body model.

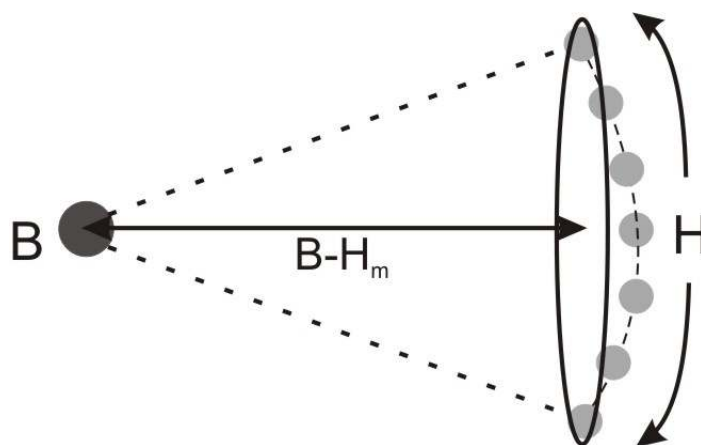


Figure 10.1 A diagram showing how a structural model is likely to model the B-H bond length when there is orientational disorder within the borohydride ion

Table 10.1 B-H and B-D bond lengths from the structures within this thesis

Structure	Radiation	B-H/D bond lengths / Å
${}^7\text{Li}^{11}\text{BD}_4$, -223 °C	Neutron	1.214(1) - 1.225(2)
${}^7\text{Li}^{11}\text{BD}_4$, -223 °C ^[176]	Neutron PDF	1.21
$\text{Li}^{11}\text{BD}_4$	X-ray	1.143(10)
$\text{Li}^{11}\text{BD}_4$	Neutron	*
${}^7\text{Li}^{11}\text{BD}_4$	Neutron	*
${}^7\text{Li}^{11}\text{BD}_4$ 150°C (HT structure)	Neutron	1.26(4)
$\text{LiK}(\text{BH}_4)_2$	X-ray	1.18(2)
$\text{LiK}({}^{11}\text{BD}_4)_2$	Neutron	1.06(3)
$\text{Na}^{11}\text{BD}_4$	Neutron	1.176(2)
KBH_4	X-ray	1.114(5)
K^{11}BD_4	Neutron	1.192(2)
$\alpha\text{-Ca}(\text{BH}_4)_2$	X-ray	1.042(10)
$\beta\text{-Ca}(\text{BH}_4)_2$	X-ray	0.81(7)
$\text{Sr}(\text{BH}_4)_2$	X-ray	0.99(2)

* rigid body model could not be fitted to the data

10.2.2 Trends in solid state ${}^{11}\text{B}$ NMR chemical shift values

The solid state ${}^{11}\text{B}$ NMR spectrum of each compound in this thesis has been discussed in the results chapters (Chapters 4 to 9). For comparison, the solid state ${}^{11}\text{B}$ NMR spectrum of $\text{Mg}({}^{11}\text{BD}_4)_2$ was also collected and the boron chemical shift is included in this discussion. The sample of $\text{Mg}({}^{11}\text{BD}_4)_2$ was supplied by Prof. Orimo of Tohoku University. The chemical shift of boron is dependent, amongst other factors, on its co-ordination number.^[160] In order to appreciate the effect of changing the cation on the ${}^{11}\text{B}$ chemical shift of a borohydride, independent of the co-ordination number, the

^{11}B chemical shift has been divided by the co-ordination number of boron to the metal cations. Figure 10.2 shows the chemical shift per co-ordinated metal ion as a function of the electronegativity of the cation. Figure 10.3 shows the chemical shift per co-ordinated metal ion as a function of the atomic ionisation energy to form the cation. For $\text{LiK}(\text{BH}_4)_2$ the average of the electronegativities and ionisation energies of lithium and potassium and the average co-ordination number of the two borohydride ions were used.

The chemical shift per co-ordinated metal ion decreases as the electronegativity or ionisation energy of the cation increases. This is the opposite trend to what might be expected where more electronegative cations pull electron density away from the borohydride ion leaving the boron atom deshielded so that the ^{11}B chemical shift decreases (becomes more negative).

The likely explanation is that the more electronegative cation only significantly attracts the electron density of the hydrogen atoms. The hydrogen electron density is pulled away from the B-H bond which weakens the bond so the boron electron density returns closer to the boron atom. This increases the shielding of the boron atoms resulting in the decreased ^{11}B chemical shift observed. Increasing cation electronegativity is associated with decreasing stability of borohydride compounds,^[60] so weaker B-H bonds would be expected for compounds with more electronegative cations.

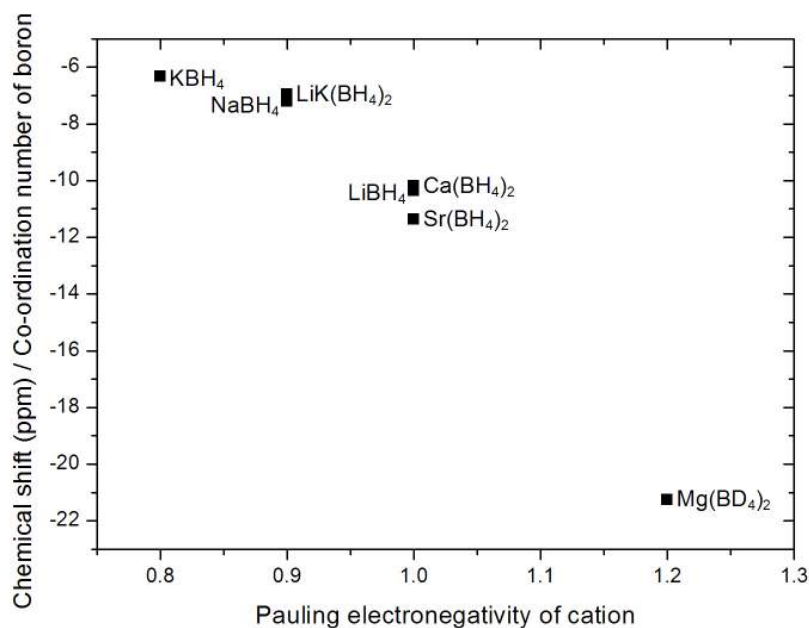


Figure 10.2 ^{11}B chemical shift / co-ordination number of boron as a function of the Pauling electronegativity of the cation for group I and II borohydrides.

