

Ammonia Borane and its Derivatives:
High Weight Percentage
Hydrogen Storage Materials

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

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A Study of Ammonia Borane and its Derivatives:
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Ammonia borane and ammonium borohydride have been considered extensively as potential hydrogen storage materials. This thesis reports their structure and functional properties, emphasising the key role that dihydrogen bonding plays in both materials.

The formation of a 'mobile phase' is considered to be the preliminary step in the decomposition of ammonia borane. The formation of this mobile phase has been studied using neutron diffraction, inelastic neutron spectroscopy and NMR. It has been found that in the mobile phase, 'end-to-end' flipping of the ammonia borane molecule occurs. This is an important precursor to the next step in the decomposition: the formation of the diammoniate of diborane. The dihydrogen bonding networks which occur in both the orthorhombic and the tetragonal phases of ammonia borane, and are the controlling factor in the decomposition process, were investigated using Density Functional Theory Molecular Dynamics (DFT-MD) simulations. It was hence shown that in the high-temperature tetragonal phase of ammonia borane, dihydrogen bonding is still an important stabilising interaction and there is little to distinguish between the three crystallographically distinct dihydrogen bonds.

A closely related hydrogen storage material, ammonium borohydride, was also studied using the same techniques. Its low temperature phase progression was examined using variable temperature neutron diffraction. The vibrational modes of ammonium borohydride were assigned by comparing vibrational spectra determined using inelastic neutron spectroscopy with the results of DFT-MD simulations. Quasielastic neutron spectroscopy was used to show that both the ammonium and borohydride groups in ammonium borohydride perform discrete 'hopping' reorientational motions at a wide range of temperatures, and that the ammonium group has a mean residence time approximately 100 times less than that of the borohydride group. Hydrogen atom densities in the ammonium group were determined from DFT-MD simulations, and from refinements of high-resolution neutron diffraction data using cubic harmonic basis functions.

The work described in this thesis was carried out whilst a student in the Inorganic Chemistry Department, University of Oxford from Michaelmas 2009 to Michaelmas 2013 under the supervision of Professor W. I. F. David and Professor P. P. Edwards. All of the work in this thesis 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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Michaelmas 2013

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Chapter 1

Introduction

Atomic Weight	1.00794(1) amu
Electron configuration	1s ¹
Isotopes	¹ H 99.985 % ² H 0.015 % ³ H trace
Melting point	14.01 K
Boiling point	20.28 K
Liquid density	0.07 g cm ⁻¹
Gas density	0.08988 g L ⁻¹ at STP

Table 1.1: The physical properties of hydrogen.

Hydrogen is the most abundant element in the universe, believed to account for 75 % of all mass [1]. As a diatomic molecule, it is a colourless, odourless and tasteless, highly combustible gas [2]. However, on Earth it is rarely found as diatomic hydrogen because it readily forms covalent bonds with other atoms, and occurs most commonly in water and organic compounds.

1.1 The Hydrogen Economy and Hydrogen Storage

Non-renewable fossil fuels are currently the main global energy source. Their combustion produces pollution: in the form of particulate matter and greenhouse gases which both contribute to global warming. In 2011, 62 % of global electricity production was obtained from fossil fuels and essentially 100 % of transportation was based on combustion engines powered by fossil fuels [3]. Estimates vary but there is a general consensus that the depletion of fossil fuels is not sustainable in the long term and that the situation will become critical some time before the end of the 21st century. Alternative energy supply options are thus essential.

Energy Density of Hydrogen		Energy Density of Petrol	
By mass	143 MJ kg ⁻¹	By mass	46.4 MJ kg ⁻¹
By volume as a liquid	10.1 MJ L ⁻¹	By volume	34.2 MJ L ⁻¹
By volume as a gas (1 bar)	0.0107 MJ L ⁻¹		
By volume as a gas (700 bar)	5.6 MJ L ⁻¹		

Table 1.2: Table comparing the energy density of hydrogen and petrol.

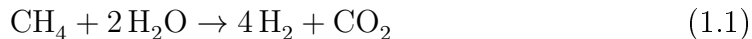
The idea of a hydrogen economy [4] was first coined and proposed by John Bockris almost 50 years ago [5]. The term is used to encompass the whole system necessary to use hydrogen as a replacement for fossil fuels; this involves production, transportation, storage and finally utilisation. As well as replacing petrol and diesel in cars, it has been proposed that hydrogen could be used as an energy store for renewable sources of energy [6]. One of the problems with renewable energy sources is their intermittency; for example, energy provision by wind or sun does not correlate with in energy demand. On the other hand, nuclear power stations run constantly and when the electricity is not needed, if not stored, it would be wasted [7]. Here, the excess electricity produced could

be used to make hydrogen, which could be stored and subsequently used to produce energy when it is required.

Hydrogen has a gravimetric energy density of 143 MJ kg^{-1} compared with 46.4 MJ kg^{-1} for petrol [8]. It is non-toxic, environmentally friendly and, in principle, continuously renewable. However, at room temperature hydrogen is a gas and its volumetric energy density is 3200 times lower than petrol [8]. As pure hydrogen is virtually non-existent on Earth, it has to be synthesised and is thus not an energy source but an energy vector. It needs to be produced using energy, a proportion of which may then be released when required. In contrast, hydrocarbons may simply be mined, drilled or, most recently accessed through hydraulic fracturing (‘fracking’) for the chemical potential energy they contain.

1.1.1 Production

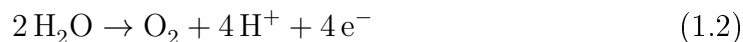
Steam Reforming Currently over 95 % of hydrogen is produced from fossil fuels [9], mainly through the steam reforming of methane [10] as shown in Equation 1.1. It is low-cost and already well established, producing the hydrogen used in the conversion of heavy petroleum fractions into lighter ones and in the production of ammonia in the Haber process.



As a method of producing ‘green’ hydrogen, it is patently not ideal since the initial feedstocks are fossil fuels. The greenhouse gas carbon dioxide is the main waste product, although it could be sequestered and stored underground. Large centralised production plants (as currently exist) do increase the efficiency of the process and could aid the green disposal of carbon dioxide. However, with

centralised plants, hydrogen would have to be transported to local networks.

Electrolysis The remaining 5 % is produced by electrolytically splitting water into hydrogen and oxygen [11]. Oxidation occurs at the anode, producing oxygen:



and reduction occurs at the cathode, producing hydrogen:



Electrolysis can be undertaken without the use of fossil fuels by using electricity from renewable sources. This is problematic as (in 2011) only 38 % of electricity produced worldwide was from renewable sources (18 % if nuclear is excluded) [3]. Electrolysis is better suited than steam reformation to the localised production of hydrogen, and electrolysis plants of almost any scale can be constructed. Producing hydrogen locally removes the need for complex distribution networks [7].

1.1.2 Transport

There are currently extensive networks of pipelines for the transport of natural gas, they cannot be turned into hydrogen pipelines. Hydrogen is a much smaller molecule than methane and so can leak out of systems which would easily contain other gases. Hydrogen can also diffuse into metals, causing hydrogen embrittlement and failure. The danger of self ignition through electrostatic charges created by hydrogen flowing through pipes must also be considered.

Currently, petrol is transferred from refineries to local petrol stations using tankers. The same principle could theoretically be applied to hydrogen. However, the same

storage problem applies to transporting hydrogen in tankers as in domestic cars: as a gas compressed to 700 bar, hydrogen is 6.1 times less energy-dense than petrol (see Table 1.2).

1.1.3 Use

Hydrogen can be used as a fuel in internal combustion engines (ICEs) with very similar designs to a petrol ICEs [12, 13]. Alternatively hydrogen can be used in fuel cells which convert chemical energy into electrical energy through a reaction between a reductant (hydrogen) and an oxidant (oxygen) in the presence of an electrolyte.

The most suitable type of fuel cell for light vehicles are polymer electrolyte membrane (PEM) fuel cells [14, 15]. The electrolyte is a polymer film, usually perfluorosulfonic acid, which, when wet, is proton permeable but will not conduct electrons. The electrodes are porous graphite impregnated with platinum. At the anode, hydrogen is split into electrons and protons; the protons migrate through the electrolyte to the cathode which is in air. The electron cannot pass through the electrolyte and is forced around through an external electrical circuit. The proton and the electron recombine with oxygen from the air at the cathode forming water.

PEM fuel cells have a relatively low optimum working temperature of 75 - 85°C. They are safe, quiet, easy-to-operate and low-maintenance. However, they are expensive, easily poisoned by contaminants and since the electrolyte must contain liquid water they will not operate below 0°C or above 100°C [7].

1.2 Storage

1.2.1 Properties of a Hydrogen Storage System

Gravimetric capacity	9 MJ kg ⁻¹
Volumetric capacity	8.23 MJ L ⁻¹
Number of cycles during lifetime	1500
Fuel purity	99.97 %
Fill time	2.5 minutes
min/max operating temperature	-30/50°C

Table 1.3: The US Department of Energy ultimate targets for on-board hydrogen storage systems for light-duty vehicles based on a mileage of 150,000 miles over the lifetime of a vehicle [16].

There are a variety of factors which have to be considered when designing a method to store hydrogen; more details of specific hydrogen stores are shown in Section 1.2.2:

- Gravimetric and volumetric energy capacity - the aim of a storage material is to increase the volumetric energy density of the hydrogen while maintaining an acceptable gravimetric energy density for the complete storage system. The United States Department of Energy (DoE) targets for such materials are 9 MJ kg⁻¹ and 8.23 MJ L⁻¹ (see Table 1.3 and Reference [16]).
- Cost - for a hydrogen-powered car to be a success, the car and the fuel must not be significantly more expensive than an equivalent petrol or diesel car. A large part of the cost of a hydrogen-powered car is likely to be the storage system.
- Durability - included in the durability and the reliability of the car is the number of cycles that the storage system will undergo during its lifetime. It must also be

able to operate over a wide range of temperatures.

- Charging and discharging rates - the car must be able to refuelled in a few minutes, the DoE target is ultimately 2.5 minutes. The rate at which hydrogen is released from the storage material also needs to be controlled.
- Hydrogen purity - PEM fuel cells need high purity hydrogen to continue to function efficiently and so the storage material must provide it.
- Safety - if hydrogen cars are to be widely used they need to be safe (and be seen by the general public to be safe). As hydrogen is more flammable than petrol (it has a lower flash point and a larger range of concentrations at which it will ignite) and leaks more easily, extra engineering controls must be considered. Another consideration is that chemical hydrogen stores are often toxic and hazardous, for example they generally release hydrogen gas on contact with water.

1.2.2 Types of Hydrogen Store

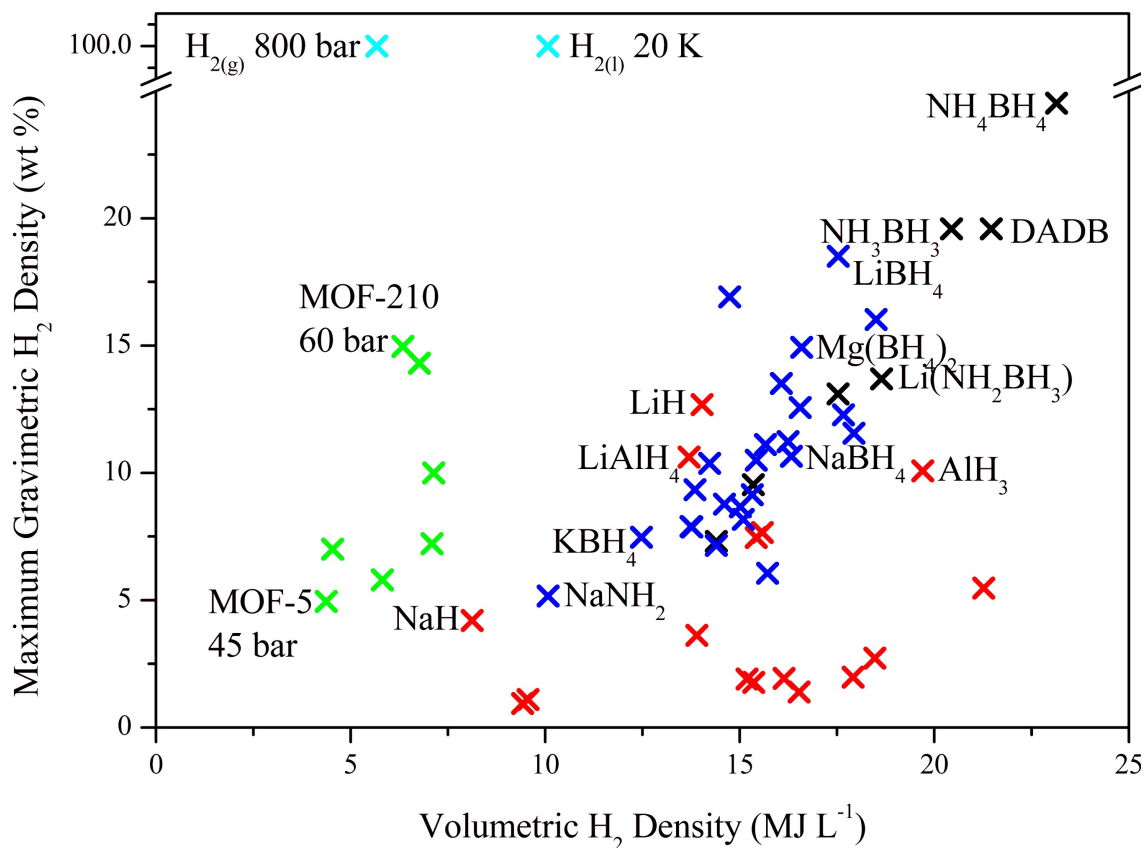


Figure 1.1: A comparison between the gravimetric and volumetric densities for various hydrogen stores. Physical stores in green, pure hydrogen in pale blue, hydrides in red, complex hydrides in dark blue and chemical hydrides in black.

Hydrogen can be physically stored as a high pressure gas, liquid or solid hydrogen, or adsorbed H₂ molecules on the surface (and internal surfaces) of a material. Hydrogen can also be stored chemically, where protic/hydridic ionic bonds or covalent bonds are formed between hydrogen atoms and other elements in the host material. A comparison of the gravimetric and volumetric densities for these various types of hydrogen store is shown in Figure 1.1.

1.2.3 Physical Stores

Compressing or liquefying hydrogen increases its volumetric energy density, making it more practical to store and transport.

Compressed Hydrogen: Compressed hydrogen is currently used as the fuel in commercial hydrogen-hybrid cars [17]. However, compressing hydrogen to 700 bar increases the energy density to only 5.6 MJ L⁻¹, still 6 times less dense than petrol. There is also an energy penalty when hydrogen is compressed, compressing to 700 bar will require 10 - 15 % of its potential chemical energy content. Gas cylinders are heavy and there are engineering constraints on their shape which make them difficult to fit into a car. However, compressed hydrogen is a more attractive option in stationary stores where size and weight are not so important.

Cryogenic Storage: The volumetric energy density of hydrogen can also be increased by storing it as a liquid or slush (a mixture of solid and liquid hydrogen). Liquefying hydrogen is a complex, energy intensive process. It is pre-cooled using liquid ammonia and liquid nitrogen to -196°C, then cooled further using helium in a multi-stage compression-expansion system. Liquid hydrogen storage tanks need to have expensive insulation, and boil-off cannot be completely prevented. Generally 1 - 5 % of the hydrogen will be lost daily, with a higher rate of loss in smaller stores [18].

Adsorption: Hydrogen can be physisorbed on to the surface of a material [19, 20].

The adsorption is generally reversible as the interaction between the hydrogen and the surface is low-energy, so there is little energy barrier to overcome when it desorbs.

There were initially very optimistic speculations for the hydrogen storage capacity of carbon-based materials. However, above its boiling point, hydrogen forms a

monolayer on the surface, and consequently the maximum capacity is directly proportional to the surface area of the material [21]. The theoretical maximum with a 1:1 ratio of hydrogen to carbon atoms is 7.7 wt%, while a more realistic maximum at room temperature is about 1 wt% [22]. The level of adsorption can be increased by reducing the temperature and increasing the pressure of hydrogen. There has been more success with metal organic frameworks (MOFs) [23], which are crystalline compounds formed by metal ions coordinated by rigid organic molecules. Some of these structures have large stable pores which increase the surface area, often to over 2500 m² g⁻¹. The metal and the organic linkers can be modified to tune the properties of the system and improve the storage capacity. Under elevated pressure, these materials are capable of storing between 1 - 7 wt% of hydrogen at -196°C and 0.01 - 1 wt% at room temperature [24].

1.2.4 Chemical Stores

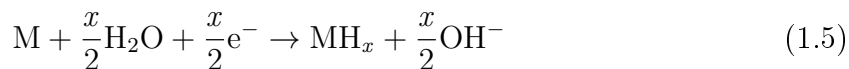
Hydrogen can be stored in compounds where it makes chemical bonds with other elements. For the gravimetric content of hydrogen to be high enough for practical applications, the other elements in the compound must be light, which typically restricts them to the first twenty or so elements of the periodic table [25]. High-purity hydrogen is needed for PEM fuel cells (see Section 1.1.3), but many potential hydrogen storage compounds will produce other gaseous impurities. Additionally the hydrogen release and resorption temperatures and pressures are often far from practical (usually too high). There are two approaches that can be taken when aiming to improve the properties of chemical hydrogen stores:

1. Altering thermodynamic properties - using additives to alter the stability of the storage material or the decomposition products.

2. Altering kinetic properties - using a catalyst to alter reaction rates or forming nanoscale structures.

1.2.4.1 Metal Hydrides

Some metal hydrides have a higher volumetric energy density than compressed hydrogen at 700 bar. However, their gravimetric energy densities are lower, as there are generally only a few hydrogen atoms for each heavy metal atom. Pure metals or metal alloys will incorporate hydrogen into their structure, forming metal hydrides, by reacting with either hydrogen or water (Equations 1.4 and 1.5).

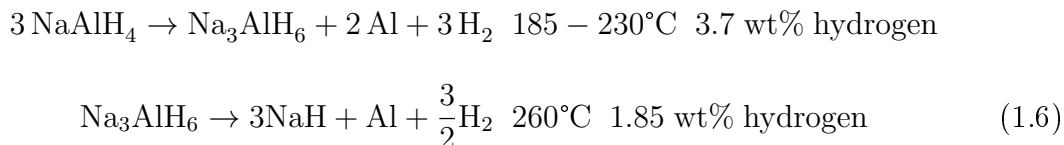


The bonds that form between the metal and hydrogen atoms are usually strong and their formation releases a large amount of heat energy. Therefore, high temperatures are needed to break the bonds for the hydrogen to desorb. Alloys, physical techniques (such as ball milling) and catalysts can also be used to reduce the desorption temperature. Hydrogenation and storage generally only require moderate pressure and the hydrogen desorbed is of a sufficiently high purity for PEM fuel cells.

1.2.4.2 Complex Hydrides

Alanates $[\text{AlH}_4]^-$, amides $[\text{NH}_2]^-$, and borohydrides $[\text{BH}_4]^-$, where hydrogen is bonded in a ‘complex’ anion, are generally termed complex hydrides. Interest in this field stems from the discovery in 1997 that adding titanium chloride to sodium aluminium hydride greatly improved its hydrogen desorption and reversibility [26]. Without any catalyst or

doping, sodium aluminium hydride (NaAlH_4) is a potential hydrogen storage material with 7.4 wt% hydrogen of which around 5.5 wt% is usable. The usable decomposition steps are shown in Equation 1.6 with the weight percentages given relative to the starting material. The third stage (the decomposition of NaH) occurs at too high a temperature to be a practical hydrogen store.

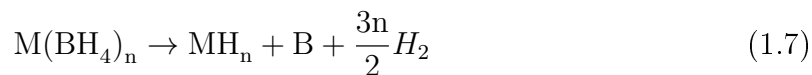


The rehydrogenation of sodium hydride and aluminium hydride using gaseous hydrogen is practically impossible due to the very high temperatures and pressures required. However, successful rehydrogenation of sodium and aluminium metal has been achieved without solvent at 180 - 240°C and >100 atm H_2 [27] or at lower temperatures and pressures in solution (150°C and 13.6 MPa) [28]. A full-scale prototype of a sodium aluminium hydride hydrogen store has been demonstrated [29].

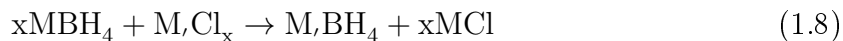
The doping of sodium aluminium hydride with titanium compounds has been found to improve both the dehydrogenation and rehydrogenation properties [26, 30]. If the titanium is added mechanically, the onset of fast decomposition is reduced from 230°C for a undoped sample to 120°C for a doped sample. Doped samples also maintain hydrogen capacity better after undergoing multiple absorption/desorption cycles.

Another important type of chemical hydrogen store are the metal borohydrides, in which four hydrogen atoms covalently bond to a boron atom, forming the anion, BH_4^- with a metal cation, M^+ . The hydrolysis of borohydrides has been exploited as single-use hydrogen stores [31]. However, it is not a suitable reversible hydrogen store, as B–O bonds have a high enthalpy of formation (808 kJ mol⁻¹ [2]). The alkali metal borohydrides ($\text{M} = \text{Li}, \text{Na}, \text{K}$) and alkaline earth metal borohydrides ($\text{M} = \text{Mg}, \text{Ca}$)

are the most relevant for hydrogen storage. The overall thermal decomposition at room temperature and pressure is shown in Equation 1.7.



Borohydride synthesis is relatively simple: they can be synthesised from the metal and diborane in an etheral solvent [32], or directly from the metal and boron under high pressures of hydrogen at high temperatures [33]. Transition metal borohydrides are often synthesised via a metathesis reaction: Group 1 borohydrides are ball milled with the transition metal chloride as shown in Equation 1.8.



The decomposition temperatures of borohydrides tend to be too high for their use with PEM fuel cells. There is a correlation between the Pauling electronegativity of a metal and the decomposition temperature of its borohydride [34] (see Figure 1.2) which, in particular, should allow metal cations to be used to tune of the decomposition temperature of a borohydride [35]. The higher the electronegativity of the cation, the greater the electron density it will attract towards it from the borohydride ion, removing electron density in the B-H bond, reducing its stability, and decreasing the decomposition temperature.

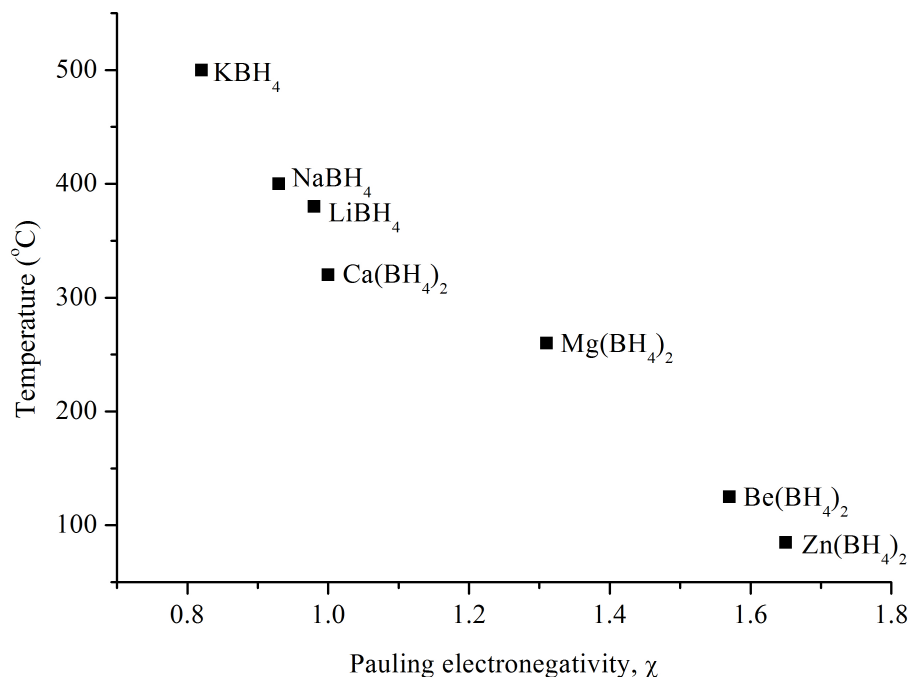
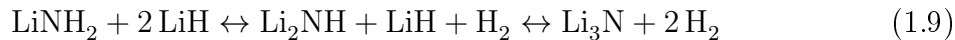


Figure 1.2: Graph showing the correlation between the Pauling electronegativity of the metal cation and the decomposition temperature of the corresponding borohydride [34].

Borohydrides have been modified using halides, oxides, amides and hydrides with the aim of reducing the decomposition temperature by alloying with, and therefore stabilising, the decomposition products. Borohydrides have also been nanoengineered, and confined in scaffolds, nanotubes and mesoporous gels [36].

The third type of complex hydrides is the metal amide-imide-hydride systems. The lithium system has a theoretical hydrogen capacity of 10.4 wt%, which is released in two steps shown in Equation 1.9. The first dehydrogenation step occurs between 150°C and 180°C, while the second step needs temperatures above 350°C [37]. Li_3N will rehydrogenate at 200°C [37]. This system has been shown to maintain a reversible

6.8 wt% of hydrogen over 500 cycles if nitrogen additives are used [38].



The first dehydrogenation step occurs via an ammonia-mediated pathway: lithium amide decomposes to form lithium imide and ammonia, and this ammonia immediately reacts with lithium hydride to form lithium amide and release hydrogen. The result is the formation of a non-stoichiometric continuous phase between lithium amide and imide, $\text{Li}_{1+x}\text{NH}_{2-x}$ [39].

As observed with the borohydrides, mixed metal amide systems have been shown to reduce both the decomposition temperatures and the release of ammonia [40]. For example, the $\text{Mg}(\text{NH}_2)_2/\text{LiH}$ system will desorb 7 wt% hydrogen starting at 140°C and is fully reversible [41].

1.3 Ammonia Borane and Related Materials

1.3.1 Ammonia Borane

The monomeric compound, NH_3BH_3 , was first synthesised by Shore et al. [42] in 1955. The first solution of the structure at room temperature was published in 1956 [43, 44]: a body-centred tetragonal unit cell with space group $I4mm$. In 1963, a face-centred orthorhombic unit cell was suggested [45]. However Hoon and Reynhardt [46] later confirmed the tetragonal structure. Discrepancies between the experimental and calculated patterns and the high R values of the structural refinements were attributed to charge transfer effects within the molecule. A neutron diffraction study by Klooster et al. [47], found that previous reports had flipped the boron and nitrogen atomic positions, and was also the first to report the hydrogen positions.

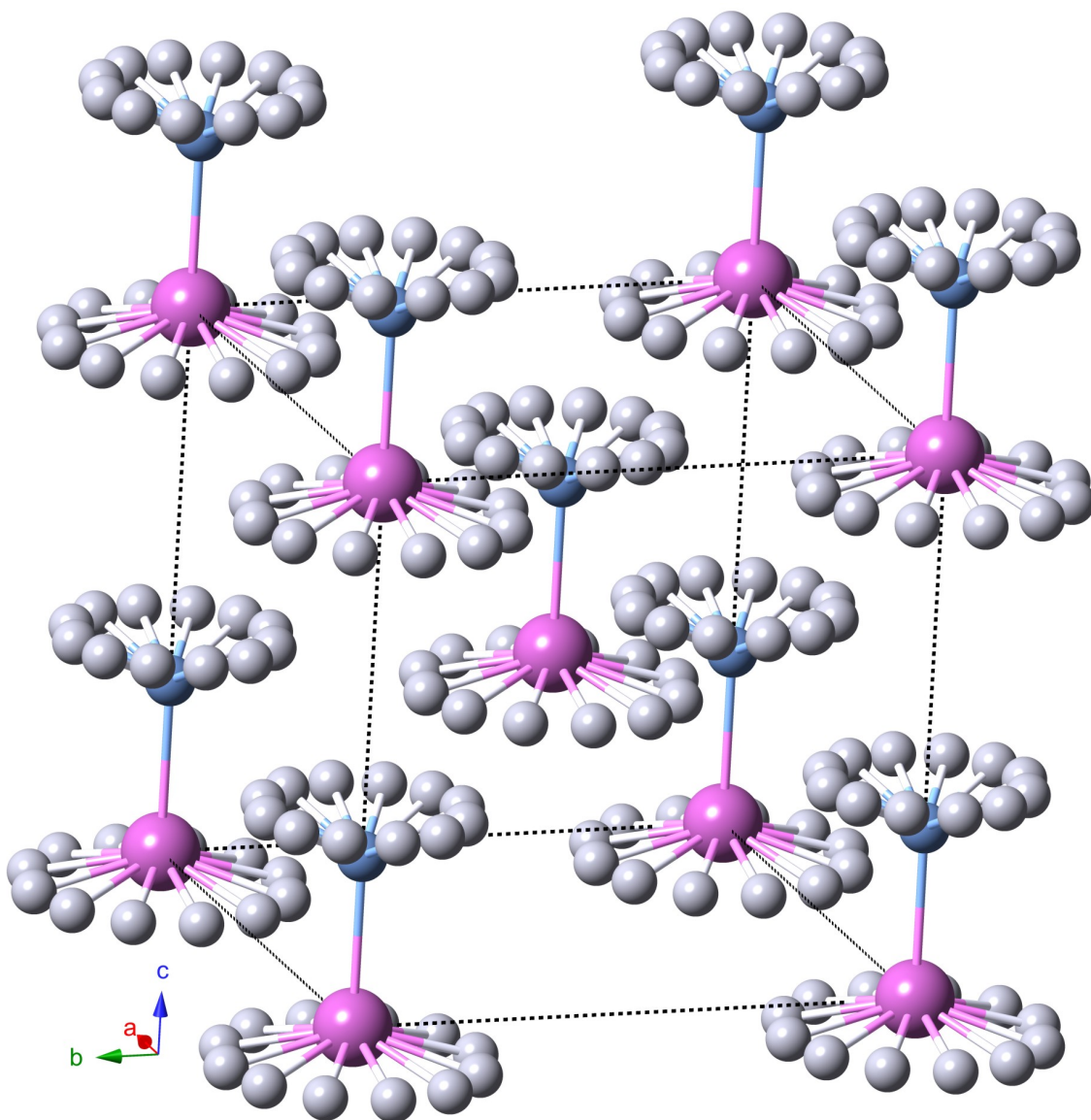


Figure 1.3: The structure of ammonia borane at 230 K (space group $I4mm$) [48]. Boron atoms in pink, nitrogen atoms, blue and hydrogen atoms, grey. The hydrogen atoms are shown as four-fold disordered.

The tetragonal $I4mm$ structure of ammonia borane (shown in Figure 1.3) is stable above 225 K. The B-N bonds are inclined at a small angle to the c -axis along a 4-fold rotation axis. The C_{3v} symmetry of the NH_3 and BH_3 groups means that the hydrogen atoms must be disordered: they must either move between at least 12 sites on each NH_3 and BH_3 group, or the individual groups must be orientated randomly, to give an

average disordered structure. 8-Fold [49, 50] and 12-fold [51] orientations have been successfully used to model the structure. Solid-state NMR studies have suggested free rotation [52] or 12-fold rotations [53] of the NH_3 and BH_3 groups. More recently, an quasielastic neutron spectroscopy study proposed 3-fold rotation [54].

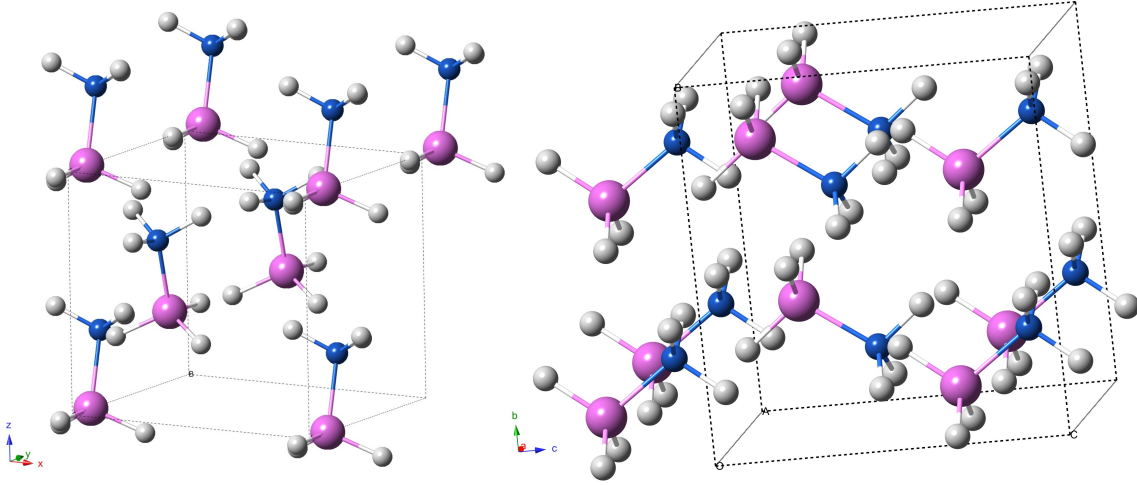


Figure 1.4: Structures of the low temperature, $Pmn2_1$ phase of ammonia borane (left) and the high pressure $Cmc2_1$ structure (right). Boron atoms in pink, nitrogen atoms, blue and hydrogen atoms, grey.

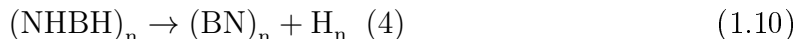
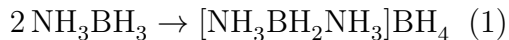
Ammonia borane has a phase transition at 225 K to a low-temperature orthorhombic phase, space group $Pmn2_1$ [46, 47], see Figure 1.4. The phase was first observed as faint lines in the X-ray powder diffraction pattern at low temperatures [44], and the structure was published in 1983 by Hoon et. al. [46]. B-N bonds alternately incline at $\pm 15^\circ$ relative to the c -axis. The 3-fold symmetry of the NH_3 and BH_3 groups is preserved by placing one hydrogen atom on a special position of the b -axis, the second hydrogen atom in a general position, and the third position is then generated by the mirror plane. The hydrogen atoms on each group can move between the 3 sites. The borane and ammonia groups move independently: at 100 K the reorientation rate of the NH_3 group is 10^4 times faster than that of the BH_3 group [55]. As the temperature increases, the rate of hopping of the BH_3 group increases faster than that of the NH_3 group, so

as the temperature approaches the phase transition they are moving at approximately the same rate.

The higher-pressure structures have been studied using Raman spectroscopy [56, 57], X-ray diffraction [58] and DFT molecular simulations [58, 59]. At pressures above 1.4 GPa, Filinchuk et al. [58] found a *c*-centred orthorhombic supercell structure with space group *Cmc2₁* (see Figure 1.4). The position of the hydrogen atoms and whether boron or nitrogen occupied the non-hydrogen positions were calculated using DFT.

Ammonia borane has a gravimetric hydrogen density of 19 wt% and the first equivalent of hydrogen is released above 70°C. At the lower temperatures at which hydrogen is released there is a substantial induction period: 10 hours at 75°C and 3 min at 90°C [60]. The mechanism for the hydrogen release is fairly well characterised. An ¹¹B NMR study [61] revealed that before the beginning of decomposition, a more mobile phase of ammonia borane formed. Further work [62] showed that in this mobile phase the volume of the unit cell increases slightly and rotation of the molecule around the B-N bond increases. This weakens the hydrogen-bonding network, facilitating the formation of the diammoniate of diborane ((NH₃BH₂NH₃)BH₄; DADB, see Section 1.3.3) from two ammonia borane molecules (Equation 1.10(1)). Under these conditions, DADB is not crystalline but its formation has been demonstrated using NMR and Raman spectroscopy [60, 61]. The addition of DADB or NH₄Cl to a sample of ammonia borane [60] significantly reduces the induction period, indicating that the formation of DADB is the rate-limiting step in the reaction. A molecule of ammonia borane will then react with a molecule of DADB as shown in Equation 1.10(2). Ammonia borane will continue to react with NH₃BH₂NH₂BH₂NH₃⁺ forming polyamidoborane chains. Evidence from NMR [60] and theoretical calculations [63] suggests the polyamidoborane chains are a

combination of linear, branched, and cyclic polymers.



Above 130°C, polyamidoborane releases another equivalent of hydrogen, producing polyimidoborane, $(\text{NHBH})_n$ (Equation 1.10(3)). Polyimidoborane at temperatures above 500°C releases a third equivalent of hydrogen, forming boron nitride (Equation 1.10(4)). Only the first two steps are at low enough temperatures for practical use in a hydrogen storage material, meaning that ammonia borane has an effective gravimetric capacity of 13 wt% (13.5 MJ L^{-1}), which is nevertheless considerably higher than the current DoE targets for a hydrogen storage systems of 8.32 MJ L^{-1} (see Table 1.3).

However, there are several downsides to the use of ammonia borane as a hydrogen store: the long induction period before hydrogen release, and the fact that when hydrogen is released it there is significant foaming. At higher temperatures and heating rates diborane, B_2H_6 and borazine, $\text{N}_3\text{B}_3\text{H}_6$ [64] are released along with hydrogen. It is very difficult to regenerate ammonia borane from its decomposition products and it cannot be done practically on board a car.

PEM fuel cells work at approximately 85°C and it would be optimal if a storage material could run off of the waste heat from the fuel cell. However, at 85°C ammonia borane has an induction period of around 3 hours and release a maximum of 1 molar equivalent of hydrogen. As ammonia borane has a high gravimetric content of hydrogen, there is scope to modify it while maintaining a usable hydrogen weight percentage.

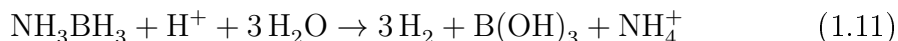
Nanoconfinement: Ammonia borane has been confined in the mesoporous silica scaffolds SBA-15 and MCM-41. It was found at loading of less than 50 % by weight, ammonia borane is completely integrated into the pores of the scaffold material [65]. At higher loading, bulk aggregate of ammonia borane started to form on the surface of the scaffold particles. For ammonia borane in the pores of the scaffold material, the reduction in average particle size and the presence of chemical interactions with the walls of the scaffold, reduces the extent of the hydrogen bonding network. This lowers the initial hydrogen release temperature to 59°C and 48°C for ammonia borane/SBA-15 and ammonia borane/MCM-41, respectively [66]. Ammonia borane in a silica scaffold also releases less borazine and diborane than bulk ammonia borane, but releases more ammonia. Lai et al. [66] suggested that this was due to interactions between oxygen on the surface of silica scaffold and the BH_3 group; ‘anchoring’ the BH_3 group and reducing the amount of diborane and borazine released. This interaction also reduces the strength of the B-N bond, allowing more ammonia to be released.

Ammonia borane in carbon cryogels shows similar properties [67]: reduction in the particle size of ammonia borane reduces the dehydrogenation temperature [68]. This is supported by the fact that ammonia borane in cryogels have increasing decomposition temperatures with increasing pore size. If bulk ammonia borane is heated at a rate of 5°C min^{-1} , the initial hydrogen release temperature will be ca. 115°C. For ammonia borane in carbon cryogels with 7 nm pores, the decomposition temperature is 98°C and for 16 nm pores, the decomposition temperature is 102°C [68]. Again, metal organic frameworks have a similar effect [69].

Ionic liquids: Ionic liquids are generally composed of weakly interacting bulky ions and have a melting point below 100°C. They will dissolve a wide range of compounds and provide an inert reaction medium. 4:1 ratios of ammonia borane to

the ionic liquid, bminCl (1-butyl-3-methylimidazolium chloride; $(\text{C}_8\text{H}_{15}\text{N}_2)\text{Cl}$) will produce 11.2 wt% hydrogen when heated at 120°C [70]. When the ammonia borane:bminCl mixture is heated at lower temperatures there is no induction period [71]. This may be because the ionic liquid stabilises the ionic intermediate DADB. There are many different ionic liquids, so that the exact properties of hydrogen release may be tuned [72].

Hydrolysis: Ammonia borane is stable in neutral and basic solution but acidic conditions will catalyse the release of hydrogen [73, 74], as shown in Equation 1.11 [75].



Various catalysts have also been used to increase the rate of hydrogen release in aqueous solution. Of the noble metal catalysts, platinum-based materials show the greatest activity. With a molar ratio of Pt metal:ammonia borane of 0.018, almost 3 wt% hydrogen will be released within 2 min of the addition of the catalyst [76]. Of the non-precious metal catalysts, iron, cobalt, nickel and copper have all shown good catalytic activity [77, 78]. The particle size of the catalyst is an important factor in its level of activity, with bulk or powdered metals showing no catalytic activity and supported nanoparticles showing high activity [76, 77]. The use of a flow reactor has been suggested to overcome the problem of the intermittent use of hydrogen in a vehicle [79, 76].

Acid catalysis: Various Lewis and Brønsted acids have been used to lower the temperature of initial hydrogen release from ammonia borane in organic solvents [80]. The mechanism suggested [80] for catalytic activity was the abstraction of a hydride by the acid from ammonia borane, forming $[\text{BH}_2\text{NH}_3]^+$ which can then react with another molecule of ammonia borane, releasing hydrogen. The resulting ion

will be consumed without the release of any more hydrogen, via the abstraction of another hydride from ammonia borane. This will limit the overall fraction of hydrogen released. Using lower concentrations of acid increases the overall yield of hydrogen, a fact that supports this mechanism. However, this may be a concentration effect: less acid will mean more ammonia borane is present.

Metal catalysis: Rhodium complexes, particularly $[\text{Rh}(1,5\text{-COD})(\mu\text{-Cl})_2]$ [81, 82]

were the first to be used to dehydrogenate ammonia borane. Initial studies of such compounds did not concentrate on the hydrogen release, but on the production of borazine and other B-N compounds. Indications that rhodium complexes proceeded via Rh(0) suggested that rhodium metal would be an efficient catalyst. This proved to be the case: the addition of rhodium on alumina [83] to ammonia borane results in immediate gas evolution, which is complete in 1 - 4 min.

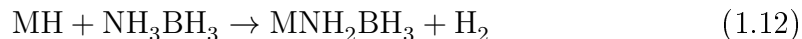
The similarity between ammonia borane and alkenes led Denney et al. [84] to investigate the alkene dehydrogenation catalyst $(\text{POCOP})\text{IrH}_2$. 0.5 mol% of this catalyst releases one equivalent of hydrogen from ammonia borane in 14 min. An alternative approach uses the electronic similarity between ammonia borane and methanol [85]. Ruthenium-based alcohol oxidation/reduction catalysts can release one equivalent of H_2 from ammonia borane within 5 min at room temperature. Nickel carbene complexes will release 2.8 equivalents of hydrogen at 60°C within 4 hours [86].

Most of the catalysts that have been investigated are homogeneous because they are easier to study, but practically they are more difficult to separate from spent fuel. Shrestha et al. [87] have shown that the heterogeneous catalysts platinum or ruthenium on alumina, and palladium on activated carbon, catalyse the dehydrogenation of ammonia borane in non-aqueous media. Platinum on alumina was the best of the three: 2 mol% of catalyst in a 0.33 M ammonia borane in

2-methoxyethyl ether will release 1.25 equivalents of hydrogen in 15 min at 70°C.

Amidoboranes, $M(\text{NH}_2\text{BH}_3)_x$: Replacing one of the hydrogen atoms in the ammonia group with a more electron-donating element alters polarity, decomposition temperature and pathway and crystal structure. The dihydrogen bonding network found in ammonia borane is destroyed and replaced with more electrostatic coordination interactions between the borohydride group and the metal. There have been investigations into amidoboranes of alkali metals (lithium [88], sodium [88] and potassium [89]), alkali earth metals (calcium [90, 91] and strontium [92]), transition metals (yttrium [93]) and various mixed metal systems [94, 95].

Amidoboranes can be synthesised from the metal hydride and ammonia borane (as shown in Equation 1.12) either in a solvent or by ball milling.

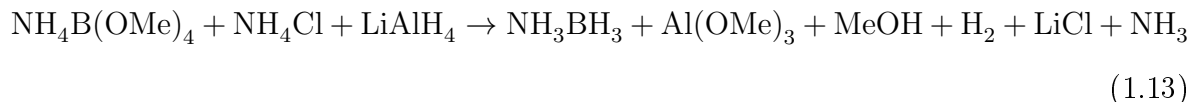


Although the addition of a metal reduces the overall gravimetric hydrogen capacity, lithium and sodium amidoborane release hydrogen at a lower temperature than ammonia borane (10.9 wt% and 7.5 wt% respectively at 90°C). At lower temperatures most amidoboranes do not release borazine and they also tend not to foam. Hydrogen release is also less exothermic than for ammonia borane, making regeneration more feasible.

Due to the unfavourable thermodynamics, the rehydrogenation of ammonia borane cannot practically occur on board a vehicle. Thermodynamic factors also mean that it is unlikely to be favourable to regenerate the system from boron nitride, limiting the usable hydrogen content to 13 wt%.

The recycling of an intermediate product in the metholysis of ammonia borane, ammonium tetramethoxyborate ($\text{NH}_4\text{B}(\text{OMe})_4$), has been proposed [96]. The ammonium

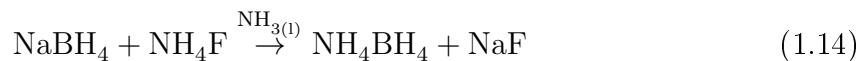
tetramethoxyborate is reduced by LiAlH_4 in the presence of an ammonia source, NH_4Cl , shown in Equation 1.13. Ammonia borane, more than 98 % pure, is produced with yields of up to 80 %.



The regeneration of ammonia borane from polyamidoborane or polyimidoborane has been achieved by reactions with an acid to give B-X bonds ($\text{X} = \text{Cl}, \text{Br}$) and then converting the B-X bonding into B-H bonds [97, 98]. An alternative method uses weaker B-S bonds [99, 100]. The yield of ammonia borane is 67 %. As well as the low yield, the heavy tin compounds are expensive to transport and there would be difficulty in scaling due to their instability. Sutton et al. [101] have used hydrazine as a reducing agent for polyborazylene, a model product for the decomposition of ammonia borane. The polyborazylene reacts with hydrazine in liquid ammonia to form hydrazine-borane, $\text{N}_2\text{H}_4\text{--BH}_3$. Ammonia will then displace the hydrazine, forming ammonia borane with a yield of -92 %.

1.3.2 Ammonium Borohydride

Ammonium borohydride was first synthesised by the United States Aerojet Engineering Corps in the early 1950s as a potential rocket fuel. The first synthesis reported in the literature was by Parry et al. [102], a metathesis reaction between sodium borohydride and ammonium fluoride in liquid ammonia, as shown in Equation 1.14.



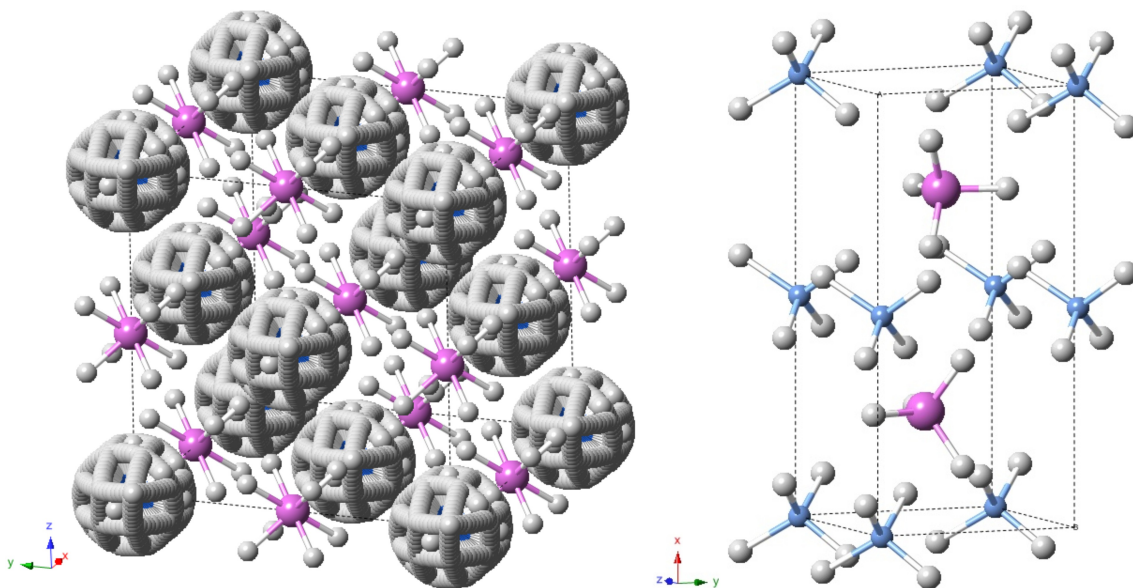


Figure 1.5: Structure of the high temperature cubic phase [103] (left) and the high pressure γ phase [104] (right) of ammonium borohydride. Boron atoms in pink, nitrogen atoms, blue and hydrogen atoms, grey.

Recently, there has been increasing interest in ammonium borohydride as a hydrogen storage material. It has the highest gravimetric ($244 \text{ g H}_2 \text{ kg}^{-1}$, 24.6 wt%) and volumetric densities ($154 \text{ g H}_2 \text{ L}^{-1}$) of any solid state store reported to date. It is unstable at room temperature; however it is stable below -40°C and can be stored for long periods.

Computational work suggested that ammonium borohydride would adopt a zinc blende structure at room temperature [105]. However, experimental work showed that it has a cubic rock salt structure, $Fm\bar{3}m$, $a = 6.978 \text{ \AA}$ [106, 107], see Figure 1.5. The structure is analogous to borohydrides with similarly sized cations (see Table 1.4). The boron atom is on the $(\frac{1}{2} \frac{1}{2} \frac{1}{2})$ site with hydrogen in the eight cubic sites on the $\langle 111 \rangle$ positions around it, meaning the tetrahedron has 2-fold disorder. The nitrogen atom is on the $(0 \ 0 \ 0)$ position; due to the symmetry of the space group, there are 48 ammonium group orientations, effectively forming a sphere of hydrogen positions around the central nitrogen atom [103]. Furthermore, detailed molecular dynamics

calculations following the experimental results ultimately predicted the cubic phase is the more stable phase [106].

borohydride cation	cation size ($\text{\AA}$)	a lattice parameter ($\text{\AA}$)
sodium	1.02	6.151
potassium	1.37	6.731
ammonium	1.43	6.978
rubidium	1.52	7.029
caesium	1.67	7.410

Table 1.4: Comparison between cation size and lattice parameter in $Fm\bar{3}m$ borohydrides [108, 109].

It has been shown that moderate pressure (~ 0.5 GPa) will stabilise ammonium borohydride at room temperature. Flacau et al. [104] have investigated the high pressure, room temperature phases of ammonium borohydride. Below 1.2 GPa, the only phase is the room temperature cubic phase described above. Over 1.3 GPa, a new phase, β , is formed, being the only phase present by 2 GPa. The new phase was thought to be disordered due to broad diffraction peaks and a structure solution was not attempted. Between 3.4 and 4.5 GPa, β and γ phases co-exist. Above 4.5 GPa the only phase present is the γ phase. The γ phase was indexed to $Pma2$ $a = 7.98$ $\text{\AA}$, $b = 3.82$ $\text{\AA}$ and $c = 3.77$ $\text{\AA}$ (see Figure 1.5), an orthorhombically distorted bcc structure with the $[\text{BH}_4]^-$ at the centre of the cell and $[\text{NH}_4]^+$ at the corners. The molecular dynamics simulation suggest that the hydrogen atoms are even more disordered than in the low pressure phase. The β phase is likely to have structure intermediate between the α and γ phases [104].

The room temperature cubic phase is stable until 60 K where a more ordered rhombohedral ‘middle’ phase forms [103], space group $R\bar{3}m$, $a = b = 4.831$ $\text{\AA}$, $c = 23.473$ $\text{\AA}$

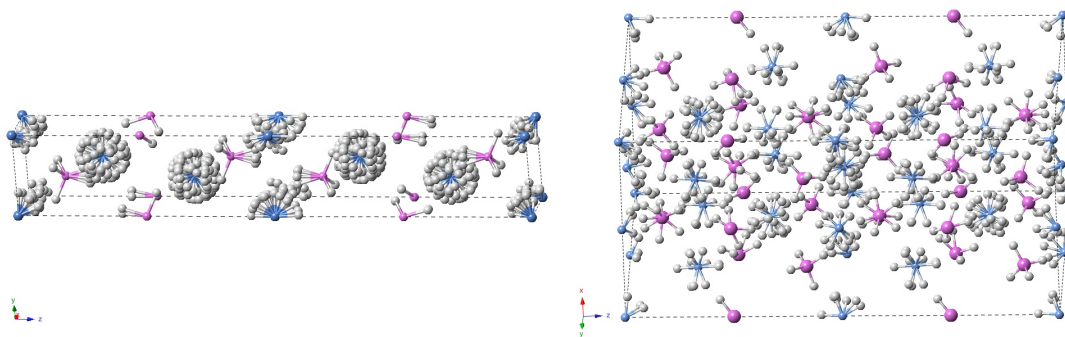


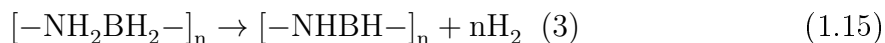
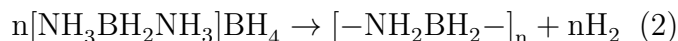
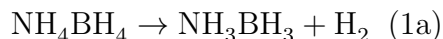
Figure 1.6: Structural diagrams of the low temperature phases of ammonium borohydride [103], top: rhombohedral ‘middle’ phase, bottom: trigonal ‘bottom’ phase. Boron atoms in pink, nitrogen atoms, blue and hydrogen atoms, grey.

(for a structural diagram see Figure 1.6). The cubic phase converts to the rhombohedral across two body diagonals. The $[\text{BH}_4]^-$ groups previously orientated along the $\langle 111 \rangle$ direction now lie along the c -axis ($\langle 001 \rangle$ direction), orientated either up or down. This explains why the rhombohedral c -axis is formed from twice the body diagonal of the cubic unit cell. The ammonium ions are in a more ordered environment than in the cubic phase, with 12-fold disorder of the tetrahedron from the lower symmetry of the site.

If a sample is then slow cooled to below 2 K it forms a third trigonal ‘bottom’ phase, space group $P-3c1$ $a = b = 9.51 \text{ \AA}$ and $c = 23.47 \text{ \AA}$ (for a structural diagram see Figure 1.6). The new phase is a supercell (with a doubling of the a and c axes) of the rhombohedral ‘middle’ phase, with increased ordering. In principle, with infinitely slow cooling a completely ordered phase would form [103].

