

A Study of Ammonia Borane and its Derivatives

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

KATHARINE RACHEL RYAN



JUNE 2011

Supervisors:

Prof. P.P. EDWARDS
Inorganic Chemistry Laboratory,
Department of Chemistry,
University of Oxford,
South Parks Road,
Oxford.

Prof. W.I.F. DAVID
ISIS Neutron Source,
Science and Technology Facilities Council,
Rutherford Appleton Laboratory,
Harwell Science and Innovation Campus,
Didcot.



The work described in this thesis was performed in the Inorganic Chemistry Laboratory, University of Oxford from October 2007 to June 2011, under the supervision of Professor W.I.F. David and Professor P.P. Edwards. All of the work is my own unless otherwise stated and has not been submitted previously for any other degree at this or any other university.

Katharine Ryan

June 2011

Acknowledgments

My doctorate could not have been completed without the help of so many people, who are both brilliant in their fields *and* very generous. It has been an honour to work with you, and I am extremely grateful to you all.

I would like to express my deep gratitude to Professor Bill David for your expert supervision, together with the infinite patience and kindness you have invariably shown me. I have learnt so much from you and it has been a privilege to have the benefit of your wisdom and trust in so many areas. My DPhil has been a rich and varied experience, encompassing so many different strands. Thank you to Professor Peter Edwards for giving me the chance to conduct research in such an exciting and interesting field.

My warm appreciation to Dr Martin Jones, for lots of advice, and for putting up with my early morning office calls! I am very grateful for all your input.

My heartfelt thanks to Dr Marco Sommariva for being a complete rock. To the other senior researchers in the group: Doctors Samantha Callear and Simon Johnson, thank you for much equipment training, guidance and making beamtime bearable! I also wish to thank Dr Christina Tang for her advice and training in Schlenk synthesis techniques.

I am hugely grateful to the past and present co-inhabitants of F21 and F23 for all their camaraderie, lab help and generally keeping me sane!: Doctors Chris Smith, Becky Lowton, Anne Nickels and Laura Richard and Doctors-in-waiting Andrew Seel, Philippe Aeberhard, Dave Royse, and Katie Hore. You have been so much fun to work with and your support was vital.

I have also benefited from the contribution of the beamline scientists who facilitated many of my experiments: Dr Timmy Ramirez Questa, thank you for all your help on TOSCA with the CASTEP / aClimax calculations and for inspiring me to 'have a bash' at using Linux! It has been great working with you! My gratitude to Dr Chris Frost for all your help during my marathon MAPs experiment; to Dr Fabia Gozzo at the SLS for such meticulous experimental help on the beamline,- and for your hospitality; taking in stray DPhil students is definitely above and beyond the call of duty!

I am particularly indebted to Professor Tony Burrell and Dr Himashinie Diyabalana for giving me the opportunity to visit Los Alamos National Laboratories and for their help and hospitality during my stay. Also for their subsequent advice and collaboration on materials synthesis.

I would like to acknowledge a major debt to Dr Liz Tull who gave me my first taste of academic research at Southampton and instilled in me the fundamental research skills which I still rely on. I am indebted to you for your friendship and care.

I have also been lucky enough to have the support of some amazing people outside of my research: thank you, Dr Rebecca Murphy and Dr Zafra Cooper for bringing the colour back into my life! I would like to thank Dr Maeve Price, Karen Kruska and Dr John Lyle for being true friends when it really mattered. And Karen again for being the best housemate ever! Finally my heartfelt gratitude to my parents for their love and unconditional support always.

I gratefully acknowledge both the EPSRC and STFC for funding.

A Study of Ammonia Borane and its Derivatives

Katharine Rachel Ryan

Submitted for the degree of Doctor of Philosophy.

Linacre College, Oxford.

Trinity 2011

Abstract

This thesis reports the investigation of molecular materials for hydrogen storage applications with a particular emphasis on alkali-metal amidoboranes. I have developed new routes for the synthesis of α -LiNH₂BH₃ and NaNH₂BH₃, and have studied their hydrogen storage properties by thermogravimetric analysis, variable temperature X-ray and neutron diffraction and inelastic neutron scattering. I report the synthesis and full structural characterization of two new materials, KNH₂BH₃ and β -LiNH₂BH₃, and have performed initial studies on a tetragonal phase of a variant of LiNH₂BH₃ with a preliminary structure solution. I have also performed variable temperature neutron diffraction on ammonium borodeuteride, ND₄BD₄, and report the full structural characterisation of the three phases identified as a result of these measurements. Furthermore, variable temperature inelastic neutron scattering (INS) measurements were performed on ammonia borane, NH₃BH₃, and the results are discussed in terms of crystallographic phase changes.

A Study of Ammonia Borane and its Derivatives

Katharine Rachel Ryan

Submitted for the degree of Doctor of Philosophy.

Linacre College, Oxford.

Trinity 2011

Extended Abstract

The *Introduction* surveys the applications of hydrogen storage materials and outlines the scope of current research. A review of the underlying materials chemistry and crystallography of ammonia borane, which forms the foundation of this thesis is also presented.

The methods of synthesis and characterisation are discussed in *Chapter 2*. A detailed discussion (theoretical background, data analysis and instrumentation) of the key techniques (including; X-ray and neutron diffraction, inelastic neutron scattering spectroscopy and gravimetric analysis) is provided.

Variable temperature neutron diffraction and inelastic neutron scattering studies are presented for both ammonia borane and ammonium borohydride in *Chapter 3*. Inelastic neutron scattering (INS) spectra were collected on $\text{NH}_3^{11}\text{BH}_3$ at eight temperatures between 25-280K (-248°C to 7°C). The full phonon density of states was calculated by DFT and used to assign the spectra and the relative onset of the NH_3 and BH_3 librations were correlated to their moments of inertia. The structure of $\text{ND}_4^{11}\text{BD}_4$ was investigated by variable temperature neutron powder diffraction between 2K and 200K (-271°C and -73°C). Three progressively more ordered phases were identified, whose formation depended strongly on the 'thermal history' of the sample. Heat capacity measurements confirmed the phase change behaviour.

In *Chapter 4* the structures of $\alpha\text{-LiNH}_2\text{BH}_3$ and $\beta\text{-LiNH}_2\text{BH}_3$ were explored in detail with synchrotron X-ray powder diffraction. $\alpha\text{-LiNH}_2\text{BH}_3$ was also investigated with neutron diffraction and variable temperature synchrotron X-ray powder diffraction to monitor the changes in crystal structure up to decomposition. Hydrogen desorption properties were studied first using combined intelligent gravimetric analysis with mass

spectrometry (IGA-MS). Low temperature and variable temperature inelastic neutron scattering studies were undertaken and used in conjunction with the crystallographic data to gain greater understanding of the decomposition mechanism. The preliminary crystal structure and desorption properties of an elusive tetragonal phase of LiNH_2BH_3 are also presented.

In *Chapter 5*, the structure of NaNH_2BH_3 is explored in detail with synchrotron X-ray powder diffraction and neutron powder diffraction. Variable temperature synchrotron X-ray powder diffraction experiments were also undertaken to monitor the changes in crystal structure up to decomposition. Hydrogen desorption properties were studied using IGA-MS and potential decomposition mechanisms discussed. NaNH_2BH_3 was found to degrade over time to an amorphous phase. A low temperature inelastic neutron scattering study and an IGA-MS study were also performed on the aged compound.

In *Chapter 6*, the structure of KNH_2BH_3 was explored in detail with synchrotron X-ray powder diffraction at the SLS and neutron powder diffraction. Variable temperature synchrotron X-ray powder diffraction measurements were also taken to monitor the changes in crystal structure up to decomposition. Hydrogen desorption properties were studied first using combined intelligent gravimetric analysis with mass spectrometry and then using the intelligent gravimetric analysis with neutrons (IGAⁿ) apparatus in conjunction with the HRPD diffractometer at the ISIS neutron source. Low temperature inelastic neutron scattering studies were undertaken and used in conjunction with the crystallographic data to gain greater understanding of the decomposition mechanism.

Finally, the *Conclusion* provides a review of the properties of the materials NH_3BH_3 , NH_4BH_4 , $\alpha\text{-LiNH}_2\text{BH}_3$, $\beta\text{-LiNH}_2\text{BH}_3$, NaNH_2BH_3 and KNH_2BH_3 . These materials are considered together in an attempt to understand the key key factors that determine their hydrogen desorption properties. The scope for further research and their industrial potential is also discussed.

Contents

1	Introduction	11
1.1	Hydrogen Storage Background	11
1.2	Hydrogen and Di-Hydrogen Bonding	15
1.2.1	Hydrogen Bonding	16
1.2.2	Dihydrogen Bonding	17
1.3	Ammonia Borane	18
1.3.1	Solid State Decomposition of NH_3BH_3	20
1.3.2	Regeneration of AB	23
1.4	Modified Ammonia Borane	26
1.4.1	Nanostructuring	26
1.4.2	Catalysis	27
1.4.3	Chemical modification	31
1.5	Ammonium Borohydride	35
2	Experimental Techniques	36
2.1	Introduction	36
2.2	Crystallography	36
2.2.1	Diffraction	39
2.2.2	X-ray Diffraction	40
2.2.3	Neutron Diffraction	50
2.2.4	Structure Determination from Powder Diffraction Data	55
2.3	Other Techniques	61
2.3.1	Gravimetric Analysis	61
2.3.2	Differential Scanning Calorimetry	63
2.3.3	Heat Capacity	65

2.3.4	Vibrational Spectroscopy	67
2.4	Synthesis Techniques and Material Manipulation	76
2.4.1	Argon Glove Box	76
2.4.2	Schlenk Line	77
2.5	Synthesis Conditions	85
2.5.1	Alkali Metal Amidoboranes	85
2.5.2	Lithiated Tetragonal Phase	86
2.5.3	^{11}B Enriched Ammonia Borane ($\text{NH}_3^{11}\text{BH}_3$)	86
2.5.4	Source and Purities of Starting Materials	88
3	Variable Temperature Studies on Ammonia Borane and Ammonium Borohydride	89
3.1	Introduction and Chapter Outline	89
3.2	Inelastic Neutron Scattering Studies of $\text{NH}_3^{11}\text{BH}_3$	90
3.2.1	Inelastic Neutron Scattering Study of $\text{NH}_3^{11}\text{BH}_3$ at 5K	90
3.2.2	Variable Temperature Inelastic Neutron Scattering Studies of $\text{NH}_3^{11}\text{BH}_3$	95
3.3	Crystal Structure of ND_4BD_4	99
3.3.1	The Cubic or 'top' phase ND_4BD_4	99
3.3.2	The Rhombohedral or 'middle' phase of NH_4BH_4	102
3.3.3	The Trigonal or 'bottom' phase of ND_4BD_4	107
3.4	Variable Temperature Neutron Diffraction on ND_4BD_4	112
3.4.1	VT Analysis of the Cubic Phase ND_4BD_4	117
3.5	Heat Capacity Measurements on ND_4BD_4	118
3.6	Conclusions	119
4	Lithium Amidoboranes	121
4.1	Introduction and Chapter Outline	121
4.2	Crystal structures of $\alpha\text{-LiNH}_2\text{BH}_3$ and $\beta\text{-LiNH}_2\text{BH}_3$	125
4.2.1	$\alpha\text{-LiNH}_2\text{BH}_3$	125
4.2.2	$\beta\text{-LiNH}_2\text{BH}_3$	129
4.3	Variable Temperature X-ray Diffraction Studies of $\alpha\text{-LiNH}_2\text{BH}_3$	132

4.3.1	Variable Temperature X-ray Diffraction Studies of α -LiNH ₂ BH ₃ at the ESRF	132
4.3.2	Variable Temperature X-ray Diffraction Studies of α -LiNH ₂ BH ₃ at the SLS	134
4.4	Thermal Analysis of α -LiNH ₂ BH ₃	136
4.4.1	Intelligent Gravimetric Analysis Of α -LiNH ₂ BH ₃	136
4.4.2	Differential Scanning Calorimetry of α -LiNH ₂ BH ₃	138
4.5	Inelastic Neutron Scattering Studies of α -LiNH ₂ BH ₃ [1]	140
4.5.1	Born Charges and Charge Density	144
4.5.2	Atomic Motion Prior to Decomposition	146
4.6	Variable Temperature INS of α -LiNH ₂ ¹¹ BH ₃ on MAPS	149
4.7	Decomposition Mechanism of α -LiNH ₂ BH ₃	153
4.8	Lithiated Tetragonal Phase	155
4.8.1	NMR of the Lithiated Tetragonal Phase	155
4.9	Raman Study of Lithiated Tetragonal Phase	157
4.10	Inelastic Neutron Scattering Studies of the Lithiated Tetragonal Phase	158
4.11	In-Situ synthesis of the Tetragonal Phase in the IGA	159
4.12	Intelligent Gravimetric Analysis of the Decomposition of the Lithiated Tetragonal Phase	162
4.13	Crystal Structure of the Lithiated Tetragonal Phase	165
4.14	Conclusions	168
5	Sodium Amidoborane	170
5.1	Introduction and Chapter Outline	170
5.2	Crystal Structure of NaNH ₂ BH ₃	174
5.3	Variable Temperature X-ray Diffraction Studies of NaNH ₂ BH ₃	177
5.4	Intelligent Gravimetric Analysis of NaNH ₂ BH ₃ and Aged NaNH ₂ BH ₃	180
5.4.1	Intelligent Gravimetric Analysis Studies of NaNH ₂ BH ₃	180
5.4.2	Intelligent Gravimetric Analysis Studies of aged NaNH ₂ BH ₃	183
5.5	Inelastic Neutron Scattering Studies of Aged NaNH ₂ BH ₃	185

5.6	Conclusions	187
6	Potassium Amidoborane	189
6.1	Introduction And Chapter Outline	189
6.2	Crystal structure of KNH_2BH_3	190
6.2.1	X-ray Diffraction of KNH_2BH_3	190
6.2.2	Neutron Diffraction of $\text{KND}_2^{11}\text{BD}_3$	190
6.2.3	Simultaneous Rietveld Refinement of KNH_2BH_3	191
6.3	Variable Temperature X-ray Diffraction Studies of KNH_2BH_3	194
6.3.1	Intelligent Gravimetric Analysis Studies of KNH_2BH_3	198
6.3.2	Intelligent Gravimetric Analysis with Neutron Diffraction Studies of $\text{KND}_2^{11}\text{BD}_3$	200
6.3.3	Differential Scanning Calorimetry of KNH_2BH_3	205
6.4	Inelastic Neutron Scattering Studies of KNH_2BH_3	207
6.5	Conclusions	213
7	Conclusions and Further Work	215
7.1	Thesis Summary	215
7.2	Structure	218
7.3	Decomposition	219
7.4	Further Work	221
7.4.1	Continuation of Thesis Research	221
7.4.2	General Ammonia Borane Derivatives for Hydrogen Storage	222
	Bibliography	223
	List of Tables	239
A	Inelastic Neutron Scattering Spectroscopy Modes and Assignments	241

Chapter 1

Introduction

1.1 Hydrogen Storage Background

Global warming is one of the main challenges that faces the world in the 21st century. There is a clear consensus that CO₂ emissions must be reduced dramatically and that part of this requires a move away from carbon-based fuels.

Hydrogen stores a large amount of chemical energy; it is light, releases only steam as its combustion product, and its oxide - water - is ubiquitous on earth. These properties combine to make it a highly promising carbon-free fuel vector for vehicles where power, cost, mobility and emissions are central considerations. Hydrogen, however, is an energy carrier not a primary energy source. As with electricity, it must be produced, transported and stored before use. One of the principal scientific and technological challenges of the early 21st century is to find green solutions to the stages that complete the cycle shown in Figure 1.1:

- Environmentally acceptable hydrogen production - The main current method of hydrogen production is by the steam reformation of methane which releases one mole of carbon dioxide for every two moles of hydrogen gas produced. This is clearly incompatible with a carbon free economy. The ideal method for hydrogen production is the direct electrolysis of water into hydrogen and oxygen using solar cells which would allow totally sustainable hydrogen production.

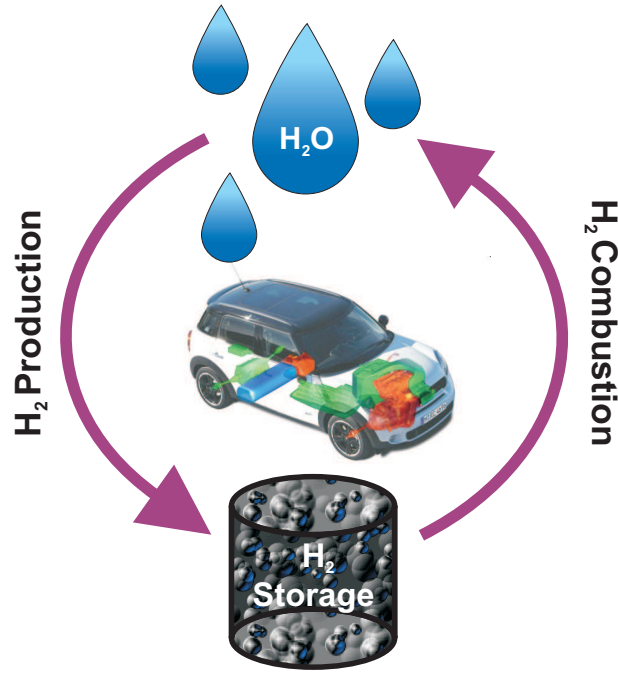


Figure 1.1: Conceptual diagram of the hydrogen cycle.

- Efficient power conversion - Hydrogen can be harnessed in two ways for vehicle applications;
 - (i) in an internal combustion engine, which has a maximum efficiency of approximately 25% because of the thermal conversion limitations of the Carnot principle [2], where T_{hot} and T_{cold} are the temperature of the system doing the work and the external surroundings respectively.

$$Carnot\ Efficiency = \eta_c = \frac{T_{hot} - T_{cold}}{T_{hot}} \quad (1.1)$$

- (ii) in an inherently more efficient (max 50-60%) electrochemical cell where the conversion is direct and hence is not limited by the Carnot principle.

- Efficient and safe storage - for hydrogen-powered vehicles to become a practical reality, one significant challenge is a method of storage that is safe, has a high gravimetric and volume density of hydrogen and is capable of rapid charge and discharge of hydrogen at reasonable temperatures (100°C to 150°C). At room temperature and atmospheric pressure, the 4 kg of hydrogen required to power an electrochemical cell for 300 miles occupies a volume of 45 m³. The U.S Department

of Energy (DoE) [3] has set objectives to develop and verify on-board hydrogen storage systems with a range of 300 miles. They include achieving 1.8 kWh/kg (5.5 wt%) by 2015. Current research in hydrogen storage may be considered in terms of three main categories which are summarized below.

Cryogenics and Compression

The energy density of hydrogen can be enhanced by compression and / or cryogenics. Modern compression tanks are capable of storing 4kg of H₂ in a 34l tank under 700 bar but the size, weight and cost of these tanks are still too high for mass production. Liquid H₂ tanks offer an even greater energy density and can store 4kg of H₂ in a 15l tank. However, cryogenic tanks are generally agreed to be less viable as they involve significant energy penalties for liquifaction and there is currently an unavoidable loss of H₂ resulting from boil-off.

Absorption within High Surface Area Materials

The most promising absorbed hydrogen systems are high surface area materials [4, 5], such as activated carbon, nanotubes, zeolites and Metal Organic Frameworks (MOFs). These materials show promise with respect to the volumetric density criteria but suffer from low absorption temperatures (77K) and very low gravimetric storage densities at room temperature.

Chemical Storage

Because of weight percent considerations, the principle chemical constituents of suitable hydrogen storage materials are limited to the early elements of the periodic table [6] (Li, Be, B, C, N, O, F, Na, Mg, Al, Si, and P.). Many interstitial metal hydrides have promising thermodynamic and kinetic properties [7], but they are too heavy and do not meet the DoE goals for vehicle-based hydrogen storage materials.

Chemical hydrides with the appropriate wt% criteria include complex non-interstitial hydrides such as borohydrides [8], alanates [9] and amides [10]. While these compounds possess the high gravimetric hydrogen content required they generally lack direct hydrogen reversibility and have unfavourable thermal desorption properties. Strategies in progress to improve the kinetic and thermodynamic properties involve doping with heavier metals cations e.g $\text{Li}_3\text{Na}(\text{NH}_2)_4$ [11], or the use of catalysts such as LaCl_3 [12].

More recently, ammonia borane (NH_3BH_3) has become the focus of a world-wide research program into its hydrogen storage properties [13], which fulfill many of the 2015 US DoE criteria for on-board hydrogen storage in light duty vehicles [3] (7.5 wt.% hydrogen, ambient stability and an operating temperature between -40-85°C). The key parameters for NH_3BH_3 include a high hydrogen content (19.6wt%), stability under atmospheric conditions [14], (resulting from uncommon intermolecular interactions) and a dehydrogenation profile which starts to occur at $\sim 75^\circ\text{C}$ (12.5 wt% hydrogen is released below 150°C , [13]).

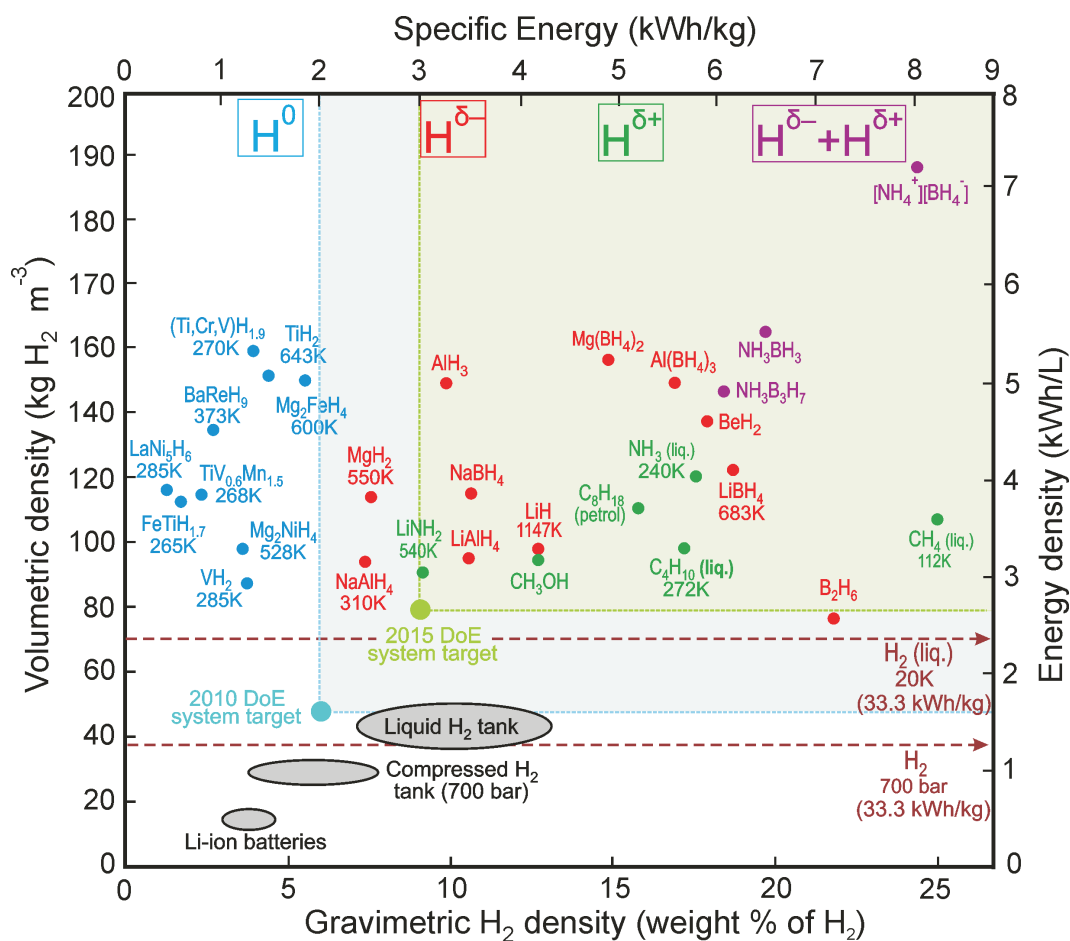


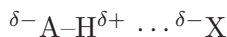
Figure 1.2: Graph showing the relationship between hydrogen interactions and hydrogen storage properties of the main chemical stores [15]. Reproduced by permission of The Royal Society of Chemistry

1.2 Hydrogen and Di-Hydrogen Bonding

Hydrogen bonding and more specifically dihydrogen bonding plays a vital role in the crystal chemistry and decomposition properties of many H storage materials as shown by Figure 1.2

1.2.1 Hydrogen Bonding

Generally hydrogen bonds can be described as a strong electrostatic interaction between two species of the form [16];



where A (the H-bond donor) and X (H-bond acceptor) are strongly electronegative elements, most commonly N, O or F and X has a lone pair.

Hydrogen bonds range in strength between 1.5 kJ mol^{-1} and 155 kJ mol^{-1} [17] but are typically between $12\text{-}30 \text{ kJ mol}^{-1}$. They are interactions of intermediate strength being approximately one order of magnitude more than dispersive (van der Waals) forces and one order of magnitude less than a chemical bond.

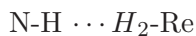
There is a strong bonding dependence on orbital overlap and consequently the ideal bonding geometry is determined by the nature of the hydrogen bond donor. For example, linear HCN adopts 180° bond with HF but pyramidal H_2O adopts a 46° bond. As such they have profound structural consequences and are responsible for the 3D tetrahedral networks in water, chains in HF and the DNA double helix.

To summarise there are four criteria for an interaction to be classified as a hydrogen bond [18]:

1. the interaction energy is measured from weak to medium
2. the interaction is accompanied by a remarkable inter-penetration of isolated electronic clouds of the two species involved. The levels of penetration can be estimated by comparing the non bonded r_H^0 and r_X^0 radii and the corresponding bonded radii r_H and r_X . $r_H + r_X$ must be less than $r_H^0 + r_X^0$.
3. the interaction results in a partial electron transfer between the two moieties.
4. the interaction exhibits a preferred geometry.

1.2.2 Dihydrogen Bonding

In 1995, Wessel *et. al.* [19] identified an unusual three-centre hydrogen bond of the form:



where the metal hydride was acting as the H-bond acceptor. These bonds have since become known as dihydrogen bonds and have been defined as follows:

- they are formed between two oppositely charged H atoms $\text{A-H}^{\delta+} \cdots \delta^-\text{H-X}$ when their separation is less than the sum of their van-der-Waals radii ($2.4\text{\AA}$)
- they are of comparable strength to classical H bonds with energies between $2.5 - 74.4 \text{ kJ mol}^{-1}$ [20]
- as with classical H bonds, electrostatic contributions dominate the charge transfer and polarisation energies. However, unlike classical H bonds, the charge transfer energy is not much greater than the polarisation energy but approximately equal to it.
- they have a more rigid geometry and $\text{A-H}^{\delta+} \cdots \delta^-\text{H}$ fragments tend to be linear whereas $\text{H}^{\delta+} \cdots \delta^-\text{H-X}$ fragments tend to be bent.
- pressure and external electric fields can have a significant affect on dihydrogen bonds. Trudel [21] and Li [22] found a negative external pressure dependence. Rozas [23] found that negative fields will also contract the dihydrogen bond.

1.3 Ammonia Borane

Ammonia borane was first synthesised in 1955 [24, 25, 26] and initial studies centred on its use as a fuel. In contrast to many chemical hydrides, pure ammonia borane can be straightforwardly synthesised [27] and easily handled in air. This has allowed many of its structural and physical properties to be extensively characterised [28].

A crystalline molecular solid at room temperature, NH_3BH_3 was first characterised by powder X-ray diffraction in 1955. Its structure was identified 1956 [25] as a tetragonal unit cell with space group $I4mm$. Sorokin et al. [29] proposed a face centred orthorhombic structure in 1963 later X-ray [30, 31] and neutron [32, 33] studies proved the tetragonal phase to be correct and the basic crystallography of NH_3BH_3 has been known since 1983 when Hoon *et. al.* discovered it undergoes a phase transition at 225K (-48C) to an orthorhombic unit cell (space group $Pmn2_1$) [30].

However, there were significant discrepancies between the initial structural studies of NH_3BH_3 regarding the exact atom positions and unit cell dimensions, that could not be accounted for by different experimental conditions or deuterium isotope effects. These discrepancies were resolved in a 1999 neutron study Koolster *et.al.* [32] which found that the B and N positions should be the inverse of those previously found; these observations have been supported by subsequent NMR [30] and Raman [34] measurements. The B-N bonds in ammonia borane are almost aligned along the c axis of both cells, while the BH_3 and NH_3 geometries are tetrahedral and adopt a staggered conformation. There is significant disorder around these sites in the high temperature tetragonal cell Figure 1.3(b).

A variable temperature neutron study [33] also observed a tilt in the 16K structure between the B-N bond and the c axis of 15° , Figure 1.3(a). The authors reported that the tilt, with respect the c axis, reduces as the orthorhombic - tetragonal phase transition is approached and becomes fully aligned in the tetragonal phase. Results in this thesis indicate that tilting still occurs in the high temperature phase and is accompanied by a four-fold disorder.

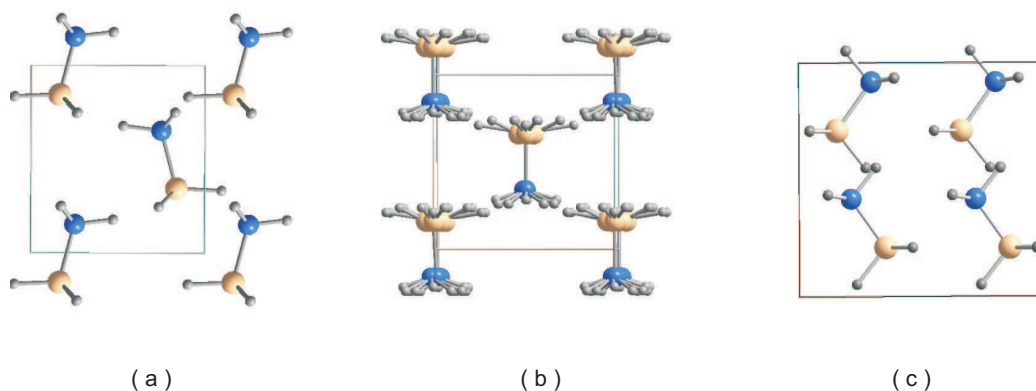


Figure 1.3: Structural diagrams of orthorhombic low temperature (a) tetragonal (b) and orthorhombic high pressure (c) NH_3BH_3 viewing along the b axes. Hydrogen is grey, nitrogen, blue and boron cream

Recently Filinchuk *et.al.* [35] observed a high pressure phase transition at 1.2GPa, from the $I4mm$ tetragonal phase to a $Cmc2_1$ orthorhombic phase shown in Figure 1.3(c) also identified by earlier Raman studies [36, 21, 37]. The most significant structural change is the large jump in tilt angle of the B-N bond along the c axis to 35° . The tilt angle increases linearly up to 79° at 4.65 GPa and is associated with the strong contraction of c axis over the same pressure regime.

The melting point of NH_3BH_3 is $+104^\circ\text{C}$ (377K) [14], which, on first consideration, is surprising as its isoelectronic analogue ethane, C_2H_6 , is a gas with a melting point of -181°C (92K). The key factor in this massive increase in melting point is the presence of strong dihydrogen bonding, see Figure 1.4. These unusual dihydrogen intermolecular interactions, see Section 1.2.2, are formed between the hydridic $\text{B-H}^{\delta-}$, acting as the Lewis base H-bond acceptor, and the protic $\text{N-H}^{\delta+}$, acting as the Lewis acid H donor, and take the form $\text{B-H}^{\delta-} \cdots \delta^+\text{H-N}$. There is a considerable interaction energy of 26 kJ mol^{-1} [38] resulting in unusually short $\text{H} \cdots \text{H}$ distances of $\sim 2\text{\AA}$, which are considerably less than the van-der-Waals radii sum of $2.4\text{\AA}$. Although there is a degree of flexibility in the geometry of these bonds, the expected preferences for linear $\text{N-H}^{\delta+} \cdots \delta^-\text{H}$, and bent $\text{B-H}^{\delta-} \cdots \delta^+\text{H}$ arrangements are upheld [32]. The polarity of NH_3BH_3 (5.2D)

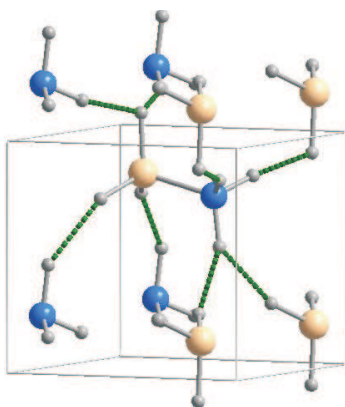


Figure 1.4: The NH_3BH_3 molecule in its orthorhombic low temperature crystalline environment showing surrounding molecular fragments indicating di-hydrogen bonding (green).

caused by the dative nature of the B-N bond is also a contributing factor to the elevated melting point.

1.3.1 Solid State Decomposition of NH_3BH_3

The generalised thermolysis of NH_3BH_3 is described below. It should be noted that the exact temperature (or temperature range) at which a decomposition step occurs and even the shapes of the thermogravimetric and differential scanning calorimetric curves are very much dependent on the heating rate. The decomposition and accompanying hydrogen release of NH_3BH_3 below 150°C (423K) occurs in two stages [13]. Firstly, NH_3BH_3 decomposes between 70°C - 120°C (343K - 393K) to give polyaminoborane $[\text{NH}_2\text{BH}_2]_n$ which subsequently decomposes to form polyiminoborane $[\text{NHBH}]_n$ over a broad temperature range according to the following equations:

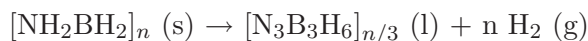


On continued heating above 500°C (773K), there is a third decomposition stage where the final mole of hydrogen is released and BN is formed [13].



The two main problems associated with the dehydrogenation profile of NH_3BH_3 are;

1. the release of borazine (extremely damaging to the hydrogen fuel cell) as a minor product resulting from a competing decomposition mechanism during the second stage of decomposition [39],

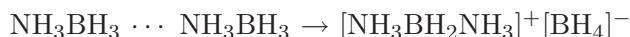


2. the non facile reversibility resulting from the unfavourable thermodynamics required to break the strong polymeric B-N bonds of the decomposition products and reform the molecular species [40].

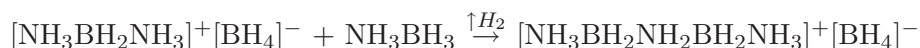
More recently, Stowe *et al.* [41] used *in-situ* ^{11}B solid state MAS NMR to follow the isothermal reaction of NH_3BH_3 at 88°C (361K). Their results revealed a more complex mechanism than previously thought and identified several new intermediates.

They proposed a three step mechanistic model comprising of:

1. An induction period where the dihydrogen bonded lattice is disrupted enabling the formation of a 'mobile phase'.
2. A nucleation stage where the diammoniate of diborane, DADB, is generated



3. A growth period where DADB reacts with ammonia-borane to form dimeric, oligomeric, and eventually polymeric products or isomerize to form the cyclic dimer.