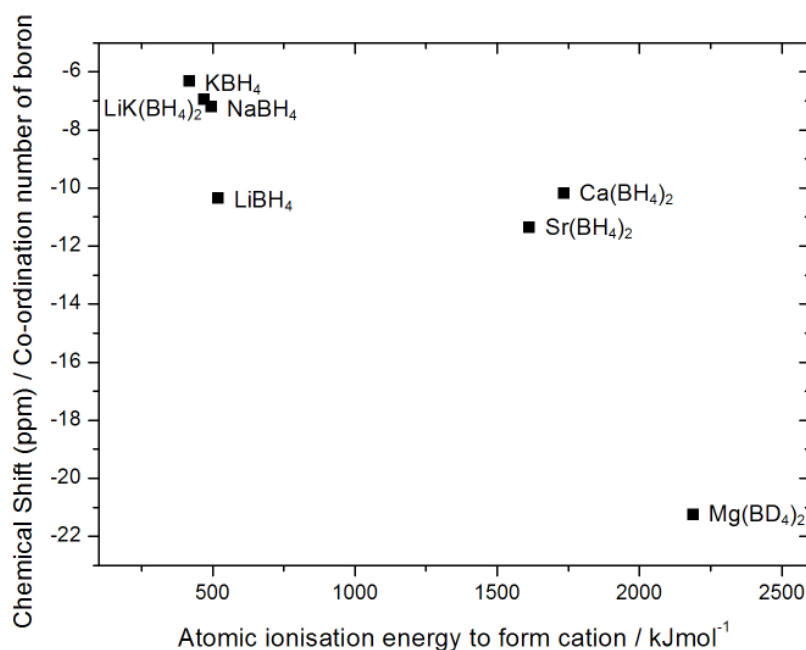


Figure 10.3 ^{11}B chemical shift / co-ordination number of boron as a function of the atomic ionisation energy to form the cation for group I and II borohydrides.

10.3 Thermal behaviour

10.3.1 Decomposition

Only LiBH_4 and $\text{LiK}(\text{BH}_4)_2$ were observed to melt before decomposition. NaBH_4 and KBH_4 have previously been reported to melt after the start of decomposition but this is difficult to identify.^[19]

Identifying decomposition temperatures is not a simple process. The temperatures depend on the heating rate and several of the borohydrides decompose in multiple stages. A summary of the temperatures where the main stage of decomposition began to occur at a significant rate producing a discernable hydrogen desorption peak or mass loss under 1 bar flowing inert gas is shown in Table 10.2. The inert gas was helium in all cases except for KBH_4 where the temperature was recorded under argon.

Table 10.2 The temperatures when significant decomposition of the borohydrides begins under 1 bar inert gas

Borohydride	Decomposition temperature / °C
LiBH_4	380
NaBH_4	500
KBH_4	560
$\text{LiK}(\text{BH}_4)_2$	400
$\text{Ca}(\text{BH}_4)_2$	340
$\text{Sr}(\text{BH}_4)_2$	300

After melting at 285 °C, LiBH_4 decomposed in two stages, the first smaller stage at 300 °C, with the second larger stage at 380 °C. NaBH_4 decomposed at 500 °C with a small event occurring before the main decomposition. When the temperature was increased continually, KBH_4 decomposed at 560 °C, however decomposition also

occurred gradually if the temperature was held at 500 °C. After melting at 230 °C, $\text{LiK}(\text{BH}_4)_2$ decomposed in two stages, the first smaller stage began at 320 °C, the main decomposition event began at 400 °C and hydrogen evolution peaked at 450 °C. $\text{Ca}(\text{BH}_4)_2$ decomposed between 340 °C and 440 °C. $\text{Sr}(\text{BH}_4)_2$ decomposed between 270 °C and 465 °C in two stages whose rates peaked at 340 °C and 372 °C (as determined by hydrogen evolution). Rapid decomposition began around 300 °C.

A very small amount of either BH_3 or B_2H_6 was detected by the mass spectrometer during all the decompositions apart from $\text{Ca}(\text{BH}_4)_2$ during the period of rapid decomposition. B_2H_6 itself decomposes at the borohydride decomposition temperatures presented in Table 10.2,^[129] so it is possible that more B_2H_6 and BH_3 were released including from $\text{Ca}(\text{BH}_4)_2$ than was detected. The main decomposition gas product in all cases was hydrogen.

10.3.2 Effect of cation electronegativity on decomposition temperature

The correlation between increasing electronegativity of the cation and decreasing decomposition temperature of the borohydride is already known.^[60] Figure 10.4 shows the trend using the decomposition temperatures determined in this thesis. The average electronegativity of lithium and potassium is used for $\text{LiK}(\text{BH}_4)_2$. The stability of the borohydrides decrease as more electronegative cations attract the electron density from the hydrogen atoms, reducing the electron density in the B-H bond.

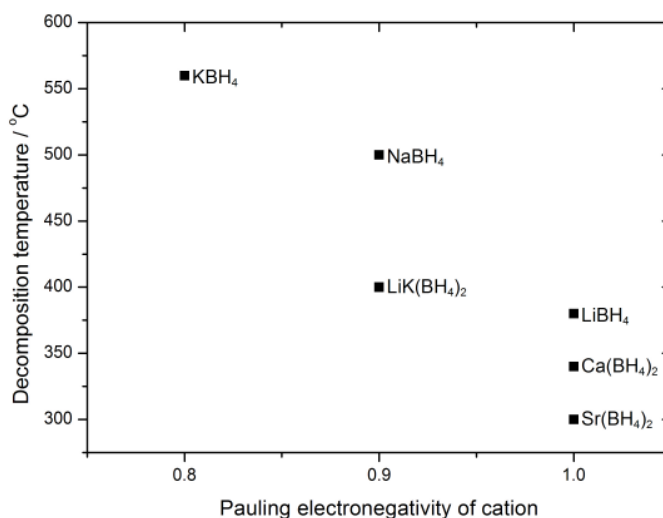


Figure 10.4 The decomposition temperature of borohydrides determined in this thesis as a function of Pauling electronegativity of the cation

10.4 New knowledge

In addition to the detailed variable temperature structural and thermogravimetric studies in this thesis, a number of new discoveries have been made.

- PDF analysis of neutron diffraction data from $^7\text{Li}^{11}\text{BD}_4$ showed that the short range B $\cdots$ D and D $\cdots$ D separations are identical meaning that the borohydride ions must be perfectly tetrahedral.
- The first mixed alkali metal borohydride, $\text{LiK}(\text{BH}_4)_2$, has been synthesised and characterised.
- New phases and phase transitions of $\text{Ca}(\text{BH}_4)_2$ have been identified.
- The first crystal structure of $\text{Sr}(\text{BH}_4)_2$ has been determined.
- Solid state ^{11}B NMR studies of a series of borohydrides have shown a trend between the ^{11}B chemical shift divided by the co-ordination number of the borohydride ion and either the electronegativity of the cation or the atomic ionisation energy to form the cation.

