Solid State Nuclear Magnetic Resonance on Quadrupolar Nuclei in Disordered Catalysis Based Materials

by

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Thesis submitted to the University of Warwick for the degree of Doctor of Philosophy

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September 2017
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<th>Abbreviation</th>
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<td>wt%</td>
<td>percentage by weight</td>
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<td>OAc</td>
<td>acetate; ([\text{O}_2\text{C}_2\text{H}_3]^-)</td>
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<td>Pressure-Composition-Temperature</td>
</tr>
<tr>
<td>PDF</td>
<td>Pair Distribution Function</td>
</tr>
<tr>
<td>PGAA</td>
<td>Prompt Gamma neutron Activation Analysis</td>
</tr>
<tr>
<td>ppm</td>
<td>Parts Per Million</td>
</tr>
<tr>
<td>PVP</td>
<td>polyvinylpyrrolidone</td>
</tr>
<tr>
<td>RF</td>
<td>Radio Frequency</td>
</tr>
<tr>
<td>SATRAS</td>
<td>SAatellite TRAnsition Spectroscopy</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>Acronym</td>
<td>Abbreviation and Description</td>
</tr>
<tr>
<td>---------</td>
<td>-----------------------------</td>
</tr>
<tr>
<td>SNR</td>
<td>Signal to Noise Ratio</td>
</tr>
<tr>
<td>ST</td>
<td>Satellite Transition</td>
</tr>
<tr>
<td>SQUID</td>
<td>Superconducting QUantum Interference Device</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric Analysis</td>
</tr>
<tr>
<td>THF</td>
<td>tetrahydrofuran; (CH\textsubscript{2})\textsubscript{4}O</td>
</tr>
<tr>
<td>QIS</td>
<td>Quadrupole Interaction Shift</td>
</tr>
<tr>
<td>VOCS</td>
<td>Variable Offset Cumulative Spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-Ray Diffraction</td>
</tr>
<tr>
<td>YAG</td>
<td>Yttrium Aluminium Garnet</td>
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Acknowledgements

I would like to firstly thank my supervisor Dr John Hanna, without whom the work in this thesis would not have been possible. I am eternally grateful to Dr Gregory Rees for his guidance, assistance and extensive proof reading throughout my research. His patience for my daily NMR inquisitions will not be forgotten. The assistance of my industrial supervisor from Johnson Matthey, Dr Nigel Powell, is also thoroughly appreciated. His knowledge of chemistry and keen research instincts made the work on palladium possible.

My thanks go to all the members of the University of Warwick Solid State NMR Group for their support and good humour over the last four years. In particular, Dr Andrew Howes deserves an individual mention for his technical expertise and for our spontaneous NMR discussions. Additionally, the Hanna group student cohort must be acknowledged, mostly for sharing the burden of my lamentations during stressful periods.

I am grateful for the help supplied by all my collaborators. My thanks go to Dr Laura Ashfield, also from Johnson Matthey, for her guidance in the synthesis of palladium nanoparticles. I am indebted to Dr Dean Keeble (Diamond Light Source) for his PDF XRD analysis. I thank Drs Dave Walker and Martin Lees (University of Warwick) for their assistance with the XRD and magnetic susceptibility measurements, respectively. I must thank Dr Ieuan Ellis, and his supervisor Dr Edman Tsang (University of Oxford), for their extensive collaboration in this thesis. Ieuan’s doped palladium nanoparticle synthesis and the accompanying knowledge made a significant part of this thesis possible. My sincere gratitude is given to Drs Kirill Okhotnikov and Thibault Charpentier (CEA Saclay) for their in-depth calculations on mullite. Their expertise was integral to the analysis of the mullite research. Alvin Panis (University of Warwick) is thanked for his assistance in the NMR study of the boron doped mullites. I am also grateful for the high-quality ceramic samples provided by Drs Hanna Lührs and Kristin Hoffman (Universität Bremen), along with their assistance in the research performed with them.

It would be remiss of me not to thank my parents, siblings and close friends for their support throughout my studies. Especially my mother and inspiration, Dr Nicola Hooper, who earned her doctorate while pregnant and raising my brother, sister and me.
Finally, I recognise that this research would not have been possible without financial backing from Johnson Matthey, the Engineering and Physical Science Research Council (EPRSC) and the University of Warwick.

Thomas J. N. Hooper
Declarations

I hereby declare that this thesis entitled Solid State Nuclear Magnetic Resonance on Quadrupolar Nuclei in Disordered Catalysis Based Materials is an original work and has not been submitted for a degree, or any other qualification, at any other university.

Results from other authors are referenced in the usual manner throughout the text. All collaborative results are indicated in the text along with the nature and extent of the collaborator’s contribution. A summary of the contributions is given here:

– Dr Gregory Rees (University of Warwick) undertook the GIPAW-DFT calculations and Dr Dean Keeble (Diamond Light Source) performed the PDF XRD analysis in Chapter 4.4.
– Dr Ieuan Ellis (University of Oxford) synthesized the boron and lithium doped palladium nanoparticles examined in Chapter 4.7
– Drs Kirill Okhotnikov and Thibault Charpentier (CEA Saclay) undertook the supercell structure generation and GIPAW-DFT calculations in Chapter 5.
– Dr Hanna Lührs (Universität Bremen) synthesized the mullite powders in Chapter 5.
– Dr Kristin Hoffman (Universität Bremen) synthesized the aluminoborate powders in Chapter 6.

The rest of the material contained within this thesis is original research performed by the author.
Abstract

The behaviour of a catalyst is intrinsically linked to its structure and, therefore, accurate structural refinements are desired to tune their overall function. Higher functional demands on catalysts systems, require more complex disordered materials which are inherently difficult to characterise with conventional analytical techniques. Solid state NMR is an excellent probe of local order and, hence, is utilised in this thesis for the structural determination of several catalytic related materials.

The first direct $^{105}$Pd solid state NMR measurements of diamagnetic (K$_2$PdCl$_6$, (NH$_4$)$_2$PdCl$_6$ and K$_2$PdBr$_6$) complexes is reported, thereby introducing an effective $^{105}$Pd chemical shift ranges with respect to the newly proposed $^{105}$Pd chemical shift reference (0.33 M H$_2$PdCl$_6$). The enormous $^{105}$Pd quadrupolar moment, makes the interaction very sensitive to small structural distortions as demonstrated by the measurable quadrupolar parameters for the three complexes, despite the high symmetry octahedral Pd coordination. The detected deviation from a cubic symmetry, was corroborated by XRD PDF analysis. The $^{105}$Pd quadrupolar parameters are shown to be more sensitive to minute disorder than conventional XRD and other quadrupolar nuclei NMR. Ambient temperature $^{105}$Pd NMR observations of Pd metal determined the Knight shift as $K = -3.205 \pm 0.006$ %, where variations in the $^{105}$Pd Knight shift allowed for detection of defects in the cubic metal structure and for differentiation of Pd nanoparticle sizes. The developed $^{105}$Pd NMR methodology was then applied in a multi-technique structural investigation of doped Pd catalysts, that confirmed the interstitial location of the dopants.

The use of the newly developed structure-generation software, supercell, in combination with GIPAW-DFT calculations and solid state NMR, is shown to be a thorough tool for structural determination of disordered materials. The methodology is applied to two phases of the aluminosilicate mullite (3:2 mullite and 2:1 mullite), and provides complete assignment of the $^{17}$O, $^{27}$Al and $^{29}$Si NMR spectra. The distribution of AlO$_4$/SiO$_4$ sites in the mullite structure is shown to be random, proving the presence of SiO$_4$ moieties in the tri-tetrahedral (T$_3$O) environments. The observation of said moieties directly contradicts Loewenstein’s avoidance principle. Additionally, a quasi-tetrahedral site with an additional long bond ((Al/Si)O$_{4+1}$) is discovered and a vacancy adjacent three-coordinated Al site (AlO$_3$□) is proposed. The findings from this investigation are then applied to the $^{27}$Al MQMAS study of boron doped mullites, providing additional evidence for the AlO$_3$□ motif.

A thorough $^{11}$B and $^{27}$Al solid state NMR investigation was undertaken on three series of aluminium borate phases (A9B$_2$, A2B and metastable Al$_{6-x}$B$_x$O$_9$ (where 1 ≤ x ≤ 3)) with varying Al/B ratios. A solid solution of AlO$_4$ and BO$_4$ tetrahedra was discovered in all three phases (to varying extents), justifying the conflicting compositional/structural reports present in the literature. Differences in the crystallinity of commercially available, sol-gel synthesized, and solid state synthesised A9B$_2$ samples were documented. The solid state NMR study of the disordered phases, A2B and metastable Al$_{6-x}$B$_x$O$_9$, utilised multiple fields and MQMAS measurements to constrain the simulation of the 1D spectra, which allowed for complete assignment of the structure and corrected previous erroneous reports. An AlO$_{4+1}$ site, analogous to the discovered mullite environment, is found in both disordered phases.
1

Solid State NMR Theory

1.1. Spin Angular Momentum

Fundamental particles possess the intrinsic property of spin angular momentum ($S$). Spin angular momentum is quantised; particles with spin $S$ have $2S + 1$ degenerate spin sublevels. Therefore, protons and neutrons with spin $S = \frac{1}{2}$ have 2 spin sublevels: spin “up” $m = +\frac{1}{2}$ and spin “down” $m = -\frac{1}{2}$. The nuclear spin quantum number ($I$) is the sum of the spins of its constituent nucleons. Nucleons can be aligned in a parallel ($\pm \frac{1}{2}, \pm \frac{1}{2}$) or antiparallel ($\pm \frac{1}{2}, \mp \frac{1}{2}$) configuration and the nuclear spin of an isotope is decided by the ground state configuration of its nucleons’ spins. Therefore, the nuclear spin number, $I$, is either equal to integer or half-integer values ($0, \frac{1}{2}, 1, \ldots$). The spin angular momentum of a nucleus, $I$, produces a magnetic moment, $\mu$, defined by

$$\hat{\mu} = \gamma \hbar \hat{I}$$  \hspace{1cm} (1.1)

where $\gamma$ is the gyromagnetic ratio, a characteristic parameter of each nucleus.$^1$

1.2. The Zeeman Interaction

The degeneracy of a nuclear state is broken in an applied magnetic field producing $2I + 1$ energy levels, due to the different magnetic moment of each spin sublevel $m$ (as shown in Figure 1.1). If the applied static magnetic field is defined in the $z$-axis giving $B = (0, 0, B_0)$ then the Zeeman Hamiltonian is given by

$$\hat{H}_Z = -\hat{\mu} \cdot \hat{B} = -\hat{\mu}_z B_0 = -\gamma \hbar \hat{I}_z B_0.$$  \hspace{1cm} (1.2)

The energy difference created by the Zeeman “splitting” is then described by the Larmor frequency $\omega_0$:

$$\omega_0 = -\gamma B_0.$$  \hspace{1cm} (1.3)

Nuclear magnetic resonance (NMR) spectroscopy excites the transitions between the splittings using electromagnetic (EM) radiation and then detects the frequency of the
transition on its return to equilibrium. Therefore, any isotope with a nuclear spin quantum number $I > 0$ is NMR active. The detected frequency, or resonance frequency, is then displayed as a peak on a frequency spectrum. The distinct Larmor frequency of each isotope, due to its characteristic gyromagnetic ratio $\gamma$, allows it to be distinguished by NMR.\(^1\)

### 1.3. Internal Interactions

If the Zeeman interaction was the only phenomena affecting the nuclear spins, then NMR would not provide any information about the nuclear environment. In fact, there are multiple interactions which are all contained in the nuclear spin Hamiltonian:

$$
\hat{H} = \hat{H}_Z + \hat{H}_{CS} + \hat{H}_J + \hat{H}_D + \hat{H}_Q + \hat{H}_K + \ldots.
$$

Each interaction alters the frequency of the transitions between the spin sublevels and, therefore, provides additional information to be detected by NMR. The interactions included above are the Zeeman interaction ($\hat{H}_Z$; Chapter 1.2), the chemical shielding interaction ($\hat{H}_{CS}$; Chapter 1.3.2), the dipolar interaction ($\hat{H}_D$; Chapter 1.3.3), the quadrupolar interaction ($\hat{H}_Q$; Chapter 1.3.4) and the Knight shift interaction ($\hat{H}_K$; Chapter 1.3.5). In solids, the strength of the interactions generally follows the hierarchy of

$$
\hat{H}_Z > \hat{H}_Q > \hat{H}_K > \hat{H}_{CS} > \hat{H}_D > \hat{H}_J
$$

\(^1\)
Other interactions, including the weak $J$-coupling interaction ($\hat{H}_J$), have not been discussed in this thesis due to their limited relevance to the results achieved.\(^2\) The relative strengths of the internal interactions, compared to the Zeeman interaction, allows them to be treated as perturbations to the Zeeman Hamiltonian.

1.3.1. Coordination Frames

Before the various NMR interactions are described, it is helpful to define the coordination frames used. Transformations between coordination frames are described by the Euler angles $\alpha$, $\beta$, and $\gamma$ as shown in Figure 1.2.

![Figure 1.2](image1.png)

Figure 1.2 The definitions of the Euler angles that define coordination frame transformations.

![Figure 1.3](image2.png)

Figure 1.3 Diagrams representing (a) the laboratory coordination frame $\Sigma_{LAB}$, (b) the principal axis system coordination frame $\Sigma_{PAS}$, (c) the rotor coordination frame $\Sigma_{ROT}$, and (d) the RF coordination frame $\Sigma_{RF}$.
The following coordination frames are discussed in this thesis: the laboratory coordination frame $\Sigma^{LAB}$ (Figure 1.3(a)) describes the $B_0$ vector in the $z$-direction; the principal axis system coordination frame $\Sigma^{PAS}$ (Figure 1.3(b)) describes the frame in which the interaction tensor is diagonalized with Euler angles $\alpha$, $\beta$, and $\gamma$ detailing the direction of the $B_0$ vector; the rotor coordination frame $\Sigma^{ROT}$ (Figure 1.3(c)) describes a rotation about the $z$-axis at a frequency of $\omega_{rot}$ with the angle $\theta$ detailing the direction of the $B_0$ vector; and the RF coordination frame $\Sigma^{RF}$ (Figure 1.3(d)) describes a rotation about the $z$-axis at a frequency of $\omega_{RF}$ with the $B_0$ vector in the $z$-direction.

1.3.2. Chemical Shielding

Due to the magnetic properties of electrons, the resonance frequency of the nucleus will be affected by its local electronic environment. In diamagnetic materials, this effect is called chemical shielding, whereas in paramagnetic materials it is the paramagnetic shift and in metals it is the Knight shift (see Chapter 1.3.5). Chemical shielding occurs because an applied magnetic field will induce currents in the electron clouds around a nucleus, which in turn will induce a small magnetic field. The nuclear spins sense the sum of the applied external field and the internal induced field. The direction of the induced field varies with the orientation of the electronic environment with respect to $B_0$. Therefore, the chemical shielding is described by a second rank tensor, $\sigma$. In the principle axis system ($\Sigma^{PAS}$), $\sigma$ is given by

\[
\sigma = \begin{bmatrix}
\sigma_{XX} & 0 & 0 \\
0 & \sigma_{YY} & 0 \\
0 & 0 & \sigma_{ZZ}
\end{bmatrix}
\]

where

\[
|\sigma_{ZZ} - \sigma_{iso}| \geq |\sigma_{XX} - \sigma_{iso}| \geq |\sigma_{YY} - \sigma_{iso}|
\]

and

\[
\sigma_{iso} = \frac{\sigma_{XX} + \sigma_{YY} + \sigma_{ZZ}}{3}. \tag{1.8}
\]

The chemical shielding Hamiltonian is then given by

\[
\hat{H}_CS = \gamma \hbar \hat{I} \cdot \sigma \cdot \hat{B} = \gamma \hbar B_0 \hat{I}_z \cdot \sigma_{ZZ} = \gamma \hbar \frac{\sigma_{ZZ}}{3}.
\]
\[ \gamma \hbar B_0 I_Z \left( \sigma_{\text{iso}} + \sigma_{\text{aniso}} \left[ \frac{(3 \cos^2 \beta - 1) + \eta_{\text{CS}} \sin^2 \beta \cos 2\alpha}{2} \right] \right) \]

when transformed into the lab frame \( \Sigma^{\text{LAB}} \). The \( \sigma_{\text{aniso}} \) term is given as

\[ \sigma_{\text{aniso}} = \sigma_{ZZ} - \sigma_{\text{iso}} \]

and the \( \eta_{\text{CS}} \) term is defined as

\[ \eta_{\text{CS}} = \frac{\sigma_{XX} - \sigma_{YY}}{\sigma_{\text{aniso}}} \]

The derivation of the chemical shielding Hamiltonian summarised here is given in full by Mackenzie and Smith.\(^2\) The chemical shielding Hamiltonian provides an additional shift to the spin energy levels, \( m \), alongside the Zeeman interaction. Chemical shielding alters the resonance frequency between the spin energy levels by the frequency

\[ \omega_{m-1,m} = \langle m - 1 | \hat{H}_{\text{CS}} | m - 1 \rangle - \langle m | \hat{H}_{\text{CS}} | m \rangle = \gamma B_0 \left( \sigma_{\text{iso}} + \sigma_{\text{aniso}} \left[ \frac{(3 \cos^2 \beta - 1) + \eta_{\text{CS}} \sin^2 \beta \cos 2\alpha}{2} \right] \right) \]

From Equation 1.12, the isotropic chemical shielding is given as \( \sigma_{\text{iso}} \), whereas the orientation dependent component is described by the reduced shielding anisotropy \( \sigma_{\text{aniso}} \) and the shielding asymmetry \( \eta_{\text{CS}} \).\(^2\) The use of these terms to describe the chemical shielding interaction follows the Haeberlen convention rather than the two other conventions in the literature: the Mehring convention and the Maryland convention.\(^4\)

In the majority of solid state NMR experiments, the sample is in powder form (i.e. containing an isotropic distribution of crystallites). Thus, the \( \Sigma^{\text{PAS}} \) of the chemical shielding tensor is randomly orientated with respect to \( B_0 \) for each crystallite. Additionally, the chemical shielding frequency shifts (Equation 1.12) are dependent on the Euler angles \( \alpha \) and \( \beta \) describing the orientation of \( B_0 \) in \( \Sigma^{\text{PAS}} \). Therefore, the isotropic distribution of crystallites produces a distribution of resonance frequencies. The population distribution over the given frequency range, forms an NMR lineshape called a powder pattern. The chemical shift anisotropy (CSA) creates distinct powder patterns with a shape dependent on \( \sigma_{\text{aniso}} \) and \( \eta_{\text{CS}} \) \((0 < \eta_{\text{CS}} < 1)\).\(^1\) Examples of such powder patterns have been simulated with \textit{dmfit}\(^5\) and are given in Figure 1.4(a).
The centre of gravity of the chemical shielding frequencies \( \delta_{\text{CSiso}} \) is given by the isotropic component. The combination of the Zeeman interaction and isotropic chemical shielding component produces a resonance frequency of

\[
\omega = -\gamma B_0 (1 - \sigma_{\text{iso}}).
\]  

The dependence of this frequency on the chemical shielding tensor, and hence the electronic environment of the nucleus, is what makes NMR a powerful analytical technique. The electronic environment of a nucleus varies from molecule to molecule due to its chemical environment and bonding. The chemical shielding adjusted frequency can therefore differentiate between nuclei in varying chemical environments.

As shown in Equation 1.13, the resonance frequency is dependent on the applied magnetic field \( B_0 \). To remove this factor, and to standardise NMR measurements, the resonance frequency is measured as the difference from a reference frequency, \( \omega_{\text{ref}} \), and is then normalised with respect to \( \omega_{\text{ref}} \), giving

\[
\delta - \delta_{\text{ref}} = \frac{\omega - \omega_{\text{ref}}}{\omega_{\text{ref}}}.  
\]  

The result, \( \delta \), is called the chemical shift. The known frequency \( \omega_{\text{ref}} \) is usually close to the Larmor frequency and provided by a chemical standard. The chemical shift of the reference, \( \delta_{\text{ref}} \), is typically chosen to be zero. The change in frequency due to the chemical shielding is small in comparison to the Larmor frequency so the chemical shift, \( \delta \), is multiplied by \( 10^6 \) and quoted in units of parts per million (ppm). From Equations 1.13 and 1.14 the chemical shift can be related to the chemical shielding by

\[
2-3 \text{ From Equations 1.13 and 1.14 the chemical shift can be related to the chemical shielding by }^2
\]
\[ \delta - \delta_{\text{ref}} = \frac{\sigma_{\text{ref}} - \sigma_{\text{iso}}}{1 - \sigma_{\text{ref}}}. \]  

1.3.3. The Dipolar Interaction

The dipolar interaction is the through space coupling between the magnetic dipoles of two adjacent nuclear spins. The Hamiltonian of the dipolar interaction combines the classical formula for the energy of two magnetic dipoles with the nuclear spin magnetic moment (Equation 1.1). Once the dipolar Hamiltonian is transformed from the \( \Sigma_{\text{PAS}} \) to the \( \Sigma_{\text{LAB}} \) it can be described by

\[ \hat{H}_D = -\frac{\mu_0}{4\pi} \frac{\hbar \gamma_I \gamma_S}{r^3} \left( \hat{I} \cdot \hat{S} - \frac{3(\hat{I} \cdot \hat{r})(\hat{I} \cdot \hat{r})}{r^2} \right) \]
\[ = -\frac{\mu_0}{4\pi} \frac{\hbar \gamma_I \gamma_S}{r^3} f(\hat{I}_z, \hat{S}_z) \left( \frac{3 \cos^2 \beta - 1}{2} \right) \]

where \( \beta \) is the angle between the vector joining the two spins and \( B_0 \). The dipolar coupling is a through space interaction dependent on the distance \( r \) between the two nuclear spins \( \hat{I} \) and \( \hat{S} \), as well as their respective gyromagnetic ratios \( \gamma_I \) and \( \gamma_S \). The derivation of the dipolar Hamiltonian is summarised above and is given in full by Levitt.\(^1\)

The resonance frequency of both coupled spins is altered by the dipolar interaction, which, like the CSA, is orientation dependent. In an isolated spin couple, the distribution of the orientation vector between the spins results in a pair of characteristic powder patterns that are superimposed, forming a Pake doublet lineshape (Figure 1.4(b)). However, in more complex spin systems the resultant powder pattern is broadened to a Gaussian/Lorentzian lineshape.\(^6\)

1.3.4. The Quadrupolar Interaction

Nuclei with spin \( I > \frac{1}{2} \) have a non-spherical charge distribution and, therefore, an electric quadrupole moment. The coupling between a nucleus’ quadrupole moment and the internal inhomogeneous electric fields in its environment is the quadrupolar interaction. The electric field gradient (EFG) is described by \( \mathbf{V} \), a second-rank diagonal tensor in the principle axis system (\( \Sigma_{\text{PAS}} \)) given by

\[
\mathbf{V} = \begin{bmatrix}
V_{XX} & 0 & 0 \\
0 & V_{YY} & 0 \\
0 & 0 & V_{ZZ}
\end{bmatrix}
\]
where $V_{xx} + V_{yy} + V_{zz} = 0$ and $|V_{xx}| \geq |V_{yy}| \geq |V_{zz}|$. Therefore, the EFG can be described by the two independent parameters:

$$eq = V_{zz}$$  \hspace{1cm} (1.18)

and

$$\eta_Q = \frac{V_{xx} - V_{yy}}{V_{zz}}.$$  \hspace{1cm} (1.19)

In axially symmetric structures the quadrupolar asymmetry parameter $\eta_Q = 0$, whereas in completely symmetrical structures the EFG is negligible and, hence, $eq = 0$ as well.

This EFG tensor leads to the expression of the Hamiltonian in the $\Sigma^{PAS}$ as

$$\hat{H}_Q = \frac{eQ}{2I(2I-1)\hbar} \hat{j} \cdot \mathbf{V} \cdot \hat{j} = \frac{e^2 qQ}{4I(2I-1)\hbar} \left[ 3l_z^2 - l(l+1) + \eta \left( l_x^2 - l_y^2 \right) \right].$$  \hspace{1cm} (1.20)

By assuming the system is in a high field regime, $\hat{H}_Q$ can be treated as first ($\hat{H}_Q^{[1]}$) and second ($\hat{H}_Q^{[2]}$) order perturbations of the Zeeman interaction. The derivation of $\hat{H}_Q^{[1]}$ and $\hat{H}_Q^{[2]}$ from the expression for $\hat{H}_Q$ in the $\Sigma^{PAS}$ involves a coordinate frame transformation to the $\Sigma^{LAB}$ using the spherical components of the tensor $V$. This derivation is described in thorough detail in the literature. The quadrupolar theory in this chapter is taken from the report by Man which should be read for further embellishment. The first and second order quadrupolar Hamiltonians are given by

$$\hat{R}_Q^{[1]} = \frac{e^2 qQ}{4l(2l-1)\hbar} \left[ 3l_z^2 - l(l+1) \right] \left[ \frac{3 \cos^2 \beta - 1 + \eta \sin^2 \beta \cos 2\alpha}{2} \right]$$  \hspace{1cm} (1.21)

and

$$\hat{R}_Q^{[2]} = \frac{1}{\omega_0} \left[ \frac{eQ}{4l(2l-1)\hbar} \right]^2 \left\{ \frac{\left[ f(\alpha, \beta, \eta_Q) \hat{L}_z [4l(l+1) - 8l^2 - 1] + \eta \right]}{2f'(\alpha, \beta, \eta_Q) \hat{L}_z [2l(l+1) - 2l^2 - 1]} \right\},$$  \hspace{1cm} (1.22)

where
\[ f(\alpha, \beta, \eta) = -\frac{3}{2}e^{2}q^{2} \left[ \left( -\frac{1}{3}\eta_{Q}^{2}\cos^{2}2\alpha + \frac{2}{3}\eta_{Q}\cos2\alpha - 3 \right)\cos^{4}\beta \right. \]
\[ \left. + \left( \frac{2}{3}\eta_{Q}^{2}\cos^{2}2\alpha - \frac{1}{3}\eta_{Q}\cos2\alpha - \frac{1}{3}\eta_{Q}^{2} + 3 \right)\cos^{2}\beta + \frac{1}{3}\eta_{Q}^{2} \right) \]  

The first and second order quadrupolar interactions shift the spin energy levels \( m \) (see Figure 1.5), resulting in a change in the resonance frequency. The corresponding frequency shifts for single transitions are given by

\[ \omega_{m-1,m}^{[1]} = \langle m - 1 | \tilde{H}_{Q}^{[1]} | m - 1 \rangle - \langle m | \tilde{H}_{Q}^{[1]} | m \rangle = \]

\[ \frac{3e^{2}qQ}{4I(2I - 1)\hbar} \left[ \frac{(3\cos^{2}\beta - 1) + \eta \sin^{2}\beta \cos2\alpha}{2} \right] (1 - 2m) \]  

for the first order interaction and

\[ \omega_{m-1,m}^{[2]} = \langle m - 1 | \tilde{H}_{Q}^{[2]} | m - 1 \rangle - \langle m | \tilde{H}_{Q}^{[2]} | m \rangle = \]
\[-\frac{1}{\omega_0}\left(\frac{eQ}{4I(2I-1)\hbar}\right)^2 \left( f(\alpha, \beta, \eta_Q)[24m(m-1) - 4I(I+1) + 9] + \right) \left( f'(\alpha, \beta, \eta_Q)[12m(m-1) - 4I(I+1) + 6] \right) \] 1.26

for the second order interaction. The quadrupole coupling constant, \(C_Q\), and the quadrupolar frequency, \(\omega_Q\), are often used for simplicity where

\[C_Q = \frac{e^2 q Q}{\hbar} \] 1.27

and

\[\omega_Q = \frac{3C_Q}{4I(2I-1)} \] 1.28

The first order interaction creates \(2I + 1\) energy levels with \(2I\) distinct transitions resulting in a multiplet in the NMR spectrum from the central transition (CT) \((m = \frac{1}{2})\) and the satellite transitions (STs). Similarly to the CSA and the dipolar interaction, the first order transition frequencies (Equation 1.25) are dependent on the Euler angles \(\alpha\) and \(\beta\), describing the orientation of \(\Sigma^{PAS}\). Therefore, the first order quadrupole interaction produces a powder pattern. The number of peaks in the first order quadrupolar powder pattern is dependent on the nuclear spin \(I\). The shape of the pattern depends on the asymmetry parameter \(\eta_Q\), as demonstrated by the examples simulated in Figure 1.6(a).

The central transition \((m = \frac{1}{2})\) is unaffected by the first order shift \((\omega_1 \frac{\omega}{2}, \frac{\omega}{2}) = 0\); see Equation 1.25), whereas the second order quadrupolar interaction alters all the transitions. Due to the lack of a first order shift, most quadrupolar NMR focuses solely on the central transition. Additionally, the wide frequency range of the first order quadrupolar powder pattern, for moderate \(C_Q\) values, makes it difficult to observe in completeness. The second order quadrupole shift at the CT is given by \(m = \frac{1}{2}\) in Equation 1.26:

\[
\omega_1^{(2)} = -\frac{1}{2\omega_0}\left(\frac{3C_Q}{2I(2I-1)}\right)^2 \left[ I(I+1) - \frac{3}{4}\right] \left[ A(\alpha, \eta_Q) \cos^4 \beta + B(\alpha, \eta_Q) \cos^2 \beta + C(\alpha, \eta_Q) \right] \] 1.29

\[
A(\alpha, \eta) = -\frac{27}{8} + 9\eta Q \cos 2\alpha - \frac{3}{8}\eta Q^2 \cos^2 2\alpha
\]

\[
B(\alpha, \eta) = \frac{30}{8} - \frac{1}{2}\eta Q^2 - 2\eta Q \cos 2\alpha + \frac{3}{4}\eta Q^2 \cos^2 2\alpha
\]

\[
C(\alpha, \eta) = -\frac{3}{8} + \frac{1}{3}\eta Q^2 - \frac{1}{4}\eta Q \cos 2\alpha - \frac{3}{8}\eta Q^2 \cos^2 2\alpha.
\]
The second order shift at the central transition is also orientation dependent and therefore results in powder patterns as demonstrated by Figure 1.6(b). The breadth of the CT, determined from Equation 1.29, is given by

$$\Delta \omega = \frac{\omega_0^2}{4\omega_0} \left[ \frac{25 + 22\eta_Q + \eta_Q^2 (\omega_0^2)}{144} \right] \left[ I(I + 1) - \frac{3}{4} \right].$$

1.3.5. The Knight Shift

In a conducting solid the nucleus is not only affected by the magnetism of electrons in its bonds (chemical shielding; Chapter 1.3.2), but also by the magnetism of the delocalised conduction electrons. The Knight shift is the relative shift, \( K \), in a metallic environment compared to an equivalent non-metallic surrounding, first discovered by Knight. Due to their similarities, the Knight shift can be described analogously to chemical shielding. The Knight shift tensor \( K \) in the principal axis system \( \Sigma_{PAS} \) is given by

$$K = \frac{\omega^2}{4\omega_0} \left[ \frac{1}{2} \right] \left[ I(I + 1) - \frac{3}{4} \right].$$

The powder patterns were simulated with dmfit and the parameter \( A \) is equal to

$$(\omega_0^2) = \frac{25 + 22\eta_Q + \eta_Q^2 (\omega_0^2)}{144} \left[ I(I + 1) - \frac{3}{4} \right].$$
\[ K = \begin{bmatrix} K_{XX} & 0 & 0 \\ 0 & K_{YY} & 0 \\ 0 & 0 & K_{ZZ} \end{bmatrix}. \]  

The frequency shift in \( \Sigma^{LAB} \) is then given by

\[ \omega = -\gamma B_0 \left( K_{iso} + K_{aniso} \left[ \frac{(3 \cos^2 \beta - 1) + \eta_K \sin^2 \beta \cos 2\alpha}{2} \right] \right) \]

where

\[ K_{iso} = \frac{K_{XX} + K_{YY} + K_{ZZ}}{3}, \]

\[ K_{aniso} = K_{ZZ} - K_{iso}, \]

and

\[ \eta_K = \frac{K_{XX} - K_{YY}}{K_{aniso}} \]

following the Haeberlen convention. Most metals are highly symmetrical and in a cubic environment \( K_X = K_Y = K_Z \) leaving only the isotropic Knight shift \( K_{iso} \).

