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High Density Ammonia Storage Materials

Author:

David M. ROYSE

New College

Supervisors:

Prof. W. I. F. DAVID

Prof. P. P. EDWARDS

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The work described in this Thesis was carried out in the Inorganic Chemistry Laboratory, University of Oxford, from October 2007 until September 2011, under the supervision of Professors William I. F. David and Peter 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.

David Royse

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Abstract

David Royse

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This Thesis considers the use of solid-state metal ammines as ammonia storage materials and endeavours to understand these materials on a fundamental chemical level. The ammines of LiBH_4 , MgCl_2 , MgBr_2 , MgI_2 and $\text{Mg}(\text{BH}_4)_2$, are investigated. The structures of lithium borohydride ammines, $\text{Li}(\text{NH}_3)_n\text{BH}_4$ with $n \in \{1, 2, 3, 4\}$, are solved using X-ray and neutron diffraction, vibrational spectroscopy, nuclear magnetic resonance, and first-principles calculations. The reversibility, bonding and ammonia storage properties of this system are discussed, and investigated using gravimetric analysis and vibrational spectroscopy. The ammines of magnesium halides are investigated using X-ray and neutron powder diffraction, gravimetric techniques, nuclear magnetic resonance, first-principles calculations and vibrational spectroscopy. Their disordered structures, bonding, and decomposition are discussed, and the trends in their properties are used to interpret the properties of other ammines. The ammines of magnesium borohydride are investigated using X-ray and neutron powder diffraction, gravimetric techniques, first-principles calculations and vibrational spectroscopy. The structure, decomposition and reversibility of $\text{Mg}(\text{NH}_3)_6(\text{BH}_4)_2$ as an ammonia store are presented. Throughout the Thesis and at the end of each Chapter the possibility of using these ammines as solid-state ammonia stores is discussed.

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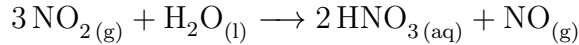
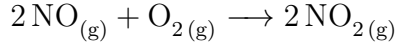
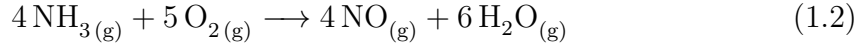
Chapter 1

Introduction

This Thesis considers the use of solid-state metal ammines as ammonia storage materials and endeavours to understand these materials on a fundamental chemical level. This Chapter contains an overview of the need for, and the requirements of, ammonia storage materials. A background to the materials investigated in later Chapters is discussed, as well as other important concepts and the aims of the Thesis.

1.1 The Widespread Use of Ammonia

Ammonia is one of the most abundantly produced inorganic chemicals in the world. Of the 124,000,000 t produced annually,¹ around 85 % is used as fertiliser either by direct application or in ammonium nitrate which is produced as shown in Reaction 1.1. One of the most important reactions involving ammonia is the Ostwald process that is shown in Reaction 1.2, and is used to produce nitric acid. This acid is hugely important to the chemical industry, finding uses in the production of; plastics, fibres, resins, explosives, dyes and pharmaceuticals. Ammonia itself is also used as an industrial scrubber to remove SO₂ from flue gas, and as a refrigerant.²⁻⁵



Alongside its already widespread uses, there are a number of emerging and potentially important uses for ammonia. When used as a fuel, pressurised ammonia has the lowest cost in terms of $\text{\$GJ}^{-1}$ compared to gasoline, LPG, methanol and hydrogen.⁶ Its potential energy may be released either by direct combustion or in a solid-oxide fuel cell.⁷⁻⁹ With a high hydrogen content of 17.6 wt% it has been speculated that, with catalytic cracking on the point of demand, ammonia may be a suitable energy vector in a hypothetical hydrogen economy. The already well-established production facilities, distribution network and simple handling procedures would help ease the transition to such an economy.¹⁰⁻¹⁴ Although the potential use of ammonia as a fuel attracts major research interest, there are other emerging uses. One of the more interesting of these, that requires an effective on-board store of anhydrous ammonia, is selective catalytic reduction (SCR).^{15,16} This process may be used to remove harmful NO_x gases from diesel exhaust fumes as shown in Reaction 1.3.



1.2 Properties of Ammonia and Gas Storage

The physical properties of ammonia have helped enable its widespread use; it is essentially non-flammable, and can be easily handled as a liquid in simple vessels

thus negating the need for expensive pressure vessels or refrigeration techniques required for handling other gases. However, it possesses a number of drawbacks, primarily its toxicity but significantly it is a corrosive gas with a high coefficient of thermal expansion and high vapour pressure at ambient conditions. Currently ammonia is stored or transported in aqueous solution, as a gas (but one that will be a liquid when stored at a pressure of greater than 7 bar), or as a refrigerated liquid at $-33\text{ }^{\circ}\text{C}$. The densities of stored ammonia vary from 0.73 gL^{-1} for gaseous ammonia at 1 atm and $15\text{ }^{\circ}\text{C}$ to 682 gL^{-1} for liquid ammonia at $-33\text{ }^{\circ}\text{C}$. Consideration of thermal expansion means that ammonia storage tanks have a practical usable capacity of only 85 %.^{13,17}

1.2.1 Solid State Ammonia Stores

Solid state ammonia stores, and in particular metal ammines, have been proposed as a useful method to store ammonia. Specific uses for such systems include; *i*) indirect hydrogen storage;¹⁸ *ii*) refrigeration;¹⁹ and *iii*) separation and storage during ammonia synthesis.^{20,21} These, and other, solid state methods may allow improvements in ammonia storage that include:

1. Reduction or control of vapour pressure.
2. Improving safety to minimise the amount of toxic ammonia release if the storage vessel were to break.
3. Increasing the storage density of the system.
4. Increasing the thermal stability of the storage medium with respect to thermal expansion.
5. Providing storage methods specific to novel uses, for example on-board SCR or hydrogen storage.

It is the group II halides that have received particular attention, with different compounds favoured for different uses. For indirect hydrogen storage and on-board SCR, $\text{Mg}(\text{NH}_3)_6\text{Cl}_2$ is favoured because of its high ammonia density and low vapour pressure.^{16,18} For separating ammonia from other gases, $\text{Ca}(\text{NH}_3)_8\text{Cl}_2$ or $\text{Ca}(\text{NH}_3)_8\text{Br}_2$ have been chosen as, along with a high ammonia density, it is possible to cycle ammonia in and out of these compounds using the pressure swing absorption method.²²

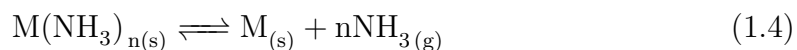
Any material that is to be used for gas storage must also consider the following criteria that are well documented in the hydrogen storage literature but adapted here to provide general guidelines for the requirements of ammonia storage systems:²³

1. The gas must be stored safely and the system must conform to appropriate standards.
2. The cost must be comparable to existing storage options or present significant system advantages.
3. There must be a high ammonia capacity.
4. The system must allow for controlled ammonia release.
5. The energy penalty for storage and release must be reasonable, especially if the gas is to be used as a fuel.
6. The system must be an improvement on existing options.

1.3 Thermodynamic Considerations

These ammine systems can be described as the reaction between a solid and ammonia as shown in Reaction 1.4. In this case, the relationship between temperature and pressure may be described by the Clausius-Clapeyron equation (Equation 1.5).

Although this relationship is normally only applied to the transformation of a single phase, if it is considered that the contribution of M remains constant then the reaction simply involves the vaporisation of NH_3 in a specific environment. Following the standard derivation available in many texts the integrated form of the Clausius-Clapeyron equation, that describes the transition from solid to gas, as shown in Equation 1.6 is obtained.²⁴ From this it is clear that in order to reduce the vapour pressure of a sample, the desorption temperature must increase. Thus balancing these two factors is the essence of producing an effective solid state ammonia store.



$$\frac{dp}{T} = \frac{\Delta H}{T\Delta V} \quad (1.5)$$

$$\frac{\ln p_1}{\ln p_2} = \frac{\Delta H_{vap}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad (1.6)$$

1.4 Magnesium Halide Ammines ($\text{Mg}(\text{NH}_3)_n\text{X}_2$)

As mentioned above, recent attention has focussed on utilising $\text{Mg}(\text{NH}_3)_6\text{Cl}_2$ as an ammonia storage material. Particularly important work by Liu et al. considers the temperature swing absorption method suitable for ammonia storage in MgCl_2 ,²⁰ while Christensen et al. have contributed many publications following their introduction of $\text{Mg}(\text{NH}_3)_6\text{Cl}_2$ as a potential hydrogen storage material.¹⁸

The MgCl_2 system has been well characterised with the most notable studies reporting; *i*) the enthalpies of desorption;²⁵ *ii*) formation of an expanded structure on desorption that allows for fast reaction kinetics;²⁶ *iii*) a calculated desorption mechanism that supports the observation of an expanded structure;²⁷ and *iv*) a detailed

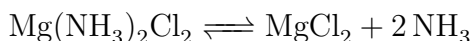
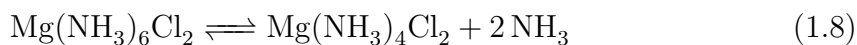
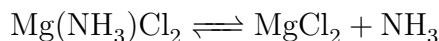
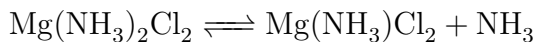
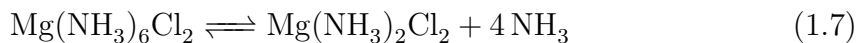
account of a model reactor that shows $\text{Mg}(\text{NH}_3)_6\text{Cl}_2$ would be a suitable material to use for SCR.¹⁶ Despite this wealth of reported knowledge, data considering the rest of the halide series are scarce. In one report, Sørensen et al. gather the desorption enthalpies of 90 metal halide ammines that include MgBr_2 and MgI_2 , though their sources are not clear.²⁷

The work of Christensen et al. shows the clear potential for the use of $\text{Mg}(\text{NH}_3)_6\text{Cl}_2$ as an ammonia storage material with a high capacity of 52 wt%. Indeed to this end, the system is well characterised, but on a fundamental level there are still areas where an increased understanding of these materials would be useful. In particular, understanding the properties of the group and how the anion affects properties is important in order to develop ammonia storage materials.

1.4.1 Ammonia Sorption Pathways

The existence of magnesium halides $\text{Mg}(\text{NH}_3)_n\text{X}_2$ (for $\text{X} = \text{Cl}, \text{Br}$ and I) with $n \in \{1, 2, 6\}$ for $\text{X} = \text{Cl}, \text{Br}$ and $n \in \{2, 6\}$ for $\text{X} = \text{I}$, was first shown by Biltz and Hüttig, who in 1921 measured the vapour pressure of NH_3 over magnesium halides as a function of temperature.²⁸ The majority of reports on $\text{Mg}(\text{NH}_3)_6\text{Cl}_2$ agree that ammonia desorption is reversible and occurs via the $n = 6, 2, 1, 0$ pathway as shown in Reaction 1.7.^{16,18,25} An alternative report suggests that desorption occurs via the $n = 6, 4, 2, 0$ pathway that is shown in Reaction 1.8.²⁹ The different experimental conditions may account for the observed differences in sorption pathways. Zhu et al. argue that carrying out thermogravimetric analysis under nitrogen on the milligram scale means that the negligible ammonia pressure promotes the alternative desorption pathway. While the majority pathway is observed by; Elmøe et al. who use a higher ammonia pressure in a demo SCR reactor to control ammonia desorption, Christensen et al. who used a similar non-negligible ammonia pressure, and Liu et al. who observed the $n = 6, 2$ and 1 phases using adsorption isotherm measurements

in a similar manner to Biltz and Hüttig.



1.4.2 Magnesium Hexa-ammine Crystal Structure and Disorder

In 1965, Olovsson referred to earlier work by Wyckoff and stated that all the $\text{Mg}(\text{NH}_3)_6\text{X}_2$ compounds have the same K_2PtCl_6 structure.^{30,31} This may be thought of as the fluorite structure with $\text{M}(\text{NH}_3)_6^{2+}$ in the Ca^{2+} sites and X^- in the F^- sites and is shown in Figure 1.1.³² It was not until 2000 that any detailed structural information of $\text{Mg}(\text{NH}_3)_6\text{Cl}_2$ was published by Hwang et al. confirming the K_2PtCl_6 structure with a cubic unit cell parameter of $a = 10.1899(4) \text{ \AA}$ and Mg–N bond length of $2.197(3) \text{ \AA}$, though they do not provide any information on hydrogen positions.³³ In contrast to the data available on $\text{Mg}(\text{NH}_3)_6\text{Cl}_2$, there are far fewer published works on either $\text{Mg}(\text{NH}_3)_6\text{Br}_2$ or $\text{Mg}(\text{NH}_3)_6\text{I}_2$. A structural analysis of $\text{Mg}(\text{NH}_3)_6\text{Br}_2$ has been performed in the PhD Thesis of M. W. Friedriszik although these data are not freely available.³⁴

The $\text{Mg}(\text{NH}_3)_6\text{X}_2$ structure belongs to the $Fm\bar{3}m$ space group in which the NH_3 molecule sits on a site with 4-fold rotational symmetry. The C_{3v} symmetry of the ammonia molecule either means that there is disorder in the hydrogen atom

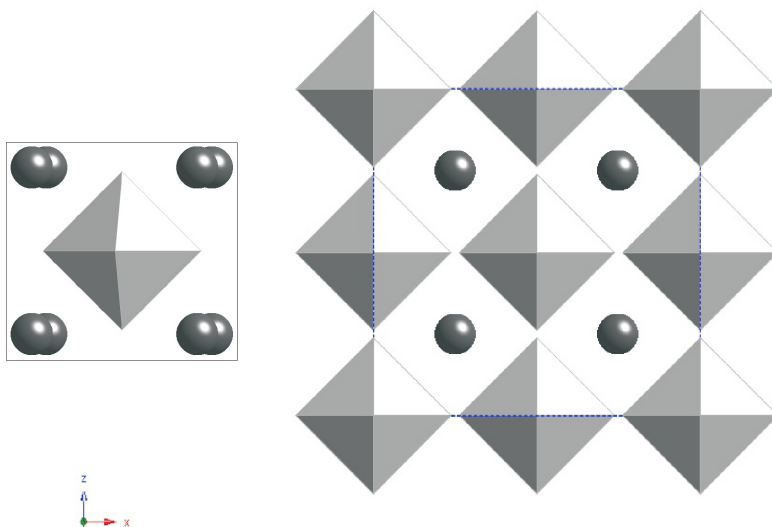


Figure 1.1: The K_2PtCl_6 structure showing PtCl_6^{2-} octahedra and K^+ atoms in light and dark grey respectively. The local coordination of a single PtCl_6^{2-} octahedron is shown in the inset on the left hand side.

positions about the nitrogen atom or that the space group assignment is incorrect. This type of disorder has been recognised, if not completely understood, for many years.^{35,36} Indeed in some of the earliest work on the isostructural $\text{Ni}(\text{NH}_3)_6\text{X}_2$, Wyckoff acknowledges that placing the nitrogen atom on the 24(a) cubic site in $Fm\bar{3}$, $F432$ or $Fm\bar{3}m$ would mean that “two of the hydrogen atoms of the ammonia in this compound are different from the third” but that “this is so contrary to what would have been expected from chemical considerations that in the absence of any satisfactory crystallographic determination of its class of symmetry, it is more natural to assign this salt to the space-group [with lower symmetry].” A number of studies of $\text{M}(\text{NH}_3)_6\text{X}_2$ ($\text{M} = \text{V}, \text{Cr}, \text{Fe}, \text{Mn}, \text{Ni}, \text{Co}$ and $\text{X} = \text{Cl}, \text{Br}, \text{I}$) suggest that the electron density of the hydrogen atoms is located around four maxima that align the N–H bonds in the direction of X^- .^{37–41} Such detailed information was not reported for the magnesium halides until 2011 when Sørby et al. published a combined neutron diffraction and molecular dynamics study of $\text{Mg}(\text{ND}_3)_6\text{Cl}_2$.⁴² They proposed 2 hydrogen sites; 96k and 96j with occupancies of 1/2 and 1/4

respectively, a model exactly in line with Wyckoff's predictions some 89 years earlier!

1.4.3 Magnesium Diammine Crystal Structure and Disorder

Leineweber et al. have published the structures of $\text{Mg}(\text{NH}_3)_2\text{Cl}_2$, $\text{Mg}(\text{NH}_3)_2\text{Br}_2$ and $\text{Mg}(\text{NH}_3)_2\text{I}_2$, concluding that all three compounds have the same local structure consisting of chains of edge sharing $\text{MgX}_4(\text{NH}_3)_2$ octahedra. The packing of these chains is such that each ammonia molecule has four nearest-neighbour halide ions, but the overall packing pattern varies from the chloride to the identical bromide and iodide, as shown in Figure 1.2. In both cases disorder is observed in the hydrogen sites, with 4 hydrogen sites per nitrogen atom and alignment of the N–H bonds in the direction of X^- once again favoured.³⁴

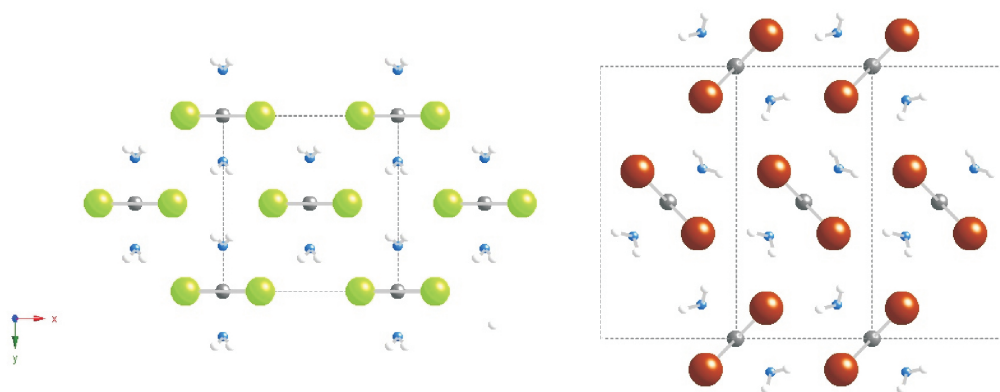


Figure 1.2: A comparison of the structures of $\text{Mg}(\text{NH}_3)_2\text{Cl}_2$ and $\text{Mg}(\text{NH}_3)_2\text{Br}_2$, both viewed along the z-axis. Mg is shown in grey, N in blue, H in off-white, Cl in lime green and Br in red-brown.

1.4.4 Low-temperature Ordered Crystal Structure

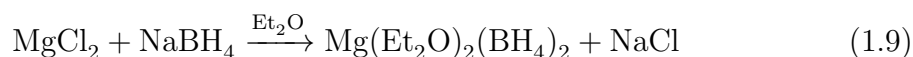
Given the room temperature disorder, it is anticipated that the ammonia molecules in $\text{Mg}(\text{NH}_3)_6\text{X}_2$ order at low temperatures. The very similar and isostructural compound $\text{Ni}(\text{NH}_3)_6\text{Cl}_2$ has been studied at low temperatures (due largely to its magnetic properties) but no experimental work has been performed on $\text{Mg}(\text{NH}_3)_6\text{Cl}_2$.

Eckert et al. reported that $\text{Ni}(\text{NH}_3)_6\text{Cl}_2$ orders to form a structure that is in a subgroup of space group $R\bar{3}$ at 27 K,⁴³ but no further structural solution has been published. A first-principles study of $\text{Mg}(\text{NH}_3)_6\text{Cl}_2$ was reported by Tekin et al., based on the assumption that $\text{N}-\text{H}^{\delta+}\cdots\text{Cl}^-$ interactions would stabilise an ordered structure they performed search algorithms to maximise the number of these interactions within potential structures.⁴⁴ The focus of this work was not on the crystal structure but they reported 4 possible space groups $R\bar{3}$, $I4/m$, $C2/m$ and $Cmmm$ with no atomic coordinates presented for the potential structures.

The chloride and bromide diammines have been well characterised in a comprehensive study by Leineweber et al. that reports low temperature ordering of ND_3 , and discusses the more subtle presence of order-disorder phase transitions.⁴⁵

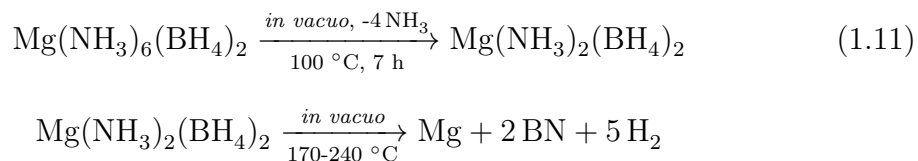
1.5 Magnesium Borohydride Ammines ($\text{Mg}(\text{NH}_3)_n(\text{BH}_4)_2$)

The borohydride compound $\text{Mg}(\text{NH}_3)_6(\text{BH}_4)_2$ has been known for over 50 years, with early research interest driven by its high hydrogen content and explosive potential.^{46,47} A number of Russian scientists carried out research on this and other borohydrides; Semenenko et al. confirmed by IR spectroscopy that $\text{Mg}(\text{NH}_3)_6\text{Cl}_2$ was “salt-like” and comprised $\text{Mg}(\text{NH}_3)_6^{2+}$ and BH_4^- ions. Their samples were synthesised in the simplest reported way by the metathesis shown in Reaction 1.9 with subsequent exposure of the etherate to ammonia as shown in Reaction 1.10. They reported that the solid crystallises in an orthorhombic unit cell though did not suggest a possible structure.⁴⁸ The synthesis of an isolated di- and tri-ammine by reaction of magnesium borohydride in benzene and ether has also been reported,⁴⁹ though has not been repeated.

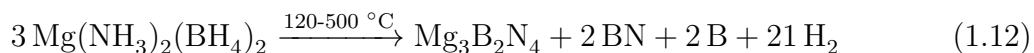




Until recently, the most complete study of decomposition pathways was reported by Konoplev et al. who observed that decomposition of the hexa-ammine occurs in two steps, releasing ammonia and then hydrogen as shown in Reaction 1.11. The hexa- and di-ammine were characterised by infra red spectroscopy.⁵⁰



Research efforts have returned to these ammines, once again motivated by the high hydrogen content, though this time for slightly different reasons. A comprehensive study by Soloveichik et al. focused on the synthesis and decomposition of $\text{Mg}(\text{NH}_3)_2(\text{BH}_4)_2$ as a potential hydrogen storage material. Observing that $\text{Mg}(\text{NH}_3)_2(\text{BH}_4)_2$ releases hydrogen at 120 °C, a temperature that is significantly lower than its parent $\text{Mg}(\text{BH}_4)_2$ at 323 °C. They propose that complete decomposition of $\text{Mg}(\text{NH}_3)_2(\text{BH}_4)_2$ occurs in a two steps beginning at 120 °C and 220 °C with the overall irreversible reaction shown in Reaction 1.12. They also suggest that $\text{Mg}(\text{NH}_3)_6(\text{BH}_4)_2$ has the K_2PtCl_6 structure with a cubic unit cell parameter of $a = 10.82(1)$ Å, but do not provide any atomic positions.⁵¹



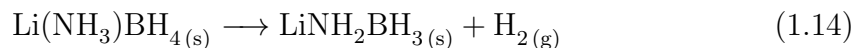
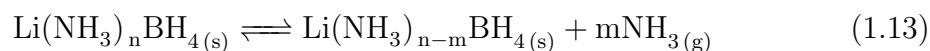
The reported crystal structure of $\text{Mg}(\text{NH}_3)_2(\text{BH}_4)_2$ is unusual; unlike the hexa-ammine, it is essentially molecular. Each Mg^{2+} cation is coordinated by two BH_4^- anions and two NH_3 molecules, these molecules pack together in a structure that appears to be stabilised by $\text{N}-\text{H}^{\delta+} \cdots \delta^- \text{H}-\text{B}$ dihydrogen bonds that are discussed further in Section 1.7. It is thought that this dihydrogen bonding promotes hydrogen

release at a lower temperatures in $\text{Mg}(\text{NH}_3)_2(\text{BH}_4)_2$ compared to $\text{Mg}(\text{BH}_4)_2$.⁵¹

Although the magnesium borohydride hexa-ammine has an ammonia content of 65 wt%, the decomposition from the diammine is irreversible. Assuming that the loss of the first four ammonia molecules is reversible, this leaves a usable ammonia storage content of 44 wt% that is released at around 100 °C.

1.6 Lithium Borohydride Ammines ($\text{Li}(\text{NH}_3)_n\text{BH}_4$)

The study of coordination compounds formed between lithium borohydride and ammonia at room temperature dates back to the discovery of borohydrides and the work of Hunt and Cowie in 1955.⁵² However, the first and only comprehensive studies of pressure-composition-temperature relationships and densities of these systems were performed by Sullivan and Johnson in 1959.⁵³ They reported that lithium borohydride forms ammines of the composition $\text{Li}(\text{NH}_3)_n\text{BH}_4$, with $n \in \{1, 2, 3, 4\}$. Thermolysis of the ammines was reported to proceed primarily through the stepwise loss of ammonia, as shown in Reaction 1.13, though a competing alternative reaction shown in Reaction 1.14 was also observed to a lesser extent.



The summary of their report in the form of a phase diagram is shown in Figure 1.3. In the diagram, the regions v, w, x and y represent the equilibrium between solid and gaseous phases as shown in Reaction 1.13 suggesting that these reactions should be observed below 15 °C. The diagram is however complex with each of the regions a to j involving a solid-liquid equilibrium. By plotting the equilibrium

pressure of the mole ratios of $\text{NH}_3/\text{LiBH}_4$ given by Sullivan and Johnson, it is in principle possible to extract the vapour pressures at one of the given temperatures for each of the phases and these data are given in Appendix B. This is the source of the estimated vapour pressure for $\text{Li}(\text{NH}_3)\text{BH}_4$ given below. There is however, a significant degree of uncertainty in the data and thus there is limited value in full analysis.

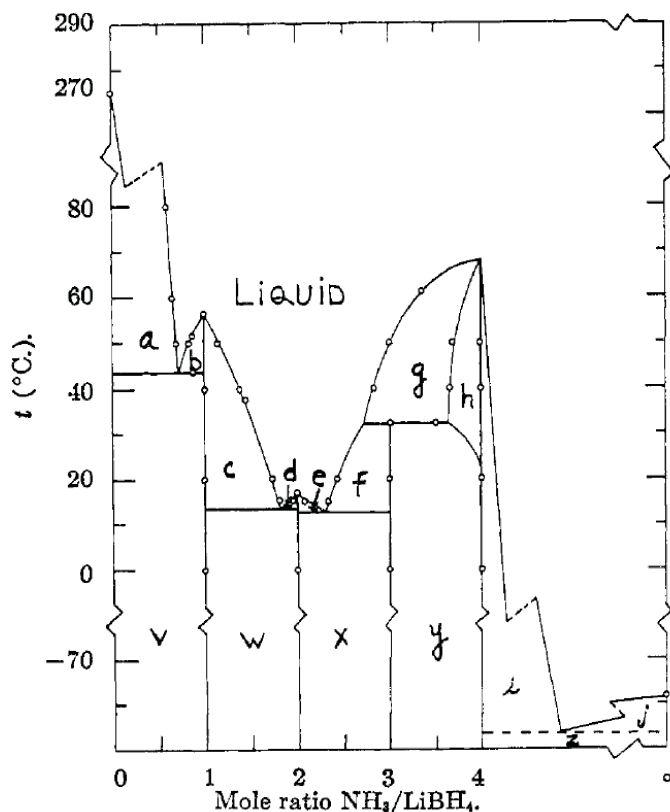


Fig. 5.— $\text{LiBH}_4\text{-NH}_3$ phase diagram.

Figure 1.3: A phase diagram for $\text{Li}(\text{NH}_3)_n\text{BH}_4$ produced by Sullivan and Johnson

Assuming that the progress of Reaction 1.14 is negligible, then these ammines have a reversible ammonia storage content of *ca.* 44, 61, 70 and 76 wt% for $n = 1, 2, 3$ and 4 respectively. The monoamine, $\text{Li}(\text{NH}_3)\text{BH}_4$, has the lowest ammonia content (*ca.* 44 wt%), but has the advantage of the lowest vapour pressure that is between 2.1 mbar and 10 mbar at 20 °C.

1.7 Hydrogen and Dihydrogen Bonding

In systems that contain ammonia and halide anions, there is a clear possibility that hydrogen bonds exist (where the definition of hydrogen bonding used in this Thesis is most generally described as “a hydrogen atom bonded to two or more other atoms.”⁵⁴) This can be thought of as the interaction of a lone pair, and typically the occupied p-orbitals of N, O or F, with the unoccupied σ^* orbital of an A–H bond. In the case of the borohydride ammines, a different type of hydrogen bond may exist, that is a dihydrogen bond between $\text{N}-\text{H}^{\delta+}$ and $\text{H}^{\delta-}-\text{B}$. Formally this interaction is described as the interaction between “ σ -bonding electron pairs of M–H bonds and traditional X–H proton donors.” These may be identified by short $\text{H}\cdots\text{H}$ interactions less than the Van der Waals radii of two hydrogen atoms at 2.4 Å, but are considered significant when the $\text{H}\cdots\text{H}$ distances are between 1.2 Å and 2.2 Å; the shorter the distance, the stronger the bond. A second indicator of dihydrogen bonding is a strongly bent $\text{XH}\cdots\text{H}-\text{M}$ angle between 90 ° and 135 °. A significant feature of these bonds is the ability to exchange weak $\text{H}\cdots\text{H}$ interactions with strong covalent ones, facilitating the release of H_2 .^{55,56}

1.8 Aims of this Thesis

This Thesis aims to synthesise and characterise materials with potential use as general purpose ammonia stores. The focus will therefore be on lowering the vapour pressure and desorption temperature of metal ammines whilst attempting to increase the gravimetric ammonia density. In fully characterising $\text{Mg}(\text{NH}_3)_6\text{X}_2$ with $\text{X} = \text{Cl}, \text{Br}, \text{I}$ and BH_4 and $\text{Li}(\text{NH}_3)_n\text{BH}_4$ both structurally and chemically it is hoped that the properties of these systems may be explained, enabling a greater understanding and ultimately development of materials for use in ammonia storage.

Chapter 2

Experimental Methods

This chapter covers all the experimental methods used within this Thesis. In the first section, practical synthetic methods are discussed. In the second section, analytical methods are described along with a brief description of the theory behind the methods.

Synthetic Methods

2.1 Storage and Handling

The vast majority of starting materials used in this Thesis were air- or moisture-sensitive, therefore all preparation and storage took place under an inert atmosphere inside an argon atmosphere glovebox. Levels of O_2 and H_2O were kept at less than 0.1 ppm by continually circulating the gas within the glovebox through columns containing molecular sieves or phosphoric acid. All glassware was dried and ports were pump-purged before use.

2.2 Sources and Purities of Starting Materials

All starting materials were anhydrous and where possible were used without further preparation. MgCl_2 (Aldrich, 99.99 %), MgBr_2 (Aldrich, 99.995 %), MgI_2 (Aldrich, 99.998 %), LiBH_4 (Aldrich, $\geq 99.99\%$), $\text{Mg}(\text{BH}_4)_2$ (Aldrich, 95 %), NH_3 (BOC Special Gases, 99.98 %), ND_3 (BOC Special Gases and CK Gases, 99.99 %), ^{11}B (Alfa Aesar, 99.9 %), Li (Aldrich, 99.95 %), Na (Aldrich, 99.95 %), D_2 (CK Gases, 99.8 %). Sodium metal was purchased in mineral oil and washed with pentane on a Schlenk line under nitrogen gas before further use.

2.3 High Pressure Furnace

Isotopically enriched (^{11}B and D) lithium and sodium borodeuteride samples were produced using a Parr Series 4740 High Pressure Vessel capable of withstanding a pressure of 200 bar at 700 °C. The instrument consists of a 75 cm³ stainless steel reactor, sealed with a steel alloy screw cap on a graphite gasket. A rigid mantle heater and temperature controller were used to control the temperature. The development of the method and the equipment is based on that of Friedrichs et al. and reported in the D. Phil. Thesis of Dr. Anne Nickels.^{57,58}

The solid elements were used in the proportions given in in Table 2.1 and were loaded into the reactor vessel inside the glovebox described in Section 2.1. The reactor vessel was then sealed and transferred to the furnace, where it was evacuated to a pressure of approximately 1×10^{-2} mbar. Following evacuation, the reactor was charged with deuterium gas to a pressure of 55 bar (an equivalent of 183 bar at 700 °C assuming a perfect gas) and then sealed. Reactions were heated to 700 °C for 12 hours; the reactor was then allowed to cool and finally re-pressurised to 55 bar and heated to 700 °C for a further 12 hours. Yields were generally poor and a significant quantity of the metal deuterides (LiD or NaD) were generated as

by-products.

Table 2.1: Amounts of reactants used in high pressure synthesis of $\text{Li}^{11}\text{BD}_4$ and $\text{Na}^{11}\text{BD}_4$

Compound	Amount of Li or Na		Amount of ^{11}B		Amount of D_2
	g	gmol^{-1}	g	gmol^{-1}	gmol^{-1}
$\text{Li}^{11}\text{BD}_4$	0.6	0.086	0.8	0.073	0.17
$\text{Na}^{11}\text{BD}_4$	2.0	0.087	0.8	0.073	0.17

2.4 Schlenk Line Synthesis and Purification

Standard Schlenk line techniques were employed for solution based synthesis of magnesium borohydride and washing of lithium and sodium borodeuteride following high pressure furnace synthesis.⁵⁹ All solvents were dried by standard methods and distilled before use.

Magnesium borohydride ($\text{Mg}(\text{BH}_4)_2$) and the isotopically enriched (^{11}B and D) magnesium borodeuteride ($\text{Mg}(^{11}\text{BD}_4)_2$) were synthesised using the solution based metathesis reaction between MgCl_2 and NaBH_4 (or $\text{Na}^{11}\text{BD}_4$) in diethyl ether (Et_2O). Reactants were ground together in a 1:2.2 molar ratio and refluxed in Et_2O for a period of 120 hours at 60 °C. The solvent was topped up at regular intervals when the level was observed to have dropped significantly. The reaction was filtered and a soluble product, $\text{Mg}(\text{Et}_2\text{O})_2(\text{BH}_4)_2$, was obtained by drying under vacuum at ca. 50 °C; desolvation of this etherate was achieved on exposure to ammonia gas.

Isotopically enriched (^{11}B and D) sodium borodeuteride was washed in di-isopropyl amine ($(i\text{-Pr})_2\text{NH}$) before use in any reactions; the mixture was stirred vigorously for a period of 2 hours and then allowed to settle overnight. The soluble product was then separated from the insoluble impurities and dried under vacuum at 40-45 °C for 2 hours. Isotopically enriched lithium borodeuteride ($\text{Li}^{11}\text{BD}_4$) was washed using the same technique, but using diethyl ether as the solvent.

2.5 Synthesis of Ammines

Syntheses involving ammonia were undertaken using a custom made glass gas handling (ammonia) line, a schematic of which is shown in Figure 2.1. All recorded gas pressures were read from the fitted pressure and vacuum gauges; the gas regulators were not used for these measurements. The maximum operating gas pressure was limited to 1500 mbar, with a minimum pressure of 1×10^{-3} mbar reached during evacuation.

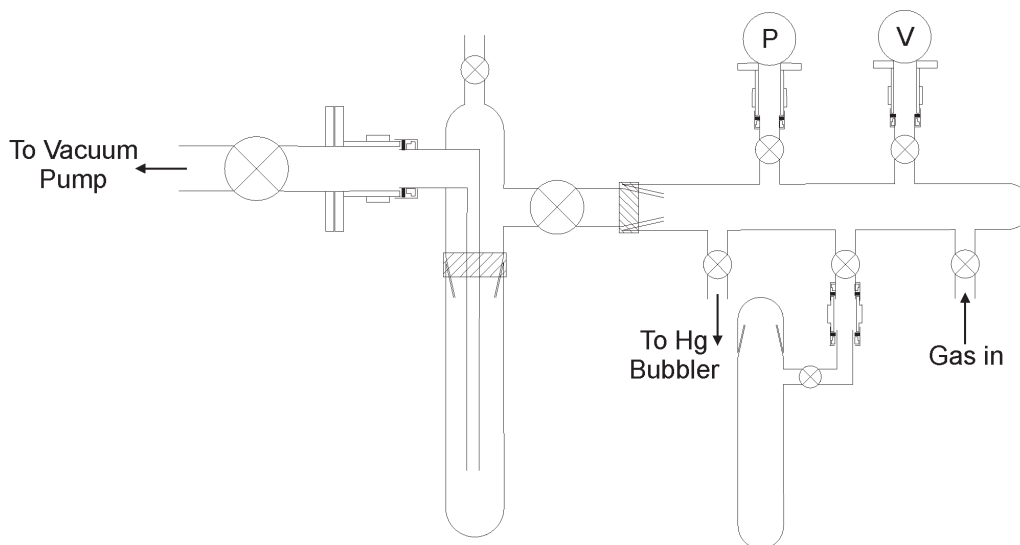


Figure 2.1: A schematic diagram of the gas line used for synthesis of ammines

Before addition of ammonia, sealed Schlenk tubes containing reactants were evacuated for a period of hours. Ammonia was slowly introduced to the system via the standard ammonia regulator until a final pressure of ca. 1000 mbar was reached. The pressure was maintained at ca. 1000 mbar for a period of several hours in an otherwise fixed system. Following exposure to ammonia, the Schlenk tube was once more evacuated and transferred to the argon atmosphere glovebox.

Single-crystals of $\text{Li}(\text{NH}_3)\text{BH}_4$ were grown using the experimental set up shown in Figure 2.2. Samples were exposed to flowing ammonia gas, until no further volume expansion nor evolution of heat was observed. The gas supply was then switched from ammonia to argon. The sample remained under flowing argon for a period of

12 hours, before being transferred to the argon atmosphere glovebox.



Figure 2.2: The apparatus used for single-crystal growth, showing a reaction between LiBH_4 and NH_3

Analytical Techniques

2.6 Diffraction Techniques⁶⁰

Diffraction techniques are based on the elastic scattering of waves from structures that have long range order. In crystalline materials where the atoms are arranged in an ordered periodic array and are of the order of a few Ångstroms apart, diffraction of X-rays, neutrons and electrons of appropriate energies occurs. Diffraction techniques are routinely used in *i*) comparison of a diffraction pattern to a known database in order to identify phase composition; *ii*) analysis of phase purity; *iii*) crystal structure determination; *iv*) identification of phase transitions; and *v*) extraction of subtle

structural aspects, including particle size and strain, and atomic disorder.

When radiation interacts with atoms, it is scattered in all directions and constructive interference only occurs in a limited number of well-defined angles. Careful analysis of the position and intensity of these diffracted beams means that the position and chemical nature of the atoms within the crystal may be deduced. The first step in analysing diffraction data is to determine the size of the unit cell. When a beam of radiation interacts with a set of planes in a crystal, defined by the Miller indices (hkl) , diffraction occurs when the geometry of the situation fulfils Bragg's Law:

$$\lambda = 2d_{hkl} \sin \theta$$

where λ is the wavelength of the radiation, d_{hkl} is the perpendicular separation of the (hkl) planes and θ is half of the diffraction angle, 2θ . There are an infinite number of (hkl) planes within a crystal or crystallite, but they will only diffract the incoming beam if they are at the appropriate angle. The complete diffraction pattern is one in which all possible angles are observed with equal (or normalised) incident radiation, application of Bragg's law to the peak positions in the diffraction pattern produces a list of d_{hkl} values for the compound. Assigning (hkl) values to these is the process of indexing the pattern, and is used to determine the unit cell size and type.

The intensities of the diffracted beams (I_{hkl}) are dependant on a number of factors (the relevance of which depends largely on how carefully diffraction data are being analysed) they are:

1. the type of radiation
2. the Bragg angle (θ) of the diffracted beam
3. the scattering power of the atoms present (the atomic scattering factor, f)

4. the arrangement of atoms in the crystal (the structure factor, F)
5. the thermal vibrations of the atoms (the temperature factor. B or W)
6. the dimensions, shape and perfection of the crystal or crystallites (the form factor)
7. the number of equivalent (hkl) planes present (the multiplicity) (in powder diffraction but not single-crystal)

These relationships are summarised as

$$I_{hkl} \propto (Lp)_{hkl} J_{hkl} F_{hkl}^2 e^{-2W_{hkl}} A_{hkl} \quad (2.1)$$

where $(Lp)_{hkl}$ is the Lorentz polarization factor, J_{hkl} is the multiplicity of the reflection, F_{hkl} is the structure factor, W_{hkl} is the atomic displacement factor (ADP) (also known as the Debye-Waller factor or the temperature factor) and A_{hkl} is the absorption factor. The crucial term is the structure factor

$$F(hkl) = \sum_{n=1}^N f_n \exp[2\pi i (hx_n + ky_n + lz_n)] \quad (2.2)$$

which may also be written

$$F(hkl) = \sum_{n=1}^N f_n (\cos 2\pi(hx_n + ky_n + lz_n) + i \sin 2\pi(hx_n + ky_n + lz_n)) \quad (2.3)$$

where f_n is the atomic scattering factor. The scattering factor varies depending on the type of radiation used, however there is also a reduction in peak intensity due to the thermal motion and/or disorder of atoms, which is parametrised in terms of the atomic displacement parameter. This motion or disorder causes a decrease in peak intensity with increasing angle, 2θ , since

$$f_B = f_a \exp \left[-B \left(\frac{\sin \vartheta}{\lambda} \right)^2 \right] \quad (2.4)$$

where $B = 8\pi^2 \langle u^2 \rangle$ and u is the displacement of the scattering centre.

2.6.1 X-ray Diffraction

The diffraction of X-rays and neutrons are both described by Bragg's law, however there is one key difference; that X-rays interact with electrons, while neutrons interact with nuclei. The atomic X-ray scattering factor of an atom may be calculated from the electron density around the atom, and is directly proportional to its atomic number. The primary consequence of this is that isoelectronic ions or atoms have equal scattering powers, so F^- and Na^+ would be indistinguishable using X-ray diffraction. It also means that in structure solution, it is often difficult to accurately locate light atoms in the presence of heavier ones. The interaction of X-rays with electrons means that there is a decrease in intensity of the scattered beam with an increase in 2θ in a manner described by the atomic form factor:

$$f(\lambda, \theta) = Zg(Q)r_e \quad (2.5)$$

where Z is the atomic number, $g(Q)$ decays from 1 at the origin to 0 as $Q \rightarrow \infty$ and r_e is the classical radius of the electron.⁶¹

2.6.2 Neutron Diffraction

While the electromagnetic component of X-rays interacts with electrons, neutrons interact with the nuclei of atoms. One of the important results of this is that instead of the scattering factor f_n varying directly with Z as it does for X-ray scattering, the scattering factor for neutrons varies in a seemingly random manner. This means that

neutron diffraction is a very useful technique for locating certain atoms, in particular light atoms that are poor scatterers of X-rays such as hydrogen in the presence of heavier atoms. An atom may scatter neutrons either coherently or incoherently; coherent, elastic, scattering produces diffraction patterns in a similar manner to X-rays, incoherent scattering does not produce Bragg reflections and is a disadvantage for diffraction (though useful for other techniques, and particularly for the study of hydrogenous materials, as discussed in Section 2.9). A selection of relevant neutron scattering data for elements encountered in this Thesis is given in Table 2.2.⁶²

Table 2.2: Selected neutron scattering data, given as coherent, incoherent, total and absorption cross sections. Absorption cross sections are quoted for neutrons with velocity 2200 ms^{-1} or energy of 25.3 meV .

Isotope	Abundance %	σ_{coh} barn	σ_{inc} barn	σ_{scatt} barn	σ_{abs} barn
^1H	99.985	1.7583	80.27	82.03	0.3326
^2H	0.015	5.592	2.05	7.64	0.000519
Li	-	0.454	0.92	1.37	70.5
^6Li	7.5	0.51	0.46	0.97	940
^7Li	92.5	0.619	0.78	1.4	0.0454
B	-	3.54	1.7	5.24	767
^{10}B	20	0.144	3	3.1	3835
^{11}B	80	5.56	0.21	5.77	0.0055
N	-	11.01	0.5	11.51	1.90
Mg	-	3.631	0.08	3.71	0.063
V	-	0.0203	5.07	5.09	4.9
Al	-	1.495	0.0082	1.503	0.231
Gd	-	29.3	151	180	49700

For experimentation, an important property of neutrons is their ability to penetrate a long distance through material, this property arises because they are charge neutral. This is with the caveat that, as shown in Table 2.2, some elemental isotopes absorb neutrons very strongly. High penetration is useful as it enables the use of various demanding experimental sample environments. Cryostats, furnaces and other custom equipment such as the IGAⁿ described in Section 2.11.3 may be used and developed with simpler and more reliable engineering processes than for X-ray

diffraction.

In structure completion (particularly in the location of deuterium atoms), neutron diffraction holds a final advantage. The small size of a nucleus compared to the wavelength of the neutron means that there is no angular dependence of the scattering factor as there is for X-ray scattering. Thus there is no drop-off in intensity of Bragg reflections with increased angle, resulting in more information available in neutron diffraction data compared with equivalent X-ray diffraction data.

2.6.3 Refinement of Structural Models

The process of structure solution, and subsequent refinement, from powder diffraction data used in this Thesis involved the following steps:

1. Obtain an accurate set of intensity values along with the position of all the Bragg reflections.
2. Determine the unit cell parameters, index the reflections, and determine the space group of the crystal.
3. Use chemical knowledge or intuition to create a possible structure model.
4. Compare the intensities or structure factors of the model with those obtained experimentally.
5. Adjust the atomic positions to obtain an improved agreement between the calculated and observed model, in an attempt to minimise the weighted profile R factor, R_{wp} as shown in Equation 2.8.

Within this general procedure, a more specific description of the methods used in this Thesis are detailed in the following sections.

Pawley Refinement

Pawley refinement is used to refine the unit cell from powder diffraction data.⁶³ Following indexing of a pattern, it is necessary to determine the precise unit cell parameters and compare the possible space groups. A Pawley refinement varies the peak profile and unit cell parameters to obtain the best possible fit to observed data — the output is a list of (hkl) values, their positions and intensities. The intensity of the (hkl) peaks can be used effectively to compare different space groups, and to monitor the changes in a phase where the atomic positions are unknown. It is particularly useful where peak overlap would make this process challenging to achieve by inspection alone.

Simulated Annealing

Simulated annealing is a very useful procedure that may be used to gain an initial structure when an obvious starting point for atomic positions in a Rietveld refinement is non-trivial. It is a global optimisation technique, that searches for the optimal solution among many possible solutions in a large search space. While in normal refinement methods, the solution can only travel “downhill,” in simulated annealing “uphill” steps are also allowed, which means that the refinement can escape from local minima. Uphill steps are introduced by replacing a current solution with a random nearby one. By analogy with physical annealing, a hypothetical temperature is used to control the movement of the trial solutions. In the case of structure solution, this “temperature” is in the units of the minimising function, R_{wp} . Higher “temperatures” allow atoms to move far from their original positions and extensively explore the parameter space. An annealing regime is used to lower the “temperature” slowly so that downhill moves are increasingly preferred as low R_{wp} solutions are increasingly explored. During this process, it is often convenient to describe the relative coordinates of known chemical units as rigid bodies, say

NH_3 or BH_4^- , and allow these to move around the unit cell, allowing a great deal of possible solutions to be explored relatively quickly.

Rietveld Refinement

Rietveld refinement is used for the refinement of the final atomic positions, thermal parameters, and other desired values within a now fixed unit cell. The basic principle of the method is to minimise the function M (Equation 2.6), that is the difference between the calculated profile and the observed data

$$M = \sum_i W_i \left\{ y_i^{obs} - \frac{1}{c} y_i^{calc} \right\}^2 \quad (2.6)$$

where y^{obs} and y^{calc} are observed and calculated data, W is a statistical weighting parameter and c is an overall scale factor such that $y_i^{obs} = c y_i^{calc}$.⁶⁴ The quality of the fit of the model to the data is typically expressed using one or all of a few key statistical parameters.⁶⁵ The perfect fit is obtained when the expected R-value (R_{exp}) is equal to the weighted profile R-value (R_{wp}).

$$R_p = \sqrt{\frac{\sum |Y_{o,m} - Y_{c,m}|}{\sum Y_{o,m}^2}} \quad (2.7)$$

$$R_{wp} = \sqrt{\frac{\sum w_m (Y_{o,m} - Y_{c,m})^2}{\sum w_m Y_{o,m}^2}} \quad (2.8)$$

$$R_{exp} = \sqrt{\frac{M - P}{\sum w_m Y_{(o,m)}^2}} \quad (2.9)$$

$$GOF^2 = \chi^2 = \left(\frac{R_{wp}}{R_{exp}} \right)^2 = \frac{\sum w_m (Y_{o,m} - Y_{c,m})^2}{\sum M - P} \quad (2.10)$$

where $Y_{o,m}$ and $Y_{c,m}$ are observed and calculated data respectively at point m ,

w_m is the weighting given to point m (which is given by $w_m = 1/\sigma(Y_{(o,m)})^2$), M is the number of data and P is the number of parameters. Of these parameters, χ^2 is perhaps the most useful as it accounts for the quality of the fit against the number of refineable parameters, avoiding the pitfall of obtaining a good fit to diffraction data by simply including a vast number of irrelevant refineable parameters. While a certain amount of experience is required to say if a model is correct, and a good visual fit to the data is important, a value of $\chi^2 < 3$ is an indicator of a good fit. While an accompanying R_{wp} value of < 10 is indicative of a well-fitted profile with a relatively low background. These statistics are particularly useful in determining the presence of subtle structural features.

2.6.4 Computational Methods

A variety of programs were used to implement the methods discussed above, the programs used were Topas Academic,⁶⁶ DASH,⁶⁷ and Crystals.⁶⁸

Topas Academic

Topas was used for analysis of all powder diffraction data including; indexing of patterns, Pawley refinement and Rietveld refinement. Topas has a number of advantages as a diffraction analysis program, it adopts a language that is both powerful and flexible enabling the easy introduction of non-standard models. The ability to perform batch refinements, using the output of a first refinement as the input to the second and so on, is also useful in analysing large numbers of diffraction patterns in a consistent manner.

DASH

Dash was used for structural solution from X-ray diffraction data, it employs a Bayesian ranking procedure in indexing and space group analysis. With the use of

rigid bodies, the inbuilt simulated annealing process often yields good results for further Rietveld refinement.

Crystals

Crystals was used for analysis of single-crystal diffraction data with the assistance of Dr. Francesco Fabbiani. In particular the Annulus model built into the program was used to model delocalised rings of electron density rather than “discrete” atoms within molecules.⁶⁹

2.6.5 Instrumentation: X-ray Facilities

All X-ray powder diffraction data were collected using synchrotron radiation sources, while the single-crystal data were collected using standard laboratory equipment. In a synchrotron, electrons fired from an electron gun are accelerated by a linear accelerator and then a booster synchrotron ring until they approach the speed of light, when they are released into a storage ring. The storage ring consists of straight sections and bending magnets. When the electron path is bent, Brehmstahlung radiation is emitted.^{70,71} The type of Brehmstahlung radiation emitted depends on the strength of the magnetic field and the speed of the electrons, in this case X-rays are produced. The wavelength of the X-rays is further tuned by passing through a Si (111) monochromator crystal.^{72,73} This tuning process is repeated in each beam cycle, so different experiments are likely to have been carried out using different wavelength X-rays.

In the laboratory based diffractometer, X-rays are produced by firing a beam of electrons, produced by an electron gun, at a metal source. The source is typically a transition metal, and X-rays are produced by absorption and excitation of electrons followed by relaxation of electrons and emission of radiation. Thus the wavelength produced depends on the metal chosen and the energy levels of its orbitals.

The advantage of using a synchrotron X-ray source is that the high intensity allows short data collection times and a vastly improved signal to noise ratio, this is useful for studying both materials which are poor scatterers of X-rays and kinetics of phase changes. There are some problems with using such powerful X-rays; the beam is prone to heat samples meaning that temperature readings may be prone to slight error, in some cases severe beam damage can also occur and result in structural changes or the destruction of samples as shown in Figure 2.3.⁷⁴

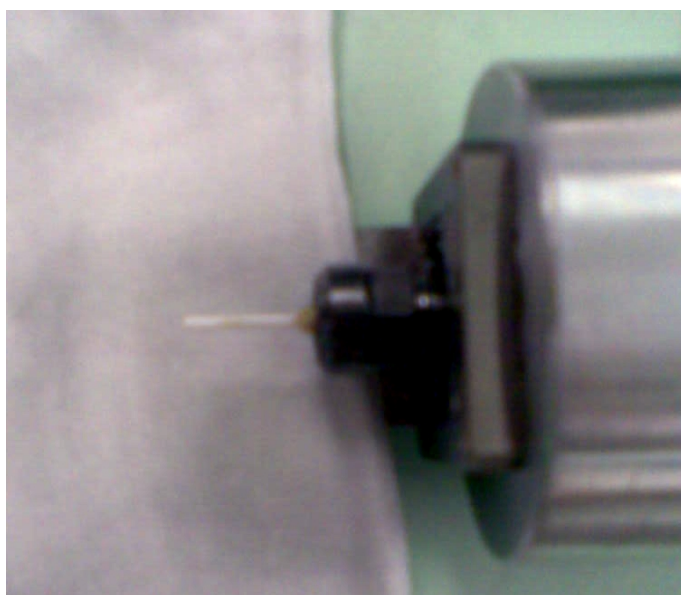


Figure 2.3: A picture showing a sample of $\text{Mg}(\text{NH}_3)_6\text{Cl}_2$ in a capillary tube after data collection at the ESRF beamline ID31, the discolouration of the sample near the centre of the capillary indicates beam damage has occurred.

European Synchrotron Radiation Facility⁷²

European Synchrotron Radiation Facility (ESRF) data were collected on the ID31 beamline, which operates at an energy range of between 5 keV and 60 keV. Diffraction data were collected using a wavelength of around $0.8 \text{ \AA}$ and a step-size of 0.003° . A bank of nine scintillation detectors, each spaced ca. 2° apart, measure the diffracted intensity as a function of 2θ , with each detector preceded by a Ge (111) crystal analyser. The nine crystals are mounted on a single rotation stage so

that only a single adjustment is to obtain a maximum range of diffraction data.

The diffractometer was operated in Debye-Scherrer transmission geometry. Samples were loaded into borosilicate glass capillary tubes (diameter 0.8 mm - 1.0 mm) within a nitrogen atmosphere glove bag. The capillaries were then packed with a glass rod to prevent sample movement and temporarily sealed using vacuum grease. After removal from the glove bag, the capillaries were sealed permanently using a natural gas-oxygen flame. The capillaries were rotated in the beam during data collection in order to provide a good powder average of intensities. Diffraction data were collected either at room temperature or during in-situ variable temperature experiments. Samples were heated by an Oxford Cryostreams cold-nitrogen-gas-blower (-193 °C to 227 °C, or 80 K to 500 K) or a Cyberstar hot-air blower (up to 950 °C).

Diamond Light Source⁷³

Diamond light source data were collected on beamline I-11. The beamline is shown in Figure 2.4 and is very similar to ID31 at the ESRF, as described above. Electrons are accelerated to approximately 30 eV under ultra high vacuum (10^{-13} bar), the resultant X-rays have energies of between 5 keV and 30 keV. A wavelength of around 0.8 Å was selected and a bank of nine detectors was used. The samples were prepared in the same manner as those for the ESRF, except that 0.7 mm capillary tubes were used and no glass rod was used to pack the samples.

Single-crystal X-ray diffraction

Single-crystal data were collected at 150 K on a Nonius Kappa CCD diffractometer ($\lambda = 0.71073$ Å) equipped with a Oxford Cryosystems low-temperature device. Suitable crystals were selected by eye and mounted on the sample holder using hair and paraffin wax, with the assistance of Dr. Amber Thompson. Crystals were

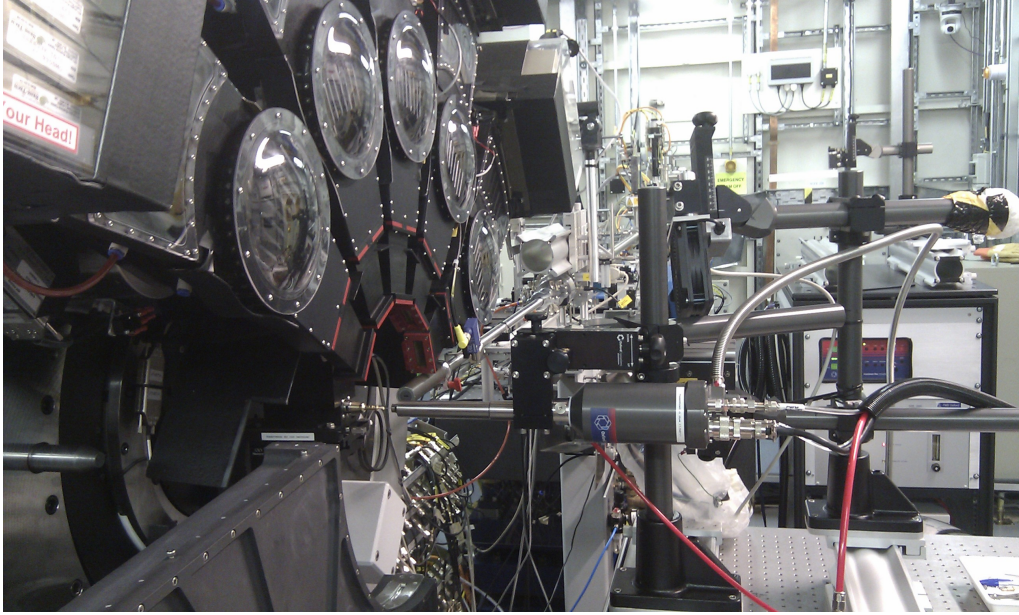


Figure 2.4: The experimental set-up of I11 at Diamond Light Source

mounted on a laboratory bench where a stream of argon gas was blown over the sample in an attempt to maintain an inert atmosphere. During data collection, the inert atmosphere was maintained via the nitrogen gas cryostream.

2.7 ISIS Spallation Neutron Source⁷⁵

It is possible to produce neutrons in a reactor by fission reactions, or to use a spallation source. Neutron experiments in this Thesis were carried out at the ISIS spallation neutron source. First H^- ions are produced by an electric discharge, and initially accelerated using a Radio Frequency Quadrupole accelerator which also divides the ions into bunches. Bunches of ions are further accelerated to 37 % of the speed of light in a linear accelerator. The accelerated ions enter a synchrotron through an alumina foil which removes the electrons, leaving protons. In the synchrotron the protons are accelerated to 86 % of the speed of light by ten radio frequency electric field cavities. When the protons reach the required speed they are extracted by kicker magnets towards the targets. The extracted protons hit the

tungsten metal target causing neutrons to be ejected. Moderators are used to slow down the neutrons to the appropriate energy levels for the required experiments. The neutrons from Target Station One pass through one of four moderators. Two of these moderators use room temperature water, one contains methane at 100 K and the other contains liquid hydrogen at 20 K. The moderators are about 0.5 L in volume and are surrounded by water-cooled beryllium reflectors which scatter divergent neutrons back into the moderator, this increases the flux of neutrons leaving the moderator and moving towards the individual beam lines and experiments.

At reactor neutron sources the neutrons produced are monochromated for use in experiments, whilst at ISIS ‘white’ neutrons with a range of wavelengths are used. As the source produces pulses of neutrons, data are collected as a function of time-of-flight. Combining Bragg’s Law with the de Broglie relationship (Equation 2.11) and substituting values for Planck’s constant (h), the neutron mass (m), and $v = L/t$, Equation 2.12 is obtained

$$\lambda = \frac{h}{mv} \quad (2.11)$$

$$t = 505.56Ld \sin \theta \quad (2.12)$$

where time-of-flight (t) is measured in microseconds, flight path (L) in metres and d -spacing (d) in Ångstrom units.⁷⁶ Fixed detector banks are used, each with its own characteristic resolution and d -spacing range. An advantage of having fixed detectors is that it is possible to use a sample environment that blocks off certain angles, as long as others remain clear. The neutron pulse provides a large number of high energy neutrons, which means that very small d -spacings are accessible on diffractometers. The resolution function for a time-of-flight diffractometer is well-approximated by the formula,

$$\frac{\Delta d}{d} = \left(\left(\frac{\Delta t}{t} \right)^2 + \left(\frac{\Delta L}{L} \right)^2 + (\Delta \theta \cot \theta)^2 \right)^{(1/2)} \quad (2.13)$$

where Δd is the width of a reflection at a d -spacing, d . The first term is approximately constant for a given moderator.⁷⁶ The second term arises from uncertainties in the flight path, and is constant for a given measurement, increasing the flight path will increase resolution but at the expense of neutron flux. The angular dispersion term arises because finite widths of the sample and detector mean that a range of wavelengths satisfy the Bragg condition for each reflection. At low angles (large $\cot \theta$) this term dominates, but it becomes vanishingly small at high angles.

2.7.1 General Materials Diffractometer⁷⁷

The General Materials Diffractometer, or GEM, was designed to be a high intensity, high resolution neutron diffractometer for both disordered materials and crystalline powders. The flight path from moderator to sample is 17 m which provides a high resolution. The 8 detector banks positioned at angles between 1.1 ° and 169.3 ° are further described in Table 2.3 and shown in Figure 2.5. The range of d -spacings accessible are 0.1 Å to ca. 15 Å. One of its advantages is the large (12 m²) detector area which means that high quality diffraction data are obtained in a matter of minutes, making this the ideal instrument for kinetic and disordered material studies.

2.7.2 High Resolution Powder Diffractometer⁷⁶

The High Resolution Powder Diffractometer, or HRPD, at ISIS is the finest diffractometer of its kind in the world, and the quality of the data is such that structure solution is possible for samples that would normally require corroboratory single-crystal or X-ray diffraction data. It is positioned at the end of a 100 m long ⁵⁸Ni super mirror neutron guide, and this exceptionally long flight path gives rise to a

Table 2.3: The detector specifications for the GEM diffractometer.

Bank	Mean Angle 2θ	Min Angle $^\circ$	Max Angle $^\circ$	L_2 m	Resolution $\Delta Q/Q$ %
0	-	1.1	3.2	2.8-2.9	5-10
1	9	5.6	12.5	2.2-2.4	4.7
2	17	13.8	21.0	1.48-2.10	2.4
3	34	24.8	45.0	0.65-1.40	1.7-2
4	62	49.9	74.9	1.03-1.44	0.79
5	92	79.0	104.0	1.38	0.51
5X	109	105.5	113.5	1.38	0.51
6	146	141.9	149.2	1.54-1.74	0.34
7	159	149.3	169.3	1.04-1.39	0.35

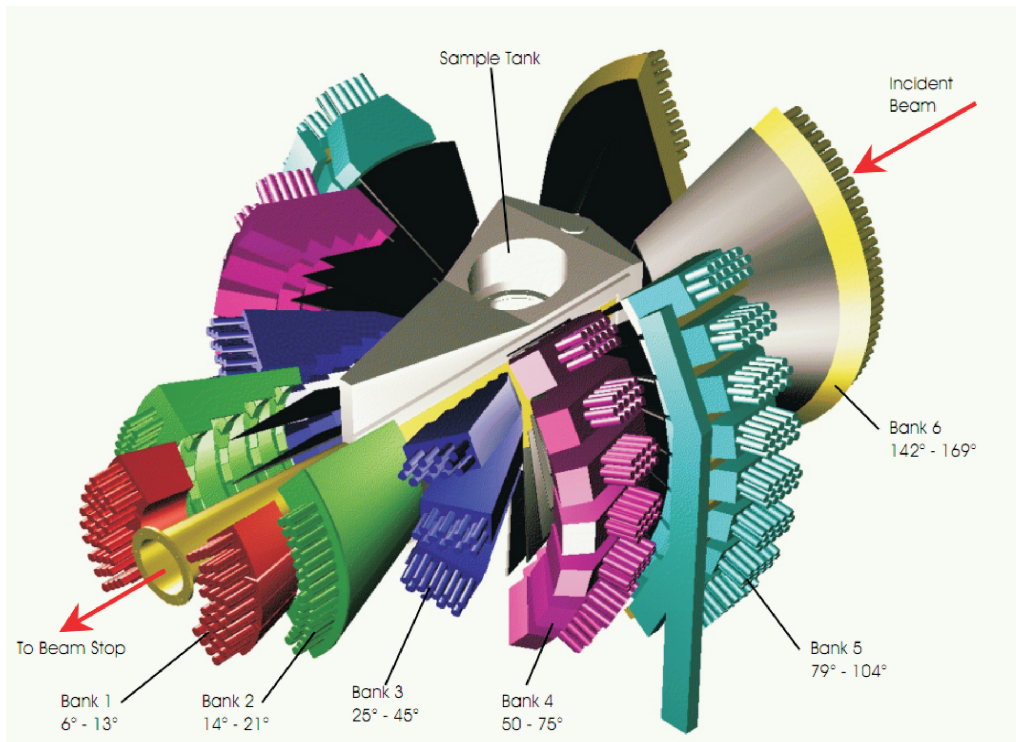


Figure 2.5: A diagram showing the orientation of the GEM diffractometer detector banks.⁷⁵

very high resolution of $\Delta d/d \approx 4 \times 10^{-4}$. The long flight path means that subsequent neutron pulses are able to overlap, to eliminate this undesirable overlap beam choppers are in place on the neutron guide, two chopper settings are available to select the desired range of neutron energies. An overall d -spacing range of 0.6–16.5 Å is accessible, though the highest resolution data of the back scattering bank is only available up to approximately 4.6 Å. There are three detector banks, positioned at 30° (bank 3), 90° (bank 2), and 168° (bank 1), that provide a range of resolutions and d -spacing ranges; the 90° bank offers the best count statistics while the 168° bank provides the highest resolution data (this is illustrated in Section 2.11.3, Figure 2.11). The instrumental configuration is shown in Figure 2.6.

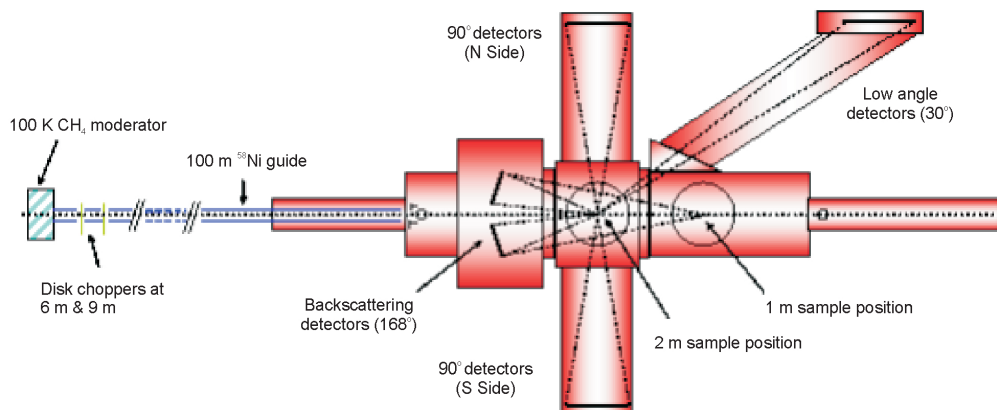


Figure 2.6: A schematic diagram of HRPD.⁷⁶

Low-temperature studies of $\text{Mg}(\text{ND}_3)_6\text{Cl}_2$ and $\text{Mg}(\text{ND}_3)_6(^{11}\text{BD}_4)_2$ were carried out using the in-house closed cycle refrigerators and cryostats to control the sample temperature between 4 K and 300 K.