Ammonium borohydride decomposes releasing $>20 \text{ wt\%}$ hydrogen in three stages below 160°C [106]. During the first stage (Equation 1.15(1)) $6.5 \text{ wt\%}$, 1 equivalent of hydrogen is released at approximately 36°C as ammonium borohydride decomposes to DADB. When ammonia borane is added to ammonium borohydride, DADB is immediately formed [106]. This is consistent with decomposition via ammonia borane,

Equations 1.15 (1a and b). In the second step (Equation 1.15(2)) at 85°C another equivalent of hydrogen is released as DADB forms polyaminoborane. At 130°C polyiminoborane formed, Equation 1.15(3), with the release of a small amount of borazine along with another equivalent of hydrogen.



Ammonium borohydride has been dispersed in meso-porous silica (MCM-41) in an attempt to stabilize it at room temperature [110]. 1:1 and 1:2 ABH₂:MCM-41 ratios by weight were prepared in liquid ammonia. It was found ammonium borohydride was destabilized by the silica framework: around half of the ammonium borohydride in the 1:1 sample and all of it in the 1:2 sample decomposed before analytical experiments could be performed. The ammonium borohydride that did not decompose in the 1:1 sample was located on the external surface of the silica and its decomposition temperature was suppressed to 17°C from 36°C for bulk ammonium borohydride.

1.3.3 The Diammoniate of Diborane (DADB)

The diammoniate of diborane, DADB, was previously believed to be the ammonia salt of diborane, $2 \text{NH}_3 \cdot \text{B}_2\text{H}_6$. It is now known to be $[\text{NH}_3\text{BH}_2\text{NH}_3]\text{BH}_4$, but the original name has been retained [111, 112]. In the mid-1950s $[\text{BH}_3\text{NH}_2\text{BH}_3]\text{NH}_4$ and

$\text{NH}_4 \cdot \text{BH}_2\text{NH}_2 \cdot \text{NH}_4$ [113] were incorrectly suggested as alternative structures. However, a series of papers published in 1958 [114, 115, 116, 117, 118, 119] provided chemical and physical evidence for the structure being $[\text{NH}_3\text{BH}_2\text{NH}_3]\text{BH}_4$. ^{11}B NMR confirmed the presence of two different boron environments [120].

DADB was initially synthesised from the reaction between diborane and solid ammonia at temperatures below -110°C [121]. In 1958, Taylor et al. [119] confirmed that DADB was the decomposition product of ammonium borohydride, providing a much easier and safer synthesis route. Twelve hours at room temperature is usually sufficient to ensure all the ammonium borohydride has decomposed to DADB [122]. Bowden et al. [122] also demonstrated this decomposition almost certainly takes place via ammonia borane (see the decomposition of ammonium borohydride, Section 1.3.2).

DADB decomposes in two steps below 200°C , each releasing approximately one equivalent of hydrogen. The initial onset of hydrogen release (85°C) is lower than that of ammonia borane (110°C). The second decomposition step is at much the same temperature in DADB and ammonia borane. Bowden et al. [122] found a small release of borazine accompanied the hydrogen release during the second decomposition. Fang et al. [123] confirmed this borazine release; their sample also released diborane with the borazine and a substantial amount of ammonia above 100°C . Different synthesis methods could account for the differing decomposition products.

Ammonia borane and DADB contain the same weight percentage of hydrogen. However, there are several advantages of DADB over ammonia borane as a hydrogen storage material:

- A lower (by approximately 35°) initial release temperature of hydrogen, and no induction period prior to hydrogen release.
- Unlike ammonia borane, DADB does not melt before or during decomposition.

- Less borazine and other contaminants are produced during the decomposition of DADB.
- DADB does not foam on decomposition.

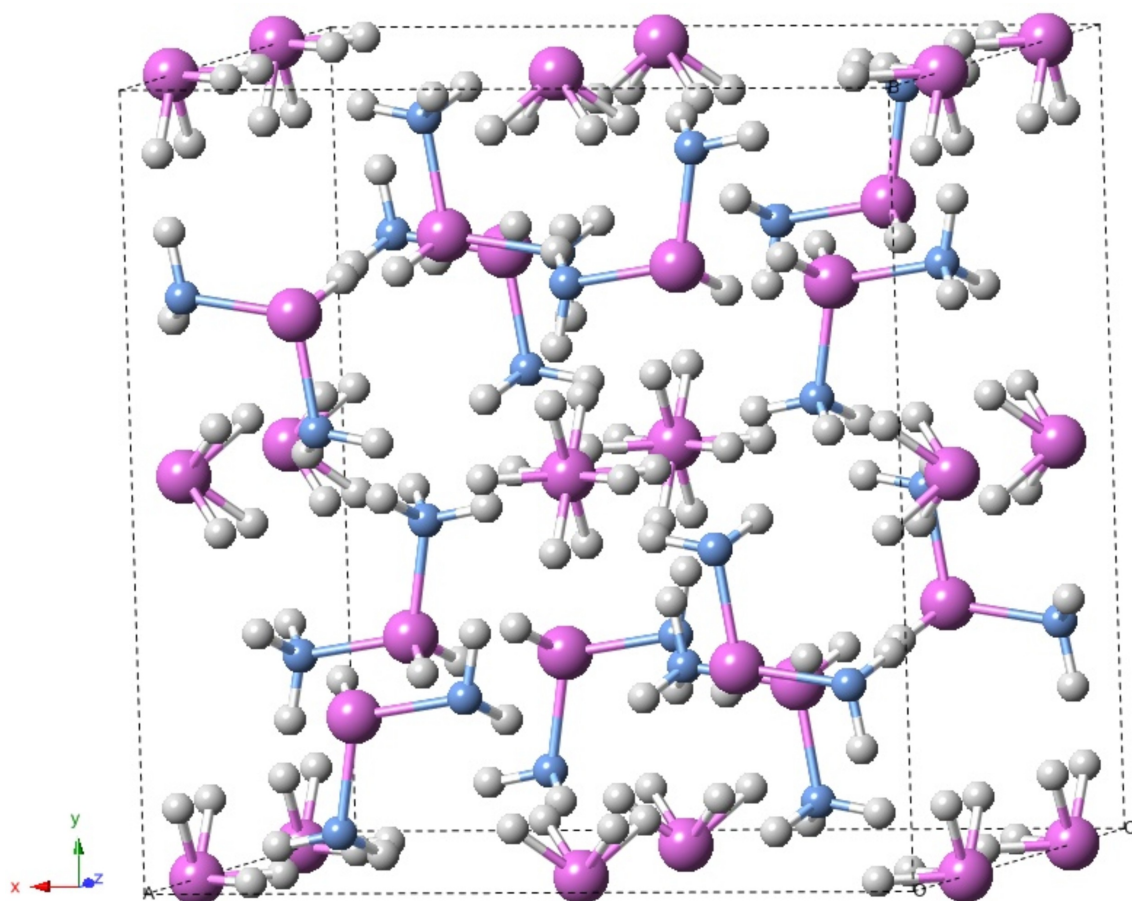


Figure 1.7: Structural diagram of the room-temperature phase of DADB [122]. Boron atoms in pink, nitrogen atoms, blue and hydrogen atoms, grey.

The room-temperature structure of DADB is tetragonal with space group $I4/mcm$, $a = b = 10.72 \text{ \AA}$, $c = 9.24 \text{ \AA}$, see Figure 1.7 [122]. The boron and nitrogen atoms are all almost tetrahedrally coordinated. The $(\text{NH}_3)_2\text{BH}_2^+$ units are aligned in rows parallel to the c -axis and related to each other by a 2_1 screw axis. The borohydride ions can have two different orientations and are equally disordered between them. The two

closest hydrogen-hydrogen distances are 1.8 Å and 2.1 Å, suggesting that the dihydrogen bonding is also important in DADB.

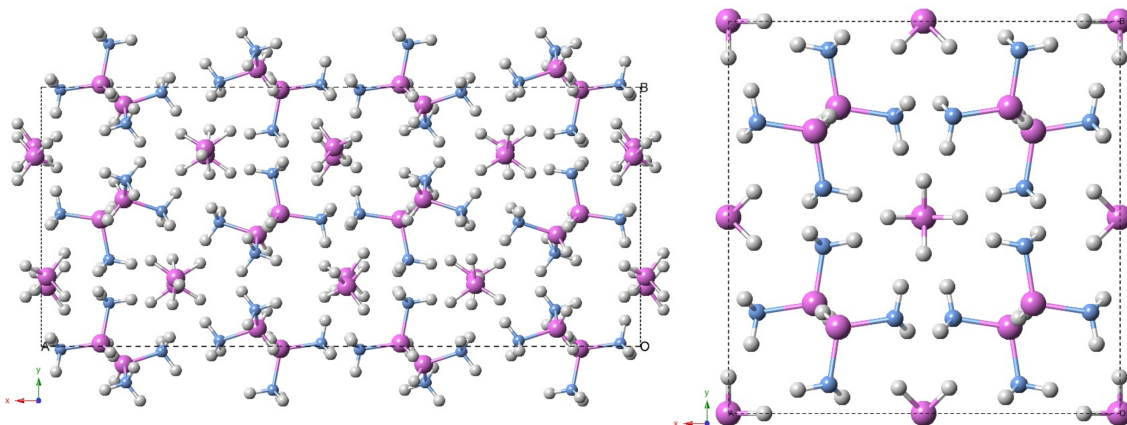


Figure 1.8: Structural diagrams of the low temperature phase of DADB [110] viewed along the *c*-axis (left) and the room temperature phase [122] (right) viewed on the same axis for comparison. Boron atoms in pink, nitrogen atoms, blue and hydrogen atoms, grey.

A lower temperature phase which forms below approximately 7°C has recently been reported [110] (see Figure 1.8). It shows considerable hysteresis: once formed it is stable up to 43°C before converting back to the room-temperature structure. Synchrotron X-ray diffraction data gave an orthorhombic cell, *Pbca*, $a = 22.78$ Å, $b = 9.84$ Å and $c = 9.54$ Å. Since the hydrogen atoms only weakly scatter X-rays, their positions, as inferred from synchrotron diffraction, cannot be regarded as reliable.

Since DADB has only recently been suggested as a hydrogen store, there are few examples of its modification to improve hydrogen storage characteristics. Fang et al. [123] ball-milled DADB with MgH_2 and found that the emission of gaseous impurities was completely suppressed. The temperature of the initial decomposition step of DADB with MgH_2 is similar to that of pure DADB. The second step is at the much higher temperature of 275°C. The study by Neilsen et al. [110] described above (in Section 1.3.2) indicated that the decomposition temperature of DADB remains unaffected by dispersion in a mesoporous silica scaffold.

1.3.4 Ammonia Borane, DADB and Ammonium Borohydride

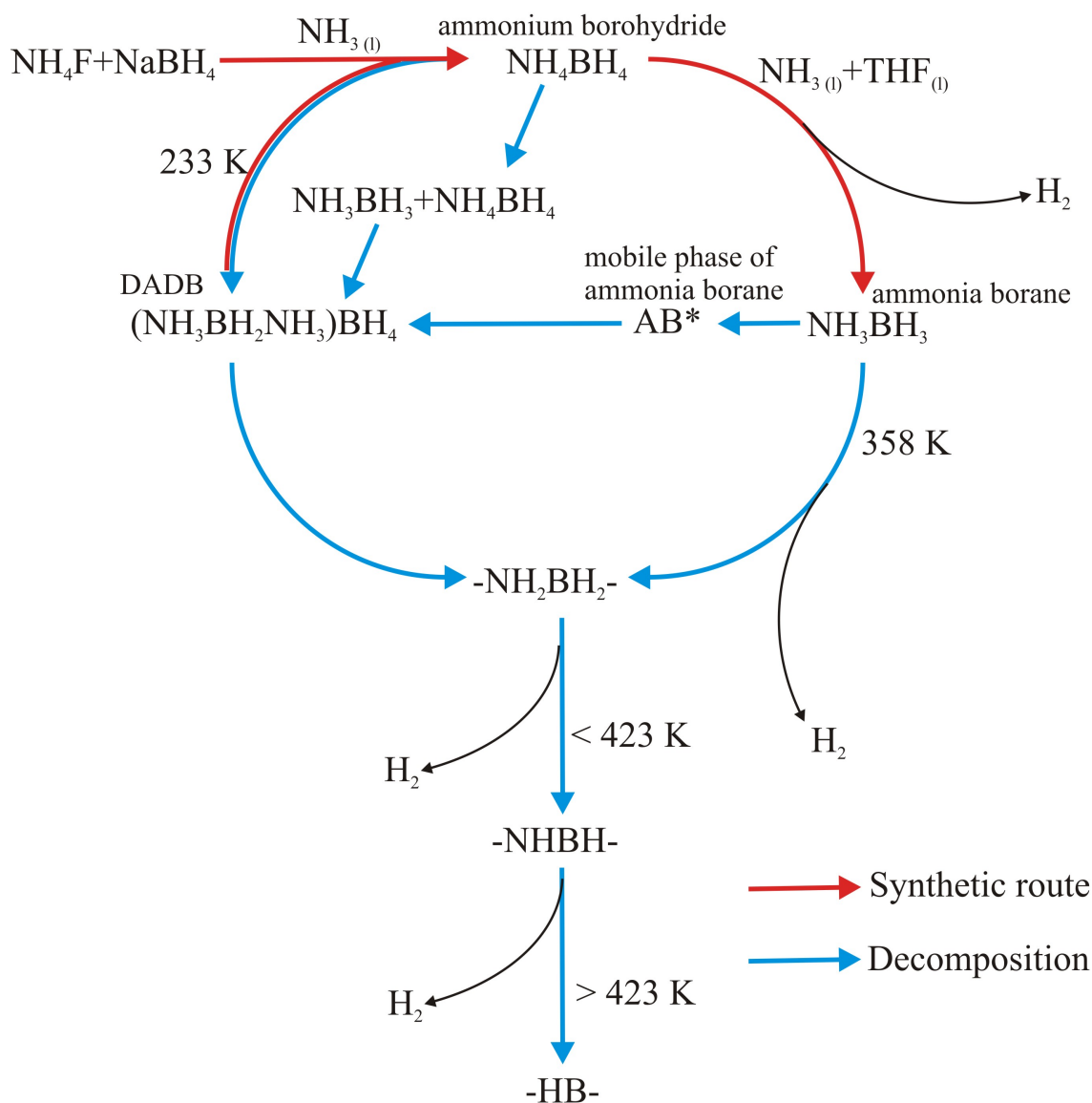
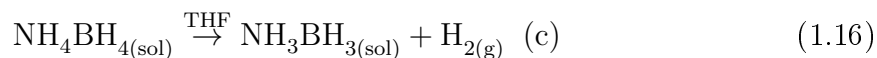


Figure 1.9: Schematic showing the synthesis and decomposition pathways of ammonium borohydride, ammonia borane and DADB.

Figure 1.9 shows the inter-relationships in the synthesis and decomposition pathways of the NH_xBH_x system. The starting point is the reaction between a metal borohydride and an ammonium halide in liquid ammonia (top LHS of the diagram). If the reaction is kept at a low temperature while the ammonia is removed the product will be ammonium

borohydride. At room temperature, ammonium borohydride will decompose to DADB, with a half-life of around 6 hours. The decomposition occurs via ammonia borane as in Equation 1.16 (a) and (b). If THF is added to the liquid ammonia, ammonia borane is formed (Equation 1.16 (c)). There are several possible explanations for these different reaction products. Firstly, the solvent removes ammonia borane from the reaction site; this may prevent it from reacting with the remaining ammonium borohydride [117]. Secondly, the solvent may remove heat after the exothermic formation (calculated to be $-70.3 \text{ kJ mol}^{-1}$ [124]) of ammonia borane, preventing reaction to form DADB [117]. Finally, any DADB formed may decompose to ammonia borane in the THF solution.



Ammonium borohydride decomposes at room temperature to stable crystalline DADB via a reaction between ammonia borane and ammonium borohydride. Ammonia borane, on the other hand, forms polyamidoborane by a similar reaction where DADB (formed from two ammonia borane molecules) reacts with another ammonia borane molecule. There is a significant induction period during the weakening of the dihydrogen bonding network and the formation of DADB.

DADB decomposes with no induction period at a slightly lower temperature also to polyamidoborane - assumed to be similar in nature to the polyamidoborane formed from the decomposition of ammonia borane. The lack of induction period and the lower temperature is at least in part due to the dihydrogen bonding network in DADB being weaker than in ammonia borane.

Once polyamidoborane is formed, all the samples will release two more equivalents

of hydrogen, forming polyimidoborane and then boron nitride.

Chapter 2

Dihydrogen Bonding in Hydrogen Storage Materials

2.1 Hydrogen bonding

Hydrogen bonds are attractive interactions formed between two molecular groups with at least one hydrogen atom involved in the bonding. Conventional hydrogen bonds are of the form $X\cdots H-Y$, where X and Y are electronegative elements, particularly fluorine, oxygen and nitrogen. The electronegativity of the Y element means that the YH moiety will have a dipole, $Y^{\delta-}\cdots H^{\delta+}$; it is termed the hydrogen bond donor or the electron acceptor. X generally has a lone pair and is the hydrogen bond acceptor or the electron donor. The interaction energies involved in hydrogen bonds are usually weak to medium, typically 8 to 150 kJ mol⁻¹ [125].

There is a variety of ways to define the nature of a hydrogen bond and to determine whether they exist between a potential donor and a potential acceptor: criteria based on the theory of Atoms in Molecules (AIM theory) were summarised by Popelier [126] as follows:

1. There are closed-shell interactions between the interacting groups. Reflecting this, the charge density, ρ_c is small (although larger than if the bonding was van der Waals) and the Laplacian of the charge density, $\nabla^2\rho_c$ is small and positive.
2. Topological analysis of the bond path to show the presence of a bond.
3. Positive mutual penetrations of the hydrogen atom on the hydrogen bond donor and the hydrogen bond acceptor atom which can be determined by comparing the non-bonded radii of the hydrogen atom and the hydrogen bond acceptor to the bonded radii or the bond critical point.
4. Loss of negative charge on the hydrogen atom, when the loss of charge is the difference between the electron population of the hydrogen atom in the hydrogen bond and of the hydrogen atom in the free bond donating group. The total charge transfer should also be negative due to the donation of electrons from one molecule to another. In other words, there must be interpenetration of the electron clouds of the hydrogen atom and the hydrogen bond acceptor with transfer of electron density between them.
5. The hydrogen atom is destabilised, the difference between the total atomic energy in the complex and in the free groups should be negative. This will cause a lengthening of the H-Y bond and a red shift in its vibrational modes.
6. The dipole moment of the bond is larger than the sum of the dipole moments of the monomers.

There are, however, more atypical types of hydrogen bonds: those with unusual hydrogen bond donors such as C-H, and those with unusual acceptors such as π -bonds, halogen atoms, carbon atoms, and the hydrogen atom in boron-hydrogen or metal-hydrogen groups. The latter two are generally known as dihydrogen bonds, $Z - H^{\delta-} \cdots H^{\delta+} - Y$

where Y-H is a conventional hydrogen bond donor such as O-H or N-H. H-Z is the hydrogen bond acceptor with Z being a less electronegative element than hydrogen, most often a boron atom or a metal such as indium or rhenium. Dihydrogen bonds are generally considered to be between 1.7-2.2 Å in length [127]: considerably less than the summed van der Waal radii of two free hydrogen atoms (2.4 Å).

2.2 M-H Dihydrogen Bonding

Hydrogen ions in group 1 metal hydrides have high negative charges, and can thus, in principle, act as excellent proton acceptors. However, they are very reactive and do not in practice, form isolable complexes. Lithium and sodium systems are relatively simple systems with few electrons and so make excellent candidates for computational studies. For example, linear dihydrogen bonds between LiH as the proton acceptor and weak proton donors (HNC, HCN and HCCH) have H...H distances (and bond energies) of 1.487 Å (55.7 kJ mol⁻¹), 1.790 Å (34.5 kJ mol⁻¹) and 1.995 Å (16.6 kJ mol⁻¹) respectively [128]. The same proton donors with NaH as a hydrogen acceptor have the following H...H distances (and bond energies): 1.451 Å (61.5 kJ mol⁻¹) for HNC, 1.770 Å (37.7 kJ mol⁻¹) for HCN and 1.987 Å (17.8 kJ mol⁻¹) for HCCH. The bond lengths are all well below 2.4 Å (double the van der Waal atomic radius of a free hydrogen atom). Lithium and sodium hydrides have also been used to study the validity of differing computational techniques [129].

Group 2 metal hydrides have fewer negatively charged hydrogen atoms and so are not such good proton acceptors. For example, from the study mentioned above [128] the hydrogen bond lengths (and bond energies) of BeH₂ and MgH₂ with HNC are 1.777 Å (13.5 kJ mol⁻¹) and 1.652 Å (26.1 kJ mol⁻¹) respectively. They are still too reactive to form isolable molecular compounds.

Transition metal hydrides (usually in transition metal complexes) generally have negatively charged hydrogen atoms and these may be hydrogen bond acceptors. However, since the M-H distances are generally short and the metal is large and has high electron density, it can be difficult to determine whether the metal d-electrons are also involved in the bond.

The rhenium system $\text{ReH}_2(\text{CO})(\text{NO})(\text{PMe}_3)_2$ [130] (shown in Figure 2.1) can form conventional hydrogen bonds using the CO and NO ligands as proton acceptors or dihydrogen bonds with the hydride ligands as proton acceptors. In a single crystal of the complex with an indole adduct, there is a short $\text{H}\cdots\text{H}$ distance ($1.79 \text{ \AA}$) between the hydrogen ligand trans to the CO and the H-N of the indole, indicating a dihydrogen bond. Further evidence is provided by the lengthening of the Re-H bond and two Re-H stretching modes in the IR spectra assigned to the free and the bonded hydrogen. In a solution of fluoro-2-methyl-2-propanol, $(\text{CF}_3)_3\text{COH}$ the hydrogen ligand trans to the NO bond forms a dihydrogen bond of length $1.78 \text{ \AA}$ [131]. The ability to form dihydrogen bonds has also been confirmed computationally [132]: water will form hydrogen bonds with CO and NO and dihydrogen bonds with the Re-H moiety (interestingly, the latter are energetically more favourable). The dihydrogen bond trans to the NO group is shorter ($1.49 \text{ \AA}$ vs $1.79 \text{ \AA}$ for the cis bond).

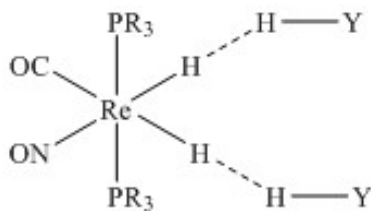


Figure 2.1: Structure of a dihydrogen bonding rhenium complex, $\text{ReH}_2(\text{CO})(\text{NO})(\text{PMe}_3)_2$ [130].

Conventional hydrogen bonds are important intermediates in proton transfer reactions [133, 134]. Dihydrogen bonds can also perform a similar process in the transfer

of protons to negatively charged hydrogen atoms as shown in Equation 2.1.



For example, the complex $\text{WH}(\text{CO})_2(\text{NO})(\text{PR}_3)_2$ will be deprotonated by weak acids as shown in Figure 2.2 [135]. Belkova et al. monitored the reaction of the complex with fluorinated alcohols using IR spectroscopy. Below 270 K, there were only signals from the initial hydride and dihydrogen bonded complex. In the presence of an excess of acid in a non-coordinating solvent, the complex will react irreversibly to form $\text{WH}(\text{OR})(\text{CO})_2(\text{NO})(\text{PR}_3)_2$, with the $\eta^2 - \text{H}_2$ complex as an unstable intermediate. The proton transfer is considered to be the rate determining step.

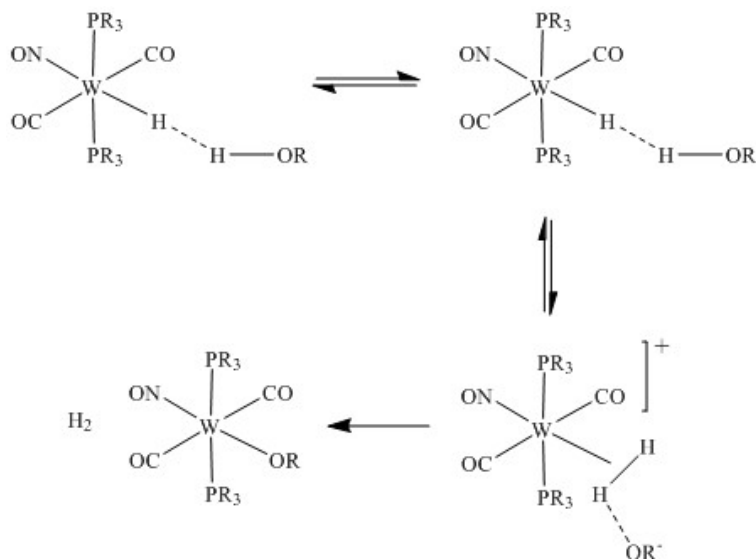


Figure 2.2: The proton transfer via dihydrogen bonding in the tungsten complex, $\text{WH}(\text{CO})_2(\text{NO})(\text{PR}_3)_2$ [135].

2.3 C-H Dihydrogen Bonding

Slightly polarised C-H groups have been suggested to be both the proton donor and the proton acceptor of a hydrogen bond, $\text{C} - \text{H}^{\delta-} \cdots \text{H}^{\delta+} - \text{C}$ in some organic compounds.

There is a significant number of compounds which have H...H distances of less than 2.4 Å (twice the van der Waal radius of hydrogen). However these interactions tend to be weak, and the short distances are often also caused by steric factors [136]. When these bonds occur they are considered to be very weak: the bond energies in compounds containing phenyl groups have been calculated at 8.3 - 12.6 kJ mol⁻¹ [137]. C-H can also act as a weak hydrogen bond acceptor to conventional hydrogen bond donors. Amino acids contain both C-H (as the acceptor) and O-H and N-H groups (as the donors) and have been shown to form intramolecular dihydrogen bonds [138, 139]. Whether or not dihydrogen bonds are important interactions in proteins and enzymes has yet to be confirmed.

2.4 B-H Dihydrogen Bonding

Dihydrogen bonds involving a B-H hydrogen bond acceptor and N-H hydrogen bond donor are generally of the form shown in Figure 2.3 [47, 140]. A systematic CSD search found 18 compounds with 26 unusually short N-H...H-B distances in the range of 1.7 - 2.2 Å, with typical energy ranges of 12 - 28 kJ mol⁻¹ [141]. The N-H...H B angle is relatively linear (typically 150 - 170°), and the B-H...H N angle is usually 95 - 115°. Both ends of the B-H bond are negatively charged, and in the N-H group the nitrogen atom has a negative dipole and the hydrogen a positive dipole [140, 142]. This explains why the N-H...H B angle is nearly linear (as in conventional hydrogen bonds), while the B-H...H N angle is bent: a smaller angle prevents an unfavourable dipole arrangement and allows the protic NH group to interact with the negatively charged boron atom.

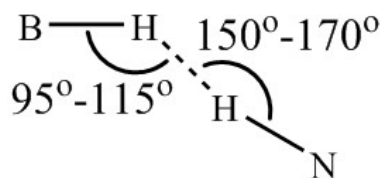


Figure 2.3: Conformation of N-H...H-B dihydrogen bond.

The presence of protic and hydridic hydrogen atoms, usually attached to nitrogen and boron atoms respectively, is important in many molecular hydrogen storage materials: they are often the determining factor in the physical properties, crystal structures and stabilities, and decomposition mechanisms which release hydrogen gas. Ammonia borane is an excellent example of a hydrogen storage material with important dihydrogen bonds. The strength of dihydrogen bonding in ammonia borane is highlighted by comparing its melting points with those of isoelectronic compounds: ethane CH_3CH_3 and fluoromethane CH_3F . The melting points and polarities are summarised in Table 2.1. The melting point of ammonia borane is almost 300°C higher than that of ethane, almost solely a consequence of dihydrogen bonding [141]. Only a small proportion of this disparity will be due to the polarity of ammonia borane. This is indicated by the melting point of (polar) fluoromethane, which is only 40°C higher than that of ethane.

Compound	Melting point ($^\circ\text{C}$)	Dipole moment (D)	Hydrogen bonding Y/N
ethane	-180	0	N
fluoromethane	-140	1.8	N
ammonia borane	$+104$	5.2	Y

Table 2.1: Comparison of the intermolecular bonding and melting points of ethane, ammonium fluoride and ammonia borane.

The low temperature orthorhombic phase of ammonia borane has three H...H dis-

tances of less than 2.4 Å [47] (shown in Figure 2.4). The closest distance is between D2 and D3 at 2.02(3) Å. The N-D...D B angle of 156(3)° is relatively linear, and the B-D...D N angle is (as expected) more acute: 106(1)°. The next two distances are longer, 2.21(4) Å between D1 and D4 and 2.23(4) Å between D2 and D4. The molecular packing means however the bond angles are less typical than in the shortest dihydrogen bond. The D1 and D4 bond deviates the most from the expected values. The N-D1...D4 B angle is 130(1)°; very much smaller than would be expected, while the D4-B...D1 N angle much larger: 156(3)°. This suggests that the bond may be weaker than the D...D distance indicates [48]. The D2 and D4 bond angles are closer to the ideal, N-D2...D4 B, 137(2)° and D4-B...D2 N, 94(2)°.

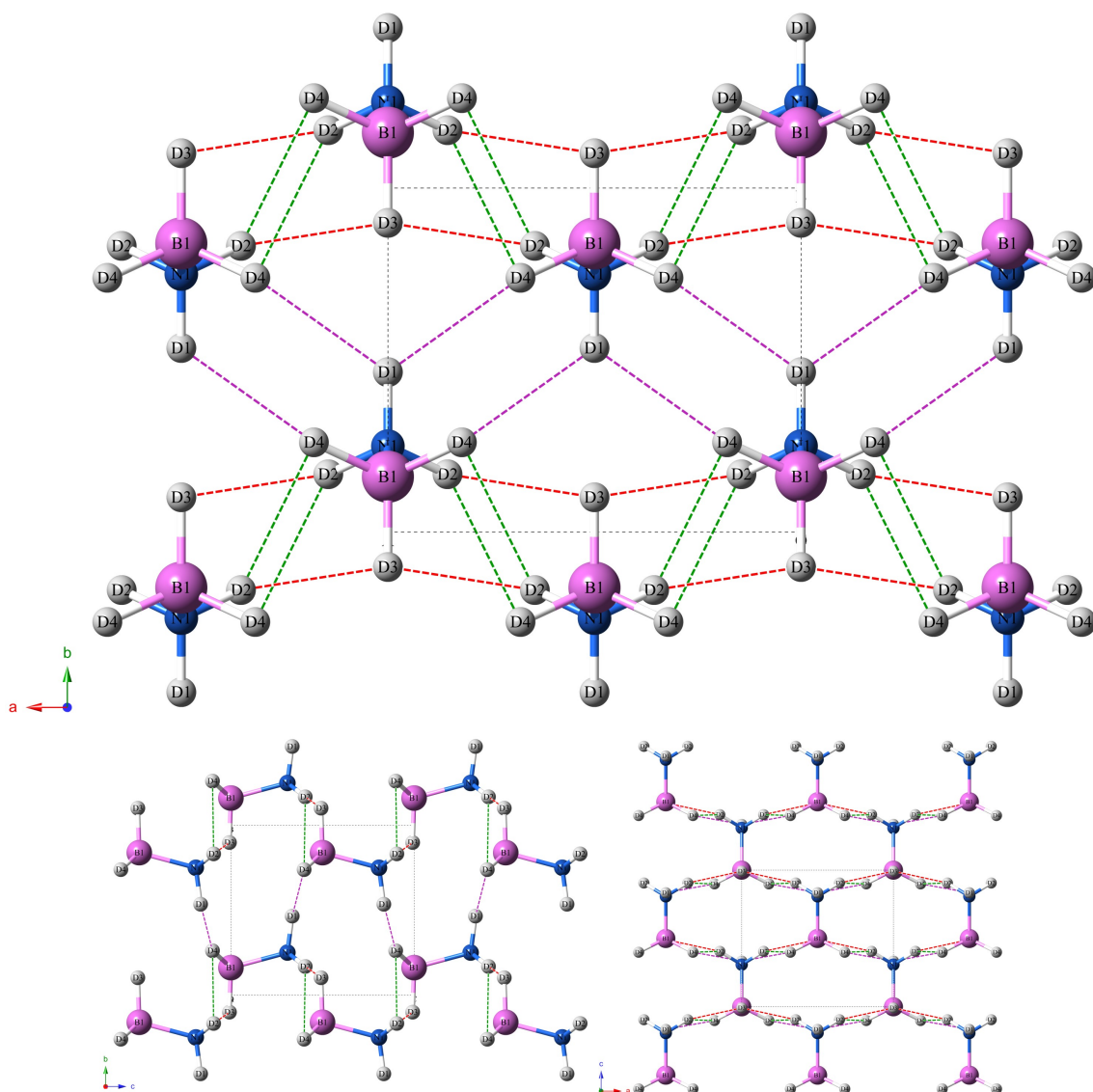


Figure 2.4: The orthorhombic phase of ammonia borane showing the short D...D bonding interactions as dashed lines. The shortest bond D2-D3 is shown in red, the next shortest D1...D4 in purple, and the longest interaction D2...D4 in green. Top: projection along the c -axis. Bottom left: projection along the a -axis. Bottom right: projection along the b -axis.

Hess et al. [48] described the phase transition of ammonia borane from the low temperature orthorhombic phase to the high temperature tetragonal phase as a pivoting of the ammonia borane molecule about the nitrogen axis to bring the B-N bond close to the c -axis while the b -axis expands and the c -axis contracts. The intramolecular geo-

metry remains the same across the phase transition. During the phase transition, the shortest dihydrogen bond in the orthorhombic phase D2...D3 increases slightly. However at 2.09(2) Å at 230 K it is still well within the range which can be considered a dihydrogen bond. The D1...D4 dihydrogen bond shortens across the phase transition becoming the shortest dihydrogen bond in the tetragonal phase with a length of 1.97(2) Å. The final orthorhombic dihydrogen bond increases by 0.5 Å to a length of 2.86(2) Å and can no longer be considered a dihydrogen bond in the tetragonal phase. The dihydrogen bonds in the tetragonal phase are shown in Figure 2.5. The relatively small transition enthalpy, 1.48 kJ mol⁻¹ [143] is consistent with the breaking of one weak dihydrogen bond during the phase transition.

The unusual bond angles of the D1...D4 dihydrogen bond found in the orthorhombic phase are continued across the phase transition into the tetragonal phase, with N-D1...D4 B = 24.5(10)° and N D1...D4-B = 170.0(11)° at 230 K [48]. This again suggests that the bond is weaker than first supposed. The D2...D3 dihydrogen bond angles are 162.2(8)° and 119.2(8)° for N-D2...D B and N D2...D3-B respectively: closer to the ideal where the N-D...D B angle is near linear and the N D...D-B angle considerably more acute.

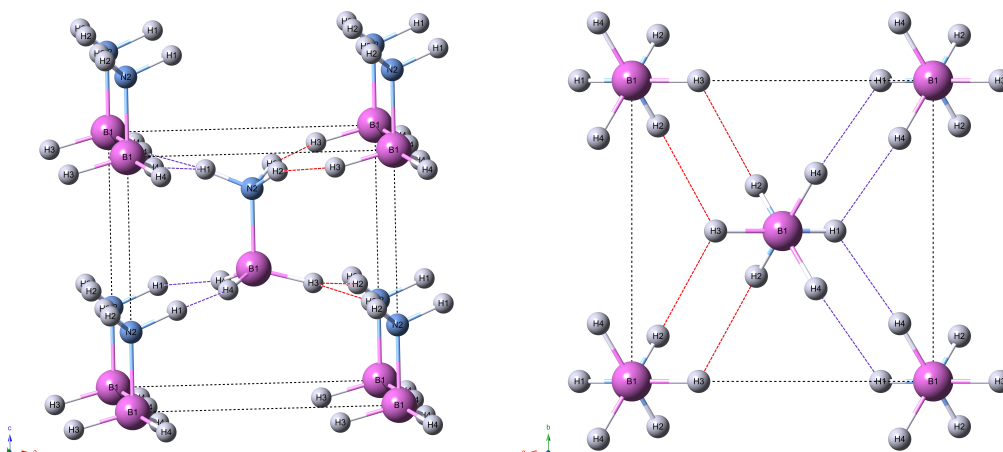


Figure 2.5: One possible tetrahedron orientation of the tetragonal phase of ammonia borane showing the short D...D bonding interactions as dashed lines, D1...D4 in green and D2...D3 in red. Left: projection almost along the *b*-axis. Right: along the *c*-axis.

There have been many computational studies of the strength of dihydrogen bonding between molecules of ammonia borane. Morrision and Siddick [144] used periodic quantum mechanical modelling to predict an average interaction energy for each dihydrogen bond of 12.7 kJ mol^{-1} , indicating that the dihydrogen bonding is relatively weak. Experimental data from the sublimation energy of ammonia borane (assuming dihydrogen bonding is responsible for all the interaction energy) estimates the energy of a dihydrogen bond to be a comparable 15.1 kJ mol^{-1} [145]. There have also been studies of ammonia borane dimers which have found two [140], three [126] and four [146, 147] dihydrogen bonds between the two molecules. Studies of larger numbers of ammonia borane molecules show that moving from the dimer to the trimer to the tetramer decreases the strength of the dihydrogen bonds, suggesting the formation of dihydrogen bonds is not a cooperative process [148]. However these studies do not necessary reflect the situation in the crystal where the molecules are not in a head-to-tail arrangement.

Autrey at al. [61, 149] have suggested the mechanism shown in Figure 2.6 for the reaction of two molecules of ammonia borane to form DADB during the induction

period of thermal decomposition. Prior to the formation of DADB the dihydrogen bond network is disrupted during the formation of the mobile phase; therefore the dihydrogen bonding in the solid state actually stabilises the material against decomposition rather than being an important mediator in the decomposition. However, protic and hydridic hydrogen atoms are still present in the mobile phase of ammonia borane and in DADB, and dihydrogen bonding may still be important in transition states in the release of dihydrogen.

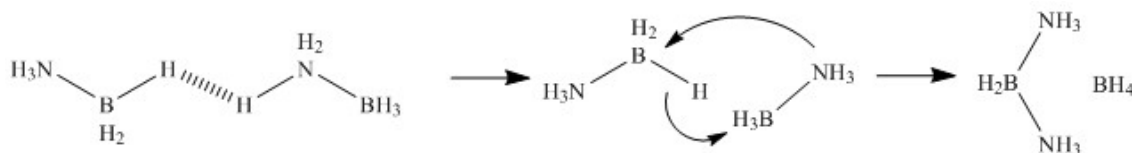


Figure 2.6: Proposed mechanism for the decomposition of ammonia borane to DADB [61, 149].

Wolstenholme et al. [150] have used hydrogen/deuterium studies to suggest that at temperatures close to the melting point of ammonia borane the main hydrogen source is the dihydrogen bonding interactions $\text{NH}^{\delta+} \cdots \delta^- \text{HB}$. However, at higher temperatures the proportion of hydrogen produced from homopolar $\text{BH}^{\delta-} \cdots \delta^- \text{HB}$ interactions increases. They suggest that in the solid, hydrogen has to come from the conventional dihydrogen bonding interactions (either between two molecules of ammonia borane molecule or between DADB and ammonia borane). Once the melt is formed, $\text{BH}^{\delta-} \cdots \delta^- \text{HB}$ conformations are now possible and hydrogen can be released via a homopolar route.

Simulations in the solid state [142] and as isolated molecules [151] have suggested alternative mechanisms for the formation of dihydrogen, involving an intramolecular reaction where a hydrogen atom moves from the ammonia end of the ammonia borane molecule to the boron atom, forming a borohydride ion. This will then eliminate dihydrogen and BH_2NH_2 will form. However, this does not take into account the formation of DADB during the decomposition.

There have been reports of two structures of DADB: tetragonal $I4/mcm$ at higher temperatures [122] and a lower temperature orthorhombic structure (space group $Pbca$) [110]. The $I4/mcm$ structure has dihydrogen bonds ranging between 1.8 Å and 2.1 Å in length. However, there have currently been no neutron studies on these structures to confirm hydrogen positions and dihydrogen bonding characteristics.

Amidoboranes decompose at lower temperatures with a higher weight percent hydrogen released than ammonia borane. The peak of hydrogen release from sodium amidoborane is at 89°C (with 6 wt% hydrogen released in 1 hour), from lithium amidoborane at 92°C (8 wt%), and from ammonia borane at 108°C (3.3 wt%). The hydrogen release is also less exothermic than for ammonia borane: -3 to -5 kJ per mol H_2 for amidoboranes compared to -21 kJ per mol H_2 for ammonia borane [88, 152]. These changes can be directly linked to changes in the structures of the compounds. Both lithium and sodium amidoborane, MNH_2BH_3 , crystallise in the same orthorhombic $Pbca$ structure, with lattice parameters of $a = 7.11274(6)$ Å, $b = 13.94877(14)$ Å, $c = 5.15018(6)$ Å and $a = 7.46931(7)$ Å, $b = 14.65483(16)$ Å, $c = 5.65280(8)$ Å respectively [88]. The structure of lithium amidoborane is shown in Figure 2.7 and shows how the addition of a metal ion will alter the structure and negate the importance of the dihydrogen bond network. The lithium ion is in a tetrahedral coordination environment with one nitrogen atom and three borohydride groups. This causes the $[NH_2BH_3]^-$ units to form sheets where the NH_2 units forming double layers with similar charges facing each other. The structure does contain $H\cdots H$ interactions between the $[NH_2BH_3]^-$ subunits [103], although they are at the upper length limit of being considered dihydrogen bonds. The shortest is 2.37 Å, as opposed to 1.97 Å in ammonia borane. The new $LiH-B$ interactions (lengths between 1.98 Å and 2.63 Å) provide the dominant interaction in the structure and counteract the unfavourable homopolar interactions. Although there are some suggestions that these homopolar interactions, especially $BH^{\delta-}\cdots^{\delta-}HB$,

may be bonding interactions and may help to stabilise the structure [150, 153].

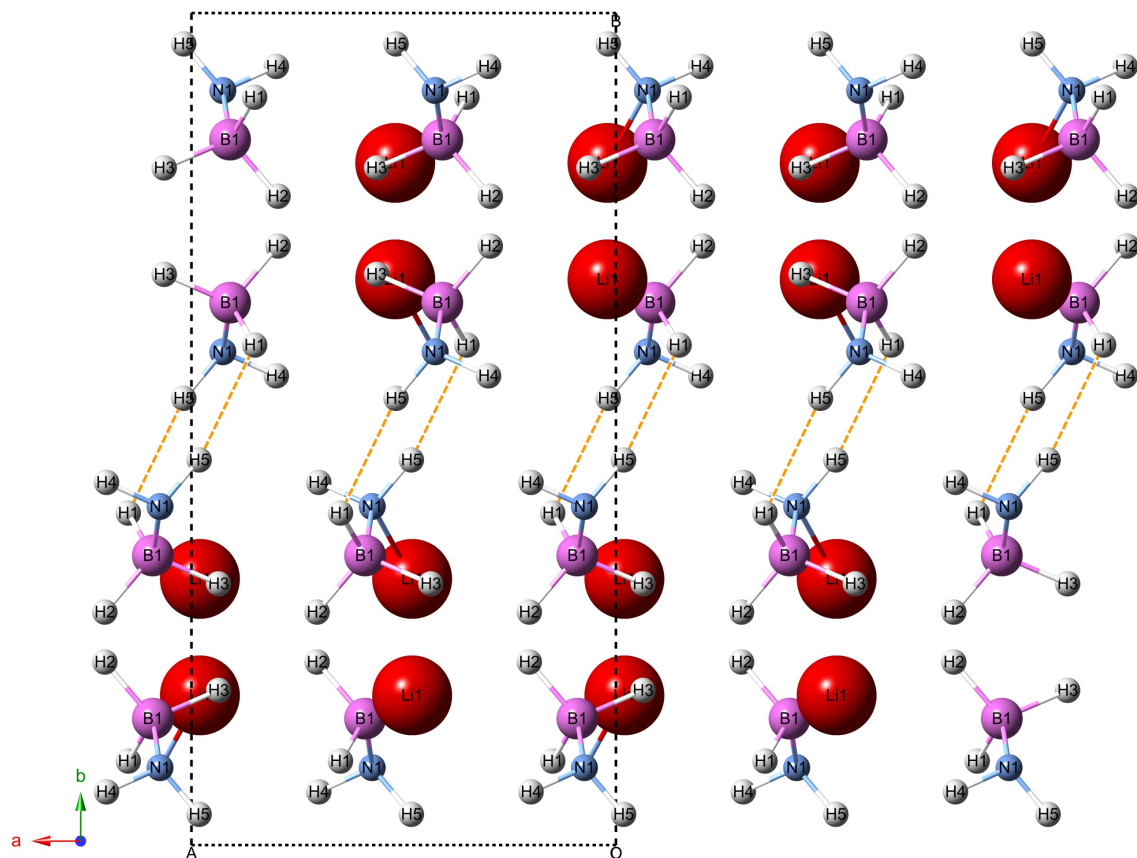


Figure 2.7: The orthorhombic *Pbca* structure of lithium amidoborane [88]. Nitrogen atoms in blue, boron in pink, lithium in red and hydrogen in grey. The ‘dihydrogen bonds’ are shown as orange dashed lines.

The presence of the metal and the protic and hydridic hydrogen atoms is also important in the decomposition mechanism. Using crystallographic and inelastic neutron spectroscopy (INS) measurements, Ryan [103] proposed a reaction between a lithium ion and $\text{B}-\text{H}^{\delta-}$. Movement of the lithium ion allows it to abstract the $\text{H}^{\delta-}$ on a boron atom. Once the $\text{H}^{\delta-}$ is bound to the lithium it is close enough to interact with a $\text{H}^{\delta+}$ bonded to a nitrogen atom and release H_2 . A new B-N bond is formed, creating the lithiated polymer $\text{Li}(\text{NHBH}_2)_n$. A similar metal-mediated reaction mechanism was proposed by Luedtke and Autrey [154] using isotope and NMR studies.

The borohydride ammoniates are another important class of systems which contain dihydrogen bonds. The ammoniates of lithium borohydride, $\text{LiBH}_4\text{x}(\text{NH}_3)$ where $\text{x} = 1 - 4$ are ammonia stores, and on decomposition will release ammonia and not hydrogen. The monoammoniate, $\text{x} = 1$ is orthorhombic (space group $Pnma$), each Li ion is coordinated by three borohydride units and one ammonia. Each borohydride unit coordinates with three lithium ions and four ammonia molecules [155]. This will give two short H...H distances of 2.160 Å and 2.284 Å [156]. When the ammoniate is heated there are two stages of gas release: firstly ammonia above 100°C and then a small release of hydrogen at approximately 280°C. If a slow heating rate (5°C min⁻¹) is used, 40.6 wt% of ammonia is lost and there is only a small hydrogen peak. But if the heating rate is increased to 15°C min⁻¹ only 35.2 wt% of ammonia is released by 280°C and the hydrogen peak is larger [88]. At higher heating rates, not all the ammonia is released by the temperature at which the molecular hydrogen will evolve from the dihydrogen bond.

The presence of protic and hydridic hydrogen atoms facilitates the structural stability of a compound through dihydrogen bonds in the absence of stronger interactions. For example, dihydrogen bonding is the predominant interaction in the structures of ammonia borane but not in the structures of amidoboranes. Protic and hydridic hydrogen atoms are also important in the formation of molecular hydrogen. However, it cannot be assumed if dihydrogen bonds form in a structure that when molecular hydrogen is released during decomposition it will have resulted from a dihydrogen interaction. For example, ammonia borane reacts to form DADB before hydrogen release, and calcium borohydride diammoniate melts [157]. However, even in these systems protic and hydridic hydrogen atoms are still present and interactions between them may play a part in the decomposition. The rehydrogenation of these materials could be hindered by the presence of partially charged hydrogen atoms. When the protic hydrogen-nitrogen

and hydridic hydrogen-boron bonds are broken strong boron-nitrogen bonds form polyamidoborane polymers. These reactions are exothermic (the enthalpy of reaction for ammonia borane to polyamidoborane is approximately -21 kJ mol^{-1} [152]) and therefore require harsh conditions and forcing reagents to break the new B-N bonds and allow the reformation of bonds with hydrogen atoms.

It is clear that dihydrogen bonds are very important in chemical hydrogen storage materials. They give extra stability to solid structures, meaning decomposition temperatures are elevated. They are also important in the mechanisms of molecular hydrogen release.

Chapter 3

Method and Theory

3.1 Diffraction

The diffraction of neutrons, electrons and electromagnetic waves are important techniques in chemistry, particularly in the study of chemical structure and the resultant properties of crystals.

3.1.1 Crystals and Crystallography

A crystal is a solid which possesses long range order ($> 100 \text{ \AA}$). The chemical and physical properties of a material are determined by the underlying atomic arrangement and so knowledge of crystal structure is essential for understanding physical characteristics and reactivity.

The concept of a crystal can be defined using an infinite lattice of points that all have identical surroundings. The crystal structure can be built up from this lattice by placing the same atom or group of atoms at or beside each lattice point.

The unit cell of the crystal is the smallest unit of volume which can be used to build up the crystal. Although more than one unit cells can be used to describe a lattice,

the simplest unit cell consistent with the potential lattice centring is generally selected. The unit cell is defined by 3 vectors **a**, **b** and **c** (of length a , b and c respectively) and the three angles α , β and γ , with α being the angle between the **b** and **c** vectors, β between **a** and **c** and γ between **a** and **b** (see Figure 3.1).

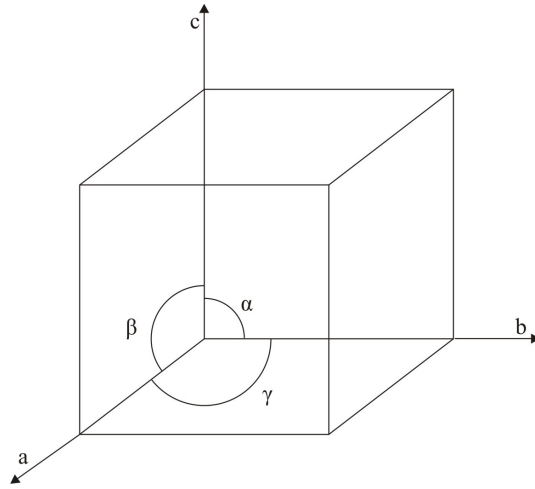


Figure 3.1: Diagram showing the lengths and angles used to define the unit cell.

There are 7 crystal systems, listed in Table 3.1 which lead to 14 possible lattice configurations, called Bravais lattices, also in Table 3.1. Where the centring system is used to define the position of lattice points in the unit cell:

- A primitive unit cell: P has one lattice point at each of the corners and contains one lattice point overall.
- Body centred: I has an additional lattice point at the centre of the unit cell.
- Face-centred: A , B or C has a lattice point on one of the faces of the unit cell, labelled according to the vector which cuts the face containing the lattice point i.e. A if the centred face cuts the a -axis etc.
- Face centred: F has a lattice point in the centre of every face.
- Rhombohedral: R consists of two additional lattice points in the unit cell.

Each of the non-primitive lattices can also be expressed as primitive unit cells. Non-primitive lattices are generally chosen because they more clearly reflect the symmetry of the crystal structure.

Crystal system	Lattice parameters
Triclinic P	$a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90^\circ$
Monoclinic P, C	$a \neq b \neq c, \alpha = \gamma = 90^\circ, \beta \neq 90^\circ$
Orthorhombic P, A, B, C, I, F	$a \neq b \neq c, \alpha = \beta = \gamma = 90^\circ$
Tetragonal P, I	$a = b \neq c, \alpha = \beta = \gamma = 90^\circ$
Trigonal R	primitive cell $a = b = c, \alpha = \beta = \gamma \neq 90^\circ$ hexagonal cell $a' = b' \neq c', \alpha' = \beta' = 90^\circ,$ $\gamma' = 120^\circ$
Hexagonal P	$a = b \neq c, \alpha = \beta = 90^\circ, \gamma = 120^\circ$
Cubic P, I, F	$a = b = c, \alpha = \beta = \gamma = 90^\circ$

Table 3.1: Table showing the crystal systems and Bravais lattices.

3.1.1.1 Reciprocal Space

Diffraction patterns and many physical properties of a crystal are best described in terms of reciprocal space. The reciprocal lattice is the representation of a Fourier transform of the spatial wave function of the original Bravais lattice. It is defined by vectors, $\mathbf{a}^*$, $\mathbf{b}^*$ and $\mathbf{c}^*$ which are perpendicular to the faces of the direct lattice unit cell. The lengths of these vectors are the inverse of the perpendicular distance from the lattice origin to the faces of the direct lattice, i.e. $a^* = 1/d_{100}$, $b^* = 1/d_{010}$ and $c^* = 1/d_{001}$. For cubic, tetragonal and orthorhombic lattices, this equates to $a^* = 1/a$, $b^* = 1/b$ and $c^* = 1/c$. A direct lattice of a particular crystal system will always give a reciprocal lattice of the same system.

3.1.2 Diffraction and Bragg's Law

When radiation with a similar wavelength to the interatomic spacing of a crystal (typically X-rays, neutrons or electrons) interacts with a crystalline sample, a distinctive diffraction pattern will be produced. The first X-ray diffraction experiment was performed by Max von Laue on a copper sulphate crystal in 1911 [158] and Bragg diffraction was first proposed by William Lawrence Bragg in 1912 [159].

Radiation is scattered when it interacts with an atom in a crystal. Each atom is a source of spherical waves radiating in every direction. Since there are multiple atoms, these waves interact with each other and diffraction occurs when there is constructive interference. This can be modelled as if the radiation is reflecting off a series of planes in a crystals called Bragg planes, defined in terms of Miller indices, $(h \ k \ l)$. Miller indices are the reciprocals of the fractions of the unit cell edge, **a**, **b** and **c** respectively, intersected by a plane. Constructive interference of the waves reflected from these planes will give a high intensity signal, called a Bragg reflection. Constructive interference will occur when the Bragg equation (see Equation 3.1 and Figure 3.2) is satisfied.

$$n\lambda = 2d \sin \theta \tag{3.1}$$

where n is an integer, λ is the wavelength of the incident wave, d is the distance between the parallel Bragg planes and θ is the angle between the incident wave and the Bragg plane.