The total Knight shift consists of multiple components where\(^{10}\)

\[ K = K_p + K_{cp} + K_{orb} + \sigma. \]

The contact interaction contribution \( K_p \) results from the Pauli paramagnetic spin susceptibility \( \chi_p \) of the conduction electrons. The conduction electrons occupy the electronic states from the lowest energy to the Fermi energy as spin “up” and spin “down” pairs as per the Pauli exclusion principle. In an applied magnetic field, spins aligned with the field become energetically favourable, resulting in an imbalance in the population of the electron spin states. Analogously to the Zeeman interaction, the difference in spin state population results in a net magnetisation, which is felt by the nucleus. The associated susceptibility of this magnetisation is the Pauli paramagnetic spin susceptibility \( \chi_p \). The \( K_p \) contribution can then be given as

\[ K_p = \frac{8\pi}{3} V_0 P_F \chi_p \]

where \( V_0 \) is the volume per atom and \( P_F \) is the average value of the electron probability density at the nucleus. Due to the dependence of \( K_p \) on the electron density at the nucleus this effect is dominated by \( s \)-electrons.
The direct interaction of $d$-electron paramagnetism with the nucleus is minimal, but it has an indirect effect called core polarisation. The $d$-electron field induces polarisation of the $s$-electrons in closed shells, or paired $s$-electrons in conduction bands below the Fermi surface. The polarisation in turn produces a field which interacts with the nucleus. The core polarisation field can be comparable to the direct $s$-electron contact interaction and is represented by $K_{\text{cp}}$.

In addition to the above interactions from the Pauli paramagnetism of the conduction electrons, is a contribution from the orbital magnetic moment of the conduction electrons induced by an applied magnetic field. The orbital contribution $K_{\text{orb}}$ is a second order effect, which results from the admixture of occupied and unoccupied orbitals in the same band due to the influence of the applied magnetic field. The mixing of these states results in a magnetisation analogous to the Van Vleck paramagnetism, which is defined by the susceptibility $\chi_v$.\(^\text{11}\)

The total Knight shift also includes a contribution from the chemical shielding ($\sigma$), as shown in Equation 1.36. The $K_p$ component is predominant in light metals, whereas $K_{\text{cp}}$ is a large contribution in heavier metals. Generally, the $K_{\text{orb}}$ contribution is small, but it can be significant in transition metals. Both $K_p$ and $K_{\text{orb}}$ are always positive, whereas $K_{\text{cp}}$ is negative. Like the chemical shift, the Knight shift is measured against a reference frequency:

$$K = \frac{\omega_{\text{metal}} - \omega_{\text{ref}}}{\omega_{\text{ref}}}.$$  \(1.38\)

The Knight shift can be expressed in ppm, however, due to the large frequency shifts produced by the Knight shift, it is often expressed as a percentage difference instead. For a full description of metallic NMR and the Knight shift, see the review by van der Klink and Brom.\(^\text{12}\)

### 1.4. Magic Angle Spinning

Magic angle spinning (MAS) is a fundamental technique for enhancing spectral resolution in solid state NMR, which involves the mechanical spinning of powder samples at a specific angle to $B_0$. NMR resonances in liquid are significantly narrower than in solids due to rapid thermal tumbling. This motion is generally of a frequency much greater than that of the internal interactions and, therefore, it averages any angular dependencies to zero, leaving
only the isotropic parts of the interactions. Hence, the NMR lineshapes of liquid samples do not present as powder patterns (see Chapter 1.3). The MAS technique attempts to emulate the removal of the anisotropic components of the interactions by motional liquid environments, through rapid rotation of the solid samples. To derive the Hamiltonians describing each interaction under MAS they must be rotated from the \( \Sigma^{\text{PAS}} \) to the rotating coordinate frame \( \Sigma^{\text{ROT}} \) before converting to \( \Sigma^{\text{LAB}} \) (Figure 1.3).

The coordination frame transformation and its effect on the interaction Hamiltonian is discussed in full detail by Mackenzie and Smith.\(^2\) In brief, Hamiltonians can be split into time-dependent and time-independent parts. The time-dependent component is averaged by the fast rotation, whereas the time-independent component is a modified version of the static Hamiltonian. Many interaction Hamiltonians can be described by a rank two tensor. In this case, the anisotropic component acquires a modulation factor equal to the second order Legendre polynomial \( P_2(\cos \theta) \) given by

\[
P_2(\cos \theta) = \frac{1}{2} (3 \cos^2 \theta - 1),
\]

where \( \theta \) is the angle between \( B_0 \) and the rotor axis. Hence, when the rotor axis is set at the “magic angle” of \( \theta = 54.74^\circ \), the anisotropic component of the Hamiltonian is reduced to zero (\( P_2(\cos \theta) = 0 \)). Sufficiently high frequency MAS can, therefore, completely remove the broadening created by the anisotropic powder patterns of interactions which can be described by second rank tensors. Hence, both the CSA and dipolar broadening can be removed by MAS.

The complete removal of the anisotropic Hamiltonian components only occurs when the spinning frequency \( \omega_r \) is greater than the static linewidth of the broadened resonance. The physical limitations on rotor spinning speeds mean this is often not the case. If \( \omega_r \) is too small, then the time-dependent Hamiltonian component is not completely averaged. The time modulated Hamiltonian produces satellite components at integer values of \( \omega_r \) from the isotropic shift. The satellite resonances in the NMR spectra are called spinning sidebands. As \( \omega_r \) increases the spinning sidebands are shifted further from the isotropic shift and become weaker. A full description of the mathematics behind the spinning sidebands is given by Duer.\(^3\)
1.4.1. Quadrupolar Interaction under MAS

The quadrupolar interaction has a more complex behaviour under MAS. As shown in Equation 1.25, the first order quadrupolar frequency shift can be given by a second rank tensor, so upon transformation from the $\Sigma^{\text{ROT}}$ coordination frame it is modulated by $1/2 (3 \cos \theta - 1)$:

$$\omega_m^{[1]R{\text{OT}}} = \frac{1}{2} (1 - 2m) \omega_Q \left( \frac{(3 \cos^2 \beta - 1) + \eta_Q \sin^2 \beta \cos 2\alpha}{2} \right) (3 \cos \theta - 1).$$  \hspace{1cm} (1.40)

Therefore, the first order quadrupole shift is reduced to zero under fast MAS ($\theta = 54.73^\circ$).

However, the second order quadrupole shift (Equation 1.26) is more complex and cannot be described by a rank two tensor alone. The transformation from $\Sigma^{\text{ROT}}$ gives the second order quadrupole shift as

$$\omega_m^{[2]R{\text{OT}}} = -\frac{4\omega_Q^2}{\omega_0} \left[ g(l, m, \eta_Q) + g'(l, m, \alpha, \beta, \eta_Q)P_2(\cos \theta) \right] + \frac{g(1, m, \alpha, \beta, \eta_Q)P_4(\cos \theta)}{\omega_0},$$  \hspace{1cm} (1.41)

where the anisotropic components are now dependent on the second and fourth order Legendre polynomials given by Equation 1.39 and

$$P_4(\cos \theta) = \frac{1}{8} (35 \cos^4 \theta - 30 \cos^2 \theta + 3).$$  \hspace{1cm} (1.42)

The magic angle is not a root of $P_4(\cos \theta)$ and no single angle reduces both the second and fourth order Legendre polynomials to zero. Therefore, the second order quadrupolar interaction cannot be fully removed by MAS and the resultant frequency shift of the CT is given by

$$\omega_m^{[2]M{\text{AS}}} = -\frac{1}{6\omega_0} \left[ \frac{3C_Q}{2l(2l - 1)} \right]^2 \left[ l(l + 1) - \frac{3}{4} \right] \left[ D(\alpha, \eta_Q) \cos^4 \beta \right] + E(\alpha, \eta_Q) \cos^2 \beta + F(\alpha, \eta_Q) \right]$$  \hspace{1cm} (1.43)

where

$$D(\alpha, \eta) = \frac{21}{16} - \frac{7}{8} \eta_Q \cos 2\alpha + \frac{7}{48} \eta_Q^2 \cos^2 2\alpha,$$

$$E(\alpha, \eta) = -\frac{9}{8} + \frac{1}{12} \eta_Q^2 + \eta_Q \cos 2\alpha - \frac{7}{24} \eta_Q^2 \cos^2 2\alpha,$$

and

15
\[ F(\alpha, \eta) = \frac{5}{16} - \frac{1}{8} \eta Q \cos 2\alpha + \frac{7}{48} \eta Q^2 \cos^2 2\alpha. \]

The orientation dependence of \( \omega_{-1/2,1/2}^{\text{[2]MAS}} \) details the anisotropic powder patterns shown in Figure 1.7. Through simulation of the quadrupolar lineshapes, an NMR spectrum can be fitted allowing the experimental determination of the quadrupolar parameters \( C_Q \) and \( \eta_Q \). As demonstrated by Equation 1.27 and 1.19, \( C_Q \) represents the magnitude of the quadrupolar interactions whereas \( \eta_Q \) is the asymmetry parameter for the EFG tensor. It is uncommon for an experimentally determined \( C_Q \) to be presented as an angular frequency, and is instead given as

\[ C_Q = \frac{e^2 q Q}{h}. \]

Figure 1.7 Powder patterns produced by the second order frequency shift at the CT in the fast MAS regime for varying values of \( \eta_Q \). The powder patterns were simulated with \textit{dmfit} and the parameter \( A \) is equal to

\[ \frac{\omega_Q^2}{4\omega_0} \left[ l (l + 1) - \frac{3}{4} \right]. \]
Although MAS cannot remove the orientation dependence of the CT, its quadrupolar lineshape is narrowed. The breadth of the CT powder pattern under fast MAS, determined from Equation 1.43, is given by

$$\Delta \left( \omega_0 \right) = \frac{(6 + \eta_q)^2}{504} \left( \frac{\omega_q}{\omega_0} \right)^2 \left[ I(I + 1) - \frac{3}{4} \right].$$  \hspace{1cm} 1.45

By comparing Equation 1.30 and 1.45, it can be shown that MAS narrows the CT lineshape by a factor of ~3. Additionally, the broadness of second order quadrupole lineshapes is inversely proportional to $\omega_0$. Hence, higher $B_0$ field strengths can be used to provide better resolution of quadrupolar spectra.\(^8\)

The centre of gravity of the second order quadrupole lineshapes of the CT ($\delta_{Qiso}$) is given by

$$\delta_{Qiso} = \frac{1}{4\pi} \int_0^\pi d\beta \sin \beta \int_0^{2\pi} d\alpha \omega^{2[MAS]} - \frac{3}{4} \omega_0 \times 10^6 =$$

$$-3 \left[ I(I + 1) - \frac{3}{4} \right] C_Q^2 \left( 1 + \frac{\eta_q^2}{3} \right) \times 10^6. \hspace{1cm} 1.46$$

Furthermore, the experimental centre of gravity of the NMR resonance, $\delta_{CG}$, is then given by

$$\delta_{CG} = \delta_{iso} + \delta_{Qiso} = \delta_{iso} + \left( \frac{P_Q}{\omega_0} \right)^2 \hspace{1cm} 1.47$$

where $\delta_{iso}$ is the isotropic chemical shift and $P_Q$ is

$$P_Q = C_Q \left( 1 + \frac{\eta_q^2}{3} \right)^{\frac{1}{2}}. \hspace{1cm} 1.48$$

Similarly, to the quadrupole broadening, the $\delta_{CG}$ of a quadrupolar lineshape is dependent on $B_0$ via $\omega_0$.\(^7\)

The simulated powder patterns presented so far, are in practice only observed in perfectly crystalline materials. Many of the systems observed in this thesis, are characterised by local disorder. Such disorder creates a distribution of quadrupolar parameters over the nuclei sites in the material. The overlapping quadrupolar powder patterns for each site sum into an amorphous lineshape devoid of the sharp quadrupolar features. However, the disordered quadrupolar pattern retains a characteristic asymmetric lineshape. A Gaussian distribution of $C_Q$ leads to the lineshapes shown in Figure 1.8, which were simulated using QuadFit.\(^{13}\)
As the width of the $C_Q$ distribution increases the lineshape broadens, presenting with a steep flank on the high frequency side and a long tail to lower frequencies.\textsuperscript{14} A distribution of $\eta_Q$, results in more subtle differences in the lineshape, that are hidden by a large $C_Q$ distribution.

Figure 1.8 Simulated NMR lineshapes of the second order quadrupolar broadened CT of an $I = \frac{5}{2}$ nucleus with $v_0 = 156.34$ MHz and $\eta_Q = 0$. Each lineshape has a Gaussian distribution of $C_Q$ defined by a centre and width parameter. The lineshapes were simulated with \textit{QuadFit}. 
2

The NMR Experiment

2.1. Net Magnetisation

The magnetic moment, $\hat{\mu}$, of a nuclear spin precesses around the direction of the applied field $B_0$ at the Larmor frequency ($\omega_0$) with only the Zeeman interaction in effect. Without an applied magnetic field, a group of nuclei will have an isotropic distribution of magnetic moments. However, due to the Zeeman interaction in an applied field $B_0$ (Chapter 1.2), magnetic moments aligned with the field have lower energy than those aligned against. This results in a slight net alignment of moments parallel to $B_0$, and therefore a net magnetisation $M_0$ in the $z$-direction as shown in Figure 2.1.

Therefore, the probability of a nucleus’ magnetic moment being aligned parallel to the magnetic field is dependent on the energy difference between the two-spin state. It also depends on the thermal energy of the system, due to thermal motion hindering the alignment of the spins. In the high-temperature limit when $\gamma \hbar B_0 \ll k_B T$ (which is appropriate for most NMR experiments), the average $z$-component of the magnetic moment is given by

$$\langle \hat{\mu}_z \rangle = \frac{(\gamma \hbar)^2 B_0 I (I + 1)}{3k_B T}$$  \hspace{1cm} 2.1

where $k_B$ is the Boltzmann constant and $T$ is the temperature. The net magnetisation from the spin system is then defined as

Figure 2.1 Representation of a nuclear magnetic moment precessing about $B_0$ and the resulting net magnetisation.
\[ M_0 = N \langle \hat{\mu}_z \rangle \]

where \(N\) is the total population of nuclei. \(^{2}\)

### 2.2. Radiofrequency Pulses

An EM wave includes a time dependent oscillating magnetic field \(B(t)\). If the magnetic field is along the \(x\)-axis with a magnitude of \(2B_1\) and oscillating at the frequency \(\omega_{\text{RF}}\) then it is given by

\[ B(t) = 2B_1 \cos(\omega_{\text{RF}}t) \hat{x}. \]

Following from the Zeeman Hamiltonian in Equation 1.2, the Hamiltonian for a nuclear spin, \(I\), under the effect of an oscillating field \(\hat{H}_{\text{RF}}\) is given by

\[ \hat{H}_{\text{RF}} = -\gamma \hbar (2B_1 \cos(\omega_{\text{RF}}t)). \]

If an oscillating magnetic field is introduced to the nuclear spin system under an applied magnetic field \(B_0\), then the spin Hamiltonian is a combination of \(\hat{H}_Z\) and \(\hat{H}_{\text{RF}}\):

\[ \hat{H} = \hat{H}_Z + \hat{H}_{\text{RF}} = -\gamma \hbar (B_0 \hat{I}_z + 2B_1 \cos(\omega_{\text{RF}}t) \hat{I}_x). \]

It is convenient to think of the oscillating magnetic field as two counter-rotating fields about the \(z\)-axis with magnitude \(B_1\) and frequencies of \(\omega_{\text{RF}}\) and \(-\omega_{\text{RF}}\). Then by transforming the Hamiltonian into a frame rotating about the \(z\)-axis at a rate of \(\omega_{\text{RF}}(\Sigma^{\text{RF}})\), only the component rotating in phase with the magnetisation has an effect and the time dependent part of the Hamiltonian can be removed giving

\[ \hat{H} = (-\gamma B_0 - \omega_{\text{RF}}) \hbar \hat{I}_z - \gamma \hbar B_1 \hat{I}_x = (\omega_0 - \omega_{\text{RF}}) \hbar \hat{I}_z - \gamma \hbar B_1 \hat{I}_x. \]

If the frequency of the oscillating magnetic field is made equal to the Larmor frequency \((\omega_{\text{RF}} = \omega_0)\), then the Hamiltonian in the frame rotating at \(\omega_0\) is in the same form as the Zeeman Hamiltonian in the lab frame:

\[ \hat{H} = -\gamma \hbar B_1 \hat{I}_x. \]

As described in Chapter 2.1, the Zeeman Hamiltonian results in a magnetisation that precesses around \(B_0\). In the described rotating frame, the effective field is \(B_1\) and, therefore, the magnetisation precesses around the \(x\)-axis. This precession is called nutation and the nutation frequency \(\omega_{\text{nut}}\) is given by

\[ \omega_{\text{nut}} = -\gamma B_1. \]
The magnetisation is nutated by an angle $\theta_{\text{nut}}$, called the flip angle, during the time $\tau_{\text{RF}}$:

$$\theta_{\text{nut}} = \omega_{\text{nut}} \tau_{\text{RF}}.$$  \hspace{1cm} (2.9)

Therefore, a pulse of EM radiation along the $x$-axis at the frequency $\omega_0$, with the correct amplitude $B_1$ and duration $\tau_{\text{RF}}$, can rotate the magnetisation to be along the $-y$-axis ($\theta_{\text{nut}} = \pi/2$); this is shown in Figure 2.2. Back in the laboratory frame $\Sigma_{\text{LAB}}$, the magnetisation still precesses around $B_0$ in the $x$-$y$ plane at $\omega_0$.

The Larmor frequencies $\omega_0$ at the $B_0$ fields used in NMR, fall within the radiofrequency range. Hence, the pulses of EM radiation used in NMR are referred to as radiofrequency (RF) pulses. The RF pulse is a fundamental component of the NMR experiment, because by flipping the magnetisation into the $x$-$y$ plane, its precession about $B_0$ can be measured (see Chapter 2.4.1).$^{1,15}$

Figure 2.2 Representation of (a) the equilibrium net magnetisation precessing about $B_0$ in $\Sigma_{\text{LAB}}$, (b) the creating of transverse magnetisation by an RF pulse magnetisation in $\Sigma_{\text{RF}}$, and (c) the precession of the transverse magnetisation about $B_0$ in $\Sigma_{\text{LAB}}$. 
2.2.1. Excitation

The determination of the nutation frequency above, assumes the presence of only the Larmor interaction and, therefore, only one precession frequency ($\omega_0$) for the RF frequency ($\omega_{RF}$) to match. However, the multiple internal interactions, described in Chapter 1.3, all cause shifts to the precession frequency based on the nuclear environment. Hence, each magnetic moment has its own effective precession frequency, or resonance. The RF pulse is required to cover the resonance frequencies of all the nuclear spins in the system to ensure the complete transition of magnetisation into transverse magnetisation. This “excitation” of a small frequency range can be achieved due to the excitation bandwidth of the pulse.

Due to the difference between the effective precession frequency and the RF frequency, it is useful to define a frequency offset, $\Omega$, as

$$\Omega = \omega - \omega_{RF}. \quad 2.10$$

The frequency domain function $A(\omega)$ corresponding to a rectangular RF pulse of frequency $\omega_{RF}$ and duration $\tau_{RF}$ is a sinc function (i.e. the Fourier transform of a rectangular function is a sinc function):

$$A(\omega) = \frac{\sin(\Omega \tau_{RF})}{\Omega \tau_{RF}}. \quad 2.11$$

Due to the sinc wave nature of the frequency domain, a range of frequencies are excited by the RF pulse. The excitation is > 90% of the maximum for frequency offsets within a range defined by

$$|\Omega \tau_{RF}| < \frac{\pi}{4}. \quad 2.12$$

Hence, a uniform excitation bandwidth, $\Delta f$, is generally defined as

$$\Delta f = \frac{2|\Omega|}{2\pi} = \frac{1}{4 \tau_{RF}}. \quad 2.13$$

![Graphical representation of a rectangular RF pulse that upon Fourier transformation becomes a sinc frequency spectrum with bandwidth $\Delta f$.](image)
A representation of a rectangular RF pulse and the resulting excitation bandwidth is shown in Figure 2.3.

Therefore, by using an RF pulse with a minimal duration, \( \tau_{RF} \), the excitation bandwidth, \( \Delta f \), can be maximised. From Equation 2.9, an RF pulse with a short \( \tau_{RF} \), requires a large \( B_1 \) amplitude to achieve the desired flip angle. Such short, high power pulses are termed hard pulses and are commonly used in solid state NMR experiments.\(^2\)

### 2.2.2 Quadrupolar Nutation

Another issue with the determination of the nutation frequency (Chapter 2.2), occurs due to the assumption that the RF pulse Hamiltonian, \( \hat{H}_{RF} \), overwhelsms the internal spin interactions. However, the quadrupolar interaction can often be on par with, or even larger than that of the RF pulse.

When \( \hat{H}_{RF} \gg \hat{H}_Q \), a hard pulse, or “non-selective” pulse, can excite the entire quadrupole frequency range. In this case the nutation frequency remains as described in Equation 2.8

\[
\omega_{nat}^{ns} = -\gamma B_1. \tag{2.14}
\]

When \( \hat{H}_{RF} \approx \hat{H}_Q \), only part of the frequency range can be excited by the “selective” pulse, usually chosen to be the CT. In this case, the quadrupolar Hamiltonian cannot be ignored, so the spin Hamiltonian given in Equation 2.5 becomes\(^16\)

\[
\hat{H} = \hat{H}_Z + \hat{H}_{RF} + \hat{H}_Q. \tag{2.15}
\]

This obviously complicates the derivation of the nutation frequency, which is given in full in the review by Freude and Haase.\(^17\) However, the result is fairly simple; the nutation frequency of the CT during a selective pulse \( \omega_{nat}^{s,CT} \) is given by

\[
\omega_{nat}^{s,CT} = \left(I + \frac{1}{2}\right) \omega_{nat}^{ns} = -\gamma B_1 \left(I + \frac{1}{2}\right). \tag{2.16}
\]

Hence, a selective excitation of the CT quadrupolar resonance causes a faster nutation of magnetisation than the excitation of a non-quadrupolar \( (C_Q = 0) \) resonance. Furthermore, if the RF amplitude \( B_1 \) is identical for both cases, then the duration of the pulse required to achieve the same flip angle is

\[
\tau_{RF}^{ns} = \left(I + \frac{1}{2}\right) \tau_{RF}^{s,CT}. \tag{2.17}
\]
This relationship is important for the calibration of RF pulses in quadrupolar NMR experiments.

Furthermore, the magnitude of the magnetisation in the x-y plane (transverse magnetisation) after an RF pulse of amplitude $B_1$ and duration $\tau_{RF}$ for both a non-quadrupolar resonance and a quadrupolar CT resonance is given by

$$M_t^{ns} = M_0 \sin \omega_{nut}^{ns} \tau_{RF}$$  \hspace{1cm} (2.18)

and

$$M_t^{s,CT} = \frac{M_0}{(I + \frac{1}{2})} \sin \left[ \left( I + \frac{1}{2} \right) \omega_{nut}^{ns} \tau_{RF} \right]$$  \hspace{1cm} (2.19)

respectively.\(^{18}\) If the duration $\tau_{RF}$ is chosen so that $\omega_{nut}^{ns} \tau_{RF} \ll \pi$, then via the small angle approximation

$$M_t^{s,CT} \approx M_t^{ns}.$$  \hspace{1cm} (2.20)

This leads to the uniform excitation condition for quadrupolar nuclei

$$\left( I + \frac{1}{2} \right) \omega_{nut}^{ns} \tau_{RF} \leq \frac{\pi}{6}$$  \hspace{1cm} (2.21)

which results in $< 5\%$ difference in the transverse magnetisation of the two resonances. Therefore, small flip angles are preferred in the selective excitation of quadrupolar nuclei to allow quantitative interpretations of NMR data.\(^{10}\) However, a smaller flip angle will not produce maximal transverse magnetisation, resulting in a weaker NMR signal (see Chapter 2.4.1). Hence, the choice of flip angle in an NMR experiment on a quadrupolar nucleus is a compromise between quantitative results and signal strength.

### 2.3. Relaxation

The net magnetisation after an RF pulse does not remain in the x-y plane indefinitely. Over time, the magnetisation will relax back to its equilibrium position parallel to $B_0$. The recovery of the $z$-component of the equilibrium magnetisation is called longitudinal ($T_1$) relaxation. The loss of magnetisation in the x-y plane is called transverse ($T_2$) relaxation.
2.3.1. Longitudinal Relaxation

As explained in Chapter 2.1, the net magnetisation is the sum of all the spin magnetic moments in the system. Immediately after the application of the static field $B_0$, the magnetic moments in the system are randomly orientated. Each magnetic moment precesses around $B_0$, forming a “cone of precession” depending on its orientation. In a perfectly isolated spin system, the orientation of the cone of precession around $B_0$ would remain constant for each spin magnetic moment. However, in real systems the nuclear spin is affected by additional small magnetic fields produced by the surrounding electrons and nuclei. These local fields are the cause of the internal spin interactions discussed in Chapter 1.3. They also act to create an effective field at the nucleus whose orientation slightly differs from $B_0$. Due to thermal agitation of the surroundings, the effective field has a slight fluctuation in direction and magnitude. Therefore, the effective field felt by any one nuclear spin is slightly different at any point in time. Hence, the orientation of the precession cone of each nuclear spin magnetic moment also fluctuates. This causes a “wandering” motion of the nuclear spin precession cones, which over time allow each nuclear magnetic moment to sample every possible orientation (Figure 2.4).

Also explained in Chapter 2.1, is the preferred alignment of the nuclear spin magnetic moments with $B_0$. The wandering thermal motion of the magnetic moments, allows the slight majority of spins aligned with $B_0$ to form, creating the equilibrium net magnetisation. The same process occurs immediately after an RF pulse. As discussed in Chapter 2.2, an RF pulse along the $x$-axis with $\theta_{\text{nut}} = \pi / 2$ rotates the magnetic polarisation to be in the $-y$ direction (i.e. there is a slight majority of magnetic moments aligned with the $-y$-axis). The wandering

![Diagram of magnetic precession and field fluctuations](image)

Figure 2.4 Representation of the fluctuating field $B$ felt by a nuclear magnetic moment resulting in a wandering precession cone.
thermal motion of the magnetic moments slowly brings them back to equilibrium with the $B_0$ field. The return of the magnetisation’s $z$-component is approximately exponential and can, therefore, be expressed as

$$M_z(t) = M_0 \left(1 - e^{-\frac{t}{T_1}}\right).$$

The rate of the longitudinal relaxation is then described by the characteristic relaxation time $T_1$. \(^1\)

In more complex cases the longitudinal relaxation can be described by a bi-exponential or a stretched-exponential function. A bi-exponential function is appropriate when nuclei in two different environments have similar frequencies but substantially different relaxation rates. The transverse relaxation is then given by

$$M_z(t) = M'_0 \left(1 - e^{-\frac{t}{T_{1}'}}\right) + M''_0 \left(1 - e^{-\frac{t}{T_{1}''}}\right),$$

where $T_{1}'$ and $T_{1}''$ are the characteristic relaxation times of the two environments, and $M'_0$ and $M''_0$ are the initial magnetisations. Bi-exponential relaxation can also occur in the magnetisation recovery of the CT of a strongly quadrupolar nuclear site. The non-exponential relaxation is due to the incomplete excitation of the complete quadrupolar lineshape (CT and STs). \(^20\)

When multiple environments have similar frequencies and separate, but similar, relaxation rates, it can be convenient to describe the range of relaxation rates as a probability distribution. In such cases the observed longitudinal relaxation can be modelled by a stretched exponential function given by

$$M_z(t) = M_0 \left(1 - e^{-\left(\frac{t}{T_1^*}\right)^x}\right),$$

where the probability distribution of relaxation rates is defined by the parameters $T_1^*$ and $x$ (where $0 < x \leq 1$). For example, a low $x$ provides a broad distribution of relaxation rates centred about $T_1^*$, whereas $x = 1$ provides a single relaxation rate (i.e. the single exponential function with $T_1 = T_1^*$). Stretched exponential functions have been found to accurately describe the longitudinal relaxation in several disordered systems (such as a system with an inhomogeneous distribution of paramagnetic impurities) and the parameter $x$ tends to fall within a defined range of $0.5 < x < 1$. \(^21\)
2.3.2. Transverse Relaxation

As the longitudinal magnetisation returns to its equilibrium position via the wandering thermal motion of the magnetic moments, there is a concurrent loss of transverse magnetisation called non-secular transverse relaxation. Hence, any longitudinal relaxation results in an equivalent non-secular transverse relaxation, and therefore their rates are equal.

However, there is an additional way in which the transverse magnetisation is lost. The effective precession frequency of a nuclear spin magnetic moment about \( B_0 \), is actually the combination of the Larmor frequency and the small frequency shifts caused by the internal spin interactions (Chapter 1.3). The thermal agitation of the surroundings, creates small variations in the frequency shifts in time. Hence, the effective precession frequency of each magnetic moment will fluctuate slightly. Over time, the precession of the individual magnetic moments will become out of phase with each other as shown in Figure 2.5. The net transverse magnetisation, which results from the slight alignment of the magnetic moments, will be reduced by this “dephasing”. This loss of transverse relaxation by dephasing of the individual precession frequencies, rather than the fluctuating direction of the precession cones, is the secular transverse relaxation contribution.