2.8 Raman Spectroscopy^{78,79}

During Raman spectroscopy a sample is exposed to intense single wavelength radiation. On impact with a molecule, photons with less energy than that required to promote an electron into an excited state may cause excitation of that electron

into a virtual excited state. This virtual state has a short lifetime, and the majority of absorbed light is re-emitted at the same energy (it is scattered elastically with ν_0). However, a small proportion of emitted light differs from the incident by an energy equivalent to some of the vibrational modes of the molecule (it is scattered inelastically with $\nu_0 \pm h\nu$). This is the Raman effect, and its concept is shown in Figure 2.7. The effect is very weak, meaning that a very intense monochromated light is required, so a laser source is usually used in spectroscopy.

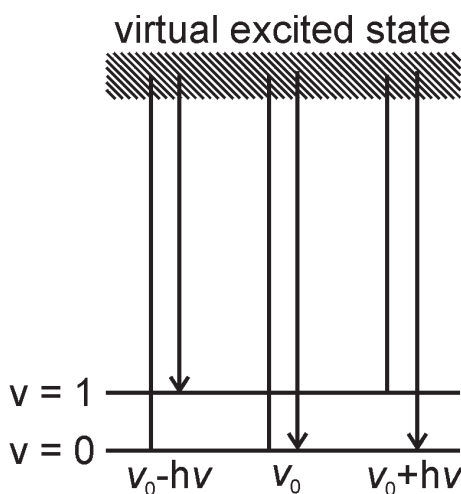


Figure 2.7: A diagram showing the concept of Raman scattering.

With respect to this Thesis, the useful result of this effect is that the scattered photons differ in wavelength from the incident beam by a vibrational frequency of the molecule in question. Assuming that the vibrations are accurately described by a quantum harmonic oscillator experiencing a force $F = kx^2$, then the energies of these modes are described by Equations 2.14 and 2.15. It should also be noted that only vibrational modes that correspond to a change in the polarisability of the molecule are active in Raman spectroscopy. Raman spectra in this Thesis were recorded with a Dilor Labram 300 spectrometer, equipped with a CCD detector, and using a wavelength of $\lambda = 514.5$ nm. Samples were loaded into glass capillaries in an inert argon atmosphere and sealed using a gas-oxygen flame before data collection.

$$E = \hbar\omega(n + 1/2) \quad (2.14)$$

$$\omega = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}} \quad (2.15)$$

where the reduced mass $\mu = \frac{m_1 \times m_2}{m_1 + m_2}$, k is the force constant of the harmonic oscillator, ω is the angular frequency and n is the vibrational quantum number.

2.9 Inelastic Neutron Scattering^{80–82}

While diffraction techniques utilise elastic scattering of neutrons, the energy gained or lost in inelastic scattering can be used in vibrational spectroscopy. A beam of neutrons with an appropriate and known velocity will pass through and transfer energy to or from a sample. The energy transfer which occurs can be written,

$$E = \hbar\omega = \tilde{\nu}hc = \frac{m_n |v|^2}{2} \quad (2.16)$$

$$E = \frac{\hbar |k|^2}{2m_n} \quad (2.17)$$

where m_n is the mass of a neutron. The incident neutron, of energy E_i , strikes the sample and after interaction has an energy E_f . The experiments in this Thesis were all carried out at low-temperature (ca. 20 K), so the incident neutron loses energy to the sample. Where the excitation of the sample is due to vibrational motions, the method is very similar to infra-red absorption spectroscopy, or Raman scattering.

While INS is conceptually similar to Raman scattering, there are significant differences in detail. The major difference, as discussed in Section 2.6, is that photons (electromagnetic radiation) interact primarily with the electrons, while neutrons in-

interact with nuclei, so the strength of the interaction is dependent on the particular nuclide involved. Another difference is that the wavelength of the electromagnetic radiation used for Raman experiments is in the visible or near UV region and is of the order of hundreds of nanometers (thousands of Ångströms). The neutrons used in these experiments have wavelengths of 0.1 Å to 2 Å. This means that the size of the neutron is comparable to, or less than, the spacing between atoms and results in there being no “selection rules” as there are for optical spectroscopy, so in principle all modes are observable.

Despite the complexities of neutron scattering, the INS technique can be simply summarised. The observed positions of transitions (the eigenvalues of the mode) are a function of the molecular structure and intramolecular forces, and correspond to energies lost from the neutron. The strength of a transition is a function of the atomic displacement occurring during the vibration (the eigenvector of the mode) and the momentum lost by the neutron. The atomic displacements are determined by the molecular structure and intramolecular forces, and the momentum transferred is determined by the neutron spectrometer. As a consequence, INS gives direct access to both the vibrational eigenvectors and eigenvalues.⁸⁰

The geometry of an INS spectrometer allows for a beam of neutrons to fall on a sample and be scattered onto a detector, of area A , at distance, d_f , and an angle, θ , relative to the sample and the incident beam. These values (d_f, θ) are the polar coordinates for the system, for which the solid angle $d\Omega$ (subtended by an angular element, $d\theta$) is $2\pi \sin \theta d\theta$.⁸⁰ The spectrometer scans the energy spectrum of the sample and records the flux in neutrons measured per second, this is the final neutron flux, J_f , and is normalised relative to the incident flux, J_i . The sample’s response is a function of energy, E , and since the polar coordinates of the detector can be changed, is also a function of solid angle.⁸⁰ The observable is the rate of change of the cross section with respect to the final energy, E_f , and solid angle, $d\Omega$, known as the double differential scattering cross section:

$$\frac{d^2\sigma}{dE_f d\Omega}$$

where

$$d\Omega = \frac{A}{d_f^2}$$

This double differential is employed in the Scattering Law which relates the momentum transfer vector, Q , and the wavenumber, ω , to the observable intensities:

$$S(\mathbf{Q}, \omega)_l = \frac{4\pi}{\sigma_l} \frac{\mathbf{k}_i}{\mathbf{k}_f} \left(\frac{d^2\Omega}{dE_f d\Omega} \right)_l \quad (2.18)$$

where σ_l is the scattering cross section of atom l and $\mathbf{k}_i$ and $\mathbf{k}_f$ are the momenta of the incident and final neutrons respectively.

Typically, spectroscopic intensities are reported as $S(\mathbf{Q}, \omega)$, which is related to the amplitude of the cross section weighted density of states. For a single molecule containing N atoms,

$$S(\mathbf{Q}, \omega)_{total} = y \sum_{l=1}^N S(\mathbf{Q}, \omega)_l \sigma_l = 4\pi \frac{\mathbf{k}_i}{\mathbf{k}_f} \left(\frac{d^2\sigma}{dE_f d\Omega} \right)_{observed} \quad (2.19)$$

The intensities, $S(\mathbf{Q}, \omega)$, are reported in scaled units, that are related to the actual units, barn (100 fm^2), by the linear factor y . The spectra become unitless and are therefore compared in terms of relative intensities. When powder samples are used then the powder averaged scattering law is

$$S(\mathbf{Q}, \omega)_{powder} = \frac{1}{4\pi} \int S(\mathbf{Q}, \omega) d\mathbf{Q} \quad (2.20)$$

Inelastic neutron spectroscopy has several advantages over analogous optical techniques:

1. INS spectra can be accurately modelled using molecular dynamics software and the intensities measured during an experiment can be straightforwardly related to the atomic displacements of the scattering atoms. This is because complications arising from electro-optic parameters are avoided. This also means that the spectra are quantitative, so for example one spectrum may be subtracted from another to reveal the spectrum of a second phase.
2. The technique is sensitive to hydrogen atoms (^1H) due to their large incoherent scattering cross section (see Section 2.6.2). Optical techniques tend to be more sensitive to larger, more electron-rich atoms.
3. There are no optical selection rules for INS, so in principle all modes are observable.
4. The high penetration of neutrons means that they pass readily through sample holders and into the bulk of samples, thus information on the bulk properties of samples is obtained.
5. There is a very wide spectral range available (16 cm^{-1} to 4000 cm^{-1}), that covers the entire molecular range. The reliability of measurements at low wavenumbers is greatly increased over optical techniques.

2.9.1 TOSCA⁸²

INS measurements discussed in this work were collected using the TOSCA Spectrometer at the ISIS pulsed neutron facility. TOSCA is an indirect geometry spectrometer optimised for the study of molecular vibrations in the solid state, it has an energy range of 0 cm^{-1} to 4000 cm^{-1} (0 meV to 500 meV), but gives best results below 2000 cm^{-1} (250 meV). Samples were crash-cooled using liquid helium before data were collected at ca. 20 K ; this low temperature was chosen to reduce the thermal effects that degrade the spectra.

2.10 Nuclear Magnetic Resonance^{78,83,84}

Nuclear magnetic resonance (NMR) spectroscopy measures the interaction of the nuclear spin of an atomic nucleus with an applied magnetic field and the nuclear spin of surrounding nuclei. In a magnetic field, there are $2I + 1$ spin states that are non-degenerate (where I is the nuclear spin quantum number). Radio frequency irradiation at the NMR frequency causes transitions between these states, as shown in Equation 2.21 and Figure 2.8;

$$\Delta E = \hbar\gamma B = hv \quad (2.21)$$

$$v_{NMR} = \frac{\gamma B}{2\pi}$$

where B is the applied magnetic field, v is the NMR frequency and γ is the gyromagnetic ratio of the nuclide in question. As a technique, sensitivity is considered low due to the small population difference between the spin states. The receptivity of a nuclide is determined by both the gyromagnetic ratio and the abundance of the nuclide, data for nuclei relevant to this Thesis are given at the end of this Section in Table 2.4.

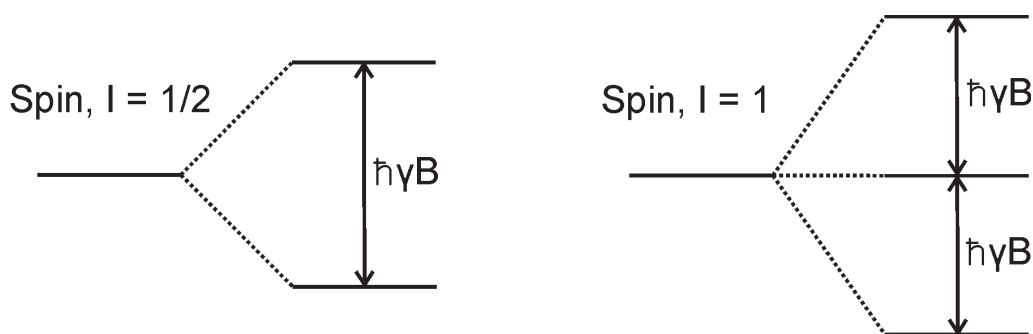


Figure 2.8: A diagram showing the splitting of energy levels in a nuclide in a magnetic field, with spin $I = 1/2$ and spin $I = 1$ on the left and right respectively.

The peaks in NMR spectra are reported using a chemical shift (δ), as defined in Equation 2.22. It is clear from Equation 2.21 that the chemical shift depends on the

nuclei, and introducing a shielding constant σ as shown in Equation 2.23 accounts for the fact that the local environment of a nucleus also effects the chemical shift. Many factors affect shielding, but in this Thesis the important factor is that electrons have a charge and will move in response to a magnetic field to generate an opposing field. This means that electrons shield nuclei from the magnetic field so in electron-rich environments σ is large and transitions occur at a lower radio frequency and a lower (more negative) chemical shift. Conversely if electron density is decreased, shielding is lower and chemical shift is higher (more positive).

$$\delta_{ppm} = \frac{v_{signal} - v_{reference}}{v_{spectrometer}} \times 10^6 \quad (2.22)$$

$$v = \frac{\gamma B(1 - \sigma)}{2\pi} \quad (2.23)$$

Another important feature of an NMR spectrum is spin-spin or J- coupling. This occurs when an NMR active nucleus (A) is bonded to another active nucleus (X), the nucleus in question (A) will experience a range of magnetic fields, with the spectral result that signals will be split into $2I + 1$ peaks (where I refers to the spin of the second nucleus (X)). The strength of the coupling varies depending on many factors but is strongest when two nuclei are covalently bonded together, it is reported as the coupling constant, J, with the units Hz. This coupling is demonstrated in Figure 2.9, where the coupling of A to a single nucleus X with $I = 1$ is shown to produce three peaks of even intensity, while coupling of A to 2 equivalent nuclei X with $I = 1/2$ produces a 1:2:1 triplet.

A further type of interaction is dipolar coupling, that originates from the through space interaction of magnetic nuclei and carries an angular dependence. In liquids this is effectively averaged to zero by molecular tumbling but in solids molecular motions are restricted, and what should be equivalent nuclei actually have slightly

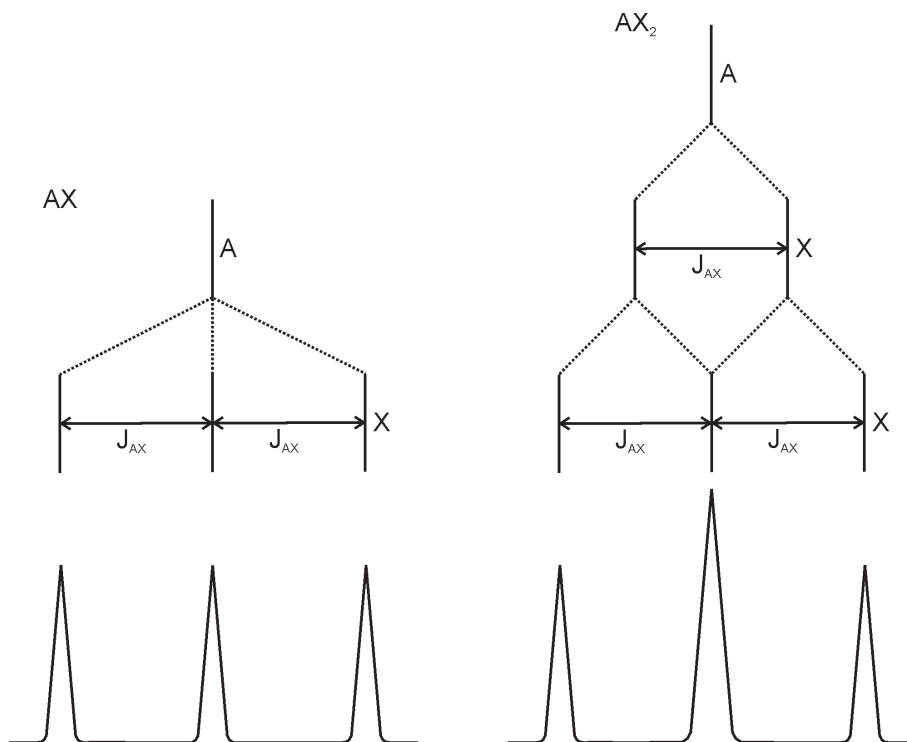


Figure 2.9: A diagram showing spin-spin coupling in the spectra of A in AX and AX₂, where $I_X = 1$ and $1/2$ respectively.

different electronic environments thence dipolar interactions may result in a broad featureless spectra. It is possible to sharpen the features of such a broad spectra by imposing motion on the nuclei and rapidly spinning the sample, and this achieves best results when the spinning axis is at an angle of 54.7° to the applied magnetic field.⁸⁵ The reason for the sharpest spectra appearing at this so called “magic angle” is that when nuclei are in a strong magnetic field all nuclear spins align with the field. Any pair of nuclear spins are then effectively separated by a distance r and an angle β to the magnetic field and the strength of dipolar coupling is given by relationship shown in Equation 2.24. Dipolar coupling may be effectively removed when the sample is spun at $\beta = 54.7^\circ$ as $3 \cos^2 \beta - 1 = 0$. This spinning technique for solid-state NMR spectroscopy is widely known as magic angle spinning (MAS).

$$d \propto \frac{3 \cos^2 \beta - 1}{2r^3} \quad (2.24)$$

A final effect to consider is that caused by quadrupolar nuclei; any nuclei with a spin greater than $1/2$ possess a non-spherical charge distribution or quadrupole. The important difference between dipolar and quadrupolar nuclei is that a dipole interacts with electric fields but a quadrupole interacts with field gradients. In solids the electric field gradient at a nucleus depends on the site symmetry and the non-uniform distribution of charge. For example a nucleus in a high symmetry octahedral site will not feel any net quadrupolar interaction, but two negative charges close to the nucleus can produce a quadrupolar interaction that causes line splitting in the spectra of single-crystals and line broadening in the spectra of powder or disordered samples. This is in fact a 2nd order effect, 1st order effects cause additional splitting in the nuclear energy levels, with the spectral result that satellite transitions are observed. These peaks are often too broad to be observed and it is possible for them to be averaged, and thus removed, by MAS. An additional type of satellite transition, known as spinning side-bands, may also be observed; these arise from gradients in the magnetic field that are orthogonal to the spinning axis, and appear as narrow side bands at multiples of the spin rate. In liquids, molecular tumbling causes quadrupolar nuclei to relax very quickly resulting in no spin-spin coupling being observed and instead the appearance of broad spectral lines.

Table 2.4: NMR data for nuclei relevant to this Thesis

Isotope	Abundance %	Spin Quantum Number I	Gyromagnetic Ratio γ $10^7 T^{-1} s^{-1}$	Receptivity relative to 1H
1H	99.985	$1/2$	36.752	1.00
^{10}B	20	3	2.874	3.95×10^{-3}
^{11}B	80	$3/2$	8.584	1.32×10^{-1}
^{14}N	99.6	1	1.934	1.01×10^{-3}
^{15}N	0.37	$1/2$	-2.713	3.85×10^{-6}
^{25}Mg	10	$5/2$	-1.634	2.68×10^{-4}

2.10.1 Solid State NMR

Solid state ^{25}Mg NMR measurements of MgX_2 and $\text{Mg}(\text{NH}_3)_6\text{X}_2$ were carried out by the EPSRC Solid-state NMR Service at Durham University. Measurements were performed at 24.48 MHz, using a pulse-acquire sequence with a $4\ \mu\text{s}$ (30°) pulse and referenced to a 1 M solution of $\text{MgCl}_2(\text{H}_2\text{O})_{6(\text{aq})}$.

2.10.2 Solution State NMR

Solution state ^1H NMR measurements of $\text{Li}(\text{NH}_3)\text{BH}_4$ were carried out using a Varian Mercury 300 MHz spectrometer. Samples were loaded into NMR tubes within a nitrogen atmosphere glove-bag, dissolved in dry THF- d_8 , sealed temporarily with a Young's tap and then sealed permanently with a natural-gas-oxygen flame.

2.11 Gravimetric Analysis Techniques

Gravimetric analysis techniques were used to investigate both the decomposition temperatures and pathways of compounds. Two techniques were used, thermogravimetric analysis (TGA) and intelligent gravimetric analysis (IGA). Both techniques record sample mass as a function of time or temperature, while with IGA it is also possible to control the pressure of a static or flowing gas in the sample chamber. One of the weaknesses of these techniques in general is the ill defined process for determining the decomposition temperature. In this Thesis, the definitions onset temperature (T_o) and peak temperature (T_p) are used throughout. Onset temperature is calculated from a plot of m vs. T and is defined as the intersection between the straight tangential lines drawn from the plateau mass and from the point of peak mass loss, as shown in Figure 2.10. Peak temperature is defined as the minimum on the section of the first derivative curve ($\frac{dm}{dT}$) relevant to the corresponding mass loss and is also shown in Figure 2.10.

2.11.1 Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was carried out using a Setaram SETSYS Evolution Thermogravimetric Analyser. The analyser was housed in a custom built nitrogen atmosphere glovebox with an oxygen content kept below 10 ppm by maintaining a constant flow of nitrogen gas. Powder samples of approximately 20 mg were first loaded into a platinum crucible in an argon atmosphere glovebox, and transferred to the analyser glove box in a sample jar sealed with Parafilm®. Measurements were carried out under an argon atmosphere flowing at a rate of 10 mlmin^{-1} and with a typical heating rate of $2 \text{ }^{\circ}\text{Cmin}^{-1}$.

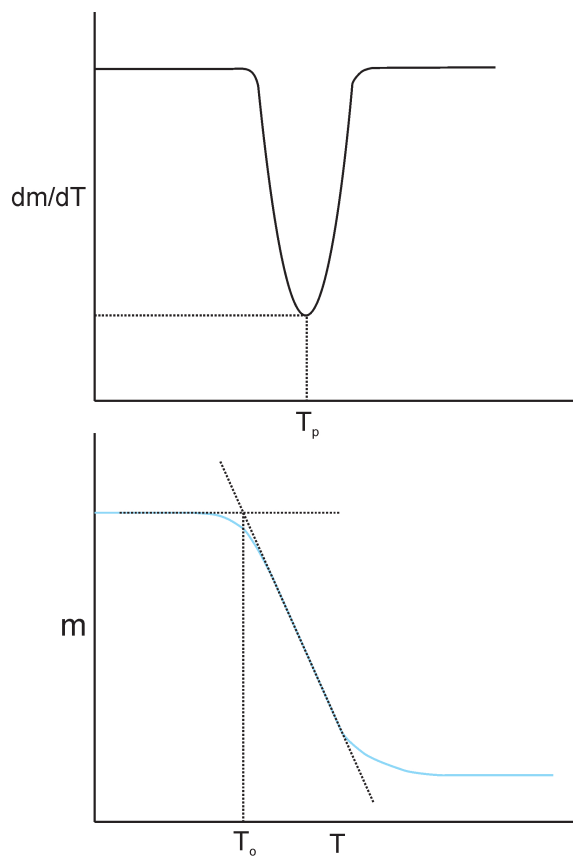


Figure 2.10: A diagram showing the definitions of T_p and T_o that are used to describe the results of gravimetric analysis experiments in this Thesis.

2.11.2 Residual Gas Analysis

Residual gas analysis (RGA) of $\text{Mg}(\text{NH}_3)_6(\text{BH}_4)_2$ was used to compliment TGA data. Measurements were carried out at Birmingham University using a “home built” temperature programmed desorption apparatus coupled to a quadrupole mass spectrometer (Thermo Electron, VG ProLab). Inside an argon atmosphere glovebox, samples of approximately 0.2 g were loaded into a quartz reaction tube that was sealed at one end. This was positioned vertically in the reaction chamber, removed from the glovebox and loaded onto the apparatus without exposing the sample to air. Measurements took place under an argon atmosphere with a flow rate of 100 ml min^{-1} . The sample was heated at $2\text{ }^\circ\text{C min}^{-1}$ up to $370\text{ }^\circ\text{C}$ and held at this temperature until gas desorption had stopped. A heated capillary was used to sample the desorbed gas species in the argon flow on the downstream side of the reaction vessel. The Faraday detector of the mass spectrometer was used to record mass channels of 2 (H_2^+), 16 (NH_2^+), 17 (NH_3^+ or OH^+), 18 (H_2O^+), 28 (N_2^+), 32 (O_2^+) and 40 (Ar^+).⁸⁶

2.11.3 In-Situ Gravimetric Analysis and Neutron Diffraction

A collaboration between the ISIS Facility, University of Oxford and Hiden Analytical has resulted in the design and commissioning of an intelligent gravimetric analyser (IGA) which can be used on GEM and HRPD the neutron diffractometers at ISIS (the IGAⁿ). The instrument allows simultaneous collection of thermogravimetric and neutron diffraction data, as a function of pressure, temperature, or time. The combination of these data allows for a more detailed analysis of both diffraction and thermogravimetric data than would be possible using either technique alone. The variety of temperature and pressure regimes accessible using a single instrument allows for greater experimental flexibility and more thorough phase characterisation.

The sample container for the IGAⁿ is a thin quartz or vanadium bucket, the

quartz bucket was used as standard during the commissioning of vanadium buckets. The reaction vessel is fitted with a standard Tomkinson flange, which allows it to be fitted into the GEM and HRPD beamlines, as well as a custom built argon atmosphere glovebox which allows for loading and unloading of air sensitive samples. The temperature is varied using two band heating elements which are located inside the reaction vessel above and below the sample. The heaters are positioned to ensure minimum interaction with the neutron beam.

Weighed amounts (0.1 - 1.0 g) of a thoroughly ground sample were loaded into the sample holder in an argon atmosphere glovebox, and then transferred to the IGAⁿ glovebox using an airtight container. The IGAⁿ glovebox was purged with argon gas for 30 minutes before the sample holder was loaded on to the tungsten hang down wire, and the reactor vessel was sealed via the Tomkinson flange. The set-up was then craned out of the glovebox and into the diffraction chamber.

For experiments involving $\text{Li}(\text{ND}_3)_n^{11}\text{BD}_4$ on GEM, neutron diffraction data were collected continuously over periods of 3 minutes. For experiments involving $\text{Li}(\text{ND}_3)_n^{11}\text{BD}_4$ on HRPD, neutron diffraction data were collected continuously over periods of 10 minutes. At various pressures and temperatures, isothermic and isobaric diffraction data were collected for extended periods of time in order to improve the signal to noise ratio within these data. Thermogravimetric data were recorded approximately every 10 seconds, with the measured mass accurate to ± 0.0001 mg and the measured temperature and pressure accurate to $\pm 0.001^\circ\text{C}$ and ± 0.01 mbar respectively. During some experiments the IGAⁿ was used without neutron diffraction, operation in this mode is denoted by the acronym IGA. Two distinct pressure regimes were used during experiments, these were: application of a static pressure of gas, and application of a dynamic vacuum where the sample vessel was continuously exposed to a vacuum pump, an operation known as ‘outgas.’

Despite its potential as a very powerful technique, the IGAⁿ system has a number of limitations; the primary ones are *i)* the instrument is not linked to the diffractome-

ter (as in house built furnaces, cryostats etc. often are), so when using a spallation neutron source (as opposed to a reactor source) which is prone to occasional ‘beam off’ period, there is a significant risk that crucial collection of data occurring around a phase transition or decomposition may be missed. Though this is as much a limitation of using a spallation source for kinetic measurements as it is an issue with the instrumentation; and *ii*) the use of the steel reactor, which despite being designed to be wide enough that the collimators in GEM would effectively remove any Bragg reflections caused by the steel, still meant that intense steel reflections were present in the diffraction data.

The problem of using the steel reactor was solved by the commissioning of a quartz reactor tube that was used in the HRPD experiments. However, the steel elements of the furnace still produced Bragg reflections in the diffraction data as shown in Figure 2.11. The application of gadolinium to the reactor vessel, as shown in Figure 2.12, enabled partial shielding of the steel elements, though given limited instrument commissioning time, it was not possible to consistently avoid the appearance of steel reflections in the diffraction data.

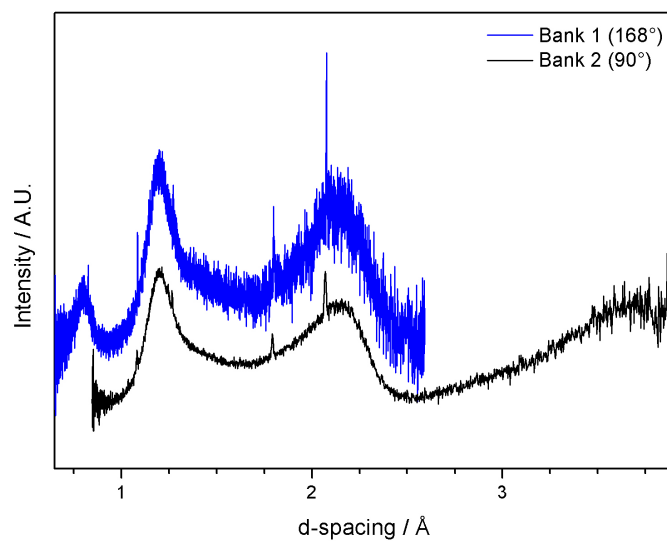


Figure 2.11: Diffraction data for the empty IGAⁿ apparatus fitted with the quartz reactor, collected using HRPD. The background shape is consistent with quartz and Bragg reflections are caused by steel.

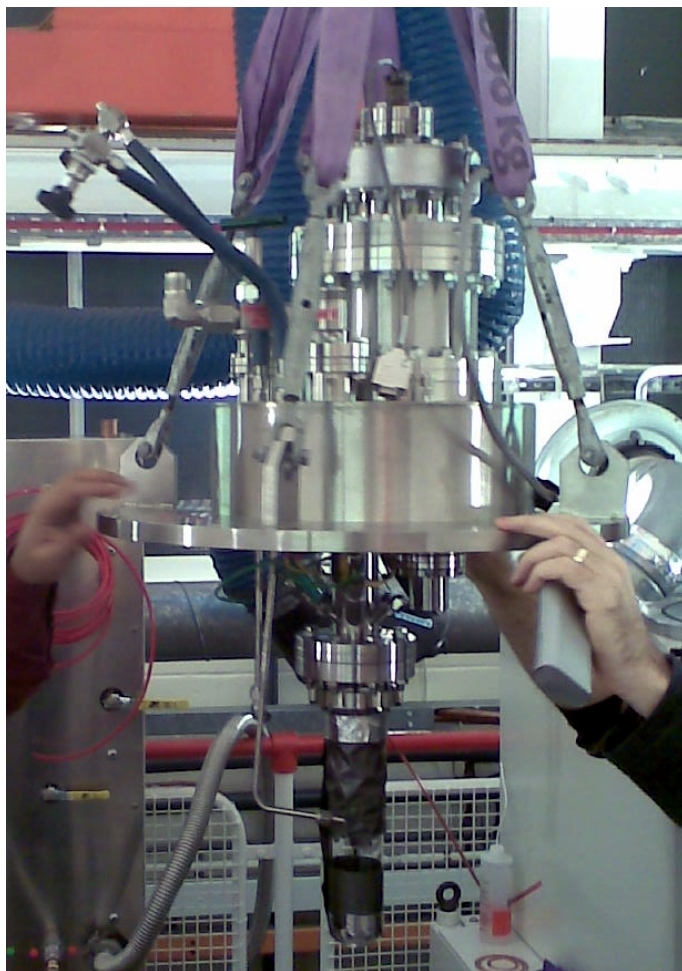


Figure 2.12: The IGAⁿ apparatus fitted with the quartz reactor and gadolinium foil neutron shielding in place.

2.12 Computational Methods

The use of computational techniques in modern science is undoubtedly important, even to an experimental Chemist! In this Thesis, computation is used primarily as a complementary technique to aid in the analysis of diffraction and vibrational spectroscopy data, though it is also used to provide an added insight into molecular motion and the thermodynamic stability of various structures.

2.12.1 Density Functional Theory^{87,88}

Density Functional Theory (DFT) started to gain popularity late 1960s following publication of seminal papers by Hohenberg and Kohn outlining its theory and Kohn and Sham implementing the theory.^{89,90} Its basis lies first with the Born-Oppenheimer approximation, that it is possible to describe a solid system by the wavefunction of electrons in the presence of an external potential that is fixed and provided by the nuclei. This means that a many electron wavefunction describes the system, however it is not practically possible to solve this many body wavefunction. The first DFT theorem states that “the external potential $V_{ext}(\vec{r})$ is (to within a constant) a unique functional of $\rho(\vec{r})$; since, in turn $V_{ext}(\vec{r})$ fixes $\hat{H}$ we see that the full many particle ground state is a unique functional of $\rho(\vec{r})$.”⁸⁹ (Where $\rho(\vec{r})$ is the electron density, and $\hat{H}$ is the Hamiltonian operator.) The ground state energy (E_0) is a functional of the ground state electron density (ρ_0), so

$$E_0[\rho_0] = T[\rho_0] + E_{ee}[\rho_0] + E_{Ne}[\rho_0] \quad (2.25)$$

where T is the kinetic energy, E_{ee} is the electron electron potential and E_{Ne} is the nuclear electron potential. This means that the total energy of a system of electrons in an external potential is a unique functional of the groundstate density ($F_{HK}[\rho]$ in Equation 2.26); if you find the density, then you can calculate the energy.

$$F_{HK}[\rho] = T[\rho] + E_{ee}[\rho] = \langle \Psi | \hat{T} + \hat{V}_{ee} | \Psi \rangle \quad (2.26)$$

where $\hat{V}$ is the potential energy operator, $\hat{T}$ is the kinetic energy operator and Ψ is the wavefunction of the system. Unfortunately this functional ($F_{HK}[\rho]$) remains the unknown holy grail of DFT, but it is known that even relatively crude approximations can give excellent results. The ground state density uniquely determines the Hamiltonian operator, which characterises all states of the system, both ground and excited. Thus, all properties of all states are formally determined by the ground state density.

The second theorem states that $F_{HK}[\rho]$, the functional that delivers the ground state energy of the system, delivers the lowest energy if and only if the input density is the true ground state density, ρ_0 .ⁱ This density is the exact single-particle ground-state density and Kohn and Sham were able to show that it is possible to replace the many-electron problem with an exactly equivalent set of solvable one-electron equations. This is a huge step forward except that there are still an infinite number of calculations to perform on an infinite number of electronic wavefunctions and an infinite basis set for each wave function.

At this point Bloch's theorem comes into play, it states that in a periodic cell each electronic wave function ($\Psi_{i,k}(\mathbf{r})$) is the product of a cell-periodic part ($f_i(\mathbf{r})$) and a wavelike part ($\exp[i\mathbf{k} \cdot \mathbf{r}]$) (Equation 2.27). The cell part can be expanded using a basis set consisting of a discrete set of plane waves whose wave vectors are the reciprocal lattice vectors ($\mathbf{G}$) of the crystal, and each electronic wave function can be written as a sum of plane waves (Equation 2.28).

$$\Psi_{i,k}(\mathbf{r}) = \exp[i\mathbf{k} \cdot \mathbf{r}] f_i(\mathbf{r}) \quad (2.27)$$

ⁱSo the energy obtained from the functional $E_0[\rho_0]$ is an upper bound to the true ground state energy, E_0 , unless the exact ground state density is known.

$$\Psi_{i,k}(\mathbf{r}) = \sum_G c_{i,\mathbf{k}+\mathbf{G}} \exp[i(\mathbf{k}+\mathbf{G}) \cdot \mathbf{r}] \quad (2.28)$$

Bloch's theorem means that electronic states are allowed only at a set of $\mathbf{k}$ points determined by the boundary conditions of the bulk solid. Therefore an infinite number of electrons is accounted for by an infinite number of $\mathbf{k}$ points but with only a finite number of states at each $\mathbf{k}$ point. The problem of how to calculate this infinite number of wavefunctions is solved by the fact that $\mathbf{k}$ points that are very close together are very similar. Thus calculation at a single $\mathbf{k}$ point represents one area in $\mathbf{k}$ space and it is only necessary to perform a finite number of calculations. The electronic wave functions at each $\mathbf{k}$ point can be expanded in terms of a discrete plane-wave basis set. In principle an infinite plane-wave basis set is required to expand the electronic wave functions, however waves of lower kinetic energy are more important than higher energy, so the basis set can be truncated to include waves below a certain cut-off. The result is that by sampling a suitable number of $\mathbf{k}$ points (formally the sampling points for Brillouin zone integration) and selecting a suitable plane-wave cut-off energy, it is possible to solve the electronic wave functions and within DFT calculate a good approximation to E_{HK} and therefore all the properties of the system.

2.12.2 CASTEP Code^{91,92}

CASTEP is a software package which uses density functional theory to provide a good atomic-level description of materials and molecules and was used for all DFT calculations in this Thesis. It employs pseudopotentials, which replace the pure Coulomb potential of a positively charged nucleus with the combined electrostatic potential of the (positive) nucleus and the (negative) core electrons. Having this weaker potential makes solving the Schrödinger equation simpler. The program then attempts to minimise the total energy functional, E_{HK} .

Through the use of CASTEP, information can be gained about total energies, forces and stress in an atomic system. In addition optimum geometries, band structures, optical spectra, phonon spectra, molecular dynamics and so on may be calculated. In this Thesis four types of calculation were performed; single-point energy, geometry optimisation, phonon, and molecular dynamics. Before performing any of the latter three calculations it is desirable to perform checks to see if the selected plane wave cut-off energy and $\mathbf{k}$ point sampling will produce an accurate result. These checks may be performed on simple results of single-point energy calculations that are observed to converge to a limit when an appropriate $\mathbf{k}$ point sampling or plane wave cut-off energy is used. These simple results are *i)* the internal energy; *ii)* the atomic forces on any atom; and *iii)* the stress on the unit cell. These convergence tests are necessary for if the cut-off energy or $\mathbf{k}$ point sampling are set too high or too frequently respectively then valuable computation time may be wasted for little improvement in the quality of information gained. This process was performed for $\text{Li}(\text{NH}_3)\text{BH}_4$ and $\text{Mg}(\text{NH}_3)_6\text{Cl}_2$ for which data in Appendix A show that convergence was achieved using a $\mathbf{k}$ point sampling of $0.08 \text{ \AA}^{-1}$ and a plane wave cut-off of 500 eV for both materials. These values were kept consistent for all $\text{Li}(\text{NH}_3)_n\text{BH}_4$ and $\text{Mg}(\text{NH}_3)_n\text{X}_2$ calculations due to the similarities of the materials and to add a level of consistency to the calculations. All calculations were performed within the generalised gradient approximation (GGA) using the Perdew Burke Ernzerhof (PBE) exchange correlation functional.⁹³

Single-point Energy

Single-point energy calculations compute the energy of a particular, fixed, arrangement of atoms. These are used in calculating the convergence criteria, and are also useful in calculating relative energies of a specific molecular or structural orientation. The result of these calculations is the internal energy of the structure, that is the energy of the arrangement of atoms with respect to a reference state where all

nuclei and electrons are infinitely separated from each other and at rest, this energy may be thought of as a ‘quantum enthalpy of formation.’

Geometry Optimisation

Geometry optimisation calculations use an optimisation algorithm to compute a minimum energy state of the system within energy and atomic force criteria. Though a powerful technique, the force minimised structure is not necessarily the most stable nor does its calculation guarantee that it will ever exist in reality. The algorithm will simply find the nearest local energy minima, not the global minima, and thus must be treated with caution. Two different regimes were used; ‘rough optimisations’ which locate atoms to allow for atomic forces less than $0.05 \text{ meV}\text{\AA}^{-1}$ which is deemed appropriate for structural information, and ‘fine optimisations’ which locate atoms to allow for atomic forces less than $0.001 \text{ meV}\text{\AA}^{-1}$ and are necessary for further phonon or molecular dynamics calculations.

Calculated bond lengths are rarely identical to those observed experimentally, and it should not be expected that they are. In the case where calculated bond lengths are shorter than those observed it may be due to the anharmonicity of the real system, calculations are carried out within the harmonic oscillator approximation and the anharmonicity of a real oscillating bond may result in longer bond lengths at higher temperatures as shown in Figure 2.13. A bending bond observed using diffraction or other averaging techniques may be seen as shorter than the same bond in a calculation. This is because when a moving or disordered atom is observed, the geometric average atomic position will be seen. If the atom is moving in an arc then the geometric average will be inside the radius of this arc and a shorter bond is observed, as shown in Figure 2.14.

The energy result of these calculations is used to calculate various enthalpies of reaction using Hess’s Law. This is possible because the internal energy is related

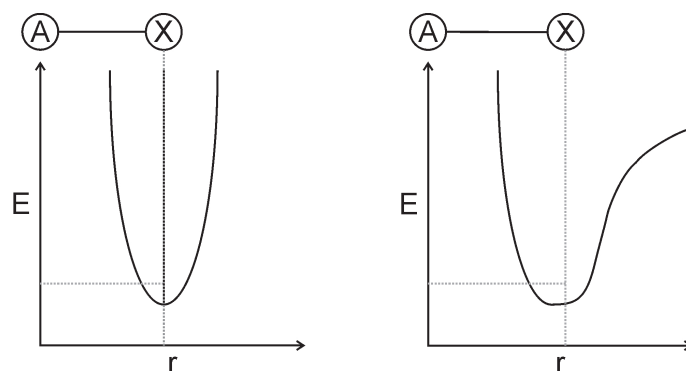


Figure 2.13: A sketch diagram to indicate how anharmonic bending or stretching bonds may appear longer in diffraction experiments (right) than in calculations (left).



Figure 2.14: A sketch to indicate how bending bonds may appear shorter in diffraction experiments (right) than in calculations (left).

to the enthalpy as shown in Equation 2.29. Where reactions involve a change in the amount of gas present as well as a change in solid phases, the dV term may be approximated to dV_{gas} as the change in the solid volume is negligible. Another consideration is that the calculations do not include any zero-point energy so will contain an error of the order of a few kJmol^{-1} .

$$dU = dH + pdV \quad (2.29)$$

Uncertainties in Optimised Atomic Positions

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Uncertainties in atomic positions are not typically quoted for calculated structures as they are for ones determined by diffraction or other experimental methods. A level of uncertainty or error may be inherent in any calculation given the method,

in the case of DFT the choice of convergence parameters (the cut-off energy and $\mathbf{k}$ point sampling), the GGA exchange correlation functional and the pseudopotentials discussed in this Section all contribute to this uncertainty. Errors resulting from use of the specific GGA exchange correlation functional or pseudopotential are largely unavoidable and hard to quantify. However, selection of the convergence parameters based on convergence testing *v.s* means that the errors in forces do not exceed those specified in the calculation, so a reasonable approximation can be made. In this Thesis, ‘rough optimisations’ allow for atomic forces (ΔF) less than $0.05 \text{ meV}\text{\AA}^{-1}$ and ‘fine optimisations’ allow for atomic forces less than $0.001 \text{ meV}\text{\AA}^{-1}$. Given a known force constantⁱⁱ, k , and assuming a simple harmonic oscillator it is reasonable to describe the atomic displacement, Δr , caused by a force as

$$\Delta r = \frac{\Delta F}{k} \quad (2.30)$$

where

$$k = (2\pi v)^2 \mu \quad (2.31)$$

$$k = \left(\frac{2\pi E}{h} \right)^2 \mu \quad (2.32)$$

and where μ is the reduced mass, E is the energy of a typical optical phonon frequency and h is Planck’s constant. Using this method the uncertainties in calculated bond lengths and thus atomic positions encountered in this Thesis were calculated and are given in Table 2.5.

Phonon

Phonon-mode calculations give all the vibrational modes of a compound, including the eigenvalues and eigenvectors of each mode. The calculations are performed by

ⁱⁱForce constants are taken from the calculated values given in Appendix D

Table 2.5: The uncertainties in bond length arising from geometry optimisation calculations used in this Thesis

Bond Type	Bond Energy (E) / meV	Uncertainty in ‘Rough’ Optimisation / Å	Uncertainty in ‘Fine’ Optimisation / Å
B–H	290	± 0.0027	± 0.00005
N–H	428	± 0.0012	± 0.00002
Li–N	59	± 0.0129	± 0.0003
Li–B	30	± 0.0543	± 0.0011
Mg–N	35	± 0.0192	± 0.0004

perturbing the atomic positions and then expanding the total energy in a perturbation series, and may be used in a number of ways. In this Thesis, they are used to produce videos of the various vibrational modes, to assess the stability of calculated structures, to calculate INS and Raman spectra, and to calculate the mean squared displacement of atoms at various temperatures. Generally a structure is considered unstable or, at least, worthy of closer inspection, if negative modes are calculated. A negative frequency mode implies a negative spring constant (k) in the description of a harmonic oscillator $E = \frac{1}{2}kx^2$ and thus a local maximum rather than minimum in energy. The consequences of this are shown in Figure 2.15(a-c). The Figure shows a) the situation for a positive value of k with the normal energy curve; b) the situation with a negative value of k resulting in a negatively sloping energy curve; and c) the reality of a negative value of k in which the energy levels would return to normal after some small displacement, resulting in a double-well potential. This is of course the most simple case, and each calculation of negative modes should be treated independently.

With phonon mode data it is possible to calculate mean squared displacement of atoms at a given temperature. In the harmonic approximation, the displacement tensors ${}^v\mathbf{B}_l$ of an atom l , vibrating in a mode v with a frequency ω_v and at temperature T , may be calculated using the relationship:⁸⁰

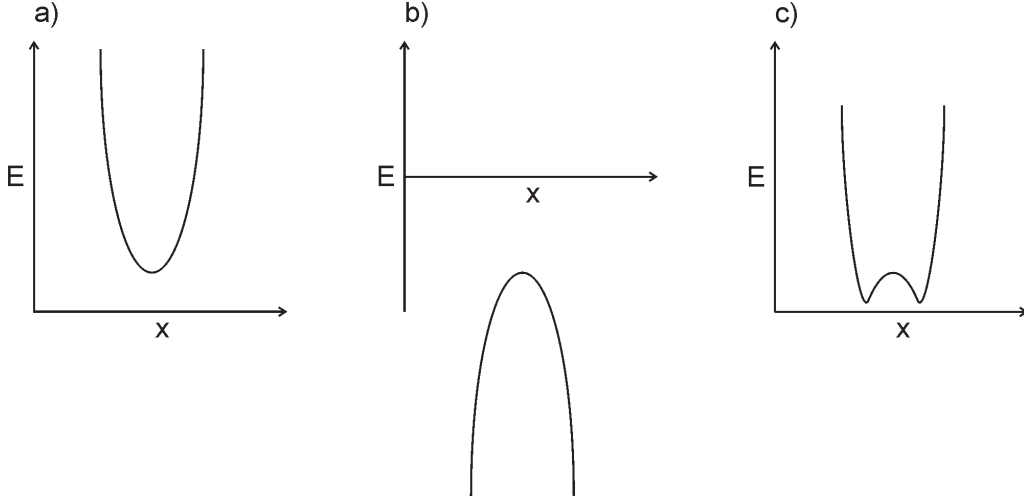


Figure 2.15: The energy curves $E = \frac{1}{2}kx^2$ for a) a positive value of k ; b) a negative value of k ; and c) a more realistic vision of a negative value of k .

$${}^v\mathbf{B}_l = {}^v u_l^2 \frac{16.9}{\mu\omega_v} \coth \frac{1.47\omega_v}{T} \quad (2.33)$$

where ${}^v u_l^2$ is the mean squared displacement of atom l and μ is the reduced mass. The individual modes are orthogonal to one another and their displacements follow a Gaussian probability distribution. Given the quadrature convolution properties of a Gaussian distribution, the total mean squared displacement of an atom at a given temperature may be calculated by summing the contributions of all the individual modes, thus:⁸⁰

$$\mathbf{B}_l = \sum_v {}^v\mathbf{B}_l(T) \quad (2.34)$$

This process was performed using a script written by Dr. Timmy Ramirez-Cuesta, and though important to consider any negative modes in these calculations it was found that their inclusion or rejection had little impact on the observed mean squared displacement of atoms.

Molecular Dynamics

Molecular dynamics (MD) calculations simulate the motion of atoms within a solid. Calculations were performed using the NVE ensemble, which maintains a constant number of particles, volume and total energy, and represents unconstrained Newtonian dynamics of the atoms with a fixed cell volume. This ensemble was chosen, with the advice of Philippe Aeberhard, as it allowed the simplest and most appropriate viewing of the motion of atoms. The value of the energy that is conserved in the calculations is the sum of the potential energy (calculated by DFT at each time step) and the kinetic energy of the ionic cores which are treated as classical particles (Born-Oppenheimer molecular dynamics). In this Thesis, the ionic velocities were randomly chosen from a Maxwell-Boltzmann distribution at 150 K, such that the total linear momentum was zero and the instantaneous temperature matched that specified and calculated using the ideal gas thermometer shown in Equation 2.35). Calculations were performed starting from the optimised structures at an MD temperature of 150 K and using a time step of 0.5 ps. Following a 3.0-6.0 ps equilibration period in which the overall kinetic energy, and therefore the temperature, was fixed by the Gaussian isokinetic thermostat,⁹⁵ a production run of 5.0 ps in the NVE ensemble was performed, during which the temperature was free to vary but typically remained close to 150 K.

$$T = \frac{2}{3Nk_B} \sum_{i=1}^N \frac{m_i \|\mathbf{v}_i\|^2}{2} \quad (2.35)$$

where N is the number of atoms, k_B is Boltzmann's constant, m_i is the mass of atom i and $\mathbf{v}_i$ is its velocity.

2.12.3 aClimax

The software package aClimax was used to calculate INS spectra from the results of CASTEP phonon calculations.⁹⁶ It is possible to do this because the intensity of the INS signal is directly proportional to the amplitude of motion and the scattering cross sections of the atoms involved. The program was also used to calculate Raman spectra. Calculated spectra shown in this Thesis include the primary modes, and 1-2, 0-2, 0-3, and 0-4 overtones.

2.13 Phase Transitions⁹⁷

The IGAⁿ and low temperature in-situ diffraction techniques used in this Thesis are very powerful techniques for observing phase transitions. In the solid state, there are three main types of phase transition, they are *i*) first-order; *ii*) second-order; and *iii*) the γ -transition. The type of change can be identified using changes in thermodynamic parameters, and a scheme known as the Ehrenfest classification. Many phase changes are accompanied by changes in volume and enthalpy, these changes have implications for the slopes of the chemical potentials of the phases at either side of the phase transition (μ_α and μ_β). For a transition from a phase α to phase β ,

$$\begin{aligned} \left(\frac{\partial \mu_\beta}{\partial p} \right)_T - \left(\frac{\partial \mu_\alpha}{\partial p} \right)_T &= V_{\beta,m} - V_{\alpha,m} = \Delta_{trs} V \\ \left(\frac{\partial \mu_\beta}{\partial T} \right)_p - \left(\frac{\partial \mu_\alpha}{\partial T} \right)_p &= -S_{\beta,m} + S_{\alpha,m} = -\Delta_{trs} S = -\frac{\Delta_{trs} H}{T_{trs}} \end{aligned} \quad (2.36)$$

When $\Delta_{trs} V$ and $\Delta_{trs} H$ are non-zero, the slopes of the chemical potential plotted against either pressure or temperature are different either side of the transition. So the the first derivatives of the chemical potentials with respect to temperature or pressure are discontinuous at the transition. Transitions where the first derivative with respect to temperature is discontinuous are classified as first-order. For a

second-order transition, the first derivative of the chemical potential with respect to temperature is continuous, but the second derivative is discontinuous. A γ -transition is not first-order, but is one where the heat capacity becomes infinite at the transition temperature (as it does for a first-order transition).

In crystallography, the volume changes associated with phase transitions are relatively easy to observe. For a first-order transition there will be a finite volume change at the transition, while for a second-order there will be no volume change at the transition. Second-order transitions are generally associated with a change in the symmetry of the crystal structure. An example of this is a tetragonal cell expanding faster along its two common directions than along the third, at a point when all the cell lengths are equal the cell will be cubic, and as all the directions are now equivalent, the cell will expand equally along them all. A phase transition has occurred, but there is no discontinuity in the volume so it is second-order.

Lithium Borohydride Ammines

3.1 Introduction

This Chapter focuses on the structural solution of the lithium borohydride ammines: $\text{Li}(\text{NH}_3)_n\text{BH}_4$, with $n = 1, 2, 3$ and 4 . The structural solution is based on X-ray and neutron diffraction, solution and solid state NMR, DFT calculations, and gravimetric analysis techniques. The themes of dihydrogen bonding and structural disorder are frequently addressed, and full structural solution for each phase is presented. Phase transformations are investigated from both experimental and theoretical results and the ammonia storage properties and potential of LiBH_4 are evaluated.

3.2 In-situ Experiments on GEM and HRPD

Isotopically enriched $\text{Li}^{11}\text{BD}_4$ was synthesised from the elements using the high pressure furnace and procedure described in Chapter 2 Section 2.3. The ammines, $\text{Li}(\text{ND}_3)_n^{11}\text{BD}_4$, were then produced in-situ using the IGAⁿ equipment (see Section 2.11.3) on the GEM and HRPD powder diffractometers at ISIS (described in Sections 2.7.1 and 2.7.2 respectively).

A summary of the initial experiment carried out on GEM is shown in Figure 3.1,

where it can be seen that four crystalline phases exist with masses corresponding to $n = 1, 2, 3$ and 4 . The starting sample of $\text{Li}(\text{ND}_3)_4^{11}\text{BD}_4$ was obtained by exposing $\text{Li}^{11}\text{BD}_4$ to ND_3 at a pressure of 1000 mbar for a period of 48 hours. By monitoring the diffraction data and the sample mass, it was possible to reduce the pressure incrementally until the pure phases were observed. The set point pressures used to isolate the phases with $n = 3, 2$, and 1 were 67 mbar, ca. 27 mbar and 3 mbar (with the IGA set to ‘outgas’) respectively, the room temperature during the experiment varied between 19 °C and 20 °C. It should be noted here that although Figure 3.1 represents real time data collection, various sections have been cut from the data to improve clarity. These include a section when the $n = 2$ phase turned amorphous and a pressure increase leading to conversion from the $n = 3$ to the $n = 4$ phase. Ideally these data would be of sufficient quality for structure solution however as Figures 3.1 and 3.2 show, intense steel reflections are present in the data. There is also significant overlap of $\text{Li}(\text{ND}_3)_n^{11}\text{BD}_4$ reflections as shown in Figure 3.2. The combination of these factors is enough to require more diffraction data with greater resolution and ideally no steel reflections. However the useful conclusion remains that 4 distinct crystalline phases exist.

The investigation was furthered using HRPD and the quartz tail of the IGAⁿ reactor which was used for the first time in this experiment, the sample mass and ND_3 pressure data from this experiment are shown in Figure 3.3. Once again, the starting $\text{Li}(\text{ND}_3)_4^{11}\text{BD}_4$ sample was obtained by exposing $\text{Li}^{11}\text{BD}_4$ to ND_3 at a pressure of 1000 mbar, but for a period of 12 hours. Transitions to phases $n = 3, 2$ and 1 were isobaric occurring at a room temperature of between 21 °C and 23 °C, and observed at set-point ammonia vapour pressures of 67 mbar, ca. 24 mbar, and 0 mbar (with the IGA set to ‘outgas’) respectively. The result of using the quartz tail was an increased (quartz) background intensity but a massively reduced appearance of steel reflections. The steel reflections still present are produced by the heating element of the IGAⁿ, as discussed in Section 2.11.3. Crystalline phases

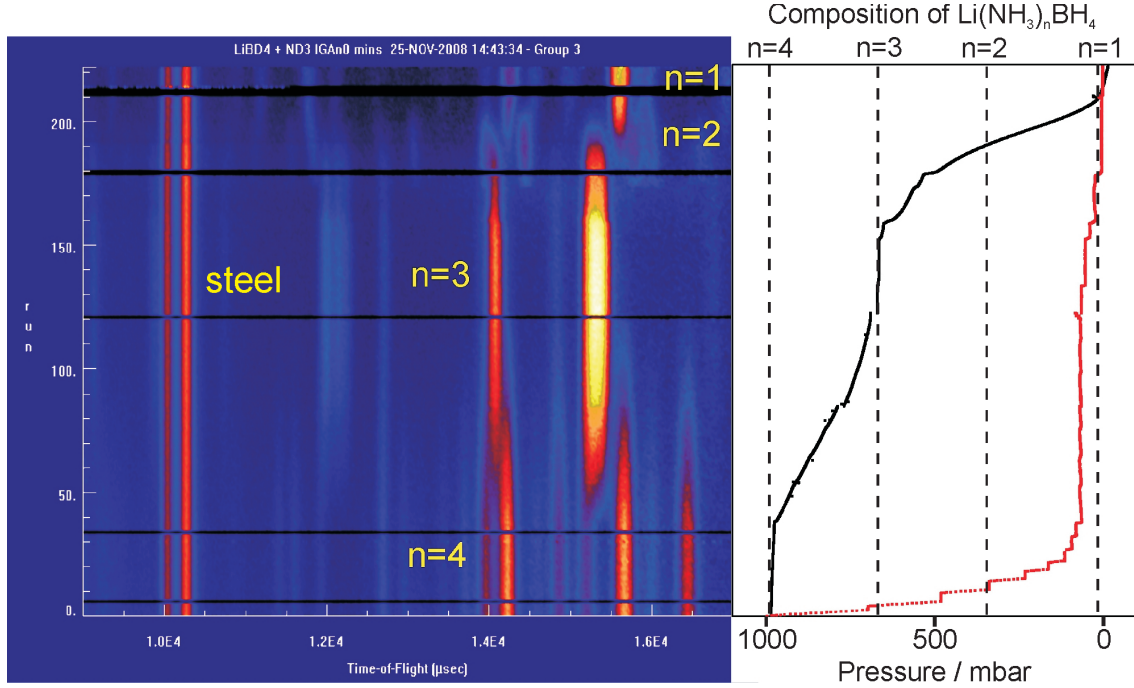


Figure 3.1: A summary of the IGA^n experiment on GEM, showing diffraction data collected using bank 4 on the left hand side (most intense peaks are yellow, background is blue) with sample mass (black) and ND_3 pressure (red) on the right hand side.

were identified for $n = 1, 3$ and 4 , and diffraction data for the $n = 3$ and 4 phases were collected for several beam hours using both of the HRPD chopper settings in order to collect high resolution data over the widest possible range of d-spacings. Data collected at each chopper setting were then normalised and merged into a single set of diffraction data covering the widest possible range of time of flight. These merged data were used for the structural solution discussed in the following Sections. Despite the mass trace showing a plateau at $n = 2$, no Bragg reflections were observed in the diffraction data collected during this period, suggesting that the $n = 2$ phase was present as a liquid as it was for part of the GEM experiment.

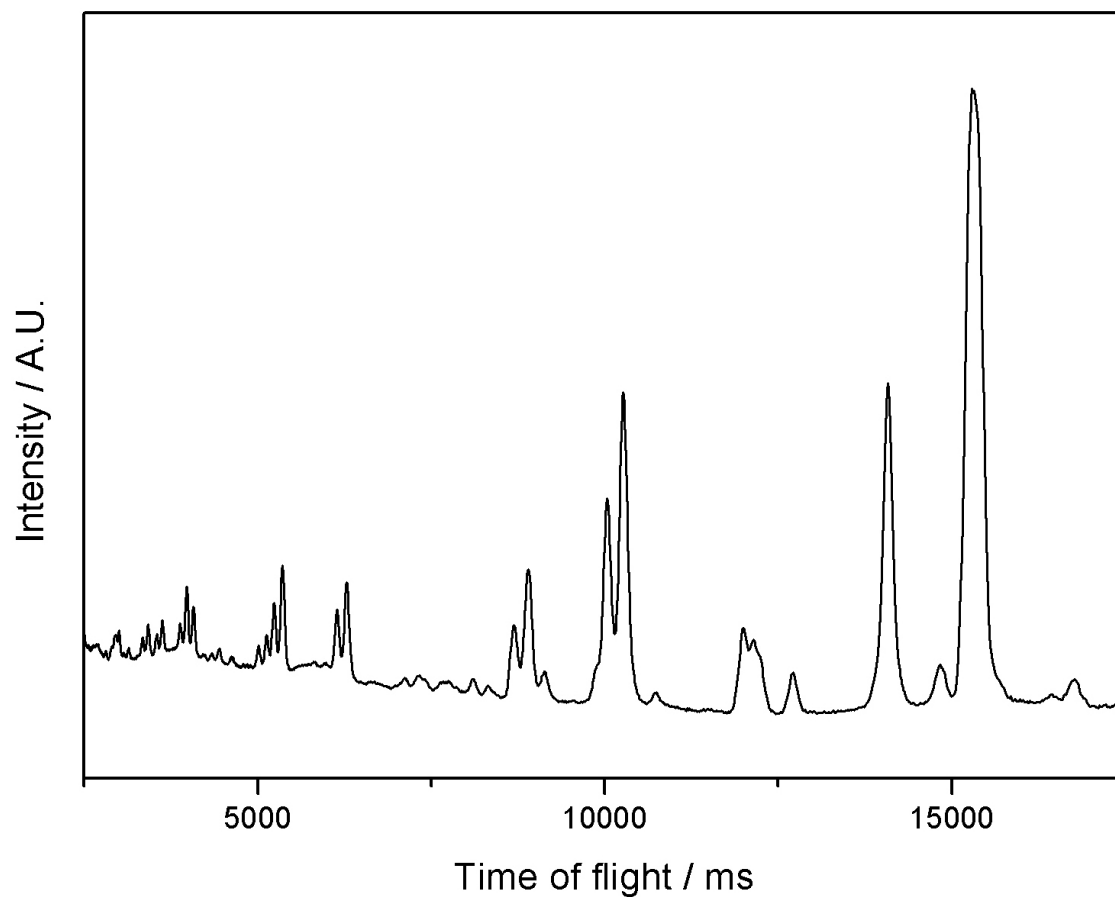


Figure 3.2: An example of the diffraction data for $\text{Li}(\text{ND}_3)_3\text{BD}_4$, collected using bank 4 of GEM. Showing significant peak overlap and steel reflections that appear as the intense doublets at ca. 10,000 ms and below.

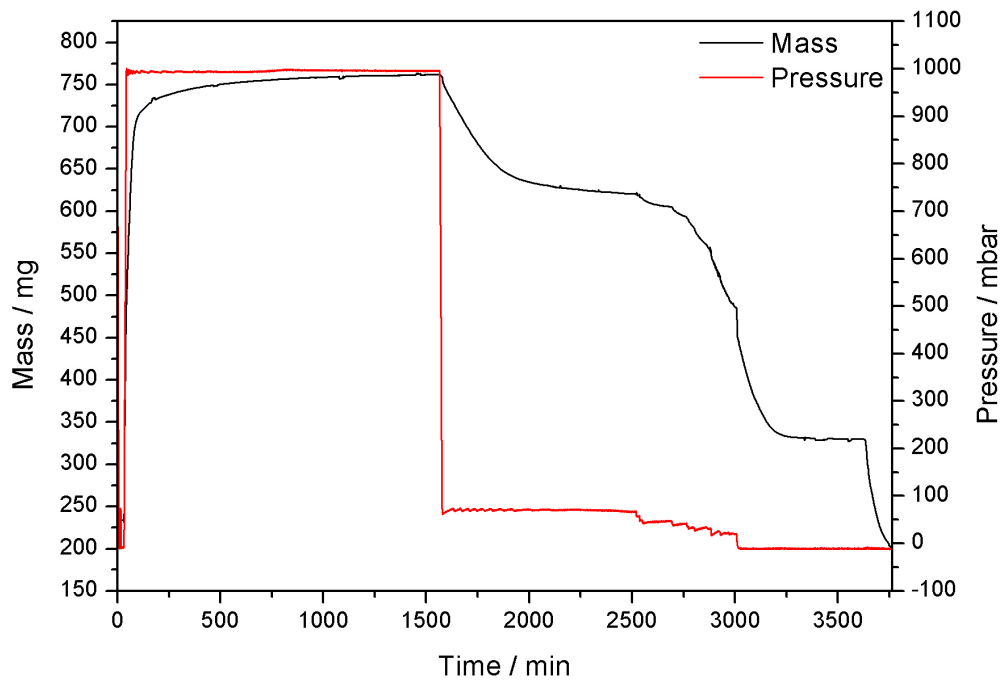


Figure 3.3: The IGAⁿ data from the HRPD experiment. Showing the sample mass, ammonia pressure and isolation of the phases $\text{Li}(\text{ND}_3)_n\text{BD}_4$ at various pressures.

3.3 Lithium Borohydride Monoammine

The monoammine of lithium borohydride exists at room temperature, with a minimal or zero overpressure of ammonia — ex-situ samples were produced as described in Section 2.5, by evacuating a sample of $\text{Li}(\text{NH}_3)_{n \geq 1}\text{BH}_4$ to 1×10^{-2} mbar — thus it has been relatively simple to use a variety of techniques to investigate its structure. The use of a variety of techniques is necessary in order to confirm assumptions made about the structure and to reduce the uncertainty arising from the sole use of diffraction data to solve structures. The principal assumptions to confirm are the presence of NH_3 and BH_4 (and not reaction products such as NH_2BH_3) and the stoichiometry of the samples.

3.3.1 Nuclear Magnetic Resonance

The ^1H NMR spectrum of $\text{Li}(\text{NH}_3)\text{BH}_4$ in THF-d_8 is shown in Figure 3.4 and confirms the presence of the NH_3 molecule and BH_4^- anion. The peaks are assigned as follows: δ ^1H (300Hz): 0.745 (3H, NH_3); 0.081, 0.351, 0.622, 0.892 (1:1:1:1 quartet, $^1\text{J}(^{11}\text{B}^1\text{H}) = 81\text{Hz}$) (BH_4 , ^{11}B); 0.214, 0.304, 0.395, 0.485, 0.575, 0.665, 0.756 (1:1:1:1:1:1:1 multiplet, $^1\text{J}(^{11}\text{B}^1\text{H}) = 27\text{Hz}$) (BH_4 , ^{10}B). The spectrum shows a classic splitting of the BH_4 signal, consisting of 4 and 7 peak multiplets in the ratio of 4:1 caused by coupling of ^1H to the 80 % naturally abundant ^{10}B (with spin $I = 3/2$) and 20 % naturally abundant ^{11}B (with spin $I = 3$). The peak corresponding to the ammonia molecule is broad, and no coupling between ^1H and ^{15}N or ^{14}N is observed. Given that THF solvent peaks appear despite using a deuterated solvent, it is possible that proton exchange between the solvent and ammonia has occurred resulting in a scrambling of the expected splitting, and peak broadening. The broadening could also be due to the coupling of the protons and the ^{14}N nuclear spin-lattice through interaction of the ^{14}N quadrupolar moment with the axial electric field gradient of the ammonia molecule. The important result with respect to this Thesis is that the

observation of BH_4 and NH_3 signals in solution suggests that these species exist in the solid state and that no aminolysis or other competing reaction has occurred. The integrated areas below the NH_3 and BH_4 peaks should be in the ratio 3:4, the observed ratio of 2.9:4 may be due to some loss of ammonia on solvation in addition to some proton exchange between the solvent and ammonia molecules.

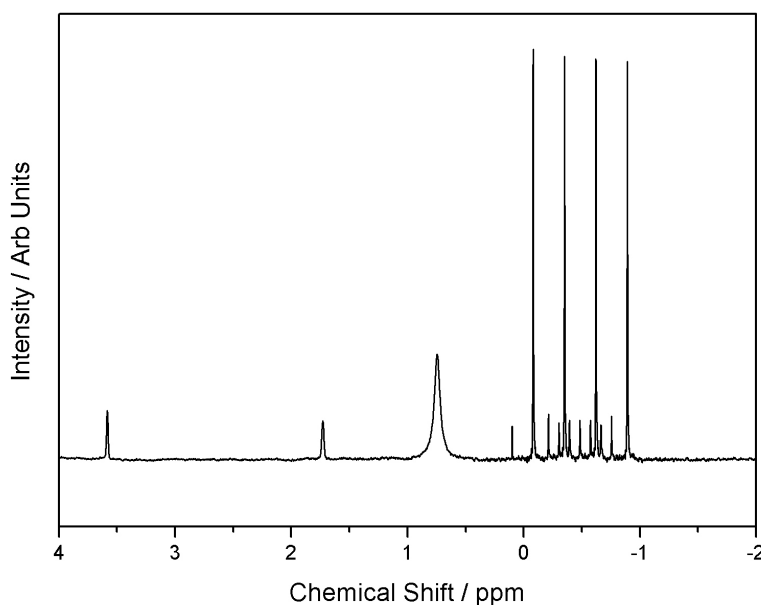


Figure 3.4: The THF- d_8 solution state ^1H NMR spectrum of $\text{Li}(\text{NH}_3)\text{BH}_4$, confirming the presence of NH_3 (broad singlet at 0.7 ppm) and BH_4 (1:1:1:1 quartet and multiplet centered around -0.5 ppm), referenced against the THF peaks at 1.73 ppm and 3.58 ppm.