Further evidence for this mechanism came from the same group who also observed the NH_3BH_3 to $[\text{NH}_3\text{BH}_2\text{NH}_3]^+[\text{BH}_4]^-$ phase change in a single crystal of NH_3BH_3 heated to 90°C (363K) [42].

Pressure has also been found to have a significant effects on the observed decomposition properties of NH_3BH_3 [43, 44].

At sub-atmospheric pressures, the induction period of a sample in a 90°C (363K) isothermal experiment was found to be remarkably reduced from 6 hours at 1040mb to 3.5 hours at 50mbar. Unfortunately unwanted volatiles such as diborane, and borazine were also observed at higher concentrations at lower pressures.

At elevated pressures above 1GPa only two distinct decomposition steps could be observed with Raman spectroscopy, occurring at 127°C and 200°C (400K and 473K) respectively [44]:



The first decomposition product $(\text{NH}_2\text{BH}_2)_x$ is also seen at ambient pressures, but the second is unique to high pressure conditions and is composed of larger segments of graphitic BN layers which are terminated by H. The decomposition steps commenced at higher temperatures as the pressure was increased further. At 5.5 GPa a previously unseen phase change emerged at 140°C and the two steps were delayed until 200°C and 237°C respectively (473K and 510K).

1.3.2 Regeneration of AB

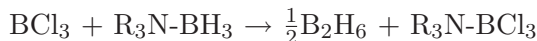
Even though reversibility is one of the key features of a successful hydrogen storage material, there is surprisingly little published on the regeneration of spent NH_3BH_3 .

Ramachandran *et al.* [45] were the first group to publish a method, which relied on the formation of B–O bonds. They used transition metal-catalyzed solvolysis to convert NH_3BH_3 into $[\text{NH}_4][\text{B}(\text{OMe})_4]$, which could be converted back to ammonia-borane at ambient temperature using NH_4Cl and LiAlH_4 .



However, this process results in the loss of H_2 and NH_3 which must be trapped and recycled and the formation of $\text{LiAl}(\text{OMe})_4$ which must be converted back to LiAlH_4 .

Later research [46, 47] used acids HX to form B–X bonds which could then be converted into B–H bonds:



It is clear that not all three equivalents of hydrogen should be released from ammonia-borane intended for regeneration, because the resulting BN is extremely inert and the energy required to reduce it would outweigh all potential benefits of using NH_3BH_3 as a hydrogen storage material. The methods described above are all spent product independent and can be used on $(\text{NH}_2\text{BH}_2)_n$ and/or $(\text{NHBH})_n$. This is advantageous because of the range of decomposition products produced by thermolysis of NH_3BH_3 . However Davis *et al.* [48] decided to restrict the product to the more well defined polyborazylene $[\text{N}_3\text{B}_3\text{H}_4]_n$ (a polymer version of borazine) produced by the transition metal catalysed dehydrogenation of NH_3BH_3 in the hope the regeneration reaction could be more easily optimised.

Davis *et al.* digested the PB under reflux with ortho-benzenedithiol which formed $(\text{C}_6\text{H}_4\text{S}_2)\text{BH}\cdot(\text{NH}_3)$ and $[\text{NH}_4][\text{B}(\text{C}_6\text{H}_4\text{S}_2)_2]$. Treatment of the mixture with excess Bu_3SnH at 60°C (333K) in THF allowed full conversion of the salt into $(\text{C}_6\text{H}_4\text{S}_2)\text{BH}\cdot(\text{NH}_3)$, which could be transformed back into ammonia-borane and $\text{C}_6\text{H}_4\text{S}_2\text{Sn}(\text{nBu})_2$ using nBu_2SnH_2 .

The above method, which suffers from a lack of scaleability due to the instability and toxicity of nBu_2SnH_2 , was improved on by Sutton [49] with the addition of an amine exchange step after the digestion with Me_3N . This step allowed nBu_3SnH to be used as the reductant instead which is more stable. The resulting products $\text{C}_6\text{H}_5\text{S-SnBu}_3$ and $\text{C}_6\text{H}_4(\text{S-SnBu}_3)_2$ could then be treated with HCl to give nBu_3SnCl and the o-benzenedithiol, which can be reused for the digestion (Figure 1.5).

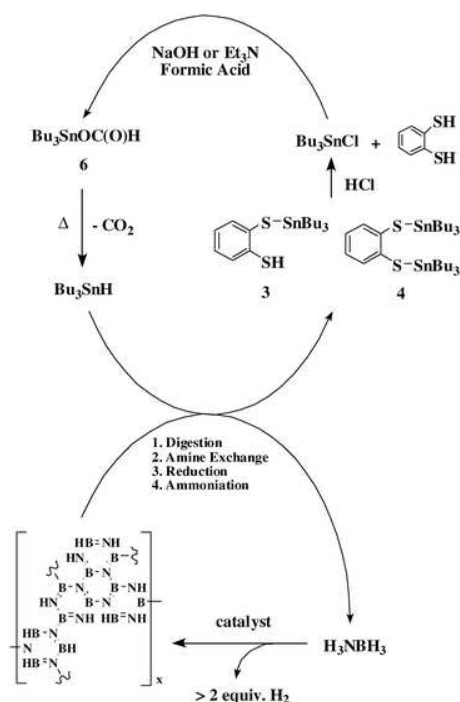
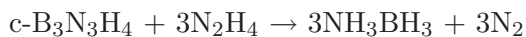


Figure 1.5: Regeneration of AB with tin recycle and ortho-benzenedithiol recovery [49]. Reproduced by permission of The Royal Society of Chemistry <http://dx.doi.org/10.1039/B919383A>.

Most recently a patent by Burrell *et al.* [50], seems to provide a more encompassing approach. Spent fuel products are digested with a thiol-containing agent (ortho-benzenedithiol) to produce at least one borosulfide compound. The borosulfide compound is then reduced with hydrazine (N_2H_4) or a hydrazine derivative to produce ammonia borane. This is particularly promising as it avoids the use altogether of the volatile tin reducing agents.

Burrell *et al.* refined this process still further and have discovered a "one-pot" method for the regeneration of PB to NH_3BH_3 using hydrazine in liquid ammonia (NH_3) at 40°C (313K) in a sealed pressure vessel. The reaction proceeds via the following pathway [50]:



1.4 Modified Ammonia Borane

Several routes have been employed to improve the dehydrogenation profile of NH_3BH_3 . Broadly these include:

1.4.1 Nanostructuring

Confinement of NH_3BH_3 at the nanoscale has been shown to significantly change its intermolecular interactions and, consequently, its dehydrogenation profile.

Mesoporous silica was the first nanoscaffold material to be used in conjunction with NH_3BH_3 [51, 52] Gutowska *et al.* reported two positive effects:

1. increased rates of H_2 release and a reduction in the peak desorption temperature to $<100^\circ\text{C}$,
2. more uniform, non-volatile decomposition products,

Further studies by Paolone [53] using anelastic spectroscopy and DCS found the orthorhombic - tetragonal phase transition at 220K (-53°C) was suppressed. The suppression occurred at silica loadings where only the internal surface of the pores were covered, suggesting monolayer deposition of NH_3BH_3 can be used to promote different thermodynamic properties.

Carbon cryogels have also been investigated and produced similar effects to the silica scaffolds in terms of suppressed borazine release and lower H_2 release temperatures [54]. Only one broad dehydrogenation step was observed at 90°C and this was lowered still further by reduction of the pore size to 5 nm. A possible catalytic effect from dangling bonds on the carbon- NH_3BH_3 interface was also postulated.

Most recently, this author has been involved in a collaboration to encapsulate NH_3BH_3 in electrospun polymer fibres. Evidence was presented that the polystyrene porous fibers contain a nano-structure that lowers the first dehydrogenation temperature of AB by 15°C - 20°C (288K-293K) and, as for the other nano-structured AB systems, the release of borazine was suppressed [55].

1.4.2 Catalysis

Catalysis of the dehydrogenation of NH_3BH_3 is a major area of research. Investigations are ongoing into both solution and solid state methods. The majority of solution based catalysis is homogeneous and centres on organometallic transition metal (TM) complexes [56, 57, 58, 59, 60] but also includes heterogeneous reactions with metal organic frameworks [61] or TM nano-particles [62]. Solid state catalysis is mainly based on doping NH_3BH_3 with TM nano-particles [63] or salts [64, 65].

Homogeneous Catalysis in Solution

The first report of organometallic catalysis of NH_3BH_3 was by Jaska *et al.* in 2001 [56]. They successfully dehydrogenated NH_3BH_3 at 25°C (298K) using Rh(I) and Rh(III) complexes. In 2006, Denny *et al.* [57] reported that Ir pincer complexes of the form $(\text{POCOP})\text{Ir}(\text{H})_2$ ($\text{POCOP} = [\eta^3\text{-}1,3\text{-(OPtBu}_2)_2\text{C}_6\text{H}_3]$) induced the rapid, room temperature evolution of 1 mole H_2 from NH_3BH_3 . The reaction mechanisms are thought to occur in a concerted fashion through B-H and N-H bond activation. The B-H hydride is bound to the Ir centre and during dehydrogenation the proton of the amine is transferred to the hydride bound to iridium [66].

Carbenes have also produced interesting results. Initially reports focused on Ni complexes [67] which facilitated the release of 2.5 moles H_2 at 60°C (333K) from NH_3BH_3 . It was found that the $\text{Ni}(\text{NHC})_2$ -catalyzed mechanism for ammonia-borane dehydrogenation was rather unusual [68, 69]. Initiation occurs through proton transfer from nitrogen to the metal-bound carbene carbon and the mechanism exhibits both N-H and B-H transition states which accounts for the release of more than two equivalents of H_2 . Recently other precious metal M(III) carbenes of the form $[(\text{NHC})_2\text{M}(\text{H})_2]^+$ ($\text{M} = \text{Rh}, \text{Ir}$) have also been investigated [60].

In 2008, a report combining in situ ^{11}B NMR monitoring, computational modeling and external trapping studies, demonstrated that selectivity and extent of H_2 release in metal-catalysed dehydrogenation of NH_3BH_3 , are determined by coordination of reactive aminoborane, NH_2BH_2 , to the metal centre [70]. If NH_2BH_2 is released from the metal centre (as in the case of carbenes) it can easily react further resulting in polyborazylene formation and the loss of ≥ 2 equivalents of H_2 . However, if NH_2BH_2 remains bound to the metal centre further reaction was hindered leading to the formation of cyclic $(\text{BH}_2\text{NH}_2)_n$ and the loss of only 1 equivalent of H_2 .

Acid catalysed reactions have the advantage of being non metallic, potentially cheaper and less toxic. The strong Lewis and Brønsted acids $\text{B}(\text{C}_6\text{F}_5)_3$, HOSO_2CF_3 and HCl initiate dehydrocoupling of NH_3BH_3 under mild conditions [71]. Lewis acids and bases which are too sterically hindered to react directly have also been exploited. An experimental study using $[\text{tBu}_3\text{PH}][\text{HB}(\text{C}_6\text{F}_5)_2]$ [72] and a theoretical study on $(\text{N-TMPN-CH}_2\text{C}_6\text{H}_4\text{B}(\text{C}_6\text{F}_5)_2)$ where TMPNH is 2,2,6,6-tetramethylpiperidiny [73] both achieved favourable results.

Ionic liquids have been shown to provide advantageous media for amineborane-based chemical hydrogen storage systems as they provide extra stability for the ionic intermediates formed e.g. $[(\text{NH}_3)_2\text{BH}_2]^+[\text{BH}_4]^-$. In 2006, Sneddon *et al.* [74] reported that both the extent and rate of hydrogen release from ammonia borane were significantly increased at 85°C , 90°C , and 95°C (358K, 363K and 368K) when the reactions were carried out in 1-butyl-3-methylimidazolium chloride compared to analogous solid-state reactions.

Heterogeneous Catalysis

There is a large body of research into the effects of transition metal nano particles on the decomposition of NH_3BH_3 in solution. Initially work centred on single metals. A wide range of non-noble metals were tested by Chandra [75] including Co, Ni, Cu and Fe, of which Co was found to have the highest activity. Noble metals (Ru, Rh, Pd, Pt and Au) have also been tested by Chandra [76] and by Shrestha *et al.* [77] both groups reported that Pt was the most effective.

Increasingly, more exotic clusters have also been explored. Yan *et al.* synthesised Au@Co Core-Shell nanoparticles which exhibited higher catalytic activity toward the dehydrogenation of ammonia borane than a simple Au-Co alloy and the pure metal counterparts. The particles caused the complete the dehydrogenation of AB within 11 minutes. Fe@Pt Core-Shell nanoparticles have also displayed high catalytic activity of up to 354% greater than Pt on its own [78].

To reduce cost and improve their stability transition metal nano-particles have also been incorporated into various supporting matrices. Oezkar et al. have confined Rh(0) [79], Cu(0) [80] and Pd(0) [81] nanoclusters in zeolites. All three metals were highly effective and promoted hydrogen release at as low as 25°C (298K). Dai *et al.* [82] prepared ruthenium (Ru) nanoparticles immobilized in montmorillonite (MMT). The Ru/MMT systems were also extremely efficient and at high loading completed the dehydrogenation of NH_3BH_3 in 1.2 minutes. Au–Ni nanoparticles embedded in SiO_2 the ability to generate hydrogen at 18°C (291K) in air.

The advent of metal organic frameworks (MOFs) provided an interesting twist on the supported catalyst theme. MOFs are attractive candidates as they offer an active metal ion already situated in an open framework. Li *et al.* [83] used a Ni-based MOF which catalysed complete hydrogen release within 2 min at 40°C (313K).

Homogeneous Catalysis in Solid State

A solid state catalyst is highly desirable given the end target of a solid state fuel tank and some promising results have been reported. However, there is less published material in this area than in solution, possibly due the inherent difficulties maintaining catalytic contact in the solid state.

The most commonly used materials are transition metals, either in the form of nanoparticles or their chlorides. He *et al.* [63] used co-precipitation to dope sample of NH_3BH_3 with Ni or Co nano-particles. Both metals successfully lowered the evolution of 1 equivalent of H_2 to 59°C (332K) and did not exhibit an induction period, undesirable byproducts or sample foaming. Kalidindi [64] preformed similar experiments to He using Ni, Co and Cu chlorides. CuCl_2 was the most effective and induced a considerable amount

of hydrogen release even at room temperature. The reaction was thought to proceed via a $[\text{NH}_4]^+[\text{BCl}_4]^-$ intermediate which prevented the formation of borazine thereby affording pure H_2 .

Neiner *et al.* [84] found the addition of nano hexagonal BN to NH_3BH_3 , decreased the dehydrogenation temperature, amount of NH_3 formed and the exothermicity of the hydrogen release reaction. These positive effects were amplified by increasing the nano-BN concentration. However, unfortunately increased amounts of borazine were also generated.

Most recently Li *et al.* [85] applied their previous work on MOFs [83] to the solid state where they observed a synergistic effect from the nanoconfinement and metallic catalysis. The small pore size of the MOF strongly confined NH_3BH_3 , enabling decomposition at a much lower temperature (75°C / 348K). The catalytic unsaturated metal Y^{3+} sites of JUC-32-Y interacted with NH_3BH_3 to completely prevent the formation of ammonia.

1.4.3 Chemical modification

Chemical modification aims to alter the intermolecular interactions and polarity of the molecular unit. An increasing body of work into the 'amidoborane' class of molecules is showing promising results. An amidoborane has the formula XNH_2BH_3 where one of H atoms on the N is replaced by X either an alkali metal [86, 87, 88, 89], alkali earth metal [90, 91], transition metal [92] or a short organic chain [93, 94, 95].

Alkali Metal Amidoboranes

The alkali amidoborane derivatives LiNH_2BH_3 and NaNH_2BH_3 [86, 87, 96, 97] were the first reported examples of solvent free modified amidoboranes as hydrogen storage materials. Both compounds have shorter B-N bonds, lower dehydrogenation temperatures ($92^\circ\text{C}/365\text{K}$ and $89^\circ\text{C}/362\text{K}$ respectively), no borazine production and almost thermally neutral dehydrogenation energies which offer hope of a low barrier to regeneration. These improved properties appear to result from the more electron donating

metal atoms, which increase the basicity of the resulting NH_2 group, thus strengthening the B-N bond as the lone pair is more available and can donate more strongly to the boron atom. This also has the effect of reducing the partial charges on the N-H and B-H hydrogens, thus removing the potential for hydrogen bonding [86]. Borazine release is suppressed, and these amidoborane molecules retain the ambient stability and high wt% of hydrogen (14% and 10% respectively) [86] of ammonia borane. The study and characterisation of LiNH_2BH_3 and NaNH_2BH_3 form two chapters of this thesis and their full history and properties are described in full in Sections 4.1 and 5.1.

There is to date only one published paper on KNH_2BH_3 [89] co-authored by this author. KNH_2BH_3 does offer advantages over NH_3BH_3 and is the subject of more detailed discussion and analysis in Chapter 6.

Alkali Earth Metal Amidoboranes

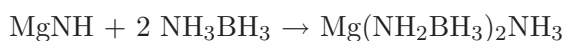
Calcium amidoborane ($\text{Ca}(\text{NH}_2\text{BH}_3)_2$) was the first alkali earth metal amidoborane which was systematically evaluated for its hydrogen storage properties [90]. It was synthesised by the reaction of CaH_2 and NH_3BH_3 in THF which formed a bis adduct that could be removed under vacuum to leave the pure product.



Its hydrogen storage properties were assessed by TGA and GC. The major weight loss occurred between 120°C and 245 °C (393K and 518K) with an inflection point at 170°C (443K) and contributed about 8 wt% out of a potential 12 wt% hydrogen. The released volatiles from this step were predominantly hydrogen, but small quantities of borazine and ammonia (below 0.1%) were also detected.

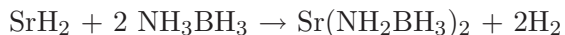
A bis-ammoniate of ($\text{Ca}(\text{NH}_2\text{BH}_3)_2$) has also displayed promising properties. $\text{Ca}(\text{NH}_2\text{BH}_3)_2(\text{NH}_3)_2$ was synthesised via the reaction of $\text{Ca}(\text{NH}_2)_2$ with NH_3BH_3 . Its decomposition properties offer an improvement compared with those of pure ($\text{Ca}(\text{NH}_2\text{BH}_3)_2$) and show that more than 8 wt% hydrogen can be released without borazine emission at 150 °C (423K).

Pure $\text{Mg}(\text{NH}_2\text{BH}_3)_2$ is a highly attractive material due to its high 12wt% of hydrogen. However there is no published data on such a phase and it only appears in the literature stabilised by adducts. This is due to the small Mg^{2+} cation which due to steric hinderance cannot be effectively stabilised by the relative large $[\text{NH}_2\text{BH}_3]^-$ which leads to an unfavourable structure under ambient conditions. Spielmann [98] reported an organometallic complex $(\text{DIPP-nacnac})\text{MgN}(\text{DIPP})\text{BH}_3$ which decomposes to release H_2 above 100°C . The most promising magnesium compound to be reported is a monoammoniate $\text{Mg}(\text{NH}_2\text{BH}_3)_2\cdot\text{NH}_3$ [99] formed by ball-milling MgNH (synthesised by thermal decomposition of $\text{Mg}(\text{NH}_2)_2$) with 2 equivalents of NH_3BH_3 :



Quantitative measurements of hydrogen desorption from $\text{Mg}(\text{NH}_2\text{BH}_3)_2\cdot\text{NH}_3$ in a closed system showed that with a heating rate of $0.5^\circ\text{C min}^{-1}$ ca. 5.3, 8.4, 9.7 and 11.4 wt% or 2.7, 4.2, 4.9 and 5.7 equivalents H_2 could be released at ca. 100, 150, 200 and 300°C (373, 423, 473 and 573K), respectively with no detectable ammonia. The solid residue has the formula $[\text{MgB}_2\text{N}_3\text{H}]$, which is thought to be equivalent to $\text{MgNH} + 2\text{BN}$.

It has been possible to form a pure $\text{Sr}(\text{NH}_2\text{BH}_3)_2$ [100] by gently milling the powder mixtures of SrH_2 and ammonia borane:

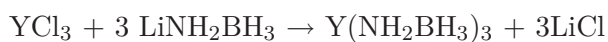


Thermal analyses showed that $\text{Sr}(\text{NH}_2\text{BH}_3)_2$ decomposed into $\text{Sr}(\text{NBH})_2$ and H_2 . The process initiated at about 60°C (333K) and became violent as the temperature increased to 93°C (366K). Small amounts of B_2H_6 and a considerable amount of NH_3 accompanied the release of H_2 due to the decomposition of $\text{Sr}(\text{NBH})_2$.

Transition Metal Amidoboranes

There has also been some limited research into transition metal amidoboranes. Hill *et al.* [101] found stoichiometric and catalytic reactions of group 3 (Sc, Y) amides with $\text{Me}_2\text{NH}\cdot\text{BH}_3$ resulted in formation of the corresponding amidoborane derivatives of the form $[\text{M}(\text{NMe}_2\text{BH}_2\text{NMe}_2\text{BH}_3)_3]$. Mild heating (30 minutes, 50°C (323K)) of $[\text{Y}(\text{NMe}_2\text{BH}_2\text{NMe}_2\text{BH}_3)_3]$ evidenced complete and selective conversion to $[\text{H}_2\text{BNMe}_2]_2$ as the sole boron-containing product by ^{11}B NMR.

Genova [92] successfully obtained polycrystalline $\text{Y}(\text{NH}_2\text{BH}_3)_3$ via mechanochemical synthesis utilizing LiNH_2BH_3 and YCl_3 .



Unfortunately $\text{Y}(\text{NH}_2\text{BH}_3)_3$ despite its attractive 8.5wt% does not hold much promise as a practical hydrogen storage compound as it is quite unstable at ambient conditions and spontaneously decomposes within several days. Additionally when heated in argon, it exothermally emits hydrogen contaminated with significant amount of ammonia in the 50°C – 250°C (323K–523K) temperature range.

1.5 Ammonium Borohydride

Ammonium borohydride, NH_4BH_4 , is a crystalline white powder which decomposes above 220K (-53°C). It was investigated in the 1950s for its potential as a rocket fuel [102] and in the 1980s as a doped material for polarised targets [103] but on the whole few investigations have been made on it and little was known about its structure or hydrogen storage properties. Now with the renewed interest in light-weight hydrogen-rich compounds for hydrogen storage applications, NH_4BH_4 is again a material of interest [104, 105]. With its high weight-percent (24.5%) and low decomposition temperature, NH_4BH_4 has two of the most important features of a commercially viable hydrogen storage material.

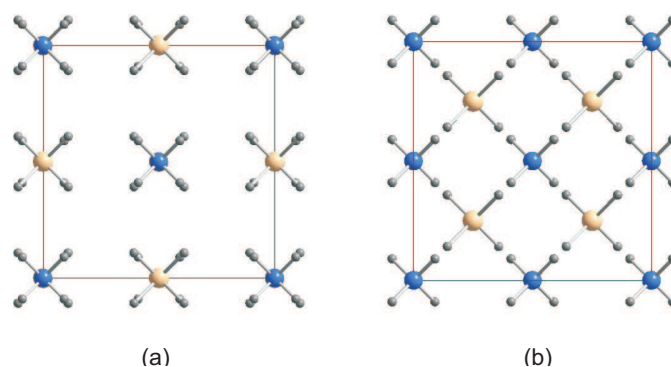


Figure 1.6: Structural diagrams of Rock Salt ($Fm-3m$) (a) and Zinc Blend ($F-43m$) (b) theoretical structures of NH_4BH_4 viewing along the b axes. Hydrogen is grey, nitrogen, blue and boron cream.

Ammonium borohydride was found to have a cubic lattice 60K (-213°C). Theoretical calculations [105] on the NH_4BH_4 resulted in two possible forms, rock salt ($Fm-3m$) and zinc blende ($F-43m$) (Figure 1.6) being identified. Of these the zinc blende space group was predicted to be the more stable but X-ray diffraction found the rock-salt structure to be correct.

Chapter 2

Experimental Techniques

2.1 Introduction

In this chapter, the methods of synthesis and characterisation used in this thesis are described and explained. Particular emphasis is placed on the handling, sourcing and preparation of precursor compounds and also the main techniques used, including; X-ray and neutron diffraction, inelastic neutron scattering spectroscopy and gravimetric analysis.

2.2 Crystallography

Solid materials can be divided in to three main classes:

1. Glasses or supercooled liquids which are made up of chemically repeating units (e.g. SiO_4) joined in a random way. They do not have long range order or sharp well defined melting points.
2. Amorphous materials also have no long range order and very small particles of less than $100\text{\AA}$ diameter
3. Crystalline materials whose constituent atoms, molecules, or ions are arranged in an orderly repeating pattern extending in all three spatial dimensions and which do have long range structural order ($>1000\text{\AA}$).

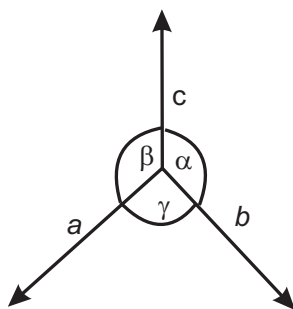


Figure 2.1: Schematic showing how the lengths and angles of a unit cell are defined.

This thesis is concerned with the synthesis and characterisation of crystalline materials and they are the focus of an in depth explanation below.

Crystalline Materials

The structure of a crystalline compound is described by two components, the lattice and the motif: The lattice is a collection of identical points in 3D space related by translation, and has no reference to the composition of the material. The motif sits on each lattice point and is the smallest repeating unit of atoms, ions or molecules whose symmetry can be described as one of 32 crystallographic point groups.

The smallest unit volume of the lattice is described by the unit cell. Unit cells must tessellate using three simple, non collinear vectors which restricts the number of possible shapes to six, representing seven different symmetry types. The unit cells are defined by three axis or lattice parameters (a, b, c) and three angles (α, β, γ) as shown in Figure 2.1.

In total there are fourteen different lattices, termed Bravais lattices, that are used to describe a crystal structure [106] (Table 2.1). These are found by combining the basic unit cell shapes with the one of five lattice centerings:

Unit Cell	Lattice Parameters	Angles	Bravais Lattice
Triclinic	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90^\circ$	P
Monoclinic	$a \neq b \neq c$	$\alpha = \gamma = 90^\circ \neq \beta$	P,C
Orthorhombic	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	P, A,B,C, F,I
Tetragonal	$a = b \neq c$	$\alpha = \beta = \gamma = 90^\circ$	P,I
Trigonal	$a = b \neq c$	$\alpha = \beta = 90^\circ \neq \gamma = 120^\circ$	P R
Hexagonal	$a = b \neq c$	$\alpha = \beta = 90^\circ \neq \gamma = 60^\circ$	P
Cubic	$a = b = c$	$\alpha = \beta = \gamma = 90^\circ$	P F I

Table 2.1: Table describing the fourteen Bravais lattices.

1. Primitive (P) - One equivalent lattice point at each corner of the unit cell.
2. Body centred (I) - One additional lattice point at the centre of the cell.
3. Face centred (F) - One additional lattice point at centre of each of the faces of the cell.
4. Rhombohedral (R) - Two additional lattice points in the unit cell.
5. Centred on a single face (A, B or C) One additional lattice point at the centre of one of the cell faces.

The addition of translational symmetry operations (screw axes and glide planes) to the symmetry of the 14 Bravais lattices and the 32 point groups leads to a total of 230 different crystallographic space groups which describe all the symmetry relationships in a structure. Each space group has its own symbol containing the Bravais lattice type and the relevant symmetry elements.

It is essential to be able to define the atomic positions within the unit cell. This is achieved using fractional coordinates x, y, z ;

$$x = \frac{X}{a}; y = \frac{Y}{b}; z = \frac{Z}{c} \quad (2.1)$$

where X, Y and Z are vectors measured in Å parallel to the a, b , and c axes.

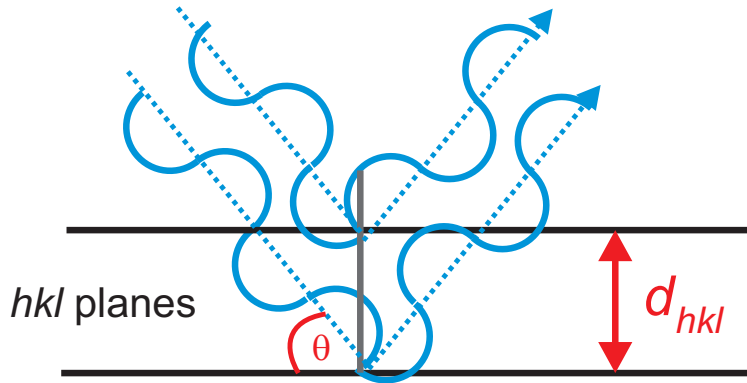


Figure 2.2: Schematic diagram of the Bragg condition for X-ray diffraction.

Planes of atoms within the crystal can be labeled with respect to the origin and the points where they intersect the a , b and c axes. There are three integers h , k , and l , called Miller indices, that define a plane intercepting a at a/h , b at b/k and c at c/l .

2.2.1 Diffraction

Diffraction is the phenomenon which occurs when a wave interacts with an obstacle. Periodic arrays of objects scatter radiation coherently and at certain angles constructive and destructive interference is observed, leading to local minima and maxima in the reflected waves.

These phenomena form the foundations of crystallography as a crystalline material is, a periodic array of atoms. When irradiated it acts as a diffraction grating where each atom site is a point source of new waves. In real space the regions of constructive interference are determined by Bragg's law [107];

$$2d\sin\theta = n\lambda \quad (2.2)$$

where d is the spacing between diffracting planes, θ is the incident angle, n is any integer, and λ is the wavelength of the incident beam, as illustrated in Figure 2.2. Using this relationship it is possible to reconstruct the framework of the crystal from the diffracted pattern.

Reconstruction works best when the diffracting planes and the wavelength of the incident beam are of a similar order of magnitude. Crystallographic planes have separations between 0.1 and 1000 Å which makes X-rays and, through wave particle duality, neutrons and electrons all suitable beams for probing a crystal structure.

2.2.2 X-ray Diffraction

Laue Equations [108]

X-rays were the first type of beam to be used for crystal structure determination. In 1912 Max Von Laue developed the equations which correlate scattering angles and the size and orientation of the unit-cell spacings in the crystal. He stated that for constructive interference to occur there must be a path difference of an integer number of wavelengths between two scattering planes.

Hence, if $\mathbf{k}_i$ is the wave-vector of the incident beam and $\mathbf{k}_o$ is the wave-vector of the outgoing beam then:

$$\mathbf{k}_i - \mathbf{k}_o = \Delta \mathbf{k} \quad (2.3)$$

For a 3D structure this condition must be satisfied simultaneously in all three directions as described by Equations 2.4-2.6;

$$\Delta k = a \sin \theta_i + a \sin \theta_o = h\lambda \quad (2.4)$$

$$\Delta k = b \sin \sigma_i + b \sin \sigma_o = k\lambda \quad (2.5)$$

$$\Delta k = c \sin \phi_i + c \sin \phi_o = l\lambda \quad (2.6)$$

where a corresponds to the lattice spacing in the unit cell, θ_i , σ_i and ϕ_i are the incident and θ_o , σ_o and ϕ_o the outgoing angles of the beam to the horizontal and h , k , l are integer values. These equations were reduced into a single formula by Bragg in 1913

His equation which is known as Bragg's law is described in detail in Section 2.2.1 went on to become the foundation of modern crystallography.

Reciprocal Space

Although Bragg's law is straightforward to use and understand it has one major limitation; it restricts the analysis of data from a three-dimensional crystal into only two-dimensions. This difficulty can be solved by converting the real lattice planes d_{hkl} into reciprocal lattice points at a distance of d_{hkl}^* from the origin [109] as shown in Equation 2.7:

$$d_{hkl}^* = \frac{1}{d_{hkl}} \quad (2.7)$$

In reciprocal space the units are $\text{\AA}^{-1}$, the unit cell parameters are labeled a^* , b^* and c^* and the angles α^* , β^* and γ^* are defined as 180° - the real space angle. This enables a hkl plane in the real lattice to be expressed as a vector in the reciprocal lattice, allowing it to be separated into its constituents as shown in Equation 2.8:

$$d_{hkl}^* = ha^* + kb^* + lc^* \quad (2.8)$$

The resolution of a reciprocal vector is especially advantageous when it comes to considering how an incident beam interacts with a crystal. For the incident beam to be diffracted to a certain point in space X from a point in the crystal C it must also be a d_{hkl}^* point in reciprocal space. Braggs Law must be satisfied in reciprocal space for this to occur as shown in Equation 2.9, where OX is the distance between the origin and the diffracted beam, CO is the radius of the sphere and IO is the diameter of the sphere (Figure 2.3)

$$OX = d_{hkl}^* = \frac{1}{d_{hkl}} = 2CO \sin \theta = IO \sin \theta \quad (2.9)$$

Braggs Law can be rearranged into the form:

$$\frac{1}{d_{hkl}} = \frac{2 \sin \theta}{\lambda} \quad (2.10)$$

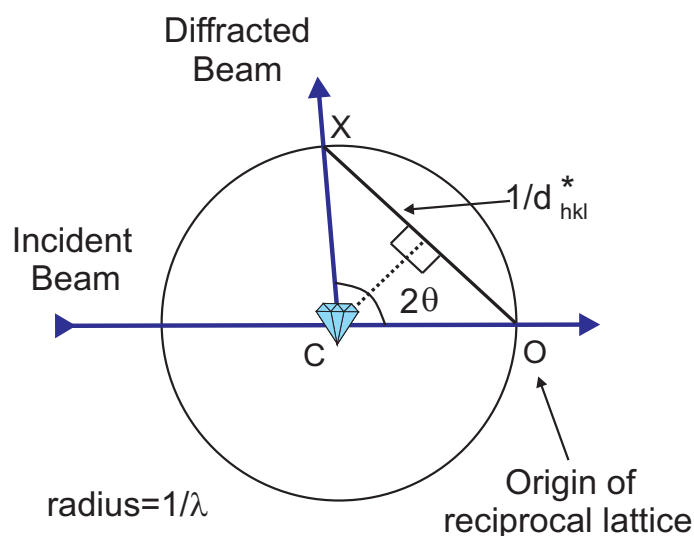


Figure 2.3: Schematic representation of Ewald's Sphere.

Simultaneous solution of both equations leads to the construction of Ewald's sphere (Figure 2.3) [109] where the reciprocal lattice points cover a sphere with radius $1/\lambda$ from the diffracting crystal. Hence, any rotation of the crystal in real space will cause all the reciprocal lattice points up to a distance of $2/\lambda$ from the origin to intersect the sphere of reflection.

Intensity

A diffraction pattern does not just depend on the geometry of the crystal. Both the X-rays and the atoms have oscillating electromagnetic fields which interact with each other, and the intensities of the diffracted beams contain a large amount of information about the actual composition of the crystal structure. Each allowed reflection is the sum of scattering from each atom in the unit cell and the combination or interference process has two main components:

1. Amplitude which differs due to the different scattering powers of the atoms which depends upon their number of electrons.
2. Individual beams will have 'phase' differences, due to the different path lengths taken through the crystal.

