EMERGENT STATES IN TRANSITION METAL OXIDES

Alexandra Gibbs

A Thesis Submitted for the Degree of PhD at the University of St Andrews

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Emergent States in
Transition Metal Oxides

A thesis presented by
Alexandra Gibbs
to the
University of St Andrews
in application for the degree of
Doctor of Philosophy
March 2013
**Declarations**

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Abstract

Transition metal oxides adopt a wide variety of crystal structures and display a diverse range of physical phenomena from Mott insulating states to electron-nematics to unconventional superconductivity. Detailed understanding of these states and how they may be manipulated by structural modifications requires both precise structural knowledge and in-depth physical property measurements using as many techniques over as wide a range of phase space as possible. In the work described in this thesis a range of transition metal oxides were studied using high-resolution powder neutron diffraction and detailed low-temperature physical property measurements. The quaternary barium orthotellurates $\text{Ba}_2\text{NiTeO}_6$, $\text{Ba}_2\text{CuTeO}_6$ and $\text{Ba}_2\text{ZnTeO}_6$ belong to an almost unstudied family of materials. The development of procedures for synthesizing large single crystals has facilitated the investigation of interesting new anisotropic magnetic states in the Cu and Ni systems and the existence of a possible structural phase transition in the Zn-based compound. YMnO$_3$ is a multiferroic with improper ferroelectricity. The study of the high-temperature structural phases described in this thesis has led to the identification both of the transition path to the ferroelectric state and the identification of an isostructural phase transition within the ferroelectric phase. BiFe$_{0.7}$Mn$_{0.3}$O$_4$ is also a multiferroic material but with proper ferroelectricity. The investigation of the structural phases of this compound have provided confirmation of the high-temperature phases with the reassignment of the symmetry of the highest-temperature phase which is intriguingly different to that of the unsubstituted material. Finally, an investigation of the electronic structures of the high conductivity delafossites PdCoO$_2$ and PdCrO$_2$ using micro-cantilever torque magnetometry measurements of quantum oscillations is described. This has resolved the warping of the Fermi surface of PdCoO$_2$ and given insights into the complicated Fermi surface of the itinerant antiferromagnet PdCrO$_2$. 
Acknowledgements

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An exciting part of my PhD was my work on the previously unexplored orthotellurate compounds. Here I have to especially thank Professor H. Takagi for arranging my stay at RIKEN as an International Program Associate during my PhD and also for the many insights and ideas he has passed on. Thanks are also
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Chapter 1

Introduction

Transition metal oxides are a broad class of materials that, as the name indicates, are oxides containing one or more transition metal ($d$-block) element(s). They are common in nature as binary compounds (pyrolusite ($\text{MnO}_2$), magnetite ($\text{Fe}_3\text{O}_4$)) and ternary and higher compounds (e.g. minerals such as olivine ($\text{Mg,Fe}_2\text{SiO}_4$) and perovskite, $\text{CaTiO}_3$). Many have been in use since ancient times, such as haematite ($\text{Fe}_2\text{O}_3$) as a pigment and magnetite ($\text{Fe}_3\text{O}_4$) in compass needles. As solid state chemistry began to develop in the 19th century, new forms of transition metal oxides were discovered and the physical properties of known materials were investigated. Many studies were driven by the realisation that even small changes in composition and structure can lead to dramatic changes in physical properties that could be useful in a practical sense. An early example of this is yttria-stabilised zirconia which was found by Nernst to be better than simple oxides in his incandescent lamp, designed to avoid some shortcomings in the tungsten filament lamps common at the time [1]. On a more fundamental level, this led to a still unfulfilled desire to understand the links between structure, composition and physical properties.

From the early 20th century there was a huge growth in synthesis and measurement of transition metal oxides spurred on by a variety of factors. One of these was the need for replacements for natural materials with dwindling or inaccessible supplies (such as mica, used as a dielectric in components such as capacitors); another was the need for better materials for emerging technologies such as radio instrumentation. A further equally important factor was the fact that despite the apparently simple structures of many materials and the general trends realised in
them, the structures could not be predicted from knowledge of the composition
and often small changes in composition would give either a different structure
and/or completely different physical properties.

The reductionist viewpoint of late 19th century science saw these compounds as
structures built from discrete building blocks following simple physical laws which
would be fully understood once thoroughly investigated. However, this dream has
still not been realised. Even with the huge computational power available now and
the deep insights that have been gained as a result, modern techniques such as
density functional theory still often are not able to reliably predict the structure of
a material or its electronic and magnetic properties. We now understand that the
reductionist viewpoint has limited applicability in many cases and that emergent
phenomena (where the collective behaviour of a large group of components is
different from that expected from the behaviour of a small number of components)
have a critical role to play in structure, physical properties and the relationships
between the two. Although the exact reductionist explanation of the structures
and behaviours of transition metal oxides may not be possible, careful study of
many systems allows underlying principles to be deduced and therefore enhances
our understanding and ability to predict and control such systems.

Modern transition metal oxide research is therefore necessarily a multifaceted
research enterprise. It often resembles a huge puzzle. The pieces of the puzzle are
information gained from a wide variety of experiments such as transport measure-
ments, neutron scattering, local probes and many others. Assembling the pieces
into a bigger picture is crucially helped by theory guiding the connection of pieces
and often pointing towards as yet undiscovered phenomena. However the task is
far more complicated than the usual puzzle with the ultimate shape being un-
known, the connections between pieces non-trivial and it not being unheard of for
pieces to change their shape midway through. For a puzzle like this the traditional
reductionist approach necessarily has to fail.

In order to understand properties of any new class of materials no single tech-
nique or experiment is sufficient. Rather, it is an interdisciplinary endeavour
spanning both aspects of physics and of chemistry. This is clearly exemplified by
the recently discovered iron-based superconductors with the first major publica-
tion describing the unconventional superconducting properties appearing in the
Journal of the American Chemical Society [2].
A modern research program covers a wide range of experiments starting with sample synthesis and characterization followed by in-depth structural studies and the detailed determination of electronic and magnetic properties. The aim of this thesis research was to combine the experience of both the chemistry side with the group of Prof. Lightfoot and the physics side with the group of Prof. Mackenzie to use such a combination of techniques on a wide variety of materials.

On the chemistry side this included experience in solid-state synthesis and structure determination by neutron and x-ray diffraction. On the physics side, Prof. Mackenzie’s group specialises in low-temperature experiments on transport and specific heat experiments on unconventional electronic states.

As I had both experience in sample synthesis by image-furnace crystal growth and also in low-temperature measurements from my undergraduate time, with interest in both, I used this chance of combining these aspects of materials research. I am very grateful to both groups for allowing me to attempt this work.

It was agreed that I would initially work on small separate projects in each group. These have, perhaps predictably, developed into larger research trains in their own right. In the chemistry-based projects research concentrated on the synthesis and structural studies of multiferroic transition metal oxides. In particular, we determined the ambient-to-high-temperature phase diagrams of YMnO$_3$ and BiFe$_{0.7}$Mn$_{0.3}$O$_3$ using a series of neutron diffraction experiments at ISIS. On the physics side I was part of a project concentrating on the electronic structure determination and physical properties of the delafossite materials PdCoO$_2$ and PdCrO$_2$ using micro-cantilever torque magnetometry measurements at low temperatures.

The project perhaps closest to the original aim was carried out in collaboration with the group of Prof. Takagi with which I had the privilege to work during the last year. In this project an almost unstudied group of materials (quaternary barium orthotellurates) was investigated, motivated by structural similarity to a recently proposed spin-liquid compound. This began with synthesis and development of flux growth methods to obtain large single crystals. The materials were then characterized by low-temperature specific heat and magnetization measurements. There is currently a neutron diffraction investigation in preparation to further investigate the detailed structures (a proposal for experiments on HRPD (High Resolution Powder Diffractometer) at ISIS involving both the groups of Prof. Lightfoot and Prof. Mackenzie as well as Prof Takagi has been accepted).
We furthermore plan to investigate the novel magnetic states discovered by detailed low-temperature experiments similar in spirit to those carried out in Prof. Mackenzie’s group. At the same time this is the least complete project described here, because it is still ongoing research at a relatively early stage.

The experimental chapters of this thesis discuss very different systems but provide some overview of a broad range of transition metal oxide physics and the crucial structure-property relationships involved.

The thesis is organized such that general theory relevant to the later chapters is discussed in chapter 2. Experimental and analysis techniques are treated in chapter 3, in which the standard techniques and concepts are discussed in a general manner. Further detailed or material-specific theory or experimental concepts are discussed as relevant in the experimental chapters.

The four experimental chapters are stand-alone but when taken together describe a range of studies from preliminary (barium orthotellurates) though to detailed experiments on well-known materials (YMnO₃) that will be faced by anyone working at the chemistry/physics interface. They also cover a range of materials from insulators to metals and magnetically ordered systems to non-magnetic materials. They give a representation of some of the currently important fields in condensed matter physics.

Chapter 4 discusses the development of sample preparation techniques and basic physical property characterization for three barium orthotellurate compounds whose physical properties have until now not been determined or investigated in detail.

Chapter 5 details high-resolution powder diffraction experiments on the high-temperature phases of BiFe₀.₇Mn₀.₃O₃ which led to a reassignment of the symmetry and space group of the highest temperature phase.

Chapter 6 focuses on the high-temperature phase transitions of YMnO₃ and the elucidation of the transition path between the high- and ambient-temperature phases.

Chapter 7 discusses micro-cantilever torque magnetometry investigations of the Fermi surfaces of PdCrO₂ and PdCoO₂.
Chapter 2

Transition Metal Oxides

2.1 Introduction

The structures of materials are fundamentally linked to their physical properties. The local environment of a transition metal ion has a strong influence on its magnetic and electronic contribution to the material as a whole. The linkages between these polyhedra further determine the nature of magnetic and electronic ordering. Face-, edge- and corner-sharing polyhedra combine to form structures based on 1D chains, 2D planes, 3D networks and more complicated structures with subunits of different dimensionality.

Due to this close structure-property relationship, detailed knowledge of a structure is required for both first principles prediction of properties through electronic structure calculations and also the more empirical predictions based upon factors such as non-centrosymmetry. A recent example of a material where the determination of correct structural information was critical for the understanding of the physical phenomena being displayed is magnetite (Fe$_3$O$_4$) [3]. It is surprising that such a binary oxide could still have an unresolved structure. However, the Verwey transition to an insulating state at 125 K was proposed to be a charge disproportionation transition in 1939 and has been the subject of debate ever since. The precise details of the structural distortions in the monoclinic $Cc$ structure of the Verwey phase have only just been elucidated. The presence of anomalously short Fe-Fe distances led to the conclusion that the localized electrons are distributed
over linear triplets of Fe sites and this trimeron quasiparticle model allowed understanding of further experimental observations [3]. This has also provided the correct structural basis for ab-initio calculations and further understanding of the magnetoelectric properties of this material [4, 5].

In this thesis a wide variety of experimental techniques are employed to study a range of transition metal oxides. In particular, crystal structure determination and the investigation of low temperature electronic properties are a main focus. In the following sections a brief theoretical background to the experiments discussed in this thesis will be given. Due to the range of different materials studied a comprehensive explanation of all relevant theory is not possible. Nevertheless, I will give an overview of the broadly applicable foundations in this chapter. More specialised theory relevant to studies of particular compounds will be discussed in the relevant experimental chapters. In section 2.2 the basic structural aspects of transition metal oxides will be covered. This will be followed by a discussion of the physics of phase transitions, as relevant to this thesis, in section 2.3. Finally we will briefly discuss the electronic and magnetic properties of transition metal oxides in section 2.4.

2.2 Crystal Structures of Transition Metal Oxides

The structures of transition metal oxides can often be considered as composed of various linkages of simple metal oxide polyhedra such as tetrahedra, octahedra and trigonal bipyramids. To give an impression of how this simple principle can lead to a wide variety of structures we will briefly discuss some common structures for binary transition metal oxides as shown in figure 2.1. The rock-salt structure adopted by e.g. periclase (MgO), shown in figure 2.1a, consists entirely of edge-sharing octahedra leaving tetrahedral voids in between. The rutile (TiO$_2$) structure in figure 2.1b is composed of chains of MO$_6$ edge-sharing octahedra linked by corner sharing octahedra. The ReO$_3$ structure in figure 2.1c is composed entirely of corner sharing octahedra. Finally, face-sharing octahedra are found in the corundum (Al$_2$O$_3$) structure shown in figure 2.1d where pairs of face-sharing octahedra are linked by edge-sharing octahedra.
Chapter 2. Transition Metal Oxides

Figure 2.1: Examples of binary transition metal oxides: (a) the rock-salt structure adopted by the cubic form of MgO, (b) the rutile TiO$_2$ structure, (c) the ReO$_3$ structure and (d) the corundum Al$_2$O$_3$ structure.

An important additional degree of freedom for physical and structural properties is the addition of one or two further cations leading to ternary and quaternary compounds which are central to this thesis. These also display a variety of structures composed of linked polyhedra. Figure 2.2 shows some common ternary structures. The delafossite (CuFeO$_2$) structure, shown in figure 2.2a, consists of sheets of edge-sharing octahedra separated by layers of the A-site element which are linearly coordinated above and below by oxygen ions. This leads to electronically active layers of oxygen coordinated transition metal ions. The resulting often quasi-two-dimensional properties are a prime example of how the crystal structure can determine the effective dimensionality of the electronic properties. The spinel structure of, for example, CuFe$_2$O$_4$ shown in figure 2.2b is composed of edge-sharing chains of octahedra linked by corner-sharing tetrahedra.

One of the best known structures is that of the mineral perovskite, CaTiO$_3$. It gives its name to the perovskite family of materials which have the same structure type and are one of the most technologically and scientifically important classes of materials. One of the first examples of this was the use of BaTiO$_3$ as a replacement for mica as a dielectric in capacitors [6]. The distorted and ideal forms of the perovskite structure, shown in figures 2.2c and 2.2d respectively, are composed
entirely of corner-sharing transition metal ion octahedra. The perovskite structure is very similar to the ReO$_3$ structure but with the additional A-site cation occupying the 12-fold coordinated vacant site in the ReO$_3$ lattice.

The three previously discussed linkage types (corner-, edge- and face-sharing) of the MO$_6$ polyhedra have not only structural significance but play a crucial role in determining the electronic and magnetic properties of materials. The distance between the metal ions is strongly dependent upon the linkage type and although transition metal oxides are usually considered to be dominantly ionic in character there are important examples of systems where metal-metal bonds play a role and structures with significant face-sharing character would be expected to have a larger susceptibility to metal-metal bonding. As a general rule, face-sharing octahedra are not generally favoured for systems with a dominantly ionic character and face-sharing octahedra are not found as commonly as edge- and corner-sharing systems. The proximity effect of different octahedral linkages can also be very important in determining the magnetic properties of materials via the exchange interaction.