The solid state ^{11}B NMR spectrum is shown in Figure 3.5. A single central transition at ca. -41 ppm is observed and confirms the presence of a single boron environment. The value of the chemical shift is very similar to that found for LiBH_4 , this infers not only that the BH_4^- anion is present in the solid but also that it is found in a very similar electronic environment to that in LiBH_4 . The additional minor peaks in the spectrum are spinning side bands as described in Section 2.10.

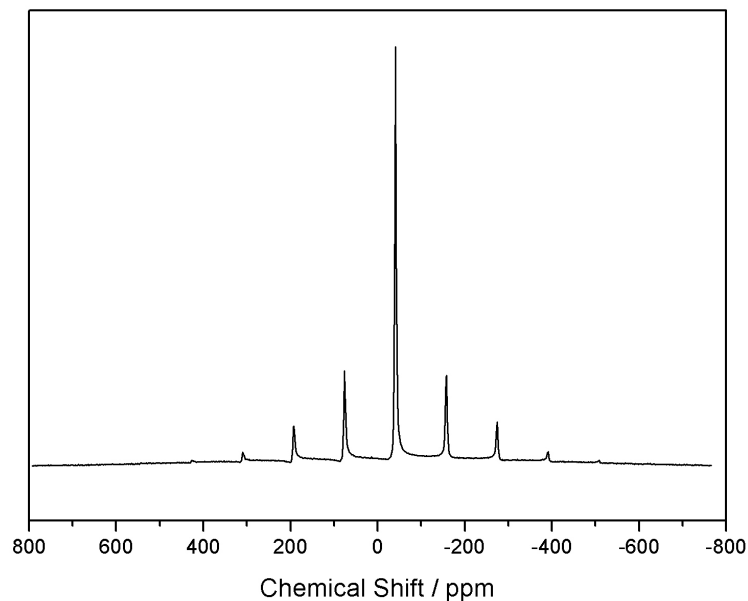


Figure 3.5: The solid state ^{11}B NMR spectrum of $\text{Li}(\text{NH}_3)\text{BH}_4$ showing a single central transition at ca. -41 ppm.

3.3.2 Thermogravimetric Analysis

Thermogravimetric analysis data are shown in Figure 3.6. Analysis was carried out using the IGAⁿ apparatus without neutron diffraction, data were collected in ‘outgas’ mode using a heating rate of $2\text{ }^\circ\text{Cmin}^{-1}$. Mass loss was observed to begin at $T_o = 47\text{ }^\circ\text{C}$, with the rate of mass loss beginning to decrease at $140\text{ }^\circ\text{C}$ and the final mass loss plateau reached at approximately $180\text{ }^\circ\text{C}$. The mass trace is uneven, which it is thought is due to gas release causing an uneven jumping of the fairly small powder sample. The total mass loss reaches approximately 40 wt% and it is most likely that this corresponds exclusively to the loss of ammonia. The reduction from the theoretical loss of 44 wt% may be due to incomplete initial formation of $\text{Li}(\text{NH}_3)\text{BH}_4$ or its partial decomposition during storage. Complete formation of the amidoborane side product, LiBH_3NH_2 , upon decomposition would result in a mass loss of only 5 wt% so this is clearly not a major product. However the slightly lower mass loss of than expected could be due to its formation at higher

temperatures, in this case 90 % of the ammonia would be given off, with 10 % forming the amidoborane. If this were the case then the ammonia storage potential upon subsequent ammonia cycles may be dramatically reduced. The decomposition product and reversibility are discussed further in Section 3.7.

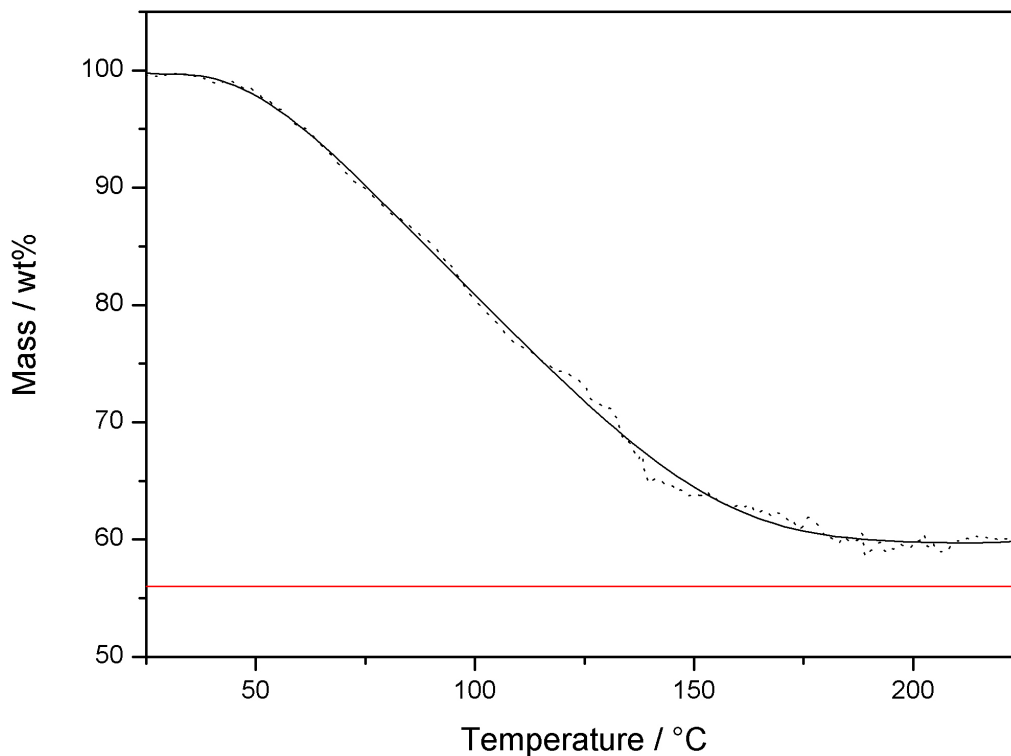


Figure 3.6: IGA data for $\text{Li}(\text{NH}_3)\text{BH}_4$, showing the sample mass in black and the mass loss corresponding to complete conversion to LiBH_4 in red. The raw mass loss data are shown as a dotted line, while fitted data are shown as a solid line.

3.3.3 Diffraction

Although the standard synthetic method produced a polycrystalline sample, it was also possible to grow single-crystals of $\text{Li}(\text{NH}_3)\text{BH}_4$ using the alternative method described in the Chapter 2. The growth of single-crystals was possible due to the formation of a liquid phase on reduction of ammonia vapour pressure during synthesis. It is expected that this liquid phase is an $\text{LiBH}_4 \cdot n\text{NH}_3$ solution, and slow evaporation of NH_3 from this solution allows for crystal growth. It is highly possible that with careful selection of evaporation temperatures and pressures, single-crystals

of all the phases may also be grown, though this was not attempted. Single-crystals varied in size, with largest observed dimensions of approximately $2 \times 1 \times 1$ mm.

X-ray Powder Diffraction

Bragg peaks in the X-ray powder diffraction pattern were indexed to a new orthorhombic unit cell. A Pawley refinement was performed in DASH using the holosymmetric orthorhombic space group $Pmmm$ and resulted in lattice parameters of $a_I = 5.96784(3)$ Å, $b_I = 4.46339(2)$ Å, $c_I = 14.34206(8)$ Å and a cell volume $V_I = 382.143(2)$ Å³. The extracted integrated intensities were analysed for systematic absences using a Bayesian ranking procedure within DASH. This yielded $Pn - a$ as the most likely extinction symbol, which corresponds to space group $Pn2_1a$ and its centrosymmetric supergroup $Pnma$. In principle, with single-crystal diffraction, it is possible to discriminate between these two space groups by an analysis of intensity statistics. However, with powders it is generally not possible to detect the presence or absence of a centre of symmetry. In such cases, it is most reasonable to presume that the material is centrosymmetric unless there is a strong physical reason to assume otherwise or if further refinement results in a significantly superior fit using the non-centrosymmetric space group.

Comparison with the parent LiBH_4 , which belongs to the space group $Pnma$, with $a_0 = 7.17858(4)$ Å, $b_0 = 4.43686(2)$ Å and $c_0 = 6.80321(4)$ Å, cell volume $V_0 = 216.685(3)$ Å³, shows a close similarity of the b-axis parameters and suggest a structural relationship between the two phases. Comparison of the unit-cell volumes for LiBH_4 and $\text{Li}(\text{NH}_3)\text{BH}_4$ suggests that $Z = 4$ formula units per unit cell for $\text{Li}(\text{NH}_3)\text{BH}_4$ as is the case for LiBH_4 . This leaves the approximate excess volume for each NH_3 molecule of $(382 - 217)/4$ Å³ = 41 Å³ which is consistent with the volumes of ammonia molecules seen in other amines.³³

While it is attractive to begin to model $\text{Li}(\text{NH}_3)\text{BH}_4$ based upon potential struc-

tural similarities with LiBH_4 , a more general approach is to reduce the symmetry to $Pn2_1a$ and then solve the structure. Unusually, there are no special positions in $Pn2_1a$ implying that global optimisation methods will explore all molecular orientations and positions, and simultaneously explore both $Pn2_1a$ and $Pnma$. The structure was solved using the simulated annealing process within the program DASH, which (as described in Section 2.6.4) uses a Z-matrix formalism to describe molecular conformation in terms of internal coordinates. Three Z-matrices were used that described *i*) one BH_4^- tetrahedral unit; *ii*) one NH_3 molecule; and *iii*) one Li^+ ion. A global minimum was repeatedly found that placed all three non-hydrogen atoms at $(x, \sim 3/4, z)$ close to the mirror plane in $Pnma$ — this is also found in LiBH_4 . Locating these atoms at $(x, 3/4, z)$ and adopting the space group $Pnma$, the structure was refined using the Rietveld method in TOPAS. No improvement in the Rietveld fit was found by retaining the lower $Pn2_1a$ symmetry. Given the difficulty in obtaining precise hydrogen positions using X-ray powder diffraction, constrained BH_4^- and NH_3 geometries were used during Rietveld refinement. Ideal tetrahedral coordination was enforced for BH_4^- , while all N–H distances and H–N–H angles were restrained to be equivalent to a free NH_3 molecule. The final results of the refinement are given in Appendix Table E.1, the final fit to the data is shown in Figure 3.7 and the structure is discussed in Section 3.3.5.

X-ray Single Crystal Diffraction

Although the structure has already been solved from the powder data, the superior structural solution possible with single-crystal data serves as a useful check of the structure refined from the powder data. Furthermore, the use of single-crystal data allows for far more accurate positioning of the hydrogen atoms and the use of more sophisticated models, with fewer constraints, compared to those which are sensible to use in analysis of powder data. The structure was solved (with the assistance of Dr. Francesca Fabbiani) by direct methods using the program SIR92, and refined against

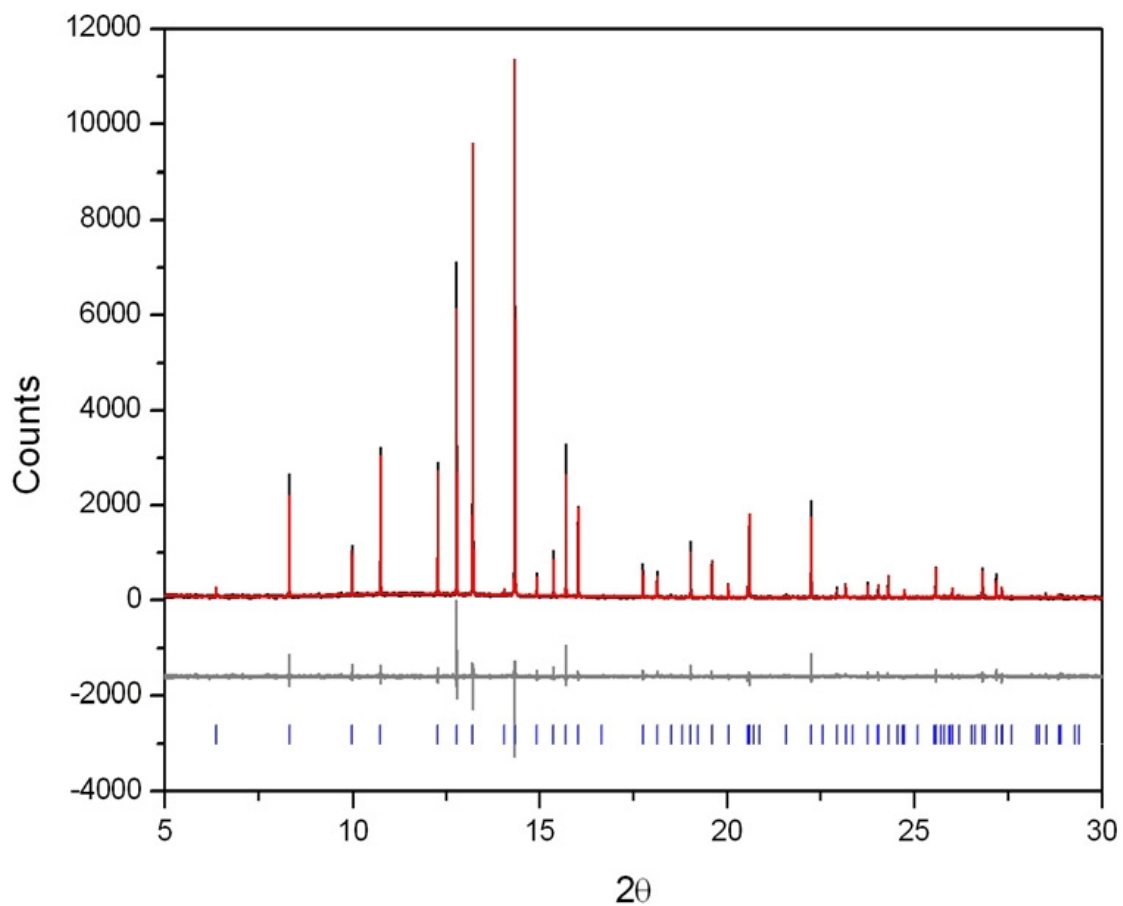


Figure 3.7: Final fit to the data for Rietveld refinement of the $\text{Li}(\text{NH}_3)\text{BH}_4$ model to X-ray powder diffraction data collected at the ESRF with a wavelength $\lambda = 0.79825 \text{ \AA}$. Space Group = $Pnma$, $R_{wp} = 5.7\%$, $R_{exp} = 2.6\%$, $\chi^2 = 4.81$. Experimental data are shown in black, calculated in red with the difference in grey, tick marks show the expected positions of Bragg reflections.

F^2 using all the available data with the program CRYSTALS (described in Section 2.6.4). All non-H atoms were modelled with anisotropic displacement parameters. H atoms attached to B were located in difference Fourier maps and their positions and isotropic atomic displacement parameters freely refined. The difference Fourier maps indicated disorder of the ammonia H atoms, thus three refinement models with varying levels of disorder associated with the NH_3 molecule were investigated; *i*) a model with ordered hydrogen atoms; *ii*) a model with disordered hydrogen atoms; and *iii*) a model with the hydrogen atom electron density distributed evenly around a ring.

The σ site symmetry of N is only compatible with the molecular C_{3v} symmetry of the NH_3 molecule given an alignment of one of the N–H bonds (in this case N1–H5) on the $(x, 1/4, z)$ mirror plane. This is the basis for the formation of the ordered model, which features large isotropic temperature factors of the NH_3 hydrogen atoms (see Figure 3.8a). The disordered model allows for positioning of one H atom (H5) with a site occupancy of 0.5 off the $(x, 1/4, z)$ mirror plane thus producing 4 hydrogen sites as shown in Figure 3.8b. Comparison of the two models reveals that the refined isotropic thermal parameter for H5 is smaller in the disordered model ($0.041 \text{ \AA}^2$, c.f. $0.114 \text{ \AA}^2$ in the ordered model), as is the R-factor (3.0 %, c.f. 3.7 % in the ordered model), at the expense of only one extra least-square parameter ($\chi^2 = 1.08$ c.f. 1.15 in the ordered model). Despite this improvement, the resulting model clearly gives unreasonable H–N–H bond angles and the thermal parameter for H4 is still too large. A satisfactory disordered model for the NH_3 molecule could not be obtained with the available data. An alternative description of disorder, which has been successfully implemented in the program CRYSTALS, involves modelling an annulus of continuous electron density as shown in Figure 3.8c. The occupancy of the annulus was set to 3 and the radius was refined to $0.825(10) \text{ \AA}$, which along with its refined position corresponds to an agreeable N–H bond angle and distance. An isotropic temperature factor, i.e. the thickness of

the annulus, as well as the declination angle between the ring normal and the z-axis of the orthogonal coordinate system were also successfully refined. A final R-factor of 3.2 % was obtained, which though slightly higher than that for the disordered model allows for a chemically reasonable NH_3 molecule. Overall, the experimental evidence suggests there is a high level of rotational disorder of the NH_3 molecule as observed in other compounds with similar NH_3 coordination.⁹⁸ Though it is not possible to tell if this disorder is static or dynamic in its nature. The successful refinement of an annulus of electron density could indicate almost full spinning for $\text{Li}(\text{NH}_3)\text{BH}_4$ at 150 K.

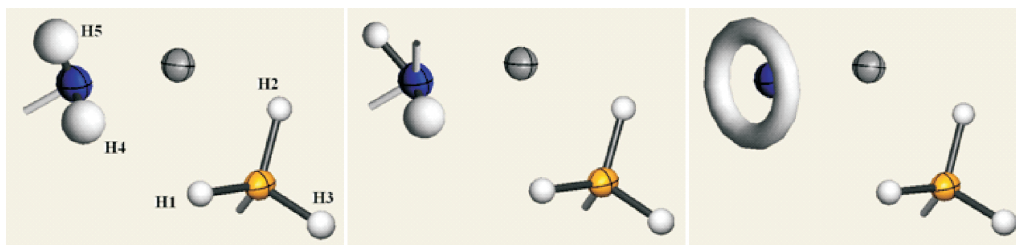


Figure 3.8: Models refined against the X-ray single-crystal diffraction data, from left to right the; a) ordered model; b) disordered model; and c) annulus model.

Full details of the refinement are given in Table 3.2, and the structure is discussed in Section 3.3.5. It is interesting to note at this stage that the presence of local $\text{N}-\text{H}\cdots\text{H}-\text{B}$ interactions is uncertain and cannot be unequivocally established given the presence of disorder. The relevant data for both the ordered and disordered models are given in Table 3.1. In both models, $\text{N}-\text{H}\cdots\text{HB}$ and $\text{B}-\text{H}\cdots\text{HN}$ angles fall within the range seen in other compounds exhibiting dihydrogen bonds. However in the ordered model, the minimum $\text{NH}\cdots\text{HB}$ distance is $2.425(17)$ Å which, greater than the sum of van der Waals radii for the H atoms, suggests the absence of dihydrogen bonding. On the contrary when the disordered model is analysed, the minimum $\text{NH}\cdots\text{HB}$ distance is $2.282(15)$ Å, which does suggest some degree of dihydrogen bonding and highlights the importance of establishing the nature of the disorder within these systems.

Table 3.1: Observed H...H distances and angles in Li(NH₃)BH₄, obtained from refinement of the ordered and disordered models against the X-ray single-crystal diffraction data.

Distance Description	Distance / Å	Angle Description	Angle / °
<i>Ordered Model</i>			
H ₄ ...H ₁	2.457(19)	N-H ₄ ...H ₁	159.7(3)
H ₄ ...H ₃	2.54(2)	N-H ₄ ...H ₃	143.0(15)
H ₅ ...H ₃	2.425(17)	N-H ₅ ...H ₃	146.2(8)
Mean	2.49	Mean	150.3
		B-H ₁ ...H ₄	102.7(7)
		B-H ₃ ...H ₄	98.5(6)
		B-H ₃ ...H ₅	156.8(8)
		Mean	104.4
<i>Disordered Model</i>			
H ₄ ...H ₁	2.448(17)	N-H ₄ ...H ₁	163.0(4)
H ₄ ...H ₃	2.57(3)	N-H ₄ ...H ₃	142.1(9)
H ₅ ...H ₃	2.282(15)	N-H ₅ ...H ₃	166.1(6)
Mean	2.43	Mean	157.1
		B-H ₁ ...H ₄	104.1(6)
		B-H ₃ ...H ₄	98.7(11)
		B-H ₃ ...H ₅	146.4(8)
		Mean	116.4

Table 3.2: The atomic coordinates obtained from the Rietveld refinement of the ordered model of Li(NH₃)BH₄ against X-ray single-crystal diffraction data. Space Group = *Pnma*, $R_{wp} = 11.3\%$, $R_{exp} = 10.6\%$, $\chi^2 = 1.15$.

atom	site	x	y	z	B _{iso} / Å ²
N	N1	0.58929(15)	0.75	0.65008(7)	0.0345(2)
B	B1	0.91710(17)	0.75	0.39957(7)	0.0240(3)
Li	Li1	0.8801(3)	0.75	0.57510(11)	0.0290(3)
H	H1	0.754(2)	0.75	0.4447(9)	0.039(3)
H	H2	1.0749(19)	0.75	0.4481(9)	0.036(3)
H	H3	0.9234(15)	0.539(3)	0.3526(6)	0.046(3)
H	H4	0.494(3)	0.602(4)	0.6402(10)	0.110(6)
H	H5	0.606(4)	0.75	0.7085(11)	0.119(9)

3.3.4 Geometry-optimised Structure

The single-crystal structure from the ordered model was used as a starting point for ‘fine’ DFT geometry optimisation calculations. These calculations were performed due to the requirement for minimal atomic forces to be present in the structure used for phonon calculations, which in-turn were necessary to perform the vibrational spectroscopy analysis discussed in Section 3.3.6. Recently Zhong et al.,⁹⁹ reported a close agreement between their optimised atomic positions and the atomic positions refined from the X-ray powder diffraction data discussed in Section 3.3.3. The optimised atomic positions reported here are also close to those experimentally observed and are given in Table 3.3. The calculations were performed with no symmetry constraints, but (within a tolerance of 0.001 Å) no change from the *Pnma* starting symmetry was observed. The similarities between the two structures are highlighted by the small change in mean bond lengths upon optimisation: B–H changes from 1.151 Å to 1.227(5) Å, N–H changes from 0.845 Å to 1.032 Å, Li–N changes from 2.014 Å to 2.041 Å, and Li–B changes from 2.550 Å to 2.52 Å. The observed global increase in bond lengths at the zero-point energy suggests disorder within the system and significant atomic motion resulting in the geometric mean of the atomic positions being observed in the diffraction data, as discussed in Section 2.12. Significantly the N–H bond length shows the largest change suggesting a large amount of rotational disorder associated with the NH₃ molecule.

3.3.5 Structural Description and Discussion

As mentioned in Section 3.3.3, the structure of Li(NH₃)BH₄ shows many similarities with that of LiBH₄. These similarities are particularly clear when both structures are viewed along the common short b-axis, as shown in Figure 3.9. The lithium cations in LiBH₄ are tetrahedrally coordinated by four BH₄[−] anions while each BH₄[−] anion is coordinated by four Li⁺ cations. In Li(NH₃)BH₄, each Li⁺ cation is tetra-

Table 3.3: The calculated atomic coordinates from the ‘fine’ geometry optimisation of the $\text{Li}(\text{NH}_3)\text{BH}_4$ structure.

atom	site	x	y	z
N	N1	0.57232(4)	0.75	0.64392(2)
B	B1	0.9254(2)	0.75	0.40042(8)
Li	Li1	0.87440(8)	0.75	0.57321(3)
H	H1	0.743780(9)	0.75	0.443390(2)
H	H2	0.935260(9)	0.52798(1)	0.349880(4)
H	H3	0.086570(9)	0.75	0.455940(4)
H	H4	0.470300(4)	0.566470(5)	0.630300(2)
H	H5	0.599310(4)	0.75	0.715590(2)

hedrally coordinated by three BH_4^- anions and one NH_3 molecule while each BH_4^- anion is linked to three Li^+ cations and four NH_3 molecules. The BH_4^- anion exhibits η^2 bonding to Li^+ , with Li–B bond distances of 2.474(1) Å and 2.545(1) Å. The observed BH...HN bond distances are 2.160 Å and 2.284 Å, these suggest the presence of some dihydrogen bonding though none that is a great deal stronger than Van der Waals forces. These distances are taken from the optimised structure as it provides the most realistic bond lengths when considering a potentially disordered system. In LiBH_4 , the $\text{Li}(\text{BH}_4)_4$ tetrahedra are linked in edge-sharing chains that run along the b-axis and are vertex-linked to neighbouring chains. $\text{Li}(\text{NH}_3)\text{BH}_4$ is composed of similar chains of edge sharing $\text{Li}(\text{NH}_3)(\text{BH}_4)_4$ tetrahedra though the polarity of the NH_3 molecule stops vertex-linking between chains resulting in the increased separation seen in Figure 3.9. The structures in Figure 3.9 show polyhedra of nearest neighbours to the Li^+ cation, more standard molecular views are presented in Figures 3.30 and 3.34, the immediate tetrahedral coordination of the Li^+ cation is shown clearly in Figure 3.14.

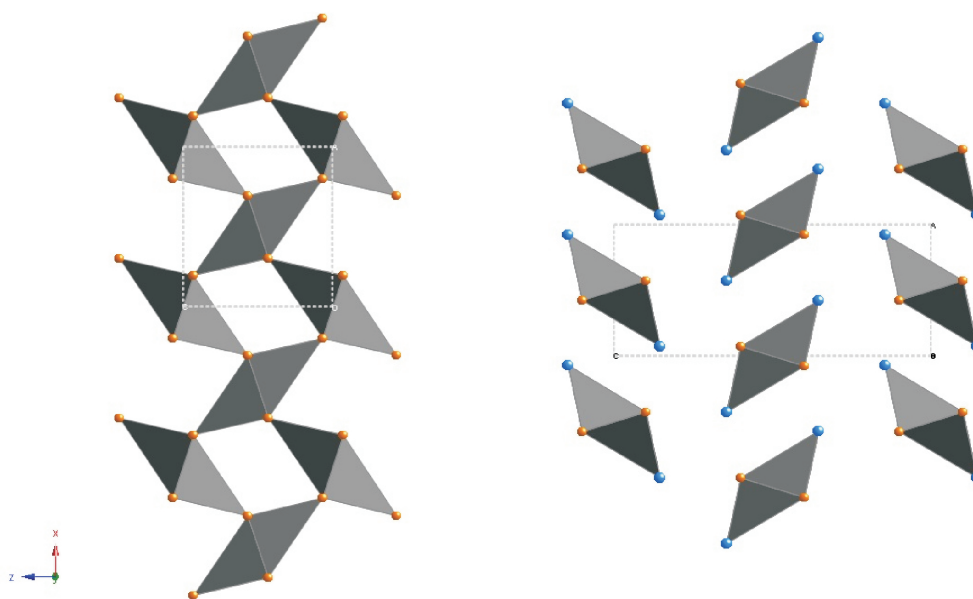


Figure 3.9: A comparison of the LiBH_4 and $\text{Li}(\text{NH}_3)\text{BH}_4$ structures, viewed down the y -axis. Hydrogen atoms are omitted for clarity, Li atoms are shown in grey, boron in brown and nitrogen in blue. $\text{Li}(\text{NH}_3)(\text{BH}_4)_3$ polyhedra are shown in grey.

3.3.6 Inelastic Neutron Scattering and Raman Spectroscopy

Vibrational spectroscopy data (INS and Raman spectroscopy) were collected as described in Chapter 2 Sections 2.8 and 2.9. The calculated and experimental INS spectra for $\text{Li}(\text{NH}_3)\text{BH}_4$ are shown in Figures 3.10 and 3.11, with the equivalent Raman spectrum shown in Figure 3.13. There is a good qualitative agreement between the calculated and observed spectra, though some discrepancy between the absolute (observed and calculated) frequencies. These differences are expected to some degree given that the calculated spectra are based on phonon modes calculated at 0 K, while the experimental spectra were collected at 20 K and 298 K for the INS and Raman data respectively. The calculation of these modes is non-trivial and errors of the magnitude seen in this work are common in many other reported studies.^{100,101} A potential source of error in comparison of the calculated and observed INS spectra is caused by the use of naturally abundant B samples rather than the isotopically enriched, and preferable, ^{11}B for which the spectra simulation methods at ISIS are

based. Modes involving B atoms will lack intensity in the observed spectra due to ^{10}B neutron absorption, and in addition the lower mass of ^{10}B will lower the frequency of certain modes. The presence of lower frequency modes of ^{10}B will have a line broadening effect due to superposition of two very similar spectra, though to some extent this will be negated by the minimal intensity of ^{10}B modes caused by absorption. However, the dominant features of spectra will be caused by the 80 % abundant ^{11}B and more importantly the hydrogen atoms connected to the boron (involved in all the boron modes), thus both the observed and calculated spectra should be similar. The combination of Raman and INS spectra show the vibrational behaviour of the compound in detail across a large range of frequencies, to a degree that would be hard to achieve using one technique alone. An important conclusion drawn from the strong agreement between the observed and calculated frequencies in both spectra is that the calculated phonon modes are realistic. A complete table of these calculated modes and their assignments is provided in Appendix Table D.1.

One of the most interesting features of the calculated modes are those at low and negative frequencies. Negative modes were calculated at -44 cm^{-1} and -21 cm^{-1} , and while these are often indicative of an inherent instability in the calculated structure in this case they are more suggestive of the atomic motion present under normal conditions. The mode at -21 cm^{-1} corresponds to the in-phase libration of ammonia molecules as shown in Figure 3.12, whilst the mode at -44 cm^{-1} shows less well defined anti-phase libration. The implication of this and the observation of a number of other low frequency librational modes at 24 cm^{-1} , 42 cm^{-1} and 68 cm^{-1} is that there is a non or minimal barrier to the rotation of the ammonia molecule. This corroborates the disorder seen in the single-crystal diffraction analysis.

A notable feature of the Raman experimental spectrum is the mode observed at around 3215 cm^{-1} , which does not appear in the calculated spectrum. The spacing between the principal mode at 3296 cm^{-1} and the side-band is around 81 cm^{-1} . It is

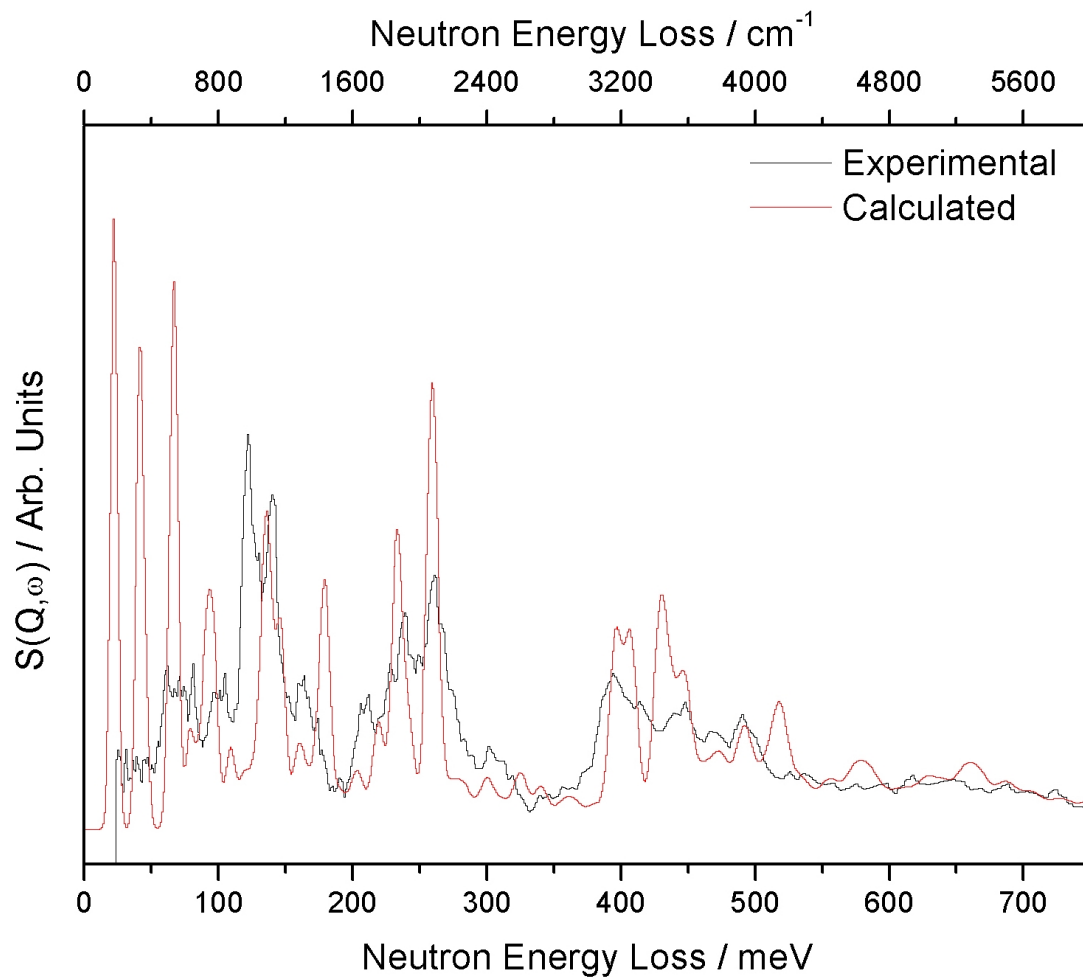


Figure 3.10: The experimental (black) and calculated (red) INS spectra for $\text{Li}(\text{NH}_3)\text{BH}_4$, shown between 0 meV and 750 meV.

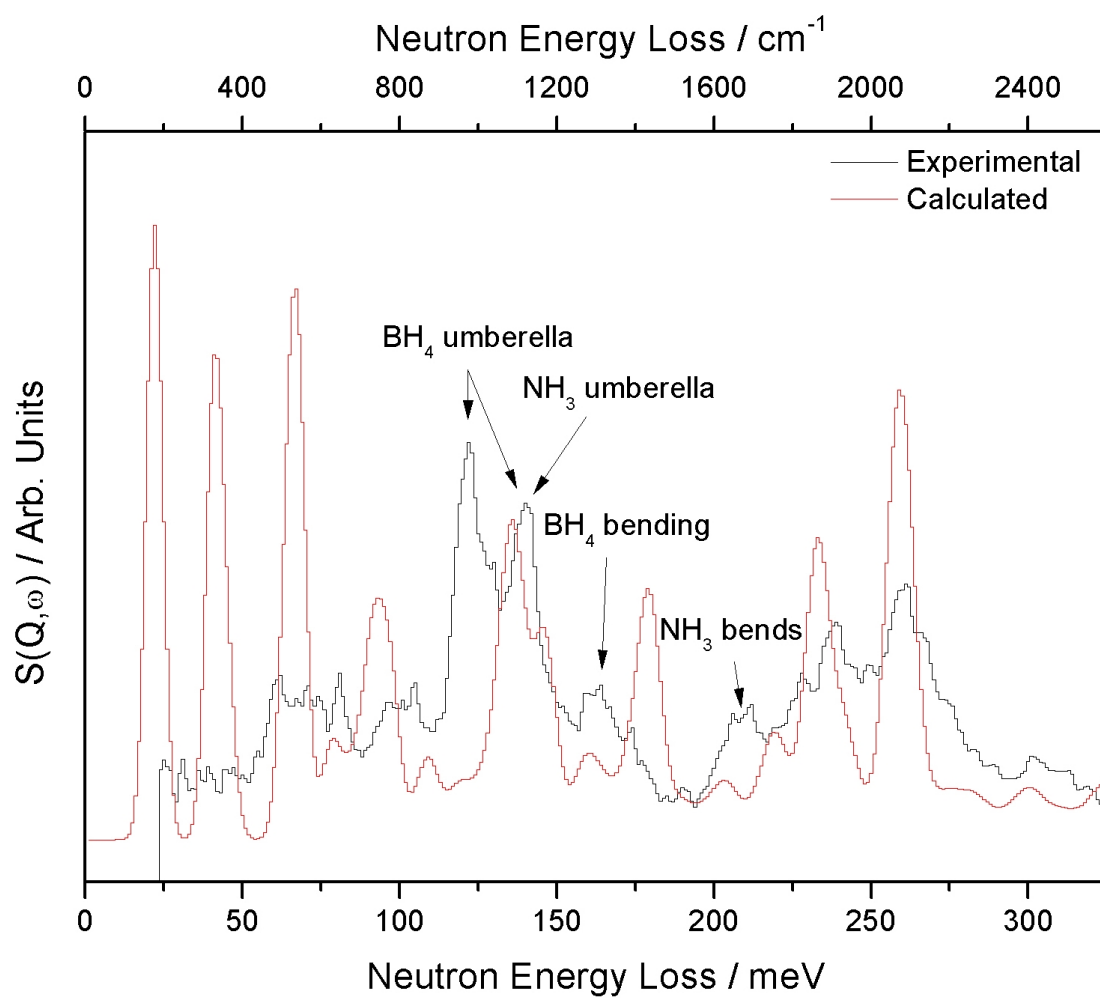


Figure 3.11: The experimental (black) and calculated (red) INS spectra for $\text{Li}(\text{NH}_3)\text{BH}_4$, shown between 0 meV and 350 meV with the position of important modes labelled.

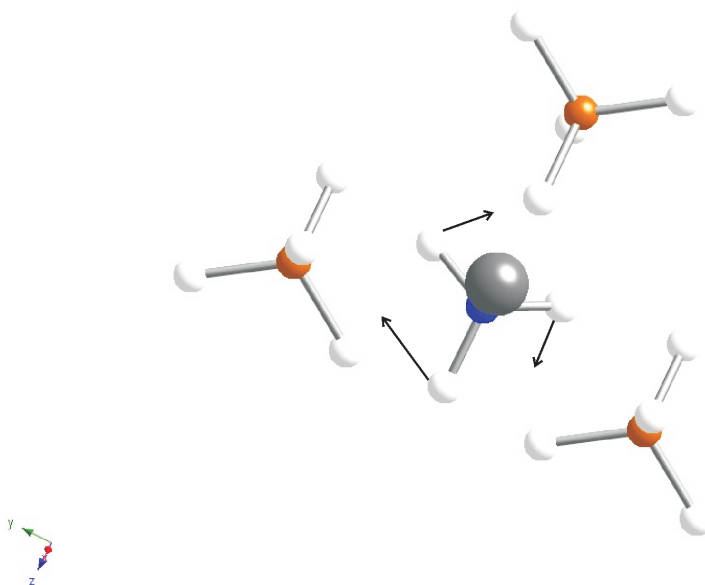


Figure 3.12: A depiction of the calculated phonon mode at -21 cm^{-1} in $\text{Li}(\text{NH}_3)\text{BH}_4$, with arrows representing the eigenvectors of the mode. Lithium is shown in grey, boron in brown, nitrogen in blue and hydrogen in off-white.

suggested that this side-band is caused by vibration-rotation coupling between NH_3 stretches and rotations. Inspection of the INS data suggests that the excited mode is the one that appears at 81 cm^{-1} , there are several calculated NH_3 librational modes in this region appearing at 68 cm^{-1} , 94 cm^{-1} and 98 cm^{-1} .

In Section 2.12, the process of calculating the Gaussian probability distribution from phonon modes is described; Figure 3.14 shows the result of these calculations at 150 K and 298 K in a single $\text{Li}(\text{NH}_3)(\text{BH}_4)_3$ unit. The massive thermal ellipsoids of the NH_3 hydrogen atoms compared to the B, Li, and N atoms show clearly the low energy barrier to NH_3 rotation and corroborate the large amount of disorder seen in the diffraction data at 150 K. The image of the 298 K structure suggests that almost unhindered spinning of the ammonia molecule occurs at room temperature. This is the case because in practice these ellipsoids would never be a perfect circle and they should never overlap, so in this example they represent a spinning molecule. There is very little change in the size of the thermal ellipsoids on the borohydric hydrogen atoms from 150 K to 298 K, especially in comparison to those of the ammonia

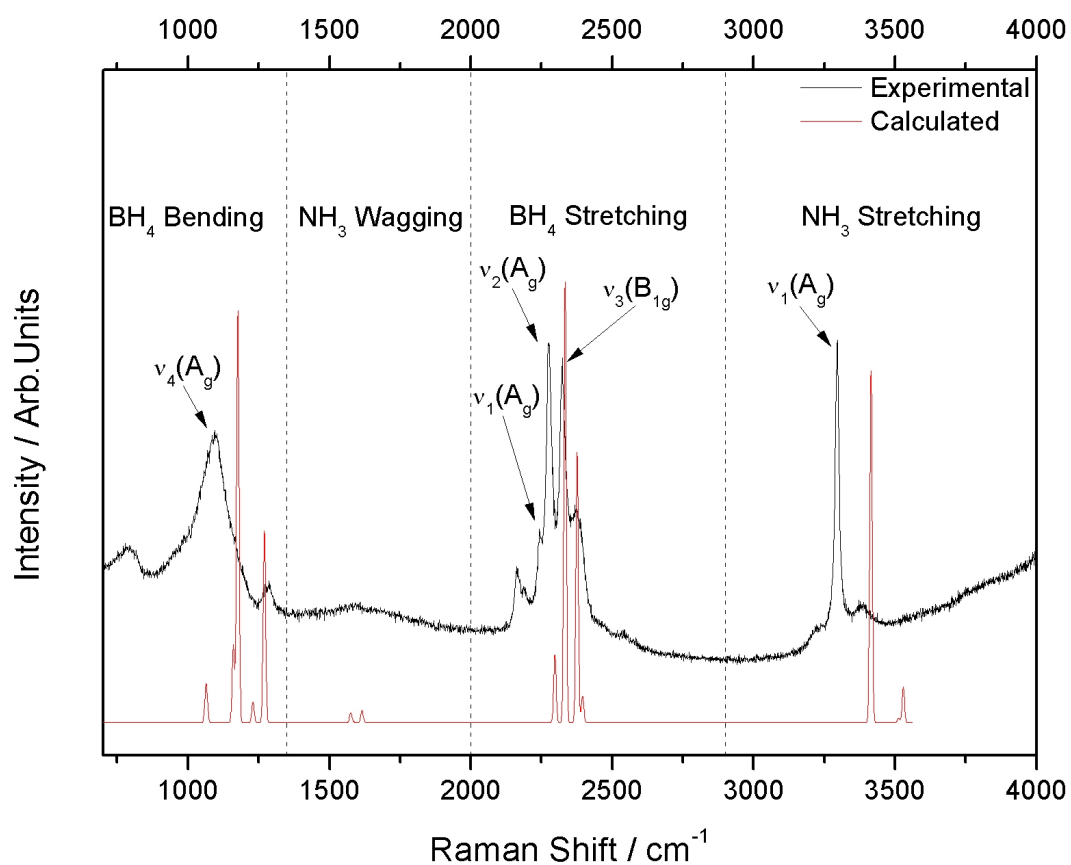


Figure 3.13: The observed and calculated Raman spectra for $\text{Li}(\text{NH}_3)\text{BH}_4$ with the position of important modes labelled.

molecule. This is to be expected given that it is primarily the low energy and highly populated modes that will contribute to the atomic motions at these temperatures, and not the higher energy BH_4 bends and stretches.

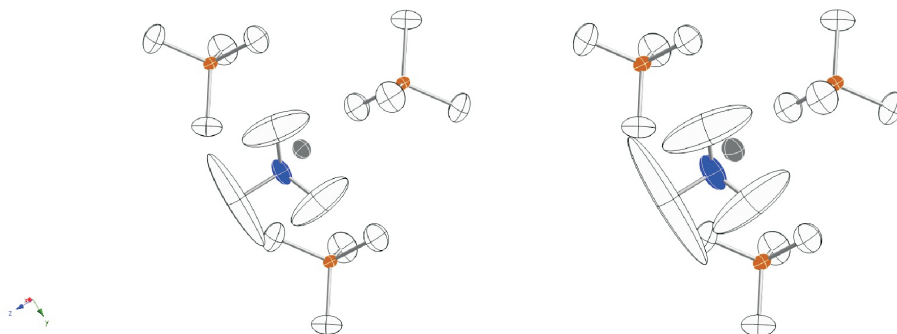


Figure 3.14: The calculated 50 % probability distributions for the mean squared displacement of atoms at 150 K (left) and 298 K (right) for a single $\text{Li}(\text{NH}_3)(\text{BH}_4)_3$ unit in $\text{Li}(\text{NH}_3)\text{BH}_4$.

In their recent publication, Zhong et al. suggested that $\text{Li}(\text{NH}_3)\text{BH}_4$ would decompose to give ammonia at 291 K and hydrogen at 371 K.⁹⁹ Observation of the mean squared displacements at these temperatures does not offer any real insight into this reaction, as they show no unexpected changes other than a straightforward extrapolation from Figure 3.14. However, a comparison of the BH_4 stretches with those reported by Racu et al. for LiBH_4 ,¹⁰⁰ confirms a weakening of the B–H bonds that must be caused by the presence of NH_3 . The calculated and experimental Raman spectra for $\text{Li}(\text{NH}_3)\text{BH}_4$ at 298 K are shown in Figure 3.13, and a comparison of the observed data and those given by Racu is shown in Table 3.4. While comparison of many of the modes is complex due to the simultaneous movement of NH_3 and BH_4 , the internal stretching modes of BH_4 do not involve the motion of any other atoms so may be compared like for like. Given the low resolution of these observed Raman data, and the 2nd overtones of the BH_4 bending modes present in the BH_4 stretching region, unambiguous assignment of the stretching modes via the Raman spectrum alone is not possible. However, strong corroboration with the calculated spectrum means the strongest modes may be reliably assigned. The $\nu_1(A_g)$

stretching mode which corresponds to all the H atoms moving in-phase in the B–H direction, features in the Raman spectra for both compounds and is shifted from 2273 cm^{-1} (2392 cm^{-1} calculated) to 2243 cm^{-1} (2298 cm^{-1} calculated) on addition of ammonia to LiBH_4 . The other directly comparable stretches are also shifted to lower wavenumbers, and provide direct evidence for weakening of the B–H bonds. This weakening is presumably caused by dihydrogen bonding and although a mode that may indicate this through simultaneous B–H and N–H stretching is not seen, a number of modes involving BH_4 and NH_3 libration, rocking, and bending are seen and detailed in Appendix Table D.1.

The symmetrical $\nu_1(A_g)$ NH_3 stretching mode, is observed at 3296 cm^{-1} and calculated to appear at 3416 cm^{-1} . There are no convenient comparisons to be made with other amines in the literature as there was for the BH_4 modes with LiBH_4 . However, Raman and infra-red spectra of other amines with comparable coordination environments have been reported. The comparison here is drawn between the symmetrical NH_3 stretch in solid-state compounds where the ammonia molecule is coordinated to the metal centre, the stretch is seen at; 3247 cm^{-1} in $\text{Zn}(\text{NH}_3)\text{Br}_2$, 3260 cm^{-1} in $\text{Ni}(\text{NH}_3)_6\text{Cl}_2$, and 3220 cm^{-1} in $\text{Cd}(\text{NH}_3)_6\text{Cl}_2$.^{102–104} These modes are observed at similar wavenumbers to the title compound, but all are at lower wavenumbers, it is suggested that in these compounds, the N–H bond is weakened by M–N interactions that are stronger than the Li–N interactions. This gives some explanation to the hydrogen release observed by Guo et al., from $\text{M}^{\text{II/III}}\text{X}_{2/3}$ doped $\text{Li}(\text{NH}_3)\text{BH}_4$ which may be a result of $\text{M}^{\text{II/III}}(\text{NH}_3)_n$ complex formation resulting in a weakening of the N–H bond. This combined with the weakening of the B–H bond observed here may lead to low-temperature hydrogen release.¹⁰⁵ The reason for the differences seen in the frequencies of these modes would be interesting to investigate further, but is beyond the scope of this Thesis.

Table 3.4: A comparison of the assignment of calculated and observed, internal and external, BH_4 modes in the Raman spectra of LiBH_4 (reported by Racu et al.) and $\text{Li}(\text{NH}_3)\text{BH}_4$ (from this Thesis).¹⁰⁰

Mode	$\text{Li}(\text{NH}_3)\text{BH}_4$		LiBH_4	
	Observed Frequency 298 K / cm^{-1}	Calculated Frequency / cm^{-1}	Observed Frequency 300 K / cm^{-1}	Calculated Frequency / cm^{-1}
		<i>internal bending</i>		
A_g		1063	1090	1063
A_g		1161	1240	1235
$v_4(A_g)$	1270(3)	1286	1320	1312
		<i>internal stretching</i>		
$v_1(A_g)$	2243(3)	2298	2273	2329
$v_2(A_g)$	2275(3)	2333	2298	2372
$v_3(B_{1g})$	2324(3)	2377	-	2388
A_g	-	2396(3)	2319	2414

3.3.7 Variable Temperature Powder X-ray Diffraction

In-situ X-ray powder diffraction is an excellent technique for the investigation of the thermal stability of materials. In addition to determining the crystal structure of $\text{Li}(\text{NH}_3)\text{BH}_4$ at room temperature, diffraction data were also collected at the ESRF in 2 °C intervals from 20 °C until the sample capillary broke as a result of raised gas pressure at ca. 54 °C. A full Rietveld analysis of $\text{Li}(\text{NH}_3)\text{BH}_4$ was performed at each temperature step and shows a positive thermal lattice expansion seen in Figure 3.15. The expansivities for the a-axis and c-axis are $\Delta a/a = 3.6(1) \times 10^{-4}$ and $\Delta c/c = 5.1(1) \times 10^{-4}$ respectively. Both are essentially linear from 20 °C to 54 °C although there is a small increase in $\Delta c/c$ as the decomposition temperature is approached. The short b-axis has a much smaller expansion as a function of temperature with $\Delta b/b = 8(1) \times 10^{-5} \text{ K}^{-1}$ below 38 °C; above 38 °C, there is a discernible decrease in the rate of expansion which correlates closely with the onset of the decomposition of $\text{Li}(\text{NH}_3)\text{BH}_4$ seen in the TGA (see Section 3.3.2). The c-axis shows the greatest rate of change, this is likely due to the fact that as ammonia leaves the structure voids are opened up. Inspection of the structure shows that it is most compressible along the longest side of the unit cell which thus shows the

greatest rate of change.

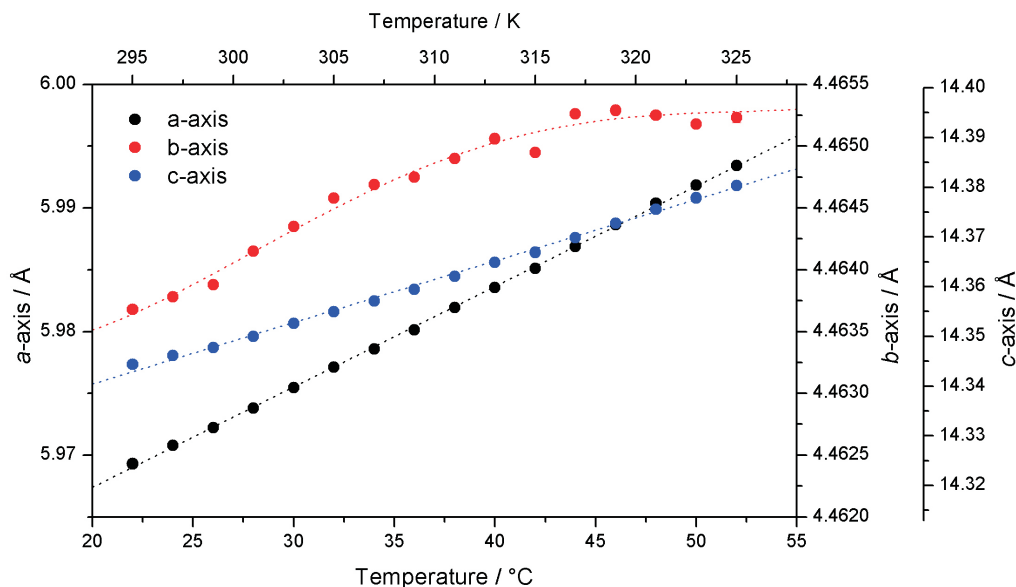


Figure 3.15: The refined lattice parameters for $\text{Li}(\text{NH}_3)\text{BH}_4$ between 22 °C and 54 °C. Error bars are included but where not visible are hidden by datum markers.

The amount of $\text{Li}(\text{NH}_3)\text{BH}_4$ present in the capillary can be assessed by plotting the scale factor associated with this phase as a function of temperature as shown in Figure 3.16. There is a small decrease in the scale factor up to 38 °C and an approximately 30 % decrease between 38 °C and 50 °C. At 50 °C, there is an abrupt drop while at 54 °C there are no detectable Bragg peaks. Examination of the sealed capillary following heating showed that it had exploded, and this explosion is attributed to a release of the absorbed ammonia. This decomposition temperature similar but slightly higher than that observed in the thermogravimetric analysis discussed in Section 3.3.2. Some difference is expected given the difference in experimental conditions, with TGA being carried out under a minimal vapour pressure of ammonia and higher pressure conditions existing inside the sealed capillary. In this case the differences are not worth investigating further, particularly as the thermodynamic conditions inside the capillary are poorly defined and pressure increase within the capillary may, as observed, suppress the decomposition temperature. Also the sam-

ple may be at a higher temperature than expected as significant beam heating can occur using high energy synchrotron light sources.

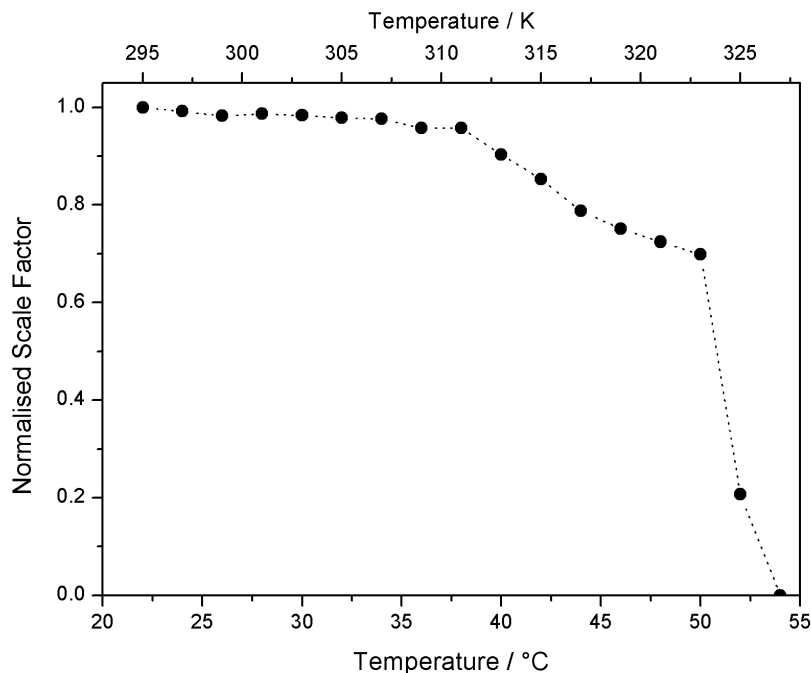


Figure 3.16: The refined scale factors for $\text{Li}(\text{NH}_3)\text{BH}_4$ between 38 °C and 50 °C.

3.3.8 Molecular Dynamics

Molecular dynamics calculations give a unique view of the likely atomic motions at a given temperature. In this case they were used to inspect the molecular motion at 150 K, the same temperature that the single-crystal diffraction data were collected. Calculations were carried out as described in Section 2.12 using time steps of 0.5 fs over a total period of 5 ps and with an equilibration period of 3.0 ps. One of the most useful ways to use the results of this calculation is a qualitative analysis based on the animation of molecular motion, analysis of this sort shows that 1) the NH_3 molecule rotates quickly, jumping between low energy sites where it spends most time, in jumps lasting between 0.5 fs and 2 fs; 2) Li^+ cations are the most mobile non-hydrogen atom, moving significantly in the y-direction; and 3) BH_4^- anions

do not rotate but oscillate about a fixed position (ie. they are not disordered). Results that can be easily pictured are displayed in Figure 3.17, where it can be seen that there is negligible movement of atoms in the z-direction, although they are all highly mobile in the y-direction. An interesting feature of this mobility is that the rows of $\text{Li}(\text{NH}_3)(\text{BH}_4)_3$ tetrahedra diffuse in opposite directions. The movement of the atoms is not obviously correlated, though this could be revealed with further calculation. These results corroborate with all the others discussed in this Section. Though many data may be extracted from these calculations (particularly with respect to ionic mobility and conductivity), such in-depth computational analysis would not befit the main body of this work.

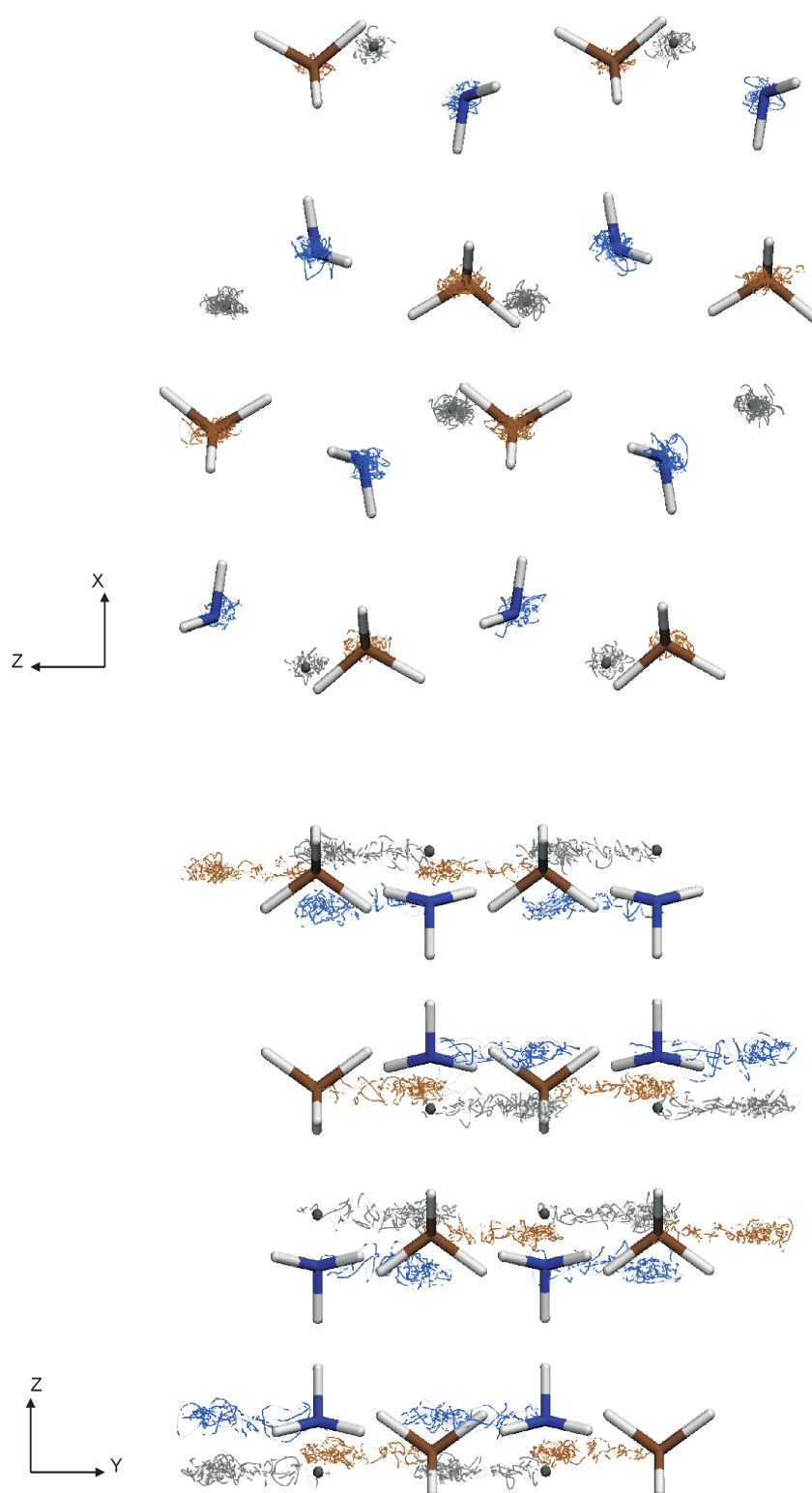


Figure 3.17: The calculated movement of Li (grey), N (blue) and B (brown) atoms in $\text{Li}(\text{NH}_3)\text{BH}_4$ at 150 K, with points representing atomic positions at 0.5 fs intervals over a period of 5 ps, viewed down the y-axis and x-axis, top and bottom respectively.

3.4 Lithium Borohydride Diammine

Structural studies of lithium borohydride diammine proved challenging; as discussed in Section 1.6 and shown in Figure 3.18, this compound exists as a liquid at temperatures of around 15 °C and above. The IGAⁿ equipment offers poor control of temperature in this region, and it was not possible to develop appropriate equipment to control ammonia gas pressure at low-temperatures. Although a crystalline phase of appropriate mass was briefly observed in the GEM-IGAⁿ experiment, the quality of the GEM data are not good enough to refine a structural model. By evacuating a sample of $\text{Li}(\text{NH}_3)_n\text{BH}_4$, where $n \geq 2$, at a temperature of 0 °C it was possible to isolate the $\text{Li}(\text{NH}_3)_2\text{BH}_4$ phase, however attempts to collect diffraction data at Diamond beamline I11 were unsuccessful due to practical difficulties of loading a sample with such a low melting point into a 0.7 mm capillary tube. Despite these problems the phase was observed in some X-ray powder diffraction data, and was characterised using these data and DFT calculations.

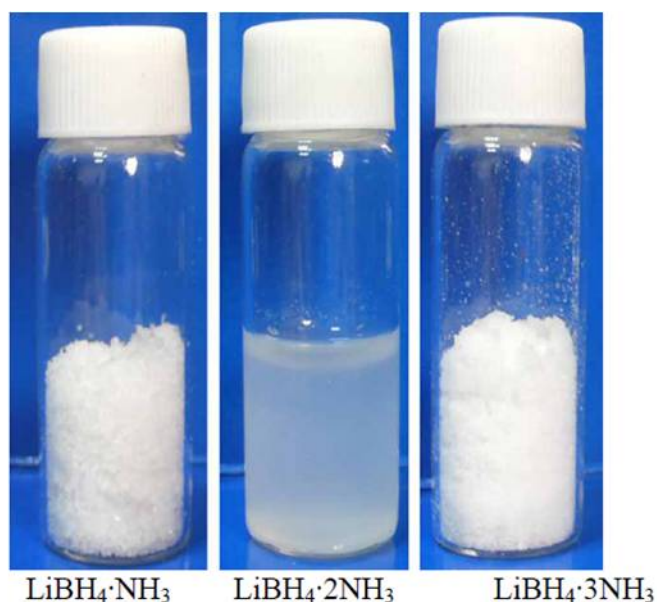


Figure 3.18: The $n = 1, 2$ and 3 phases of $\text{Li}(\text{NH}_3)_n\text{BH}_4$ isolated under ammonia pressures by Guo et al.¹⁰⁵

3.4.1 Diffraction

X-ray Powder Diffraction

An unknown phase was observed in diffraction data of a sample produced by reaction between liquid ammonia and lithium borohydride at $-78\text{ }^{\circ}\text{C}$. On repeated attempts using the same method only the single phase $\text{Li}(\text{NH}_3)\text{BH}_4$ was observed. The unknown phase was indexed in an orthorhombic cell with refined lattice parameters of $a = 9.6227(4)\text{ \AA}$, $b = 4.44268(2)\text{ \AA}$, $c = 13.75357(6)\text{ \AA}$, and cell volume $V = 587.959(4)\text{ \AA}^3$. Via Pawley refinements and extinction symbol analysis in DASH the space group $Pnma$ was chosen. The structure was then solved by simulated annealing in DASH, using four Z-matrices representing one BH_4^- tetrahedral unit, two NH_3 molecules and one Li^+ ion. As was the case with $\text{Li}(\text{NH}_3)\text{BH}_4$, discussed in Section 3.3.3, simulated annealing was performed in the lower symmetry space group $Pn2_1a$ in order to explore a wider number of possible solutions. The obtained solution was then refined using the Rietveld method in TOPAS, and using the centrosymmetric space group, $Pnma$. The similarities with $\text{Li}(\text{NH}_3)\text{BH}_4$ and LiBH_4 are seen not only in the unit cells that feature a common short b-axis, but also in the highly similar arrangement of atoms that is also implied in this case by the common space group. The final fit to the data is shown in Figure 3.19, the goodness of fit parameters, $R_{wp} = 12.146$, $R_{exp} = 5.649$, $\chi^2 = 4.62$, show a relatively poor fit of the model to the data though observing the fit, this can be largely attributed to the poor fit of the peak at $2\theta = 6.7\text{ }^{\circ}$ despite the good fit to the large number of remaining peaks which give the model increased credibility. It is also strange that this phase is seen to coexist with LiBH_4 as one may expect only $\text{Li}(\text{NH}_3)\text{BH}_4$ and LiBH_4 to exist together, however the thermodynamics of the phase transitions are not well known and it may be possible for these phases to coexist (especially in a capillary environment). For example, $\text{Li}(\text{NH}_3)\text{BH}_4$ could ‘dissociate’ into $\text{Li}(\text{NH}_3)_2\text{BH}_4$ and LiBH_4 under certain conditions. The similarities to $\text{Li}(\text{NH}_3)\text{BH}_4$ which along with

the similar bond lengths and atomic positions found in the geometry optimisation calculations strengthen the case that this is the correct structure, as discussed further in Section 3.4.3. The structure is discussed further in Section 3.4.2.