Path and hence phase differences will depend on the orientation of the crystal, and the relative positions of the atoms in the unit cell, with the origin of the unit cell being used as a reference point. Phases of the diffracted beam for the real atomic lattices are then phase differences between the their individual diffracted beams and the one which would be formed by the 'origin' lattice. This is given by P in Equation 2.11 [110];

$$P = 2\pi(hx + ky + lz) \quad (2.11)$$

where hkl are the indices of the reflection and x, y, z the fractional coordinates of the atom.

The final observed diffracted beam is made up by the combination of all the individual atomic beams and is defined by the structure factor F_{hkl} . In the case of a structure with N atoms in the unit cell it is defined by Equation 2.12;

$$F_{hkl} = \sum_{j=1}^N f_j \exp(i.P_j) \quad (2.12)$$

where $i.P_j = P = 2\pi i(hx_j + ky_j + lz_j)$

Complex numbers are used as the most elegant way of representing the diffracted beam that has both magnitude and phase associated with it. For any wave motion, intensity is proportional to the square of the amplitude hence the intensity of a diffracted beam is proportional to $|F|^2$.

Electron density in a structure is a continuous repetitive function and can be represented as a Fourier series as shown in Equation 2.13 [110];

$$\rho_{xyz} = \sum \sum \sum |F_{hkl}| \cos 2\pi(hx + yk + zl - \Phi_{hkl}) \quad (2.13)$$

where ρ_{xyz} is the electron density at point xyz , and Φ is the phase of the reflection hkl . Φ is unmeasurable which means direct reconstruction of the electron density map from the beam intensities is not possible and other methods must be employed to first recapture this lost information.

The most popular solutions to the phase problem are the Direct [111] and Patterson [112] methods:

- Direct Methods is a statistical approach, most applicable for crystals containing many light atoms. A detailed statistical analysis of the distribution of intensities in the diffraction pattern is performed and trigonometry is used to derive the relationships between phases of reflections and their related indices. This leads to the generation of a set of equations that define the probabilities for values of phases.
- Patterson methods create a vector map of the structure with a Fourier summation of the phaseless ($|F_{hkl}|$)². This is most useful for structures containing a few heavy atoms and many light ones as the vectors between heavy atoms are very prominent.

X-ray Powder Diffraction (XRPD)

The techniques and equations described above in sections were formulated for use on single crystal samples, i.e. a macroscopic crystal over 1mm in size with no flaws or occlusions. Unfortunately, it is not always possible to grow single crystals of sufficient size or quality to allow good diffraction data to be collected. In these cases a polycrystalline or 'powder' sample can be used instead with some modifications to the detector setup and analysis methods.

Powder samples have by their very nature an enormous number of crystallites in them and inevitably there will be some orientated, with respect to the incident beam, at the Bragg angle for every hkl plane. Thus, every hkl plane will be simultaneously irradiated for all angles of the incident beam.

This has implications for reciprocal space as well - averaging means the 3D space of a single crystal now reduces to a 2D plane. The scattering vectors are on sphere surfaces with a radii of d_{hkl}^* and not individual lattice points. Now the condition for constructive interference is only satisfied when the scattering vectors lie at the intersection of the Ewald sphere and a series of concentric spheres located at the origin of the reciprocal lattice [106]. This results in a series of concentric cones, known as the Debye-Scherrer

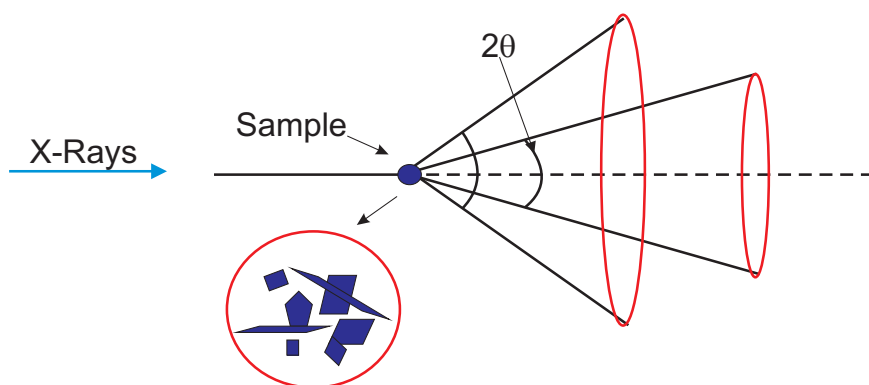


Figure 2.4: Schematic showing the generation of Debye-Scherrer cones from a powder sample.

cones, being projected and when intersected by a detector there are seen as rings of varying intensity as shown in Figure 2.4.

Unfortunately there are difficulties in assigning the absolute intensities of the rings to specific hkl reflections. This because the 2D nature of the data collection makes it impossible to distinguish lattice planes that have the same d spacing but different hkl values. Also, planes with similar scattering angles often have overlapping peaks due to their finite width. These factors combine to make *ab initio* structure solution from powder data very difficult and previously this was only possible from single crystal data. This left the main uses of powder diffraction data as fingerprinting (phase identification of known phases) and structural refinement where the experimental data is compared to a calculated model and the difference minimised using an iterative process (see Section 2.2.4).

However, in recent years there have been a huge number of advances in the resolution obtainable from high intensity synchrotron beam lines and it is now possible to collect data of high enough quality for full structure solution [113].

Experimental Equipment

High-resolution X-ray powder diffraction data were collected on many samples using the MS X04SA beamline at the Swiss Light Source, Villigen, Switzerland and the ID31 beamline at the European Synchrotron Radiation Facility, Grenoble, France.

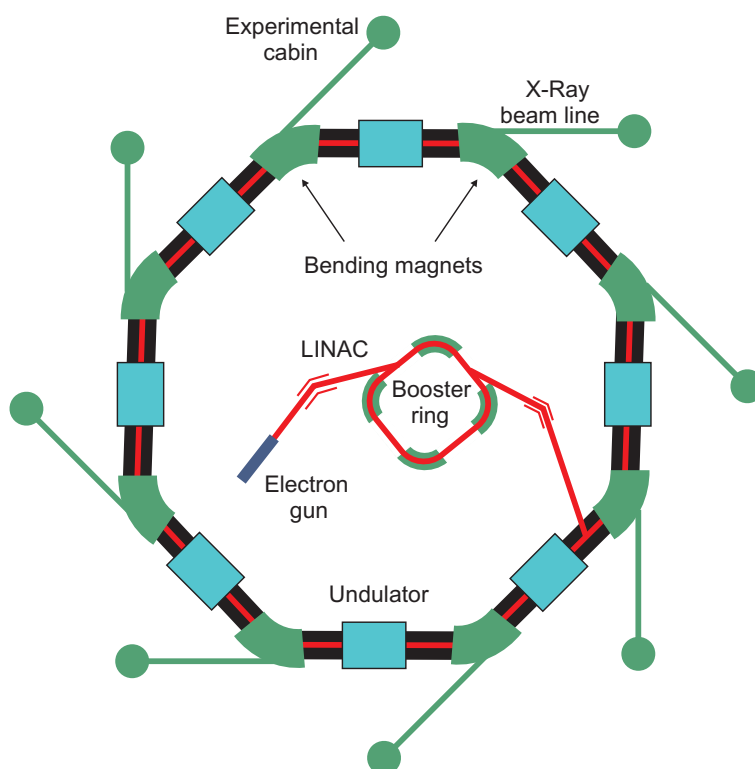


Figure 2.5: Schematic of a Synchrotron.

Synchrotron X-ray Powder Diffraction The intensity and collimation of synchrotron radiation are many orders of magnitude higher than those generated using conventional laboratory X-ray tubes. They depend on the phenomenon of bremsstrahlung. Bremsstrahlung describes the radiation emitted from the tangent of an electrons path when it is deflected by a magnetic field. To the observer the electron is approaching at virtually the speed of light. This has the effect of shrinking space and thus reducing the wavelength of the energy from microwaves to X-rays. It also folds space into a very tight cone making the light very highly collimated.

At a synchrotron electrons from an electron gun are accelerated to close to the speed of light (several billion eV) in a linac and booster ring. They are then injected into storage ring with a series of bending magnets. Light sources or beamlines utilize the cones of light produced at each bend in the storage ring as shown in Figure 2.5.

The MS X04SA beamline at the Swiss Light Source (SLS) [114] [115] [116]

The Swiss Light Source (SLS) is a third-generation synchrotron facility (2.4 GeV, 400 mA) and uses the straight sections of the booster ring for more complex magnet arrays, allowing great flexibility with the energy and intensity of the light produced.

The hardest X-rays at the SLS (5–40 keV) are generated at the Materials Science (MS) Beamline which uses a novel mini gap wiggler at its radiation source and has typical fluxes of 10^{13} photons s^{-1} at 13 keV and 2×10^{12} photons s^{-1} at 20 keV. Collimation and monochromation are achieved by a vertically collimating mirror, a fixed-exit double-crystal monochromator (DCM), in which the second Si $\langle 111 \rangle$ crystal provides horizontal focusing, and a vertically focusing mirror.

The powder diffraction section of the beamline has two independent detector systems:

1. a multi-crystal analyzer detector for high angular resolution (better than 0.005°).
2. a wide-angle silicon microstrip detector for high-speed (sub-ms) data acquisition at angular resolution better than 0.02° . It consists of 15,360 integrated semiconductor detector elements with a channel spacing of $50\mu\text{m}$ spread over 60° in 2θ , corresponding to an intrinsic resolution of 0.004° .

The combination of speed and resolution offered by the microstrip detector was essential for the compounds studied in this thesis as they had been found to suffer from severe radiation damage at other synchrotron beamlines e.g. the ESRF and Diamond which decomposed the samples into amorphous compounds and their corresponding metal hydride. The microstrip detector also allowed very detailed time resolved experiments to be conducted where the diffractometer was fitted with a cryostream or heater and crystallographic changes studied over a wide range of temperatures.

SLS Sample Preparation Samples were loaded into borosilicate glass capillary tubes (diameter 0.7 mm - 1.1 mm) within a N₂ atmosphere glove bag. The capillaries were then temporarily sealed using vacuum grease. After removal from the glove bag, the capillaries were sealed permanently using a gas-oxygen flame. The capillaries were mounted on a brass spinner using Araldite so they could be rotated in the beam during data collection in order to give good powder averaging. The data in this thesis was collected using a wavelength of around 0.8Å and a step-size of 0.004°.

The ID31 Beamline at the European Synchrotron Radiation Facility (ESRF)

The European Synchrotron Radiation Facility (ESRF) is also a third generation synchrotron facility but has a much higher energy than the SLS (6 GeV, 200 mA). ID31 is the dedicated High Resolution Powder Diffraction beamline at the ESRF. Three 11-mm-gap ex-vacuum undulators are used to generate X-rays between 5 to 60 keV with typical fluxes of 1.5×10^{12} photons mm⁻² s⁻¹ at 29 keV and 6.1×10^{12} photons mm⁻² s⁻¹ at 15 keV being measured at the sample. Monochromation is achieved by a cryogenically cooled double-crystal monochromator, with Si <111> crystals. There is no collimation of the beam to allow better powder averaging of the sample [117].

The ID31 diffractometer is comprised of a bank of 9 detectors, each preceded by a Si <111> analyser crystal. The detector channels are 2° apart and the whole bank is scanned vertically to capture the diffracted intensity over the entire 2θ range.

ESRF Sample Preparation Samples were loaded into borosilicate glass capillary tubes (diameter 0.7 mm - 1.1 mm) within a N₂ atmosphere glove bag. The capillaries were then temporarily sealed using vacuum grease. After removal from the glove bag, the capillaries were sealed permanently using a gas-oxygen flame. The capillaries mounted on a brass spinner using high melting point wax so they could be rotated in the beam during data collection in order to give good powder averaging. The data in this thesis was collected using a wavelength of around 0.8Å and a step-size of 0.003°.

Drawbacks of X-ray diffraction

Unfortunately X-ray diffraction has a number of limitations which means it is not the most suitable technique for studying all types of crystalline material. As previously stated in Section 2.2.2. the intensity of the diffracted pattern depends on the square of the structure factor $(|F_{hkl}|)^2$ of all the atoms. is in turn related to the electron density of the atoms present or more simply the atomic number (Z). This is shown explicitly in Equation 2.14 [106]:

$$f(\theta) = \frac{1}{2}(1 + \cos 2\theta) \frac{e^2}{mc^2} \psi \psi^* e^{i\mathbf{k} \cdot \mathbf{r}} dT \quad (2.14)$$

There are three important implications for this dependence:

1. Firstly, and with probably the greatest implications for this research is that with only one electron, hydrogen atoms are almost impossible to observe using X-ray diffraction. This also results in the anomalous shortening of E-H bonds
2. Secondly, it is very difficult to differentiate between atoms with similar Z.
3. Thirdly, if a compound is predominantly comprised of light atoms with only one or two heavy atoms the diffraction pattern will be dominated by scattering from the heavy atoms, thus making it difficult to elucidate information about the light elements.

Another problematic variable in Equation 2.14 is the inverse dependence on 2θ . This relationship occurs because destructive interference increases with θ and accordingly data collected at $2\theta > 70^\circ$ is often too weak to resolve.

Atomic motion is not included in Equation 2.14 and this has the effect of "smearing out" the observed electron cloud, making it seem larger than it is and also leading to a drop in intensity with increasing θ most notably for crystals with many light atoms, atoms with very similar Z and or large amounts of thermal motion.

2.2.3 Neutron Diffraction

Neutrons are electrically neutral but magnetically polar particles which interact with nuclei through the strong nuclear force and also with magnetic fields moments. Through the phenomena of wave particle duality and the relationship described by the de Broglie equation, (Equation 2.15) which relates a particles momentum (mv) to a wavelength, λ [118];

$$\lambda = \frac{h}{mv} \quad (2.15)$$

it can be shown that neutrons can have wavelengths suitable for crystallographic purposes. Neutrons have three ways of interacting with nuclei:

1. Elastic scattering where no energy transfer takes place and can be coherent or incoherent.
2. Inelastic scattering where the energy of the scattered radiation is different from the incident radiation.
3. Absorption where the incident neutron is incorporated into sample nuclei.

Coherent elastic scattering is the interaction harnessed for diffraction. All atoms and isotopes have a different coherent scattering length b which can be used to calculate the scattering cross section σ , given by Equation 2.16 [119]

$$\sigma = 4\pi b^2 \quad (2.16)$$

Equation 2.16 is the equivalent of the X-ray atomic form factor described in Section 2.2.2.

Whilst being a powerful technique in its own right, neutron diffraction also offers several advantages over X-ray diffraction:

1. As neutrons interact with the nuclei and not the electron clouds the effective size of the atoms are drastically reduced making it possible accurately gauge bond lengths.
2. No angular dependence of scattering makes structural refinements much easier.

3. Scattering abilities are not proportional to Z which makes electronically similar elements potentially easier to differentiate and also may give much more information on light elements.
4. As neutrons also interact with magnetic moments it is also possible to elucidate the magnetic ordering of a crystal.
5. The weak interaction of neutrons with matter means they are very useful for high pressure or variable temperature experiments necessitating thick sample environments, as they can penetrate them more easily.

Of course neutron diffraction is not without its drawbacks as well. The chief problems for the research undertaken in this thesis are:

The very high incoherent but low coherent scattering lengths for hydrogen which cause diffraction patterns to have high backgrounds lower resolution. This means for accurate structure refinement substitution of ^1H for ^2D is required as ^2D has low incoherent and high coherent scattering lengths.

The enormous absorption cross section of ^{10}B which is over 10,000 times greater than that of ^{11}B , permitting its use as a shielding material in nuclear reactors. This means the scattering is very weak for samples containing ^{10}B and requires either ^{11}B enrichment or very long collection times.

Other problems are lack of contrast between elements such as O and F, requirements for large sample sizes of the order of 1-2g due to the weak interactions of neutrons with matter, and the very high cost of building and running a neutron beamline which means access is limited to a few days at a time and is only awarded after a stringent application process.

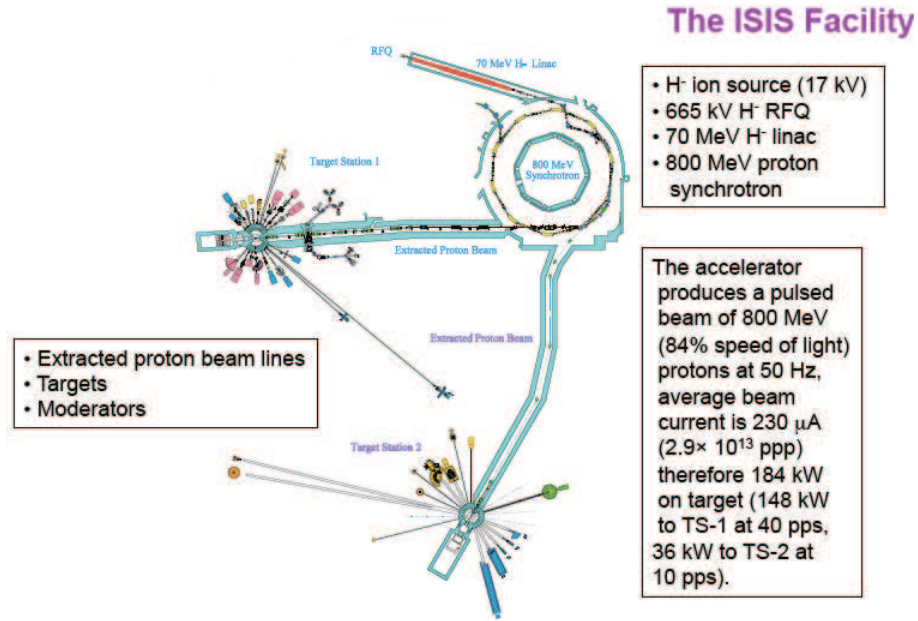


Figure 2.6: Schematic of the ISIS Beam Hall [120]. Reproduced with the permission of the STFC

ISIS Pulsed Neutron Facility

ISIS is a pulsed source which generates its neutrons by spallation. The process begins with H^- production by an electron gun. The H^- are then bunched and accelerated by a Radio Frequency Quadrupole accelerator and then a LINAC to 70 MeV. As they leave the LINAC they are stripped of their electrons by a thin alumina foil and the resulting H^+ collected in a synchrotron storage ring. Once a critical number has been reached they are accelerated further to 800 MeV and separated into two bunches. Kicker magnets are used to extract the bunches and send them to the tungsten target [120].

The huge energy of H^+ and the impact on the target forces the tungsten atoms to release some of their neutrons, creating in an intense sharp pulse. The pulses are then moderated and slowed to energies suitable for non destructive condensed matter interactions and separated for use in the different beamlines.

At ISIS the wavelength of the neutrons is determined by the time of flight (ToF) method where the time taken by the neutrons to travel the known distance from the source down a beamline to the sample and through to the detector is measured and used to calculate their velocity. The de Broglie relationship stated earlier can then be used to determine the wavelength (λ) as shown in Equation 2.17 [118]

$$\lambda = \frac{h}{mv} = \frac{hT}{mL} \quad (2.17)$$

where m is the mass of the neutron and h is Plank's constant, v is the velocity in $\text{m } \mu \text{ s}^{-1}$, T is the time of flight in $\mu \text{ s}$ and L is the path length in m . This allows the polychromatic neutrons arriving in the pulse to be distinguished by λ from their arrival times at the detector. As a consequence all the d spacings can be measured from the same scattering angle using the following form of the Bragg equation:

$$\lambda_{hkl} = 2d_{hkl} \sin \theta_0 \quad (2.18)$$

The neutron diffraction data presented in this thesis were measured from powdered, deuterated samples, which were loaded into 6mm vanadium cans.

The GEneral Materials Diffractometer (GEM) [121, 122]

The GEneral Materials diffractometer (GEM) is a high-intensity, medium-resolution instrument, suitable for structural studies of both crystalline powders and disordered materials.

The GEM detector array is divided into six banks and has a total area of 7.270m² and a large range in scattering angles from 1.2° to 117.4. GEM has a reasonably long 17m flight path which increases the resolution of the instrument, particularly the at the 90° detector bank which has a constant resolution of $\delta d/d = 5 \times 10^{-3}$ across all d-spacings.

Distributed along the flight path are two disc choppers which are used to control the wavelength range and a nimonic chopper to remove high energy neutrons which increase the background signal. Additionally there are five apertures and a beam-scraper for beam collimation. The beam scraper precisely defines the dimensions of the beam which is incident on the sample.

High Resolution Powder Diffractometer (HRPD) [123]

HRPD is the highest resolution neutron diffractometer in the world and is finely balanced to give the maximum attainable resolution whilst still maintaining reasonable counting times.

The spread in the Bragg reflection $\Delta d/d$ for a given d spacing is determined by the resolution of the diffractometer. In case of a pulsed neutron source there are three major sources of uncertainty; the flight time Δt , the flight path length ΔL , and the scattering angle $\Delta\theta$ which are combined in Equation 2.19 below:

$$R(d) = \frac{\Delta d}{d} = [\Delta\theta^2 \cot^2 \theta + (\frac{\Delta t}{t})^2 + (\frac{\Delta L}{L})^2]^{1/2} \quad (2.19)$$

From this it can be seen that the longer the flight path the better the resolution and the optimum geometry is backscattering for $\theta = 90$ as here $\cot \theta \approx 0$. As such HRPD was designed to have a very long flight path of 100m and 3 detector banks in backscattering geometry at angles of 30, 90 and 168°.

WISH - Wide angle In a Single Histogram [124]

WISH is a new instrument on the 2nd target station at ISIS - (TS-II) and like HRPD is also a TOF powder diffractometer. It is specifically designed to operate at long wavelengths on magnetic structures, and other crystals with big unit cells such as metal organic frameworks (MOFs), to resolve the multiple nearly overlapping Bragg peaks that occur at long d-spacings.

Neutrons coming from the TS-II are moderated by a decoupled solid methane moderator and have a thermalised flux peaking around 4 Å. This coupled with an optimised path length of 50m allows high resolution data collection over a d-spacing range from 0.7-17 Å with a single frame bandwidth of 8Å. All scattering angles between 10° and 170° covered by ZnS scintillator, position sensitive detectors situated at a constant $L\sin\theta$ from both sides of the sample, where L is 2.2m. The extrinsic background is kept low by careful collimation with oscillating radial collimator and by enclosing the detector modules in a boron rich material.

2.2.4 Structure Determination from Powder Diffraction Data

Collection of a good diffraction pattern from a new compound is only the first step in the journey to solve its structure and the processes used in this thesis are outlined below:

- Indexing - The reflection positions of the pattern are analysed and the unit cell determined. Symmetry operations within the unit cell reduce the number of reflections seen and these systematic absences are used to determine the space group. This was achieved using the auto indexing function in Refinement program TOPAS academic [125] (more detailed information is available in Section 2.2.4.2).

- Pawley refinement [126] - This breaks down the pattern into its constituent integrated intensities I_{hkl} using a least squares analysis. It requires no structural model because unlike the those for the peak positions and widths, the variables for the peak areas are not functions of anything other than those shown in Equation 2.20, where χ^2 is the 'goodness of fit', M_i is the model diffraction pattern, y_i is the observed diffraction pattern and σ_i is the standard deviation at point i [127]:

$$\chi^2 = \sum_{i=1}^N \frac{1}{\sigma_i^2} (y_i - M_i)^2 \quad (2.20)$$

- Solution of the phase problem - The single crystal methods described in Section 2.2.2 can be used to introduce chemical information in the unit cell. However for the molecular compounds used in this thesis the simulated annealing technique can also be used to great effect. A known molecular structure or fragment is allowed to move around the unit cell by translations and rotations in an attempt to find an energy minima. The technique utilises a Bayesian algorithm and was performed in the computer program DASH [128].

Once these stages have been completed the coarse structure produced must be optimised against the experimental data by one of several possible refinement methods. The Rietveld method [129] is widely agreed to be the most powerful for powder diffraction data as it minimises the impact of overlapping reflections and it is described below in more detail [127].

Rietveld Refinement

In 1969 Rietveld [129] formulated a method that could be applied to the complex patterns from low symmetry materials that were beginning to be resolved due to the advances in experimental equipment. It is based on a curve fitting procedure and, by means of a least squares refinement, minimises the difference between the observed and calculated patterns instead of individual reflections. This parameters is termed the residual S_y ;

$$S_y = \sum_i w_i (y_i - y_{ci})^2 \quad (2.21)$$

where $w_i = 1/y_i$, y_i is the observed intensity at point i and y_{ci} is the calculated intensity.

The Rietveld method models shape of the Bragg reflections on a peak function such as Gaussian, Lorentzian or pseudo-Voigt. From there it assumes the calculated intensity at any point on the pattern can be found by summing the contributions from all overlapping peaks at that point. It requires additional parameters to the usual least squares parameters of atomic coordinates, scale and temperature factors. These are; a zero point error for the detector, lattice parameters and functions which describe the FWHM intensity of the peak model with scattering angle and are shown in Equation 2.22;

$$y_{ci} = y_{bi} + s \sum_K L_K |F_K|^2 \phi(2\theta_i - 2\theta_K) P_K A \quad (2.22)$$

where y_{bi} is background intensity, s is scale factor, K is miller indices of the Bragg reflection L_K , Lorentz polarisation and multiplicity factors $|F_K|^2$ structure factor for the K^{th} Bragg reflection, ϕ is peak shape $(2\theta_i - 2\theta_K)$ resolves sample displacement and instrument misalignment, $P_K A$ preferred orientation, A absorption.

For the Rietveld method to work well it is essential to have a good starting structure and care must be taken in the early stages of structure determination to ensure it converges correctly. Visual inspection of the fit is important but ultimately the success of the refinement is quantified several statistical R-values.

1. the profile R value $R_p = \frac{\sum |y_i - y_{ci}|}{\sum |y_i|}$.
2. the weighted profile R value $R_{wp} = \left[\frac{\sum w_i y_i - y_{ci}^2}{\sum w_i y_i^2} \right]^{1/2}$. it is often seen as the most meaningful because the numerator is minimised and best demonstrates the progress of the refinement.
3. the expected profile R value $R_{exp} = \left[\frac{(N-P)}{\sum w_i y_i^2} \right]^{1/2}$ where N is the number of number of observables and P is the number of refined parameters.

The ratio of R_{wp} to R_{exp} is know as the χ^2 or 'goodness of fit' value. Obviously the closer χ^2 is to 1 the better but values up to 2.5 are considered acceptable.

TOPAS Academic Refinement Software

All structural refinements discussed in this thesis were performed using the Rietveld method in the program TOPAS Academic [125].

The first stage of a refinement was to model the background with high order polynomials. For X-ray data a Lorentz polarisation factor was added to account for changes in peak position and the angular dependency of the X-rays. Then structural information on the phases potentially present were added one by one. Initially only parameters affecting the peak positions were varied e.g. the lattice constants and zero point error. Once the best possible fit was achieved, factors affecting the peak intensity were also allowed to vary e.g. scale, atomic positions and temperature factors.

Sequential Rietveld Refinement of Variable Temperature Data - Batch refinements The variable temperature diffraction experiments performed in this thesis frequently generated hundreds of files to be analysed which would be extremely time consuming to do individually. However, provided temperature increments are small, it can be assumed the difference between consecutive files is also small and the converged refinement for the n^{th} file makes a good starting point for the $n+1^{th}$.

This assumption forms the basis of the 'Batch refinement' in TOPAS Academic [125] which allows the sequential refinement of any number of diffraction pattern in one go and the simultaneous output of the refining parameters. A seed file was prepared by careful refinement of the first diffraction pattern of the sequence and the zero error and background fixed.

A batch file is also generated which specifies the data files for refinement and code for the production of a .inp file for each refinement, using the seed file or previous refinement file as its starting point. The technique works best for smoothly varying crystals and compounds which exhibited large discontinuities in the refining parameters or which underwent phase changes needed more than one batch file per run.

The main parameters allowed to vary in a batch refinement are the lattice constants, scale factor and the temperature factors. Other parameters that could be varied depending on the compound of interest were bond lengths, bond angles and site occupancies.

Z-Matrices Z matrices are internal coordinate representations of an atomic system. Each atom is described in terms of its internal coordinates; atomic number, bond length, bond angle, and dihedral angle.

Z-matrices can be converted to Cartesian coordinates and back, as the information content is identical. This interconversion means Z-matrices can be used to incorporate a 'rigid body' in a crystallographic refinement that is explicitly defined in terms of bond lengths and angles rather than Cartesian coordinates. Once defined several operations can be performed on them including; translation, rotation around a point, or rotation around a line. The bond lengths and angles can also be allowed to refine between specified limits.

The advantages of including a rigid body in a refinement are three fold:

1. During structure solution a known molecular unit may be specified and used during simulated annealing to help convergence into a 'chemically sensible' solution.
2. During Rietveld refinement to optimise and/or constrain a specific geometry.
3. Refining parameters may be labeled and output for data mining during a batch refinement.

An example Z-matrix for a NH_4 tetrahedron is shown below:

```

z_matrix N1
z_matrix H1 N1 NHbond 1.08' min 0.9 max 1.1
z_matrix H2 N1 NHbond 1.08' min 0.9 max 1.1 H1 !NHang 109.5
z_matrix H3 N1 NHbond 1.08' min 0.9 max 1.1 H1 !NHang 109.5 H2 !NHdihed 120.0
z_matrix H4 N1 NHbond 1.08' min 0.9 max 1.1 H1 !NHang 109.5 H2 !NHdihed2 -120.0
rotate @ -311.66934' qa 1
rotate @ -239.19284' qb 1
rotate @ -77.79973' qc 1

```

```

Translate( tranx231 =N1x; , trany231 =N1y; , tranz231 =N1z;)

```

2.3 Other Techniques

2.3.1 Gravimetric Analysis

Gravimetric analysis monitors the change in a samples mass as a function of time when an external condition is applied. The samples in this thesis were analysed using Intelligent Gravimetric Analysis (IGA) which measures mass changes as a function of temperature, pressure or a combination of the two. The technique was predominantly used in conjunction with simultaneous mass spectrometry to investigate the desorption products of the samples. However it was also used in conjunction with the HRPD diffractometer at ISIS for monitoring the changes in crystal structure during decomposition.

The IGA system used for all experiments was a Hiden Isochema IGA-003 Two Stream Dynamic Gas Sorption Analyser. A UHV stainless steel reaction vessel sheathes a stainless steel mesh sample bucket, a platinum resistance thermocouple (accurate to $\pm 0.2^{\circ}\text{C}$) and a gas inlet/outlet tube. The sample holder is attached to a large capacity microbalance (5g) with a resolution of $0.1\text{ }\mu\text{g}$ via a fine gold chain and a tungsten wire hangdown.

The reaction vessel is capable of with standing pressures from 10^{-6} mbar to 20 bar and temperatures between -5 and 500°C (268K-773K). Temperature control was via a low thermal mass linear ramp 500°C (773K) fast response furnace capable of ramp rates between 0.2 and $20^{\circ}\text{C min}^{-1}$. Measurements can be made in a sealed system or under a flow of gas of up to 500 ml min^{-1} .

Software compensations for non ideal gas behaviour and buoyancy effects due both to the different temperatures and volumes of the sample and counterweight are integrated into the system. Air sensitive samples were loaded inertly using a special 'dry loading' chamber and pod.

For a typical experiment 50 mg of sample was loaded in the glove box into a stainless steel mesh bucket and sealed into the dry loading pod. The pod was then inserted in to the IGA dry loading chamber and the chamber purged with N_2 for 30 minutes. The pod was then opened and the bucket transferred to the tungsten hangdown using a system reminiscent of an arcade game. The reactor was then raised and sealed with

a copper gasket. The dry loader was then removed from the IGA and the sample left under dynamic vacuum for 12 hours to remove all traces of contaminant gases. The chamber was refilled with the requisite pressure of He, the furnace attached and the experiment commenced. All variables are sampled every 12.5 seconds. Upon completion of the experiment the sample was removed again using the dry loader for further analysis.

Intelligent Gravimetric Analysis with Mass Spectrometry (IGA-MS)

Using the mass spectrometer in conjunction with the IGA requires it to be operated in flowing mode with an inert background gas. The flowing background gas (in this case He) then carries a small aliquot of the desorbed gas to the mass spectrometer chamber through a 10 bar capillary tube.

The Mass spectrometer used is a Hiden Analytical Dynamic Sampling Mass Spectrometer system (DSMS type HPR-20). The gauge fitted is type HAL 201, type 124100, with dual a Faraday/Electron Multiplier detector capable of detecting an atomic mass range 200 AMU with a limit of 0.1 to 1ppm, subject to spectral interference. Ionisation is via electron impact using a thorium coated iridium filament and the system can follow the partial pressures of up to six molecular ions simultaneously.

Intelligent Gravimetric Analysis with Neutron Diffraction (IGAⁿ)

Neutrons are extremely suitable for dynamic experiments as they have a much higher penetration the complex sample environments required than other types of radiation. With this in mind a collaboration was formed between Hiden Isochema, ISIS and Oxford University to create an IGA system capable of being used *in situ* in a neutron beamline at ISIS.

The result was a new and powerful technique; Intelligent Gravimetric Analysis with Neutron Diffraction or IGAⁿ. The potency comes from the simultaneous monitoring of the mass change with temperature or pressure while collecting neutron diffraction data. This means phase changes can be precisely pinpointed and additionally any transitory intermediates or non stoichiometric phases that may be formed [130].

There are four main differences between the standard IGA and the IGAⁿ

1. Loading takes place in a custom built glove box and then the IGAⁿ is craned out and into the beamline.
2. The reactor is made of quartz to minimise interference with the neutron beam.
3. Samples are loaded into thin vanadium buckets also to minimise interference with the neutron beam (quartz buckets could not be used due to static interactions with the reaction vessel).
4. Temperature is controlled with two coil heaters situated inside the reaction vessel above and below the sample to minimise beam interaction.

Neutron diffraction data was collected every 2.5 minutes and heating rates were as slow as possible to allow the enough time for the neutron diffraction data capture the changes occurring. The measured mass is accurate to ± 0.0001 mg and the measured temperature and pressure are accurate to $\pm 0.001^\circ\text{C}$, $\pm 0.01\text{mbar}$, respectively.

2.3.2 Differential Scanning Calorimetry

Differential Scanning Calorimetry or DSC is a thermal analysis method which measures the difference in the amount of heat required to increase the temperature of a sample and reference as a function of temperature [131]. The sample and the reference are situated in separate cells, each supplied with their own heating element and thermocouple. During an experiment, the same temperature regime, selected to cause a physical transformation in the sample such as a phase transition, is applied to both cells. When the sample undergoes a physical transformation more or less heat will need to flow to it than the reference to maintain both at the same temperature. As the sample temperature starts to deviate from the reference temperature the device detects it and modifies the heat supplied to the cell in order to maintain a 'null balance' between them [132].