Analogous to the longitudinal relaxation, the loss of transverse magnetisation can be represented as

\[
M_t(t) = M_0 \left( e^{-\frac{t}{T_2}} \right).
\]

2.25

The rate of the transverse relaxation is then described by the characteristic relaxation time \( T_2 \). [15]

![Figure 2.5 Representation of two transverse magnetisation components with effective precession frequencies \( \omega_0 \) and \( \omega_0' \) becoming out of phase with each other.](image)
2.4. Signal Detection

2.4.1. Free Induction Decay

The transverse magnetisation immediately after a $\pi/2$ pulse along the $x$-axis is given as

$$M_y = -M_0$$ \hspace{1cm} 2.26

if measured in the rotating frame $\Sigma_{RF}$. The transverse magnetisation precesses around the $z$-axis at the frequency offset $\Omega$ of its effective precession frequency (Equation 2.10) and relaxes following Equation 2.25. Therefore, the transverse magnetisation, in its $x$ and $y$ components, is given by

$$M_y = -M_0 \cos \Omega t \left( e^{-\frac{t}{\tau_z}} \right); \quad M_x = -M_0 \sin \Omega t \left( e^{-\frac{t}{\tau_z}} \right).$$ \hspace{1cm} 2.27

The oscillating magnetic field induces a current in the detection apparatus creating a signal for both magnetisation components. It is convenient to combine the two generated signal components into a complex signal of the form

$$S(t) = S_x + iS_y = S_0 e^{i\Omega t} e^{-\frac{t}{\tau_z}}.$$ \hspace{1cm} 2.28

This time-domain signal is called the free induction decay (FID). The single pulse NMR experiment described so far, and the resulting FID is schematically represented in Figure 2.6.

2.4.2. Fourier Transform

By Fourier transforming the time-domain signal a frequency domain signal (or frequency spectrum) is produced. The Fourier transform of Equation 2.28 gives

![Figure 2.6: A schematic pulse sequence diagram of a single pulse NMR experiment which includes a $\pi/2$ pulse and the acquisition time $t_{aq}$](image-url)
\[
S(\omega) = A(\omega) + iD(\omega)
\]

where
\[
A(\omega) = \frac{\left(\frac{1}{T_2}\right)}{\left(\frac{1}{T_2}\right)^2 + (\omega - \Omega)^2}
\]

and
\[
D(\omega) = \frac{-(\omega - \Omega)}{\left(\frac{1}{T_2}\right)^2 + (\omega - \Omega)^2}.
\]

The real part of the signal (Equation 2.30) gives an absorption Lorentzian centred at \(\Omega\). Multiple components with different frequencies \(\Omega\) in the time-domain signal will result in multiple Lorentzian lineshapes in the frequency-domain signal. This provides the desired result of a frequency spectrum with resonances whose positions are related to the effective precession frequencies of different chemical environments.

So far, the direction of the RF pulse has been assumed to be along the x-axis. However, the pulse can be along any direction in the x-y plane. The direction of the pulse is described by the phase \(\phi\), which affects the resultant magnetisation producing
\[
M(t) = M_0 e^{i\omega t} e^{i\phi} e^{-\frac{t}{T_2}}.
\]

If the measurement of the signal does not occur in the same phase as the magnetisation then an arbitrary phase \(\phi'\) is carried into the time-domain signal
\[
S(t) = S_0 e^{i\omega t} e^{i\phi'} e^{-\frac{t}{T_2}}.
\]

This results in the real part of the frequency-domain becoming a mixture of the absorption and dispersion lineshapes \(A(\omega)\) and \(D(\omega)\). To rationalise this a correction phase \((\phi_{corr})\) can be added post detection to remove the arbitrary phase \(\phi'\) if
\[
e^{i\phi'} e^{i\phi_{corr}} = 0.
\]

This process is called phasing.\(^15\)

2.4.3. Phases and Coherences

The phase of the signal added by the RF pulse can be used advantageously by applying a technique called phase cycling. To describe phase cycling, it is first necessary to introduce
the concept of coherences. As described in Chapter 2.1, a spin system at equilibrium with an applied magnetic field will be polarized due to the difference in populations of the two spin states. Once the net magnetisation is rotated into the $x$-$y$ plane by an RF pulse, the polarisation is now perpendicular to the external field. The transverse synchronisation of the magnetic moments resulting from the polarisation between the two spin states is called a coherence. It is useful to define a coherence with the quantum number coherence order, $p$.

For a non-interacting $I = \frac{1}{2}$ spin system there are two spin states $m = \pm \frac{1}{2}$. Hence, there are three possible coherence orders: $p = 0$ for longitudinal magnetisation and $p = \pm 1$ for transverse magnetisation. The RF pulse, therefore, alters the coherence order by $\Delta p = \pm 1$. The $p = \pm 1$ coherences (single quantum coherence) are the only coherences that can produce a directly observable signal.

In more complicated spin systems, like for a quadrupolar system, there are multiple spin states. Therefore, there are higher order coherences (multiple quantum coherences) with coherence order of $p = \pm 2, \pm 3$, etc. An RF pulse will excite all coherences but only the single quantum coherence can be detected. However, if a sequence of pulses is applied then these multiple quantum coherences can affect the observable single quantum coherence and be indirectly detected.

A coherence order pathway describes the evolution of the coherences during a specific pulse sequence. Each pulse produces a change in coherence order of $\Delta p$. The change of phase produced by the pulse $\Delta \phi$, results in a coherence phase shift of $\Delta p \cdot \Delta \phi$. Therefore, by varying the phase of the pulses a distinct phase shift can be applied to a desired coherence order pathway. By matching the phase of detection to the appropriate coherence phase shift, the desired coherence order pathway can be detected, while the other coherence order pathways are ignored.

The use of phase shifts to select a desired coherence pathway is called phase cycling. It allows NMR experiments to manipulate the multiple quantum coherences, which can provide further details about the interactions in the system. This has led to the development of increasingly complex NMR techniques with multiple pulse sequences. A full description of coherences, and therefore phase cycling, requires knowledge of the density matrix formalism of spin systems, which is described in detail by Duer.\(^3\)
2.5. Solid State NMR Instrumentation

The NMR experiment detailed so far requires a basic set of equipment that make up the NMR spectrometer. These components include: a magnet to provide the static $B_0$ field; an NMR probe to place the sample into the $B_0$ field, apply RF pulses to the sample, measure the resultant transverse magnetisation and to spin the sample at the MAS frequency; a transmitter to generate RF pulses; a receiver to record the NMR signal; and a computer to store the digital signal and Fourier transform it into a frequency spectrum.

The NMR signal strength and resolution are improved by higher $B_0$ fields, which has led to increasing strengths of NMR magnets. The highest commercially available NMR magnet at the time of writing is 24 T. The high $B_0$ fields used in most modern NMR spectrometers is provided by a superconducting solenoidal magnet. The solenoid coil sits in a liquid helium bath to maintain the necessary temperature for superconductivity. To conserve helium, temperature losses must be minimised. This is achieved via an enclosing sacrificial liquid nitrogen reservoir, vacuum chamber layers and heat shields. Magnet uniformity is improved through multiple smaller cryo-shimming coils which apply gradient fields to correct for inhomogeneity.

Modern MAS NMR probes use high pressure gas to spin cylindrical sample containers with fluted caps, called rotors. Smaller rotors can be spun very fast (up to 111 KHz), and can therefore achieve great resolution. However, this is a trade off with the weaker NMR signal provided by the small volume of sample. To survive the high spinning speeds, the rotors themselves must have a high strength-to-mass ratio while preferably being relatively NMR inactive. Partially stabilised zirconia is the generally preferred material for NMR rotors. The probe contains a solenoidal coil that acts to transmit the RF pulse and receive the NMR signal. The probe circuitry must be finely tuned to ensure efficient transmission and reception of the desired Larmor frequency. Different probes cover select frequency ranges and are designed for a specific rotor size. Specialised probes can also offer other features, such as variable temperature or multi-resonance acquisition. Therefore, choosing the correct probe for one’s experimental needs is a key part of the NMR experiment.

The console contains the rest of the electronics involved in the NMR experiment. The transmitter must be able to provide all the possible Larmor frequencies for the field strength of its magnet. A frequency synthesizer produces the desired frequency which is then amplified to the correct $B_1$ field strength. The RF signal is then gated to produce the RF
pulses. The receiver must amplify the weak NMR signal before detection. Great care must be taken to ensure the high power transmitted frequencies do not damage the sensitive receiver electronics. The pre-amplification at the receiver adds noise to the signal as an unwanted side effect. The signal is then digitized to be stored by the computer. The computer Fourier transforms the NMR signal to produce the frequency spectrum, alongside additional processing such as phasing.²

A very important gauge of the NMR experiment is the signal-to-noise ratio (SNR) of the NMR signal. Naturally, it is effected by the instrumentation used. The SNR is defined as the peak signal voltage $V_{\text{signal}}$ over the root mean square of the noise voltage $V_{\text{noise}}$ which can be roughly calculated using

$$SNR = \frac{V_{\text{signal}}}{V_{\text{noise}}} = N_T^{\frac{1}{2}} \frac{M_0 \omega_0 V_s}{(k_B T (R_s + R_c))^\frac{1}{2} \Delta f^\frac{1}{2}}$$

where $M_0$ is the equilibrium magnetisation (Equation 2.2); $\omega_0$ is the Larmor frequency (Equation 1.3); $V_s$ is the sample volume; $B_1/i$ is the strength of the RF field per unit current which gives the sensitivity of the coil; $k_B$ is the Boltzmann constant; $T$ is the temperature of the sample/coil; $R_s$ and $R_c$ are the resistances of the sample and coil respectively; and $\Delta f$ is the frequency bandwidth. An NMR signal is naturally quite insensitive, so in most NMR experiments multiple repeated NMR signals, or transients, are acquired and then averaged. This averaging increases the SNR by the square root of the number of transients ($N_T$) averaged over. From Equation 2.35, it is of interest to note that the SNR is proportional to the cube of the gyromagnetic ratio of the observed nucleus.³³
3

Analytical Techniques

3.1. NMR Techniques

The single pulse NMR experiment described in Chapter 2, provides an excellent analytical technique by itself. However, by using a sequence of multiple pulses the spin system and its interactions can be manipulated further. These pulse sequences can assist in the acquisition of the NMR signal, extract additional information about the nuclear spins or suppress specific internal interactions. In addition to single pulse NMR experiments this thesis makes use of the following pulse sequence NMR techniques.

3.1.1. The Spin Echo Experiment

Chapter 2.3.2 assumes a perfectly homogenous $B_0$ field where transverse relaxation is only caused by differences in the local field. In reality, the applied field $B_0$ is spatially inhomogeneous. The variations in the applied field felt by each nuclear spin result in transverse magnetisation loss just as the variations in the local fields do. Therefore, the observed transverse relaxation is a combination of both the “homogenous” and “inhomogeneous” contributions. The transverse magnetisation decay is then given by

$$M_t(t) = M_0 \left( e^{-\frac{t}{T_2^*}} \right)$$

where

$$\frac{1}{T_2^*} = \frac{1}{T_2} + \frac{1}{T_2'}.$$  \hspace{1cm} 3.2

The rates of the observed transverse relaxation and the homogenous and inhomogeneous transverse relaxation contributions are given by the characteristic relaxation times $T_2^*$, $T_2$ and $T_2'$ respectively.

The homogenous relaxation is the result of the time-dependent local fields from the internal interactions (see Chapter 2.3.2). The inhomogeneous relaxation is instead caused by spatial variations in the static field, and as such the produced differences in the precession...
frequencies of the individual nuclear spins are time independent. Therefore, the inhomogeneous relaxation can be reversed. The reversal of inhomogeneous relaxation is used advantageously in a spin echo experiment, which consists of two pulses separated by a time delay $\tau$ as shown in Figure 3.1. The first pulse ($\pi/2$) creates the transverse magnetisation that dephases over time $\tau$. In a Hahn echo pulse sequence, the second pulse ($\pi$) rotates the dephased magnetisation components $180^\circ$ around the pulse axis. The order of precession of the dephased components is now reversed allowing faster precessing components to catch up to the slower ones. Therefore, the magnetisation refocuses after a further delay of $\tau$. Hence, the time domain signal then consists of a signal ‘echo’ at $\tau$ which then decays normally.

Echo techniques are useful due to the delayed appearance of the echo signal. The RF pulse in a strong magnetic field can induce mechanical oscillations in the structure of the probe, especially at low frequencies. These acoustic vibrations can in turn generate a signal that is detected by the NMR experiment. The detected “acoustic ringing” in the NMR signal decays rapidly but can overshadow fast relaxing components. The delay in measurement, post an RF pulse in spin echo experiments, allows for the ringing to be avoided.

The Hahn echo ($\pi/2$)-$\tau$-($\pi$) sequence is used for relaxation caused by first order interactions (i.e. those described by a second rank tensor; see Chapter 1.4). However, the refocusing of relaxation due to the quadrupolar interaction (which cannot be described by a second rank tensor alone) is more complex.\(^3\)

For non-selective excitation of an entire quadrupolar lineshape ($\hat{H}_{RF} \gg \hat{H}_Q$), the echo pulse sequence must refocus the magnetisation from the central and satellite transitions created by the first order quadrupolar interaction (see Figure 1.5). Due to the complex evolution of the
multiple quantum coherences, the magnetisation from each transition is maximally refocused by a second pulse with a different flip angle. For the full derivation of the echo amplitudes please refer to the review by Freude and Haase.\textsuperscript{17} The total echo produced by the sequence is therefore a combination of the refocused magnetisation of the separate transitions. The total echo is maximal when using a $(\frac{\pi}{2})$-\(\tau\)-(\(\frac{\pi}{2}\)) sequence, where the two pulses are $\frac{\pi}{2}$ out of phase with each other. Such a pulse sequence is referred to as a solid (or quadrupolar) echo. It is most commonly used for static measurements of quadrupolar nuclei. An additional advantage of using a solid echo, rather than a Hahn echo, for broad quadrupolar lineshapes is the larger uniform excitation bandwidth provided by using a shorter second pulse.

For selective excitation of a quadrupolar lineshape ($\mathcal{H}_{RF} \approx \mathcal{H}_Q$) only the central transition needs to be refocused by an echo pulse sequence. The excitement of the single transition can be imagined as the excitement of a fictitious spin $\frac{1}{2}$ system and, therefore, the Hahn echo sequence, using selective pulse durations (see Chapter 2.2.2), provides the most efficient refocusing of the magnetisation. Smaller flip angles can also be incorporated into a Hahn echo pulse sequence to ensure quantitative results from quadrupolar nuclei, analogously to a single pulse experiment.\textsuperscript{24}

3.1.2. The Saturation Recovery Experiment

The rate of the longitudinal relaxation of an NMR resonance can be useful for determining its environment, due to its relation to the behaviour of the surrounding electrons and nuclei. The saturation recovery experiment is used to find the characteristic relaxation time $T_1$ of an NMR resonance, which describes the rate of the longitudinal relaxation (see Chapter 2.3.1). The basic principle behind this sequence is to apply a $\frac{\pi}{2}$ pulse to remove any longitudinal magnetisation. The longitudinal magnetisation is then allowed to recover for time $t_1$. Then a second $\frac{\pi}{2}$ pulse rotates the recovered longitudinal magnetisation into the $x$-$y$ plane where it is detected. By varying the time $t_1$ and measuring the intensity of the resultant NMR resonances, the recovery of the longitudinal magnetisation can be followed. The plotted results of the saturation recovery will give a function which can be fitted to Equation 2.22 and, therefore, the characteristic relaxation time $T_1$ can be determined.

With this basic experiment, the magnetisation must be allowed to completely return to equilibrium prior to repetition with a different $t_1$ delay. In a system with long $T_1$, this can
cause excessive experimental times and requires some a priori knowledge of $T_1$. In actuality, a chain of $\frac{\pi}{2}$ pulses are rapidly applied with separation times $\tau$ (where $T_2 < \tau \ll T_1$), in place of the singular initial pulse, as shown in Figure 3.2. This ensures the destruction of all net magnetisation due to the complete saturation of the spin system. The recovery profile of the longitudinal magnetisation remains the same, but experiments can be repeated without a delay, as the saturation pulse train removes any remaining magnetisation.\(^{25}\)

3.1.3. The Multiple Quantum MAS Experiment

Frydman and Harwood developed a 2D MAS NMR experiment that manipulates the undetectable multiple-quantum (MQ) transitions to remove the anisotropic components of the second order quadrupole interaction (see Chapter 1.4.1), called MQMAS.\(^{26}\) The frequency shift in the fast MAS regime of the symmetric $\frac{p}{2} \leftrightarrow -\frac{p}{2}$ transitions, which are not affected by the first order interaction, can be separated into isotropic and anisotropic components as described by Freude:\(^{18}\)

$$\omega_0^{[2]_{\text{MAS}}} = \frac{p\omega Q^2}{\omega_0} \left( \frac{2(1 + \eta Q^2)}{15} \left[ I(I + 1) - \frac{3}{4}p^2 \right] - \frac{h(\alpha, \beta, \eta Q)}{3240} [36I(I + 1) - 17p^2 - 10] \right).$$

The phase development $\varphi(t)$ of the multiple-quantum coherence $p$ is described by

$$\frac{\varphi(t)}{t} = \omega_0^{[2]_{\text{MAS}}} - \omega_p^{\frac{p}{2} \rightarrow -\frac{p}{2}}.$$
The sign of the phase development at the multiple-quantum coherence $p$ is inverted for the observable coherence $p = -1$. Therefore, the anisotropic components of the quadrupolar interaction can be cancelled out by manipulating the coherences. The MQMAS sequence allows the phase to develop at coherence $p$ for a duration of $t_1$, before converting to $p = -1$ where it freely evolves over a time of $t_2$. From Equation 3.3, the anisotropic components of the quadrupolar interaction are removed when

$$t_2 = \frac{36I(I + 1) - 17p^2 - 10}{36I(I + 1) - 27} pt_1 = R(I,p)t_1.$$  \hspace{1cm} 3.5

A 2D Fourier transform of the time domain signal with respect to $t_1$ and $t_2$, provides a 2D correlation spectrum with axes $\delta_1$ and $\delta_2$, which represent shifts in the multiple and single quantum dimensions respectively. The 2D spectrum consists of narrow resonance bands, with ridges along the slope of the anisotropic axis, which is given by

$$\delta_1 = R(I,p)\delta_2,$$ \hspace{1cm} 3.6

A projection of the 2D spectrum perpendicular to the slope $R(I,p)$ yields an 1D isotropic spectrum free from quadrupolar broadening.

A shearing transformation can align the ridges along the $\delta_2$ direction, transforming $\delta_1$ into a new isotropic dimension $\delta_{1,\text{shear}}$. The isotropic components of $\delta_1$ and $\delta_2$ are

$$\delta_1 = \delta_{\text{CSiso}} + \delta_{\text{Qiso}}(p) = \delta_{\text{CSiso}} - \frac{2\omega_Q^2 \left(1 + \frac{\eta_Q^2}{3}\right)}{15\omega_0^2} \left[I(I + 1) - \frac{3}{4}p^2 \right]$$ \hspace{1cm} 3.7

and

$$\delta_2 = \delta_{\text{CSiso}} + \delta_{\text{Qiso}}(p = -1) = \delta_{\text{CSiso}} - \frac{2\omega_Q^2 \left(1 + \frac{\eta_Q^2}{3}\right)}{15\omega_0^2} \left[I(I + 1) - \frac{3}{4}\right]$$ \hspace{1cm} 3.8

respectively. The terms $\delta_{\text{CSiso}}$ and $\delta_{\text{Qiso}}$ represent the isotropic components of the chemical shielding shift and the quadrupolar shift. In Equation 3.8, $\delta_2$ gives the centre of gravity of the anisotropic ridge, which is not affected by the transformation. The $\delta_{1,\text{shear}}$ coordinate after the transformation is given by

$$\delta_{1,\text{shear}} = \delta_{\text{CSiso}} + \delta_{\text{Qiso}}^{\text{shear}} = \delta_{\text{CSiso}} + \frac{4\omega_Q^2 \left(1 + \frac{\eta_Q^2}{3}\right)}{51\omega_0^2} \left[I(I + 1) - \frac{3}{4}\right],$$ \hspace{1cm} 3.9
where the quadrupolar shift is positive and $p$ independent. After shearing, the projection of the resonances at the $\delta_1^{\text{shear}}$ and the $\delta_2$ axes provide isotropic and MAS spectrums respectively. To reflect this, $\delta_1^{\text{shear}}$ and $\delta_2$ axes are labelled as $\delta_{\text{iso}}$ and $\delta_{\text{MAS}}$ in this work. The line $\delta_1^{\text{shear}} = \delta_2$ (labelled CS) describes the variable isotropic chemical shift where the quadrupolar shift is zero. The slope $\delta_1^{\text{shear}} = -\frac{10}{17}\delta_2$ (labelled QIS) describe the variable quadrupolar shift at a constant $\delta_{\text{CSiso}}$ value defined by the chosen intercept of CS and QIS. The 1D projections of the individual anisotropic resonances can be obtained from slices in the $\delta_2$ direction in the 2D spectra. Therefore, the 2D MQMAS spectrum distinguishes between NMR resonances by both their isotropic chemical shift and their quadrupolar shift, which greatly assists in the deconvolution of complex NMR lineshapes.

A basic MQMAS experiment requires: RF excitation of the multiple quantum coherences $p$; evolution of these coherences during time $t_1$; reconversion of the coherences into the observable $p = -1$ coherence; and detection of the resultant signal as a function of time $t_2$. The most common pulse sequence for achieving this, and the one used in this thesis, is the $z$-filtered 3QMAS shown in Figure 3.3. The first non-selective pulse excites all coherences and after time $t_1$ the second pulse converts them back to $p = 0$. Both are high power (hard) pulses to optimise the excitation/reconversion efficiency. After a short duration, the third pulse ($z$-filter), which is a weaker (soft) pulse to allow accurate excitation of the CT only,
converts the non-observable $p = 0$ coherence into the observable coherence, allowing detection. The 3-pulse $z$-filter sequence allows simultaneous excitation of both coherence pathways $0 \rightarrow \pm p \rightarrow 0 \rightarrow -1$, compared to a 2-pulse experiment which requires consecutive experiments for the excitation of both the $0 \rightarrow -p \rightarrow -1$ and $0 \rightarrow +p \rightarrow -1$ pathways. Selection of the desired coherence pathway ($p = \pm 3$ for 3QMAS; see Figure 3.3) is achieved by phase cycling.\textsuperscript{18}

3.1.4. Variable Offset Cumulative Spectroscopy

Occasionally, NMR lineshapes are so broad that the frequency range cannot be covered by the excitation bandwidth from a single pulse, as a sufficiently large frequency bandwidth would require an unachievably short pulse duration (Equation 2.13). In these cases, the simple solution is to perform multiple NMR experiments at incremental frequencies across the required frequency range. The sum of the resultant spectra provides a cumulative spectrum that accounts for the entire lineshape. This technique is called variable offset cumulative spectroscopy (VOCS). To ensure that the entire lineshape is uniformly excited the pulse profiles must remain constant, with frequency increments that are less than the excitation bandwidth of an individual pulse. The downside to this technique is the necessary retuning of the probe before each frequency stepped acquisition.\textsuperscript{27}

3.2. Other Analytical Techniques

In addition to solid state NMR this thesis has made use of a few other analytical techniques. A brief description of each is given.

3.2.1. Powder X-ray Diffraction

X-Ray diffraction (XRD) is a useful analytical technique for the determination of crystalline structures. A crystal lattice can act as a set of 3D diffraction gratings for an X-ray beam of similar wavelength to the spacing of planes in the lattice. Constructive interference of the diffracted X-rays upon interaction with the crystalline sample produce a diffraction pattern. Detection and analysis of the diffraction pattern provides information about the spacing of the planes and, therefore, the crystal structure can be inferred.

Constructive interference of the diffracted rays occurs when conditions satisfy Bragg’s law
where \( n\lambda \) are integer multiples of the incident x-ray wavelength, \( d \) is the planar spacing and \( \theta \) is the angle between the incident X-ray and the diffraction plane. The XRD experiment fires a monochromatic X-ray beam at the sample and the detector, at \( 2\theta \), records the intensity of the diffracted X-rays. In a powdered sample, every possible crystalline orientation is represented equally. Therefore, by scanning over a range of \( 2\theta \) angles, all possible diffraction directions of the lattice are attained. The resultant diffractogram plot (intensity versus \( 2\theta \)), maps out all the lattice spacings, \( d \), in the crystal structure. Hence, the crystal structure can be determined.\(^{11}\)

### 3.2.2. Pair Distribution Function XRD

The Bragg peaks in an X-ray diffractogram accurately describe long-range order. Therefore, powder XRD provides accurate structural determination on highly periodic (small unit cell) crystals. However, in more disordered materials the lower periodicity (large unit cells) reduces the long-range order. Instead, the short-range order can be examined to provide the local atomic structure. The short-range order is present in the broad, less well-defined features at high diffraction angles in the diffractogram. By analysing the complete powder XRD pattern, which contains both the Bragg scattering and diffuse scattering data the local structure can be determined.

By Fourier transforming the total diffraction pattern, the pair distribution function (PDF) can be obtained. The PDF function gives the probability of finding atomic pairs separated by a distance \( r \). To describe it, we first must consider the momentum transfer \( Q \) of the scattered X-rays which is given by

\[
Q = \frac{4\pi}{\lambda} \sin \theta
\]

where \( 2\theta \) is the scattering angle. The total diffraction pattern is then described by the normalised structure function \( S(Q) \), which Fourier transformed provides the PDF function \( G(r) \) as

\[
G(r) = \frac{2}{\pi} \int_0^\infty Q[S(Q) - 1] \sin(Qr) \, dQ.
\]

When \( G(r) \) is plotted it presents peaks at \( r \) values corresponding to the interatomic distances. Hence, the PDF can be used for structural determination. To ensure sufficient spatial
resolution for the study of local atomic structure, the diffraction data must be performed using high energy X-rays and with very good counting statistics. Therefore, the majority of PDF XRD experiments are performed using synchrotron X-rays.\textsuperscript{28}

3.2.3. Magnetic Susceptibility Measurements

A magnetic property measurement system (MPMS) can be used to determine the magnetic susceptibility of a material. When introduced to an applied magnetic field $H$, all materials are magnetically polarised due to permanent or induced magnetic dipole moments resulting from the behaviour of the electrons and nuclei (see Chapter 2.1) in the material. The magnetisation $M$ is the measure of the polarisation and is related to the applied field by

$$M = \chi H.$$ \hspace{1cm} 3.13

where $\chi$ is the magnetic susceptibility of the material. The magnetic susceptibility, therefore, defines the magnetic properties of the material. The total flux density, $B$, in the material is then given by

$$B = H + 4\pi M$$ \hspace{1cm} 3.14

in Gaussian cgs units (the preferred unit system of magnetic properties). Notice the different notation used for fields in the discussion of magnetic properties compared to NMR.

The magnetisation, $M$, of a material is measured by the MPMS and therefore the susceptibility, $\chi$, can be determined. The MPMS achieves this by moving the sample through a coil of superconducting wire, in the applied field $H$ produced by a superconducting magnet. The changing flux density $B$ at the coil, due to the magnetisation of the material, induces a current in the coil. The current is detected by a superconducting quantum interface device (SQUID) which is protected from the strong fields by a superconducting magnetic shield. The SQUID acts as a highly linear current-to-voltage converter. Variations in the SQUID output voltage provide a highly accurate measurement of the material’s magnetisation.

For some materials, the magnetic susceptibility, $\chi$, is dependent on $H$. To account for this, $\chi$ is determined by measuring $M$ over a range of $H$ values. In paramagnetic and diamagnetic materials $M$ is linearly dependent on $H$. An applied magnetic field in a diamagnetic material induces a field in the opposite direction and, hence, such materials have a negative $\chi$ value. Conversely, paramagnetic materials produce an induced field in the direction of the applied field and have positive $\chi$ values. Diamagnetic susceptibility is almost completely independent of temperature. The temperature dependence of the paramagnetic susceptibility...
is different for the several types of paramagnetism. In general, the paramagnetic susceptibility is reduced at higher temperatures.\textsuperscript{29}
4

The Development of $^{105}$Pd Solid State NMR Methodology and its Application to Pd Catalyst Systems

4.1. Background

The accessible oxidation states and versatility of palladium, make it a desirable option in many technological applications such as electronics, dentistry and catalysis. The most predominant use of palladium is in automobile catalytic converters, where it catalyses the oxidation of CO.$^{30-31}$ Palladium is also known to be one of the most active and selective alkyne hydrogenation catalysts, with applications in the petrochemical and food industries.$^{32}$ In the pharmaceutical and fine chemical synthesis industries, palladium catalysts play a significant role through the catalysis of carbon-carbon coupling and a range of hydrogenation reactions.$^{33}$ Additionally, palladium catalysts are popular in the development of hydrogen fuel cell materials.$^{34}$

The functional demands on modern catalysts require highly accurate refinements of their proposed crystal structures. A small structural change can significantly alter the function of a catalyst. Most catalytic applications of Pd involve the use of organometallic Pd systems, or the deployment of pure or alloyed Pd metal nanoparticles on various substrates.$^{31-34}$ This renders characterisation by conventional techniques, such as X-ray diffraction (XRD), somewhat problematic as these systems often lack the effective long-range order that enables these measurements. The short-range, element specific nature of solid state NMR provides a useful alternative that can readily probe structural aspects of materials that lack any long-range periodicity. It is an excellent probe for characterising disordered systems, and exhibits great complementarity with other techniques such as diffraction, for long range order information, and vibrational spectroscopies, for motional information.

No thorough NMR investigation of the $^{105}$Pd nucleus in diamagnetic materials has ever been undertaken and the field of $^{105}$Pd solid state NMR is undeveloped and unexplored. The dearth of $^{105}$Pd solid state NMR studies is predominantly a consequence of the extremely large
quadrupole moment \((Q = 66 \text{ fm}^2)\), low gyromagnetic ratio \((\gamma = 1.95 \text{ MHzT}^{-1})\), and modest natural abundance (22 %) of the \(^{105}\text{Pd}\) nucleus.\(^{35}\) The NMR parameters of the \(^{105}\text{Pd}\) nucleus are displayed in Table 4.1 and are compared to other popular quadrupolar NMR nuclei.\(^{35}\)

As shown, \(^{105}\text{Pd}\) has one of the largest \(Q\) values in the NMR periodic table which can cause extreme quadrupole broadening even in systems with small EFGs. For example, by inputting these values into Equation 1.45, the solid state NMR observation of the central transition of a \(^{105}\text{Pd}\) complex is determined to be \(~115\) times broader than a \(^{27}\text{Al}\) complex in the same environment. Unfortunately, the meagre \(\gamma\) and low natural abundance of \(^{105}\text{Pd}\) only further inhibits matters. Even if the NMR line shape of a \(^{105}\text{Pd}\) and a \(^{27}\text{Al}\) nucleus had the same breadth, Equation 2.35 determines that the \(^{105}\text{Pd}\) nucleus would require \(~700,000\) times the number of transients to achieve a similar SNR.