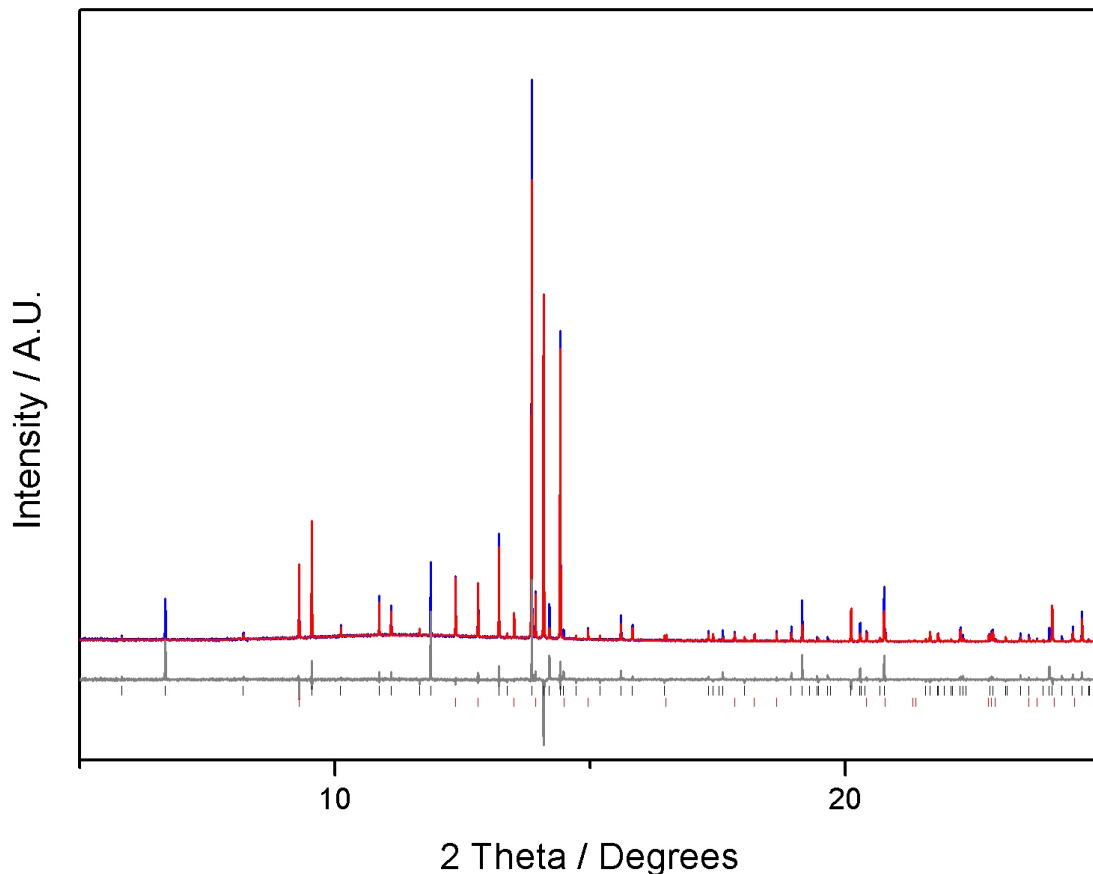


Figure 3.19: Final fit to the data for Rietveld refinement of the $\text{Li}(\text{NH}_3)_2\text{BH}_4$ model to X-ray powder diffraction data, data were collected at the ESRF with a wavelength $\lambda = 0.8022$ Å. Space group = $Pnma$, $R_{wp} = 12.146$, $R_{exp} = 5.649$, $\chi^2 = 4.62$. Experimental data are shown in blue, calculated in red with the difference in grey, tick marks show the expected positions of Bragg reflections for $\text{Li}(\text{NH}_3)_2\text{BH}_4$ in black and LiBH_4 in red.

Neutron Powder Diffraction

A phase was observed in the IGAⁿ experiment on GEM that corresponds in mass to $\text{Li}(\text{NH}_3)_2\text{BH}_4$, however this phase turned into a liquid so only very limited diffraction data were collected. The phase was observed again in a vanadium can though the conditions of its production are unrepeatable due to an experimental error: the

experiment was stopped when $\text{Li}^{11}\text{BD}_4$ was formed, with the intention of removing the sample from the IGAⁿ and collecting diffraction data with the sample in a vanadium can. However $\text{Li}^{11}\text{BD}_4$ was not observed, and it is thought that some residual ammonia in the IGAⁿ pipework reached the sample causing conversion into the $n = 2$ phase. The data are also unrefineable due to the small size of the sample recovered from the IGAⁿ producing a poor signal to noise ratio in the data. Though in both cases it was possible to fit the orthorhombic unit cell described in Section 3.4.1 to the data using a Pawley refinement.

3.4.2 Structure Description

Figure 3.20 shows the structure of $\text{Li}(\text{NH}_3)_2\text{BH}_4$, when this is compared to Figure 3.9 the many similarities with LiBH_4 and $\text{Li}(\text{NH}_3)\text{BH}_4$ are clear. Molecular images of the structure are shown in Figures 3.21, 3.31 and 3.35. The diammine consists of chains of edge-sharing $\text{Li}(\text{NH}_3)(\text{BH}_4)_3$ tetrahedra that run along the b-axis, in a near identical fashion to those seen in the monoammine. The additional second ammonia molecule (N2) sits in-between these chains, with an interatomic N–H...N distance of 2.269 Å and N–H...N angle of 158.9 °, comparison of these figures with those seen in solid ammonia (2.398 Å and 162.98 °) suggests the presence of hydrogen bonding between the two molecules (N1 and N2). Each N1 molecule is bonded in this way to 2 equidistant N2 molecules. With a minimum observed distance of 2.32 Å, the BH...HN contacts seen in $\text{Li}(\text{NH}_3)\text{BH}_4$ are not observed to the same degree here and this may be a contributing factor to the low melting point of the phase.

The openness of the structure provides an appealing explanation of its low melting point: the already well established network of ammonia molecules can easily solvate the LiBH_4 chains. A preliminary inspection of the refined thermal parameters suggests a great deal of disorder in the second ammonia molecule, which is less pronounced in both the ammonia molecule bonded to the lithium atom, and the

borohydride unit. While it is not appropriate to report these here given the poor fit of the model to the diffraction data, the implications of disorder from the calculated data are discussed in Sections 3.4.3 and 3.4.4.

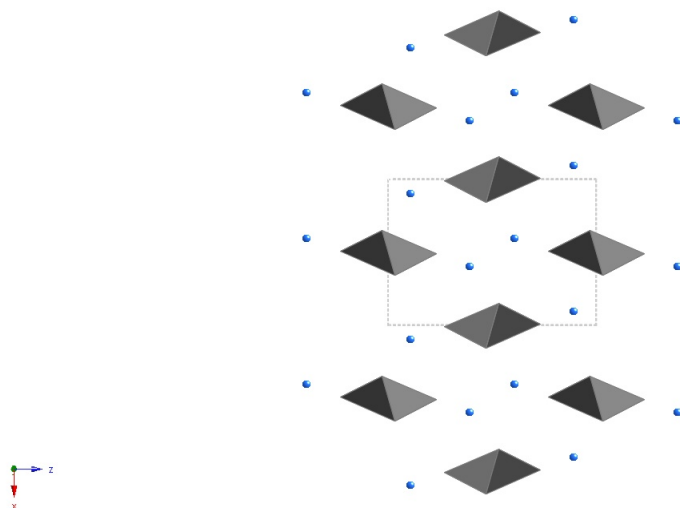


Figure 3.20: The $\text{Li}(\text{NH}_3)_2\text{BH}_4$ structure, viewed down the y-axis. Hydrogen atoms are omitted for clarity, Li atoms are shown in grey, boron in brown and nitrogen in blue. $\text{Li}(\text{NH}_3)(\text{BH}_4)_3$ polyhedra are highlighted in grey.

3.4.3 Geometry-optimised Structure and Properties

The structure refined from the X-ray diffraction data was used as a starting point for ‘fine’ DFT geometry optimisation. There was little observable change in the structure and as was the case for $\text{Li}(\text{NH}_3)\text{BH}_4$ (within a tolerance of 0.001 Å) there was no change from the *Pnma* starting symmetry. Similar bond lengths are observed before and after optimisation, with Li–B at 2.63 Å before and 2.54 Å after, and Li–N at 2.05 Å both before and after. There is a significant change in N–H⋯N bond length changing from 1.79 Å before to 2.27 Å after optimisation with a change in N–H⋯N bond angle from 167.3 ° before to 158.9 ° after. The changes in N–H⋯N distances are in part due to the N–H bond length being fixed to 0.90 Å during simulated annealing and allowed to vary in optimisation to reach a relaxed average of 1.03 Å. This movement brings the calculated NH_3 bond lengths more in line with

those seen in solid ammonia.

Despite problems with gathering adequate diffraction data, the similarities to LiBH_4 and $\text{Li}(\text{NH}_3)\text{BH}_4$, with similar bond lengths and atomic positions, strengthen the case that Section 3.4.2 details the correct structure. Furthermore, phonon calculations were carried out to check the stability of the structure. No negative modes were calculated, suggesting the structure is stable and exists in a local minimum on the potential energy surface. The final calculated atomic positions are given in Table 3.5.

Table 3.5: The calculated atomic coordinates from ‘fine’ geometry optimisation of the $\text{Li}(\text{NH}_3)_2\text{BH}_4$ structure.

atom	site	x	y	z
H	H1	0.954380(3)	0.437050(6)	0.767460(2)
H	H2	0.288780(3)	-0.027230(6)	0.934200(2)
H	H3	0.354560(6)	0.56707(1)	0.577580(4)
H	H4	0.097670(3)	0.25	0.742240(2)
Li	Li5	0.95115(5)	0.25	0.58476(3)
N	N6	0.99187(3)	0.25	0.73097(2)
H	H7	0.335070(6)	0.75	0.057040(4)
H	H8	0.469890(6)	0.75	0.944210(4)
H	H9	0.504830(3)	0.75	0.578120(2)
B	B10	0.3460(1)	0.75	0.96803(8)
N	N11	0.40585(3)	0.75	0.60666(2)
H	H1	0.954380(3)	0.437050(1)	0.767460(2)

In the results of the phonon calculation, a number of low energy NH_3 librational modes are observed. The first significant one appears at 128 cm^{-1} and involves the movement of N2. Several other low energy, N2, librational modes are observed, though none as low in energy as the some of the N1 modes seen in $\text{Li}(\text{NH}_3)\text{BH}_4$. The N1 librational modes in $\text{Li}(\text{NH}_3)_2\text{BH}_4$ are found at higher energy than in $\text{Li}(\text{NH}_3)\text{BH}_4$. In the case of the N1 modes, the higher energy is thought to be due to hydrogen bonding between N1 and N2 increasing the rotational energy barrier. Figure 3.21 shows the calculated mean squared displacement of the atoms nearest

to the lithium site at 298 K. Here it can be seen that the displacement of hydrogen atoms bonded to N2 is greater than hydrogen atoms bonded to N1, which may be explained by localisation of N1 hydrogen atoms that is forced by hydrogen bonding. Comparison of the N1 ammonia molecule thermal ellipsoids with its equivalent in $\text{Li}(\text{NH}_3)\text{BH}_4$, that is shown in Figure 3.14 is striking.

The full assignment of calculated modes is given in Appendix Table D.3. A number of interesting features are observed in particular the coupling of N1 and N2 modes; consistently the motion of N1 coincides with the motion of N2 but not vice versa, showing the strong interaction between the two ammonia molecules. The large number of low energy translational modes, in particular those for N2 show that there is a large amount of ammonia mobility in this structure, and corroborate the observation of a low melting point.

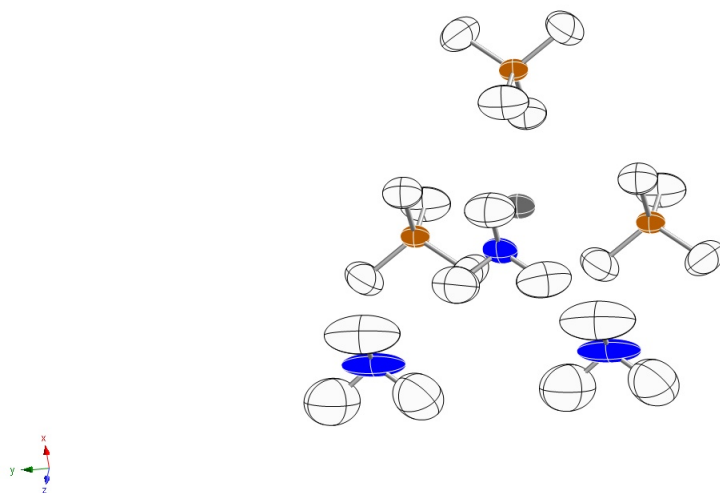


Figure 3.21: The calculated 50 % probability distributions for the mean squared displacement of atoms at 298 K for a single $\text{Li}(\text{NH}_3)(\text{BH}_4)_3$ unit and nearest NH_3 molecules in $\text{Li}(\text{NH}_3)_2\text{BH}_4$. The ammonia molecule referred to as N1 is seen closest to the Li atom, with N2 appearing in duplicate towards the bottom of the image.

3.4.4 Molecular Dynamics

The molecular dynamics calculations performed on $\text{Li}(\text{NH}_3)_2\text{BH}_4$ were identical to those for $\text{Li}(\text{NH}_3)\text{BH}_4$, discussed in Section 3.3.8, and were performed at 150 K for a time of 5.0 ps to aid direct comparison between the two structures. From observation of the movies it is clear that 1) the N2 ammonia molecule rotates quickly; 2) the N1 ammonia molecule rotates notably less frequently than the N2 molecule; and 3) BH_4^- anions do not rotate but oscillate about a fixed position (i.e. they are not disordered). Results that can be easily pictured are displayed in Figure 3.22, here it can be seen that there is significant movement of all atoms. The N2 molecules move more than other atoms and the network of ammonia molecules resulting in low melting point is clear, particularly where the 2 ammonia sites close to the centre of the unit cell are close to exchanging. A fascinating comparison of these calculations with those performed on $\text{Li}(\text{NH}_3)\text{BH}_4$ is the absence of significant atomic movement and/or migration in the y-direction. It could be that this is due to increasing separation of the $\text{Li}(\text{NH}_3)(\text{BH}_4)_3$ chains, which would suggest that those compounds with greater ammonia content will have lower ionic conductivity. If this were the case then an ammonia storage system utilising LiBH_4 would have a simple and direct way of monitoring ammonia content within the solid.

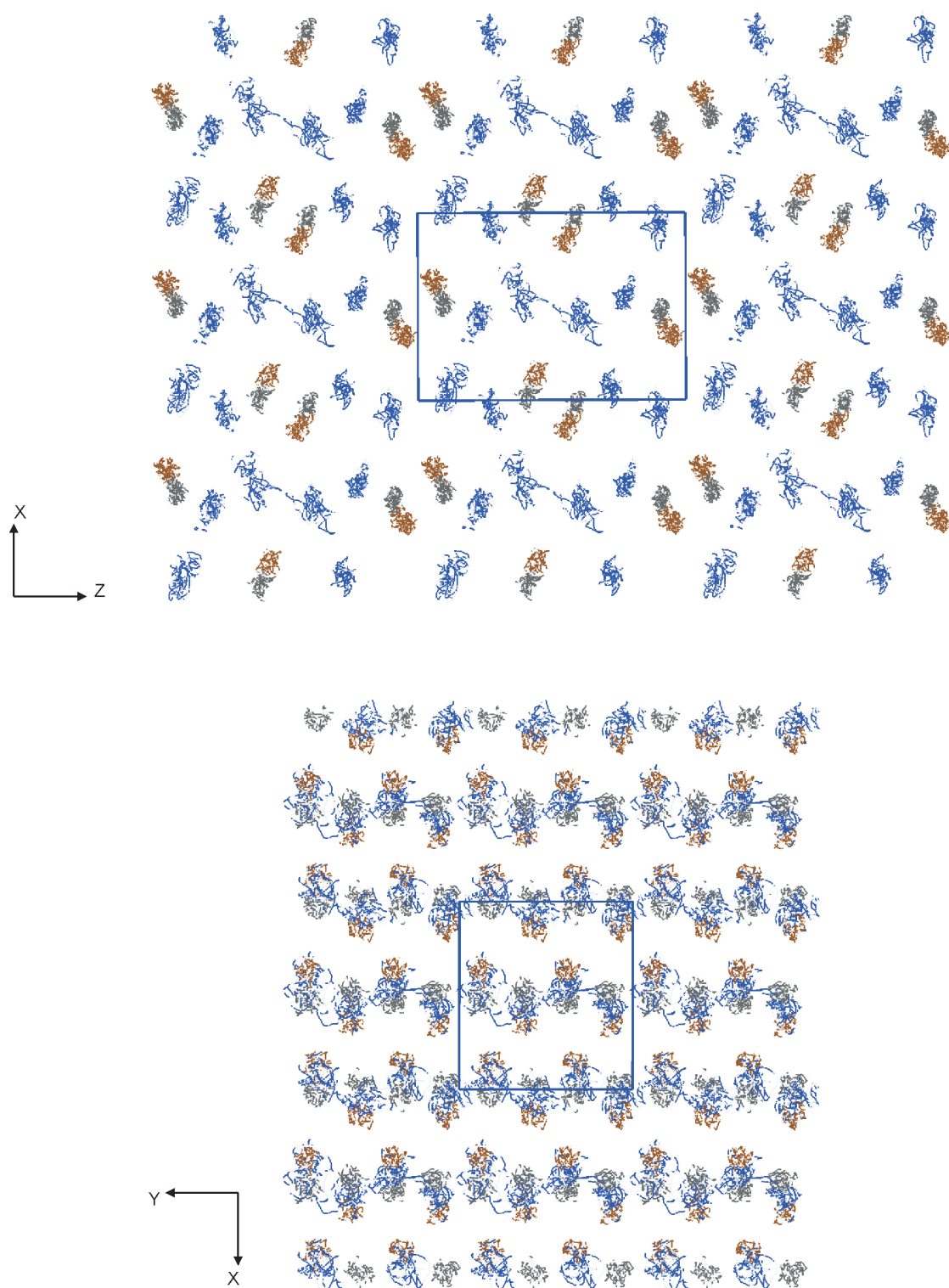


Figure 3.22: The calculated movement of Li (grey), N (blue) and B (brown) atoms in $\text{Li}(\text{NH}_3)_2\text{BH}_4$ at 150 K, with points representing atomic positions at 0.5 fs intervals over a period of 5.5 ps, viewed down the y-axis and z-axis, above and below respectively.

3.5 Lithium Borohydride Triammine

The triammine was produced and characterised in-situ using the IGAⁿ apparatus. The phase was isolated at room temperature using a set-point ammonia vapour pressure of 67 mbar on both GEM and HRPD. Although the HRPD data are good, a combined approach using both Rietveld refinement and DFT calculations was used in structure solution.

3.5.1 Combined Neutron Diffraction and DFT Structure Solution

Bragg peaks in the HRPD diffraction pattern were indexed to a new orthorhombic unit cell. Lattice parameters of $a = 8.08499(7) \text{ \AA}$, $b = 9.81191(8) \text{ \AA}$, $c = 8.20782(7) \text{ \AA}$ and cell volume $V = 651 \text{ \AA}^3$ were refined using the Pawley method in TOPAS. Comparing the unit cell volume with that of LiBH_4 , and assuming that $Z = 4$ for $\text{Li}(\text{ND}_3)_3^{11}\text{BD}_4$, it is observed that the approximate excess volume for each ND_3 molecule is $(651 - 217)/12 \text{ \AA}^3 = 36 \text{ \AA}^3$. This value is slightly small but still consistent with other ammines, so it follows that the unit cell is of reasonable size. The extracted integrated intensities from the refinement were analysed for systematic absences, the concluding reflections were; the absent (021) suggesting $Cc - -$ is preferred, the present (310) suggesting $C - -2_1$, $C - c-$, $Cc - -$, or $Ccc-$, and the present (401) suggesting $C - -2_1$, $C - -(ab)$, $Cc - -$, or $Cc - (ab)$. Thus the structure belongs to one of the space groups $Ccm2_1$, $Cc2m$ or $Ccmm$. It is worth noting here that in these space groups the order of the final two characters $m2_1$, $2m$ and mm is interchangeable with the y- and z- axes.

The structure was solved using the simulated annealing process within TOPAS. It was assumed that each lithium cation would be coordinated by three ND_3 molecules and one $^{11}\text{BD}_4^-$ anion, the preceding arrangement was described using a single rigid body in the simulated annealing process. Three ND_3 molecules and one BD_4 unit were fixed in an ideal tetrahedron about the central Li atom, the ammonia molecules

were allowed to rotate freely and the BD_4 unit was allowed to tumble, whilst bond lengths were constrained to vary within the reasonable limits: 0.95 Å to 1.05 Å for N–D, 2.3 Å to 2.7 Å for Li–B, 1.5 Å to 2.5 (2.2) Å for Li–N, and 1.21 Å for B–D, the Li–N–D angle was constricted to vary within the limits 109 ° to 112 °. Through a series of refinements, in each of the possible space groups, the occupancies of sites were also allowed to vary in order to account for the symmetry of the various space groups. A global minimum was repeatedly found that placed N, Li and B atoms at (x, ca. 1/2, z), close to the mirror plane in Ccm -. Locating these atoms at (x, 1/2, z), further simulated annealing was performed. It was observed that of the three possible space groups, $Ccm2_1$ consistently produced the most chemically reasonable structure. Using this space group, a new rigid body was defined that accounted for placement of the boron, lithium and one nitrogen atom of the $\text{Li}(\text{ND}_3)_3\text{BD}_4$ tetrahedron on the (x, 1/2, z) mirror plane.

The neutron data show a greater reduction of intensity at low d-values than would normally be expected, it is suggested that this is due to some level of disorder within the structure. The data are also somewhat lacking, with very few intense Bragg reflections available to refine a complicated model. Despite employing a number of different models and allowing free movement of atoms, it was not possible to obtain a high quality fit of the model to the data. For these reasons DFT calculations were also employed in the structure solution.

‘Rough’ DFT geometry optimisation was carried out using the result of the initial Rietveld refinement as a starting structure. The resultant structure is virtually indistinguishable from the starting one, with small differences in bond-lengths, Li–B was 2.28 Å before optimisation and 2.54(5) Å after, and Li–N were 2.19 Å and 2.20 Å before and 2.10(2) Å and 2.11(2) Å after optimisation. The calculated structure, with no change to the atomic positions and without allowing for any disorder, produced a good fit to the diffraction data with the parameters: $R_{wp} = 4.608$, $R_{exp} = 2.950$, and $\chi^2 = 2.44$. The diffraction data, with the final fit of

the Rietveld refinement of the model to the data, are shown in Figure 3.23. Final calculated atomic positions are given in Table 3.6.

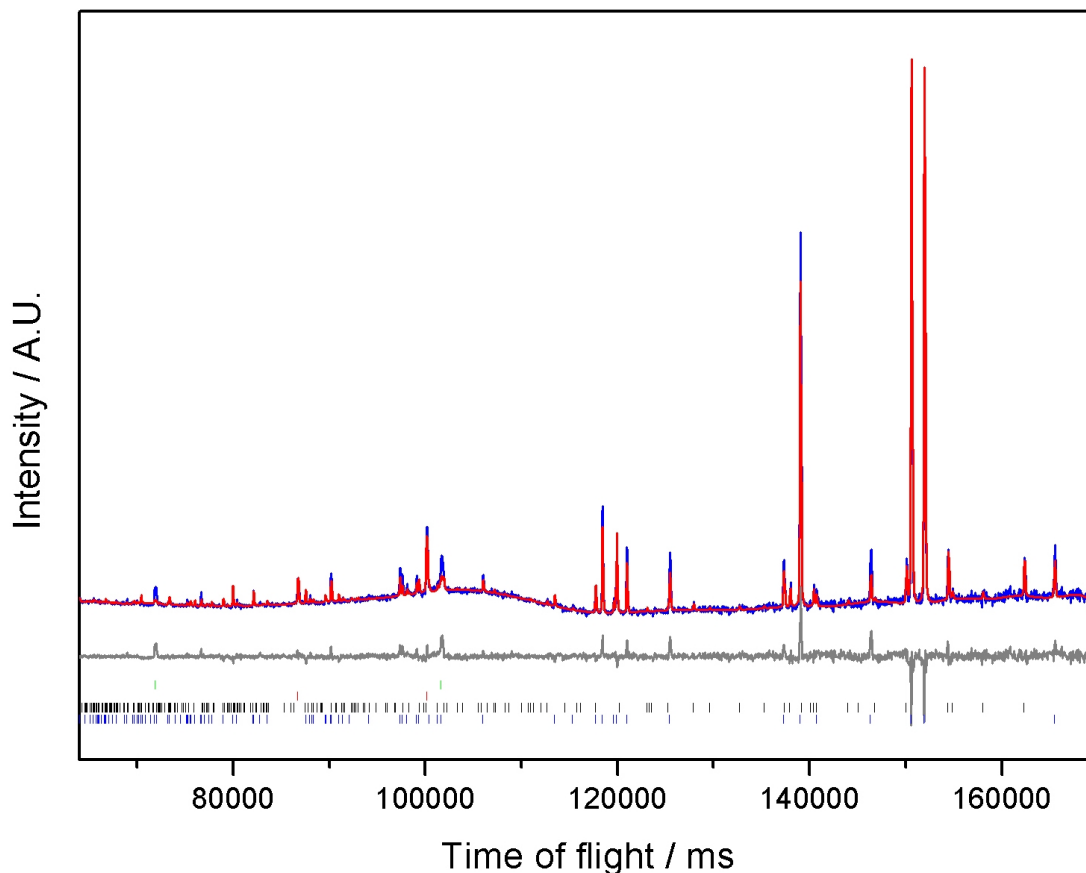


Figure 3.23: Final fit to the data for Rietveld refinement of the $\text{Li}(\text{NH}_3)_3\text{BH}_4$ model to neutron powder diffraction data collected using HRPD. Space group = $Ccm2_1$, $R_{wp} = 4.608$, $R_{exp} = 2.950$, $\chi^2 = 2.44$. Experimental data are shown in blue, calculated in red with the difference in grey, tick marks show the expected positions of Bragg reflections for (from top to bottom) V, Fe, $\text{Li}(\text{NH}_3)_4\text{BH}_4$ and $\text{Li}(\text{NH}_3)_3\text{BH}_4$.

3.5.2 Structural Description and Discussion

During structural solution it was assumed that the molecules would be arranged in $\text{Li}(\text{NH}_3)_3\text{BH}_4$ tetrahedra rather than in a more open arrangement as seen with $\text{Li}(\text{NH}_3)_2\text{BH}_4$. This assumption holds, and the final structure is reasonable, given that 1) an open structure would be likely to have a low melting point, as seen with $\text{Li}(\text{NH}_3)_2\text{BH}_4$; 2) as observed in the spectrochemical series, bonding between Li^+

Table 3.6: The atomic coordinates from ‘rough’ geometry optimisation calculation and B_{iso} from Rietveld refinement of the final $\text{Li}(\text{NH}_3)_3\text{BH}_4$ structure.

atom	site	x	y	z	B_{iso}
H	H1	-0.3977(2)	0.2507(1)	0.6426(1)	9.5(0.2)
H	H2	-0.6250(3)	0.2641(3)	0.1870(3)	9.5(0.2)
H	H3	-0.7952(2)	0.4425(1)	0.4674(1)	9.5(0.2)
H	H4	-0.6735(2)	0.5792(1)	0.4742(1)	9.5(0.2)
H	H5	-0.7754(2)	0.5410(1)	0.3065(1)	9.5(0.2)
N	N6	-0.710(2)	0.499(1)	0.402(2)	9.5(0.2)
H	H7	-0.5	0.1417(1)	0.5289(1)	9.5(0.2)
H	H8	-0.5	0.0899(3)	0.1532(3)	9.5(0.2)
H	H9	-0.5	0.2342(3)	0.9784(3)	9.5(0.2)
Li	Li10	-0.5	0.375(2)	0.368(3)	9.5(0.2)
B	B11	-0.5	0.213(6)	0.126(3)	9.5(0.2)
N	N12	-0.5	0.241(1)	0.569(2)	9.5(0.2)

and NH_3 should be stronger than bonding between Li^+ and BH_4^- ; 3) while with X-ray diffraction it would be hard to see a difference between the isoelectronic NH_3 and BH_4^- , the total coherent scattering of 27.8 barn for ND_3 and 22.4 barn for $^{11}\text{BD}_4^-$ mean that the two sites should be distinguishable; and 4) the stabilisation of the structure via dihydrogen bonding should be a significant thermodynamic factor on formation of the structure, it is hard to conceive a structure with a greater number of these bonds than the one presented in Figure 3.24.

When considering the structure as part of the $\text{Li}(\text{NH}_3)_n\text{BH}_4$ group, it is convenient to view down the z-axis where it can be seen that the $\text{Li}(\text{NH}_3)_3\text{BH}_4$ tetrahedra are arranged in pairs which form rows running in the z-direction. These rows join together to form layers that run in the yz-plane and are discussed further in Section 3.7, where a clear image of the molecular structure is also shown. The $\text{BH}\cdots\text{HN}$ distances suggest that there is a significant number of both inter- and intra-layer dihydrogen bonds that act to stabilise the structure. The different $\text{BH}\cdots\text{HN}$ distances are given in Table 3.7 and reveal that the mean inter- and intra-layer bond distances are 2.290(4) Å and 2.340(4) Å respectively. Even though these distances suggest

relatively weak bonds, their importance in stabilising the structure is reflected in their sheer number, as shown in Figure 3.24.

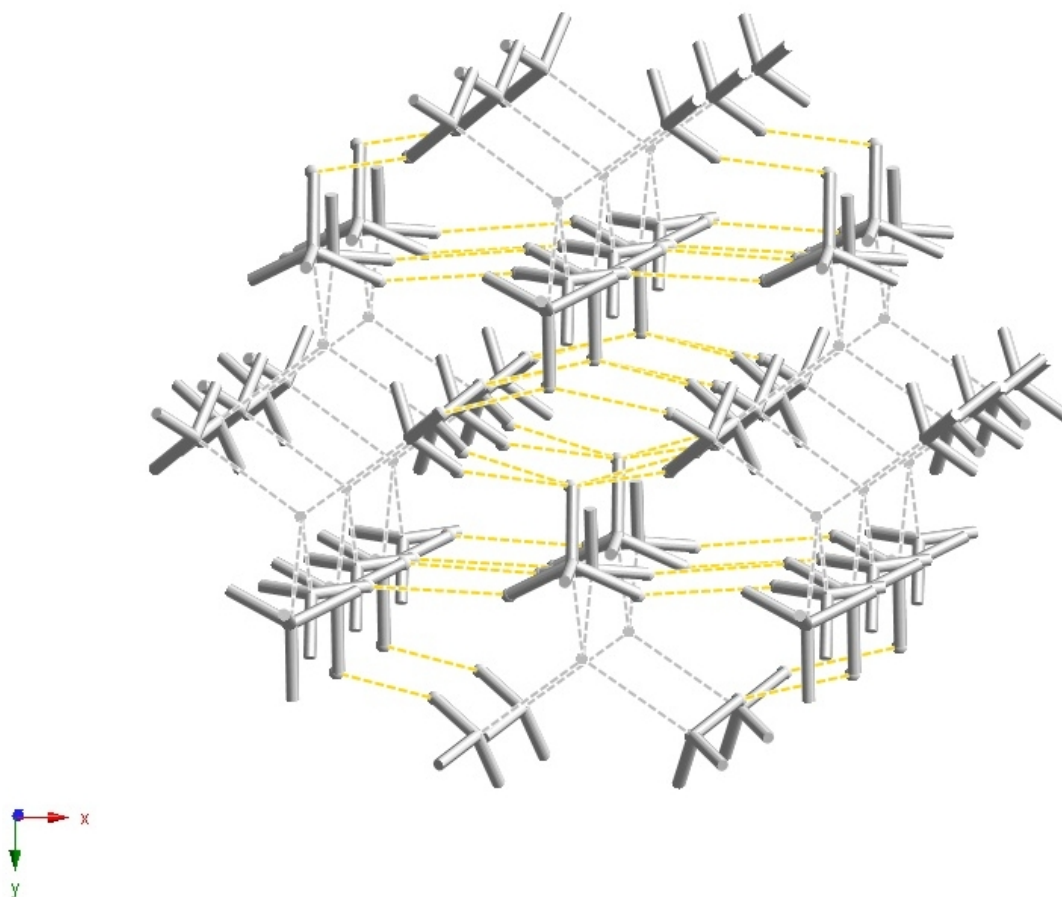


Figure 3.24: The structure of $\text{Li}(\text{NH}_3)_3\text{BH}_4$, with Li–B and Li–N bonds shown as dashed grey lines, and H...H contacts of $\leq 95\%$ of the Van der Waals radii (i.e. $2.28 \text{ \AA}$) shown as dashed gold lines

Table 3.7: BH...HN distances observed in the final $\text{Li}(\text{NH}_3)_3\text{BH}_4$ structure.

Hydrogen Atom Sites	Inter- or Intra-row	Number of Bonds	Distance / Å
8-3	Inter-	2	2.270(4)
8-5	Inter-	2	2.260(4)
9-3	Intra-	2	2.400(4)
9-4	Inter-	2	2.310(4)
2-4	Inter-	1	2.360(4)
2-1	Intra-	1	2.240(4)

3.6 Lithium Borohydride Tetra-ammine

Lithium borohydride tetra-ammine was produced and characterised in-situ using the IGAⁿ apparatus. The phase was isolated at room temperature using a set-point ammonia vapour pressure of 1000 mbar on both GEM and HRPD, though was observed to exist with vapour pressures as low as 96 mbar. A combined approach using both Rietveld refinement and DFT calculation was once again used in the structural solution process.

3.6.1 Neutron Diffraction and DFT Structure Solution

Bragg peaks in the HRPD diffraction data were indexed to a new orthorhombic unit cell. Pawley refinements were performed using TOPAS in each of the possible orthorhombic space groups, and resulted in lattice parameters of $a = 11.9345(1) \text{ \AA}$, $b = 7.06904(7) \text{ \AA}$, $c = 9.96326(8) \text{ \AA}$, and cell volume $V = 841 \text{ \AA}^3$. Performing a check on volume and assuming that $Z = 4$, it can be seen that $(841-217)/16 = 39 \text{ \AA}^3$ are left for each ammonia molecule which is consistent with other amines and thus the size of the unit cell is considered reasonable. The structures of $\text{Li}(\text{NH}_3)_4\text{Br}$ and $\text{Li}(\text{NH}_3)_4\text{I}$ have been reported,¹⁰⁶ and comparison between them and the cell for $\text{Li}(\text{NH}_3)_4\text{BH}_4$ is given in Table 3.8. It appears likely that the three compounds are isostructural and share the space group $Pnma$.

Table 3.8: A comparison of the unit cells of $\text{Li}(\text{NH}_3)_4\text{Br}$, $\text{Li}(\text{NH}_3)_4\text{I}$ and $\text{Li}(\text{NH}_3)_4\text{BH}_4$

	Compound		
	$\text{Li}(\text{NH}_3)_4\text{Br}$	$\text{Li}(\text{NH}_3)_4\text{BH}_4$	$\text{Li}(\text{NH}_3)_4\text{I}$
x	11.947(5)	11.9345(1)	12.646(3)
y	7.047(4)	7.06904(7)	7.302(1)
z	9.472(3)	9.96326(8)	9.790(2)
Volume	797.5	840.6	904.0
Space group	$Pnma$	$Pnma$	$Pnma$

The ideal approach to solve this structure would perhaps be to locate the heavier atoms within the cell using X-ray diffraction and then locate the hydrogen atoms using neutron diffraction data. In absence of X-ray data and given the bulk of the scattering from the cell is due to deuterium atoms, it was necessary to model the $\text{Li}(\text{ND}_3)_4$ and BD_4 tetrahedra as rigid bodies constrained to vary within sensible limits during the refinement process. As a starting point, lithium and boron positions were interpolated from the lithium and halide sites in $\text{Li}(\text{NH}_3)_4\text{Br}$ and $\text{Li}(\text{NH}_3)_4\text{I}$. Fractional coordinates of the Li, ^{11}B and two of the three possible N sites were fixed in the $(x, 1/4, y)$ mirror plane but otherwise allowed to vary freely. It was clear during the refinement process that a significant amount of disorder was present within the structure. As was the case with the $\text{Li}(\text{NH}_3)_3\text{BH}_4$ data, there is a significant drop in the intensity of Bragg peaks at low d-spacing, also the vapour pressure of > 96 mbar required to isolate the phase suggests a large amount of ammonia mobility. Disorder was modelled by increasing the number of hydrogen sites around the nitrogen atom to 6 instead of 3, conceptually representing a spinning ammonia molecule, and modelling the hydrogen sites around the boron atom, and nitrogen sites around the lithium atom as a cube. The occupancies of these disordered sites were allowed to vary freely while maintaining the appropriate Li:N, N:D and ^{11}B :D ratios. The inclusion of disorder within the model greatly improved the goodness of fit to the data, whilst taking into account the additional refineable variables. It was observed that there was disorder present in the hydrogen sites about the N and B atoms, but a single set of N sites was preferred. The best fit of the model to the data is shown in Figure 3.25, and produced the fit statistics: $R_{wp} = 3.316$, $R_{exp} = 1.876$ and $\chi^2 = 3.13$. It was possible to achieve a better fit while only refining the model against part of the data but this approach is limited as without considering the entire pattern there is not enough data to accurately refine a disordered model. Within the disorder a site preference was shown for the ‘b’ sites of BD_4 that were occupied at 75 % and the ‘a’ sites in ND_3 that were occupied at 60 %, though why

this preference is shown is not clear.

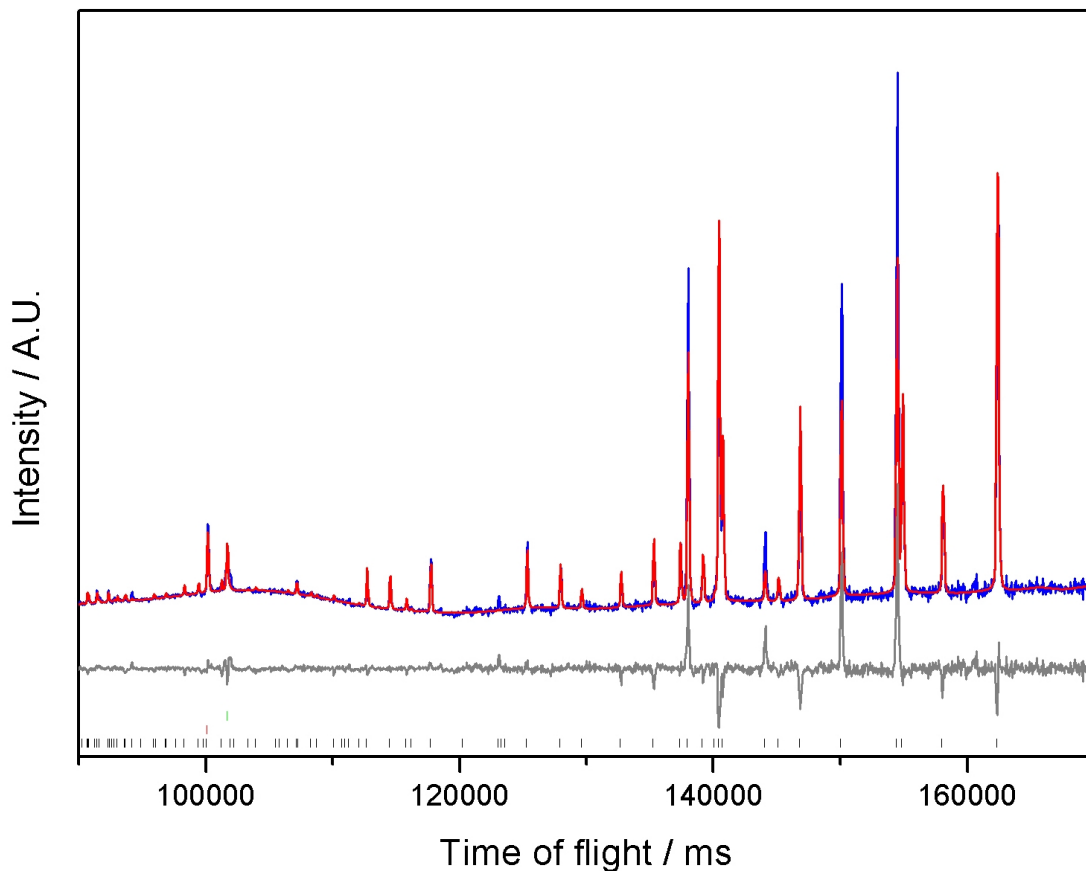


Figure 3.25: Final fit to the data for Rietveld refinement of the $\text{Li}(\text{ND}_3)_4\text{BD}_4$ model to neutron powder diffraction data collected using HRPD. Space group = $Pnma$, $R_{wp} = 3.32$, $R_{exp} = 1.88$ and $\chi^2 = 3.13$. Experimental data are shown in blue, calculated in red with the difference in grey, tick marks show the expected positions of Bragg reflections for V, steel and $\text{Li}(\text{ND}_3)_4\text{BD}_4$.

To confirm the structure, DFT geometry optimisation was performed using a structure that positioned the disordered hydrogen atoms on the sites with highest occupancy. The resulting structure showed a great deal of similarity with the starting one; Table 3.9 shows there was a negligible increase in the mean bond lengths, except in the case of NH_3 where the small increase in bond length may be due to some rotational disorder as discussed in Section 2.12. The biggest discrepancies in bond lengths arise for those associated with NH_3 . These discrepancies may be a result of significant ammonia mobility and rotational motion at room temperature.

Although there are large changes in the N–Li–N bond angles, both models show irregular LiN_4 tetrahedra. The refinement of the calculated structure with fixed atomic coordinates did not provide a good fit to the data. It is proposed that the reason for this and the observed differences in bond angles is significant disorder present at room temperature. These differences are exaggerated by the fact that the calculated structure is effective at 0 K in a fixed system with no net forces acting on atoms while the experimental structure is at 298 K with a dynamic ammonia equilibrium in force. The final atomic positions from Rietveld refinement are given in Appendix Table E.5 and Table 3.10 gives the final calculated atomic positions. The images presented are, unless otherwise stated, produced from the calculated structure as these offer the most reasonable bond angles.

Table 3.9: A comparison of bond lengths in $\text{Li}(\text{NH}_3)_4\text{BH}_4$ before and after geometry optimisation

Bond	Length Before Optimisation / Å	Length After Optimisation / Å
Li–N	1.95(5)	2.08(1)
	2.01(4)	2.10(1)
	2.17(3)*	2.08(1)
Mean Li–N	2.08(4)	2.09(1)
B–H	1.23(2)	1.230(3)
N–H	0.96(2)	1.030(1)

3.6.2 Structural Description and Discussion

During the refinement process, ammonia molecules were fixed in tetrahedra around the Li atoms. The alternative would be to have an arrangement of $\text{Li}(\text{NH}_3)_{4-n}\text{BH}_n$ tetrahedra with n free NH_3 molecules as is seen in $\text{Li}(\text{NH}_3)_2\text{BH}_4$ though this would presumably produce a low melting point solid. It is also unlikely that the 4th ammonia molecule will be free, as this is not a feature of the $\text{Li}(\text{NH}_3)_4\text{Br}$ or $\text{Li}(\text{NH}_3)_4\text{I}$ and NH_3 is generally considered a better ligand than BH_4^- so should bond to Li^+ preferentially. Furthermore, when BH_4^- is not bonded to the Li^+ cation, it is available

Table 3.10: The calculated atomic coordinates from the ‘rough’ geometry optimisation of $\text{Li}(\text{NH}_3)_4\text{BH}_4$.

atom	site	x	y	z
H	H1	0.3380(2)	0.3924(4)	0.2441(3)
H	H2	0.7390(1)	0.1328(2)	0.5833(1)
H	H3	0.0964(1)	0.3657(2)	0.5361(1)
H	H4	0.9851(1)	0.5634(2)	0.8265(1)
H	H5	0.8489(1)	0.5705(2)	0.7903(1)
H	H6	0.8949(1)	0.4380(2)	0.9167(1)
N	N7	0.913(1)	0.483(2)	0.821(1)
H	H8	0.3875(2)	0.25	0.4088(3)
H	H9	0.2256(2)	0.25	0.3563(3)
H	H10	0.8020(1)	0.25	0.4605(1)
H	H11	0.1400(1)	0.25	0.6686(1)
Li	Li1	0.926(1)	0.25	0.694(1)
B	B1	0.322(5)	0.25	0.313(5)
N	N1	0.788(1)	0.25	0.563(1)
N	N2	0.079(1)	0.25	0.595(1)

for an increased number of dihydrogen bonds that act to stabilise the structure.

Clear images of the structure are shown in Figures 3.33 and 3.37, where it can be seen that $\text{Li}(\text{NH}_3)_4^+$ tetrahedra run in rows in the y-direction, and these are connected to neighbouring rows via the BH_4^- anion. Neighbouring rows form layers that span the the yz-plane, the layers are made up of either $\text{Li}(\text{NH}_3)_4^+$ or BH_4^- and dihydrogen bonding is observed between alternate layers as highlighted in Figure 3.26. These layers are also seen in $\text{Li}(\text{NH}_3)_4\text{Br}$ and $\text{Li}(\text{NH}_3)_4\text{I}$, however in $\text{Li}(\text{NH}_3)_4\text{BH}_4$ they are more clearly defined.

Both $\text{Li}(\text{NH}_3)_4\text{Br}$ (and $\text{Li}(\text{NH}_3)_4\text{I}$) have previously been described as having a distorted CsCl structure,¹⁰⁶ similar to that shown in Figure 3.27. This is because each Li atom is coordinated by 8 Br atoms at Li–Br distances of; 4.75, 4.58, 4.73, 4.73, 5.43, 5.48, 5.43, and 7.54 Å (with similar distances seen in the iodide). The comparison with CsCl is attractive, but the single longer bond length raises concern. In $\text{Li}(\text{NH}_3)_4\text{BH}_4$, the equivalent Li–B distances are; 4.72, 4.81, 4.92, 4.81, 4.91, 4.92,

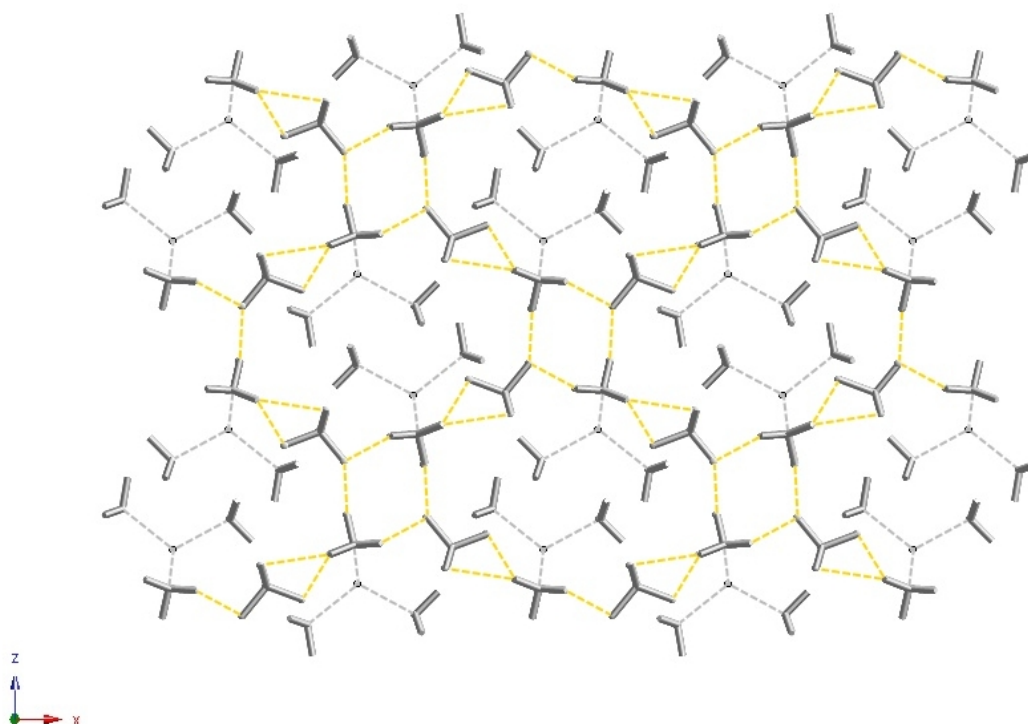


Figure 3.26: The structure of $\text{Li}(\text{NH}_3)_4\text{BH}_4$, highlighting dihydrogen bonding. Li–B bonds are shown as dashed grey lines and $\text{NH}\cdots\text{HB}$ contacts of $\leq 95\%$ of the Van der Waals radii (i.e. $2.28\text{ \AA}$) as dashed gold lines

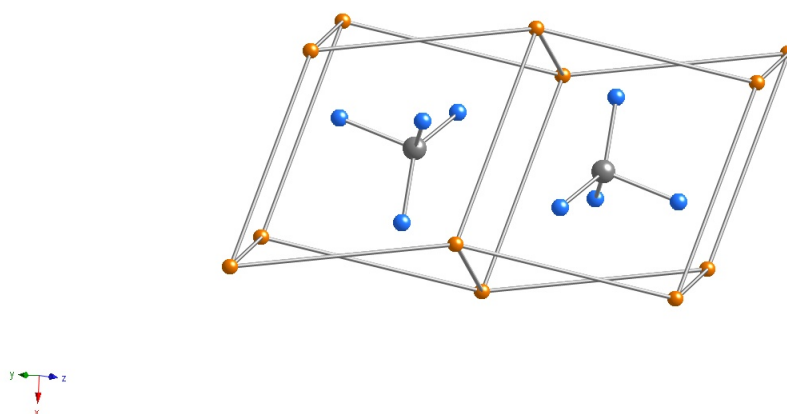


Figure 3.27: $\text{Li}(\text{NH}_3)_4\text{BH}_4$ showing the distorted CsCl motif as observed in the Rietveld refined structure and originally proposed by Jacobs et al. for $\text{Li}(\text{NH}_3)_4\text{Br}$ and $\text{Li}(\text{NH}_3)_4\text{I}$. H atoms are omitted for clarity, Li in grey, B in brown and N in blue.

6.11, and 7.84 Å. In this case the two long bond-lengths are towards the atoms on opposite corners of the distorted CsCl cell. When considering just the 6 nearest neighbours it is apparent that the Li atoms sit inside distorted LiB_6 octahedra. At this point the experimental and calculated structures differ significantly; in the experimental structure the LiB_6 octahedra are arranged in face sharing chains that are vertex linked to neighbouring chains, in the calculated structure these chains are edge-sharing, as shown in Figure 3.28. The environment of the B atoms is more striking; in the experimental structure the B atoms sit inside edge sharing but distorted BLi_6 trigonal prisms, while in the calculated structure the arrangement is of edge-sharing BLi_6 octahedra, as shown in Figure 3.29. These structure types are well known, albeit somewhat distorted, as NiAs and NaCl for the experimental and calculated structures respectively. Typically the NiAs structure is observed where metal-metal bonding is favourable; in this case it is proposed that the proximity of $\text{Li}(\text{NH}_3)_4^+$ cations allows for increased NH_3 mobility, thus promoting the observed disorder. This ammonia mobility has not been modelled in the DFT calculations, and therefore the energy is lowered as the $\text{Li}(\text{NH}_3)_4^+$ tetrahedra move apart and NaCl type structure is calculated as an energy minimum.

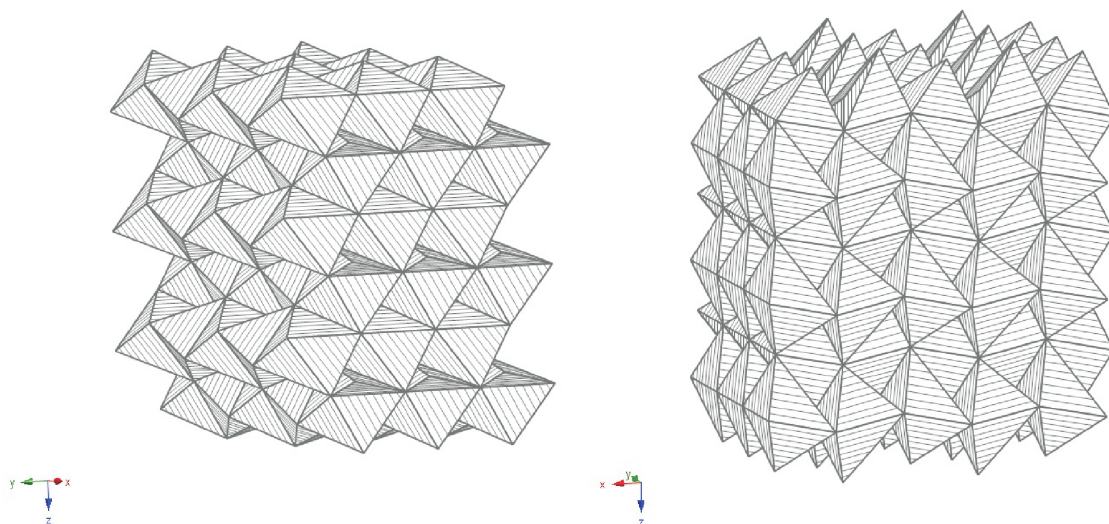


Figure 3.28: Experimental (left) and calculated (right) $\text{Li}(\text{NH}_3)_4\text{BH}_4$ structures showing the LiB_6 environments. B atoms sit on the corners of the displayed polyhedra.

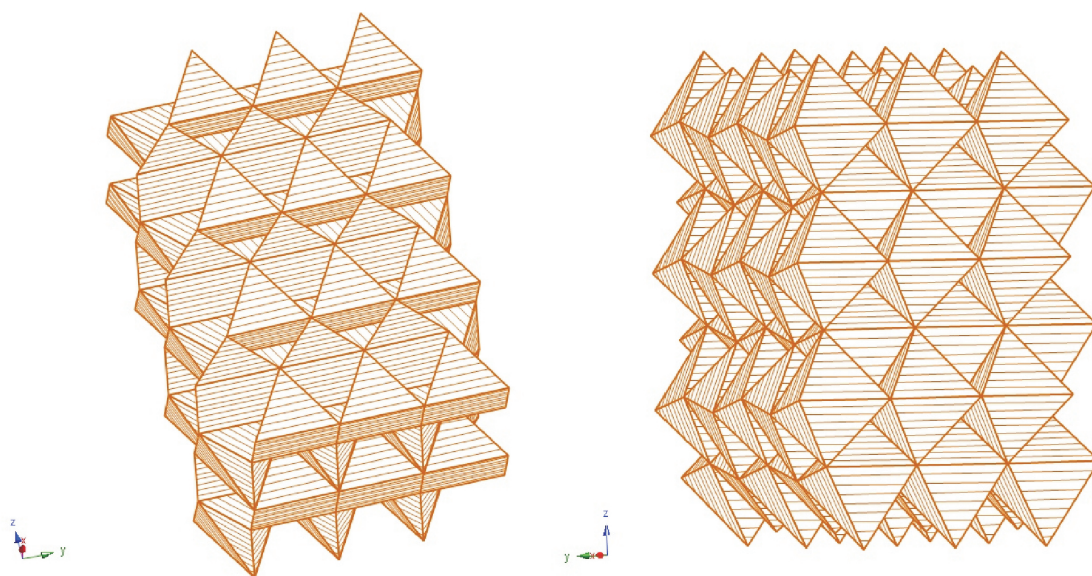


Figure 3.29: Experimental (left) and calculated (right) $\text{Li}(\text{NH}_3)_4\text{BH}_4$ structures showing the BLi_6 environments. Li atoms sit on the corners of the displayed polyhedra.

3.7 Phase Overview and Transitions

All of the presently discussed structures show common features and the evolution from each to the next is clear. Figures 3.30 to 3.33 show that the Li atoms are arranged in pairs that run in rows along either the y-axis or in the case of $\text{Li}(\text{NH}_3)_3\text{BH}_4$ the z-axis. Adjacent rows are organised in layers that run in the yz-plane as Figures 3.34 to 3.37 show. Dihydrogen bonding has been discussed throughout this Chapter and is an important feature in these structures. In each case, adjacent layers appear to be held together by dihydrogen bonding interactions. The different structures are characterised by an increase in both inter- and intra-layer Li–Li distances, with the exception that the inter-layer Li–Li distances are shorter than the intra-layer distances in $\text{Li}(\text{NH}_3)_3\text{BH}_4$.

The enthalpy changes for the reactions of $n = 4$ to 3, 3 to 2, 2 to 1, and 1 to 0 are calculated from the results of geometry optimisation as 32 kJmol^{-1} , 63 kJmol^{-1} , 22 kJmol^{-1} , and 56 kJmol^{-1} respectively. The phase diagram for these compounds reported by Sullivan and Johnson suggests that these enthalpy changes may only be realistic below about 15°C , where change between the solid phases occurs.⁵³ The numbers highlight the similarities and differences between the structures, in particular the low enthalpy change between $n = 2$ and $n = 1$ shows the close similarity between these structures while the large enthalpy change between $n = 3$ and $n = 2$ highlights the significant change occurring over this transition.

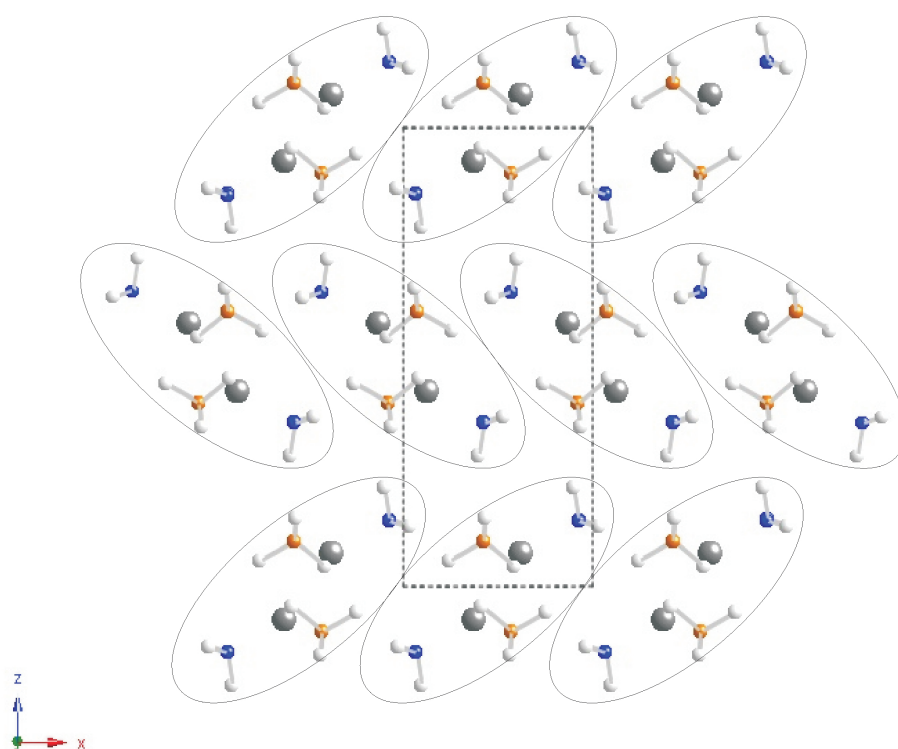


Figure 3.30: The $\text{Li}(\text{NH}_3)\text{BH}_4$ structure, showing the arrangement of rows of atoms running in the y -direction. H atoms are shown in off-white, Li in grey, B in brown and N in blue.

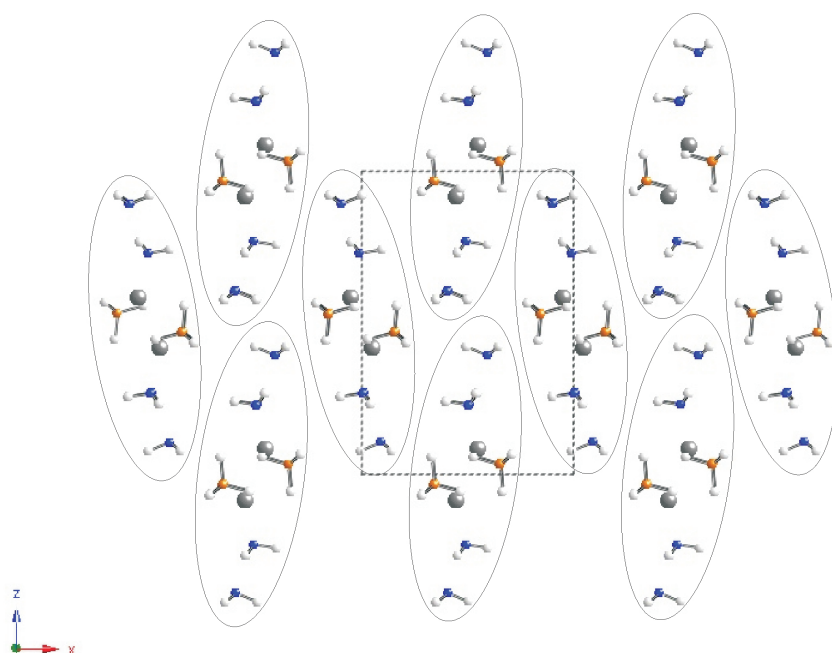


Figure 3.31: The $\text{Li}(\text{NH}_3)_2\text{BH}_4$ structure, showing the arrangement of rows of atoms running in the y-direction. H atoms are shown in off-white, Li in grey, B in brown and N in blue.

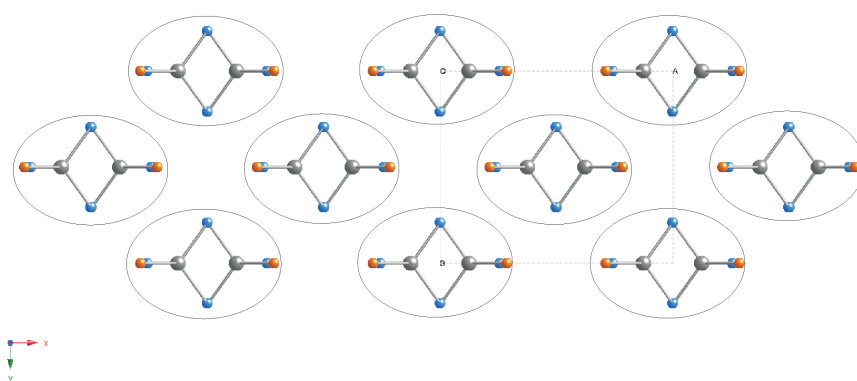


Figure 3.32: The $\text{Li}(\text{NH}_3)_3\text{BH}_4$ structure, showing the arrangement of rows of atoms running in the z-direction. H atoms are omitted and Li–N and Li–B bonds are shown for clarity, with Li shown in grey, B in brown and N in blue.

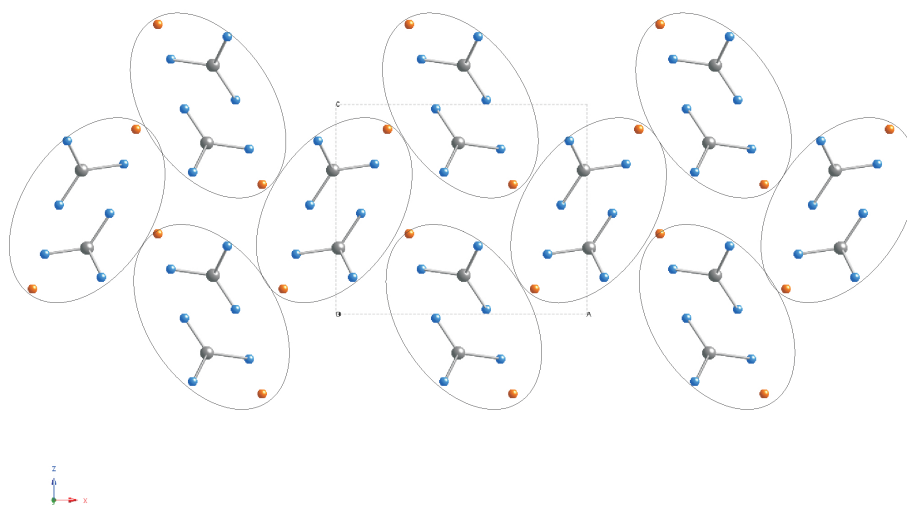


Figure 3.33: The $\text{Li}(\text{NH}_3)_4\text{BH}_4$ structure, showing the arrangement of rows of atoms running in the y-direction. H atoms are omitted and Li–N and Li–B bonds are shown for clarity, with Li shown in grey, B in brown and N in blue.

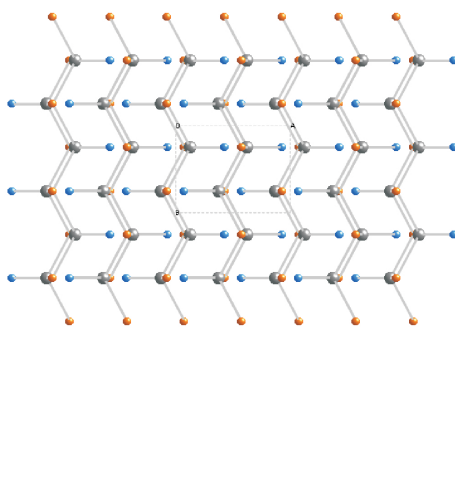


Figure 3.34: The $\text{Li}(\text{NH}_3)_4\text{BH}_4$ structure, showing the arrangement of layers of atoms running in the yz-plane. H atoms are omitted and Li–N and Li–B bonds are shown for clarity, with Li shown in grey, B in brown and N in blue.

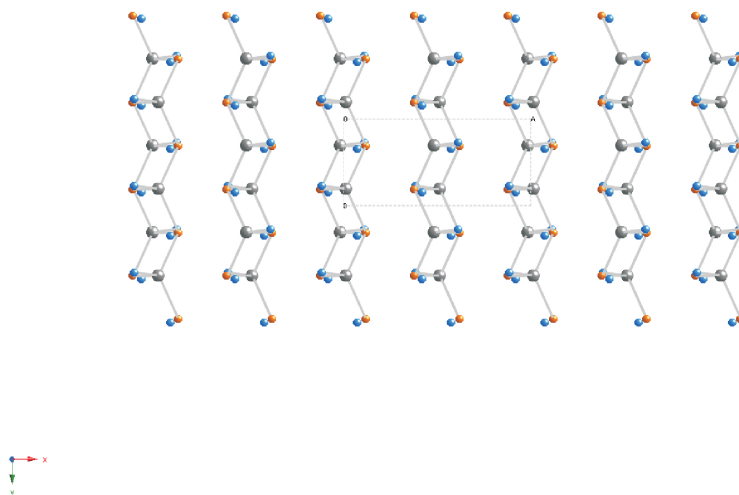


Figure 3.35: The $\text{Li}(\text{NH}_3)_2\text{BH}_4$ structure, showing the arrangement of layers of atoms running in the yz -plane. H atoms are omitted and Li–N and Li–B bonds are shown for clarity, with Li shown in grey, B in brown and N in blue.