The heat flow to the sample may be reduced or increased depending on whether the transformation is exo- or endo- thermic. For example a melt transition would be endothermic but a vigorous decomposition would be exothermic. The electrical energy

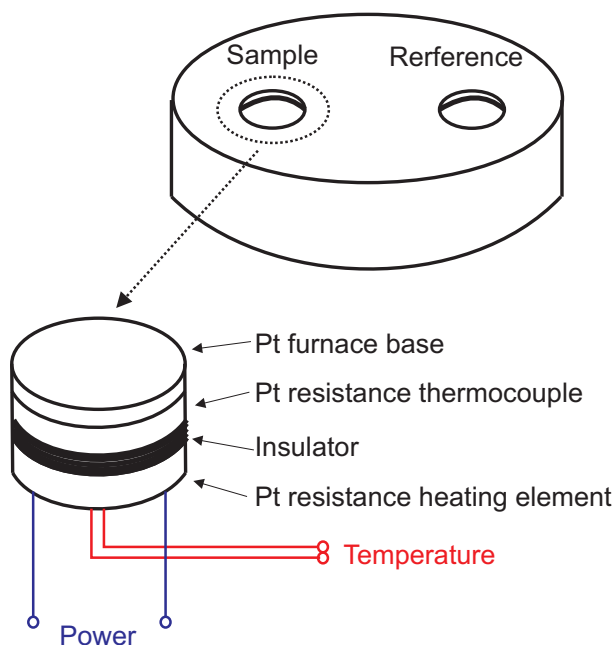


Figure 2.7: Schematic of a power compensated differential scanning calorimeter.

in W or mW required to maintain the null balance is assumed to be proportional to the heat released by the sample. Consequently the result of a DSC experiment is a curve of heat flux vs. temperature or vs. time. There are two possible conventions with respect to exothermic reactions in the sample and they can be shown positive or negative peak depending on the technology used. Integration of the area under a peak corresponding to a given transition can be used to calculate its enthalpy of transition ΔH , as shown by Equation 2.23

$$\Delta H = KA \quad (2.23)$$

where A is the area under the peak and K is the calorimetric constant. K is instrument specific and may be determined by analysing a well-characterised sample with known enthalpies of transition, subsequent data sets can then be normalised for that value [133].

Differential Scanning Calorimetry Experimental Conditions

DSC measurements were made at Los Alamos National Laboratory, New Mexico, on a Setaram SENSYS evo DSC [134]. Approximately 15mg of powdered sample was loaded into a closed 250 μ L aluminium crucible in a glove box. A small hole was punctured in the crucible to allow gas release during the experiment. The crucible was then sealed in sample vial, removed from the glove box and transported to the DSC apparatus. No inert sample loading was available for the DSC so, when ready the crucible was quickly removed from the vial and placed in the sample chamber of the DSC under a stream of flowing Ar. The sample chamber was then purged with Ar (100ml min⁻¹) for 20 mins prior to commencing the experiment.

The following temperature regime was used for all samples:

- 20 min dwell 20°C (293K)
- 20°C $\rightarrow$ 300°C (573K) @ 1°C min⁻¹
- 300°C $\rightarrow$ 20°C @ 5°C min⁻¹

2.3.3 Heat Capacity

Heat capacity is a measure of the heat absorbed by a system undergoing no chemical change. For a change in temperature of 1K at constant pressure the heat capacity C_v is defined thus:

$$C_v = \left(\frac{\partial H}{\partial T} \right)_v \quad (2.24)$$

For a pure sample the C_v can be decoupled from the mass and volume effects and expressed in terms of moles as an intensive property C_{vm} :

$$C_{vm} = \left(\frac{\partial C}{\partial n} \right)_{vm} \quad (2.25)$$

where n = number of moles in the sample and C is the heat capacity of a body made of the material in question. This molar heat capacity now depends on how the vibrational and rotational modes are populated or how many degrees of freedom the sample has. The more the degrees of freedom the higher the heat capacity of the sample [135].

For solid samples at low temperatures the phonon contribution to the heat capacity is most successfully estimated by the Debye model [136] which has a T^3 dependency:

$$\frac{C_v}{Nk} = 9 \left(\frac{T}{T_D} \right)^3 \int_0^{T_D/T} \frac{x^4 e^x}{(e^x - 1)^2} dx \quad (2.26)$$

where N = the number of atoms, T = temperature, k the Boltzmann constant and T_D = Debye temperature. Deviation of the experimental data from this fit is usually indicative of a phase change, the order of which can be determined by taking successive derivative of the data.

Heat Capacity Experimental Conditions

Heat capacity measurements were made in the materials characterisation laboratory at ISIS the on a Quantum Design PPMS-9 [137]. Approximately 20mg of the sample was loaded into a 5mm die set in a glove bag whilst being cooled on dry ice. The die set was then transfered to a pellet press and subjected to 10 tones to form a pellet.

The pellet was mounted onto the heat capacity 'puck' with Apiezon N cryogenic grease. The sample platform is suspended by eight thin wires that serve as the electrical leads for an embedded heater and thermometer. The wires also provide a well-defined thermal connection between the sample platform and the puck. An additional thermometer embedded in the puck provides a highly accurate determination of the puck temperature, and a thermal shield aids in maintaining stable sample temperature and uniformity.

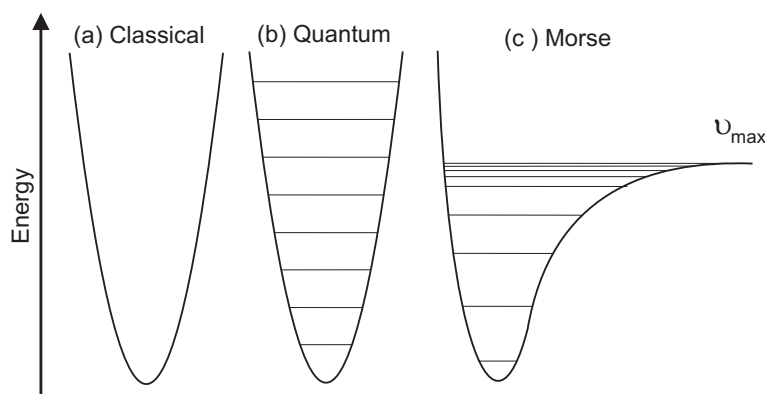


Figure 2.8: Diagram of the different potential energy curves used to describe an oscillating bond (a) Classical, (b) Quantum (c) Morse.

2.3.4 Vibrational Spectroscopy

All molecules have some form of vibrational motion. It occurs when atoms in the molecule are in periodic motion while the molecule as a whole has constant translational and rotational motion. There are six possible types of molecular vibration:

1. Bending - changing the angle between two bonds.
2. Rocking - changing the angle between a group of atoms and the rest of the molecule.
3. Wagging - changing the angle between a plane in a group of atoms and a plane bisecting the rest of the molecule.
4. Twisting - changing the angle between the plane in two groups of atoms.
5. Out of plane - a central atom moving in and out of the plane of the surrounding atoms.
6. Stretching - changing a bond length.

The number of possible vibrations for a given molecule depends on the number of atoms, N , and its geometry. All molecules have $3N$ degrees of freedom, linear molecules have $3N-5$ vibrational modes and nonlinear molecules have $3N-6$. For example linear CO_2 has 2 stretching and 2 bending modes, bent H_2O has 2 stretching and one bending mode [16].

The vibrational modes can be modelled classically by treating the molecule as a simple harmonic oscillator Figure 2.8(a). The atoms are large spheres joined by 'springs' the electronic bonds and are assumed to obey Hooke's Law, Equation 2.27 [16];

$$V(x) = \frac{1}{2}kx^2 \quad (2.27)$$

where $V(x)$ is the potential energy of the vibration, x is the displacement from the neutral positions and k is the force constant which defines the strength of the spring / bond. The frequency of the vibration ω_i is then given by Equation 2.28;

$$\omega_i = \sqrt{\frac{k}{\mu_i}} \quad (2.28)$$

where μ_i is the reduced mass of the vibrating atom.

However, the continuous parabolic potential well described by Equations 2.27 and 2.28 needs some modifications to make it a more accurate description of systems at the molecular level. On this scale energy is quantized Figure 2.8(b) and the allowed vibrational frequencies are now discrete with energies E_v given by;

$$E_v = h\mu_i(v + \frac{1}{2}) \quad (2.29)$$

where v is the vibrational quantum number, h is Plank's constant divided by 2π and the $1/2$ corresponds to the vibrational zero-point energy of the system.

Anharmonicity must also be included in the model as the current set of equations do not allow a bond to dissociate. For very high energy vibrations the atoms have enough energy to enter poorly modelled regions of the potential well. Here the motion is said to become anharmonic as the restoring force is no longer proportional to the displacement. Energy levels become closer together the higher in energy they are to account for the wider spread of the parabola in these regions (Figure 2.8(c)).

The Morse potential is a much closer model for the actual shape of the potential well and has a finite number of vibrational levels, the highest equaling the bond dissociation energy v_{max} [16]

$$E_{vMorse} = \hbar\omega_i(v + \frac{1}{2}) - x_e(v + \frac{1}{2})^2 \quad (2.30)$$

Molecules can be excited in to the different vibrational modes by exposure to heat or appropriate energy radiation all the way up to v_{max} .

Vibrational spectroscopy uses the interaction of an incident beam of radiation with a sample to probe its molecular vibrations. It is extremely useful for determining the structural features present in a molecule and highlighting possible decomposition pathways.

Raman Spectroscopy

Raman Spectroscopy uses the inelastic interaction of monochromatic photons with matter to probe the rotational and vibrational structure of a sample [16].

The sample is excited to a 'virtual state' by a laser, normally IR, visible or UV, and the photons emitted on relaxation are analysed. Most of the molecules relax to the same ground state and photons have the same energy as the incident radiation, elastic or Rayleigh scattering.

However, some molecules relax to a different ground state and the energies of those photons are changed, inelastic scattering. If the molecule is excited by the interaction then the photon leaves with less energy (Stokes scattering). If the molecule is stabilised by the interaction the photon leaves with more energy (anti-Stokes scattering). See Figure 2.9.

Excitation to the virtual state occurs because the interaction of the molecule with the oscillating electric vector of the incident radiation polarises the electron cloud. As a result, only vibrational modes that change the polarisability of the molecule are Raman

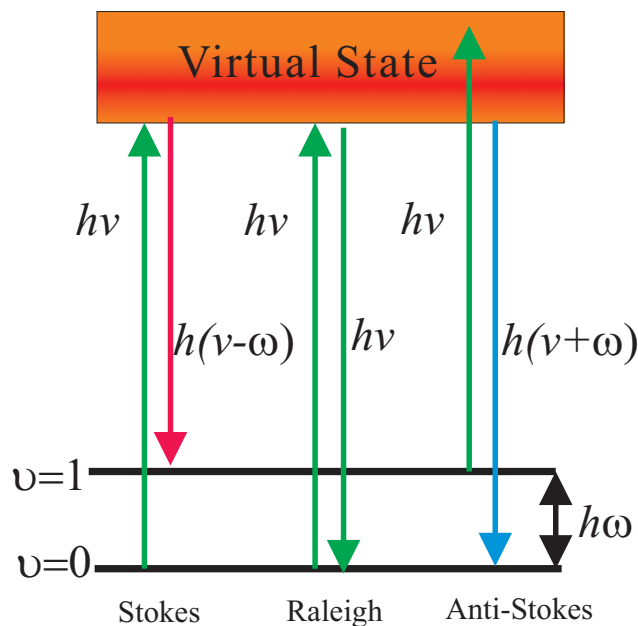


Figure 2.9: Schematic of Stokes, Raleigh and Anti-Stokes scattering.

active. Additionally, the vibrational quantum number v must change by ± 1 , ($\Delta v = \pm 1$) to comply with the conservation of energy principal. Stokes scattering is dominant ($\Delta v = +1$) as the population of the vibrational energy levels follows the Boltzmann distribution so the majority of the molecules will be in the v_0 state.

The Raman spectra in this thesis were recorded on a Jobin Yvon spectrometer (Labram 1B) equipped with a microscope, through a 50-fold magnification objective (Olympus Co.). A 20mW He-Ne laser (632 nm) was used. The 1800 L/mm grating provides a resolution that ranges from 1.0 cm^{-1} at 200 cm^{-1} to 0.5 cm^{-1} at 3600 cm^{-1} . The abscissa was calibrated with a silicon standard and the sharp Raman shifts are accurate to $\pm 2 \text{ cm}^{-1}$. Polycrystalline powder c.a. 100mg was loaded into a glass melting point tube which was flame sealed. The microscope was then focused on the surface of the capillary and spectra were collected over a period of 4 hours at room temperature.

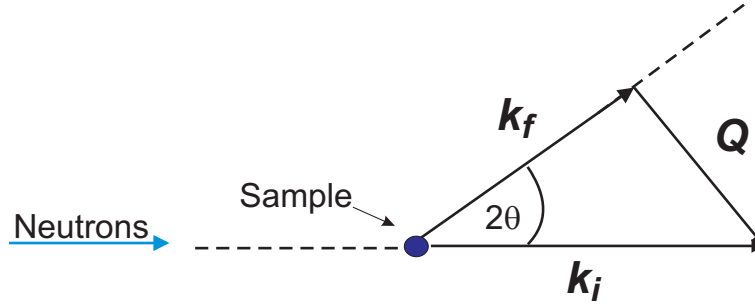


Figure 2.10: Schematic of the 'scattering triangle'.

Inelastic Neutron Spectroscopy (INS)

As the name suggests Inelastic Neutron Spectroscopy (INS) uses the inelastic interactions of neutrons with matter to probe the vibrational structure of a sample [119].

In an inelastic scattering event the energy of the incident beam E_i is changed due to momentum transfer with the sample and the energy transfer, ΔE can be calculated by;

$$\Delta E = E_i - E_f \quad (2.31)$$

where E_f is the final energy of the beam and from this it is also possible to calculate the momentum transfer $\hbar\mathbf{Q}$;

$$\hbar\mathbf{Q} = \hbar(\mathbf{k}_i - \mathbf{k}_f) \quad (2.32)$$

where $\mathbf{k}_i$ is the wave vector of the incident neutrons and $\mathbf{k}_f$ is the wave vector of the scattered neutrons. The real space relationship between these vectors, known as the scattering triangle, is shown in Figure 2.10.

During collection of an INS spectrum, the intensity of the scattered neutrons $S(\mathbf{Q}, \omega)_{total}$ (a function of their energy and momentum transfer) is recorded against neutron energy loss. $S(\mathbf{Q}, \omega)_{total}$ is also closely related to the 'amplitude and cross section weighted density of states' as shown by Equation 2.33

$$S(\mathbf{Q}, \omega)_{total} = y \sum_{l=1}^{N_{atom}} S(\mathbf{Q}, \omega)_{l\sigma_l} = 4\pi \frac{\mathbf{k}_i}{\mathbf{k}_f} \left(\frac{d^2\sigma}{dE_f d\Omega} \right)_{observed} \quad (2.33)$$

for a given vibrational mode ν at energy ω there is always a peak value for $S(\mathbf{Q}, \omega)$ determined by the degree of momentum transfer. For small transfers the intensity increase is driven by a pre exponential term $(Q \cdot^\nu u_l)^2$ where u is the atomic displacement. For large transfers the intensity is suppressed by an exponential term $-(Q \cdot \sum_\nu u_l)^2$ also known as the Debye Waller factor. The Debye Waller factor has its physical origin in the thermal motion of the atoms.

$$S(\mathbf{Q}, \omega_\nu)_{ln} = y\sigma_l \frac{[(Q \cdot^\nu u_l)^2]^n}{n!} e^{-(Q \cdot \sum_\nu u_l)^2} \quad (2.34)$$

The final state of the excited mode is denoted by n which is an integer and signifies the number of quantum events that have occurred. $n=0$ signifies elastic scattering, the most likely event, and is seen as the most intense line at $\Delta E=0$. $n=1$ is the fundamental and $n > 1$ corresponds to multiscattering events and $n-1^{th}$ overtone.

INS has five main advantages over vibrational spectroscopy techniques such as IR and Raman:

1. Wide spectral range - typically $0-4000 \text{ cm}^{-1}$ which is difficult experimentally for IR and Raman spectrometers.
2. No optical selection rules - as it is based on momentum transfer INS measurements are not limited to the Brillouin zone like photon techniques and all vibrations are allowed.
3. Highly sensitive to hydrogenic vibrations - the intensity of an INS band is proportional to the product of the incoherent scattering cross-section and the amplitude of vibration. Since the scattering cross-section for hydrogen is at least 20 times larger than for any other type of atom present in the molecule, the INS spectrum emphasises the modes that involve significant hydrogen motion either directly (such as a N-H bend) or where the hydrogen is 'carried' on another atom (e.g. torsions).

4. Neutrons are penetrating - this means INS is inherently a bulk technique and as with neutron diffraction, sample environments have a much lower impact on the measurement.
5. INS can be effectively modelled - INS intensity is related to the displacement of the scattering atom, which as shown in section can be calculated using classical harmonics. This means there are none of the problems from electro optic parameters which complicate photonic spectra and *ab initio* computation has a very high success rate.

TOSCA [138, 139, 140]

The inelastic neutron scattering (INS) experiments were in this thesis were performed using the high resolution broadband spectrometer TOSCA at the ISIS pulsed spallation neutron source at the Rutherford Appleton Laboratory, Chilton, UK. The instrument is optimised for vibrational spectroscopy and has an optimal energy range of 0-4000 cm^{-1} .

TOSCA is an inverted geometry time-of-flight spectrometer where a pulsed, polychromatic beam of neutrons illuminates the sample at 17 m from the source. The wavelength of the backscattered neutrons are fixed by Bragg reflecting them with a pyrolytic graphite analyser and those with a final energy of $\sim 32 \text{ cm}^{-1}$ are passed to the ^3He detector bank situated at 45° , multiples of this wavelength are removed by a longpass beryllium filter.

Measurements are undertaken in neutron energy loss mode and would normally be performed on a ^{11}B enriched sample to avoid the high neutron absorption of natural boron. However, TOSCA covers an extended energy transfer, E , range: $3 \text{ meV} < E < 500 \text{ meV}$, providing an excellent energy resolution, ΔE , ($\Delta E/E = 1.5\%$) and allowed excellent data to be collected despite the natural boron content of most of the samples used. Approximately 1g of sample was required for a good spectrum. The samples were loaded in the glove box in to an Al foil sachet 4x4 cm. The sachets were then screwed into a flat back Al sample can using indium wire as the sealant.

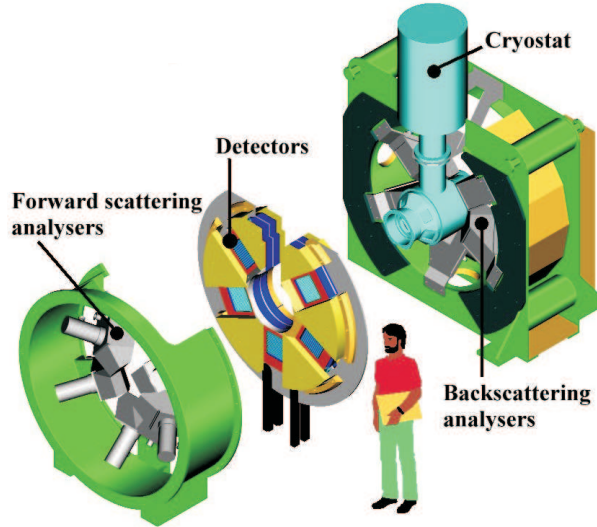


Figure 2.11: Schematic of the TOSCA INS spectrometer at ISIS. Reproduced with the permission of the STFC

The signals of the empty aluminium sample holder and a flat background have been subtracted and the raw data was corrected to obtain $S(\mathbf{Q}, \omega)_{total}$ using standard routines available at ISIS, which corrects for the term $1/\omega$, the polarization factor, and the Debye-Waller factor.

Periodic density functional theory calculations were carried out using a plane wave basis-set and pseudopotentials as implemented in the CASTEP code. The PBE [141] version of the localised density approximation within DFT was used in conjunction with optimised norm conserving Opium pseudopotentials [142] generated using the Qc-tuning method [143]. The Brillouin zone sampling used a $5 \times 5 \times 4$ grid of k-points generated using the Monkhorst-Pack method. A full geometry optimization, with a plane-wave cut-off energy of 850 eV, of the internal atomic co-ordinates was performed to reduce the residual atomic forces to better than 1.5 meVÅ. Phonon modes were calculated using density functional perturbation-theory [144] to compute the dynamical matrix at the Γ -point. The CASTEP output includes the atomic displacements for each mode. This enables visualisation of the modes in Jmol [145] and are all that is needed to generate the INS spectrum using the in-house program ACLIMAX [146]. Calculations were performed on the complete unit cell using our experimental crystallographically determined structure as the initial structure.

MAPS [147]

Variable temperature INS measurements were made on the MAPS time-of-flight spectrometer at ISIS. MAPS allows very wide areas of the Brillouin zone to be sampled in great detail due to its high resolution, broad energy range (meV to several eV) and large detector solid angle coverage (-20 to $+60^\circ$ in the horizontal plane and $\pm 20^\circ$ in the vertical plane). To achieve this, MAPS employs position sensitive detectors (PSDs) that provide close to continuous coverage over large solid angles. Its 16 m^2 area is approximately divided into 36864 square detector pixels. A total of ≈ 160000 detector pixels are used there in the forward direction. In addition, narrower strips of detectors provide additional angular coverage within the horizontal plane. The raw data each detector registers comprises of histograms representing neutron counts *vs.* arrival time taken with respect to an external reference. A data set thus consists of histograms of neutron counts *vs.* time stored by each individual detector situated at set of angular coordinates with respect to the incident beam.

The data are represented as an intensity (i.e. neutron counts) measured along some trajectories within wave-vector energy space versus time of arrival at a given detector-pixel position. For a given detector element such trajectories are set by the neutron kinematics once the energy of the neutrons impinging upon the sample is selected. They define a two-dimensional (2D) grid and so a set of trajectories defines a data volume. The data format of interest for most scientific applications corresponds to projections within a four-dimensional space constituted by the three components of the momentum-transfer vector $\mathbf{Q}$ as well as a scalar quantity that is the energy transfer (ϵ). Practical performance of such measurements by the TOF technique requires to set one of the variables to a fixed value, which reduces the dimensionality of the problem. The raw data were mapped into $S(\mathbf{Q}, \omega)$ and two-dimensional projections were produced by the MSlice software [148].

This precise imaging of the Brillouin zone make MAPS a model instrument for high resolution studies of non-dispersive excitations in powders. The sample, 1 g of polycrystalline powder, was sealed in an 11mm vanadium can with indium wire, cooled to 20K

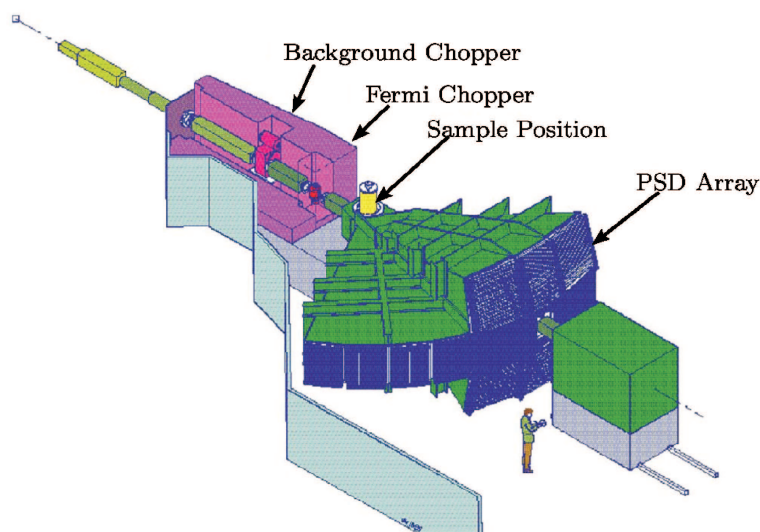


Figure 2.12: A schematic drawing of the MAPS TOF chopper spectrometer at the ISIS neutron source. Reproduced with the permission of the American Institute of Physics

(-253°C) and the spectrum recorded for 12 h. The combinations of (incident neutron energy E_i , Fermi chopper frequency, typical integrated beam current) used for the measurements were (200 meV, 400 Hz, 5,000 $\mu\text{A h}$), (300 meV, 450 Hz, 9,000 $\mu\text{A h}$) and (500 meV, 500 Hz, 7,000 $\mu\text{A h}$).

2.4 Synthesis Techniques and Material Manipulation

2.4.1 Argon Glove Box

All handling of materials was carried out in an argon atmosphere glove-box as the materials used in this thesis are both air and moisture sensitive.

The glove box used was an MBruan Unilab capable of maintaining an argon atmosphere with $\text{H}_2\text{O} < 1$ ppm, $\text{O}_2 < 0.1$ ppm. A closed loop gas recirculation system was used for this purpose and continuously passed the internal gas through two columns containing molecular sieves and phosphoric acid. The integrity of the glove box atmosphere was maintained on a daily basis by the drying of all glassware in an oven and the

thorough pump-purging of the ports before use.

2.4.2 Schlenk Line

Air sensitive solution based synthesis was preformed using a Schlenk line apparatus (Figure 2.13) which allows reactions to be preformed under a protective nitrogen atmosphere.

A Schlenk line consists of combined vacuum and inert gas (normally nitrogen) lines connected via double oblique taps. Reaction vessels are connected to the line flexible tubing and the orientation of the double oblique taps selects whether the vessel is under nitrogen or vacuum. The nitrogen pressure can be used to transfer liquids via a cannula between vessels and cannulae fitted with filters can be used for filtration. Upon completion of a reaction, solvent may be evaporated under reduced vacuum via the vacuum section of the Schlenk line.

For a typical reaction, solid reagents were loaded into a Schlenk flask within an argon atmosphere glove box. The flask was then sealed, removed from the glove box and connected to the Schlenk line via the flexible tubing, along with a solvent Schlenk flask. The tubing is pump-purged with nitrogen three times over a period of 30 mins before the taps to the flasks are opened. Solvent is added to the flask via a cannula and rubber septa. The reaction is stirred under nitrogen at room temperature or whilst refluxing. When the reaction time is complete and the solution is cooled, the solution is filtered to separate precipitates which can be washed with more solvent if necessary and then dried under reduced pressure. Further drying by mild heating is sometimes necessary.

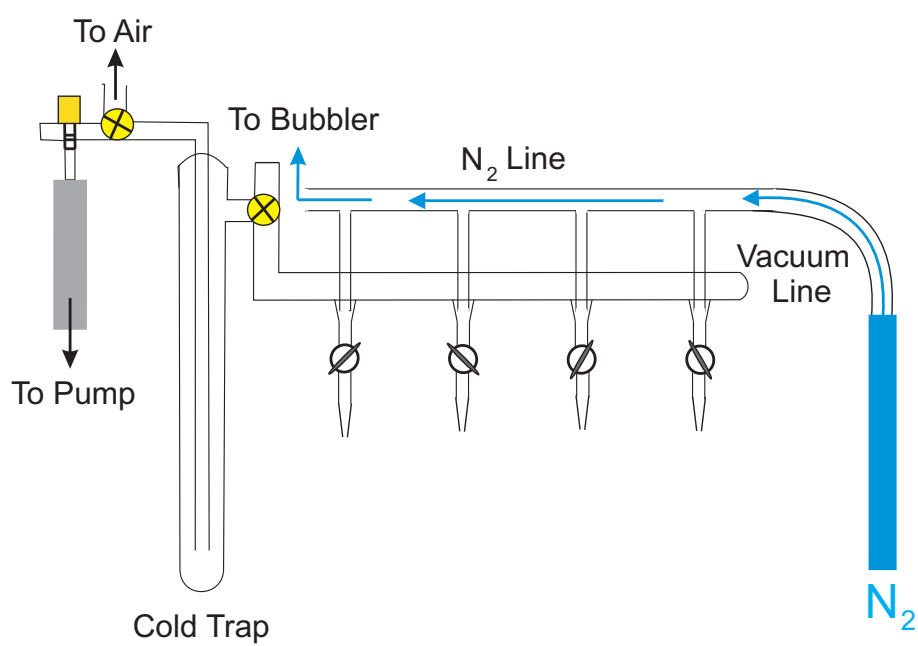


Figure 2.13: Schematic of a Schlenk line.

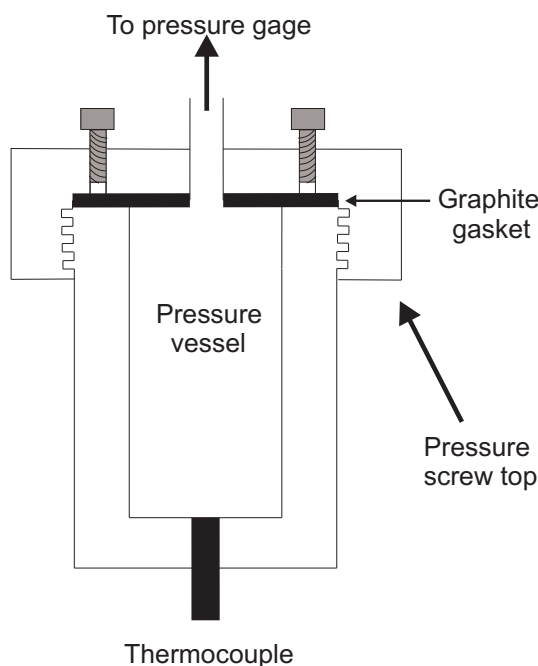


Figure 2.14: Schematic diagram of the high pressure Parr furnace.

High Pressure Furnace

Very high temperatures and pressures of hydrogen were required to synthesis the borohydride precursors in this thesis. These reactions took place in a Parr Series 4740 High Pressure Vessel capable of withstanding 200 bar at 700°C (973K).

The instrument, shown in Figure comprises of a 75 ml stainless steel reactor, closed with an alloy steel screw cap which includes six cap screws to develop the sealing force on a flat, flexible graphite gasket. A Parr gage block assembly which acts as a inlet / outlet valve, pressure gage and safety rupture disc is attached to the screw cap via a cone pressure fitting. A ridged mantle heater and thermocouple are used to control the temperature.

The reactants were loaded into the reaction vessel and the screws tightened to 15 lb/feet using a torque wrench. The gage block assembly was attached and sealed and the entire unit removed from the glove box. A Swagelock connector was attached and the residual argon inside the vessel was removed through the gage block using a turbo pump and then back filled with the desired pressure of the reactive gas. The vessel was

sealed, the Swagelok connector removed and a thermo couple connected. The vessel was then sheathed with the furnace and left to heat to the desired temperature. Upon completion of the reaction the vessel was allowed to cool and the residual gas removed with the turbo pump. The vessel was then taken in to the glove box the product was retrieved using a considerable amount of force.

Elemental Analysis

Elemental Analysis of sample for carbon, nitrogen, and hydrogen were outsourced to The London Metropolitan University Science Centre. The air sensitive samples were loaded into sample vials and sealed in a kilner jar in the glove box prior to postage.

The CHN ratio, was accomplished by combustion analysis. The samples were burned in an excess of oxygen, and the combustion products of interest (carbon dioxide, water, and nitric oxide) collected in separate traps. The weights of these combustion products were then used to calculate the composition of the unknown sample.

Melting Point Analysis

Melting point analysis of some samples was undertaken using a melting point apparatus. Normally samples are loaded into a sealed capillary that is then placed in the apparatus, which has a magnifying viewing window and thermometer holder. The sample is then heated by a heating block and as the temperature increases the sample is observed to determine when / if the phase change from solid to liquid occurred.

However because gas release from the samples in this thesis was very likely, the capillaries were sealed with vacuum grease rather than flame sealed to allow for gas expansion.

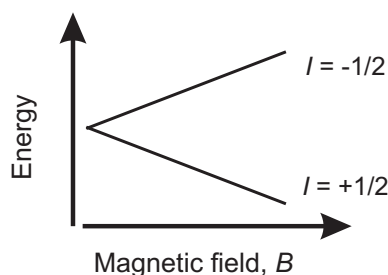


Figure 2.15: Effect of placing a nucleus with $I = 1/2$ in an external magnetic field.

Nuclear Magnetic Resonance (NMR) [149]

All atomic nuclei possess a property called Nuclear Spin (I) which, depending on its value, gives rise to nuclear magnetism. In NMR an external magnetic field is applied to the chemical of interest and radiofrequency waves are used to interrogate the substance.

The value of an atom's spin originates from the number of protons and neutrons in the nucleus and how they interact. There are three main classes of nuclei:

1. Nuclei with $I = 0$, have an even number of protons and neutrons and do not exhibit an NMR effect. e.g. ^{12}C ^{16}O
2. Nuclei with $I = 1/2$ e.g. ^1H , ^{13}C , and ^{31}P
3. Nuclei with $I > 1/2$ e.g. ^{11}B , ^{14}N , and ^{27}Al

How magnetic a nucleus is is determined by its gyromagnetic ratio γ_N . γ_N is defined as the ratio of the magnetic moment to the spin and is a fundamental property of each nuclear isotope.

When a magnetic field, B , is applied to a nucleus in its ground state it splits into

$$2I + 1 \text{ levels where } m_I = -I, -I + 1 \dots + I \quad (2.35)$$

This effect is known as Zeeman splitting, the size of which is proportional to B and γ_N , as shown in Figure 2.15 and Equation 2.36:

$$E_{m_I} = -\gamma_N \hbar B m_I \quad (2.36)$$

Therefor the energy gap ΔE_{Zeeman} is:

$$\Delta E_{Zeeman} = \frac{-\gamma_N \hbar B}{2\pi} = E_{photon} = h\nu \quad (2.37)$$

The nuclear spins 'precess' about the magnetic field with a frequency, known as the Larmor frequency ν_{Larmor} equal to:

$$\nu_{Larmor} = \frac{-\gamma_N B}{2\pi} \quad (2.38)$$

As the spins precess they absorb and emit radiowaves at the same frequency as their Larmor frequency. The precise vale of the Larmor frequency also depends on the local magnetic field at the site of the nucleus, which is influenced by:

- The main magnetic field in which the nucleus is placed
- Magnetic fields generated by the electrons (the chemical shift, δ) which effect the position of a peak.
- Magnetic fields generated by other nuclei (spin-spin coupling) which effect the fine structure and 'splitting' of a peak

The chemical shift is defined by where ν^0 is the Larmor frequency of the same isotope in a standard reference compound

$$\delta = \frac{\nu_{Larmor} - \nu^0}{\nu^0} \quad (2.39)$$

Chemical shifts are very small c.a. 10^{-5} and it is customary to quote them the in 'parts per million' ppm. Generally, if the nucleus of interest is attached to highly electronegative atoms / groups the δ will be high. This is because the electronegative atoms withdraw electron density and decrease the magnetic shielding of the nucleus. If the nucleus of interest is attached to electropositive atoms / groups the δ will be low or even negative as the shielding is increased.

There are two types of spin spin coupling, indirect dipole-dipole coupling which is mediated by the bonding electrons (J-coupling) and direct dipole-dipole coupling (DD coupling) which only occurs in solids.