4.1.1. Literature Review

To date, the difficulty of measuring \(^{105}\text{Pd}\) NMR has hampered studies to only very high-symmetry Pd environments generally in beneficial conditions, such as solutions or very low temperatures (< 10 K).
Most of the measurements in the literature occurred on cubic Pd metal. The first $^{105}$Pd NMR measurement was achieved by Seitchik, Gossard and Jaccarino in 1964, where they achieved a continuous wave NMR measurement of Pd metal at temperatures of 1.4 to 300 K. This provided the first measurement of the Pd Knight shift as $-3.1 \pm 0.4 \%$. In 1966, Narath, Fromhold and Jones measured the $^{105}$Pd nuclear relaxation rates for Pd metal at temperatures of 1 - 4 K and this work was later expanded to include measurements of the longitudinal relaxation rate at temperatures of 4 - 300 K (Takigawa and Yasuoka in 1981). By 1973 the scientific community’s interest in palladium hydride pushed Brill and Voitlander to measure the $^{105}$Pd Knight shift of α phase palladium hydride at 75 K.

In 1984, Fedotov and Likholobov claimed to present the first direct observation of $^{105}$Pd NMR in solution. Their measurements were performed on $\text{H}_2\text{PdCl}_6$ in concentrated acid. However, work by Brevard and Granger reported a $^{105}$Pd solution NMR measurement on $\text{K}_2\text{PdCl}_6$ ($\text{D}_2\text{O}$) in 1981.

In 1977 the first solid state $^{105}$Pd NMR measurement on intermetallic Pd was reported by Matsuda, Kohori and Kohara. They performed $^{105}$Pd NMR measurements on the superconductor $\text{UPd}_2\text{Al}_3$, albeit at 4.2 K. Since then no direct measurement of $^{105}$Pd NMR has occurred. In 2004, Rüegger detected in direct spin-spin coupling of $^{105}$Pd nuclei to $^{31}$P using $^{31}$P NMR on Pd(II) complexes. This led to the successful determination of the $J$-coupling constants between $^{105}$Pd and $^{31}$P.

4.2. Chemical Shift Reference

A first step in the development of a methodology to study an under-developed NMR-active nucleus is to determine an appropriate isotropic chemical shift reference; this is to standardize all future $^{105}$Pd chemical shift measurements. The IUPAC recommends a $^{105}$Pd reference of $\text{K}_2\text{PdCl}_6$ in a saturated $\text{D}_2\text{O}$ solution presumably following the report of Brevard and Granger. However, the low solubility of this complex in aqueous solutions limits its use as a $^{105}$Pd chemical shift reference, as a higher concentration solution is preferred to maximise Pd content.

Conversely, this report proposes the solution $\text{H}_2\text{Pd(IV)Cl}_6$ (aq), which was examined by Fedotov and Likholobov and boasts octahedral Pd point symmetry, as an appropriate
chemical shift reference. However, their reported synthetic route facilitates the fast reduction to H₃Pd(II)Cl₄ (planar Pd point symmetry), an observation supported by many industrial processes and extractions at low pH. This species yields a very broad \(^{105}\text{Pd}\) resonance in solution giving limited resolution and accuracy as a chemical shift standard. This study suggests a 0.33 M solution of H₃PdCl₆ in \textit{aqua regia} as the \(^{105}\text{Pd}\) primary chemical shift reference following the synthetic route described by

\[
Pd(s) + 4\text{HNO}_3(aq) + 6\text{HCl}(aq) \rightarrow H_2\text{PdCl}_6(aq) + 4\text{NO}_2(aq) + 4\text{H}_2\text{O}(l).
\]

To synthesize the proposed reference 0.125g of Pd metal sponge was dissolved in 2 mL of concentrated (70 %) nitric acid. Then 2 mL of concentrated (36 %) hydrochloric acid was added dropwise producing a dark red solution. An excess of oxidizing acid is required to hinder the reduction of H₃Pd(IV)Cl₆ to H₃Pd(II)Cl₄. As demonstrated in Figure 4.1, the \(^{105}\text{Pd}\) chemical shift of H₃PdCl₆(aq) exhibits a minor concentration dependence. Despite the shift variation decreasing at lower concentrations of \(\leq 0.15\) M, the relatively high concentration of 0.33 M was selected as the proposed reference to maximise the Pd content and therefore minimise experimental time required.

Furthermore, the proximity to the \(^{39}\text{K}\) (γ = 1.99 MHz/T⁻¹) solid state reference, KCl(s), is very convenient. It allows the use of KCl(s) as an external secondary reference for \(^{105}\text{Pd}\) NMR, eliminating the repetitive handling of \textit{aqua regia} solutions in solid state NMR probes, while requiring only minimal retuning of the NMR probe upon switching observation. The utility of both H₃PdCl₆(aq) and KCl(s) referencing approaches is shown in Figure 4.2, which demonstrates the consistency of these shifts across multiple \(B_0\) field strengths. The cubic

\[
\text{Figure 4.1 The }^{105}\text{Pd NMR chemical shift of H}_3\text{PdCl}_6(aq) \text{ at various concentrations acquired at 7.05 T.}
\]
point symmetry of K in the KCl(s) lattice rigorously restricts the $^{39}$K quadrupolar coupling constant ($C_Q$) to zero\textsuperscript{45} thus creating a field independent reference in the solid state; this has been verified against KCl\textsubscript{(aq)}\textsuperscript{46-47}. The H$_2$PdCl$_6$\textsubscript{(aq)} solution reference shift was set to 0.0 ppm and the $^{39}$K resonance of KCl\textsubscript{(s)} was recorded at a shift position of 17,647 ppm at three fields (14.1 T, 11.7 T and 7.05 T). The field independence of the $^{105}$Pd chemical shift confirms that H$_2$PdCl$_6$\textsubscript{(aq)} does not have a measurable $^{105}$Pd $C_Q$, as observed in some solution species which possess large quadrupole moments $Q$\textsuperscript{48}.

4.3. Experimental

4.3.1. NMR Measurements

Both the static and MAS NMR experiments in this study were performed at room temperature across a range of different magnetic field strengths ($B_0$) using Bruker Avance II+600 (14.1 T), Bruker Avance III-500 (11.7 T), Bruker Avance HD-400 (9.40 T), Bruker HD-300 (7.05 T) and Varian Infinity+300 (7.05 T) spectrometers. All NMR data was processed using TOPSPIN. Simulations of Gaussian/Lorentzian lineshapes were performed with dmfit\textsuperscript{49}.

Solid state NMR of metallic materials has several complications due to the conductivity of the samples. Firstly, the skin effect in conductors causes an exponential decay in the intensity
of EM radiation the deeper it penetrates the material. Therefore, the conducting volume of the sample needs to be small enough to ensure that the RF radiation is exciting nuclei throughout the sample, rather than just the surface. The skin depth $\delta$ is defined as the depth below the surface when the intensity of the radiation has fallen to $\frac{1}{e}$ of its initial value, and is given for conductors in Equation 4.2 where $\rho$ is the resistivity, $\nu$ is the EM frequency, and $\mu$ is the magnetic permeability. The skin depth for Pd metal at a couple of relevant frequencies is stated in Table 4.2, using known values of $\rho$ and $\mu$.\textsuperscript{50-51}

\[
\delta = \sqrt{\frac{\rho}{\pi\nu\mu}} \tag{4.2}
\]

Table 4.2 The skin depth of palladium at the EM frequencies equal to $\nu_0$ ($^{105}$Pd) at 14.1 and 7.05 T.

<table>
<thead>
<tr>
<th>EM Frequency/(MHz)</th>
<th>Skin Depth ((\mu m))</th>
</tr>
</thead>
<tbody>
<tr>
<td>26.6</td>
<td>31.7</td>
</tr>
<tr>
<td>13.3</td>
<td>44.8</td>
</tr>
</tbody>
</table>

Particles with a radius below the skin depth were generally used in this investigation, however to prevent agglomeration of these particles into a mass larger than the skin depth, an insulator was mixed in with the metal. The insulator diluent has the added benefit of reducing the necessary re-tuning of an NMR probe when a conducting material is placed inside the coil. Regardless, care must be taken to ensure precise tuning when changing between metallic samples. Any conducting materials examined in this work were all diluted with 50-75% NaCl\(_{(s)}\). Additionally, a conductive material is difficult to analyse using MAS due to heating caused by the build-up of eddy currents. Therefore, most metallic NMR measurements in this work were taken under static conditions.

4.3.2. $^{105}$Pd Solid State NMR Measurements

All $^{105}$Pd NMR experiments at 14.1, 11.7 and 9.40 T were undertaken using a Varian 9.5 mm MAS probe with a low gamma attachment whereas the 7.05 T experiments were completed using a 9.5 mm Otsuka MAS probe. All data was referenced to the proposed standard of $\text{H}_2\text{PdCl}_6(aq)$ ($\delta_{iso} = 0$ ppm) and the neighbouring KCl\(_{(s)}\) ($\delta_{iso} = 17,647$ ppm).
The $^{105}$Pd NMR experiments on non-metallic samples were performed at 14.1 T ($\nu_0$ ($^{105}$Pd) = 27.49 MHz), 11.7 T ($\nu_0$ ($^{105}$Pd) = 22.93 MHz), 9.40 T ($\nu_0$ ($^{105}$Pd) = 18.30 MHz) and 7.05 T ($\nu_0$ ($^{105}$Pd) = 13.75 MHz) employing an MAS frequency of ~3 KHz where appropriate. A $\pi/2$ pulse length was determined on H$_2$PdCl$_6$(aq) resulting in a selective $\pi/4$ pulse length of 10, 6, 5 and 4 $\mu$s at 14.1, 11.7, 9.40 and 7.05 T respectively. A ($\pi/4$)-$\tau$-($\pi/2$) echo sequence was utilised to diminish ringing effects present at low frequencies. A recycle delay of 0.1 s was used throughout and a rotor synchronised $\tau$ period of 323, 327, 659 and 330 $\mu$s was used for the 14.1, 11.7, 9.40 and 7.05 T experiments, respectively.

The wide line shapes produced by $^{105}$Pd NMR on metallic materials required VOCS (Chapter 3.1.4), to achieve full, uniform excitation. The VOCS frequency range and step-size is dependent on the line shape characteristics of each sample alongside the experimental parameters used; they are provided in Table 4.3. A solid-echo ($\pi/2$)-$\tau$-($\pi/2$) sequence was utilised to avoid ringing effects present at low frequencies, with $\pi/2$ pulse lengths of 10 and 7.5 $\mu$s on the 14.1 and 7.05 T instruments respectively. A recycle delay of 0.01 s was used throughout and a $\tau$ period of 30 and 150 $\mu$s was used for the 14.1 and 7.05 T experiments respectively. The larger $\tau$ period at 7.05 T reflects the greater ringing present in the Otsuka probe.

### Table 4.3 Details of the VOCS $^{105}$Pd static NMR experiments performed on metallic samples.

<table>
<thead>
<tr>
<th>Name</th>
<th>Field (T)</th>
<th>$\nu_0$ Range (MHz)</th>
<th>$\nu_0$ Step-size (MHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd sponge</td>
<td>14.1 T</td>
<td>26.57 - 26.61</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>7.05 T</td>
<td>13.29 - 13.44</td>
<td>0.03</td>
</tr>
<tr>
<td>Pd black</td>
<td>14.1 T</td>
<td>26.57 - 26.61</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>7.05 T</td>
<td>13.23 - 13.38</td>
<td>0.03</td>
</tr>
<tr>
<td>Pd PVP16</td>
<td>14.1 T</td>
<td>26.57 - 26.69</td>
<td>0.02</td>
</tr>
<tr>
<td>Pd/C</td>
<td>14.1 T</td>
<td>26.58 - 26.64</td>
<td>0.02</td>
</tr>
<tr>
<td>Dehydrogenated Pd</td>
<td>14.1 T</td>
<td>26.60 - 26.64</td>
<td>0.02</td>
</tr>
</tbody>
</table>

The $^{105}$Pd NMR experiments on non-metallic samples were performed at 14.1 T ($\nu_0$ ($^{105}$Pd) = 27.49 MHz), 11.7 T ($\nu_0$ ($^{105}$Pd) = 22.93 MHz), 9.40 T ($\nu_0$ ($^{105}$Pd) = 18.30 MHz) and 7.05 T ($\nu_0$ ($^{105}$Pd) = 13.75 MHz) employing an MAS frequency of ~3 KHz where appropriate. A $\pi/2$ pulse length was determined on H$_2$PdCl$_6$(aq) resulting in a selective $\pi/4$ pulse length of 10, 6, 5 and 4 $\mu$s at 14.1, 11.7, 9.40 and 7.05 T respectively. A ($\pi/4$)-$\tau$-($\pi/2$) echo sequence was utilised to diminish ringing effects present at low frequencies. A recycle delay of 0.1 s was used throughout and a rotor synchronised $\tau$ period of 323, 327, 659 and 330 $\mu$s was used for the 14.1, 11.7, 9.40 and 7.05 T experiments, respectively.

The wide line shapes produced by $^{105}$Pd NMR on metallic materials required VOCS (Chapter 3.1.4), to achieve full, uniform excitation. The VOCS frequency range and step-size is dependent on the line shape characteristics of each sample alongside the experimental parameters used; they are provided in Table 4.3. A solid-echo ($\pi/2$)-$\tau$-($\pi/2$) sequence was utilised to avoid ringing effects present at low frequencies, with $\pi/2$ pulse lengths of 10 and 7.5 $\mu$s on the 14.1 and 7.05 T instruments respectively. A recycle delay of 0.01 s was used throughout and a $\tau$ period of 30 and 150 $\mu$s was used for the 14.1 and 7.05 T experiments respectively. The larger $\tau$ period at 7.05 T reflects the greater ringing present in the Otsuka probe.

#### 4.3.3. $^{39}$K and $^{35}$Cl Solid State NMR Measurements

The $^{39}$K NMR experiments at 14.1 T were undertaken using a Varian 9.5 mm MAS probe with a low gamma attachment whereas the experiments at 9.40 T and 7.05 T were completed
using a 9.5 mm Otsuka MAS probe respectively. All data was referenced with respect to KCl\((s)\) \((\delta_{iso} = 47.8 \text{ ppm})\). The \(^{39}\text{K}\) NMR experiments performed at 14.1 T \((\nu_0 \ (^{39}\text{K}) = 27.97 \text{ MHz})\), 9.40 T \((\nu_0 \ (^{39}\text{K}) = 18.61 \text{ MHz})\) and 7.05 T \((\nu_0 \ (^{39}\text{K}) = 13.98 \text{ MHz})\) employed an MAS frequency of 3 KHz throughout. A \(\pi/2\) pulse length was determined on KCl\((s)\) resulting in a selective \(\pi/6\) pulse length of 3, 3 and 2 \(\mu\)s at 14.1, 9.40 and 7.05 T respectively. The single-pulse experiments used a recycle delay of 5 s.

The \(^{35}\text{Cl}\) NMR experiments were performed at 11.7T \((\nu_0 \ (^{35}\text{Cl}) = 49.00 \text{ MHz})\) with an MAS frequency of 12 KHz. The \(^{35}\text{Cl}\) NMR experiments were completed using a Bruker 4 mm HX MAS probe with all data referenced with respect to NaCl\((s)\) \((\delta_{iso} = -46 \text{ ppm})\). A \(\pi/2\) pulse length was determined on NaCl\((s)\) resulting in a selective \(\pi/4\) pulse length of 1 \(\mu\)s being used in the single-pulse experiments, with a recycle delay of 10 s.

4.3.4. \(^1\text{H}, ^{11}\text{B}\) and \(^7\text{Li}\) Solid State NMR Measurements

The \(^1\text{H}\) NMR experiments were performed at 14.1 T \((\nu_0 \ (^{1}\text{H}) = 600.00 \text{ MHz})\) with an MAS frequency of 12 KHz where appropriate. The experiments were completed using a Bruker 4 mm HX MAS probe with all data referenced with respect to alanine\((s)\) \((\text{C}_3\text{H}_7\text{NO}_2; \delta_{iso} = 1.1, 3.5, 8.5 \text{ ppm})\). A \(\pi/2\) pulse length was determined on alanine\((s)\) resulting in a pulse length of 2.5 \(\mu\)s being used in the single-pulse experiments, with a recycle delay of 3 s.

The \(^{11}\text{B}\) NMR experiments were performed at 14.1 T \((\nu_0 \ (^{11}\text{B}) = 192.50 \text{ MHz})\) with an MAS frequency of 12 KHz. The experiments were completed using a boron-free Varian 4 mm HXY MAS probe with all data referenced with respect to NaBH\(_4\)(s) \((\delta_{iso} = -42.06 \text{ ppm})\). A \(\pi/2\) pulse length was determined on NaBH\(_4\)(s) resulting in a selective \(\pi/4\) pulse length of 2.6 \(\mu\)s being used throughout, with a recycle delay of 0.1 s for the single-pulse experiments. The saturation recovery experiments used 300 pulses in the saturation train with a delay of 30 \(\mu\)s.

The \(^7\text{Li}\) NMR experiments were performed at 11.7 T \((\nu_0 \ (^{11}\text{B}) = 194.32 \text{ MHz})\) with an MAS frequency of 30 KHz. The experiments were completed using a Bruker 2.5 mm HX MAS probe with all data referenced with respect to LiCl\((s)\) \((\delta_{iso} = -0.77 \text{ ppm})\). A \(\pi/2\) pulse length was determined on LiCl\((s)\) resulting in a selective \(\pi/4\) pulse length of 2.25 \(\mu\)s being used throughout, with a recycle delay of 600 s for the single-pulse experiments. The saturation recovery experiments used 200 pulses in the saturation train with a delay of 45 \(\mu\)s.
4.3.5. GIPAW-DFT Calculations

Density functional theory (DFT) calculations were performed by G.J. Rees (University of Warwick) using the CASTEP 16 code with the ultrasoft pseudopotential approximation. The generalized gradient approximation (GGA) was employed and adjacent geometry optimisation calculations were performed on all systems. NMR parameter calculation (δiso, CQ, ηQ) invoked the gauge included projector augmented-wave (GIPAW)-DFT method. The GIPAW-DFT calculations were performed with a 2x2x2 k-point grid and a kinetic energy cut-off of 1400 eV.

4.3.6. Powder XRD

XRD patterns were measured on a Panalytical X-Pert Pro MPD diffractometer using Cu Kα1 radiation (λ = 1.5406 Å) at ambient temperature. Scans were between 10 - 70° 2θ for the Pd complexes and 30 - 90° 2θ for the metallic Pd samples. Step sizes varied depending on the timescales required for signal acquisition. XRD patterns were fitted using Rietveld refinement where appropriate.

4.3.7. Pair Distribution Function XRD

Total x-ray scattering experiments were performed by D.S. Keeble on XPDF (beamline I15-1) at Diamond Light Source (Harwell Science and Innovation Campus, UK). Samples were packed into 1 mm borosilicate capillaries and were illuminated with photons of energy 78.34 keV (λ = 0.1583 Å). The scattered intensity was acquired on a Perkin Elmer 1611 CP3, calibrated against a CeO2 standard and integrated in DAWN. The integrated 1D scattering patterns were used directly for Rietveld refinement and were converted to pair distribution functions in GudrunX, while the structural refinements against both the real and reciprocal space data were performed in TOPAS Academic.

4.3.8. Magnetic Susceptibility Measurements

Magnetic susceptibility measurements were performed on a Quantum Design MPMS 5S SQUID Magnetometer. Powder samples were packed into gel capsules and measurements were performed at temperatures of 300 and 5 K and with magnetic fields of 0 to 50,000 Oe. Gaussian cgs units are used with magnetic field strength $H$ in Oe, (mass) magnetisation $M_{mass}$ in emug$^{-1}$ and (mass) susceptibility $\chi_{mass}$ in emug$^{-1}$. 

51
4.3.9. Transmission Electron Microscopy

Transmission electron microscopy (TEM) analysis was used to determine particle sizes of the Pd nanoparticles. Samples were prepared for TEM by sonicating the nanoparticles in ethanol until fully dispersed. The suspension was then placed onto a holey carbon coated Cu grid and dried. Different microscopes were used depending on the location of the experimentation (University of Warwick/ Johnson Matthey Technology Centre/ University of Oxford).

4.4. High Symmetry Palladium Complexes

Once a chemical shift reference has been established for a burgeoning NMR nucleus, the next step is to develop an idea of its chemical shift range by examining a variety of compounds. Three cubic hexa-halogen palladates with octahedral Pd point symmetry (see Figure 4.3) were chosen as model complexes for this initial $^{105}\text{Pd}$ solid state NMR study: $(\text{NH}_4)_2\text{Pd(IV)Cl}_6$, $\text{K}_2\text{Pd(IV)Cl}_6$ and $\text{K}_2\text{Pd(IV)Br}_6$. These complexes are commercially available (Alfa Aesar) and have relatively high Pd contents which will keep experimental

![Crystal structures of complexes](image)

Figure 4.3 The crystal structures of (a) $(\text{NH}_4)_2\text{PdCl}_6$, (b) $\text{K}_2\text{PdCl}_6$ and (c) $\text{K}_2\text{PdBr}_6$ giving the relative atomic positions of Pd (grey), Cl (green), Br (burgundy), N (blue), H (pink) and K (purple).
time minimal. Most importantly, the difficult quadrupolar interaction should be negligible due to the highly symmetrical environment.

4.4.1. $^{105}$Pd NMR Chemical Shift Range

The $^{105}$Pd solid state NMR spectra of the three complexes are displayed in Figure 4.4 and reveal the sensitivity of the $^{105}$Pd NMR chemical shift to changes in the Pd environment. The change in anion from $[\text{PdCl}_6]^2^-$ to $[\text{PdBr}_6]^2^-$ produces a large $\sim$800 ppm shift to lower frequency. This greater shielding of the Pd nucleus in $\text{K}_2\text{PdBr}_6$, is due to the lower

![Figure 4.4](image-url)

Figure 4.4 The multifield $^{105}$Pd MAS (3 KHz) NMR spectra of the three inorganic palladium complexes $(\text{NH}_4)_2\text{PdCl}_6$ (red), $\text{K}_2\text{PdCl}_6$ (blue) and $\text{K}_2\text{PdBr}_6$ (green) acquired at 14.1 T, 11.7 T, 9.40 T and 7.05 T.
electronegativity of the heavier halogen.\textsuperscript{57} Changing the cation in the second coordination sphere from K\textsuperscript+ to (NH\textsubscript{4})\textsuperscript{+}, also produces a significant shift of \textasciitilde10 ppm towards higher frequency. This sensitivity to positional substitution of next nearest neighbours is very promising for the use of \textsuperscript{105}Pd solid state NMR as an analytical tool for structural determination.

4.4.2. Evidence of a Quadrupolar Interaction in the \textsuperscript{105}Pd NMR Results

A closer look at the line shapes of the (NH\textsubscript{4})\textsubscript{2}PdCl\textsubscript{6} and K\textsubscript{2}PdCl\textsubscript{6} resonances in Figure 4.4 reveals an asymmetric tailing to lower frequencies. This asymmetry, instead of the expected Gaussian/Lorentzian line shape, is indicative of a second order quadrupolar interaction in a disordered system, as detailed in Chapter 1.4.1.\textsuperscript{58-59} To investigate further, the \textsuperscript{105}Pd NMR spectra for the three complexes was compared across multiple fields: 14.1 T, 11.7 T, 9.40 T

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4_5.png}
\caption{The $\delta_{CG}(^{105}\text{Pd})$ of (NH\textsubscript{4})\textsubscript{2}PdCl\textsubscript{6} (red), K\textsubscript{2}PdCl\textsubscript{6} (blue) and K\textsubscript{2}PdBr\textsubscript{6} (green) against the inverse square of the Larmor frequency $\nu_0$.}
\end{figure}

<table>
<thead>
<tr>
<th>Complex</th>
<th>$\delta_{iso}$ (exp.) /MHz</th>
<th>$P_Q$ (exp.) /MHz</th>
<th>$P_Q$ (calc.) /MHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>(NH\textsubscript{4})\textsubscript{2}PdCl\textsubscript{6}</td>
<td>209.3 ± 0.9</td>
<td>0.47 ± 0.05</td>
<td>0.00</td>
</tr>
<tr>
<td>K\textsubscript{2}PdCl\textsubscript{6}</td>
<td>200.7 ± 0.3</td>
<td>0.50 ± 0.02</td>
<td>0.00</td>
</tr>
<tr>
<td>K\textsubscript{2}PdBr\textsubscript{6}</td>
<td>−585.0 ± 1.0</td>
<td>0.81 ± 0.05</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Table 4.4 Experimental (NMR) and calculated (CASTEP) values of the isotropic shift and quadrupolar product of the three Pd complexes.
and 7.05 T. Figure 4.4 shows that the three complexes all present a field dependent chemical shift. As previously discussed in Chapter 1.4.1, a field dependent chemical shift is often due to a second order quadrupolar shift.

By plotting the centre of gravity of each resonance ($\delta_{CG}$) against the inverse square of the Larmor frequency squared ($\nu_0^{-2}$) at each field (Figure 4.5), and then applying Equation 1.47, the quadrupolar parameters for each complex can be determined. The complexes (NH$_4$)$_2$PdCl$_6$, K$_2$PdCl$_6$ and K$_2$PdBr$_6$ have small, but certainly not insignificant, quadrupolar products $P_Q$ in the range of 0.47 to 0.81 MHz (Table 4.4; $P_Q = C_Q$, assuming an $\eta_Q$ of 0). This conflicts with the complexes’ reported crystal structures which depict octahedral Pd(IV) centres (see Figure 4.3).$^{60-61}$ The high symmetry Pd environment should ensure that there are

![Figure 4.6](image_url)

Figure 4.6 The powder XRD patterns for (NH$_4$)$_2$PdCl$_6$ (s), K$_2$PdCl$_6$ (s) and K$_2$PdBr$_6$ (s) displayed with relative intensities against 2$\theta$. The data is presented with the XRD pattern in black, the Reitveld refinement fitting in red, the cubic $Fm-3m$ profile in blue, and the tetragonal $P4/mmm$ profile in green.
no EFGs present, as demonstrated by the DFT calculations on these structures, which produced $P_Q$ values of 0.00 MHz (Table 4.4). Disagreement with the published XRD structures suggests that these complexes contain some deviation from the predicted cubic structure.

The samples were tested with powder XRD to verify their high purity. The Rietveld refinement fitting of the patterns for each sample confirmed the structure as the cubic $Fm\bar{3}m$ phase, as shown in Figure 4.6. Each of the samples contain a small impurity (2 - 3%) of their respective tetragonal $P4/mmm$ phases: $(NH_4)_2Pd(II)Cl_4$, $K_2Pd(II)Cl_4$ and $K_2Pd(II)Br_4$. It is unlikely that these impurity phases are causing the quadrupolar interaction observed in the $^{105}$Pd NMR spectra. The square planar Pd symmetry of the tetrahalides would present a significant EFG and, therefore, an extremely broad NMR resonance that is presumed to be undetectable by these measurements.

However, to ensure that the tetrahalide impurities had no effect on the $^{105}$Pd NMR spectra, $K_2PdCl_6$ was washed with aqua regia. Stirring the powder into an aqua regia solution for 30 minutes before filtering, washing and drying will remove/oxidise any of the soluble $K_2Pd(II)Cl_4$, leaving only the insoluble $K_2PdCl_6$. The $^{105}$Pd MAS NMR spectra of this “washed” sample is compared to the original sample in Figure 4.7(a, b). There is no discernible difference between the two spectra, indicating that the tetrahalide impurities present in the complexes are not the cause of the observed quadruple interactions. Additionally, Figure 4.7(c) compares the MAS and static $^{105}$Pd NMR of $K_2PdCl_6$ to rule out

![Figure 4.7](image-url)

Figure 4.7 The $^{105}$Pd NMR spectra acquired at 9.40 T of (a) unmodified $K_2PdCl_6(s)$ and (b) aqua regia washed $K_2PdCl_6(s)$ under MAS (3KHz) alongside (c) unmodified $K_2PdCl_6(s)$ under static conditions. Spinning sidebands are marked by an asterix.
varying temperatures due to MAS as an alternative cause of the different chemical shifts at each field. The determined shifts of $\Delta CG = 197 \pm 2$ ppm ($\Delta iso = 200.7 \pm 0.3$ ppm/$P_Q$ value of 0.50 MHz) from both conditions confirms that the observed field-dependent behaviour of the resonance is a second-order quadrupole contribution.

4.4.3. $^{39}$K and $^{35}$Cl Solid State NMR

The K containing complexes, $K_2$PdCl$_6$ and $K_2$PdBr$_6$, were investigated with multi-field $^{39}$K MAS NMR. The spectra, shown in Figure 4.8(a), display single narrow resonances at $\delta_{iso} = −10.3 \pm 0.5$ ppm and $\delta_{iso} = −16.4 \pm 0.5$ ppm for $K_2$PdCl$_6$ and $K_2$PdBr$_6$ respectively. Figure 4.8(b) reveals that the $^{39}$K chemical shifts do not exhibit a field dependence; the less substantial $^{39}$K quadrupole moment does not produce a large enough $P_Q$ to influence the shift position by a measurable amount at accessible magnetic fields. However, the spinning sideband manifolds, highlighted in the $^{39}$K spectra, indicate the presence of non-zero EFGs at the K site.

Figure 4.8(a) The $^{39}$K MAS (3 kHz) NMR spectra of $K_2$PdCl$_6$(s) and $K_2$PdBr$_6$(s), in blue and green respectively, acquired at 14.1 T, 9.40 T and 7.05 T. Spinning sidebands are marked by an asterisk and have been enlarged for the 14.1 T spectra. (b) The $\delta_{CG}(^{39}$K) of $K_2$PdCl$_6$(s) in blue and $K_2$PdBr$_6$(s) in green against the inverse square of the Larmor frequency $\nu_0$. (c) The $^{35}$Cl MAS (12 kHz) NMR spectra of $(NH_4)2$PdCl$_6$(s) and $K_2$PdCl$_6$(s), in red and blue respectively, acquired at 14.1 T. The resonance given by the internal NaCl(s) reference is marked with a dashed grey line.
For a nucleus in a perfect cubic environment the quadrupole effects are non-existent; however, “close-to-cubic” local environments will produce quadrupole satellite spinning sidebands. Dislocations, defects and impurities in the material create a discernible quadrupole interaction that produces STs that are detectable once reduced to a spinning sideband manifold, despite not always producing a resolvable quadrupolar NMR line-shape. In fact, it is this phenomenon that allows nominally cubic KBr to be used as the default method of setting the magic angle via $^{81}\text{Br}$ NMR spinning sideband analysis. These quadrupolar spinning sideband manifolds are also observable in the $^{105}\text{Pd}$ NMR data (Figure 4.7(a, b)).