There are several standard ways of characterising and classifying structures of
transition metal oxides. The most relevant of these will now be briefly discussed for ABO$_3$-type compounds with reference to the perovskite structure as a simple and well-known example.

2.2.1 Characterisation and Classification

The perovskite structure could be argued to be the most important in transition metal oxides due to its high flexibility of both distortion and composition. The mineral perovskite adopts a distorted corner-linked octahedral structure with the space group $Pbnm$ at ambient temperature$^1$. The aristotype$^2$ for the perovskite family is, however, the high-temperature form of perovskite, stable above 1523 K. This is cubic with undistorted octahedra and the space group $Pm\bar{3}m$ [8]. This structure is adopted by few compounds at room temperature but by many perovskite-type compounds at high temperature. Perovskite structures are typically discussed as distorted forms of the aristotype with a notation developed by Glazer [9] being commonly used to describe the various octahedral tilts. The notation is straightforward, with three letters relating to the relative magnitudes of tilts around each crystallographic axis. These letters are the same for tilts of the same magnitude and different for unequal magnitude tilts. Therefore, equal tilts in all directions will be written as $aaa$ and unequal tilts in all directions $abc$. The superscript to the letter is either +, - or 0 symbolising in-phase tilts, out of phase tilts or the absence of tilts between adjacent layers of octahedra. The ideal cubic perovskite, therefore, has the Glazer tilt system $a^0a^0a^0$, i.e. tilts of zero magnitude around each axis. The ambient temperature form of CaTiO$_3$ has the Glazer tilt system $a^{-}a^{-}b^{+}$. Further details and examples can be found in the article by Glazer [9].

The perovskite structure is adopted by a large number of compounds with a wide range of compositions. The range of stability of the structure is often described in terms of the tolerance factor developed by Goldschmidt [11]. The tolerance factor, $t$, is defined using the cation ionic radii $R_A$ and $R_B$ and oxygen anion ionic radius $R_O$. It was expressed by Goldschmidt [11] as:

$$ (R_A + R_O) = \alpha \cdot \sqrt{2}(R_B + R_O) $$

$^1$A brief overview of symmetry and space group notations is given in Appendix A. A more thorough treatment can be found e.g. in Burns and Glazer [7].

$^2$Ideal undistorted parent structure.
and is now commonly formulated as:

\[ t = \frac{(R_A + R_O)}{\sqrt{2(R_B + R_O)}}. \]  

(2.2)

This relates the cation and anion sizes to determine how well the ions will fit into a perovskite structure. A perfect fit of ions into their respective sites will give a tolerance factor of \( t = 1 \). A structure-field diagram can be drawn for the structure types of \( \text{ABO}_3 \) composition expected for different relative ionic sizes as shown in figure 2.3. For tolerance factors less \( 0.9 \geq t > 0.85 \), distorted perovskite structures tend to be stable. When \( t \leq 0.85 \), non-perovskite structures usually form such as the layered hexagonal structure of \( \text{Y MnO}_3 \) (\( t = 0.85 \)) with trigonal bipyramids of oxygens coordinating the Mn site rather than the octahedral coordination of perovskites. \( \text{Y MnO}_3 \) and the details of its crystal structure will be discussed in detail in chapter 6.

Figure 2.3: A structure-field map for \( \text{A}^{3+}\text{B}^{3+}\text{O}_3 \) compounds [10].
The aristotype and distorted forms of the perovskite structure will be particularly important in chapter 5 where the high temperature phase transitions of BiFe$_{0.7}$Mn$_{0.3}$O$_3$ are investigated.

When quaternary (or higher) perovskite materials have fractional occupancies on the B-site which correspond to ratios such as 1:1, 1:2, 1:3, they often (depending upon details of the relative sizes and valencies of the ions involved) order in the structure.

In the case of a 1:1 ratio this causes doubling of the unit cell. These ordered double perovskites, with the general formula $A_2BB'O_6$ with B and B' being transition metal ions, are also commonly called 'elpasolites' after the mineral elpasolite $K_2NaAlF_6$. The space group of the aristotype structure for these materials is the face-centred cubic $Fm\bar{3}m$ as shown in figure 2.4a. This is the structure that is expected for materials with a tolerance factor $0.8 \leq t \leq 1.0$. For materials with tolerance factor $t \geq 1.0$, hexagonal structures are predicted and often involve face-sharing octahedra [12]. An example of this is the $12L$ structure$^3$ of Ba$_2$NiTeO$_6$ with $t = 1.05$ which is shown in figure 2.4b. This compound will be investigated in chapter 4.

$^3$Layered structures are often described using the notation $nL$ where $n$ is the number of layers in a unit cell. If the symmetry of the structure is known $L$ can be replaced with, for example, $R$ signifying a rhombohedral cell, $H$ a hexagonal unit cell or $C$ a cubic unit cell.

Figure 2.4: Two common structures of elpasolite-type compounds. The most simple ordered structure, a $3C$ cubic double perovskite, is shown in (a). Panel (b) shows the $12L$ Ba$_2$NiTeO$_6$-type structure. The green and blue octahedra represent the two different B-site ion octahedra with the A-site ion in grey.
The details of the electronically and magnetically ordered states of transition metal oxides can often be better understood by studying the details of the transition to the ordered state. The changes in properties at the phase transition and the elucidation of the order parameter give information on the underlying causes and mechanisms of the transition and therefore the most relevant parameters for understanding the ordered phase. The next section will discuss phase transitions in solids in general followed by the methods of analysis of second order phase transitions and of quantifying differences between related structures.
2.3 Phase Transitions in Solids

Phase transitions were first classified thermodynamically by Ehrenfest in 1933 [13]. The classification was based upon derivatives of the Gibbs free energy, $G$. Infinitesimal changes of the Gibbs free energy $dG$ as a function of infinitesimal changes in the temperature $dT$ and pressure $dP$ are given by

$$dG = -SdT + VdP,$$  \hspace{1cm} (2.3)

where as usual $S$ is the entropy, $T$ the temperature, $V$ the volume and $P$ the pressure. Since $G$ is an analytic function it follows:

$$\left(\frac{dG}{dP}\right)_T = V, \quad \left(\frac{dG}{dT}\right)_P = -S.$$  \hspace{1cm} (2.4)

Ehrenfest defined the order of a transition as the lowest order at which a derivative of the Gibbs free energy shows a discontinuity at the transition. Therefore, first order transitions show discontinuities in entropy and volume. Discontinuities in thermal expansivity, specific heat and compressibility without jumps in (i.e. continuous) volume and entropy are often properties of a second-order (or continuous) phase transition:

$$\left(\frac{\partial^2 G}{\partial P \partial T}\right)_P = \left(\frac{dV}{dT}\right)_P = \alpha V,$$  \hspace{1cm} (2.5)

$$\left(\frac{\partial^2 G}{\partial P^2}\right)_T = \left(\frac{dV}{dT}\right)_T = -\beta V,$$  \hspace{1cm} (2.6)

$$\left(\frac{\partial^2 G}{\partial T^2}\right)_P = \left(\frac{dS}{dT}\right)_P = \frac{C_P}{T}.$$  \hspace{1cm} (2.7)

Phase transitions are also often described in terms of an order parameter, $\eta$, which is normally finite below the transition temperature $T_C$ and zero above $T_C$. Examples of order parameters are the magnetization in a ferromagnetic transition, the polarization in a ferroelectric transition, the magnitude of an octahedral tilt in a perovskite structural phase transition or any other parameter which may be measured and whose magnitude can be related to the phase transition. First order transitions show a discontinuity in the order parameter at a phase transition as shown in figure 2.5a and second order transitions show continuous evolution of the
order parameter as in figure 2.5b, often of the form

$$\eta \propto |T_C - T|^{\beta}.$$  \hfill (2.8)

### 2.3.1 The Landau Theory of Phase Transitions

The free energy close to a transition can be expanded in $\eta$, as proposed by Landau [14], giving:

$$G = G_0 + \alpha \eta + A\eta^2 + C\eta^3 + B\eta^4 + \ldots.$$  \hfill (2.9)

The constraint for a second order phase transition that $G(\eta)$ should be independent of the sign of $\eta$ ($\eta=0$ at the transition) leads to the removal of the terms with odd powers of $\eta$, leaving:

$$G = G_0 + A\eta^2 + B\eta^4 + \ldots.$$  \hfill (2.10)

The fundamental physics of a second order phase transition can be captured by considering only terms up to fourth order. The equilibrium value of $\eta$ is at a minimum in $G$, defined by $\frac{\partial G}{\partial \eta} = 0$ and $\frac{\partial^2 G}{\partial \eta^2} > 0$. Positive values for the coefficients $A$ and $B$ lead to a single minimum at $\eta=0$. This is the expected form of the free energy above a second order phase transition. If $A$ is negative and $B$ positive (as they must be if there are no higher order terms in order to ensure stability) then the free energy has a maximum at $\eta=0$ and two minima at finite $\eta$, the new possible equilibrium values of the order parameter below $T_C$. The free energies for both of these cases are shown in figure 2.6. Due to the sign of $A$ controlling the stability of the high and low symmetry phases, the assumption of $A$ changing sign
at \( T_C \) is usually made and the simplest way of expressing this is used\(^4\):

\[
A = a(T - T_C), \quad a > 0.
\]  

(2.11)

Therefore, the Landau free energy is usually written\(^5\) as:

\[
G_L = G_0 + \frac{1}{2}a(T - T_C)\eta^2 + \frac{1}{4}B\eta^4.
\]  

(2.12)

Second order structural transitions were shown by Landau to be necessarily between two group-subgroup related space groups\([15]\). This can be used in analysis of structural phase transitions to first narrow down the candidate space groups for the low (or high) symmetry phase. An example of a group-subgroup diagram for perovskite structures is shown in figure 2.7 (after Howard and Stokes\([16]\)). It also allows the use of distortion modes based upon irreducible representations of space groups as order parameters, thus allowing mapping of the distortion (order parameter) as a function of temperature (or pressure). The amplitudes of the various candidate order parameters can be compared to select the most probable order parameter and hence the most likely subgroup.

This method can be particularly helpful in cases such as ferroelectric materials with multiple possible transition paths to the ferroelectric phase (often corresponding to different mechanisms driving the ferroelectricity). Although distortions can sometimes be relatively small, the use of symmetry arguments from the mode

---

\(^4\)This is simply the assumption that \( A \) can be linearised in the vicinity of the transition.

\(^5\)With the half and quarter constants to give simpler derivative expressions upon minimisation.
decomposition can clarify the problem substantially, especially in temperature regimes where reliable physical property measurements are difficult to obtain. For first order transitions, however, there is no constraint on whether structural symmetry breaking takes place or not and so the above methods are not applicable.

2.3.2 Distortion Mode Analysis of Structures and Phase Transitions

In chapters 5 and 6 we will make use of the technique of symmetry-mode analysis of structural phase transitions. In this method, one takes advantage of the fact that the free energy close to a structural phase transition can be expanded in the amplitudes of structural distortion modes consistent with the irreducible representations of the structures under consideration [17]. This analysis is rather complicated in nature but has recently been facilitated by the development of programs such as the ISOTROPY suite [18] and AMPLIMODES [17, 19]. An in-depth discussion of the theoretical foundations of this technique is out with the scope of this thesis, the details can be found in references such as Stokes et al. [20], Howard et al. [16], Hatch et al. [21], Orobengoa et al. [17], Perez-Mato et al. [19] and references therein as well as textbooks on group theory in physics and chemistry such as those by Jacobs [22] and Dresselhaus, Dresselhaus and Jorio
Here the basic outline of the technique applicable to its practical use in phase transition analysis will be discussed.

A symmetry group can be defined as a set of operations under which an object is invariant. A subgroup is a set of elements within a symmetry group that also form a group. A group-subgroup transition between the high-symmetry phase with space group $G$ and the low symmetry phase with space group $H$ (a subgroup of $G$) can be described using distortion modes with the symmetries of irreducible representations of $G$. Irreducible representations may be most easily envisaged first in terms of point groups, as the translational operations of space groups introduce additional complications.

The symmetries of free molecules (not arranged in a lattice) or specific points in a crystal lattice may be described by point groups, composed of combinations of specific symmetry operations such as rotations, roto-inversions and mirror planes. There are a total of 32 three-dimensional crystallographic point groups.

The point groups and their symmetry operations are usually expressed in Schönhardt’s notation when discussing molecules or in spectroscopy. The equivalent Hermann-Mauguin notation is often used when discussing crystal symmetry. The relevant operations and their symbols in both notations are tabulated in table 2.1.

The point groups are represented by combinations of the symbols of the symmetry operations they contain. This can be seen in the example of a water molecule which has the point group $C_{2v}$. This point group consists of a $C_2$ rotation, two vertical mirror planes $\sigma_v(xz)$ and $\sigma_v(yz)$ and the identity operation $E$. It can be seen from figure 2.8 that the molecule is symmetrical under these four operations.

Elements of a structure can transform differently under these symmetry operations. Each element or set of elements which have identical transformation properties under the symmetry operations have the same irreducible representation. The orbitals (and other functions) can be used as bases to generate the irreducible representations of the point group. A point group will have a number of irreducible representations which is equal to the number of different ways objects can transform under its symmetry operations.

---

Crystalline materials also have translational symmetries. These, combined with the point group symmetries, lead to space groups which are used to describe crystal symmetry. There are 230 three-dimensional space groups, details of which can be found in the International Tables for Crystallography.
Table 2.1: The symmetry operations of point groups and their symbols in Schönflies and Hermann-Mauguin notation.

<table>
<thead>
<tr>
<th>Operation</th>
<th>Schönflies</th>
<th>Hermann-Mauguin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Identity</td>
<td>$E$</td>
<td>1</td>
</tr>
<tr>
<td>Inversion</td>
<td>$i$</td>
<td>$\bar{1}$</td>
</tr>
<tr>
<td>$n$-fold proper rotation</td>
<td>$C_n$</td>
<td>$n$</td>
</tr>
<tr>
<td>(360°/n rotation around an axis)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$n$-fold improper rotation</td>
<td>$S_n$</td>
<td>$\bar{n}$</td>
</tr>
<tr>
<td>(360°/n rotation around an axis</td>
<td></td>
<td></td>
</tr>
<tr>
<td>followed by reflection in a plane</td>
<td></td>
<td></td>
</tr>
<tr>
<td>perpendicular to rotation axis</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Mirror plane

<table>
<thead>
<tr>
<th></th>
<th>$\sigma_d$, $\sigma_h$, $\sigma_v$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$m$</td>
</tr>
</tbody>
</table>

Figure 2.8: The symmetry operations of the $C_{2v}$ point group of the water molecule.