J-coupling may be homo or hetero nuclear but couplings between magnetically equivalent spins may be ignored. J-couplings to a magnetically equivalent group of spins give rise to multiplets with binomial intensity patterns. J-coupling of a spin to a group of n magnetically equivalent spins I splits the peak into $2nI + 1$ lines with amplitudes proportional to the binomial coefficients.

$${}_nC_r = n!/r!(n-r) \text{ where } r = (0, 1, \dots, n) \quad (2.40)$$

In solution NMR the molecules are free to move and transient interactions between them are averaged out. However in solids the fixed orientations mean the molecules can interact and isolated environments can no longer be observed. Dipolar coupling makes a large contribution to the spectra resulting in very broad lines of up to several kHz wide.

Several methods can be used to reduce the line width in solid state spectra including:

- Spin dilution - if the nucleus is of low abundance or well dispersed in the solid (can be achieved by grinding with an inert material) the number of interactions will be reduced.
- Decoupling the spectra from other NMR active nuclei present in the sample.
- Magic angle spinning (MAS). The chemical shift is dependent on the orientation of the molecule in the magnetic field. This effect, called the chemical shift anisotropy (CSA), is very well known in solid state NMR as it is responsible (in part) for the very wide line width observed on a static sample. Chemical shift anisotropy (CSA) has an angular dependence :

$$CSA \propto 3\cos^2\theta - 1 \quad (2.41)$$

which means if $\theta = 54^\circ 44'$ then $3\cos^2\theta = 1$ and CSA is minimised.

NMR Experimental Conditions Solution state ^1H NMR studies of LiNH_2BH_3 , NaNH_2BH_3 and KNH_2BH_3 were undertaken using a Varian Mercury 300 MHz spectrometer. The powder samples (c.a. 10mg) were loaded into standard borosilicate NMR tubes within an argon atmosphere glove box and then dissolved in THF-d_8 or diglyme- d_8 within a nitrogen filled glove bag. Prior to removal from the glove bag the NMR tubes were sealed with parafilm.

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

2.5 Synthesis Conditions

2.5.1 Alkali Metal Amidoboranes

Lithium and Sodium Amidoborane (LiNH_2BH_3 and NaNH_2BH_3)

Schlenk line methods described in section were used for the solution based preparation of LiNH_2BH_3 and NaNH_2BH_3 . Diethyl ether was dried in an in-house solvent drying system and distilled before use. LiH or NaH and NH_3BH_3 were used in a 1:1 molar ratio. Dry diethyl ether was added with rigorous stirring and the mixture left to stir at room temperature for two days. The mixtures were then filtered and pumped dry of diethyl ether over 5 hrs on a high-vacuum line ($1 \times 10^{-4} \text{mb}$) whilst being warmed in an oil bath to 40°C (313K).

LiNH_2BH_3 elemental analysis H 13.68%, C $<0.01\%$, N 38.02% (expected H 13.7%, C $<0.01\%$, N 38.06%), ^{11}B {H} NMR (THF- d_8 room temperature): $\delta = -22.08$ ppm (BH_3) NaNH_2BH_3 elemental analysis H 9.47%, C $<0.01\%$, N 26.65% (expected H 9.53%, C $<0.01\%$, N 26.51%), ^{11}B {H} NMR (THF- d_8 room temperature): $\delta = -21.46$ ppm (BH_3).

Potassium Amidoborane (KNH_2BH_3)

Schlenk line methods described in section were used for the solution based preparation of KNH_2BH_3 . Benzene was dried by standard methods and distilled before use. KH and NH_2BH_3 were used in a 1:1 molar ratio. Dry benzene was added with rigorous stirring and the mixture left to stir at room temperature for two days. The mixtures were then filtered and pumped dry of benzene over 5 hrs on a high vacuum line ($1 \times 10^{-4} \text{mb}$) whilst being warmed in an oil bath to 40°C .

KNH_2BH_3 elemental analysis H 7.21%, C $<0.01\%$, N 20.17% (expected H 7.30%, C $<0.01\%$, N 20.31%) ^{11}B {H} NMR (diglyme- d_8 room temperature): $\delta = -19.62$ ppm (BH_3).

2.5.2 Lithiated Tetragonal Phase

LiH and NH_3BH_3 were ground to intimate mixture in a 1:2 molar ratio under an inert atmosphere. The mixture was then heated in a quartz tube to 80°C (353K) for 12 hours under flowing argon.

Lithiated Tetragonal Phase elemental analysis H 15.83%, C <0.01%, N 27.72% (expected H 15.93%, C <0.01%, N 27.66%) ^{11}B {H} NMR (THF- d_8 room temperature) δ -21.46ppm

2.5.3 ^{11}B Enriched Ammonia Borane ($\text{NH}_3^{11}\text{BH}_3$)

$\text{NH}_3^{11}\text{BH}_3$ was synthesised via the method detailed by Heldebrant *et. al* [27]. Anhydrous NH_3 was condensed in an oven-dried, three-neck, round-bottom flask fitted with a stirrer bar. The flask was open to a nitrogen atmosphere and cooled in a dry-ice/acetone bath ($-78^\circ\text{C}/195\text{K}$). Equimolar quantities of NH_4Cl and $\text{Na}^{11}\text{BH}_4$ were added by a solids addition funnel to the three-neck flask, and the reaction was stirred for 3 h under nitrogen at ($-78^\circ\text{C}/195\text{K}$). The NH_3 was removed under vacuum to leave $\text{NH}_4^{11}\text{BH}_4$ and NaCl . Anhydrous THF was slowly added to the flask via a canula, and residual NH_3 and H_2 were allowed to evaporate while thawing the reaction to room temperature. At room temperature, the flask was stirred for another hour. The precipitated NaCl was removed by filtration, and the THF was removed under vacuum, and the remaining microcrystalline powder dried for 12 hours under high vacuum ($1 \times 10^{-4}\text{mb}$).

^{11}B enriched Sodium Borohydride ($\text{Na}^{11}\text{BH}_4$)

The $\text{Na}^{11}\text{BH}_4$ required for the above reaction was synthesised from its elements using the high pressure furnace described in Section 2.4.2.

Na metal was cut into very fine slices and then ground to an intimate mixture with ^{11}B powder. This was transferred to the high pressure furnace and heated under 100 bar of H_2 at 700°C (973K) for 12 hours to yield a dark grey solid confirmed by X-ray diffraction to be $\text{Na}^{11}\text{BH}_4$ and ^{11}B . The powder was then washed using the Schlenk line. The impure $\text{Na}^{11}\text{BH}_4$ was dissolved in isopropyl amine to purify and the excess boron was removed by filtration. The isopropyl amine was removed under vacuum and the resulting white powder dried on a high vacuum line ($1 \times 10^{-4}\text{mb}$) for 5 hours while being warmed in an oil bath to 50°C (323K).

^{11}B Enriched Deuterated Ammonia Borane ($\text{ND}_3^{11}\text{BD}_3$)

The $\text{ND}_3^{11}\text{BD}_3$ was synthesised using the same method described in Section 2.5.3 but the $\text{Na}^{11}\text{BH}_4$, NH_4Cl and NH_3 were replaced with $\text{Na}^{11}\text{BD}_4$, ND_4Cl and ND_3 .

^{11}B Enriched Sodium Borodeuteride ($\text{Na}^{11}\text{BD}_4$)

The $\text{Na}^{11}\text{BD}_4$ required for the above reaction was synthesised using the same method described in Section 2.5.3 but using 100 bar of D_2 instead of H_2 .

2.5.4 Source and Purities of Starting Materials

Na metal (99.95% cubes in mineral oil, Sigma Aldrich) ^{11}B (99.99% purity 96% ^{11}B 100 mesh) LiH (98%, Alpha Aesar), NaH (95%, Sigma Aldrich), KH (30 wt% in mineral oil, Sigma Aldrich), NH_4Cl (99.5%, Sigma Aldrich), ND_4Cl (98% atom D, Sigma Aldrich), NH_3BH_3 (97.5% Sigma Aldrich), ND_3 anhydrous (99.99% atom D, CK Gas Products), NH_3 anhydrous (BOC special gases) D_2 (99.99% atom D, CK Gas Products) H_2 (99.999%, CK Gas Products).

All starting materials were used without further purification with the exceptions of:

- KH which was washed with light petroleum, filtered and the remaining solvent removed under vacuum to leave the pure product.
- Na metal which was washed with light petroleum, filtered and the remaining solvent removed under vacuum to leave the pure product.
- ^{11}B powder was ball milled before use in a Retch planetary mill for 1 hour at 300rpm.

Chapter 3

Variable Temperature Studies on Ammonia Borane and Ammonium Borohydride

3.1 Introduction and Chapter Outline

The early structural confusion described Section 1.3 and more recent discoveries of molecular motion even at low temperatures clearly show how complex and disordered the seemingly simple NH_3BH_3 and NH_4BH_4 systems are. Accurate variable temperature structural and vibrational studies of both these materials are required to probe and understand the detailed molecular behaviour of these prototypic compounds.

In this chapter, variable temperature neutron diffraction and inelastic neutron scattering studies are presented for both ammonia borane and ammonium borohydride. The variable temperature neutron diffraction measurements were performed using the HRPD and WISH diffractometers (Section 2.2.3) for ND_4BD_4 . The variable temperature inelastic neutron scattering was conducted on the TOSCA INS spectrometer (Section 2.3.4). All instruments are situated at the ISIS pulsed neutron facility at the Rutherford Appleton Laboratory, UK (Section 2.2.3).

3.2 Inelastic Neutron Scattering Studies of $\text{NH}_3^{11}\text{BH}_3$

The general experimental details of INS studies on TOSCA are described in more detail in Section 2.3. but have the following additional details. The 1g sample, of fully enriched $\text{NH}_3^{11}\text{BH}_3$ was held in an aluminium sachet, cooled to 5K and a spectrum recorded for 12 hours (Section 3.2.1). The sample was then warmed and a series of spectra were collected at 25, 30, 35, 40, 80, 100, 180, 240 and 280K for 8 hours each (discussed in Section 3.2.2).

3.2.1 Inelastic Neutron Scattering Study of $\text{NH}_3^{11}\text{BH}_3$ at 5K

Below 220K $\text{NH}_3^{11}\text{BH}_3$ crystallises in the orthorhombic space group $Pmn2_1$ with 4 molecules per unit cell each on a site of 2 symmetry as shown in Figure 1.3. Each fundamental vibration of the isolated molecule gives rise to 24 factor group modes of the crystal.

To assign the spectra, we have performed Density Functional Theory (DFT) calculations on the complete unit cell using CASTEP [150, 151, 152] Comparison of the observed and calculated bond distances for the complete unit cell with the experimental data shows good agreement: bond distances are generally within 0.02 Å or 1.9%. Two exceptions are the N-H and B-H bonds co-axial with the b axis which are anomalously short (0.06 Å) in the calculated structure. Largest deviations are for the N-H bond lengths where the distances are 0.07 Å longer than the experimental values. Nevertheless, it was concluded that the *ab initio* calculations for the complete unit cell accurately reproduced the experimental structure.

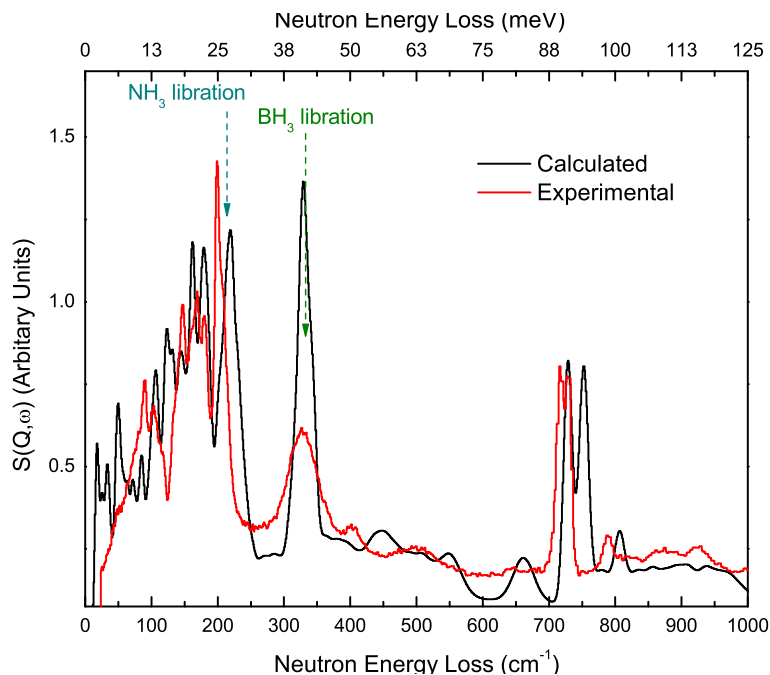


Figure 3.1: Comparison of INS spectra: experimental (red) and calculated by CASTEP for the complete unit cell (black) in the 0-1500 cm^{-1} region.

Figure 3.1 shows a comparison of the INS spectra calculated from the DFT results and the experimental spectrum. There is a good agreement between the calculated and observed spectra. Generally there is a slight over estimation of the mode frequencies by the DFT calculations but there is one major discrepancy which must be accounted for. The band at 329cm^{-1} is much broader and weaker than predicted from calculated spectrum. The most likely cause of this anharmonicity [153] is di-hydrogen bonding. As can be seen from Figure 3.2, which shows the vector motion of the mode at 349cm^{-1} , the B-H libration is directly along the di-hydrogen bonds. This means there is direct compression of the di-hydrogen bond when that mode is populated which costs energy and therefore makes the mode anharmonic. Conversion of the phonon frequency to units of energy revealed the di-hydrogen bond compression energy to be 3.9 kJ mol^{-1} .

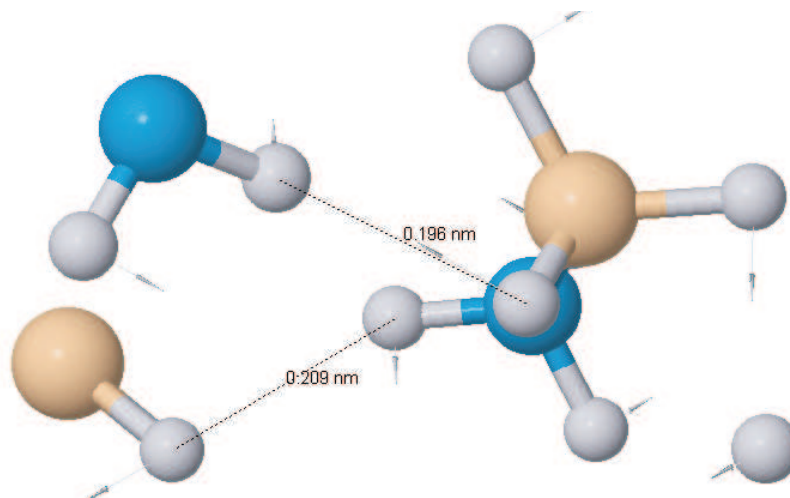


Figure 3.2: Structural diagram of NH_3BH_3 viewing along the b axis showing the vector motion of the anharmonic mode at 349cm^{-1} . Hydrogen is grey, nitrogen blue, and boron cream.

Similar effects are also observed on IR and Raman peaks [154]. This is because bulk samples have a large number of molecules all of which may be involved in di-hydrogen bonding to a slightly different extent due to the different crystallite sizes and orientations in the sample. Hence the signal is broadened and averaged due to all the slightly different modes.

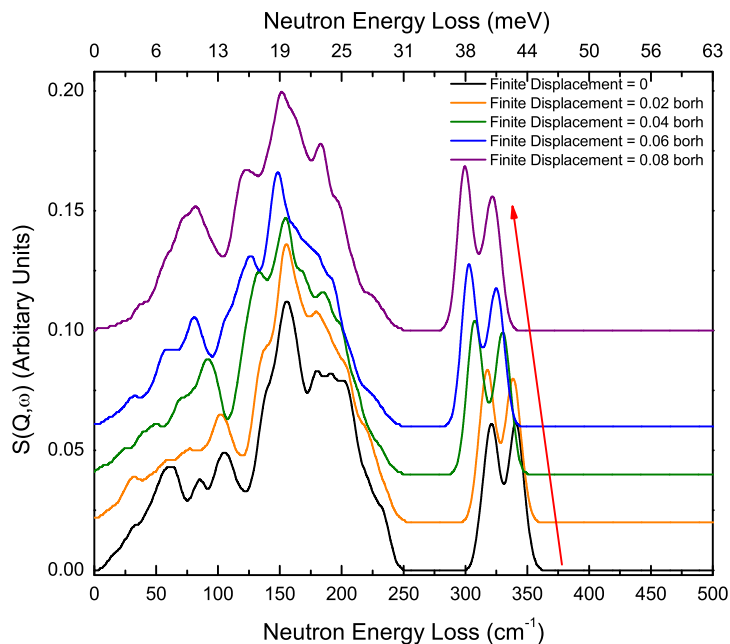


Figure 3.3: Graph showing the INS spectra generated from the finite displacement calculation on $\text{NH}_3^{11}\text{BH}_3$ in the $0\text{-}500\text{ cm}^{-1}$ region.

Another way of probing the anharmonicity of certain modes is to perform a finite displacement calculation in CASTEP. The calculation proceeds by shifting each atom by a small amount, then performing a Self Consistent Field (SCF) calculation (an initial set of orbitals is used to generate a new set of orbitals and the procedure is repeated until some convergence criteria is met) to evaluate the forces on the perturbed configuration. Both positive and negative displacements are performed in each direction so that the corresponding force constants can be evaluated using the accurate “central difference” method of numerical differentiation [155].

Figure 3.3 shows the INS spectra generated from the finite displacement calculation on $\text{NH}_3^{11}\text{BH}_3$ and it is clear that the modes between $300\text{-}355\text{ cm}^{-1}$ do move significantly as the displacement increases. Whereas, the rest of the modes remain fairly static.

The NH_3 librations occur at lower energies ($189\text{-}252\text{ cm}^{-1}$) than the BH_3 librations ($290\text{-}383\text{ cm}^{-1}$). The onset of NH_3 libration has also been shown by NMR [156], quasi-elastic neutron scattering (QENS) [157] and incoherent inelastic neutron scattering [158] to have a lower activation energy than for BH_3 . The relative onset of the NH_3 and BH_3 librations can be correlated to their moments of inertia I [159].

$$I = cML^2 \quad (3.1)$$

where c is a dimensionless inertial constant, M is the mass and L is the 'size' of the body in the direction perpendicular to the axis of rotation. A comparison of the two values, taking c to be 1 can be seen in Table 3.1 where the I for BH_3 is significantly larger than for NH_3 . As I is proportional to M and L^2 it is clear that I increases more with L than with M . Hence even though the BH_3 unit is lighter than the NH_3 the greater size of the BH_3 unit has more of an impact and more energy is required to rotate it.

Unit	M (AMU)	L (Å)	I (AMU Å ²)
NH_3	17	1.86	58.81
BH_3	14	2.23	75.35

Table 3.1: Data comparing the relative moment of inertia for NH_3 and BH_3 when c is take to be 0.

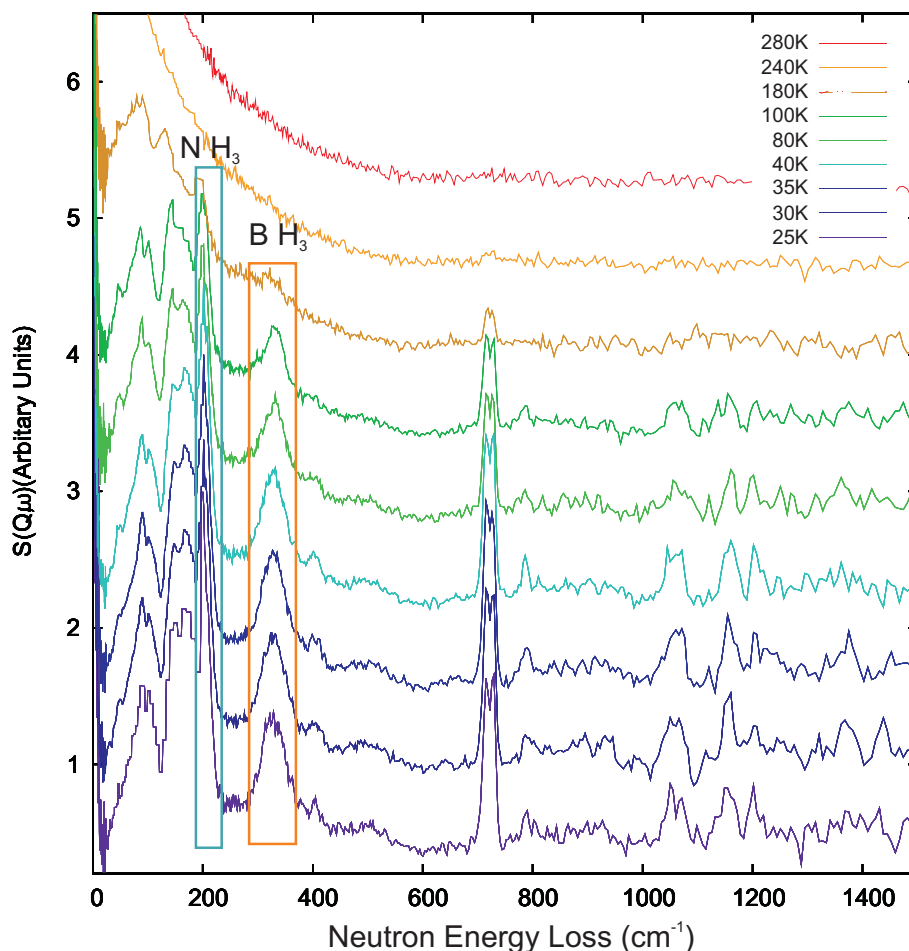


Figure 3.4: VT INS spectra of $\text{NH}_3^{11}\text{BH}_3$ in the $0\text{--}1500\text{ cm}^{-1}$ region collected at 25K, 30K, 35K, 40K, 80K, 100K, 180K, 240K and 280K.

3.2.2 Variable Temperature Inelastic Neutron Scattering Studies of $\text{NH}_3^{11}\text{BH}_3$

In the low-T phase, NH_3BH_3 is a reasonably well ordered crystal which allows a straightforward comparison of the structure refined from diffraction data with the one obtained from *ab initio* calculations. In the present section, the dynamical properties of $\text{NH}_3^{11}\text{BH}_3$ have been investigated by means of inelastic neutron scattering (INS) performed at various temperatures (25, 30, 35, 40, 80, 100, 180, 240 and 280K) above and below the structural phase transition. The spectral series are presented below in Figure 3.4.

From Figure 3.4, it is clear that the spectra collected between 25K-40K changed only slightly. Once the sample reached 80K more noticeable changes started to occur and the peak intensities decreased steadily up to 180K, the last spectra collected before the phase change at 220K.

The principle cause of the intensity reduction is thermal motion and an increased Debye Waller factor (Section 2.3.4) are of the major causes of the peak reduction. However, there may also be another cause particular to $\text{NH}_3^{11}\text{BH}_3$; namely the onset of NH_3 and BH_3 'hopping' or stepwise rotation. In their 2008 VT NMR study on NH_3BH_3 , Cho *et al.* [156] found:

- The onset of NH_3 and BH_3 'hopping' to be at 60K and 100K respectively.
- The activation energy of the NH_3 hopping changed from 5.80 kJ mol^{-1} at $T \leq 80\text{K}$ to $22.40 \text{ kJ mol}^{-1}$ at $T \geq 85\text{K}$ within the NMR time scale.

Further analysis of the peak intensities associated with NH_3 and BH_3 libration (Figure 3.5) supports the findings of Cho *et al.* [156].

Between 25K-80K the intensity of the BH_3 libration peak does not change outside of experimental error. At 100K, the BH_3 libration peak starts to decrease sharply consistent with the 100K hopping onset. But in the case of the NH_3 libration there is little change between 30K-40K and the peak starts decrease sharply at 80K. Regrettably no spectrum was collected at 60K so it is not possible to see if the NH_3 behaviour changes there. The NH_3 peak also decreases by a greater amount than the BH_3 peak (43.5% and 28.3% respectively) consistent with its earlier onset of libration.

By the time the sample had under gone the orthorhombic - tetragonal phase transition the spectra looked very different (Figure 3.4). All the peaks in the $32\text{-}488 \text{ cm}^{-1}$ region of the spectra collected at 240K and 280K are now masked by an exponential region leading up to the elastic line.

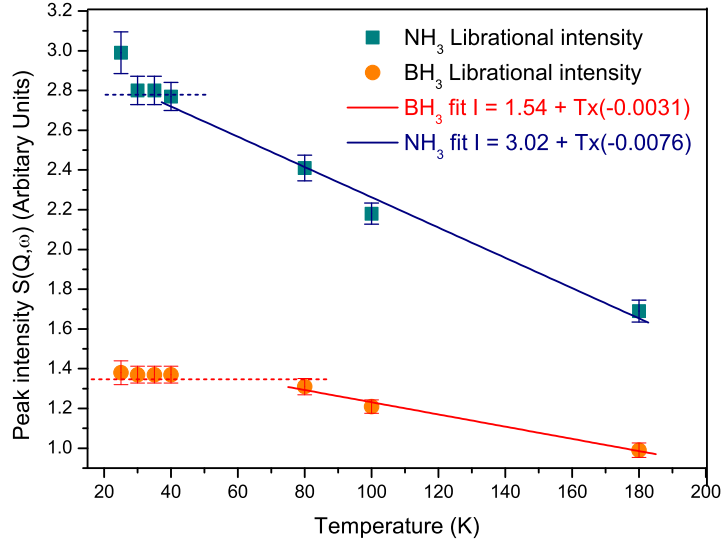


Figure 3.5: Graph showing the changes in intensity of the NH₃ (teal squares) and BH₃ (orange circles) libration peaks with increasing temperature.

This exponential region is thought to be a type of "boson peak", a distinct feature of most glasses and some disordered crystalline solids [160]. The boson peak results from an excess of the low-energy density of states (DOS) $g(\omega)$, where ω is the frequency, relative to the Debye squared-frequency law:

$$g(\omega) \propto \omega^2 \quad (3.2)$$

Grigera *et al.* [161] report that the boson peak signals a crossover at frequency ω_{BP} between a (phonon dominated) ω^2 scaling of $g(\omega)$ to an ω^γ scaling ($\gamma < 2$) where molecular motion is no longer ruled by rare 'activated' jumps between inherent structures, but by motion along the unstable directions of 'saddle points'.

The boson peak has been attributed *inter alia* to rotation of SiO₄ [162] and BH₄ [163] tetrahedral units and to the collective addition of a number of modes [164]; in all cases it has been modelled by an exponential function as shown in Figure 3.6.

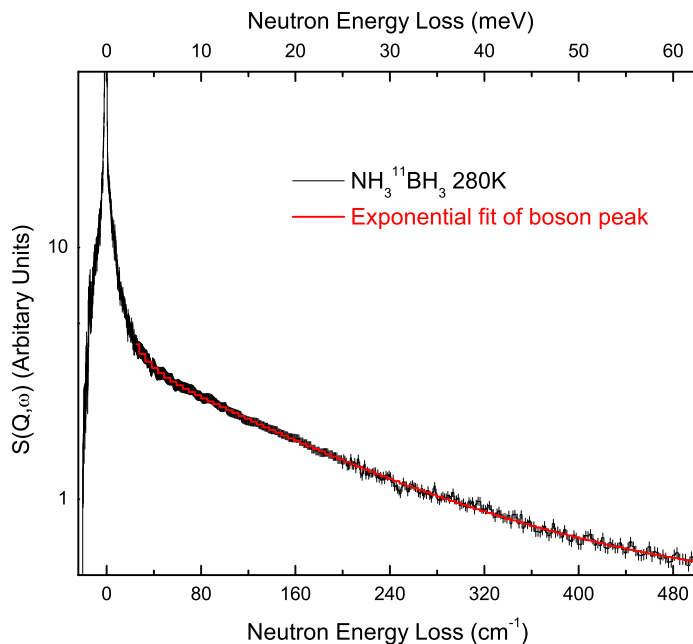


Figure 3.6: Graph showing the exponential fit of the boson peak region of the 280K INS spectrum of $\text{NH}_3^{11}\text{BH}_3$.

In the case of $\text{NH}_3^{11}\text{BH}_3$, the boson peak is thought to originate from the almost free rotation of the NH_3 and BH_3 units in the tetragonal phase especially as the region has also been seen in the spectra of zeolites loaded with NH_3 [165]. Crystallographically, in the tetragonal unit cell, the NH_3BH_3 molecule is modelled on 8 site disorder. As a result of this and the NMR studies by Cho *et al.* [156] the NH_3 and BH_3 units are believed to have different 'hopping' mechanisms with the NH_3 having a three fold hop and the BH_3 having a four fold hop.

3.3 Crystal Structure of ND_4BD_4

NH_4BH_4 has three phases, two of which were solved as part of this thesis. All three are discussed and result, as a function of temperature, from progressive ordering of the BH_4 and NH_4 units. Between 60-300K, the 'top phase' NH_4BH_4 adopts a disordered rock salt structure but below 60K the 'thermal history' of the sample has a strong influence on the phases observed (described in more detail in Section 3.4.1). The intermediate or 'middle' phase is rhombohedral and transforms across two body diagonals of the cubic phase. The 'bottom phase' is a trigonal $a \times b$ super cell of the middle phase.

A detailed account of the structure solution and refinement of each of the three NH_4BH_4 phases is described below.

3.3.1 The Cubic or 'top' phase ND_4BD_4

At 60K ND_4BD_4 was found to have cubic lattice $a = 6.868(3)$ Å with space group, $Fm\bar{3}m$ as illustrated in Figure 3.7 and the full structural data is found in Table 3.2. The N atom occupies the 0, 0, 0, position and the B atom the $\frac{1}{2}, \frac{1}{2}, \frac{1}{2}$. The BD_4 molecular anion is 2-fold disordered indicating that there is dynamic hopping in this phase in agreement with the findings of Karkamkar *et. al* [105]. Hydrogen bonding considerations indicated that the hopping is likely to occur around the $\langle 100 \rangle$ directions. The D atoms were refined with an occupancy of 0.5 on the eight cubic site along the $\langle 111 \rangle$ directions. The resulting B-D bond length of 1.20 Å was similar to those observed in other borohydride compounds[166].

Flacau *et al.* [167], have recently reported the same geometry for the ammonium ion, the same geometry is not observed for the ND_4 unit. Placing the D atoms in the same cubic geometry around the N atom resulted in a very low refined site occupancy indicating a different orientation of ND_4 unit with respect to BD_4 . In an attempt to find the most favourable orientation other D sites were added around the N atom along the $\langle 100 \rangle$ and the $\langle 110 \rangle$ directions. Surprisingly, the highest occupancy was found to be for those sites along the $\langle 100 \rangle$ direction. This is unusual because of the difficulty in resolving the octahedral symmetry of the site with the tetrahedral symmetry of the ND_4 unit. For both conditions to be satisfied a significant amount of disorder and rotation of

Atom	x/a	y/b	z/c	Occupancy	$B_{iso} \text{ \AA}^2$	Wyckoff Positions
N	0.00000	0.00000	0.00000	1.000	1.00	4a
D11	0.00000	0.00000	-0.15284	0.166	1.00	24e
D00	0.14410	0.00000	0.05094	0.003	3.69	96j
D05	0.14355	0.01255	0.05094	0.005	3.69	192l
D10	0.14191	0.02502	0.05094	0.008	3.69	192l
D15	0.13919	0.03729	0.05094	0.010	3.69	192l
D20	0.13541	0.04928	0.05094	0.008	3.69	192l
D25	0.13060	0.06090	0.05094	0.005	3.69	192l
D30	0.12479	0.07205	0.05094	0.003	3.69	192l
D35	0.11804	0.08265	0.05094	0.005	3.69	192l
D40	0.11039	0.09262	0.05094	0.008	3.69	192l
D45	0.10189	0.10189	0.05094	0.010	3.69	96k
B1	0.50000	0.50000	0.50000	1.000	1.00	4b
D2	0.60297	0.60297	0.60297	0.500	1.00	32f

Table 3.2: Refined crystallographic data for cubic ND_4BD_4 space group, $Fm\bar{3}m$ $a = 6.868(2)$ $\text{\AA}$ $R_{wp} = 3.48$ $R_{exp} = 2.03$ $\chi^2 = 1.72$.

the ND_4 unit is necessary. The result is 48-fold disorder of ND_4 leading to an essentially spherical distribution of D atoms around the N with a radius of the refined N-D bond length (1.02 $\text{\AA}$).

The 48-fold disorder of the ND_4 unit comes from:

1. 6-fold disorder automatically conferred by the $\langle 100 \rangle$ orientation.
2. 4-fold disorder conferred by the C_3 axis of the tetrahedron being co-axial with the C_4 unit cell axes
3. 2-fold disorder conferred by the mirror plane of the unit cell

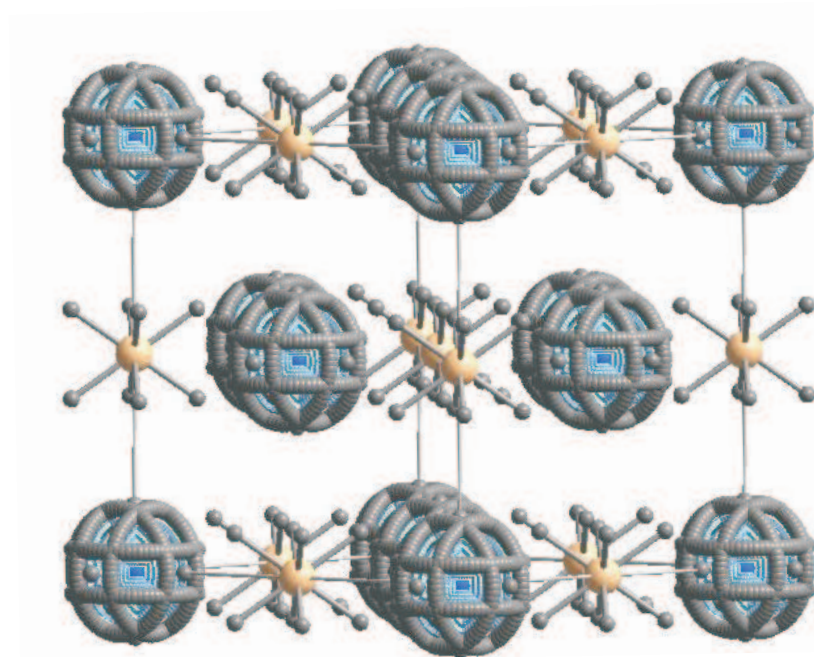
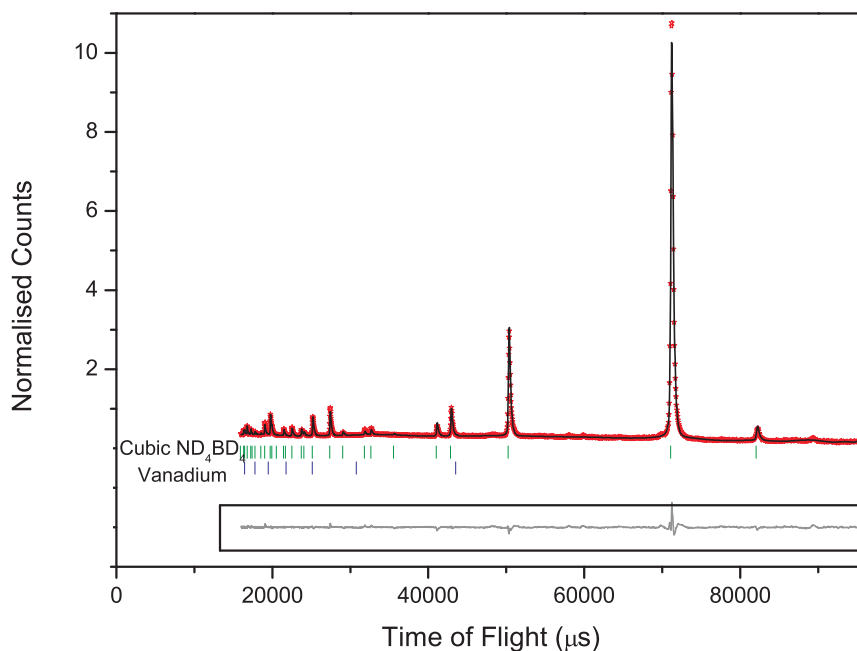


Figure 3.7: Top: Observed (dots) and calculated (line) room temperature diffraction patterns of rhombohedral ND_4BD_4 (top tick marks) and Vanadium (bottom tick marks). The highlighted box is the difference between the observed and the calculated data. $R_{wp} = 3.48$ $R_{exp} = 2.03$ $\chi^2 = 1.72$. Bottom: Structural diagram of cubic ND_4BD_4 nitrogen is blue, boron cream and deuterium grey.