Similarly, the Cl containing complexes, (NH$_4$)$_2$PdCl$_6$ and K$_2$PdCl$_6$, were investigated with $^{35}\text{Cl}$ MAS NMR as shown in Figure 4.8(c). The spectra present single narrow resonances at $\delta_{\text{iso}} = 74 \pm 2$ ppm and $\delta_{\text{iso}} = 3.6 \pm 0.8$ ppm for (NH$_4$)$_2$PdCl$_6$ and K$_2$PdCl$_6$ respectively. The resonances are accompanied by low intensity spinning sideband manifolds giving further credence to the presence of EFGs in the structures.

4.4.4. PDF Analyses

The detection of EFGs in the structures, by the $^{105}\text{Pd}$ NMR studies, suggests the technique is sensitive to some deviation from the perfect cubic structure reported by the literature, that cannot be detected by powder XRD. To find this “deviation”, high resolution X-ray PDF analysis was performed on the three Pd complexes.

The real space PDF data and fits are presented in Figure 4.9. The very sharp reflection at just over 2 Å in each fit represents a well-defined rigid PdX$_6$ (X = Cl, Br) bond. The Pd-X bond lengths are highly uniform and the local symmetry of the octahedral unit is strictly preserved, as reported by the literature. The octahedral hexahalopalladate unit is so well defined that the reflection is, surprisingly, narrower than the resolution of the experiment; hence the truncation artefacts collaring the reflection. Therefore, it is highly unlikely that the deviation from cubic symmetry occurs within the octahedral units.

The modelling of the real space PDF for K$_2$PdB$_6$ required the additional refinement of a large atomic displacement parameter for the K site, exceeding what would be expected for a normal thermal parameter range. This can be seen in the PDF fits by comparing the data for K$_2$PdCl$_6$ and K$_2$PdBr$_6$. The bond lengths determined from the literature structures are
presented in Table 4.5, where X represents the halogen atom \((X = \text{Cl}/\text{Br})\).\(^{61}\) Both contain a narrow Pd-X reflection, as discussed, and then a broader reflection \((3 - 4 \, \text{Å})\) which
encompasses the following bond lengths: X-X within the octahedral unit, X-X between the octahedral units and K-X. The PDF fit for $K_2PdCl_6$ then has a reflection at 4.2 Å representing the K-Pd bond length. Importantly, this K-Pd bond length is “missing” from the $K_2PdBr_6$ PDF fit due to the hypothesized positional disorder on the K ($\frac{1}{4}, \frac{1}{4}, \frac{1}{4}$) positions.

It is noted from Table 4.4 that $K_2PdBr_6$ exhibits the largest $^{105}$Pd EFG of the three complexes ($P_Q = 0.81$ MHz). In contrast, the complexes with lower $P_Q$, $(NH_4)_2PdCl_6$ and $K_2PdCl_6$, did not require an atomic displacement parameter on the cation position for accurate fitting. It is therefore suggested that these PDF experiments are sensitive to the larger positional disorder on the K site in $K_2PdBr_6$, whereas the $^{105}$Pd NMR technique is also sensitive to the hypothesized smaller disorder at the cation sites in the chloride complexes.

### 4.5. Palladium Metal Particles

As discussed in Chapter 4.1.1, Pd metal is one of the few materials that has previously been investigated with $^{105}$Pd solid state NMR. This is due to its fcc structure reducing the EFG in the Pd environment to a minimum, similarly to the octahedral Pd complexes. All the previous $^{105}$Pd NMR studies on Pd metal examined pure Pd powders with particle sizes > 40 μm.\(^{36-39}\)

Not only does this work provide a more thorough study of $^{105}$Pd solid state NMR on Pd metal, but it also studies particle sizes and systems that are more relevant to Pd metal’s use in catalysis. The various Pd metal systems that have been investigated are detailed in Table 4.6. Pd black, Pd nanoparticles on carbon and polyvinylpyrrolidone (PVP) stabilised nanoparticles are all commonly used as catalysts.\(^{63-65}\)

#### 4.5.1. Synthesis

Pd sponge is commercially available from Alfa Aesar with a 100+325 mesh size (44 - 149 μm) and 99.95% purity. The Pd black sample was produced by the Johnson Matthey Technology Centre in Sonning Common, UK. A typical synthesis involves the precipitation of Pd black from a solution of $(NH_4)_2PdCl_6$, formic acid and KOH.\(^{65}\) The carbon supported Pd nanoparticles were produced by I.T. Ellis from the University of Oxford. The synthesis is described in Chapter 4.7.1 and in greater detail in the thesis of Ellis.\(^{66}\)
The PVP stabilised Pd nanoparticles were synthesized by the author via two different methods to produce the different particle sizes. The methodology for producing Pd PVP16 involves refluxing 40 ml of water, 200 ml of ethylene glycol, 2.432 g of Pd(acac)$_2$ (palladium acetylacetonate), and (palladium acetylacetonate), and 13.34 g of PVP$_8000$ (molecular weight = 8,000 gmol$^{-1}$) for 4 hours at 400 K. The methodology for producing Pd PVP6 is slightly different, refluxing 120 ml of H$_2$O, 104 ml of methanol, 7 ml of 12.1 wt% solution Na$_2$PdCl$_4$, and 6g of PVP$_{8000}$ for 3 hrs at 350 K. The alcohol reduces the Pd(II) complex and the PVP enwraps the Pd nanoparticles before they can agglomerate. Changing the reactants and temperature alters the speed of the decomposition of the Pd(II) complexes allowing different sized particles to be produced. The resultant solutions were then washed with acetone and centrifuged to acquire colloids that produced the Pd nanoparticles upon evaporation.

### 4.5.2. $^{105}$Pd Solid State NMR

As discussed in Chapter 1.3.5, metallic materials have an additional interaction: the Knight shift. In $^{105}$Pd NMR of Pd metal the Knight shift is the dominant interaction, despite the strength of its quadrupole moment. The electron configuration of Pd is simplistically described as [Kr]$4d^{10}\cdot{}^5s^1$ due to its overlapping $s$ and $d$ bands at the Fermi level. Unpaired electrons in the $d$ orbital contribute to the paramagnetic susceptibility of Pd and result in a large $K_{cp}$ component of the Knight shift. The negative $K_{cp}$ component is responsible for the very large $K$ of $-3.0 \pm 0.4$ \% reported by Seitchik, Gossard and Jaccarino. $^{36}$

The multifield $^{105}$Pd NMR spectra of Pd metal sponge and Pd black are presented in Figure 4.10. Both Pd metal samples present with one identical, broad NMR resonance as expected. No quadrupole interaction is observed in either of the metal samples evidenced by the lack

<table>
<thead>
<tr>
<th>Name</th>
<th>Particle diameter / (nm)</th>
<th>Support</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd sponge</td>
<td>44 - 149 (10$^3$)</td>
<td>-</td>
<td>Alfa Aesar</td>
</tr>
<tr>
<td>Pd black</td>
<td>20 - 150</td>
<td>-</td>
<td>JMTC$^\gamma$</td>
</tr>
<tr>
<td>Pd/C</td>
<td>13 ± 9</td>
<td>C$^\beta$</td>
<td>Oxford</td>
</tr>
<tr>
<td>Pd PVP16</td>
<td>16 ± 3</td>
<td>PVP$^a$</td>
<td>JMTC$^\gamma$</td>
</tr>
<tr>
<td>Pd PVP6</td>
<td>6 ± 5</td>
<td>PVP$^a$</td>
<td>JMTC$^\gamma$</td>
</tr>
</tbody>
</table>

Table 4.6 Particle diameter, loading, support type and source of the various Pd metal samples investigated. Particle diameters were determined via TEM analysis.

$^a$polyvinylpyrrolidone; $^\beta$carbon black; $^\gamma$Johnson Matthey Technology Centre
of any field dependence in their shifts. Any quadrupolar shift resulting from the cubic structure will be negligible, at least when overshadowed by the paramagnetic broadening of the Pd metal resonance. The Pd metal sponge gives a more precise \( K \) of \(-3.205 \pm 0.006\) % (at room temperature), which is corroborated by the Pd black shift and is in agreement with the previously reported value.

The \(^{105}\text{Pd}\) NMR of the Pd metal samples are then compared to the other Pd nanoparticle samples in Similarly, it is believed that the reduced particle size in the Pd metal particles results in the observed \( K \) distribution. Adding to this, deviation from cubic symmetry will cause a; their NMR parameters are presented in Table 4.7. The results show no discernible difference in the structure of the micron-sized Pd sponge and the nano-sized Pd black. However, supported nanoparticles present very different NMR spectra. Pd PVP16 and the Pd/C samples have similar particle diameters (16 ± 3 and 13 ± 9 nm respectively); both present with broad resonances and give a \( K \) that is shifted to higher frequencies. This is due to a distribution of reduced Knight shift values presumably caused by a deviation from the cubic Pd metal structure.

Comparative results were observed by Rees et al. in their investigation of Pt nanoparticles using \(^{195}\text{Pt}\) NMR.\(^{69}\) Their results showed that 5 nm diameter Pt particles produced a broad line shape consisting of resonances with a range of \( K \) values. Each resonance represented a sub-surface layer of the Pt particle, with the core layer resonance presenting with the bulk Pt

Figure 4.10 The \(^{105}\text{Pd}\) static VOCS NMR of Pd sponge (red) and Pd black (black), at 14.1 T and 7.05 T.
metal $K$ and the other layers having a reduced $K$ moving towards the surface. In particles that are sufficiently small, the ratio of atoms in these subsurface layers to in the bulk is large enough that they can be observed by NMR.

Similarly, it is believed that the reduced particle size in the Pd metal particles results in the observed $K$ distribution. Adding to this, deviation from cubic symmetry will cause a quadrupolar broadening, unlike in $^{195}$Pt ($I = 1/2$). It could also be argued that the support

<table>
<thead>
<tr>
<th>Name</th>
<th>$K$ (ppm)</th>
<th>FWHM (KHz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd sponge</td>
<td>$-32,050 \pm 60$</td>
<td>$13 \pm 1$</td>
</tr>
<tr>
<td>Pd black</td>
<td>$-32,110 \pm 90$</td>
<td>$16 \pm 1$</td>
</tr>
<tr>
<td>Pd/C</td>
<td>$-31,500 \pm 400$</td>
<td>$80 \pm 10$</td>
</tr>
<tr>
<td>Pd PVP16</td>
<td>$-31,100 \pm 400$</td>
<td>$80 \pm 10$</td>
</tr>
<tr>
<td>Pd PVP6</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 4.7 The experimentally determined $^{105}$Pd NMR parameters, Knight shift $K$ and full-width at half-maximum FWHM, of the various Pd metal particles.
systems introduced the disorder to the metallic structure instead. However, the similarity in the spectra between the two different support types examined puts doubt on this hypothesis, as does the different NMR result from Pd PVP6 (6 ± 5 nm). No observable NMR resonance could be detected on these smaller particles. This can be explained by the smaller particles having a greater ratio of Pd atoms in a disordered environment allowing for such a large $K$ distribution, alongside the associated quadrupolar broadening, that the resonance was too broad to be observed in the given timeframe.

4.6. Palladium Hydride

Palladium hydride is a system of great scientific interest. It was first examined as early as 1866\textsuperscript{70} and has continued to be studied extensively, with a wide range of experimental and theoretical techniques, up to the present day.\textsuperscript{71-73} The most exceptional of Pd metal’s interactions with hydrogen is its affinity for hydrogen absorption. At room temperature and atmospheric pressure, Pd will readily absorb a volume of $\text{H}_2(\text{g}) \sim 900$ times its own volume. By heating the material, the hydrogen is easily expelled from the Pd lattice. Additionally, the palladium structure suffers virtually no macro-disruption under bulk hydrogenation, in comparison to the other transition metals which can also absorb large amounts of hydrogen.\textsuperscript{71} Accordingly, the use of palladium as a hydrogen storage material has driven much of the interest in the material. However, the study of the mechanics behind the hydrogen absorption

![Diagram of the fcc Pd metal lattice highlighting the octahedral (red) and tetrahedral (blue) interstitial sites.](image.png)

Figure 4.12 A diagram of the $fcc$ Pd metal lattice highlighting the octahedral (red) and tetrahedral (blue) interstitial sites.
are also useful for better understanding the role of Pd in catalysing hydrogenation reactions. Therefore, palladium hydride is an attractive material to be investigated with the newly developed $^{105}$Pd solid state NMR methodology.

Hydrogen inserts into the octahedral interstitial sites of the $fcc$ Pd lattice, as shown by Figure 4.12, causing an isotropic lattice expansion. Pd-H$^{\text{int}}$ is described as having two phases, $\alpha$ and $\beta$, which differ only in their hydrogen content and increased lattice parameters. The dilute $\alpha$-(PdH$_x$) exists when $x < 0.015$ (at room temperature) and its lattice parameter increases to 0.3894 nm, when compared to 0.3890 nm for pure Pd. Above that hydrogen concentration (and below a critical temperature) the $\alpha$ and $\beta$ phases coexist, until the pure $\beta$-(PdH$_x$) phase begins at $x > 0.607$ (at room temperature) with a significantly larger lattice parameter of 0.4025 nm. The Pd-H$^{\text{int}}$ P-C-T (pressure-composition-temperature) isotherms have been thoroughly studied and the saturation H/Pd ratio achieved under ambient conditions is $\sim$0.7.

Hydrogenation and dehydrogenation is known to cause permanent changes in the mechanical and electrical properties of Pd. These changes are also evident in the hysteresis of pressure isotherms, and various other physical measurements, of hydrogenation and dehydrogenation cycles. These physical variations are manifestations of dislocations and vacancies in the Pd structure caused by the $\alpha/\beta$ miscibility gap. The difference in volume between the two phases causes dislocations to arise during the $\alpha \rightarrow \beta$ and $\beta \rightarrow \alpha$ phase transitions. Positron lifetime spectroscopy determined the concentration of vacancies formed under a hydrogenation and dehydrogenation cycle to pure $\beta$ phase (at room temperature) to be of the order of $10^{-3} - 10^{-2}$, significantly higher than Pd at thermal equilibrium.

4.6.1. Synthesis

Pd-H$^{\text{int}}$ samples for solid state NMR were produced by exposing Pd sponge (Chapter 4.5.1) to a H$_2$ atmosphere (ambient conditions) for at least 30 minutes and then packing the modified metal into NMR rotors while under the same conditions. For the $^1$H NMR measurements, 4 mm MAS rotor inserts, provided by cortecnet, were used to keep the samples in air tight conditions. Similarly, the $^{105}$Pd NMR was performed on samples contained in custom made 9.5 mm glass inserts sealed with Precision Seal® rubber septa caps. Dehydrogenated samples were synthesized by leaving a Pd-H$^{\text{int}}$ sample exposed to the atmosphere, allowing the H to escape the Pd lattice as H$_2$(g) over several days.
4.6.2. $^1$H Solid State NMR

The prepared Pd-H$^{19}$ samples were examined with $^1$H solid state NMR. Figure 4.13(a) shows the spectrum for the synthesized palladium hydride sample in an H$_2$ atmosphere, which contains three distinct resonances. A large narrow resonance at $\delta_{iso} = 4.3 \pm 0.1$ ppm is assigned as free H$_2(g)$, a broader resonance at $\delta_{iso} = 32.9 \pm 0.2$ ppm is assigned as hydrogen within the Pd lattice, and a small resonance at $\delta_{iso} = 0.9 \pm 0.1$ ppm is believed to be an organic impurity. The H$_2(g)$ resonance confirms that the rotor has retained its hydrogen atmosphere and, therefore, the palladium hydride will be at saturation as $\beta$-PdH$_{0.7}$.

The large positive chemical shift, relative to the normal $^1$H chemical shift range, is from a Knight shift effect due to the metallic environment of the Pd lattice, which confirms the presence of palladium hydride. The positive $K$ of $\beta$-PdH$_{0.7}$ corroborates the previous results collated by Brill and Voitlander on $\beta$-PdH$_x$. However, results presented here give a higher chemical shift than the $\beta$-PdH$_x$ chemical shift range determined by their study (19 - 26 ppm at 298 K).

Figure 4.13(b) shows a spectrum of the same sample once the H$_2$ atmosphere has been removed, allowing the hydrogen to escape the Pd lattice. The resonances assigned to $\beta$-PdH$_{0.7}$ and H$_2(g)$ are both removed whereas the small contaminant resonance has remained,

![Figure 4.13](image)

Figure 4.13 The $^1$H NMR of palladium hydride samples acquired at 14.1 T including: MAS (12 KHz) NMR spectra of (a) PdH$_{0.7(s)}$ in a H$_2(g)$ atmosphere and (b) the same sample once the hydrogen has been released; and (c) static in-situ measurements of palladium hydride at 32 s, 152 s, 482 s, 662 s, 1427 s and 3992 s after the H$_2(g)$ atmosphere was first released; and (d) a static measurement of the rotor background present in this setup.
which corroborates the NMR assignments. To investigate the Pd-H$^{\text{int}}$ phases with lower hydrogen content, the H was allowed to escape from the Pd lattice in-situ while being observed with $^1$H NMR. Figure 4.13(c,d) shows the $\beta$-PdH$_x$ resonance gradually diminishing in intensity over a period of ~1 hr, as expected. Additionally, as the H/Pd ratio decreases the $\beta$-PdH$_x$ shift moves towards lower values of 24 - 21 ppm, suggesting that Brill and Voitlander were working with a lower H concentration.

The dependence of $K$ on the H/Pd ratio is due to the changes in the electron configuration. As H is first absorbed in the $\alpha$ phase, its electrons fill the holes in the Pd 4$d$ orbital, which decreases the density of $d$ states at the Fermi level, therefore reducing the susceptibility and decreasing the resultant negative $K_{\text{cp}}$ component.$^{39,67,80}$ This has been observed by Brill and Voitlander$^{39}$ and corroborated by studies on the varying susceptibility of palladium hydride systems.$^{67,80-81}$ The pure $\beta$ phase begins once the susceptibility has reached zero. Now, as hydrogen content increases, the electron density of the 5$s$ orbital increases. As seen in Equation 1.37, this results in an increase of the positive $K_{\rho}$ component.$^{39,81}$ This causes the Knight shift to increase with hydrogen content over the whole H concentration range, and explains why the $^1$H Knight shift range observed in this study is positive.

4.6.3. $^{105}$Pd Solid State NMR

Once the $\beta$-PdH$_{0.7}$ synthesis had been confirmed via $^1$H NMR, the system was studied using $^{105}$Pd static VOCS NMR. The spectrum of PdH$_{0.7}$ is shown in Figure 4.14(b) and clearly

![Figure 4.14 The $^{105}$Pd static VOCS NMR of (a) Pd metal sponge, (b) PdH$_{0.7(a)}$ in a H$_2(g)$ atmosphere and (c) the same sample once the hydrogen has been released at 14.1 T.](image-url)
does not return an observable $^{105}\text{Pd}$ NMR resonance. This is despite sweeping a Knight shift range down to 0 ppm, far beyond that shown in Figure 4.14. However, due to the large predicted change in $K$ and the long $^{105}\text{Pd}$ NMR experimental times, it is possible that the resonance was missed in the search. However, it is more likely that the significant lattice expansion of PdH$_{0.7}$ may have introduced enough disorder in the structure, that the combined Knight shift and quadrupolar interactions have broadened the resonance beyond detection of the current methodology, similarly to the Pd PVP6 results.

A more successful result was obtained on the Pd sponge sample post hydrogen release, as shown in Figure 4.14(c). However, the NMR result does not return to that given by the unmodified Pd sponge (Figure 4.14(a)). The $^{105}\text{Pd}$ resonance has shifted to a less negative $K$ of $-31,300 \pm 100$ ppm and has broadened (FWHM = $24 \pm 1$ KHz). This result is due to the dislocations introduced into the Pd metal structure during the hydrogenation/dehydrogenation cycle.\textsuperscript{75-78} The deviation from cubic symmetry presents in the NMR as a reduced Knight shift and a broader resonance, as seen in the Pd nanoparticles (Chapter 4.5.2). The dislocations have previously been directly detected only by positron lifetime spectroscopy,\textsuperscript{78} once again demonstrating the sensitivity of $^{105}\text{Pd}$ NMR to structural distortions.

4.7. Boron and Lithium Interstitial Doping of Pd Nanoparticles

As demonstrated by the palladium hydride system, light elements can be inserted into the octahedral interstitial sites in the Pd lattice, significantly altering the geometry and electronic properties of the system. Therefore, interstitial modification of Pd can be used to alter its catalytic properties. The most simple alteration, occurs when the filling of the interstitial sites with a different atom blocks the formation of Pd-H\textsuperscript{int}, which can improve catalytic selectivity in hydrogenation.\textsuperscript{82} An advantage over other catalyst modifications, is that interstitial doping does not block active sites on the Pd surface.\textsuperscript{83}

Palladium with interstitial carbon has been studied previously and has been found to have a maximum C/Pd ratio of 0.15.\textsuperscript{84} Like Pd-H\textsuperscript{int}, Pd-C\textsuperscript{int} undergoes a lattice expansion increasing the lattice parameter up to 0.399 nm.\textsuperscript{85} The electronic properties are altered via a band overlap between the C 2$p$ and the Pd 4$d$ electrons.\textsuperscript{86} Pd-C\textsuperscript{int} has been shown to be a selective catalyst in a number of reactions.\textsuperscript{87-88}
Additionally, Pd-B\textsuperscript{int} has been previously studied and was found to have a maximum B/Pd ratio of 0.20, alongside a lattice parameter increase to 0.402 nm.\textsuperscript{89} A higher B/Pd ratio has recently been reported, although the heavier B doping resulted in structural rearrangement of the Pd lattice into a hexagonal crystal structure.\textsuperscript{90} Electronically, Pd-B\textsuperscript{int} is similar to Pd-C\textsuperscript{int}, as the B 2p band is almost degenerate with the Pd 4d band. Pd-B\textsuperscript{int} has been found to be an effective catalyst in selective hydrogenations and formic acid decomposition.\textsuperscript{91-92}

Recently, I.T. Ellis (University of Oxford) has further investigated the synthesis, physical structure, electronic properties and catalytic abilities of Pd-B\textsuperscript{int}. The novel Pd-Li\textsuperscript{int} is also synthesized for the first time and investigated in parallel to Pd-B\textsuperscript{int}.\textsuperscript{66,93} In addition to his analyses, this work used the newly developed \textsuperscript{105}Pd solid state NMR alongside \textsuperscript{11}B solid state NMR, \textsuperscript{7}Li solid state NMR and magnetic susceptibility measurements to assist in the determination of the structure of the interstitially modified Pd nanoparticles.

4.7.1. Synthesis

The Pd-B\textsuperscript{int} and Pd-Li\textsuperscript{int} catalysts were previously synthesized as nanoparticles supported on carbon with a catalyst loading of 5 wt\%. This work focuses on systems with a loading of 45 ± 2 wt\%. This higher loading is not representative of how the materials would be used in catalysis, but is useful for structural determination by techniques that benefit from a higher Pd content such as \textsuperscript{105}Pd NMR. By investigating the higher loaded materials, it is hoped that structural information can be inferred about the viable catalysts. The various methods for the synthesis of Pd-B\textsuperscript{int} and Pd-Li\textsuperscript{int} with different loadings, discussed in detail by Ellis, are summarised here.\textsuperscript{66}

The synthesis of the interstitially modified nanoparticles begins with the production of palladium metal nanoparticles on a carbon support. I.T. Ellis produced a 5 wt\% loaded Pd/C, by first dispersing activated carbon in butan-1-ol. A solution of Pd(NO\textsubscript{3})\textsubscript{2} was then added dropwise and stirred before being filtered, washed and dried. The catalyst was then reduced in a furnace at 770 K with a 1:1 H\textsubscript{2}:N\textsubscript{2} atmosphere. For this work, a 45 wt\% loaded Pd/C was achieved by grinding activated carbon with Pd(OAc)\textsubscript{2} (palladium acetate; Pd(O\textsubscript{2}C\textsubscript{2}H\textsubscript{3})\textsubscript{2}) until homogeneous before heating in an N\textsubscript{2} atmosphere above the Pd(OAc)\textsubscript{2} decomposition temperature (478 K). These “base catalysts” were then used to synthesize the interstitially modified catalysts. The 45 wt\% loaded Pd/C has previously been discussed in Chapter 4.5.
The synthesis of Pd-B\textsuperscript{int} began by suspending the base Pd/C catalyst in THF (tetrahydrofuran; (CH\textsubscript{2})\textsubscript{4}O) under a N\textsubscript{2} atmosphere, followed by the addition of BH\textsubscript{3}-THF. The solvent was evaporated leaving a black powder that was heated at 470 K, still under N\textsubscript{2}, to drive the boron into the Pd lattice before being washed and dried. The synthesis of Pd-Li\textsuperscript{int} involved grinding LiOAc and the base Pd/C into a homogenous powder which is then heated at 520 K (to decompose the acetate) under an N\textsubscript{2} atmosphere before being washed and dried. Samples of the Pd-B\textsuperscript{int} and Pd-Li\textsuperscript{int} catalysts were also prepared with an additional acid wash to remove surface contaminants. These were stirred in 0.1 M HCl\textsubscript{(aq)} for 30 mins before being washed with distilled water and dried.

4.7.2. Verification of the Synthesis Methods

To ensure that the 45 wt% and the 5 wt% loaded samples are sufficiently structurally similar to justify the investigation of the higher loaded materials, they were both compared via powder XRD and solid state NMR. Additionally, these catalysts are compared to their acid washed counterparts.

The success of the interstitial modification of the Pd nanoparticles can be confirmed by using powder XRD to observe the resultant lattice expansion. The XRD patterns for this suite of catalysts is shown in Figure 4.15. As expected the 5 wt% loaded Pd/C (Figure 4.15 (a)) presents reflections that match the fcc structure of Pd metal. The interstitial modification of the structure is evident in the patterns for 5 wt% loaded Pd-B\textsuperscript{int}/C and Pd-Li\textsuperscript{int}/C (Figure 4.15(b,d)); the reflections are shifted towards lower 2\texttheta values, indicative of the expected lattice expansion.\textsuperscript{66}

The 45 wt% loaded Pd/C (Figure 4.15 (f)) is shown to contain two phases: Pd and the expanded lattice Pd-C\textsuperscript{int}. The different synthesis method for producing the 45 wt% loaded material appears to drive C into the Pd lattice. However, the 45 wt% loaded Pd-B\textsuperscript{int}/C and Pd-Li\textsuperscript{int}/C (Figure 4.15(g,i)) have very similar XRD patterns as the 5 wt% loaded catalysts. Hence, the presence of Pd-C\textsuperscript{int} does not substantially affect the interstitial modification. It is hypothesized that the interstitial carbon is reduced out of the lattice during the synthesis of Pd-B\textsuperscript{int}/C and Pd-Li\textsuperscript{int}/C. The 45 wt% loaded materials have slightly broadened reflections; this is believed to be due to slight variations of the success of the interstitial doping throughout the material. The acid washed materials all present XRD patterns (Figure 4.15(c, e, h, j) that are similar to their original materials. Each present with a small shift in
the reflections towards higher $2\theta$ values. This suggests that the additional washing has removed some of the interstitial dopant, slightly reducing the lattice expansion.

The different loadings of the Pd-B$^{\text{int}}$/C and Pd-Li$^{\text{int}}$/C samples were also compared with $^{11}$B and $^7$Li NMR respectively, as shown in Figure 4.16. The 45 wt% and 5 wt% loaded materials are virtually indistinguishable via NMR. The powder XRD and NMR results have confirmed that the 45 wt% loaded versions of Pd-B$^{\text{int}}$/C and Pd-Li$^{\text{int}}$/C are structurally very similar to
the 5 wt% loaded catalysts. Therefore, from this point onwards this investigation will examine only the higher loaded samples to determine the structures of these systems.

4.7.3. $^{11}$B Solid State NMR of Pd-$^{\text{int}}$/C

As seen in Figure 4.16(a,b) the $^{11}$B NMR spectra of Pd-$^{\text{int}}$/C contains at least two resonances corresponding to multiple B environments. One of these resonances corresponds to the interstitial B whereas the other(s) will be surface B contaminants. To determine which resonance corresponds to the interstitial B, $T_1$ relaxation measurements have been performed using the saturation recovery method described in Chapter 3.1.2. The spectrum was preliminarily deconvoluted into two resonances at 13 ± 1 ppm and 1 ± 1 ppm as shown in Figure 4.17(a); the relaxation results for both resonances are shown in Figure 4.17(c). As detailed in Chapter 3.1.2, the characteristic relaxation time $T_1$ can be procured by fitting the saturation recovery data. When a single-exponential was inadequate, bi-exponential and stretched-exponential fits were also attempted. The resultant $T_1$ values are detailed in Table 4.8.

The relaxation profile of the 1 ± 1 ppm resonance is adequately described by a single exponential with a $T_1$ of 0.64 ± 0.04 s. The relaxation profile of the 13 ± 1 ppm resonance is best fit with a bi-exponential function with a $T_1'$ of 0.848 ± 0.007 s and a $T_1''$ of 0.003 ± 0.009 s. The necessity of two relaxation rates suggests that two separate components from different B environments, hence two different values of $T_1$, form the resonance at 13 ± 1 ppm. Therefore, it is believed that three B environments exist in the Pd-$^{\text{int}}$/C system.
that result in the observed NMR lineshape. Two of the components have similar relaxation rates \( T_1 \approx 1 \, \text{s} \) whereas the other component relaxes exceptionally quickly \( T_1 < 0.01 \, \text{s} \). It is thought that the fast relaxing component is interstitial B, as a B atom inside the Pd lattice will take on the fast relaxation rate of its metallic environment.\(^{94}\) The slower relaxing components are assigned as B compounds on the surface of the Pd/C. However, a bi-exponential relaxation profile can also be caused by a single environment with a strong quadrupolar interaction.\(^{20}\) The quadrupolar nature of \(^{11}\)B puts doubt on the assignment of the interstitial B component.

Further confirmation is provided by the \(^{11}\)B NMR of the acid washed Pd-B\text{int}/C. The acid wash should remove surface elements leaving the interstitial B intact. In fact, the acid wash has greatly reduced the B content by removing surface B compounds and reducing the amount of interstitial B (as seen in Chapter 4.7.2). This is demonstrated by the \(^{11}\)B NMR
spectrum of the acid washed Pd-B\textsuperscript{int}/C (Figure 4.17(b)) which required ~60 times the number of transients as the spectrum of the original (Figure 4.17(a)). A greatly reduced resonance is still present at 13 ± 1 ppm, where the fast-relaxing component occurred in the original Pd-B\textsuperscript{int}/C. However, due to the reduction in B content a saturation recovery experiment is unfeasible. Instead, the relaxation rate can be crudely estimated by varying the recycle delay of a one-pulse NMR experiment and observing any changes in the SNR. If the recycle delay is < 5 × \( T_1 \) then saturation effects will occur, reducing the SNR of the produced spectrum. The results of such an experiment are shown in Figure 4.17(d). Increasing the recycle delay from 0.1 s shows no increase in the SNR at 13 ± 1 ppm. Therefore, the \( T_1 \) of the component must be < 0.02 s, confirming the presence of a very fast relaxing component that is not completely removed by an acid wash. Hence, the interstitial B component can be confidently assigned at 13 ± 1 ppm. The \(^{11}\text{B} \) NMR also presents evidence of surface B compounds which may be of significant importance to the catalytic abilities of the material.