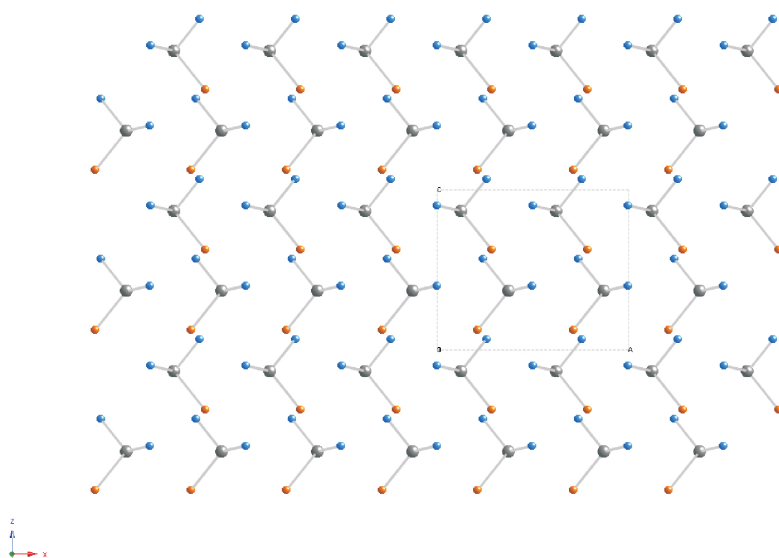


Figure 3.36: The $\text{Li}(\text{NH}_3)_3\text{BH}_4$ structure, showing the arrangement of layers of atoms running in the yz -plane. H atoms are omitted and Li–N and Li–B bonds are shown for clarity, with Li shown in grey, B in brown and N in blue.

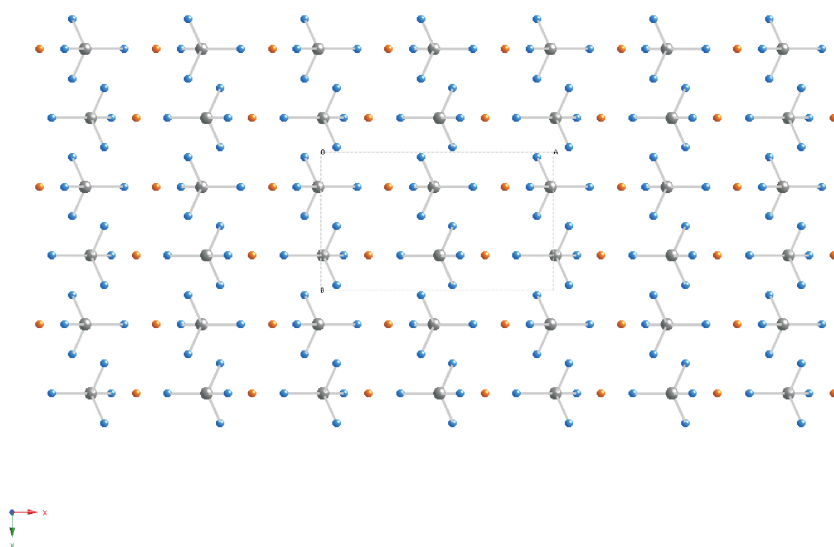


Figure 3.37: The $\text{Li}(\text{NH}_3)_4\text{BH}_4$ structure, showing the arrangement of layers of atoms running in the yz -plane. H atoms are omitted and Li–N and Li–B bonds are shown for clarity, with Li shown in grey, B in brown and N in blue.

3.7.1 Phase Transitions

During the HRPD IGAⁿ experiment phase transitions were carried out under isobaric conditions, providing ideal data for studying the kinetics of these transitions. However, the neutron flux on HRPD is low so in order to gain statistically usable data collection times of 15 minutes were required. Ideally the GEM data would be used for this task given GEM's higher neutron flux, but given the consistent conditions of the HRPD experiment and the improved resolution of the data, these HRPD data are more reliable. In order to study the transition from the $n = 4$ to the $n = 3$, 2 and 1 phases, Pawley refinements in the appropriate space groups (given in this Chapter) were carried out across multiple data sets. During refinement all variables were fixed other than the scale factor, which therefore directly represents the proportion of each phase present.

The refined scale factors for the transition between $\text{Li}(\text{NH}_3)_4\text{BH}_4$ and $\text{Li}(\text{NH}_3)_3\text{BH}_4$ are shown in Figure 3.38. As expected it can be seen that the concentration of $\text{Li}(\text{NH}_3)_4\text{BH}_4$ decreases as the concentration of $\text{Li}(\text{NH}_3)_3\text{BH}_4$ increases. The decrease in $\text{Li}(\text{NH}_3)_4\text{BH}_4$ concentration occurs at a slower rate than the increase in $\text{Li}(\text{NH}_3)_3\text{BH}_4$ concentration, though the reason for this unclear at this stage of investigation.

The transition from $\text{Li}(\text{NH}_3)_3\text{BH}_4$ to $\text{Li}(\text{NH}_3)_2\text{BH}_4$ and $\text{Li}(\text{NH}_3)\text{BH}_4$ is shown in Figure 3.39. It can be seen that (unlike the previous transition) as the intensity of $\text{Li}(\text{NH}_3)_3\text{BH}_4$ reflections decreases, the intensities of the alternative phase reflections do not increase. The non-zero scale factors for $\text{Li}(\text{NH}_3)_2\text{BH}_4$ and $\text{Li}(\text{NH}_3)\text{BH}_4$ below 350 minutes are anomalous and result from the broad peak shape meaning that it is possible to model the data incorrectly using too many trial phases. The fact that these anomalous scale factors decrease along with those for the singularly present $\text{Li}(\text{NH}_3)_3\text{BH}_4$ is indicative of the overall decrease in intensity of all Bragg reflections, which is caused by the formation of liquid $\text{Li}(\text{NH}_3)_2\text{BH}_4$. It should be noted here

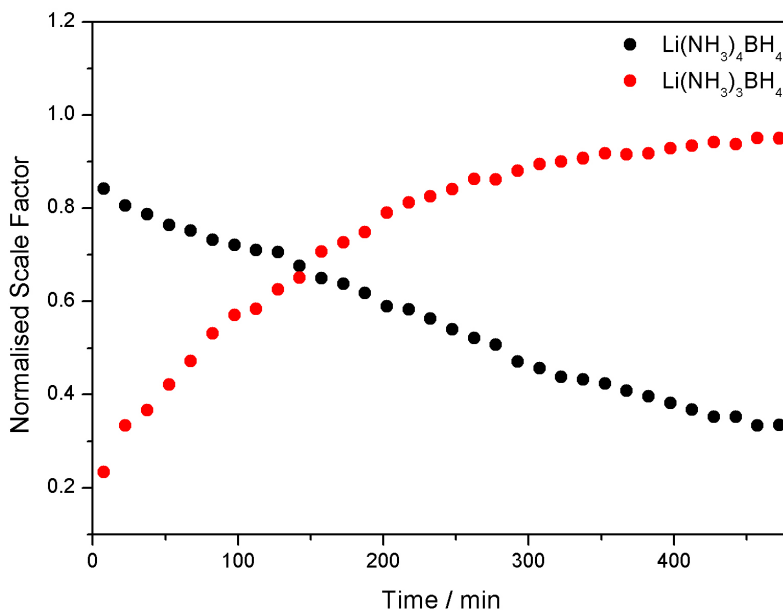


Figure 3.38: The normalised scale factors for the transition between $\text{Li}(\text{NH}_3)_4\text{BH}_4$ and $\text{Li}(\text{NH}_3)_3\text{BH}_4$. Data were collected over continuous 15 minute periods using the IGAⁿ equipment on HRPD and an ammonia pressure of 70 mbar.

that refinements were carried out using all available data and sections of Figure 3.39 where datum points at the expected 15 minute intervals are absent are a result of the neutron beam cutting out. It can be seen that from a time of 473 minutes $\text{Li}(\text{NH}_3)\text{BH}_4$ begins to crystallise out of the liquid phase, completing the transition from $\text{Li}(\text{NH}_3)_3\text{BH}_4$ to $\text{Li}(\text{NH}_3)\text{BH}_4$ via the liquid $\text{Li}(\text{NH}_3)_2\text{BH}_4$. As may be expected from a crystalline sample grown in-situ, significant preferred orientation is seen in these $\text{Li}(\text{NH}_3)\text{BH}_4$ diffraction data.

The transition from $\text{Li}(\text{NH}_3)\text{BH}_4$ to LiBH_4 is demonstrated in Figure 3.40. For these data, due to the neutron beam instability, the plot of scale factors is insufficient to provide any real insight into the reaction. Preferred orientation of both phases also limits the use of inspecting the entire diffraction pattern, however the Figure shows clearly that as the intensity of the $\text{Li}(\text{NH}_3)\text{BH}_4$ reflections drops, the intensity of the LiBH_4 reflections increases. It was also observed that in order to model the

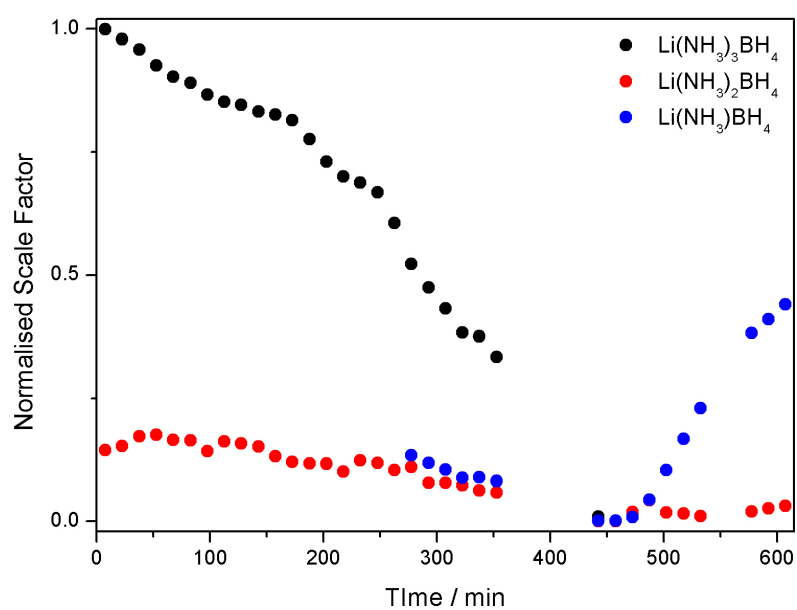


Figure 3.39: The normalised scale factors for the transition between $\text{Li}(\text{NH}_3)_3\text{BH}_4$, $\text{Li}(\text{NH}_3)_2\text{BH}_4$ and $\text{Li}(\text{NH}_3)\text{BH}_4$. Data were collected over continuous 15 minute periods using the IGAⁿ equipment on HRPD, the ammonia pressure was reduced sequentially from 70 mbar to 5 mbar before switching to dynamic vacuum.

LiBH_4 phase it was necessary to vary the lattice parameters (a step that was not necessary for modelling any of the other data). This change in lattice parameter is particularly great along the c-axis, as exemplified by the movement of the (002) peak to lower d-spacing that is seen in Figure 3.40. This suggests that as ammonia leaves $\text{Li}(\text{NH}_3)\text{BH}_4$, an intermediate and expanded LiBH_4 structure remains and takes some time to relax into the normal LiBH_4 phase. This would be an interesting reaction to investigate in greater detail though a greater level of analysis is not possible using the existing data.

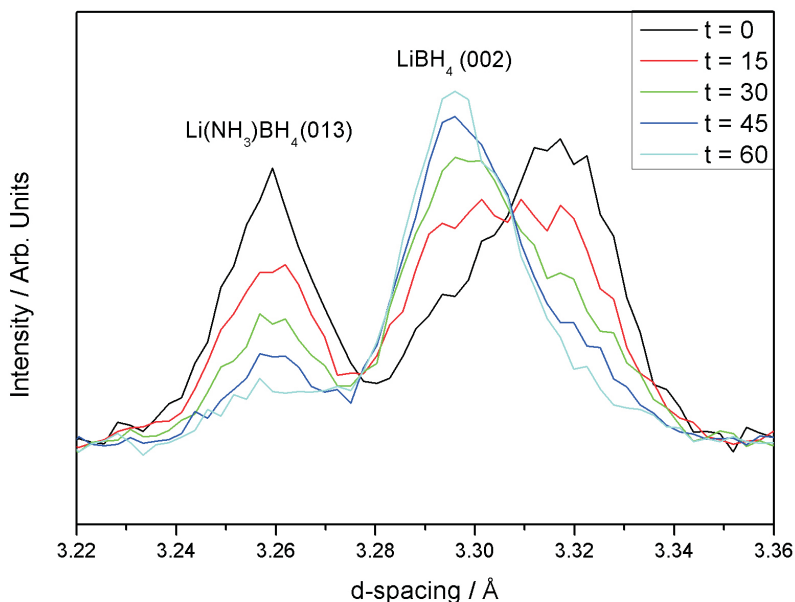


Figure 3.40: Diffraction data for the transition between $\text{Li}(\text{NH}_3)\text{BH}_4$ and LiBH_4 , showing the (013) and (002) reflections for $\text{Li}(\text{NH}_3)\text{BH}_4$ and LiBH_4 respectively. Data were collected over continuous 15 minute periods using the IGAⁿ equipment on HRPD, at a temperature of 50 °C and under dynamic vacuum.

The evidence shown in Figure 3.40 suggests that transition from $\text{Li}(\text{NH}_3)\text{BH}_4$ to LiBH_4 occurs completely and there is no trace of other decomposition products. In order to confirm this reversibility a sample of $\text{Li}(\text{NH}_3)\text{BH}_4$ was placed under vacuum in a Schlenk tube and heated to a temperature of 55 °C for a period of 12 hours. The product was a white powder and the diffraction data (shown in Figure 3.41)

show only LiBH_4 with no trace of either $\text{Li}(\text{NH}_3)\text{BH}_4$ or LiNH_2BH_3 . This confirms the reversibility of the $\text{Li}(\text{NH}_3)_n\text{BH}_4$ system.

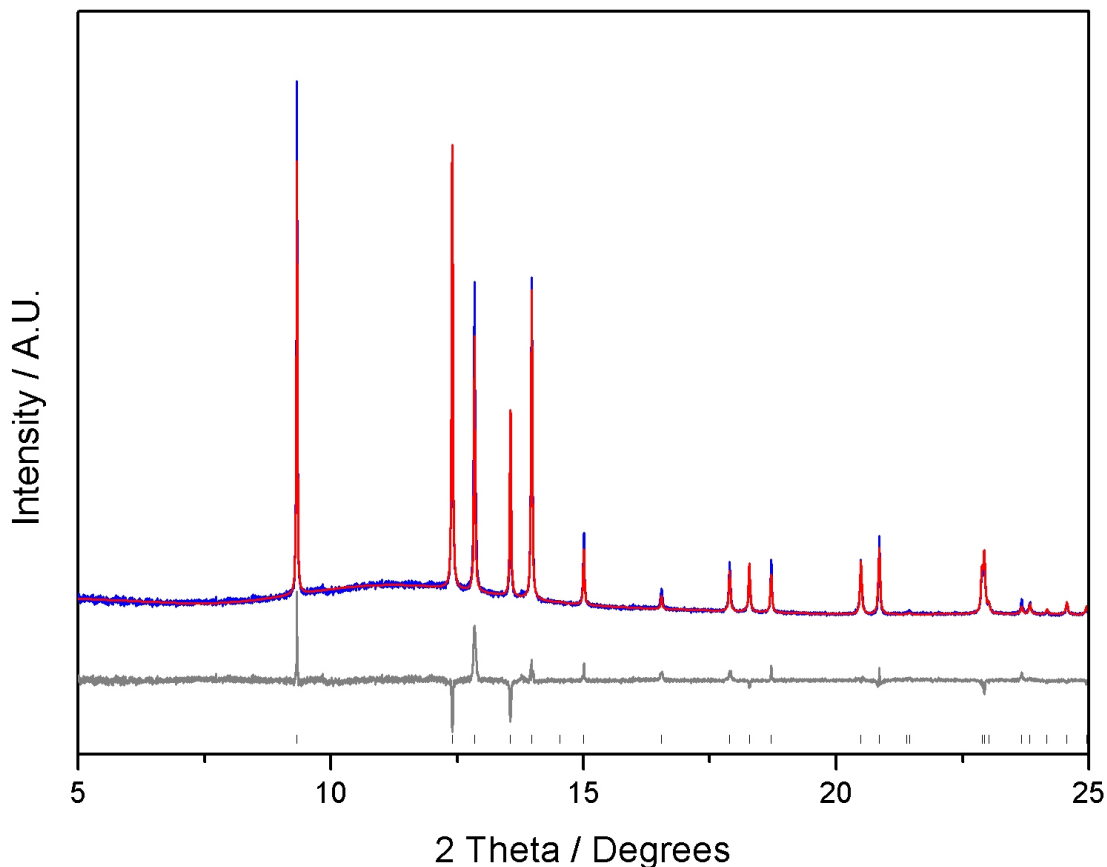


Figure 3.41: Final fit to the data for Rietveld refinement of the LiBH_4 model to X-ray powder diffraction data from a sample produced by heating $\text{Li}(\text{NH}_3)\text{BH}_4$ to 55 °C under vacuum. Data were collected at the ESRF with a wavelength $\lambda = 0.80268 \text{ \AA}$. Space group = $Pnma$, $R_{wp} = 6.5\%$, $R_{exp} = 4.1\%$, $\chi^2 = 2.44$. Experimental data are shown in blue, calculated in red with the difference in grey, tick marks show the expected positions of Bragg reflections.

3.7.2 Low-temperature Phase Transitions

Attempts to isolate $\text{Li}(\text{NH}_3)_2\text{BH}_4$ are briefly discussed in Section 3.4. Two low-temperature samples were produced in an attempt to isolate and collect X-ray diffraction data for this phase. The first, ‘high-temperature,’ sample was prepared by producing a sample of $\text{Li}(\text{NH}_3)_n\text{BH}_4$ in the normal way, and then evacuating the

Schlenk tube at 0 °C. The second, ‘low-temperature,’ sample was produced in the same way but evacuating at -78 °C. Both samples were transferred to the Diamond Light Source in sealed Schlenk tubes packed in dry ice, and were loaded into capillaries within an argon atmosphere glove bag at temperatures as close to -78 °C as possible. While it was not possible to load the high-temperature sample into a capillary tube, data were collected from the low-temperature sample. Data collection started at 200 K (-73 °C) and the sample was heated until Bragg reflections disappeared at 358 K (85 °C).

A surface plot of the diffraction data collected between 201 K and 295 K is shown in Figure 3.42, where it can be seen that at least 2 phases exist over this temperature range. Diffraction data (collected at 256 K) for the higher temperature phase are shown in Figure 3.43 where it can be seen that this phase is consistent with $\text{Li}(\text{NH}_3)_4\text{BH}_4$, though in the presence of a 2nd unknown phase that is observed in all these diffraction data. In the lower temperature phase it appears that $\text{Li}(\text{NH}_3)_4\text{BH}_4$ has undergone a monoclinic distortion, the transition between the two phases is complete at ca. 231 K upon heating. The phase transition is characterised by the clear splitting of (amongst others) the (111), (011), (112) and (212) peaks, while the (201), (002), (200) and (210) peaks do not split. The new low-temperature phase was indexed in the space group $P2_1/n11$, with the lattice parameters of $a = 11.6936(6)$ Å, $b = 6.9649(3)$ Å, $c = 10.0324(3)$ Å and monoclinic angle $\alpha = 84.247(6)$ °C determined by Pawley refinement using Topas. The final fit of the Pawley refined unit cell to the data is shown in Figure 3.44.

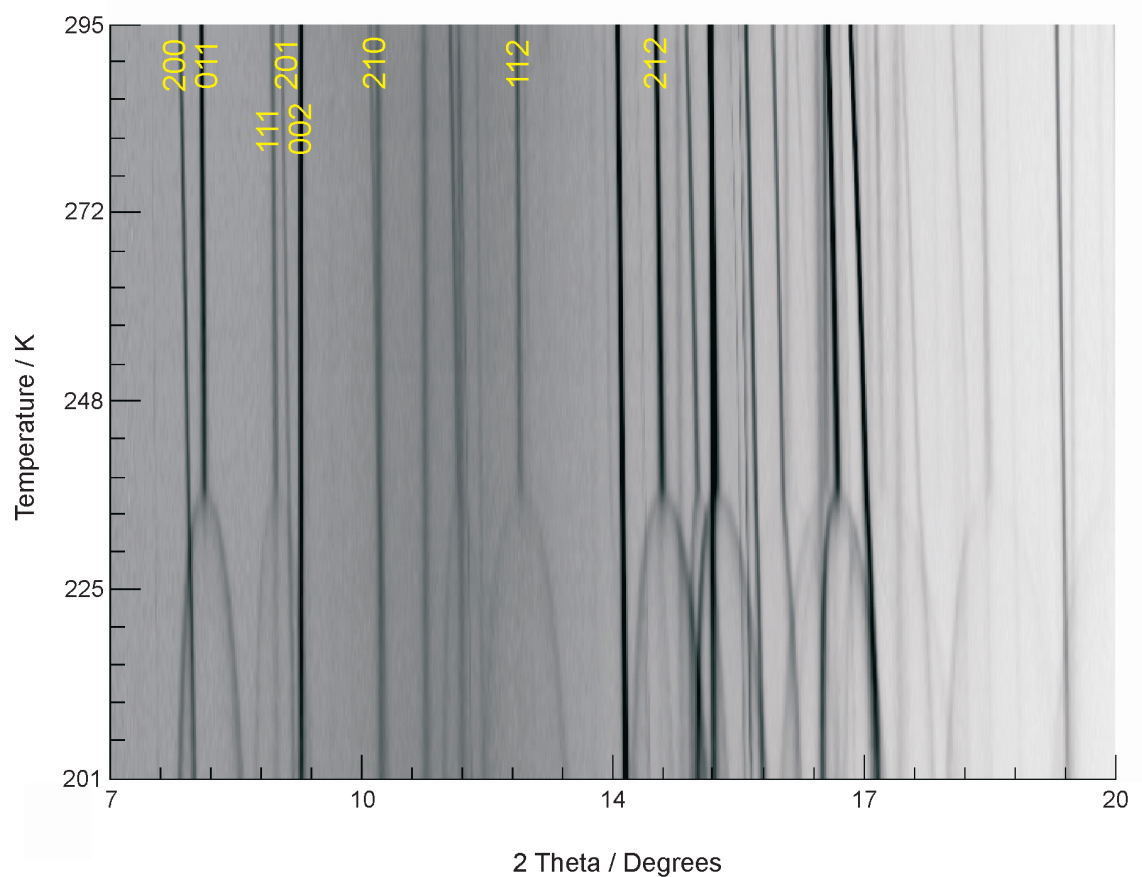


Figure 3.42: Surface plot of the diffraction data for the transition between $\text{Li}(\text{NH}_3)_4\text{BH}_4$ low-temperature and room temperature phases. Data were collected at Diamond with a wavelength $\lambda = 0.826008 \text{ \AA}$ and are plotted with the darkest areas representing the highest intensity peaks. The y-axis represents the run numbers of data that were summed every 10 s when heating between 201 K (top) and 295 K (bottom).

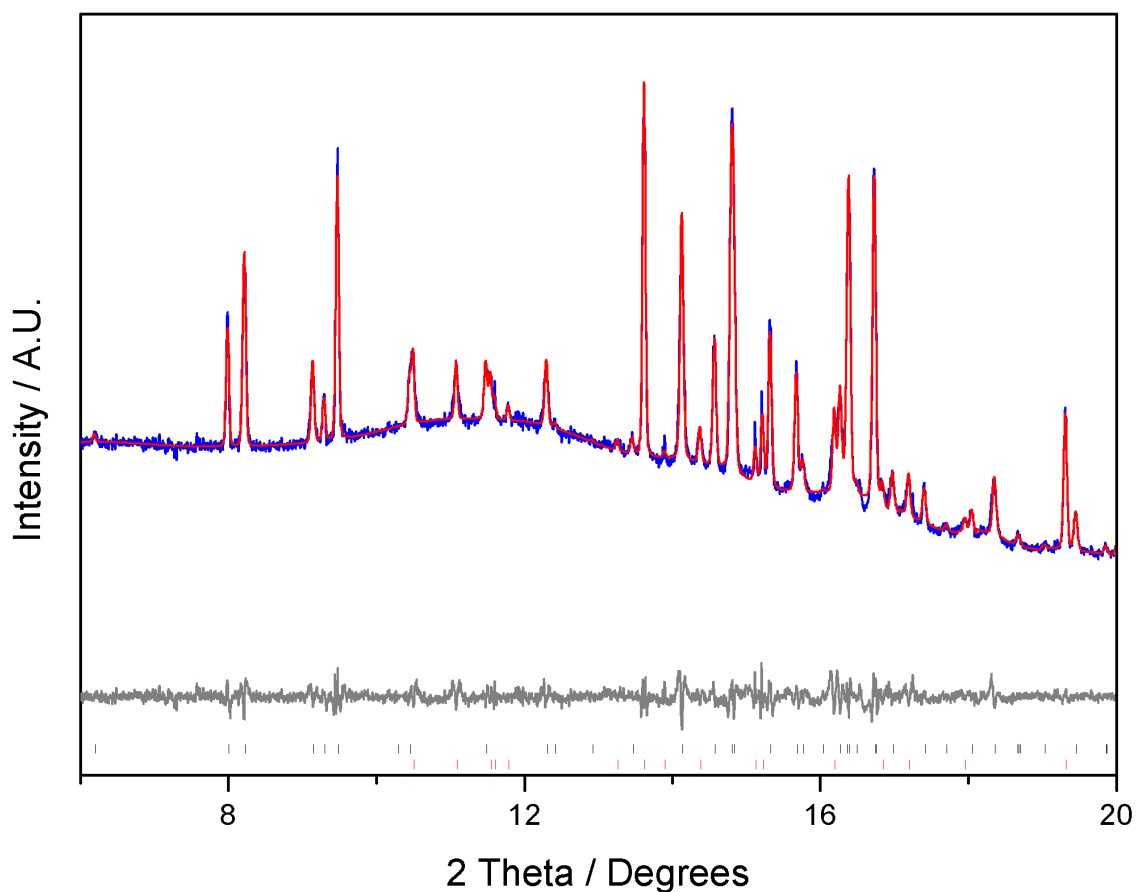


Figure 3.43: A Pawley refinement of the $\text{Li}(\text{NH}_3)_4\text{BH}_4$ unit cell to X-ray powder diffraction data collected at the Diamond light source at 256 K and with a wavelength $\lambda = 0.826008 \text{ \AA}$. Space Group = $Pnma$, $R_{wp} = 2.38\%$, $R_{exp} = 1.52\%$, $\chi^2 = 2.46$. Experimental data are shown in blue, calculated in red with the difference in grey, tick marks show the expected positions of Bragg reflections for $\text{Li}(\text{NH}_3)_4\text{BH}_4$ in black and an unknown phase in red.

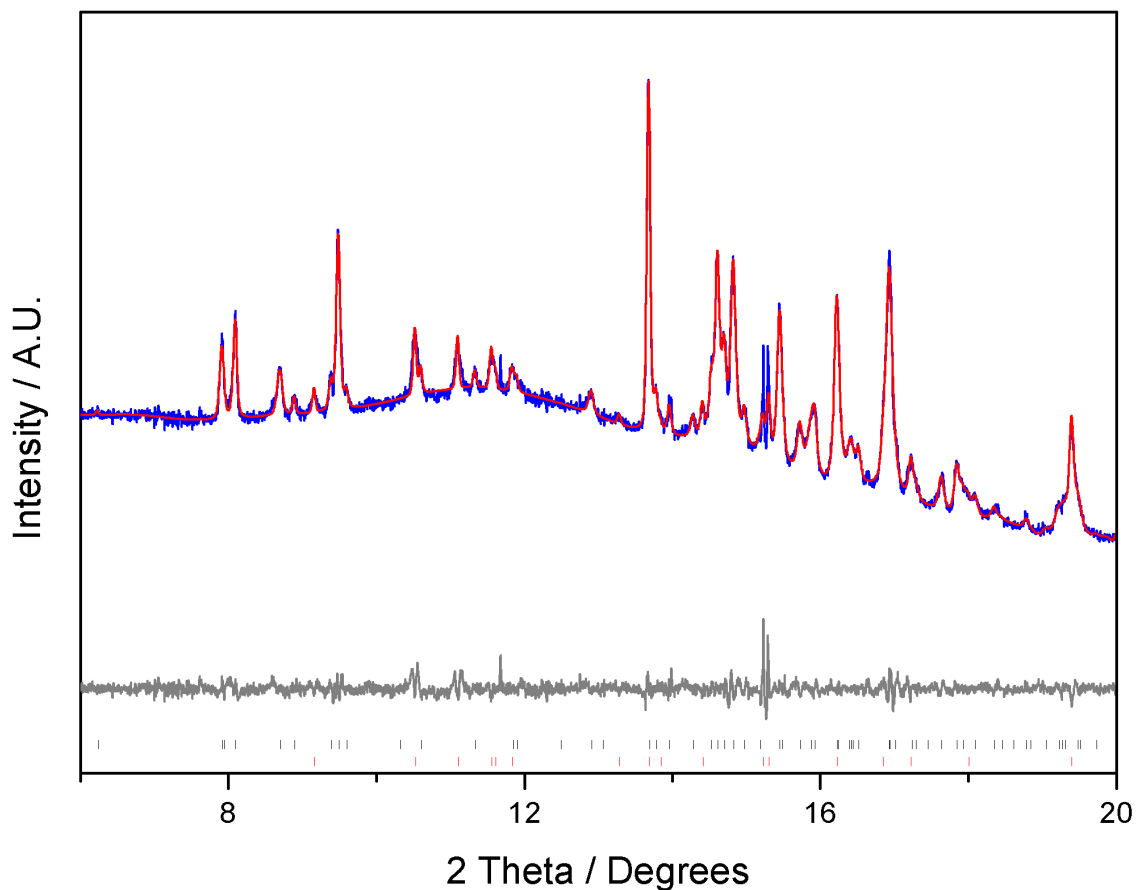


Figure 3.44: A Pawley refinement of the LT, monoclinic, phase of $\text{Li}(\text{NH}_3)_4\text{BH}_4$ unit cell to X-ray powder diffraction data collected at the Diamond light source at 201 K and with a wavelength $\lambda = 0.826008 \text{ \AA}$. Space Group = $P2_1/n11$, $R_{wp} = 2.10\%$, $R_{exp} = 1.52\%$, $\chi^2 = 1.91$. Experimental data are shown in blue, calculated in red with the difference in grey, tick marks show the expected positions of Bragg reflections for the LT $\text{Li}(\text{NH}_3)_4\text{BH}_4$ phase in black and an unknown phase in red.

3.8 Conclusions and Further Work

The structures of $\text{Li}(\text{NH}_3)_n\text{BH}_4$, with $n = 4, 3, 2, 1$ have been solved using a combination of Rietveld refinement from powder diffraction data and first-principles calculation. Each of the phases has been produced and identified in-situ and thus it has been shown that complete conversion from LiBH_4 to $\text{Li}(\text{NH}_3)_4\text{BH}_4$ and back again is possible — LiBH_4 acts as a fully reversible ammonia store. Disorder is a common feature of each structure, primarily in the form of multiple ammonia-hydrogen sites but also about the BH_4^- anion in the case of $\text{Li}(\text{NH}_3)_4\text{BH}_4$. A large amount of either dihydrogen or hydrogen bonding is also seen in each case and these bonds act to stabilise the structures.

$\text{Li}(\text{NH}_3)\text{BH}_4$ is easily synthesised and isolated, dynamic disorder associated with spinning of the ammonia molecule has been observed. Dihydrogen bonding interactions have been shown to be at their greatest within the disordered structure, and explain the weakening of the B–H bond compared to LiBH_4 . Heating of the sample at a temperature of 50 °C leads to complete conversion to the starting LiBH_4 .

$\text{Li}(\text{NH}_3)_2\text{BH}_4$ has been difficult to study due to its low melting point. This low melting point is explained by its open structure and loosely intercalated ammonia. In this compound, $\text{NH}\cdots\text{HB}$ dihydrogen bonds are reduced in strength compared to LiBH_4 , and are replaced by $\text{NH}\cdots\text{N}$ hydrogen bonds which to some extent stabilise the structure but also allow it to melt at low-temperatures.

$\text{Li}(\text{NH}_3)_3\text{BH}_4$ exists at room temperature ammonia pressures of between 30 mbar and 70 mbar. It is stabilised by many weak dihydrogen bonds and adopts a layered structure. It shows low levels of disorder compared to both $\text{Li}(\text{NH}_3)\text{BH}_4$ and $\text{Li}(\text{NH}_3)_4\text{BH}_4$.

$\text{Li}(\text{NH}_3)_4\text{BH}_4$ exists at room temperature ammonia pressures of greater than 70 mbar and is also stabilised by many weak dihydrogen bonds. High levels of disorder are observed and associated with both the BH_4^- anion and the NH_3 molecule. In the case of the NH_3 molecule this disorder is likely to be due to a high level of translational ammonia mobility within the structure. It has been shown that this phase orders and undergoes a monoclinic distortion at low-temperatures, suggesting that the disorder is dynamic in its nature.

Further work in this area would require a detailed study of the reversibility and kinetics of ammonia loading in the system, over tens and hundreds of loading cycles in order to establish the suitability of LiBH_4 as a commercially viable ammonia storage material. Further study into the structure of $\text{Li}(\text{NH}_3)_2\text{BH}_4$ and successful isolation of this phase would also be beneficial. Solving the low-temperature $\text{Li}(\text{NH}_3)_4\text{BH}_4$ structure may well enable a greater understanding of both its structure and the nature of the observed disorder. Another hugely beneficial avenue of research would be to attempt the growth of single-crystals of each phase. This may be possible through choosing the correct vapour pressure and slowly evaporating ammonia from a solution of $\text{LiBH}_4 \cdot n\text{NH}_3$. Subsequent neutron single-crystal diffraction experiments could then be used to both confirm the structures and also gain high quality data with which the nature of the disorder may be unequivocally established.

3.8.1 Evaluation as an Ammonia Storage Material

The results presented here clearly establish LiBH_4 as a very promising ammonia storage material. Table 3.11 compares the storage properties of the $\text{Li}(\text{NH}_3)_n\text{BH}_4$ group with liquid ammonia; while these ammines give a reduced ammonia density, significantly they offer greatly reduced vapour pressures. Compared to other ammines with comparable ammonia capacities, for example $\text{Mg}(\text{NH}_3)_6\text{Cl}_2$ or $\text{Ca}(\text{NH}_3)_8\text{Cl}_2$,

they have the significant advantage that 75 % of the bonded ammonia molecules may be removed by small changes in the ammonia pressure, with the remaining 25 % of stored ammonia released at the low-temperature of ca. 50 °C. Overall these properties mean that storage using LiBH_4 may be considered more favourable than liquid ammonia as vapour pressures are reduced, and than existing amines as lower temperatures are required to recover the stored ammonia. Reaction 3.1 shows that that $\text{Li}(\text{NH}_3)\text{BH}_4$ allows storage of 57 wt% ammonia using the room temperature PSA storage method operating between ca. 24 mbar and 110 mbar, this compares preferably to $\text{Ca}(\text{NH}_3)_8\text{Cl}_2$ that can be used to store 41 wt% ammonia using PSA between 700 mbar and 2.1 mbar as shown in Reaction 3.2

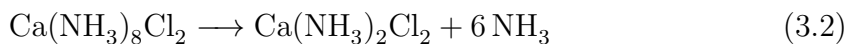
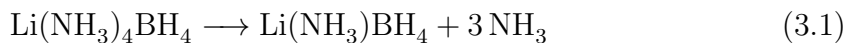


Table 3.11: Summary of ammonia storage properties of $\text{Li}(\text{NH}_3)_n\text{BH}_4$ in comparison with liquid NH_3

Compound	Reversible Ammonia Content / wt%	Ammonia Density / gL^{-1}	Vapour Pressure at 25 °C / mbar	Temperature required for complete ammonia release / °C
$\text{Li}(\text{NH}_3)\text{BH}_4$	41	296	6.7	50
$\text{Li}(\text{NH}_3)_2\text{BH}_4$	61	385	24	50
$\text{Li}(\text{NH}_3)_3\text{BH}_4$	70	526	96	50
$\text{Li}(\text{NH}_3)_4\text{BH}_4$	76	539	110	50
$\text{NH}_{3(l)} -33^\circ\text{C}$	100	682	1017	-

Magnesium Halide Ammines

4.1 Introduction

Considerable research has been carried out on magnesium halide hexa-ammines, $\text{Mg}(\text{NH}_3)_6\text{X}_2$, but the majority of this has focussed on the chlorides and studies that consider the properties of the group as a whole are uncommon. In this Chapter, the magnesium halides are considered in order to evaluate their ammonia storage properties and to gain an understanding of their chemistry that may be used to interpret the decomposition behaviour of other ammines. Analysis of these ammines has been carried out for the first time using ^{25}Mg NMR, INS and low-temperature diffraction. Though previous studies have used X-ray diffraction, structural understanding is here developed using unique models and neutron diffraction. The use of DFT has featured heavily in the work of Christensen et al., and in this work some important properties of the $\text{Mg}(\text{NH}_3)_n\text{X}_2$ system have been calculated and investigated, as discussed in Chapter 2.

4.2 Room Temperature Diffraction Studies

All of the $\text{Mg}(\text{NH}_3)_6\text{X}_2$ group are expected to share the same K_2PtCl_6 structure, and as discussed in Section 1.4.2 the $Fm\bar{3}m$ space group does not allow for a molecule with 3-fold rotational symmetry, thus the hydrogen atoms of the NH_3 molecules must be disordered. The disorder within the structure means that it can be challenging to model diffraction data, but successful modelling may lead to greater understanding of the structure and material properties. In order to gain a greater understanding of these structural intricacies, both neutron and X-ray diffraction experiments were carried out at room temperature and at variable temperatures from 10 K to 150 K.

4.2.1 X-Ray Powder Diffraction

Room temperature X-ray powder diffraction studies of $\text{Mg}(\text{NH}_3)_6\text{X}_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) were carried out using beam line I11 at the Diamond Light Source. The cubic ($Fm\bar{3}m$) K_2PtCl_6 structure was used to model the data using Rietveld refinement. The cubic lattice parameter, a , was allowed to vary freely while the positions of the Mg and X atoms were fixed on the appropriate special positions within the unit cell. The positions of the N and H atoms were allowed to vary freely along the y-direction. The N–H bond length was constrained between values of 0.9 Å and 1.1 Å, and the MgNH bond angle between 105 ° and 115 °.

To model the disorder in its most general form, the scattering from the hydrogen atoms of the NH_3 molecules is best delocalised around a ring of radius and position determined by the N–H bond length and MgNH bond angle; the overall occupancy of this ring should give an H:N ratio of 3:1.ⁱ In practice it was simpler to model the hydrogen atoms positioned at 15 ° intervals around the ring, giving each of the 24 hydrogen sites an occupancy of 3/24, an image of this model is shown in Figure 4.1. In principle with neutron or single-crystal diffraction data it would

ⁱThis approach is exemplified in analysis of the single crystal data discussed in Section 3.3.3

be possible to determine the favoured hydrogen sites about the ring. From powder X-ray diffraction alone it is not possible to unambiguously determine the hydrogen atom positions on this circular locus. However, for the purposes of comparison within a series of isostructural materials this approach provides the most accurate and appropriately constrained model for structural solution. Figure 4.2 shows a typical fit of the model to diffraction data, in this case the $\text{Mg}(\text{NH}_3)_6\text{I}_2$ data are shown with the remaining diffraction data displayed in Appendix Figures E.4 and E.5.

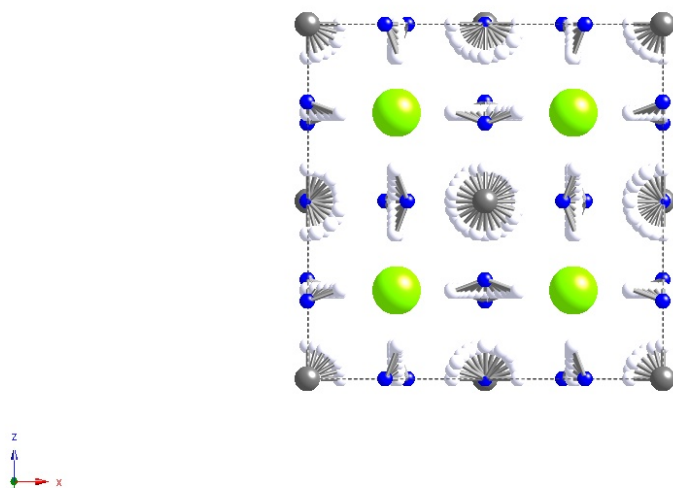


Figure 4.1: The disordered $\text{Mg}(\text{NH}_3)_6\text{Cl}_2$ model used for analysis of diffraction data showing hydrogen sites positioned every 15° about a circular locus. Magnesium is shown in grey, nitrogen in blue, hydrogen in off-white and chlorine in lime green.

The refinements confirm that each of the ammines shares the cubic K_2PtCl_6 structure, as reported for $\text{Mg}(\text{NH}_3)_6\text{Cl}_2$, and suggested for $\text{Mg}(\text{NH}_3)_6\text{Br}_2$ and $\text{Mg}(\text{NH}_3)_6\text{I}_2$.^{30,31,33,34} A comparison of the refined unit cell sizes and bond lengths is given in Table 4.1. It can be seen that the Mg–N distance increases slightly as the size of the anion increases. This suggests that the strength of the Mg–N bonding decreases with increasing size of the anion. This can be explained by the smaller more electronegative anions causing a reduced electron density on the en-

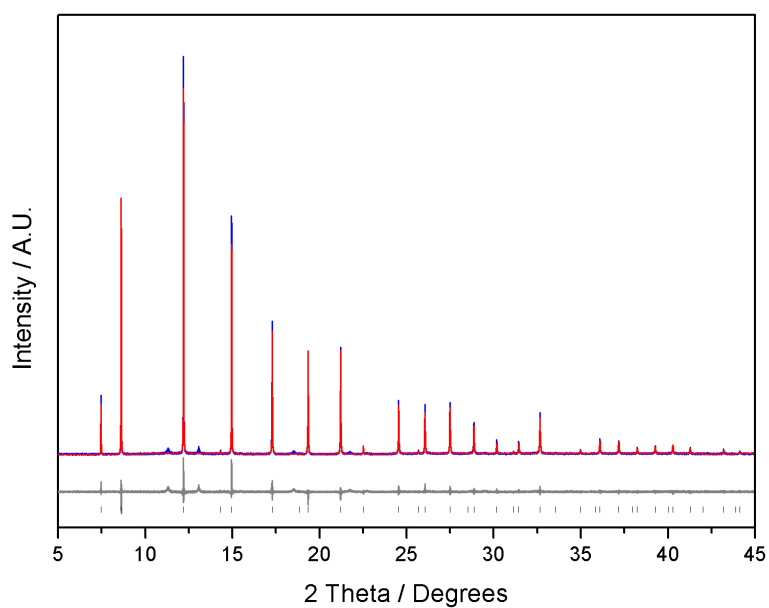


Figure 4.2: Final fit to the data for Rietveld refinement of the $\text{Mg}(\text{NH}_3)_6\text{I}_2$ model to X-ray powder diffraction data collected at the Diamond Light Source with a wavelength $\lambda = 0.82000 \text{ \AA}$. Space group = $Fm\bar{3}m$, $R_{wp} = 14.9\%$, $R_{exp} = 12.7\%$, $\chi^2 = 1.37$. Experimental data are shown in blue, calculated in red with the difference in grey, tick marks show the expected positions of Bragg reflections.

tire $\text{Mg}(\text{NH}_3)_6^{2+}$ cation. Given its lower electronegativity, this positive charge will remain principally on the Mg nucleus, resulting in stronger Mg–N bonding, though the effect is small in magnitude. The Mg–N bond lengths are similar in magnitude to those observed in the crystal structures of $\text{Mg}(\text{NH}_3)_2\text{X}_2$ for which Leineweber reports 2.125(3) Å for $\text{X} = \text{Cl}$ and 2.108(3) Å for $\text{X} = \text{Br}$.³⁴ The implication from these two bond lengths is that the bond strength trend is reversed in the di-ammine. However, the data for the bromide were collected at a temperature of 25 K, lower than those for the chloride and this may well account for the reduced bond length. Further investigation would be required to comment on this trend and its significance. There was no significant change in the N–H bond length or MgNH angle although this may be due to limitations of the X-ray powder diffraction data. The final refined atomic positions are given in Appendix Tables E.2, E.3 and E.4.

Table 4.1: Unit cell parameters and Mg–N bond lengths in $\text{Mg}(\text{NH}_3)_6\text{Cl}_2$, refined from X-ray powder diffraction data.

	$\text{Mg}(\text{NH}_3)_6\text{Cl}_2$	$\text{Mg}(\text{NH}_3)_6\text{Br}_2$	$\text{Mg}(\text{NH}_3)_6\text{I}_2$
a / Å	10.12258(3)	10.40693(1)	10.91487(2)
Mg–N Length / Å	2.161(2)	2.167(3)	2.181(4)

4.2.2 Neutron Powder Diffraction

Neutron powder diffraction data for $\text{Mg}(\text{ND}_3)_6\text{Cl}_2$ were collected using GEM at ISIS. Data were collected by the research group of P. J. van Ekeren but as no publications arose from their measurements and the group later disbanded, these data were released by ISIS for analysis in this Thesis. Data were collected at various temperatures and pressures, and analysis was preceded by subtraction of the complicated background pattern from all data. In-depth analysis of the experiment is hard given that the conditions are vague and on inspection of the data with the best count statistics it was observed that most of the data are of poor quality. A single

set of data collected under 1.5 bar ND_3 at 120 °C (393 K) produces a reasonable pattern. Extrapolating from the TGA data discussed in Section 4.5, $\text{Mg}(\text{ND}_3)_6\text{Cl}_2$ should be the predominant phase under these conditions. Using the same model that was refined against the X-ray diffraction data, and refining against data collected using GEM banks 3, 4 and 5 (34 °, 62 ° and 92 ° respectively) a good fit to the data, with $\chi = 1.699$, was achieved. The quality of the fit was similar for each bank, exemplified by that for bank 3 as shown in Figure 4.3. In principle, neutron data should allow the positions of greatest deuterium density about the locus to be determined. Allowing the the occupancies of the four deuterium sites to vary gave values of 0.009, 0.003, 0.084 and 0.490 for the 0 °, 15 °, 30 ° and 45 ° sites respectively. These occupancies may not be quantitatively correct, but a clear preference for the 45 ° site is shown. Referring to Figure 4.1, the 0 ° site is in line with any of the axes, and the 45 ° site aligns the N–D bond with a Cl^- anion. The refined $\text{ND}\cdots\text{Cl}^-$ distance is 2.660 Å, which is similar to the $\text{ClH}\cdots\text{ClH}$ distance of 2.589 Å seen in solid HCl .¹⁰⁷ The implication of this is that the ammine shows slightly weakened hydrogen bonding between N–D and X^- compared to that in HCl . This result agrees with the observations of Lienweber et al. and Hoser et al. who report hydrogen bond driven site preference in the disordered structures of $\text{Mg}(\text{ND}_3)_2\text{Cl}_2$ and $\text{Ni}(\text{ND}_3)_6\text{Br}_2$ respectively.^{39,45}

Diffraction data for $\text{Mg}(\text{ND}_3)_6\text{Cl}_2$ were also collected using HRPD at a temperature of 95 K during the low-temperature experiment discussed in Section 4.3. The high flux of GEM should make it the superior instrument for studying this kind of disorder, but the HRPD data has the advantage of not being subject to any post collection manipulation (the improved resolution of HRPD does not help in this case as the highly symmetrical cubic structure produces few Bragg reflections that are close to their neighbours). Using the same model as for the GEM data and refining against data collected using banks 1 and 2 (168 ° and 90 ° respectively) a good fit to the data, with $\chi = 2.137$, was obtained. Repeating the same process and allowing

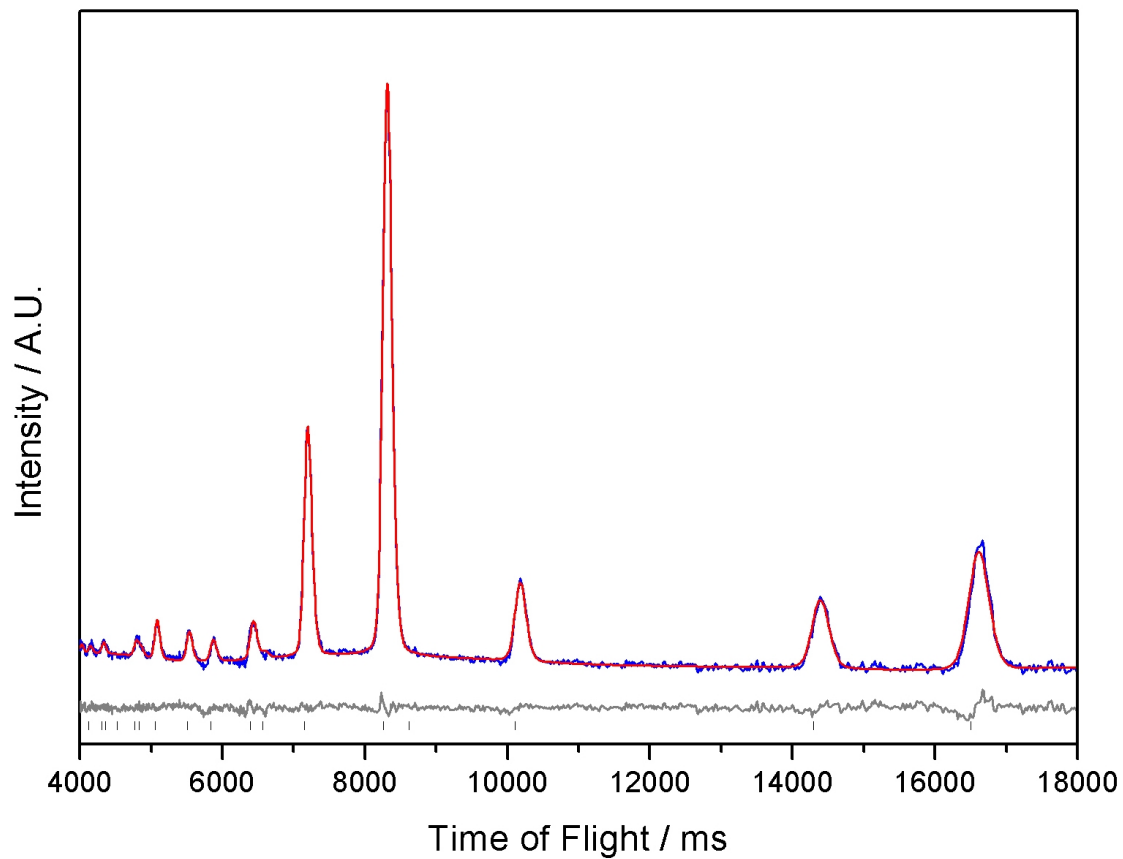


Figure 4.3: Final fit to the data for Rietveld refinement of the $\text{Mg}(\text{NH}_3)_6\text{Cl}_2$ model to neutron powder diffraction data, collected using GEM bank 3 (34°) by van Ekeren et al.. Space group = $Fm\bar{3}m$, $R_{wp} = 4.49\%$, $R_{exp} = 3.37\%$, $\chi^2 = 1.77$. Experimental data are shown in blue, calculated in red with the difference in grey, tick marks show the expected positions of Bragg reflections.

the occupancies of the four deuterium sites to vary gave values of 0.014, 0.001, 0.083 and 0.500 for the 0 °, 15 °, 30 ° and 45 ° sites respectively. Once again a strong preference for the 45 ° site is observed. Compared to the GEM refinement, a shorter ND...Cl distance of 2.634 Å reflects a global reduction in unit cell parameters, which is expected for a lower temperatures. A comparison of some useful data from the GEM and HRPD refinements is given in Table 4.2.

Table 4.2: A comparison of selected $\text{Mg}(\text{ND}_3)_6\text{X}_2$ data, refined from neutron powder diffraction data collected using GEM and HRPD.

	GEM	HRPD
T / K	393	95
a / Å	10.2450(11)	10.0899(17)
Mg–N Length / Å	2.272(4)	2.210(3)
N–D Length / Å	0.995(56)	0.995(26)

4.3 Low Temperature Diffraction Studies

Given the disorder at room temperature, it is highly likely that $\text{Mg}(\text{NH}_3)_6\text{Cl}_2$ adopts an ordered structure at low temperatures. Initial experiments were carried out at the ESRF to investigate any low temperature phases, these experiments were then extended using HRPD at ISIS.

4.3.1 X-ray Powder Diffraction

Initial analysis shows that two phases exist; the $Fm\bar{3}m$ high temperature (HT) phase, and a second low temperature (LT) phase, though the HT phase was observed in all collected data. Initial inspection of the ESRF data revealed transitions occurring at different temperatures, with the high temperature phase dominant at temperatures as low as 12 K, and the low temperature phase dominant up to temperatures of 66 K. To some degree this disparity in transition temperatures may be

due to hysteresis, however on cooling from 54 K to 10 K negative thermal expansion, that was not seen in other parts of the experiment, was observed. Furthermore, and crucially, when the sample position was moved a different phase was observed in a nonirradiated section of the sample. These two facts suggest that the sample was prone to beam damage and possibly that beam heating was also occurring. Thus the transition temperatures observed are not reliable, but data collected from a section of a sample that was only in the X-ray beam for a short time should provide reliable phase information. Beam damage is thought to be predominant in systems exhibiting hydrogen bonding, and acts to destroy those bonds.⁷⁴ Thus the appearance of the high temperature phase at lower temperatures than expected may suggest that hydrogen bonding is an important factor in formation of the low temperature phase.

4.3.2 Neutron Powder Diffraction

The neutron diffraction data show the same HT and LT phases as the X-ray data and once again the HT phase was observed at all temperatures. The maintained presence of the high temperature phase at low temperatures may be a result of disorder being frozen into the system due to the cooling rate, although it is possible that even with an infinitely slow cooling rate some disorder may remain in the system. Observation of the diffraction data shows that reflections from the low temperature phase appear at 90 K and reach full intensity at 80 K upon cooling. Upon heating they start to disappear at 85 K and are completely absent at 90 K. The observed transition temperatures are more reliable than those seen in the X-ray data, as neutron irradiation does not induce the same type of beam damage or heating as X-ray.

A theoretical study produced by Tekin et al. suggested an ordered phase would exist in one of the space groups; $R\bar{3}$, $I4/m$, $C2/m$ or $Cmmm$, with the $R\bar{3}$ structure calculated to have the lowest energy.⁴⁴ None of the proposed sets of unit cell

parameters allowed a good fit to the data, however doubling the parameters of the $R\bar{3}$ cell did allow a good fit to the data. Without any further knowledge of the proposed structure, the space group $R\bar{3}$ is not a clear choice, there was no significant improvement in the fit of the Pawley refinement using either $R\bar{3}$ or its supergroup $R\bar{3}m$. In absence of any reason to lower the symmetry and given that it is also a subgroup of $Fm\bar{3}m$, the higher symmetry $R\bar{3}m$ was chosen. The final fit of the $R\bar{3}m$ cell to the neutron diffraction data is shown in Figure 4.4, the refined lattice parameters for the hexagonal cell are $a = 15.92(3) \text{ \AA}$ and $b = 32.3(2) \text{ \AA}$ with a volume $V = 7304(52) \text{ \AA}^3$. The uncertainties in these lattice parameters are huge and this reflects the broad peak shape which itself indicates significant strain in the sample. These uncertainties combined with the huge unit cell meant that attempts to solve the structure using the simulated annealing technique did not yield any useful results. Using computational methods to try and maximise the number of $\text{NH}\cdots\text{Cl}^-$ interactions would probably be the best method to try and solve this structure.

The changes in lattice parameter of the HT phase with respect to temperature are shown in Figure 4.5, which highlights the lack of hysteresis in the neutron data. The change in lattice parameters suggest that the phase transition occurs between 70 K and 90 K, which agrees with the *prima facie* analysis. An interesting feature of the data is the expanded lattice of the HT phase when coexistent with the LT phase. It is proposed that formation of $\text{NH}\cdots\text{Cl}^-$ bonds, in a manner analogous to the expansion of ice cf. water, causes this expansion of the lattice. This is strong evidence for dynamic disorder existing above the transition temperature in the high temperature phase. Unfortunately the diffraction data are not of sufficient quality to analyse this in more detail. Investigation of the low temperature phase shows a more normal volume expansion with increasing temperature, though without any structural information and given the large number of potential reflections contributing to the broad peaks, detailed analysis of these lattice changes is a moot point.

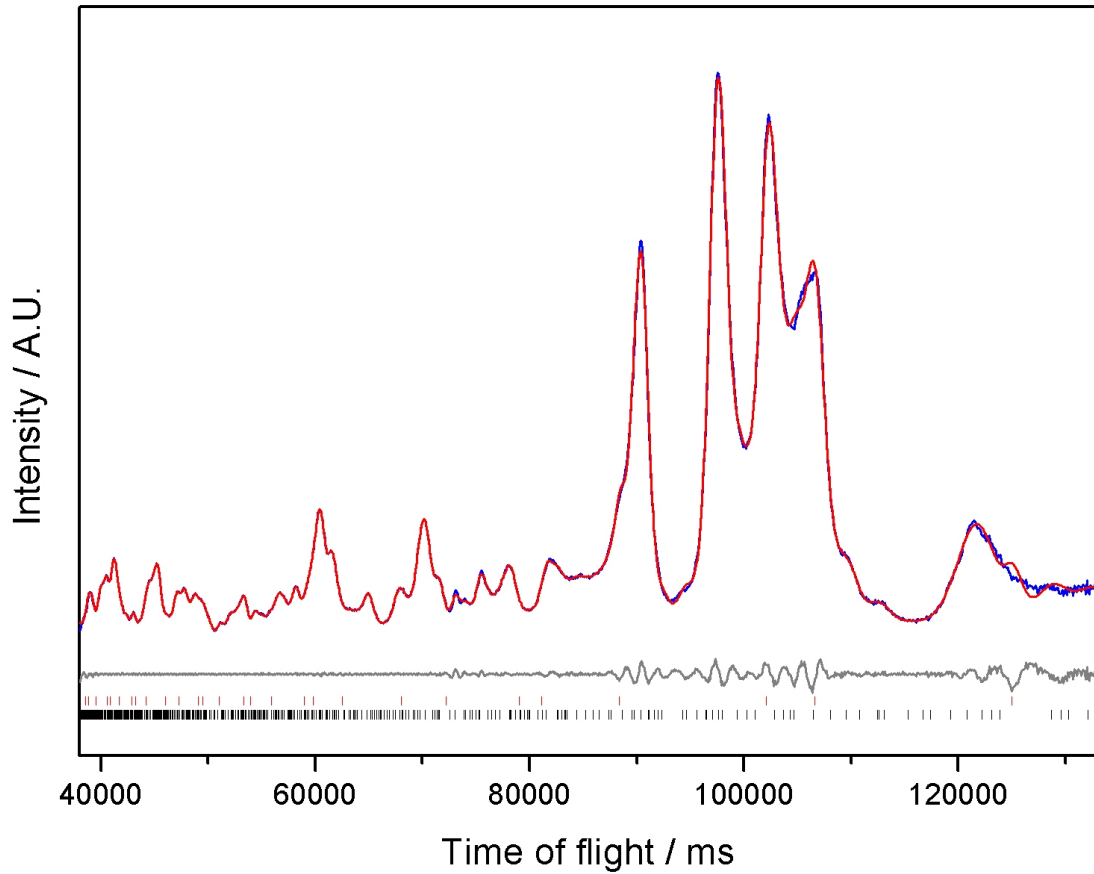


Figure 4.4: Final fit to the data for Pawley refinement of the $\text{Mg}(\text{NH}_3)_6\text{Cl}_2$ low temperature ($R\bar{3}m$) unit cell to neutron powder diffraction data, collected using HRPD bank 2 (90°) at a temperature of 20 K. $R_{wp} = 0.75\%$, $R_{exp} = 0.27\%$, $\chi^2 = 7.44$. Experimental data are shown in blue, calculated in red with the difference in grey, tick marks show the expected positions of Bragg reflections with the high temperature ($Fm\bar{3}m$) phase in red and the low temperature phase in black.

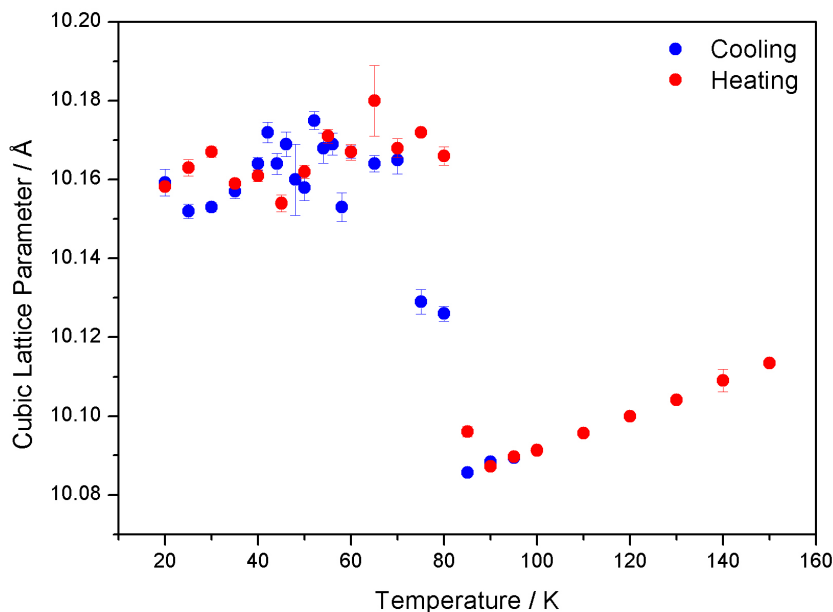


Figure 4.5: The lattice parameters of the $\text{Mg}(\text{NH}_3)_6\text{Cl}_2$ high-temperature phase between 20 K and 150 K, refined from neutron diffraction data collected using HRPD bank 2 (90 °).

4.4 Nuclear Magnetic Resonance

^{25}Mg NMR measurements were carried out at Durham University via the EPSRC solid-state NMR service and initial analysis was aided by Dr David Apperley. The purpose of these experiments was to investigate the influence of the anion on the Mg nuclei and Mg–N bonding in MgX_2 and $\text{Mg}(\text{NH}_3)_6\text{X}_2$. The very low resonant frequency of the ^{25}Mg nucleus means that it can be hard to observe using NMR as most spectrometers are unable to operate at such a low frequency. Thus, and given the nature of shared resources and the requirements of this Thesis, it was not possible to follow some of the more interesting spectroscopic results with further investigation.

The spectra of MgI_2 and all $\text{Mg}(\text{NH}_3)_6\text{X}_2$ each show a narrow symmetric line, typified by the $\text{Mg}(\text{NH}_3)_6\text{Cl}_2$ spectrum shown in Figure 4.6 (the remaining spectra are shown in Appendix Figures E.1 to E.3). The narrow and symmetric lines show

that there is no second-order quadrupolar broadening so the magnesium must be in a high-symmetry (octahedral) environment. This is consistent with the K_2PtCl_6 structures of $\text{Mg}(\text{NH}_3)_6\text{X}_2$ and the CdI_2 structure of MgI_2 .

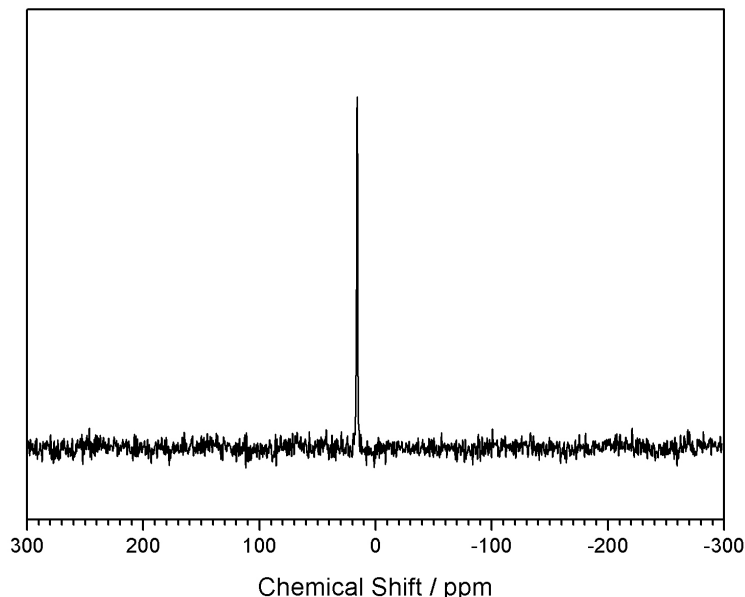


Figure 4.6: The ^{25}Mg NMR spectrum of $\text{Mg}(\text{NH}_3)_6\text{Cl}_2$, showing a sharp line at 15.921 ppm (referenced to a 1 M solution of $\text{Mg}(\text{H}_2\text{O})_6\text{Cl}_{2(\text{aq})}$).

The spectrum of MgBr_2 is shown in Figure 4.7. As with MgI_2 there is a single line but in this case second order quadrupolar broadening is observed. This suggests a lower symmetry environment than that found in MgI_2 but one that is still axially symmetric. This is not consistent with the crystal structure, as MgBr_2 also adopts the CdI_2 structure under these conditions and changing the proximity of neighbouring ions alone should not introduce any second order effects. This is certainly an interesting spectrum, though for the purposes of this work the region of the chemical shift is the most important result.

The spectrum of MgCl_2 is shown in Figure 4.8, again a single sharp line is observed, but with the presence of 2 additional peaks. It does not appear that these peaks are part of the quadrupolar bandshape, and it is likely that they belong

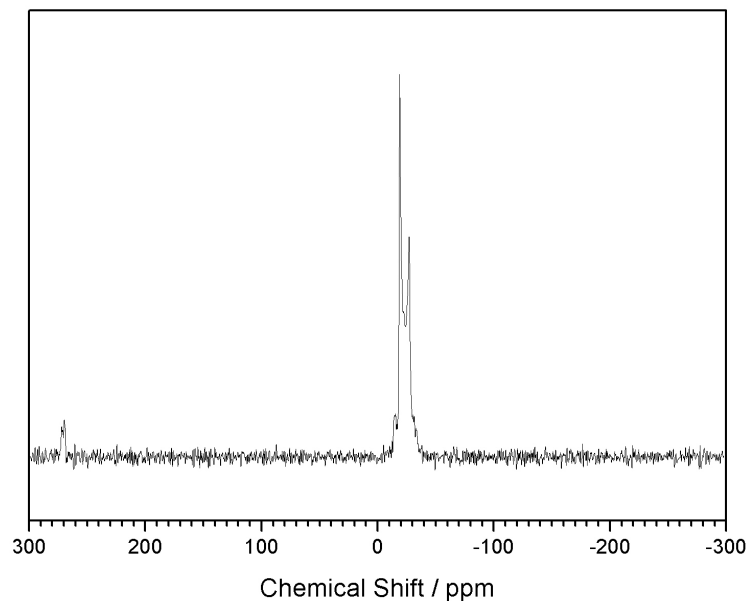


Figure 4.7: The ^{25}Mg NMR spectrum of MgBr_2 , showing sharp lines at 19.000 ppm and -27.111 ppm (referenced to a 1 M solution of $\text{Mg}(\text{H}_2\text{O})_6\text{Cl}_2(\text{aq})$).

either to a secondary phase or an impurity. There is a broad signal underlying the narrow lines that suggests some disorder in the system and may also be associated with an impurity. If this sample, or the MgBr_2 sample, did contain impurities then they should also appear in the spectra of the ammines. The absence of these impurities in the spectra of the ammines suggests the presence of disorder that still allows conversion to the ammine, that impurities were introduced to the sample during pre-measurement handling, or that they were removed during formation of the ammine. Once again the significant result for this work is the region of the chemical shift.