The reason for the seemingly energetically unfavourable orientation must be dihydrogen bonding. The closest $D^{\delta+} \cdots D^{\delta-}$ distances are ≈ 1.9 Å and the additional symmetry conferred on the structure must more than compensate for the energy debt incurred by the symmetry disparity [168]. This behaviour is also seen in the $Fd\bar{3}m$ phase of NH_4I [166].

3.3.2 The Rhombohedral or 'middle' phase of NH_4BH_4

Rapid cooling of NH_4BH_4 to below 60K results in the formation of a more ordered 'middle' phase. The structure was solved from neutron powder diffraction data collected on the WISH diffractometer at the ISIS pulsed neutron facility (Section 2.2.3).

At 40K NH_4BH_4 was indexed to the $R\bar{3}m$ space group (number 166) with unit cell parameters $a = b = 4.831(3)$ Å and $c = 23.473(2)$ Å (Figure 3.8). The rhombohedral lattice parameters are related to the cubic lattice parameters by Equations 3.3 and 3.4:

$$a_{rhombohedral} = \sqrt{2 \left(\frac{a_{cubic}}{2} \right)^2} \quad (3.3)$$

$$c_{rhombohedral} = 2\sqrt{3a_{cubic}^2} \quad (3.4)$$

which indicates the cubic phase transforms to the rhombohedral phase across two body diagonals. Rietveld analysis of the diffraction data collected from the samples studied here was undertaken utilizing the $R\bar{3}m$ space group and the lattice parameters identified by cell indexing. The B and N atomic positions were added mathematically to preserve the 3.4 Å distances seen in the cubic phase of ND_4BD_4 and taken as a starting model for the refinement. The D sites were then built up around the B and N sites using tetrahedral rigid body matrices.

The BD_4 sites were modelled first as they were well ordered. A single D atom was tethered between 1.15- 1.25 Å from the B site and allowed to rotate freely. Once the refinement converged 1-3 extra D atoms (depending on the symmetry of the site) were added to the z-matrix to construct the rest of the tetrahedron. The angles were fixed to

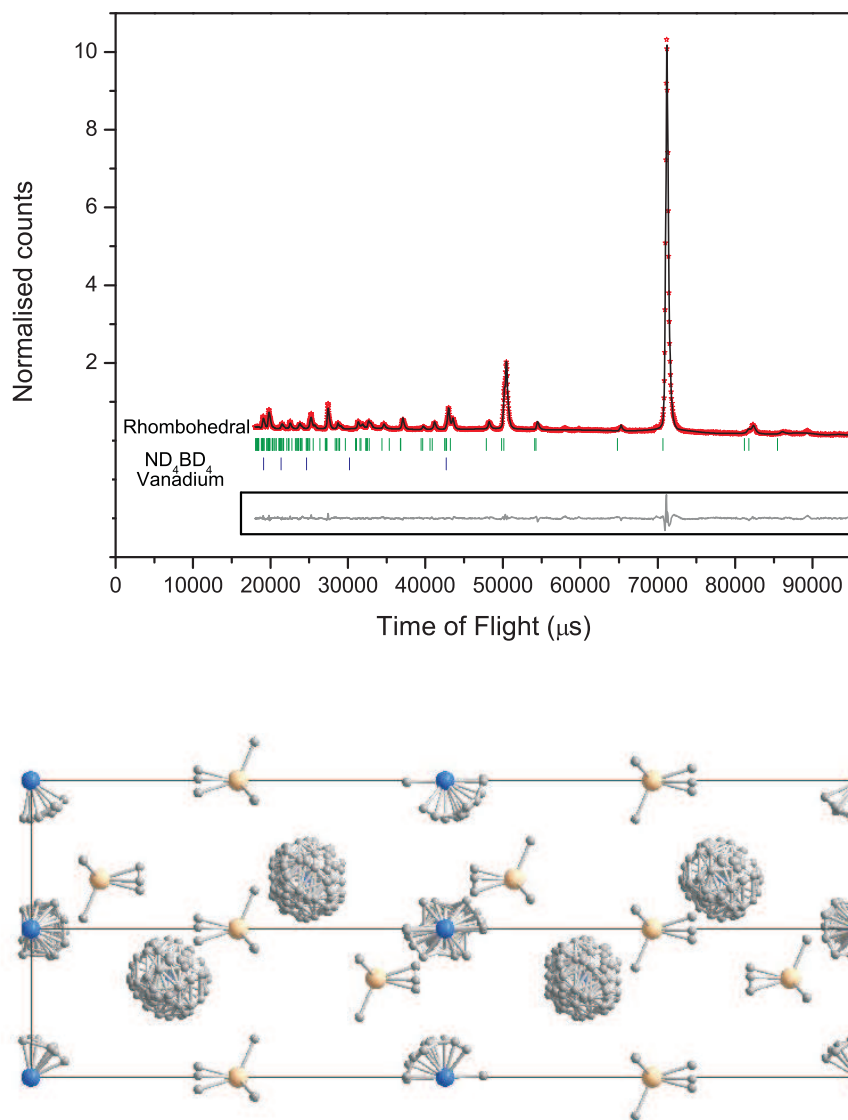


Figure 3.8: Top: Observed (dots) and calculated (line) room temperature diffraction patterns of rhombohedral ND₄BD₄ (top tick marks) and Vanadium (bottom tick marks). The highlighted box is the difference between the observed and the calculated data. $R_{wp} = 4.31$ $R_{exp} = 1.88$ $\chi^2 = 2.29$. Bottom: Structural diagram of rhombohedral ND₄BD₄ nitrogen is blue, boron cream and deuterium grey.

the ideal value of 109.45° , and the bond lengths made equivalent but allowed to refine between 1.15- 1.25Å. The unit was allowed to rotate freely. The refinement was then run again to allow the optimum geometry to be reached.

The ND_4 were significantly more disordered and added an additional layer of complexity to the structure solution. To model the ND_4 disorder successfully several Z-matrices needed to be constructed around the same N site.

When building up the D atoms around the N sites, the initial Z-matrices were added in the same manner described above for the BD_4 units (the only difference being the N-D bond length was constrained between 0.90- 1.09Å) and then fixed. The next Z-matrix was added and allowed to refine. Finally both matrices were allowed to refine simultaneously and the process repeated for any additional Z-matrices required.

There is, however, one significant drawback to the multiple Z-matrix method. It generates a very large number of refinement parameters, which meant the refinements were struggling to converge. It also became apparent that there were a large number of unnecessary reflections generated by the $R\text{-}\bar{3}$ space group. So it was decided to investigate other, higher symmetry, space groups to try and alleviate both problems.

Several Pawley refinements were performed using related higher symmetry space groups and $R\text{-}\bar{3}m$ was found to give the best fit. The Rietveld parameters were adjusted accordingly allowing the 0,0,0.25 B site and two Z-matrices to be removed from the refinement. The final atomic positions are shown in Table 3.3.

As the rhombohedral unit cell transformed along the body diagonal of the cubic phase, the BD_4 units which were orientated along the $\langle 111 \rangle$ are now orientated along the *rhombohedral* axis, $\langle 001 \rangle$ and can 'point' up or down it (see Figure 3.8) In this more ordered structure the tetrahedra alternate in an up - down array which explains why the transformation is over two body diagonals of the cubic phase. The cubic unit cell adopts an A B C layered repeat which requires two body diagonals for the up down ordering of the rhombohedral phase to be satisfied, as shown in Figure 3.9.

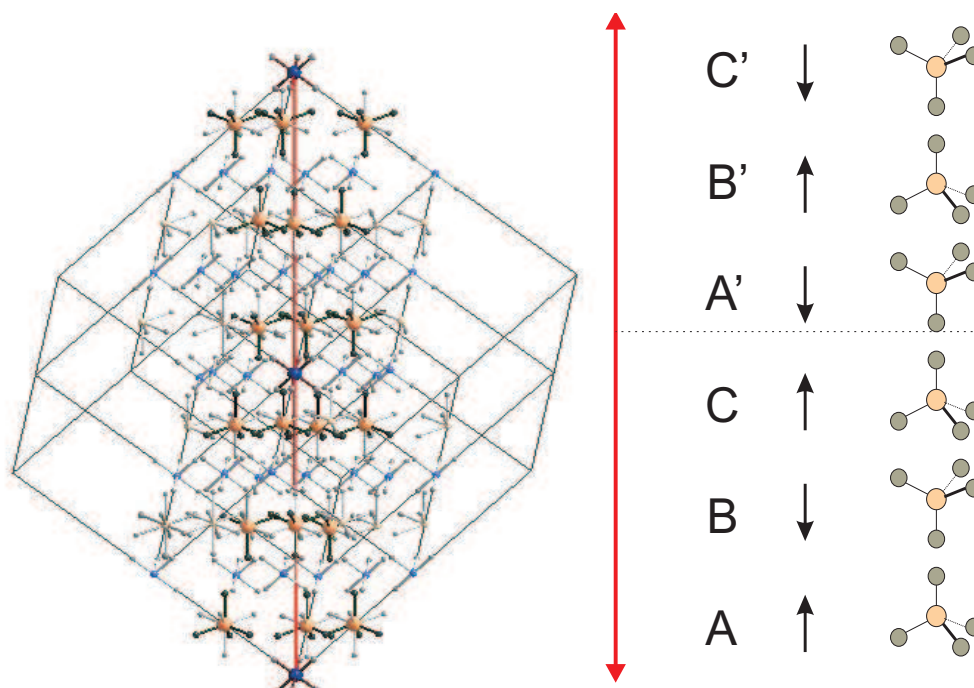


Figure 3.9: Diagram showing how cubic ND_4BD_4 transforms along the $\langle 111 \rangle$ axis to rhombohedral ND_4BD_4

The ND_4 unit has a 12-fold disorder, a factor of four less than in the cubic phase. This is because there is not a C_4 axis in the $R\bar{3}m$ unit cell that needs to be resolved with the C_3 axis of the tetrahedral ND_4 unit.

The 12-fold disorder of the ND_4 unit comes from:

1. 3 fold disorder automatically conferred by the $\langle 001 \rangle$ orientation.
2. 2 fold disorder conferred by the centre of inversion
3. 2 fold disorder conferred by the mirror plane of the unit cell

CHAPTER 3. VARIABLE TEMPERATURE STUDIES ON AMMONIA BORANE
AND AMMONIUM BOROHYDRIDE

Atom	x/a	y/b	z/c	Occupancy	$B_{iso} \text{ \AA}^2$	Wyckoff Positions
B1	0.00000	0.00000	0.75000	1.00	0.96	6c
D1	0.26077	0.13379	0.72999	0.42	0.65	36i
D2	0.01147	0.08318	0.79799	0.18	0.65	36i
N1	0.00000	0.00000	0.00000	1.00	0.28	3a
D11	-0.06452	-0.12907	0.03985	0.10	1.88	36i
D12	0.15075	-0.06293	-0.02419	0.00	1.88	36i
D13	-0.21379	-0.06181	-0.02407	0.00	1.88	36i
D14	0.12755	0.25382	0.00840	0.10	1.88	36i
D15	0.17564	0.17116	0.02904	0.00	1.88	36i
D16	-0.19795	-0.18298	0.02395	0.00	1.88	36i
D17	-0.08523	0.11995	-0.02769	0.00	1.88	36i
D18	0.10754	-0.10813	-0.02529	0.19	1.88	36i
D19	-0.12165	-0.25797	-0.00090	0.00	1.88	36i
D110	0.18231	0.08776	0.03257	0.00	1.88	36i
D111	0.10928	0.09302	-0.04094	0.00	1.88	36i
D112	-0.16995	0.07718	0.00926	0.00	1.88	36i
N2	0.00000	0.00000	0.50000	1.00	0.28	3b
D21	0.21966	0.09922	0.52408	0.10	1.88	36i
D22	-0.15700	0.07302	0.51902	0.10	1.88	36i
D23	0.05233	0.08541	0.45661	0.10	1.88	36i
D24	-0.11500	-0.25766	0.50028	0.10	1.88	36i
D25	0.05962	-0.17999	0.51182	0.10	1.88	36i
D26	-0.22099	-0.10983	0.47620	0.10	1.88	36i
D27	-0.02760	0.11024	0.53797	0.10	1.88	36i
D28	0.18897	0.17958	0.47399	0.10	1.88	36i
D29	0.11824	-0.12103	0.48272	0.10	1.88	36i
D210	0.12088	0.24512	0.48555	0.10	1.88	36i
D211	-0.24542	-0.11876	0.48574	0.10	1.88	36i
D212	0.00628	-0.00532	0.54597	0.10	1.88	36i

Table 3.3: Refined crystallographic data for rhombohedral ND_4BD_4 space group, $R\bar{3}m$ $a = b = 4.831(3) \text{ \AA}$ and $c = 23.473(2) \text{ \AA}$ $R_{wp} = 4.31$ $R_{exp} = 1.88$ $\chi^2 = 2.29$

3.3.3 The Trigonal or 'bottom' phase of ND_4BD_4

Slow cooling of ND_4BD_4 to below 2K results in the formation of an even more ordered 'bottom' phase. The structure was solved from neutron powder diffraction data collected on the WISH diffractometer at the ISIS pulsed neutron facility (Section 2.2.3).

Comparison of 2K ND_4BD_4 data with the 40K ND_4BD_4 data revealed a number of the 40K peaks had split, indicating a supercell structure. The bottom was indexed to the $P\bar{3}$ space group (number 147) with unit cell parameters $a = b = 9.51(4)$ Å and $c = 23.47(9)$ Å (Figure 1). The trigonal a and b lattice parameters are indeed double those of the rhombohedral phase and to the cubic lattice parameters by Equations 3.5 and 3.6.

$$a_{\text{trigonal}} = \sqrt{2a_{\text{cubic}}^2} \quad (3.5)$$

$$c_{\text{trigonal}} = 2\sqrt{3a_{\text{cubic}}^2} \quad (3.6)$$

Rietveld analysis of the diffraction data collected from the samples studied here was undertaken utilizing the $P\bar{3}$ space group and the lattice parameters identified by cell indexing. The B and N atomic positions from the cubic phase of NH_4BH_4 were transformed on to the rhombohedral axes and taken as a starting model for the refinement. The D sites were then built up around the B and N sites using tetrahedral rigid body matrices.

The BD_4 sites were first modelled as ordered anions. A single D atom was tethered between 1.15- 1.25Å from the B site and allowed to rotate freely. Once the refinement converged, 1-3 extra D atoms (depending on the symmetry of the site) were added to the z-matrix to construct the rest of the tetrahedron. The angles were fixed to the ideal value of 109.45° , and the bond lengths made equivalent but allowed to refine between 1.15- 1.25Å. The unit was allowed to rotate freely. The refinement was then run again to allow the optimum geometry to be reached.

The ND_4 were still somewhat disordered and again needed several Z-matrices needed to be constructed around the same N site to model the ND_4 disorder successfully .

When building up the D atoms around the N sites the initial Z-matrices were added in the same manner described above for the BD₄ units (the only difference being the N-D bond length was constrained between 0.9- 1.09Å) and then fixed. The next Z-matrix was added and allowed to refine. Finally both matrices were allowed to refine simultaneously and the process repeated for any additional Z-matrices required.

The initial Rietveld refinements were performed using the *P-3* space group to allow more control over the individual placing of atoms. Due to the large unit cell and the substantial number of parameters the refinements became very slow to converge. There were also a number of unnecessary reflections.

Trial of related higher symmetry space groups using Pawley refinements found *P-3c1* to give the best fit. Due to the increased ordering of the ND₄ in this expanded trigonal cell the BD₄ units no longer simply orientate along the <001> direction. Instead they order above or below the <102> and <204> hkl planes as shown in Figure 3.10.

In an ideal case with an infinite amount of cooling time the ND₄ would probably become completely ordered as well. However, due to practical time and experimental constraints it was not possible for this state to be observed. As such a 3-fold disorder around the N atoms still remains in the trigonal structure which comes from the 3-fold axis of the *P-3c1* unit cell.

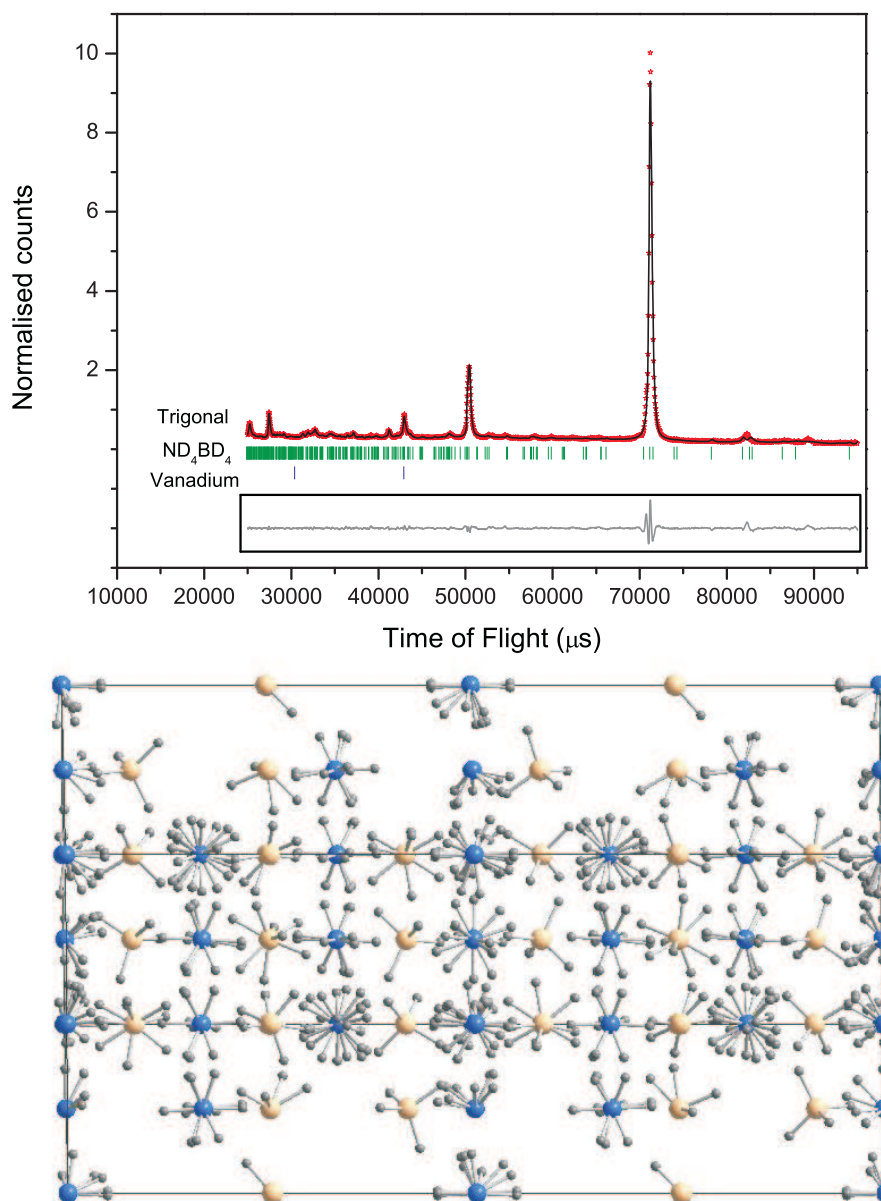


Figure 3.10: Top: Observed (dots) and calculated (line) room temperature diffraction patterns of trigonal ND_4BD_4 (top tick marks) and vanadium (bottom tick marks). The highlighted box is the difference between the observed and the calculated data. The weighted profile R-factor, R_{wp} , and expected R-factor, R_{exp} , are 4.48% and 1.97% respectively ($\chi^2=2.29$). Bottom: Structural diagram of trigonal ND_4BD_4 , nitrogen is blue, boron cream and deuterium grey.

CHAPTER 3. VARIABLE TEMPERATURE STUDIES ON AMMONIA BORANE
AND AMMONIUM BOROHYDRIDE

Table 3.4: Refined crystallographic data for trigonal ND_4BD_4 space group, $P\bar{3}c1$ $a = b = 9.51(4)$ Å and $c = 23.47(9)$ Å $R_{wp} = 4.48$, $R_{exp} = 1.97$, $\chi^2 = 2.29$.

Atom	x/a	y/b	z/c	Occupancy	B_{iso} Å ²	Wyckoff Positions
N1	0.00000	0.00000	0.00000	1.00	12.25	2b
H111	0.11877	0.01467	0.01381	0.10	2.46	12g
H112	-0.01041	0.10444	0.01568	0.10	2.46	12g
H113	-0.00851	-0.00461	-0.048143	0.10	2.46	12g
H114	-0.09984	-0.11451	0.018647	0.10	2.46	12g
H115	0.03301	0.12353	-0.015768	0.10	2.46	12g
H116	-0.07934	-0.09121	-0.032527	0.10	2.46	12g
H117	0.11204	-0.00738	0.006409	0.15	2.46	12g
H118	-0.06571	-0.02493	0.041886	0.10	2.46	12g
N2	0.00000	0.50000	0.00000	1.00	2.26	6e
H121	0.07476	0.48030	-0.03214	0.18	2.46	12g
H122	-0.10986	0.48853	-0.02173	0.23	2.46	12g
H123	-0.03714	0.40775	0.03530	0.10	2.46	12g
H124	0.07223	0.62341	0.01864	0.10	2.46	12g
H125	0.09332	0.61082	0.02240	0.25	2.46	12g
H126	0.03723	0.50182	-0.04571	0.10	2.46	12g
H127	-0.01216	0.39062	0.02257	0.16	2.46	12g
H128	-0.11838	0.49673	0.00074	0.10	2.46	12g
N5	0.66666	0.33333	0.16670	1.00	2.26	4d
H151	0.59601	0.20177	0.15662	0.00	2.46	12g
H152	0.72823	0.35037	0.20936	0.15	2.46	12g
H153	0.75905	0.39778	0.13239	0.25	2.46	12g
H154	0.58336	0.38339	0.16841	0.20	2.46	12g
H155	0.76489	0.42722	0.13919	0.1	2.46	12g
H156	0.55836	0.25766	0.13934	0.1	2.46	12g
H157	0.70931	0.25511	0.18733	0.39	2.46	12g
continued overleaf..						

CHAPTER 3. VARIABLE TEMPERATURE STUDIES ON AMMONIA BORANE
AND AMMONIUM BOROHYDRIDE

Atom	x/a	y/b	z/c	Occupancy	$B_{iso} \text{ \AA}^2$	Wyckoff Positions
H158	0.63409	0.39333	0.20093	0.1	2.46	12g
N7	0.83335	0.16670	0.33333	1.00	8.59	12g
H171	0.89426	0.29191	0.35087	0.25	2.46	12g
H172	0.90967	0.11071	0.34226	0.10	2.46	12g
H173	0.71323	0.09303	0.35447	0.25	2.46	12g
H174	0.81622	0.17112	0.28571	0.10	2.46	12g
H175	0.82484	0.16427	0.28518	0.29	2.46	12g
H176	0.89224	0.09678	0.34800	0.30	2.46	12g
H177	0.90676	0.29438	0.34802	0.10	2.46	12g
H178	0.70954	0.11135	0.35212	0.10	2.46	12g
H179	0.70625	0.09578	0.31736	0.34	2.46	12g
H1710	0.88645	0.29544	0.31929	0.13	2.46	12g
H1711	0.83465	0.15996	0.38150	0.10	2.46	12g
H1712	0.90603	0.11560	0.31517	0.10	2.46	12g
B1	0.00000	0.00000	0.25000	1.00	0.10	2a
H211	0.06447	-0.04777	0.21863	0.41	3.53	12g
B2	0.00000	0.50000	0.25000	1.00	0.10	6f
H221	0.05827	0.42128	0.26531	0.38	3.53	12g
H222	-0.09194	0.49337	0.28566	0.10	3.53	12g
H223	0.10360	0.63646	0.24337	0.27	3.53	12g
H224	-0.06993	0.44884	0.20569	0.56	3.53	12g
B4	0.33333	0.66666	0.08335	1.00	0.10	4d
H241	0.26715	0.68829	0.12259	0.35	3.53	12g
H242	0.25140	0.63518	0.04123	0.63	3.53	12g
H243	0.45942	0.78554	0.07481	0.29	3.53	12g
B6	0.16670	0.83335	0.41667	1.00	0.10	12g
H261	0.25263	0.86716	0.45774	0.52	2.46	12g
H262	0.22310	0.94203	0.38282	0.10	2.46	12g
H263	0.15374	0.71536	0.39495	0.24	2.46	12g
H264	0.03731	0.80883	0.43114	0.18	2.46	12g

3.4 Variable Temperature Neutron Diffraction on ND_4BD_4

Variable temperature neutron diffraction studies of ND_4BD_4 were made on the WISH and HRPD beamlines at ISIS (Section 2.2.3).

The HRPD study was performed first, over a wide temperature range (2-200K). The sample was packed on dry ice, in a glovebox into a 2cm flat vanadium can which was then sealed with indium wire. The can was then mounted on to a vented centre stick, cooled rapidly to 2K using a cryostat.

Upon reaching 2K, data were collected for 2 hours and the sample was warmed in 5K steps up to 200K. Upon reaching 200K, the process was reversed and the sample was cooled in 5K steps to 2K where data were then collected for a further 2 hours.

Surface plots of the heating and cooling runs are presented in Figure 3.11 and it is clear that below 60K the sample undergoes different phase transitions depending on the cooling rate. Initially this was quite confusing but once the phases had been indexed, and later solved (Section 3.3), the reasons became clear.

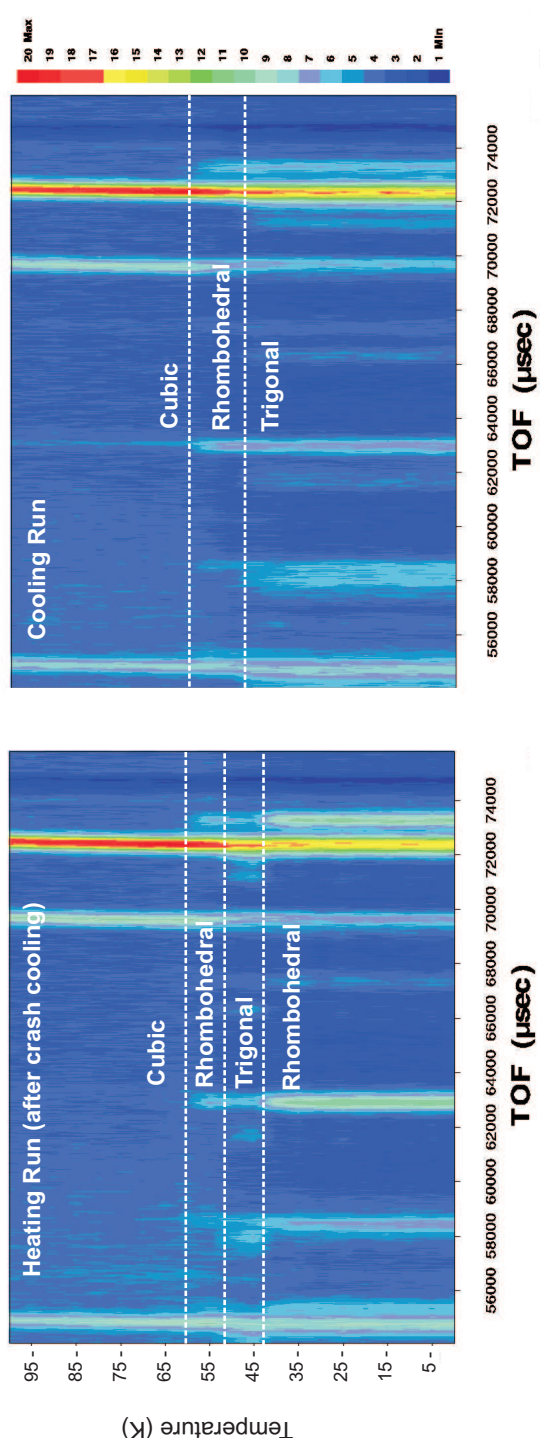


Figure 3.11: Surface plot of the heating and cooling time of flight neutron diffraction data collected at ISIS on HRPD for ND_4BD_4 . Data displayed between 2-100K in the 54000-76000 μs region. Lines corresponding to the phase transitions are indicated in white.

Rapid cooling to 2K resulted in the compound being trapped in the rhombohedral phase (Section 3.3.2) with a $R\bar{3}m$ space group lattice parameters $a = b = 4.8429(6)\text{\AA}$, $c = 23.524(4)\text{\AA}$. The phase transforms from the cubic lattice over two body diagonals. The BD_4 disorder was eliminated but which occupy tetrahedral sites but the ND_4 units still retained a 12 fold disorder.

As the sample was warmed slowly, additional peaks appeared at 45K and were consistent with the rhombohedral phase doubling along the a and b axes and moving to primitive trigonal (Section 3.3.3) unit cell lattice parameters $a = b = 9.6858(6)\text{\AA}$, $c = 23.5241(9)\text{\AA}$. unit cell. This phase was short lived and was assumed to be an intermediary phase to allow a final phase change to a cubic, $Fm\bar{3}m$ structure at 60K to occur.

To test the hypothesis and collect better data for structural refinement a short period of beam time on WISH was allocated to corroborate the HRPD findings. Due to time constraints it was not possible to do a slow cooling experiment so the sample was crash cooled to 35K and data collected at 42.4 44.6 50.3 53.8 59.9 62.3 66.7 71.4 and 75.6K for 15 mins each.

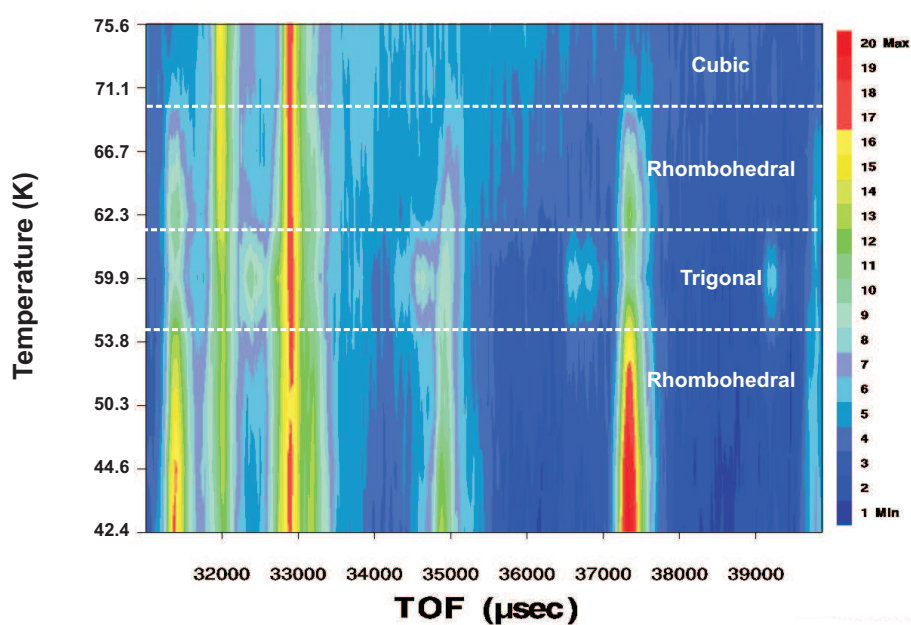


Figure 3.12: Surface plot of the heating and cooling time of flight neutron diffraction data collected at ISIS on WISH for ND_4BD_4 . Data displayed between 42K-76K in the 31000-40000 μs region. Lines corresponding to the phase transitions are indicated in white.

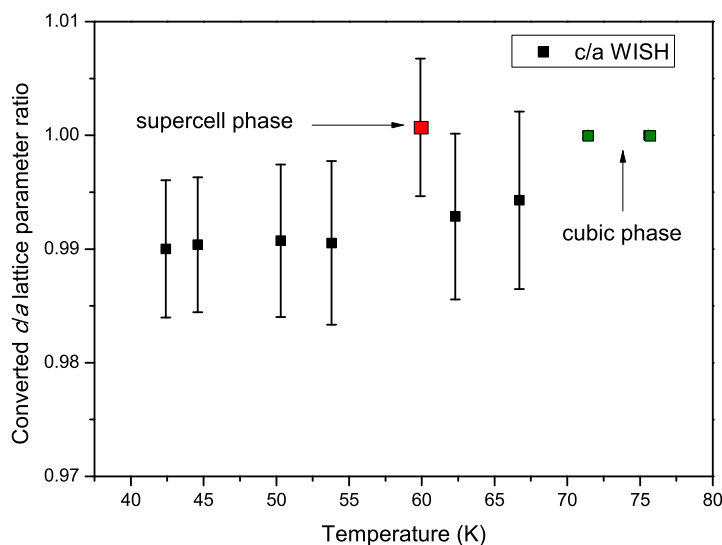


Figure 3.13: Graph showing the converted c/a lattice parameter ratio of the trigonal, rhombohedral and cubic phases of ND_4BD_4 as a function of temperature. Data calculated from Rietveld analysis of neutron diffraction data. Cubic points are green, trigonal red and rhombohedral black.

A surface plot of the WISH data is presented in Figure 3.12 and it is clear that the experiment was successful in replicating the HRPD heating run. Albeit with the phase changes occurring at slightly different temperatures (probably due to different cryostat calibration). In this case the first transition from rhombohedral to primitive occurs between 54K-60K, the primitive cell transforms back to the rhombohedral at 62K and then finally to the cubic cell between 67K-71K.