10.5 Further work

Future work on the alkali and alkaline earth metal borohydrides should focus on learning more about the behaviour of the new structures discussed in this thesis and gaining an even greater understanding of the synthesis and decomposition pathways of all of these borohydrides.

The method for the synthesis of borohydrides from the elements should be optimised; in the case of $\text{Na}^{11}\text{BD}_4$ and K^{11}BD_4 , the reaction is likely to occur in less than 12 hours. The yield could be improved by using a modified reaction vessel which did not allow the metal to rise above the boron powder as a vapour; this would increase the probability of the metal reacting with boron as well as the deuterium gas. The next stage in attempting high pressure solid-gas reactions would be to investigate using metal hydrides and borides as starting materials. In some cases, the synthesis from the elements is thought to occur via the metal hydride^[43] so this would remove a step from the synthesis. In addition, the metal hydrides usually take the form of crystalline powders which would be easier to grind or mechanically mill before heating than the metallic element; if the starting materials were more intimately mixed, the reaction yield may be higher. Metal borides such as MgB_2 should be investigated because there is a lower activation energy to remove boron atoms from boron layers in MgB_2 than from icosahedra in elemental boron.^[100]

In the future, the thermal decomposition of LiBH_4 could be studied using the IGAⁿ (thermogravimetric analysis with simultaneous neutron diffraction, see Chapter 2). It is not possible to collect neutron diffraction data during the decomposition of LiBD_4 with the sample contained within a sealed vanadium can because of the gas released during decomposition. On the other hand if the variable temperature neutron diffraction study had been completed within the IGAⁿ, the data would have been of

poorer quality due to the presence of the IGAⁿ within the neutron beam. The decomposition of LiBD_4 needs further investigation to determine the reason for the multiple decomposition stages and the presence of any decomposition intermediates such as $\text{Li}_2\text{B}_{12}\text{H}_{12}$ whose significance is still being debated.^[195]

Further work studying NaBH_4 and KBH_4 could include thermogravimetric analysis with mass spectrometry to higher temperatures than were possible during this project in order to better understand the decomposition process. Neutron diffraction studies with *in situ* Raman spectroscopy of the decomposition of $\text{Li}^{11}\text{BD}_4$, $\text{Na}^{11}\text{BD}_4$ and K^{11}BD_4 would be useful in order to determine when diffraction peaks disappear, whether it is due to the melting or decomposition of the compound.

The synthesis of $\text{LiK}(\text{BH}_4)_2$ has lead to many new questions. Alternative synthesis methods need to be attempted in order to both discover a method to produce a pure sample and also to understand why a starting ratio of 2:1 $\text{LiBH}_4\text{:KBH}_4$ is necessary to produce the optimum yield. One possible synthesis route to investigate is from LiBH_4 and either metallic potassium or a compound containing potassium ions such as a potassium halide. This would determine if all of the borohydride ions in $\text{LiK}(\text{BH}_4)_2$ come only from LiBH_4 , hence the requirement for twice as much LiBH_4 as KBH_4 in the starting mixture. Further analysis of the decomposition process is also required to determine if decomposition occurs directly from $\text{LiK}(\text{BH}_4)_2$ or via LiBH_4 and KBH_4 as has been suggested by a theoretical study.^[75]

Further work on $\text{Ca}(\text{BH}_4)_2$ should focus on determining the identity and structure of the high temperature phase; whether it is another polymorph of $\text{Ca}(\text{BH}_4)_2$ or a decomposition intermediate.

The structures of the unsolved $\text{Sr}(\text{BH}_4)_2$ phases also need to be determined. If it is possible, the variable temperature X-ray diffraction study of $\text{Sr}(\text{BH}_4)_2$ should be

repeated using a single sample. This is likely to require the use of a PSD detector so that data can be collected quickly enough to avoid radiation damage to the sample. A neutron diffraction study could also be used to determine the orientation of the borohydride ions.

The properties of the experimental parameters used by the IGA (Intelligent Gravimetric Analyser, see Chapter 2) should be further investigated in order to better understand the conditions which cause the apparent gains in sample mass to be recorded and then to avoid these conditions.

Work should then focus on the synthesis of more mixed metal borohydride systems. In particular the mixed $\text{LiBH}_4\text{-Ca}(\text{BH}_4)_2$ system has recently attracted attention. The composite has a eutectic melting temperature at approximately 200 °C and decomposes at a lower temperature than both LiBH_4 and $\text{Ca}(\text{BH}_4)_2$ in the pure form.^[139]

10.6 Borohydrides for hydrogen storage

Presently, the borohydrides discussed in this thesis cannot be used in reversible hydrogen storage systems due to their high decomposition temperature and poor reversibility of the dehydrogenation reaction. However, the high pressure synthesis of the isotopically enriched borohydrides (Chapter 3) showed that direct synthesis from the elements is possible and therefore synthesis from decomposition products could be the next step. With titanium halide catalysts, there is evidence that $\text{Ca}(\text{BH}_4)_2$ can be synthesised from CaH_2 , CaB_6 and H_2 at low temperatures making the dehydrogenation process of $\text{Ca}(\text{BH}_4)_2$ more reversible.^[196]

The synthesis of $\text{LiK}(\text{BH}_4)_2$ (Chapter 7) has proved the concept of producing a borohydride material from other alkali metal borohydrides where the properties of the new material are intermediate to those of the parent compounds.

The way forward for borohydride hydrogen storage is likely to be more mixed metal borohydrides of the alkali, alkaline earth and transition metals possibly combined with transition metal-based catalysts to produce a compound which reversibly releases sufficient hydrogen at low temperatures.