Interstitial B is expected to display a Knight shift due to its environment in the metal Pd lattice. The Knight shift of B in a variety of metallic environments has been reported previously and the determined shift of 13 ± 1 ppm is within the reported range.\textsuperscript{95}

4.7.4. \(^{7}\text{Li} \) Solid State NMR of Pd-Li\textsuperscript{int}/C

The \(^{7}\text{Li} \) NMR investigation of Pd-Li\textsuperscript{int}/C closely follows the parallel \(^{11}\text{B} \) NMR investigation of Pd-B\textsuperscript{int}/C. The \(^{7}\text{Li} \) NMR lineshape of Pd-Li\textsuperscript{int}/C is also found to contain at least two resonances as shown in Figure 4.18(a). Unlike the \(^{11}\text{B} \) NMR spectrum, the multiple resonances are difficult to deconvolute due to the featurelessness of the \(^{7}\text{Li} \) NMR lineshape. However, the multiple resonances become clear when observing the changing lineshape

<table>
<thead>
<tr>
<th>Resonance</th>
<th>Single</th>
<th>Exponential fits</th>
<th>Stretched</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \delta_{CG} / \text{(ppm)} )</td>
<td>( T_1 / \text{(s)} )</td>
<td>( T_1' / \text{(s)} )</td>
<td>( T_1'' / \text{(s)} )</td>
</tr>
<tr>
<td>13 ± 1</td>
<td>0.848 ± 0.007</td>
<td>0.848 ± 0.007</td>
<td>0.003 ± 0.009</td>
</tr>
<tr>
<td>1 ± 1</td>
<td>0.64 ± 0.04</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 4.8 The parameters of single, bi and stretched exponential fits of the saturation recovery data from the \(^{11}\text{B} \) NMR resonances present in Pd-B\textsuperscript{int}/C (45 wt% loaded). Errors on the relaxation parameters were determined via the fitting program (Origin Pro), and therefore may not fully account for the experimental uncertainty in the intensity measurements.
during saturation recovery experiments. The spectrum was preliminarily deconvoluted into two resonances at 0.9 ± 0.2 ppm and −0.6 ± 0.2 ppm. The saturation recovery results for both resonances are presented in Figure 4.18(c) and the resultant $T_1$ values are given by Table 4.10.

The exponential fits are poorer in the $^7$Li saturation recovery data, compared to the $^{11}$B data, due to the longer relaxation times. This enforces the use of less transients per acquisition to keep experimental time sufficiently low. However, Figure 4.18(c) demonstrates that bi-exponential fits give the best match for both components, producing four different $T_1$ times which, therefore, suggests four different Li environments exist in Pd-Li\textsubscript{int}/C. Similarly to Pd-B\textsubscript{int}/C, one of the components at −0.6 ± 0.2 ppm relaxes very fast ($T_1 < 0.01$ s), with a $T_1$ of
which designates it as Li located in the interstitial sites of the Pd lattice. The other components relax slower so they are assigned as surface Li environments.

Once again, the quadrupole nature of the nuclei and its effect on relaxation cannot be ignored; therefore, the acid washed Pd-Li\textsubscript{int}/C sample is investigated. The \textsuperscript{7}Li MAS NMR spectrum of acid washed Pd-Li\textsubscript{int}/C is shown in Figure 4.18(b) and appears to contain a single component at −0.7 ± 0.2 ppm. The saturation recovery data for this resonance is shown in Figure 4.18(d) and the resultant $T_1$ values are detailed in Table 4.9.

The lower Li content further impedes the fitting due to the poorer SNR. However, the bi and stretched exponentials fits are not superior to the single exponential fit, and, therefore, it is believed that a singular Li environment remains. This component has a $T_1$ of 0.007 ± 0.001 s which, alongside its chemical shift, agrees with the designation of the interstitial Li component in Pd-Li\textsubscript{int}/C. The acid wash has been successful in removing all the surface Li while leaving the interstitial Li intact.

<table>
<thead>
<tr>
<th>Resonance</th>
<th>Single</th>
<th>Bi</th>
<th>Stretched</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta_{CG}$ (ppm)</td>
<td>$T_1$ (s)</td>
<td>$T_1'$ (s)</td>
<td>$T_1''$ (s)</td>
</tr>
<tr>
<td>0.9 ± 0.2</td>
<td>40 ± 10</td>
<td>140 ± 40</td>
<td>0.07 ± 0.05</td>
</tr>
<tr>
<td>−0.6 ± 0.2</td>
<td>1.7 ± 0.8</td>
<td>70 ± 30</td>
<td>0.006 ± 0.004</td>
</tr>
</tbody>
</table>

Table 4.10 The parameters of single, bi and stretched exponential fits of the saturation recovery data from the \textsuperscript{7}Li NMR resonances present in Pd-Li\textsubscript{int}/C (45 wt% loaded). Errors on the relaxation parameters were determined via the fitting program (Origin Pro), and therefore may not fully account for the experimental uncertainty in the intensity measurements.

<table>
<thead>
<tr>
<th>Resonance</th>
<th>Single</th>
<th>Bi</th>
<th>Stretched</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta_{CG}$ (ppm)</td>
<td>$T_1$ (s)</td>
<td>$T_1'$ (s)</td>
<td>$T_1''$ (s)</td>
</tr>
<tr>
<td>−0.7 ± 0.2</td>
<td>0.007 ± 0.001</td>
<td>0.0014 ± 0.0005</td>
<td>0.046 ± 0.002</td>
</tr>
</tbody>
</table>

Table 4.9 The parameters of single, bi and stretched exponential fits of the saturation recovery data from the \textsuperscript{7}Li NMR resonances present in acid washed Pd-Li\textsubscript{int}/C (45 wt% loaded). Errors on the relaxation parameters were determined via the fitting program (Origin Pro), and therefore may not fully account for the experimental uncertainty in the intensity measurements.
Mirroring the Pd-B\textsuperscript{int}/C results, the NMR investigation has revealed the presence of non-interstitial Li, which could significantly alter catalytic function, and has confirmed the position of the interstitial Li at \(-0.7 \pm 0.2\) ppm. The \(^{7}\text{Li}\) Knight shift of Li metal is 0.026 \%,\(^{94}\) so it is reasonable to assume that Li in the metallic environment of the Pd lattice should present with a larger chemical shift than \(-0.7 \pm 0.2\) ppm. However, DFT calculations included in the work of Ellis, predict that Li is situated in the Pd interstitial sites as Li\(^{+}\).\(^{66,93}\) This would vastly alter the Knight shift making comparison to the \(K\) of Li metal unviable.

4.7.5. Magnetic Susceptibility Measurements

The magnetic susceptibility of the Pd-H\textsuperscript{int} system has been thoroughly studied previously.\(^{39,67,80-81}\) It has been clearly demonstrated that the magnetic susceptibility of the system decreases linearly with increasing H content.\(^{80-81}\) As mentioned in Chapter 4.5.2, Pd metal is paramagnetic due to the Pauli susceptibility of holes in the 4\(d\) orbital, which is enhanced by the density of \(d\) states at the Fermi level (Stoner enhancement factor).\(^{68}\) Donation of the H electrons into holes in the Pd 4\(d\) orbital, reduces the density of states at the Fermi level.

Figure 4.19 The magnetisation \(M\) versus applied field \(H\) measurements of Pd sponge (grey), Pd/C (black), Pd-B\textsuperscript{int}/C (blue), Pd-Li\textsuperscript{int}/C (red), activated C (orange) at a temperature of (a) 300 K and (b) 5 K.
As the H content becomes sufficiently high ($\beta$-PdH$_{0.607}$ at room temperature), Pd-H$_{\text{int}}$ becomes diamagnetic. Therefore, the magnetic susceptibility of the interstitially modified catalysts is of interest.

Magnetic susceptibility measurements have been made on the (45 wt% loaded) Pd/C, Pd-B$_{\text{int}}$/C and Pd-Li$_{\text{int}}$/C catalysts. By measuring the (mass) magnetisation $M_{\text{mass}}$ versus the applied magnetic field $H$, the (mass) magnetic susceptibility $\chi_{\text{mass}}$ can be determined from Equation 3.13, where the gradient of the line is given by

$$\chi_{\text{mass}} = \frac{M_{\text{mass}}}{H}.$$  \hfill (4.3)

As detailed in Chapter 3.2.3, a paramagnetic material has a positive $\chi_{\text{mass}}$ whereas a diamagnetic material has a negative $\chi_{\text{mass}}$. Figure 4.19(a) shows the $M$ versus $H$ measurements of the three carbon supported catalysts, pure Pd sponge and activated C at a temperature of 300 K. The carbon supported catalysts, including Pd/C, are diamagnetic at 300 K in contrast to the paramagnetism of pure Pd. This is due to the diamagnetism of the C support overshadowing the paramagnetism of the Pd nanoparticles. To circumvent this, the $M$ versus $H$ measurements on the carbon supported catalysts were also performed at a temperature of 5 K (Figure 4.19(b)). Diamagnetism is temperature independent, whereas $\chi$ is larger at lower temperatures in paramagnetic materials, including Pd metal.

Hence, reducing the temperature will allow any paramagnetism present to dominate the diamagnetism of the C support. At 5 K, all three carbon supported catalysts demonstrate a paramagnetic $\chi_{\text{mass}}$. As shown in Table 4.11, the interstitial modification of Pd/C with B and Li significantly reduces the $\chi_{\text{mass}}$ of the system, akin to Pd-H$_{\text{int}}$. This further confirms the interstitial location of B and Li in the Pd lattice.

As mentioned in Chapter 4.7, the 2$p$ orbital of interstitial B is degenerate with the Pd 4$d$ band. This reduces the density of states at the Fermi level and therefore reduces the Pd

<table>
<thead>
<tr>
<th>Name</th>
<th>$\chi_{\text{mass}}/(10^{-6} \text{ emug}^{-1})$</th>
</tr>
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<tbody>
<tr>
<td>Pd/C</td>
<td>10.72 ± 0.07</td>
</tr>
<tr>
<td>Pd-B$_{\text{int}}$/C</td>
<td>0.55 ± 0.01</td>
</tr>
<tr>
<td>Pd-Li$_{\text{int}}$/C</td>
<td>2.79 ± 0.02</td>
</tr>
</tbody>
</table>

Table 4.11 The experimentally determined $\chi_{\text{mass}}$ for the C supported Pd nanoparticles at a temperature of 5 K.
paramagnetism, as observed. DFT calculations in the work of I.T. Ellis suggest that no such overlap occurs between Li and Pd. Instead Li is thought to enter the lattice as Li\(^+\), donating electrons to the Pd \(d\) band and, therefore, reducing the paramagnetism. The resultant negative charge is then spread over the Pd lattice, so that the metal remains virtually charge neutral. Interstitial Li does not reduce the density of states at the Fermi level which may explain the more paramagnetic nature of Pd-Li\(^\text{int}\) in comparison to Pd-B\(^\text{int}\) and Pd-H\(^\text{int}\).

4.7.6. \(^{105}\)Pd Solid State NMR

The use of powder XRD, solid state NMR and magnetic susceptibility measurements have helped provide a thorough understanding of the Pd-B\(^\text{int}\)/C and Pd-Li\(^\text{int}\)/C systems. Finally, the novel \(^{105}\)Pd solid state NMR was applied to these systems, the results of which are shown in Figure 4.20. Despite the 45 wt\% loaded Pd/C containing a phase of Pd-C\(^\text{int}\), the Pd phase still produces a \(^{105}\)Pd resonance. The \(^{105}\)Pd NMR parameters of Pd/C is detailed in Chapter 4.5.2.

The \(^{105}\)Pd NMR results from Pd-B\(^\text{int}\)/C and Pd-Li\(^\text{int}\)/C were fruitless. Similarly to PdH\(_{0.7}\), no NMR resonance could be detected for either system despite sweeping a wide \(K\) range. Once again, the unknown \(K\) and the lattice expansion related disorder/broadening combined with long experimental times puts detection via \(^{105}\)Pd NMR beyond the limits of this investigation. However, the negative \(^{105}\)Pd NMR result gives even further confirmation of successful interstitial modification. If the B and Li remained only on the surface of the Pd, then the NMR spectra would resemble that of Pd/C.

![Figure 4.20 The \(^{105}\)Pd static VOCS NMR of 45 wt\% loaded Pd/C (black), Pd-B\(^\text{int}\)/C (blue) and Pd-Li\(^\text{int}\)/C (red) at 14.1 T.](image-url)
4.8. Conclusions

This study proposes a standard chemical shift reference of 0.33 M H_{2}PdCl_{6(aq)} alongside a secondary chemical shift reference of KCl(s). It also demonstrates the feasibility of supscript{105}Pd solid state NMR on diamagnetic compounds and begins to develop a supscript{105}Pd NMR chemical shift range. Combined with the more accurate determination of the room temperature Knight shift for Pd metal, these findings will greatly aid any future studies using supscript{105}Pd solid state NMR.

The sensitivity of supscript{105}Pd solid state NMR to structural distortions, due to its large quadrupole moment and the EFG it produces, is shown to be exemplary. Study of the hexa-halogen palladates demonstrated its sensitivity to be beyond that of NMR from other quadrupole nuclei and lab source X-ray diffractometers. X-ray PDF refinements were necessary to confirm the detected distortions in the complexes. The large Knight shift in supscript{105}Pd is also shown to be a sensitive probe of disorder by its ability to detect defects in Pd metal and differentiate between different sizes of Pd metal nanoparticles.

However, its sensitivity is also very limiting. The large quadrupole moment constrains supscript{105}Pd solid state NMR to studies of highly symmetrical materials. Otherwise the quadrupole broadening becomes so severe that experimental times become unfeasible. Additionally, the large Knight shift range and long experimental times make studies of Pd systems with varying Knight shifts often unachievable. This was demonstrated by the studies on the catalysis related Pd systems, which often relied heavily upon various other analytical techniques for structural determination. Nevertheless, this work forms a solid basis for any further supscript{105}Pd NMR studies and verifies the technique as a sensitive probe to structural distortion, which could have significant applicability to catalytic structural determination.

The study of PdLi_{int}/C and PdB_{int}/C catalysts provided conclusive proof of the interstitial location of the dopants. The similarities of the interstitial doped materials to the palladium hydride system was also demonstrated. It is hoped that the additional structural characterisation of these catalysts will aid in future improvement of their functionality.
5

The Study of Disorder in Mullite Using Multi-Nuclear Solid State NMR and supercell Enabled GIPAW-DFT Calculations

5.1. Background

The ceramic aluminosilicate mullite occurs rarely in nature, forming when magma interacts with alumina rich sediments. It was first discovered on the Isle of Mull (Scotland), hence where the name originates. Mullites have excellent mechanical and thermal properties such as low thermal expansion, low thermal conductivity, high corrosion stability, and excellent creep resistance. Due to their stability in challenging conditions, mullite ceramics have a diverse range of applications including: tableware, construction ceramics, electronic devices, optically translucent ceramics for furnace windows, barrier coatings for tube furnaces, and heat shields for space re-entry vehicles.96-97 Most relevant to this thesis is mullite’s role in catalysis. Mullite is most commonly used as a substrate for catalytic converters, and is the support of choice for many supported metal catalysts.98-102 The structure of the support is often equally as important as the structure of the metal to the overall function of a supported catalyst. Additionally, mullite structured mixed oxides have been reported as having impressive catalytic ability.103 Therefore, a full structural characterisation of mullite is of great interest, so its catalytic function can be better understood and, hence, improved.

The majority of mullite materials are produced synthetically, with the nominal composition of:

\[
Al_2(Al_{2+2x}Si_{2-2x})O_{10-x} \quad 0.2 < x < 0.9. \quad 5.1
\]

Theoretically, mullite can form any composition between sillimanite (Al₂SiO₅) and alumina (Al₂O₃), but, in reality there is a miscibility gap between \( x = 0 \) and \( x = 0.2 \) due to the differing founding conditions (moderate pressure/temperature for sillimanite and low pressure/high temperature for mullite). Mullite has two stoichiometric forms when \( x = 0:25 \) (3Al₂O₃:2SiO₂), and \( x = 0:4 \) (2Al₂O₃: SiO₂), so called 3:2 and 2:1 mullite respectively.
The structure of mullite is proposed to be closely related to that of crystalline sillimanite.\textsuperscript{104} The suggested refined structure consists of edge sharing AlO\textsubscript{6} octahedral chains running along the c-axis, which are cross linked with SiO\textsubscript{4} and AlO\textsubscript{4} motifs.\textsuperscript{105} Sillimanite consists of four oxygen environments; one is a two-coordinated oxygen (O\textsubscript{b}) site while the rest are three-coordinated (O\textsubscript{t}). The O\textsubscript{b} site bridges between the two tetrahedral double chains forming a moiety that is termed T\textsubscript{2}O.

The mullite system is characterised by a fundamental difference in an increase of Al with respect to Si, with some of the corner shared O linking the tetrahedral SiO\textsubscript{4} sites being removed due to charge compensation:

\[ 2Si^{4+} + O^{2-} \rightarrow 2Al^{3+} + \square. \] 

Figure 5.1 (a) A diagram of the sillimanite structure highlighting the T\textsubscript{2}O moiety and the bridging oxygen site O\textsubscript{b}. (b) A diagram of the proposed mullite structure highlighting the vacancy at the O\textsubscript{b} site that causes the T\textsubscript{2}O units to back bond towards adjacent T\textsubscript{3}O moieties, forming T\textsubscript{3}O environments. The Al octahedra are in blue, the Al/Si tetrahedra are in green and the oxygen atoms are in black.
This produces oxygen vacancies (□) in the structure, as demonstrated in Figure 5.1. Crystallographic refinements suggest that the bridging oxygen (O₆) in the T₂O moiety is removed, displacing the disconnected cations. The oxygen deficient tetrahedral units (T₂□) back bond to connect with an adjacent T₂O unit, forming a three-coordinated oxygen. This moiety containing three tetrahedral units connected at an O₆ site, termed T₃O, is a distinctive feature in mullite’s structure. The T₃O moiety directly defies the Loewenstein avoidance principle, which states that two AlO₄ units cannot share an O site. The literature often uses T* or tricluster to refer to this formation; for clarity, this thesis will refer to the moiety as T₃O throughout. Despite the general structure of mullite being well understood, plenty of debate still remains about the finer points, as demonstrated by the numerous studies in the literature. Ongoing debate on the mullite structure is focused on a few key areas. While some evidence of the existence of the T₃O moiety has been presented, absolute confirmation is still sought. Additionally, a structural characterisation of T₃O has proven elusive. Some report that SiO₄ is present in T₃O environments, whereas others have implied that the SiO₄ contribution is immeasurable. Another unresolved aspect of the mullite structure is the configuration of the Al/Si tetrahedral units. The tetrahedral double chains in sillimanite contain alternating AlO₄ and SiO₄ units. Due to the additional Al, the same cannot be true for mullite. Whether any order exists in the AlO₄/SiO₄ distribution is still an open question.

Figure 5.2 A diagram of the proposed boron doped mullite structure highlighting the BO₃ units that have substituted for the tetrahedral units of a T₂O moiety. The Al octahedra are in blue, the Al/Si tetrahedra are in green, the oxygen atoms are in black and the trigonal B units are highlighted in red.
Due to the disordered nature of the material, solid state NMR is one for the most suited analytical tools for further structural determination, because of its ability to study local order in systems lacking long range periodicity. Several $^{27}$Al NMR investigations of mullite have been reported, with the majority attempting to detect the presence of the AlO$_4$ units in the T$_3$O moiety.\textsuperscript{116,119} King presented a deconvoluted $^{27}$Al MAS NMR spectrum containing an AlO$_6$ site, and AlO$_5$ site and two AlO$_4$ sites, claiming that AlO$_4$ in the T$_3$O environment provides a distinct resonance.\textsuperscript{120} Previous $^{29}$Si MAS NMR studies have shown that the mullite structure possesses several Si environments.\textsuperscript{115,117,119} The most intense resonance (~88 ppm) is attributed to a sillimanite type environment.\textsuperscript{119} King, following the calculations of Ban and Okada, tentatively assigned the other resonances to Si environments with different configurations of Al/Si tetrahedral units as next nearest neighbours.\textsuperscript{110,120}

Another area of interest arises due to mullite’s ability to accommodate a variety of different dopant cations. By doping with boron, materials can be created that share the properties of pure aluminosilicate mullites with that of aluminoborates. Aluminoborates have a wide range of uses due to several beneficial attributes, that are discussed in detail in Chapter 6.1. Therefore, these intermediate materials have great potential for material science and engineering applications, hence the numerous studies in the literature.\textsuperscript{121-125} Several studies report that B incorporates into the mullite structure in a BO$_3$ coordination.\textsuperscript{120-122,124-125} It is believed that BO$_3$ substitutes for the tetrahedral units in the T$_3$O moiety (see Figure 5.2), via a substitution mechanism analogous to increased Al content:

$$2\text{Si}^{4+} + \text{O}^{2-} \rightarrow 2\text{B}^{3+} + \Box.$$ \text{5.3}

This work uses the newly developed supercell program alongside DFT calculations to thoroughly model the structure of 3:2 and 2:1 mullite. These models are then compared to a rigorous study of both mullites with $^{29}$Si, $^{27}$Al and $^{17}$O solid state NMR approaches. The findings of these studies are then applied to the analysis of a $^{27}$Al solid state NMR study of several B doped mullites.

5.2. Experimental

5.2.1. Synthesis

The synthesis of all mullite samples used in this investigation was performed by H. Lührs (Universität Bremen) and complete details of the methodology have been reported.
To allow a thorough $^{29}\text{Si}$ and $^{17}\text{O}$ NMR investigation, isotopically enriched samples of 3:2 and 2:1 mullite were synthesized via a solid state method. The samples were prepared using stochiometric amounts of $^{29}\text{Si}$ or $^{17}\text{O}$ enriched $\text{SiO}_2$ and amorphous $\text{Al}_2\text{O}_3$, that were homogenised and pressed into a pellet. The pellets were inductively heated, under $\text{N}_2(\text{g})$, to ~1970 K to crystallize. An unenriched single crystal 2:1 mullite sample was also acquired, which was grown via the Czochralski method. The boron doped variants were produced via a sol-gel method which provides greater control over the product. Stochiometric amounts of aluminium nitrate nonahydrate ($\text{Al(NO}_3\text{)}_3\cdot9\text{H}_2\text{O}$), tetraethoxysilane ($\text{C}_8\text{H}_{20}\text{O}_4\text{Si}$) and boric acid ($\text{H}_3\text{BO}_3$) were dissolved in ethanol to produce a gel. The gel is then dried, ground and calcined before being heated at a temperature of 1470 K for 5 hrs.

All samples were powdered for the NMR investigation and the initial compositions of each sample are shown in Table 5.1.

### Table 5.1

<table>
<thead>
<tr>
<th>Name</th>
<th>Initial Composition /(%)</th>
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<tr>
<td></td>
<td>$\text{Al}_2\text{O}_3$</td>
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<tr>
<td>3:2</td>
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</tr>
<tr>
<td>1% $\text{B}_2\text{O}_3$</td>
<td>60.76</td>
</tr>
<tr>
<td>4% $\text{B}_2\text{O}_3$</td>
<td>61.89</td>
</tr>
<tr>
<td>6% $\text{B}_2\text{O}_3$</td>
<td>63.86</td>
</tr>
<tr>
<td>2:1</td>
<td>66.5</td>
</tr>
</tbody>
</table>

Previously, to allow a thorough $^{29}\text{Si}$ and $^{17}\text{O}$ NMR investigation, isotopically enriched samples of 3:2 and 2:1 mullite were synthesized via a solid state method. The samples were prepared using stochiometric amounts of $^{29}\text{Si}$ or $^{17}\text{O}$ enriched $\text{SiO}_2$ and amorphous $\text{Al}_2\text{O}_3$, that were homogenised and pressed into a pellet. The pellets were inductively heated, under $\text{N}_2(\text{g})$, to ~1970 K to crystallize. An unenriched single crystal 2:1 mullite sample was also acquired, which was grown via the Czochralski method.

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All samples were powdered for the NMR investigation and the initial compositions of each sample are shown in Table 5.1.

#### 5.2.2. supercell Structure Generation

The supercell program is a newly developed combinatorial structure-generation approach for the description of vacancy or substitution defects in otherwise periodically-ordered materials. Disorder in a material is approximated by a set of generated structures which can then undergo GIPAW-DFT calculations.

Two approaches were used for the structure generation of the 3:2 mullite. The first approach began with the structure of sillimanite and is, therefore, referred to as the “sillimanite” approach. A 2x2x1 sillimanite structure, provided by Burnham Charles, was modified by

85
substituting four Al into tetrahedral Si positions and two vacancies at the \( \text{O}_b \) sites. By varying the positions of the additional Al and vacancy sites, the *supercell* program was used to generate all the possible, symmetrically unique configurations of the structure. From these generated structures, 100 were randomly sampled to represent the disordered 3:2 mullite structure. This approach maintains the premise of the \( \text{AlO}_4/\text{SiO}_4 \) order present in sillimanite, whereas the next approach uses a random distribution of Al/Si tetrahedra.

The “random” approach began with a 2x2x2 initial structure based on the XRD refined 3:2 mullite structure reported by Balzar and Ledbetter.\(^{129}\) The partial occupancy on the \( \text{O}_b \) site (\( \text{O}_b:\square = 0.871:0.129 \)) was extrapolated by the *supercell* program, generating 9 symmetrically unique structures, that model the oxygen vacancy disorder. Then all the Al/Si tetrahedra were made interchangeable, while preserving the correct Al/Si ratio. From the symmetrically unique structures generated by the random \( \text{AlO}_4/\text{SiO}_4 \) disorder, 10 are randomly sampled from each of the 9 vacancy configurations, totalling 90 generated structures to represent the disordered 3:2 mullite structure.

The *supercell* treatment of 2:1 mullite was similar to the 3:2 “random” approach, using the same structure with an additional vacancy and a stochiometric Al/Si ratio. The increased number of vacancies generates 23 unique symmetry structures for the oxygen vacancy disorder. Once again, 10 of the generated structures representing \( \text{AlO}_4/\text{SiO}_4 \) disorder are randomly sampled for each vacancy configuration, totalling 230 structures to represent the disordered 2:1 mullite structure.

### 5.2.3. GIPAW-DFT Calculations

The supercell structure generation and subsequent calculations were performed by K. Okhotnikov and T. Charpentier (C.E.A. Saclay). The DFT-GGA calculations of each of the generated structures, were completed with the pseudopotential approximation in the *VASP* package.\(^{130}\)

These calculations were carried out in three sequential stages. Firstly, a rough relaxation geometry optimisation was accomplished on the generated structures, using a reduced k-point grid (1x1x2). The output of these calculations then underwent a precise relaxation geometry optimisation with a finer k-point grid (2x2x5), to give the final structures. Both relaxation stages employed a kinetic energy cut-off of 500 eV. In the final step, GIPAW-DFT calculations were performed on the products of the precise relaxation to provide NMR
parameters (δ\text{iso}, C_Q, \eta_Q). The GIPAW-DFT calculations were performed with a 2x2x5 k-point grid and an energy cut-off of 550 eV while the isotropic chemical shift values were determined via a reference shielding of 308.8, 561.1 and 261.3 ppm for ²⁹Si, ²⁷Al and ¹⁷O respectively.

5.2.4. Solid State NMR Measurements

The MAS NMR experiments in this study were performed at room temperature across a range of different magnetic field strengths (B₀) using Bruker Avance III-850 (19.9 T), Bruker Avance II+600 (14.1 T), Bruker Avance II+500 (11.7 T) and Varian Infinity+-300 (7.05 T) spectrometers. All NMR data was processed using TOPSPIN and MQMAS data were sheared using the TOSPSPIN program xfshear. Simulations of Gaussian/Lorentzian lineshapes were performed with dmf.

The ²⁹Si NMR experiments at 19.9 T and 7.05 T were undertaken using a Bruker 4 mm HX probe and a Bruker 7 mm broadband MAS probe respectively. All data was referenced with respect to kaolinite(s) (Al₂Si₂O₅(OH)₄; \delta_{\text{iso}} = -93 ppm). The ²⁹Si NMR experiments performed at 19.9 T \( (\nu_0 (²⁹Si) = 168.84 \text{ MHz}) \) and 7.05 T \( (\nu_0 (²⁹Si) = 59.59 \text{ MHz}) \) employed an MAS frequency of 12 KHz and 5 KHz respectively. A \( \frac{\pi}{2} \) pulse length was determined on kaolinite(s) resulting in a pulse length of 4 \( \mu \)s for the single pulse experiments, with a recycle delay of 4,500 s.

The ²⁷Al NMR experiments were performed at 11.7 T \( (\nu_0 (²⁷Al) = 130.29 \text{ MHz}) \) and 14.1 T \( (\nu_0 (²⁷Al) = 156.34 \text{ MHz}) \) with an MAS frequency of 20 KHz. The experiments were completed using a Bruker 3.2 mm HX probe with all data referenced with respect to yttrium aluminium garnet(s) (YAG; Y₃Al₅O₁₂; \delta_{\text{iso}}[AlO₆] = 0.7 ppm). A \( \frac{\pi}{2} \) pulse length was determined on YAG(s) resulting in a selective \( \frac{\pi}{12} \) pulse length of 2 \( \mu \)s being used for the single-pulse experiments, with a recycle delay of 4 s used throughout. The 2D MQMAS experiments utilised a z-filtered 3QMAS pulse sequence with a 3.75 \( \mu \)s excitation pulse, a 1.25 \( \mu \)s conversion pulse and a 25 \( \mu \)s selective z-filter pulse.

The ¹⁷O NMR experiments were performed at 11.7 T \( (\nu_0 (¹⁷O) = 67.78 \text{ MHz}) \) with an MAS frequency of 20 KHz. The experiments were completed using a Bruker 3.2 mm HX probe with all data referenced with respect to ¹⁷O enriched (10 %) H₂O(l) \( (\delta_{\text{iso}} = 0 \text{ ppm}) \). A \( \frac{\pi}{2} \) pulse length was determined on ¹⁷O enriched H₂O(l) resulting in a selective \( \frac{\pi}{4} \) pulse length of 2 \( \mu \)s. A \( \frac{\pi}{4} - \tau - \frac{\pi}{2} \) echo sequence was utilised to diminish ringing effects present at low
frequencies. A recycle delay of 750 s was used throughout and a rotor synchronised \( \tau \) period of 47 \( \mu s \) was used in the echo experiments. The 2D MQMAS experiments utilised a \( z \)-filtered 3QMAS pulse sequence with a 3 \( \mu s \) excitation pulse, a 0.9 \( \mu s \) conversion pulse and a 20 \( \mu s \) selective \( z \)-filter pulse.