The diffraction patterns were analysed sequentially by hand, (due to the complexity of the phase transitions the use of a batch file was not practical) and the lattice parameters output as a function of temperature. To allow ease of comparison between all three phases, the lattice parameters of the trigonal and rhombohedral phases were converted to their equivalent cubic lattice parameters using the equations given in Sections 3.3.3 and 3.3.2 and the new c/a ratio calculated. The results are shown in Figure 3.13.

3.4.1 VT Analysis of the Cubic Phase ND_4BD_4

The HRPD data, whilst not as high quality as the WISH data and hence not suitable for the very detailed Rietveld refinement, was still good enough to allow accurate information on the lattice parameters to be mined. In contrast to the trigonal and rhombohedral phases, the cubic phase behaved identically on heating and cooling between 60K-200K.

The heating data is shown in Figure 3.14 along with a fit to the data calculated by the Fortran program 'Fitter' [169]. The program uses a polynomial function with terms involving Debye [136] and Einstein [170] models of thermal expansion.

$$a(T) = p_1 + p_2 V_D T + p_3 V_E T \quad (3.7)$$

where the Einstein model V_E represents the phonon density of states with a single phonon frequency.

$$V_E = \frac{\alpha_E e^{-\alpha_E}}{1 - e^{-\alpha_E}} \quad (3.8)$$

$$\alpha_E = \frac{T_E}{T} \quad (3.9)$$

and the Debye model V_D which uses a distribution of phonon frequencies.

$$V_D = \frac{\pi^4}{5\alpha_D^3} - \sum_{k=1}^{\infty} \left(3 + \frac{9}{k\alpha_D} + \frac{18}{k^2\alpha_D^2} + \frac{18}{k^3\alpha_D^3} \right) \frac{e^{-k\alpha_D}}{k\alpha_D} \quad (3.10)$$

$$\alpha_d = \frac{T_D}{T} \quad (3.11)$$

The Debye model should be a more satisfactory formulation however David *et al.* [171] found during their work on C_{60} a significantly better fit was achieved when using both models in conjunction than using them singly. The final fit to the lattice parameter between 60K-200K, shown in Figure 3.14 is given by the following formula.

$$a(T) = 6.850679 + (3.191 \times 10^{-4} \times 155.30) + (4.711 \times 10^{-4} \times 595.5386) \quad (3.12)$$

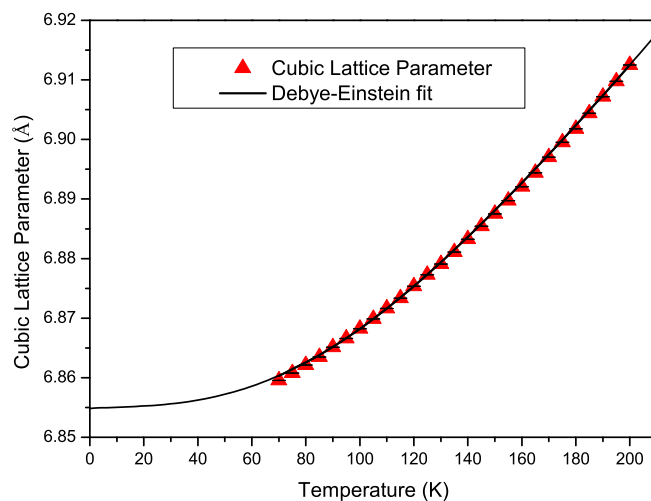


Figure 3.14: Graph showing the refined ND_4BD_4 a lattice parameter, calculated from Rietveld analysis of neutron diffraction data (via batch refinement) collected during the heating of ND_4BD_4 between 0K-200K. Mean errors, $a \pm 0.000005$, error bars only shown if larger than data markers. Debye-Einstein fit of the relationship between temperature and the axis length is displayed on the graph.

3.5 Heat Capacity Measurements on ND_4BD_4

The neutron diffraction findings were also confirmed by heat capacity measurements made on the same sample. For the 1st run the sample was cooled very slowly over a period of 20 hours to 2K and then allowed to warm up to 80K with measurements being taken every 1K. For the 2nd run the sample was crash cooled to 2K and again allowed to warm to 80K. It should be noted that the noise present above 50K is due to the sample lifting away from the contacts on the sample puck.

The results are shown in Figure 3.15. The fast cooling run (a) shows two transformations, a 1st order between 37K-47K consistent with the rhombohedral cell relaxing into the trigonal cell and a 2nd order between 57K-64K again consistent with a transformation from the primitive trigonal cell to the cubic cell. The slow cooling run (b) shows a single 2nd order phase transition, between 49K-59K consistent with a transformation from the most stable primitive trigonal cell to the cubic cell.

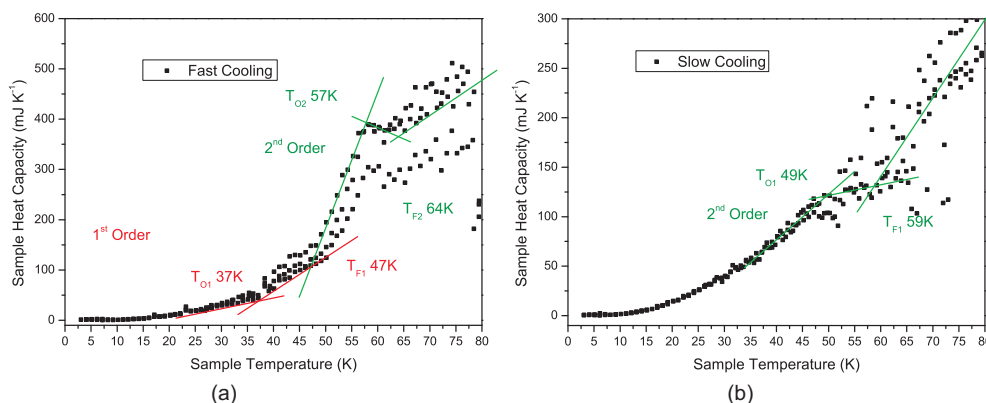


Figure 3.15: Graphs of the sample heat capacity of ND_4BD_4 after fast (a) and slow (b) cooling to 2K.

3.6 Conclusions

A fully boron enriched sample of $\text{NH}_3^{11}\text{BH}_3$ was synthesised and used for a variable temperature inelastic neutron scattering (INS) study. One long 12 hour scan was collected at 5K and then a series of 8 hour scans collected at 25, 30, 35, 40, 80, 100, 180, 240 and 280K.

The full phonon density of states was calculated by DFT for the $Pmn2_1$ unit cell and used to assign the 5K spectrum. There was generally good agreement between the two apart from the band at 329cm^{-1} which was much broader and weaker than predicted. Compression of di-hydrogen bonding was proposed as the explanation. The energy required for this compression was calculated to be 3.9 kJ mol^{-1} . The relative onset of the NH_3 and BH_3 librations were correlated to their moments of inertia I [159].

Evaluation of the variable temperature spectra revealed some interesting features. The spectra collected between 25K-40K changed only slightly. Once the sample reached 80K more noticeable changes started to occur and the peak intensities decreased steadily up to 180K. Above 220K when the sample had undergone the orthorhombic - tetragonal phase transition all the peaks in the $32\text{-}488\text{ cm}^{-1}$ region of the spectra collected at 240K and 280K were masked by an exponential region leading up to the elastic line.

Analysis of the peak intensities associated with NH_3 and BH_3 libration supports the findings of Cho *et al.* [156] that NH_3 libration has an earlier onset than the BH_3 . The exponential regions of the 240K and 280K spectra were assigned as boson peaks, attributed to almost free rotation of the NH_3 end of the molecule.

The structure of $\text{ND}_4^{11}\text{BD}_4$ was investigated by variable temperature neutron powder diffraction. Three progressively more ordered phases were identified. Above 60K $\text{ND}_4^{11}\text{BD}_4$ was found to have cubic lattice $a = 6.868(3)$ Å with space group, $Fm\bar{3}m$. The BD_4 and ND_4 units are 2 and 48 fold disordered respectively.

The 'thermal history' of the sample has a strong influence on the phases observed below 60K. Fast cooling to 2K resulted in the compound being trapped in a rhombohedral phase with a $R\bar{3}m$ space group lattice parameters $a = b = 4.8429(6)$ Å, $c = 23.524(4)$ Å. No disorder is present for the BD_4 which occupy tetrahedral sites but the ND_4 units have a 12 fold disorder. Slow cooling of ND_4BD_4 to below 2K results in the formation of an even more ordered 'bottom' phase space group, $P\bar{3}c1$ $a = b = 9.5148(6)$ Å and $c = 23.4732(9)$ Å. Again no disorder is present for the BD_4 sites but the ND_4 units have a 3 fold disorder.

In contrast to the trigonal and rhombohedral phases, the cubic phase behaved identically on heating and cooling between 60K-200K and the lattice parameters were fitted with a polynomial function with terms involving Debye [136] and Einstein [170] models of thermal expansion.

The phase changes identified by the variable temperature neutron diffraction studies were also confirmed by heat capacity measurements made on the same sample.

Chapter 4

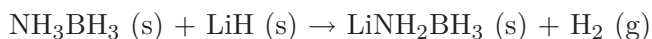
Lithium Amidoboranes

4.1 Introduction and Chapter Outline

Lithium amidoborane (LiNH_2BH_3) was first reported in the literature in the mid 1990's [172, 173] as a reducing agent, able selectively to transform a tertiary amide into the corresponding primary alcohol. However, it was only formed *in situ* and though some early computational calculations [174, 175] were made on LiNH_2BH_3 nothing was known about its behaviour in the solid state.

It was not until 2008 that evidence for the elusive solid state phase was published by Xiong *et al.* [86] along with some decomposition properties. This seminal paper opened the field for alkali metal amidoboranes as potential solid state hydrogen stores. Xiong *et al.* determined the structure of LiNH_2BH_3 to be *Pbca* $a=7.11274(6)$ Å, $b=13.94877(14)$ Å, $c=5.15018(6)$ Å, $V=510.970(15)$ Å³, and although solving the structure did not include the atomic coordinates. Their findings were confirmed experimentally by Wu *et al.* who published the atomic coordinates in 2008 [91] and from *ab initio* calculations by Ramzan *et al* [176].

Initially crystalline samples of LiNH_2BH_3 were formed using high impact ball milling synthesis techniques [86, 91]:

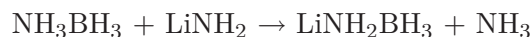


However, there are a number of disadvantages to ball milling as a synthesis technique:

- Samples produced by this route also contain impurities from the milling process, normally metallic iron or tungsten carbide depending on the milling apparatus.
- Very small particles are formed (depending on milling time, but may be as small as 5Å) making it difficult to decouple milling effects from the bulk sample properties during thermogravimetric analysis [177].
- It is energy inefficient to scale up for industrial applications.

As a result, other solution based synthetic avenues were explored and there broadly included:

- A $\text{NH}_3\text{BH}_3 + \text{LiH}$ suspension in THF [178, 179, 180] The LiNH_2BH_3 formed is soluble and isolated by vacuum removal of the THF. Unfortunately, complete removal of the THF can be difficult due to the strong O - Li interaction which leads to the formation of an $\text{LiNH}_2\text{BH}_3\text{-THF}$ adduct [181].
- A $\text{NH}_2\text{BH}_3 + \text{LiNH}_2$ suspension in THF [182, 183] thought to proceed via the reaction



LiNH_2BH_3 samples produced by this method have been found to be poorly crystalline [181] and contain significant amounts of NH_3BH_3 and LiNH_2 . It is thought that the excess THF allows continual exchange between residual NH_3 still dissolved in the THF and LiNH_2 and the BH_3 unit of the NH_3BH_3 . This prevents the LiNH_2BH_3 from crystallizing well and also accounts for the presence of LiNH_2 and NH_3BH_3 in the sample.

- $\text{NH}_3\text{BH}_3 + \text{LiNH}_2$ will also react on contact when ground together in the solid state [184]. A viscous foaming mixture is produced which when left to dry forms the LiNH_2BH_3 .

In this thesis, a modified synthesis route LiNH_2BH_3 (and NaNH_2BH_3), utilizing NH_3BH_3 and the appropriate metal hydride in Et_2O . As both reactants are only sparingly soluble and LiNH_2BH_3 is insoluble Et_2O offers an improvement over the THF methods as the Et_2O can be removed with ease. The reaction occurs at room temperature in excellent yield and purity and has potential to be scaled up for bulk synthesis.

LiNH_2BH_3 has been well characterised by thermogravimetric and NMR studies.

There is generally good agreement between the NMR studies with the solid state MAS $^{11}\text{BH}_3$ shift of ca. -20ppm [173, 86]. This is deshielded with respect to the $^{11}\text{BH}_3$ shift of NH_3BH_3 suggesting electron withdrawal by the Li metal from the BH_3 unit in the crystal structure. Some very elegant time resolved studies have been performed on solution state reactions [179, 183], which have provided valuable insights into the formation mechanisms.

There is considerable variation in the reported hydrogen release properties of LiNH_2BH_3 [179, 86, 91, 183, 87]. For example, in the solid state Xiong *et al.* [86] report a single step hydrogen release at 92°C (365K), Wu *et al.* [91] report a two stage release at 92 and 120°C (365K and 393K), where as in solution Xiong *et al.* [179] reported hydrogen evolution at as low as 40°C (313K). These differences are likely to be as a result of different synthesis methods and measurement conditions and are the subject of further discussion in Section 4.4.

The dehydrogenation mechanism of LiNH_2BH_3 has been rather under studied, which could in part be due to the difficulty in characterizing its decomposition products. To date, there have been three gas phase computational studies of note [185, 186, 187] and one detailed experimental study [180] into its dehydrogenation mechanism. All of the calculations predicted a bimolecular mechanism involving a lithium hydride intermediate to be the lowest energy pathway and these findings were supported by the experimental study. The mechanism is considered in more depth in Section 4.6.

The above work all centres on the α phase of LiNH_2BH_3 , which was assumed to be the only allotrope of the compound. However in 2009 [87], a minor β phase was detected as part of the reaction product of ball milling experiment, the structure of which is described in Section 4.2.2.

The structure of $\alpha\text{-LiNH}_2\text{BH}_3$ was explored in detail with synchrotron X-ray powder diffraction on the MS X04SA, high-resolution beamline at the SLS (Section 2.2.2) and neutron powder diffraction on GEM at ISIS (Section 2.2.3). Variable temperature synchrotron X-ray powder diffraction measurements were also taken to monitor the changes in crystal structure up to decomposition. Hydrogen desorption properties were studied first using combined intelligent gravimetric analysis with mass spectrometry (IGA-MS, Section 2.3.1). Low temperature and variable temperature INS studies were undertaken on the TOSCA and MAPS spectrometers at ISIS (Section 2.3.4) and used in conjunction with the crystallographic data to gain greater understanding of the decomposition mechanism.

Finally in the last part of this chapter, the preliminary crystal structure and desorption properties of an elusive tetragonal phase of LiNH_2BH_3 are presented.

4.2 Crystal structures of α -LiNH₂BH₃ and β -LiNH₂BH₃

4.2.1 α -LiNH₂BH₃

The structure of α -LiNH₂BH₃, was initially solved using X-ray powder diffraction data [86] [91]. However, the final refinement presented in this thesis was obtained from a simultaneous Rietveld analysis of synchrotron X-ray data from the SLS(Section 2.2.2) and neutron powder diffraction data from GEM and consequently enable the H positions to be determined with a high degree of accuracy (Figure 4.1(a)).

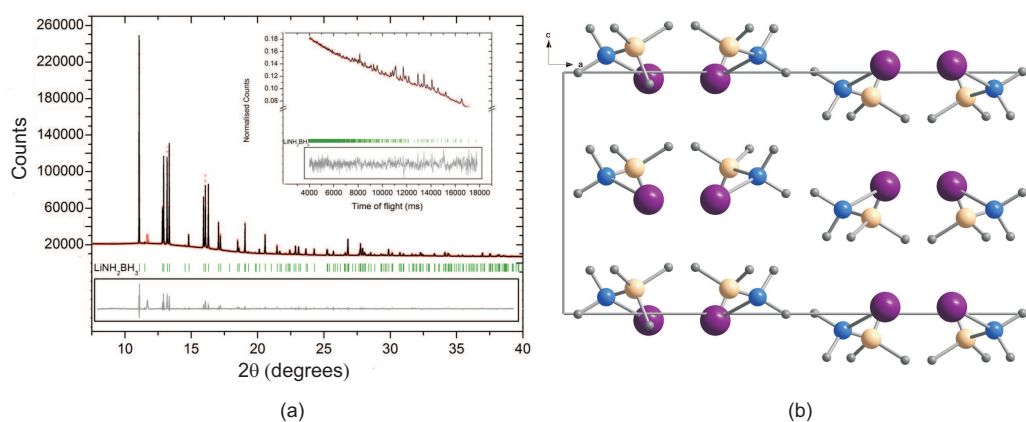


Figure 4.1: (a) Final Rietveld refinement plots for X-ray and neutron (inset) diffraction data showing observed (blue), calculated (red) and difference (grey) plots. Bragg peak positions for the α -LiNH₂BH₃ (green) are indicated. Figure 4.1(b) Structural diagram of α -LiNH₂BH₃ viewing along the b axis. Lithium is purple, nitrogen blue, and boron cream.

Notably, the neutron data was collected on samples with naturally occurring isotopes using the GEM powder diffractometer at ISIS. The presence of natural boron results in very high absorption which dramatically reduces the diffraction signal, while the incoherent scattering contribution from the hydrogens results in a large background (Figure 4.1a inset). However, the high count rate of GEM can enable diffraction patterns of sufficient quality for accurate refinement to be collected in approximately four hours. α -LiNH₂BH₃ has an orthorhombic unit cell and with $Pbca$ space group and room temperature lattice constants of ($a = 13.94682(7)$ Å, $b = 5.14883(3)$ Å, $c = 7.11254(3)$ Å and $V = 510.748(4)$ Å³) and is shown in Figure 4.1(b). The atomic coordinates are given in Table 4.1.

Atom	x/a	y/b	z/c	Occupancy	B_{iso} Å ²	Wyckoff Positions
B	0.15003	0.03647	0.10351	1	2.4(8)	8c
H1	0.10735	-0.13982	0.18258	1	4.1(4)	8c
H2	0.22166	0.09826	0.19220	1	4.1(4)	8c
H3	0.18117	-0.03568	-0.04861	1	4.1(4)	8c
N	0.08996	0.28316	0.06866	1	3.0(6)	8c
H4	0.03038	0.24579	-0.00201	1	6.2(5)	8c
H5	0.05595	0.35184	0.18026	1	6.2(5)	8c
Li	0.17955	0.55381	-0.02769	1	4.1(3)	8c

Table 4.1: Refined crystallographic data for α -LiNH₂BH₃ space group *Pbca* $a = 13.94682(7)$ Å, $b = 5.14883(3)$ Å, and $c = 7.11254(3)$ Å $R_{wp} = 1.66$ $R_{exp} = 0.72$ $\chi^2 = 2.37$.

The structure of α -LiNH₂BH₃ differs substantially from that of NH₃BH₃. Instead of a neutral NH₃BH₃ molecule, α -LiNH₂BH₃ is more akin to an ionic salt [Li]⁺[NH₂BH₃][−]. This changes the intermolecular forces present from dihydrogen bonds to electrostatic interactions. The structure can be constructed in three stages (see Figure 4.2).

1. The strongest characteristic feature of α -LiNH₂BH₃ is the discrete [NH₂BH₃][−] molecular unit (Figure 4.2(a)). There are significant changes to the [NH₂BH₃][−] unit on replacement of the hydrogen by lithium. The most notable is the contraction of the B-N bond which decreases from 1.59(5)Å in NH₃BH₃ to 1.54(4) Å in α -LiNH₂BH₃. The ionic nature of α -LiNH₂BH₃ increases the electron density on the nitrogen. This increases the availability of the lone pair and the Lewis basicity of the nitrogen, allowing greater electron donation to the Lewis acid BH₃ unit, resulting in a stronger, shorter bond. The N-H bond was observed to lengthen slightly from 0.96(3) Å in NH₃BH₃ to 0.99(2) Å in α -LiNH₂BH₃ probably due to increased steric repulsion from the [Li]⁺. There is an increase in B-H bond length (1.15(4) Å to 1.22(2)Å), due to an increase in electron density on the boron from the more available nitrogen lone pair. The increased availability of the nitrogen

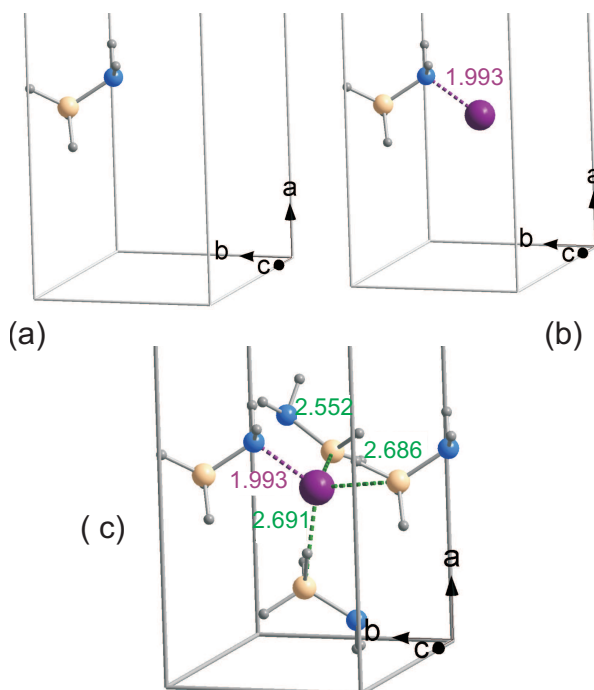


Figure 4.2: Schematic showing the three stage construction of the α - LiNH_2BH_3 structure. (a) the $[\text{NH}_2\text{BH}_3]^-$ molecular unit. (b): the electrostatic interaction between the $[\text{Li}]^+$ ion and the $[\text{NH}_2\text{BH}_3]^-$. (c): tetrahedral electrostatic interactions between $[\text{Li}]^+$ and the 3 closest BH_3 units. (All bond lengths in Angstroms calculated from refined powder data).

lone pair, demonstrated by the shorter B-N bond, reduces the electron deficiency of the boron atom. Consequently, there is a decrease its affinity for the electrons centred on the $\text{H}^{\delta-}$, resulting in a weaker, longer bond.

2. The electrostatic interaction between the $[\text{Li}]^+$ ion and $[\text{NH}_2\text{BH}_3]^-$ (Figure 4.2(b) top right) results in a strong, directed Li-N bond. This bond is 1.0 Å longer than the N-H bond it replaces and results in a unit cell expansion and the disappearance of dihydrogen bonding. The closest intermolecular $\text{H}^{\delta+} \cdots \text{H}^{\delta-}$ distances to increase from 1.96 Å (NH_3BH_3) to 2.37 Å α - LiNH_2BH_3 , close to the expected van-der-Waals distance and too far for the significant $\text{H}^{\delta+} \cdots \text{H}^{\delta-}$ interactions to occur. The length of the Li-N interaction, 1.99 Å, is analogous to those observed in LiNH_2 [188], Li_2BNH_6 and $\text{Li}_4\text{BN}_3\text{H}_{10}$ [189] (2.14 Å, 2.09 Å and 2.07 Å respectively).

3. The next significant interactions in the α - LiNH_2BH_3 structure are the tetrahedral electrostatic interactions between $[\text{Li}]^+$ and the three closest BH_3 units. (Figure 4.2(c)). The presence of these $\text{BH}^{\delta-} \cdots \text{Li}^+$ interactions supersede the dihydrogen bonding seen in NH_3BH_3 as the stabilising factor of the extended structure. These are of significant energy so that α - LiNH_2BH_3 remains a solid at room temperature despite the removal of the dihydrogen bonding. The $[\text{NH}_2\text{BH}_3]^-$ units face each other forming a layered structure which allows the coordination of the $[\text{Li}]^+$ atom by three close $\text{BH}_3^{\delta-}$ units (Li-B distances of 2.55 Å, 2.69 Å and 2.69 Å). The BH_3 units form the base of a tetrahedron with the associated N atom at the apex. This structural feature is also seen in the analogous compounds LiBH_4NH_3 and α - LiNH_2BH_3 . A consequence of this geometry is that the NH_2 units point towards each other down the centre of the unit cell. This is an unfavourable interaction which must be significantly compensated by the $\text{B-H}^{\delta-} \cdots \text{Li}^+$ interactions for the compound to exist. The longer N-H bonds may reduce the partial charges on the H atoms, weakening their repulsion, though facile shearing between the molecular layers (perpendicular to the a axis c.f graphite or mica) is still an expected feature of α - LiNH_2BH_3 .

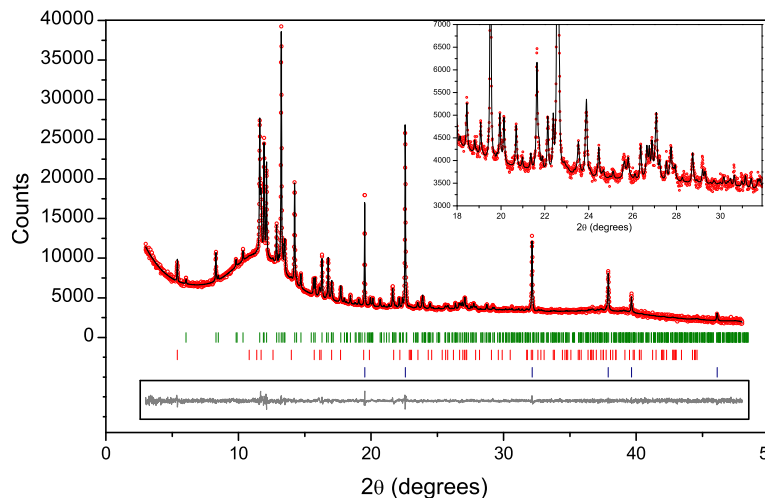


Figure 4.3: Observed (dots) and calculated (line) room temperature diffraction patterns of β -LiNH₂BH₃ (top tick marks) and LiH (bottom tick marks) with a small amount (10%) of an unknown tetragonal phase (middle tick marks). The highlighted box is the difference between the observed and the calculated data. The weighted profile R-factor, R_{wp} , and expected R-factor, R_{exp} , are 2.38% and 1.50% respectively ($\chi^2 = 2.51$) indicating an excellent fit to the data as evidenced by the close agreement at higher angles (inset).

4.2.2 β -LiNH₂BH₃

The structure of β -LiNH₂BH₃, was solved using synchrotron X-ray powder diffraction data from the ESRF (Section 2.2.2). A typical data set is shown in Figure 4.3 and indicates a mixture of phases that includes unreacted LiH a minority lithiated tetragonal phase, see Section 4.8, and the majority new phase. The computer program DASH [128] was used both to determine the space group and subsequently solve the crystal structure of the majority phase β -LiNH₂BH₃. The final detailed structural Rietveld analysis of β -LiNH₂BH₃ was performed using the profile refinement program TOPAS Academic [125] with the LiNH₂BH₃ units independently restrained using a z-matrix formalism. The unknown tetragonal phase was accounted for using the Pawley refinement method.

In common with α -LiNH₂BH₃, β -LiNH₂BH₃ has an orthorhombic unit cell with $Pbca$ space group. However, the β -LiNH₂BH₃ unit cell ($a=15.146(6)$, $b=7.721(3)$, $c=9.268(4)$ Å and $V=1083.7(8)$ Å³) is essentially a factor of two larger than the α -LiNH₂BH₃ ($a=13.94682(7)$, $b=5.14883(3)$, and $c=7.11254(3)$ Å); the β -phase has two different Li, N

Atom	x/a	y/b	z/c	Occupancy	$B_{iso} \text{ \AA}^2$	Wyckoff Positions
B1	0.25892	-0.11524	0.12724	1	4.1	8c
H1	0.21760	-0.13470	0.23390	1	7.1	8c
H2	0.30440	0.00880	0.12590	1	7.1	8c
H3	0.30170	-0.24230	0.11610	1	7.1	8c
N1	0.19691	-0.11399	-0.00986	1	5.2	8c
H4	0.15930	-0.21800	-0.02120	1	7.1	8c
H5	0.15960	-0.00860	-0.01140	1	7.1	8c
Li1	0.27864	-0.11881	-0.18508	1	6.3	8c
B2	0.05994	0.17457	0.38353	1	5.5	8c
H6	0.02420	0.21700	0.49590	1	7.1	8c
H7	0.10380	0.30000	0.34800	1	7.1	8c
H8	0.10290	0.04130	0.38990	1	7.1	8c
N2	-0.01796	0.11644	0.28008	1	7.8	8c
H9	0.01160	0.06230	0.19610	1	7.1	8c
H10	-0.05820	0.21630	0.26680	1	7.1	8c
Li2	-0.07661	-0.0844	0.35876	1	6.3	8c

Table 4.2: Refined crystallographic data for β -LiNH₂BH₃.space group *Pbca* $a = 15.146(6) \text{ \AA}$, $b = 7.721(3) \text{ \AA}$, $c = 9.268(4) \text{ \AA}$ $R_{wp} = 2.38$ $R_{exp} = 1.50$ $\chi^2 = 2.51$.

and B sites while the α phase has one. The atomic coordinates are shown in Table 4.2.

The crystal structure of β -LiNH₂BH₃ can be considered to be an intergrowth of two LiNH₂BH₃ layers oriented perpendicular to the a -axis (Figure 4.4(a)). As with α -LiNH₂BH₃, the strongest intermolecular interactions are the principally ionic bonds between Li⁺ and the nitrogen atoms in the amidoborane anions; at 1.99(4) $\text{\AA}$ and 2.04(4) $\text{\AA}$, the Li-N distances are similar to the equivalent distance in α -LiNH₂BH₃. β -LiNH₂BH₃ also displays a tetrahedral molecular coordination of Li⁺ (Figure 4.4b)).

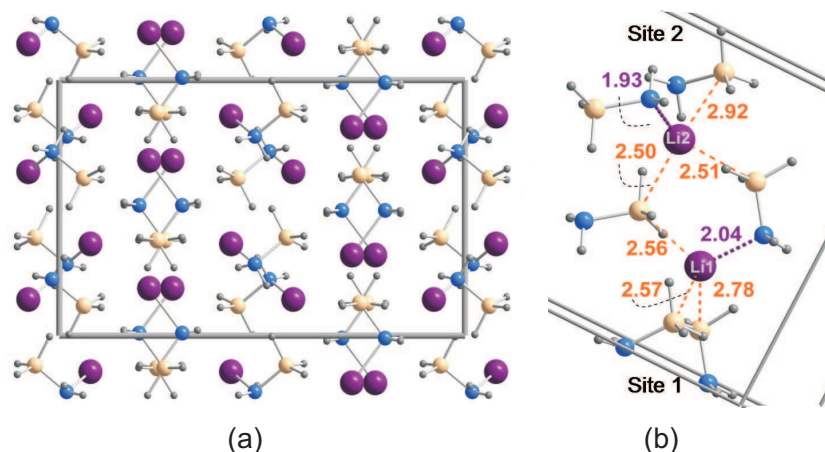


Figure 4.4: (a) b -axis projection of β - LiNH_2BH_3 showing the alternating layers of LiNH_2BH_3 molecules perpendicular to the long a -axis, (b) the tetrahedral coordination of Li^+ ions highlighting the short Li-N bonds and Li - BH_3 close contacts in Å.

It is believed that β - LiNH_2BH_3 is less stable than the previously reported [86] α - LiNH_2BH_3 polymorph for the following reasons:

- β - LiNH_2BH_3 , the compound only seems to be accessible by ball milling and has not been found in any of the products made via wet chemical methods.
- β - LiNH_2BH_3 has a lower density than α - LiNH_2BH_3 (0.902gcm^{-3} and 0.957gcm^{-3} respectively) which commonly suggests a less stable polymorph [190].
- The occurrence of two crystallographically distinct formula units of lithium amidoborane in chemically very similar environments in β - LiNH_2BH_3 suggests that the structure is trapped in a local thermodynamic minimum.
- The tetrahedral coordination of Li^+ ions amidoborane anions is more distorted in β - LiNH_2BH_3 . In α - LiNH_2BH_3 , the three distances are similar at 2.51Å , 2.69Å , 2.69Å but in β - LiNH_2BH_3 , the Li1-B distances are 2.56Å , 2.57Å , 2.78Å and for Li2-B are 2.50Å , 2.51Å , 2.92Å . Each Li^+ ion has a long Li-B distance which implies weaker bonding with the associated amidoborane anion. This weaker bond is characteristic of a less stable structure.

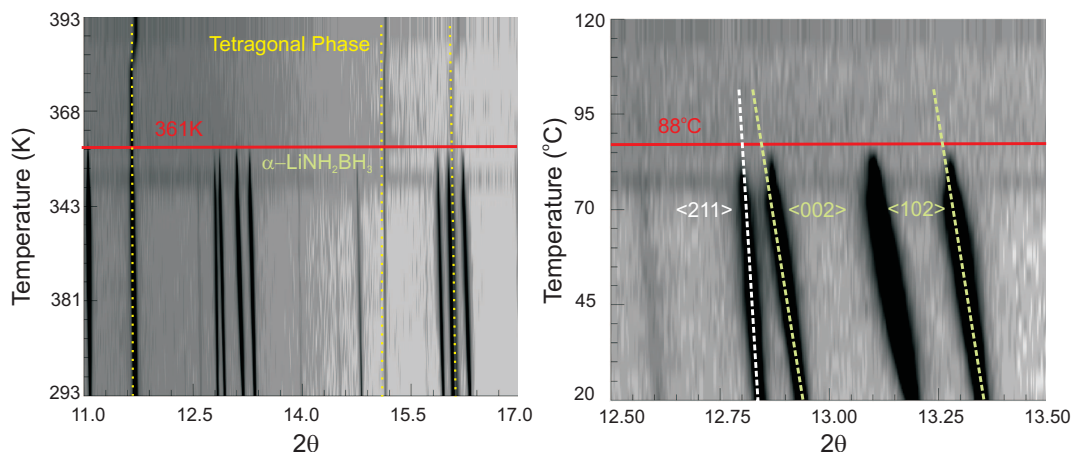


Figure 4.5: Surface plot of synchrotron X-ray diffraction data collected at the ESRF where α -LiNH₂BH₃ was heated to 408K (135°C) in a sealed glass capillary tube. Lines corresponding to Bragg reflections of the various phases are indexed.

4.3 Variable Temperature X-ray Diffraction Studies of α -LiNH₂BH₃

4.3.1 Variable Temperature X-ray Diffraction Studies of α -LiNH₂BH₃ at the ESRF

The first variable temperature X-ray diffraction studies of α -LiNH₂BH₃ were performed at the ESRF (Section 2.2.2) between 293K and 408K (20°C-135°C) in a sequential series of experiments performed at 5 degree increments. The data are presented as a surface plots in Figure 4.5.

Inspection of the Bragg peaks during these experiments revealed they broadened and flattened with increasing temperature, with a complete disappearance of crystallinity after 361K (88°C), in accordance with the observed dehydrogenation temperature [86]. The Bragg peaks were shifted on heating, but by differing amounts, (see Figure 4.5), indicating anisotropic thermal expansion of the unit cell. For example, the peaks at 12.93° and 13.19° at room temperature are shifted by 0.07° at the decomposition temperature while the peak at 12.84° is shifted by 0.05°. Sequential refinement of the data with a batch file (Section 2.2.4) showed that the *a* and *c* axes increased monotonically with temperature by 0.64 and 0.53% respectively.