One simple example illustrating this concept is the case of the $s$-orbitals and $p$-orbitals of atoms in the water molecule. The symmetry operations of the $C_{2v}$ molecular point group are, as previously discussed, $E$, $C_2$, $\sigma_v(xz)$ and $\sigma_v(yz)$. An $s$-orbital is isotropic and therefore transforms identically to itself with any of these four operations. A $p_z$ orbital is also transformed into itself under all of these operations and therefore has the same irreducible representation as the $s$-orbital. The $p_x$ and $p_y$ orbitals, however, respond differently. A $p_x$ orbital has its phases swapped by the $C_2$ operation and also by the $\sigma_v(yz)$ reflection and therefore is antisymmetric under these operations. A $p_y$ orbital is antisymmetric to the $C_2$ and $\sigma_v(xz)$ operations.
This information is collected in the form of character tables which describe the possible irreducible representations for a point group. These tables contain entries of 1 and -1 (for 1D representations) corresponding to symmetry or antisymmetry under the symmetry operations. The character table for the point group $C_{2v}$ is shown in table 2.2. The symmetry elements are shown in the top row and the irreducible representations in the first column. The penultimate and last columns give examples of the basis functions which generate the irreducible representations. It can be seen that the $s$ and $p_z$ orbitals have irreducible representation $A_1$. The $p_x$ and $p_y$ orbitals have irreducible representations $B_1$ and $B_2$. It can be deduced from inspection of the last column of quadratic basis functions that a $d_{xy}$ orbital would have irreducible representation $A_2$ in $C_{2v}$. The notation commonly used for irreducible representations of point groups was developed by Placzek and Mulliken [29–31]. The capital letter denotes the dimensionality with $A$ and $B$ being used to indicate a 1D irreducible representation, $E$ for 2D and $T$ for 3D irreducible representations. $A$ indicates that the irreducible representation is symmetric with respect to rotation about the principal axis and $B$ indicates antisymmetry under this operation. The numerical subscripts show the effect of a rotation on the sign of the wavefunction with 1 indicating no change and 2 indicating a change of sign. The subscripts $g$ and $u$ indicate the behaviour of the wavefunction with respect to inversion with $g$ indicating it is symmetric (derived from the German gerade for even) and $u$ antisymmetric (ungerade = uneven).

The irreducible representations for space groups have the same theoretical basis but due to the translational symmetry present the irreducible representations are commonly described around specific high-symmetry points in the Brillouin zone. An example which will be relevant later is the space group $Pm\bar{3}m$ (No. 221). The Wyckoff sites (symmetry equivalent atomic sites) of space groups each have

<table>
<thead>
<tr>
<th>E</th>
<th>$C_2(z)$</th>
<th>$\sigma_v(xz)$</th>
<th>$\sigma_v(yz)$</th>
<th>linear, rotations</th>
<th>quadratic</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>$z$, $x^2$, $y^2$, $z^2$</td>
</tr>
<tr>
<td>$A_2$</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>$R_z$, $xy$</td>
</tr>
<tr>
<td>$B_1$</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>$x$, $R_y$, $xz$</td>
</tr>
<tr>
<td>$B_2$</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>$y$, $R_x$, $yz$</td>
</tr>
</tbody>
</table>

Table 2.2: The character table for point group $C_{2v}$.
a site symmetry corresponding to a point group. Therefore, the irreducible representations of high-symmetry points are directly equivalent to those of the relevant point group. In space group $Pm\bar{3}m$ the high-symmetry point $\Gamma = (0, 0, 0)$ has site symmetry $O_h$ ($m\bar{3}m$ in Hermann-Mauguin notation), which has the character table shown in table 2.3. There are ten irreducible representations for this point, $\Gamma_1^+, \Gamma_1^-, \Gamma_2^+, \Gamma_2^-, \Gamma_3^+, \Gamma_3^-, \Gamma_4^+, \Gamma_4^-, \Gamma_5^+, \Gamma_5^-$ with the symbol labelling the high-symmetry point and superscripts indicating parity with respect to inversion. The point group $O_h$ has four 1D representations, two 2D and four 3D representations. Irreducible representations can be expressed in terms of transformation matrices which are $n \times n$ matrices for $n$-dimensional representations. The character, $\chi$, for an $n$-dimensional representation can have integer values in the range $-n \leq \chi \leq n$ as the character is equal to the trace of the matrix of the irreducible representation for the basis under consideration.

As previously mentioned, a second order transition between a high-symmetry phase with space group $G$ and a low symmetry phase with space group $H$ (a subgroup of $G$) can be described using distortion modes which have the symmetries of irreducible representations of $G$. The atomic positions of the subgroup structure can be written as:

$$ r(\mu, i) = r_0(\mu, i) + u(\mu, i) $$

(2.13)

where $\mu$ labels the atomic positions in the asymmetric unit and $i = 1, \ldots, n_\mu$

<table>
<thead>
<tr>
<th></th>
<th>$E$</th>
<th>4</th>
<th>2</th>
<th>3</th>
<th>$2'$</th>
<th>I</th>
<th>4</th>
<th>m</th>
<th>3</th>
<th>$m'$</th>
<th>functions</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{1g}$</td>
<td>$\Gamma_1^+$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>$x^2+y^2+z^2$</td>
</tr>
<tr>
<td>$A_{1u}$</td>
<td>$\Gamma_1^-$</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td></td>
</tr>
<tr>
<td>$A_{2g}$</td>
<td>$\Gamma_2^+$</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td></td>
</tr>
<tr>
<td>$A_{2u}$</td>
<td>$\Gamma_2^-$</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td></td>
</tr>
<tr>
<td>$E_g$</td>
<td>$\Gamma_3^+$</td>
<td>2</td>
<td>0</td>
<td>2</td>
<td>-1</td>
<td>0</td>
<td>2</td>
<td>0</td>
<td>2</td>
<td>-1</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td></td>
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<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$x^2-y^2)$</td>
</tr>
<tr>
<td>$E_u$</td>
<td>$\Gamma_3^-$</td>
<td>2</td>
<td>0</td>
<td>2</td>
<td>-1</td>
<td>0</td>
<td>-2</td>
<td>0</td>
<td>-2</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>$T_{2g}$</td>
<td>$\Gamma_5^+$</td>
<td>3</td>
<td>-1</td>
<td>-1</td>
<td>0</td>
<td>1</td>
<td>-3</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>-1</td>
</tr>
<tr>
<td>$T_{2g}$</td>
<td>$\Gamma_5^-$</td>
<td>3</td>
<td>-1</td>
<td>-1</td>
<td>0</td>
<td>1</td>
<td>3</td>
<td>-1</td>
<td>-1</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>$T_{1u}$</td>
<td>$\Gamma_4^+$</td>
<td>3</td>
<td>1</td>
<td>-1</td>
<td>0</td>
<td>-1</td>
<td>-3</td>
<td>-1</td>
<td>1</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>$T_{1g}$</td>
<td>$\Gamma_4^-$</td>
<td>3</td>
<td>1</td>
<td>-1</td>
<td>0</td>
<td>-1</td>
<td>3</td>
<td>1</td>
<td>-1</td>
<td>0</td>
<td>-1</td>
</tr>
</tbody>
</table>

Table 2.3: The character table for point group $O_h$ ($m\bar{3}m$). The symmetry elements are labelled in Hermann-Mauguin notation in the first row with the equivalent in Schönflies notation below.
labelling the split positions coming from a single Wyckoff position in $G$. This and the following equations will use the notation of Orobengoa et al. and Perez-Mato et al. [17, 19]. The distortions from the parent structure, $u(\mu, i)$, which have the symmetry of $H$ fully define the distortion relating the two structures. These distortions can be represented using a basis composed of symmetry-adapted basis modes which consist of an amplitude ($A_{\tau,m}$ with units of length, usually in Å) and a set of atomic displacements ($\epsilon(\tau, m|\mu, i)$). These modes are linearly combined to express the distortion relating $G$ and $H$:

$$u(\mu, i) = \sum_{\tau,m} A_{\tau,m} \epsilon(\tau, m|\mu, i)$$

(2.14)

where $\tau$ labels the symmetry and $m$ indexes the possible modes for a given symmetry $\tau$. The displacements $\epsilon(\tau, m|\mu, i)$ also called the the polarization vector of the mode fully define the symmetry-adapted basis mode $(\tau, m)$ when combined with the amplitude.

The modes are normalized by the condition

$$\sum_{\mu,i} \text{mult}(\mu, i) |\epsilon(\tau, m|\mu, i)|^2 = 1$$

(2.15)

with mult($\mu, i$) being the multiplicity of the Wyckoff position within the primitive cell of the structure with space group $H$ and therefore the sum is over the asymmetric unit.

The modes are also chosen with polarization vectors fulfilling the orthogonality condition

$$\sum_{\mu,i} \text{mult}(\mu, i) \epsilon(\tau, m|\mu, i) \cdot \epsilon(\tau', m'|\mu, i) = \delta_{\tau\tau'}\delta_{mm'}.$$  

(2.16)

The amplitudes of the modes which are the relevant quantity for analysis of experimental data can be obtained as a scalar product using the relation

$$A_{\tau,m} = \sum_{\mu,i} \text{mult}(\mu, i) \epsilon(\tau, m|\mu, i) \cdot u(\mu, i).$$

(2.17)

The basis modes have the symmetry of irreducible representations of $G$ and are therefore labelled with the names of the irreducible representations (i.e. $\Gamma_{4}^{-}$).

As well as describing a group-subgroup transition, this method can be used
Chapter 2. Transition Metal Oxides

2.4 Electronic Properties of Transition Metal Oxides

Transition metal oxides show a huge range of electronic states from simple metals and band insulators to unconventional superconductors, electronic-nematic phases and Mott insulators. To this date, no unified theoretical framework that allows the prediction of these unconventional electronic states from first principles exists. Advances in insight are often gained by the postulation of model Hamiltonians capturing the essential emerging physics of the relevant problem. It is beyond the scope of this thesis to describe or review in detail all modern developments in electronic structure research. In this section we mainly concentrate on the basic concepts relevant to the materials discussed in this thesis with more details given in the respective experimental chapters.

2.4.1 The Free Electron Gas

The most basic quantum mechanical description of electrons in solids is the free electron model developed by Sommerfeld. The model assumes free and independent electrons (i.e. interactions with the ion cores and electron-electron interactions between collisions are neglected) within a confined space and, crucially, subject to the Pauli exclusion principle.

The model is based upon wavefunctions constrained by the Born-von Karman periodic boundary condition with a periodicity based, in the simplest case, upon a cube of side length $L$:

$$\psi(x + L, y + L, z + L) = \psi(x, y, z).$$

(2.18)
This leads to wavefunctions of the form

$$\psi(x, y, z) = \frac{1}{V^{1/2}} e^{i\mathbf{k} \cdot \mathbf{r}}$$  \hspace{1cm} (2.19)

with

$$k_x = \frac{2\pi p}{L}, \quad k_y = \frac{2\pi q}{L}, \quad k_z = \frac{2\pi r}{L}.$$  \hspace{1cm} (2.20)

where $p$, $q$ and $r$ are integers. The electron energies are then given by

$$\epsilon(k) = \frac{\hbar^2 k^2}{2m}$$  \hspace{1cm} (2.21)

and the momenta by

$$p = \hbar k.$$  \hspace{1cm} (2.22)

The Pauli exclusion principle dictates that each of these allowed energy states can be occupied by one electron only (modulo spin degeneracy). This leads to filling up of the allowed states at zero temperature to the chemical potential $\mu$ (also called the Fermi energy $E_F$). The filled states, at zero temperature, form in momentum space a sphere of radius

$$k_F = \left( \frac{3\pi^2 N}{V} \right)^{1/3}.$$  \hspace{1cm} (2.23)

with energy at the Fermi surface given by

$$E_F = \frac{\hbar^2}{2m} \left( \frac{3\pi^2 N}{V} \right)^{2/3}.$$  \hspace{1cm} (2.24)

The distribution function, $f$, for such a sphere would be equal to one at and below the Fermi energy (corresponding to one electron per state) and zero above $E_F$:

$$f(T = 0) = \begin{cases} 0 & \text{for } \epsilon > E_F \\ 1 & \text{for } \epsilon \leq E_F \end{cases}$$  \hspace{1cm} (2.25)

At finite temperature, however, the surface of this sphere is smeared out by the excitation of electrons to states above $E_F$ which leave corresponding holes below the Fermi level. This temperature effect is captured by the Fermi-Dirac distribution

$$f(\epsilon, T) = \frac{1}{e^{(\epsilon - \mu)/k_B T} + 1}.$$  \hspace{1cm} (2.26)

The distribution can be seen in figure 2.9. As can be seen only a small fraction
of electrons participate in the temperature excitations contributing to quantities
such as specific heat and thermal transport.

An important quantity is the density of states, \( g(\epsilon) \), which (in 3D) can be derived as

\[
g(\epsilon) = g(k) \frac{dk}{d\epsilon} = \frac{1}{2\pi^2} \frac{(2m)^{3/2}}{h^3} \epsilon^{1/2}.
\]  

(2.27)

It can be shown [32] that the specific heat of a Fermi gas at low temperature is

\[
c_v = \frac{\pi^2}{3} k_B T g(E_F).
\]  

(2.28)

This can be reformulated in terms of the mass of the electron to give

\[
c_v = \frac{mk_F}{3h^2} k_B T.
\]  

(2.29)

Similarly the magnetic susceptibility of a free electron gas is given by [32]:

\[
\chi = \frac{mk_F}{h^2 \pi^2} \mu_B^2.
\]  

(2.30)

The expression for specific heat was a particularly important development as the
experimental data on specific heats of metals could not be reconciled with the
values expected from the classical expression of \( c_v = 3nk_B/2 \).
2.4.2 The Effect of a Weak Periodic Potential

So far we have only considered a free electron gas (the dispersion of which is shown in figure 2.10a) ignoring the effect of the lattice. To illuminate some basic effects one can in a first step assume that the lattice is only a week perturbation. Though far from reality it helps to introduce some important basic concepts. We will take the example of a one-dimensional chain of atoms which gives a potential which has a period equal to the interatomic spacing. This can be represented using a potential $V$ which is the difference between the constant potential assumed for the free electron gas and the ion core potential seen in reality. This potential can be written as a Fourier sum consistent with the periodicity, $a$, of the lattice

$$V = -\sum_{n=1}^{\infty} V_n \cos \left( \frac{2\pi n x}{a} \right). \quad (2.31)$$

First order perturbation theory for the unperturbed wavefunctions $\psi_k$ gives

$$\Delta \epsilon_k^{(1)} = \frac{\int \psi_k^* V \psi_k dx}{\int \psi_k^* \psi_k dx}. \quad (2.32)$$

which is identical to zero. A more advanced treatment of (nearly) degenerate energy levels in second order perturbation theory is required with detailed descriptions given in, for example, the textbooks by Ashcroft and Mermin [32] and Rae [33]. Here we only summarize the main points. The periodic potential predominantly affects those states with wavevectors $k$ close to the Fourier components of $V$ situated at $k_n = \pm \frac{\pi n}{a}$. For wavevectors at the $n^{th}$ zone boundary a gap of size $\epsilon_n^{(2)} = V_n$ opens, as shown in figure 2.10b. The corresponding wavefunctions are standing waves given by $\sin (kx)$ and $\cos (kx)$. Away from the zone boundaries the dispersion has to smoothly approach the unperturbed quadratic dispersion of the free electron model (shown in figure 2.10a).