Bragg's Law can be derived as follows and the derivation is illustrated in Figure 3.2: the incident beam can reflect off either the top or bottom planes; if it reflects at B it will travel further than if it reflects at A. For the waves to interfere constructively they will need to be in the same phase after they reflect. To have the same phase, the difference in the distance travelled by the two beams must be a multiple of the

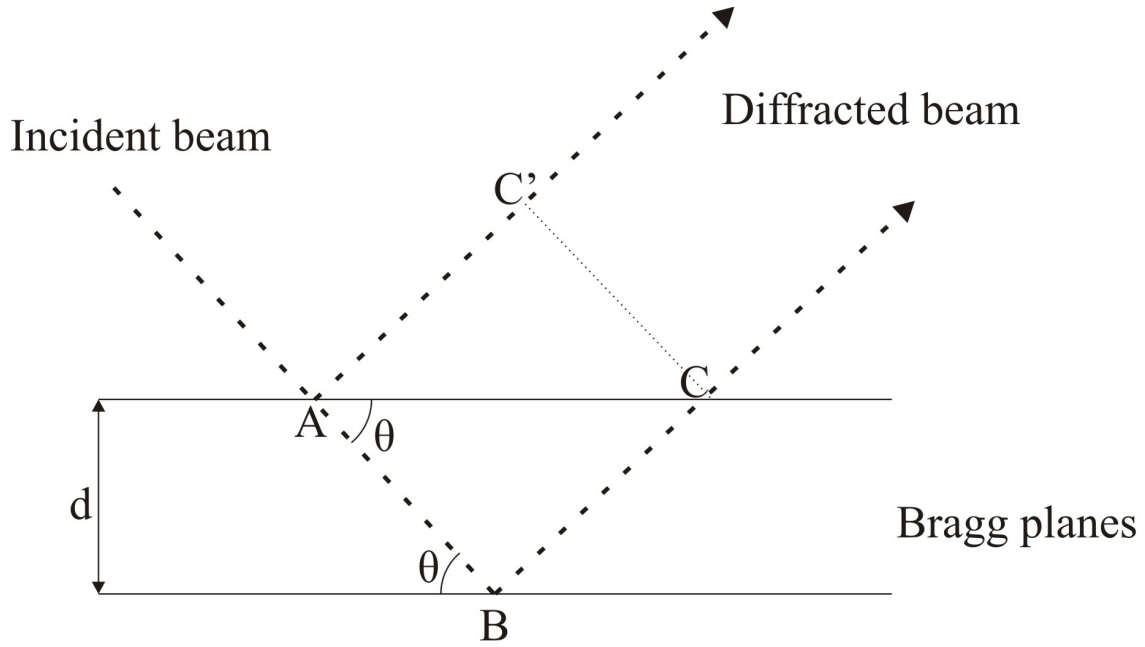


Figure 3.2: Diagram showing Bragg scattering. When the Bragg equation is satisfied, radiation will interfere constructively producing a Bragg reflection.

wavelength, Equation 3.2.

$$(AB + BC) - AC' = n\lambda \quad (3.2)$$

The distances in question can be defined as:

$$AB = BC = \frac{d}{\sin \theta} \quad (3.3)$$

$$AC = \frac{2d}{\tan \theta} \quad (3.4)$$

$$AC' = \frac{2d \cos \theta}{\tan \theta} = \frac{2d \cos^2 \theta}{\sin \theta} \quad (3.5)$$

Substituting Equations 3.3 and 3.5 into Equation 3.2 gives Bragg's Law

$$n\lambda = \frac{2d}{\sin \theta} - \frac{2d \cos^2 \theta}{\sin \theta} = \frac{2d}{\sin \theta} (1 - \cos^2 \theta) = 2d \sin \theta \quad (3.6)$$

3.1.2.1 Ewald Sphere

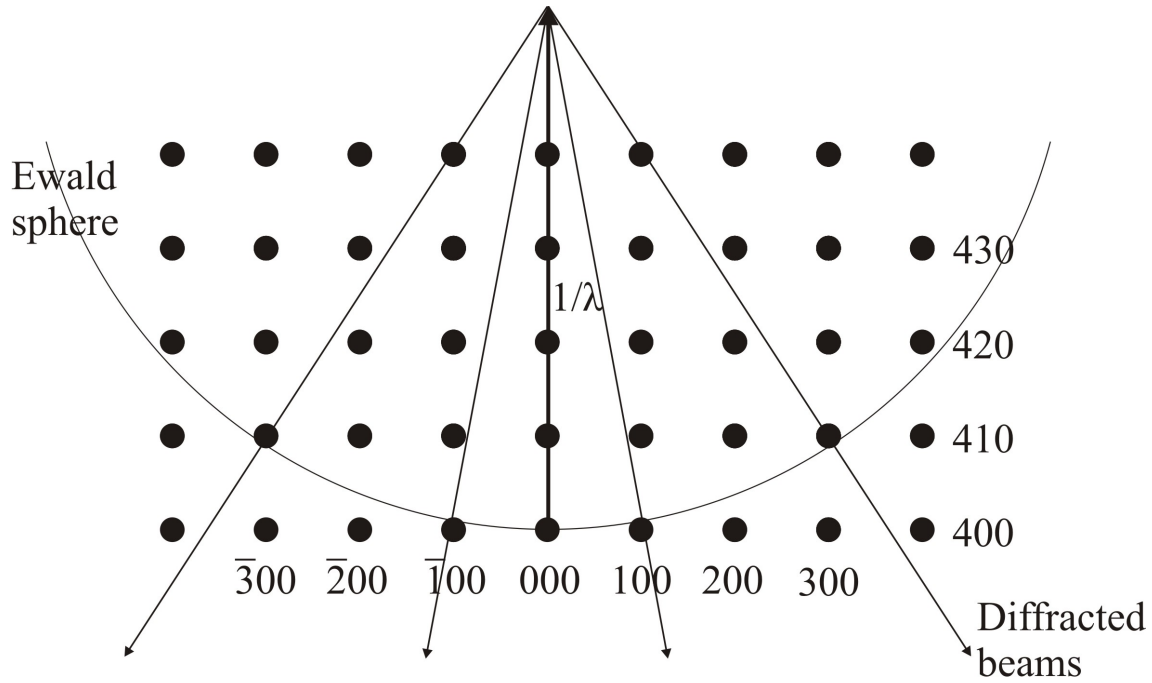


Figure 3.3: The construction of the Ewald sphere including the reciprocal lattice, showing the $\mathbf{r} = \frac{1}{\lambda}$ vector parallel to the incident beam, the Ewald sphere (projected as a circle in the 2D representation), and the diffracted beams.

The Ewald sphere is a useful way of visualizing how different Bragg planes in a crystal diffract [160]. It is the reciprocal space equivalent of Bragg's Law in real space. The construction of the Ewald sphere is simple:

1. Draw the reciprocal lattice of the crystal, as described in Section 3.1.1.1
 2. Add a vector of length $\frac{1}{\lambda}$ (where λ is the wavelength of the incident beam) from the origin of the lattice, parallel and in the opposite direction to the incident beam.
 3. The Ewald sphere is constructed with a radius of $\frac{1}{\lambda}$ around the end of the vector.
- Where the sphere touches lattice points, the incident beam will be diffracted.

The Ewald sphere in reciprocal space can be easily related to real space. The distance from the origin of the reciprocal lattice to the hkl reciprocal lattice point is $\frac{1}{d_{hkl}}$ where d_{hkl} is the distance between the planes in the real space. Therefore:

$$\sin \theta = \frac{1/2d_{hkl}}{1/\lambda} = \frac{\lambda}{2d_{hkl}}$$

which rearranges to Bragg's Law:

$$n\lambda = 2d \sin \theta \quad (3.7)$$

3.1.2.2 Intensity

For a single crystal diffraction pattern, where one crystal is mounted and rotated in the X-ray beam, the diffracted beams will produce a series of spots. If the intensity and location of the spots is recorded, they can easily be assigned their hkl indices. Interaction with electrons in an atom will change both the direction and the phase of the incident X-rays. Therefore the scattered intensity depends on two main factors; the scattering from each individual atom in the structure, f_0 , which depends on the number of electrons possessed by each atom and the phases of the individual beams which differ as their different paths take them through different amounts of the crystal.

The structure factor, F_{hkl} (see Equation 3.8) is a combination of the two above contributions. Its imaginary component is used to indicate the phase of the diffracted beam.

$$F_{hkl} = \sum_{j=1}^{\text{atoms}} f_j \exp[2\pi i(hx_j + ky_j + lz_j)] \quad (3.8)$$

where f_j is the structure factor of atom j and x , y and z are the fractional coordinates of the atom in question.

The intensity for a particular reflection can be calculated from the structure factor

as shown in Equation 3.9.

$$I = K |F_{hkl}|^2 m L_p A \quad (3.9)$$

where K is the scale factor, m is a multiplicity factor, L_p is the Lorentz polarisation factor and A is an absorption factor. The Lorentz polarisation factor contains both the Lorentz correction (a geometric correction accounting for the amount of time a particular plane remains in the diffracting position) and the polarization correction which accounts for the partial polarization of the diffracted beam. They are generally combined into a single correction factor as they depend on the instrument and the spacing of the Bragg planes and not on the structure of the crystal.

3.1.2.3 The Phase Problem

The structure factor can easily be calculated from the crystal structure, and therefore the diffraction pattern can be predicted. But is it not so easy to infer the structure from the diffraction pattern. Since the structure factor is a continuous function, a Fourier transform (Equation 3.10) can be performed to give the electron density, ρ_{xyz} map of the crystal and hence its structure.

$$\rho_{xyz} = \frac{1}{V} \sum_h \sum_k \sum_l F_{hkl} \exp[-2\pi \cdot i(hx + ky + lz)] \quad (3.10)$$

However as shown in Equation 3.9 the magnitude of the structure factor can be calculated, but not the phase. Not being able to calculate the phase of the diffracted beam is called the phase problem. There are a variety of ways to determine the phases of the reflections:

- The Patterson function: A Patterson map [161] can be used to determine interatomic vectors and the scattering factors of the atoms at either end of the

vectors. These can then be used to find the structure. It is more effective for heavy and widely-spaced atoms, as many similar atoms will give overlapping peaks which can be difficult to resolve.

- Direct methods [162]: The initial phases are estimated using a triplet relationship between the phases of three reflections.
- Isomorphous replacement: This is particularly used in determining the structure of proteins; a heavy metal is added to the protein structure by soaking crystals in a heavy metal solution. The relationships between the structure factors of the original protein, the protein with the heavy metal, and the heavy metal alone can be used to determine the phases.
- Multi-wavelength anomalous diffraction [163]: The inner electrons of an atom can absorb X-rays of a particular wavelength and after a time delay re-emit them, which induces a phase shift in the reflections. The analysis of this phase shift at different wavelengths of synchrotron X-ray light gives the phase.
- Multiple trial and error: In some systems there are special features which make it possible to guess at one or more plausible crystal structures. Trial and error can then be used to distinguish between and improve these initial structures iteratively. Although this method is time consuming, modern computing capabilities make it feasible. For example a Bayesian algorithm can be used in an optimisation routine with the aim of finding the structure corresponding to an energy minimum, by moving a known molecular structure or fragment around the unit cell. This minimisation is often carried out using simulated annealing in order to avoid numerical problems associated with the presence of local energy minima.

3.1.2.4 Structure Solution

Once the initial phases have been found, an initial map of the electron density can be produced and a structure can be constructed by adding atoms at regions of high electron density. The structure can then be refined until a good fit with experimental data is obtained.

3.1.3 Powder Diffraction

Growing a large enough crystal for single crystal diffraction can be difficult, and often impossible. Powder diffraction uses a polycrystalline sample containing many small crystallites, usually smaller than 10 μm in diameter.

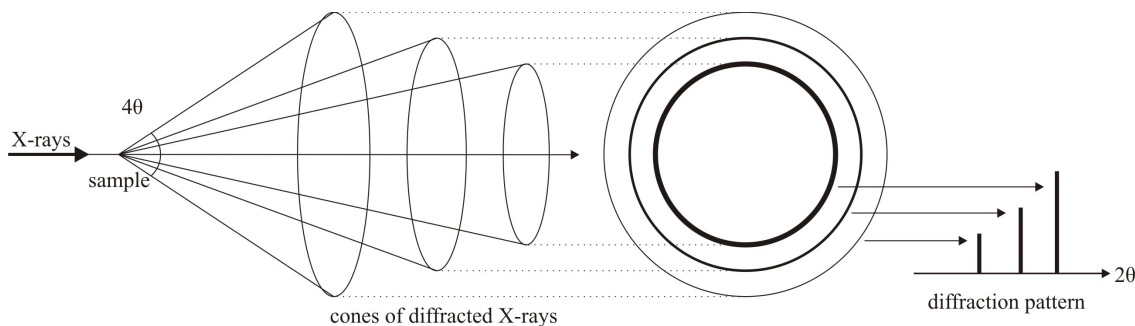


Figure 3.4: Schematic of X-ray diffraction Debye-Scherrer cones generating the X-ray pattern.

The theory and the analysis of powder diffraction data is very similar to single crystal data. Single crystal diffraction produces a pattern which consists of a series of spots. A powder sample is made up of multiple crystallites in random different orientations. Consequently, the individual set of spots from each crystallite will have a different orientation, and the spots for the different crystallites will merge to produce cones, called Debye-Scherrer cones, as shown in Figure 3.4. The 2D diffraction pattern seen is a thin radial slice across these rings.

3.1.3.1 Uses of Powder Diffraction

Powder diffraction is an easy and quick way to determine the composition of a crystalline product or mixture of products without the need for difficult and time-consuming sample preparation. Patterns can be compared with those from known compounds stored in databases such as the Inorganic Crystal Structure Database [164]. Variable temperature experiments are generally easier for powder samples, as single crystals may not be stable during phase changes and many solid state reactions require an intimate mixture. Changes in lattice parameters can be tracked in response to changes in temperature or pressure. These lattice constants can be determined from the position of peaks known to correspond to particular lattice planes. Although the solution of structures is more difficult than for single crystal measurements, it is still an important use of powder diffraction, especially for samples which do not form large crystals.

3.1.3.2 Structure Solution from Powder Diffraction

The solution of a structure from a powder diffraction pattern is rather more complicated than for single crystal data. However, modern computing power is allowing more and more complex structures to be solved. The stages necessary for the solution of a structure (from either a single crystal or powder pattern) are as follows [165]:

- Index the diffraction patterns and define the unit cell.
- Identify the space group of the crystal.
- Calculate the integrated intensity of the peaks.
- Solve the phase problem.
- Refine the model until there is a good match between the calculated and experimental patterns.

Indexing the reflections in a single crystal pattern is simple, since it is effectively the reciprocal lattice, so the hkl values can be counted from the origin. For simple crystal structures, a powder diffraction pattern can be assigned by simple trial and error or by using the systematic absences caused by the symmetry of the unit cell. However, for more complex indexing this is generally achieved using autoindexing programs. In this work, patterns were indexed automatically using TOPAS-academic [166] (see Section 3.1.4.5).

The experimental intensities are determined and the modelled intensities are calculated as part of a Pawley refinement which breaks the pattern down into its intensities. No structural model is required at this stage; only details of the unit cell parameters. The phase problem and structure solution for a powder pattern is often performed in the same way as for a single crystal pattern. However, techniques such as simulated annealing also work well [165] and have been used to solve the structures of many of the new hydrogen storage materials.

3.1.3.3 Laboratory Powder Diffraction X-ray Sources

In a conventional X-ray tube, X-rays are produced by firing electrons at a target metal, usually copper or molybdenum. The impact of the high energy electron on an atom causes an electron from an inner shell to be ejected. When a higher energy electron falls to fill the resulting hole, excess energy is emitted as electromagnetic radiation. There are usually several higher energy electrons that can fill the hole, resulting in a radiation spectrum with a set of characteristic peaks.

In the case of copper, the electron ejected is from the 1s shell, so the hole can be filled by either of the two electrons in the 2p shell or an electron from the 3p shell. This produces X-rays of three distinct energies, a doublet at $K_\alpha = 1.5418 \text{ \AA}$ and a singlet $K_\beta = 1.3922 \text{ \AA}$. The differing spins of the two electrons in the 2p orbitals means that

the energy lost during their transition to the lower orbital is slightly different, resulting in a doublet with $K_{\alpha 1}$ and $K_{\alpha 2}$ lines. In most diffractometers, filters are used to remove all but the $K_{\alpha 1}$ line.

3.1.3.4 Synchrotron X-ray Sources

There are many advantages to using a synchrotron as an X-ray source for powder diffraction. The very high brightness and intensity of the X-rays produced allows high intensity diffraction patterns to be collected. This can either be used to obtain patterns good enough to allow structure solution, often including the hydrogen positions, or to monitor fast processes such as reactions and phase changes.

In a synchrotron, electromagnetic radiation is produced by the radial acceleration of electrons (acceleration in a direction perpendicular to their direction of movement). The electrons are initially produced by an electron gun and accelerated in a Linear Particle Accelerator (linac) before being injected into the main synchrotron ‘ring’. The ring is not completely circular, but a polygon with a series of straights and corners. At the corners, bending magnets cause the electrons to lose energy as electromagnetic radiation which can then pass through the walls of the synchrotron and into the experimental cabins. On the straights, there are two types of insertion devices. Wigglers produce electromagnetic radiation across a broad spectrum, with the very high energy radiation being particularly useful. Undulators produce tunable very bright light in a very narrow beam. There are also accelerating magnets which replace the energy which the electrons lose in producing radiation, increasing the lifetime of the electrons in the ring.

3.1.3.5 Problems with X-Ray Diffraction

Although X-ray diffraction is a very powerful technique, it is not suitable for every situation. The X-rays interacting with electrons in an atom presents several problems:

- Hydrogen only has one electron and so will have a small scattering factor and will contribute little to the diffraction pattern, making accurately determining its position in the structure difficult. The position of hydrogen atoms can often be inferred from the position of heavier atoms. However, in hydrogen storage materials the precise location of the position of hydrogen atoms is important.
- If a structure contains heavy and light atoms, the pattern will be dominated by scattering from the heavy atoms and it can be difficult to distinguish the lighter atoms.
- It can be difficult to distinguish between atoms with a similar number of electrons.
- The form factor fall off caused by the extended size of the electron cloud leads to low intensities at short d-spacings which can lead to less precise atom locations.

3.1.4 Neutron Diffraction

All particles exhibit wavelike properties; the wavelength associated with a particle can be calculated using the de Broglie equation shown in Equation 3.11.

$$\lambda = \frac{h}{mv} \quad (3.11)$$

where λ is the wavelength, h is Planck's constant, m the mass of the particle and v the velocity of the particle. For large particles the wavelength is too small to be measurable or useful, but for small particles such as neutrons, protons and electrons the wavelengths are comparable with interatomic spacings, and so make ideal tools for diffraction. When a neutron interacts with an atom, one of three things can occur:

1. The neutron can be elastically scattered by the atom, with no energy exchange between them. The final energy of the neutron is the same as its initial energy.

2. The neutron can be inelastically scattered by the atom with an exchange of energy (see Section 3.2.2).
3. The neutron can be absorbed by the atom and incorporated into the nucleus.

There are several advantages of neutron diffraction. Unlike X-rays which are scattered by electrons, neutrons interact with the nucleus of the atom. The neutron cross-section is not proportional to the mass of the atom: light elements often have the highest cross sections and different isotopes of the same element generally have different cross sections. This allows the lighter atoms in samples containing both heavier and lighter atoms to be investigated. Neutrons are scattered by the nucleus and so there is no form factor fall off associated with the chemical structure. Well-defined peaks at high angles allow atomic positions to be determined with high certainty. Neutrons are non-interacting and so do not damage delicate or reactive samples in contrast to X-rays which can cause samples to decompose.

Due to large incoherent scattering cross sections or large absorption cross sections of some isotopes, it is not always possible to perform successful neutron diffraction experiments with elements in natural abundance. The compounds studied in this thesis primarily contain hydrogen, boron and nitrogen. A comparison between the neutron and X-ray cross sections of these elements is given in Figure 3.5. ^1H has a large incoherent neutron diffraction cross section which during elastic diffraction experiments results in a high background. All of the neutron diffraction samples were therefore enriched with deuterium (^2H). Natural abundance boron is 20 % ^{10}B and 80 % ^{11}B ; ^{10}B has a high neutron absorption cross section and will dramatically reduce the overall intensity of the neutron data collected, therefore samples were made using 100 % enriched ^{11}B .

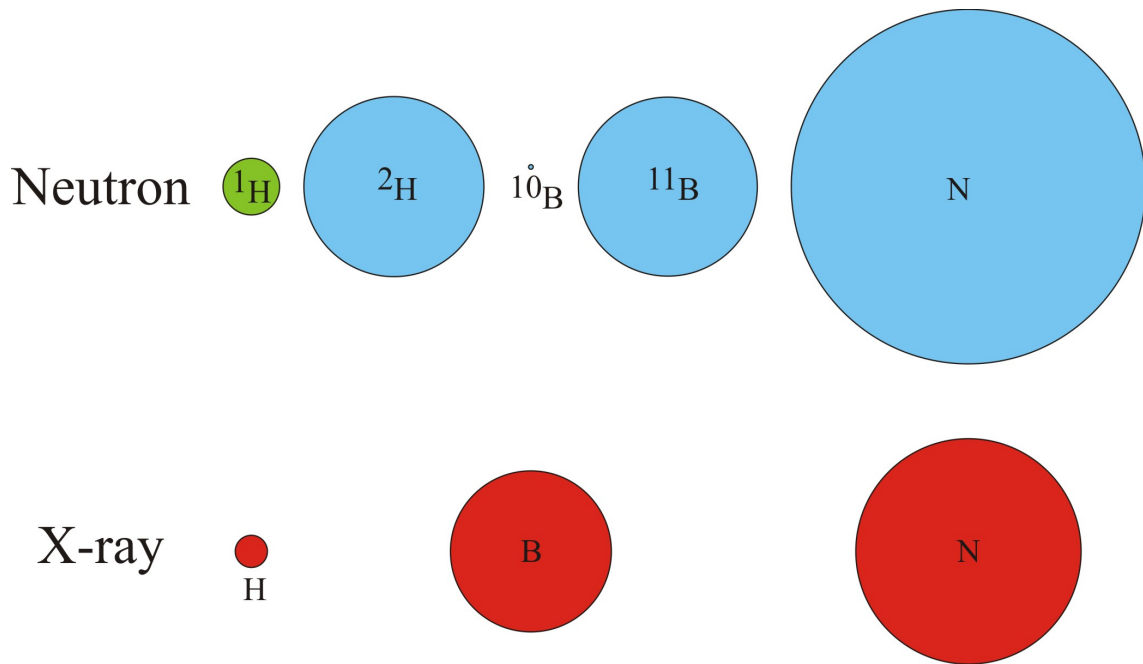


Figure 3.5: Schematic comparing neutron and X-ray cross sections. Neutron cross sections in green (negative) and blue (positive) and X-ray cross sections in red.

3.1.4.1 Neutron Sources

There are two main types of neutron sources used for research: reactor sources and spallation sources. Reactor sources such as the Institut Laue-Langevin (ILL) in Grenoble, France, produce neutrons using the nuclear fission of uranium-235 in a reactor (Equation 3.12).



For each uranium atom that breaks apart on average 2.5 neutrons are produced, one returns to the core to continue the reaction, and 0.5 of a neutron is lost through absorption, leaving one neutron to be used in experiments. The neutrons emanating from the reactor are moderated by the pool of water thus producing thermal neutrons. Reactor sources typically have high average neutron flux, (the highest is the ILL, 58.3 MW with

a flux of 1.5×10^{15} neutrons/s/cm²) [167] and are a particularly good source of thermal neutrons. However, time-of-flight experiments are more difficult with reactor sources.

The neutron results reported in this thesis were collected at ISIS, Rutherford Appleton Laboratories, Didcot, UK [168, 169]. ISIS is a spallation neutron source which produces neutrons by firing protons at a heavy metal target. Initially, an ion source produces H⁺ ions that are accelerated and bunched by a radio frequency quadrupole accelerator. A linear accelerator accelerates the H⁺ ions to 70 MeV (37 % of the speed of light). The H⁺ ions are stripped of their electrons as they are injected into the synchrotron ring. The protons in the ring are accelerated and focused in the synchrotron ring. After approximately 10,000 cycles, the protons have been accelerated to 800 MeV (84 % of the speed of light) and are fired at the target. Two 100 ns pulses of protons are delivered to the target, and the process is repeated 50 times a second giving a mean proton current of 200 μ A.

Four out of five pulses are directed at the Target Station 1 target. The Target Station 1 target consists of heavy-water-cooled tungsten plates. The protons trigger an intranuclear cascade releasing neutrons; each proton that hits the target will produce 15 neutrons. The high energy neutrons produced are cooled by four small moderators. The small size of the moderators means that the neutrons do not entirely reach thermal equilibrium, which maintains a compact pulse length. The moderated neutrons pass down 18 neutron channels to the experimental instruments.

The fifth proton pulse generated is directed to Target Station 2 which is optimised for colder neutrons. The target is a tungsten cylinder, designed to allow the moderators very close to the target and thereby increase the neutron flux. The neutron flux at Target Station 2 is higher than Target Station 1 despite receiving only a fifth of the neutrons. Spallation sources produce higher energy neutrons than reactor sources. The pulse structure of the neutrons on spallation sources allows time-of-flight neutron

experiments to be easily preformed.

3.1.4.2 Wish

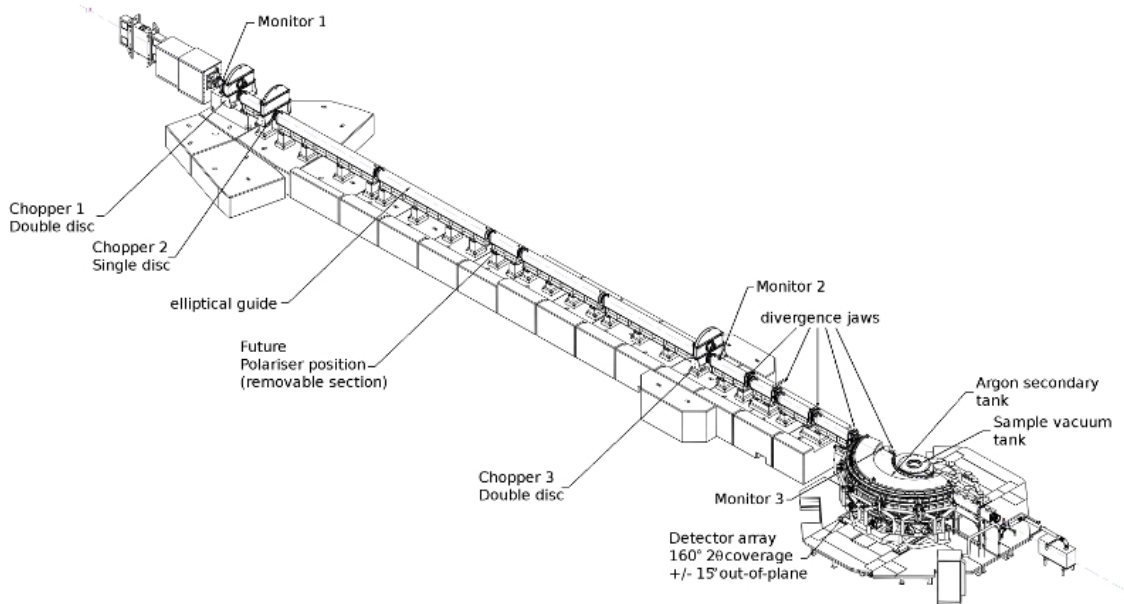


Figure 3.6: Schematic of the Wish diffractometer on target station 2 at ISIS [170].

Wish (Figure 3.6) [170] is a high resolution long wavelength neutron diffractometer optimised for long d-spacing systems ($0.7 - 50 \text{ \AA}$) such as large unit cell and magnetic samples. At short d-spacings, Bragg peaks tend to overlap but they can be deconvoluted using high resolution instruments such as Wish.

The neutrons are moderated using a decoupled solid methane moderator and detected using an array of pixellated ^3He detectors covering a range of scattering angles from $10 - 170^\circ$. The background is reduced by using careful collimation with an oscillating radial collimator and protection of the detectors with boron rich materials.

On Wish, data can be collected in the more traditional normal mode in which the data are collected and saved at the end of each scan. Alternatively, there is a continuous mode in which data are collected continuously over a long period of time and can be

processed into time slices at the end of the experiment. This is used for fast processes where crucial data might be missed while the data are being saved. It also allows data to be reprocessed into differently-sized time slices if necessary.

3.1.4.3 HRPD

HRPD (High Resolution Powder Diffraction) is the highest resolution neutron powder diffractometer in the world. The spread in the Bragg reflections, $\frac{\Delta d}{d}$ is approximately 4×10^{-4} . There are three factors which affect $\frac{\Delta d}{d}$, timing uncertainty, ΔT , flight path uncertainty, ΔL , and angular uncertainty, $\Delta\theta$:

$$\frac{\Delta d}{d} = \left[\Delta\theta^2 \cot^2 \theta + \left(\frac{\Delta T}{T}\right)^2 + \left(\frac{\Delta L}{L}\right)^2 \right]^{\frac{1}{2}} \quad (3.13)$$

Therefore increasing the length of the flight path will decrease the amount of uncertainty in the time and the path length. The detector angle is when $\cot \theta = 0^\circ$, $\theta = 90^\circ$ will have the highest resolution. HRPD has ZnS scintillator detectors at 30° , 90° and 168° .

3.1.4.4 The Rietveld Method

Rietveld analysis [171] is the primary technique for the characterisation of powder X-ray or neutron diffraction patterns of crystalline materials. A least-squares refinement is used to obtain the best possible match between a calculated diffraction pattern and the experimental results. The calculated pattern is obtained from the model containing the crystal structure (or structures), machine/instrument parameters, lattice and thermal parameters and so on. The least squares refinement attempts to minimise iteratively the residual, S_y which is defined in Equation 3.14.

$$S_y = \sum_i \omega_i (y(obs)_i - y(calc)_i)^2 \quad (3.14)$$

where $y(obs)_i$ and $y(calc)_i$ are the observed and calculated intensities at the i th step and $\omega_i = \frac{1}{\sigma_i^2}$ where σ_i is the estimated error associated with $y(obs)_i$. After each iteration, the new calculated parameters are fed back into the model, improving the model structure, until S_y converges and the model cannot be further improved.

The Rietveld method makes no attempt to deconvolute overlapping peaks or to allocate particular Bragg peaks to particular observed intensities. Therefore the original model must be reasonably accurate. The intensity at any particular point, i , in the pattern will typically be made up of many Bragg reflections. Therefore the calculated intensities, $y(calc)_i$ are determined from the structure factor values found by summing the calculated contributions of all the Bragg peaks over a specific range and the background over that range (Equation 3.15).

$$y(calc)_i = s \sum_K L_K |F_K|^2 \phi(2\theta_i - 2\theta_K) P_K A + y(back)_i \quad (3.15)$$

where s is the scale factor, K represents the Miller indices for a particular Bragg reflection, L_K is a factor which contains the Lorentz, polarization and multiplicity factors, ϕ the reflection profile function, P_K the preferred orientation function, A an absorption factor, F_K the structure factor for the K th Bragg reflection and $y(back)_i$ is the intensity of the background for the i th step.

The peak shapes can be modelled using a variety of functions, the most common being Gaussian, Lorentzian and Voigt. The progression of a refinement can be judged using a variety of statistical measures:

1. R_{wp} is the weighted pattern R factor and is the usual measure to show the progress

of the refinement:

$$R_{wp} = \frac{\{\sum_i \omega_i [y(obs)_i - y(calc)_i]^2\}^{\frac{1}{2}}}{\{\sum_i \omega_i y(obs)_i^2\}^{\frac{1}{2}}} \quad (3.16)$$

2. The profile R factor, R_p is based on the difference between the calculated and the observed diffraction patterns:

$$R_p = \frac{\sum_i |y(obs)_i - y(calc)_i|}{\sum_i |y(obs)_i|} \quad (3.17)$$

3. χ , the ‘goodness of fit’ parameter, is useful since it includes R_e (see Equation 3.19), the R expected value for the refinement:

$$\chi = \frac{R_{wp}}{R_e} = \left[\frac{S_y}{(N - P + C)} \right]^{\frac{1}{2}} \quad (3.18)$$

where S_y is the residual (see Equation 3.14), N is the number of observations, P is the number of variables and C is the number of variables restraints, and:

$$R_e = \left[\frac{(N - P)}{\sum \omega_i y(obs)_i^2} \right]^{\frac{1}{2}} \quad (3.19)$$

However, it is also crucial to determine how well the fit is progressing is by visually assessing how well the calculated pattern fits the observed pattern, and how plausible the newly refined model structure is.

3.1.4.5 Fitting Software

The refinement program TOPAS-Academic [166] was used for all the refinements reported in this thesis. A text editor was used to construct and edit the TOPAS input files. Typically, a refinement progressed as follows:

- Initially, the instrument parameters are refined to take account of the instrument-dependent factors and the background modelled using a high order polynomial function.
- Details for the phases are added one by one with Lorentzian and Gaussian functions modelling the peak shapes. Initially, factors which affect the peak position, such as lattice parameters, are allowed to refine. After a good fit has been obtained, other parameters such as thermal parameters will be allowed to refine to improve the fit.

In variable temperature experiments, there can be tens or hundreds of diffraction patterns which must be analysed, each which only differs slightly from the previous and next patterns. The refinement of these patterns can be achieved using a ‘batch refinement’. The batch refinement constructs input files for the diffraction patterns, with the parameters from the end of the previous refinement as the initial parameters for the refinement of the next pattern. A carefully refined initial file, where the background and the zero error parameters are (usually) fixed, is used as the starting point for the batch refinement. Parameters of interest are allowed to vary and can be programmed to output into a text file for further analysis. Batch refinements work well when the changes between the patterns are small. For example, the increase in lattice parameters of a phase due to thermal expansion as its temperature increases. If the differences between subsequent patterns are larger, such as may be caused by a phase transition, it may be necessary to manually perform the refinements across the phase transition.

3.2 Spectroscopy

3.2.1 Vibrational Spectroscopy

Vibrations of a molecule occur when its atoms are in periodic motion. All molecules have $3N$ degrees of freedom, where N is the number of atoms the molecule contains.

- Three of these degrees of freedom are the translational motion of the centre of mass of the molecule.
- Non-linear molecules have three rotational degrees of freedom and linear molecules have two (they have no rotational axis along the bond axis).
- The remainder of the degrees of freedom will be vibrational modes, hence non-linear molecules have $3N-6$ vibrational modes and linear molecules have $3N-5$.

There are six types of vibrational motion that a molecule can experience:

- Bending - a change of the angle between two bonds.
- Out of plane - an atom moving perpendicular to the plane of surrounding atoms.
- Rocking - a change in the angle between a group of atoms and the rest of the molecule.
- Stretching - a change in the bond length.
- Twisting - a change in the angle between the plane of two groups of atoms.
- Wagging - a change in the angle between a plane in a group of atoms and a plane bisecting the rest of the molecule.

Particularly at low energies, molecular vibrations can be described by treating the atoms and the bonds between them as masses joined by a spring. For a two particle

system, assuming the bond obeys Hooke's Law the potential energy of the system, V is given by Equation 3.20.

$$V = \frac{1}{2}kx^2 \quad (3.20)$$

where k is the force constant of the spring (bond) and x is the displacement from the equilibrium position. The frequency, ν of the bond is shown in Equation 3.21.

$$\nu = \frac{1}{2\pi} \sqrt{\frac{k}{m_r}} \quad (3.21)$$

where m_r is the reduced mass associated with this frequency. The allowable energy states of molecular vibrations are however not continuous but are quantized. If the Schrödinger equation for the relative motion of two atoms is solved using the harmonic oscillator potential as the potential energy term, it will give the discrete quantized vibrational energy levels, Equation 3.22.

$$E_v = (n + \frac{1}{2})h\nu \quad (3.22)$$

where n is the is the vibrational quantum number and the $\frac{1}{2}$ refers to the ground state of the atom. The harmonic approximation is too simple, especially at higher energies, where it does not allow bonds to break. Modelling the bond as an anharmonic oscillator using a Morse potential is more accurate. The allowed vibrational energy levels (Equation 3.23) will no longer be equally spaced as in the harmonic model but will move closer together at higher energies until they eventually merge at the dissociation limit when the bond will break.

$$E_v = (n + \frac{1}{2})h\nu - (n + \frac{1}{2})^2 h\nu x_e \quad (3.23)$$

where x_e is the anharmonicity constant. Heat or electromagnetic radiation can excite molecules from a lower energy level to a higher level. Spectroscopy uses the interaction of radiation with a molecule to determine its vibrational states, which can be used to investigate the structure of a material and possible reaction and decomposition pathways.

3.2.2 Inelastic Neutron Spectroscopy

Inelastic neutron spectroscopy, INS [172], is used to probe the atomic and molecular motions of an element or compound using the inelastic interaction of neutrons. The scattering involves a exchange of energy and momentum between the neutron and the scatterer (the sample).

The energy change of the neutrons is the difference between the initial energy of the incident neutron beam, E_i and the final energy after interaction with the sample, E_f Equation 3.24.

$$\Delta E = E_i - E_f \quad (3.24)$$

and therefore the momentum transfer can be written as in Equation 3.25.

$$\hbar Q = \hbar(k_i - k_f) \quad (3.25)$$

where k is the wave vector of the neutron and Q is the neutron momentum. The neutron energy loss is usually recorded as $S(Q, \omega)$ the neutron momentum transfer vector, which is defined using the scattering law, Equation 3.26.

$$S(Q, \omega)_l^n = y\sigma_l \frac{[(Q \cdot u_l)^2]^n}{n!} \exp(-(Q \cdot \sum_{\nu} u_l)^2) \quad (3.26)$$

where y is a scaling factor, u_l the atomic displacement, σ_l is the total incoherent scattering cross section of an atom l and n is the final state of the excited mode.

In an INS spectrum, the elastic line is $n = 0$ (analogous to the Rayleigh line in Raman scattering), it is the most probable event leading to the large intense line at $\Delta E = 0$. It is generally not displayed in the final spectrum. $n = 1$ is the fundamental transition and will be the next most intense line, less intense overtones ($n = 2, 3, 4 \dots$) will also be observed.

Neutron spectroscopy has several advantages over Raman and IR spectroscopy:

- Wider energy range available: The whole range of molecular vibrations is accessible ($0 - 4000 \text{ cm}^{-1}$). This is especially useful in the low energy range below 400 cm^{-1} which can be difficult to access using optical spectroscopes.
- No selection rules: All vibrations are active in INS spectroscopy, as it is not subject to the optical selection rules.
- Scattering cross sections are not dependent on atomic number: The scattering of photons in optical spectroscopes is generally proportional to the number of electrons an element has, meaning heavier elements will scatter more strongly. The interaction of neutrons is proportional to the incoherent scattering cross section, which does not depend on the size of the atom. Hydrogen has by far the largest scattering cross section of any element: 80 barns compared to less than 5 barns for most other elements. Where hydrogen is present, INS spectra will be dominated by hydrogen vibrations and the technique is therefore perfect for investigating highly hydrogenous compounds.
- Neutrons are highly penetrating: A photon will only interact with the surface of a sample, meaning surface effects can distort the spectrum. Neutrons however are far more penetrating, giving a more representative measurement of the bulk

properties of a sample. Neutrons will also pass through thin layers of aluminium or vanadium, allowing easier containment of the sample and larger, more complex sample environments.

- Easy modelling of spectra: The band positions and intensities of an INS spectrum can often be accurately calculated using ab initio computational methods, therefore bands can be easily and accurately assigned.

3.2.3 The Debye Waller Factor

As temperature increases peak intensities will decrease. This is generally caused by increased thermal motion of the atoms in a sample and is described using the Debye Waller Factor, $\exp(-(Q \cdot \sum_{\nu} u_l)^2)$ which relates to the scattering law as:

$$S(Q, \omega)_l^n = y \sigma_l \frac{[(Q \cdot^{\nu} u_l)^2]^n}{n!} \exp(-(Q \cdot \sum_{\nu} u_l)^2) \quad (3.27)$$

where y is a scaling factor, Q is the neutron momentum, u_l the atomic displacement, σ_l is the total incoherent scattering cross section of an atom l and n is the final state of the excited mode. As temperatures increase, the thermal motion of the atoms (indicated by the atomic displacement) becomes the dominant term in the scattering until the peaks are no longer discernible.

The Debye Waller factor also explains the fall-off in peak intensities at high energy transfers (larger wave numbers) where the Debye Waller term is the dominant term in the peak intensity. At small energy transfers the intensity is influenced more by the initial term in the scatter law, $\frac{[(Q \cdot^{\nu} u_l)^2]^n}{n!}$.

3.2.4 Tosca

Tosca[173] is an indirect geometry time-of-flight spectrometer which is optimized for INS. Indirect time-of-flight spectrometers use a white energy neutron beam and fix the energy of the final neutron beam. A pulse of neutrons with a wide energy range is produced from the moderator, the neutrons arrive at the sample (fastest first) and are scattered changing energy and direction. The scattered neutrons impinge on a crystal which acts as a filter by Bragg scattering: the selected neutrons are directed towards the detectors. By recording the arrival time of the neutrons relative to the initial time the energy loss or gain in the sample can be investigated.

On Tosca, neutrons that are scattered by 45° or 135° will be filtered by a graphite crystal. This will select a single wavelength of neutrons (there will also be overtones which are removed using a cooled beryllium filter). The neutrons are then detected using ^3He filled detector tubes.

Tosca also has diffraction capabilities covering Q -space from 0.5 - 35 $\text{\AA}$, which is useful for confirming the structure of the sample being studied. On Tosca 0.5 - 1 g of sample will typically give a good spectrum in 6 hours.

3.2.5 Maps

Maps[174] is a direct geometry time-of-flight neutron spectrometer with a broad energy range (meV to several eV) and a large detector coverage. As it is a direct geometry instrument, the incident monochromatic neutron beam is chosen using a Fermi chopper. The neutron beam is scattered by the sample and detected using position-sensitive ^3He filled tube detectors. The Fermi chopper can be run at between 50 - 600 Hz phased to the neutron pulse to select different incident energies.

Selecting the incident energy reduces the intensity of the beam at the sample; this is

compensated for by having a large detector bank, -20° to $+60^\circ$ in the horizontal plane and -20° to $+20^\circ$ in the vertical plane with minimal gaps between banks, a total area of approximately 16 m².

Unlike indirect geometry instruments, direct geometry spectrometers measure both momentum and energy independently of each other. For neutrons scattered with the same energy transfer (and therefore the same final energy) but at different angles, there will be a different momentum transfer for each angle. Detectors positioned at the different angles will be able to measure neutrons with the same energy but with differing momentum. Conversely, neutrons that are scattered by the same angle but with a differing energy transfer allow the measurement of energy transfer for a given momentum transfer. However, direct geometry instruments do not have such high resolution at low energies as indirect geometry instruments.

3.2.6 Quasielastic Neutron Spectroscopy

Quasielastic Neutron Spectroscopy (QENS) is the limiting case for INS, where the scattering is almost elastic. The energy transfer when the neutrons hit a sample is very small. The spectrum generally appears as a broadening of the elastic line rather than discrete peaks. QENS is used to study a wide range of dynamic behaviour, particularly diffusion in the solid state and in viscous liquids, and the slower modes in crystals.

3.2.6.1 Iris

Iris is a high resolution, long-wavelength quasi-elastic and elastic neutron spectrometer. Like Tosca, it is a direct geometry instrument: neutrons at a wide range of energies impinge on the sample and are then selected after they have been scattered. The neutrons are moderated by liquid hydrogen at 25 K, which produces a high flux of cold, long wavelength neutrons. The wavelength range of neutrons which impinge on

the sample is selected by two choppers located at 6.3 m and 10 m from the moderator. Two choppers are used to prevent overlap between neutron pulses. Once the neutrons have been scattered from the sample, they are monochromated by either a pyrolytic graphite or a fluorinated mica crystal. Each crystal has its own detector bank of 51 ZnS scintillator detectors.

3.3 NMR

Nuclear magnetic resonance (NMR) is a technique that uses the magnetic properties of certain nuclei to probe their physical and chemical environments. NMR-active nuclei have an odd numbers of protons and/or neutrons which means they have a non-zero spin. S is the spin quantum number. If the number of protons and neutrons in a nucleus is even, $S = 0$ and the nucleus is not NMR active. If both the number of protons and neutrons are odd, S is an integer ($S = 1, 2, 3 \dots$). If only the number of protons or the number of neutrons is odd, then $S = \frac{1}{2} + \text{integer}$ ($S = \frac{1}{2}, \frac{3}{2}, \frac{5}{2} \dots$). Nuclei with a non-zero spin will have an intrinsic magnetic moment and angular momentum. The nuclei discussed in this thesis are ^1H ($S = \frac{1}{2}$), ^2H ($S = 1$) and ^{11}B ($S = \frac{3}{2}$).

When a magnetic field is applied to an active nucleus, the magnetic quantum number, m can take values from $+S$ to $-S$ in integer steps, i.e. $m = S, S - 1, S - 2 \dots - S$. In the case of a nucleus with a spin of $\frac{1}{2}$, $m = \frac{1}{2}$ or $m = -\frac{1}{2}$ with the spins tending to align with the external field or against it, see Figure 3.7.

If the sample is then irradiated with electromagnetic radiation, some of the lower energy spins will flip to a higher energy spin state. The frequency needed to promote a nucleus from the lower to the higher energy spin state is given in Equation 3.28.

$$\nu = \frac{\gamma B}{2\pi} \quad (3.28)$$

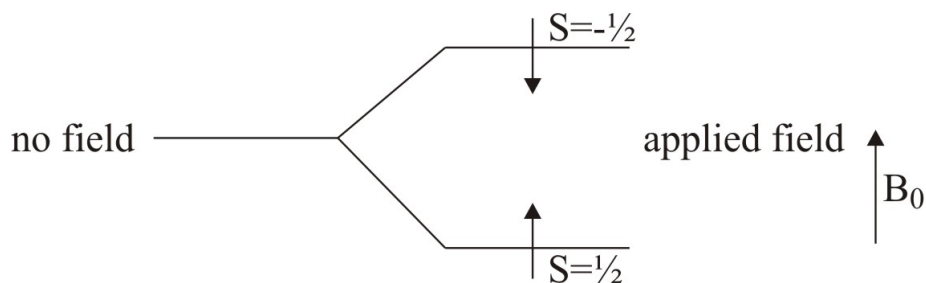


Figure 3.7: Schematic showing the splitting of the nuclear spin of a spin $\frac{1}{2}$ nucleus in an external magnetic field.

where ν is the frequency, B is the magnetic flux density at the nucleus and γ is the gyromagnetic ratio, a unique property for each particular nucleus. For protons at room temperature in a magnetic field of 23,500 G, the two states will be almost equally populated. However, it is possible to detect the small absorption of energy when the sample is irradiated with electromagnetic radiation at *ca.* 100 MHz. The resonance frequencies of the nuclei are called chemical shifts and are quoted relative to a standard; for example, tetramethylsilane is usually used for proton NMR. It is always reported in parts per million (ppm) (see Equation 3.29) - quoting in Hz would cause problems as the values will vary between spectrometers:

$$\delta = \frac{\nu - \nu_{(\text{standard})}}{\nu_0} \times 10^6 \text{ ppm} \quad (3.29)$$

where ν is the frequency of the resonance, $\nu_{(\text{standard})}$ is the resonant frequency of the standard and ν_0 is the operating frequency of the spectrometer.

The protons in the nucleus will be surrounded by a cloud of electrons which in an applied magnetic field, B_0 will circulate and produce an induced magnetic field, B_i in the opposite direction to the applied field, see Figure 3.8. Therefore the effective magnetic field, B at the nucleus will be reduced, see Equation 3.30.

$$B = B_0 - B_i \quad (3.30)$$

In electron-rich environments, a larger magnetic field will be induced and the effective magnetic field at the nucleus will be reduced. Consequently, the nucleus will be shielded. In electron-poor environments the nucleus will be relatively deshielded. This means that nuclei in different chemical environments will resonate at slightly different frequencies. This is called diamagnetic shielding. The differences are generally small; for a proton on a 100 MHz instrument the difference will be ± 1 MHz.

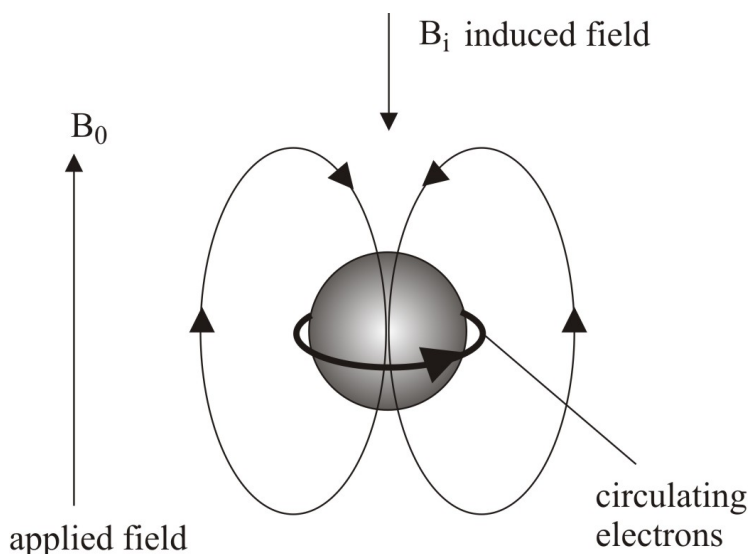


Figure 3.8: Diagram of the induction of a magnetic field in an electron cloud producing diamagnetic shielding.

The observed frequency at the nucleus is also modified by the spin of neighbouring nuclei. The effect is relayed through shared electron density in bonds and so will rapidly fall away with distance from the nucleus. The multiplicity of the splitting (the number of lines a resonance consists of) is related to the number of nuclei being coupled with, and with the spin of those nuclei. It can be calculated as shown in Equation 3.31. The magnitude of the splitting is called the coupling constant and is measured in Hz since

it is dependent on the strength of the interaction and not on the spectrometer field.

$$\text{splitting} = 2nI + 1 \quad (3.31)$$

where n is the number of nuclei being coupled to and I is the spin of the nuclei. The splitting from other nuclei can be removed or reduced using a technique called spin decoupling. A pulse of radio waves is used to fully saturate the spin state of the coupling nuclei, this removes the influence of the coupling on the neighbouring nuclei. It is used to simplify the resulting spectrum and can help in determining the molecular structure.

An NMR experiment can be performed in two ways: by keeping the magnetic field constant and sweeping the frequency, or by keeping the frequency constant and sweeping the field until resonance is observed. Historically, almost all machines swept the field, but newer machines use a different approach called Fourier Transform NMR spectroscopy.

Spectra were measured by the Durham solid-state NMR service on a Varian VNMRs 400 NMR spectrometer with a 9.4 T magnet. The references used were BF_3 in OEt_2 for ^{11}B and neat tetramethylsilane for ^1H and ^2H

3.4 Density Functional Theory

Density function theory (DFT) is a quantum mechanical modelling method for various atomic and molecular systems. The Schrödinger equation is solved using the electron density which depends on three spatial coordinates rather than the much more complex many-body wave function.

A molecular system can be described by the Schrödinger equation (shown in Equa-

tion 3.32).

$$\hat{H}\Psi_n(r_1, \dots, r_N, x_1, \dots, x_{N_e}) = E_n\Psi_n(r_1, \dots, r_N, x_1, \dots, x_{N_e}) \quad (3.32)$$

where $\hat{H}$ is the Hamiltonian operator, Ψ are eigenstates, r_N are the coordinates of the nuclei and x_{N_e} are the coordinates of the electrons. The Hamiltonian can be expressed as the combination of the potential and kinetic energies of the system (see Equations 3.33).

$$\hat{H} = \hat{K}_e + \hat{K}_n + \hat{V}_{ne} + \hat{V}_{ee} + \hat{V}_{nn} \quad (3.33)$$

where $\hat{K}$ and $\hat{V}$ are operators corresponding to the kinetic and potential energies of the nuclei, n and electrons, e . The Hamiltonian operator can be simplified using the Born-Oppenheimer approximation. The Schrödinger equation can only be solved directly for very simple systems. DFT aims to determine the energy of molecular systems as a function of electron density; this energy will have a minimum at the equilibrium electron density.

All the simulated data presented in this thesis were kindly performed by Phillippe Aeberhard.

3.5 Laboratory Equipment

3.5.0.2 Gravimetric Analysis

Gravimetric analysis is a technique which accurately measures changes in the mass of a sample with changing temperature, pressure or a combination of the two.

All the measurements in this thesis were performed using a Setaram SETSYS Evolution TGA. Around 20 mg of sample was packed into an alumina crucible and hung from a balance (35 g capacity, with a resolution of 0.002 μ g) using platinum wires. The furnace was capable of temperatures up to 1750°C (generally temperatures up to 800°C

were used) and ramp rates of $1^{\circ}\text{C min}^{-1}$ were used. 1 bar of argon was flowed over the sample at a rate of 5 mL min^{-1} . The whole instrument was housed in a nitrogen atmosphere glove box with O_2 and H_2O content below 10 ppm.

3.5.0.3 Schlenk Line

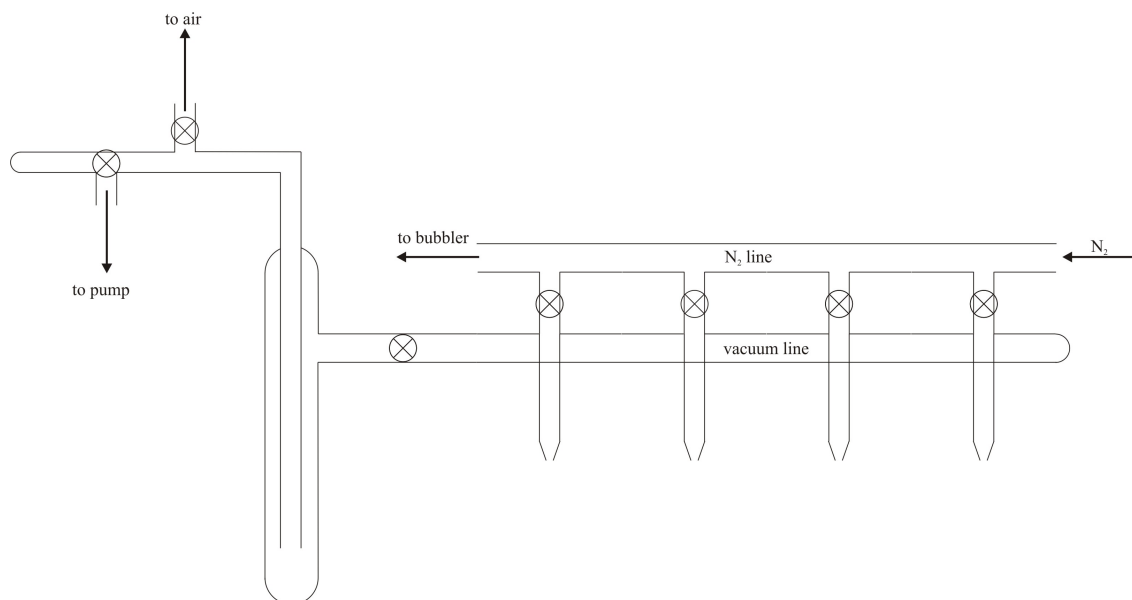


Figure 3.9: Schematic diagram of a Schlenk line.