The most unusual feature of the data was the negative thermal expansion observed in the short b axis which decreased by -0.02% between 293K and 351K (20°C-78°C) and but then expanded by +0.07% between 351K and 361K (78°C-88°C), the last run before decomposition.

Negative thermal expansion is a rare phenomenon arising from several possible high order mechanisms at the supramolecular level of the solid [191] including, ferroelectric, magnetostrictive or displacive phase transitions, low frequency phonon modes [192], the presence of rigid unit modes and libration.

The origin of the negative thermal expansion in α -LiNH₂BH₃ was thought to be two fold due to:

1. Libration of the BH₃ unit.
2. Low energy shearing modes between the structural layers along the $\langle 200 \rangle$ direction of the unit cell.

Both of which were seen in the inelastic neutron scattering data collected on TOSCA at ISIS (see Section 4.5).

However when further VT diffraction measurements were performed at the SLS (see Section 4.3.2) the negative thermal expansion was not observed. This lead to the conclusion that it was a radiation induced artifact caused by the very high flux of the beam at the ESRF; amidoboranes are highly susceptible to radiation damage. As a result, all future synchrotron measurements were conducted at the comparatively low-flux SLS to avoid any further radiation damaged to the samples.

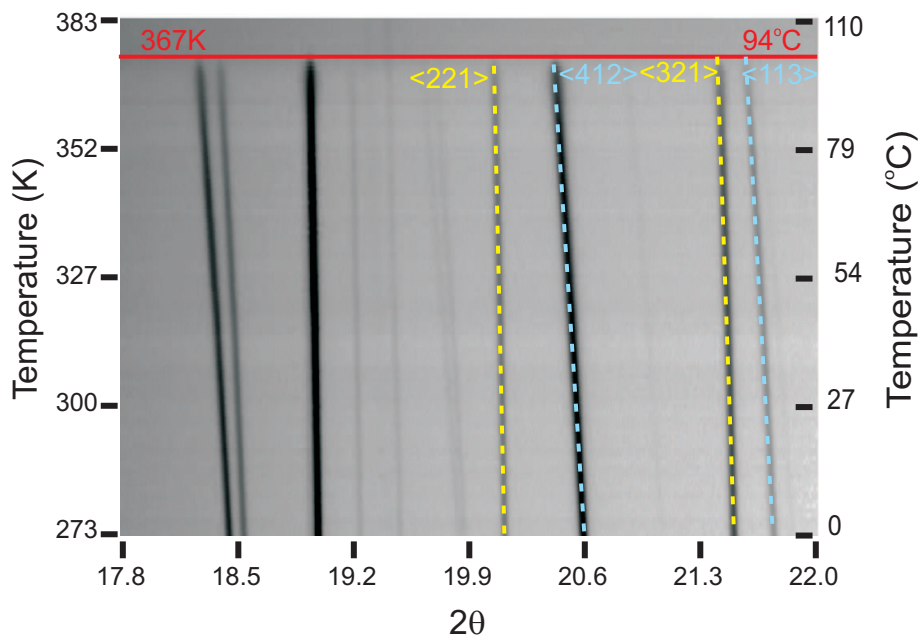


Figure 4.6: Surface plot of synchrotron X-ray diffraction data collected during the heating of α - LiNH_2BH_3 400K (127°C) in a sealed glass capillary tube. Lines corresponding to Bragg reflections of the various phases are indexed.

4.3.2 Variable Temperature X-ray Diffraction Studies of α - LiNH_2BH_3 at the SLS

Variable temperature X-ray powder diffraction patterns of α - LiNH_2BH_3 were collected between 200-400K (-73-127°C) in 1 degree steps on MS X04SA, the high-resolution beamline at the SLS (see Section 2.2.2) The data sets were refined sequentially in a batch file as detailed in Section 2.2.4.

Inspection of the Bragg peaks during variable temperature X-ray diffraction experiments reveals peak broaden and flattening with increasing temperature, with a complete disappearance of crystalline α - LiNH_2BH_3 at 363K (90°C)(see Figure 4.6). Sequential refinement of the diffraction patterns revealed all the lattice parameters to increase linearly with temperature, but with significant anisotropic expansion. The a axis expanded by +1.554% , the b axes by +0.203% and the c axis by +1.243% as shown in Figure 4.7(a).

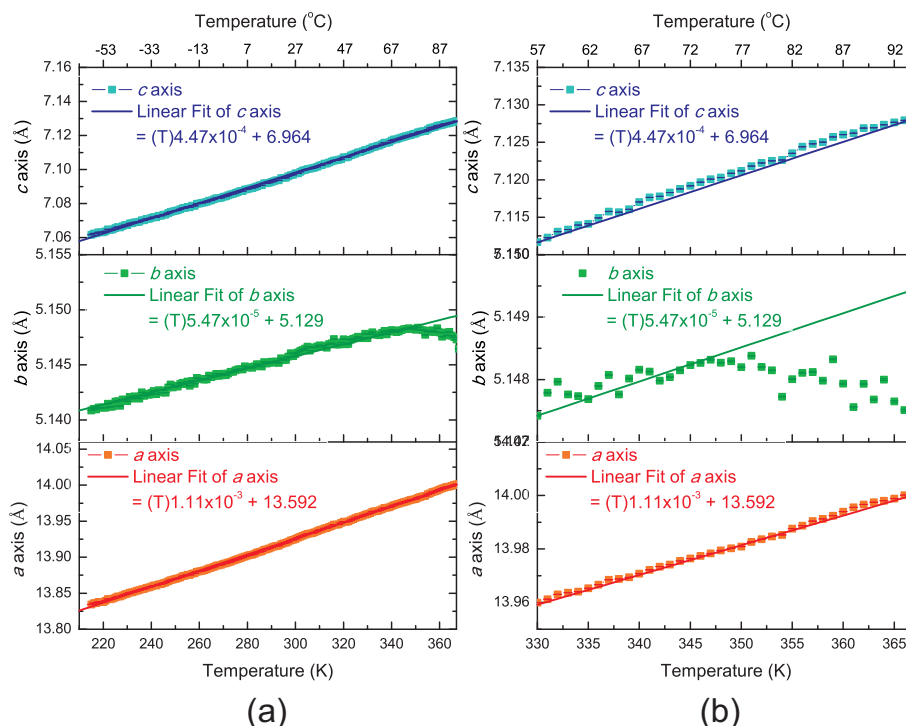


Figure 4.7: Refined α -LiNH₂BH₃ lattice parameters, calculated from Rietveld analysis of synchrotron diffraction data (via batch refinement) collected during the heating of α -LiNH₂BH₃ between (a) 200K-367K (-73°C - 94°C) and (b) 330K-367K (57°C-94°C). Mean errors, $a \pm 0.000015$, $b \pm 0.000007$, $c \pm 0.000006$. Error bars only shown if larger than data markers. Linear fits of the relationship between temperature and the axis length are displayed on the graphs.

Unsurprisingly, the largest expansion is observed down the long a axis. But whilst the a and c axes still vary linearly until the sample decomposes the b axis begins to deviate significantly. From Figure 4.7(b) the b axis starts to decrease at 350K (77°C) and has contracted by 0.00097Å. Although, not marked as the negative thermal expansion seen in the ESRF data (Section 4.3.1) it is reasonable to suppose that the origins are similar - namely the onset of BH₃ libration and low energy shearing modes between the structural layers along the $\langle 200 \rangle$ direction of the unit cell, described in more detail in Section 4.5.

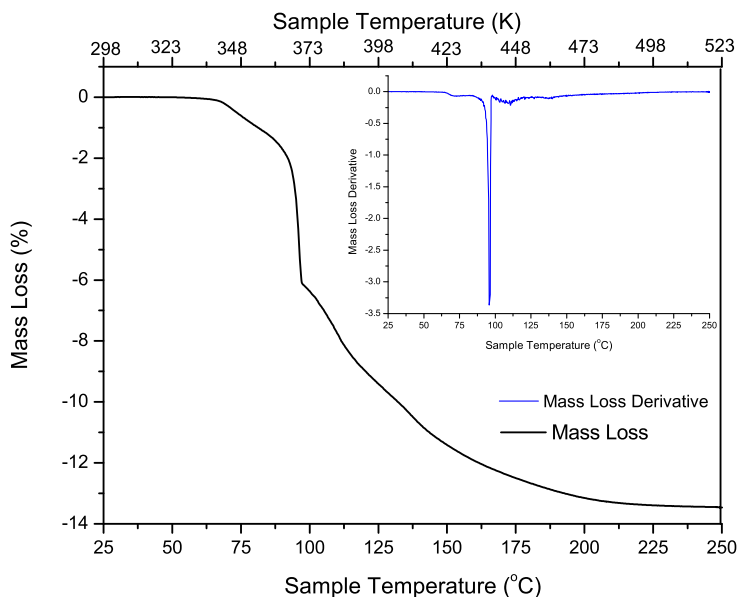


Figure 4.8: Thermogravimetric data of the decomposition of α - LiNH_2BH_3 collected using intelligent gravimetric analysis, with heating rate 2°C min^{-1} and target temperature of 250°C (523K). The black line represents the sample mass loss in % Insert: differential of sample mass loss % with respect to time.

4.4 Thermal Analysis of α - LiNH_2BH_3

4.4.1 Intelligent Gravimetric Analysis Of α - LiNH_2BH_3

The thermogravimetric data for the decomposition of α - LiNH_2BH_3 , is presented in Figure 4.8a. A total mass loss of 13.4% over two events was observed during the decomposition of the α - LiNH_2BH_3 sample. The first mass loss of 5.4 % was observed as the temperature of the sample increased from 69°C to 97°C (344K-385 K) and the second mass loss of 1.5 % occurred between temperatures of 116°C to 246°C (389K-519 K). Differentiation of the mass loss with respect to time (see Figure 4.9 inset) confirmed these findings and revealed peak mass losses of the two events to be at 92°C (365K) and 110°C (383K).

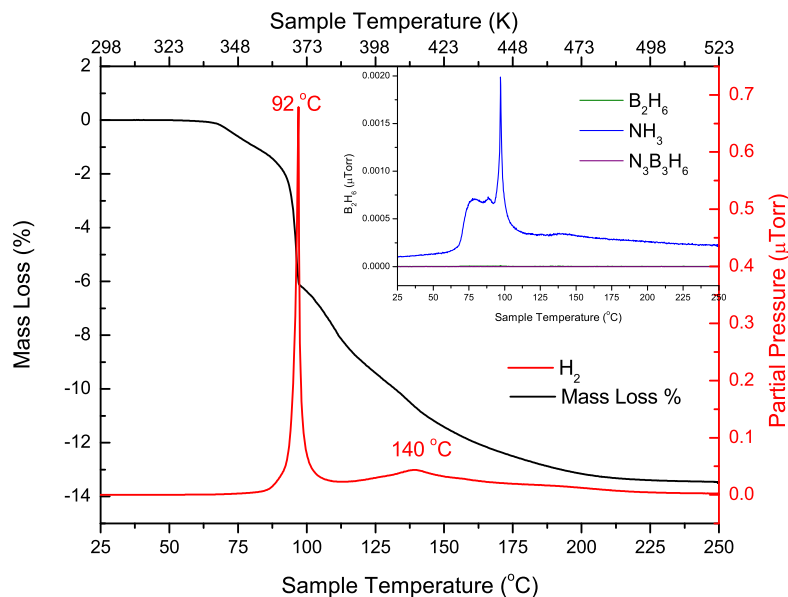
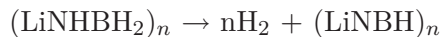


Figure 4.9: Thermogravimetric data of the decomposition of LiNH_2BH_3 collected using intelligent gravimetric analysis, with heating rate 2°C min^{-1} and target temperature of 250°C (523K) (black line) and the partial pressures of H_2 (red line), recorded using in-situ mass spectrometry. Inset: partial pressures of NH_3 (blue line), B_2H_6 (green line), and $\text{N}_3\text{B}_3\text{H}_6$ (purple line) recorded using in-situ mass spectrometry are also presented.

The partial pressures of H_2 , NH_3 , B_2H_6 , $\text{B}_3\text{N}_3\text{H}_6$ (2, 17, 28 and 81 AMU respectively) recorded by in-situ mass spectrometry, are presented in Figure 4.9. As can be seen from the data, H_2 is the major decomposition product. No $\text{B}_3\text{N}_3\text{H}_6$ and B_2H_6 were observed at any point. Only very small amounts of NH_3 ($7 \times 10^{-4} \mu\text{Torr}$) were observed, just prior to the first rapid mass loss event and accompanying the two H_2 release events see Figure 4.9 inset.

Integration of the area under the H_2 peaks gave an approximate ratio of 1 : 1. This indicates 1 mole of H_2 is released in each step and leading to a total mass loss of 11% the additional 2.4% is believed to be from the small amount of NH_3 released. X-ray diffraction on the decomposed sample found it to be amorphous which meant the final product was likely to be a Li decorated N-B-H polymer. The combination of the above data provides evidence for the following two stage decomposition pathway:



4.4.2 Differential Scanning Calorimetry of $\alpha\text{-LiNH}_2\text{BH}_3$

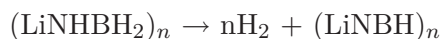
The experimental details of the DSC data collected in this thesis are described in Section 2.3.2 and the data are presented in Figure 4.10. The trace agrees well with the IGA data (Section 4.4.1) and indeed is extremely similar to the differential of the mass loss trace (Figure 4.8). Two exothermic events are observed, corresponding to the two H_2 desorptions seen in this temperature regime. The first event, between 79°C - 101°C (352 - 374K), is sharp and peaks at 91°C (364K). The second event is broader, between 107°C - 156°C (380 - 429K) and has its peak at 131°C (404K).

Integration of the area under the peaks with respect to time allowed the molar enthalpy changes to be calculated for each event (Section 2.3.2). The calculated value for the first event was $\Delta H = -4.9 \text{ kJ mol}^{-1}$ corresponding to the reaction;



agrees well with the literature value of -3 - -5 kJ mol^{-1} [86] which is significantly less exothermic than the NH_3BH_3 value of about -20 kJ mol^{-1} [193].

The calculated value for the second event is slightly lower than the first at $\Delta H = -3.7 \text{ kJ mol}^{-1}$ and corresponds to the reaction:



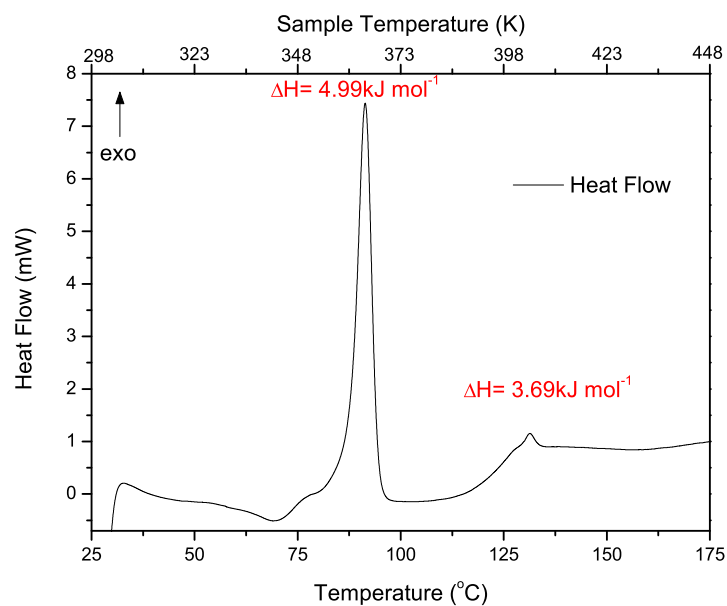


Figure 4.10: DSC trace of the decomposition of α -LiNH₂BH₃ heated to 175°C (448K) at 1°C min⁻¹

There is no published data for the second event as it was not observed by Xiong *et al.* [86], probably as a result of different synthesis and measurement conditions.

4.5 Inelastic Neutron Scattering Studies of α -LiNH₂BH₃ [1]

The INS spectrum in this section was collected on the TOSCA time of flight spectrometer at ISIS(Section 2.3.4)

At room temperature α -LiNH₂BH₃ crystallises in the orthorhombic space group *Pbca* with eight molecules per unit cell 1 each on a site of 8c symmetry as shown in Figure 4.1(b). Each fundamental vibration of the isolated molecule gives rise to 8 factor group modes of the crystal.

To assign the spectra, we have performed density functional theory (DFT) calculations on the complete unit cell using CASTEP [150, 151, 152] Comparison of the observed and calculated bond distances for the complete unit cell with the experimental data shows good agreement: bond distances are generally within 0.03Å or 1.8%. The largest deviations are for the N-H bond length where the distances are 3.1% longer than the experimental values. The full data can be seen in Appendix A. The *ab initio* bond angles are generally within 3° of the experimental values, the largest deviation is for the H-N-H bond where the calculated angle is 104.7° versus 94.3° (experimental). It was concluded that the *ab initio* calculations for the complete unit cell have accurately reproduced the experimental structure.

Figure 4.11 shows the INS and Raman spectra of α -LiNH₂BH₃. Similarities and differences are apparent between the two spectra and emphasise the need to have both types of spectra for a complete vibrational analysis. Raman spectroscopy requires a change in polarisability of the molecule and thus is more sensitive to the non-polar motions of the molecule. The technique provides information on the heavy atom motions. The INS spectra show all the possible vibrational modes for the structure, as unlike Raman spectroscopy, there are no selection rules in INS. Here, the spectrum is dominated by the hydrogenic motions, since the intensity of an INS band is proportional to the product of the incoherent scattering cross-section and the amplitude of vibration [119]. As the scattering cross-section for hydrogen is at least 20 times larger than that for all the other atoms present in α -LiNH₂BH₃, the INS spectrum emphasises the modes that involve significant hydrogen motion either directly (such as a N-H bend) or where the hydrogen is carried by another atom (e.g. torsions). A complete list of all the observed

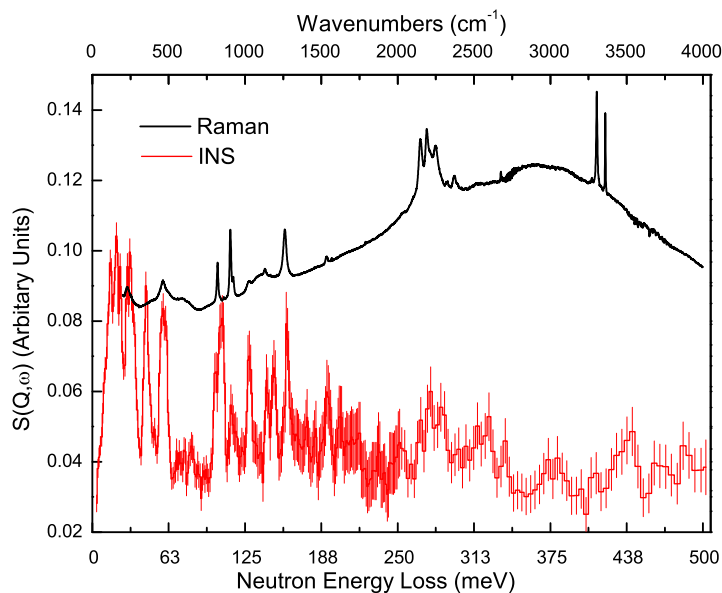


Figure 4.11: INS(red) and Raman(black) spectra of polycrystalline α - LiNH_2BH_3 in the 0-4000 cm^{-1} region

bands and their assignments is provided in Appendix A, Table A.1.

The Raman spectrum as calculated by CASTEP is compared to the experimental spectrum in Figure 4.12. It is clear that there is a good agreement between the two, particularly in the lower energy region (Li-N stretch experimental and calculated are 231cm^{-1} and 232cm^{-1} respectively). However in higher energy regions (above 2000cm^{-1}) the calculation has over estimated the vibrations associated with the B-H and N-H stretching regions. This is most likely to be a consequence of the calculated longer bond lengths in the optimised structure.

Figure 4.13 shows a comparison of the INS spectra calculated from the DFT results and the experimental spectrum. It is clear there is very good agreement between the calculated and observed spectra, although there are some discrepancies with the vibrations involving boron. These are probably due to the presence of ^{10}B in the un-enriched sample as the DFT calculations are performed using the assumption of ^{11}B . The most notable discrepancy being lower than predicted intensity for the BH_3 libration band at 362cm^{-1} .

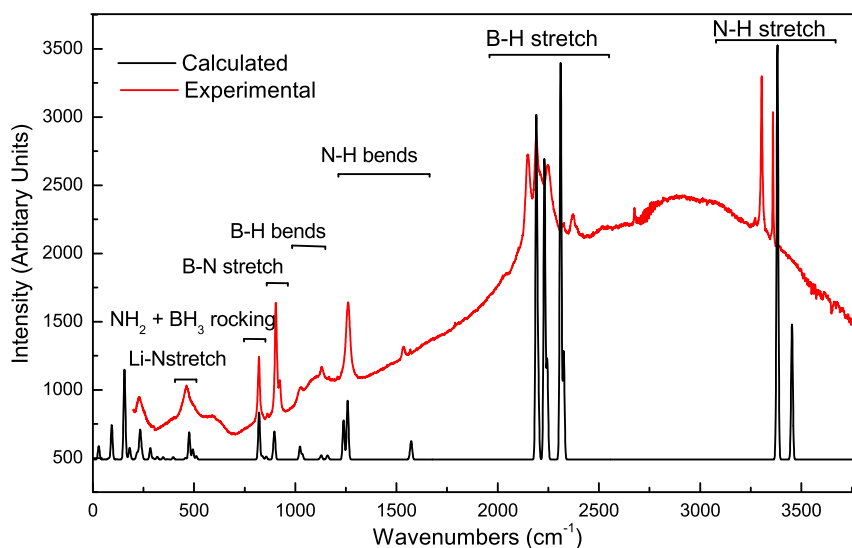


Figure 4.12: Comparison of Raman spectra: experimental (red) and calculated by CASTEP for the complete unit cell (black) in the 0-4000 cm^{-1} region.

and the BH_3 rocking band at 818cm^{-1} . There is also a shift to higher wavenumbers for the BH_3 wagging modes (1232 cm^{-1} calculated vs. 1268 cm^{-1} experimental). It is thought that this shift to higher wavenumbers occurs because of an underestimation of the electrostatic forces between the Li^+ and the BH_3 units. In the crystal structure, each Li^+ is tetrahedrally coordinated by 1 NH_2^- and 3 BH_3 units and these interactions replace the dihydrogen bonding observed in NH_3BH_3 [34] as the stabilising factor of the extended structure. Stronger than calculated forces further emphasise their importance as the stabilisers of the structure and vibrate at higher frequencies.

Interestingly, the BH_3 librations occur at lower energies ($340\text{-}398\text{ cm}^{-1}$) than the NH_2 librations ($416\text{-}529\text{ cm}^{-1}$). This is the opposite of ammonia borane where the onset of NH_3 libration has been shown by NMR, quasielastic neutron scattering (QENS) [157] and INS (Section 3.2) to have a lower activation energy than for BH_3 . The reason for this change in behaviour is the close association of the Li^+ and NH_2 in $\alpha\text{-LiNH}_2\text{BH}_3$. In this case Li^+ acts as an anchor for its end of the molecule because it takes more energy to overcome the electrostatic interactions and displace it.

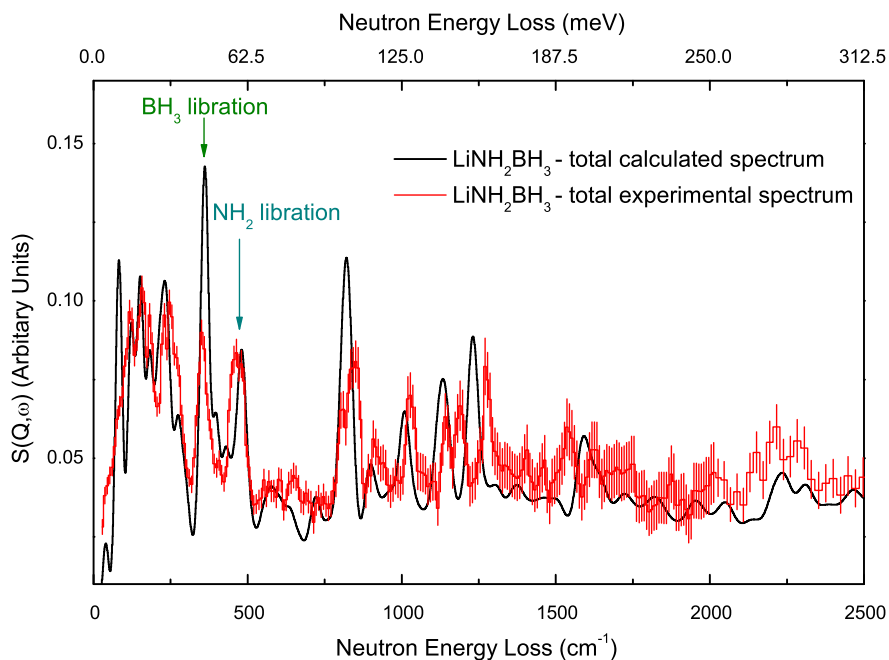


Figure 4.13: Comparison of INS spectra: experimental (red) and calculated by CASTEP for the complete unit cell (black) in the 0-2500 cm^{-1} region.

The DFT calculations also revealed some surprising features which are rare in ionic compounds. There are two imaginary modes at -11 and -16 cm^{-1} and additionally a low frequency real mode at 38 cm^{-1} . These correspond to shearing modes perpendicular to the a axis along a central planar break with one half of the unit cell moving rigidly with respect to the other as shown in Figure 4.14. This is indicative of a very shallow double well potential for which the correct quantum nuclear solution in the anharmonic potential still predicts zero displacement even at 0K. Negative phonon modes are often associated with a lowering of symmetry and their presence could indicate anomalous shearing behaviour if the cell is exposed to high pressure or very low temperature [194].

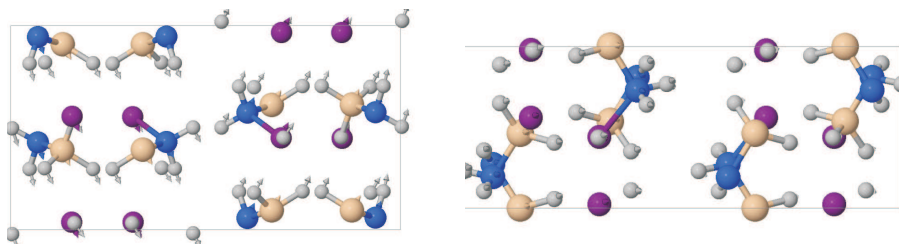


Figure 4.14: Structural diagram of α -LiNH₂BH₃ viewing along the b axis showing the vector motion of the negative mode at -16.74cm^{-1} . Lithium is purple, nitrogen blue, and boron cream.

4.5.1 Born Charges and Charge Density

The coupling between optical phonons and electric fields for an atom can be quantified by Born effective charges Z^* , which are defined through:

$$Z_{\kappa,\beta,\alpha}^* = V \frac{\partial P_\beta}{\partial x_{\kappa,\alpha}} = \frac{\partial F_{\kappa,\alpha}}{\partial E_\beta} \quad (4.1)$$

where Z^* is polarisation per unit cell caused by displacement of atom κ in direction α or force exerted on atom by macroscopic electric field [195].

Figure 4.15 is a schematic displaying the atomic charge ellipsoids for α -LiNH₂BH₃. The colours of the atoms correspond to their calculated Born charges depicted by a RWB gradient: tints of blue for high electron density, tints of red for low electron density, white for neutral. The range of values for partial charge was adjusted to the minimum and maximum values present in the file. A complete list of all the values is provided in Table 4.3.

The partial charge colouring clearly shows the ionic nature of α -LiNH₂BH₃. The largest charges are located on the Li and N atoms which have charges of $+1.02$ and -0.97 respectively. The B atom has a partial charge of 0.67 and the hydrogen atoms also have a significant amount of charge. The $\text{H}^{\delta+}$ on the N atom range between $0.21 - 0.23$ and $\text{H}^{\delta-}$ on the B atom are between $0.35 - 0.42$.

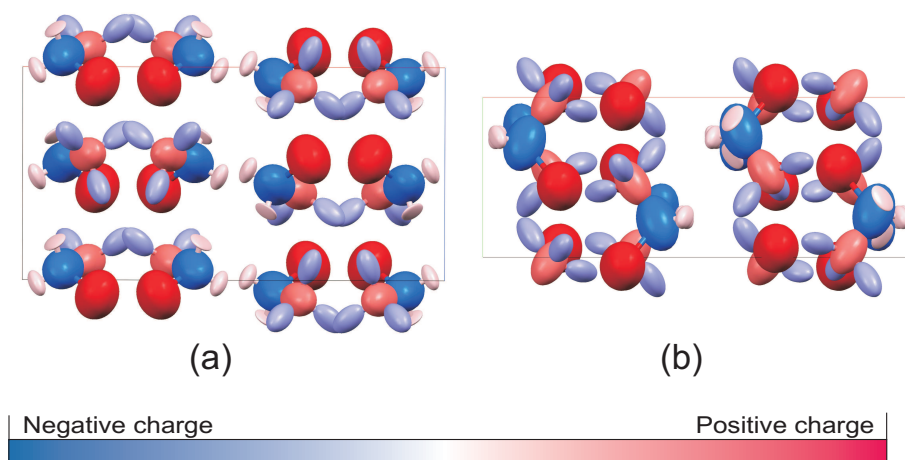


Figure 4.15: Structural diagram of α -LiNH₂BH₃ viewing along the b axis (a) and the c axis (b) showing atomic charge ellipsoids. The colours of the atoms correspond to their calculated Born charges depicted by a RWB gradient: tints of blue for high electron density, tints of red for low electron density, white for neutral.

The charge ellipsoids are very informative about the directionality of the inter and intra molecular bonds. Usually charge density is located along bonds and this is certainly the case with the N, B and H ^{δ^-} charge ellipsoids. The majority of the N and B charge density is located along the U₂₂ direction of their ellipsoids, illustrating the strong dative bond from the lone pair of the N atom to the electron deficient B. The H ^{δ^-} charge density is mainly located along the B-H bonds which point towards the Li.

However, charge density for the Li⁺ ion is not strongly polarised toward the N atom (presumably because the majority of the charge on the N atom is localised in the dative bond). Instead the Li charge density is orientated orthogonally to the N atom and extends between its three nearest BH₃ units. The preference of the Li for the BH₃ units over the N atom again emphasises the importance of the Li⁺ $\cdots$ H ^{δ^-} interactions in stabilising the α -LiNH₂BH₃ structure.

Table 4.3: Calculated Born charge tensor for α -LiNH₂BH₃.

Atom	q_{11}	q_{22}	q_{33}	q_{23}	q_{13}	q_{12}
H1	-0.11428	-0.17528	-0.12744	0.06089	0.03972	-0.06006
H2	-0.14906	-0.07380	-0.12364	-0.02856	-0.05881	-0.01488
H3	-0.08683	-0.11426	-0.18155	-0.04977	0.04181	0.02611
H4	0.04859	0.07771	0.09714	-0.02309	-0.02960	0.01423
H5	0.06910	0.09538	0.04320	-0.01739	0.03008	0.04036
Li	0.29166	0.34311	0.36900	0.02631	0.04024	0.00533
B	0.20115	0.28676	0.17458	-0.02807	0.00894	-0.08635
N	-0.26031	-0.43961	-0.25126	-0.07826	0.01836	0.06990

The H ^{δ +} charge ellipsoids are also orthogonal to the N⁻ H ^{δ +} bond. This unusual orientation is especially obvious when looking at the plane down the centre of the unit cell. The H ^{δ +} seem to form a 'wall' of positive charge between the layers and it is thought that they adopt their orthogonal orientation to maximise the separation, and thus minimise repulsion between the layers.

4.5.2 Atomic Motion Prior to Decomposition

The displacement tensors ${}^\nu B_l$ of an atom l vibrating in mode ν at temperature T in K can be calculated through Equation 4.1.

With the transition at ω in cm⁻¹ and the reduced mass μ in atomic mass units, the atomic mean square is in Å². Hence the total mean square displacement of an atom at a given temperature can be calculated by summing the contributions of all the individual modes.

$${}^\nu B_l = {}^\nu u_l^2 = \frac{16.9}{\nu \mu_l \omega_\nu} \coth \left(\frac{1.47 \omega_\nu}{T} \right) \quad (4.2)$$

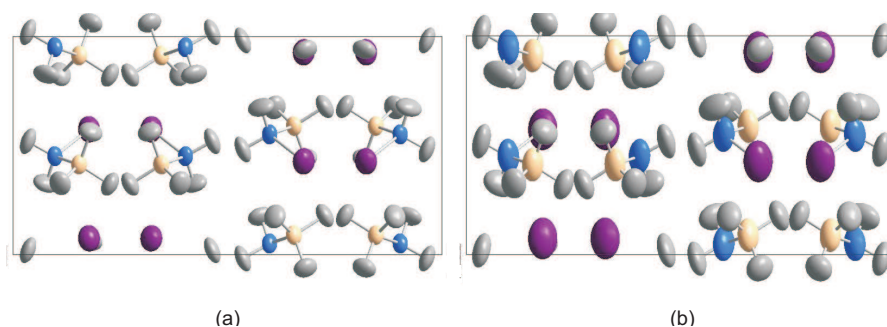


Figure 4.16: Structural diagrams of α -LiNH₂BH₃ viewing along the *b* axis showing the total mean square displacement of the atoms at 70 K (a) and 370K (b)(-203°C and 97°C)

Figure 4.16 shows how the atomic motions of α -LiNH₂BH₃ change with increasing temperature between 100K and its decomposition at 370K (-203°C and 97°C). Figure 4.17 gives a quantitative representation of these changes between 100K - 300K (-203°C and 27°C).

From Figures 4.16 and 4.17 it is clear the Li atomic motion transforms the most. It changes from a chiefly spherical motion at 70K (-203°C) to a strong ellipsoidal motion predominantly along the *c* axis at 370K (97°C). The B vibrations also become more ellipsoidal but along the *a* axis, orthogonal to the Li motion. Surprising the hydrogen motion changes relatively little over the temperature range depicted here (Figure 4.17). It could be assumed that for the compound to decompose and release hydrogen the hydrogenic motion at the decomposition temperature must be considerable. However, because the decomposition temperature is relatively low (365K/92°C) the higher energy modes are not thermally populated and only the lower energy lattice modes (250cm⁻¹ or less) contribute significantly to the atomic motions.

The orthogonal motion of the Li and B atoms is thought to be one of the key factors causing the low decomposition temperature. It means that the crystal is being stressed simultaneously along the *a* and *c* axes, generating a large amount of strain within the lattice. Thus it seems that by 365K (92°C) the amplitudes of these vibrations are sufficient to destabilise to cause crystal structure of α -LiNH₂BH₃.