As indicated in figure 2.10b, the dispersion is broken up into energy bands, each of which can be fully characterised by momenta in the $1^{st}$ Brillouin zone $\pm \pi/a$.

This model gives an important first indication of the impact of crystal structure on the electronic structure and properties of a material.

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7Details of the calculation can be found in standard text books such as [32].
2.4.3 Tight-Binding Theory

The description of electronic properties in the previous section was based upon the electrons in a solid being subject to a weak potential at the ionic sites. Naturally, the opposite point of view can also be taken, i.e. the electrons are predominantly localised at ionic sites with small overlaps of the wavefunctions between atomic sites. This is the far more natural point of view for the electronic structures in transition metal oxides. In this tight-binding approach, the true wavefunctions of the crystal are constructed as linear superpositions of the localized atomic orbitals $\phi_n$ ($n$ refers to the atomic orbital). It can be shown [32] that (for a 1D chain) the resulting wavefunctions are

$$\psi_{nk}(r) = \sum_R \exp(i k R) \phi_n(r - R), \quad (2.33)$$

where $R$ indicates the atomic site position. Here $k$ is running over allowed momenta within the first Brillouin zone.

This leads to a dispersion of

$$E = E_0 - 2t \cos(ka), \quad (2.34)$$

where $t$ is the transfer integral between neighbouring orbitals indicating the strength of the inter-site hopping. The range of $k$ used to calculate the dispersion is that...
of the first Brillouin zone, $-\pi/a \leq k \leq \pi/a$. In other words, the more the electron wavefunctions overlap, the larger $t$ and the wider the resulting bandwidth. That means in terms of the previously discussed structures that more distorted structures tend to have weaker hopping and narrower bands depending upon the differences in overlap.

In a 3D material with multiple sites per unit cell the dispersion may be written

$$E = E_0 - \sum_{m,n} t_m \cos(k \cdot r_n)$$

(2.35)

where $m$ labels the different site types (i.e. nearest neighbour, next nearest neighbour etc.) and $r_n$ is the vector joining the atomic sites under consideration. This model is often useful for first-order approximations of transition metal oxide band structures as the transition metal $d$-orbitals are usually dominant at the Fermi energy. Therefore, a simple tight-binding model using the known superexchange paths often gives a useful first approximation to the band structure of a material. This is especially useful in cases such as high-symmetry quasi-2D transition metal oxides where a simple intuitive picture of the band structure is easy and quick to calculate. Tight-binding models are also often used to fit experimental band structure data to get an approximation of the relative magnitudes of the hopping integrals. It is also a useful concept to approximate DFT band structure calculations for further theoretical studies. Importantly, the introduction of strong ionic potentials changes the dispersion but not the fundamental concepts of band structure, Brillouin zone, Fermi energy etc. In particular expressions for specific heat and magnetic susceptibility in terms of density of states carry over from the free electron picture.

### 2.4.4 Fermi Liquid Theory

The quantum mechanical theories of Sommerfeld and others worked well in general when compared with experimental data for simple metals and $^3$He. However, these theories were based upon non-interacting electrons aside from the Pauli exclusion principle. The success of these theories was surprising since materials such as the fermionic $^3$He were known to have strong inter-atomic interactions and it was not understood how a theory ignoring such an apparently important component could work so well for these materials. This problem was solved by Landau, in fact for
He initially, using the adiabatic continuity principle. He hypothesised that if the evolution of the eigenstates of a system could be observed as they evolved with the continuous ‘turning on’, from zero, of electron interactions then the low-energy eigenstates of the original and evolved system could be mapped on to one another with a one-to-one correspondence. He also proposed that good quantum numbers for the excitations of the original system, such as crystal momentum, would remain applicable to the new system at low energy. Therefore, the interacting system may still be described using the eigenstate labels of its non-interacting equivalent. The excitations of the new system are excitations of quasiparticles - electrons or holes with properties such as effective mass modified by their interactions. The picture has thus changed from one in which weakly-interacting electrons are excitations of a Fermi sea to one in which non-interacting quasiparticles take this role. In essence the non-interacting picture is still visible but as people had intuitively realised before Landau developed his theory, the non-interacting electron model cannot be a true description. It had to be replaced by a theory including interactions but which retains the same general form as the original picture. Achieving this was the success of Landau Fermi liquid theory (so-called due to the inclusion of finite-strength interactions) which with very few assumptions included the role of interactions whilst at the same time explained why the non-interacting picture had worked so well.

As indicated earlier, Landau Fermi liquid quasiparticles can be treated similarly to electrons with modified parameters. These modifications were encoded in so-called Landau parameters. Examples of these are seen in the expressions for specific heat and susceptibility. The specific heat for a Fermi liquid may be recognised as the Fermi gas form from equation 2.29 with the use of the effective mass $m^*$ rather than the band mass to represent the fact that the Fermi surface is now one of quasiparticles rather than electrons.

$$c_v = \frac{m^* k_F}{3h^2} k_B^2 T$$

(2.36)

The change in effective mass can in an isotropic system such as $^3$He be encoded in a single parameter $F_1^s$ via

$$\frac{m^*}{m} = 1 + \frac{1}{3} F_1^s.$$  

(2.37)

The susceptibility of a Fermi liquid is very similar to the Fermi gas expression in
equation 2.30, modified only by the effective mass and the inclusion of the term involving the Landau parameter $F_0$:

$$\chi = \frac{m^* k_F}{\pi^2 \hbar^2} \frac{1}{1 + F_0 \mu_B^2}$$  \hspace{1cm} (2.38)

The $\frac{1}{1 + F_0}$ term in the susceptibility is also known as the Sommerfeld-Wilson ratio and can be used as a gauge of the strength of magnetic interactions between quasiparticles.

2.4.4.1 Effect of Magnetic Field

In the study of itinerant systems the topology of the Fermi surface is one of the most fundamental pieces of knowledge required. Information on this can be obtained using a variety of complementary techniques. Angle Resolved Photoemission Spectroscopy (ARPES) gives high resolution ($\lesssim 3$ meV) energy and $k$-space resolved information about the geometry of the Fermi surface sheets and their position in the Brillouin zone. However, the spectra are usually measured in the $ab$-plane in layered transition metal oxides, leading to a lack of information about the $k_z$-dependence of the Fermi surface. Additionally, ARPES is sensitive to any surface reconstruction present and determining which signals are from the bulk may sometimes be difficult. A complementary technique which does give this information, and also has the benefit of higher energy and $k$-space resolution than ARPES [34], is quantum oscillations - originally discovered as the de Haas-van Alphen effect.

The de Haas-van Alphen effect was first discovered in 1930 by W. J. de Haas and P.M. van Alphen when measuring the magnetization as a function of applied magnetic field, $M(H)$, in bismuth [35–37]. Oscillations periodic in $1/H$ were observed but their origin was not understood at the time. This was resolved in 1952 by L. Onsager [38]. He discovered that there was a simple relationship between the oscillation period in $1/H$ and the extremal cross sectional area of a Fermi surface pocket perpendicular to the applied field direction:

$$\frac{1}{F} = \frac{2\pi e}{\hbar c} \frac{1}{A_e}$$  \hspace{1cm} (2.39)
In a uniform magnetic field,

\[
\hbar \dot{k} = -e \mathbf{v} \times \mathbf{B} \tag{2.40}
\]

This means that the electrons orbit contours of constant energy which are also at constant \( k_\parallel \) relative to the field direction. The above semiclassical equation would allow continuous variation of the orbit radius but the electron orbits are quantized, described by the Bohr-Sommerfeld condition \[39\]:

\[
\oint p \cdot dr = \left(n + \frac{1}{2}\right) \hbar \tag{2.41}
\]

in real space where \( p \) is the momentum and \( n \) an integer. An orbit in real space being quantized directly corresponds to a quantized \( k \)-space orbit.

For a spherical Fermi surface, this quantization condition in an applied field leads to ‘Landau tubes’ of allowed orbits with areas proportional to \( \sqrt{B} \) as shown in figure 2.11. This means that as \( B \) is increased, the tube radii increase and eventually pass through the Fermi surface. This gives oscillations in the density of states as a function of inverse field leading to oscillations in physical quantities such as magnetization, conductivity and entropy. Although all orbits perpendicular to the applied field are allowed and indeed occur, phase smearing leads to the fact that only extremal orbits such as the ones shown in figure 2.12 lead to an experimentally observable signal.

This means that a measurement of these oscillations will allow the areas of the Fermi surface pockets to be determined directly. The multiplicity and position in \( k \)-space, however, can not be determined by this method.

Figure 2.11: The Landau tubes for a 2D cylindrical Fermi surface with field applied parallel to \( k_z \).
2.4.5 Insulating Systems

The tight-binding model discussed in section 2.4.3 is based on a reasonably strong on-site potential meaning that the electrons may be thought of as being mostly localized in atomic orbitals. The trivial case of a band insulator is simply due to filled bands in a solid but another more interesting class of insulator, Mott insulators, can be developed from an extension of the tight-binding model. In this case strong correlations add an additional on-site potential, $U$, to the Hamiltonian due to a repulsive interaction between the electrons. In the case $U \gg t$ when this on-site interaction is strong enough to overcome the inter-site hopping an insulating state occurs. This is the case for BiFeO$_3$ which will be discussed in Chapter 5.

Equation 2.42 shows the Hubbard model Hamiltonian in second quantized notation:

$$\mathcal{H} = -t \sum_{\langle i,j \rangle, \sigma} \left(c_{i\sigma}^\dagger c_{j\sigma} + c_{j\sigma}^\dagger c_{i\sigma}\right) + U \sum_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow} \quad (2.42)$$

The operator $c_{i\sigma}^\dagger$ corresponds to creation of an electron on site $i$ with spin $\sigma$ and $c_{j\sigma}$ to the destruction of one on site $j$ with spin $\sigma$. In the case of $U = 0$, this simply corresponds to the tight-binding model discussed earlier. For a Mott insulator
(\(U \gg t\)), the sites are half-filled (\(\hat{n}_{i\uparrow} + \hat{n}_{i\downarrow} = 1\)). When \(U \gg t\), it can be seen that the on-site repulsion term will overcome the hopping term leading to an insulating state. This achieved in terms of density of states by separation into a lower and upper Hubbard band as shown in figure 2.13.

In an oxide Mott insulator the bands involving dominant oxygen \(p\)-orbital character are usually well below the Fermi energy and therefore also below the relevant transition metal \(d\)-orbitals at the Fermi energy as shown schematically in figure 2.13a. Therefore the charge-transfer gap, \(\Delta\), which corresponds to the energy required for an excitation between the oxygen \(p\)-levels below the Fermi energy and the relevant transition metal \(d\)-levels above is greater than \(U\).

An important modification to the above picture occurs in charge-transfer insulators. In a charge-transfer insulator the states at the Fermi energy are half-filled and as in a Mott insulator would be expected to lead to a metallic state. In this case, \(U\) is large enough to give a Mott insulating state. However, the bands originating primarily from the oxygen \(p\)-orbitals now lie in between the lower and upper Hubbard bands as shown in figure 2.13b. In this case, \(\Delta < U\) and therefore a charge-transfer insulator is formed.

For transition metals, the magnitude of \(U\) in general increases with the filling of the \(d\)-shell as can be seen in figure 2.14a. Conversely, the magnitude of \(\Delta\) decreases with filling, as in figure 2.14b, and so insulating materials containing transition metals from the left-hand side of the \(d\)-block in general tend to be Mott insulators and those containing transition metals from the right-hand side tend to

![Figure 2.13: A schematic diagram of the relative band locations in (a) a Mott insulator and (b) a charge transfer insulator.](image-url)
Figure 2.14: The trend in (a) the Coulomb repulsion energy, $U$, and (b) the charge-transfer energy, $\Delta$, across the 3$d$ transition metals (from [40]). The crossover from Mott-type insulators to charge-transfer type insulators is shown in (c) (from [41]).

be charge-transfer insulators. The transition point is often around chromium ($d^3$ for $Cr^{3+}$) as can be seen in figure 2.14c.

2.4.5.1 Ferroelectricity

I will now discuss an electronic property of certain insulating systems that is particularly relevant to this thesis: ferroelectricity. This is a particularly clear instance of a structure-property relationship as the presence of ferroelectricity is only possible for a specific number of space groups due to symmetry considerations, as will be discussed in the following section.

The phenomenon of ferroelectricity, where a material develops spontaneous electric polarization which is switchable by an applied electric field, has been known since the 1920s. The first full report was in 1921 by Valasek who reported "an electric hysteresis in $P$ analogous to the magnetic hysteresis in iron" for Rochelle salt (potassium sodium tartrate tetrahydrate, KNaC$_4$H$_{4}$O$_{6}$·4H$_2$O) [42].

Since this discovery, many more ferroelectric materials have been discovered and continue to be discovered as predictions based upon symmetry analysis are investigated. Some materials which show behaviour characteristic of ferroelectricity are actually ferrielectric, that is they have opposite but unequal dipole moments which result in a net polarization within the unit cell, analogous to ferrimagnets$^8$.

$^8$varying definitions can be used for ferrielectricity but the simple definition given here will be assumed throughout this thesis.
In the following descriptions of types of ferroelectrics, ferrielectric materials will be implicitly included.

There are specific constraints on the space groups that allow ferroelectric states. All space groups can be classified into one of 32 crystal classes (or crystallographic point groups). Of these, 21 are non-centrosymmetric but only 10 of these non-centrosymmetric classes can contain a unique polar axis and therefore accommodate a ferroelectric state, this is shown schematically in figure 2.15.