It was not possible to obtain a spectrum from MgF_2 . This is likely due to a much higher quadrupole coupling constant than for the rest of the group resulting in a signal that is more diffuse or broad and difficult to detect. Dipolar coupling to fluorine may add additional line broadening that complicates matters further.

A summary of all NMR data is given in Table 4.3. In the MgX_2 series, the

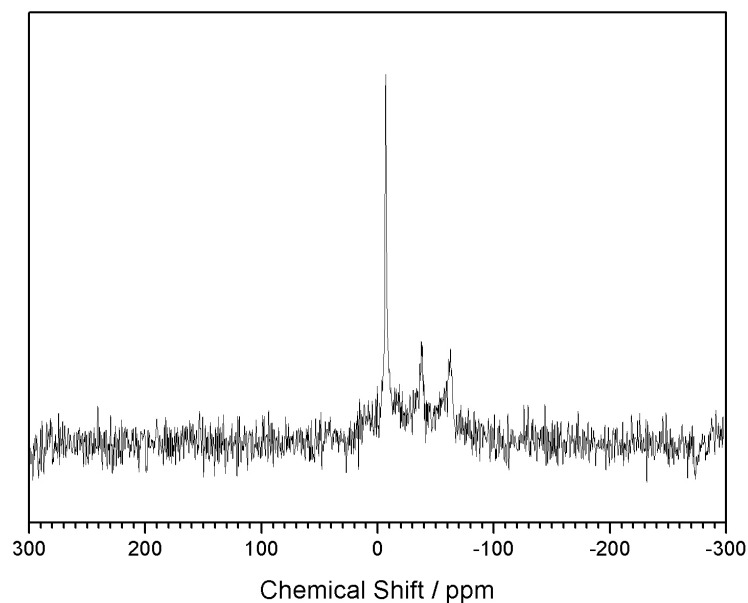


Figure 4.8: The ^{25}Mg NMR spectrum of MgCl_2 , showing a sharp line at -6.909 ppm (referenced to a 1 M solution of $\text{Mg}(\text{H}_2\text{O})_6\text{Cl}_{2(\text{aq})}$).

^{25}Mg chemical shift was observed to decrease with increasing atomic number of the anion X. This decrease in chemical shift is indicative of an increase in diamagnetic shielding of the Mg cation, and hence an increase in the electron density around the Mg nucleus. Which is a result of the change in electronegativity of the anion, with the larger less electronegative anions allowing a greater electron density to reside on the Mg nuclei.

The chemical shifts seen in the $\text{Mg}(\text{NH}_3)_6\text{X}_2$ series are shifted downfield relative to those in MgX_2 ; this corresponds to a lower electron density on the Mg nucleus in $\text{Mg}(\text{NH}_3)_6\text{X}_2$ than in the corresponding MgX_2 . This reduced electron density most probably arises as nitrogen is a weaker σ -donor than any of the halides.

Within the $\text{Mg}(\text{NH}_3)_6\text{X}_2$ series, the chemical shift decreases with increasing atomic number of X. This trend is the same as that observed in MgX_2 though an order of magnitude smaller. The small increase in Mg–N bond lengths discussed in Section 4.2.1 corroborate this effect, as increasing the electron density of the Mg^{2+}

cation will result in a weaker and longer bond. However, the differences in chemical shifts and Mg–N bond lengths of the $\text{Mg}(\text{NH}_3)_6\text{X}_2$ series are very small (covering a range of 0.8 ppm and 0.02 Å respectively), thus varying the anion does not appear to have any significant effect on the strength of the Mg–N bond.

Table 4.3: Summary of ^{25}Mg data for the MgX_2 and $\text{Mg}(\text{NH}_3)_6\text{X}_2$ series, chemical shifts referenced to a 1 M solution of $\text{MgCl}_2(\text{H}_2\text{O})_6(\text{aq})$.

Compound	Chemical Shift ppm	Compound	Chemical Shift ppm
MgCl_2	-6.9	$\text{MgCl}_2(\text{NH}_3)_6$	15.9
MgBr_2	-19.0	$\text{MgBr}_2(\text{NH}_3)_6$	15.2
MgI_2	-81.1	$\text{MgI}_2(\text{NH}_3)_6$	15.1

4.5 Thermogravimetric Analysis

Thermogravimetric analysis of $\text{Mg}(\text{NH}_3)_6\text{X}_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) was carried out using the procedure described in Section 2.11.1. Measurements were carried out using a heating rate of $2\text{ }^\circ\text{Cmin}^{-1}$ under a 1 bar argon atmosphere with a flow rate of 5 mlmin^{-1} . A comparison of each set of data is shown in Figure 4.9 and summarised in Table 4.4. Figure 4.10 shows each mass loss with the first derivative of the mass loss with respect to time ($\frac{dm}{dt}$) also plotted, these data are also summarised in Table 4.4. The derivative plots show that ammonia loss occurs in a three step process for each compound. These three steps have mass losses consistent with the process described in (Section 1.4) Equation 1.7, that is the evolution of 4 ($\text{T} = \text{T}_1$) and sequentially 2×1 ($\text{T} = \text{T}_2$ and $\text{T} = \text{T}_3$) ammonia molecules. The temperature required for each decomposition step is seen to increase down the halide group. It appears that the lifetime of the $\text{Mg}(\text{NH}_3)_2\text{X}_2$ intermediates decreases with increasing atomic number of X. A clear stability plateau may be observed in the desorption step for $\text{Mg}(\text{NH}_3)_2\text{Cl}_2$ to $\text{Mg}(\text{NH}_3)\text{Cl}_2$, which is less well defined for $\text{Mg}(\text{NH}_3)_2\text{Br}_2$

to $\text{Mg}(\text{NH}_3)\text{Br}_2$ and difficult to distinguish for $\text{Mg}(\text{NH}_3)_2\text{I}_2$ to $\text{Mg}(\text{NH}_3)\text{I}_2$. These trends are discussed further in Section 4.8.1.

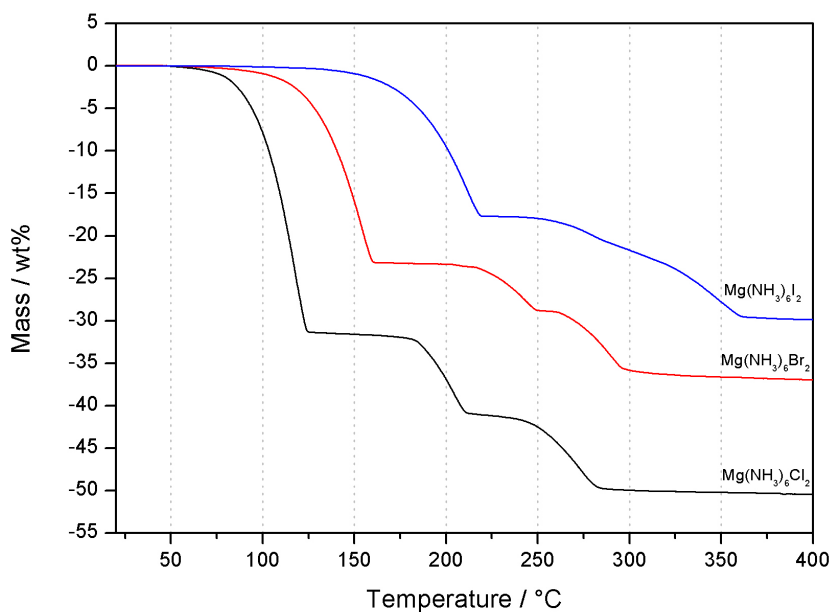


Figure 4.9: Mass loss of $\text{Mg}(\text{NH}_3)_6\text{Cl}_2$ as a function of temperature for in black, $\text{Mg}(\text{NH}_3)_6\text{Br}_2$ in red and $\text{Mg}(\text{NH}_3)_6\text{I}_2$ in blue.

Table 4.4: A summary of TGA data on the decomposition of $\text{Mg}(\text{NH}_3)_6\text{X}_2$.

Starting Compound	Desorption Step 1			Desorption Step 2			Desorption Step 3		
	T_{1o}	T_{1p}	wt%	T_{2o}	T_{2p}	wt%	T_{3o}	T_{3p}	wt%
$\text{Mg}(\text{NH}_3)_6\text{Cl}_2$	98	117	32	187	204	10	250	274	9
$\text{Mg}(\text{NH}_3)_6\text{Br}_2$	130	155	23	223	243	6	270	292	9
$\text{Mg}(\text{NH}_3)_6\text{I}_2$	182	212	18	na	282	na	na	349	na

Figure 4.11 shows a linear relationship between the anionic radii and the peak rate of desorption (T_p) for each of the three desorption steps, T_1 , T_2 and T_3 . The gradients of the lines of best fit are approximately equal for T_2 and T_3 ($197 \text{ K}\text{\AA}^{-1}$), whilst that for T_1 is greater ($275 \text{ K}\text{\AA}^{-1}$). The most appropriate analysis of these data considers all data presented in this Chapter, and is discussed in Section 4.8.1.

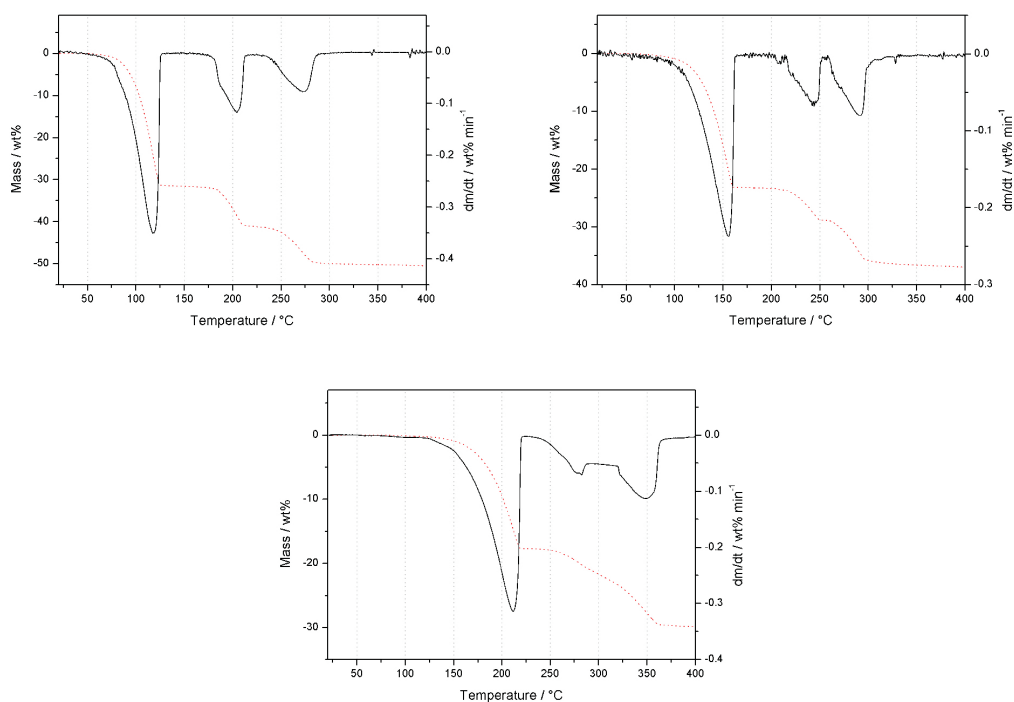


Figure 4.10: Mass loss as a function of temperature in red and the change in mass loss with respect to time (in this case $T = f(t)$) ($\frac{dm}{dt}$) in black for (from top left to bottom) $\text{Mg}(\text{NH}_3)_6\text{Cl}_2$, $\text{Mg}(\text{NH}_3)_6\text{Br}_2$ and $\text{Mg}(\text{NH}_3)_6\text{I}_2$.

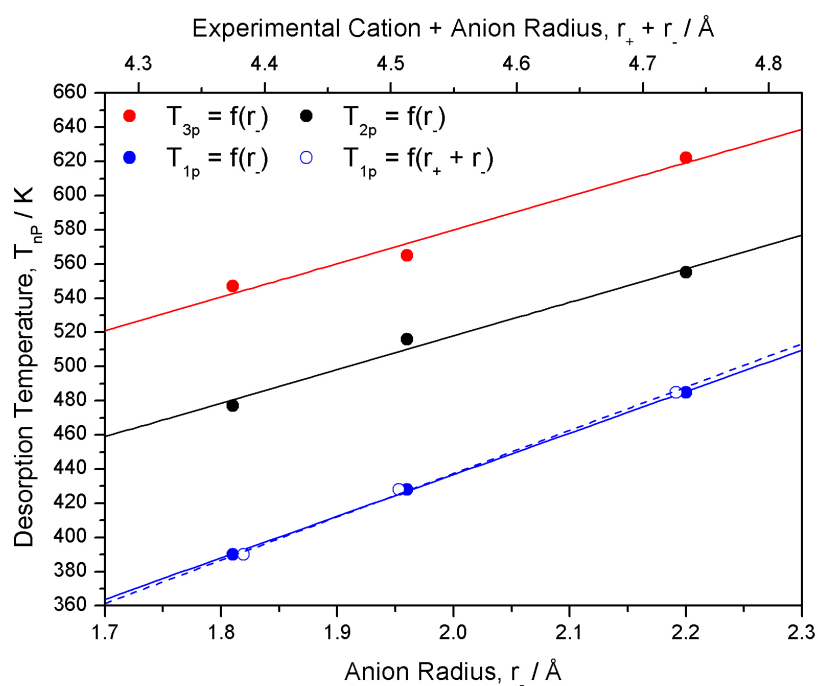


Figure 4.11: A plot of T_{nP} against ionic radii the X^- in $Mg(NH_3)_6X_2$ ($X = Cl, Br, I$). The lower x-axis shows the reported radii of X^- ,¹⁰⁸ whilst the upper axis shows the radii of the cation plus anion as calculated from the X-ray powder diffraction data. The lines show linear fits to the data. Error bars are included but where not visible are hidden by datum markers.

4.6 Inelastic Neutron Scattering

Inelastic neutron spectroscopy data were collected using TOSCA at ISIS. Samples of $\text{Mg}(\text{NH}_3)_6\text{Cl}_2$, $\text{Mg}(\text{NH}_3)_6\text{Br}_2$, and $\text{Mg}(\text{NH}_3)_6\text{I}_2$ were produced as described in Section 2.5 and loaded into aluminium sample holders in an argon atmosphere glove box. The spectra of all three compounds are shown in Figure 4.12, a large amount of common features reflect their structural similarity though to gain a better understanding of them it was necessary to model the data using DFT and aClimax. INS data were collected at 20 K, (as seen in Section 4.3) two phases of $\text{Mg}(\text{NH}_3)_6\text{Cl}_2$ coexist at this temperature and this is assumed to be the case for $\text{Mg}(\text{NH}_3)_6\text{Br}_2$ and $\text{Mg}(\text{NH}_3)_6\text{I}_2$. As the structure of the low temperature phase remains elusive and it is not possible to model the disordered phaseⁱⁱ, any analysis becomes increasingly complicated. However, the fact that the disordered phase remains at low temperatures means a range of NH_3 orientations will exist in the solid. Simply modelling the data using the high-temperature cubic structure of $\text{Mg}(\text{NH}_3)_6\text{Cl}_2$ with an arbitrary set of ammonia orientations produces a calculated spectrum, shown in Figure 4.13, that agrees strongly with the observed spectrum. Analysing these simply calculated phonon modes should allow for reasonable assignment of modes seen in the experimental spectrum, without the need for the more rigorous calculation required to find the most stable low temperature structure. A full description of the calculated modes is given in Appendix Table D.2.

Figure 4.14 highlights a number of common modes that are observed to move as the anion is changed. All the labelled modes are detailed in Table 4.5 and relate to motion of NH_3 molecules in a manner associated with libration for modes 1 and 2; rocking (with some minor libration) for 3, 4, and 5, and; an umbrella motion for 6. The range of the observed shifts varies from 14 cm^{-1} to 95 cm^{-1} , and while at the lower end the magnitude of the shifts may be outside the resolution of the instrument ($\delta\omega/\omega \approx 1.5\%$), the trends are still compelling. The decrease

ⁱⁱWithin the computational limits of using a sensible amount processor time.

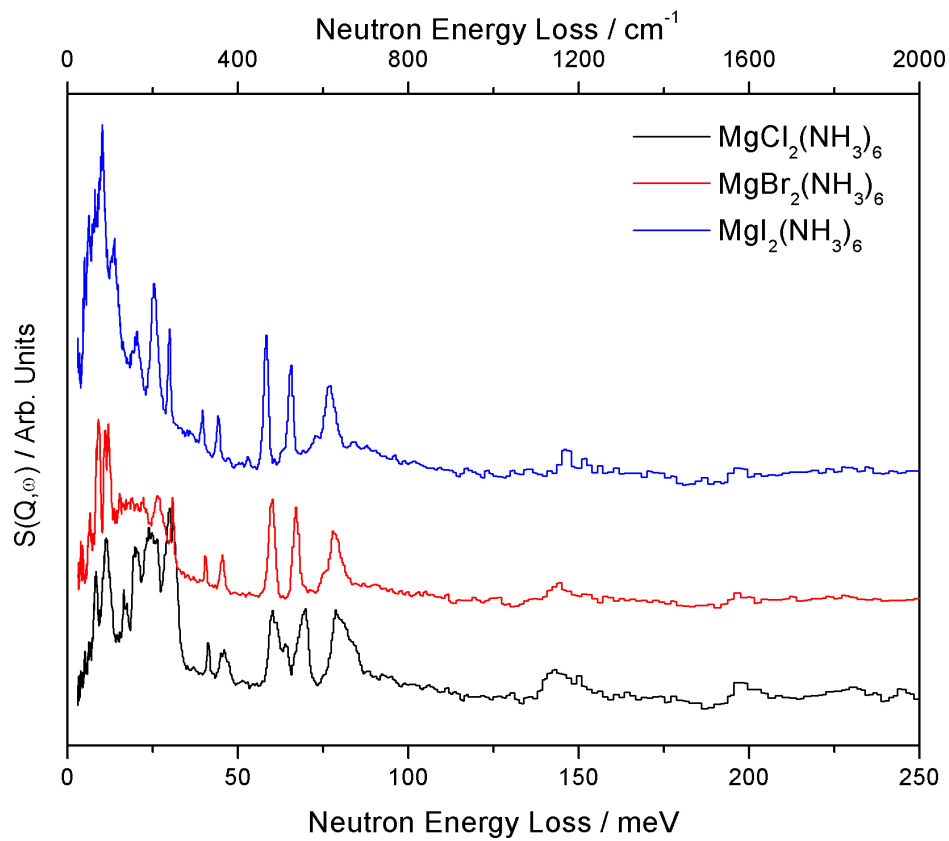


Figure 4.12: The INS spectra of $\text{Mg}(\text{NH}_3)_6\text{Cl}_2$ (black), $\text{Mg}(\text{NH}_3)_6\text{Br}_2$ (blue) and $\text{Mg}(\text{NH}_3)_6\text{I}_2$ (red). Data were collected using TOSCA at a temperature of 20 K.

in energy of rotational modes with increasing anion size suggests that there is a small but significant $\text{NH}\cdots\text{X}^-$ interaction. The lower charge densities of the larger anions reduce the electrostatic strength of this interaction and thus the rotational energy barrier is reduced. The movement of the rocking and bending modes can be explained by considering a molecular orbital description of the bonding. Figure 4.15 shows how the NHX angle of a hydrogen bond is important in allowing maximum overlap between the $\text{N-H } \sigma^*$ and the appropriate X^- p orbitals. The closer to 180° the bond is then the greater the potential orbital overlap and the stronger it becomes. The rocking modes (3 – 5) cause a reduced overlap of the orbitals, hence they decrease in energy as the anion size increases for the same reason that the rotational modes do: the weaker bonds of the larger anions are easier to disrupt. Mode 5 shifts 95 cm^{-1} compared to 24 cm^{-1} and 35 cm^{-1} for modes 3 and 4, because it involves significant movement of all 6 ammonia molecules rather than modes 3 and 4 that involve significant movement of only 2 ammonia molecules, thus the magnitude of the shift seen for mode 5 is a factor of 3 greater. The umbrella mode (6) follows a reversed trend, it increases in energy as the size of the anion increases, the reason for this is that the umbrella motions bring the $\text{N-H } \sigma^*$ orbitals towards the same plane as the appropriate X^- p orbitals. Though the orbitals may not be physically able to move into the same plane, the angle of incidence between the σ^* orbital and the relevant p orbital is reduced. This will have a stabilising effect, so in the case of the smaller anions where there is a stronger bonding interaction, this mode is lowered in energy.

4.7 Calculated Structure and Properties

Within disordered systems calculating properties can be hard as electronic calculations require sites of unit occupancy. However, selected calculations may still develop a greater understanding of these systems. Here the site preference of the

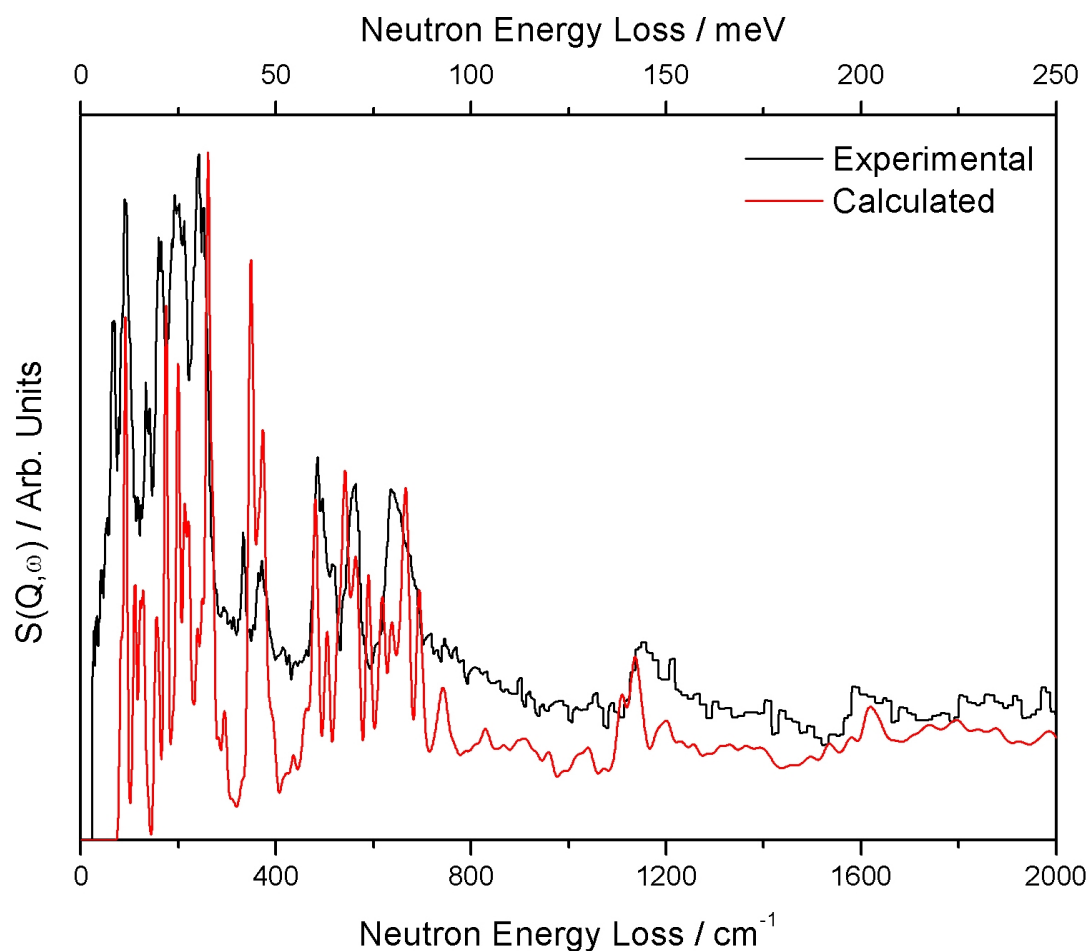


Figure 4.13: The experimentally observed (black) and calculated (red) INS spectra of $\text{Mg}(\text{NH}_3)_6\text{Cl}_2$.

Table 4.5: The observed positions and descriptions of selected modes in INS spectra for $\text{Mg}(\text{NH}_3)_6\text{X}_2$.

Mode Description	$\text{Mg}(\text{NH}_3)_6\text{Cl}_2$ ω / cm^{-1}	$\text{Mg}(\text{NH}_3)_6\text{Br}_2$ ω / cm^{-1}	$\text{Mg}(\text{NH}_3)_6\text{Br}_2$ ω / cm^{-1}
1) Single NH_3 rotation	333	327	319
2) Multiple NH_3 rotations and Mg–N breathing	370	365	354
3) In-phase, off N–H axis rocking	495	482	470
4) Anti-phase, off N–H axis rocking	563	541	528
5) All NH_3 molecules rocking	641	628	546
6) NH_3 umbrella modes	1155	1161	1178

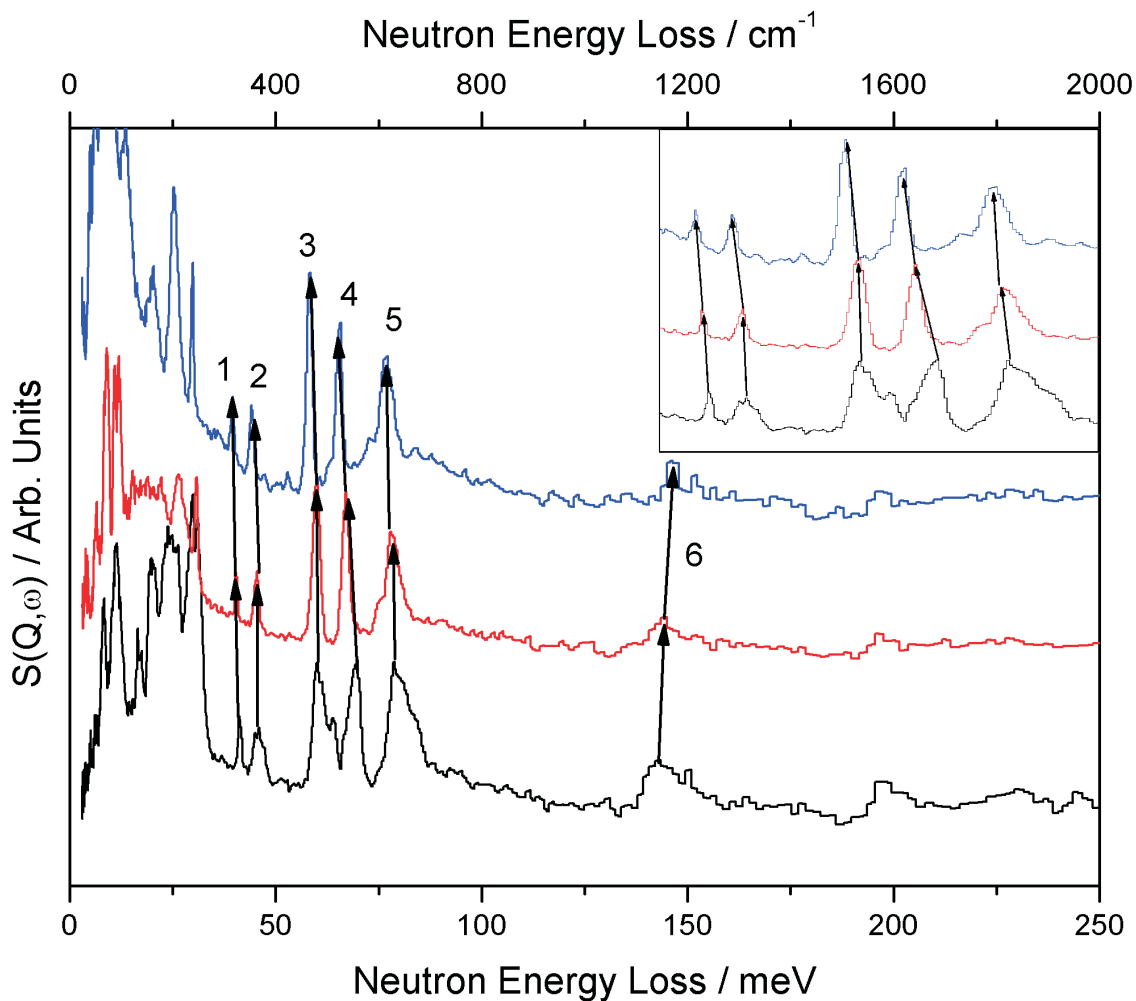


Figure 4.14: The INS spectra of $\text{Mg}(\text{NH}_3)_6\text{Cl}_2$, $\text{Mg}(\text{NH}_3)_6\text{Br}_2$ and $\text{Mg}(\text{NH}_3)_6\text{I}_2$, highlighting the movement of selected modes. The inset shows the spectra between 35 meV and 90 meV.

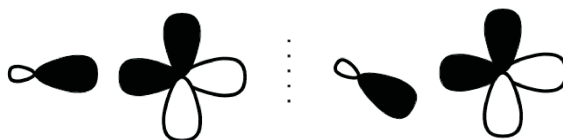


Figure 4.15: A diagrammatic representation of the possible effect of bond angle on σ^* and p-orbital overlap.

hydrogen atoms and unknown enthalpies of reaction are investigated.

In order to investigate the preference for different rotational hydrogen sites a series of single point energy calculations were performed that used a completely fixed unit cell with subsequent iterations varying only in the position of 3 hydrogen atoms. The remaining 69 hydrogen atoms were kept constant in the 0° position *v.i.*. The 3 moveable hydrogen atoms were rotated clockwise in 5° steps between 0° defined in Figure 4.16 and 120° (the exact equivalent of the 0° position).ⁱⁱⁱ The results of the calculations are shown in 4.17, and show that there is no clear site preference for the hydrogen atoms. While there are several energy minima, the energy range of 0.00435 eV is small and this suggests that the energy barrier to NH_3 rotation is small and would be equal to thermal energy (kT) at 51 K. Given the use of a simple model, this corroborates well with hydrogen bond driven phase transition observed between 80 K and 90 K in the low temperature diffraction data discussed in Section 4.3, it also suggests that the disorder observed at room temperature is dynamic. A more accurate model would need to include rotation of all hydrogen atoms in the cell as their rotation is unlikely to be independent.

Geometry optimisation calculations were performed in an attempt to find the lowest energy ammonia conformations, as an extension of the single point energy calculations discussed above and in order to calculate the enthalpies of formation for the known phases. The structures of $\text{Mg}(\text{NH}_3)_6\text{X}_2$ and $\text{Mg}(\text{NH}_3)_2\text{X}_2$ were optimised using the room temperature structures and positioning all hydrogen atoms in the 0° position. Calculations converged quickly and the final atomic positions are given in Appendix Tables E.6 to E.11. The results do not show any rotation of the ammonia molecules, but do show a distortion of the MgN_6 octahedra causing all new structures to belong to the Cm space group. Attempts to calculate a structure for $\text{Mg}(\text{NH}_3)\text{X}_2$ beginning with $\text{X} = \text{Cl}$ and using the atomic coordinates of $\text{Ni}(\text{NH}_3)\text{Cl}_2$ but replacing Ni for Mg and allowing the unit cell to relax were unsuccessful; the

ⁱⁱⁱA script enabling this process to be performed is given in Appendix C

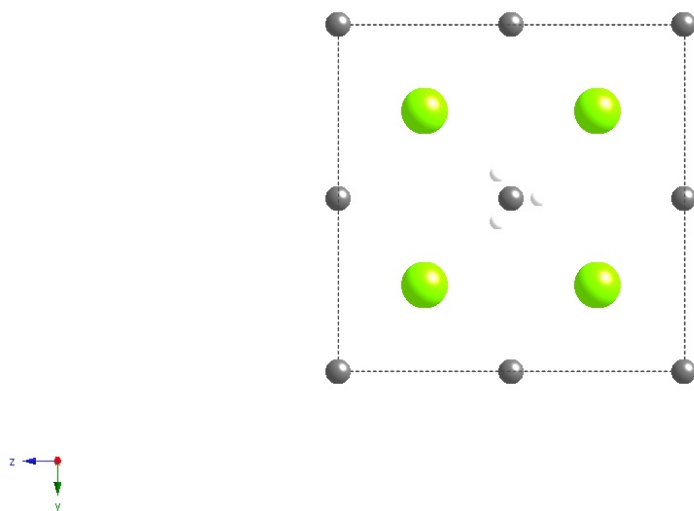


Figure 4.16: A representation of the $\text{Mg}(\text{NH}_3)_6\text{Cl}_2$ model used for DFT single-point energy calculations of different hydrogen sites. All H atoms are hidden other than those that change in subsequent calculations and are shown in the 0° position. Magnesium is shown in grey, hydrogen in off white and chlorine in lime green. Nitrogen atoms are omitted for clarity.

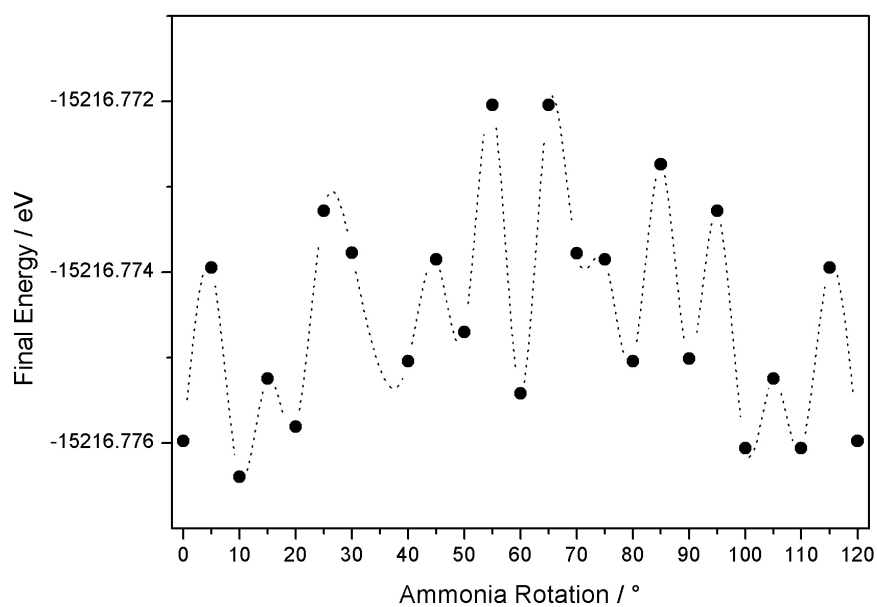


Figure 4.17: The internal energy of $\text{Mg}(\text{NH}_3)_6\text{Cl}_2$ with varying degrees of NH_3 rotation.

iterative calculations failed to converge. This in itself does not suggest that the $\text{Ni}(\text{NH}_3)\text{Cl}_2$ structure is unstable when Ni is replaced with Mg, but is a common problem when attempting to optimise such “soft” systems where dispersion or Van der Waals forces feature heavily and are not always successfully modeled using DFT.

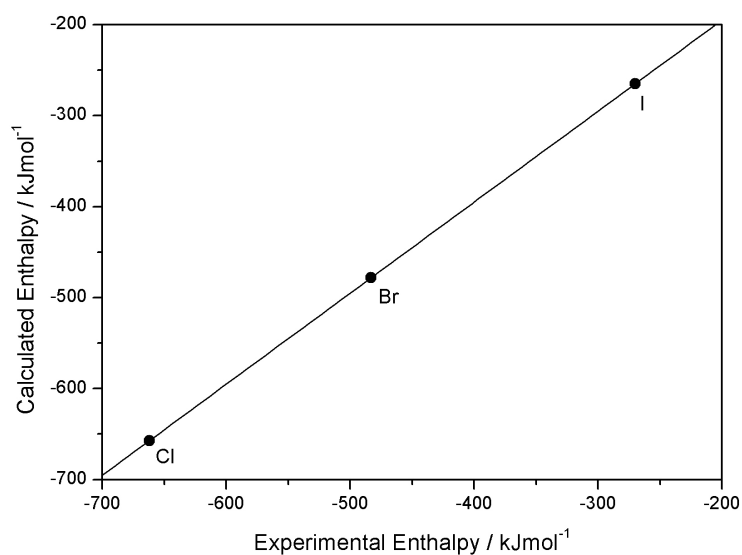
During geometry optimisation calculations the internal energy of the atomic arrangement is calculated, which as discussed in Section 2.12 enables the enthalpy of various reactions to be calculated. Initially the enthalpies of formation were calculated for $\text{MgX}_{2(\text{s})}$, $\text{Mg}(\text{NH}_3)_2\text{X}_{2(\text{s})}$, $\text{Mg}(\text{NH}_3)_6\text{X}_{2(\text{s})}$ and $\text{NH}_{3(\text{g})}$. These are reported in Table 4.6 where a comparison is made to MgX_2 as an assessment of the uncertainty of the calculations. Figure 4.18 confirms the close match between the experimental and calculated enthalpies of formation for MgX_2 . The linear fit to the data has a gradient of 1.0(2) and an intercept of 5(1), which suggest a reasonable and consistent uncertainty of 5 kJmol^{-1} in the calculated values compared to the experimental. These uncertainties may arise from errors in the structures used in calculations, in the lack of consideration of any zero-point energy, and in the lack of adjustment from the calculated enthalpy at 0 K and the experimental enthalpy which is not possible given the unknown heat capacities of the phases. Another source of error may arise from problems associated with modelling of polarisable anions using DFT. To some extent in all these compounds, and in particular in MgI_2 , dispersion forces are likely to make a significant contribution to the cohesive energy.¹⁰⁹ These forces may be modelled in a semi-empirical way using ‘DFT-D’ that may be implemented in CASTEP, but in this case the close agreement to the experimental data and the consistency of the calculations when varying the anion from Cl to Br to I meant that corrections of this type were not used.^{110,111}

Using the calculated enthalpies of formation, the enthalpies of reactions 4.1 to 4.3 were calculated. A reasonable agreement to experimental results^{iv} for reaction 4.1 and 4.2, is shown in Figure 4.19, the linear fits to the data have gradients of 0.90(9)

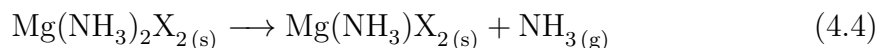
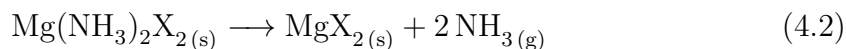
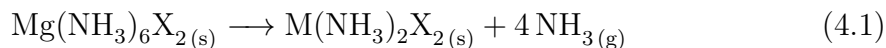
^{iv}Calculated using Hess’s law and the relevant available data.¹¹²

Table 4.6: Calculated and experimental enthalpies of formation of $\text{Mg}(\text{NH}_3)_n\text{X}_2$ given in kJmol^{-1} .

	MgX_2		$\text{Mg}(\text{NH}_3)_2\text{X}_2$	$\text{Mg}(\text{NH}_3)_6\text{X}_2$
	Exp. ²⁷	Calc.	Calc.	Calc.
Cl	-657	-662(5)	-894	-1316
Br	-478	-483(5)	-737	-1182
I	-265	-270(5)	-534	-1015

**Figure 4.18:** A comparison of the calculated and experimental enthalpies of formation of MgX_2 .²⁷

and 1.2(3), and intercepts of 9(6) and -25(25) for reactions 4.1 and 4.2 respectively. The errors in this case are larger than those in the enthalpy of formation calculations, though this is expected largely due to the compounding of calculative and experimental uncertainty. There is greatest error in the calculation of the enthalpy of reaction 4.2 due to the lack of structural information on $\text{Mg}(\text{NH}_3)_2\text{X}_2$ meaning that it may not be considered as an intermediate of any reactions, so the enthalpy of the theoretical reaction 4.2 is the best approximation to the real reaction 4.4. The calculated enthalpies of reaction for reaction 4.3 are -94 kJmol^{-1} , -105 kJmol^{-1} and -117 kJmol^{-1} for $\text{X} = \text{Cl}$, Br and I respectively. These data are discussed further in Section 4.8.1.



4.8 Conclusions

In this Chapter, a number of trends and similarities have been shown to exist in the magnesium halide ammines. While the most in-depth analysis has been carried out for the chlorides, the similarities of the group suggest that most conclusions may be extended to include the bromides and iodides. Using diffraction techniques, the structures of $\text{Mg}(\text{NH}_3)_6\text{X}_2$ have been confirmed and it has been shown that a dynamic ammonia disorder exists down to 90 K in $\text{Mg}(\text{NH}_3)_6\text{Cl}_2$ at which temperature a phase transition occurs. It is likely that weaker hydrogen bonding in the bromide and iodide will result in a lower transition temperature. At room temperature, hy-

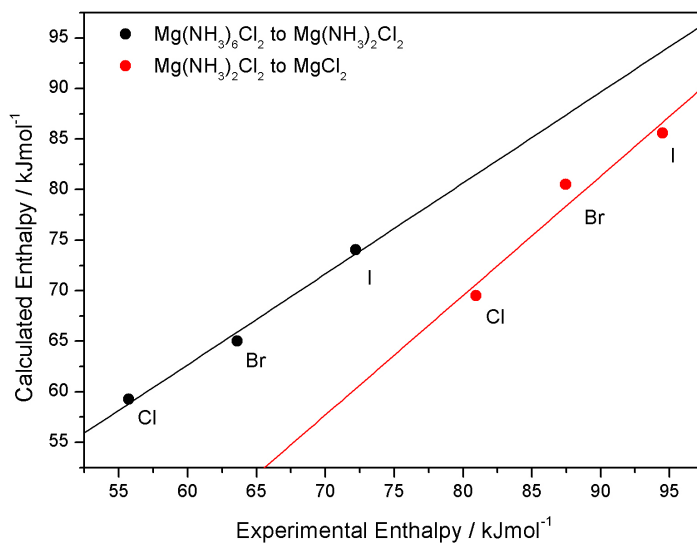


Figure 4.19: A comparison of the experimental and calculated enthalpies of reaction per mole of ammonia for the decomposition of $\text{Mg(NH}_3)_6\text{X}_2$ to $\text{Mg(NH}_3)_2\text{X}_2$, and $\text{Mg(NH}_3)_2\text{X}_2$ to MgX_2 .²⁷ Lines are linear fits to the data, with black and red lines corresponding data of the same colour.

hydrogen bonding is evidenced through a preference for the 45 ° site that aligns the the N–H with the X^- anion. Simple energy calculations of possible hydrogen sites do not reflect this site preference, but do confirm a low energy barrier to rotation resulting in the low temperature phase transition. The presence of hydrogen bonding has also been confirmed using inelastic neutron spectroscopy for all three halides. Thermogravimetric analysis confirms that each compound decomposes by the 3 step process with the evolution of 4 and sequentially 2×1 ammonia molecules, a linear relationship between anion size and decomposition temperature is observed. Both diffraction and NMR confirm that changing the anion has only a small effect on the state of Mg–N bonding. The unknown enthalpies of formation of $\text{Mg(NH}_3)_6\text{X}_2$ and $\text{Mg(NH}_3)_2\text{X}_2$ have been calculated, as has the enthalpy of reaction for ammonia adsorption in MgX_2 . An increasingly detailed analysis of the presented data follows in Section 4.8.1.

4.8.1 Thermodynamic Consideration of Decomposition

The NMR data and Mg–N bond lengths refined from the powder diffraction data suggest that the anion does not have a significant effect on the state of Mg–N bonding. Given that the desorption temperature increases with increasing anion atomic size, it is sensible to suggest that the overall driving force for loss of ammonia is the negative lattice enthalpy ($U_L[\text{MX}_2]$) gained on formation of MgX_2 . $U_L[\text{MX}_2]$ will naturally be expected to be less favourable for large radius anions. Consequently, where $U_L[\text{MX}_2]$ is more favourable (Cl), the temperature for ammonia loss is expected to be low, and equally where $U_L[\text{MX}_2]$ is less favourable the temperature for ammonia loss is expected to be higher (Br, I). This relationship is summarised in the Hess cycle shown in Figure 4.20, and also provides an explanation for the experimental observation that MgF_2 does not react with ammonia under the same conditions as for $\text{X} = \text{Cl}, \text{Br}$ or I ; because of the thermodynamic stability of MgF_2 . The calculated enthalpies of ammonia adsorption, that increase in magnitude with increasing anion size, support this theory; as the (MgX_2) lattice energy becomes less favourable the energy gained on NH_3 sorption increases.

If each desorption step is considered individually and an ionic model is assumed, such that each decomposition intermediate is composed of $\text{Mg}(\text{NH}_3)_n^{2+}$ and X^- ions as shown in Figure 4.21, then similar reasoning may be applied: the driving force for each desorption step is the negative lattice enthalpy gained as a result of reducing cation size.

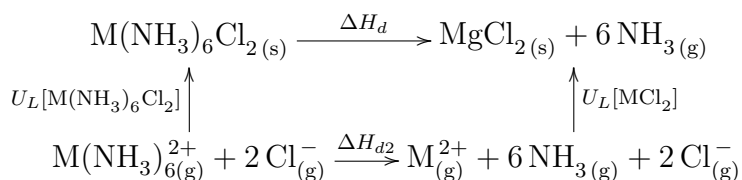


Figure 4.20: A Hess cycle for conceptual decomposition of $\text{Mg}(\text{NH}_3)_6\text{X}_2$ directly to MgX_2 .

Increasing the size of the anion, X, will lead to a less favourable lattice energy for $M(NH_3)_nX_2$ for all values of n. The contribution of the lattice terms (U_L) to the enthalpy of reaction (ΔH_r , ΔH_{r3} and ΔH_{r5}) will always be negative as $U_L[M(NH_3)_{n+x}X_2]$ must be lower in magnitude than $U_L[M(NH_3)_nX_2]$, (where $x > 0$). Assuming that the enthalpy of ammonia desorption (ΔH_{r2} , ΔH_{r4} and ΔH_{r6}) is approximately constant and independent of anion, as determined by X-ray diffraction and NMR. The negative contribution of $U_L[M(NH_3)_{n+x}X_2]$ and $U_L[M(NH_3)_nX_2]$ to the enthalpy of reaction will decrease proportionally with increasing size of X (as both terms will decrease). Thus, as X increases in size, the enthalpy of ammonia desorption becomes a more significant factor in the overall enthalpy of reaction and the decomposition temperature is observed to increase. The dominance of the cation size in the lattice energy terms is reflected in the relative enthalpies of formation that are shown in Table 4.7. As the cation increases in size from Mg^{2+} to $Mg(NH_3)_2^{2+}$ and $Mg(NH_3)_6^{2+}$ its radius becomes a more dominant term in determining the lattice energy and as this term is constant for each X the relative stabilities of each phase decrease as the cation size increases.

Table 4.7: Calculated enthalpies of formation of $Mg(NH_3)_nX_2$, and the relative stabilities of Br cf. Cl and I cf. Br for each cation, all values are given in kJmol^{-1} .

	MgX_2		$Mg(NH_3)_2X_2$		$Mg(NH_3)_6X_2$	
	Calc.	Rel.	Calc.	Rel.	Calc.	Rel.
Cl	-662	-	-894	-	-1316	-
Br	-483	+179	-737	+157	-1182	+134
I	-270	+213	-534	+203	-1015	+167

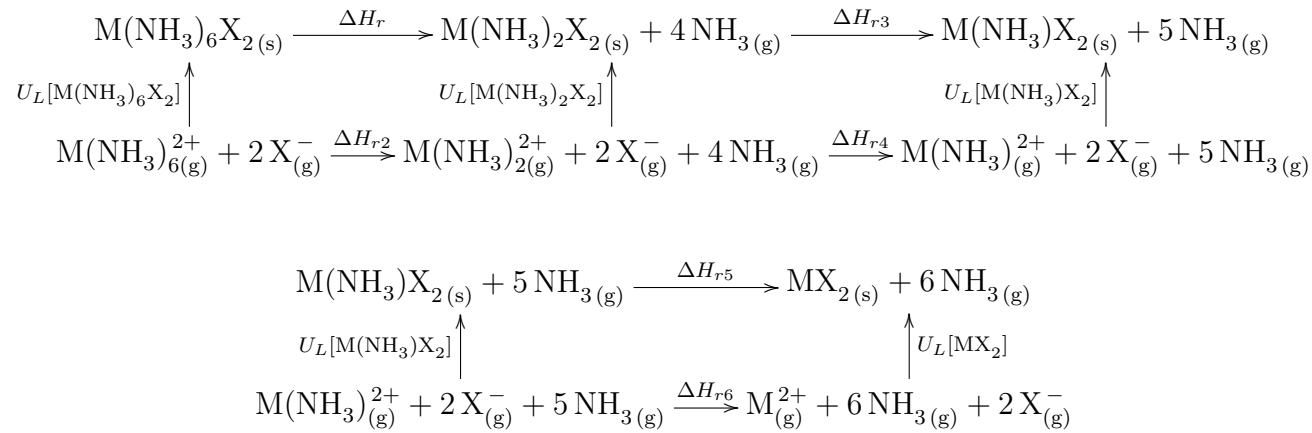


Figure 4.21: A Hess cycle for full decomposition of $\text{Mg}(\text{NH}_3)_6\text{X}_2$ to MgX_2 including the two intermediate steps determined by TGA. Each of the odd numbered steps are the enthalpies of (decomposition) reaction and each of the even numbered steps are the enthalpies of ammonia desorption.

In Section 4.5, Figure 4.11 shows a plot of T_{nP} against ionic radii for the decomposition of $\text{Mg}(\text{NH}_3)_6\text{X}_2$ and reveals a linear relationship between the anionic radii and the peak rate of desorption (T_p) for each of the three steps D_1 , D_2 and D_3 at temperatures T_1 , T_2 and T_3 . The gradients of the lines of best fit are approximately equal for D_2 and D_3 ($197 \text{ K}\text{\AA}^{-1}$), while that for D_1 is greater ($275 \text{ K}\text{\AA}^{-1}$). These trends in behaviour may be explained by considering the expression for ΔH_r obtained from Figure 4.21. Assuming an ionic model, it is possible to calculate the lattice enthalpies for $\text{Mg}(\text{NH}_3)_6\text{X}_2$ using the Kapustinskii equation,¹¹³ and assuming that T_{dec} is proportional to ΔH_{dec} the expression for the gradient of the linear fit in Figure 4.11 is obtained in Equations 4.5 to 4.8, where L^+ , S^+ , and X^- represent large and small cations, and an anion respectively.

$$T_{dec} \propto U_L[LX] - U_L[SX] \quad (4.5)$$

$$T_{dec} \propto \frac{1}{r_{L^+} + r_{X^-}} - \frac{1}{r_{S^+} + r_{X^-}} \quad (4.6)$$

$$T_{dec} \propto \frac{r_{S^+} - r_{L^+}}{(r_{L^+} + r_{X^-})(r_{S^+} + r_{X^-})} \quad (4.7)$$

$$\frac{dT_{dec}}{dr_{X^-}} \propto \frac{(r_{L^+} - r_{S^+})(r_{L^+} + r_{S^+} + 2r_{X^-})}{((r_{L^+} + r_{X^-})(r_{S^+} + r_{X^-}))^2} \quad (4.8)$$

The expression in Equation 4.8 shows that the rate of change of the decomposition temperatures is governed by the change in size of the cation and the anion. As the change in the anion size is constant then the rate of change of T_{dec} with respect to anion radius, $\frac{dT_{dec}}{dr_{X^-}}$, for the first desorption step (D_1) is larger than for the second and third desorption steps (D_2 and D_3) since:

$$r_{\text{Mg}(\text{NH}_3)_6^{2+}} - r_{\text{Mg}(\text{NH}_3)_2^{2+}} > r_{\text{Mg}(\text{NH}_3)_2^{2+}} - r_{\text{Mg}(\text{NH}_3)^{2+}} \approx r_{\text{Mg}(\text{NH}_3)^{2+}} - r_{\text{Mg}^{2+}}$$

4.8.2 Evaluation as Ammonia Storage Materials

Although the ammonia storage properties of the magnesium halide compounds have been reported in part in other studies, here the group is considered as a whole; decomposition data have been clarified, and ammonia densities and enthalpies of reaction have been determined. The ammonia storage properties of the halides are compared to liquid ammonia in Table 4.8. One of the advantages of using halides as an ammonia store are that they are robust and structural changes or decomposition occur well outside the temperature range required for ammonia sorption, and they allow a lowering of vapour pressure compared to liquid ammonia. A disadvantage is the high temperatures of 100 °C to 180 °C required for release of the first ammonia molecules. With knowledge of the effect changing the anion has on decomposition it is possible, in principle, to tune the decomposition temperature or vapour pressure to the specific requirements of a system or catalyst. A mixed system would also have the potential to produce a constant ammonia pressure over a range of temperatures, avoiding the stepwise lose of ammonia associated with a single halide system.

Table 4.8: Summary of ammonia storage properties of $\text{Mg}(\text{NH}_3)_6\text{X}_2$, compared to liquid NH_3

Compound	Reversible Ammonia Content / wt%	Ammonia Density / gL^{-1}	ΔH_{abs} / kJmol^{-1} of NH_3	Temperature required for complete ammonia release / °C
$\text{Mg}(\text{NH}_3)_6\text{Cl}_2$	52	654	-94	250
$\text{Mg}(\text{NH}_3)_6\text{Br}_2$	36	602	-105	270
$\text{Mg}(\text{NH}_3)_6\text{I}_2$	27	522	-117	330
$\text{NH}_3_{(l)}$ -33°C	100	682	-	-

4.9 Further Work

A large amount of research has already been carried out on these ammines, however a few areas for further work remain. In particular solving the structure of $\text{Mg}(\text{NH}_3)\text{X}_2$ and the low temperature phases would increase the understanding of these compounds. In the case of $\text{Mg}(\text{NH}_3)\text{X}_2$ it should be possible to isolate this phase (in-situ and possibly ex-situ) by heating a sample of $\text{Mg}(\text{NH}_3)_6\text{X}_2$ to the appropriate temperature (T_o) found in Section 4.5. The low temperature phases should exist for all X and it is expected that the transition temperatures would be reduced with increasing anion size. It would also be interesting to investigate the use of mixed anion systems, as this may present the opportunity to tune the decomposition temperature and vapour pressures for desired applications. In terms of applying these materials as commercial ammonia stores, the properties upon cycling must be ascertained, as must methods of dissipating the large amount of heat produced upon ammonia adsorption.

Magnesium Borohydride Ammines

5.1 Introduction

Recently the basic structure of $\text{Mg}(\text{NH}_3)_6(\text{BH}_4)_2$ was reported by Soloveichik et al. as part of a paper that focused on the use of $\text{Mg}(\text{NH}_3)_2(\text{BH}_4)_2$ as a promising hydrogen storage material.⁵¹ This Chapter focuses on $\text{Mg}(\text{NH}_3)_6(\text{BH}_4)_2$, its structure and disorder, decomposition pathway and the bonding interactions that explain its properties. Analysis was carried out using X-ray and neutron diffraction, vibrational spectroscopy and thermogravimetric analysis, the data and results are frequently compared to those presented in Chapters 3 and 4 in order to fully understand these materials.

5.2 Room Temperature Diffraction Studies

$\text{Mg}(\text{NH}_3)_6(\text{BH}_4)_2$ has been reported to share the same K_2PtCl_6 structure as the magnesium ammine halides, though reports are not detailed and provide no data on hydrogen positions or disorder. In addition to the inherent NH_3 disorder *v.s.*, the BH_4^- anions may also be disordered. The B atom is positioned on the $\bar{4}3m$ site at $(1/4, 1/4, 1/4)$; when choosing a hydrogen atom position near this site there are

three logical options 1) using the $3m$ site at (x, x, x) that has a multiplicity of 32; 2) using the m site at (x, x, z) that has a multiplicity of 96; or 3) using both these sites. These three options would produce a BH_4^- anion exhibiting 1-, 3-, or 4- fold disorder respectively. In order to gain a greater understanding of these structural intricacies, both neutron and X-ray diffraction experiments were carried out at room temperature and at variable temperatures from 4 K to 300 K.

5.2.1 X-Ray Powder Diffraction

Samples analysed using X-ray powder diffraction were produced using the method described in Section 2.5 to ammoniate $\text{Mg}(\text{BH}_4)_2$ purchased from Sigma Aldrich. Room temperature X-ray powder diffraction data were collected using beam line ID31 at the ESRF. The cubic ($Fm\bar{3}m$) K_2PtCl_6 structure was used to model the data using Rietveld refinement, with the same model of ammonia disorder and atomic constraints discussed in Section 4.2. The possible boronic hydrogen atoms were positioned at either (x, x, x) or $(x, x, 0.25)$ using the a B–H bond length that was allowed to vary within the limits of 1.0 Å and 1.4 Å. The final fit to the data, with $\chi^2 = 3.52$ is shown in Figure 5.1, the refined cubic lattice parameter was $a = 10.7663(1)$ Å.

Though it is not appropriate to use these X-ray diffraction data to unambiguously ascertain the level of disorder associated with hydrogen atoms, an improvement in the fit of the model to the data was observed when greater levels of disorder were included. The refined B–H bond length of 1.06(2) Å is shorter than expected, though this may indicate disorder of the BH_4^- anion *v.i.*. The refined Mg–N bond length of 2.161(4) Å is similar to those observed in $\text{Mg}(\text{NH}_3)_6\text{Cl}_2$ and $\text{Mg}(\text{NH}_3)_6\text{Br}_2$, at 2.161(2) Å and 2.167(3) Å respectively. This suggests that any difference in the strength of Mg–N bonding is negligible when changing from a halide to borohydride anion.

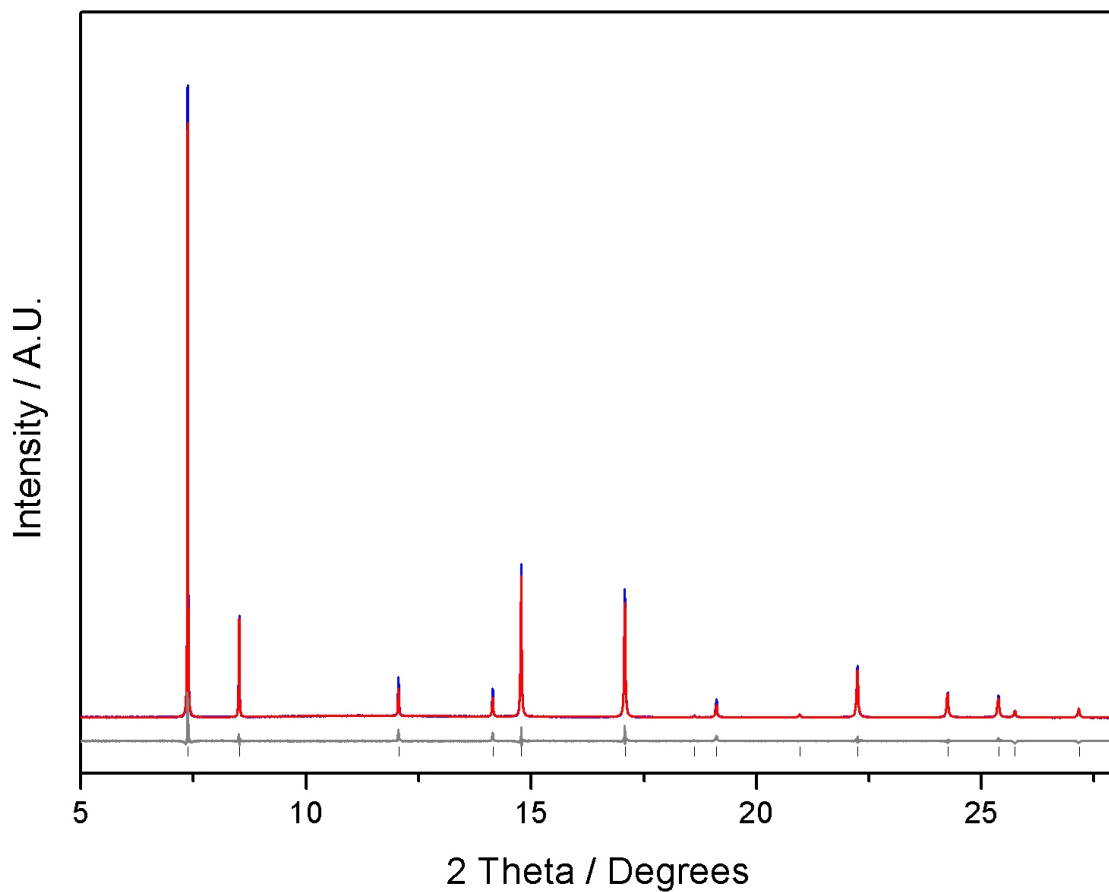


Figure 5.1: Final fit to the data for Rietveld refinement of the $\text{Mg}(\text{NH}_3)_6(\text{BH}_4)_2$ model to X-ray powder diffraction data collected at the ESRF with a wavelength $\lambda = 0.7996 \text{ \AA}$. Space group = $Fm\bar{3}m$, $R_{wp} = 7.71\%$, $R_{exp} = 4.12\%$, $\chi^2 = 3.52$. Experimental data are shown in blue, calculated in red with the difference in grey, tick marks show the expected positions of Bragg reflections.

5.2.2 Neutron Powder Diffraction

Samples analysed using neutron powder diffraction were produced using the method described in Section 2.5 to ammoniate $\text{Mg}({}^{11}\text{BD}_4)_2$ that was produced via the metathesis reaction (described in Section 2.4) between $\text{Na}^{11}\text{BD}_4$ (synthesised from the elements as described in Section 2.3) and MgCl_2 in diethyl ether. Data were collected using GEM and HRPD, but in depth analysis was performed only on data collected using GEM as its high flux lends itself to studying disordered systems, while the high resolution of HRPD is less useful in this case.

Analysis was carried out using the same model as for the X-ray diffraction data and refining it against data collected using GEM banks 2, 3, 4, and 5, the final fit to the data is shown in Figure 5.2. During the refinement process the disorder of the BD_4^- anion was clear, subsequent refinements varying only in the level of BD_4^- disorder showed an improvement in the quality of fit with each added level of disorder. A second indicator of disorder was the refined thermal parameters that were seen to decrease with each added level of disorder. A final indicator was a shorter than expected B–D bond length seen in most ordered model, this suggested a bending or rotating BD_4^- anion meaning the geometric average of deuterium nuclear position was observed. The disordered model allows for this average nuclear positioning so a more realistic B–D bond length of $1.24(2)$ Å was observed, which agrees strongly with the $1.18(1)$ Å seen in $\text{Mg}(\text{BD}_4)_2$.¹¹⁴

The refined Mg–N bond length of $2.29(4)$ Å, is similar to the bond length of $2.272(4)$ Å seen in $\text{Mg}(\text{NH}_3)_6\text{Cl}_2$ (discussed in Section 4.2.2). According to the X-ray diffraction data discussed in Section 4.2.1, the Mg–N bond length in $\text{Mg}(\text{NH}_3)_6\text{Br}_2$ is slightly longer than in $\text{Mg}(\text{NH}_3)_6\text{Cl}_2$, if this is also the case for $\text{Mg}(\text{ND}_3)_6\text{Br}_2$ then it is expected that the observed Mg–N bond lengths in $\text{Mg}(\text{ND}_3)_6({}^{11}\text{BD}_4)_2$ are similar to those found in $\text{Mg}(\text{ND}_3)_6\text{Br}_2$. Essentially this means that BD_4^- behaves as a spherical anion in its interaction with ND_3 , the presence of the local B–D

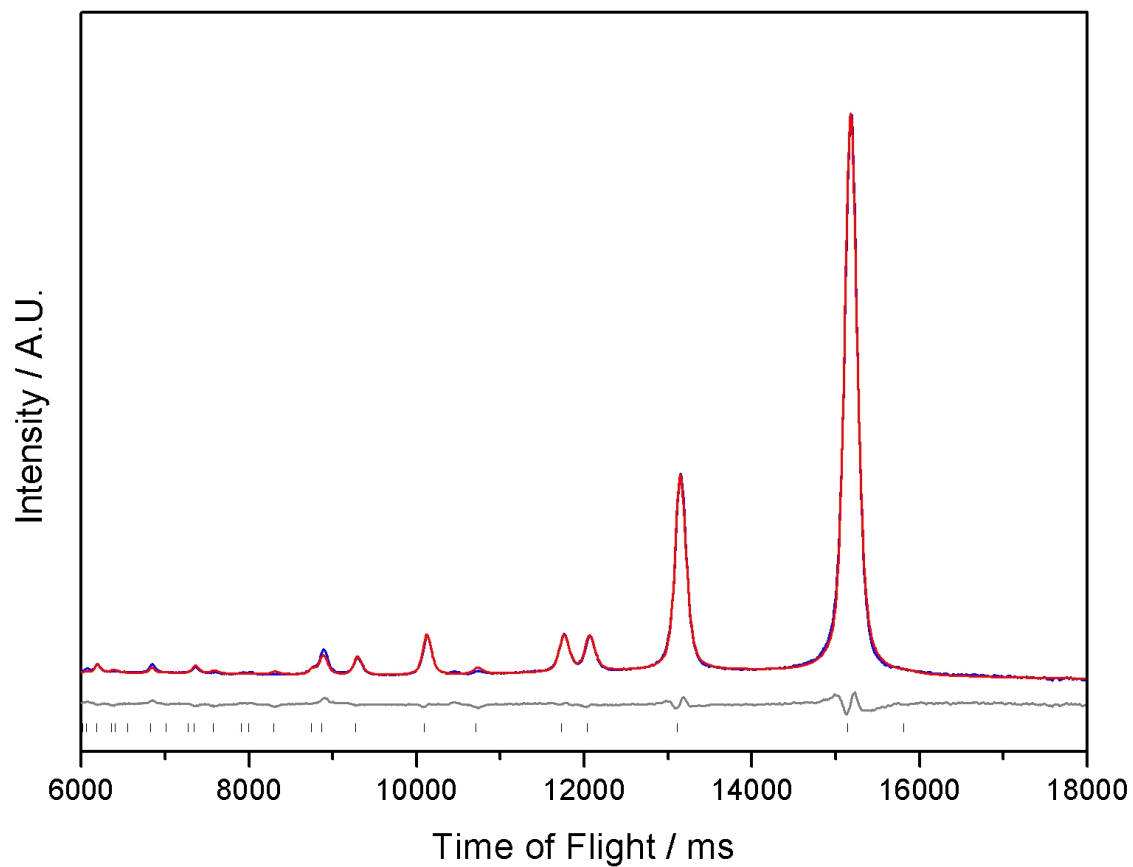


Figure 5.2: Final fit to the data for Rietveld refinement of the $\text{Mg}(\text{NH}_3)_6(\text{BH}_4)_2$ model to neutron powder diffraction data, collected using GEM bank 4 (62°). Space group = $Fm\bar{3}m$, $R_{wp} = 0.976\%$, $R_{exp} = 0.529\%$, $\chi^2 = 3.37$. Experimental data are shown in blue, calculated in red with the difference in grey, tick marks show the expected positions of Bragg reflections.

polarity and (as discussed in Chapter 4) the anion as a whole has little or no effect on the state of Mg–N bonding.