The task of finding new mixed metal hydrides for use as hydrogen storage materials is currently being engaged with by a collaboration between the University of Oxford, the Rutherford Appleton Laboratory, (RAL), Johnson Matthey and Ilika Technologies using a high-throughput combinatorial approach. Combinatorial arrays of metal hydride thin films are produced by physical vapour deposition for initial screening using a thermal imaging camera. The synthesis of hydrides which show potential for hydrogen storage can then be scaled up, allowing for structural, thermodynamic and gravimetric characterisation. The hydrogen desorption and absorption processes can also be studied by neutron diffraction with *in-situ* gravimetric analysis. This high-throughput combinatorial approach will allow the investigation of a wide range of multinary hydrides including borohydrides in order to find the optimum hydrogen storage material.^[197]

11 Bibliography

- [1] P. Hoffman, *Tomorrow's Energy: Hydrogen Fuel Cells and the Proposals for a Cleaner Planet*, MIT Press, Cambridge, MA, **2001**.
- [2] G. Marbán, T. Valdés-Solís, *Int. J. Hydrogen Energy* **2007**, 32, 1625.
- [3] L. Schlapbach, A. Züttel, *Nature* **2001**, 414, 353.
- [4] W. Grochala, P. P. Edwards, *Chem. Rev. (Washington, DC, U. S.)* **2004**, 104, 1283.
- [5] T. K. Mandal, D. H. Gregory, *Annu. Rep. Prog. Chem., Sect. A* **2009**, 105, 21.
- [6] <http://www1.eere.energy.gov/hydrogenandfuelcells/>, Accessed April 2009.
- [7] U. Bossel, B. Eliasson, G. Taylor, *European Fuel Cell Forum* **2003**.
- [8] P. Bénard, R. Chahine, *Scripta Materialia* **2007**, 56, 803.
- [9] C. E. Housecroft, A. G. Sharpe, *Inorganic Chemistry*, Prentice Hall, **2001**.
- [10] G. Sandrock, *J. Alloys Compd.* **1999**, 293-295, 877.
- [11] M. Dornheim, S. Doppiu, G. Barkhordarian, U. Boesenberg, T. Klassen, O. Gutfleisch, R. Bormann, *Scr. Mater.* **2007**, 56, 841.
- [12] B. Sakintuna, F. Darkrim-Lamari, M. Hirscher, *Int. J. Hydrogen Energy* **2007**, 32, 1121.
- [13] P. Bo, J. Chen, *Energy Environ. Sci* **2008**, 1, 479.
- [14] H. Wu, *Chem. Phys. Chem.* **2008**, 9, 2157.
- [15] T. Umegaki, J.-M. Yan, X.-B. Zhang, H. Shioyama, N. Kuriyama, Q. Xu, *Int. J. Hydrogen Energy* **2009**, 34, 2303.
- [16] S. Orimo, Y. Nakamori, J. R. Eliseo, A. Züttel, C. M. Jensen, *Chem. Rev. (Washington, DC, U. S.)* **2007**, 107, 4111.
- [17] M. Au, A. Jurgensen, *J. Phys. Chem. B* **2006**, 110, 7062.
- [18] J. J. Vajo, S. L. Skeith, F. Mertens, *J. Phys. Chem. Let.* **2005**, 109, 3719.
- [19] A. Züttel, P. Wenger, S. Rentsch, P. Sudan, P. Mauron, C. Emmenegger, *J. Power Sources* **2003**, 118, 1.
- [20] A. Züttel, A. Borgschulte, S. Orimo, *Scr. Mater.* **2007**, 56, 823.
- [21] Y. Filinchuk, D. Chernyshov, V. Dmitriev, *Z. Kristallogr.* **2008**, 223, 649.
- [22] H. I. Schlesinger, H. C. Brown, B. Abraham, A. C. Bond, N. Davidson, A. E. Finholt, J. R. Gilbreath, H. C. Hoekstra, L. Horvitz, E. K. Hyde, J. J. Katz, J. Knight, R. A. Lad, D. L. Mayfield, L. R. Rapp, D. M. Ritter, A. M. Schwartz, I. Sheft, L. D. Tuck, A. O. Walker, *J. Am. Chem. Soc* **1953**, 75, 186.
- [23] K. N. Semenenko, A. P. Chavgun, V. N. Surov, *Zhurnal Neorganicheskoi Khimii* **1971**, 16, 513.
- [24] V. I. Mikheeva, L. V. Titov, *Russian Journal of Inorganic Chemistry* **1964**, 9, 789.

- [25] V. I. Mikheeva, L. N. Tolmacheva, *Russian Journal of Inorganic Chemistry* **1973**, *18*, 1703.
- [26] L. V. Titov, E. R. Eremin, *Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya* **1975**, *5*, 1188.
- [27] V. I. Mikheeva, V. N. Konoplev, *Zhurnal Neorganicheskoi Khimii* **1965**, *10*, 2108.
- [28] B. D. James, M. G. H. Wallbridge, *Prog. Inorg. Chem.* **1970**, *11*, 97.
- [29] <http://www.chemistry.sdsu.edu/research/BNMR/>, Accessed **March 2010**.
- [30] H. Li, S. Orimo, Y. Nakamori, K. Miwa, N. Ohba, S. Towata, A. Züttel, *J. Alloys Compd.* **2007**, *446-447*, 315.
- [31] F. Schuth, B. Bogdanovic, M. Felderhoff, *Chem. Commun.* **2004**, *2004*, 2249.
- [32] J. Clayden, N. Greeves, S. Warren, P. Wothers, *Organic Chemistry*, Oxford University Press, **2001**.
- [33] W. H. Rapson, *Vol. 3017316* (Ed.: U. S. P. Office), **1962**.
- [34] R. C. Wade, (Ed.: U. S. P. Office), Ventron Corporation, **1976**.
- [35] C. P. de Leon, F. C. Walsh, D. Pletcher, D. J. Browning, J. B. Lakeman, *J. Power Sources* **2006**, *155*, 172.
- [36] B. H. Liu, Z. P. Li, *J. Power Sources* **2009**, *187*, 291.
- [37] A. Züttel, S. Rentsch, P. Fischer, P. Wenger, P. Sudan, P. Mauron, C. Emmenegger, *J. Alloys Compd.* **2003**, *356-357*, 515.
- [38] L. Mosegaard, B. Møller, J.-E. Jørgensen, U. Bosenberg, M. Dornheim, J. C. Hanson, Y. Cerenius, G. Walker, H. J. Jakobsen, F. Besenbacher, T. R. Jensen, *J. Alloys Compd.* **2007**, *446-447*, 301.
- [39] H. I. Schlesinger, H. C. Brown, *J. Am. Chem. Soc* **1940**, *62*, 3429.
- [40] H. I. Schlesinger, H. C. Brown, H. C. Hoekstra, L. R. Rapp, *J. Am. Chem. Soc* **1953**, *75*, 199.
- [41] H. I. Schlesinger, H. C. Brown, E. K. Hyde, *J. Am. Chem. Soc* **1953**, *75*, 209.
- [42] H. C. Brown, Y. M. Choi, S. Narasimhan, *Inorganic Chemistry* **1982**, *21*, 3657.
- [43] O. Friedrichs, F. Buchter, A. Borgschulte, A. Remhof, C. N. Zwicky, P. Mauron, M. Biemann, A. Züttel, *Acta Materialia* **2008**, *56*, 949.
- [44] S. Orimo, Y. Nakamori, G. Kitahara, K. Miwa, N. Ohba, S. Towata, A. Züttel, *J. Alloys Compd.* **2005**, *404-406*, 427.
- [45] A. Remhof, O. Friedrichs, F. Buchter, P. Mauron, A. Züttel, *Phys. Chem. Chem. Phys.* **2008**, *10*, 5859.
- [46] F. Pendolino, P. Mauron, A. Borgschulte, A. Züttel, *J. Phys. Chem. C* **2009**, *113*, 17231.
- [47] Ç. Çakanyildirim, M. Gürü, *Renewable Energy* **2008**, *33*, 2388.
- [48] F. Agresti, A. Khandelwal, *Scr. Mater.* **2009**, *60*, 753.
- [49] W. Haiping, W. Weidong, L. Tiecheng, W. Xuemin, G. Fangfang, C. Linhong, B. Li, D. Yang, *Materials Letters* **2010**, *64*, 320.
- [50] P. M. Harris, E. P. Meibohm, *J. Am. Chem. Soc* **1945**, *69*, 1231.