Two classes of ferroelectric materials have been recognised: proper and improper ferroelectrics.

Proper ferroelectrics are materials which exemplify one of two mechanisms of ferroelectricity. The first of these occurs in materials with a B-site transition metal ion with an empty $d$-shell, commonly termed ‘$d^0$’ materials, the classic example of this being BaTiO$_3$ (shown in figure 2.16). In this case, the dipoles result from covalent bonding between the $d^0$ ion and oxygen leading to off-centring within the oxygen octahedra. The second case is that seen in BiFeO$_3$ (to be discussed in chapter 5) where the mechanism is the off-centring of a ‘lone pair’ ion such as Pb$^{2+}$ or Bi$^{3+}$. These proper ferroelectrics are structurally unstable towards the polar state and the polarization will be the primary order parameter in transition to the ferroelectric state.

![Figure 2.15: The 32 crystal classes. There are 21 non-centrosymmetric crystal classes and 10 of these are polar.](image-url)
Improper ferroelectrics are materials in which the polarization is not the primary order parameter. The ferroelectric state is the consequence of another property such as charge ordering, magnetic ordering or ionic size effects. In case of ionic size effects being the property primarily causing the transition, a structural transition is driven by the imbalance in ionic sizes leading to distortions which as a by-product give a net polarization. An example of this which will be discussed in detail in chapter 6 is YMnO$_3$. This has a hexagonal structure with layers of MnO$_5$ trigonal bipyramids separated by layers of Y$^{3+}$ ions. The structure in the state above the ferroelectric transition has untitled trigonal bipyramids. The transition to the polar state is driven by tilting of the bipyramids which triples the unit cell. As a by-product the combination of this tilting with the corrugation it induces in the Y$^{3+}$ ion layer leads to a ferrielectric state with a (small) net polarization. The primary distortion mode for this transition is antiferroelectric and therefore without the further distortions which are non-linearly coupled to the primary mode, no net polarization would result.
2.4.6 Magnetism in Transition Metal Oxides

Many transition metal oxides are magnetic due to the unfilled $d$-shells present. The type of ordering and the ordering temperature are dependent on many complex interactions influenced by factors such as the geometry of the magnetic sublattice, the local coordination of the transition metal ions, electron correlation strength and electronic structure. A good introduction to and overview of the complex field of magnetism in transition metal oxides can be found in [43]. The next two sections will briefly outline two concepts which are important for the materials to be discussed in the later experimental chapters: magnetic frustration and multiferroic materials.

2.4.6.1 Magnetic Frustration

Magnetic frustration may occur for both itinerant and insulating systems. It is primarily a product of the geometry of the lattice of magnetic transition metal ions combined with the exchange interaction between the ions. For example, $S = 1/2$ ions with antiferromagnetic exchange interactions on a triangular lattice will be ‘frustrated’ as any two spins in an isolated triangle may order antiferromagnetically with respect to each other but the third spin will have competing and balanced interactions and therefore no energetically favoured orientation. Ordering does usually occur for such systems but at a much reduced temperature compared to mean-field theory predictions (the preferred ground state solution for a Heisenberg spin triangular lattice is a structure with 120° angles between the spins).

The strength of the frustration in a system may be described by an empirical ‘frustration parameter’, $f = |θ_W|/T_N$, which is the ratio of the predicted mean-field ordering temperature, as extracted from a high-temperature Curie-Weiss fit for example, to the actual ordering temperature [44]. A frustration parameter much greater than 1 indicates frustration as the system has not ordered down to temperatures lower than the mean-field predicted ordering temperature. The determination of the Weiss temperature, however, often has large errors due to limited fit ranges or non-Curie-Weiss behaviour. Due to this and other complications such as the applicability range of mean-field theory, frustration parameters of greater than $f = 5$ are usually required for a reliable indication of non-negligible
frustration and \( f \geq 10 \) for indication of strong frustration which would be expected to be outside the range of validity of mean-field theory \[44\]. One of the largest frustration parameters reported to date is that of FeSc\(_2\)S\(_4\) with \( f \geq 1000 \) \[45\].

This concept is of particular importance to the magnetism of some of the barium orthotellurates, for example Ba\(_2\)NiTeO\(_6\) with \( f \approx 16 \), discussed in chapter 4. It is also important in the context of PdCrO\(_2\), with \( f = 13 \), discussed in chapter 7.

### 2.4.6.2 Multiferroics

Multiferroics were originally defined as materials which display at least two simultaneous ferroic orders in the same phase. This definition is now commonly extended to include antiferroic orders. The multiferroics discussed in this thesis are of interest due to their magnetolectric multiferroicity: concurrent magnetic and ferroelectric order. Such materials are interesting from a fundamental physics viewpoint but are also of particular importance for potential spintronics applications as they would allow magnetic control of electric order and vice versa. From a naive viewpoint, these concurrent orders should not be possible assuming that the ferroelectricity is driven by a \( d^0 \) non-magnetic B-site cation in a perovskite-type material\(^9\). This lack of unpaired \( d \)-electrons would not allow for any magnetic moment on the transition metal sites.

In reality, this problem is circumvented in several ways. One example is BiFeO\(_3\) in which the mechanism of ferroelectricity is based upon lone-pair-driven polar distortions involving the A-site ion. For materials without a ‘lone-pair’ A-site ion the ferroelectricity must come from another source. A relevant example for this thesis is the geometric ferroelectricity in YMnO\(_3\) which is driven by a tendency towards close-packing and therefore not sensitive, to first order, to the \( d \)-electron count on the B-site. A third way around this problem is to have an elpasolite-type double perovskite with B-site occupancy shared between one \( d^0 \) transition metal ion and one magnetic transition metal ion as is the case in materials such as Pb\(_2\)Fe\(^{3+}\)Nb\(^{5+}\)O\(_6\).

\(^9\)It could, of course, be possible in a material composed of subunits of ferroelectric and magnetic character. However, in this case the magnetolectric coupling would be expected to be weak due to the spatial separation of the subunits.
In magnetoelectric multiferroic materials the magnetoelectric effect describes the coupling between the electric and magnetic orders. The free energy, $F$, of such systems can be expressed as

$$F(E, H) = F_0 - P_s^i E_i - M_s^i H_i - \frac{1}{2} \epsilon_0 \epsilon_{ij} E_i E_j - \frac{1}{2} \mu_0 \mu_{ij} H_i H_j$$

$$- \alpha_{ij} E_i H_j - \frac{1}{2} \beta_{ijk} E_i H_j H_k - \frac{1}{2} \gamma_{ijk} H_i E_j E_k - \ldots$$

(2.43)

(2.44)

where $P$ is the polarization, $M$ the magnetization, $E$ the electric field, $H$ the magnetic field, $\epsilon_{ij}$ the dielectric susceptibility, $\mu_{ij}$ the magnetic susceptibility and $\alpha_{ij}$, $\beta_{ij}$ and $\gamma_{ij}$ are magnetoelectric coupling coefficients. The relations between the magnetization and polarization can be obtained from the differentiation of the free energy with respect to the applied electric and magnetic fields $E$ and $H$ [46]:

$$P_i(E, H) = - \frac{\partial F}{\partial E_i}$$

$$= P_{s}^i + \epsilon_0 \epsilon_{ij} E_j + \alpha_{ij} H_j + \frac{1}{2} \beta_{ijk} H_j H_k + \gamma_{ijk} H_i E_j - \ldots$$

(2.45)

(2.46)

$$M_i(E, H) = - \frac{\partial F}{\partial H_i}$$

$$= M_{s}^i + \mu_0 \mu_{ij} H_j + \alpha_{ij} E_i + \beta_{ijk} E_i H_j + \frac{1}{2} \gamma_{ijk} E_j E_k - \ldots$$

(2.47)

(2.48)

Generally, the study of the magnetoelectric effect in materials is restricted to the linear component, the coupling strength of which is parametrized by the tensor $\alpha$.

The ideal situation for technological uses of multiferroics would be to have a strong magnetoelectric coupling (large $\alpha$) which would allow the development of magnetically switchable electronic memory and electronically switchable magnetic memory. Unfortunately, however, due to the constraints on the mechanisms of concurrent ferroelectricity and magnetic order, these effects are usually site-separated with one site being responsible for the ferroelectricity and one for the magnetic order such as in BiFeO$_3$. This site separation necessarily weakens the coupling strength and currently limits the technological uses of multiferroics.

The nature of the magnetoelectric coupling is restricted by the symmetry of the system and in a more general consideration the occurrence of multiferroicity is restricted to certain point groups [46, 47]. Therefore, experimentally the identification of the symmetry of the polarization can in principle allow identification of
the symmetry of the magnetic structure. However, the study of complex multiferroics with incommensurate magnetism is ongoing and the refinement of symmetry analysis techniques for multiferroics is currently a fast developing field [48–51].

The materials discussed in this thesis all show electronic and/or magnetic states which are strongly dependent upon the details of their structures. The next chapter will provide an overview of the measurement and analysis techniques used in this thesis for structural and electronic property investigations.
Chapter 3
Experimental Techniques and Analysis Procedures

The experiments detailed in this thesis are of two general types: crystal structure determination and physical property measurements. The structure determination methods that will be discussed here are time-of-flight neutron scattering (which was used for high-resolution structure investigations) and x-ray diffraction which was used for characterisation of samples during synthesis development and to check phase purity of samples prior to more detailed neutron investigations. The physical properties measurements to be discussed are: quantum oscillation measurements with the torque magnetometry technique, resistivity, specific heat and magnetization. The quantum oscillation measurements were used in an angle-dependent study of the Fermi surfaces of PdCrO$_2$ and PdCoO$_2$. The magnetization, specific heat and resistivity measurements were used for basic sample characterisation either before detailed measurements or in the investigation of novel compounds. The experimental details and analysis techniques for both types of measurement will be discussed in the following sections.

3.1 Structural Techniques

The experimental structure determination techniques described in the following two sections are both diffraction techniques: time-of-flight neutron scattering and laboratory x-ray diffraction. They have the same basic principle but the diffraction
of x-rays and neutrons are fundamentally different from a structure determination point of view. X-rays scatter from the electronic charge distribution in a material whereas neutrons scatter via nuclear interactions with the nuclei and via magnetic interactions with the spin density of a material. Both methods have their advantages and disadvantages with regards to structure determination. For example, neutron scattering has an intrinsically greater sensitivity to oxygen positions but require longer counting times and larger scale experiments than x-ray diffraction due to neutrons being a weakly interacting probe.

For the specific cases discussed in this thesis, x-ray diffraction has been used as a characterisation method during synthesis and to check sample quality before further measurements. This was used during all sample synthesis procedures described in this thesis. Powder neutron diffraction, on the other hand, has been used for the in-depth structural measurements of the two multiferroics presented in chapters 5 and 6, BiFe$_{0.7}$Mn$_{0.3}$O$_3$ and YMnO$_3$. In these studies the choice of neutron diffraction for the detailed structure and phase transition investigations was due to the fact that subtleties of the oxygen polyhedral tilts were a key factor and neutron diffraction has a better sensitivity to the oxygen positions than x-ray diffraction.

The basis of both diffraction methods is the well-known Bragg condition that relates the wavelength $\lambda$ of the incident beam of radiation with a periodic scatterer of periodicity $d$ and the scattering angle $2\theta$ via $n\lambda = 2d \sin \theta$ where $n$ is an integer. The wavelength of the incident particle is related to its momentum, $p$, by the de Broglie relation $\lambda = \frac{h}{p}$.

There are many experimental realisations of utilising this scattering condition for structural investigations. In the following sections I will first discuss the basics of neutron diffraction and in particular the time-of-flight method and the instruments used. X-ray diffraction as used in the laboratory for routine characterisation will then be introduced. Finally Rietveld refinement, the crucial structural analysis technique for both methods, will be discussed from a theoretical and practical point of view.
3.1.1 Neutron Scattering

3.1.1.1 Interaction of Neutrons with Single Nuclei

Neutron diffraction is a key technique in modern materials science, allowing high precision magnetic and structural determination as well as investigation of excitations over a wide energy range. The diffraction of neutrons was first performed in 1936 by Mitchell & Powers [52] and von Halban & Preiswerk [53] followed by the first diffraction pattern reported in 1948 by Wollan and Shull for powders including aluminium, graphite, NaCl, NaH and NaD [54].

The fact that neutrons are charge neutral particles means that the non-magnetic scattering in a neutron diffraction experiment is not based upon an interaction with the electrons in a material. Instead, the interaction is predominantly with the nucleus which gives an advantage to structure determination over that by x-ray or electron diffraction. The nuclear scattering gives a position which is independent of the shape or deformation of the electron cloud, a property which is especially important in materials such as ferroelectrics where the electron distributions around ion cores may be distinctly non-spherical and therefore lead to difficulties in obtaining the true ion core positions by other methods\(^1\). Of course, the fact that neutrons are spin 1/2 particles allows magnetic properties to be probed as well. The first measurement of the neutron magnetic moment was by Alvarez & Bloch in 1940 [55]. Elastic and inelastic magnetic neutron scattering is a subject in its own right. However, this aspect has not been utilised in the work presented here. An introduction to this field can be found, for example, in [56].

One of the most fundamental quantities measured in scattering experiments is the differential scattering cross section \(\frac{d\sigma}{d\Omega}\), which is the total number of neutrons scattered per second into the solid angle \(d\Omega\) in the direction of the measurement normalised by the incident flux. The total cross section \(\sigma_{\text{tot}}\) is the integral of the differential cross section over all angles

\[
\sigma_{\text{tot}} = \int \frac{d\sigma}{d\Omega} d\Omega.
\]

\(^1\)Having said this, the fact that x-rays are probing the shape of the electron cloud has been key in the recent development of maximum entropy methods (MEM) analysis of charge distribution which has significant importance in studies of properties such as bonding in materials.
The strength of the scattering of neutrons is dependent on the element, isotope of the element and energy of the neutrons. The scattering strength of the nucleus may be most simply described by the parameter $b$ called the scattering length. This can currently only be obtained experimentally. It can be calculated from the total scattering cross section \( \sigma = 4\pi b^2 \). To illustrate the origin of this relation it is instructive to consider the experimentally relevant case where the incident neutron wavelength in a scattering experiment is far larger than the size of the nucleus. The nucleus therefore appears as a point scatterer producing isotropic scattering. The incident neutrons may be represented as a plane wave of the form $e^{ikz}$. The scattered wave is an isotropic spherical wave $\frac{-b}{r} e^{ikr}$. $b$ encodes the properties of the scattering potential and has units of length. It is in general a complex number, the magnitude and sign of the real part describing the strength of the repulsive or attractive scattering potential with the imaginary part describing the absorption properties. This allows the relationship between $\sigma$ and $b$ to be expressed as:

\[
\sigma = 4\pi r^2 v \left| \frac{(-b/r)e^{ikr}}{v|e^{ikz}|^2} \right|^2 = 4\pi b^2, \tag{3.2}
\]

where $v$ is the velocity of the neutrons [57], resulting in the previous expression (equation 3.1) used for experimental determination of the scattering length.