By allowing the occupancy of the ammonia deuterium sites to vary, the nature of the ND₃ interactions may be established. The refined occupancies of 0.065, 0.043, 0.102 and 0.423 for the 0 °, 15 °, 30 ° and 45 ° sites respectively show that there is a strong preference for the 45 ° site. The level of preference is similar, though slightly less well defined than that seen in Mg(ND₃)₆Cl₂, this may be because if the disordered BD₄[−] anion behaves like a sphere then its lower charge density cf. Cl[−] means that any ND...X interactions are weaker and the stabilisation achieved in the 45 ° site is reduced. The minimum ND...DB distances observed were 2.08(2) Å and 1.68(3) Å in the 1-fold and 3-fold disorder models respectively, these distances suggest a dihydrogen bonding interaction. However, there is no evidence here to suggest that this is significantly different from the ND...Cl[−] hydrogen bonding observed in Mg(ND₃)₆Cl₂ and the other halides.

5.3 Low-temperature Diffraction Studies

The low-temperature phase changes of Mg(ND₃)₆Cl₂ were discussed in Section 4.3, given the similarities in structure it is expected that Mg(NH₃)₆(BH₄)₂ will also form low-temperature ordered phases. Initial experiments were carried out using beamline ID31 at the ESRF to investigate any low-temperature phases, these experiments were then extended using HRPD at ISIS.

5.3.1 X-ray Powder Diffraction

Initial visual analysis of the X-ray diffraction data shows that three phases exist; the *Fm* $\bar{3}$ *m* high-temperature (HT) phase, a low-temperature (LT) phase and an intermediate (MT) phase. On cooling, a gradual transition between the MT and

LT phases was observed to begin at 85 K with the LT phase reflections reaching maximum intensity at 50 K. The LT phase was not isolated and at all temperatures it was observed to coexist with the MT phase. On changing the sample position it was clear that a different phase existed in a nonirradiated section of the sample. This suggests that, as was the case with $\text{Mg}(\text{NH}_3)_6\text{Cl}_2$ (discussed in Section 4.3), the sample was prone to either beam damage or beam heating. The appearance of the high temperature phase at lower temperatures than expected may suggest that hydrogen bonding is an important force in formation of the low-temperature phase. The MT phase contains all the Bragg reflections of the HT phase, though with additional reflections of very low intensity. On heating, transition between the MT and HT phase was observed to begin at 238 K with the additional reflections disappearing at 267 K.

5.3.2 Neutron Powder Diffraction

The neutron diffraction data show the same three HT, MT and LT phases as the X-ray data. During this experiment it was possible to cool the sample off-line, employing a slow rate to reach a temperature of 4 K over a period of 24 hours. The result, that at 4K only reflections from the LT phase were observed. The reflections from the LT phase were indexed to a hexagonal unit cell, belonging to the space group $R\bar{3}m$ which as discussed in Section 4.3 is a subgroup of $Fm\bar{3}m$. The lattice parameters of the LT phase at 4K were refined against the data collected using HRPD banks 1, 2 and 3 as $a = 15.369(1) \text{ \AA}$ and $c = 34.966(7)$ with a cell volume of $V = 7152(2) \text{ \AA}^3$, the final fit to the data is shown in Figure 5.3. The reduced uncertainty compared to the refined $\text{Mg}(\text{ND}_3)_6\text{Cl}_2$ LT unit cell parameters reflects the improvement in the quality of data that was a result of utilising a slow cooling rate.

As seen in the X-ray diffraction data, the MT phase shares all the reflections of

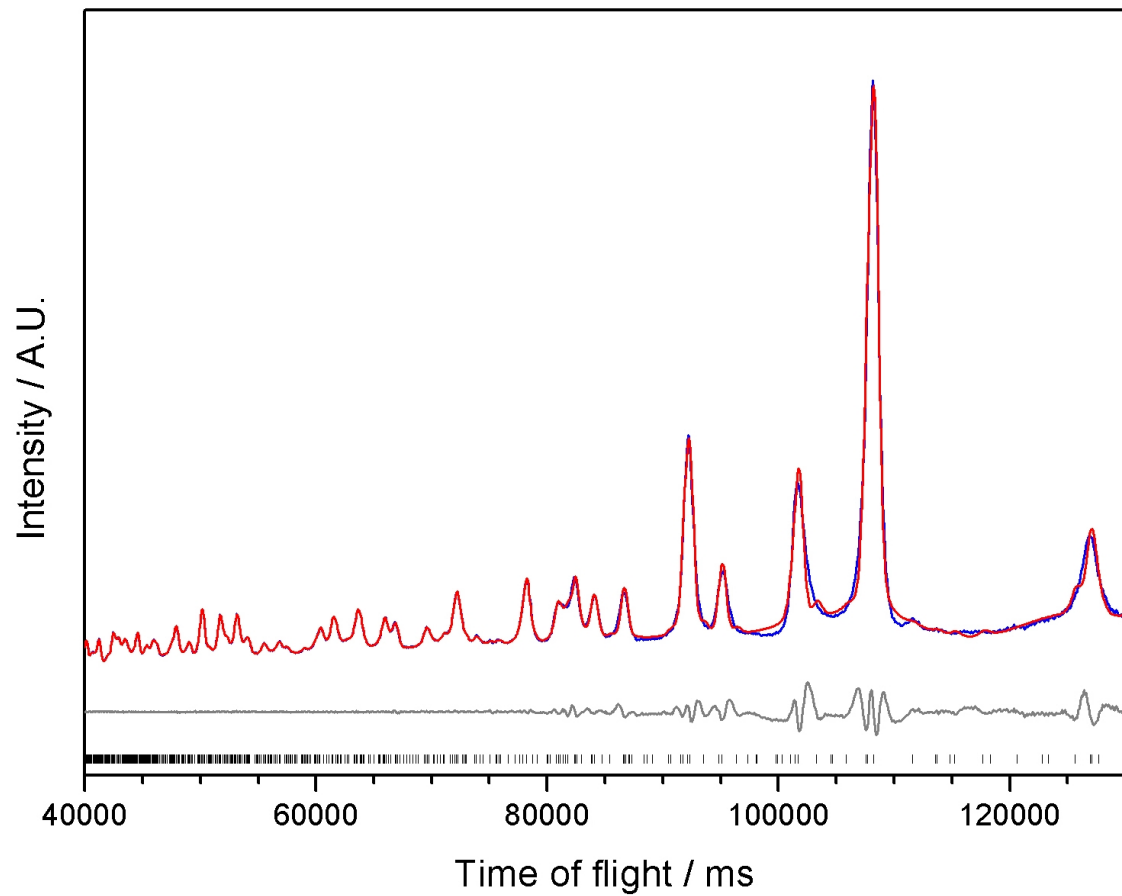


Figure 5.3: The fit to the data for the Pawley refinement of the LT ($R\bar{3}m$) unit cell of $\text{Mg}(\text{ND}_3)_6(^{11}\text{BD}_4)_2$ to the neutron powder diffraction data collected using HRPD bank 2. $R_w p = 2.60\%$, $R_{exp} = 0.56\%$, $\chi^2 = 21.6$

the HT ($Fm\bar{3}m$) phase, with several additional reflections of weak intensity. All the reflections of this new phase were indexed in the cubic space group $Fd\bar{3}m$, which was chosen as a subgroup of $Fm\bar{3}m$ that provided the best fit to the data shown in Figure 5.4. The cubic unit cell parameter refined from data collected using HRPD banks 1, 2 and 3 at 150 K is $a = 21.2620(2)$ Å, with a cell volume of $V = 9611.9(3)$ Å³, thus the MT phase is a $2 \times 2 \times 2$ supercell of the HT phase. It is suggested that as the equivalent cell was not observed in the $\text{Mg}(\text{ND}_3)_6\text{Cl}_2$ data that the transition from the HT to MT phase is a result of ordering of the BD_4^- anions. The similar unit cells of the LT phases of the chloride and borodeuteride suggests that their formation is driven by ND_3 ordering. With such large unit cells and so many H/D atoms, the ideal approach to structure solution would be to position the non-H atoms using X-ray diffraction data. However, the X-ray data are mixed phase so the reliability of the refinements is reduced and the practical difficulty is increased, no attempts at structure solution have been successful thus far.

Phase Transitions

On visual inspection of the neutron diffraction data, it appears that when heating, the transition between the LT and MT phases begins at 95 K and ends when all of the LT phase reflections disappear at 120 K. Transition between the MT and HT phases also occurs over a large range, with the MT reflections reducing in intensity at 200 K and ceasing to appear at 255 K. The change in lattice parameters of the LT phase as a function of temperature is shown in Figure 5.5, with the equivalent plot for the volume shown in Figure 5.6. These Figures show that a first order phase transition occurs between 60 K and 70 K, but that both phases either have the same space group, or that one phase is in a subgroup of the other. It is possible that the lower temperature phase belongs to the lower symmetry $R\bar{3}$ space group that was predicted to contain the LT structure of $\text{Mg}(\text{NH}_3)_6\text{Cl}_2$,⁴⁴ and in this case is not distinguishable from $R\bar{3}m$ using Pawley refinement. The data for the LT phase of

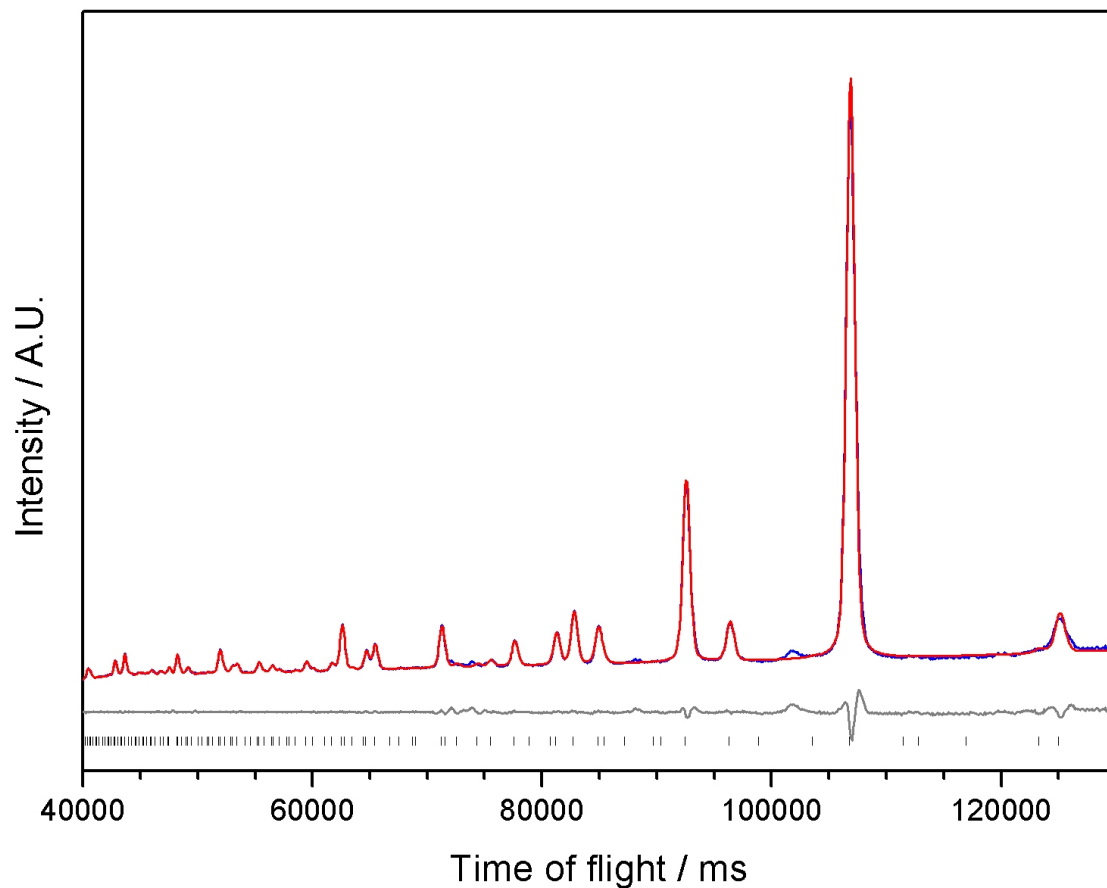


Figure 5.4: The fit to the data for the Pawley refinement of the MT ($Fd\bar{3}m$) unit cell of $\text{Mg}(\text{ND}_3)_6(^{11}\text{BD}_4)_2$ to the neutron powder diffraction data collected using HRPD bank 2. $R_{wp} = 2.42\%$, $R_{exp} = 0.99\%$, $\chi^2 = 2.45$.

$\text{Mg}(\text{ND}_3)_6\text{Cl}_2$ do not show any similar phase transition. The transition between the LT and MT phases of $\text{Mg}(\text{NH}_3)_6(\text{BH}_4)_2$ occurs at higher temperature than the LT to HT phase transition of $\text{Mg}(\text{NH}_3)_6\text{Cl}_2$, this implies that weaker hydrogen bonding exists in $\text{Mg}(\text{NH}_3)_6(\text{BH}_4)_2$ and that BH_4^- still behaves as a spherical anion even in the low-temperature phases. The potential $\text{NH}\cdots\text{HB}$ interactions are not significant compared to the overall $\text{NH}\cdots\text{BH}_4^-$ interactions.

The transition between the MT and HT phases can be followed by observing the intensity of the (731) reflection (I_{731}), as shown in Figure 5.7. The plot of I_{731} shows that a gradual phase transition occurs between approximately 140 K and 260 K, and that the I_{731}^3 shows an almost linear variation in response to temperature in this range. The lattice parameters shown in Figure 5.8 show more clearly that the transition is second order and occurs between 160 K and 260 K, with two distinct rates of change seen for the HT and MT lattices confirming that there is a difference in the chemistry and behaviour of the two phases.

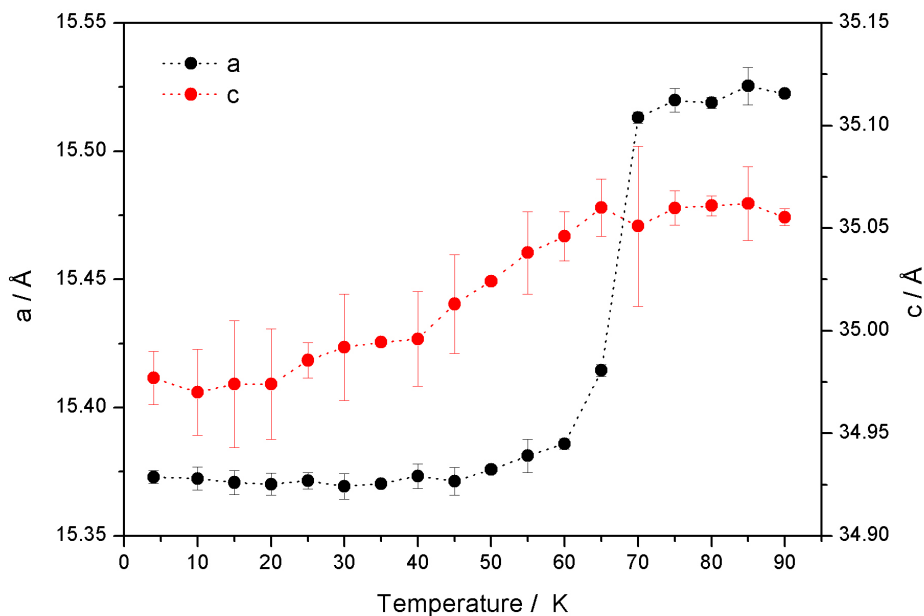


Figure 5.5: The lattice parameters of the LT phase of $\text{Mg}(\text{ND}_3)_6(^{11}\text{BD}_4)_2$ as a function of temperature.

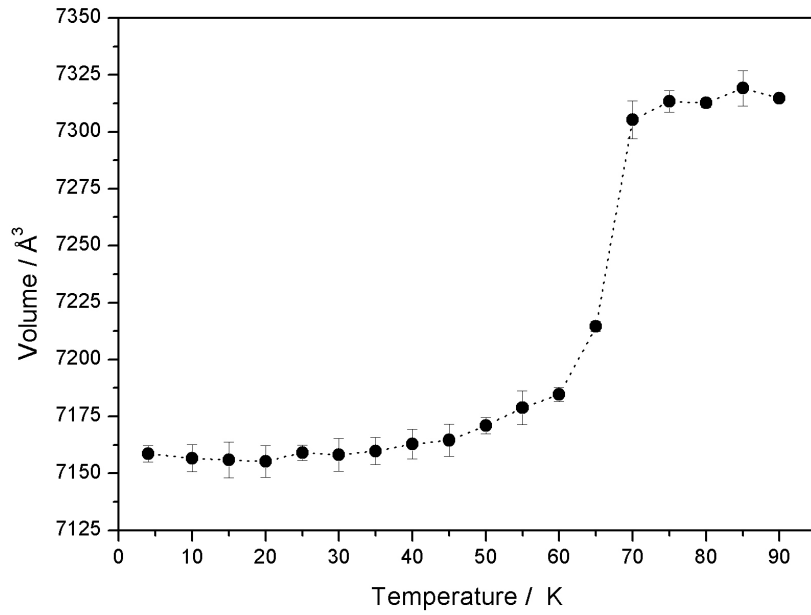


Figure 5.6: The volume of the LT phase of $\text{Mg}(\text{ND}_3)_6(^{11}\text{BD}_4)_2$ as a function of temperature. Error bars are included but where not visible are hidden by datum markers.

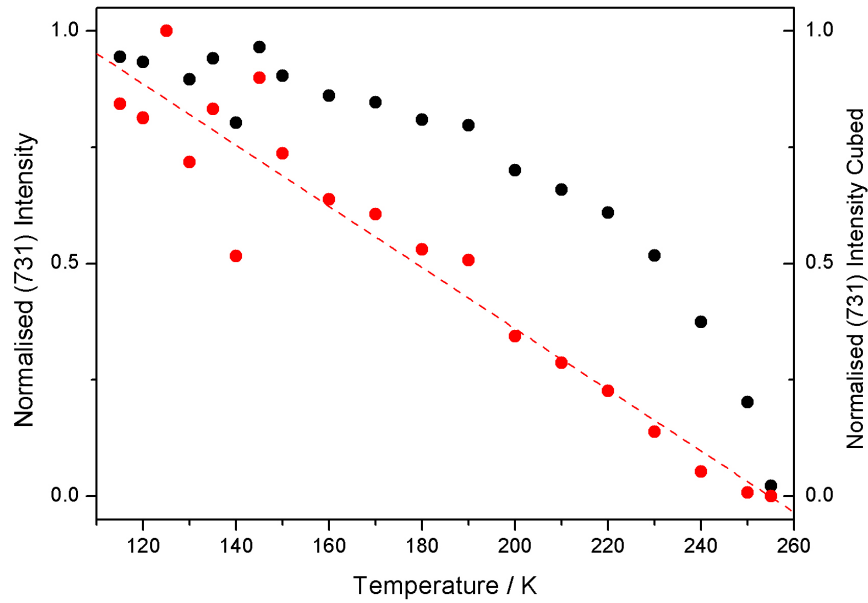


Figure 5.7: The intensity of the (731) reflection (I_{731}) of the MT phase of $\text{Mg}(\text{ND}_3)_6(^{11}\text{BD}_4)_2$ in black and $I_{(731)}^3$ in red as a function of temperature, the dashed line indicates a linear fit to all $I_{(731)}^3$ data.

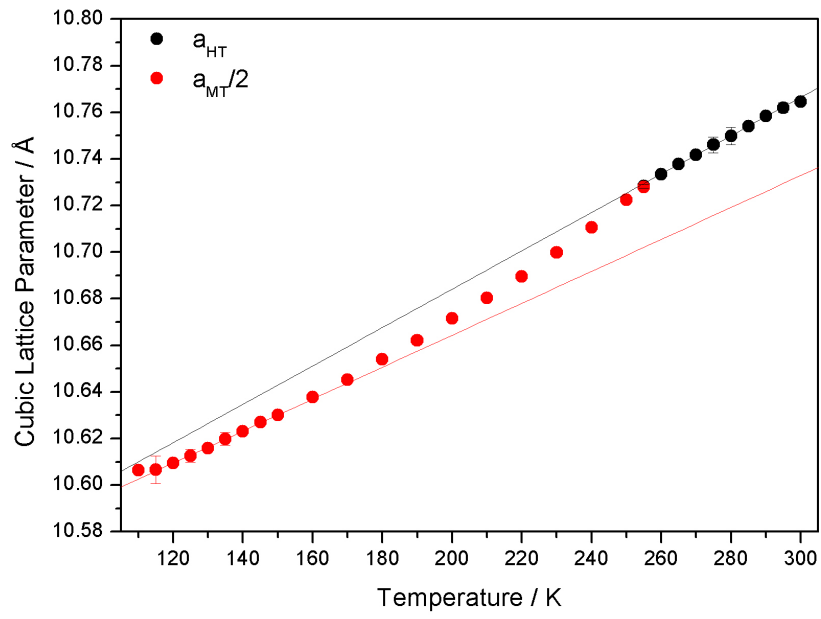


Figure 5.8: The lattice parameters of the HT (a_{HT}) and MT/2 ($a_{\text{MT}}/2$) phases of $\text{Mg}(\text{ND}_3)_6(^{11}\text{BD}_4)_2$ as a function of temperature. Error bars are included but where not visible are hidden by datum markers.

5.4 Raman Spectroscopy

The Raman spectrum of $\text{Mg}(\text{NH}_3)_6(\text{BH}_4)_2$ is shown in Figure 5.9, where the similar spectrum of $\text{Li}(\text{NH}_3)\text{BH}_4$ that is discussed in detail in Section 3.3.6 is also shown for comparison. The principal mode in the BH_4^- region appears at the same wavenumber in both spectra, confirming the existence of discrete BH_4^- anions in both materials. The lower intensity of the side bands in the BH_4^- stretching region of the $\text{Mg}(\text{NH}_3)_6(\text{BH}_4)_2$ spectrum may suggest that the anion here is in a higher symmetry environment than in $\text{Li}(\text{NH}_3)\text{BH}_4$, which is consistent with the disorder seen in the diffraction data. The shape of the NH_3 stretching bands is highly similar in both spectra, with the most intense line observed at a frequency of 3267 cm^{-1} in $\text{Mg}(\text{NH}_3)_6(\text{BH}_4)_2$ and 3296 cm^{-1} in $\text{Li}(\text{NH}_3)\text{BH}_4$. This suggests a weakening of the N–H bond in the magnesium compound, most likely caused by stronger M–N bonding rather than $\text{NH}\cdots\text{BH}_4^-$ interactions. In the spectrum of LiBH_4 , a mode that was not calculated was observed at 3172 cm^{-1} and was attributed to vibration rotation coupling between NH_3 stretches and NH_3 rotations. This mode is also observed in $\text{Mg}(\text{NH}_3)_6(\text{BH}_4)_2$ and in this case the spacing between the main mode and the additional mode is 124 cm^{-1} . This is compared to an observed spacing of 81 cm^{-1} in the $\text{Li}(\text{NH}_3)\text{BH}_4$ spectrum, and suggests that the NH_3 rotational modes appear at higher energies in $\text{Mg}(\text{NH}_3)_6(\text{BH}_4)_2$. The increased barrier to rotation and stronger $\text{NH}\cdots\text{BH}_4^-$ interactions are attributed to the local (albeit weak) interaction with 4 nearest neighbour anions per ammonia molecule in $\text{Mg}(\text{NH}_3)_6(\text{BH}_4)_2$ compared to the local interaction with just one anion seen in $\text{Li}(\text{NH}_3)\text{BH}_4$.

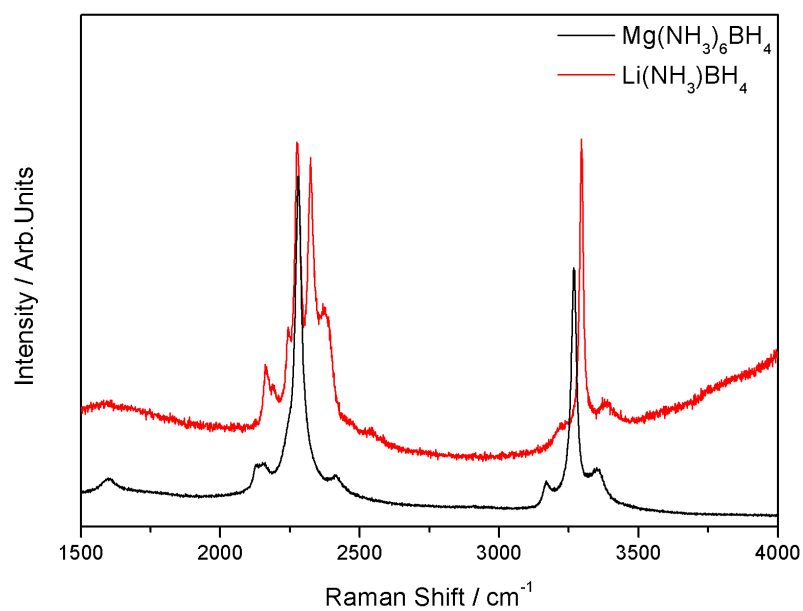


Figure 5.9: The Raman spectra of $\text{Mg}(\text{NH}_3)_6(\text{BH}_4)_2$ in black and $\text{Li}(\text{NH}_3)\text{BH}_4$ in red.

5.5 Inelastic Neutron Spectroscopy

INS data for a sample of $\text{Mg}(\text{NH}_3)_6(\text{BH}_4)_2$ (with all elements at their natural isotopic abundance) were collected using TOSCA at 20 K, the resulting spectrum is shown in Figure 5.10. The similarities to spectra of the $\text{Mg}(\text{NH}_3)_6\text{X}_2$ halides are clear and this reflects the structural similarities of the group. For ease of comparison the relative positions of common NH_3 libration, rocking and umbrella modes (discussed in detail in Section 4.6) are highlighted by dashed lines, and it is clear that the modes for the borohydride sit at an intermediate position between bromide and iodide. This suggests that the trends follow the size of the anion; the hydrogen atoms present in BH_4^- do not effect the movement of the NH_3 molecules and the charge density of the BH_4^- anion is the most important factor. It is proposed that this is because the orientation of the BH_4^- unit in the high temperature phase does not allow for directional dihydrogen bonding to all NH_3 molecules. The phase present during the measurements is likely to have frozen BH_4^- disorder, thus the average hydrogen atom position produces a spherical ion of radius 2.05 Å.

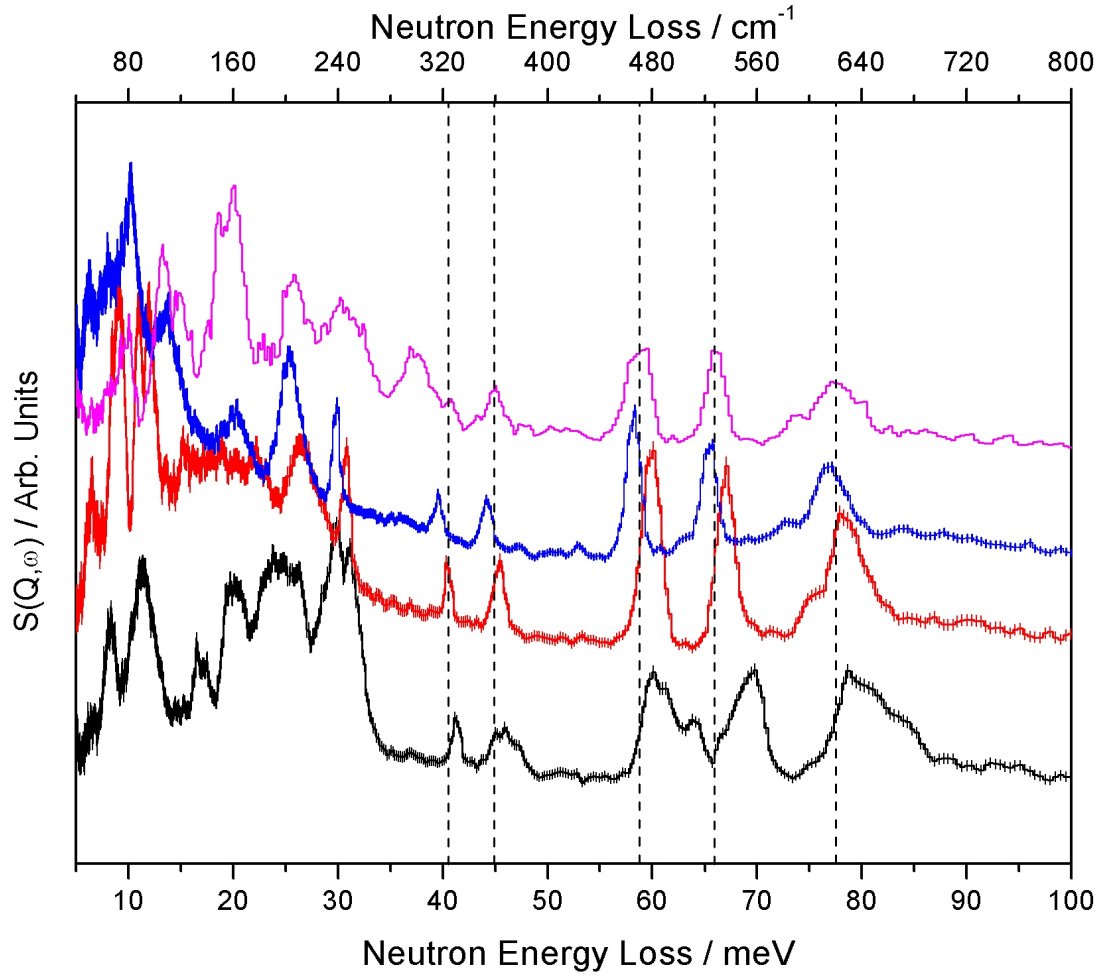


Figure 5.10: The INS spectra of $\text{Mg}(\text{NH}_3)_6\text{X}_2$ with $\text{X} = \text{BH}_4$, I, Br and Cl shown in pink/purple, blue, red and black respectively. Positions of particular modes in $\text{Mg}(\text{NH}_3)_6(\text{BH}_4)_2$ are indicated by dashed lines.

5.6 Gravimetric Analysis

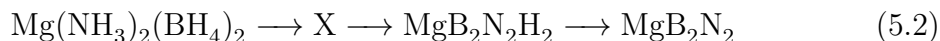
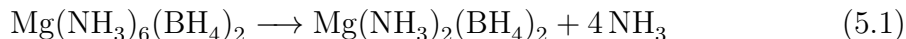
Gravimetric analysis was carried out using the TGA, RGA, and IGA equipment detailed in Chapter 2. The use of a variety of techniques allows for a thorough analysis of decomposition, that is necessary both for comparison with other data presented in this Thesis and to clarify the contradicting reports in the literature.^{50,51}

5.6.1 Thermogravimetric Analysis (TGA)

Thermogravimetric, TGA, analysis of $\text{Mg}(\text{NH}_3)_6(\text{BH}_4)_2$ was carried out using the procedure described in Section 2.11.1. Measurements were carried out using a heating rate of $2\text{ }^\circ\text{Cmin}^{-1}$ under a 1 bar argon atmosphere with a flow rate of 5 mlmin^{-1} . Data are shown in Figure 5.11, where it can be seen from the plot of $(\frac{dm}{dt})$ that up to $575\text{ }^\circ\text{C}$ there are four mass loss steps with $T_{p1} = 144\text{ }^\circ\text{C}$, $T_{p2} = 200\text{ }^\circ\text{C}$, $T_{p3} = 226\text{ }^\circ\text{C}$ and $T_{p4} = 427\text{ }^\circ\text{C}$. No plateaus distinguishing between steps one, two and three are observed meaning that it is hard to assign the intermediates, though T_{p2} matches the $200\text{ }^\circ\text{C}$ reported for $\text{Mg}(\text{NH}_3)_2(\text{BH}_4)_2$, suggesting this phase has formed after the first step and then decomposed. The subsequent two-step decomposition of $\text{Mg}(\text{NH}_3)_2(\text{BH}_4)_2$ below $400\text{ }^\circ\text{C}$ is also consistent with reported data.⁵¹

It is assumed, that the lowest mass reached corresponds to complete hydrogen loss and an empirical formula of MgB_2N_2 . The fourth mass loss at $T_{p4} = 427\text{ }^\circ\text{C}$ is close to the decomposition temperature of MgH_2 ,¹¹⁵ and if this is present or not an empirical formula of $\text{MgB}_2\text{N}_2\text{H}_2$ is consistent with the first plateau product. Taking the mean molar amount of sample from these two points gives a starting sample of $\text{Mg}(\text{NH}_3)_{5.4}(\text{BH}_4)_2$, that is to say either the starting ammine was produced with 90 % yield or some ammonia was lost from the sample on evacuation of the sample vessel during synthesis. The masses of these assumed products are shown in Figure 5.11. Overall, the analysis shows that decomposition occurs according to Reactions 5.1 and 5.2. The small amount of sample available after the TGA experiment

meant that no additional data to help identify the decomposition products could be obtained.



The first mass loss step has an onset temperature of $T_o = 105^\circ\text{C}$, this is lower than the equivalent bromide or iodide, but higher than the chloride. The evidence in the diffraction and vibrational spectroscopy data suggests that the disordered BH_4^- acts as a spherical anion. Considering the argument for decomposition of $\text{Mg}(\text{NH}_3)_6\text{X}_2$ based on an ionic model presented in Section 4.8.1 and shown for $\text{Mg}(\text{NH}_3)_6(\text{BH}_4)_2$ in Figure 5.12; $\text{Mg}(\text{NH}_3)_6(\text{BH}_4)_2$ should decompose at a temperature close to the halide with the most similar anionic radii, $\text{Mg}(\text{NH}_3)_6\text{Br}_2$ ($2.03 \text{ \AA}$ for BH_4^- cf. $1.96 \text{ \AA}$ for Br^-).^{108,116} The lower than expected T_1 shows that in this case the purely ionic model is no longer appropriate and its breakdown may be explained by the presence of dihydrogen bonding that acts to stabilise the intermediate $\text{Mg}(\text{NH}_3)_2(\text{BH}_4)_2$ but not the starting $\text{Mg}(\text{NH}_3)_6(\text{BH}_4)_2$, the presence of such bonding was proposed by Soloveichik et al..⁵¹

5.6.2 Residual Gas Analysis (RGA)

The decomposition products were investigated using RGA, with measurements carried out at Birmingham University. A sample of $\text{Mg}(\text{NH}_3)_6(\text{BH}_4)_2$ was heated at a rate of 3°Cmin^{-1} with the output gas scanned for the presence of matter with masses between 1 a.m.u. and 50 a.m.u.. The strong signals that were detected for NH_3 and H_2 and are shown in Figure 5.13. The two stages of gas release that are observed fit with the TGA data and are consistent with the decomposition pathway shown in Reactions 5.1 and 5.2. The multiple maxima of the H_2 plot suggest

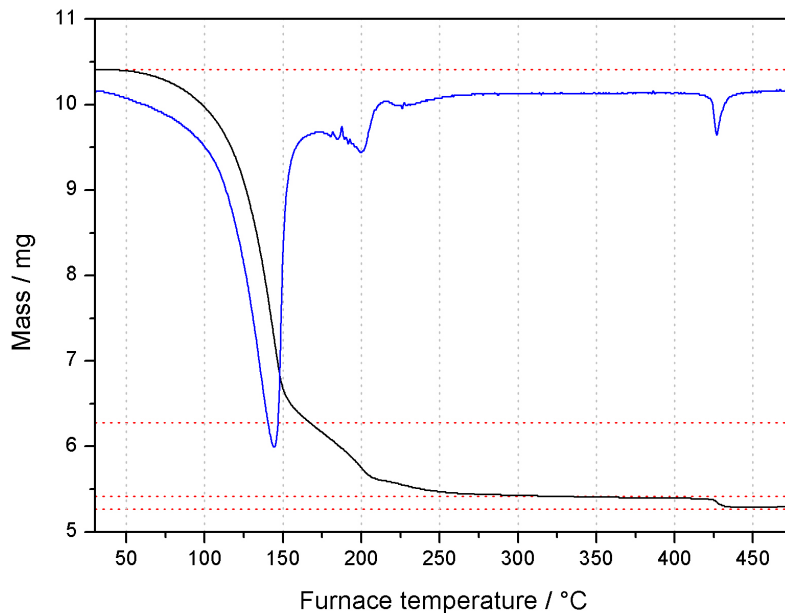


Figure 5.11: Mass loss as a function of temperature for $\text{Mg}(\text{NH}_3)_6(\text{BH}_4)_2$ in black, with the first derivative of the mass with respect to time ($\frac{dm}{dt}$) in blue. Red dotted lines indicate masses corresponding to (from top to bottom) $\text{Mg}(\text{NH}_3)_{5.4}(\text{BH}_4)_2$, $\text{Mg}(\text{NH}_3)_2(\text{BH}_4)_2$, $\text{MgN}_2\text{B}_2\text{H}_2$ and MgN_2B_2 .

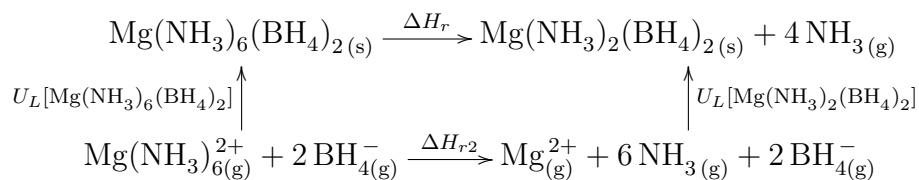


Figure 5.12: Hess cycle for decomposition of $\text{Mg}(\text{NH}_3)_6(\text{BH}_4)_2$ to $\text{Mg}(\text{NH}_3)_2(\text{BH}_4)_2$.

that there are several intermediates associated with the decomposition that leads to hydrogen release. The apparent hydrogen release below 150 °C is not attributed to the sample but is an experimental artefact that is typical of the instrument when ammonia is also detected.

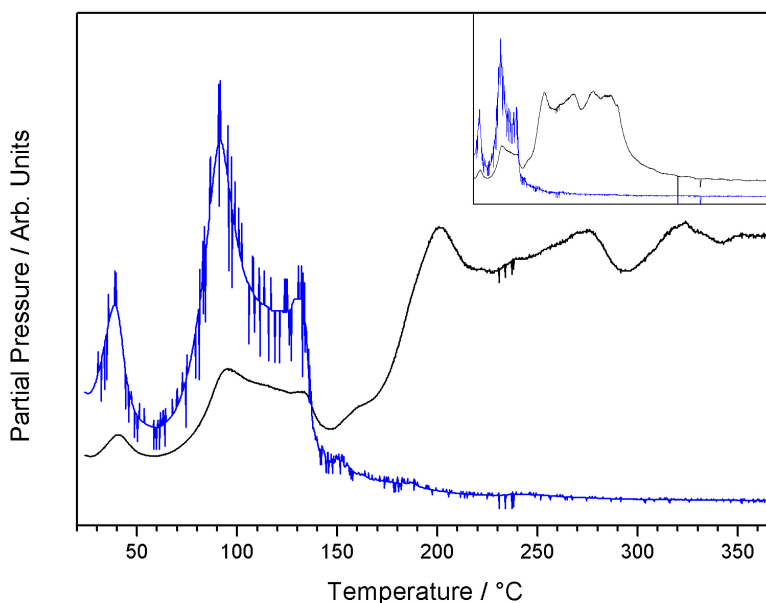


Figure 5.13: The partial pressures of NH_3 in blue and H_2 in black produced during heating of $\text{Mg}(\text{NH}_3)_6(\text{BH}_4)_2$.

5.6.3 Intelligent Gravimetric Analysis (IGAⁿ)

In order to assess the stability of $\text{Mg}(\text{NH}_3)_2(\text{BH}_4)_2$ and to establish the potential suitability of $\text{Mg}(\text{NH}_3)_6(\text{BH}_4)_2$ as an ammonia storage material, a cycling experiment was carried out using the IGAⁿ equipment with and without neutron diffraction. The data collected without neutron diffraction are shown in Figure 5.14. Here it can be seen that at a constant temperature of 75 °C it was possible to convert between the $\text{Mg}(\text{NH}_3)_6(\text{BH}_4)_2$ and $\text{Mg}(\text{NH}_3)_2(\text{BH}_4)_2$ by changing the pressure between 250 mbar of ammonia and the ‘outgas’ mode of the IGAⁿ (nominally 0 bar).

Attempts to perform this experiment in-situ whilst collecting neutron diffrac-

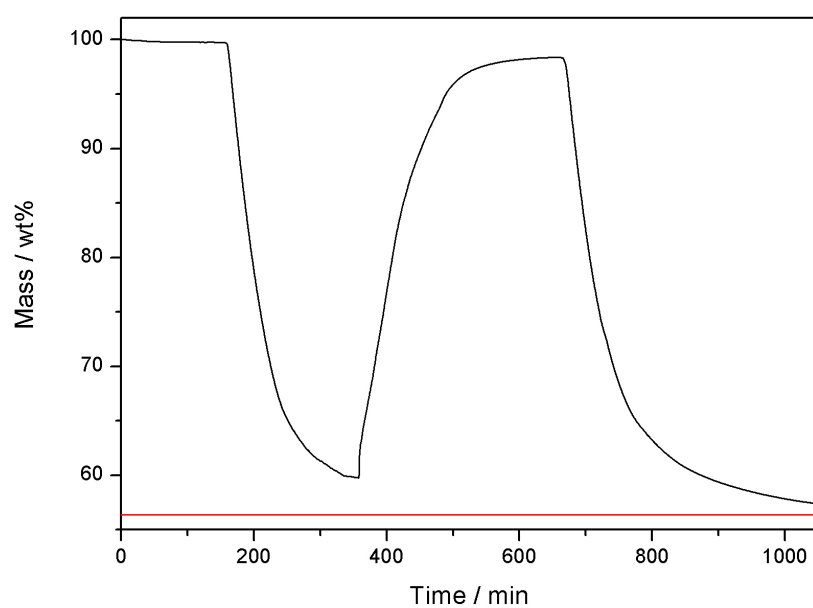


Figure 5.14: Mass as a function of time for $\text{Mg}(\text{NH}_3)_6(\text{BH}_4)_2$, data were collected cycling between an ammonia pressure of 250 mbar and ‘outgas’ at a temperature of 75 °C. The red line corresponds to complete conversion to $\text{Mg}(\text{NH}_3)_2(\text{BH}_4)_2$ assuming a starting sample of 100 % $\text{Mg}(\text{NH}_3)_6(\text{BH}_4)_2$.

tion data were of limited added value. It was found that the Bragg reflections for $\text{Mg}(\text{ND}_3)_6(^{11}\text{BD}_4)_2$ decreased in intensity as ammonia loss occurred. The mass trace showed a lumpiness that is characteristic of a gas loss from a liquid with a solid crust, it is proposed that at this temperature $\text{Mg}(\text{ND}_2)_2(^{11}\text{BD}_4)_2$ is a liquid and thus did not produce Bragg reflections. Attempts to cool the sample resulted in the appearance of some reflections, though with a poor signal to noise ratio, such that no useful data were gained for further analysis.

5.7 Conclusions

In this Chapter it has been shown that the properties of $\text{Mg}(\text{NH}_3)_6(\text{BH}_4)_2$, including its vibrational spectrum, its initial decomposition and the size of its unit cell, may all be explained by considering it as part of the $\text{Mg}(\text{NH}_3)_6\text{X}_2$ series where the anion BH_4^- sits between Br^- and I^- . The nature of disorder within $\text{Mg}(\text{NH}_3)_6(\text{BH}_4)_2$ has been established using a variety of techniques, at room temperature the BH_4^- anion exhibits a fourfold disorder which is why it behaves in an analogous manner to the halides. The similarity with the halides is further reflected in the similar Mg–N bond lengths and favoured occupancy of the 45° NH_3 hydrogen site. The additional B–H bonds are irrelevant until it comes to the formation of $\text{Mg}(\text{NH}_3)_2(\text{BH}_4)_2$, where the formation of dihydrogen bonds allow significant stabilisation of the diammine compared to the equivalent halides.

5.7.1 Evaluation as an Ammonia Storage Material

It has been shown that it is possible to reversibly cycle between the hexa- and diammines, though the potential for irreversible decomposition of the diammine may limit the effective lifetime of the material. The storage properties are compared to $\text{Mg}(\text{NH}_3)_6\text{Cl}_2$ in Table 5.1, where it can be seen that the useful ammonia content

of $\text{Mg}(\text{NH}_3)_6(\text{BH}_4)_2$ is reduced as a result of the irreversible decomposition of the diammine. The advantage of the using the borohydride over the chloride is the low and constant temperature required for complete ammonia release. The conclusion that a stabilised intermediate may help to lower the desorption temperature of ammines may be used in attempts to design ammonia storage materials with lower decomposition temperatures.

Table 5.1: Summary of ammonia storage properties of $\text{Mg}(\text{NH}_3)_6(\text{BH}_4)_2$, compared to $\text{Mg}(\text{NH}_3)_6\text{Cl}_2$ and liquid NH_3 .

Compound	Reversible Ammonia Content / wt%	Ammonia Density / gL^{-1}	Temperature required for complete ammonia release / $^{\circ}\text{C}$
$\text{Mg}(\text{NH}_3)_6\text{Cl}_2$	52	654	250
$\text{Mg}(\text{NH}_3)_6(\text{BH}_4)_2$	50	543	75
$\text{NH}_3_{(l)} -33^{\circ}\text{C}$	100	682	-

5.7.2 Further Work

The use of $\text{Mg}(\text{NH}_3)_6(\text{BH}_4)_2$ as an ammonia store may be limited given the instability of $\text{Mg}(\text{NH}_3)_2(\text{BH}_4)_2$ around the temperatures that ammonia is released from the hexa-ammine, however a number of interesting areas for further work remain. In particular determining the decomposition products formed using in-situ ^{25}Mg and ^{11}B NMR, diffraction and possibly pair distribution function (PDF) analysis would be useful in determining the potential reversibility of the decomposition and the suitability of $\text{Mg}(\text{NH}_3)_2(\text{BH}_4)_2$ as a hydrogen storage material. The hydrogen storage properties of $\text{Mg}(\text{NH}_3)_2(\text{BH}_4)_2$ have only been discussed briefly but is a material with huge potential. Solving the low-temperature structures would increase the general understanding of this material and provide an interesting crystallographic study. A potential use for the borohydride anion in ammonia storage materials may be in producing mixed anion systems with bromine or chlorine, wherein the borohydride

may act to stabilise intermediates and reduce decomposition temperatures.

Conclusions and Further Work

In this Thesis, $\text{Li}(\text{NH}_3)_n\text{BH}_4$ and $\text{Mg}(\text{NH}_3)_n\text{X}_2$ (with $\text{X} = \text{Cl}, \text{Br}, \text{I}$ and BH_4) have been investigated as potential ammonia storage materials. Detailed conclusions are discussed at the end of Chapters 3 to 5, but a brief summary and some common features are presented here. In this Chapter, the potential use as ammonia storage materials is concluded and discussed. This is followed by a summary of the points of more general interest and some final conclusions.

As reported in Chapter 1, $\text{Mg}(\text{NH}_3)_6\text{Cl}_2$ has been proposed as a promising ammonia storage material,¹⁸ with the primary benefit of having a high ammonia density of 654 gl^{-1} and a low vapour pressure. This ammonia density is higher than the novel materials investigated in this Thesis, with $\text{Li}(\text{NH}_3)_4\text{BH}_4$ at 539 gl^{-1} and $\text{Mg}(\text{NH}_3)_6(\text{BH}_4)_2$ at 543 gl^{-1} . Moreover, $\text{Mg}(\text{NH}_3)_6(\text{BH}_4)_2$ falls short in its gravimetric ammonia density, containing only 50 wt% of recoverable ammonia compared to $\text{Mg}(\text{NH}_3)_6\text{Cl}_2$ with 52 wt% — $\text{Li}(\text{NH}_3)_4\text{BH}_4$ excels in this respect as it contains 76 wt% ammonia. The borohydride compounds succeed in lowering the energy exchange associated with ammonia cycling, as they require temperatures of 50°C and 75°C respectively to release all adsorbed ammonia, compared to 250°C for the chloride system. These comparisons are assuming a desorption method that involves elevated temperatures (in the style of TGA), but a key benefit of using

$\text{Li}(\text{NH}_3)\text{BH}_4$ is that, as reaction 6.1 shows, it allows storage of 57 wt% ammonia using the room temperature pressure swing absorption (PSA) method operating between ca. 24 mbar and 110 mbar. This compares favourably to the leading PSA candidate $\text{Ca}(\text{NH}_3)_8\text{Cl}_2$, that can be used to store 41 wt% ammonia using PSA between 700 mbar and 2.1 mbar as shown in Reaction 6.2.²⁵ Some key ammonia storage data collated from Chapters 3, 4 and 5 are given in Table 6.1.

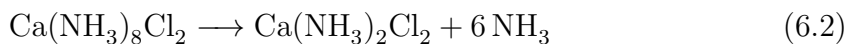
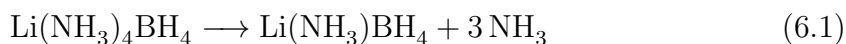


Table 6.1: A summary of the ammonia storage properties of materials investigated in this Thesis in comparison to liquid ammonia

Compound	Reversible Ammonia Content / wt%	Ammonia Density / gl^{-1}	Vapour Pressure at 25 °C / mbar	Temperature required for complete ammonia release / °C
$\text{Li}(\text{NH}_3)\text{BH}_4$	41	296	6.7	50
$\text{Li}(\text{NH}_3)_2\text{BH}_4$	61	385	24	50
$\text{Li}(\text{NH}_3)_3\text{BH}_4$	70	526	96	50
$\text{Li}(\text{NH}_3)_4\text{BH}_4$	76	539	110	50
$\text{Mg}(\text{NH}_3)_6\text{Cl}_2$	52	654	1.97 ²⁵	250
$\text{Mg}(\text{NH}_3)_6\text{Br}_2$	36	602	-	270
$\text{Mg}(\text{NH}_3)_6\text{I}_2$	27	522	-	330
$\text{Mg}(\text{NH}_3)_6(\text{BH}_4)_2$	50	543	-	75
$\text{NH}_{3(l)} -33^\circ\text{C}$	100	682	1017	-

In terms of developing these materials as viable, large scale, ammonia stores, careful thought must be given the final application. The borohydrides may produce good lightweight storage materials but they suffer from relatively facile decomposition, which means that these systems are less robust than those based on halides which have substantially higher melting points and decomposition temperatures. The choice of starting material must depend on the end-use application. There may be requirement to operate at specific temperatures or pressures and withstand more

aggressive heating or loading regimes in an ‘industrial’ environment compared to the laboratory.

Considering future research, the next step for each system must be to perform cycling experiments to determine any loss of capacity on repeated cycles. It would also be necessary to determine the effect of pelletisation and use of bulk samples on storage properties. A key consideration will be the heat of absorption; this was calculated (in Chapter 4) to range between -91 kJmol^{-1} and -117 kJmol^{-1} for the magnesium halides. It would be useful for these to be experimentally determined in order to assess the thermal conductivity requirements of any large scale system. Investigating pressure-composition relationships at elevated and fixed temperatures, in a method similar to the $\text{Mg}(\text{NH}_3)_6(\text{BH}_4)$ 75°C cycling experiments, would also be beneficial as varying just the temperature or the pressure will create the simplest system in terms of engineering and manufacture. An interesting investigation would involve determining if mixes of anions allow steady ammonia release over a temperature range, or even allow a combination of the seemingly exclusive properties of low vapour pressure and low-temperature desorption. For example, in an ammine consisting of MgCl_2 and MgI_2 , the chloride would release ammonia at lower temperatures while the iodide would adsorb at low vapour pressures.

Besides the ammonia storage capacity of these materials, they have provided a number of interesting results. Discussion presented throughout this Thesis concludes that disorder is present in all these ammines and is primarily associated with rotating ammonia molecules. The nature of the disorder has proved a determining factor in the material properties, for example in $\text{Mg}(\text{NH}_3)_6(\text{BH}_4)_2$ the BH_4^- anion is disordered and behaves analogously to the halides, but in $\text{Mg}(\text{NH}_3)_2(\text{BH}_4)_2$ the BH_4^- anion is ordered and instead of decomposing as the halides do to release ammonia, this diammine decomposes to release hydrogen.⁵¹ In the lithium borohydride ammines, ammonia motion and disorder explains a number of the properties; in the case of $\text{Li}(\text{NH}_3)\text{BH}_4$ the disordered ammonia molecule shows close $\text{NH}\cdots\text{HB}$ contacts

which may allow the hydrogen release that has been seen by Guo et al..¹⁰⁵ In the diammine, it is the ammonia motion that determines the low melting temperature. While the triammine results provide less insight, the tetra-ammine shows a great deal of disorder and ammonia mobility that explains why it requires stabilisation with an ammonia vapour pressure of 110 mbar. Most of this disorder and ammonia motion has been determined through combinations of diffraction experiments and DFT calculations. Using such techniques in combination has provided a level of insight into the materials that neither could provide individually.

There are a number of areas of investigation that have been started in this Thesis where further work would strengthen the understanding of the nature of ammonia coordination in the solid state. A clear place starting point is the solution of the low-temperature crystal structures for all the compounds. The ammonia molecule orders at low-temperatures making its interactions with local ions clearer; observing the subsequent phase changes and higher temperature disordering will provide a better understanding of the materials. Accurate low-temperature structures will also mean that INS data may be modelled more accurately, and this will allow for calculations that are accurate enough to reliably calculate a range of important thermodynamic properties and obtain a better understanding and assignment of the critical low energy modes seen in the INS data. Understanding of the $\text{Li}(\text{NH}_3)_n\text{BH}_4$ system will be further developed by studying $\text{Li}(\text{NH}_3)_n\text{Cl}$ and $\text{Li}(\text{NH}_3)_n\text{Br}$; in particular pressure-temperature-composition studies of both halides and borohydride will help determine the nature of the stabilising BH_4^- and NH_3 interactions and the presence of dihydrogen bonding.

The release of hydrogen has been observed from $\text{Mg}(\text{NH}_3)_2(\text{BH}_4)_2$ and $\text{Li}(\text{NH}_3)\text{BH}_4$ and this provides another interesting avenue of research.^{51,105} If it is possible to release all the hydrogen in these materials then their hydrogen contents of 16.0 wt% and 18.2 wt% (for $\text{Mg}(\text{NH}_3)_2(\text{BH}_4)_2$ and $\text{Li}(\text{NH}_3)\text{BH}_4$ respectively) place them high in the rankings of high hydrogen content materials. While much of this Thesis has

focused on the role of the anion, the role of the cation must also be examined in more depth to understand hydrogen release. It appears that increasing the polarisation of the N–H bond may promote NH...HN interactions and facilitate hydrogen release upon heating. One route to achieve this may be to use similar cations with higher charge densities, such as Fe^{2+} , Co^{2+} or Ni^{2+} instead of Mg^{2+} . Experiments to determine the properties of these, and other, transition metal halides and borohydrides would provide an interesting comparison and help develop a deeper understanding of these systems. Isolation of transition metal borohydrides is difficult, given their high reduction potential in the presence of BH_4^- . However, synthesis of the borohydride ammines in liquid ammonia may be possible as the cation would become solvated and be protected by ammonia molecules.

In summary, this Thesis has reported the synthesis and structural characterisation of materials that have potential use as ammonia stores. The compounds $\text{Li}(\text{NH}_3)_n\text{BH}_4$ with $n = 1, 2, 3$ and 4 have been structurally and thermogravimetrically characterised and their properties have been explained principally in terms of ammonia mobility and hydrogen bonding interactions. It has been shown that this system has a high gravimetric ammonia density and provides energy efficient storage. The compounds $\text{Mg}(\text{NH}_3)_6\text{X}_2$ have also been characterised structurally and studied with a variety of techniques. In these materials, the disorder of the ammonia molecule indicates the strength of the ammonia-anion interaction. Where high levels of rotational disorder exist the anion size is the determining factor in desorption properties, when disorder decreases and ammonia-anion interactions are stronger, alternative reaction pathways become favourable. The general understanding of the magnesium halides has been improved, and magnesium borohydride has been shown as a lightweight ammonia storage material that allows for energy efficient cycling of ammonia. The study of the materials in this Thesis has shown them to be viable high density ammonia stores and produced a detailed understanding of the chemistry of solid state ammines.

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DFT Convergence Tests

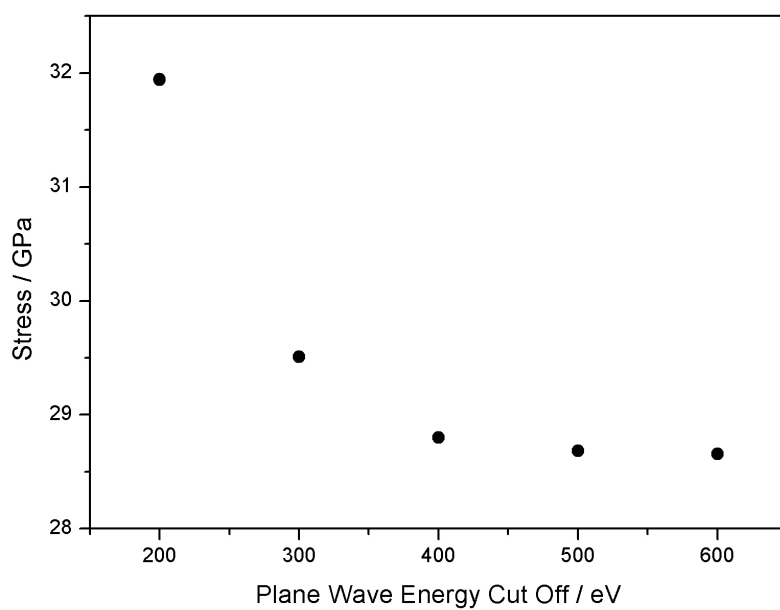


Figure A.1: The calculated stress in Li(NH₃)BH₄ as a function of plane wave cut-off energy

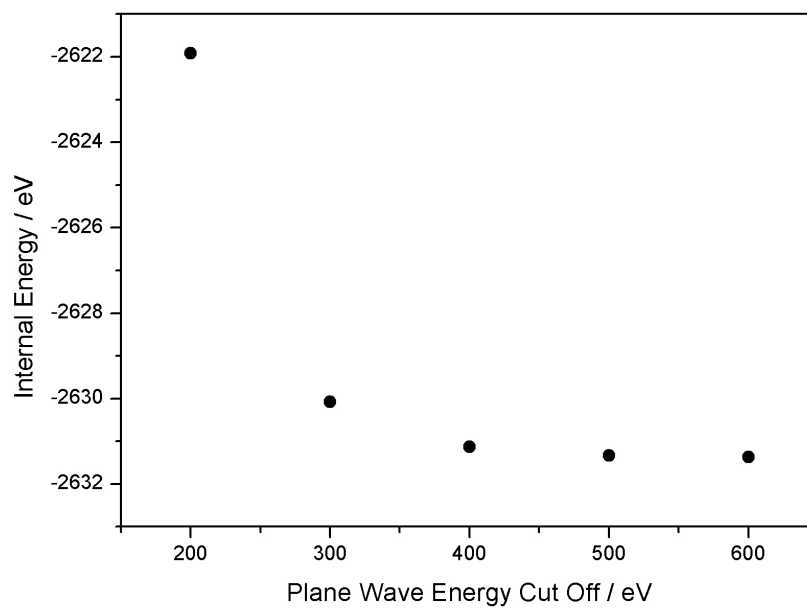


Figure A.2: The calculated internal energy of $\text{Li}(\text{NH}_3)\text{BH}_4$ as a function of plane wave cut-off energy

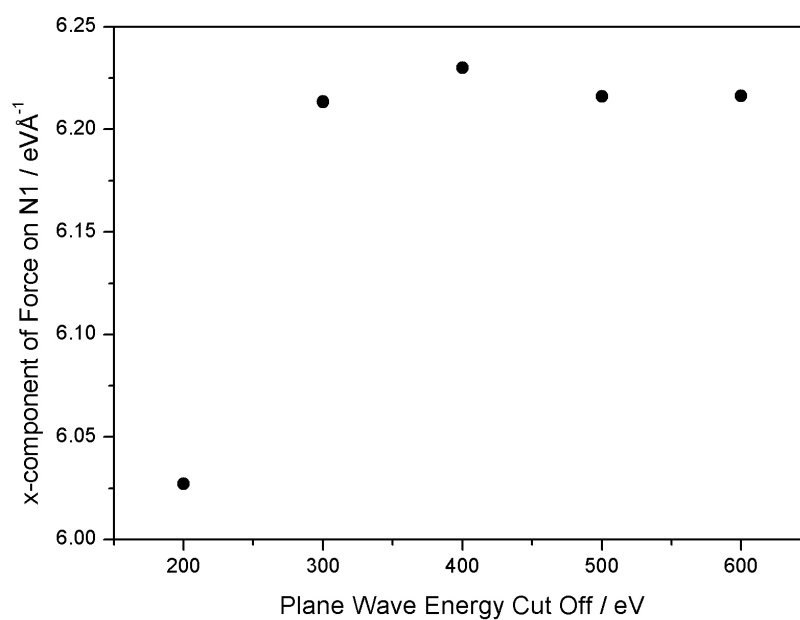


Figure A.3: The calculated x-component of the force on atom N1 in $\text{Li}(\text{NH}_3)\text{BH}_4$ as a function of plane wave cut-off energy

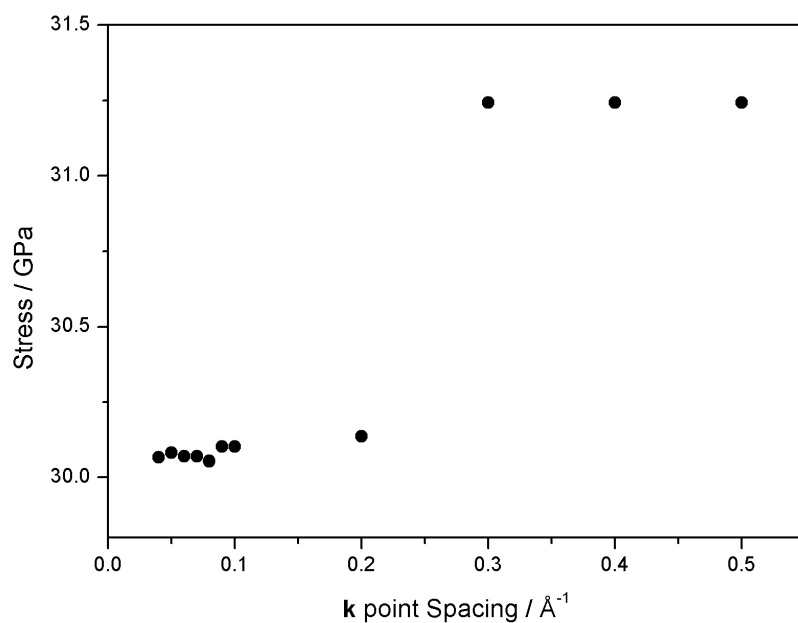


Figure A.4: The calculated stress in $\text{Li}(\text{NH}_3)\text{BH}_4$ as a function of $\mathbf{k}$ -point sampling

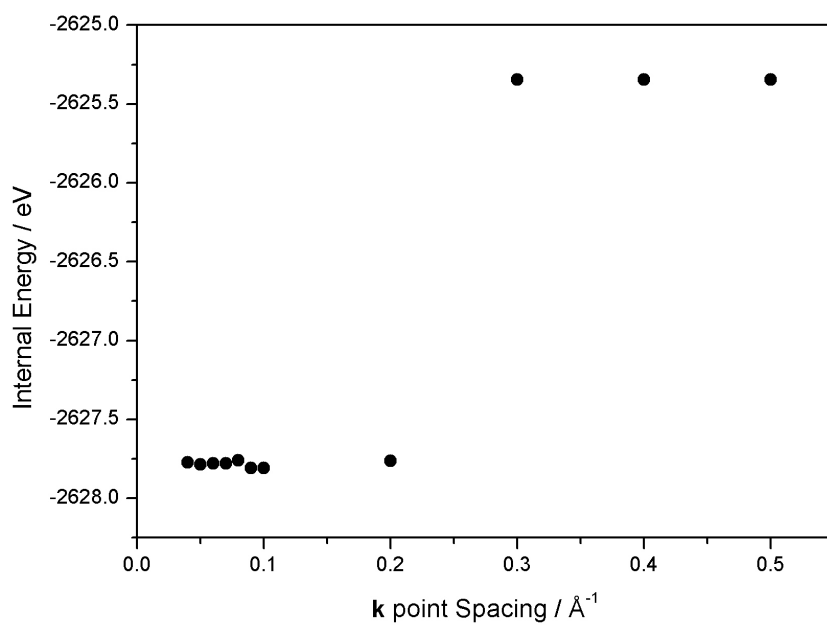


Figure A.5: The calculated internal energy of $\text{Li}(\text{NH}_3)\text{BH}_4$ as a function of $\mathbf{k}$ -point sampling

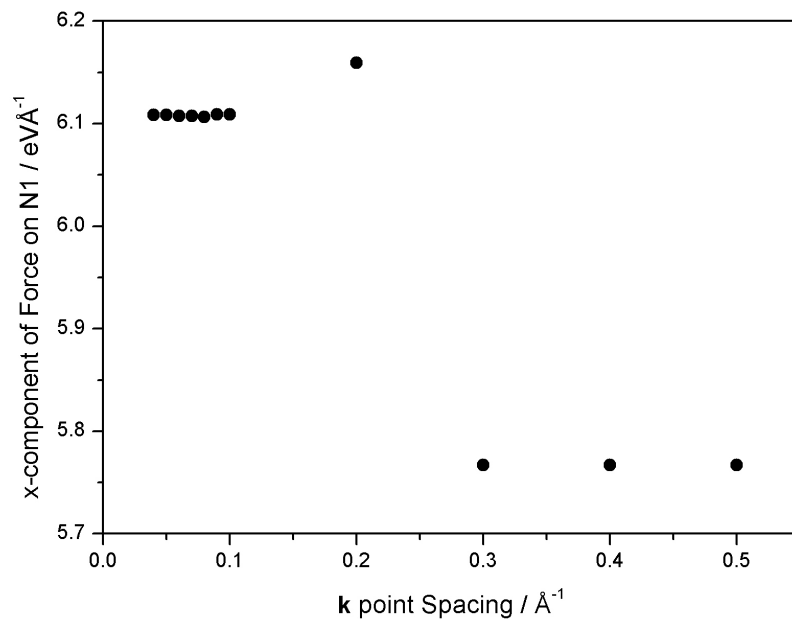


Figure A.6: The calculated x-component of the force on atom N1 in $\text{Li}(\text{NH}_3)\text{BH}_4$ as a function of $\mathbf{k}$ -point sampling