- [51] J.-P. Soulie, G. Renaudin, R. Černý, K. Yvon, *J. Alloys Compd.* **2002**, 346, 200.
- [52] M. R. Hartman, J. J. Rush, T. J. Udovic, R. C. Bowman Jr., S.-J. Hwang, *J. Solid State Chem.* **2007**, 180, 1298.
- [53] Z. Łodziana, T. Vegge, *Phys Rev Lett* **2004**, 93, 145501.
- [54] F. Buchter, Z. Łodziana, P. Mauron, A. Remhof, O. Friedrichs, A. Borgschulte, A. Züttel, D. Sheptyakov, T. Strässle, A. J. Ramirez-Cuesta, *Phys Rev B* **2008**, 78, 094302.
- [55] Y. Filinchuk, D. Chernyshov, R. Černý, *J. Phys. Chem. C* **2008**, 112, 10579.
- [56] W. D. Davis, L. S. Mason, G. Stegeman, *J. Am. Chem. Soc* **1949**, 71, 2775.
- [57] M. B. Smith, G. E. Bass Jr., *J. Chem. Eng. Data* **1963**, 8, 342.
- [58] P. Mauron, F. Buchter, O. Friedrichs, A. Remhof, M. Biemann, C. N. Zwicky, A. Züttel, *J. Phys. Chem. B* **2007**, 112, 906.
- [59] K. Miwa, N. Ohba, S. Towata, Y. Nakamori, S. Orimo, *Phys Rev B* **2004**, 69, 245120.
- [60] Y. Nakamori, K. Miwa, A. Ninomiya, H. Li, N. Ohba, S. Towata, A. Züttel, S. Orimo, *Phys. Rev. B: Condens. Matter* **2006**, 74, 045126.
- [61] S. Orimo, Y. Nakamori, N. Ohba, K. Miwa, M. Aoki, S. Towata, A. Züttel, *Appl. Phys. Lett.* **2006**, 89, 021920.
- [62] M. Au, W. Spencer, A. Jurgensen, C. Zeigler, *J. Alloys Compd.* **2008**, 462, 303.
- [63] <http://www.sigmaaldrich.com>, **Accessed October 2009**.
- [64] B. Bogdanović, M. Felderhoff, G. Streukens, *J. Serb. Chem. Soc* **2009**, 74, 183.
- [65] J. S. Kasper, L. V. McCarty, A. E. Newkirk, *J. Am. Chem. Soc* **1949**, 71, 2583.
- [66] A. M. Soldate, *J. Am. Chem. Soc* **1947**, 69, 687.
- [67] Y. Wu, J. C. Brady, M. T. Kelly, J. V. Ortega, J. L. Snover, *Am. Chem. Soc., Div. Fuel Chem.* **2003**, 48, 938.
- [68] Y. Filinchuk, H. Hagemann, *Eur. J. Inorg. Chem* **2008**, 2008, 3127.
- [69] R. L. Davis, C. H. L. Kennard, *J. Solid State Chemistry* **1985**, 59, 393.
- [70] S. C. Abrahams, J. Kalnajs, *J. Chem. Phys.* **1954**, 22, 434.
- [71] P. Fischer, A. Züttel, *Paul Scherrer Institute Annual Reports.* **2001**, Available from <http://num.web.psi.ch/reports/2001/pdf/g09.pdf>.
- [72] P. Fischer, A. Züttel, *Materials Science Forum* **2004**, 443-444, 287.
- [73] J. Urgnani, F. J. Torres, M. Palumbo, M. Baricco, *Int. J. Hydrogen Energy* **2008**, 33, 3111.
- [74] O. A. Babanova, A. V. Soloninin, A. P. Stepanov, A. V. Skripov, Y. Filinchuk, *J. Phys. Chem. C* **2010**, 114, 3712.
- [75] K. C. Kim, D. S. Sholl, *J. Phys. Chem. C* **2010**, 114, 678.
- [76] E. Kim, R. Kumar, P. F. Weck, A. L. Cornelius, M. Nicol, S. C. Vogel, J. Zhang, M. Hartl, A. C. Stowe, L. Daemen, Y. Zhao, *J. Phys. Chem. B letters* **2007**, 111, 13873.