5.3. 3Al\(_2\)O\(_3\):2SiO\(_2\) Mullite

5.3.1. \(^{29}\)Si Results

The deconvoluted \(^{29}\)Si MAS NMR spectrum of 3:2 mullite is presented in Figure 5.3(a), alongside the simulated spectra of the \textit{supercell}-GIPAW DFT structures generated from the “sillimanite” and “random” starting approaches (Figure 5.3(c) and (d) respectively). It is clear that the “random” approach produces a spectrum in better agreement with the experimental data, as the “sillimanite” approach simulation is missing several lower frequency components. While the “random” approach does not produce a perfect simulation, it is sufficient to provide a comprehensive assignment of the deconvoluted resonances in the \(^{29}\)Si MAS NMR spectrum (Table 5.2). The SiO\(_4\) environments predicted by the calculations are schematically represented in Figure 5.3(e). The nomenclature used for each environment,

<table>
<thead>
<tr>
<th>Experimental ( \delta_{iso} ) (ppm)</th>
<th>Intensity (%)</th>
<th>Calculated ( \delta_{iso} ) (ppm)</th>
<th>Intensity (%)</th>
<th>Assignment</th>
<th>Moiety</th>
</tr>
</thead>
<tbody>
<tr>
<td>-79.9 (\pm 0.5)</td>
<td>1</td>
<td>-82.3</td>
<td>7</td>
<td>8Al(O(_t))</td>
<td>T(_3)O</td>
</tr>
<tr>
<td>-81.9</td>
<td>2</td>
<td>-83.4</td>
<td>5</td>
<td>7Al(O(_t)) : 1Si(O(_t))</td>
<td></td>
</tr>
<tr>
<td>-83.7</td>
<td>4</td>
<td>-87.3</td>
<td>4</td>
<td>6Al(O(_t)) : 2Si(O(_t))</td>
<td></td>
</tr>
<tr>
<td>-87.5</td>
<td>37</td>
<td>-89.8</td>
<td>36</td>
<td>1Al(O(_b)) : 6Al(O(_t))</td>
<td>T(_2)O</td>
</tr>
<tr>
<td>-90.3</td>
<td>25</td>
<td>-92.9</td>
<td>23</td>
<td>1Si(O(_b)) : 6Al(O(_t))</td>
<td></td>
</tr>
<tr>
<td>-92.5</td>
<td>9</td>
<td>-94.9</td>
<td>15</td>
<td>1Al(O(_b)) : 4Al(O(_t)) : 2Si(O(_t))</td>
<td></td>
</tr>
<tr>
<td>-95.1</td>
<td>9</td>
<td>-98.1</td>
<td>11</td>
<td>1Si(O(_b)) : 4Al(O(_t)) : 2Si(O(_t))</td>
<td></td>
</tr>
<tr>
<td>-97.8</td>
<td>3</td>
<td>-102.5</td>
<td>0</td>
<td>4Si(O(_b))</td>
<td>SiO(_2)</td>
</tr>
<tr>
<td>-106.9</td>
<td>10</td>
<td>-</td>
<td>-</td>
<td>SiO(_2)</td>
<td></td>
</tr>
</tbody>
</table>

Table 5.2 The experimental and simulated (“random” approach \textit{supercell} enabled GIPAW-DFT) NMR parameters of the deconvoluted resonances of the \(^{29}\)Si spectrum of \(^{29}\)Si labelled 3:2 mullite, with each resonance assigned a corresponding SiO\(_4\) environment.
89 describes the number of next nearest Al or Si neighbours and the nature of the shared O between them (Oₖ or Oₐ) (e.g. the sillimanite Si environment 1Al(Oₖ):6Al(Oₐ) is bonded to one Al through a bridging oxygen and three pairs of Al via three-coordinated oxygens).

Figure 5.3(a) The $^{29}$Si MAS (12 KHz) NMR spectrum of $^{29}$Si enriched 3:2 mullite at 19.9 T with (b) an insert displaying the magnified, quantitative $^{29}$Si MAS (5 KHz) NMR spectrum of $^{29}$Si enriched 3:2 mullite at 7.05 T with the SiO$_{4+1}$ resonance labelled. The supercell enabled GIPAW-DFT simulated $^{29}$Si spectra of the (c) “sillimanite” and (d) “random” approaches to 3:2 mullite. Experimental spectra are in black, with simulated lineshapes in red and deconvoluted/simulated resonances in colours corresponding to (e) the schematic representation of the assigned Si environments.
The $^{29}$Si MAS spectrum contains multiple SiO$_4$ resonances, with the most dominant assigned to a sillimanite environment at $-87.5 \pm 0.5$ ppm, which splits the spectrum into two distinct regions. At lower frequencies are the four SiO$_4$ environments, including the sillimanite environment, which exist in T$_2$O moieties. At higher frequencies are three environments that represent T$_3$O moieties, and, thus, confirm the existence of the T$_3$O moiety in the mullite structure and the presence of SiO$_4$ in said moiety. In both the T$_2$O and T$_3$O regions of the spectrum, the various environments produce distinct resonances due to the different number of SiO$_4$ units each has as next nearest neighbours. Additional small resonances exist in the lowest frequency region of the NMR spectrum that are not observable in the simulations. The resonance at $-97.8 \pm 0.5$ ppm is predicted by the calculation, albeit in negligible quantities, and can be assigned to an SiO$_2$ environment within the mullite structure. The resonance at $-106.9 \pm 0.5$ ppm is assigned to an amorphous silica impurity remaining from the starting material of the solid state synthesis method. The calculations also predict a small amount of SiO$_4$ with an additional long bond, dubbed SiO$_{4+1}$. A corresponding resonance can be observed in the longer, quantitative $^{29}$Si MAS measurement (Figure 5.3(b)) at $-135$ ppm, between the expected shifts for SiO$_4$ ($-60$ to $-120$ ppm) and SiO$_5$ ($-150$ ppm). The presence of this distorted SiO$_{4+1}$ polyhedra is discussed in greater detail in the next section (Chapter 5.3.2).

The “random” approach calculations produce a minor $\delta_{\text{iso}}$ inaccuracy and the component intensities (site populations) are slightly misrepresented, as demonstrated in Table 5.2. Despite, this the combined use of NMR and supercell enabled DFT calculations, provides a complete understanding of the mullite structure which allows total assignment of the $^{29}$Si NMR spectrum. The $^{29}$Si assignments are in partial agreement with those previously reported,$^{110, 120}$ but correct the exact assignment of some of the resonances.

The “sillimanite” approach completely under represents the T$_2$O environments, overpredicting T$_3$O formation. The failure of this approach, that assumed some of the sillimanite AlO$_4$/SiO$_4$ order remained, compared with the success of the no order “random” approach, implies a lack of order in the AlO$_4$/SiO$_4$ configuration in mullite’s structure. A random configuration of Al and Si tetrahedral units proves that the mullite structure defies the Loewenstein avoidance principle. It is hypothesized that by ignoring this principle, the “random” approach may ignore an inequivalence of charge which could result in the observed $\delta_{\text{iso}}$ inaccuracy. Further investigation of this hypothesis was beyond the scope of this study.
From this point forward, only the results from the calculations performed on the structures generated by the “random” approach will be discussed.

5.3.2. $^{27}$Al Results

The calculated $^{27}$Al NMR parameters ($\delta_{\text{iso}}$ and $C_Q$) from the 3:2 mullite generated structures are presented in Figure 5.4(a). Unlike the $^{29}$Si NMR study, the quadrupolar broadened $^{27}$Al NMR does not have the resolution to distinguish environments by their different next nearest neighbours. Instead, the data is classified by the Al coordination number, with AlO$_4$ sites
divided into T₂O and T₃O moieties (labelled AlO₄(T₂O) and AlO₄(T₃O) respectively). The predicted environments are then assigned to the resolved resonances in the ²⁷Al 2D 3QMAS spectrum (Figure 5.4(b)). As expected, the most populated environments in both the simulated and NMR data are the moieties found in the parent sillimanite: AlO₄(T₂O) and AlO₆.¹⁰⁴

The AlO₄(T₃O) environments are indistinguishable from AlO₄(T₂O) environments via modern NMR methodology, with mean calculated δiso values of 64 ± 9 ppm and 67 ± 6 ppm respectively. This contrasts with published work that assigned the resolved resonance at δiso ≈ 50 ppm as AlO₄(T₃O).¹²⁰ Instead, AlO₄⁺₁(T₃O), an environment analogous to the Si environment SiO₄⁺₁, is assigned to that resonance in the GIPAW-DFT calculations. These quasi-tetrahedral environments form as part of the T₃O moiety, but have an additional long bond to an adjacent Oₜ site creating a four-coordinated oxygen site (Oₜq). Due to the elongated bond the resonance is situated at a mean calculated δiso of 45 ± 5 ppm, between the shifts of AlO₄ (80 - 50 ppm) and AlO₅ (40 - 30 ppm) giving further support to the proposal of the AlO₄⁺₁ moiety.² The simulation also predicts some AlO₅ formation that is not observable in the 2D 3QMAS NMR data. However, the low population (< 1%) and wide spread NMR parameters of the proposed AlO₅ sites would significantly hinder detection.

The oxygen deficient tetrahedral units (AlO₃□), formed by vacancy substitution at T₂O moieties in the generated structures, almost completely form T₃O polyhedra post DFT geometry optimisation. However, a very small percentage (< 1%) remain as AlO₃□ in the relaxed structure with a calculated δiso of 81 ± 9 ppm. This metastable environment, that is predicted in mullite for the first time, is tentatively assigned to the small, high frequency resonance in the 2D 3QMAS NMR spectrum (Figure 5.4). Despite the low site population, it has a concentrated population of predicted δiso and CQ values, and, hence, may be detected by ²⁷Al 3QMAS NMR.

An unpredicted resonance at δiso ≈ 16 ppm in the ²⁷Al NMR spectra can be assigned to an α-Al₂O₃ impurity remaining from the starting material of the solid state synthesis method.² The good agreement between the calculated and experimental ²⁷Al NMR parameters lends further credence to the strength of the supercell method of disorder simulation, which has allowed a complete assignment of the ²⁷Al NMR data.
5.3.3. $^{17}$O Results

The GIPAW-DFT calculated $^{17}$O NMR parameters, $\delta_{\text{iso}}$ and $C_Q$, from the 3:2 mullite generated structures are presented in Figure 5.5(a). The generated structures contain 53 unique O sites, therefore only the 10 sites with $> 1\%$ of the total O population are illustrated in Figure 5.5(a). Each unique environment is classified by its coordination with O$_b$, O$_t$ and

![Figure 5.5(a) A plot of the GIPAW-DFT calculated $^{17}$O $\delta_{\text{iso}}$ and $C_Q$ values of the environments (with $> 1\%$ total O population) in the supercell generated 3:2 mullite structures. (b) The $^{17}$O 3QMAS (20 KHz) NMR 2D spectrum of $^{17}$O enriched 3:2 mullite at 11.7 T with the MAS spectrum above and the projected $\delta_{\text{iso}}$ spectrum on the right. The predicted environments from the simulations are assigned to distinct resonances in the 2D spectrum with the addition of an $\alpha$-$\text{Al}_2\text{O}_3$ contaminant.](image-url)
O_q representing two, three and four coordinate oxygen sites respectively. The sites are further labelled by the coordination of their nearest neighbours, detailed by the subscript (h = six-coordinate; q = four-coordinate; q* = 4+1-coordinate). For example, O_t(2Al_h:Al_q) is a three-coordinate oxygen shared by two AlO_6 and one AlO_4 polyhedra.

As mentioned in Chapter 5.1, the sillimanite structure contains four oxygen sites: O_t(2Al_h:Al_q), O_t(2Al_h:Si_q), O_t(Al_h:Al_q:Si_q) and O_b(Al_q:Si_q). Compared to sillimanite, the disorder in the 3:2 mullite structure has introduced many additional environments, as demonstrated by Figure 5.5(a). However, only the four most populated O environments can be assigned in the ^17O 3QMAS 2D spectrum of 3:2 mullite (Figure 5.5(b)). These environments are: O_t(2Al_h:Al_q) with a predicted δ_{iso} of 65 ± 8 ppm; O_t(2Al_h:Si_q) with a predicted δ_{iso} of 79 ± 7 ppm; O_t(Al_h:Al_q:Si_q) with a predicted δ_{iso} of 62 ± 5 ppm; and O_t(Al_h:2Al_q) with a predicted δ_{iso} of 45 ± 6 ppm. Similarly to the ^27Al NMR, the ^17O spectra also contains a resonance from the α-Al_2O_3 impurity which has a δ_{iso} ≈ 75 ppm.\(^{2,131}\)

The only sillimanite site not observable in the experimental data is the bridging oxygen O_b(Al_q:Si_q), predicted at δ_{iso} = 62 ± 13 ppm. It is overshadowed in the NMR data by the more popular sites that surround it. This fate is shared by several other environments presented in Figure 5.5(a), including the T_3O site O_t(2Al_q:Si_q). Two other environments, O_t(Al_h:2Si_q) and O_b(2Si_q), are shown to have distinct NMR parameters from the popular sites. However, these are not observed in the 2D NMR spectrum due to their stronger quadrupole interaction (C_Q ≈ 6 MHz) and low population (< 4%).\(^{132}\) Unfortunately, the four-coordinated sites O_q, whose detection via ^17O NMR would confirm the presence of the (Al/Si)O_{4+1} moieties, are predicted to have a combined population of ~1 % and, therefore, are not observed.

Similarly to the ^29Si data, the predicted δ_{iso} values are all underestimated by a few ppm. Still, the close agreement between the predicted and experimental ^17O NMR parameters lends credence to the proposed 3:2 mullite structure, despite not directly confirming the presence of moieties of greatest interest (T_3O, (Al/Si)O_{4+1}, etc.). Once again, the supercell enabled GIPAW-DFT calculations have allowed complete assignment of the ^17O NMR spectra.
5.4. 2Al₂O₃:SiO₂ Mullite

5.4.1. ²⁹Si Results

The ²⁹Si MAS NMR of 2:1 mullite is presented in Figure 5.6(a), alongside the simulated spectrum of the structures generated by the supercell GIPAW-DFT approach (Figure 5.6(b)). The simulated spectrum for 2:1 mullite has several differences to the calculated ²⁹Si spectrum for 3:2 mullite (Figure 5.3(c)). As shown by Table 5.3, there are less Si habituated in the T₂O environments, whereas the higher frequency T₃O moieties have an increased presence. An additional T₃O site, 3Al(O₉):6Al(O₆) (Figure 5.6(c)), is sufficiently populated to affect the simulation. This Si site is bonded to an O₉ site in a T₃O moiety that contains the quasi-tetrahedral AlO₄+₁ unit. The higher population of the T₃O environments is in line with the increased vacancies in the 2:1 mullite structure. Unfortunately, the ²⁹Si NMR of 2:1 mullite does not reflect these differences. As shown in Figure 5.6(a), the spectrum is overshadowed by an amorphous SiO₂ impurity produced by the single crystal synthesis method. This impurity makes structural determination of 2:1 mullite by ²⁹Si NMR on this sample fruitless, while the solid state ¹⁷O enriched 2:1 mullite sample was produced in too small of a quantity to study with ²⁹Si NMR.

![Figure 5.6(a) The ²⁹Si MAS (5 KHz) NMR spectrum of 2:1 mullite (single crystal) at 7.05 T. (b) The supercell enabled GIPAW-DFT simulated ²⁹Si spectra of 2:1 mullite. Experimental spectra are in black, with simulated lineshapes in red and deconvoluted/simulated resonances in colours corresponding to Figure 5.3(e) and the insert (c), which together show schematic representations of the most popular (> 2 %) predicted Si environments in 2:1 mullite.](image)
5.4.2. $^{27}$Al and $^{17}$O Results

The calculated $^{27}$Al NMR parameters ($\delta_{iso}$ and $C_Q$) from the 2:1 mullite generated structures are presented in Figure 5.7(a). In comparison to the 3:2 mullite predictions (Table 5.4), there is an expected increase in the number of Al in $\text{AlO}_{4+1}(T_3\text{O})$, $\text{AlO}_4(T_3\text{O})$ and $\text{AlO}_3\square$ moieties due to the increase in vacancies. The $^{27}$Al 2D 3QMAS spectrum of 2:1 mullite (single crystal) is presented in Figure 5.7(b). Unfortunately, the increase in population of the $\text{AlO}_{4+1}(T_3\text{O})$ and $\text{AlO}_3\square$ sites is too small to give any appreciable difference in the NMR spectrum.

<table>
<thead>
<tr>
<th>Site</th>
<th>Calculated Al Population Share / (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{AlO}_6$</td>
<td>42.8</td>
</tr>
<tr>
<td>$\text{AlO}_4(T_2\text{O})$</td>
<td>48.4</td>
</tr>
<tr>
<td>$\text{AlO}_4(T_3\text{O})$</td>
<td>4.4</td>
</tr>
<tr>
<td>$\text{AlO}_{4+1}(T_3\text{O})$</td>
<td>2.2</td>
</tr>
<tr>
<td>$\text{AlO}_3\square$</td>
<td>1.8</td>
</tr>
<tr>
<td>$\text{AlO}_5$</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Table 5.4 The calculated Al population, as a percentage of all Al sites, of the NMR observed environments in the supercell generated structures of 3:2 and 2:1 mullite.
2D 3QMAS NMR spectrum does, however, show an ostensible increase in intensity at \( \delta_{\text{iso}} \approx 65 \) ppm which is credited to the larger population of the \( \text{AlO}_4(T_3O) \) environment in 2:1 mullite.

The calculated \(^{17}\text{O} \) NMR parameters, \( \delta_{\text{iso}} \) and \( C_Q \), from the 2:1 mullite generated structures are presented in Figure 5.8(a). In comparison to the 3:2 mullite predictions (Table 5.5), there is an expected decrease in the number of Si containing moieties due to the increased Al:Si ratio. The \(^{17}\text{O} \) 2D 3QMAS spectrum of 2:1 mullite is presented in Figure 5.8(b). Similarly
The $^{17}$O $^{\alpha}$QMAS for 2:1 mullite produced a lower SNR, due to a smaller quantity of the sample, which is responsible for the apparent reduction in intensity of some resonances. The solid state synthesised 2:1 mullite is shown to have an α-$\text{Al}_2\text{O}_3$ impurity in the $^{17}$O NMR data (Figure 5.8(b)), as seen in the $^{27}$Al and $^{17}$O data on the solid state synthesised 3:2 mullite (Figure 5.4(b) and Figure 5.5(b) respectively). However, due to the different synthesis, the

Figure 5.8(a) A plot of the GIPAW-DFT calculated $^{17}$O $\delta_{\text{iso}}$ and $C_Q$ values of the various environments in the supercell generated 2:1 mullite structures. (b) The $^{17}$O 3QMAS (20 KHz) NMR 2D spectrum of $^{17}$O enriched 2:1 mullite at 11.7 T with the MAS spectrum above and the projected $\delta_{\text{iso}}$ spectrum on the right. The predicted environments from the simulations are assigned to distinct resonances in the 2D spectrum.
single crystal 2:1 mullite does not contain such an impurity and, therefore, it is not detected in the $^{27}\text{Al}$ NMR data on 2:1 mullite (Figure 5.7(b)). Due to the small changes in site population it appears that only $^{29}\text{Si}$, out of the NMR nuclei examined, has the resolution to confidently confirm differences in the 2:1 mullite. Unfortunately, this would require a new sample to be synthesized that does not contain such a large amorphous SiO$_2$ contaminant, perhaps by the sol-gel method.

5.5. Boron Doped Mullite

The study of 1%, 4% and 6% B$_2$O$_3$ doped mullites (see Table 5.1) began with the work of Lührs et al., and was continued with a thorough NMR investigation by King.\textsuperscript{120, 124-126} They confirmed that the B dopant was incorporating into the structure as BO$_3$ using $^{11}\text{B}$ NMR, which also verified the varying B content in the samples. Their use of $^{29}\text{Si}$ and $^{27}\text{Al}$ NMR revealed structures identical to 3:2 mullite, presenting no discernible trends with increasing B content. However, due to the new information on mullite structure, revealed by the supercell enabled calculations in this study, the three B doped mullites have been reinvestigated using $^{27}\text{Al}$ 3QMAS 2D NMR.

5.5.1. $^{27}\text{Al}$ Results

The $^{27}\text{Al}$ 3QMAS 2D NMR spectra of 1%, 4% and 6% B$_2$O$_3$ mullites are displayed in Figure 5.9. Except for the missing $\propto$-Al$_2$O$_3$ contaminant resonance, the same resonances are observed in the spectra of 3:2 and 2:1 mullite, confirming that the mullite structure can incorporate B without significant structural changes. The only other change occurs at the resonance ($\delta_{\text{iso}} \approx 80$ ppm), which was tentatively assigned to the AlO$_3$□ moiety. Although

<table>
<thead>
<tr>
<th>Site</th>
<th>Calculated O Population Share / (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3:2 mullite</td>
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<tr>
<td>$O_t(2\text{Al}^h:\text{Al}^q)$</td>
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<tr>
<td>$O_t(\text{Al}^h:\text{Al}^q:\text{Si}^q)$</td>
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<tr>
<td>$O_t(\text{Al}^h:2\text{Al}^q)$</td>
<td>13.9</td>
</tr>
<tr>
<td>$O_t(2\text{Al}^h:\text{Si}^q)$</td>
<td>13.8</td>
</tr>
</tbody>
</table>

Table 5.5 The calculated O population, as a percentage of all O sites, of the NMR observed environments in the supercell generated structures of 3:2 and 2:1 mullite.
Figure 5.9 The $^{27}\text{Al}$ 3QMAS (20 KHz) NMR 2D spectrum of (a) 1 %, (b) 4% and (c) 6% B$_2$O$_3$ doped mullites at 14.1 T with the MAS spectrum above and the projected $\delta_{\text{iso}}$ spectrum on the right. The resonance corresponding to AlO$_3$($T_2$□) is labelled.
observable in the 2D spectrum, the low intensity resonance could not be distinguished in the projected $\delta_{\text{iso}}$ spectra for either aluminosilicate mullite. However, in all three of the B doped mullites the resonance is not only larger in the 2D spectrum, but clearly visible in the projected $\delta_{\text{iso}}$ spectra. The intensity of the resonance at $\delta_{\text{iso}} \approx 80$ ppm also increases as the $\text{B}_2\text{O}_3$ content increases. Although projected $\delta_{\text{iso}}$ spectra are not strictly quantitative,\textsuperscript{133} it is clear that increasing B content increases the Al site occupancy of the $\text{AlO}_3\square$ moiety.

The current opinion on B doped mullites states that $\text{BO}_3$ substitutes for the tetrahedral units in the $\text{T}_2\text{O}$ moiety, as represented in Figure 5.2. It is hypothesized that, due to their similar configuration in the structure, the $\text{BO}_3$ substitution may stabilise adjacent $\text{AlO}_3\square$ polyhedra (see Figure 5.10), encouraging their formation. Additionally, it is also possible that the increased number of vacancies introduced by the $\text{BO}_3$ substitution, inherently leads to an increase in $\text{AlO}_3\square$ sites. Regardless, the $^{27}\text{Al}$ NMR results on B doped mullite further justify the existence of the $\text{AlO}_3\square$ moiety in mullite.

5.6. Conclusions

This study has successfully answered several of the remaining questions about mullites structure. Firstly, the configuration of $\text{AlO}_4$ and $\text{SiO}_4$ units in 3:2 mullite was shown to lack order due to the success of the “random” approach over the “sillimanite” approach for structure generation. Secondly, the investigation provided a complete assignment of all
components in the $^{29}$Si MAS spectrum of 3:2 mullite, confirming the existence of the T₃O moiety and conclusively proving the inclusion of SiO₄ tetrahedra in its formation.

Additionally, this study unveiled some new features of mullites structure. The $^{29}$Si and $^{27}$Al investigations determined the presence of quasi-tetrahedral polyhedra (AlO₄+/SiO₄+) that contain an additional long bond to a four-coordinate oxygen site. The discovery of the AlO₄+ environment at ~50 ppm, allowed the previously reported assignments of the $^{27}$Al MAS spectrum of mullite to be corrected. The $^{27}$Al investigation also proposed AlO₃ as an environment in the mullite structure, which was verified by the investigation into boron doped mullites. In the B doped mullites, the AlO₃ environment was shown to increase in population with B content.

Unfortunately, the differences in structure between 3:2 and 2:1 mullite could not be confirmed with this method, due to the large amorphous SiO₂ contaminant in the 2:1 mullite sample. However, the close agreement of the supercell generated NMR simulations with the experimental $^{29}$Si, $^{27}$Al and $^{17}$O NMR data on all the mullite samples proved the strength of the described methodology for the modelling of disordered systems, which could be applied to other catalyst systems.
The Study of Mullite-like Aluminoborates using Solid State NMR

6.1. Background

Mullite type materials consist of characteristic edge sharing octahedral chains along the c-axis, which are cross linked with three, four or five coordinated polyhedral motifs. As discussed in Chapter 5, several aluminosilicate phases, including those doped with small quantities of substitutional boron, belong to the mullite family. Figure 6.1 demonstrates the mullite type compositional field in the Al$_2$O$_3$ - SiO$_2$ - B$_2$O$_3$ ternary system, as reported by Werding and Schreyer. The aluminoborates Al$_{18}$B$_4$O$_{33}$ (9Al$_2$O$_3$:2B$_2$O$_3$ or A9B2) and Al$_4$B$_2$O$_9$ (2Al$_2$O$_3$:B$_2$O$_3$ or A2B) are the two thermodynamically stable phases in the Al$_2$O$_3$ - B$_2$O$_3$ system. Both phases are known to have mullite-like structures, however the complex details of both crystal structures are yet to be solved.

![Ternary plot of Al$_2$O$_3$ - SiO$_2$ - B$_2$O$_3$ system showing known compounds with mullite-like structures (●) and known compounds with structures differing from mullite’s (■). The boron-mullite compositional field is shown in blue.](image)
The A9B2 phase has been utilised as a model sample for advanced quadrupolar $^{27}$Al NMR techniques due to the ordered, yet convoluted, nature of its Al environments. Double rotation (DOR) NMR, $^{13}$ MQMAS NMR, ultrahigh field MAS NMR$^{139}$ and satellite transition spectroscopy (SATRAS)$^{140}$ have all been applied to the study of the material. Alongside $^{11}$B MAS NMR, these studies have revealed a crystalline structure composed of AlO$_6$, AlO$_5$, AlO$_4$ and BO$_3$ polyhedra.$^{136}$ However, the exact chemical composition of this phase is still a matter of debate. Various chemical analyses have provided the stated composition of Al$_4$B$_5$O$_9$ (termed A9B2).$^{135,141-142}$ In contrast, crystallographic structure refinements, with an ordered distribution of Al and B, suggest a composition closer to Al$_5$BO$_9$ (A5B rather than A9B2)$^{136,143}$ The crystal structure reported by Garsche et al. is shown in Figure 6.2(a).$^{143}$ A substitution of less than 2 % of Al atoms with B in the A5B composition would yield A9B2. This discrepancy in the two proposed compositions has previously been rationalised by the possibility of a solid solution of Al and B at the tetrahedral site, with 9 % of AlO$_4$ sites replaced with BO$_4$. However, Fisch et al. found no evidence of BO$_4$ sites in their $^{11}$B MAS NMR investigation.$^{136}$ In this thesis, the phase will be termed A9B2 throughout, following the nomenclature used by the majority of the literature to avoid confusion. A9B2 is commercially available under the trade names Alborex and Alborite.

The A2B phase has a structure closely related to that of borasilite (Al$_{16}$Si$_2$B$_6$O$_{37}$; see Figure 6.1), with B replacing Si sites. Fischer et al. confirmed the presence of AlO$_6$, AlO$_5$, AlO$_4$, BO$_4$ and BO$_3$ motifs using $^{11}$B and $^{27}$Al MAS NMR. They reported the crystal structure shown in Figure 6.2(b).$^{97}$ At certain sites boron can exist as three or four-coordinate, with the BO$_4$ moiety having an additional bond to an adjacent bridging oxygen. In the BO$_4$ environment, this oxygen site is shared by three tetrahedral units analogous to the observed T$_3$O sites in aluminosilicate mullites (Chapter 5). The variation in coordination at the B site and the displacement of the adjacent O creates the disorder that is observed by NMR. The exact details of the oxygen disorder and the positions of the BO$_4$ moieties are not solved yet.

A series of Al$_{6-x}$B$_x$O$_9$ compounds (where $1 \leq x \leq 3$) can be synthesized between the two stable A9B2 and A2B phases.$^{144}$ Further heat treatment of these phases yields either A9B2 or A2B, hence the phases are thought to be metastable. The disordered structure of this series of aluminoborate compounds (Figure 6.2(c)) is close to that of mullite. Mackenzie et al. have previously performed an $^{11}$B and $^{27}$Al NMR study on a similar series of compounds.$^{145}$ They revealed the presence of both BO$_4$ and BO$_3$ sites in the structure, where an increase in B content caused an increase in the BO$_4$:BO$_3$ ratio. Their tentative $^{27}$Al NMR assignments
show the structure to be composed of two AlO$_6$ motifs and three AlO$_5$/AlO$_4$ motifs, where the configuration of the three non-octahedral motifs varies with boron content. They showed that the structure contained one AlO$_5$ and two AlO$_4$ sites at low B content, whereas at high B content an additional AlO$_5$ unit replaced one of the AlO$_4$ sites.

The A9B2 and A2B ceramics are of high research interest due to their novel properties, which include: high elastic modulus, high tensile strength, low thermal expansion, low thermal conductivity and high corrosion resistance. Hence, aluminoborates have

Figure 6.2 The reported crystal structures of the three aluminoborate phases (a) A9B2, (b) A2B and (c) Al$_{6-x}$B$_x$O$_9$. AlO$_6$ octahedra are in blue and Al, B and O atoms are in green, red and black respectively.
applications in optics, tribology, fire insulation, nuclear reactor components, refractory linings, nanomaterials and structural materials. The majority of structural applications focus on the utilisation of aluminoborate needles or whiskers for the reinforcement of other materials, such as light metals (Al, Mg), other ceramics, and epoxy resins. Most relevant to this thesis is the role of aluminoborates in catalysis. Due to their refractory nature and their ability to be prepared with a high surface area, they are well suited as catalyst materials. Aluminoborates are most commonly used as solid acid catalysts, which are important to many industrial reactions such as catalytic reforming, cracking, isomerisation, and (de)alkylation. Similarly to aluminosilicate mullites, they are also used as a catalyst support. Multiple studies have shown that varying the synthesis and composition of these materials has a significant effect on the acidity and activity of the catalysts.