Air sensitive solution-based chemistry was performed on a Schlenk line (schematic in Figure 3.9), allowing experiments to be carried out in an inert nitrogen atmosphere. A Schlenk line consists of two glass lines, one under nitrogen and the other under vacuum, connected by two-way taps allowing the sample to be under either nitrogen or vacuum. The nitrogen was passed through a molecular sieve column to ensure it was dry, and vented through an oil bubbler to prevent air passing back into the system. The vacuum was provided by an Edwards rough pump and the system was fitted with a liquid nitrogen cold trap to prevent solvents damaging the pump.

Solvent can be transferred via cannula between reaction vessels using nitrogen pressure, and the reaction vessel can be left open to nitrogen during the reaction to prevent

pressure build up or sealed to reduce solvent loss. After the reaction, solvent can be removed under vacuum and collected in the cold trap.

3.5.0.4 Ammonia Line

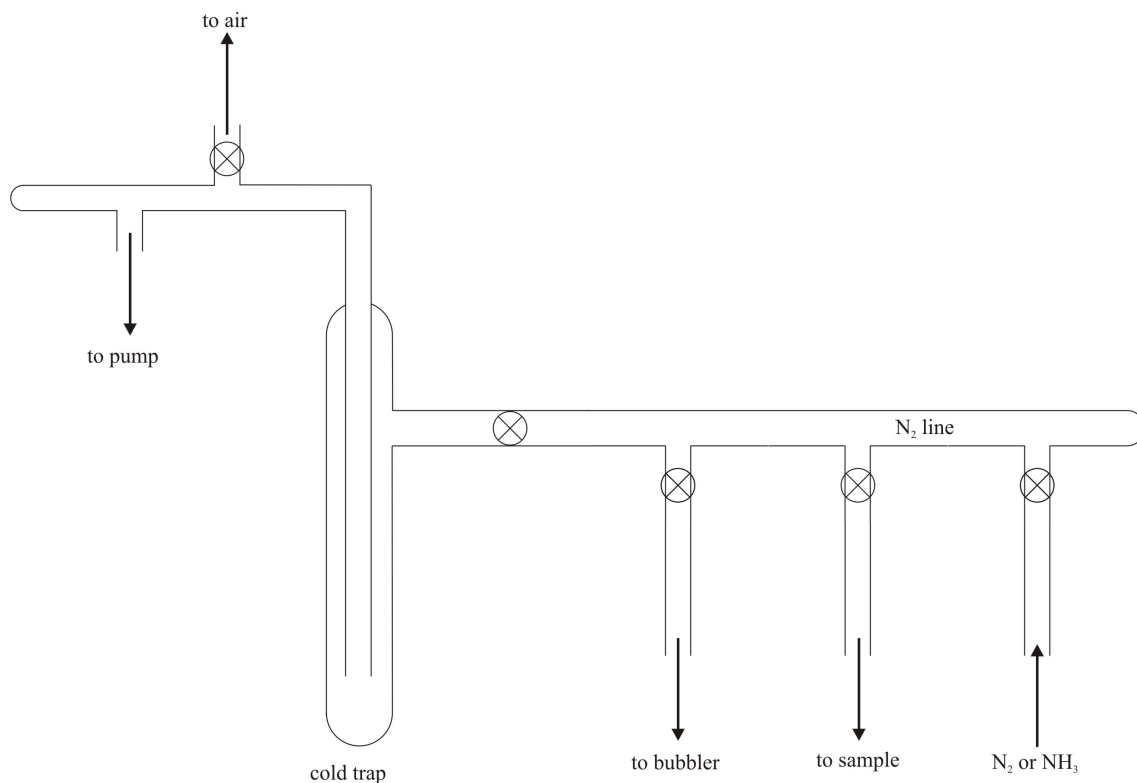


Figure 3.10: Schematic diagram of an ammonia line.

The ammonia line (schematic in Figure 3.10) was a single-manifold glass line designed to allow the condensing of ammonia in a reaction vessel. A Swagelok snap fitting allows the gas inlet to be changed between nitrogen and ammonia. A sample in a round-bottom flask was attached using a Swagelok metal-to-glass fitting, cooled in a dry ice/acetone bath to -78°C . Ammonia at approximately 1 bar was introduced and allowed to condense in the reaction vessel (boiling point of ammonia is -33°C). After the experiment was completed, nitrogen was introduced into the line and exhausted through the bubbler, the dry ice bath was removed and the ammonia allowed to boil

off. Alternatively the ammonia could be removed under vacuum and condensed into the liquid nitrogen cold trap.

3.5.0.5 High Pressure Furnace

A high pressure furnace was used for synthesising boron-11 enriched sodium borohydride or borodeuteride precursors. The pressure vessel used was a Parr series 4740 reactor capable of withstanding pressures up to 200 bar and temperatures up to 700°C. The 75 mL stainless steel reactor was capped with an alloyed steel screw cap containing six screws and sealed with a graphite gasket. The gas inlet and outlet, pressure gauge and pressure relief valve was contained within a Parr gauge block attached to the top of the screw cap with a cone fitting. The temperature was controlled using a ridged mantle heater and a thermocouple attached to the bottom of the reaction vessel.

The sample was loaded, and the vessel sealed, in an argon glove box. Outside of the glove box the vessel was attached to a pressure/vacuum rig and the remaining argon in the sample chamber was removed using a rough pump and a turbo pump. The pressure vessel was pressurised with hydrogen or deuterium in 20 bar stages using the cylinder regulator. After the desired pressure was reached, the vessel was isolated and the pressure/vacuum rig was removed; the vessel was then heated. When the experiment was complete and the vessel had cooled, the pressure/vacuum rig was reattached. Any remaining pressure was released slowly through the pump using a small volume T-piece to ensure high pressure did not damage the pump. When the reaction vessel had been completely evacuated it was returned to the glove box and the sample collected.

3.6 Synthesis

All samples were handled in an argon-filled Unilab Bruker glove box with less than 1 ppm O₂ and H₂O. Solution chemistry was done using a standard nitrogen Schlenk line (details in Section 3.5.0.3) and standard Schlenk glassware. Ammonia solution chemistry used a single line ammonia line (details in Section 3.5.0.4). Ammonia borane [175], ammonium borohydride [102] and DADB [119] were synthesised as previously reported; more details are given below in Section 3.6.1.

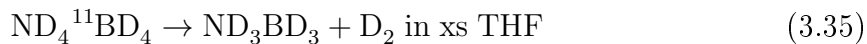
3.6.1 Samples for Neutron Experiments

3.6.1.1 Boron-11 Enriched Deuterated Ammonia Borane and Ammonium Borohydride

Ammonia borane and ammonium borohydride for the Wish experiments were synthesized at the Pacific Northwestern National Laboratory in Washington DC, USA from boron-11 enriched sodium borodeuteride, Na¹¹BD₄ and deuterated ammonium fluoride, ND₄F. ND₄F was ground in an inert atmosphere, transferred to a 100 mL round-bottom flask, and cooled in dry ice. Liquid deuterated ammonia, ND₃ was condensed onto the sample using a cold finger condenser. Once it had been ensured that all the ND₄F was dissolved, Na¹¹BD₄ was added using a solid addition funnel. The solution was stirred under an inert nitrogen atmosphere for 2 hours to allow the reaction shown in Equation 3.34 to occur. The apparatus was sealed and transferred, while being kept at -78°C , to a Schlenk line. The ND₃ was then filtered through a frit to separate the soluble ND₄¹¹BD₄ from the insoluble NaF. ND₃ was allowed to boil off and half the NH₄¹¹BH₄ was stored in a -80°C freezer.

The remaining ND₄¹¹BD₄ was used to make ND₃¹¹BD₃. The ND₄¹¹BD₄ was re-dissolved in liquid ND₃ in a round-bottom flask in dry ice and excess tetrahydrofuran

(THF) was added. While stirring, the sample was allowed to warm to room temperature, the THF was removed under vacuum and the sample was dried at 40°C for a further 4 hours.



For the Wish neutron experiment, approximately 2 g of each of the samples were loaded into cylindrical aluminium alloy sample cans with a diameter of 10 mm and sealed with indium wire. At higher temperatures, where the samples were decomposing, argon gas was flowed over the sample and exhausted through a bubbler.

3.6.1.2 Deuterated Sodium Borohydride Synthesis

$\text{Na}^{11}\text{BD}_4$ was synthesized at the University of Oxford using the high pressure furnace (Section 3.5.0.5). Approximately 0.8 g boron-11 was intimately ground with 2 g sodium metal in an inert atmosphere. The mixture was pressurized with approximately 55 bar of deuterium at room temperature and heated to 700°C for 12 hours, reaching a maximum pressure of 120 bar.

3.6.1.3 Deuterated Ammonium Fluoride Synthesis

ND_4F was synthesized from NH_4F and D_2O , NH_4F was dissolved in D_2O and the D_2O removed by rotor evaporation. This was repeated twice to give a theoretical 99.9 % substitution of hydrogen with deuterium.

3.6.1.4 Boron-11 Enriched Ammonia Borane and Ammonium Borohydride Synthesis

$\text{NH}_4^{11}\text{BH}_4$ for Tosca and $\text{NH}_3^{11}\text{BH}_3$ for Maps was prepared as described above in Section 3.6.1.1 using $\text{Na}^{11}\text{BH}_4$ purchased from Katchem and NH_4F from Sigma Aldrich. For the Tosca experiments, the sample was contained in 10 mm cylindrical passivated vanadium cans, sealed with indium wire and topped with a Swagelock tap. At high temperatures where samples may decompose, argon gas was flowed over the sample and exhausted through a bubbler. For Maps around 1.2 g of sample was sealed in a cylindrical aluminium can with indium wire.

3.6.2 X-ray Sample Preparation

Laboratory X-rays: The samples were ground and mounted onto greased glass slides an argon atmosphere and sealed in an airtight sample holder with a clear acetate window.

Synchrotron X-rays: The samples were intimately ground in an argon glove box or a nitrogen glove bag and loaded into 0.5 mm or 1 mm quartz capillaries. The capillaries were temporarily sealed using vacuum grease and then flame sealed outside of the glove box/bag. They were mounted on brass studs and aligned to allow the sample to be spun while remaining in the beam.

Chapter 4

The Mobile Phase of Ammonia Borane

4.1 Current Literature

The mobile phase of ammonia borane, NH_3BH_3 was first observed by Stowe *et al.* [61]. Variable-temperature boron-11 NMR spectroscopy of the decomposition of ammonia borane showed a narrow BH_3 signal before the formation of DADB (the diammoniate of diborane, $(\text{NH}_3\text{BH}_2\text{NH}_3)\text{BH}_4$) and further decomposition products [61] (see Figure 4.1). The very narrow resonance observed in the NMR spectra suggests that the new phase could be isotropically tumbling or even completely melting to a liquid. The T_1 relaxation time of the hydrogen atoms bonded to boron atoms was 0.05 s in the mobile phase at 90°C compared to 0.4 s for non-mobile ammonia borane [62]. As the sample was heated further the relaxation time continued to reduce. Direct observation and calorimetry ruled out melting [60, 152].

Shaw *et al.* [62] demonstrated that the conversion to the new phase is irreversible and the increased mobility was maintained when a heated sample was returned to room temperature. The T_1 relaxation time after heating at 90°C for 14 min was 0.0025 s and after the same sample was cooled to room temperature $T_1 = 0.0032$ s. There was also

no hysteresis in the overall heating time required for hydrogen release if the sample was cooled and reheated during the induction period.

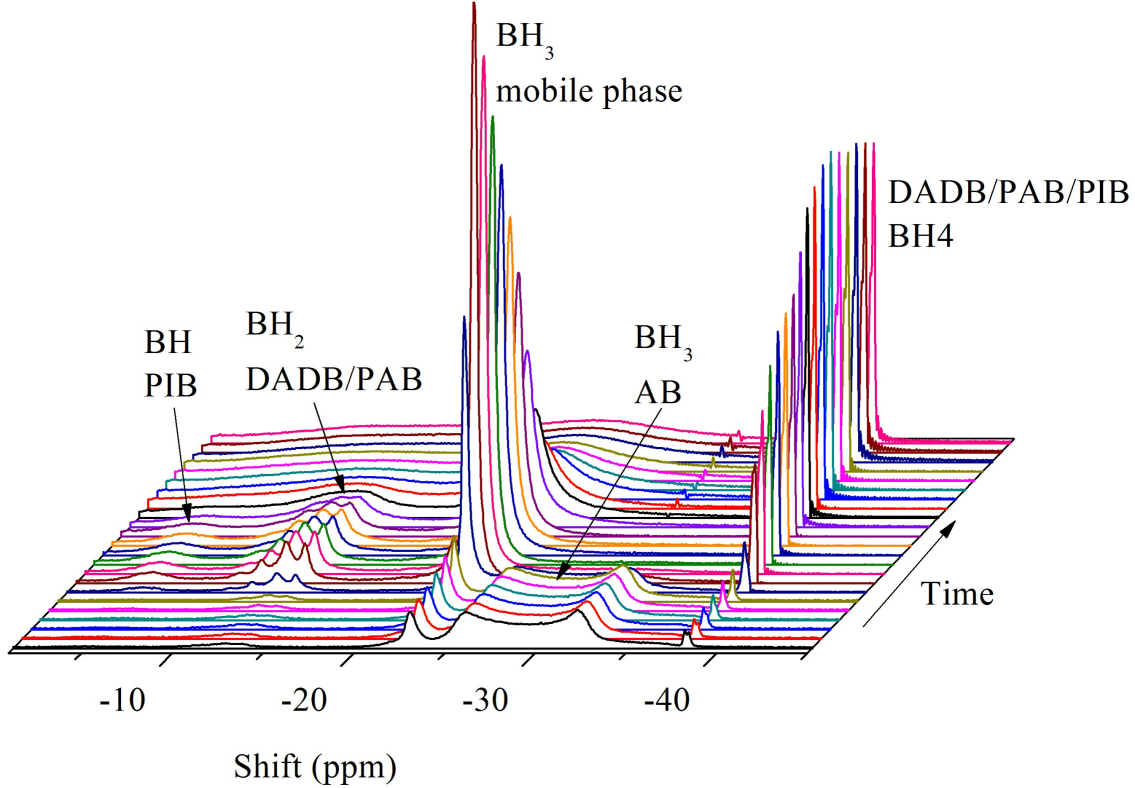


Figure 4.1: ^{11}B NMR spectra of the decomposition of ammonia borane (AB) at 78°C . The first spectrum is shown after 138 min of heating and the subsequent spectra were measured every minute. PAB/PIB are the decomposition products of ammonia borane, polyamidoborane and polyimidoborane respectively. Repeat of work performed in [62].

The same study [62] used synchrotron X-ray diffraction indicated that the structure of the mobile phase is essentially the same as the structure of ammonia borane. There was a small increase in the lattice parameters (0.05 %) and a slight increase in the inclination angle between the B–N bond and the c -axis, from 16° to 19° . Although this is not truly a new phase as there is no change in the overall symmetry of the structure, it is referred to as the ‘mobile phase’.

This new ‘mobility’ is considered by Shaw *et al.* [62] to be an increased rotation of the ammonia borane molecule around the B–N bond and precession of the molecule

around the c -axis. Increasing temperature causes hydrogen bonds between molecules to break or weaken, allowing the increase in rotation. The best analogues for the mobile phase of ammonia borane are considered to be the rotor phases of alkanes [176, 177, 178], which have increased rotational disorder along the chain lengths while maintaining packing order of the chains.

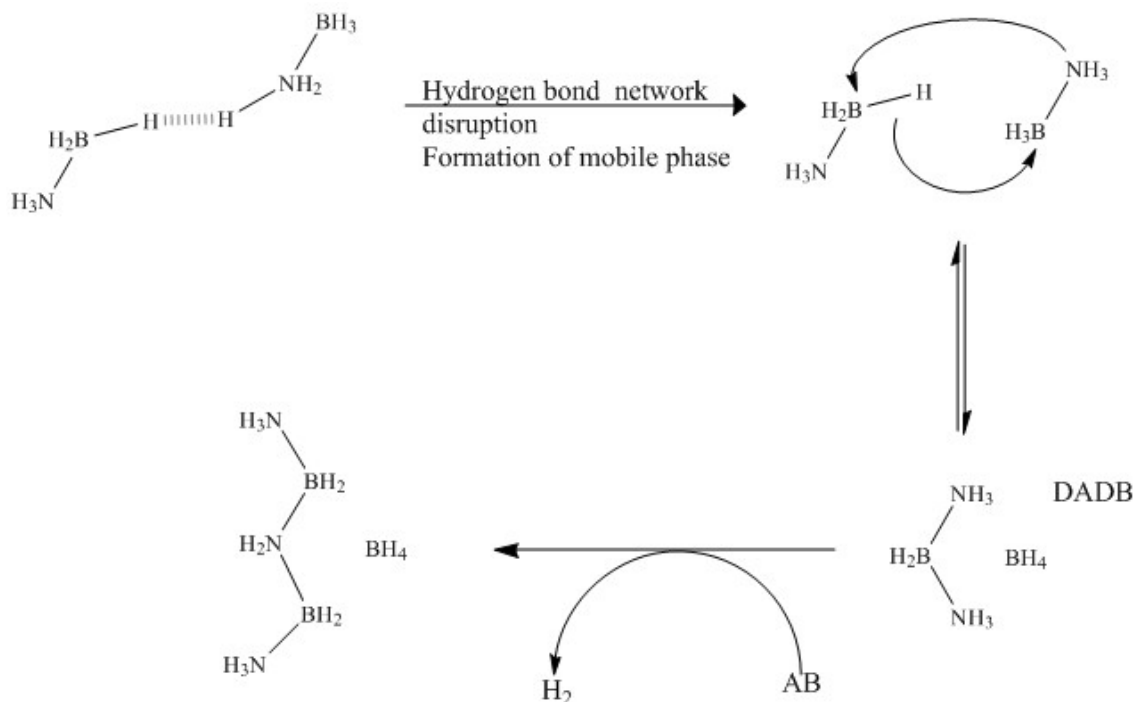


Figure 4.2: The proposed mechanism for the thermal decomposition of ammonia borane [61].

A mechanism for the decomposition of ammonia borane was proposed by Stowe *et al.* [61] and is shown in Figure 4.2. Two molecules of ammonia borane react to form a molecule of DADB. To react one of the ammonia borane molecules may flip end-to-end along the B-N bond, with the boron and nitrogen atoms exchanging positions (see Figure 4.3). A molecule of DADB will then react with a molecule of ammonia borane starting a $-\text{H}_2\text{BNH}_2-$ polymer, which will react with further ammonia borane molecules to produce polyamidoborane.

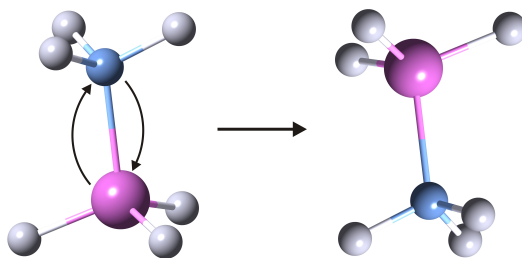


Figure 4.3: Diagram showing the end-to-end flipping of ammonia borane necessary for the formation of DADB.

Figure 4.4 shows two possible mechanisms for the formation of DADB, one for the low temperature structure of ammonia borane where all the B-N bonds are aligned parallel. The other is at higher temperatures where the central molecule has flipped by 180°. In the lower temperature structure, the distance between the borane and ammonia groups which are forming a new bond is 3.8 Å (compared to 4.5 Å in the flipped structure). However, the conformation in the flipped structure is closer to the most stable calculated conformation of DADB [151].

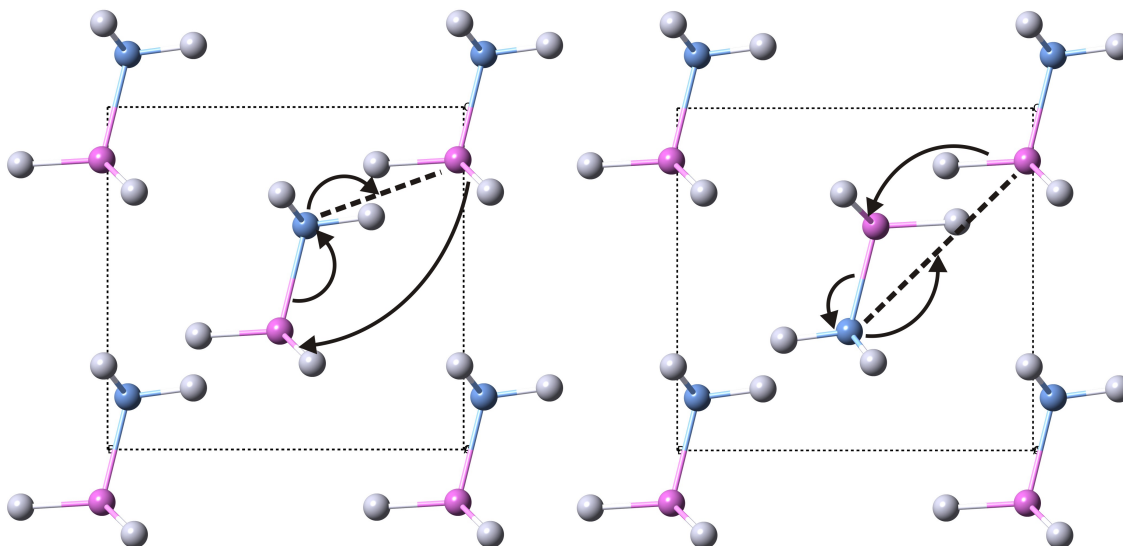


Figure 4.4: Possible mechanism for the reaction of two molecules of ammonia borane to form DADB. Left, unflipped. Right, when the central ammonia borane molecule has flipped.

4.2 Variable-Temperature Neutron Diffraction of Ammonia Borane

Neutron experiments are able to locate the hydrogen/deuterium positions accurately and determine if there is end-to-end flipping in the mobile phase of ammonia borane. So far only X-ray diffraction studies on the mobile phase of ammonia borane have been performed [62]. It is possible to locate hydrogen positions using synchrotron X-ray diffraction. The large neutron scattering cross section of deuterium atoms means their positions can be determined with much greater ease and accuracy. Boron and nitrogen have a similar number of electrons and it can be difficult to distinguish between them using X-ray diffraction [46]. As neutron scattering cross sections vary significantly and non-monotonically across the periodic table, these two atoms are easier to distinguish using neutron diffraction.

4.2.1 Experimental Details

A deuterated boron-11 enriched sample of ammonia borane was packed into a 12 mm aluminium alloy sample can in an argon glove box. It was loaded onto a gas handling centre-stick. Below room temperature the sample was under static vacuum; above room temperature argon was flowed over the top of the stick to allow hydrogen formed during decomposition to vent.

On Wish the sample was heated from 180 K to 278 K at 1 K min^{-1} , encompassing the phase transition at approximately 230 K. Subsequently the sample was cooled to 260 K. To study the decomposition, the sample was heated to 343 K at approximately 0.5 K min^{-1} and then held isothermally at 343 K. 1 hour long continuous mode scans were taken, which were then processed into 1 min or 5 min time slices.

4.2.2 Results

The phase transition from the orthorhombic to tetragonal phase has already been well characterised [46, 47, 48, 62, 179]. The results of these experiments (shown in Figure 4.5) are in good agreement with previous results and are not discussed further in this thesis.

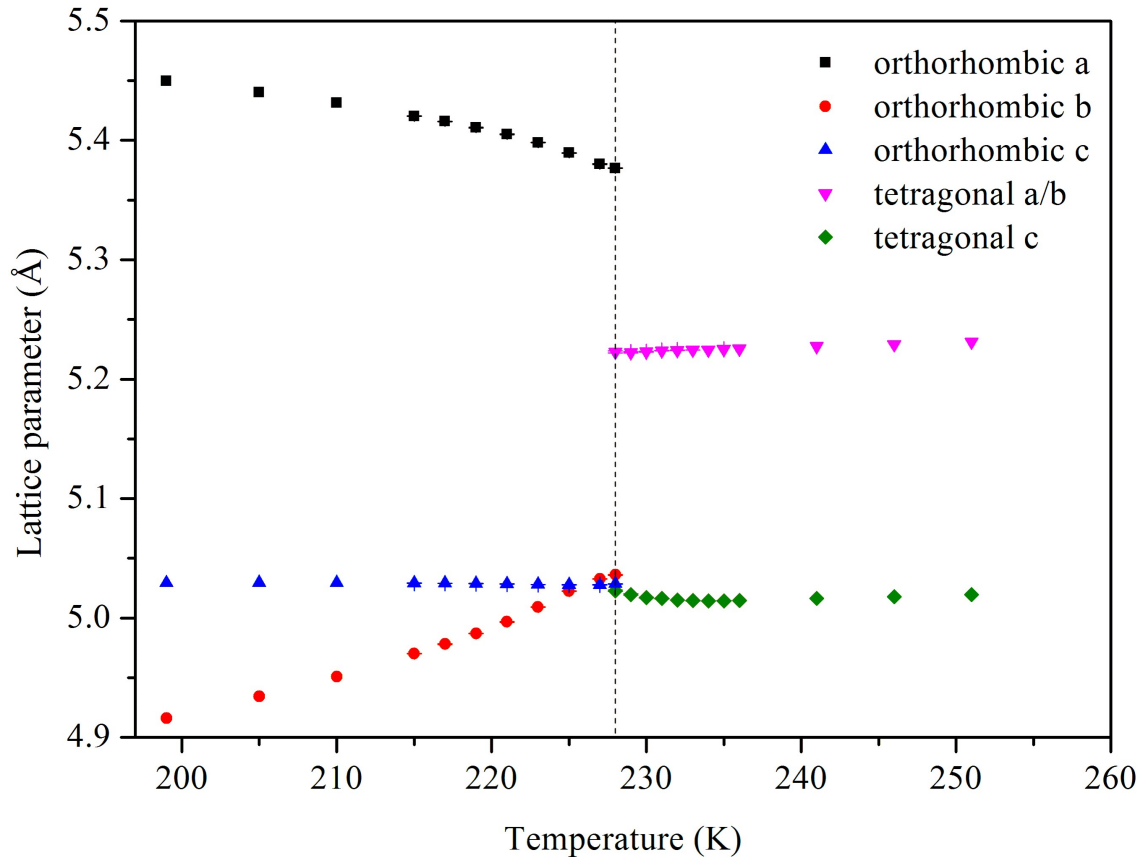


Figure 4.5: The lattice parameters before and after the orthorhombic to tetragonal phase transition from data collected on the Wish diffractometer at ISIS. The error bars are contained within the data points.

Figure 4.6 shows the variations in the lattice parameters *vs* temperature. The gap in the data results from the neutron beam being off due to a fault in a radio-frequency magnet. A second order polynomial has been fitted to the data before the break. Before the break there are no anomalies in the lattice parameters and the overall trend fits well to all the points. However, after the break the lattice parameters are larger than

would be expected from the trend. This indicates that the mobile phase has formed, although unfortunately the transition occurred during the beam off period, so there are no data for the transition. At 340 K, the a lattice parameter is 0.023 % larger than expected and the c lattice parameter, 0.022 %. These values are slightly smaller than those previously reported [62].

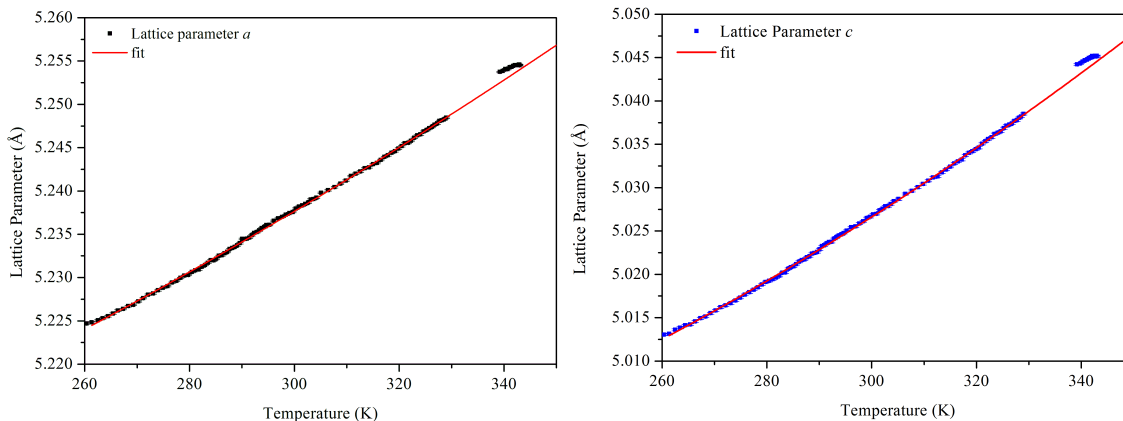


Figure 4.6: Lattice parameters of the high temperature phase of ammonia borane left- a and right- c with extrapolated 2nd order polynomial fits of the data up to 343 K.

A refinement was constructed which allowed the bond angle, ϕ between the B-N bond and the c -axis to vary and refines the occupancies of boron and nitrogen atoms in each of the boron and nitrogen sites. For the B-N bond to be tilted at an angle to the c -axis, while maintaining the $I4mm$ symmetry, the ammonia borane molecule must be precessing around the c -axis. The refinement has four possible boron/nitrogen atom sites around the c -axis at either end of the B-N bond with 12 possible hydrogen atom positions around each of the central atoms (see Figure 4.7).

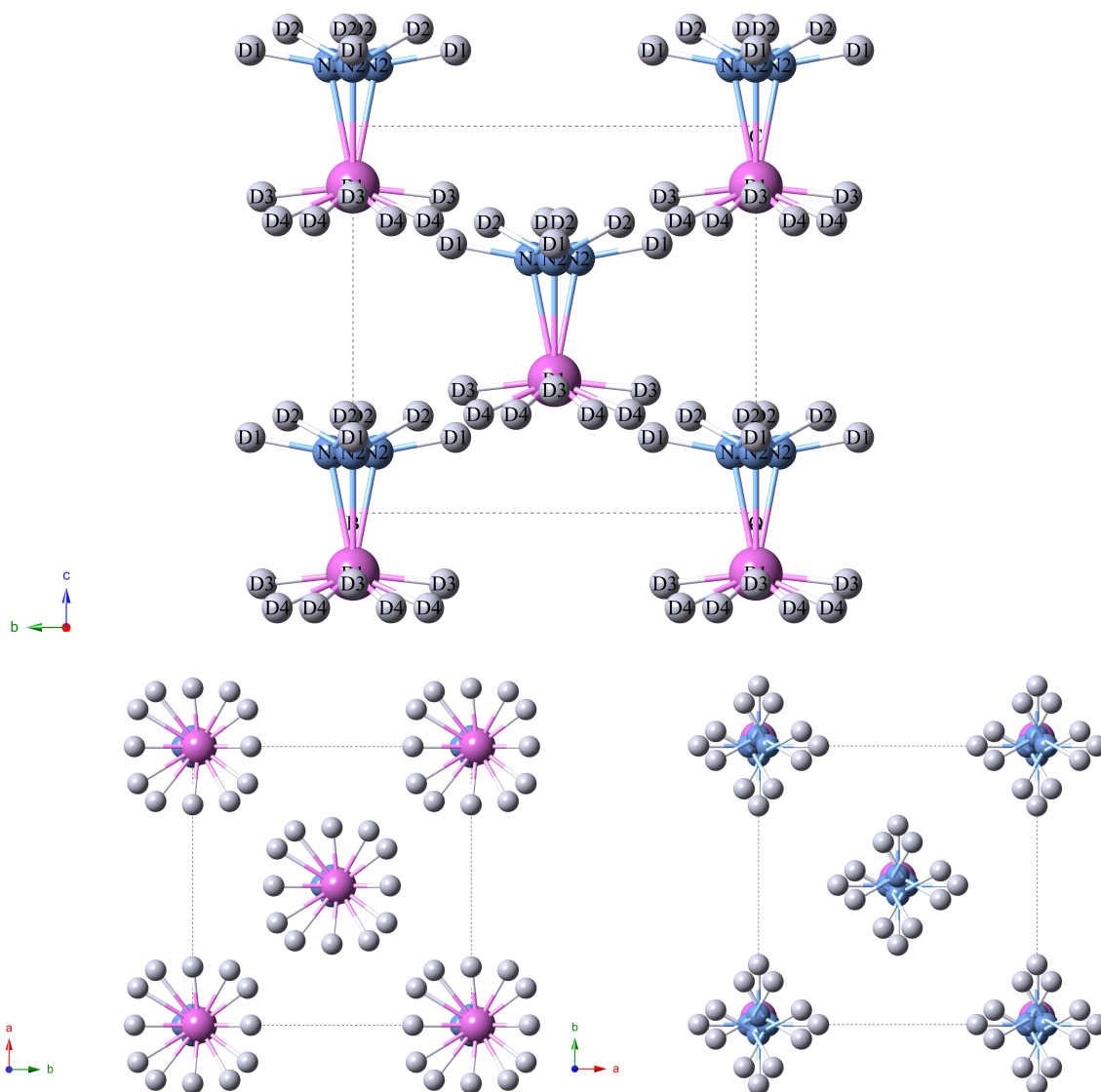


Figure 4.7: Structural diagram of ammonia borane at 260 K. Top: along the *a*-axis. Bottom: along the *c*-axis to show the positions of the hydrogen atoms. For clarity the hydrogen atoms in the ammonia groups have been removed in the left hand image and the hydrogen atoms in the borane group in the right. Boron atoms in pink, nitrogen atoms, blue and deuterium atoms, grey.

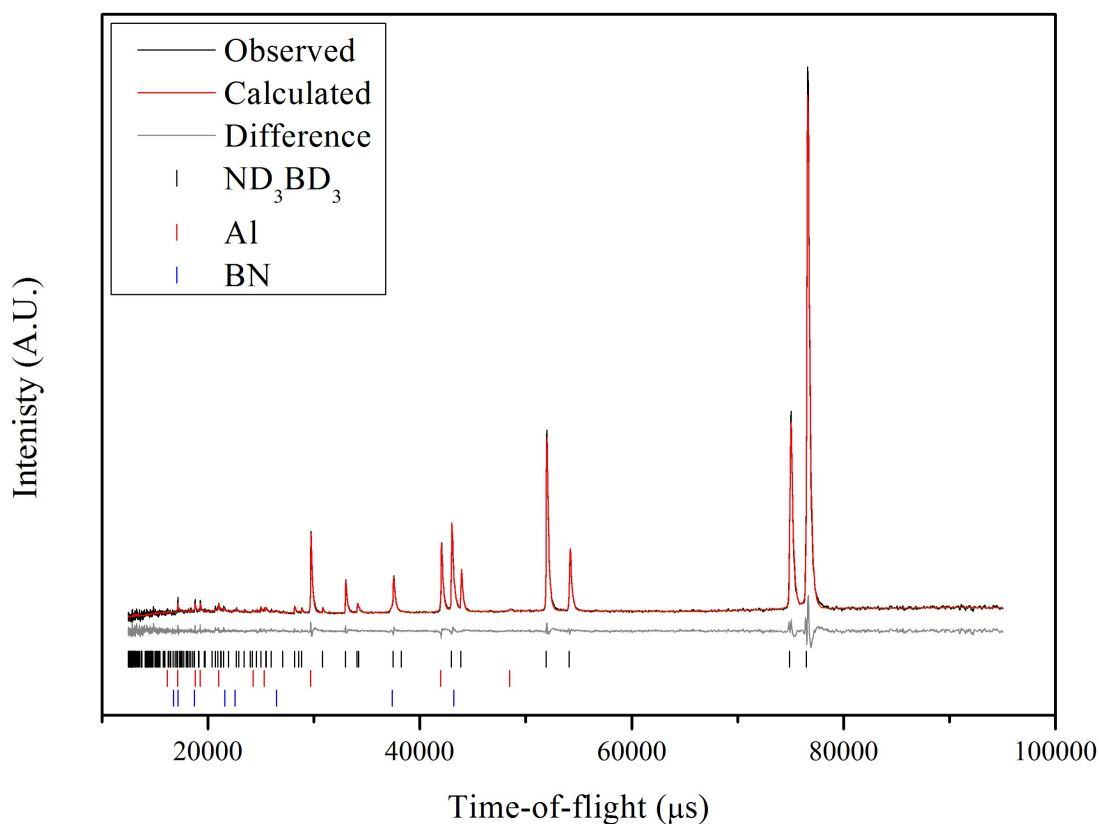


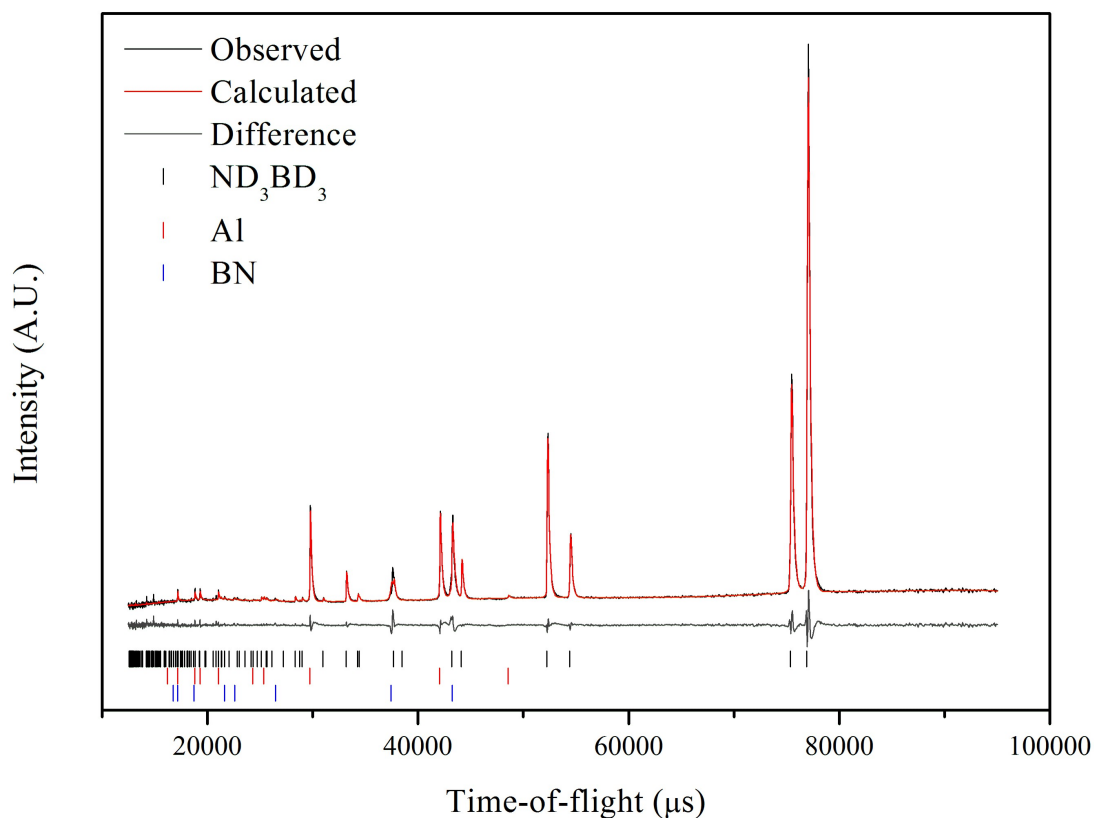
Figure 4.8: Top: Observed (black) and calculated (red) diffraction patterns of the tetragonal phase of ammonia borane at 260 K before the start of thermal decomposition. The grey line under the diffraction pattern is the difference between the observed and calculated patterns. Ammonia borane (black tick marks), aluminium (red ticks) and boron nitride (blue ticks). Bottom: Crystallographic data from the refinement. Space group, $I4mm$, $a = 5.22513(4)$ Å and $c = 5.01361(5)$ Å, $\varphi = 11(1)^\circ$, $R_{wp} = 4.08$, $R_{exp} = 2.97$ and $\chi^2 = 1.37$.

Figure 4.8 shows the refinement and crystallographic data of ammonia borane at 260 K. The best refined fit of the data is if no flipping of the B-N bond has occurred. The $(0, 0, -0.1566(6))$ position has 100 % boron atom occupancy and the $(0, 0.0578(6), 0.1566(6))$ sites are fully occupied by nitrogen atoms. The angle between the B-N axis and the c -axis is $11(1)^\circ$, which is, within experimental errors, in good agreement with the angle computed by Hess *et al.* [48] of $10(5)^\circ$.

At 343 K (after being heated at temperatures above 333 K for 268 min) the scale factor has fallen significantly, decomposition has started, and the a and c lattice parameters are 0.02 % larger than expected (Figure 4.6), indicating that the mobile phase of ammonia borane has formed. The refinement and crystallographic data at this temperature are shown in Figure 4.9. The occupancy of the boron and nitrogen sites are now each split 50/50 between boron and nitrogen atoms, indicating that the molecular orientation is flipping between orientations. This would allow two adjacent molecules of ammonia borane to be in the correct conformation to react easily to form DADB.

The bond angle, φ increases from $11(1)^\circ$ before the decomposition to $14(2)^\circ$ after the transitions. Although these values are 5° smaller than those previously reported from X-ray data [62], the size of the increase is similar. The difference could be due to the more accurate determination of the hydrogen/deuterium positions using neutron diffraction or an effect from the deuteration of the neutron diffraction sample.

The single sharp mobile phase NMR peak of ammonia borane indicates that this flipping must be occurring on a very fast time scale, to give not only a single time-averaged NMR peak, but a very sharp one.



Atom	x	y	z	Occupancy	$B_{\text{iso}}(\text{\AA}^2)$
B1	0.000	−0.02(1)	−0.154(1)	0.12(12)	13.8(7)
N1	0.000	0.05(1)	0.154(1)	0.12(12)	3.4(3)
B2	0.000	0.05(1)	0.154(1)	0.12(12)	3.4(3)
N2	0.000	−0.02(1)	−0.154(1)	0.12(12)	13.8(7)
H1	0.000	0.000	0.24(2)	0.25	7.2(2)
H2	0.162(6)	0.15(1)	−0.01(1)	0.25	7.2(2)
H3	0.000	0.000	−0.25(2)	0.25	7.2(2)
H4	0.188(5)	0.19(1)	0.07(1)	0.25	7.2(2)

Figure 4.9: Observed (black) and calculated (red) diffraction patterns for the high temperature tetragonal mobile phase of ammonia borane at 343 K. The grey line under the diffraction pattern is the difference between the observed and calculated patterns. Ammonia borane (black tick marks), aluminium (red ticks) and boron nitride (blue ticks). Crystallographic data for the refinement, space group, $I4mm$, $a = 5.25470(5)$ Å and $c = 5.04542(5)$ Å, $\varphi = 14(2)^\circ$, $R_{\text{wp}} = 4.04$, $R_{\text{exp}} = 1.66$ and $\chi^2 = 2.43$.

4.3 Inelastic Neutron Spectroscopy of Ammonia borane and the Mobile Phase at Room Temperature

Inelastic neutron spectroscopy measurements of ammonia borane and its mobile phase were performed on the MAPS spectrometer at ISIS. The aim was to determine how the changes caused by the formation of the mobile phase affected the vibrational modes.

4.3.1 Experimental

Spectra of boron-11 enriched unheated ammonia borane were recorded at 25 K and at room temperature, and the spectrum of the mobile phase (synthesised ex-situ) was recorded at room temperature. The samples were packed into flat vanadium cans in an argon glovebox. In-situ synthesis and variable temperature INS experiments were attempted; however a pump breaking on the MAPS spectrometer meant there was not enough time for variable-temperature experiments. Raw data were plotted, projected as $S(Q, \omega)$ and the program MSlice [180] was used to produce two-dimensional projections. Two energy ranges were used: incident neutron energies of 300 meV with a Fermi chopper frequency of 450 Hz, and 600 meV with a Fermi chopper frequency of 600 Hz. Two distinct ranges were used as the lower energy data have better Q resolution but a lower maximum energy. The formation of the mobile phase was confirmed using boron-11 NMR.

The room temperature Raman spectra of natural abundance unheated ammonia borane and heated ammonia borane, the mobile phase, were recorded. Natural abundance ammonia borane has 20 % boron-10 and 80 % boron-11.

4.3.2 Results

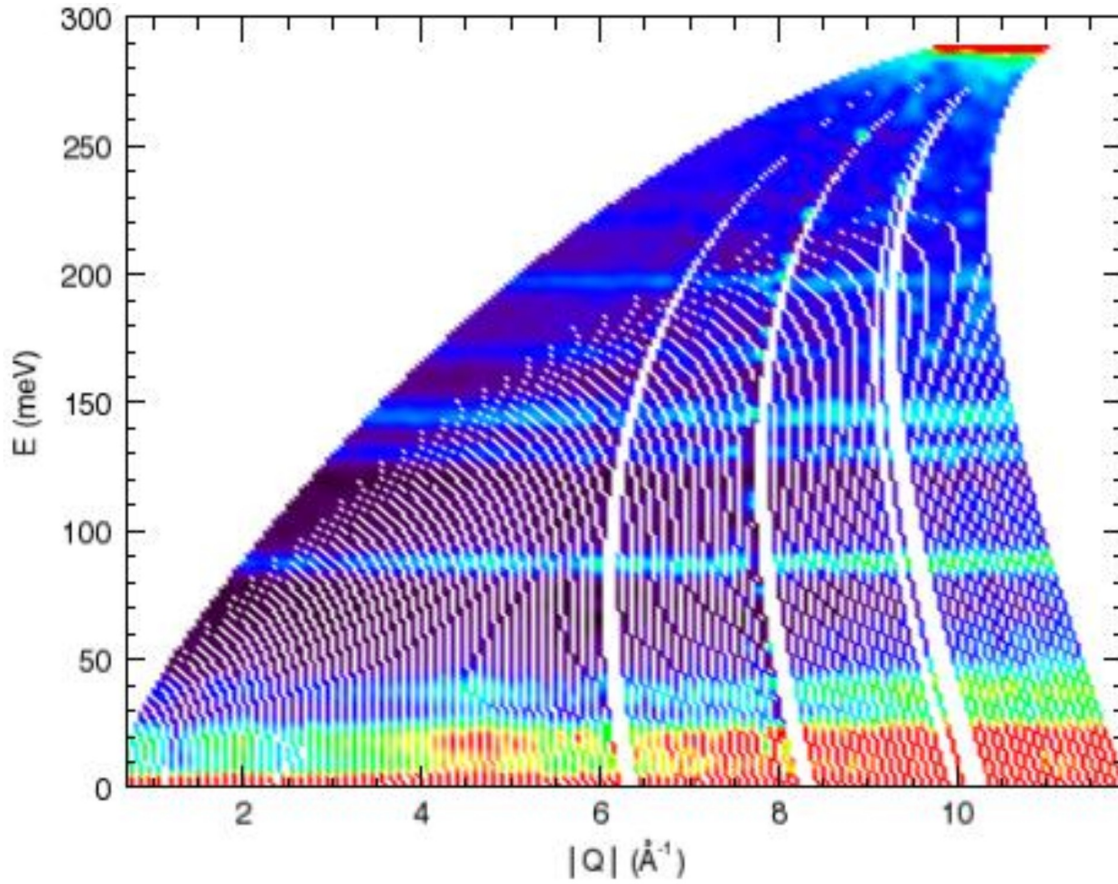


Figure 4.10: Surface plot of the 300 meV inelastic neutron spectrum of ammonia borane measured on MAPS at 25 K

A $S(Q, \omega)$ surface plot of the low temperature orthorhombic phase of ammonia borane at 25 K is shown in Figure 4.10. A slice of the data from $Q = 5 \text{ \AA}^{-1}$ to $Q = 6 \text{ \AA}^{-1}$ is shown in Figure 4.11 and peak assignments are summarised in Table 4.1. The spectrum can be broken down into several regions:

- Up to 500 cm^{-1} which contains the lattice modes and external molecular modes. Although these modes have been assigned to BH_3 or NH_3 they were shown by Kathmann *et al.* [181] to be highly coupled.
- 500 cm^{-1} - 2000 cm^{-1} the BH_3 and NH_3 modes.

- 2000 cm^{-1} - 2750 cm^{-1} the BH stretching modes.
- The NH stretching modes are at higher energies than were measured: 3000 cm^{-1} - 3400 cm^{-1} .

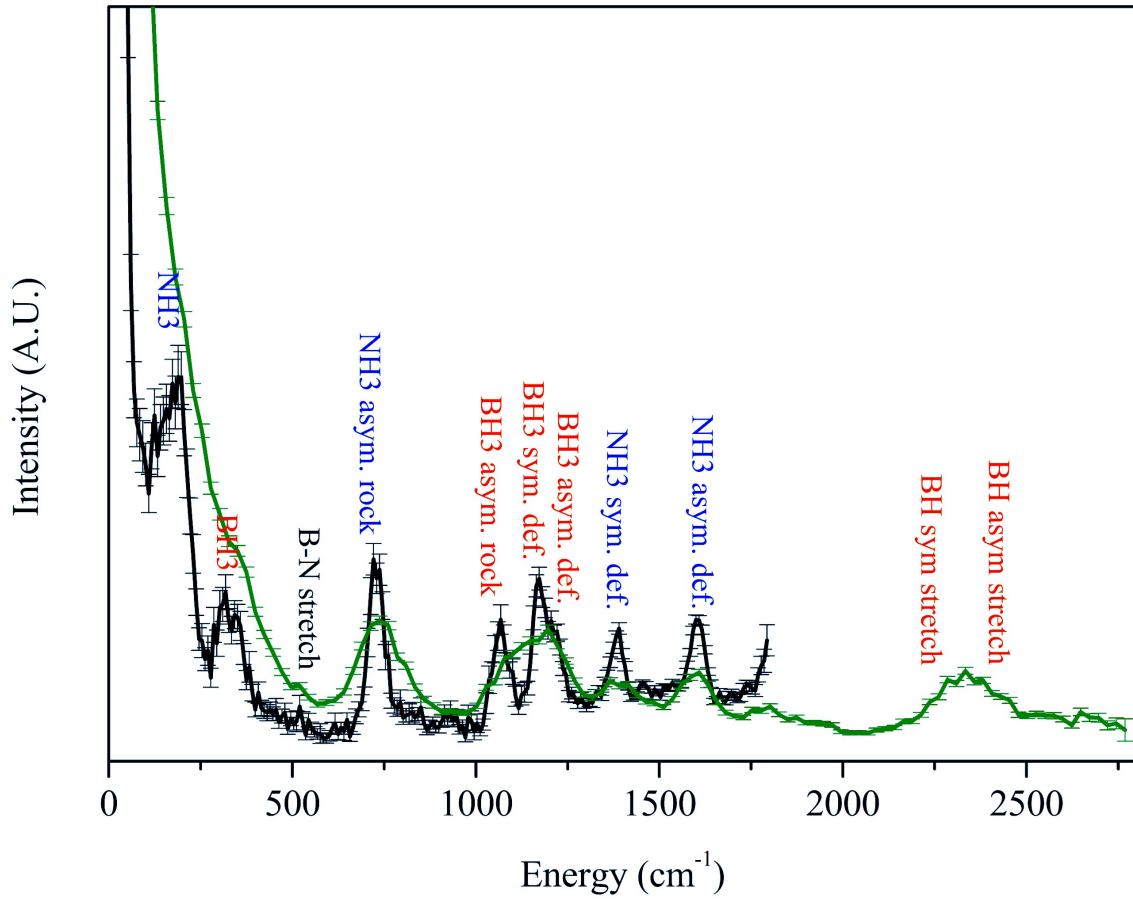


Figure 4.11: 300 meV (black) and 600 meV (green) inelastic neutron spectrum of ammonia borane at 25 K with peak assignments, BH_3 in red, NH_3 in blue and BN in black [182, 183].

Wavenumber of mode (cm^{-1})	Mode assignment
157	NH_3 lattice modes
326	BH_3 lattice modes
721	NH_3 asymmetric rock
1067	BH_3 asymmetric rock
1172	BH_3 symmetric deformation (umbrella)
1221	BH_3 asymmetric deformation (scissors)
1390	NH_3 symmetric deformation (umbrella)
1600	NH_3 asymmetric deformation (scissors)
2285	BH_3 symmetric stretch
2381	BH_3 asymmetric stretch

Table 4.1: The mode assignments of the 25 K INS spectra of ammonia borane [182, 183, 184].

Crystallography indicates there is little change in the B-N bond length in mobile ammonia borane; however, it has been used as a sensitive indicator of the environment of the ammonia borane molecule. In the solid state, the bond shortens by 0.08 Å and the stretching frequency increases by 200 cm^{-1} compared with a molecule in the gas phase [184]. Dillen and Verhoeven also used *ab initio* calculations to show that the shortening was caused primarily by short-range interactions [184].

When the mobile phase of ammonia borane forms, the number or strength of hydrogen bonds decreases [62]. The reduction in short range interactions could cause the B-N bond to lengthen, which should be detectable using vibrational spectroscopy [184]. There could also be changes in the frequencies of the individual group motions. The whole group motions (the asymmetric rocks), which depend on the moments of inertia

of the whole BH_3 or NH_3 groups may be affected less than modes involving N/B-H bonds which will be more sensitive to small changes in electron density in the bonds.