- [77] D. R. Lide, *CRC Handbook of Chemistry and Physics*, CRC Press, **2003-2004**.
- [78] P. Martelli, R. Caputo, A. Remhof, P. Mauron, A. Borgschulte, A. Züttel, *J. Phys. Chem. C* **2010**, *114*, 7173.
- [79] S. Orimo, Y. Nakamori, A. Züttel, *Materials Science and Engineering* **2004**, *B104*, 51.
- [80] Z. P. Li, B. H. Liu, N. Morigasaki, S. Suda, *J. Alloys Compd.* **2003**, *354*, 243.
- [81] Q. Liu, D. Zhang, L. Duan, G. Zhang, L. Wang, Y. Cao, Y. Qiu, *Jap. J. Applied Phys.* **2009**, *48*, 080205.
- [82] M. D. Banus, R. W. Bragdon, (Ed.: U. S. P. Office), **1956**.
- [83] W. S. Fedor, M. D. Banus, D. P. Ingalls, *Industrial and Engineering Chemistry* **1957**, *49*, 1664.
- [84] D. L. Chamberlain, (Ed.: U. S. P. Office), **1962**.
- [85] R. L. Luck, E. J. Schelter, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1999**, *55*, IUC9900151 (cif access).
- [86] G. Renaudin, S. Gomes, H. Hagemann, L. Keller, K. Yvon, *J. Alloys Compd.* **2004**, *375*, 98.
- [87] R. Kumar, E. Kim, A. L. Cornelius, *J. Phys. Chem. C* **2008**, *112*, 8452.
- [88] X.-B. Xiao, W.-Y. Yu, B.-Y. Tang, *J. Phys.: Condens Matter* **2008**, *20*, 445210.
- [89] S. V. Zapol'skii, L. N. Tolmacheva, V. I. Mikheeva, *Russian Journal of Inorganic Chemistry* **1970**, *15*, 413.
- [90] S. V. Zapol'skii, V. M. Bakulina, V. I. Mikheeva, *Zhurnal Neorganicheskoi Khimii* **1967**, *12*, 1310.
- [91] D. S. Stasinevich, G. A. Egorenko, *Zhurnal Neorganicheskoi Khimii* **1968**, *13*, 654.
- [92] Y. Nakamori, H. Li, K. Kikuchi, M. Aoki, K. Miwa, S. Towata, S. Orimo, *J. Alloys Compd.* **2007**, *446-447*, 296.
- [93] E. Jeon, Y. W. Cho, *2006* **2006**, *422*, 273.
- [94] E. Rönnebro, E. H. Majzoub, *J. Phys. Chem. B* **2007**, *111*, 12045.
- [95] J.-H. Kim, S.-A. Jin, J.-H. Shim, Y. W. Cho, *Scr. Mater.* **2008**, *58*, 481.
- [96] J. Kollonitsch, O. Fuchs, V. Gabor, *Nature* **1954**, *173*, 125.
- [97] J. Kollonitsch, O. Fuchs, V. Gábor, *Nature* **1955**, *175*, 346.
- [98] L. V. Titov, *Russian Journal of Inorganic Chemistry* **1968**, *13*, 1797.
- [99] K. Miwa, M. Aoki, T. Noritake, N. Ohba, Y. Nakamori, S. Towata, A. Züttel, S. Orimo, *Phys. Rev. B: Condens. Matter* **2006**, *74*, 155122.
- [100] G. Barkhordarian, T. R. Jensen, S. Doppiu, U. Bosenberg, A. Borgschulte, R. Gremaud, Y. Cerenius, M. Dornheim, T. Klassen, R. Bormann, *J. Phys. Chem. C* **2008**, *112*, 2743.
- [101] F. Buchter, Z. Łodziana, A. Remhof, O. Friedrichs, A. Borgschulte, P. Mauron, A. Züttel, D. Sheptyakov, G. Barkhordarian, R. Bormann, K. Chłopek, M. Fichtner, M. H. Sorby, M. D. Riktor, B. C. Hauback, S. Orimo, *J. Phys. Chem. B* **2008**, *112*, 8042.
- [102] K. Chłopek, C. Frommen, A. Léon, O. Zabara, M. Fichtner, *J. Mat. Chem.* **2007**, *17*, 3465.

- [103] Y. Kim, D. Reed, Y.-S. Lee, J.-H. Shim, H. N. Han, D. Book, Y. W. Cho, *J. Alloys Compd.* **2010**, 492, 597.
- [104] F. Buchter, Z. Łodziana, A. Remhof, O. Friedrichs, A. Borgschulte, P. Mauron, A. Züttel, D. Sheptyakov, L. Palatinus, K. Chłopek, M. Fichtner, G. Barkhordarian, R. Bormann, B. C. Hauback, *J. Phys. Chem. C* **2009**, 113, 17223.
- [105] P. Vajeeston, P. Ravindran, H. Fjellvag, *J. Alloys Compd.* **2007**, 446-447, 44.
- [106] M. Aoki, K. Miwa, T. Noritake, N. Ohba, M. Matsumoto, H.-W. Li, Y. Nakamori, S. Towata, S. Orimo, *Applied Physics A* **2008**, 92, 601.
- [107] Y.-S. Lee, Y. Kim, Y. W. Cho, D. Shapiro, C. Wolverton, Ozoliņš, *Phys. Rev. B: Condens. Matter* **2009**, 79, 104107.
- [108] M. Fichtner, K. Chłopek, M. Longhini, H. Hagemann, *J. Phys. Chem. C* **2008**, 112, 11575.
- [109] E. H. Majzoub, E. Rönnebro, *J. Phys. Chem. C* **2009**, 113, 3352.
- [110] Y. Filinchuk, E. Rönnebro, D. Chandra, *Acta Materialia* **2009**, 57, 732.
- [111] M. D. Riktor, M. H. Sørby, K. Chłopek, M. Fichtner, B. C. Hauback, *J. Mat. Chem.* **2009**, 19, 2754.
- [112] T. Noritake, M. Aoki, M. Matsumoto, K. Miwa, S. Towata, H.-W. Li, S. Orimo, *J. Alloys Compd.* **2010**, 491, 57.
- [113] V. N. Konoplev, N. N. Mal'tseva, V. S. Khain, *Soviet Journal of Coordination Chemistry* **1992**, 18, 1143.
- [114] L.-L. Wang, D. D. Graham, I. M. Robertson, D. D. Johnson, *J. Phys. Chem. C* **2009**, 113, 20088.
- [115] K. A. Solntsev, N. T. Kuznetsov, L. N. Kol'ba, V. M. Agre, V. I. Ponomarev, *Russian Journal of Inorganic Chemistry* **1977**, 22, 313.
- [116] J.-H. Kim, S.-A. Jin, J.-H. Shim, Y. W. Cho, *J. Alloys Compd.* **2008**, 461, L20.
- [117] Y. Kim, D. Reed, Y.-S. Lee, J. Y. Lee, J.-H. Shim, D. Book, Y. W. Cho, *J. Phys. Chem. C* **2009**, 113, 5865.
- [118] J.-H. Kim, J.-H. Shim, Y. W. Cho, *J. Power Sources* **2008**, 181, 140.
- [119] E. Wiberg, H. Nöth, R. Hartwimmer, *Zeitschrift für Naturforschung* **1955**, 10b, 292.
- [120] E. Wiberg, R. Hartwimmer, *Zeitschrift für Naturforschung* **1955**, 10b, 294.
- [121] E. Wiberg, R. Hartwimmer, *Zeitschrift für Naturforschung* **1955**, 10b, 295.
- [122] V. I. Mikheeva, A. S. Sizareva, *Zhurnal Neorganicheskoi Khimii* **1977**, 22, 1706.
- [123] M. Bremer, H. Nöth, M. Thomann, M. Schmidt, *Chemische Berichte* **1995**, 128, 455.
- [124] D. S. Marynick, W. N. Lipscomb, *Inorganic Chemistry* **1972**, 11, 820.
- [125] R. Černý, Y. Filinchuk, H. Hagemann, K. Yvon, *Angew. Chem. Int. Ed.* **2007**, 46, 5765.
- [126] R. Černý, N. Penin, H. Hagemann, Y. Filinchuk, *J. Phys. Chem. C* **2009**, 113, 9003.