As mentioned previously, the scattering length has a dependence upon the energy of the incident neutron. For most elements and isotopes the dependence is effectively flat in the thermal energy range (5-100 meV corresponding to $\lambda = 1 - 4\, \text{Å}$)\(^3\). One notable exception is $^{113}\text{Cd}$. Absorption of neutrons may also occur, with varying strength depending upon isotope and element. Absorption is particularly overwhelming in the natural isotope composition of elements such as Cd, Gd and B, leading to very limited applicability of neutron scattering for materials containing these elements. A further complication is that the scattering length can have a strong incoherent contribution. In some elements/isotopes the incoherent part provides such a large background to spectra that structure determination is hampered. This is the case for hydrogen and so samples with high hydrogen densities are often isotopically substituted with deuterium to counteract this. The coherent

\(^2\)In neutron scattering this is defined as an effective area with the unit of barns (1 barn = $10^{-28}\text{m}^2$).

\(^3\)Other commonly used terms for energy ranges are cold neutrons (0.1-10 meV/3-30 Å), hot neutrons (100-500 meV/0.4-1 Å), fast neutrons (energies of 1 MeV or more) and epithermal which refers to the short-wavelength neutrons produced by spallation sources with wavelengths at the low-energy end of the hot neutron range.
scattering lengths, $b_{coh}$, for thermal ($\approx 2,200 \text{ m/s}$) neutrons of the natural isotopic mixtures of the elements are shown in figure 3.1 and the absorption cross sections in figure 3.2.

**Figure 3.1:** The coherent scattering lengths, $b_{coh}$, for the naturally occurring isotopic mixtures of the elements. Values taken from Sears [58].

**Figure 3.2:** The absorption cross sections, $\sigma_{abs}$, on a logarithmic scale, of the naturally occurring isotopic mixtures of the elements for $2,200 \text{ m/s}$ (thermal) neutrons. Values taken from Sears [58].
3.1.1.2 The Time-of-Flight Technique

The time-of-flight technique is based upon detecting neutrons as a function of time rather than as a function of angle and is most commonly used at spallation sources which produce a pulsed beam composed of a range of wavelengths. This is in contrast to the more familiar technique of angle-dependent diffraction used in laboratory x-ray diffraction and continuous-wave neutron diffraction (usually at reactor sources) which uses monochromatic radiation. The basic experimental setup is shown in figure 3.3. A neutron pulse with a distribution of wavelengths travels from the neutron source to the sample and is scattered with angle $2\theta$. The time-of-flight $t$ is the total time the neutron travels over distance $L = L_1 + L_2$.

The fundamental equation for the time-of-flight technique can be obtained by combining the Bragg condition $n\lambda = 2d\sin\theta$ with the de Broglie relation $\lambda = \frac{h}{p}$. If one expresses the momentum $p$ as the product of mass $m$ and velocity $v$ (the energy ranges considered are non-relativistic) and furthermore the time-of-flight $t$ for the neutron over distance $L$ as $t = \frac{L}{v}$ then one obtains

$$t = \frac{L}{v} = \frac{L}{p/m} = \frac{mL\lambda}{h} = \frac{2m}{nh}Ld\sin\theta \quad (3.3)$$

This equation therefore relates the $d$-spacing to the time-of-flight between the source moderator and the detector.

The time-of-flight technique often allows better determination of the details of crystal structures than continuous-wave techniques as short-wavelength 'epithermal' neutrons are included in the pulse. This allows low-$d$-spacing measurements and gives a high real space resolution. Furthermore, a measurement at a single angle can provide a complete $d$-space spectrum.

![Figure 3.3: A schematic of the time-of-flight technique. The total path length is $L = L_1 + L_2$. Further details are given in the text.](image-url)
The resolution function for a time-of-flight instrument is

\[
\frac{\Delta d}{d} = \left[ \left( \frac{\Delta L}{L_1 + L_2} \right)^2 + \left( \frac{\Delta t}{t} \right)^2 + (\Delta \theta \cot \theta)^2 \right]^{1/2}, \tag{3.4}
\]

where \(\Delta L\) is the uncertainty in the distance between the moderator and detector and is dominated by the moderator thickness with additional contributions from the finite detector and sample thickness, \(\Delta t\) is the uncertainty in the time-of-flight and \(\Delta 2\theta\) is the uncertainty in the scattering angle [57].

### 3.1.1.3 Instrument Characteristics - HRPD and GEM at ISIS

The ISIS spallation neutron source at Didcot in Oxfordshire has been a world-leading spallation source since its completion in 1984. It has benefited from a constant program of upgrades, most recently with the addition of a second target station. ISIS is a spallation source which uses protons from an 800 MeV synchrotron hitting a tantalum-clad tungsten target to produce \(\approx 4 \mu s\) long pulses of neutrons. A schematic diagram of the neutron production apparatus is shown in figure 3.4. The spallation process involves capture of an oncoming high energy proton followed by an intra-nuclear cascade process, then emission of high energy particles causing internuclear cascade processes and finally ‘evaporation’ of lower energy protons, neutrons, photons and neutrinos.

![Figure 3.4: The ISIS beam production layout. A 70 MeV linear accelerator feeds an 800 MeV synchrotron from which the beam is extracted and hits the tantalum-lined tungsten target to produce the neutron and muon beams [59].](image-url)
As these spallation neutrons are fast neutrons (with energies of the order of 1 MeV) their wavelengths are in general too short for use in diffraction experiments. To modify the wavelength distribution and make it suitable for the relevant experiment the beam is then passed through a moderator. Target station 1 at ISIS uses three types of moderator - water, methane or hydrogen. Target Station 2 has been equipped with solid methane moderators for long-wavelength ‘cold’ neutron experiments. The layout of instruments at Target Station 1, which is the one at which the experiments described in this thesis were carried out, can be seen in figure 3.5.

Both instruments used for the structural investigations described in this thesis (HRPD and GEM) use neutrons which have passed through the gadolinium ‘poisoned’ liquid methane moderator which is kept at 100 K. The use of the gadolinium poison allows greater control over the pulse length [61]. The moderator is designed

![Figure 3.5: The ISIS target station 1 instruments. Those shown in blue receive liquid methane-moderated neutrons, those in orange water-moderated neutrons and those shown in green receive liquid hydrogen-moderated neutrons [60]. The relevant instruments for this thesis are HRPD which has an extremely long path length to provide high resolution and GEM which is a high-flux medium-resolution instrument.](image)
to slow down the fast spallation neutrons released from the target whilst keeping the short pulse length. Epithermal neutrons are slowed down without thermalisation but the longer wavelength thermal neutrons are thermalised and the resultant wavelength at peak flux is approximately 1.8 Å. An example spectrum of neutrons from the methane moderator is shown in figure 3.6. Further general details of ISIS can be found in [62] and references therein.

**Figure 3.6:** An example of the flux spectrum as a function of neutron wavelength from a liquid methane moderator (red). HRPD and GEM both receive liquid methane moderated neutrons. The distribution shape is due to the combination of a thermal Maxwellian spectrum (green) and a $1/E$-type epithermal component (blue) typical of a spallation source.

**HRPD - High Resolution Powder Diffractometer**

HRPD (High Resolution Powder Diffractometer) is an instrument specially designed for high-resolution structural studies of powder materials (although single-crystal measurements are possible). It has a flight path length of moderator to detector of approximately 100 m which greatly increases the resolution (determined by equation 3.4). It is the highest resolution machine of its type in the world. Despite being one of the original suite of ISIS instruments it has benefitted from upgrades which have kept it performing at world-class level such as the recent supermirror\(^4\) upgrade for the 100 m flight path which gave a large increase in neutron flux [63].

\(^4\)This is a neutron guide made of multilayers of different thicknesses of $^{58}$Ni or more recently $^{58}$Ni and Ti which act as highly reflecting supermirrors for neutrons minimising flux loss along long path lengths. More details are given in [63].
A schematic diagram of HRPD is shown in figure 3.7. HRPD has two disk choppers at 6 m and 9 m from the liquid methane moderator. The 6 m chopper rotates at the ISIS pulse frequency of 50 Hz and its time offset relative to the ISIS pulse selects the wavelength range. The second chopper at 9 m from the moderator is necessary to avoid ‘frame overlap’. This is an issue for long flight-path instruments as the pulse disperses over the long path meaning that the shorter wavelength neutrons from the next pulse catch up with the longer wavelength neutrons from the initial pulse. The use of the secondary chopper allows this to be avoided by selecting a window of wavelengths (dependent on the chopper frequency) to be transmitted to the sample whilst blocking other wavelengths to prevent frame overlap. This secondary chopper on HRPD has a variable frequency but is commonly set to 10 Hz. This gives a wavelength window of $\Delta \lambda \approx 2 \text{Å}$. The phase of the chopper rotation determines where in the wavelength spectrum this window occurs. As the chopper places constraints on the incoming wavelengths and rotates at a frequency lower than the pulse repetition rate its use necessarily reduces the incident flux.

HRPD has three pairs of detector banks: a low-angle bank centred on $30^\circ$, a $90^\circ$ centred bank and a backscattering bank centred on $168^\circ$. The bank characteristics are tabulated in table 3.1. The backscattering bank has the highest resolution as would be expected from equation 3.4. Due to this, the back-scattering bank data alone is commonly used for structure determination. The low-angle banks give

![Figure 3.7: A schematic diagram of the HRPD instrument at ISIS. The sample position is indicated by the black circle. There are three sets of detector banks centred on $30^\circ$, $90^\circ$ and $168^\circ$.](image-url)
access to larger \( d \)-spacings which may be useful for magnetic structures or larger unit cell materials.

**GEM - GEneral Materials Diffractometer**

The second ISIS instrument used for work relating to this thesis is GEM (GEneral Materials Diffractometer) shown in figure 3.8a. This is a high-flux, medium-resolution instrument. Its main design feature is a large angular coverage of detector banks (from 1.1° to 169.3°) allowing collection over a large volume of reciprocal space. The flight path from the moderator to the sample position is 17 m minimising loss of flux. GEM has two disk choppers at 6.5 m and 9.75 m to prevent frame overlap which normally give a wavelength range of 0.05 Å-3.40 Å (an additional nimonic chopper\(^5\) at 9.45 m can be used to remove fast neutrons to reduce the background). Due to the good detector coverage and wide incoming wavelength

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\(^5\)nimonic is the name of the nickel-based alloy from which these choppers are made.

![Figure 3.8](image)

**Figure 3.8:** (a) The GEM detector banks and (b) the relative count rates of the GEM detector banks as a function of \( d \)-spacing and momentum transfer \( Q \) [64].
spectrum a large range of $d$-spacings can be measured in a short space of time (compared to HRPD). This is useful for materials with large unit cells or magnetic structures where the longer $d$-spacings must be accessed. The relative count rates of the various detector banks as a function of $d$-spacing and momentum transfer $Q$ for the detector banks of GEM can be seen in figure 3.8b. Although GEM has advantages in flux and $d$-spacing range over HRPD, this must be balanced against the resolution. The backscattering banks for GEM have a resolution of $\Delta d = \frac{\Delta Q}{Q} = 3.5 \times 10^{-3}$ which is approximately an order of magnitude lower than the back-scattering bank resolution of HRPD. Further details on GEM may be found in [64].

### 3.1.2 X-ray Diffraction

As previously mentioned, x-ray diffraction differs fundamentally from neutron scattering as x-rays scatter predominantly from the electronic charge density in a material. There are many advanced synchrotron-based x-ray techniques (such as resonant techniques and magnetic scattering). A detailed introduction to x-ray scattering may be found in textbooks such as that by Warren [65]. Here only basic laboratory-based characterisation will be discussed as relevant to the work in this thesis.

X-ray diffraction is a convenient laboratory characterization technique as the sources are inexpensive and compact (compared with neutron sources). Patterns may be collected in a few minutes to a couple of hours, allowing basic checks of phase purity and material structure.

The scattering length for x-rays is to first order proportional to the total electronic charge and therefore the atomic number $Z$ of the atom being scattered from. The scattering cross section is therefore proportional to $Z^2$. This in contrast to the random distribution of neutron scattering lengths and cross sections.

X-ray diffraction is in most cases a useful check of phase purity. However, in cases where heavier elements are present the large scattering intensity from phases containing these atoms can make the smaller magnitude scattering from lighter element containing phases difficult to detect.

X-ray diffraction measurements can be performed every few hours during solid state synthesis to monitor reaction progress. Over this period of time the patterns
evolve from those of the reactants to those of the product, often with intermediate impurity phases being present. This can be useful for determining how long a complete reaction takes and also identify the other phases that may form. An example of such a process can be seen in figure 3.9 for the synthesis of Ba$_2$NiTeO$_6$ which is discussed further in chapter 4.

The instrument used for the projects based in St Andrews was a Stoe STADI P diffractometer with Cu $K_{\alpha 1}$ radiation in flat-plate transmission mode.

The instrument used for the barium orthotellurate project at RIKEN discussed in chapter 4 was a Rigaku Ultima with Cu radiation using Bragg-Brentano geometry with a silicon plate.

![Graph showing the evolution of x-ray diffraction patterns with reaction time during material synthesis of Ba$_2$NiTeO$_6$. The arrows indicate peaks from reactant phases which decrease in volume fraction with time.](image)
3.1.3 Rietveld Refinement

The methods of single crystal structure solution are in general not applicable to powder diffraction due to the overlapping reflections in powder patterns. Therefore, methods based upon calculating the pattern for a plausible model structure and then refining the model parameters with the aim of improving the correspondence of model and data are used. This can be implemented as a non-linear least-squares fit.

The Rietveld method is the standard method for structure analysis from powder diffraction data. There are many programs currently available for Rietveld refinement such as Fullprof [66], GSAS [67], Rietan [68] and Topas [69]. The program used throughout this thesis was GSAS and so the parameters discussed in this section (for the case of time-of-flight neutron diffraction), while included in all modern Rietveld refinement programs, will often be referred to by their GSAS variable name.