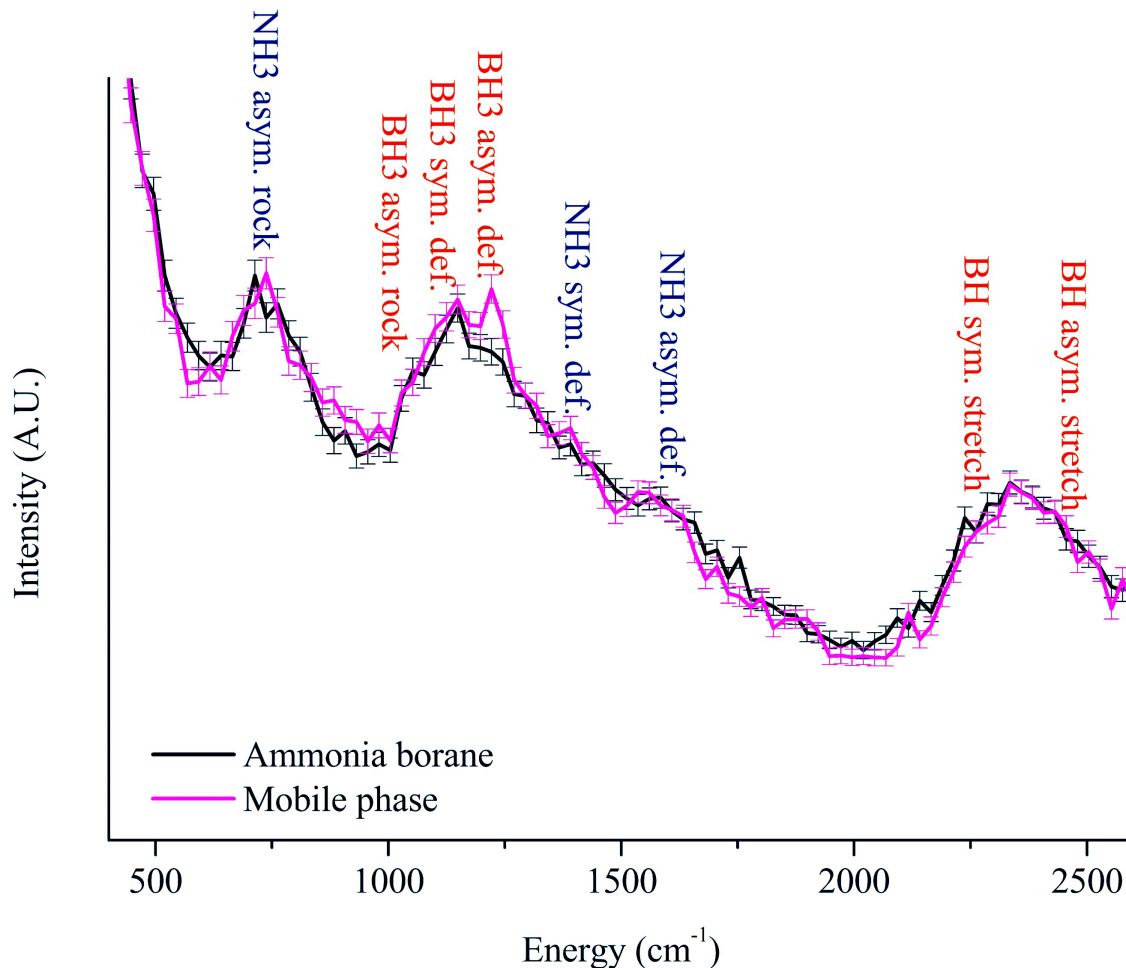


Figure 4.12: Inelastic neutron spectrum of ammonia borane and the mobile phase at 600 meV, peak assignments BH_3 in red and NH_3 in blue.

Figure 4.12 shows the INS spectra of the tetragonal room temperature phase of unheated ammonia borane and heated ammonia borane, the mobile phase. At this temperature the resolution is poor; there are however observable differences between the two spectra. The intensity of the BH_3 asymmetric deformation (and to a lesser extent the BH_3 symmetric deformation) has increased. The increase in intensity may be because this is a precursor motion to the flipping of the boron and nitrogen atoms.

However, the positions of these peaks and the B-H symmetric and asymmetric stretches have not changed, indicating that there is little change in the BH bond strength.

There appears to have been a reduction in the frequency of the NH_3 asymmetric deformation. However, the deformation of the BH_2 group of DADB is at about 1550 cm^{-1} [60, 119] and the NMR spectrum shows that there is DADB (10 %) and some further PAB decomposition products (13 %) present in the sample. This new signal is probably responsible for the perceived shift. The large background and the DADB peaks mean that although there may well be changes in the intensities of the NH_3 deformation peaks, they cannot be discerned.

The neutron scattering cross sections of boron and nitrogen are considerably smaller than the scattering cross section of hydrogen and so the effect on the INS spectrum of motions that do not involve hydrogen will be very small. The B-N stretching signal is just discernible in the low-temperature spectrum at around 520 cm^{-1} . The boron and nitrogen signals are, however, observed by Raman spectroscopy (see Figure 4.13). The two natural isotopes of boron in the sample causes the double B-N stretching peak, shown in detail in the inset. There is clearly no change in the position of the B-N stretch, which agrees with the crystallography results in that the transition to the mobile phase does not affect the B-N bond.

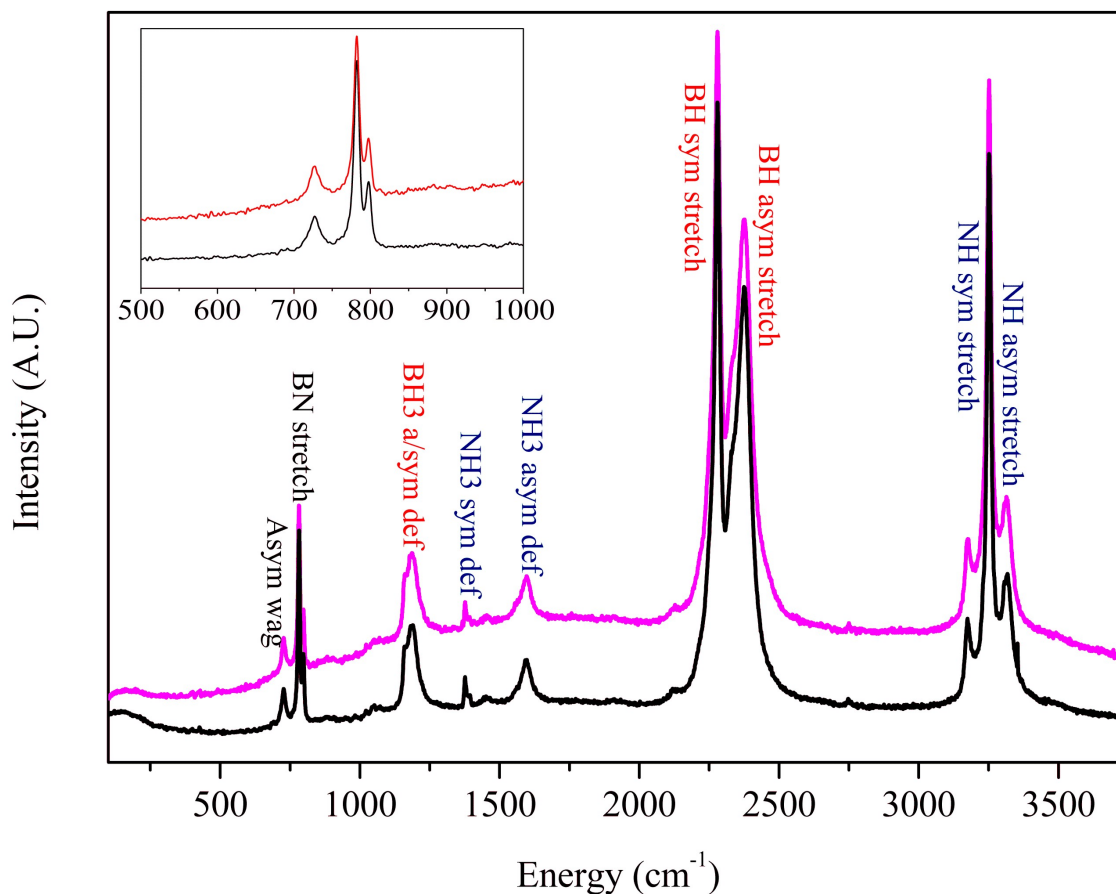


Figure 4.13: Raman spectra of natural abundance ammonia borane (black) and the mobile phase (pink), inset shows the B-N stretching vibrations. Peak assignments, BH₃ in red, NH₃ in blue and BN in black.

4.4 Conclusion

Neutron diffraction experiments were used to show that the mobile phase of ammonia borane has the same structure as the room temperature phase, but with the unit cell lattice parameters 0.022 % larger and the angle between the B-N bond and the *c*-axis increased from 11(1)° to 14(2)°. It was also found that B-N bond is flipping end-to-end which supports the mechanism published by Shaw *et al.* [62] for the formation of DADB.

Neutron spectroscopy experiments were not as conclusive: due to the high temperature of the experiments, the energy resolution is poor. However, there are changes in the borohydride and ammonium deformation modes, which are likely to be associated with the flipping of the ammonia borane molecule. Variable temperature experiments, which would have helped to define the changes, were attempted but were not successful.

In conclusion, the mobile phase of ammonia borane is structurally broadly similar to the room temperature structure, but with a slight increase in size of the unit cell caused by an increase in the angle between the B-N bond and the *c*-axis. The ammonia borane molecule in the mobile phase can flip end-to-end, producing a conformation where two molecules can react to form DADB during the first stage of the thermal decomposition.

Chapter 5

Dihydrogen Bonding in Ammonia Borane

An important class of dihydrogen bonds are those which involve a B-H hydrogen bond acceptor and N-H hydrogen bond donor. The most common conformation of bond angles is shown in Figure 5.1. The near linear N-H...H B angle and the bent B-H...H N angle allows the protic NH group to interact favourably with the negatively charged boron atom while preventing an unfavourable dipole arrangement [140, 142].

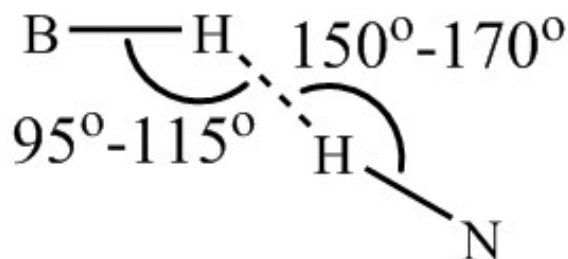


Figure 5.1: Conformation of N-H...H-B dihydrogen bond, $150 - 170^{\circ}$ for N-H...H B and $95 - 155^{\circ}$ for B-H...H N angles.

The low temperature orthorhombic phase of ammonia borane contains three crystallographically distinct pairs of hydrogen atoms which can be described as having

dihydrogen bonding characteristics. The shortest (bond A, see Figure 5.2) is approximately 2.02(3) Å with N-D...D B and B-D...D N angles of 156(3)° and 106(1)° respectively. There are two longer dihydrogen bonds of 2.21(4) Å and 2.23(4) Å. The bond angles in bond B (as for bond A) follow the general trend for B-H...H-N dihydrogen bonds: a bent B-D...D N angle of 94(2)° and a more obtuse N-D...D B angle of 137(2)°. Bond C however has the opposite configuration of bond angles: a B-D...D N angle of 156(3)° and a N-D...D B angle of 130(1)°. In the high temperature tetragonal phase, bond B lengthens to 2.86(2) Å (greater than the combined van der Waal’s radii of two hydrogen atoms, 2.4 Å) and can no longer be considered a dihydrogen bond. Bond C shortens to 1.97(2) Å and the unusual bond angles remain: 125(1)° for N-D...D B and 170(1)° for B-D...D N. Bond A increases in length to 2.1 Å with bond angles of 162(1)° for N-D...D B and 119(1)° for B-D...D N. A series of DFT calculations were performed by Hess *et al.* [48] at temperatures between 5 K and 373 K to study the structural changes of ammonia borane with changing temperature. In this Chapter, these simulations will be re-analysed to interpret the dihydrogen bonding.

5.1 Experimental Details

Details of the computational methods used in this chapter can be found in [48]. Briefly, the simulations were performed using DFT with a PBE function [185], Goedecker pseudopotentials and a TZVP basis set [186, 187] on a $2 \times 2 \times 2$ unit cell containing 16 ammonia borane molecules (128 atoms). The CP2K *ab initio* molecular simulation package was used [188]. All the simulations were carried out at constant temperature and pressure. A Nosé-Hoover chain [189] was used to ensure thermalisation. The simulation temperatures were: 15 K, 100 K, 120 K, 175 K, 220 K, 230 K, 240 K, 250 K, 330 K and 373 K; the orthorhombic to tetragonal phase transition occurs at approxi-

ately 225 K [48]. All the simulations apart from 15 K contained 15,000 steps of 0.5 fs. The 15 K simulation contained only 5000 steps and the results were scaled so they could be compared with the larger data sets [48].

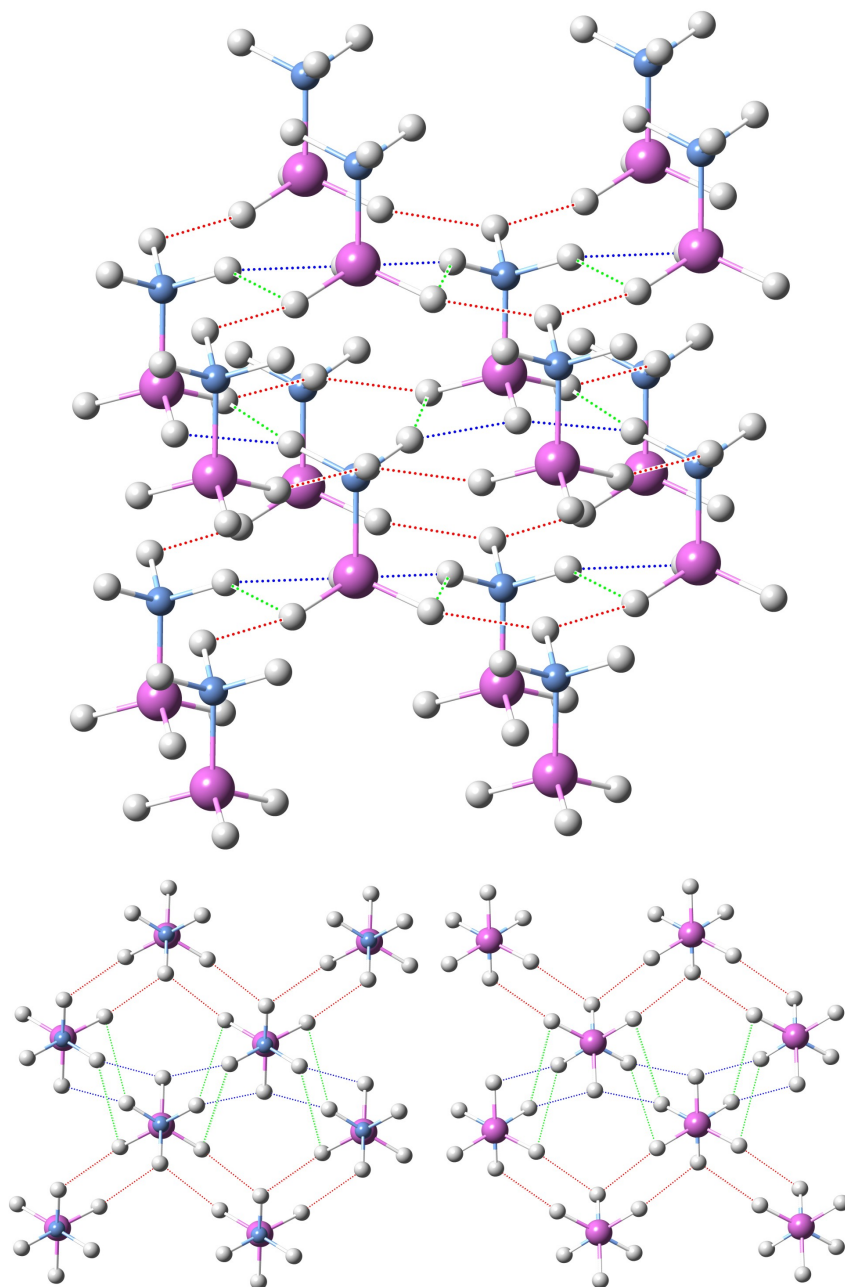


Figure 5.2: The dihydrogen bonds in the initial simulation structure of ammonia borane. The shortest dihydrogen bond (bond A) is in blue. Bond B is green, and bond C is in red.

There has not, to date, been an analysis of the dihydrogen bonds in these simulations. The three different dihydrogen bonds (specified above) were identified in the simulation cell: Figure 5.2 shows the positions of the dihydrogen bonds in the initial structure used for all of the calculations. The distance between each pair of atoms was recorded at each calculated time step. Since this distance is measured between two particular atoms, if the ammonia and borane groups rotate the measured ‘bond’ length can increase to a maximum of approximately 6 Å. The first 1000 time steps were disregarded to allow the system to thermalise and equilibrate. The number density, n , of bonds of a particular length follows a Boltzmann distribution give by:

$$n = \alpha \exp \left(\frac{V(r)}{k_B T} \right) \quad (5.1)$$

where α is a constant, $V(r)$ is the classical potential energy of the system, k_B is the Boltzmann constant and T is temperature. $V(r)$ was calculated at 0.02 Å steps by inverting Equation 5.1:

$$V(r) = k_B T \ln(n) + C \quad (5.2)$$

where C is a constant, $C = k_B T \ln(\alpha)$. The resulting potential energy wells were fitted using a Morse potential shown in Equation 5.3.

$$V(r) = D_e (1 - e^{(-a(r-r_e))})^2 + c \quad (5.3)$$

where D_e is the dissociation energy of the bond, a is a measure of the width of the potential well, r is the distance between the two atoms forming the bond, r_e is the equilibrium bond length and c is a constant. The force constant at the equilibrium

bond length, k , can be calculated using the relationship in Equation 5.4.

$$k = 2a^2D_e \quad (5.4)$$

5.2 Results and Discussion

5.2.1 Orthorhombic phase

Figure 5.3 shows the bond length distributions for the three dihydrogen bonds in orthorhombic ammonia borane. In the simulation, in the orthorhombic phase, neither the ammonia nor the borane groups are able to rotate freely. At 15 K, the distribution of lengths for the strongest bond (bond A) is centred at 2.01 Å with a maximum and minimum of 2.21 Å and 1.83 Å. The two weaker bonds (bond B and bond C) have average bond lengths of 2.24 Å and 2.14 Å with ranges of 0.50 Å and 0.57 Å, respectively. These values agree well with the bond lengths measured experimentally by Hess et al. [48] using neutron diffraction; the largest deviation being the length of bond B which was reported as 2.211(4) Å. As the temperature rises, the amplitude of the molecular vibration increases, and therefore the distribution of bond lengths widens. The hydrogen atoms are still localised at their original position and there is no free rotation of the ammonia and borane groups. This is demonstrated by the atom trajectories in Figure 5.4.

Experimental NMR data show that the ammonia group begins to rotate at approximately 60 K and the borane group begins to rotate at 100 K [53, 179]. Deuterium NMR of selectively deuterated ammonia borane has shown that at approximately 110 K the ammonia group rotates at a rate of $5.4 \times 10^7 \text{ s}^{-1}$ [179] and the borane group at $3 \times 10^4 \text{ s}^{-1}$ [53]. The simulations reported in this Chapter are relatively short (7.5 ps long) and therefore rotations at these rates are infrequent events on the time scale of

the simulation. As the temperature increases towards and above the phase transition the rotation rate of both groups increases by several orders of magnitude and therefore several rotation events will occur during the simulation.

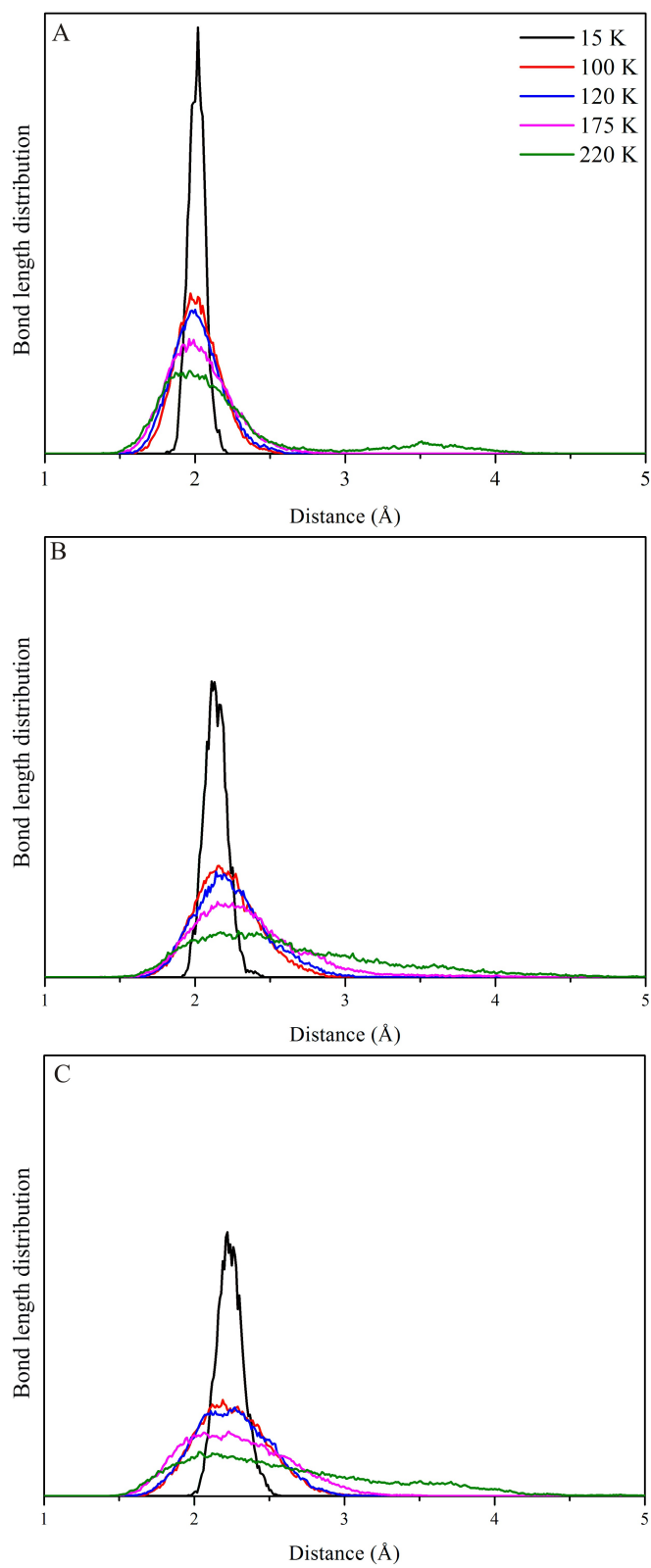


Figure 5.3: The bond length distributions of the three dihydrogen bonds, A, B and C as a function of temperature.

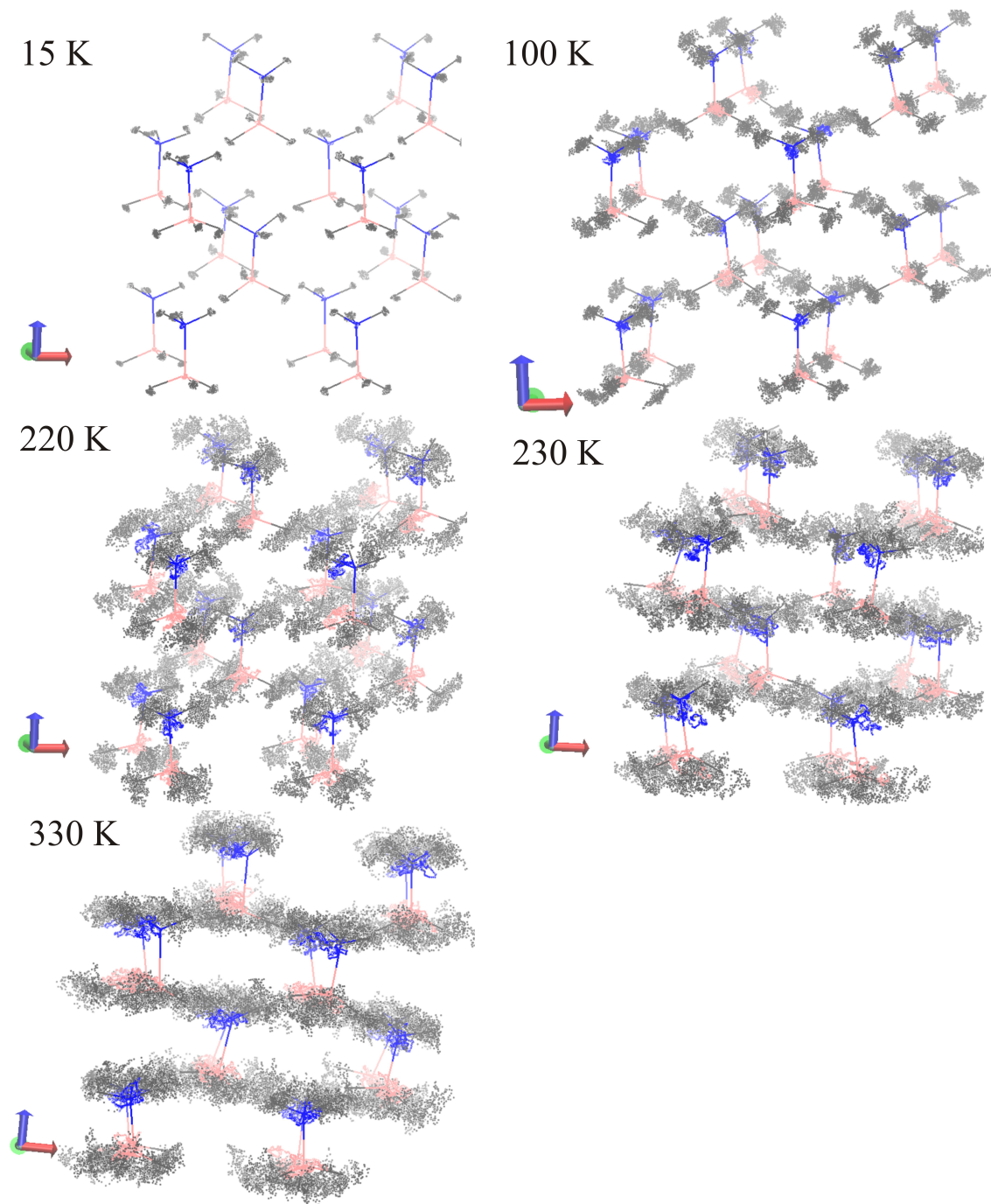


Figure 5.4: Trajectories of the atoms in ammonia borane at different temperatures. The atomic positions are shown for 400 steps at 5 fs time intervals.

In the 220 K simulations, the final temperature before transformation to the tetragonal phase, the ammonia and borane groups begin to rotate. However, the groups

do not perform complete 360° rotations around the B-N bond, but rather rotations of a few tens of degrees either side of the equilibrium position (see the trajectories in Figure 5.4). For bond A there are now two peaks in the bond length distributions, which occur at 2.01 Å and 3.49 Å (see Figure 5.3). The first peak (2.01 Å) also has a shoulder at 2.27 Å. This is due to the bifurcated nature of the bond between one B-H moiety and two N-H moieties. Figure 5.5 illustrates the bond distances which are measured when a borane or ammonia group reorientates. If the borane group rotates by 120° both of the bonds will break, giving rise to two new distances between the N-H moieties and the reorientated B-H moieties of approximately 2.2 Å (this is bond B) and 3.5 Å. If the nitrogen atom rotates by the same amount, two bonds between the N-H moieties and the B-H moieties in two different borane groups will be broken. The new H-H distances will both be approximately 3.5 Å. This explains the second peak and the shoulder in the first peak in the length distribution for bond A in ammonia borane at 220 K (Figure 5.3 A). Bonds B and C have less well defined peaks because these weaker bonds ‘tether’ the hydrogen atoms less and so they can vibrate more freely around their equilibrium position, which increases the width of the first peak.

The bond length distributions shown in Figure 5.3 were used to calculate potential energy curves for each bond using Equation 5.1. The potential curves were then fitted to Morse potentials. For simulations which resulted in more than one energy minimum only the first potential curve was fitted. The data from the simulations at 15 K, especially for bond A, did not fit well to a Morse potential due to the low temperature and small number of calculation steps. Therefore, they were also fitted to a harmonic potential as in Equation 5.5.

$$V(r) = \frac{1}{2}k(r - r_e)^2 \quad (5.5)$$

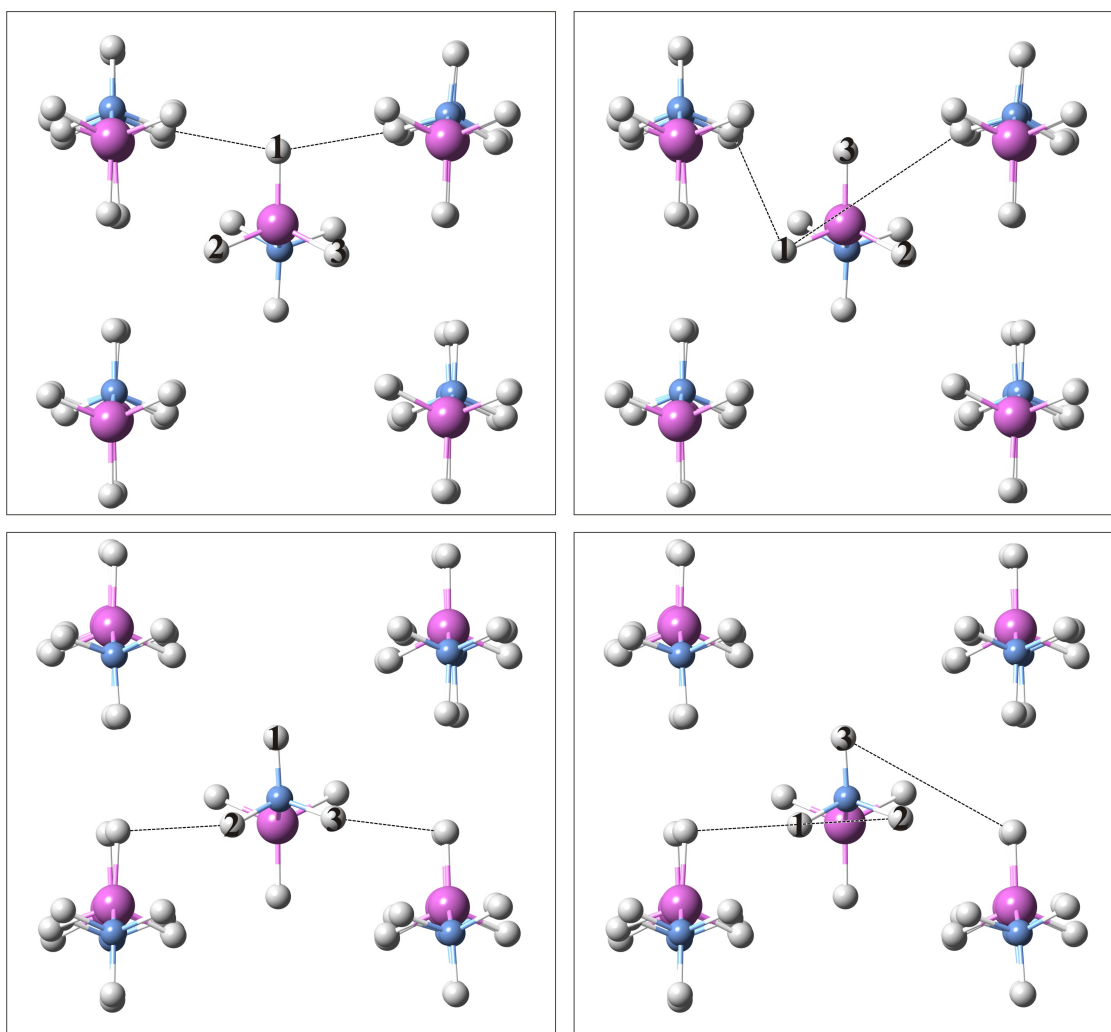


Figure 5.5: The measured lengths of bond A during rotation of the borane (top) and ammonia (bottom) groups.

As a consequence of the low temperature, only the vibration levels in the bottom of the potential curve will be filled and so it is valid to use a harmonic approximation. The potential curves calculated from the simulated data and the corresponding fitted Morse potentials are shown in Figure 5.6.

Table 5.1 shows the equilibrium bond lengths, the force constant of the dihydrogen bonds (from Morse and harmonic potential fits) and the depth of the potential curve for all three bonds. The force constants calculated using the Morse potentials and the

harmonic potentials at 15 K are in good agreement. The force constant of bond A (the strongest dihydrogen bond) at 15 K is 6.13 N m^{-1} , for bond B is 4.02 N m^{-1} , for bond C is 2.72 N m^{-1} . These bond strengths correlate well with the experimental bond lengths, bond A is the shortest and strongest bond, bond B and C are longer and weaker with the anomalous bond angles further weakening bond C. The small force constants of the bonds support the view that the dihydrogen bonding in ammonia borane is relatively weak [144, 145]. By comparison, one of the strongest hydrogen bonds - between an ammonia molecule lone pair (the hydrogen acceptor) and a hydrogen fluoride (the hydrogen donor) - has a force constant of 37.5 N m^{-1} . For the hydrogen bond between two water molecules the force constant is 17.4 N m^{-1} [190].

Due to the shape of the Morse potential fits for the computational potential curves at 220 K, the equilibrium bond lengths and the force constant values are relatively uncertain. This accounts for the drop in the force constants at 220 K and the large change in the bond length between 175 K and 220 K for bond C.

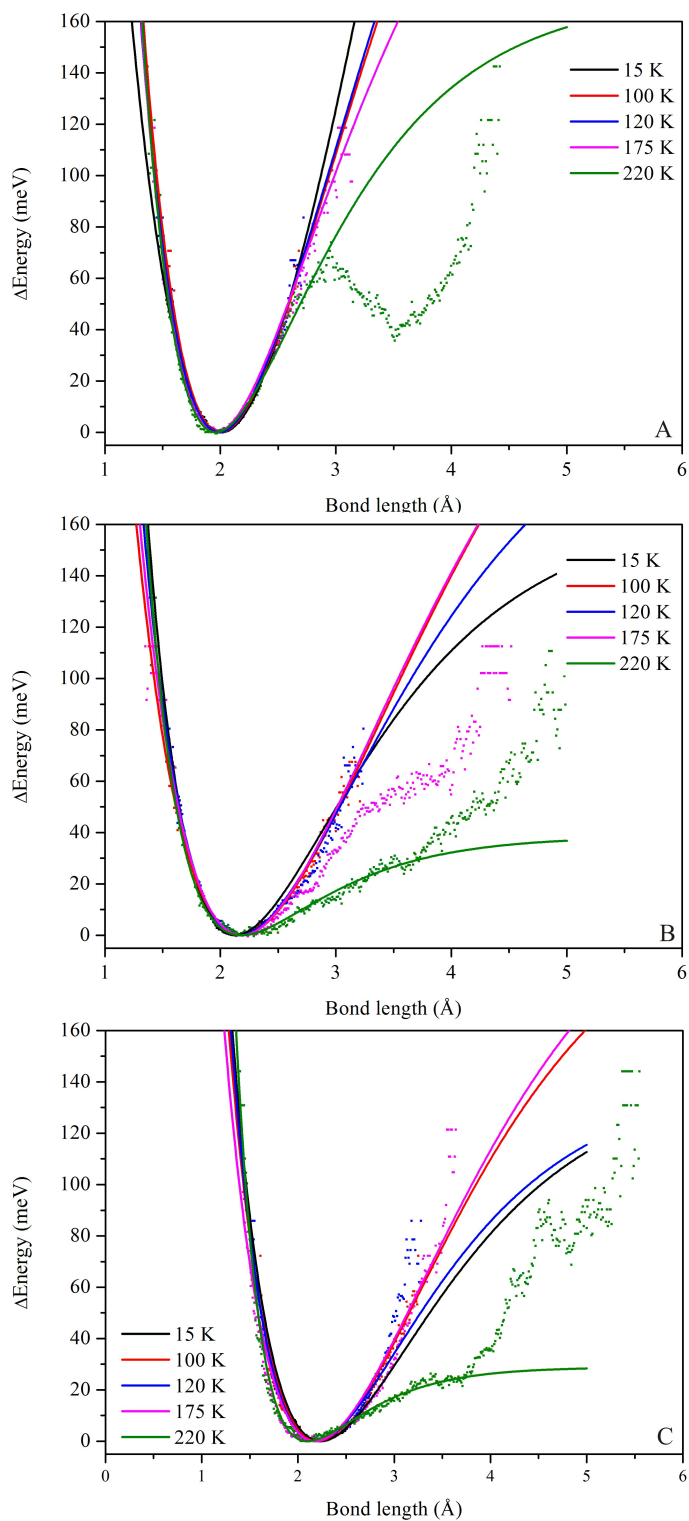


Figure 5.6: Potential curves for bonds A, B and C, calculated from the simulated length distributions (dots), and corresponding fitted Morse potentials (solid lines), for the low temperature orthorhombic phase of ammonia borane.

Temperature	r_e (Å)	k (N m ⁻¹)	Depth of well (meV)
Bond A			
15 K	2.01*	-/6.13(35)*	-11.6(2)*
100 K	2.00	6.91(69)	-70.6(8)
120 K	1.99	6.77(77)	-84(1)
175 K	1.96	6.90(22)	-119(1)
220 K	1.96	6.19(18)	-143(1)
Bond B			
15 K	2.13	4.0(27)/4.02(21)*	-11.5(1)*
100 K	2.18	3.57(40)	-67.8(1)
120 K	2.17	3.88(32)	-81(1)
175 K	2.18	3.8(24)	-114(1)
220 K	2.18	2.2501(91)	-132(1)
Bond C			
15 K	2.23	2.8(12)/2.72(12)*	-11.3(1)*
100 K	2.20	3.20(30)	-66.6(7)
120 K	2.18	3.09(48)	-79.1(5)
175 K	2.18	3.08(65)	-110.6(1)
220 K	2.10	2.459(97)	-131(1)

Table 5.1: The equilibrium bond length, r_e , the force constant, k and the depth of well of the models fitted to the dihydrogen bond potential curves of the orthorhombic phase for ammonia borane (shown in Figure 5.3). The fits using the harmonic oscillator model are marked with an asterisk. The Morse potential fit for Bond A at 15 K is not shown.

5.2.2 Tetragonal Phase

Above 230 K, ammonia borane adopts the high temperature tetragonal phase, and both the ammonia and borane groups are rotating. The simulated trajectories are fairly short (in terms of the time interval simulated) and therefore due to the infrequent nature of rotation events, the results could be skewed if only a few rotations occur within the time interval of the simulation. In the tetragonal phase, bond B (determined to be 2.9 Å) from crystallographic refinements [48]) is considered too long to be a dihydrogen bond. However, the bond length distribution is broadly similar to those for the other two bonds, especially just after the phase transition, suggesting that it can be considered a dihydrogen bond. Bond length distributions are shown in Figure 5.7. The similarity between the three bonds can also be seen in the potentials curves shown in Figure 5.8. The high level of disorder and molecular motion at temperatures above the phase transition (see the trajectories in Figure 5.4) allows the hydrogen atoms to move into close enough proximity to form a dihydrogen bond. This disorder also has the consequence that bond C is no longer necessarily the shorter dihydrogen bond and bond A the longer one. However, for all three bonds there are still maxima in the bond length distributions when the tetrahedral groups have rotated by 0°, 120° and 240° (see Figure 5.3) - the angles at which the hydrogen groups are as close together as possible. This indicates that dihydrogen bonding is still important in stabilising the high temperature phase. A three site jump model was also reported by Hess *et al.* using quasielastic neutron spectroscopy [51].

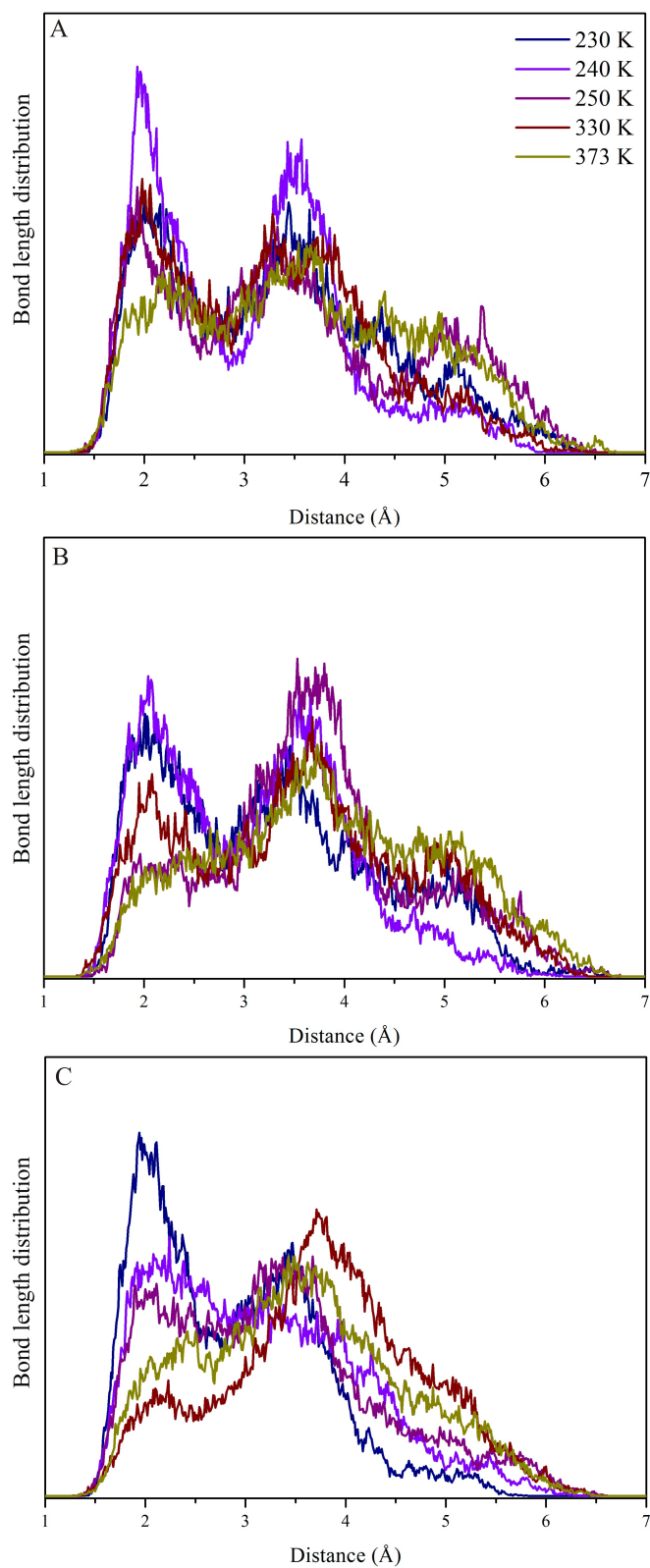


Figure 5.7: The bond length distributions of the three dihydrogen bonds, A, B and C as a function of temperature.

Potential curves for the high temperature tetragonal phase at 230 K and 373 K are shown in Figure 5.8. The depths of the first minima of the curves are approximately 124 meV, 126 meV and 133 meV for bonds A, B and C respectively at 230 K. The fitted Morse potentials for the curves at 230 K are shown in Figure 5.8. Especially above the tetragonal phase transition the curves determined from simulation are broad with multiple minima and do not follow ideal Morse-like behaviour. This will reduce the reliability of the force constants and equilibrium bond lengths; however they can still be used as indications of the bonds strength. The force constants for the bonds at this temperature are: bond A, $3.04(16) \text{ N m}^{-1}$, bond B, $3.44(7) \text{ N m}^{-1}$ and bond C, $3.42(11) \text{ N m}^{-1}$. The equilibrium bond lengths are; $1.98 \text{ \AA}$, $1.96 \text{ \AA}$ and $2.00 \text{ \AA}$ respectively. The bond lengths determined experimentally by Hess et al. [48] for bond C and bond A at 230 K are $1.97(2) \text{ \AA}$ and $2.09(2) \text{ \AA}$ respectively, and agree well with the equilibrium bond lengths determined numerically. However, the length of bond B, $2.86(2) \text{ \AA}$ found experimentally is considerably longer than the value found numerically ($1.96 \text{ \AA}$). This again suggests that molecular vibration allows the hydrogen atoms to approach close enough to form dihydrogen bond B as well as bond A and bond C. Similarly, the unusual bond angles in bond C do not have an effect on the bond strength. The calculated potential curves at 240 K and 250 K (not shown) are very similar to that at 230 K.

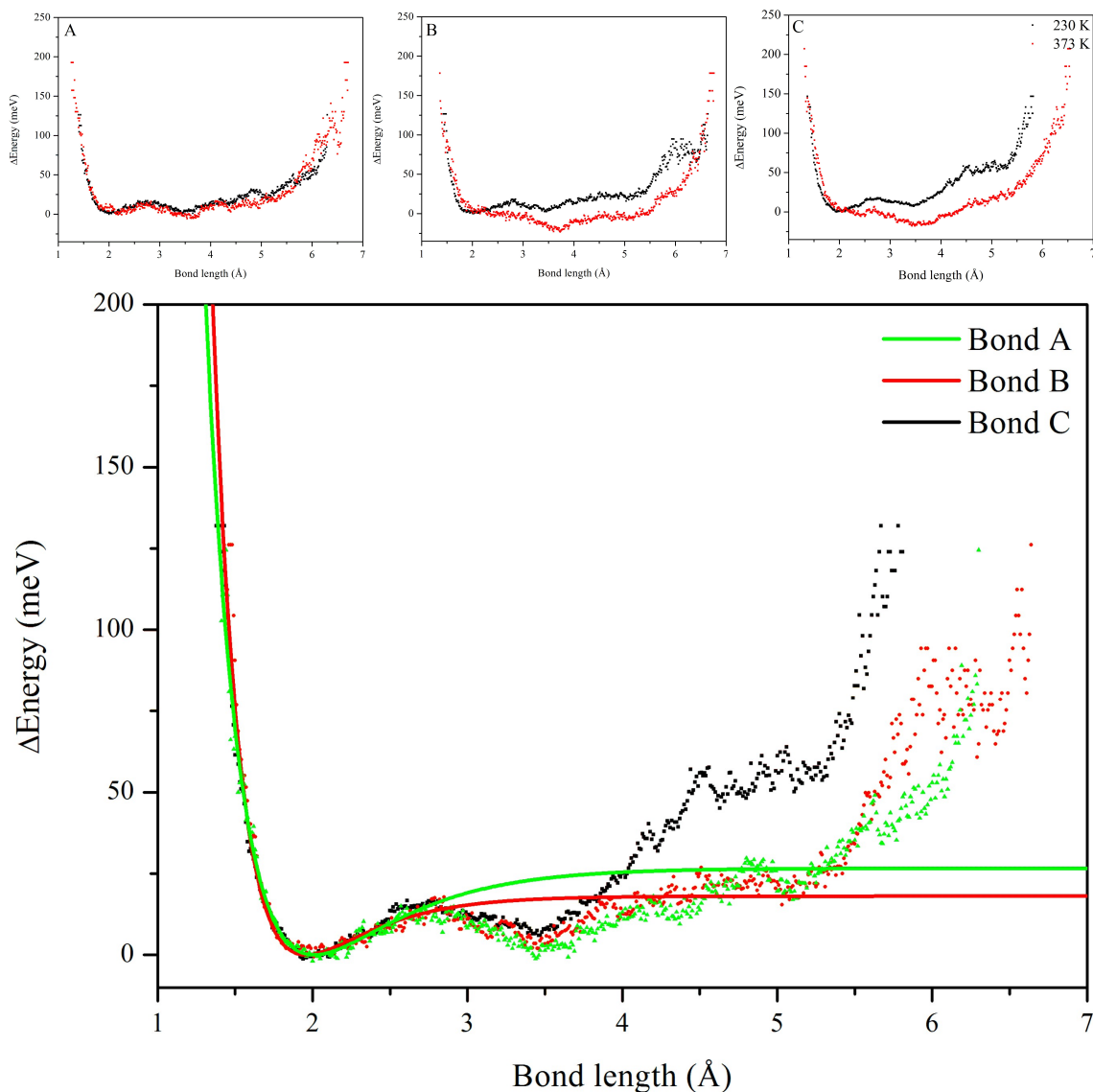


Figure 5.8: Top: Computationally-determined potential curves for dihydrogen bonds in ammonia borane 230 K (black) and 373 K (red). Bonds A to C, left to right. Bottom: Computationally-determined potential curves (dots) and fitted Morse potentials (solid lines) for ammonia borane at 230 K.

At higher temperatures (330 K and 373 K in the simulations), the potential curves deepen further and the distinction between the potential well minima is reduced, especially in bonds B and C. The reduction in the barrier between the first and second wells means that at higher temperatures Morse potential fits are no longer meaningful. At

these temperatures ammonia borane decomposes (albeit with a long induction period at 330 K). The flatter potential curves suggest a reduction in the formation of directional dihydrogen bonds. This supports the view that the formation of the mobile phase of ammonia borane is caused by a reduction in dihydrogen bonding between adjacent molecules (see Chapter 4). However, unlike in the neutron diffraction data presented in Chapter 4, no end-to-end flipping of the whole ammonia borane molecule is observed in these simulations is possibly because, on the timescale of the simulations, end-to-end flipping is a rare event.

5.3 Summary

The DFT simulations performed by Hess et al. [48] were analysed to study dihydrogen bonding in the tetragonal and orthorhombic phases of ammonia borane. Morse and harmonic potentials were fitted to the potential curves of each of the crystallographically distinct dihydrogen bonds in the ammonia borane molecule. In the orthorhombic phase, all three dihydrogen bonds are well defined, with no rotation of the ammonia and borane groups. Force constants determined from fits to the calculated potential wells confirm that the dihydrogen bonds are relatively weak. After the tetragonal phase transition the ammonia and borane groups begin to rotate. Multiple minima occur in the potential curves for the tetragonal phase, showing that the dihydrogen bonds are still present and important in stabilising the high temperature tetragonal structure. At even higher temperatures, when ammonia borane will decompose, simulated potential curves of two of the dihydrogen bonds in the structure display some distinct local minima. This indicates that the dihydrogen bonds become a very weak bonding interaction - supporting the view that the formation of the mobile phase of ammonia borane occurs via a reduction in the dihydrogen bonding network.

Chapter 6

Ammonium Borohydride

6.1 Crystallographic Phases and Decomposition of Ammonium Borohydride

6.1.1 Current Literature

Previous studies have emphasised the dependence on thermal history of the low temperature phases of ammonium borohydride [103]. The high temperature phase has been well characterized [106, 107, 103] (cubic, space group $Fm\bar{3}m$, $a = 6.868(2)$ Å). The boron atoms occupy the $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ positions and the hydrogen atoms in the borohydride group occur in the $\frac{1}{2}$ -occupancy cubic positions along the $\langle 111 \rangle$ directions. The nitrogen atoms occupy the $(0, 0, 0)$ positions and the hydrogen atoms in the ammonium group are highly disordered, due to the 48-fold disorder of the ammonium tetrahedron [103]. The cubic phase is stable between 60 K and 230 K, above which it begins to slowly decompose to DADB while releasing hydrogen. Ryan [103] reported two low-temperature phases: a rhombohedral and a trigonal phase. The more ordered rhombohedral structure ($R\bar{3}m$ $a = b = 4.831(3)$ Å and $c = 23.473(2)$ Å) occurred

when the cubic phase transformed along two body diagonals to form a rhombohedral cell. In this phase, the borohydride groups are aligned along the $\langle 001 \rangle$ direction, with the tetrahedra alternately pointing up and down. The ammonium groups have 12-fold disorder; the new space group no longer has a 4-fold axis, which reduces the level of disorder 4-fold. The lower-temperature phase is a trigonal super cell of the higher temperature rhombohedral phase ($P\bar{3}c1$ $a = b = 9.51(4)$ Å and $c = 23.47(9)$ Å). In this phase the ammonium groups are further ordered, with only 3-fold disorder.

Ryan [103] found that when ammonium borohydride was slowly cooled to base temperature the phases occurred in the expected order: the cubic phase above 60 K, the rhombohedral phase between 60 K and 45 K, and the trigonal phase below 45 K. However, when the sample was crash-cooled (shown in Figure 6.1) it remained in the rhombohedral phase on cooling below 45 K. As the temperature was increased it transformed to the trigonal phase, before returning to the rhombohedral phase when enough energy was available for the transformation.

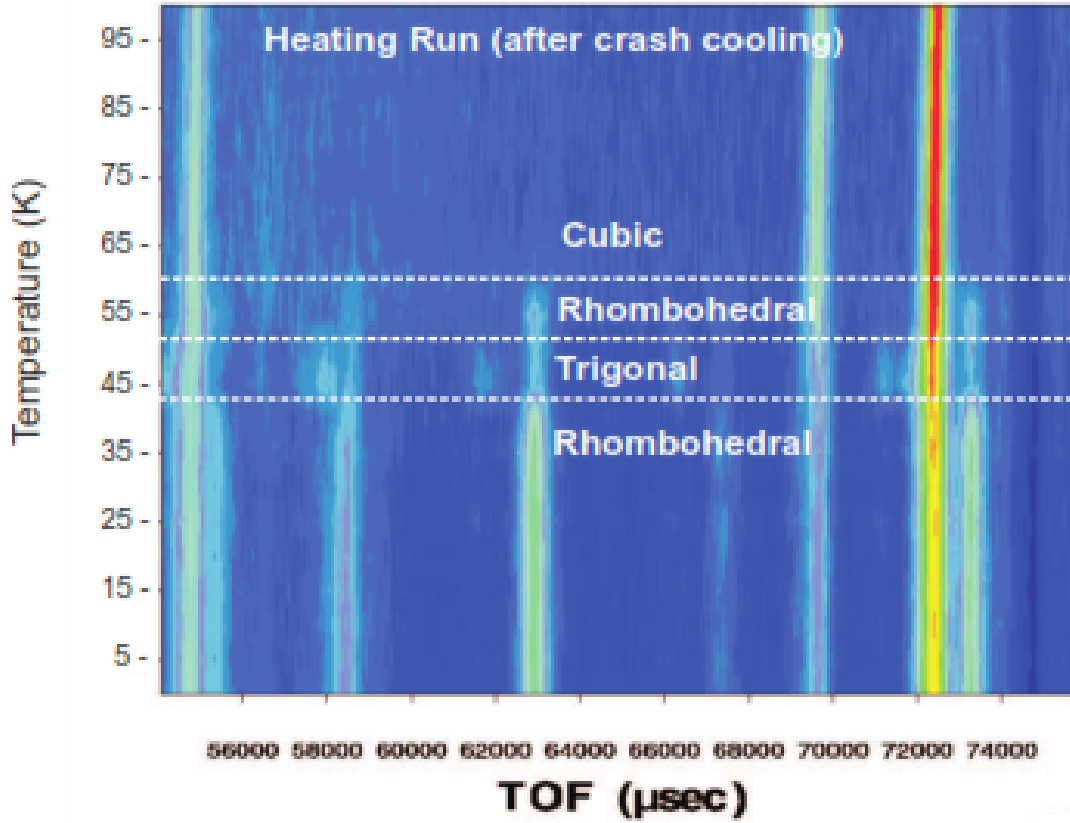


Figure 6.1: Surface plot of the heating of ammonium borohydride; time-of-flight neutron diffraction data collected at ISIS on HRPD. The broken lines indicate the phase transitions. [103] reproduced with permission.