- [127] K. Miwa, N. Ohba, S. Towata, Y. Nakamori, A. Züttel, S. Orimo, *J. Alloys Compd.* **2007**, 446-447, 310.
- [128] S. Aldridge, A. J. Blake, A. J. Downs, R. O. Gould, S. Parsons, C. R. Pulham, *J. Chem. Soc., Dalton Trans.*, **1997**, 1007.
- [129] H. Fernández, J. Grotewold, C. M. Previtali, *J. Chem. Soc., Dalton Transactions: Inorganic Chemistry* **1973**, 20, 2090.
- [130] Y. Nakamori, S. Orimo, *J. Alloys Compd.* **2004**, 370, 271.
- [131] H. Smithson, C. A. Marianetti, D. Morgan, A. Van der Ven, A. Predith, G. Ceder, *Phys Rev B* **2002**, 66, 144107.
- [132] K. Miwa, N. Ohba, S. Towata, *J. Alloys Compd.* **2005**, 404-406, 140.
- [133] H. Hagemann, M. Longhini, J. W. Kaminski, T. A. Wesolowski, R. Cerny, N. Penin, M. H. Sørby, B. C. Hauback, G. Severa, C. M. Jensen, *J. Phys. Chem. A* **2008**, 112, 7551.
- [134] R. Černý, G. Severa, D. Ravnsbæk, Y. Filinchuk, V. D'Anna, H. Hagemann, D. Haase, C. M. Jensen, T. R. Jensen, *J. Phys. Chem. C* **2010**, 114, 1357.
- [135] D. Ravnsbæk, Y. Filinchuk, Y. Cerenius, H. J. Jakobsen, F. Besenbacher, J. Skibsted, T. R. Jensen, *Angew. Chem. Int. Ed.* **2009**, 48, 6659.
- [136] L. Seballos, J. Z. Zhang, E. Rönnebro, J. L. Herberg, E. H. Majzoub, *J. Alloys Compd.* **2009**, 476, 446.
- [137] J. S. Hummelshøj et al, *J. Chem. Phys.* **2009**, 131, 014101.
- [138] Z.-Z. Fang, X.-D. Kang, P. Wang, H.-W. Li, S. Orimo, *J. Alloys Compd.* **2010**, 491, L1.
- [139] J. Y. Lee, D. Ravnsbæk, Y.-S. Lee, Y. Kim, Y. Cerenius, J.-H. Shim, T. R. Jensen, N. H. Hur, Y. W. Cho, *J. Phys. Chem. C* **2009**, 113, 15080.
- [140] R. L. Lowton, M. O. Jones, W. I. F. David, S. R. Johnson, M. Sommariva, P. P. Edwards, *J. Mat. Chem.* **2008**, 18, 2355.
- [141] J. Huot, S. Boily, V. Güther, R. Schulz, *J. Alloys Compd.* **1999**, 383, 304.
- [142] E. A. Nickels, M. O. Jones, W. I. F. David, S. R. Johnson, R. L. Lowton, M. Sommariva, P. P. Edwards, *Angew. Chem. Int. Ed.* **2008**, 47, 2817.
- [143] A. J. Du, S. C. Smith, G. Q. Lu, *Phys. Rev. B: Condens. Matter* **2006**, 74, 193405.
- [144] R. Tilley, *Crystals and Crystal Structures*, John Wiley and Sons, Ltd, **2006**.
- [145] http://reference.iucr.org/dictionary/Ewald_sphere, **Accessed November 2009**.
- [146] A. Putnis, *Introduction to Mineral Sciences*, Cambridge University Press, **1992**.
- [147] L. E. Smart, E. A. Moore, *Solid State Chemistry, An Introduction*, 3 ed., CRC Press.
- [148] J. Als-Nielsen, D. F. McMorrow, *Elements of Modern X-ray Physics*, John Wiley and Sons Ltd, **2001**.
- [149] <http://www.esrf.eu/UsersAndScience/Experiments/StructMaterials/ID31>, **Accessed November 2009**.