This investigation aims to produce a detailed structural characterisation of the phases in the $\text{Al}_2\text{O}_3$ - $\text{B}_2\text{O}_3$ system using $^{11}$B and $^{27}$Al solid state NMR. The structural changes of the A9B2, A2B and metastable $\text{Al}_{6-x}\text{B}_x\text{O}_9$ phases are investigated as a function of initial B content. Solid state and sol-gel synthesized A9B2 samples are also compared to the commercially available materials.

6.2. Experimental

6.2.1. Synthesis

Three series of powder samples with varying precursor Al/B ratios were produced for this investigation: the A9B2 phase series (A), the A2B phase series (B), and the metastable $\text{Al}_{6-x}\text{B}_x\text{O}_9$ series (C). The synthesis method and initial precursor composition (in wt% $\text{Al}_2\text{O}_3$/B$_2$O$_3$) of each compound is given in Table 6.1. Alborite and Alborex were obtained from Shikoku Chemical Corporation (Japan). The synthesis of all remaining samples was performed by K. Hoffman (Universität Bremen) and complete details of the methodology have been reported previously.

Samples A1-A3, series B and series C were all synthesised via a sol-gel method. Stochiometric amounts of aluminium nitrate nonahydrate (Al(NO$_3$)$_3$•9H$_2$O) and boric acid (H$_3$BO$_3$) were dissolved in glycerol to produce a gel. The gels are then crystallised at 1373 K for 5 hrs, 1223 K for 44 hrs, or 1173 K for 6hrs to produce the A9B2, A2B, and $\text{Al}_{6-x}\text{B}_x\text{O}_9$ phases, respectively. Samples A4, A5 and A6 (A9B2 phase) were synthesized via a solid
state reaction. Powdered $\alpha$-Al$_2$O$_3$ and B$_2$O$_3$ were mixed in corresponding ratios (Table 6.1), pressed into a pellet and crystallised at 1473 K for 10 hrs.

Hoffman et al. verified the phases of the samples in series A and B (as A9B2 and A2B respectively) with XRD. The precursor ratios of series C indicate compositions of Al$_{6-x}$B$_x$O$_9$ where $x = 1.09, 1.38, 1.61, 1.79$ and $2$ for C1, C2, C3, C4, and C5 respectively. However, due to volatilisation of boron during synthesis the actual composition of the product may be different to the initial composition.

<table>
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<th>Initial comp.</th>
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<tr>
<td></td>
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<td>Al$_2$O$_3$/(wt%)</td>
</tr>
<tr>
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<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Alborex</td>
<td>-</td>
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<tr>
<td>C5</td>
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Table 6.1 The synthesis methods and initial compositions of the three series of aluminoborates studied: A (A9B2), B (A2B) and C (Al$_{6-x}$B$_x$O$_9$). The initial compositions are given in corresponding ratios of Al$_2$O$_3$ and B$_2$O$_3$. G - sol-gel method; S - solid state method.
6.2.2. Solid State NMR Measurements

The MAS NMR experiments in this study were performed at room temperature across a range of different magnetic field strengths ($B_0$) using Varian-600 (14.1 T), Bruker Avance II+–600 (14.1 T), and Bruker Avance III HD–400 (9.40 T) spectrometers. All NMR data was processed using TOPSPIN and MQMAS data was sheared using the TOSPSPIN program xfshear. Simulations of non-quadrupolar ($C_Q = 0$) lineshapes (Gaussian) and second-order quadrupolar lineshapes were performed with dmfit. The distributions are defined by a $C_Q$ centre, a $C_Q$ width and a broadening factor ($\Delta$).

The $^{11}$B NMR experiments were performed at 14.1 T ($\nu_0 ^{11}$B) = 192.50 MHz) with an MAS frequency of 12 KHz. The experiments were completed using a boron-free Varian 4 mm HXY MAS probe with all data referenced with respect to NaBH$_4$(s) ($\delta_{iso} = -42.06$ ppm). A $\pi/2$ pulse length was determined on NaBH$_4$(s) resulting in a selective $\pi/2$ pulse length of 5 $\mu$s being used, with a recycle delay of 20 s used throughout. The quantitative nature of these experiments was tested on selected samples, by comparison with experiments using smaller flip angles that satisfy the uniform excitation condition for quadrupolar nuclei (see Equation 2.21). In this case, a selective $\pi/9$ pulse length of 1.1 $\mu$s was used resulting in a much longer acquisition time (>24 hr). The difference in relative ratio of the intensity of BO$_3$ and BO$_4$ resonances was negligible and therefore the longer experiment was deemed unnecessary.

The $^{27}$Al NMR experiments were performed at 14.1 T ($\nu_0 ^{27}$Al) = 156.34 MHz) and 9.40 T ($\nu_0 ^{27}$Al) = 104.23 MHz) with an MAS frequency of 20 KHz. The experiments were completed using a Bruker 3.2 mm HX probe with all data referenced with respect to yttrium aluminium garnet(s) (YAG; $\delta_{iso}[\text{AlO}_6] = 0.7$ ppm). A $\pi/2$ pulse length was determined on YAG(s) resulting in a selective $\pi/6$ pulse length of 0.8 $\mu$s and 1 $\mu$s being used for the single-pulse experiments at 14.1 T and 9.40 T, respectively. At 9.40 T a recycle delay of 10 s was utilised, whereas a shorter delay of 2 s was used at 14.1 T to minimise experimental time. The 14.1 T 2D MQMAS experiments utilised a z-filtered 3QMAS pulse sequence with a 3.5 $\mu$s excitation pulse, a 1.5 $\mu$s conversion pulse and a 17.0 $\mu$s selective z-filter pulse.
6.3. The A9B2 Phase

6.3.1. $^{11}$B Solid State NMR

The $^{11}$B MAS NMR spectra of the A9B2 samples (series A) is presented in Figure 6.3. The NMR parameters are determined via simulated fitting of each spectrum and the results are given in Table 6.2. As expected, each spectrum is dominated by a second-order quadrupolar broadened lineshape with parameters indicative of trigonal planar BO$_3$ ($C_Q \approx 2.6$ MHz, $\delta_{iso} \approx 16.5$ ppm, and $\eta_Q \approx 0.07$ - 0.12). The $^{11}$B lineshape of Alborex is subtly distinct from the rest of the species. In Figure 6.3(b) the low frequency shoulder of the BO$_3$ resonance is raised, which is not matched by the simulated second-order quadrupole lineshape. This is due to the whisker macrostructure of Alborex, as observed by Hoffman et al. using scanning electron microscopy (SEM) imaging. The stacking of the needle shaped crystal formations in the NMR rotor causes a preferred orientation of crystals, altering the second-order quadrupolar powder pattern (see Chapter 1.4.1). Under MAS conditions, this results in an increase in intensity at the low frequency shoulder position.

Each sample also presents with small resonances at $\delta_{iso}$ values between 2.6 and $-$0.7 ppm, which are assigned to BO$_4$ moieties. Fisch et al. did not observe these environments with $^{11}$B NMR as they were obscured by the broad BO$_3$ resonance, a product of the lower B$_0$ field used in their study. The detection of BO$_4$ environments confirms the hypothesis that a solid solution of AlO$_4$ and BO$_4$ units is present in the A9B2 structure. This explains the different chemical compositions given by structural refinements and chemical analysis in the literature. The BO$_4$ to BO$_3$ ratio increases with increasing initial B content for both synthesis methods in series A, which is concurrent with the replacement of AlO$_4$ sites with BO$_4$ units. The varied BO$_4$ content of the compounds in series A (Table 6.2) suggests a range of compositions close to Al$_{18}$B$_2$O$_{33}$, which has been confirmed previously by prompt gamma neutron activation analysis (PGAA). The majority of the compounds in series A have multiple BO$_4$ components (Figure 6.3), indicating disorder at the BO$_4$ site.

6.3.2. $^{27}$Al Solid State NMR

The $^{27}$Al MAS NMR spectra of the A9B2 samples (series A) is presented in Figure 6.4. Due to the convoluted nature of the MAS lineshape, $^{27}$Al 2D 3QMAS NMR experiments (Figure 6.5) were performed on a selected range of samples: Alborite, A1, A4 and A6. The 3QMAS
Figure 6.3 The $^{11}$B MAS (12 KHz) NMR spectra at 14.1 T of series A (A9B2): (a) Alborite, (b) Alborex, (c) A1, (d) A2, (e) A3, (f) A4, (g) A5 and (h) A6. The experimental spectra, the simulated lineshapes and the deconvoluted resonances are presented in black, red and blue, respectively.
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<th>(\eta_Q)</th>
<th>FWHM</th>
<th>Species</th>
<th>Intensity</th>
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<td>(KHz)</td>
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<td>(%)</td>
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<tr>
<td></td>
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<td>((\pm 0.05))</td>
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<tr>
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<td>-</td>
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Table 6.2 The \(^{11}\)B NMR parameters of series A (A9B2) determined via simulated fitting.
Figure 6.4 The $^{27}$Al MAS (20 KHz) NMR spectra at 14.1 T of series A (A9B2): (a) Alborite, (b) Alborex, (c) A1, (d) A2, (e) A3, (f) A4, (g) A5 and (h) A6. The experimental spectra, the simulated lineshapes and the deconvoluted resonances are presented in black, red and blue, respectively.
Figure 6.5 The $^{27}$Al 2D 3QMAS (20 KHz) NMR spectra at 14.1 T of selected (a) alborite, (b) A1, (c) A4 and (d) A6. The MAS spectrum is displayed above and the projected $\delta_{\text{iso}}$ spectrum on the right. Distinct resonances in the 2D spectrum are labelled with their assigned environments.
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114
data allowed accurate simulated fitting of the MAS lineshapes. The NMR parameters determined via simulated fitting of each spectra are given in Table 6.

Each sample is shown to contain one AlO$_6$, one AlO$_4$ and two AlO$_5$ sites as previously determined. The NMR parameters of each component are similar to those determined by Kunath et al. and Massiot et al., although some variation occurs across the series. Similarly, the predicted site occupation ratio of 2:1:1:1 for AlO$_6$:AlO$_5$:AlO$_5$:AlO$_4$ is approximately followed throughout. However, an additional small AlO$_6$ resonance is detected in the spectra of Alborex, A3, A5 and A6 (Figure 6.4(b, e, g, h)). This AlO$_6$ component is only observed in the compounds that have a high initial B content, and, hence, contain a high BO$_4$ content. Therefore, it is hypothesized that the AlO$_6$ units adjacent to the BO$_4$ unit are distorted by a decreased bond length, creating a distinct AlO$_6$ site. This hypothesis also explains the disorder seen at the BO$_4$ site by $^{11}$B NMR (Figure

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<th>AlO$_6$</th>
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</tr>
<tr>
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<tr>
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<td></td>
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<td></td>
<td>14 -   - 6.13 Al$_2$O$_3$ 14 -</td>
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Table 6.3 The $^{27}$Al NMR parameters of series A (A9B2) determined via simulated fitting.
6.3). The smaller AlO$_6$ resonance has been fitted with a narrow Gaussian/Lorentzian lineshape in the simulations, despite the probable quadrupolar nature of the component. The small observed intensity is thought to be one of the singularities present in a full second-order quadrupole lineshape (see Figure 1.7), with the rest of the shape overshadowed by the larger AlO$_6$ resonance. There is tentative evidence for the second singularity of the proposed quadrupole lineshape at ~0 ppm in Figure 6.4(b).

The samples A4 and A5 (Figure 6.4(f, g)) have a resonance at ~14 ppm that is assigned to an amorphous α-Al$_2$O$_3$ impurity from the starting materials. The α-Al$_2$O$_3$ impurity only occurs in these high initial Al$_2$O$_3$ content samples produced via the solid state methodology, and its intensity increases with the initial Al$_2$O$_3$ content. The sol-gel samples A1 and A2, which were produced with the same initial Al$_2$O$_3$:B$_2$O$_3$ ratios, do not contain an observable quantity of α-Al$_2$O$_3$. This is replicated in the aluminosilicate mullites (Chapter 5), verifying that the α-Al$_2$O$_3$ is a by-product of the solid state synthesis method and that the sol-gel synthesis method provides a greater control over the end product.

The samples A1 and A2 (Figure 6.4(c, d)) are observed to have more disturbed lineshapes in their MAS spectra. This is visible in the AlO$_6$ resonances, which are less accurately fitted by the simulations. Additionally, both present an increased AlO$_4$:AlO$_5$ ratio with the intensity of the AlO$_4$ components reaching ~30%. This is believed to be due to local disorder in the crystal structure of the high initial Al content, sol-gel synthesized systems, as disorder effects were also detected in the diffraction data acquired by Hoffman et al.\textsuperscript{164}

6.4. The A2B Phase

6.4.1. $^{11}$B Solid State NMR

The $^{11}$B MAS NMR spectra of the set of A2B samples (series B) is presented in Figure 6.6. The NMR parameters determined via simulated fitting of each spectra are given in Table 6.4. The $^{11}$B NMR spectra confirm the presence of both BO$_3$ and BO$_4$ components in the A2B phase. For each of the samples the trigonal BO$_3$ moiety is represented by a second-order quadrupole lineshape with a $C_Q$ of 2.6 ± 1 MHz, a $\delta_{iso}$ of 16.8 ± 1 ppm and a $\eta_Q$ of 0.11 ± 0.01. The BO$_4$ resonances fall into the $\delta_{iso}$ range of 1.0 to −1.3 ppm.
Figure 6.6 The $^{11}$B MAS (12 KHz) NMR spectra at 14.1 T of series B (A2B): (a) B1, (b) B2, (c) B3 and (d) B4. The experimental spectra, the simulated lineshapes and the deconvoluted resonances are presented in black, red and blue, respectively.

Figure 6.7 The $^{27}$Al MAS (20 KHz) NMR spectra at 14.1 T of series B (A2B): (a) B1, (b) B2, (c) B3 and (d) B4.
The relative site occupancies of BO$_4$ to BO$_3$ determined by the $^{11}$B MAS NMR results disagree with those predicted by Fischer et al. $^{97}$ Their crystal structure refinements suggest a maximum relative BO$_4$ site occupancy of 25%, which is at odds with the 31% occupancy determined on sample B4. Similarly to the A9B2 phase (Chapter 6.4.1), there is an observed trend of increasing BO$_4$ relative site occupancy (BO$_4$:BO$_3$ ratio), with the increasing initial B content. Therefore, the extra BO$_4$ content is hypothesised to be due to the substitution of B into tetrahedral Al sites, as observed in the A9B2 phase. This substitution would result in an additional BO$_4$ environment in the structure. The multiple BO$_4$ sites observed in the $^{11}$B

<table>
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<th>$\eta_Q$</th>
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<th>Species</th>
<th>Intensity</th>
<th>Species Int.</th>
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<td>/ (KHz)</td>
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Table 6.4 The $^{11}$B NMR parameters of series B (A2B) determined via simulated fitting.
spectra (Table 6.4) lend credence to this hypothesis. Additionally, the decreased bond length of the BO$_4$ units, compared to AlO$_4$, would result in disorder at the site. Therefore, this hypothesis could also justify the disordered oxygen configuration detected via diffraction.$^{164}$

6.4.2. $^{27}$Al Solid State NMR

The $^{27}$Al MAS NMR spectra of the set of A2B samples (series B) is presented in Figure 6.7. Due to the extremely convoluted nature of the lineshapes, $^{27}$Al 2D 3QMAS NMR experiments, alongside additional $^{27}$Al MAS NMR experiments at 9.40 T, were performed on selected samples: B1 and B4 (Figure 6.8). The deconvolutions of the 1D MAS spectra of B1 and B4 were constrained by simulating the MAS spectra at two different fields (14.1 T and 9.40 T) and by simulating the 3QMAS projections of each site. This thorough methodology provides confidence in the accurate simulation of complicated quadrupolar spectra. The NMR parameters determined via simulated fitting of the spectra for B1 and B4 are given in Table 6.5.

The spread of the contours along the QIS axis in the 2D 3QMAS data, and the long asymmetric tails of the resonances in the 1D MAS spectra, are indicative of significant distributions in the quadrupolar parameters of each component. Hence, the $^{27}$Al NMR data proves that the A2B structure is characterized by significant short-range disorder, especially when compared to A9B2. The spectra of B1 and B4 can be deconvoluted into 6 distinct components assigned as four AlO$_4$/AlO$_5$ sites and two AlO$_6$ sites. The relative site occupancy of six-coordinated sites is ~50 % for both compounds which is in good agreement with the previous $^{27}$Al data on A2B, reported by Fischer et al.$^{97}$ However, the thorough $^{27}$Al NMR investigation reported here, improves on the published material by clearly distinguishing four non-octahedral sites, rather than three. This provides a better match with the published refined crystal structure which details the distinct Al sites as two AlO$_4$, two AlO$_5$ and three AlO$_6$ environments. Two of the crystallographic AlO$_6$ sites are thought to be insufficiently distinct to be resolved by NMR, hence the difference in the number of six-coordinated sites observed in the NMR and the crystallographic data.

Additionally, the refined crystal structure reports two AlO$_4$ sites whereas the corresponding NMR resonances are assigned to one AlO$_4$ and one AlO$_{4+1}$ moiety. The AlO$_{4+1}$ moiety is a quasi-tetrahedral unit with an additional long bond to an adjacent O. This assignment is parallel to the discovery of an AlO$_{4+1}$ moiety in aluminosilicate mullites. The moiety is
Figure 6.8 The $^{27}$Al 2D 3QMAS (20 KHz) NMR spectra at 14.1 T of (a) B1 and (b) B4. The MAS spectrum is displayed above and the projected $\delta_{iso}$ spectrum on the right. Distinct resonances in the 2D spectrum are labelled with their assigned environments. The $^{27}$Al MAS (20 KHz) NMR spectra at 14.1 T and 9.40 T for (c) B1 and (d) B4. The experimental spectra, the simulated lineshapes and the deconvoluted resonances are presented in black, red and blue, respectively.
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<th>$C_Q$ width</th>
<th>$\eta_Q$</th>
<th>$\Delta$</th>
<th>Species</th>
<th>Intensity</th>
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<td>10 ± 1</td>
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Table 6.5 The $^{27}$Al NMR parameters of series B (A2B) determined via simulated fitting using a Gaussian distribution of $C_Q$. 
represented by a component with a $\delta_{\text{iso}}$ of 49 ± 1 ppm, which is corroborated by the similar NMR parameters observed for the AlO$_4^{+1}$ site in mullite (Chapter 5.3.2).

The $^{27}$Al MAS spectra of series B (Figure 6.6) do not exhibit any observable trends and the determined NMR parameters of the resonances in B1 and B4 are close to identical. Therefore, the varied BO$_4$ content, and the varied initial B content that precedes it (see Chapter 6.4.1), appear to have no effect on the overall structure of the A2B phase.

6.5. The Metastable Al$_{6-x}$B$_x$O$_9$ Phase

6.5.1. $^{11}$B Solid State NMR

The $^{11}$B MAS NMR spectra of the metastable Al$_{6-x}$B$_x$O$_9$ samples (series C) is presented in Figure 6.9. The NMR parameters determined via simulated fitting of each spectra are given in Table 6.6. The $^{11}$B NMR spectra of series C are analogous to those of the A2B phase (see Figure 6.6) as both contain a trigonal BO$_3$ resonance ($C_Q \approx 2.6$ MHz, $\delta_{\text{iso}} \approx 16.8$ ppm and $\eta_Q \approx 0.15$), multiple BO$_4$ resonances ($\delta_{\text{iso}}$ values between 1.6 and −1.1 ppm), and a trend of increasing BO$_4$ relative site occupancy with the increasing B content. As discussed for both the stable phases, the multiple BO$_4$ resonances indicate some local disorder at this site.

The major differences occur in the larger range of BO$_4$ site occupancies that the C series contains. The site is virtually unpopulated (1 %) for sample C1 but increases up to 20% relative BO$_4$ site occupancy for sample C5, demonstrating a broad AlO$_4$/BO$_4$ solid solution. The structural model proposed by Mazza et al. for Al$_{6-x}$B$_x$O$_9$, suggest that sample C5 should have 50 % BO$_4$, rather than the 20 % detailed in Table 6.6. This demonstrates a clear preference of boron to populate a three-fold coordination and, therefore, the proposed structural model requires revaluation.

These findings are all in agreement with Mackenzie et al.’s $^{11}$B NMR investigation of a similar series in the Al$_{6-x}$B$_x$O$_9$ phase.
Figure 6.9 The $^{11}$B MAS (12 KHz) NMR spectra at 14.1 T of series C (Al$_{1-x}$B$_x$O$_9$): (a) C1, (b) C2, (c) C3, (d) C4 and (e) C5. The experimental spectra, the simulated lineshapes and the deconvoluted resonances are presented in black, red and blue, respectively.
The $^{27}$Al MAS NMR spectra of the $\text{Al}_6\text{x}\text{B}_x\text{O}_9$ samples (series C) is presented in Figure 6.10. The $^{27}$Al NMR investigation of series C was performed analogously to the investigation of series B (Chapter 6.4). Accurate deconvolution of the complex $^{27}$Al MAS spectra for selected samples (C1, C3 and C5) was completed via the simultaneous simulation of multi-field (14.1 T and 9.40 T) MAS spectra and 3QMAS projections (Figure 6.11). The NMR parameters determined via simulated fitting of the spectra for C1, C3 and C5 are given in Table 6.7. Once again, the NMR results include significant distributions in the quadrupolar parameters

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<th>$C_Q$/(MHz)</th>
<th>$\eta_Q$/(± 0.01)</th>
<th>FWHM/(KHz)</th>
<th>Species</th>
<th>Intensity/(%)</th>
<th>Species Int./(± 0.5)</th>
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| Table 6.6 | The $^{11}$B NMR parameters of series C ($\text{Al}_6\text{x}\text{B}_x\text{O}_9$) determined via simulated fitting.

6.5.2. $^{27}$Al Solid State NMR

The $^{27}$Al MAS NMR spectra of the $\text{Al}_6\text{x}\text{B}_x\text{O}_9$ samples (series C) is presented in Figure 6.10. The $^{27}$Al NMR investigation of series C was performed analogously to the investigation of series B (Chapter 6.4). Accurate deconvolution of the complex $^{27}$Al MAS spectra for selected samples (C1, C3 and C5) was completed via the simultaneous simulation of multi-field (14.1 T and 9.40 T) MAS spectra and 3QMAS projections (Figure 6.11). The NMR parameters determined via simulated fitting of the spectra for C1, C3 and C5 are given in Table 6.7. Once again, the NMR results include significant distributions in the quadrupolar parameters.
for each component, proving that the $\text{Al}_{6-x}\text{B}_x\text{O}_9$ structures are highly disordered despite longer range periodicity giving rise to measured diffraction data.\textsuperscript{59} The 3QMAS data reveal that the structure of all three compounds consists of two AlO$_6$ sites, one AlO$_{4+1}$ site, and an AlO$_4$ site. Samples C3 and C5 boast two additional AlO$_5$ sites (see Figure 6.11(c)) whereas sample C1 has an additional AlO$_4$ (see Figure 6.11(a)). In the $^{27}\text{Al}$ MAS NMR investigation of $\text{Al}_{6-x}\text{B}_x\text{O}_9$ compounds with similar initial contents as C3 and C5 performed by Mackenzie et al., they could only distinguish three AlO$_{4/5}$ moieties rather than the four moieties discovered in this investigation.\textsuperscript{145} Furthermore, the simulated fittings of the $^{27}\text{Al}$ data reveal the AlO$_6$ site occupancies to be split between a populated site and a marginally populated site, contrary to the results of Mackenzie et al.\textsuperscript{145} The highly resolved 3QMAS measurements reported here, alongside the thorough simulation methodology utilised, permit a more accurate identification of all the Al speciation, than in the previous reports.

Figure 6.10 The $^{27}\text{Al}$ MAS (20 KHz) NMR spectra at 14.1 T of series C (Al$_{6-x}$B$_x$O$_9$): (a) C1, (b) C2, (c) C3, (d) C4 and (e) C5.
Figure 6.11 The $^{27}$Al 2D 3QMAS (20 KHz) NMR spectra at 14.1 T of (a) C1, (b) C3 and (c) C5. The MAS spectrum is displayed above and the projected $\delta_{iso}$ spectrum on the right. Distinct resonances in the 2D spectrum are labelled with their assigned environments. The $^{27}$Al MAS (20 KHz) NMR spectra at 14.1 T and 9.40 T for (d) C1, (e) C3 and (f) C5. The experimental spectra, the simulated lineshapes and the deconvoluted resonances are presented in black, red and blue, respectively.
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<td>AIO$_4$</td>
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Table 6.7 The $^{27}$Al NMR parameters of series C (Al$_{6-x}$B$_x$O$_9$) determined via simulated fitting using a Gaussian distribution of $C_Q$. 
Similarly to the A2B phase (Chapter 6.3), a quasi-tetrahedral AlO$_{4+1}$ moiety is detected in the three series C compounds. Due to the observable similarities between the $^{27}$Al MAS spectra of series C and aluminosilicate mullites (Figure 5.4), the presence of an AlO$_{4+1}$ site is not surprising. The structural models proposed by Mazza et al. for Al$_{6-x}$B$_x$O$_9$ do not contain AlO$_5$ sites, and therefore may adequately describe the structure of sample C1. However, the detection of two AlO$_5$ sites in the samples C3 and C5 via $^{27}$Al NMR, alongside the results of the $^{11}$B NMR investigation (Chapter 6.5.1), cast severe doubts on the veracity of these models. The detection of AlO$_5$ sites is assured, due to their presence in the structures of both stable aluminoborate phases and Mackenzie et al.’s corroborative $^{27}$Al NMR results.

The observed increase in the number of distinct AlO$_5$ sites, and with it the increase in relative AlO$_5$ site occupancy (Table 6.7), is a function of increasing initial B content which mirrors the concomitant increase in relative BO$_4$ site occupancy. Furthermore, the observed disorder in the more populated AlO$_6$ site also increases with increasing initial B content. These observations are compatible with an AlO$_4$/BO$_4$ solid solution, where the smaller BO$_4$ units induce distortion to adjacent AlO$_6$ units and the increased disorder favours the formation of AlO$_5$ moieties.

6.6. Conclusions

This study has successfully improved upon the previous $^{11}$B and $^{27}$Al NMR studies of the three mullite-like aluminoborate phases: A9B2, A2B and metastable Al$_{6-x}$B$_x$O$_9$. The thorough $^{27}$Al NMR investigation of the three phases used 3QMAS and multi-field MAS NMR experiments, which allowed accurate assignment of the Al speciation. For the A9B2 phase, the accurate $^{27}$Al NMR data detected a variety of differences in the structure of commercially, solid state and sol-gel synthesized materials. The $^{27}$Al NMR results (using the knowledge gained from the mullite study in Chapter 5) discovered the quasi-tetrahedral AlO$_{4+1}$ moiety in both the A2B and Al$_{6-x}$B$_x$O$_9$ structures, correcting the previous assignments in the literature. The improved $^{27}$Al assignments in the Al$_{6-x}$B$_x$O$_9$ phase also disproved the existing structural model by confirming the presence of five-coordinate Al sites.

By studying a series of each phase with varying initial B contents this study has improved the understanding of the crystal structures. The $^{11}$B NMR results determined a solid solution of tetrahedral Al and B in each series. In the A9B2 phase the narrow solid solution explained the disagreement between Al$_{18}$B$_4$O$_{33}$ and Al$_8$BO$_9$ compositions reported in the literature.
Additionally, the discovered substitution of BO₄ for AlO₄ units in the A2B phase justified the literature structural models with the NMR results.

Overall, the study has shown the utility of quadrupolar solid state NMR for structural determination. It is hoped that the improved understanding of the structures may aid in the application of these materials, especially in catalysis where small structural changes can result in large differences in function.
Summary

Despite the relatively disparate areas of research covered by this thesis, there is a common theme carried throughout. Namely, the structural determination of materials related to catalysis and containing local disorder, through investigation by quadrupolar solid state NMR. Each chapter approached this task with different methodologies, while investigating a diverse selection of catalytic materials.

Before an investigation into palladium catalyst materials with $^{105}$Pd solid state NMR could take place in Chapter 4, the previously unexplored technique required fundamental development. This was achieved with the proposal of a standard chemical shift reference (0.33 M H$_2$PdCl$_6$(aq)) and the inaugural study of three Pd complexes (K$_2$PdCl$_6$, (NH$_4$)$_2$PdCl$_6$ and K$_2$PdBr$_6$) with direct observation $^{105}$Pd solid state NMR. What began as a routine initial study into the chemical shift range instead became a key part of the research, as $^{105}$Pd solid state NMR was found to be sensitive to minute structural deviations from the nominal cubic structure of the complexes. The study of Pd metal particles provided more evidence for this sensitivity, where it was shown that $^{105}$Pd solid state NMR could detect defects in the metal structure and classify Pd metal nanoparticle sizes. Once these developmental studies were complete, $^{105}$Pd NMR was applied to the more catalytical relevant doped Pd metal systems. At this point the limitations of $^{105}$Pd solid state NMR were brought to light. In more disordered systems, the previously lauded sensitivity, in the form of both quadrupolar and Knight shift interactions, became its downfall, as the NMR resonances were often broadened beyond detection. Regardless, the study of the catalysts with $^{105}$Pd solid state NMR alongside multi-nuclear solid state NMR, XRD and magnetic susceptibility measurements provided valuable structural information, specifically the interstitial location of the dopant.

The feasibility of a novel methodology for structural determination in disordered systems was explored in Chapter 5. The recently developed structure-generation program supercell was combined with GIPAW-DFT calculations and solid state NMR to probe the structure of the aluminosilicate, mullite. Mullite was chosen for this study due to its disordered structure, which had not yet been completely solved, and its relevance to catalysis. This methodology proved successful on 3:2 mullite, as the supercell led simulations allowed complete assignment of the $^{17}$O, $^{27}$Al and $^{29}$Si solid state NMR spectra. Hence, the remaining questions...
concerning mullite’s structure could be answered. The application of this methodology to other mullite phases, was only limited by the synthetic challenges of making stochiometric samples.

Three mullite-like aluminoborate phases (A9B2, A2B and metastable Al_{6.5}B_{2}O_{9}) were investigated in Chapter 6, instead utilising the tried-and-tested method of solid state NMR in conjunction with (previously reported) diffraction results for structural determination. The $^{11}$B and $^{27}$Al solid state NMR study of the disordered aluminoborate phases utilised MQMAS and multiple field measurements. The thoroughness of this study, alongside the information gleaned from the mullite investigation mentioned above, allowed complete assignment of the NMR spectra for each phase, which corrected previous erroneous reports. Each of the phases were also studied for changes under varying synthesis conditions, which verified additional structural features in the aluminoborates.

It is hoped that the discovered structural information contained in this thesis may lead to improved function of the related catalysts and that the developed methodologies can be applied to studies of other disordered systems.


147. Hernández, M. F.; Suárez, G.; Cipollone, M.; Conconi, M. S.; Aglietti, E. F.; Rendtorff, N. M., Formation, microstructure and properties of aluminum borate ceramics obtained from alumina and boric acid. *Ceramics International* 2017, 43 (2), 2188-2195.