6.1.2 Low Temperature Phases of Ammonium Borohydride

Experimental Details

An experiment on the Wish diffractometer at ISIS was designed to confirm the phase progression of ammonium borohydride and to determine whether phases with further ordering existed. A fully deuterated and boron-11 enriched sample, $\text{ND}_4^{11}\text{BD}_4$, was packed into a 12 mm cylindrical aluminium alloy sample can in an argon glove box. It was loaded on to a gas handling centre stick with the capability to have the sample under vacuum or flowing argon. For the experiments described in this Section, the

sample was kept under vacuum.

The sample was slow-cooled from approximately 200 K to 4 K over 5 days (1.63 K hr^{-1}) in a cryostat out of the beam. Unfortunately, while being loaded into the beam the sample temperature increased to approximately 40 K; however this is still below the first phase transition observed and so should not have had an effect on the phases reported. Due to the need to anneal the Target Station 2 methane moderator (for 8 hours in every 24 hours) the beam was only usable for two 8 hour periods per day. The slow-cooled sample was heated from 4 K to 86 K with 4.5 min diffraction patterns collected every 1 K. During the annealing break the sample was cooled slightly to give overlapping data, and was heated from 70 K to 182 K with a diffraction pattern collected every 1.1 K. The sample was then crash-cooled, taking approximately 2 hours to reach 4 K. It was not possible to record data during this crash-cooling due to moderator annealing. Finally, the sample was reheated from 4 K to 200 K with a diffraction pattern collected every 2 K.

The sample can was made of an aluminium alloy; aluminium and the other alloying elements have a significant neutron cross section and so will produce diffraction peaks. The diffraction pattern of the sample can was modelled using a Pawley refinement of the cubic space group ($Fm\bar{3}m$) and lattice parameters ($a = 4.05830(6) \text{ \AA}$) of pure aluminium. The samples also had a small impurity of boron nitride, introduced during the synthesis of the sodium borohydride. The main can and impurity peaks are highlighted in Figure 6.3.

Slow Cooled

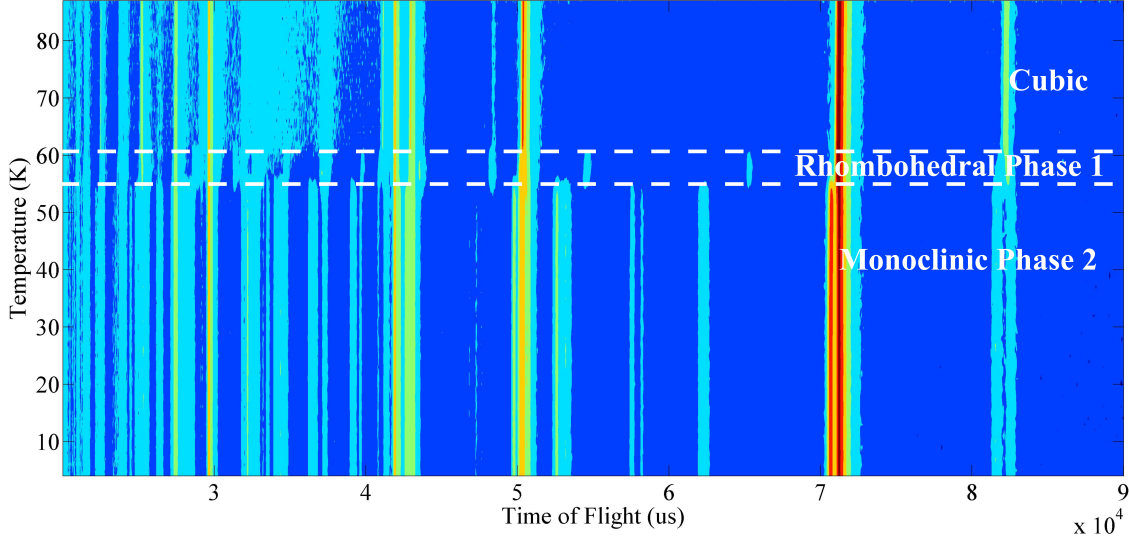


Figure 6.2: Surface plot of the heating of ammonium borohydride from 4 K to 80 K after it has been slow-cooled; time-of-flight neutron diffraction data (20,000 μs to 90,000 μs shown). The broken white lines indicate phase transitions.

On heating the sample after slow-cooling, three phases were observed (shown in Figure 6.2). However, two of these phases were different to those previously reported. The low temperature phase (referred to here as Phase 2) was observed between 4 K and 55 K. It is different from the ‘bottom’ trigonal phase reported by Ryan [103]. A rhomboidal phase (Phase 1) observed between 55 K and 66 K, also shows differences from the previously reported ‘middle’ rhomboidal phase (see Section 6.1.2).

The transition temperatures between the phases are similar to those reported by Ryan [103]. The greatest difference is that the transformation from Ryan’s [103] rhomboidal middle phase to trigonal bottom phase occurs at 45 K, whereas in this study the transformation of the rhomboidal Phase 1 to the low temperature Phase 2 was observed at 55 K. This could be due to the differences in the phases or it could be a hysteresis effect, since the previously reported data were recorded during cooling.

Crash Cooled

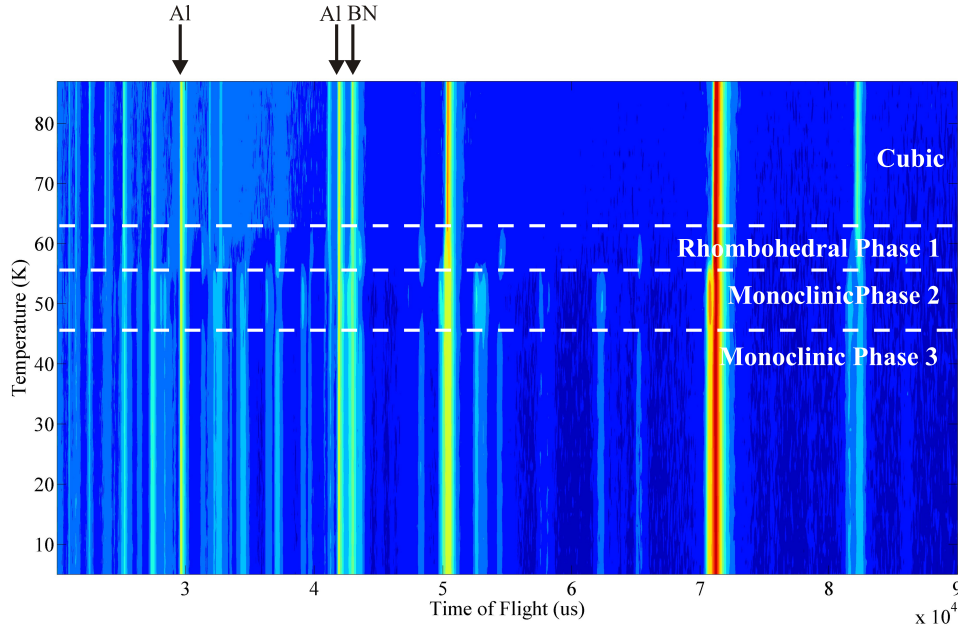


Figure 6.3: Surface plot of the heating of ammonium borohydride from 4 K to 80 K after it has been crash-cooled; time-of-flight neutron diffraction data (20,000 μs to 90,000 μs shown). The broken white lines indicate phase transitions.

The phase progression during re-heating of the crash-cooled sample was more complex (shown in Figure 6.3), although it also showed similar behaviour to that observed in Ryan's earlier study [103]. Below 45 K, there is a new phase which has not been previously observed, and is referred to here as Phase 3. On heating above 47 K the sample transforms to Phase 2 and at 57 K to the rhombohedral Phase 1.

Phase 2 and Phase 3 are very similar; using a Pawley refinement both of the phases have been indexed to the monoclinic space group $P2/m$ $a = 9.69 \text{ \AA}$, $b = 9.76 \text{ \AA}$, $c = 13.67 \text{ \AA}$ and $\beta = 89.5^\circ$. No further attempts were made to solve the structures. If the low temperature Phase 3 is less ordered than Phase 2 but more ordered than the rhombohedral phase (Phase 1), the progression is similar to that observed by Ryan. Under these circumstances, crash-cooling would trap it in a disordered phase (Phase 3). When heated, the sample would eventually have enough energy to transform into a more

ordered phase (Phase 2) and finally into the rhombohedral phase.

The Rhombohedral Phase

The new rhombohedral phase observed in both the crash-cooled and the slow-cooled experiments (referred to above as Phase 1) has the same space group and lattice parameters as the rhombohedral phase previously reported by Ryan [103]. However due to ordering differences, a different structural solution is required - this is presented below.

The rhombohedral cell can be explained in terms of the relationship with the high temperature cubic unit cell. The c -axis of the hexagonal rhombohedral cell is double the $\langle 111 \rangle$ direction of the original cubic cell (see Figure 6.4). The a - and b -axes are defined by the cubic lattice points $(\frac{1}{2}, -\frac{1}{2}, 0)$ and $(0, -\frac{1}{2}, \frac{1}{2})$. The relationships between the rhombohedral and cubic lattice parameters are given by Equation 6.1.

$$a_r = \sqrt{2 \left(\frac{a_c}{2} \right)^2}$$

$$c_r = 2\sqrt{3a_c^2} \tag{6.1}$$

where a_r and c_r are the a/c lattice parameters for the rhombohedral phase and a_c is the cubic lattice parameter.

In the rhombohedral phase the boron atoms all occupy the $(0, 0, \frac{1}{4})$ symmetry-equivalent positions. The boron hydrogen atom site at $(\frac{1}{2}+x, \frac{1}{2}+x, \frac{1}{2}+x)$ in the cubic structure becomes the $(0, 0, z_B + \frac{1}{2}x)$ position in the rhombohedral phase which is the ‘up/down point’ of the tetrahedron (z_B is the z coordinate of the boron atom). The other three positions (on the ‘base’ of the tetrahedron) are symmetry equivalent, with the $(\frac{1}{2}-x, \frac{1}{2}-x, \frac{1}{2}+x)$ position in the cubic structure becoming the $(-\frac{4}{3}x, -\frac{8}{3}x, z_B + \frac{1}{6}x)$ position in the rhombohedral structure. Figure 6.4 shows how the borohydride groups

order in the rhombohedral structure. In the cubic structure, the borohydride tetrahedra have 2-fold disorder (the dark and pale grey hydrogen positions): they point either up or down. In the rhombohedral structure the borohydride groups order, and point either up or down in alternate planes (the pale grey hydrogen positions). Therefore two cubic $\langle 111 \rangle$ axes become the rhombohedral c -axis.

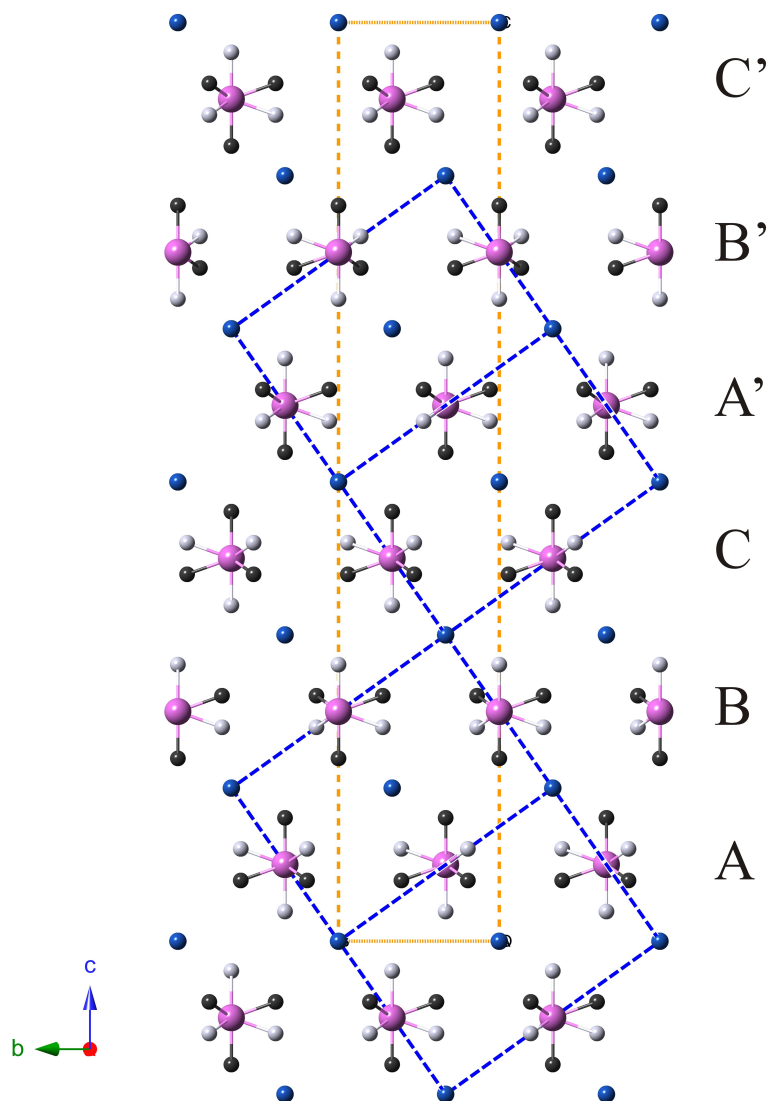


Figure 6.4: Schematic showing the transformation from the cubic unit cell (blue dashed lines) to the rhombohedral unit cell (orange dashed lines).

In the rhombohedral phase there are two distinct nitrogen positions, $(0, 0, 0)$ and

$(0, 0, \frac{1}{2})$. The ammonium tetrahedron has 12-fold disorder. The cubic ammonium group hydrogen atom position $(x, 0, 0)$ transforms to the rhombohedral $(\frac{4}{3}x, \frac{2}{3}x, \frac{1}{6}x)$ position for the ammonium group centred on the nitrogen atom at $(0, 0, 0)$, and to $(\frac{4}{3}x, \frac{2}{3}x, \frac{1}{6}x + \frac{1}{2})$ for the $(0, 0, \frac{1}{2})$ nitrogen position. The 6-fold disorder of this position is maintained, giving six symmetry-equivalent positions. The remainder of the hydrogen atoms (and how they are transformed) are listed in Table 6.1. The 12-fold disorder of the nitrogen tetrahedron now comes from the 3-fold disorder of the 3-fold rotation along the c -axis, the 2-fold disorder at the centre of inversion and the 2-fold disorder of the mirror plane.

Axis	Cubic position	Rhombohedral position for the $(0,0,0)$ nitrogen site	Rhombohedral position for the $(0,0,\frac{1}{2})$ nitrogen site
x	$-\frac{1}{3}R$	$-\frac{2}{9}R(2 + \sqrt{8}(\sin \phi + \cos \phi))$	$-\frac{2}{9}R(2 + \sqrt{8}(\sin \phi + \cos \phi))$
y	$\frac{\sqrt{8}}{3}R \sin \phi$	$-\frac{2}{9}R(2 + \sqrt{8}(\sin \phi + \cos \phi))$	$-\frac{2}{9}R(2 + \sqrt{8}(\sin \phi + \cos \phi))$
z	$\frac{\sqrt{8}}{3}R \sin \phi$	$-\frac{2}{9}R(2 + \sqrt{8}(\sin \phi + \cos \phi))$	$-\frac{2}{9}R(2 + \sqrt{8}(\sin \phi + \cos \phi)) + \frac{1}{2}$

Table 6.1: The transformation of the general position of hydrogen atoms from the cubic high temperature phase of ammonium borohydride to the rhombohedral phase, $R = b_{N-H}/a_c$ where b_{N-H} is the N-H bond length, a_c is the cubic lattice parameter and $\phi = n\pi/12$.

Once the structure had been inferred from the transformation geometry, a refinement using the Rietveld method [171] was performed on data from the slow-cooled experiment at 59 K. The B-D and N-D bond lengths were allowed to refine, along with the lattice parameters, the thermal factors and the positions of the boron atoms. The occupancies of the deuterium atoms were defined using the symmetry of the atom positions; $\frac{1}{6}$ occupancy in the $(0, 0, z_B + \frac{1}{2}x)$ position. The lower symmetry positions initially had an occupancy of $\frac{1}{48}$, which was allowed to refine while maintaining the three-fold rotational

symmetry of the space group. On fitting, it was found that although the majority of the borohydride groups follow the up/down conformation (approximately 90 %), there is a significant proportion that are disordered. The structure of the rhombohedral $R\bar{3}m$ phase of ammonium borohydride is shown in Figure 6.5. The borohydride position with the lower occupancy is not shown for clarity.

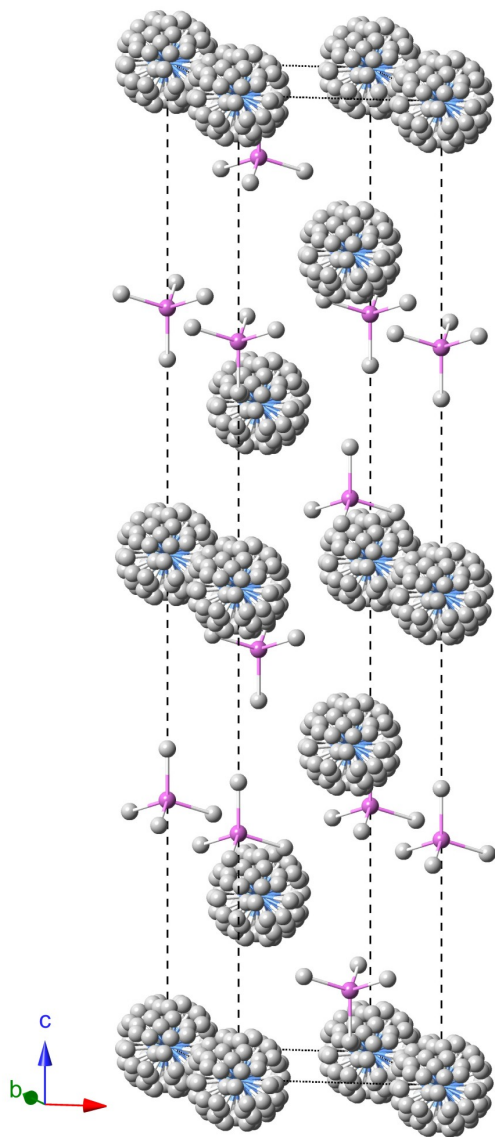


Figure 6.5: Structure of the rhombohedral phase of ammonium borohydride. Boron atoms in pink, nitrogen atoms in blue and deuterium atoms in grey. Only the borohydride tetrahedron position with the larger occupancy is shown to emphasise the symmetry.

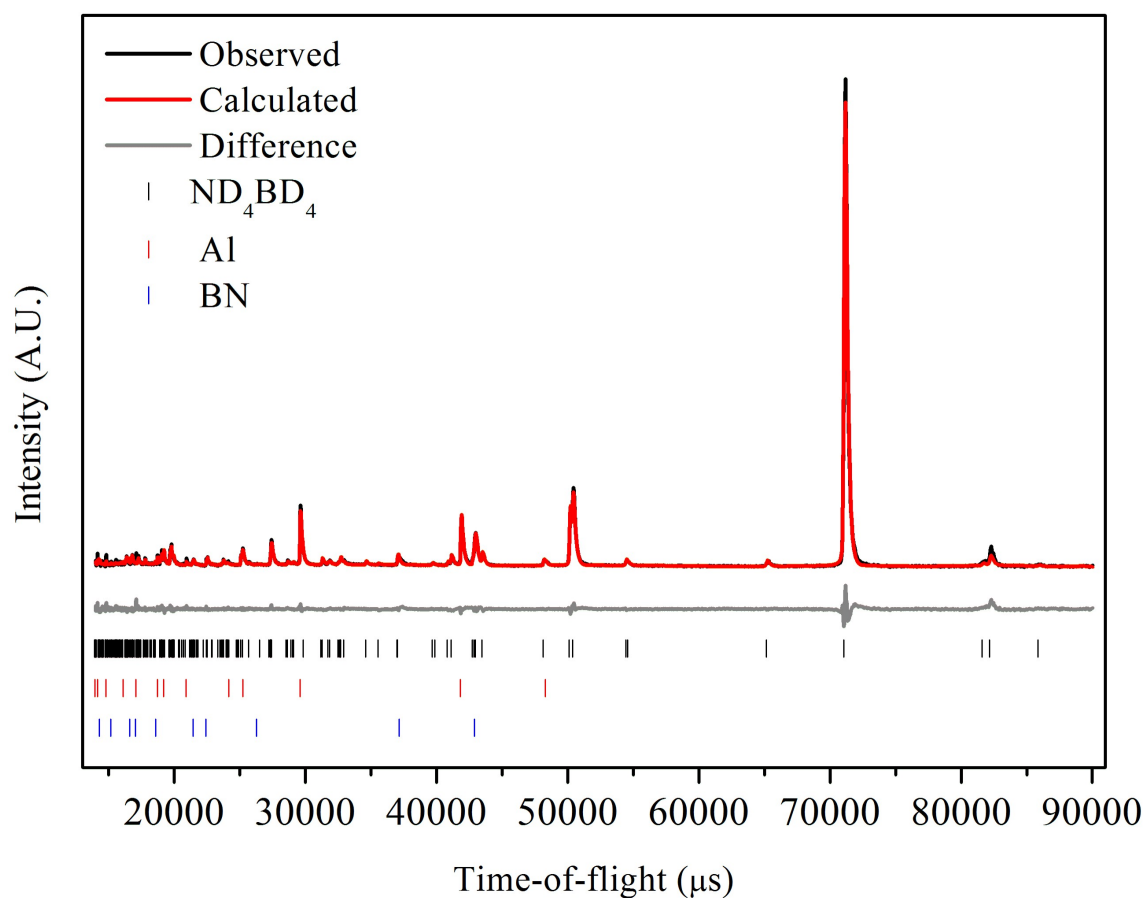


Figure 6.6: Observed (black) and calculated (red) diffraction patterns of the rhombohedral phase of ammonium borohydride at 59 K. The grey line under the diffraction pattern is the difference between the observed and calculated patterns. Ammonium borohydride (black tick marks), aluminium (red ticks) and boron nitride (blue ticks).

Atom	x	y	z	Occupancy	B_{iso} ($\text{\AA}^2$)	Wyckoff position
B1	0	0	0.24994(14)	1	1.527(93)	6c
H11	0	0	0.30191(19)	0.904(2)	2.491(68)	6c
H12	-0.13756(34)	0.13756(34)	0.23261(14)	0.904(2)	2.491(68)	18h
H21	0	0	0.19797(19)	0.095(2)	2.491(68)	6c
H22	0.11913(30)	0.27511(68)	0.26726(14)	0.095(2)	2.491(68)	18h
N1	0	0	0	1	0.957(68)	3a
H31	0.20597(55)	0.10298(28)	0.02575(07)	0.167	-1.26(10)	18h
H32	-0.16575(45)	-0.22852(61)	0.01569(04)	0.035(2)	1.82(20)	36i
H33	-0.20129(54)	-0.15395(41)	0.02458(07)	0.021(0)	1.82(20)	36i
H34	-0.20129(54)	-0.04734(13)	0.02458(07)	0.007(3)	1.82(20)	36i
H35	-0.16575(45)	0.06277(17)	0.01569(04)	0.021(0)	1.82(20)	36i
H36	-0.10420(28)	0.14685(39)	0.00030(00)	0.035(3)	1.82(20)	36i
H37	-0.03312(09)	0.18239(49)	-0.01747(05)	0.021(0)	1.82(20)	36i
H38	0.02844(08)	0.15986(43)	-0.03286(09)	0.007(3)	1.82(20)	36i
H39	0.06398(17)	0.08530(23)	-0.04174(11)	0.021(0)	1.82(20)	36i
H310	0.06398(17)	-0.02132(06)	-0.04174(11)	0.035(3)	1.82(20)	36i
H311	0.02844(08)	-0.13142(35)	-0.03286(09)	0.021(0)	1.82(20)	36i
H312	-0.03312(09)	-0.21551(58)	-0.01747(05)	0.007(3)	1.82(20)	36i
H313	-0.10420(28)	-0.25105(68)	0.00030(00)	0.021(0)	1.82(20)	36i
N2	0	0	0.5	1	0.956(68)	3b
H41	0.20597(55)	0.10298(28)	0.52575(07)	0.167	-1.26(10)	18h
H42	-0.16575(45)	-0.22852(61)	0.51569(04)	0.035(2)	1.82(20)	36i
H43	-0.20129(54)	-0.15395(41)	0.52458(07)	0.021(0)	1.82(20)	36i
H44	-0.20129(54)	-0.04734(13)	0.52458(07)	0.007(3)	1.82(20)	36i
H45	-0.16575(45)	0.06277(17)	0.51569(04)	0.021(0)	1.82(20)	36i
H46	-0.10420(28)	0.14685(39)	0.50030(00)	0.035(3)	1.82(20)	36i
H47	-0.03312(09)	0.18239(49)	0.48253(05)	0.021(0)	1.82(20)	36i
H48	0.02844(08)	0.15986(43)	0.46714(09)	0.007(3)	1.82(20)	36i
H49	0.06398(17)	0.08530(23)	0.45826(11)	0.021(0)	1.82(20)	36i
H410	0.06398(17)	-0.02132(06)	0.45826(11)	0.035(3)	1.82(20)	36i
H411	0.02844(08)	-0.13142(35)	0.46714(09)	0.021(0)	1.82(20)	36i
H412	-0.03312(09)	-0.21551(58)	0.48253(05)	0.007(3)	1.82(20)	36i
H413	-0.10420(28)	-0.25105(68)	0.50030(00)	0.021(0)	1.82(20)	36i

Table 6.2: Crystallographic data from the refinement of the rhombohedral phase of ammonium borohydride at 59 K. Space group, $R\bar{3}m$, $a = b = 4.872659(82)$ $\text{\AA}$ and $c = 23.69317(66)$ $\text{\AA}$, $R_{wp} = 8.513$, $R_{exp} = 4.920$ and $\chi^2 = 1.730$.

Figure 6.6 and Table 6.2 show the refined diffraction pattern and the crystallographic data for the rhombohedral $R\bar{3}m$ phase of ammonium borohydride. The B-D and N-D

bond lengths are 1.2314(31) Å and 1.0542(28) Å respectively and are similar to those reported for related compounds [48, 191, 192]. When allowed to refine, the z -coordinate of the boron atom is 0.24994(14) - barely changed from the high-symmetry value of 0.25. The thermal parameters for the atoms are in the range to be expected for this compound at low temperatures, except those for the deuterium atoms (H31 and H41) at the ‘point’ of the borohydride tetrahedron. These deuterium atoms have a negative thermal parameter of $-1.26(10)$ Å². This is because the assumed distribution of deuterium atoms in the ammonium groups limits the number of available positions, while in reality there is greater disorder. Spherical harmonic distributions and occupancies such as those used in Section 6.4.2 would provide a more accurate value. However, defining harmonics for anything other than high symmetry space groups is difficult and the improvement would be small.

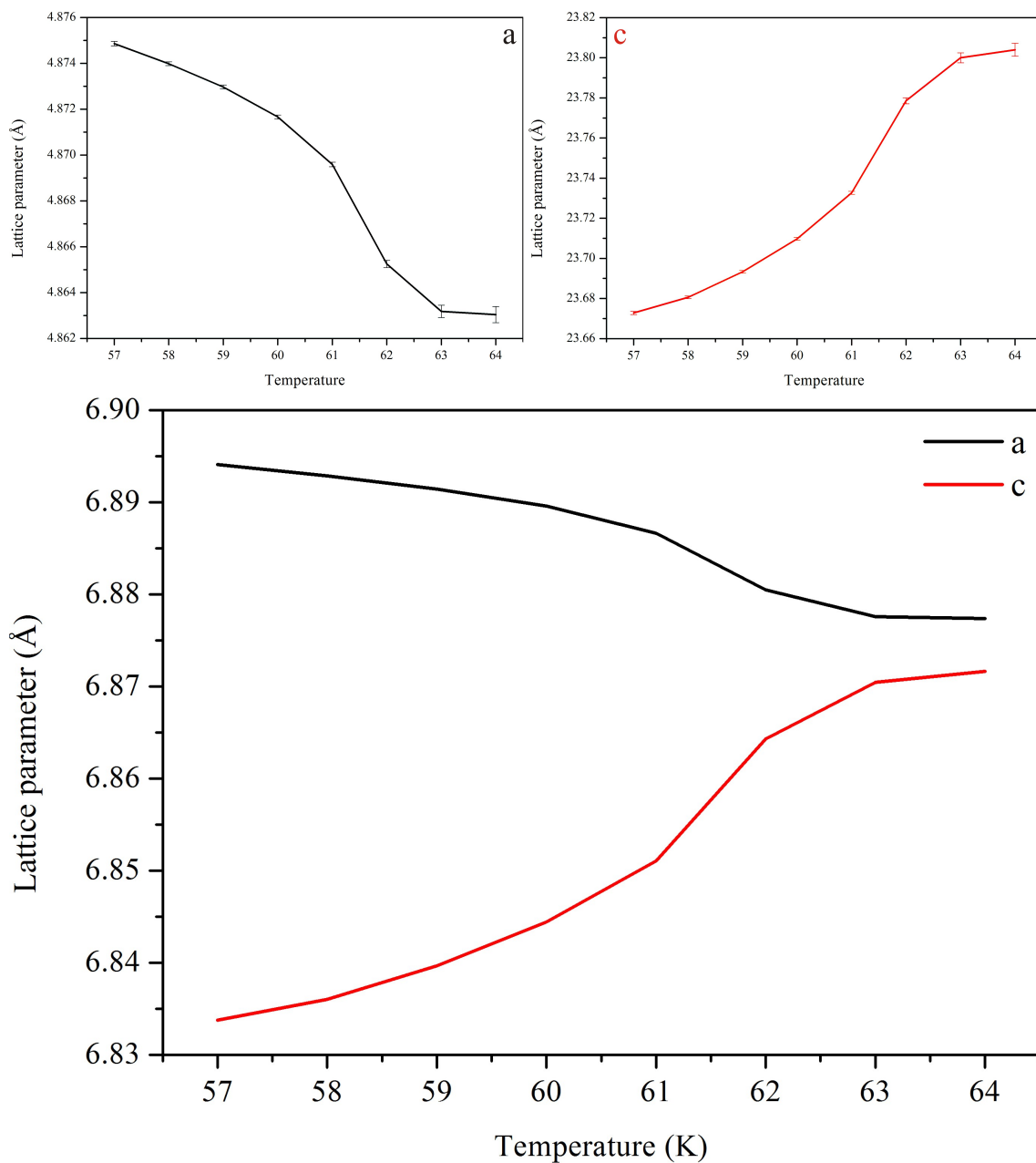


Figure 6.7: Top: The variation in the a and c lattice parameters of the rhombohedral phase of ammonium borohydride with temperature. Bottom: the rhombohedral lattice parameters converted to cubic notation (see Equation 6.1).

Figure 6.7 shows the variation of the rhombohedral lattice parameters with temperature (top) and their conversion into cubic parameters using the relationships shown in Equations 6.1 (bottom). As the temperature increases, the a lattice parameter de-

creases and the c lattice parameter increases making the rhombohedral phase increasingly strained. When this change is considered in the context of the transformation to the cubic phase, using the relationship between the cubic and rhombohedral lattice parameters, the a and c lattice parameters converge as would be expected on the formation of a cubic phase. Another indication of the impending phase transformation is the increased amount of disorder in the borohydride groups as shown in Figure 6.8. As the phase transition approaches the amount of disorder increases towards the 50:50 occupancy of the two tetrahedron positions found in the cubic phase.

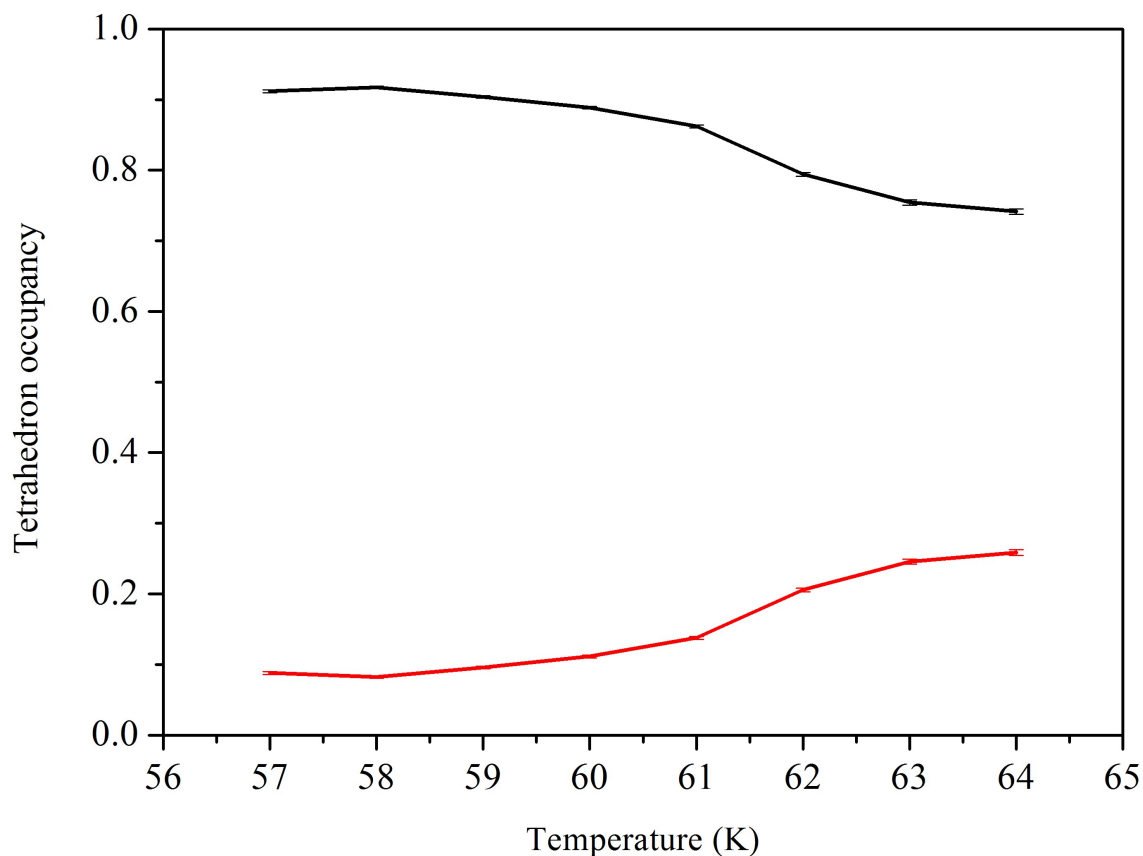


Figure 6.8: The occupancy of the deuterium positions in the borohydride tetrahedron in the rhombohedral phase of ammonium borohydride.

6.1.3 Decomposition of Ammonium Borohydride

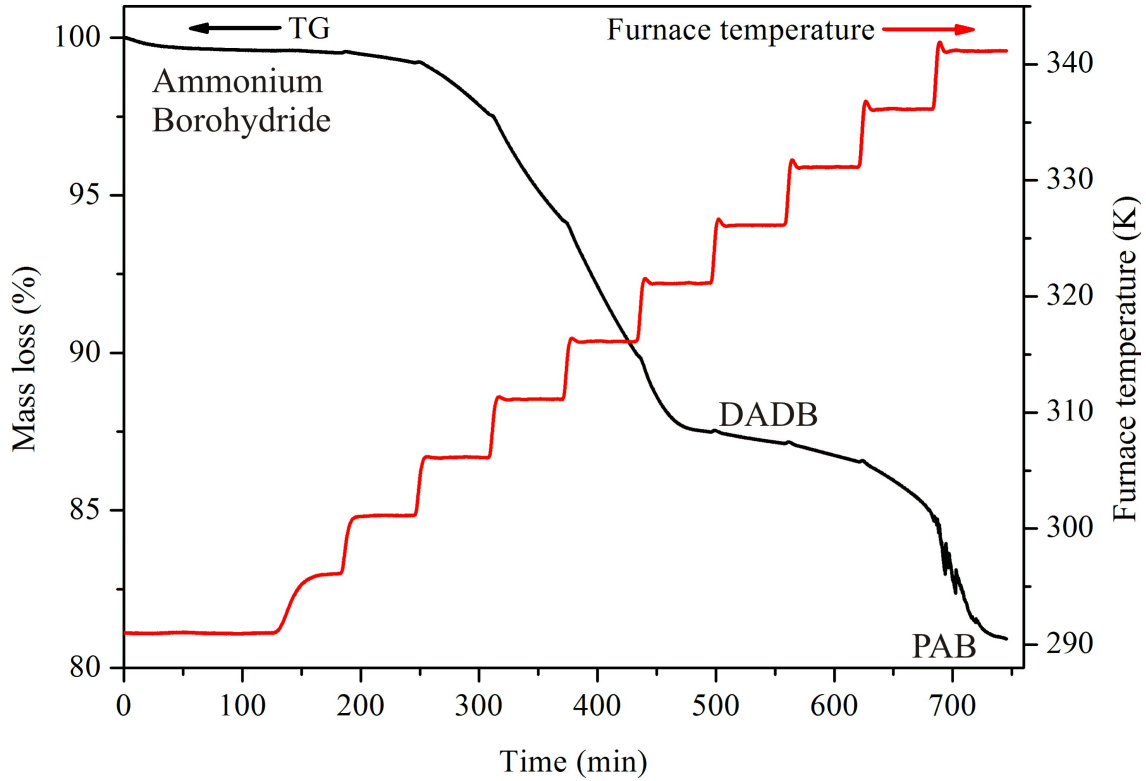


Figure 6.9: Thermal gravimetric analysis of the decomposition of deuterated and boron-11 enriched ammonium borohydride to DADB in 5° temperature steps.

Figure 6.9 shows the decomposition of deuterated and boron-11 enriched ammonium borohydride (the same sample as used in the Wish experiment). The sample was removed from a 200 K freezer and loaded into an alumina crucible while being kept cold in dry ice. The sample was at room temperature for approximately 5 min before the beginning of the data recording. Although ammonium borohydride does decompose slowly at room temperature, it will not immediately begin to decompose as shown by these TGA data. Decomposition starts once the temperature reaches 300 K (at 190 min in Figure 6.9) and speeds up significantly once the sample reaches 305 K (255 min).

The mass loss during the decomposition of ammonium borohydride to DADB (~250 - 500 min) is 11.9 %, which is consistent with the loss of one equivalent of

duterium. It is slightly higher than the stoichiometric value of 9.75 % due to borazine and diborane during decomposition [106]. The small mass loss (0.4 %) at the beginning of the experiment is due to the loss of a small amount of ammonia solvent remaining after the sample synthesis. Starting at 336 K there is a second mass loss of 5.78 %, which results from the loss of one equivalent of deuterium (5.40 %) from DADB to form amidoborane. The ‘noise’ in the mass loss between 680 min and 706 min is due to foaming of DADB during the decomposition.

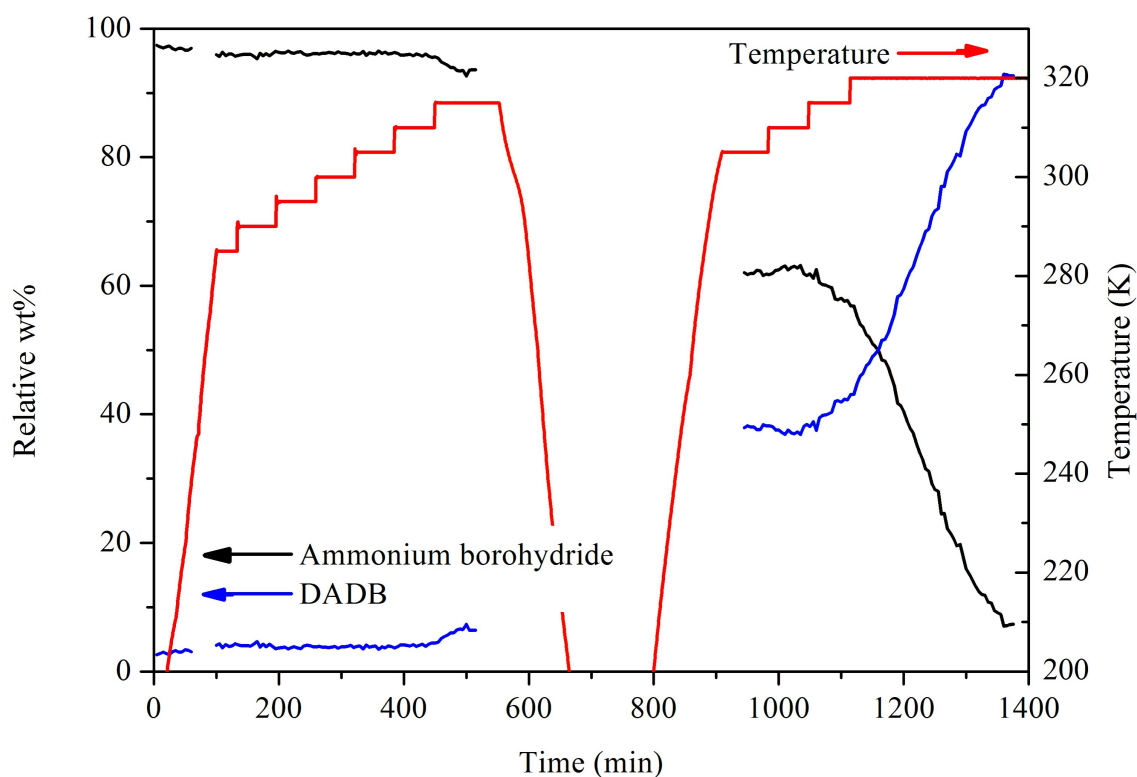


Figure 6.10: Mass fractions of ammonium borohydride and DADB during the thermal decomposition of ammonium borohydride; calculated from neutron diffraction data (Wish, ISIS).

Following the gravimetric analysis, further information on the decomposition of ammonium borohydride was obtained using neutron diffraction. Following the low-temperature experiment described in Section 6.1, the same sample of ammonium borohydride was heated under flowing argon from 200 K to 285 K at 1.4 K min^{-1} . The

sample was held isothermally for 60 min at 285 K, 290 K, 295 K, 300 K, 305 K and 310 K, and for 175 min at 315 K. Unfortunately, in the neutron diffraction experiment a larger sample volume and lower argon flow rate caused the sample to decompose more slowly than in the TGA experiment. During the moderator annealing break the sample was crash-cooled to pause the decomposition (see Figure 6.10, 600 - 850 min). Once the beam returned, the sample was heated to 305 K at 1.6 K min^{-1} , for 60 min isotherms at 305 K, 310 K and 315 K, and then isothermally at 315 K for the remainder of the experiment (190 min). The continuous collection feature on Wish was used; a single scan was used for each temperature step. After the experiment, these long scans were processed into 5 min diffraction patterns.

The sample began to decompose at 310 K after 350 min of heating. The crash-cool (starting at 315 K and 600 min) was not sufficient to halt the decomposition completely. When measurements recommenced, approximately 60 wt% ammonium borohydride remained; the colour map in Figure 6.11 shows this second heating period. There was a reduction in the induction period when the sample was heated for the second time; 60 min in the second compared with 350 min in the first. The temperature at which the decomposition begins also decreases; 305 K compared with 310 K for the first heating period. This supports the classic nucleation and growth model for the decomposition. During the first induction period the initial nucleation of ammonia borane occurs, allowing the ammonium borohydride to decompose. When the sample is reheated after crash-cooling, DADB and ammonia borane will already be present and so there is a reduced induction period before the decomposition continues.

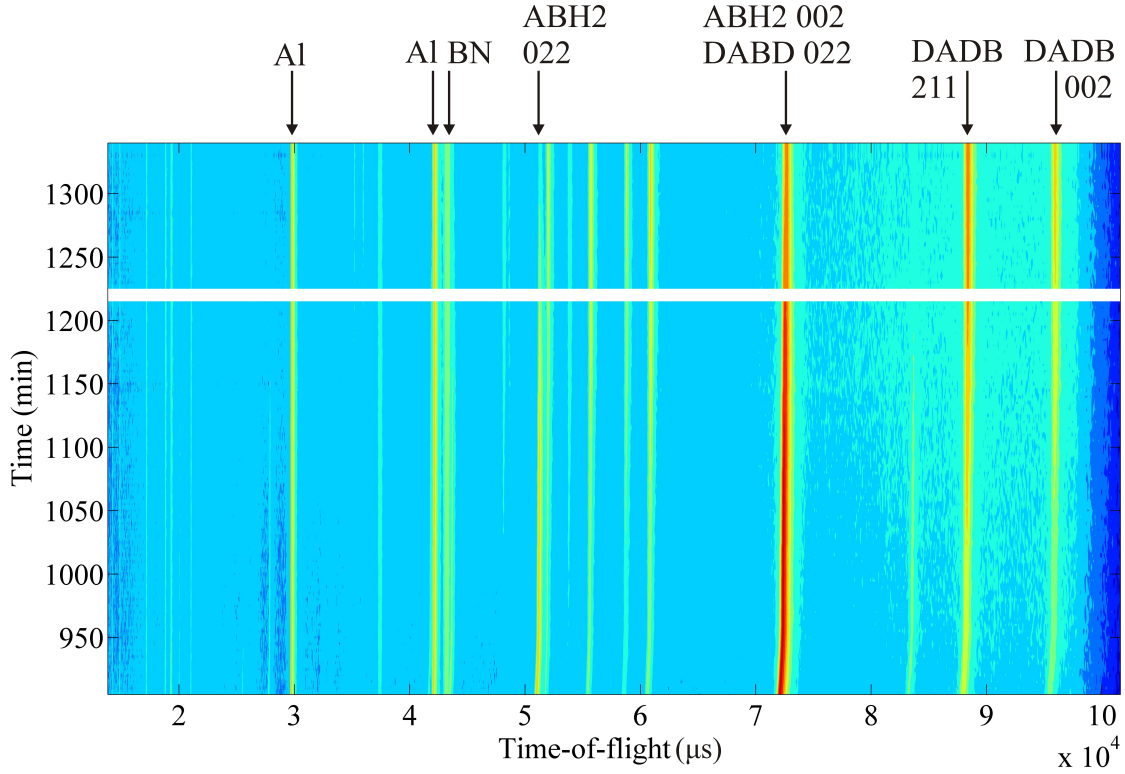


Figure 6.11: Colour map of the decomposition of ammonium borohydride to DADB during the second heating period (905 min to 1340 min). No data were collected during the period 1215 - 1225 min.

6.1.4 Conclusion

The low temperature phases of ammonium borohydride have been investigated using neutron diffraction. The phase progression observed was different to that previously reported by Ryan [103]. The high-temperature cubic phase and the transition temperature from this cubic phase to a lower-temperature rhombohedral phase at 65 K were the same as previously reported. The structure of this rhombohedral phase was solved: it has space group $R\bar{3}m$, with $a = 4.872659(82)$ Å and $c = 23.69317(66)$ Å at 59 K. Around 10 % of the borohydride tetrahedra are disordered, and the nitrogen groups have 12-fold disorder. The unit cell showed increasing strain as the transition to the cubic phase approached. In the slow-cooled sample, a new base temperature phase

was found (monoclinic, space group $P2/m$ $a = 9.69$ Å, $b = 9.76$ Å, $c = 13.67$ Å and $\beta = 89.5^\circ$). In addition to this, a more disordered form of this phase with near identical lattice parameters was found in the crash-cooled sample.

The decomposition of ammonium borohydride was investigated using TGA and neutron diffraction. Ammonium borohydride decomposes above 300 K and there is a reduction in the induction period if the decomposition has previously been interrupted.

6.2 The Inelastic Neutron Spectroscopy of Ammonium Borohydride

Raman spectroscopy of ammonium borohydride has been used to confirm the presence of N–H and B–H bonds in solution [119, 193, 194] and in the solid state [106, 107]. Flacau et al. used Raman spectroscopy to track the phase transitions of ammonium borohydride when subjected to pressures of up to 10 GPa [104].

6.2.1 Experimental Details

INS spectra were recorded on the TOSCA spectrometer, at 4 K, 53 K, 61 K, 80 K, 120 K, 180 K for 6 hours. On heating up to room temperature the sample swiftly decomposed making further measurements impossible. During a second experiment (unfortunately with a smaller sample and therefore with lower intensity), spectra were recorded at 4 K, 120 K, 180 K, 220 K, 250 K. Again higher temperature measurements were not possible due to the decomposition of the sample.

The DFT-MD can be used to calculate the vibration spectra which are usually termed power spectra. The power spectra of NH_4BH_4 , ND_4BH_4 and NH_4BD_4 at 120 K (shown in Figure 6.12) were calculated (for more details of the DFT-MD see Section 6.4.1). The calculated power spectra can be used to assign vibrational modes to the peaks in an experimental spectrum. An X-D bond vibrates at lower energy than an X-H bond, so the signal from an X-D bond occurs at lower vibrational frequencies.

The phonon density of states of ammonium borohydride cannot be calculated since the phases in which it occurs are highly disordered. However, broad regions in the INS spectra can be assigned by comparison with spectra of similar systems.

6.2.2 Simulated Power Spectra

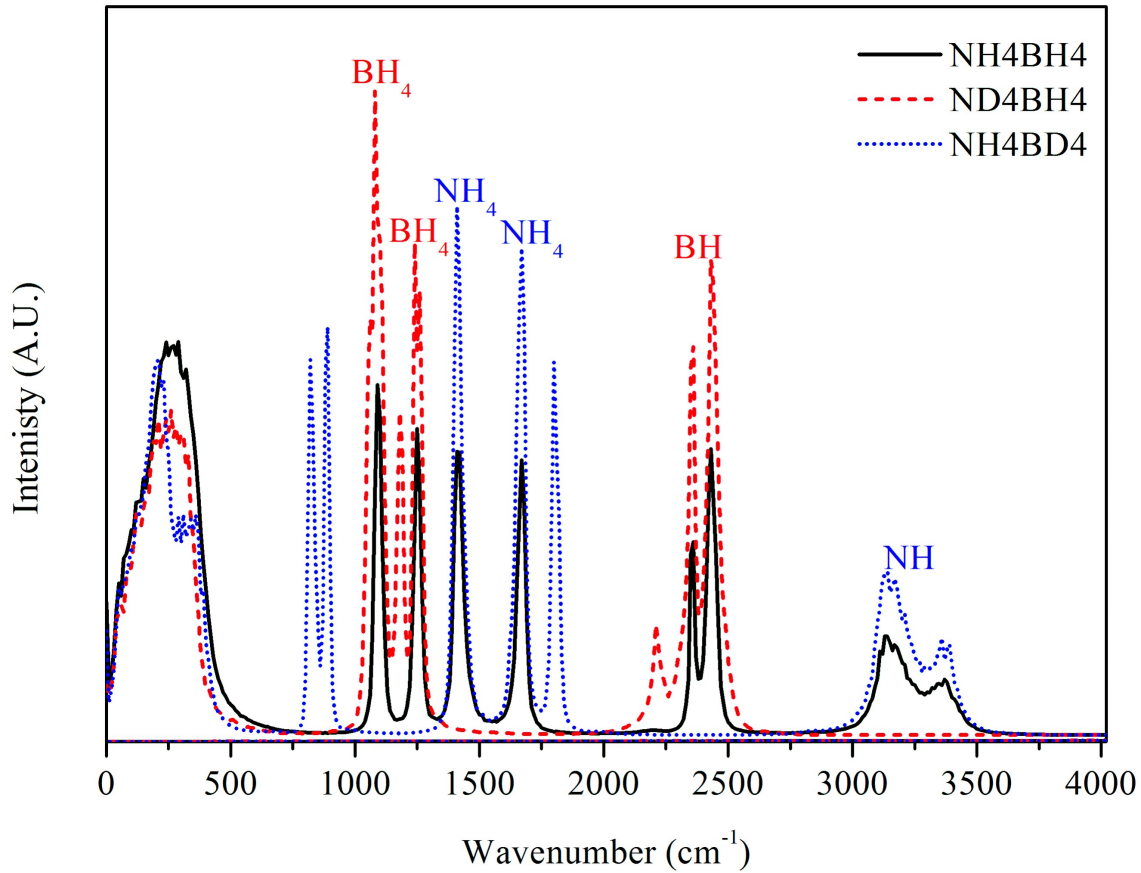


Figure 6.12: The calculated power spectra at 120 K of fully hydrogenated, NH_4BH_4 and partially deuterated, ND_4BH_4 and NH_4BD_4 , ammonium borohydride.

The power spectra of the partially deuterated ammonium borohydride shown in Figure 6.12 can be used to determine whether ammonium or borohydride motions are responsible for particular peaks in the fully hydrogenated spectrum. The initial broad peak in the fully hydrogenated spectrum from 0 cm^{-1} to 500 cm^{-1} results from both NH_4 and BH_4 groups. There is a similar peak in the spectrum of ammonia borane [106] in which the boron group and the nitrogen group motions are highly coupled. In the ammonium borohydride spectrum the BH_4 group contributes slightly more to higher frequencies ($> 250\text{ cm}^{-1}$) and NH_4 to the lower frequencies ($< 250\text{ cm}^{-1}$). This is also

seen in the ammonia borane spectrum.

Between 1000 cm^{-1} and 2000 cm^{-1} there are four peaks which are due to the BH_4 and NH_4 group modes. The first two peaks (at 1090 cm^{-1} and 1250 cm^{-1}) are from the borohydride group. The peak in the ND_4BH_4 spectrum at 1180 cm^{-1} and the broadening of the 1090 cm^{-1} peak are ND_4 motions shifted to lower frequencies compared with NH_4 vibrations. The peaks at 1410 cm^{-1} and 1670 cm^{-1} are due to the ammonium group. In the NH_4BD_4 spectrum, the two borodeuteride peaks occur at lower frequencies: 820 cm^{-1} and 890 cm^{-1} .

The peaks between 2250 cm^{-1} and 2750 cm^{-1} are due to B-H stretching vibrations. There is no signal in the NH_4BD_4 spectrum and in the ND_4BH_4 spectrum the B-H signals are superimposed with the N-D signals. The 2250 cm^{-1} to 3750 cm^{-1} region contains the N-H stretching vibrations; in the NH_4BD_4 spectrum the B-D signals are shifted down to the peak at 1800 cm^{-1} and incorporated into the 1670 cm^{-1} peak.