- [150] <http://www.diamond.ac.uk/Home/Beamlines/I11/>, **Accessed May 2010.**
- [151] <http://sls.web.psi.ch/view.php/beamlines/ms/index.html>, **Accessed May 2010.**
- [152] B. D. Patterson, R. Abela, H. Auderset, Q. Chen, F. Fauth, F. Gozzo, G. Ingold, H. Kühne, M. Lange, D. Maden, D. Meister, P. Pattison, T. Schmidt, B. Schmitt, C. Schulze-Briesse, M. Shi, M. Stamparoni, P. R. Willmott, *Nuclear Instruments and Methods in Physics Research A* **2005**, 540, 42.
- [153] E. N. Kaufmann, *Characterization of Materials, Vol. 2*, John Wiley and Sons, Ltd, **2003**.
- [154] <http://www.isis.stfc.ac.uk/>, **Accessed November 2009.**
- [155] A. C. Hannon, *Nuclear Instruments and Methods in Physics Research A* **2005**, 551, 88.
- [156] S. Gomes, H. Hagemann, K. Yvon, *J. Alloys Compd.* **2002**, 346, 206.
- [157] R. Gremaud, Z. Łodziana, P. Hug, B. Willenberg, A.-M. Racu, J. Schoenes, A. J. Cuesta-Ramirez, S. J. Clark, K. Refson, A. Züttel, A. Borgschulte, *Phys. Rev. B: Condens. Matter* **2009**, 80, 100301.
- [158] K. B. Harvey, N. R. McQuaker, *Can. J. Chem* **1971**, 49, 3282.
- [159] G. Herzberg, *Molecular Spectra and Molecular Structure II. Infrared and Raman Spectra of Polyatomic Molecules*, D. Van Nostrand Company, Inc., **1968**.
- [160] J. A. Iggo, *NMR Spectroscopy in Inorganic Chemistry*, Oxford University Press, **1999**.
- [161] S. Hayashi, K. Hayamizu, *Bull. Chem. Soc. Jpn.* **1989**, 62, 2429.
- [162] W. Clegg, A. J. Blake, R. O. Gould, P. Main, *Crystal Structure Analysis: Principles and Practice*, Oxford University Press.
- [163] W. I. F. David, K. Shankland, L. B. McCusker, C. Baerlocher, *Structure Determination from Powder Diffraction Data*, Oxford University Press.
- [164] R. A. Young, *The Rietveld Method*, Oxford University Press.
- [165] H. M. Rietveld, *Acta Crystallogr.*, **1967**, 22, 151.
- [166] H. M. Rietveld, *J. Appl. Crystallogr.* **1969**, 2, 65.
- [167] A. Coelho, *TOPAS Academic* © 1994 - 2004
- [168] W. I. F. David, K. Shankland, J. van de Streek, E. Pidcock, W. D. S. Motherwell, J. C. Cole, *J. Appl. Crystallogr.* **2006**, 39, 910.
- [169] <http://www.ncnr.nist.gov/resources/n-lengths/elements/h.html>, **Accessed March 2010.**
- [170] J. A. Beattie, O. C. Bridgeman, *J. Am. Chem. Soc* **1928**, 50, 3133.
- [171] G. Severa, E. Rönnebro, C. M. Jensen, *Chem. Commun.* **2010**, 46, 421.
- [172] H. Wu, W. Zhou, T. Yildirim, *J. Am. Chem. Soc* **2008**, 130, 14834.
- [173] J. B. Yang, J. Lamsal, Q. Cal, W. J. James, W. B. Yelon, *Appl. Phys. Lett.* **2008**, 92, 091916.
- [174] C. B. Hübschle, M. Messerschmidt, D. Lentz, P. Luger, *Z. Anorg. Allg. Chem.* **2004**, 630, 1313.
- [175] V. Dmitriev, Y. Filinchuk, D. Chernyshov, A. V. Talyzin, A. Dzwilewski, O. Andersson, B. Sundqvist, *Phys Rev B* **2008**, 77, 174112.

- [176] S. K. Callear, E. A. Nickels, M. O. Jones, M. Matsuo, S. Orimo, P. P. Edwards, W. I. F. David, *Submitted, J. Mat. Chem* **2010**.
- [177] D. A. Keen, *J. Appl. Cryst.* **2001**, *34*, 172.
- [178] A. Borgschulte, A. Züttel, P. Hug, A.-M. Racu, J. Schoenes, *J. Phys. Chem. A* **2008**, *112*, 4749.
- [179] A.-M. Racu, J. Schoenes, Z. Lodziana, A. Borgschulte, A. Züttel, *J. Phys. Chem. A* **2008**, *112*, 9716.
- [180] B. E. Smith, B. D. James, R. M. Peachley, *Inorganic Chemistry* **1977**, *16*, 2057.
- [181] L. M. Arnbjerg, D. Ravnsbæk, Y. Filinchuk, R. T. Vang, Y. Cerenius, F. Besenbacher, J.-E. Jørgensen, H. J. Jakobsen, T. R. Jensen, *Chem. Mater.* **2009**, *21*, 5772.
- [182] G. L. Soloveichik, X.-Y. Gao, J. Rijssenbeek, M. Andrus, S. Kniajanski, R. C. Bowman Jr., S.-J. Hwang, J.-C. Zhao, *Int. J. Hydrogen Energy* **2009**, *34*, 916.
- [183] A. C. Stowe, W. J. Shaw, J. C. Linehan, B. Schmid, T. Autrey, *Phys. Chem. Chem. Phys.* **2007**, *9*, 1831.
- [184] G. Guella, B. Patton, A. Miotello, *J. Phys. Chem. C* **2007**, *111*, 17844.
- [185] A. Ammar, M. Menetrier, A. Villesuzanne, S. Matar, B. Chevalier, J. Etourneau, G. Villeneuve, J. Rodriguez-Carvajal, H.-J. Koo, A. I. Smirnov, M. Whangbo, *Inorganic Chemistry* **2004**, *43*, 4974.
- [186] R. Juza, *Angew. Chem. Int. Ed.* **1964**, *3*, 471.
- [187] S. R. Johnson, W. I. F. David, D. M. Royse, M. Sommariva, C. Y. Tang, F. P. A. Fabbiani, M. O. Jones, P. P. Edwards, *Chem. Asian J.* **2009**, *4*, 849.
- [188] L. Pauling, *J. Am. Chem. Soc* **1929**, *51*, 1010.
- [189] S. J. Smith, R. Stevens, S. Liu, G. Li, A. Navrotsky, J. Boerio-Goates, B. F. Woodfield, *American Mineralogist* **2009**, *94*, 236.
- [190] D. J. Reidy, J. D. Holmes, M. A. Morris, *Journal of the European Ceramic Society* **2006**, *26*, 1727.
- [191] J.-H. Her, P. W. Stephens, Y. Gao, G. L. Soloveichik, J. Rijssenbeek, M. Andrus, J.-C. Zhao, *Acta Crystallogr., Sect. B: Struct. Sci.* **2007**, *63*, 561.
- [192] T. Hahn, *International Tables for Crystallography, Volume A*, Springer for International Union of Crystallography, **2005**.
- [193] J.-H. Her, M. Yousufuddin, W. Zhou, S. S. Jalisatgi, J. G. Kulleck, J. A. Zan, S.-J. Hwang, R. C. Bowman Jr., T. J. Udovic, *Inorganic Chemistry* **2008**, *47*, 9757.
- [194] S. Filatov, N. Bendeliani, B. Albert, J. Kopf, T. Dyuzheva, L. Lityagina, *Solid State Sciences* **2005**, *7*, 1363.
- [195] O. Friedrichs, A. Remhof, S.-J. Hwang, A. Züttel, *Chemistry of Materials* **2010**, *22*, 3265.
- [196] C. Rongeat, V. D'Anna, H. Hagemann, A. Borgschulte, A. Züttel, L. Schultz, O. Gutfleisch, *J. Alloys Compd.* **2010**, *493*, 281.
- [197] D. Nikbin, *The Fuel Cell Review* **2006**, *3*, 15.