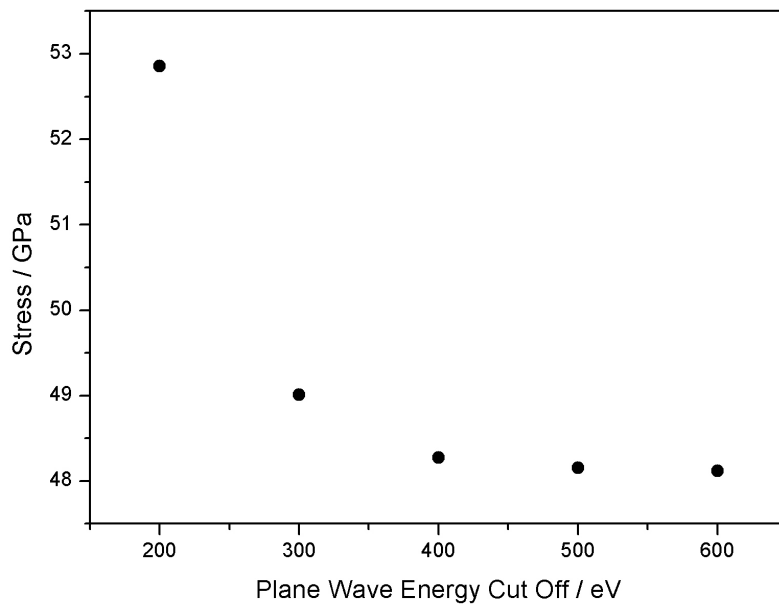


Figure A.7: The calculated stress in $\text{Mg}(\text{NH}_3)_6\text{Cl}_2$ as a function of plane wave cut-off energy

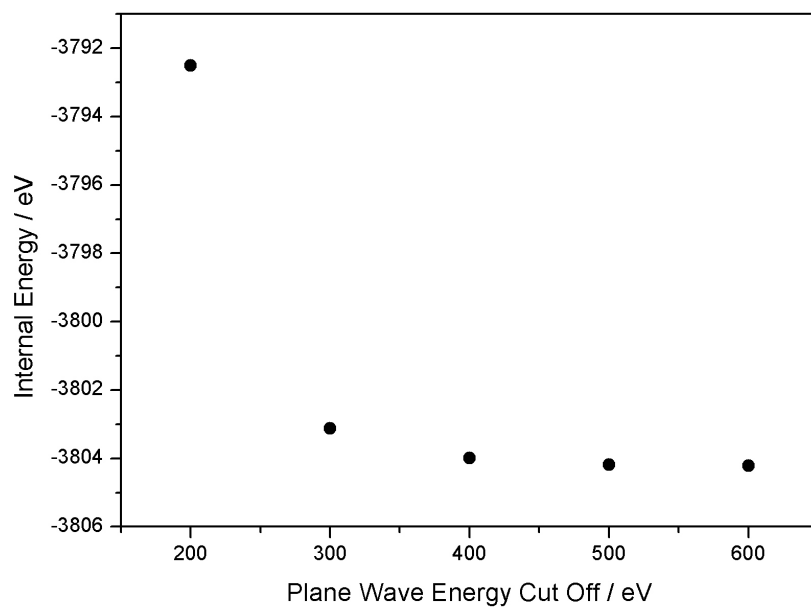


Figure A.8: The calculated internal energy of $\text{Mg}(\text{NH}_3)_6\text{Cl}_2$ as a function of plane wave cut-off energy

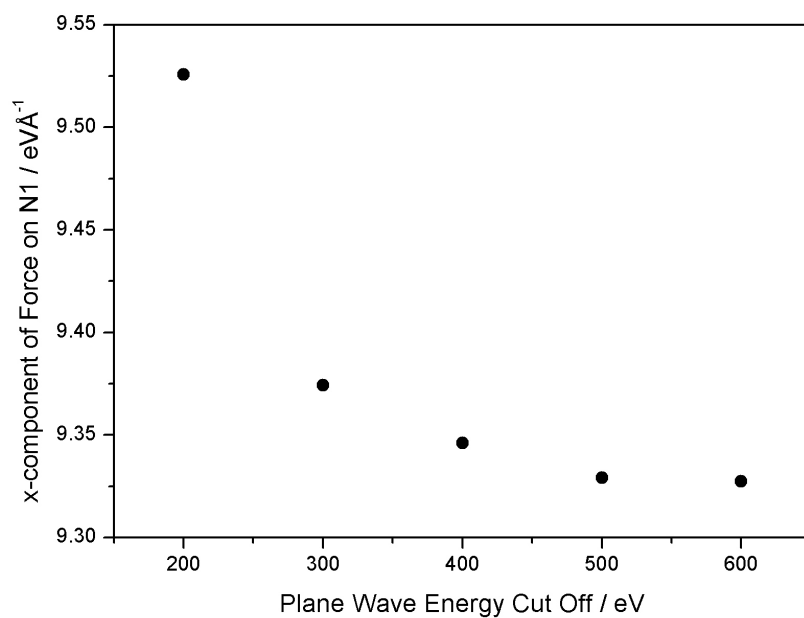


Figure A.9: The calculated x-component of the force on atom N1 in $\text{Mg}(\text{NH}_3)_6\text{Cl}_2$ as a function of plane wave cut-off energy

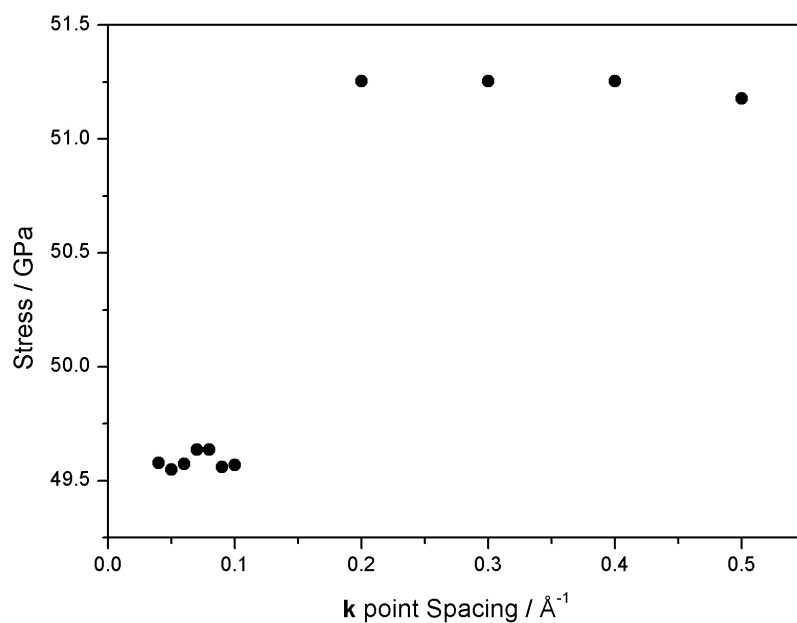


Figure A.10: The calculated stress in $\text{Mg}(\text{NH}_3)_6\text{Cl}_2$ as a function of $\mathbf{k}$ -point sampling

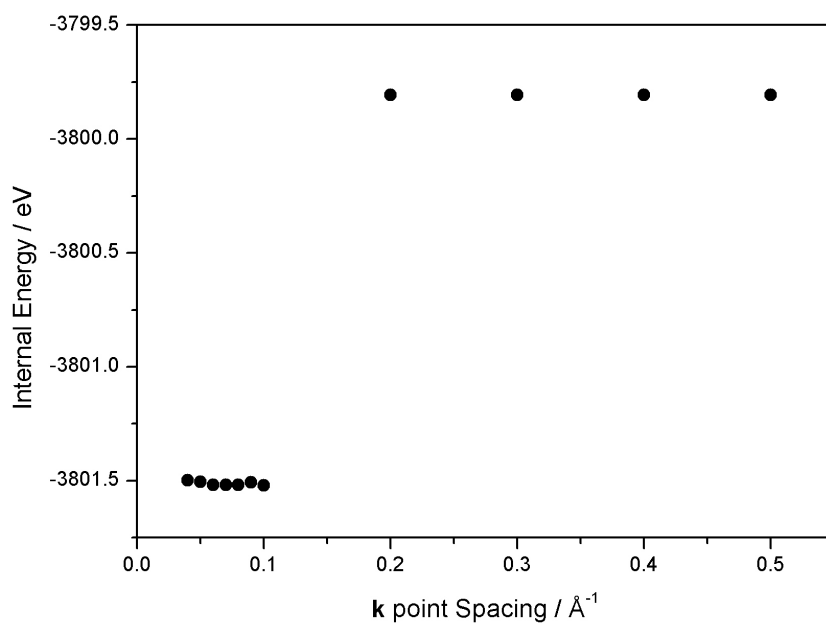


Figure A.11: The calculated internal energy of $\text{Mg}(\text{NH}_3)_6\text{Cl}_2$ as a function of $\mathbf{k}$ -point sampling

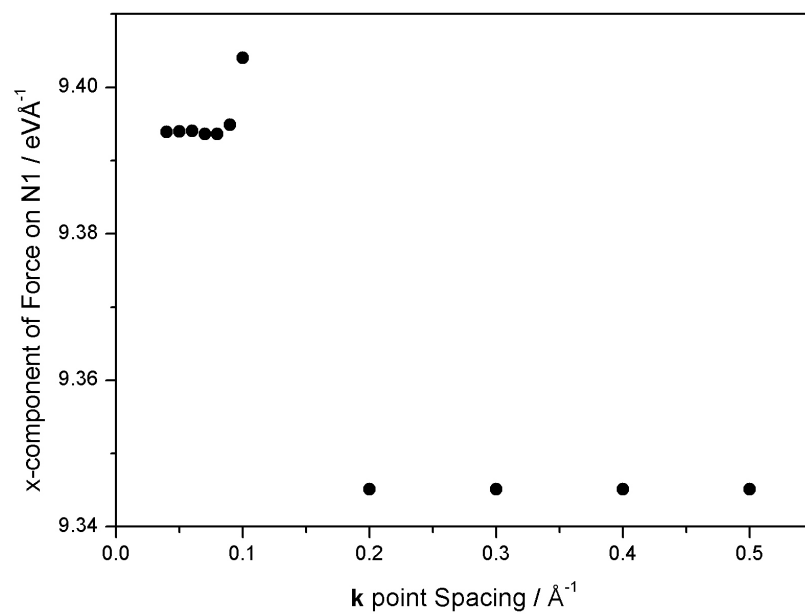


Figure A.12: The calculated x-component of the force on atom N1 in $\text{Mg}(\text{NH}_3)_6\text{Cl}_2$ as a function of $\mathbf{k}$ -point sampling

Lithium Borohydride Ammine Vapour Pressures

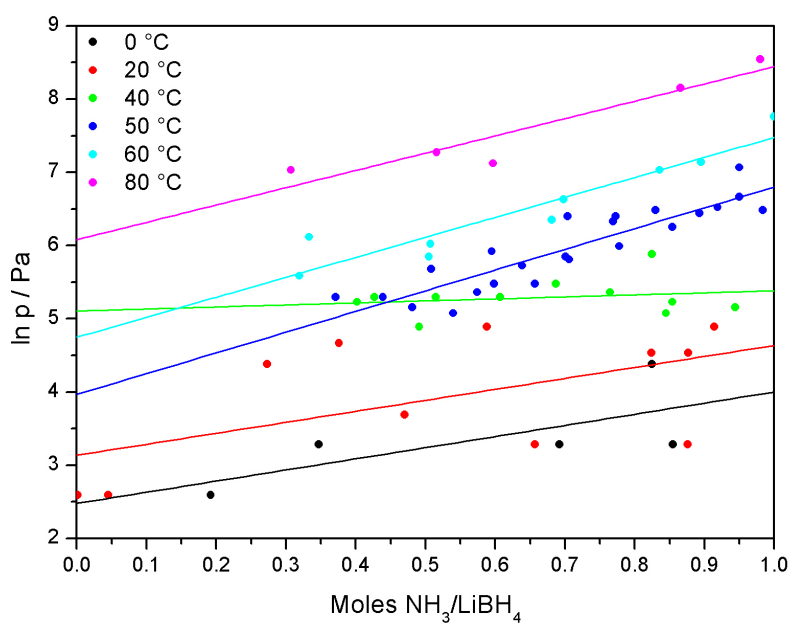


Figure B.1: The vapour pressures $\text{Li}(\text{NH}_3)_n\text{BH}_4$, $n = 0-1$, at various temperatures. Extracted from data reported by Sullivan and Johnson⁵³

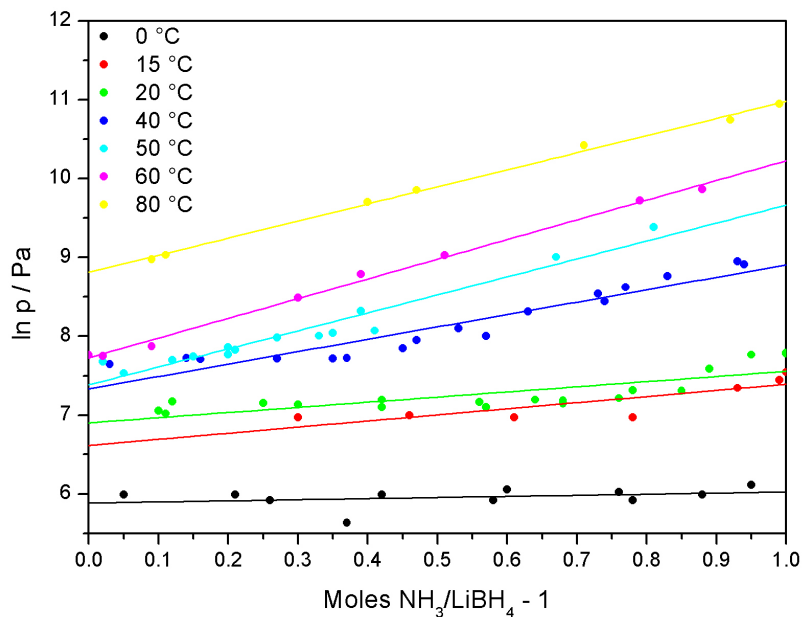


Figure B.2: The vapour pressures $\text{Li}(\text{NH}_3)_n\text{BH}_4$, $n = 1-2$, at various temperatures. Extracted from data reported by Sullivan and Johnson⁵³

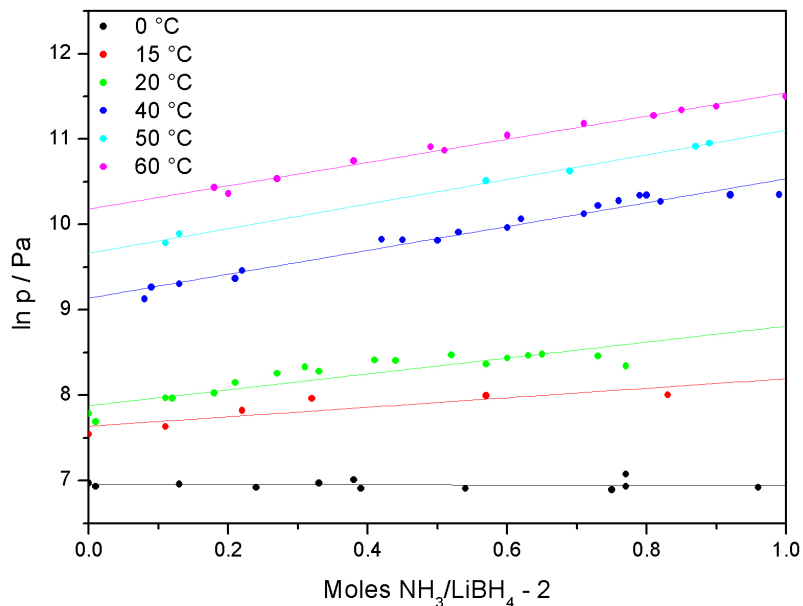


Figure B.3: The vapour pressures $\text{Li}(\text{NH}_3)_n\text{BH}_4$, $n = 2-3$, at various temperatures. Extracted from data reported by Sullivan and Johnson⁵³

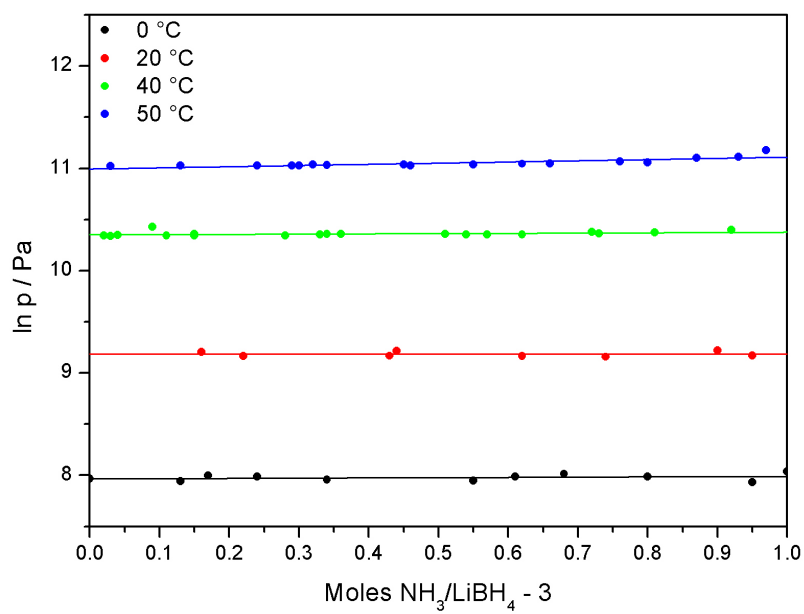


Figure B.4: The vapour pressures $\text{Li}(\text{NH}_3)_n\text{BH}_4$, $n = 3-4$, at various temperatures. Extracted from data reported by Sullivan and Johnson⁵³

Script for Creating Ammonia Molecules in a Unit Cell

The script used to position hydrogen atoms of an ammonia molecule within a known unit cell given position of atoms M and N. Written in Python 2.5.4.

```

from math import *
from numpy import *
from Scientific.Geometry.Quaternion import Quaternion
# Unit cell matrix
# p = [a b c alpha beta gamma]
p = [10, 10, 10, 90, 90, 90]
a = p[0]
b = p[1]
c = p[2]
alpha = (p[3] * pi) / 180.0
beta = (p[4] * pi) / 180.0
gamma = (p[5] * pi) / 180.0
ax = a
bx = b * cos(gamma)
by = sqrt(b**2 - bx**2)
cx = c * cos(beta)
cy = (b * c * cos(alpha) - cx * bx) / by
cz = sqrt(c**2 - cx**2 - cy**2);
A = array([[ax, 0, 0],
           [bx, by, 0],
           [cx, cy, cz]])
invA = linalg.inv(A)
# this converts coordinate system with x = a
# invA * mat converts x to a
# A * mat converts a to x

```

```
# M-N vector N.B. real space from now on
M_a = array([0.3338, 0.00000, 0.8480])
N_a = array([0.360, 0.000, 0.994])
M = dot(A, M_a)
N = dot(A, N_a)
MN = N - M
# axis and M-N vector, find the unit normal and angle
x_ax = array([1, 0, 0])
y_ax = array([0, 1, 0])
z_ax = array([0, 0, 1])
axis = z_ax
n_full = cross(axis, MN)
n_mod = sqrt(dot(n_full, n_full))
n = array([n_full[0]/n_mod, n_full[1]/n_mod, n_full[2]/n_mod])
MN_mod = sqrt(dot(MN, MN))
theta = arccos((vdot(MN, axis)) / MN_mod)
# Create quaternion and rotation matrices
w = cos(theta/2)
x = (sin(theta/2)) * n[0]
y = (sin(theta/2)) * n[1]
z = (sin(theta/2)) * n[2]
q_full = Quaternion(w, x, y, z)
q = Quaternion.normalized(q_full)
R_mem = Quaternion.asRotation(q)
R = R_mem.tensor.array
# Create hydrogen atoms
NH_bond = 0.847
MNH = 109.5
xNH = math.radians((MNH - 90))
r_angle = math.radians(62)
a_0 = r_angle
a_1 = r_angle + (2 * pi / 3)
a_2 = r_angle - (2 * pi / 3)
Rz_0 = array([[cos(a_0), -sin(a_0), 0],
               [sin(a_0), cos(a_0), 0],
               [0, 0, 1]])
Rz_1 = array([[cos(a_1), -sin(a_1), 0],
               [sin(a_1), cos(a_1), 0],
               [0, 0, 1]])
Rz_2 = array([[cos(a_2), -sin(a_2), 0],
               [sin(a_2), cos(a_2), 0],
               [0, 0, 1]])
H_base = array([(NH_bond * (cos(xNH))), 0, (NH_bond * (sin(xNH)))])
H_0 = dot(Rz_0, H_base)
H_1 = dot(Rz_1, H_base)
```

```
H_2 = dot(Rz_2, H_base)
# Rotate hydrogen vectors to face in direction MN and add to N coordinates
H_0_R = dot(R, H_0)
H_1_R = dot(R, H_1)
H_2_R = dot(R, H_2)
NH_0_R = N + H_0_R
NH_1_R = N + H_1_R
NH_2_R = N + H_2_R
# Convert H coordinates into the unit cell
H1 = dot(invA, NH_0_R)
H2 = dot(invA, NH_1_R)
H3 = dot(invA, NH_2_R)
print H1
print H2
print H3
```


Appendix

D

Lithium Borohydride Ammine Phonon Modes

Table D.1: The calculated phonon modes for $\text{Li}(\text{NH}_3)\text{BH}_4$.

Number	Energy		Description
	cm^{-1}	meV	
1	-44.8	-5.56	NH_3 libration
2	-21.2	-2.63	NH_3 libration
3	-0.1	-0.01	anharmonic phonon mode
4	-0.1	-0.01	anharmonic phonon mode
5	-0.1	-0.01	anharmonic phonon mode
6	22.9	2.84	NH_3 libration
7	41.5	5.15	NH_3 libration
8	41.9	5.20	xz-plane shearing
9	67.2	8.33	xz-plane lattice vibration
10	67.7	8.40	NH_3 libration
11	68.1	8.44	xz-plane shearing
12	78.1	9.69	xz-plane shearing
13	93.5	11.60	NH_3 libration
14	97.8	12.13	NH_3 libration
15	126.3	15.66	xz-plane lattice vibration
16	132.5	16.43	NH_3 libration
17	136.5	16.93	xz-plane lattice vibration
18	136.7	16.95	xz-plane lattice vibration
19	137.6	17.06	NH_3 libration
20	142.7	17.70	xz-plane lattice vibration
21	147.0	18.23	NH_3 and BH_4 rocking ⁱ

Continued on next page

ⁱsignificant Li movement

Table D.1 – continued from previous page

Number	Energy		Description
	cm ⁻¹	meV	
22	147.3	18.27	NH ₃ and BH ₄ rocking ⁱ
23	174.8	21.68	xz-plane lattice vibration
24	179.3	22.23	BH ₄ and NH ₃ rocking ⁱ
25	180.4	22.36	BH ₄ and NH ₃ rocking ⁱ
26	180.5	22.38	BH ₄ rocking
27	220.0	27.27	xz-plane lattice mode
28	220.9	27.39	xz-plane lattice mode
29	233.1	28.90	BH ₄ rocking
30	233.2	28.92	BH ₄ rocking
31	241.6	29.96	xz-plane lattice mode ⁱ
32	241.8	29.98	xz-plane lattice mode ⁱ
33	256.4	31.79	xz-plane lattice mode ⁱ
34	258.5	32.06	BH ₄ libration
35	259.8	32.21	BH ₄ libration
36	260.8	32.34	BH ₄ rocking
37	262.0	32.49	BH ₄ rocking
38	262.5	32.54	Li–B stretching ⁱ
39	322.1	39.94	NH ₃ rocking ⁱ
40	341.7	42.37	NH ₃ rocking ⁱ
41	395.5	49.04	BH ₄ rocking
42	397.2	49.25	BH ₄ rocking
43	407.4	50.51	BH ₄ libration
44	407.6	50.53	BH ₄ libration
45	427.2	52.97	BH ₄ rocking
46	429.4	53.25	BH ₄ rocking
47	430.1	53.33	NH ₃ rocking
48	432.8	53.67	BH ₄ libration and NH ₃ rocking
49	435.9	54.05	NH ₃ rocking
50	440.3	54.59	BH ₄ libration and NH ₃ rocking
51	447.2	55.45	BH ₄ libration and NH ₃ rocking
52	448.8	55.65	BH ₄ libration and NH ₃ rocking
53	458.7	56.88	NH ₃ rocking ⁱ
54	460.0	57.04	BH ₄ rocking ⁱ
55	472.4	58.57	BH ₄ rocking ⁱ
56	474.4	58.82	Li–N bond stretch ⁱ
57	487.0	60.39	NH ₃ rocking
58	507.8	62.97	NH ₃ rocking ⁱ
59	512.0	63.48	NH ₃ rocking
60	516.0	63.98	NH ₃ rocking
61	1062.3	131.71	BH ₄ umbrella

Continued on next page

Table D.1 – continued from previous page

Number	Energy		Description
	cm ⁻¹	meV	
62	1062.7	131.77	BH ₄ umbrella
63	1062.8	131.78	BH ₄ wagging
64	1063.2	131.83	BH ₄ wagging
65	1063.4	131.85	BH ₄ umbrella
66	1064.1	131.94	BH ₄ umbrella
67	1067.8	132.39	BH ₄ wagging
68	1067.8	132.40	BH ₄ wagging
69	1159.1	143.71	BH ₄ and NH ₃ umbrella
70	1160.6	143.90	BH ₄ and NH ₃ umbrella
71	1166.1	144.59	BH ₄ umbrella
72	1166.3	144.61	BH ₄ umbrella
73	1176.2	145.84	BH ₄ and NH ₃ umbrella
74	1177.5	146.01	BH ₄ and NH ₃ umbrella
75	1195.5	148.24	NH ₃ umbrella
76	1202.3	149.07	NH ₃ umbrella
77	1227.5	152.20	BH ₄ bending
78	1227.6	152.21	BH ₄ bending
79	1230.8	152.61	BH ₄ bending
80	1230.9	152.62	BH ₄ bending
81	1263.5	156.66	BH ₄ bending
82	1264.7	156.81	BH ₄ bending
83	1270.2	157.50	BH ₄ bending
84	1270.9	157.58	BH ₄ bending
85	1573.2	195.07	NH ₃ wagging
86	1575.9	195.39	NH ₃ wagging
87	1581.1	196.05	NH ₃ wagging
88	1584.0	196.41	NH ₃ wagging
89	1615.3	200.29	NH ₃ clapping
90	1617.4	200.54	NH ₃ clapping
91	1622.1	201.13	NH ₃ clapping
92	1623.2	201.27	NH ₃ flapping
93	2297.8	284.91	BH ₄ stretch
94	2297.8	284.91	BH ₄ stretch
95	2300.6	285.25	BH ₄ stretch
96	2301.5	285.37	BH ₄ stretch
97	2333.3	289.31	BH ₄ stretch
98	2333.8	289.38	BH ₄ stretch
99	2338.4	289.95	BH ₄ stretch
100	2338.6	289.96	BH ₄ stretch
101	2376.8	294.70	BH ₄ stretch

Continued on next page

Table D.1 – continued from previous page

Number	Energy		Description
	cm ⁻¹	meV	
102	2377.1	294.74	BH ₄ stretch
103	2378.1	294.87	BH ₄ stretch
104	2378.4	294.91	BH ₄ stretch
105	2385.8	295.82	BH ₄ stretch
106	2396.0	297.09	BH ₄ stretch
107	2396.5	297.15	BH ₄ stretch
108	2398.0	297.33	BH ₄ stretch
109	3415.8	423.53	NH ₃ stretch
110	3416.2	423.58	NH ₃ stretch
111	3416.6	423.63	NH ₃ stretch
112	3417.0	423.69	NH ₃ stretch
113	3513.0	435.58	NH ₃ stretch
114	3513.0	435.59	NH ₃ stretch
115	3513.0	435.59	NH ₃ stretch
116	3513.0	435.59	NH ₃ stretch
117	3529.9	437.68	NH ₃ stretch
118	3530.1	437.70	NH ₃ stretch
119	3532.9	438.05	NH ₃ stretch
120	3535.0	438.31	NH ₃ stretch

Table D.2: The calculated phonon modes for Mg(NH₃)₆Cl₂.

Number	Energy		Description
	cm ⁻¹	meV	
1	-0.1	-0.01	anhormonic phonon mode
2	-0.1	-0.01	anhormonic phonon mode
3	0.0	0.00	anhormonic phonon mode
4	76.0	9.42	translational mode
5	88.7	11.00	translational mode
6	107.0	13.26	translational mode
7	117.1	14.52	translational mode
8	123.3	15.29	translational mode
9	134.7	16.70	translational mode
10	154.0	19.09	Mg–N bond bending
11	176.0	21.82	Mg–N bond bending
12	177.1	21.96	Mg–N bond bending
13	187.1	23.20	Mg–N bond bending
Continued on next page			

Table D.2 – continued from previous page

Number	Energy		Description
	cm ⁻¹	meV	
14	207.3	25.70	Mg–N bond bending
15	224.2	27.80	Mg–N bond bending
16	229.7	28.48	Mg–N bond bending
17	234.4	29.06	Mg–N bond bending
18	238.3	29.55	Mg–N bond bending
19	239.9	29.74	Mg–N bond bending
20	247.9	30.74	Mg–N bond bending
21	259.3	32.15	Mg–N bond bending
22	262.9	32.60	Mg–N bond bending
23	285.8	35.44	Mg–N bond bending
24	312.3	38.72	NH ₃ rotation
25	313.0	38.81	NH ₃ rotation
26	328.8	40.77	NH ₃ rotation
27	331.5	41.11	NH ₃ rotation
28	339.1	42.05	NH ₃ rotation
29	348.9	43.26	NH ₃ rotation
30	352.9	43.76	NH ₃ rotation
31	358.7	44.48	NH ₃ rotation
32	361.0	44.76	NH ₃ rotation
33	366.9	45.50	NH ₃ rotation
34	493.8	61.22	NH ₃ rocking
35	510.0	63.23	NH ₃ rocking
36	533.3	66.13	NH ₃ rocking
37	545.7	67.67	NH ₃ rocking
38	552.7	68.53	NH ₃ rocking
39	606.8	75.24	NH ₃ rocking
40	616.7	76.47	NH ₃ rocking
41	634.1	78.62	NH ₃ rocking
42	639.6	79.31	NH ₃ rocking
43	665.0	82.46	NH ₃ rocking
44	672.9	83.44	NH ₃ rocking
45	697.7	86.51	NH ₃ rocking
46	1121.9	139.10	NH ₃ umbrella
47	1143.1	141.73	NH ₃ umbrella
48	1146.9	142.21	NH ₃ umbrella
49	1158.7	143.67	NH ₃ umbrella
50	1166.7	144.66	NH ₃ umbrella
51	1196.9	148.41	NH ₃ umbrella
52	1552.7	192.52	NH ₃ bending
53	1561.3	193.59	NH ₃ bending

Continued on next page

Table D.2 – continued from previous page

Number	Energy		Description
	cm ⁻¹	meV	
54	1565.1	194.06	NH ₃ bending
55	1572.1	194.93	NH ₃ bending
56	1574.4	195.21	NH ₃ bending
57	1587.3	196.82	NH ₃ bending
58	1588.6	196.97	NH ₃ bending
59	1599.1	198.28	NH ₃ bending
60	1603.3	198.79	NH ₃ bending
61	1609.1	199.52	NH ₃ bending
62	1628.4	201.92	NH ₃ bending
63	1631.5	202.30	NH ₃ bending
64	3317.8	411.38	NH ₃ stretch
65	3318.5	411.46	NH ₃ stretch
66	3331.8	413.12	NH ₃ stretch
67	3337.1	413.78	NH ₃ stretch
68	3373.6	418.30	NH ₃ stretch
69	3379.8	419.08	NH ₃ stretch
70	3427.6	424.99	NH ₃ stretch
71	3428.0	425.04	NH ₃ stretch
72	3436.1	426.05	NH ₃ stretch
73	3446.1	427.29	NH ₃ stretch
74	3475.2	430.89	NH ₃ stretch
75	3485.0	432.11	NH ₃ stretch
76	3571.3	442.82	NH ₃ stretch
77	3573.2	443.05	NH ₃ stretch
78	3573.3	443.07	NH ₃ stretch
79	3574.3	443.18	NH ₃ stretch
80	3584.5	444.45	NH ₃ stretch
81	3585.6	444.58	NH ₃ stretch

Table D.3: The calculated phonon modes for Li(NH₃)₂BH₄.

Number	Energy		Description		
	cm ⁻¹	meV	BH ₄	NH ₃ , N(1)	NH ₃ , N(2)
1	-0.1	-0.01	—	anharmonic phonon mode	—
2	-0.1	-0.01	—	anharmonic phonon mode	—
3	0.0	-0.01	—	anharmonic phonon mode	—
4	17.7	2.19	—	NH ₃ translation	—

Continued on next page

Table D.3 – continued from previous page

Number	Energy		Description		
	cm ⁻¹	meV	BH ₄	NH ₃ , N(1)	NH ₃ , N(2)
5	28.3	3.51	— NH ₃ translation —		
6	40.4	5.01	— NH ₃ translation —		
7	44.4	5.50	— —		
8	54.5	6.76	— lattice shearing —		
9	58.2	7.22	— lattice shearing —		
10	61.6	7.64	— lattice shearing —		
11	63.0	7.82	— translation —		
12	70.7	8.76	— translation with N(2) rocking —		
13	72.8	9.03	— translation —		
14	79.6	9.87	— translation —		
15	83.6	10.36	— translation —		
16	93.0	11.53	— translation with N(2) rocking —		
17	94.4	11.71			translation
18	106.1	13.16	— translation —		
19	107.4	13.32	— translation —		
20	119.1	14.76	— translation —		
21	121.3	15.04	— translation —		
22	128.2	15.90	— translation —		
23	128.5	15.93			rotation
24	129.8	16.09	— translation with N(2) breathing —		
25	130.7	16.21			rotation
26	134.7	16.71	— translation —		
27	145.2	18.01	— translation with N(2) translation —		
28	158.8	19.69	— translation with N(2) translation —		
29	160.9	19.95	rotation		rotation
30	161.9	20.07	rotation with significant Li movement		
31	168.8	20.93			rotation
32	169.0	20.95			rotation
33	170.4	21.12			rotation
34	172.9	21.44	— translation, pronounced in N(2) —		
35	179.0	22.19			rotation
36	181.9	22.55	— translation, pronounced in N(2) —		
37	193.3	23.97	rotation		rocking
38	193.8	24.03	rotation		rotation
39	196.3	24.34	rocking		
40	197.4	24.48			rocking
41	198.3	24.59	rocking		
42	201.7	25.01	rotation		
43	211.7	26.25	rocking	rotation	rocking
44	212.2	26.31	rocking	rotation	rocking

Continued on next page

Table D.3 – continued from previous page

Number	Energy		Description		
	cm ⁻¹	meV	BH ₄	NH ₃ , N(1)	NH ₃ , N(2)
45	212.9	26.40		rotation	bending
46	215.1	26.67		— translation —	
47	225.4	27.95		— translation —	
48	226.1	28.03		rotation	rocking
49	229.9	28.50		— translation —	
50	232.8	28.87		— translation —	
51	244.0	30.25	Li–B stretch		
52	244.9	30.36	Li–B stretch		
53	244.9	30.37	Li–B bend	Li–N bend	
54	246.6	30.57	Li–B bend	Li–N bend	
55	277.3	34.38	Li–B bend	Li–N bend	
56	292.4	36.25		rotation	
57	292.9	36.31	Li–B bend	Li–N bend	
58	293.6	36.41		rotation	rocking
59	302.9	37.56		rotation	rocking
60	306.6	38.02		rotation	rocking
61	366.0	45.38	rocking		rocking
62	370.3	45.92	rocking		
63	370.5	45.94	rotation		
64	372.0	46.13		rocking	rocking
65	373.5	46.32	rocking		rocking
66	375.7	46.59	rotation		
67	390.0	48.36	rocking		rocking
68	391.1	48.49	rocking		
69	397.6	49.30			rocking
70	400.4	49.64	rocking		rocking
71	417.6	51.78	rotation		
72	419.9	52.06	rotation		
73	471.7	58.48		Li–N stretch	
74	474.6	58.84		Li–N stretch	
75	477.0	59.14		Li–N stretch	
76	482.6	59.83		Li–N stretch	
77	497.0	61.63		rocking	
78	508.3	63.02		rocking	rocking
79	517.7	64.19		rocking	
80	519.7	64.44		rocking	rocking
81	567.6	70.38		rocking	rocking
82	568.1	70.45		rocking	rocking
83	568.5	70.49		rocking	rocking
84	569.6	70.63		rocking	rocking

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Table D.3 – continued from previous page

Number	Energy		Description	NH ₃ , N(1)	NH ₃ , N(2)
	cm ⁻¹	meV			
85	1057.3	131.09	umbrella		
86	1057.5	131.12	umbrella		
87	1061.1	131.57	umbrella		
88	1061.1	131.57	umbrella		
89	1062.7	131.76	umbrella		
90	1064.0	131.93	umbrella		
91	1066.1	132.19	umbrella		
92	1066.3	132.22	umbrella		
93	1095.9	135.89			umbrella
94	1105.7	137.10			umbrella
95	1106.1	137.15			umbrella
96	1107.0	137.25			umbrella
97	1156.0	143.33	umbrella		
98	1156.7	143.42	umbrella		
99	1156.8	143.43	umbrella		
100	1156.9	143.45	umbrella		
101	1192.8	147.90		umbrella	
102	1193.4	147.97		umbrella	
103	1198.8	148.65		umbrella	
104	1209.3	149.95		umbrella	
105	1229.4	152.43	clapping		
106	1229.4	152.44	clapping		
107	1233.1	152.89	clapping		
108	1233.1	152.90	clapping		
109	1264.6	156.80	clapping		
110	1264.7	156.81	clapping		
111	1268.9	157.33	clapping		
112	1269.1	157.36	clapping		
113	1566.4	194.22			clapping
114	1567.5	194.35			clapping
115	1586.1	196.67			clapping
116	1587.7	196.86			clapping
117	1603.4	198.81		clapping	clapping
118	1605.3	199.05		clapping	clapping
119	1605.6	199.08		clapping	
120	1607.8	199.36		clapping	clapping
121	1611.4	199.80		clapping	clapping
122	1612.4	199.93		clapping	clapping
123	1612.6	199.95		clapping	clapping
124	1615.2	200.28		clapping	clapping

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Table D.3 – continued from previous page

Number	Energy		Description		
	cm ⁻¹	meV	BH ₄	NH ₃ , N(1)	NH ₃ , N(2)
125	1651.3	204.75		clapping	clapping
126	1654.2	205.11		clapping	clapping
127	1656.0	205.33		clapping	clapping
128	1659.0	205.70		clapping	clapping
129	2284.8	283.30	stretching		
130	2285.2	283.34	stretching		
131	2289.5	283.88	stretching		
132	2289.5	283.89	stretching		
133	2340.1	290.16	stretching		
134	2340.4	290.19	stretching		
135	2343.9	290.62	stretching		
136	2346.6	290.96	stretching		
137	2365.0	293.24	stretching		
138	2365.0	293.24	stretching		
139	2365.4	293.29	stretching		
140	2365.4	293.29	stretching		
141	2379.0	294.98	stretching		
142	2381.8	295.33	stretching		
143	2382.1	295.36	stretching		
144	2384.2	295.62	stretching		
145	3356.1	416.13		stretching	
146	3356.3	416.16		stretching	
147	3356.7	416.21		stretching	
148	3358.8	416.47		stretching	
149	3411.2	422.97			stretching
150	3411.3	422.98			stretching
151	3414.9	423.42			stretching
152	3415.2	423.46			stretching
153	3431.9	425.53			stretching
154	3431.9	425.53		stretching	
155	3432.0	425.54		stretching	
156	3432.0	425.54		stretching	
157	3515.1	435.85			stretching
158	3515.2	435.86			stretching
159	3515.3	435.87			stretching
160	3515.4	435.89			stretching
161	3534.5	438.26		stretching	
162	3534.7	438.27		stretching	
163	3534.9	438.31		stretching	
164	3535.1	438.32		stretching	

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Table D.3 – continued from previous page

Number	Energy		Description		
	cm ⁻¹	meV	BH ₄	NH ₃ , N(1)	NH ₃ , N(2)
165	3549.9	440.16			stretching
166	3549.9	440.16			stretching
167	3551.3	440.33			stretching
168	3551.3	440.34			stretching

Appendix E

Additional Data

Table E.1: The atomic coordinates obtained from the Rietveld refinement of the ordered model of $\text{Li}(\text{NH}_3)\text{BH}_4$ against X-ray powder diffraction data. Space Group = $Pnma$, $R_{wp} = 5.7\%$, $R_{exp} = 2.6\%$, $\chi^2 = 4.81$.

atom	site	x	y	z	$B_{iso} / \text{\AA}^2$
N	N1	0.6081(4)	0.75	0.6514(1)	5.9(1)
B	B1	0.9059(4)	0.75	0.3993(1)	4.6(1)
Li	Li1	0.8903(8)	0.75	0.5752(3)	4.7(2)
H	H1	0.754(2)	0.75	0.451(1)	5.5(3)
H	H2	0.073(2)	0.75	0.442(1)	5.5(3)
H	H3	0.898(1)	0.536(2)	0.352(1)	5.5(3)
H	H4	0.519(2)	0.584(1)	0.632(2)	5.5(3)
H	H5	0.585(3)	0.75	0.717(1)	5.5(3)

Table E.2: The atomic coordinates obtained from the Rietveld refinement of the disordered model of $\text{Mg}(\text{NH}_3)_6\text{Cl}_2$ against X-ray powder diffraction data. Space group = $Fm\bar{3}m$, $R_{wp} = 12.7\%$, $R_{exp} = 13.1\%$, $\chi^2 = 0.939$.

atom	site	x	y	z	occ.	B_{iso}
Mg	Mg1	0	0	0	1	2.24(4)
Cl	Cl1	0.25	0.25	0.25	1	3.7(3)
N	N1	0	0	0.2140(2)	1	4.2(6)
H	H1	-0.074(1)	0	0.2426(9)	0.125	4.2(6)
H	H2	-0.072(1)	-0.0192(3)	0.2426(9)	0.125	4.2(6)
H	H3	-0.0641(8)	-0.0370(5)	0.2426(9)	0.125	4.2(6)
H	H4	-0.0524(7)	-0.0524(7)	0.2426(9)	0.125	4.2(6)

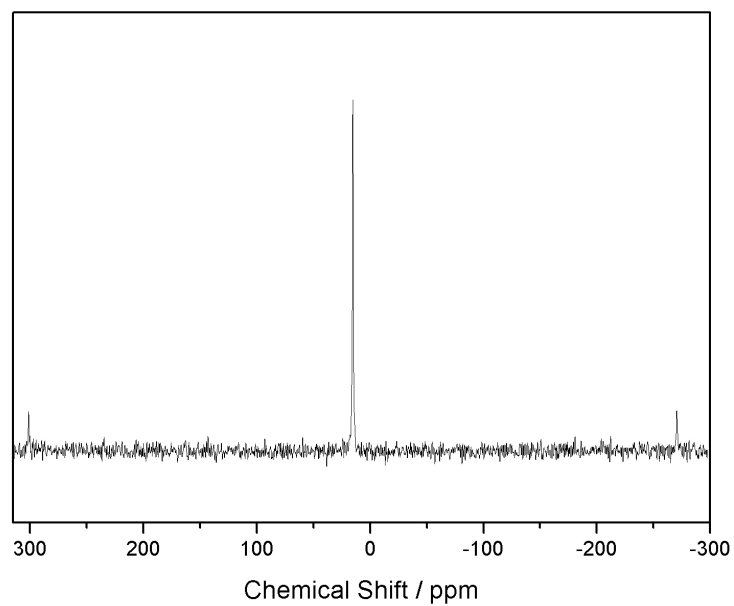


Figure E.1: The ^{25}Mg NMR spectrum of $\text{Mg}(\text{NH}_3)_6\text{Br}_2$, showing a sharp line at 15.245 ppm (referenced to a 1 M solution of $\text{Mg}(\text{H}_2\text{O})_6\text{Cl}_2(\text{aq})$).

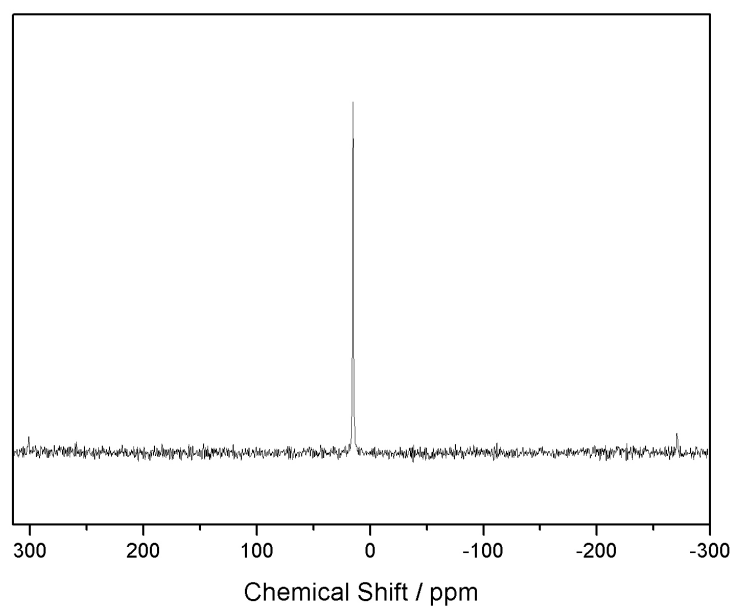


Figure E.2: The ^{25}Mg NMR spectrum of $\text{Mg}(\text{NH}_3)_6\text{I}_2$, showing a sharp line at 15.095 ppm (referenced to a 1 M solution of $\text{Mg}(\text{H}_2\text{O})_6\text{Cl}_2(\text{aq})$).

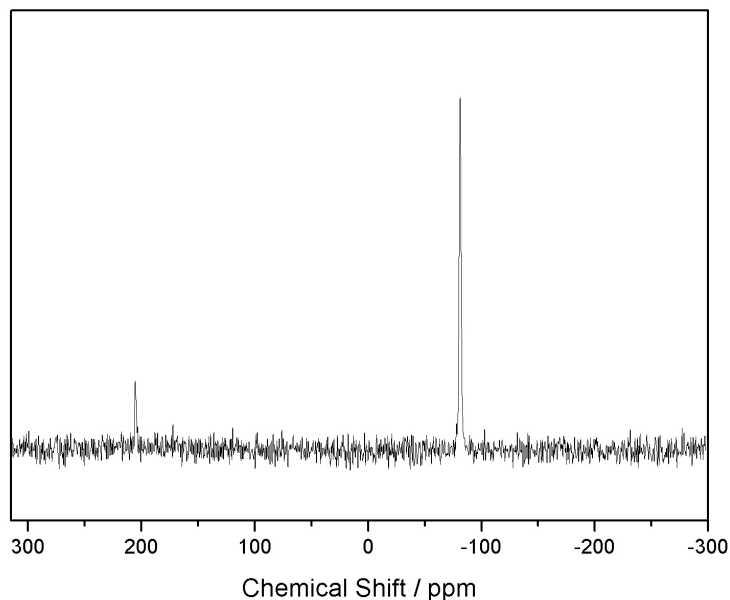


Figure E.3: The ^{25}Mg NMR spectrum of MgI_2 , showing a sharp line at -81.109 ppm (referenced to a 1 M solution of $\text{Mg}(\text{H}_2\text{O})_6\text{Cl}_{2(\text{aq})}$).

Table E.3: The atomic coordinates obtained from Rietveld refinement of the disordered model of $\text{Mg}(\text{NH}_3)_6\text{Br}_2$ against X-ray diffraction data. Space group = $Fm\bar{3}m$, $R_{wp} = 15.2\%$, $R_{exp} = 16.6\%$, $\chi^2 = 0.841$.

atom	site	x	y	z	occ.	B_{iso}
Mg	Mg1	0	0	0	1	2.50(7)
Br	Br1	0.25	0.25	0.25	1	3.54(3)
N	N1	0	0	0.2082(3)	1	3.2(1)
H	H1	-0.078(1)	0	0.245(2)	0.125	3.2(1)
H	H2	-0.076(1)	-0.0202(4)	0.245(2)	0.125	3.2(1)
H	H3	-0.068(1)	-0.0392(7)	0.245(2)	0.125	3.2(1)
H	H4	-0.055(1)	-0.055(1)	0.245(2)	0.125	3.2(1)

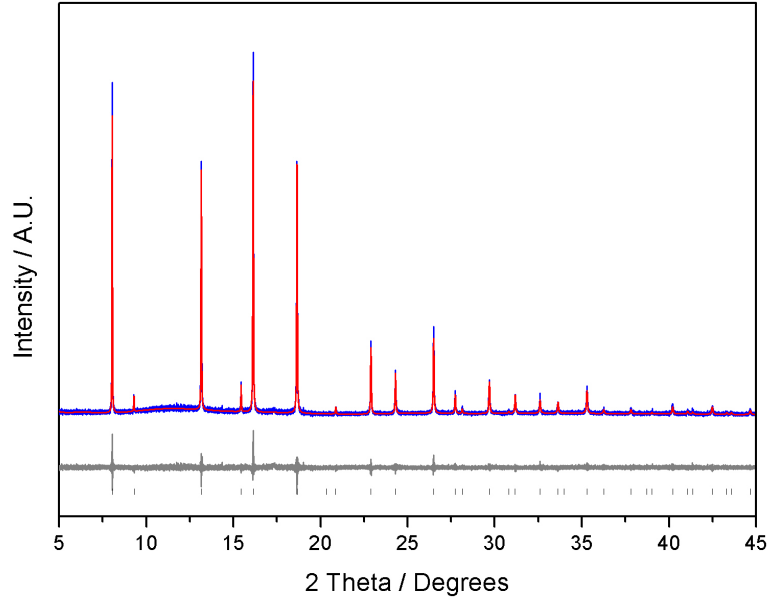


Figure E.4: Final fit to the data for Rietveld refinement of the $\text{Mg}(\text{NH}_3)_6\text{Cl}_2$ model to X-ray powder diffraction data collected at the Diamond Light Source with a wavelength $\lambda = 0.82000 \text{ \AA}$. Space group = $Fm\bar{3}m$, $R_{wp} = 12.7\%$, $R_{exp} = 13.1\%$, $\chi^2 = 0.939$. Experimental data are shown in blue, calculated in red with the difference in grey, tick marks show the expected positions of Bragg reflections.

Table E.4: The atomic coordinates from the Rietveld refinement of the disordered model of $\text{Mg}(\text{NH}_3)_6\text{I}_2$ against X-ray diffraction data. Space group = $Fm\bar{3}m$, $R_{wp} = 14.9\%$, $R_{exp} = 12.7\%$, $\chi^2 = 1.37$.

atom	site	x	y	z	occ.	B_{iso}
Mg	Mg1	0	0	0	1	2.37(9)
I	I1	0.25	0.25	0.25	1	3.53(2)
N	N1	0	0	0.1998(3)	1	2.5(1)
H	H1	-0.075(2)	0	0.235(2)	0.125	2.5(1)
H	H2	-0.072(2)	-0.0193(4)	0.235(2)	0.125	2.5(1)
H	H3	-0.065(1)	-0.0374(8)	0.235(2)	0.125	2.5(1)
H	H4	-0.053(1)	-0.053(1)	0.235(2)	0.125	2.5(1)

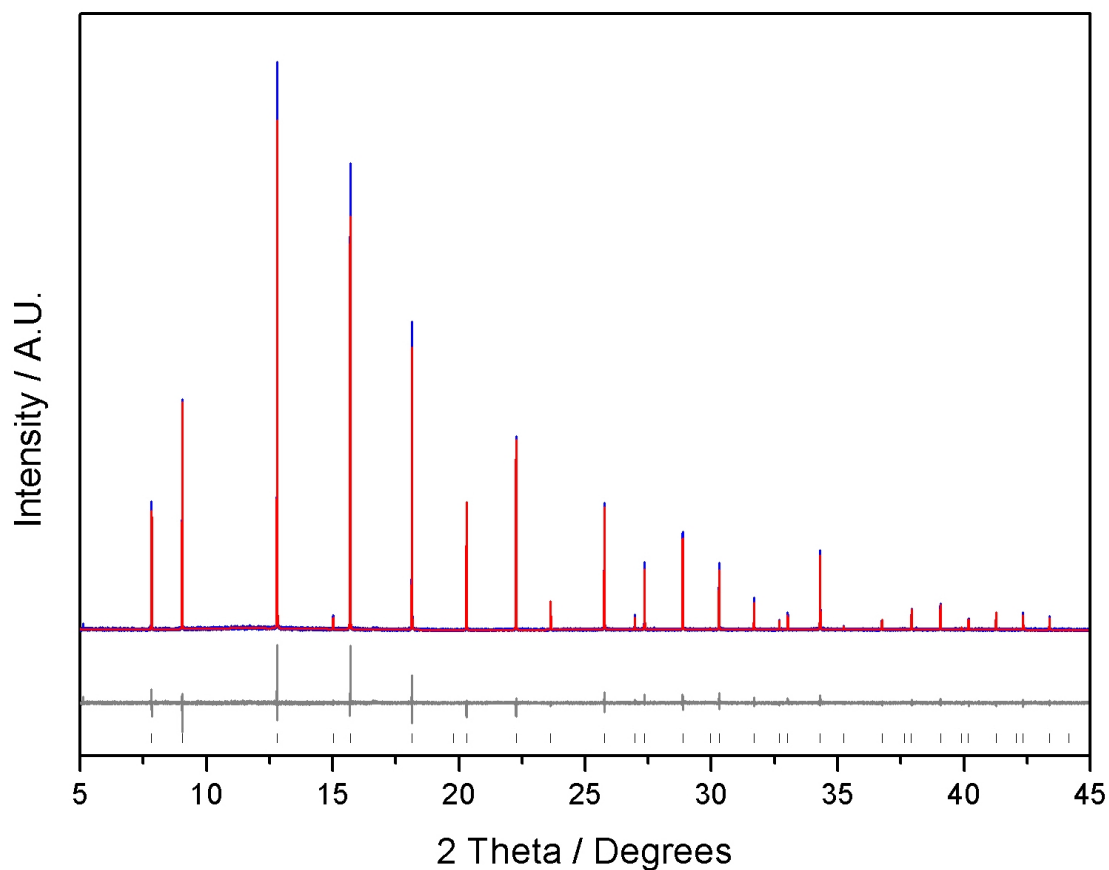


Figure E.5: The final fit to the data for Rietveld refinement of the $\text{Mg}(\text{NH}_3)_6\text{Br}_2$ model to X-ray powder diffraction data collected at the Diamond Light Source using a wavelength $\lambda = 0.82000 \text{ \AA}$. Space group = $Fm\bar{3}m$, $R_{wp} = 15.2\%$, $R_{exp} = 16.6\%$, $\chi^2 = 0.841$. Experimental data are shown in blue, calculated in red with the difference in grey, tick marks show the expected positions of Bragg reflections.

Table E.5: The atomic coordinates obtained from Rietveld refinement of the disordered model of $\text{Li}(\text{NH}_3)_4\text{BH}_4$ against neutron diffraction data. Space group = $Pnma$, $R_{wp} = 3.32$, $R_{exp} = 1.88$ and $\chi^2 = 3.13$.

atom	site	x	y	z	occ.
Li	Li1	0.989(3)	0.25	0.684(4)	1.0
B	B1	0.292(1)	0.25	0.382(1)	1.0
D	H24a	0.293(3)	0.25	0.505(3)	0.26
D	H25a	0.196(3)	0.25	0.341(3)	0.25(2)
D	H26a	0.342(3)	0.39(4)	0.340(3)	0.25(2)
D	H24b	0.293(3)	0.25	0.258(3)	0.26
D	H25b	0.390(3)	0.25	0.423(3)	0.75(2)
D	H26b	0.245(3)	0.10(4)	0.423(3)	0.75(2)
N	N1	0.899(4)	0.25 (7)	0.521(5)	0.75(2)
D	H1a	0.945(6)	0.25	0.441(7)	1.0
D	H2b	0.851(6)	0.140(9)	0.515(7)	0.40(2)
D	H1a	0.819(6)	0.25	0.540(7)	0.40(2)
D	H2b	0.914(6)	0.140(9)	0.466(7)	0.60(2)
N	N2	0.157(3)	0.25	0.713(4)	0.60(2)
D	H4a	0.176(5)	0.25	0.808(6)	1.0
D	H6a	0.192(5)	0.360(8)	0.674(6)	0.40(2)
D	H4b	0.198(5)	0.25	0.629(6)	0.40(2)
D	H6b	0.182(5)	0.140(8)	0.763(6)	0.60(2)
N	N3	0.931(2)	0.003(4)	0.823(3)	0.60(2)
D	H10a	0.975(4)	0.468(7)	0.906(5)	1.0
D	H11a	0.936(4)	0.592(7)	0.785(5)	0.40(2)
D	H12a	0.854(4)	0.447(7)	0.850(5)	0.40(2)
D	H10b	0.990(4)	0.558(7)	0.844(5)	0.40(2)
D	H11b	0.868(4)	0.537(7)	0.788(5)	0.60(2)
D	H12b	0.907(4)	0.413(7)	0.909(5)	0.60(2)

Table E.6: The calculated atomic coordinates obtained from the ‘fine’ geometry optimisation of $\text{Mg}(\text{NH}_3)_6\text{Cl}_2$, space group Cm , $a = 10.1226 \text{ \AA}$, $c = 7.1578 \text{ \AA}$, $\alpha = \gamma = 90^\circ$, $\beta = 135^\circ$.

atom	site	x	y	z
H	H1	-0.67440(2)	0.41801(2)	-1.85474(2)
H	H2	0.31397(2)	0.91763(2)	-0.51246(2)
H	H3	0.32942(2)	0.25908(2)	-1.17330(2)
H	H4	-0.46624(2)	0.23599(2)	-1.07592(2)
H	H5	0.52264(2)	0.24239(2)	-0.85312(2)
H	H6	-0.18740(2)	0.41769(2)	-1.86944(2)
H	H7	-0.18035(2)	0.08219(2)	-1.49890(2)
N	N8	0.47061(4)	0.28187(4)	-1.02730(4)
Cl	Cl1	-0.00844(6)	0.25236(6)	-0.51138(6)
H	H10	0.16106(2)	0.5	-0.13814(2)
H	H11	0.69522(2)	0.5	-0.46686(2)
H	H12	0.69027(2)	0.5	-0.15352(2)
H	H13	0.15863(2)	0.5	-1.53636(2)
N	N14	-0.69993(4)	0.5	-1.96288(4)
N	N15	-0.26785(4)	0.5	-0.56858(4)
N	N16	-0.26985(4)	0.5	-1.97580(4)
N	N17	-0.70360(4)	0.5	-1.43942(4)
Mg	Mg1	0.49643(4)	0.5	-0.00532(4)

Table E.7: The calculated atomic coordinates obtained from the ‘fine’ geometry optimisation of $\text{Mg}(\text{NH}_3)_6\text{Br}_2$, space group Cm , $a = 10.4069 \text{ \AA}$, $c = 7.3588 \text{ \AA}$, $\alpha = \gamma = 90^\circ$, $\beta = 135^\circ$.

atom	site	x	y	z
H	H1	-0.67935(2)	0.42030(2)	-1.87102(2)
H	H2	0.30438(2)	0.92014(2)	-0.51562(2)
H	H3	0.34119(2)	0.26237(2)	-1.15916(2)
H	H4	-0.46426(2)	0.24565(2)	-1.07702(2)
H	H5	0.53412(2)	0.24627(2)	-0.85098(2)
H	H6	-0.19578(2)	0.42015(2)	-1.87762(2)
H	H7	-0.18080(2)	0.07970(2)	-1.48902(2)
N	N8	0.47766(2)	0.28714(2)	-1.02192(2)
Br	Br1	-0.00541(6)	0.25165(6)	-0.50558(6)
H	H10	0.16570(2)	0.5	-0.14770(5)
H	H11	0.68206(2)	0.5	-0.48368(5)
H	H12	0.68088(2)	0.5	-0.15438(5)
H	H13	0.16541(2)	0.5	-1.51960(5)
N	N14	-0.70037(4)	0.5	-1.97350(5)
N	N15	-0.27683(4)	0.5	-0.57610(5)
N	N16	-0.27714(4)	0.5	-1.97914(5)
N	N17	-0.70105(4)	0.5	-1.42766(5)
Mg	Mg1	0.49787(4)	0.5	-0.00236(5)

Table E.8: The calculated atomic coordinates obtained from the ‘fine’ geometry optimisation of $\text{Mg}(\text{NH}_3)_6\text{I}_2$, space group Cm , $a = 10.9149 \text{ \AA}$, $c = 7.7180 \text{ \AA}$, $\alpha = \gamma = 90^\circ$, $\beta = 135^\circ$.

atom	site	x	y	z
H	H1	-0.68987(2)	0.42439(2)	-1.90310(3)
H	H2	0.28284(2)	0.92399(2)	-0.53386(3)
H	H3	0.41221(2)	0.25481(2)	-1.16852(3)
H	H4	-0.37948(2)	0.26358(2)	-0.90660(3)
H	H5	0.47098(2)	0.26293(2)	-0.90274(3)
H	H6	-0.21770(2)	0.42418(2)	-1.90548(3)
H	H7	-0.18928(2)	0.07567(2)	-1.48028(3)
N	N8	0.49817(4)	0.29567(4)	-0.99836(5)
I	I1	-0.01451(7)	0.24891(7)	-0.51930(7)
H	H10	0.16960(2)	0.5	-0.16700(3)
H	H11	0.65929(2)	0.5	-0.51656(3)
H	H12	0.65827(2)	0.5	-0.16974(3)
H	H13	0.17151(2)	0.5	-1.49498(3)
N	N14	-0.70429(4)	0.5	-1.99706(5)
N	N15	-0.29577(4)	0.5	-0.59730(5)
N	N16	-0.29678(4)	0.5	-1.99910(5)
N	N17	-0.70277(4)	0.5	-1.41418(5)
Mg	Mg1	0.49423(4)	0.5	-0.00760(5)

Table E.9: The calculated atomic coordinates obtained from the ‘fine’ geometry optimisation of $\text{Mg}(\text{NH}_3)_2\text{Cl}_2$, space group $Amm2$, $a = 3.7550 \text{ \AA}$, $b = 8.2067 \text{ \AA}$, $c = 8.1810 \text{ \AA}$.

atom	site	x	y	z
H	H1	0.78403(7)	0.69122(3)	-0.06225(3)
H	H2	1	0.68082(3)	-0.88670(3)
N	N3	1	0.2627(1)	-0.99936(5)
Mg	Mg1	0	0	-0.99316(5)
Cl	Cl1	0.5	0	-0.2076(8)
Cl	Cl2	0.5	1	-0.7781(8)

Table E.10: The calculated atomic coordinates obtained from the ‘fine’ geometry optimisation of $\text{Mg}(\text{NH}_3)_2\text{Br}_2$, space group $P1$, $a = 5.9440 \text{ \AA}$, $b = 11.8760 \text{ \AA}$, $c = 3.9830 \text{ \AA}$.

atom	site	x	y	z
H	H1	0.89849(4)	0.40160(2)	0.13555(6)
H	H2	0.70736(4)	0.30143(2)	0.11869(6)
H	H3	0.81927(4)	0.35040(2)	0.77038(6)
H	H4	0.60179(4)	0.89919(2)	0.14217(6)
H	H5	0.79438(4)	0.80008(2)	0.11726(6)
H	H6	0.68207(4)	0.85219(2)	0.77303(6)
H	H7	0.39755(4)	0.10021(2)	0.14461(6)
H	H8	0.20648(4)	0.20004(2)	0.11780(6)
H	H9	0.32047(4)	0.14778(2)	0.77479(6)
H	H10	0.09957(4)	0.59891(2)	0.85136(6)
H	H11	0.29050(4)	0.69912(2)	0.86751(6)
H	H12	0.18283(4)	0.64832(2)	0.21675(6)
N	N13	0.25870(7)	0.12570(3)	0.00754(9)
N	N14	0.74184(7)	0.87434(3)	0.00685(9)
N	N15	0.24040(7)	0.62520(3)	0.98253(9)
N	N16	0.75908(7)	0.37474(3)	0.00202(9)
Mg	Mg1	0.99989(7)	0.00023(3)	0.99727(9)
Mg	Mg2	0.49984(7)	0.50004(3)	0.99187(9)
Br	Br1	0.27821(8)	0.38582(5)	0.4876(2)
Br	Br2	0.72109(8)	0.61433(5)	0.4929(2)
Br	Br3	0.22188(8)	0.88587(5)	0.5030(2)
Br	Br4	0.77831(8)	0.11446(5)	0.4986(2)

Table E.11: The calculated atomic coordinates obtained from the ‘fine’ geometry optimisation of $\text{Mg}(\text{NH}_3)_2\text{I}_2$, space group $P1$, $a = 6.2850 \text{ \AA}$, $b = 12.5590 \text{ \AA}$, $c = 4.3020 \text{ \AA}$.

atom	site	x	y	z
H	H1	0.62604(4)	0.90719(2)	0.86427(6)
H	H2	0.80503(4)	0.81211(2)	0.89806(6)
H	H3	0.69517(4)	0.86415(2)	0.21199(6)
H	H4	0.87675(4)	0.40673(2)	0.14293(6)
H	H5	0.69787(4)	0.31184(2)	0.10337(6)
H	H6	0.37599(4)	0.09502(2)	0.14215(6)
H	H7	0.19691(4)	0.18986(2)	0.10412(6)
H	H8	0.30836(4)	0.13689(2)	0.79266(6)
H	H9	0.80976(4)	0.36522(2)	0.79283(6)
H	H10	0.12707(4)	0.59456(2)	0.86551(6)
H	H11	0.30630(4)	0.68965(2)	0.89654(6)
H	H12	0.19723(4)	0.63836(2)	0.21206(6)
N	N13	0.24716(6)	0.11859(3)	0.0088(1)
N	N14	0.75539(6)	0.88312(3)	0.9958(1)
N	N15	0.25679(6)	0.61888(3)	0.9958(1)
N	N16	0.74817(6)	0.38324(3)	0.0089(1)
Mg	Mg1	0.00135(6)	0.00079(3)	0.0025(1)
Mg	Mg2	0.50249(6)	0.50109(3)	0.0028(1)
I	I1	0.2721(2)	0.3812(3)	0.4972(4)
I	I2	0.7328(2)	0.6209(3)	0.5080(4)
I	I3	0.2317(2)	0.8810(3)	0.5078(4)
I	I4	0.7713(2)	0.1208(3)	0.4970(4)