6.2.3 Experimental INS Spectroscopy

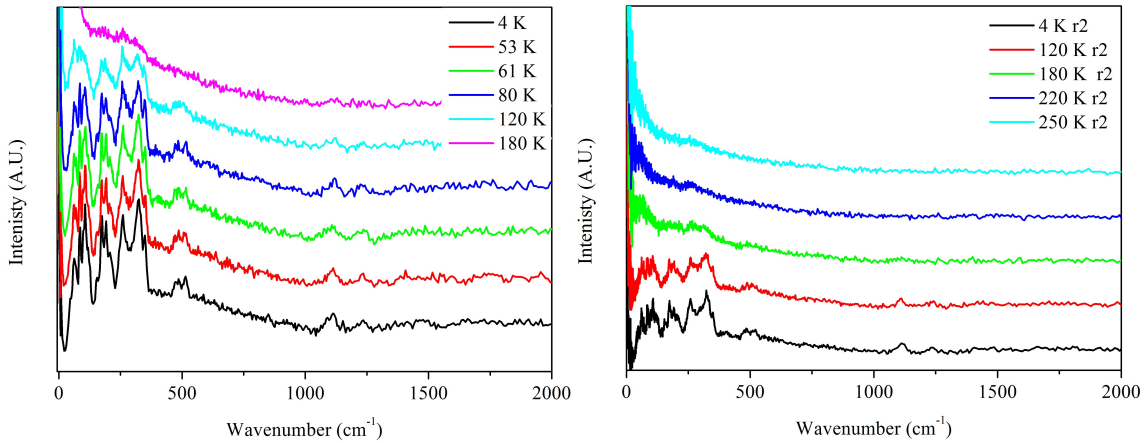


Figure 6.13: Variable temperature experimental INS spectra of ammonium borohydride. Left: first sample. Right: repeat sample.

Figure 6.13 shows the variable temperature experimental INS spectra for ammonium

borohydride. There is good agreement between the two different experiments. The majority of the analysis has been performed using the first experiment due to the higher intensity. The peak resolution begins to reduce above 80 K with the increased background masking all peak structure by 180 K. The majority of this reduction is due to the Debye-Waller factor (see Section 3.2.3), although the onset of rotational hopping motion can also cause a drop in peak intensity. The intensity reduction between the 120 K and the 180 K spectra correlates with the large increase in the rotational motions of the borohydride group (at 160 K) as seen in the QENS experiment reported in Section 6.3.3.

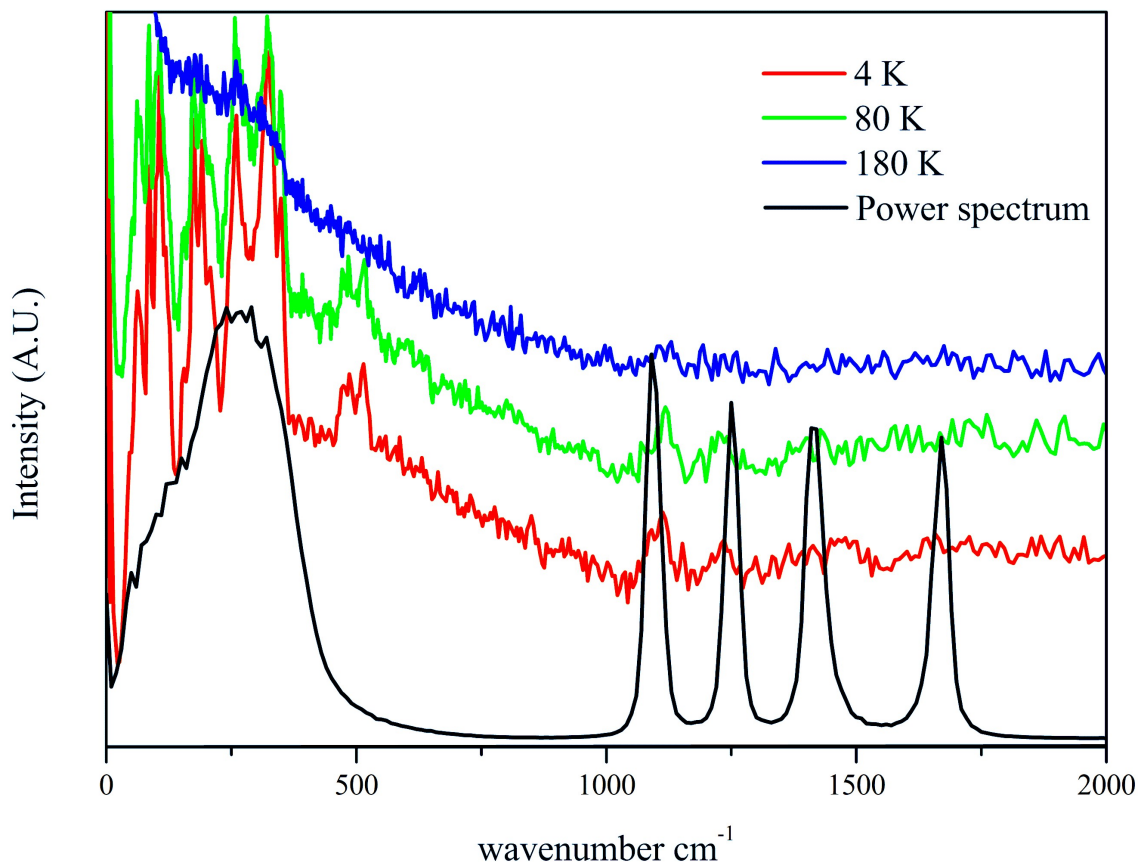


Figure 6.14: Comparison of the calculated power spectrum at 120 K and the experimental INS spectra at 4 K, 80 K and 180 K of NH_4BH_4 .

Figure 6.14 shows a comparison between the calculated power spectra at 120 K

and the experimental spectra at 4 K, 80 K and 180 K of NH_4BH_4 . The molecular dynamics calculations were performed for the high temperature cubic phase of ammonium borohydride at 120 K. Although the structure affects the vibrational modes, the general appearance of the spectra will be similar regardless of the phase. There is good agreement between the calculated and the experimental spectra. The lattice modes at low energy transfers are resolved in the experimental TOSCA spectra, but are represented by a broad peak in the calculated power spectrum. The four borohydride and ammonium group modes between 1000 cm^{-1} and 2000 cm^{-1} are all present in the experimental spectra.

The internal modes of the borohydride and ammonium groups cannot be clearly resolved due to the high background at higher energies. The increase in background at high energy transfers is due molecular motion which is quantified by the Debye-Waller factor. The borohydride group modes are at 1236 cm^{-1} and 1113 cm^{-1} in the experimental spectrum. They can be assigned to the symmetric bend, ν_2 and the antisymmetric bend, ν_4 respectively. The positions of the peaks do not change with temperature and the intensities of the peaks do not decrease until 180 K.

Table 6.3 shows a comparison between the ν_2 and ν_4 modes of ammonium borohydride and group 1 metal borohydrides. Even accounting for the differing temperatures of the experimental spectra, ammonium borohydride fits the general trend of decreasing frequency of the bending mode with increasing cation size, confirming the borohydride peak assignments. Compared with the other borohydride vibrations both the ν_2 and ν_4 modes of ammonium borohydride vibrate at a slightly higher energy. This may be due to the effect of the dihydrogen bonding in ammonium borohydride, which stabilises the B-H bond and increases the vibrational frequency.

The ammonium internal modes are at higher energy transfers and therefore have a further reduced resolution. They can similarly be assigned to the symmetric (ν_2)

Compound	Cation radii (pm) [109]	Spectroscopy technique, Temperature	BH ₄ ν_2 (cm ⁻¹)	BH ₄ ν_4 (cm ⁻¹)
NaBH ₄ [108, 195]	116	INS, 15 K	1287	1136
		Raman, RT	1274	1124
KBH ₄ [108, 195]	152	INS, 15 K	1244	1120
		Raman, RT	1246	1119
RbBH ₄ [108]	166	Raman, RT	1234	1112
NH ₄ BH ₄ (this work)	175	INS, 15 K	1236	1113
		DFT, 120 K	1250	1090
CsBH ₄ [108]	181	Raman, RT	1220	1103

Table 6.3: Comparison of INS and Raman frequencies of the borohydride bending modes of group 1 metal borohydrides and ammonium borohydride.

bending mode at approximately 1700 cm⁻¹ and antisymmetric (ν_4) bending mode at approximately 1480 cm⁻¹. The borohydride ion (206 pm [109]) is closest in size to the iodide anion (203 pm [109]). Conveniently, iodine has the *Fm-3m* space group at room temperature and so can be compared to ammonium borohydride directly. Table 6.4 shows the ν_2 and ν_4 bending modes for ammonium iodide and ammonium borohydride, which are in good agreement.

There are three peaks in the experimental spectra shown in Figure 6.14 (at 486.2 cm⁻¹, 471.9 cm⁻¹ and 514.2 cm⁻¹) which do not appear in the simulated power spectra. These are overtones which are not included in the spectrum simulation. The peaks below 400 cm⁻¹ are external phonon modes, which are difficult to assign without low energy simulations due to the contributions of the entire lattice rather than the internal modes from individual groups. Such simulations have not been attempted due to the difficulty

Compound	Anion radii (pm) [109]	Spectroscopy technique, Temperature	NH ₄ ν_2 (cm ⁻¹)	NH ₄ ν_4 (cm ⁻¹)
NH ₄ BH ₄ (this work)	203	INS, 4 K	approx. 1700	approx. 1480
		DFT, 120 K	1670	1410
NH ₄ I [196, 197]	206	Raman, 85 K	1632	1367
				1383
				1410

Table 6.4: Frequencies of the ammonium bending modes of ammonium borohydride and ammonium iodide. The INS ammonium borohydride frequencies are approximate due to the low resolution at high wavenumbers.

of phonon density state simulations on systems with high disorder.

6.2.4 Summary

Inelastic neutron spectra of ammonium borohydride were collected at a range of temperatures. Power spectra calculated from DFT simulations of partially deuterated ammonium borohydrides were used to assign vibrational modes to the experimental spectra. Further assignments were possible by comparison with similar compounds. Low energy lattice modes could not be assigned due to the difficulty of performing phonon density calculations on systems which are highly disordered.

6.3 Quasielastic Neutron Spectroscopy of Ammonium Borohydride

6.3.1 Theory

Quasielastic neutron scattering, QENS uses low energy neutrons to investigate the rotational and translational motions of molecules. It is the limiting case of inelastic neutron spectroscopy: QENS studies the area of the spectrum close to the elastic line. The energy transfers between the neutrons and the atoms of the sample are small, typically ± 2 meV. These correspond to motions of particles on a time scale of 1 - 100 ps.

A QENS spectrum generally consists of an elastic line, where the neutrons have been scattered completely elastically and quasielastic scattering which causes broadening of the elastic line. The typical time scale that is accessible using QENS is so short that no long-range translational diffusion will contribute to the scattering law, $S(Q, \omega)$. Therefore, assuming only reorientational motion contributes:

$$S(Q, \omega) = A_0(Q)\delta(\omega) + \sum_{j=0}^n A_j(Q)L_j(\omega) \quad (6.2)$$

where $A_0(Q)$ is the elastic incoherent structure factor (EISF) see Equation 6.4, $\delta(\omega)$ is a delta function which describes the elastic scattering, $A_j(Q)$ is the quasielastic structure factor and $L_j(\omega)$ is a Lorentzian function used to fit the quasielastic scattering. The experimental spectra can be related to the scattering law by convolution with the instrument resolution, $R(Q, \omega)$:

$$S_{exp}(Q, \omega) = R(Q, \omega) \otimes \left(A_0(Q)\delta(\omega) + \sum_{j=0}^n A_j(Q)L_j(\omega) \right) \quad (6.3)$$

The EISF can be used to determine the geometry of the reorientations:

$$\text{EISF} = \frac{I_{el}}{I_{el} + I_{inel}} \quad (6.4)$$

where I_{el} and I_{inel} are the elastic and inelastic intensities respectively.

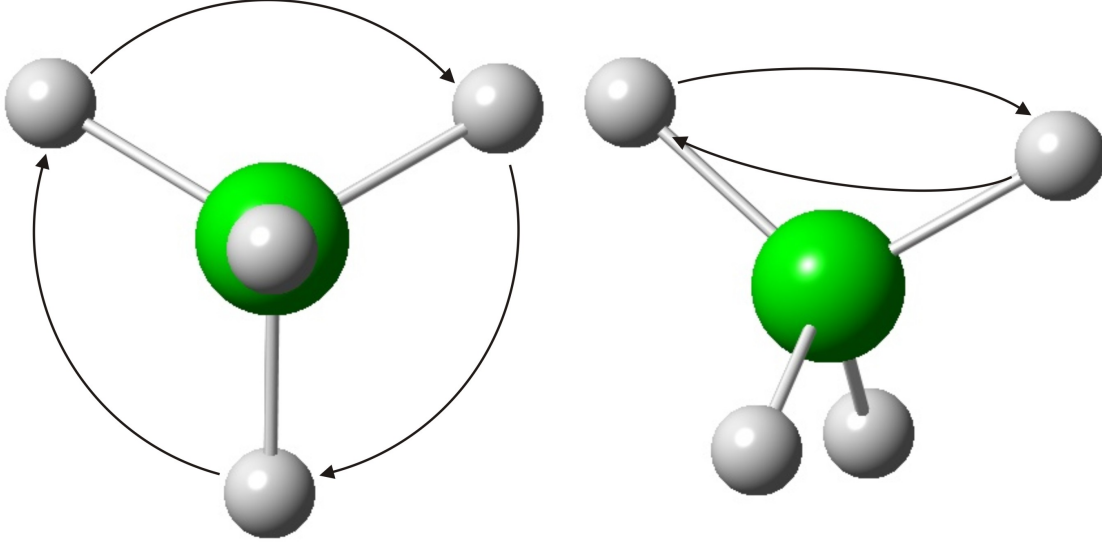


Figure 6.15: Schematic showing the 3-site (left) and 2-site (right) jumps of a tetrahedral group.

Considering only the tetrahedral geometry of the borohydride and ammonium groups there are two types of rotation (see Figure 6.15):

- Three 2-fold axes running between the bonds, which will cause all of the hydrogen atoms to change position.
- Four 3-fold axes running along each of the bonds, with three hydrogen atoms exchanging positions and the hydrogen atom on the axis remaining stationary.

In the special case of a tetrahedral group, the EISF of a rotation around one of the C_3 or one of the C_2 axes is the same (Equation 6.5), because the jump distance is identical for both of the rotations, and one of the hydrogen atoms is immobile during the 3-fold

jump [198]. The EISF for this case is:

$$\text{EISF} = \frac{1}{2}[1 + j_0(Qd)] \quad (6.5)$$

where Q is the neutron momentum, d is the distance between the sites that the hydrogen atom is jumping to/from and $j_0(x) = \frac{\sin x}{x}$, the zeroth order spherical Bessel function. The immobility of a hydrogen atom in the C_3 rotation would allow one hydrogen bond to remain unbroken, suggesting that this would be a lower-energy rotation than the C_2 rotation (in which all four hydrogen bonds would be broken).

The 2-fold and 3-fold rotations can also occur at the same time; in which case the positions of all the atoms will change. The EISF would then be the product of the 2-fold and the 3-fold jumps:

$$\text{EISF} = \frac{1}{4}[(1 + j_0(Qd))(1 + j_0(Qd))] \quad (6.6)$$

If the rotation axis changes, either changing among the C_2 or C_3 axes or between them, the EISF would then be:

$$\text{EISF} = \frac{1}{4}[1 + 3j_0(Qd)] \quad (6.7)$$

If the high temperature structure of ammonium borohydride (Figure 6.16) is also considered there are other rotations which can occur. There are two possible conformations of the borohydride group giving eight hydrogen sites, at the eight vertices of a cube. Each BH_4 could remain in one tetrahedral position and reorient along the C_2 or C_3 axes (as above), or there could be a 4-fold rotation along the tetrahedral 2-fold axis allowing hopping between all eight corners of the cube. During the C_2 or C_3 reorientations the conformation of the borohydride group is the same at the beginning and the

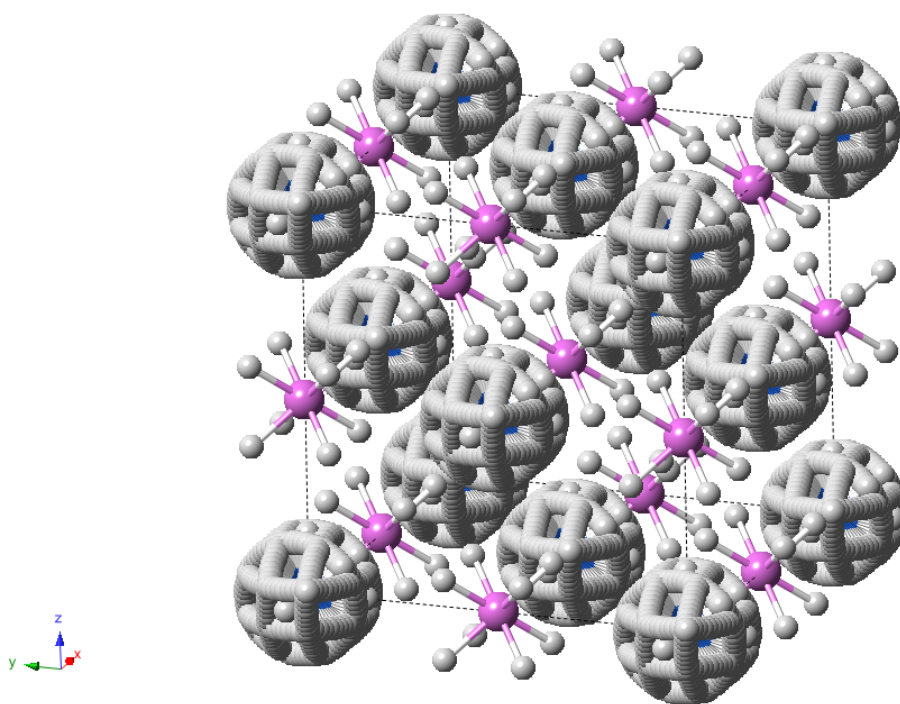


Figure 6.16: Structure of the high temperature cubic phase of ammonium borohydride. High levels of hydrogen disorder, and therefore the larger number of hydrogen atom positions, make the borohydride ions appear as ‘hydrogen spheres’. Boron atoms in pink, nitrogen atoms (mostly hidden), blue and hydrogen atoms, grey.

end of the rotation meaning there is no overall energy change. However in the 4-fold rotation the borohydride group changes from one conformation to the other meaning the starting and the end conformation will be different energies.

The symmetry of the ammonium site means that there are 48 possible tetrahedral positions and 192 hydrogen atom sites. The hydrogen atoms of an ammonium ion could be visiting every possible site, effectively freely rotating on the surface of a sphere. However, it is unlikely that all of the hydrogen bonds which hold the structure together would be broken during such a rotation. If one hydrogen atom remains stationary, and one hydrogen bond remains unbroken, the other hydrogen atoms could reorient around a three-fold axis as described above. Alternatively, the large number of possible hydrogen sites might allow higher-order rotations around the C_3 axis.

The intensity of the elastic line, usually termed the elastic window scan, can be used to determine how the quasielastic motion varies with temperature. At low temperatures, the elastic intensity will generally have a gentle downward gradient with respect to increasing temperature, as the lattice vibrations (associated with the Debye-Waller factor) increase (for examples see Figure 6.17). Then there will be a swift drop in elastic intensity as the reorientational motions begin. At higher temperatures, the quasielastic signal will broaden to the extent that it becomes part of the background and the Debye-Waller behaviour will again dominate.

There has, to date, been one previous study of the dynamics of ammonium borohydride. Solid state ^1H and ^2H NMR of NH_4BH_4 [107] showed a single narrow signal indicating that the ions reorient rapidly in a pseudo-isotropic manner (relative to the NMR time-scale), $\ll \sim 1.5 \times 10^6 \text{ s}^{-1}$. The activation energies were calculated using the spin-lattice relaxation time, T_1 . It was not possible to separate the motions of the two ions, so the activation energies calculated were an average of the two motions. $E_a = 11.5 \pm 0.1 \text{ kJ mol}^{-1}$ and $E_a = 10.7 \pm 0.1 \text{ kJ mol}^{-1}$ for ^1H and ^2H respectively. The barriers of each individual group were calculated at rather higher values since no cooperative interactions were included in the calculations: 20.1 - 37.4 kJ mol^{-1} for BH_4 and 16.3 - 19.5 kJ mol^{-1} for NH_4 . The authors of this study also suggested the possibility of tunnelling at low temperatures.

6.3.2 Experimental

A QENS experiment was performed on Iris, a time-of-flight spectrometer at ISIS. Three Q ranges were used: 0.42 meV to 1.85 meV (with a high resolution of 17.5 μeV), a wider Q range of -3.5 meV to 4 meV with a lower resolution of 54.5 μeV and reduced intensity, and a range which extends to high Q values of -0.3 meV to 7.2 meV with a resolution of 17.5 μeV to determine if tunnelling was occurring. The samples were

sealed in aluminium sachets and packed into annular vanadium cans in a nitrogen glove bag. They were loaded onto gas handling centre sticks and kept at 195 K in dry ice until they could be loaded into the Iris Closed cycle refrigerator (CCR) at 200 K.

Hydrogen has a much higher incoherent scattering cross section than any other element and therefore if it is present in a sample it will dominate any QENS signal. The incoherent scattering cross section of deuterium is 40 times lower than that of hydrogen. Therefore deuterating part of a sample will effectively remove the signal from the deuterated group(s) allowing the remaining parts of a molecule to be studied separately. Three samples were studied: the ammonium and borohydride groups were separately deuterated in different samples (ND_4BH_4 and NH_4BD_4) to allow the remaining hydrogenated groups to be studied separately. A fully hydrogenated sample (NH_4BH_4) was also measured to check for any deuteration effects.

For each sample a series of long (600 μA) and short (20 μA) spectra were recorded: long scans for detailed analysis and shorter scans to ensure there were enough data for elastic window scans. Due to time constraints, only high resolution 0.42 meV to 1.85 meV Q -range data were collected for ND_4BH_4 . After the data were reduced using MANTID [199], the spectra were fitted using DAVE [200]. A constant background was assumed. The elastic scattering component was fitted using a delta function, and the inelastic component was fitted using between one and three Lorentzian functions. Both the elastic and inelastic functions were convoluted with a base temperature spectrum of the same sample to account for the instrument resolution.

6.3.3 Results and Discussion

Figure 6.17 shows the elastic window scans. The ammonium group begins to reorientate at 30 K. This is similar to the reorientation temperature for ammonium ions in a tungsten trioxide framework [201]. However it is considerably lower than for the ammonium

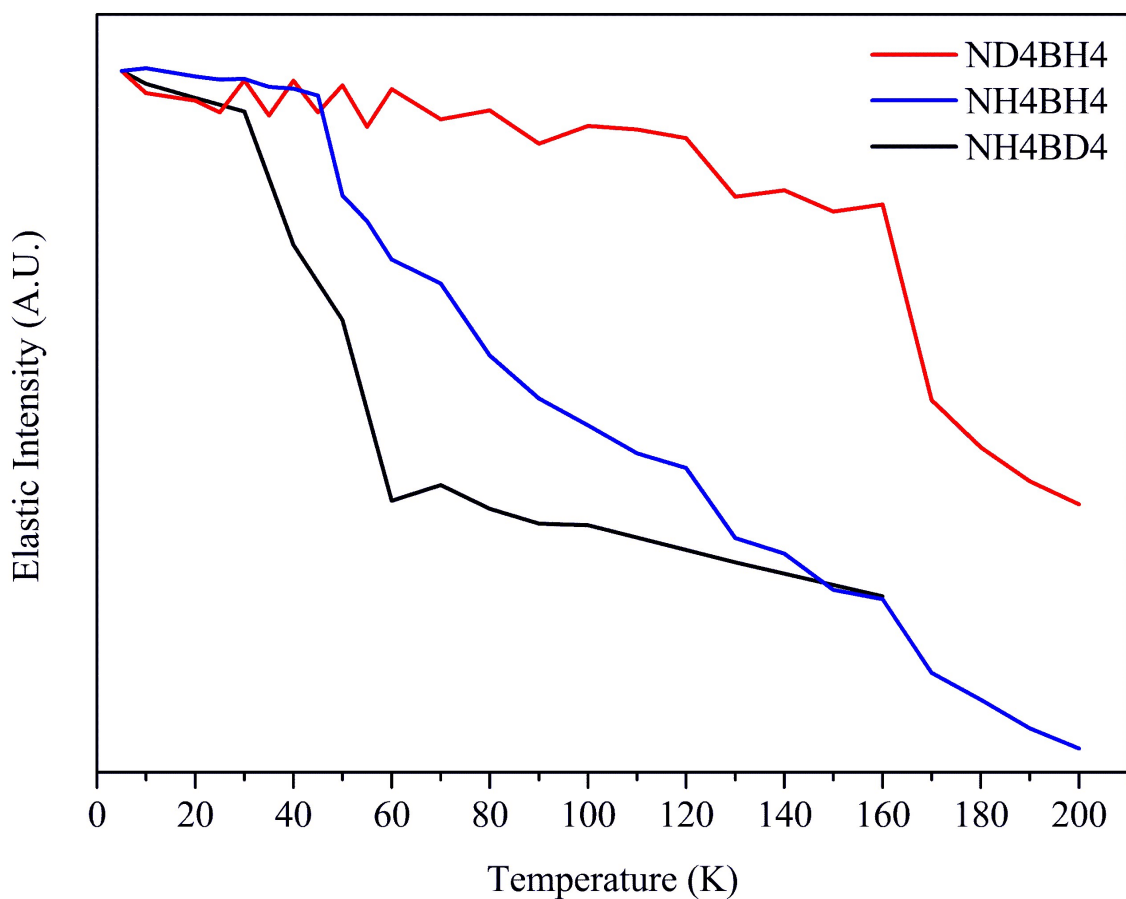


Figure 6.17: Elastic window scans for ND_4BH_4 (red), NH_4BD_4 (black) and NH_4BH_4 (blue) normalised to allow comparison.

ions in ammonium chloride [202] and ammonium cyanide [203], both of which begin to move at ~ 200 K. The borohydride group begins to reorientate at 160 K. This is at a considerably higher temperature than the borohydride group in $\text{Ca}(\text{BH}_4)_2$ which begins to reorientate at 90 K [204]. The reorientation of the nitrogen and boron containing groups in ammonia borane follow a similar trend, with the ammonia groups beginning to reorientate at approximately 60 K and the borane group at approximately 100 K [52, 179].

The reduction in elastic intensity in the fully hydrogenated sample occurs at 45 K (see Figure 6.17). The higher temperature of the initial movement in the hydrogenated

analogue (45 K *vs* 30 K in the partially deuterated analogue) is likely to be a deuteration effect. The motion of the borohydride group in the ND_4BH_4 (red line in Figure 6.17) and NH_4BH_4 (blue line) samples is still increasing at 200 K, but higher temperatures measurements were not attempted due to the instability of ammonium borohydride above 220 K.

Borohydride Reorientations

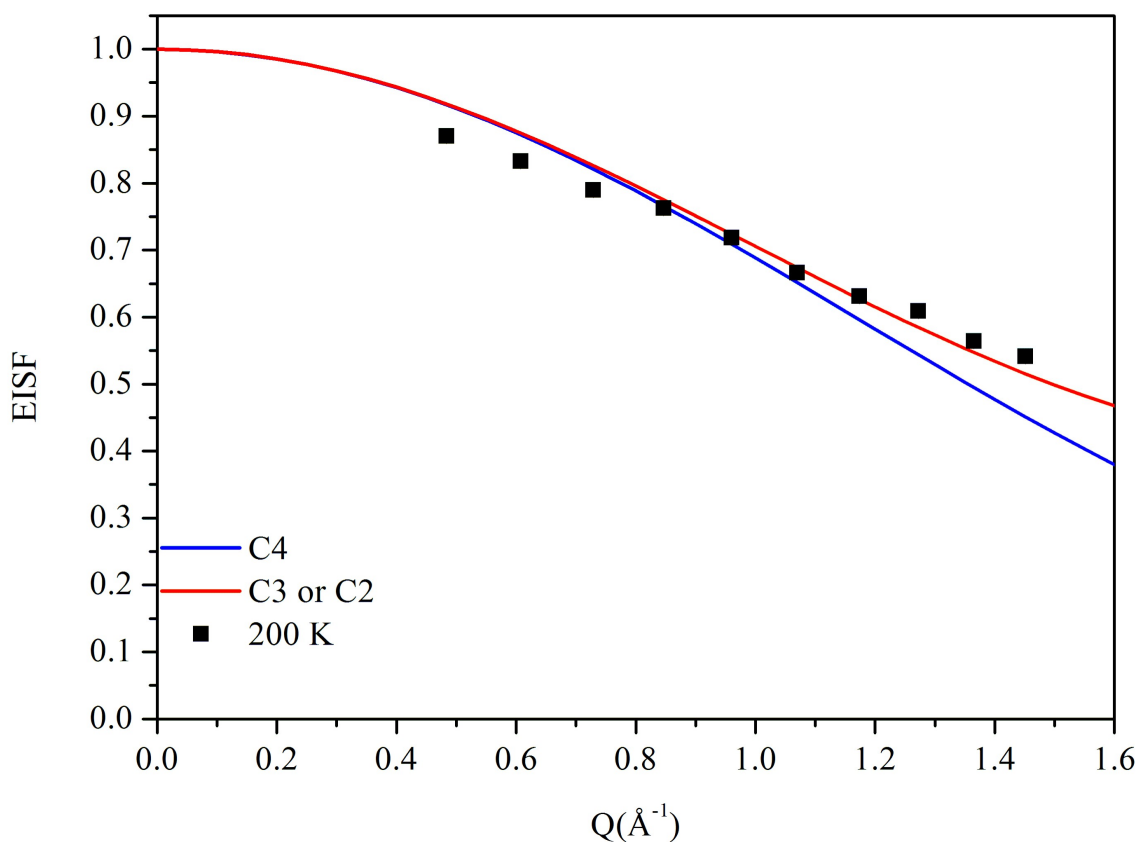


Figure 6.18: The observed EISF for ND_4BH_4 at 200 K with the EISFs calculated from the C_3 or C_2 and the C_4 models.

For the ND_4BH_4 sample, at temperatures below 80 K the scattering is predominantly elastic. Above 80 K, a single Lorentzian is required to fit the inelastic component. The width of the Lorentzian is independent of Q and therefore the inelastic component is

entirely due to molecular reorientations rather than diffusional motion. Various models of the rotation were considered; the closest fits were the C_3 or C_2 model, and the C_4 model shown in Figure 6.18. The C_3 or C_2 model produced the best fit. The jump distance was $2.1(1) \text{ \AA}$ which corresponds to a B-H bond distance of $1.29 \text{ \AA}$. This is comparable to the B-D bond distance of $1.225 \text{ \AA}$ at 80 K from neutron diffraction of ND_4BD_4 .

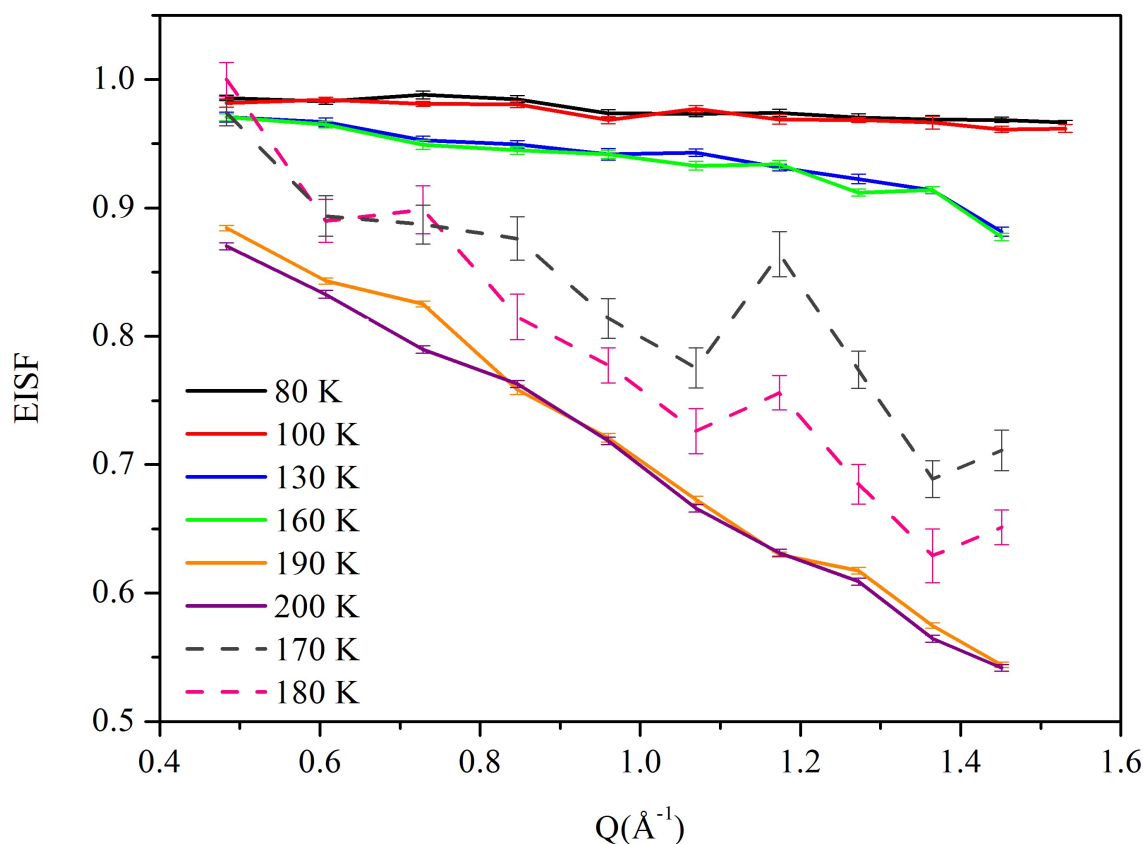


Figure 6.19: The observed EISF for ND_4BH_4 at temperatures between 80 K and 200 K. The solid lines are from longer scans and the dashed lines are from shorter, lower resolution spectra and should only be considered as indications of behaviour.

At lower temperatures not all of the borohydride groups are moving, so there is a reduced quasielastic contribution to the EISF, see Figure 6.19. At the two lowest temperatures, 80 K and 100 K, the fraction of reorientating groups is very low (8.1 %). At the next two temperatures, 130 K and 160 K, this percentage increases to 21.7 %

and by 190 K 100 % of the groups are reorientating. This is consistent with the elastic window scan (Figure 6.17) where there is no discernible decrease below 120 K but a small drop between 120 K and 160 K when a significant fraction of the borohydride groups are beginning to reorient. Above 160 K, there is a sharp drop in the elastic scan which indicates that an increasing number of groups are reorientating. The EISFs of the lower resolution spectra have been included in Figure 6.19 as an indication of the increasing percentage of borohydride ions moving at 190 K compared with at 160 K.

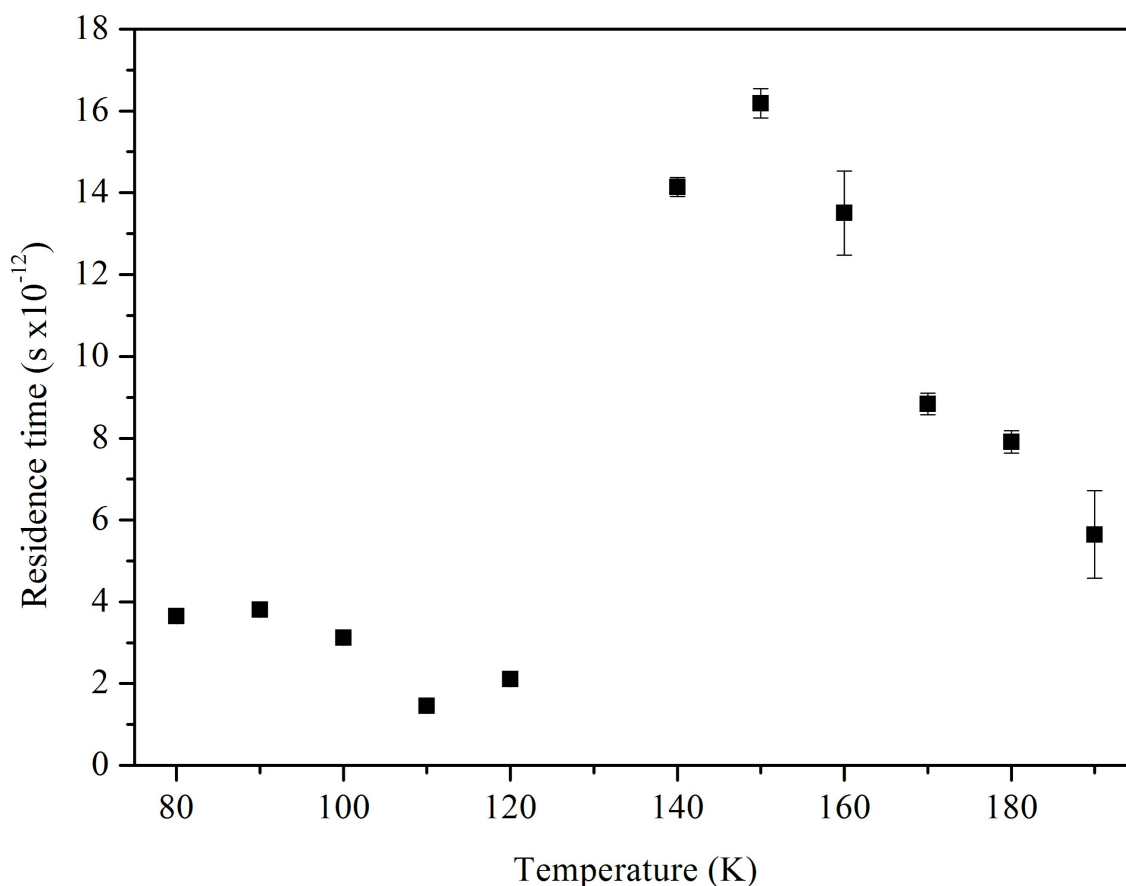


Figure 6.20: The temperature dependence of the mean residence time between hops of the borohydride group assuming a C_2 mechanism.

The mean residence time, the average length of time a hydrogen atom spends in a site before it moves to the next site, can be calculated from the Q -independent half-width-half-maximum of the Lorentzian used to model the quasielastic signal. The rates

for the C₂ and C₃ rotations can be calculated using Equations 6.8 and 6.9 respectively:

$$\tau_2 = \frac{2\hbar}{\Gamma_{C2}} \quad (6.8)$$

$$\tau_3 = \frac{3\hbar}{2\Gamma_{C3}} \quad (6.9)$$

where τ is the residence time, and Γ is the half-width-half-maximum of the Lorentzian.

The residence times follow Arrhenius behaviour, so the activation energy of the motion can be calculated using a form of the Arrhenius equation:

$$\tau = \tau_0 \exp\left(\frac{E_a}{RT}\right) \quad (6.10)$$

where τ_0 is a pre-factor constant, E_a is the activation energy, R is the universal gas constant and T is the temperature.

Figure 6.20 shows the temperature dependence of the hopping rate of the C₂ rotation of BH₄ (the C₃ rotation would clearly show the same trend). The data unexpectedly show that there are two temperature regions with two different activation energies and rate constants, as shown for the C₂ and the C₃ rotations in Table 6.5. The low temperature region from 80 K to 120 K has a lower activation energy (1.6 kJ mol⁻¹) than the higher temperature region from 130 K to 200 K (which has an activation energy of 4.4 kJ mol⁻¹). Flacau et al. [104] calculated much larger values for the activation energy of the ammonium group: 20.1 - 37.4 kJ mol⁻¹. However they did point out these were upper limits and cooperative motions would cause experimental values to be lower. The most likely cause of a change in the rate constant is a phase transition, which would modify the potential energy environment around a group. However, as shown by multiple diffraction experiments, ammonium borohydride does not undergo a phase transition above 60 K (Section 6.1 and [103]).

Type of Reorientation	Temperature range (K)	Activation energy (kJ mol ⁻¹ /eV)	Pre-factor constant (ps)
C ₂	80 - 120K	1.62/0.017	3.64
C ₂	130 - 200K	4.42/0.046	3.71
C ₃	80 - 120K	1.62/0.017	2.73
C ₃	130 - 200K	4.42/0.046	2.78

Table 6.5: The activation energies and pre-factor constant for the two different temperature regions for the C₂ and C₃ reorientations.

The transition in the rotation rates occurs between 120 K and 130 K. This coincides with the increase in the percentage of reorientating groups evident from the change in EISF (see Figure 6.19). It is possible that, at low temperatures, a rotational mode with a low activation energy is occurring with only a small percentage of the borohydride groups in motion. Then, at higher temperatures a second rotational mode becomes active and the quasielastic signal from the first (weaker) mode becomes obscured by the second mode, in which a much greater percentage of groups are moving.

The EISF suggests a C₂ or a C₃ rotation. Given the lower energy of the C₃ rotation, it is most likely that the first low temperature rotation is around the C₃ axis, allowing one hydrogen bond to remain intact. At higher temperatures, there is sufficient energy to break the fourth hydrogen bond and so rotation around the C₂ axis dominates.

Ammonium Reorientations

As shown by the elastic window scan, the ammonium groups start reorientating at 30 K (see Figures 6.17 and 6.21). After an initial heating run, the NH₄BD₄ sample was cooled back to 30 K to increase the number of temperature points at the beginning of the reorientation. However, the difference in the results of the second set of temperature

measurements compared with the original heating run again highlights how dramatically the thermal history affects the behaviour of ammonium borohydride (see Section 6.1).

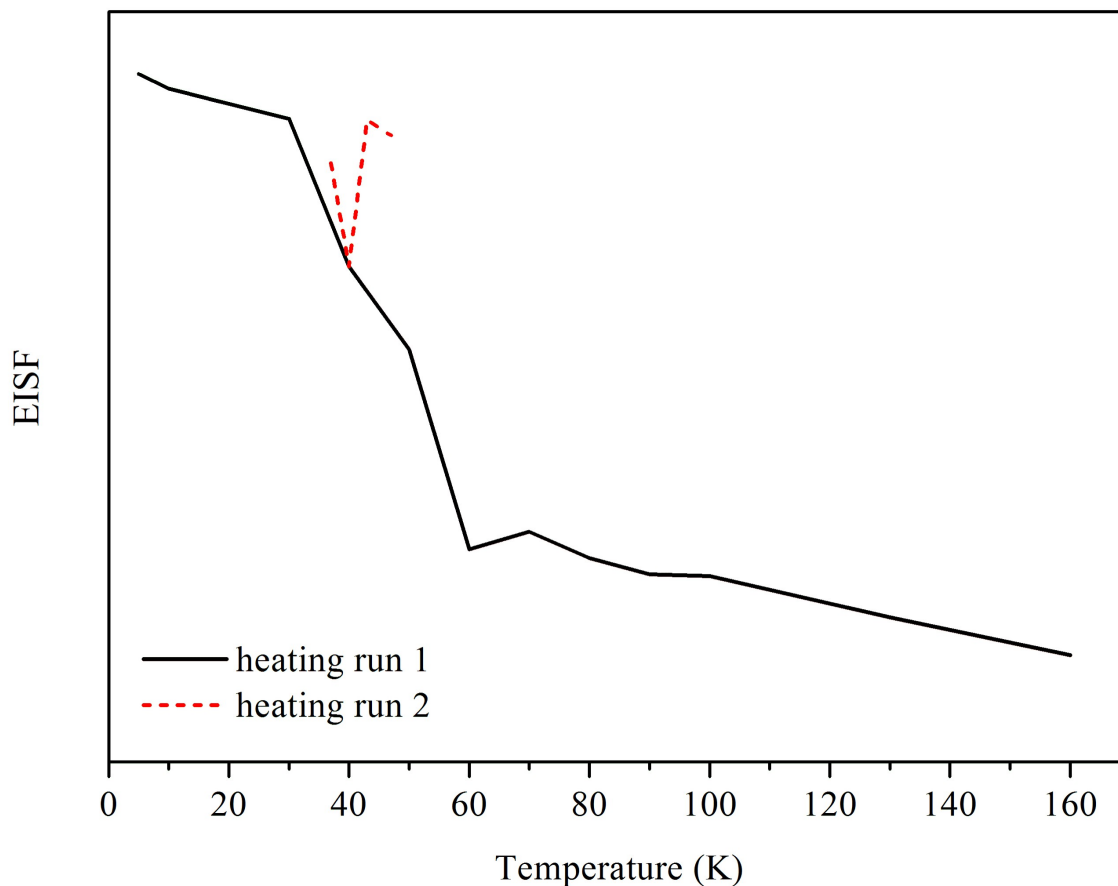


Figure 6.21: The elastic window scan of NH_4BD_4 for the first (black line) and second (broken red line) heating runs.

The diffraction patterns of NH_4BD_4 measured concurrently with the QENS data are shown in Figure 6.22. During the first temperature run, above 60 K only the high temperature cubic phase was present. Below 50 K the sample is in the rhombohedral phase. On the second temperature run, the sample was cooled to 37 K and it transformed back to the rhombohedral phase. As the temperature was increased to 47 K it reverted to one of the ordered trigonal low temperature phases. Due to the small number of peaks and the low resolution of the diffraction data the exact structure of the phase could

not be determined. The progression of phases is similar to that found during neutron diffraction on WISH (see Section 6.1) but most closely follows the experiments reported by Ryan [103].

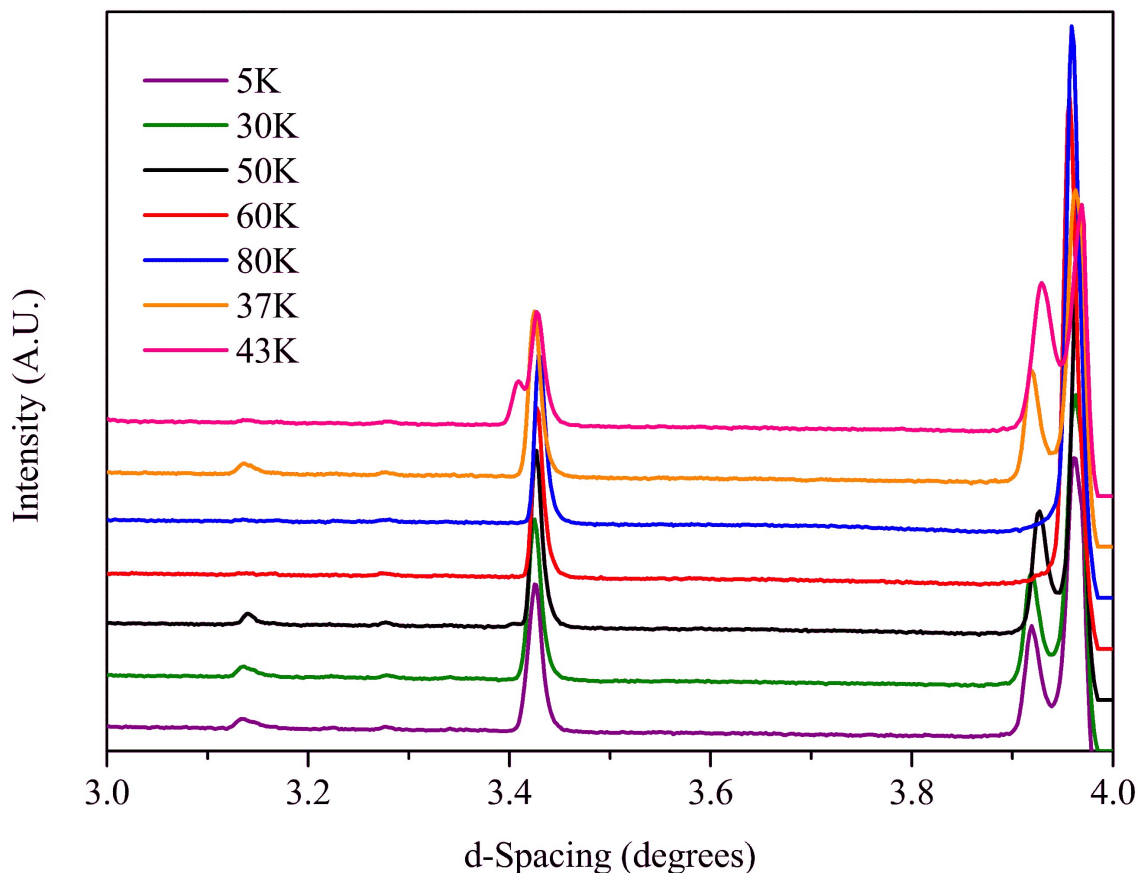


Figure 6.22: Variable temperature neutron diffraction of NH_4BD_4 recorded simultaneously with the quasielastic spectra using the diffraction detectors of the Iris spectrometer.

The effects of the different phases can also be seen in the elastic window scan, Figure 6.21. For the first temperature run the ammonium groups start to rotate at 30 K and reach a maximum at 60 K where the low temperature rhombohedral phase converts to the high temperature cubic phase. During the second run, where the sample is in the rhombohedral phase, the elastic intensities are similar to the first run, as would be expected. After the phase transition to the trigonal phase the elastic intensity increases,

indicating a decrease in the rotation of the borohydride groups. At 100 K and above, the quasielastic signal has broadened to the extent that it can no longer be distinguished from the background.

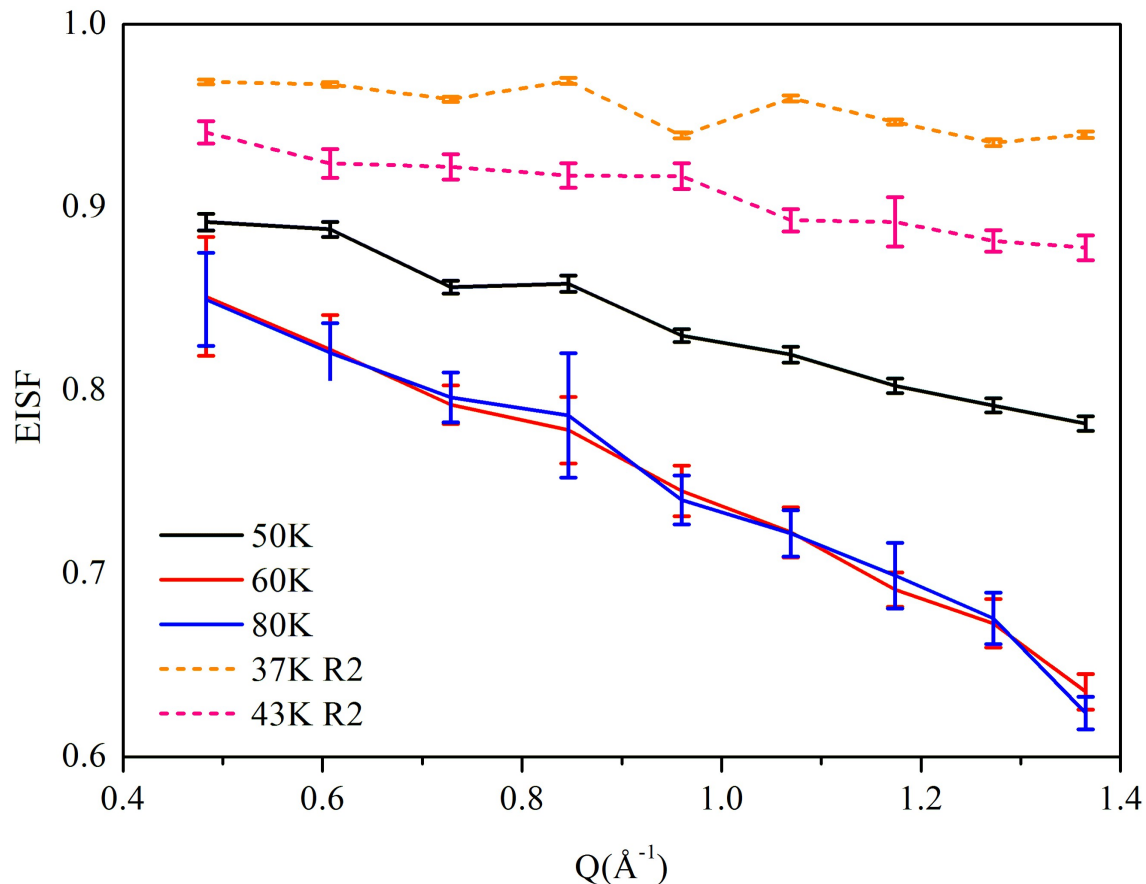


Figure 6.23: The observed EISFs for NH_4BD_4 . The solid lines are from the initial heating experiment, the dot-dash lines are from the second heating run.

Fitting of the observed EISFs for the ammonium group was not as straightforward as for the borohydride group. For the ammonium group at temperatures below 47 K one EISF was used to fit the quasielastic signal. At higher temperatures two Lorentzians were required. The widths of the Lorentzians were independent of Q and therefore the motion is entirely reorientational. Two Lorentzians would indicate four-fold rotation, however the calculated EISF for a 4-fold rotation along the 2-fold axis is a poor fit for the experimental data.

The observed EISFs do not extrapolate to unity at $Q = 0 \text{ \AA}^{-1}$; most likely due to multiple scattering. The synthesis methods used meant that the NH_4BD_4 and NH_4BH_4 samples had a higher purity than the ND_4BH_4 sample. The increased concentration of hydrogen (the element with the largest neutron scattering cross section) in the purer samples would be expected to increase the amount of multiple scattering. Multiple scattering generally affects scattering at low Q more than at high Q and therefore fits will deviate more from the experimental data at low Q . Figure 6.24 shows the best-fitting calculated EISF: at both 50 K and 80 K the best fit is C_2 or C_3 rotations with a jump distance of $1.6(1) \text{ \AA}$. This equates to a bond distance of $0.98 \text{ \AA}$. This is in good agreement with the N-D bond length of $1.05 \text{ \AA}$ from the neutron diffraction of ND_4BD_4 and N-H bond lengths in similar compounds (Section 6.1 and [192]). At 50 K, approximately 30 % are reorientating and at 80 K all of the ammonium groups are reorientating. The other possible rotations considered were free rotation of all four hydrogen atoms on the surface of a sphere, C_2 or C_3 rotations occurring at the same time, and high order rotation around the C_3 axis. However, for a good fit to the calculated EISF, it has to be assumed that a proportion of the groups are not rotating. At 80 K, where the EISF have reached a maximum this is considered to be unlikely given the high mobility of the ammonia group.