The fundamental approach of Rietveld refinement is basic. It uses the fact that experimentally observed intensities can be well represented by a calculated intensity $Y_c(p)$ as a function of parameter $p = d$-spacing, time-of-flight... of the form

$$Y_c(p) = Y_b(p) + \sum_{k=k_1}^{k_n} Y_k(p).$$

(3.5)

This describes diffraction peaks for reflections $k = k_1 \ldots k_n$ with a smooth background contribution $Y_b(p)$ [70].

The observed count number in an experimental dataset, $Y_{raw}$, is normalised with incident intensity $Y_i$ and bin size $W$ by the relation

$$Y_o = \frac{Y_{raw}}{W Y_i}.$$  

(3.6)

The Rietveld refinement is a weighted least squares fit ($w$ is the weight function) which minimises the function

$$M = \sum_{\text{spectrum}} w (Y_o - Y_c)^2.$$  

(3.7)
The function is non-linear and the fit is performed iteratively with partial derivatives taken with respect to the parameters $p_j$

$$\frac{\partial Y_c}{\partial v_i} = U_{ij} \frac{\partial Y_c}{\partial p_j}. \quad (3.8)$$

The weighted residual for the Rietveld refinement is calculated as [57]:

$$R_{wp} = \sqrt{\frac{M}{\sum w Y_o^2}}, \quad (3.9)$$

and the quality of fit (commonly called ‘goodness of fit’) by

$$\chi^2 = \frac{M}{N_{obs} - N_{var}}. \quad (3.10)$$

The calculated intensity function is highly non-linear with many parameters $p_i$ determining peak shapes, peak functions, background etc. Carrying out a Rietveld refinement is far from an automatic task. It depends most crucially on the correct parametrization of the model, the inclusion of only physical parameters and a good knowledge of the physically reasonable range of these. Even for simple structures appropriate refinements can have over 30 free parameters. In the following section I will introduce some of the main parameters influencing the model spectrum.

**Peak Position**

In a time-of-flight experiment the peak positions in the calculated pattern are dependent upon the instrumental parameters. The instrumental parameters included in the refinement are involved in the relation between the time-of-flight and the $d$-spacing (equation 3.3). The total time-of-flight can be expressed as

$$t = C d + A d^2 + Z \quad (3.11)$$

where $C$ (called DIFC in GSAS) is equal to $C = 505.56 L \sin \theta$ for a given bank, $A$ (DIFA in GSAS) corrects for the expected effects of absorption of the sample on the time-of-flight which have been empirically determined to have a quadratic $d$ dependence [67]. $Z$ (ZERO in GSAS) is a correction for timing signals and finite electronic response times. The parameters $C$, $A$ and $Z$ are determined separately.
for each detector bank of an instrument using a standard sample (commonly National Bureau of Standards silicon). These are then fixed during refinement with the exception of $A$. The physical range of $A$ will be dependent on the sample composition and therefore this is a refinable parameter.

**Peak Intensity Parameters**

The intensities seen at various angles in a diffraction experiment can be expressed as:

$$Y_h = F_h^2 \times H(T - T_h) \times K_h$$  \hspace{1cm} (3.12)

with $H(T - T_h)$ being the peak profile shape function value at point $T$ with $T_h$ being the predicted reflection position and $K_h$ being the correction factor composed of various intensity correction factors for the reflection, discussed below [70].

$F_h$ is the structure factor for the reflection given by

$$F_h = \sum_j f_j e^{2\pi i(hx_j + ky_j + lz_j)} e^{(-8\pi^2 U_j \sin^2 \theta / \lambda^2)}$$  \hspace{1cm} (3.13)

with $f_j$ being the scattering factor of atom $j$ which combined with the first exponential gives the geometric structure factor. The second exponential represents the effect of thermal displacement with $U_j$ being the thermal displacement parameter (Debye-Waller factor) for atom $j$ in Å$^2$.

$K_h$ is a combination of the intensity correction factors $A_h$ for absorption, $E_h$ for extinction, $O_h$ for preferred orientation, $m_h$ for reflection multiplicity, $L$ a wavelength dependent Lorentz term and $V$ the unit cell volume:

$$K_h = \frac{E_h A_h O_h m_h L}{V}.$$  \hspace{1cm} (3.14)

The absorption term depends on the elements and isotopes present in the sample and is also wavelength dependent. For a cylindrical sample with low linear absorption $A_B \lambda = \mu R < 3$ cm$^{-1}$ (the case in the neutron diffraction experiments presented in this thesis) the correction used is an empirical one developed by N.N. Lobanov and L. Alte da Veiga [71] (absorption function 0 in GSAS [67]) of the form

$$A_h = \exp \left[ -k_0 A_B \lambda - k_1 (A_B \lambda)^2 - k_2 (A_B \lambda)^3 - k_3 (A_B \lambda)^4 \right]$$  \hspace{1cm} (3.15)
with the empirically determined coefficients

\[ k_0 = 1.697653 \]

\[ k_1 = (25.99978 - 0.01911 \sin^{1/2} \theta) \exp(-0.024514 \sin^2 \theta) + 0.109561 \sin \theta - 26.0456 \]

\[ k_2 = -0.02489 - 0.39499 \sin^2 \theta + 1.219077 \sin^3 \theta - 1.31268 \sin^4 \theta + 0.871081 \sin^5 \theta - 0.2327 \sin^6 \theta \]

\[ k_3 = 0.003045 + 0.018167 \sin^2 \theta - 0.03305 \sin^4 \theta \]

(3.16)

The absorption correction behaves in a similar way to thermal displacements of atoms and so care must be taken in the refinement to prevent unphysical results due to this.

Extinction is an effect related to the mosaic size of the polycrystalline material (the size of the crystallites of which there can be more than one in a single grain). Extinction is caused by attenuation of the incident beam due to successive diffraction events as it travels through a crystallite. It is therefore larger for larger crystallites. It is often a negligible contribution when powder samples have a very small mosaic size. The correction to the intensity is of the form

\[ E_h = E_B \sin^2 \theta + E_L \cos^2 \theta. \]

(3.17)

with

\[ E_B = \frac{1}{\sqrt{1 + x}} \]

(3.18)

\[ E_L = \left\{ \begin{array}{ll}
1 - \frac{x}{2} + \frac{x^2}{4} - \frac{5x^3}{48} \ldots & \text{if } x < 1 \\
\sqrt{\frac{2}{\pi x}} \left[ 1 - \frac{1}{8x} - \frac{3}{128x^2} \ldots \right] & \text{if } x > 1
\end{array} \right. \]

(3.19)

where

\[ x = E_x \left[ \frac{\lambda F_h}{V} \right]^2 \]

(3.20)

The variable \( E_x \) gives the mosaic size for the sample in units of \( \mu \text{m} \) [67].

For time-of-flight experiments the Lorentz term [57], which is a geometric factor for the range of wavelengths a reflection will meet the Bragg condition, corrects for the wavelength dependence of the scattered intensity by

\[ L = d^4 \sin \theta. \]

(3.21)
These are a set of the standard parameters refined for powder samples although
different programs may use different functional forms or approximations. Further
details of the parameters and their physical meanings in GSAS can be found in
[67].

**Peak Profile Shape**

The peak shape of a time-of-flight instrument can be represented by the convo-
lation of two back-to-back exponentials representing the effect of the moderator
convolved with a peak-shape function such as a Gaussian or pseudo-Voigt. In
the refinements of HRPD data presented in this thesis the convolution with a
pseudo-Voigt is used as the inclusion of the Lorentzian term (a component of
the pseudo-Voigt) allows refinement of the Lorentzian-type strain commonly seen
in samples. Therefore, the relevant terms of this profile function will be briefly
discussed here\(^6\).

The peak-shape function for the back-to-back exponentials with the pseudo-
Voigt is

\[
H(\Delta T) = \int E(\Delta T - t)P(t)dt
\]  

(3.22)

where the back-to-back exponentials are

\[
E(\tau) = \begin{cases} 
2Ne^{\alpha\tau} & \text{for } \tau < 0 \\
2Ne^{-\beta\tau} & \text{for } \tau > 0 
\end{cases}
\]  

(3.23)

and the pseudo-Voigt with

\[
P(t) = \eta L(t, \Gamma) + (1 - \eta)G(t, \Gamma)
\]  

(3.24)

where \(L\) is the Lorentzian component, \(G\) the Gaussian component, \(\Gamma\) is the total
full-width at half-maximum and \(\eta\) the mixing parameter [67].

The Gaussian variance, \(\sigma^2\), is mostly instrument-dependent with the \(d\)-spacing
dependence

\[
\sigma^2 = \sigma_0^2 + \sigma_1^2d^2 + \sigma_2^2d^4.
\]  

(3.25)

\(^6\)This profile function corresponds to time-of-flight profile function 3 in GSAS [67]
The Lorentzian coefficient of the total full-width at half-maximum, $\gamma$, which is mostly sample-dependent, has the $d$-spacing dependence

$$\gamma = \gamma_0 + \gamma_1 d + \gamma_2 d^2 + (\gamma_4 d + \gamma_5 d^2) \cos \phi + \gamma_L.$$  \hspace{1cm} (3.26)

$$\gamma_L = \gamma_{11} h^2 + \gamma_{22} k^2 + \gamma_{33} l^2 + 2\gamma_{12} hk + 2\gamma_{13} hl + 2\gamma_{23} kl$$  \hspace{1cm} (3.27)

The coefficients $\alpha$ and $\beta$ are not refined as they are dependent on the target and moderator and are fixed during calibration.

Strain broadening is generally proportional to $d$ and particle-size broadening proportional to $d^2$. This therefore means that $\sigma_1$ and $\gamma_1$ will be affected by strain broadening and $\gamma_2$ by particle size broadening. $\gamma_L$ expands the anisotropic description of the strain anisotropy.

The empirical expression in equation 3.27 is a tensor description of $hkl$-dependent microstrain and has no physical meaning except in a few special cases. For a more physically-founded refinement of micro-strain parameters another profile function can be used which is the same as that described above except that the microstrain is instead described by Gaussian and Lorentzian components with symmetry-constrained parameters based upon the Bravais lattice. A full description of this can be found in [67].

**Refinement Procedure and Evaluation**

The Rietveld refinement process consists of a series of steps. As there are many parameters involved in the fit, some of which can be correlated, care must be taken to prevent the fit finding false minima rather than the true minimum. A simple example is the anticorrelation between absorption and thermal displacement parameters which both decrease peak intensity with increasing magnitude.

The refinement usually begins with the background contribution (commonly represented by expansion series such as Chebyshev polynomials or Fourier series) being refined to convergence followed by the instrumental factors and lattice parameters. After these basic parameters have been refined the detailed parameters may be added to the refinement step-by-step until the refinement is satisfactory and all important factors have been included. The number of parameters that can
be included for a physically meaningful result depends on the data quality and characteristics of the sample.

To evaluate the fit the most important first step is an inspection by eye. The usual plots showing the data, fit and the difference profile between the two. An example of such a plot is shown in figure 3.10 which is taken from the experiments of $\text{YMnO}_3$ in chapter 5.

A more objective way is the detailed examination of the weighted residual $R_{wp}$ and the goodness-of-fit $\chi^2$. The fit is monitored as it progresses and once convergence with all necessary parameters included is obtained the final $R_{wp}$, $\chi^2$ and visual fit can be examined. An evaluation of whether the fit is as good as could be expected for the data and sample quality and also whether the parameters obtained from the fit are physically reasonable can be made at this stage.

![Figure 3.10: An example Rietveld refinement plot of $\text{YMnO}_3$. The raw data is shown in blue, the calculated Rietveld fit in green and the lower red line is the difference profile. The black tick marks indicate predicted reflection positions. Details are given in chapter 5.](image-url)
3.2 Physical Property Measurement Techniques

An integral part of materials investigation is the determination of physical properties such as specific heat, transport and magnetization. More explicitly it is the identification of phases and transitions between them that is studied by these methods. Here I will discuss several methods of physical property measurements related to the experiments carried out in this thesis.

3.2.1 Transport

From a materials science point of view, resistivity is an excellent indication of sample purity for metallic samples. The residual resistivity $\rho_0$, which is due to defect and impurity scattering, is a direct indication of sample purity. In practice, one often uses the residual resistivity ratio RRR. This is the ratio between the room temperature resistivity (dominated by sample purity independent processes\(^7\)) and low-temperature resistivity (dominated by defect scattering). For a material this gives a direct comparison of the impurity content between different samples without the necessity of knowing the absolute resistivities.

From a physical properties point of view, resistivity is a very important tool for both the identification of phase transitions and the identification of phases themselves. One only has to think of metal-superconductor transitions to illustrate this point.

It has particularly been useful in identifying Fermi liquid regimes. For those the temperature dependent part of the resistivity $\rho$ has a $T^2$ dependence resulting in the functional form

$$\rho = \rho_0 + AT^2.$$  \hspace{1cm} (3.28)

Deviations from this form are routinely used to identify metallic non-Fermi liquids [72].

For resistivity measurements the sample is mounted by attaching four leads with conductive silver epoxy. Two of these leads are used for passing current through the sample and the second pair for a voltage measurement along the sample (called a four-point measurement). Figure 3.11 shows an example of a mounted sample.
As there is negligible current passing through the voltage measurement contacts the resistance obtained from conversion of the measured current is intrinsic to the sample with no contribution from the contact resistance. The measurements described in this thesis were performed using a helium flow cryostat giving a temperature range of roughly 3.5 K to 300 K for the measurements. Rather than using a DC current method (which can be influenced by e.g. ground loops) AC measurements were carried out. As the samples usually have a very small resistance, passive transformers are used to amplify the signal obtained\textsuperscript{8}. Due to the frequency dependence of the amplification only a narrow range of frequencies can be used for measurement at maximum amplification ($\approx 100$ Hz for the transformers used for the measurements relevant to this thesis).

The resistive characterization of metallic samples is particularly relevant to the materials PdCrO$_2$ and PdCoO$_2$ discussed in chapter 4, which show significant deviation from the simple Fermi liquid temperature dependence expectation.

### 3.2.2 Specific Heat

From a statistical point of view, specific heat is a measure of degrees of freedom and their characteristic energy scales. This, and the fact that it is a thermodynamic probe of phase transitions makes specific heat extremely useful for understanding the properties and nature of different phases and the transitions between them. For example, some states such as Fermi liquids and spin liquids have a linear specific heat for temperature $T$ approaching 0.