The C_3 or C_2 rotation would give quasielastic scattering profile which could be fitted using a single Lorentzian. However, two Lorentzians were required to fit the data at higher temperatures. The extra Lorentzian could be fitting another process which is occurring but which cannot be resolved from the data. The second Lorentzian could also be an extra background function necessary because of the multiple scattering. Both of the Lorentzians are approximately 10 times broader than the Lorentzian fit to the ND_4BH_4 sample. The mean residence times for the ammonium groups are approximately $10^{-14} - 10^{-15} \text{ s}$ compared to $10^{-11} - 10^{-12} \text{ s}$ for the borohydride group.

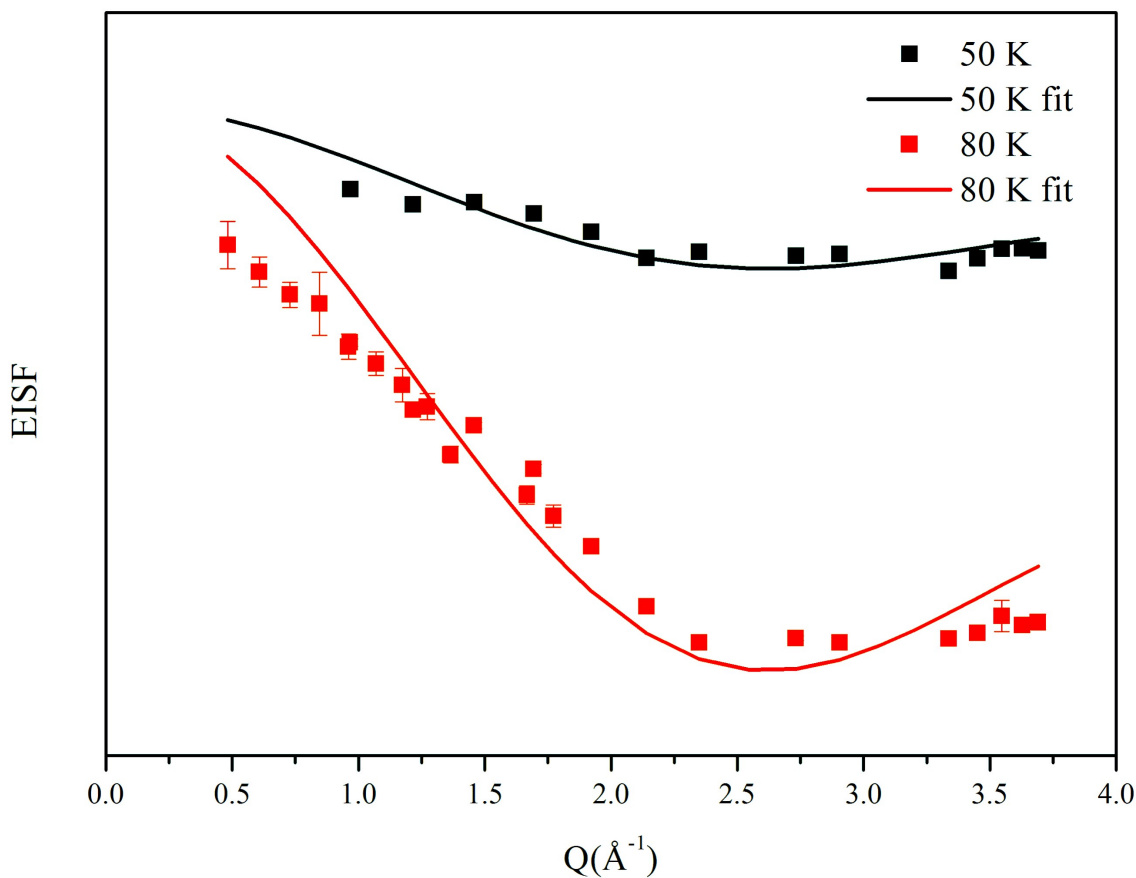


Figure 6.24: The observed EISF for NH_4BD_4 at 50 K and 80 K with the EISF calculated for the C_3 or C_2 rotation.

Activation energies for the ammonium group motions are approximately $1 - 2 \text{ kJ mol}^{-1}$, again considerably lower than those previously calculated [104]. The fast motion and lower activation energy of the ammonium group is consistent with the faster motion of the ammonia/ammonium group in other systems [52, 179]. This increased mobility is due to the smaller size of the ammonium cation relative to the borohydride anion (175 pm compared with 203 pm), which allows the ammonium ion to rotate more easily than the larger borohydride ion.

Fully Hydrogenated Ammonium Borohydride

A full hydrogenated sample, NH_4BH_4 was also measured to ensure that the effects of deuterating part of the sample are minimal. The elastic window scan (Figure 6.17) has already shown that deuteration has an effect on the onset of the ammonium reorientations; increasing it from 30 K to 45 K. This is because deuteration strengthens the dihydrogen bonding network [205], hence increasing the energy barrier for rotational motion.

Assuming the temperatures at which the reorientations of the ammonium and borohydride groups in the partially deuterated compounds occur are similar to the temperatures at which the reorientations occur in the fully hydrogenated compound, there will be no overlap in the temperature windows of the motions of the ammonium and borohydride groups. The ammonium groups begins to reorientate at 30 K and by 100 K the quasielastic signal has become too broad to discern from the background. Only above 100 K does a substantial proportion of the borohydride groups begin to reorientate.

Due to the multiple scattering at high temperatures, fits have been performed using only the the $Q = -3.5 - 4$ meV data above $1.2 \text{ \AA}$, data and fits are shown in Figure 6.25. At 50 K, only the ammonium group will be reorientating: the C_2 or C_3 EISF for the ammonium group fits the data with a fraction of 17 % mobile hydrogen atoms. If the stationary borohydride groups are taken into account, this indicates that around 34 % of the ammonium groups are reorientating. This corresponds well with the approximately 30 % of the ammonium groups reorientating at 50 K in the NH_4BD_4 sample.

At 120 K in the deuterated samples approximately 27 % of the borohydride groups are reorientating, as is 100 % of the ammonium groups (however it is no longer detectable in the data). The NH_4BH_4 EISF at 120 K does not fit well to a model which only includes the borohydride group motions. Due to the higher temperature of initial reorientation and the increased interactions between the ions in the hydrogenated

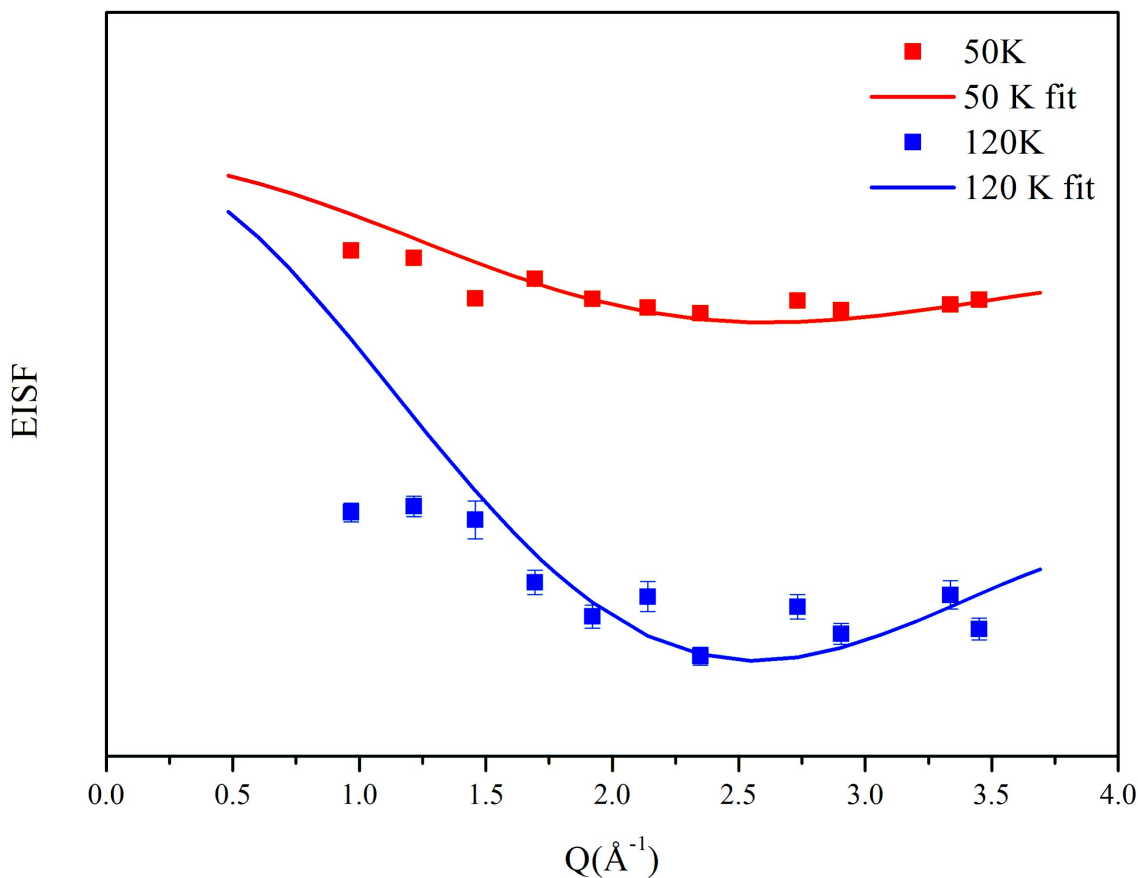


Figure 6.25: Observed and calculated EISFs for NH_4BH_4 at 50 K and 120 K.

sample, the ammonium groups may still contribute to the quasielastic scattering. If it is assumed that all the ammonium groups are reorientating and contribute to quasielastic scattering, the calculated EISF shown in Figure 6.25 indicates that 24 % of the borohydride groups are also reorientating, which is in reasonable agreement with the 22 % of the borohydride groups which are reorientating at 120 K ND_4BH_4 data.

Data were also collected over a wider Q range (-1.3 - 7.2 meV) for the NH_4BH_4 sample at 5 K to determine whether there was any tunnelling occurring during the rotations, but no evidence of this was found.

6.3.4 Summary

Quasielastic neutron scattering has been used to show that both the ammonium and borohydride groups in ammonium borohydride reorientate along the C_2 or the C_3 axis. Unfortunately, due to the tetrahedral geometry of the ammonium and borohydride ions the EISF C_2 and C_3 reorientations are identical and so it cannot be determined which of these two motions is occurring.

In the borohydride group motions are first observed at temperatures above 80 K. Above 190 K, all of the borohydride groups are in motion. The mean residence time shows an unusual discontinuity between 120 K and 130 K with differing activation energies before and after; possibly due to conversion from C_3 to C_2 rotation.

The NH_4BD_4 data indicated considerable multiple scattering. However, reorientation starts at 30 K and the predominant type of movement occurring was again C_2 or C_3 rotations. A second temperature run highlighted the effect of thermal history on phase of the sample and the effect of the phase on the reorientation.

A fully hydrogenated sample (NH_4BH_4) was used to confirm that deuteration had no significant effect on the reorientations and that no detectable tunnelling occurred even at low temperatures.

6.4 The Behaviour of Hydrogen in Ammonium Borohydride

Flacau *et al.* [107] published the first determination of hydrogen atom positions in ammonium borohydride. They concluded that both the ammonium and borohydride hydrogen atoms were placed in eight positions along the $\langle 111 \rangle$ directions with half occupancy. Ryan [103] confirmed the positions of the borohydride hydrogen atoms on the $(\frac{1}{2} \frac{1}{2} \frac{1}{2})$ sites. However, she also found that the hydrogen atoms in the ammonium ion are more disordered than suggested by Flacau *et al.*, with hydrogen sites present on the $\langle 100 \rangle$ directions. The $Fm\bar{3}m$ symmetry means that the ammonium group has 48-fold disorder. In this section, the disorder of the hydrogen atoms in the ammonium ion are investigated using neutron diffraction and density functional theory.

6.4.1 Molecular Dynamics Density Functional Theory

Experimental Details

Ab initio Born-Oppenheimer molecular dynamics calculations were performed using the CP2K package [188]. A canonical ensemble with a constant number of particles, constant volume and constant temperature was used. The Nosé-Hoover chain thermostat of length three [189] was used to ensure thermalisation of the system and the velocity-Verlet integrator to calculate the particle trajectories. The total potential energy and the forces on the atoms at each step were calculated by a full-wave function optimisation using density functional theory. The Quickstep method [206] with a dual basis set of plane waves (with a cut-off energy of 280 Ry), atom-centred Gaussian functions and the PBE exchange-correlation functional were used [185], along with the double-zeta (DZVP) Gaussian basis set [207] in combination with the Goedeck-

er-Teter-Hutter pseudopotentials for all elements.

The cell used was a 2 x 2 x 2 super-cell, containing 320 atoms (32 formula ammonium borohydride units) with cubic lattice parameter $a = 13.786 \text{ \AA}$ at 120 K. The diffraction pattern collected on WISH (see Section 6.1) at 120 K was used to calculate the initial atomic positions. The overall trajectory time was 50 ps, with 0.5 fs time steps. The first 5,000 steps were disregarded to allow the system to fully relax. 120 K was chosen as a temperature where the atoms would be in motion, but not moving too fast for the individual jumps to be distinguished. This temperature also allows comparison with the TOSCA INS spectra (Section 6.2) and the IRIS QENS spectra (Section 6.3). These calculations were kindly performed by Philippe C. Aeberhard.

These calculations allowed examination of the trajectories of the hydrogen atoms. Summed trajectories of all the hydrogen atoms around a particular type of atom in the centre of the tetrahedron were calculated. The trajectories of individual hydrogen atoms were also examined.

Eckert Projections

Eckert projections are pseudocylindrical map projections and have been used in this Section to graphically illustrate the hydrogen atom density on a spherical shell around the central atom of the ammonium and borohydride ionic groups. Figure 6.26 shows the eight $\langle 111 \rangle$ and six $\langle 100 \rangle$ crystallographic directions on an Eckert projection and on the surface of a sphere. In this projection, the $\langle 111 \rangle$ positions are located in the centre of each quarter of the sphere. The $\langle 100 \rangle$ positions are on the equatorial and polar sites. One of the equatorial positions is split between either end of the projection and the polar positions will be projected across the top of the map.

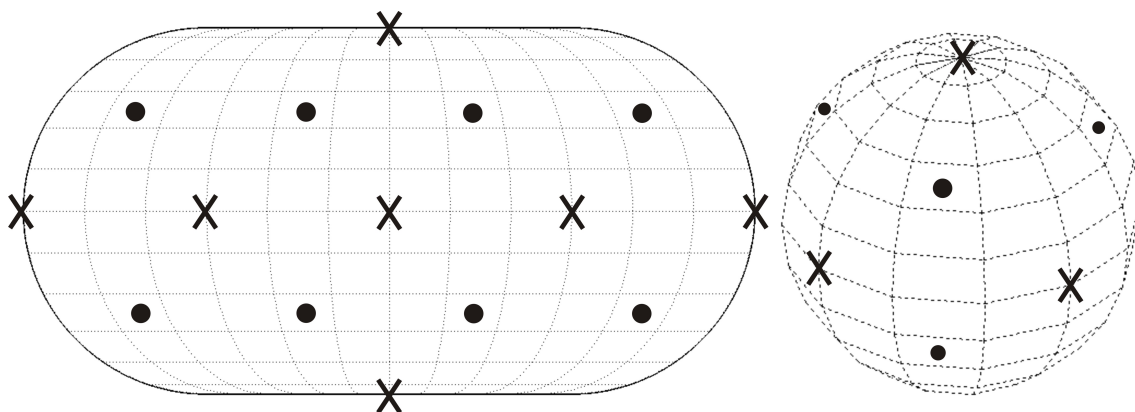


Figure 6.26: Eckert projection and sphere indicating the $\langle 111 \rangle$ (circles) and $\langle 100 \rangle$ (crosses) positions.

Results

Borohydride groups

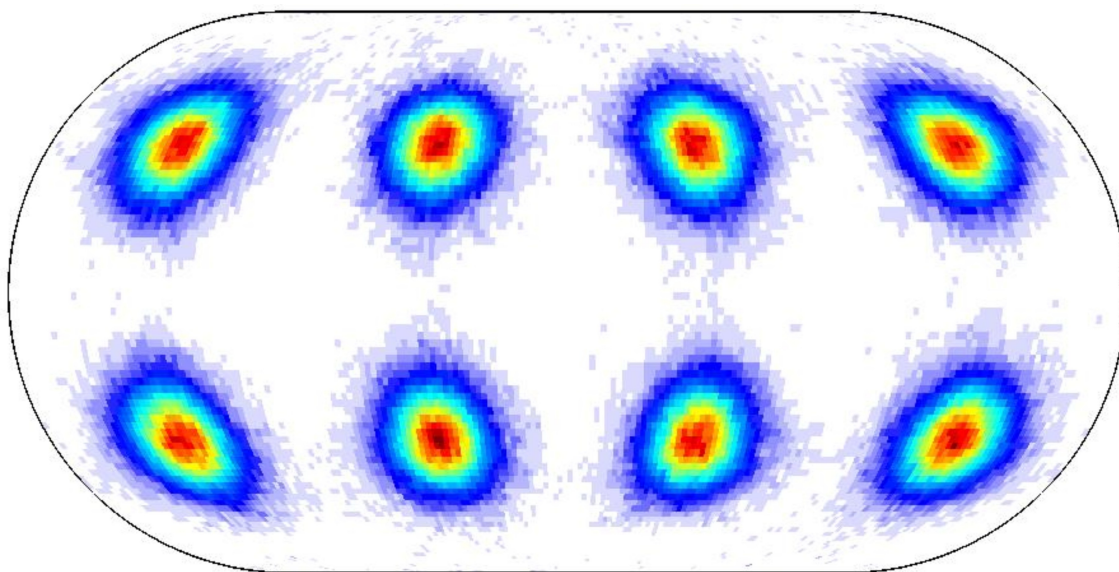


Figure 6.27: Eckert projection of the distribution of the hydrogen atoms in the borohydride group in the DFT of ammonium borohydride at 120 K.

It has previously been shown experimentally [107] that in ammonium borohydride, the boron atoms occupy the $(\frac{1}{2} \frac{1}{2} \frac{1}{2})$ positions and the hydrogen atoms are in $\frac{1}{2}$ occupancy

cubic positions along the $\langle 111 \rangle$ directions. Therefore, the computed distributions of the hydrogen atoms shown in Figure 6.27 are as expected, with the intensity averaged evenly over eight possible positions along the $\langle 111 \rangle$ directions. Figure 6.28 shows examples of the trajectories of single hydrogen atoms in the borohydride group. The hydrogen atoms are performing jumps around any one of the three tetrahedral 2-fold axes, from one $\langle 111 \rangle$ site to the adjacent one. This is in contrast to the results of the quasielastic spectroscopy (see Section 6.3) which indicate that each borohydride group occupies one of the two possible tetrahedral orientations, with the hydrogen atoms in the borohydride group hopping around one of the C_3 or C_2 axes.

The quasielastic neutron experiments (see Chapter 6.3) indicate that hydrogen atoms in the borohydride group have an average residence time of around 2 ps between hops at 120 K. However, the DFT calculations give between 1 and 4 jumps in the 47.5 ps of the trajectory analysed: a considerably longer residence time. The QENS data shows an unusually large change in the mean residence time of the hydrogen atoms between 120 K and 140 K (Section 6.3.3). The gradient in residence time over this temperature interval may explain the disparity between the measured and calculated jump rates at 120 K. QENS data for 140 K indicates a mean residence time of 14 ps, which is closer to the values calculated via DFT. The DFT calculations also suggest that the change in rate and residence time in the QENS data is caused by a change in the reorientation from 2-fold or 3-fold hops to 4-fold jumps around the 2-fold axis.

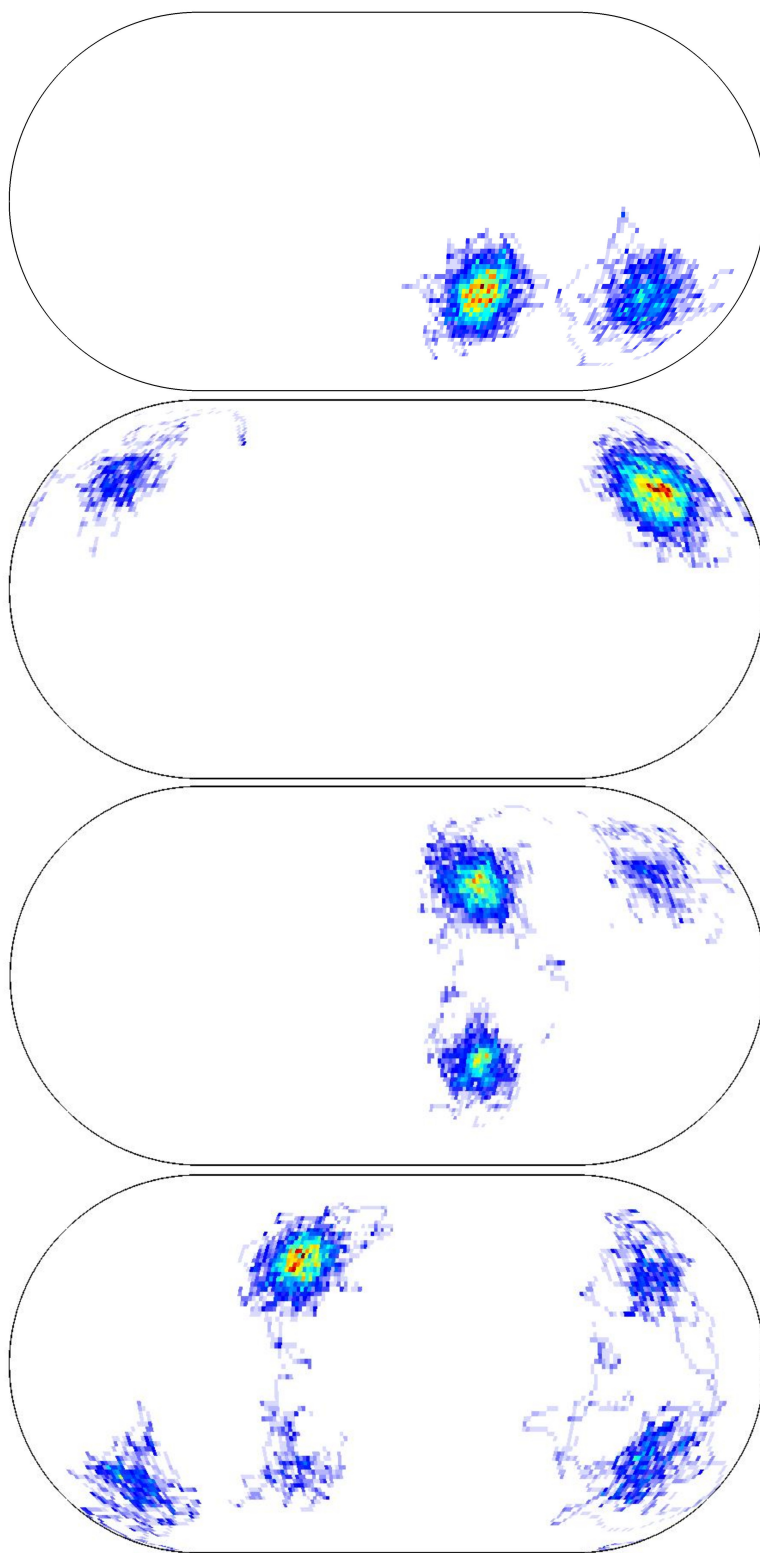


Figure 6.28: Eckert projections of four hydrogen atoms in the borohydride group to illustrate individual hydrogen motions in the computational model.

Ammonium Group

It is known from previous neutron diffraction data presented by Ryan [103], that the nitrogen atom occupies the (0 0 0) site in the cubic structure of ammonium borohydride. It can be also be inferred from these results that the hydrogen atoms in the ammonium group are not placed in the cubic sites in the same way as those in the borohydride group; the optimum refinement has hydrogen atoms located in sites along the $\langle 100 \rangle$ direction. Once the tetrahedral group symmetry and the octahedral site symmetry are satisfied there are 48 possible ammonium orientations and 192 possible hydrogen sites. In the same work, it was also shown that there is not equal occupancy of all the hydrogen atom positions [103]. Higher occupancy occurs in the $\langle 100 \rangle$ positions than on the other sites.

An Eckert projection of the distribution of hydrogen atoms on the ammonium group from DFT calculations is shown in Figure 6.29. The highest occupancy areas are the $\langle 100 \rangle$ sites, as shown by higher intensities at the four equatorial and the two polar sites. There are also areas of medium intensity on the $\langle 111 \rangle$ positions and on the sites linking together the $\langle 100 \rangle$ and the $\langle 111 \rangle$ positions, forming a hexagonal pattern.

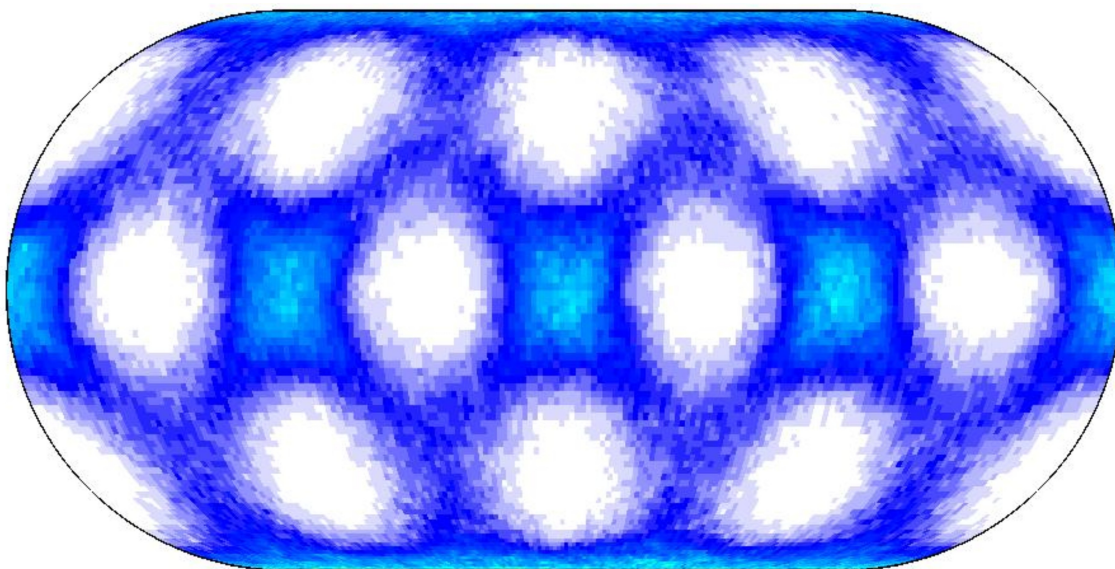


Figure 6.29: Eckert projection of the distribution of hydrogen atoms in the ammonium group of ammonium borohydride at 120 K, calculated using DFT.

The individual hydrogen trajectories (Eckert projections shown in Figure 6.30) do not show jumps between well-defined sites, but effectively undirected diffusion across the surface of the sphere. This is not supported by the QENS analysis, which suggests site-to-site hopping across a small number of sites. However, residence times for these hydrogen atoms calculated from QENS data (1 - 10 fs) do agree with the very fast motion shown in the calculated hydrogen trajectories.

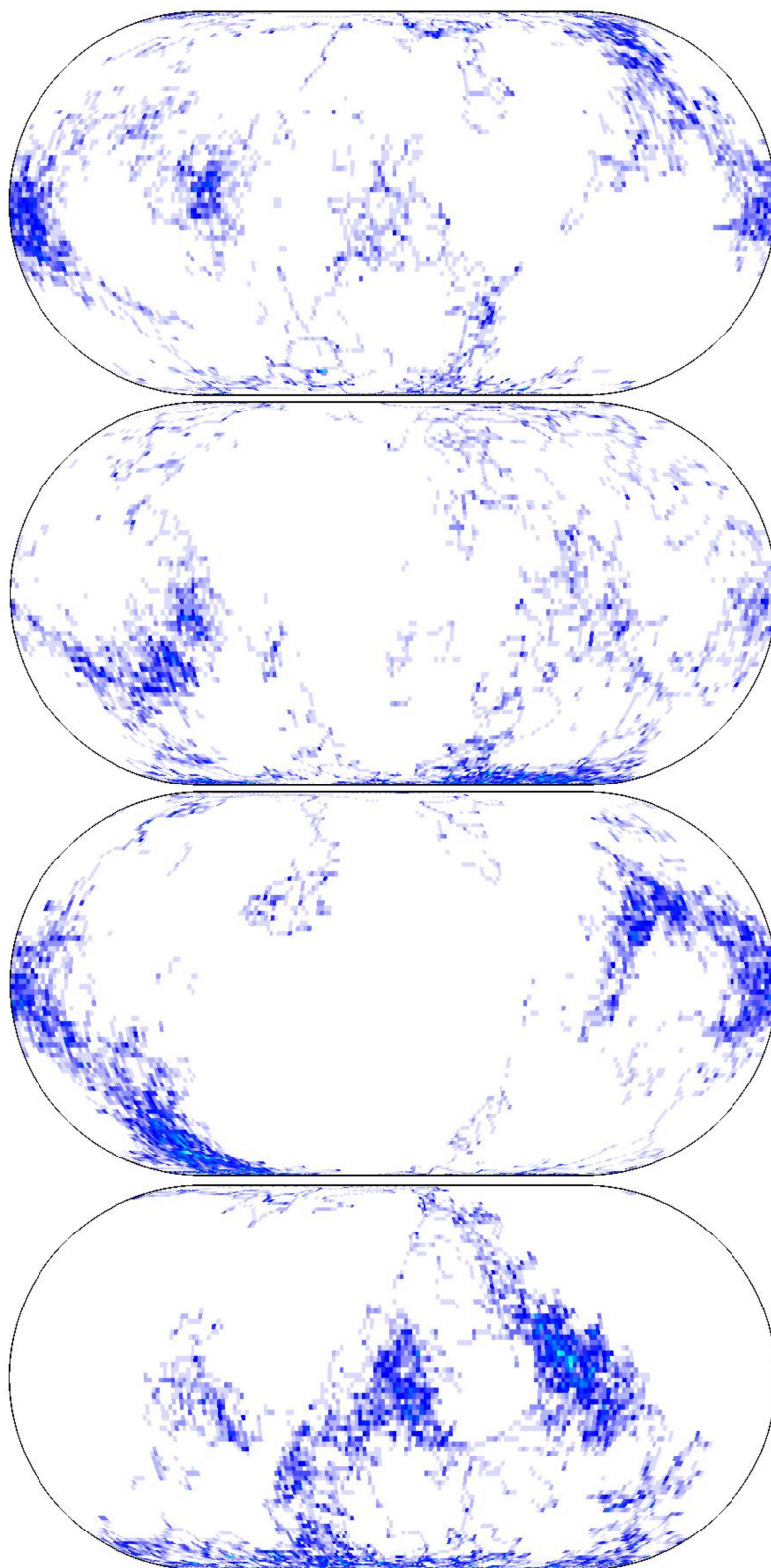


Figure 6.30: Eckert projections of four representative hydrogen atoms in the ammonium group, to illustrate individual hydrogen motions in the computational model.

6.4.2 Cubic Harmonics

In this section, cubic harmonics are used to determine the hydrogen distribution in the ammonium group in ammonium borohydride. Cubic harmonics are a special symmetrised form of spherical harmonics.

Spherical harmonics, $Y_l^m(\theta, \phi)$ (Equation 6.11) are the angular portions of a set of solutions to Laplace's equation. They are important for many applications; for example, the computation of atomic orbitals.

$$Y_l^m(\theta, \phi) = \sqrt{\frac{2l+1}{4\pi} \frac{(l-m)!}{(l+m)!}} P_l^m(\cos \theta) e^{im\phi} \quad (6.11)$$

where θ is the polar coordinate, ϕ is the longitudinal coordinate, $P_l^m(z)$ is the associated Legendre polynomial, l is the degree of the function and $m = -l, -(l-1), \dots, 0, \dots, l-1, l$. Table 6.6 shows the spherical harmonics for $l = 0, 1, 2$.

Spherical harmonics can be symmetrised so that they obey the point symmetry operations of a crystal. Cubic harmonics are linear combinations of spherical harmonics that obey the O_h cubic symmetry. Symmetrisation is used to represent the symmetry of the crystal structure, or because it offers computational benefits. Table 6.7 shows cubic harmonics up to the 8th order, in Cartesian coordinates. Spherical coordinates as given in Table 6.6 can be converted to the Cartesian coordinates used in Table 6.7 via the relationships $x = r \sin \theta \cos \varphi$, $y = r \sin \theta \sin \varphi$ and $z = r \cos \theta$.

$l m$	$Y_l^m(\theta, \phi)$
0 0	$(\frac{1}{4\pi})^{\frac{1}{2}}$
1 0	$(\frac{3}{4\pi})^{\frac{1}{2}} \cos \theta$
1 1	$-(\frac{3}{8\pi})^{\frac{1}{2}} e^{i\phi} \sin \theta$
1 - 1	$(\frac{3}{8\pi})^{\frac{1}{2}} e^{-i\phi} \sin \theta$
2 0	$(\frac{5}{16\pi})^{\frac{1}{2}} (3 \cos^2 \theta - 1)$
2 1	$-(\frac{15}{8\pi})^{\frac{1}{2}} e^{i\phi} \sin \theta \cos \theta$
2 - 1	$(\frac{15}{8\pi})^{\frac{1}{2}} e^{-i\phi} \sin \theta \cos \theta$
2 2	$(\frac{15}{32\pi})^{\frac{1}{2}} e^{2i\phi} \sin^2 \theta$
2 - 2	$(\frac{15}{32\pi})^{\frac{1}{2}} e^{-2i\phi} \sin^2 \theta$

Table 6.6: Spherical harmonics for $l = 0, 1, 2$.

lm	$K_{lm}(\theta, \varphi)$
00	1
41	$2.5(x^4 + y^4 + z^4) - 1.5$
61	$21.65625(x^6 + y^6 + z^6) - 29.53125(x^4 + y^4 + z^4) + 8.43750$
81	$\frac{1}{3}[97.5(x^8 + y^8 + z^8) - 182(x^6 + y^6 + z^6) + 105(x^4 + y^4 + z^4) - 17.5]$

Table 6.7: The first four cubic harmonics for the $Fm\bar{3}m$ space group.

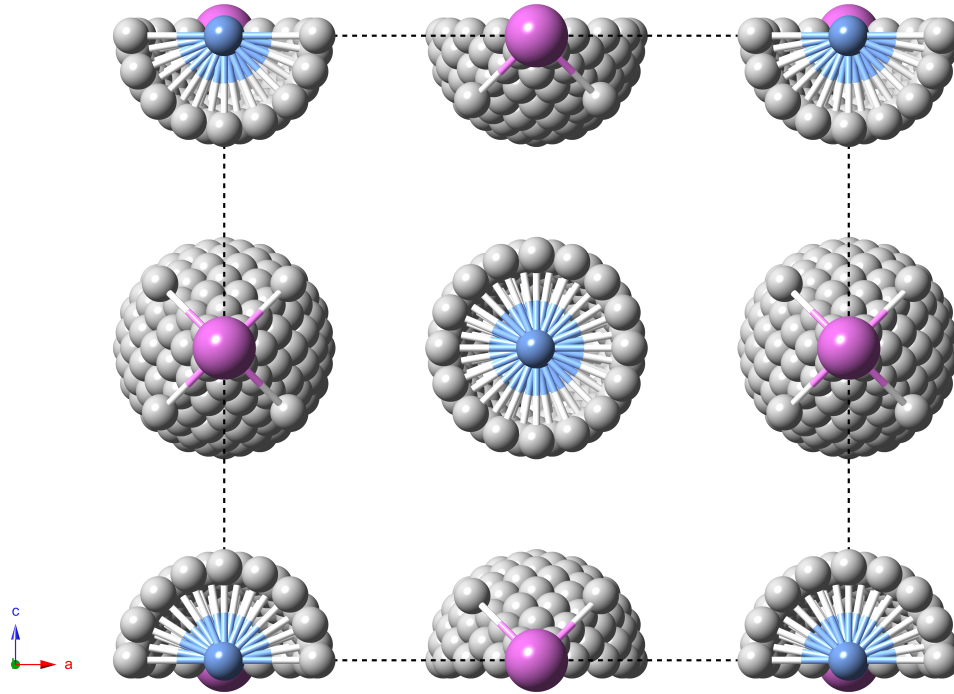


Figure 6.31: The structure of ammonium borohydride used in the refinement, showing the allowable ammonium hydrogen positions.

The hydrogen atoms of the ammonium group in ammonium borohydride are disordered. This is known from the number of hydrogen sites in the crystal structure [103]

and from the calculated hydrogen pathways shown in Figure 6.30. Cubic harmonics can be used to obtain further information on this disorder from the experimental neutron diffraction patterns presented in Chapter 6.1. A refinement scheme was constructed with hydrogen positions on the surface of a sphere with a radius of 1.036(2) Å around the nitrogen atom as shown in Figure 6.31. The symmetry of the site meant that it is only necessary to calculate 9 hydrogen positions. A linear combination of cubic harmonics (up to $l = 10$) was used to define the occupancies of the hydrogen positions as shown in Equation 6.12.

$$\text{occ} = c_{\text{norm}}(c_0 + c_4K_{41} + c_6K_{61} + c_8K_{81} + c_{10}K_{101}) \quad (6.12)$$

where $K_n(\theta, \phi)$ are the cubic harmonics and c_n and c_{norm} are constants to be refined. Hydrogen density maps were produced from the refinement and compared with the computational density plots found using DFT (Section 6.4.1).

This refinement scheme was applied to a diffraction pattern of ammonium borohydride at 120 K collected on the WISH diffractometer at ISIS (see Chapter 6.1). The diffraction pattern, calculated Rietveld-refined fit and crystallographic data are shown in Figure 6.32 and Table 6.32. The diffraction pattern has a fairly low intensity and it was only possible to accurately define the contribution of the cubic harmonics up to $l = 8$.

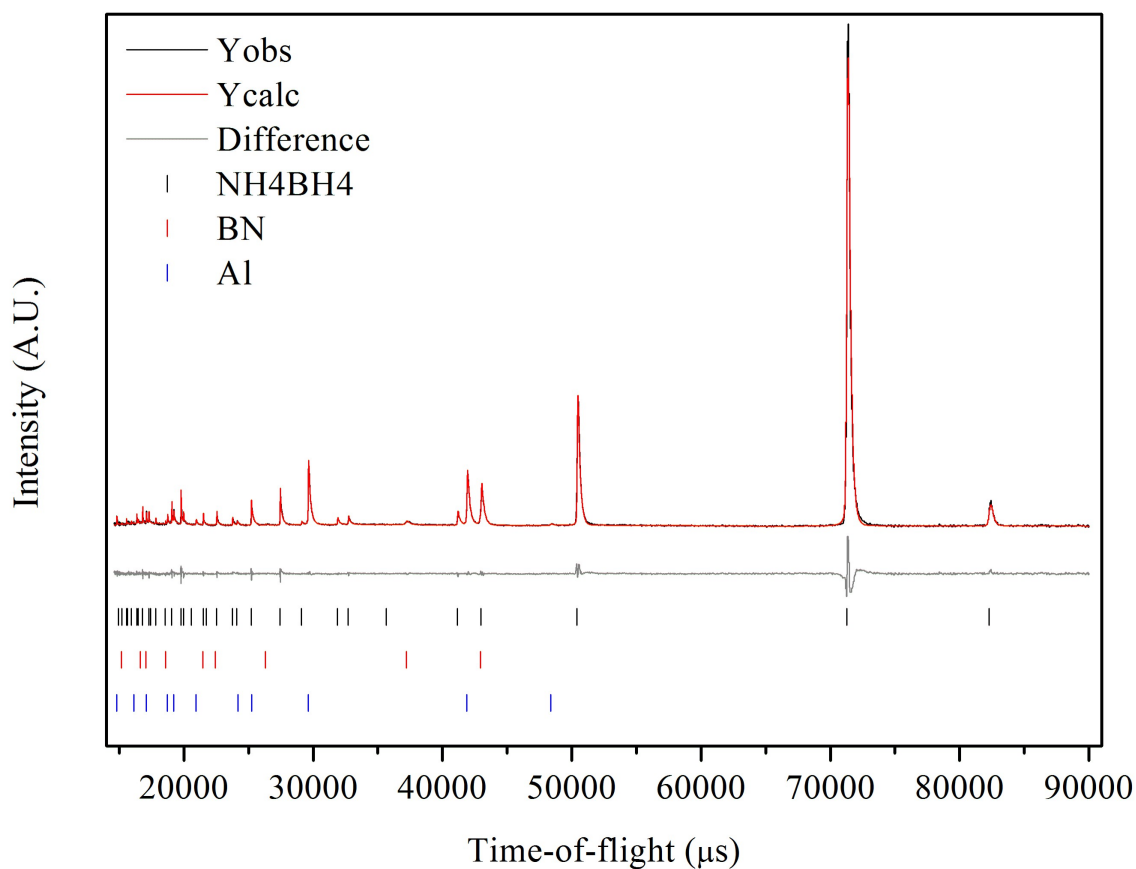


Figure 6.32: Observed (red) and calculated (black) diffraction patterns of the cubic phase of ammonium borohydride at 120 K. The grey line under the diffraction pattern is the difference between the observed and calculated patterns. Ammonium borohydride (black tick marks), boron nitride (red ticks) and aluminium (blue ticks). Crystallographic data in Table 6.8.

Atom	a	b	c	Occupancy	$B_{\text{iso}}(\text{\AA}^2)$
B1	0.5	0.5	0.5	1	1.71(8)
H1	0.60167	0.60167	0.60167	0.5	2.77(8)
N1	0	0	0	1	1.58(7)
H2	0	0	0.15025	0.15(2)	2.4(2)
H3	0.10624	0.10624	0	0.01(1)	2.4(2)
H4	0.08674	0.08674	0.08674	0.028(7)	2.4(2)
H5	0.13343	0.04884	0.04884	0.00(1)	2.4(2)
H6	0.13881	0.05750	0	0.025(5)	2.4(2)
H7	0.14598	0.02513	0.02513	0.080(4)	2.4(2)
H8	0.12434	0.08045	0.02534	0.000(2)	2.4(2)
H9	0.09935	0.09935	0.05324	0.015(5)	2.4(2)
H10	0.11330	0.06977	0.06977	0.006(3)	2.4(2)

Table 6.8: Crystallographic data from the cubic harmonics refinement of the cubic phase of ammonium borohydride at 120 K. Space group, $Fm\bar{3}m$, $a = 6.89466(4)\text{\AA}$, $c_{\text{norm}} = 0.0216(2)$, $c_0 = 1.0$, $c_4 = 1.17(3)$, $c_6 = 0.55(7)$, $c_8 = 0.9(3)$, $R_{\text{wp}} = 7.553$, $R_{\text{exp}} = 4.751$ and $\chi^2 = 1.590$.

An Eckert projection of hydrogen atom density in the ammonium group, refined from the diffraction data, is shown in Figure 6.33. This bears good resemblance to the distribution calculated via DFT (Figure 6.29). Areas of high hydrogen atom intensity on the $\langle 100 \rangle$ positions and on the $\langle 111 \rangle$ positions occur in both the calculated and refined distributions. However, the low intensity of the diffraction pattern leads to a relatively low spatial resolution of the refined hydrogen distribution. Higher-intensity diffraction patterns would allow more detail to be resolved.

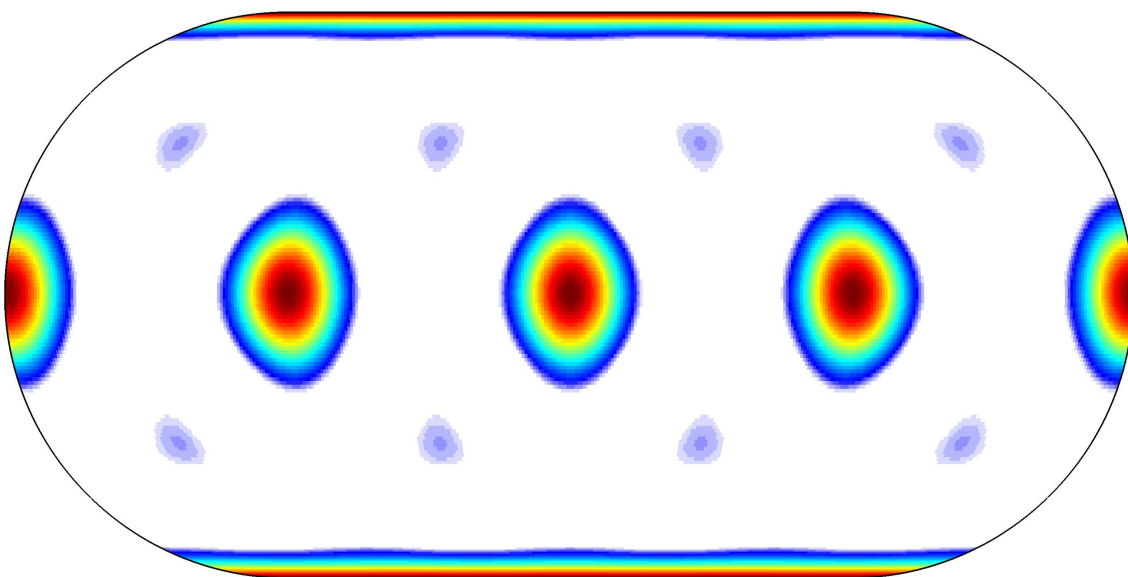


Figure 6.33: The hydrogen atom distribution around the nitrogen atom in ammonium borohydride at 120 K, refined from neutron diffraction data.

6.4.3 Summary

DFT MD calculations have been used to determine the distribution of hydrogen atoms in the ammonium and borohydride groups in ammonium borohydride. In the results of these calculations, as in previous experimental data, the borohydride hydrogen atoms occupy the $\langle 111 \rangle$ positions in the crystal lattice. The positions of the hydrogen atoms in the ammonium groups were also determined from experimental neutron diffraction data using a refinement scheme based on cubic harmonics. The result of the DFT calculations shows the hydrogen atoms located on the $\langle 100 \rangle$ positions, with connecting regions through the $\langle 111 \rangle$ positions. The experimental data show similar areas of high intensity on the $\langle 100 \rangle$ and the $\langle 111 \rangle$ positions, but no substantial hydrogen density between these areas. It is believed that this disparity is due to the low intensity of the available neutron diffraction spectrum, which affects the accuracy of the refinement.

Chapter 7

Conclusions and Further Work

7.1 Conclusions

As highlighted in Chapter 2, dihydrogen bonds and interactions are important in a variety of hydrogen storage materials. In this thesis, the dihydrogen bonding and behaviour of hydrogen atoms in solid ammonia borane and ammonium borohydride have been investigated. The formation of a mobile phase of ammonia borane via the breaking of dihydrogen bonds has been studied using neutron diffraction and inelastic neutron spectroscopy (INS) (Chapter 4). It was shown that the mobile phase is structurally very similar to the room temperature phase, with an increase in the lattice parameters of 0.02 % and a 3° increase in the angle of inclination between the B-N bond and the *c*-axis. It was also found that once the mobile phase had formed, end-to-end ‘flipping’ of the ammonia borane molecule occurred, reversing the positions of boron and nitrogen atoms. This allows the formation of DADB, an intermediate compound in the decomposition of ammonia borane to polyamidoborane and hydrogen. DFT-MD simulations of ammonia borane at temperatures where decomposition is energetically favourable suggest that the breaking of dihydrogen bonds causes formation of the mobile

phase (Chapter 5).

Analysis of DFT-MD calculations (Chapter 5) at a variety of temperatures gave an insight into dihydrogen bonding in ammonia borane, and how this varies with temperature. In the orthorhombic phase of ammonia borane there are three crystallographically distinct dihydrogen bonds. The DFT-MD simulations indicated that all of these bonds have clearly defined potential wells. The force constants of the bonds (calculated from the simulations) indicate that they are relatively weak. As the temperature is increased towards the phase transition to the tetragonal phase, the ammonia and borane groups begin to rotate. In the tetragonal phase, there is little difference between the potential wells of each of the three dihydrogen bonds. There are, however, local minima in the wells, which indicate that although dihydrogen bonds in the tetragonal phase are being continually broken and reformed, they are still important stabilising interactions.

During the variable temperature neutron diffraction experiments described in Section 6.1, four distinct solid phases of ammonium borohydride were observed. These include a cubic high-temperature phase which is stable above 65 K and a rhombohedral phase stable between 65 K and 55 K. The structure of the latter (rhombohedral) phase was solved; it has space group $R\bar{3}m$ and lattice parameters $a = 4.872659(82)$ Å and $c = 23.69317(66)$ Å. The occurrence of lower-temperature phases are dependent on the thermal history. When ammonium borohydride is slow-cooled below 55 K it forms a single monoclinic phase. When crash-cooled below 45 K, it forms another, distinct, monoclinic phase. In the analysis described in Section 6.2, the molecular modes of ammonium borohydride were assigned using variable-temperature INS data and simulated power spectra calculated from DFT-MD simulations.

Results from quasielastic neutron spectroscopy of ammonium borohydride showed that both the ammonium and borohydride groups perform two- or three-fold reorientations (Section 6.3). The ammonium group was shown to have a higher mobility than

the borohydride group; it was observed to reorient approximately 1000 times faster. Between 120 K and 130 K, the borohydride group shows an unusual discontinuity in the residence time between reorientations, which increases ~3.5 fold over this temperature interval. This does not coincide with a phase transition and may indicate that a change has occurred in the type of reorientation performed by the borohydride group.

DFT-MD simulations were used to probe the hydrogen atom density around the ammonium and borohydride ions in ammonium borohydride (Section 6.4). The greatest density of hydrogen atoms in the borohydride group occurs on the $\langle 111 \rangle$ direction - this is consistent with the borohydride orientations in the crystal structure previously reported [103]. The DFT-MD results also show that in the ammonium group the areas of greatest hydrogen atom density occur on the $\langle 100 \rangle$ positions. However in these results, unlike in the previously calculated crystal structure, there are also regions of high hydrogen density connecting the $\langle 100 \rangle$ sites through the $\langle 111 \rangle$ sites. A similar pattern of hydrogen density was also observed in refinements of neutron diffraction data, in which cubic harmonic basis functions were used to calculate hydrogen occupancies in ammonium ion.

7.2 Further Work

7.2.1 Pertaining to this Study

The formation of a mobile phase is an important step in the decomposition of ammonia borane. While it has been demonstrated here that the structure of ammonia borane does change on the formation of the mobile phase, a further neutron diffraction study would be required to demonstrate how this change occurs. An issue of particular importance is whether the B-N bond tilt causes an increase in the lattice parameters during the formation of the mobile phase, or whether the increased lattice parameters

allow the angle of the bond to increase. This information would be useful in designing dopants to reduce the decomposition temperature of ammonia borane. Furthermore, high-resolution heat capacity measurements of the decomposition of ammonia borane would provide valuable information on the thermodynamics of the formation of ammonia borane; however, these would be difficult to obtain due to foaming.

In this work, it has been shown that the structure of ammonium borohydride is highly dependent on its thermal history. A comprehensive study of the low temperature phases of ammonium borohydride would increase the understanding of the hydrogen atom disorder in the system, along with the temperature-dependence of its low temperature phases, and possible dihydrogen bonding. This could be achieved using synchrotron X-ray diffraction. Once the phase progression is understood, the structure of specific phases could be examined using neutron diffraction. In this study, areas of high hydrogen atom density in ammonium borohydride were calculated using DFT-MD. Higher intensity and higher resolution neutron diffraction of the cubic phase of ammonium borohydride (than those reported in this work) would allow the fine detail of the distribution of ammonium hydrogen atoms determined computationally to be confirmed experimentally.

Despite the difficulty in performing phonon density state calculations on disordered phases, they would be helpful in assigning the lattice modes in the INS spectra of ammonium borohydride presented in Section 6.2. Once modes have been assigned, information on the low temperature phase transitions of ammonium borohydride could be obtained. Further INS experiments on an instrument with a higher resolution at room temperature (such as the MAPS spectrometer at ISIS) could be used to provide mechanistic information on the decomposition of ammonium borohydride.

In Section 6.3, an unusual change in the reorientation rate of the borohydride group in ammonium borohydride was observed in variable-temperature QENS data. NMR

experiments on partially deuterated ammonium borohydride samples (NH_4BD_4 and ND_4BH_4 from 4 K to 200 K) would provide additional information on the rotational dynamics and confirm the presence of the unusual change in borohydride group reorientation rate. A more detailed low temperature QENS study to rule out the possibility of tunnelling could also be performed. Furthermore, DFT-MD calculations on ammonium borohydride at a wide range of temperatures could be used to study the stability of the low temperature phases and provide further information on the rotation and molecular dynamics. In Chapter 5, DFT-MD simulations on ammonia borane were analysed to provide information about the dihydrogen bonding pairs. In ammonium borohydride at low temperatures, where there is minimal rotation of the ionic groups, similar investigations could be performed to provide information on whether hydrogen bonding is a significant stabilising interaction.

7.2.2 Ammonia Borane and its Derivatives as Hydrogen Storage Materials

Ammonia borane, ammonium borohydride and DADB all contain very high weight percentages of hydrogen. However there are significant issues to be overcome before they can be considered as practical hydrogen stores. Particular problems are the decomposition temperature, regeneration of the storage compound, and the release of contaminants along with the desired hydrogen [64, 106]. The thermal stabilities of ammonia borane and ammonium borohydride present different problems: the decomposition (with no induction period) of ammonia borane occurs at too high a temperature [60], while the decomposition temperature of ammonium borohydride is too low [106]. There have been multiple studies which have successfully reduced the decomposition temperature/induction period and the foaming of ammonia borane [66, 87, 88]. However, there have been no successful attempts to stabilise ammonium borohydride, other

than by simply increasing pressure [104].

The reduction of impurities in the released hydrogen can be achieved either by preventing their release from the storage material or by removal using a filter/scrubber system. For both ammonia borane and ammonium borohydride, the conditions of hydrogen release affect the quantity and nature of the impurities released. There have been many studies on reducing the impurities in hydrogen released from ammonia borane [66, 80, 89], but not ammonium borohydride. Methods of regenerating ammonia borane have been proposed [97, 98, 99, 100, 101]. These techniques, particularly where they relate to the breaking of the B-N bond in polyamidoboranes, will also be applicable to ammonium borohydride regeneration.

The utility of DADB as a hydrogen storage material has only been briefly discussed in this thesis. However, its properties are potentially more promising than those of ammonia borane and ammonium borohydride. DADB decomposes at a lower temperature than ammonia borane with less of an induction period and less foaming. However, very little work on this compound has been reported to date.

The hydrogen storage abilities of ammonia borane and its derivatives have been discussed for nearly two decades. It is now evident that considerable modifications to their properties would be required to produce a practical hydrogen storage material.

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