\footnote{CMR type LTT-m-up}
The fundamental connection to statistical physics is made by the connection to the concept of entropy, with $C$ being proportional to the temperature derivative of entropy

$$C = T \frac{\partial S}{\partial T}. \quad (3.29)$$

The most basic method of specific heat measurement is the relaxation time method. This is the method employed by the Quantum Design PPMS used for the measurements in this thesis. Figure 3.12a shows a conceptual schematic of a typical setup. The sample $S$ is strongly coupled to the thermometer $Th$ and the heater $H$ ($k_{S-Th}$ and $k_{S-H}$ respectively), ensuring rapid thermalization between these components. Contrary to this, the link $k_{S-TB}$ from the sample to the thermal bath $TB$ of constant temperature is weak. Figure 3.12b illustrates the relaxation method experiment protocol. The technique involves applying a known heater power to the sample for a known length of time between $t_1$ and $t_2$ and measuring the thermal relaxation (of the form $T = Ae^{-t/\tau}$) of the sample temperature back to that of the thermal bath it is linked to. The total heat capacity of the sample and independently determined addenda can then be determined using the relation

$$\tau_1 = \frac{C_{\text{sample}} + C_{\text{addenda}}}{k_1}, \quad (3.30)$$

where $k_1$ is the thermal conductivity of the weak link to the thermal bath. An example PPMS experimental puck from this thesis is shown in figure 3.12c. It is prepared for measurement of an array of single crystals of Ba$_2$NiTeO$_6$ described in chapter 4. An example relaxation curve is shown in figure 3.13.

The coupling between the sample and thermal bath must be weak compared to

![Figure 3.12: (a) A schematic of the measurement setup for the relaxation time method (taken from [73]) (b) the relaxation method measurement protocol (taken from [73]) (c) An example PPMS experimental puck from this thesis with a Ba$_2$NiTeO$_6$ single crystal array.](image)
the coupling between the sample and addenda (thermometer/heater) to prevent errors in measurement due to an additional weak coupling in the system and the resulting temperature gradients. Apiezon-N grease, which is a standard material for specific heat measurements, was used to thermally couple and mechanically attach the sample to the sample platform of the measurement puck. The addenda (sample stage and grease) are measured separately before the sample is added to allow extraction of the sample specific heat from the total.

In this thesis, specific heat measurements were used for basic characterisation of the barium orthotellurate materials in chapter 4.

### 3.2.3 Magnetization/Susceptibility

Magnetization is one of the most basic properties of materials. It gives details of bulk magnetic properties in contrast to probes such as magnetic neutron diffraction or muon techniques. It can also be used to give an indication of whether a transition metal ion is in a low-spin or high-spin configuration if this is not known. Several methods exist for measurement. For the measurements presented here
the SQUID-based Quantum Design MPMS was used and will be described in the following.

The MPMS uses the movement of the sample through a superconducting second-order gradient coil to generate a current in the coil (the basic setup is shown in figure 3.14). The change of flux through the coil generates superconducting currents in it. The gradient coil is connected to a SQUID (Superconducting QUantum Interference Device) which converts the current to a voltage proportional to the magnetization of the sample. More details can be found in [74]. The MPMS is calibrated using a standard sample such as palladium to ensure accurate conversion.

An example case of a raw scan, from this thesis, of SQUID output voltage as a function of sample position is shown in figure 3.15. The centre of the coils is at 1.5 cm in the figure and for a correctly positioned sample the maximum signal will be at this position which allows the most accurate measurement of the moment. To increase signal to noise, the measurement is repeated a number of times before averaging the obtained magnetization to give a data point at a particular temperature/field. The MPMS has its own built-in fitting software to extract the magnetic moment from the voltage-position curve. However, when the sample signal is small compared to the background this may not give a good fit (due to the shape and magnitude of the sample holder signal) and in certain cases manual fitting must be performed to get an accurate magnetization value. The main reason for the manual fit being more successful than the automated procedure is the possibility of setting the initial fit parameters to physically sensible ranges.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{second_derivative_coil.png}
\caption{The second-order gradient coil used in the MPMS. From [74]}
\end{figure}
This was the case for the small single crystals of Ba$_2$CuTeO$_6$ and Ba$_2$NiTeO$_6$ discussed in chapter 4 for which I analysed all raw voltage-position traces.

The fitting equation [75] is

\[
 f(Z) = X_1 + X_2Z + X_3 \left[ \frac{2 (R^2 + (Z + X_4)^2)^{-3/2}}{2} - \frac{R^2 + (\Lambda + (Z + X_4))^2}{2}^{-3/2} \right] - \frac{R^2 + (\Lambda + (Z + X_4))^2}{2}^{-3/2} \]  

where $X_1$ is a constant offset voltage, $X_2$ is a constant linear SQUID drift, $X_4$ is sample shift along magnet axis and $X_3$ is the signal amplitude. $R = 0.97 \text{ cm}$ represents the longitudinal radius and $\Lambda = 1.519 \text{ cm}$ is the longitudinal coil separation.

The moment, in emu, can then be calculated using

\[
 M = \frac{X_3 \times \text{longitudinal regression factor}}{\text{SQUID calibration factor} \times \text{sensitivity factor} \times \text{correction factor}} \]  

where the longitudinal regression and SQUID calibration factors are device-dependent, the correction factor is 0.9125 and the sensitivity is dependent upon the range and gain used in the measurement. A Matlab script was written to perform the fitting procedure and moment extraction for small samples.

An overview of the temperature- and field-dependences of the magnetization/susceptibility behaviour of different magnetic systems is beyond the scope of this
thesis, a good introduction can be found in textbooks such as Blundell [76] and Ashcroft and Mermin [32].

Magnetic susceptibility is defined as
\[ \chi = \frac{\partial M}{\partial H}, \]  
(3.33)
which in the limit of a linear magnetization with magnetic field reduces to
\[ \chi = \frac{M}{H}. \]  
(3.34)

Most of the experiments discussed in chapter 4 were performed in the low-field regime and showed a linear relationship between magnetization and field and therefore used equation 3.34 for determining magnetic susceptibility.

Magnetization was used in particular for the characterization of the barium orthotellurite materials discussed in chapter 4. Another technique related to magnetization, torque magnetometry, was used for the measurement of quantum oscillations in \( \text{PdCoO}_2 \) and \( \text{PdCrO}_2 \) (Chapter 7) and will now be discussed.

### 3.2.4 Magnetic Torque

For magnetically anisotropic materials, application of a magnetic field away from high-symmetry directions generates a torque. The torque, \( \tau \), on a magnetic moment, \( \mathbf{m} \), in an applied field \( \mathbf{B} \) can be written
\[ \tau = \mathbf{m} \times \mathbf{B}. \]  
(3.35)

For obtaining accurate magnetization information from the torque one needs to know details of the magnetic structure. However, even without this information the torque magnetization technique can be used for measurements such as quantum oscillations due to the high signal-to-noise ratios that can be achieved.

The magnetic torque measurements described in this thesis were carried out using a piezo-resistive micro-cantilever technique [77]. This involves attaching the sample to a piezo-resistive microcantilever and measuring the resistance of the lever relative to an empty dummy lever. A photograph of the experimental realization of this is shown in figure 3.16.
Figure 3.16: The micro-cantilever setup used for measuring magnetic torque. The sample shown is a single crystal of PdCrO$_2$ which is approximately 500 $\mu$m across.

The piezo-resistive cantilevers used in the measurements were model SSI-SS-ML-PRC120 from SII NanoTechnology Inc. They have a length of 120 $\mu$m, width 50 $\mu$m and thickness 4-5 $\mu$m. The spring constant is 40 N/m and resistance $\approx 500 \Omega$.

The cantilever resistance is measured by a balanced AC Wheatstone bridge. The Wheatstone bridge setup is shown schematically in figure 3.17.

This method is ideal for extremely small samples where other measurements (such as coil-based measurements) are difficult. This was the case for the PdCoO$_2$ and PdCrO$_2$ samples discussed in chapter 7. These experiments were performed in a dilution refrigerator equipped with a 17 T magnet.

The details of the analysis of the quantum oscillations are discussed in the following section.

Figure 3.17: The Wheatstone bridge circuit used for the micro-cantilever torque experiments. The measurement signal is the voltage recorded by the lock-in amplifier which to first order is a linear function of the change in cantilever resistance due to the deflection.
3.2.5 Analysis Procedures

An example trace of a typical cantilever measurement as a function of magnetic field $B$ representative of the work in this thesis is shown in figure 3.18. The oscillations that are periodic in $1/B$ are clearly visible (for general aspects of quantum oscillations see section 2.4.4.1). The smoothly varying $B^2$ background is intrinsic to the torque technique and is removed prior to data analysis. The analysis scripts used by me are based upon scripts previously developed by Dr E. A. Yelland in Matlab.

In the first step the data are interpolated linearly in $1/B$ as a preparation for the second step which is a Fast Fourier Transform (FFT) in $1/B$. This is necessary since the built-in FFT algorithms require an equally-spaced dataset. The FFT can be carried out over any field range. This is advantageous, for example, if there is a phase transition as a function of field in the sample.

In order to minimise artefacts resulting from the finite field range the data is ‘windowed’. This means the data is multiplied by a smooth function that is zero at the lower and upper limit of the field range and 1 at the mean. An example of a typical windowing function is half a period of a sine function.

The FFT of a real valued function is of course complex. The result is presented as the square root of the power spectral density, i.e. $\sqrt{\text{Im} \{\text{FFT}\}^2 + \text{Re} \{\text{FFT}\}^2}$. An example of such an analysis is shown in the inset of figure 3.18. As discussed in section 2.4.4.1 the frequencies seen are directly proportional to the Fermi surface.

![Figure 3.18: An example micro-cantilever torque magnetometry quantum oscillation trace and in the inset an example Fourier transform.](image)
cross-sectional area.

In order to perform an analysis of the variation of amplitude with temperature equivalent datasets (i.e. same field range, sweep rate and cantilever measurement conditions) are taken for a range of temperatures. In this approach the amplitude of the square root of the power spectral density of the FFT follows the predicted Lifshitz-Kosevich formula. In particular, this ensures that the peak shape is unaltered between measurements.

This concludes the overview of experimental techniques used in this thesis. Typically, for an unknown sample, all of these techniques are used in order to study the phase diagram and determine the basic physical properties. The projects presented in the following main chapters were at different stages at the time of writing and address different aspects of a wide variety of materials. Consequently, only a subset of the discussed techniques was used for each of them. Each individual measurement must always be seen in the context of the overall knowledge of the material from all techniques available in modern condensed matter physics. Having given a brief introduction to the techniques used during the experiments presented in this thesis I will now discuss the experiments and results themselves in the following chapters.
This chapter discusses work on a new class of magnetic materials, barium orthotellurates. Those under investigation are the insulators $\text{Ba}_2\text{NiTeO}_6$, $\text{Ba}_2\text{CuTeO}_6$ and $\text{Ba}_2\text{ZnTeO}_6$, with the last one being a non-magnetic member of the family. The interest in these materials comes from their structural similarity to the proposed spin liquid $\text{Ba}_3\text{CuSb}_2\text{O}_9$ [78, 79]. The research project is at an early stage of development. Here I discuss the optimisation of sample preparation methods and first characterisation measurements of the materials involved. The goal of the project was to develop the crystal growth methods to obtain large single crystals and establish the basic physical properties of the materials as a platform for further detailed study. Of particular interest was the first measurement of the magnetic susceptibility and specific heat, as good indicators of potentially interesting magnetic physics. The combination allows changes in susceptibility to be compared with the presence (or absence) of signatures of phase transitions in specific heat. These first steps have been accomplished, laying the foundations for neutron diffraction experiments and high-field studies which are to be performed in the near future. Due to the early stage of the research on these materials a brief discussion of the current results and their possible implications will be given in this chapter. Firm conclusions as to the exact details of the magnetism and structural details of these compounds will not be possible until further measurements of larger samples and a greater range of techniques are completed.
4.1 Introduction

In the 1970s many of the known orthotellurates were synthesised by Köhl et al. [80, 81]. These were elpasolite-type compounds with the general formula $A_2B\text{TeO}_6$ with $B=\text{Ni, Cu, Zn}$. The tellurium ion will be in a $6^+$ valence state if the B-site ion is in a $2^+$ state. $\text{Te}^{6^+}$ has electronic configuration $[\text{Kr}]4d^{10}$ which makes it electronically and magnetically ‘inert’ therefore leaving the physics of the system to be dominated by the partially filled $d$-shell electrons of the B-site ion ($3d^8$ for Ni, $3d^9$ for Cu). There are relatively few inorganic compounds of tellurium and of these, the majority contain the Te$^{4^+}$ ion. Compounds of Te$^{4^+}$ are often referred to as ‘tellurates’ and the compounds of Te$^{6^+}$ as ‘orthotellurates’. This is based upon the common nomenclature used to distinguish between the two oxyanions of tellurium. The tellurate ion is formally $[\text{TeO}_4]^{2^-}$ and orthotellurate $[\text{TeO}_6]^{6^-}$ in the IUPAC nomenclature [82]. Compounds of Te$^{6^+}$ generally require oxidising synthesis conditions or high pressure to stabilise the higher oxidation state.

As mentioned above, the motivation to work on these quaternary barium orthotellurate compounds came initially from their structural similarity with $\text{Ba}_3\text{CuSb}_2\text{O}_9$ which was recently proposed to be a spin liquid [78]. The possibility of spin and/or orbital liquid physics in such compounds provided the motivation for a study of related systems which had been little researched. The $6H\text{Ba}_3\text{CuSb}_2\text{O}_9$ structure, shown in figure 4.1a, is composed of pairs of face-shared trigonally distorted octahedra which are linked by corner-sharing. Until now, the related systems studied here were, as far as we are aware, only investigated briefly in the 1970s. They form part of one of many related families, of general formula $A_x(B,B')_x\text{O}_{3x}$ ($x = 1, 2, 3, ..., \infty$), with varying numbers of face-shared trigonally distorted octahedra in the subunits and various orderings or lack of ordering between the B- and B’-site ions. The magnetic properties of these compounds are dependent upon the arrangement of the magnetic ions in the chains of face-shared trigonally distorted octahedra, their presence/absence in the trigonally distorted octahedra involved in the corner-sharing and also whether or not they are ordered. This gives a huge potential playground for exotic magnetism.

The possible spin liquid state in $\text{Ba}_3\text{CuSb}_2\text{O}_9$ arises largely because, as shown in figure 4.1b, the Cu ions in the hexagonal structure form a honeycomb-type lattice in the $ab$-plane with out-of-plane Cu ions forming isosceles triangles with two Cu ions in a honeycomb unit [79]. This leads to spin and orbital frustration and
long-range ordering has not yet been observed down to 110 mK [79]. The Weiss temperature for $\text{Ba}_3\text{CuSb}_2\text{O}_9$ is $\theta_W = -42$ K and so the lack of order to below 110 mK indicates an extremely strong frustration, phenomenologically expressed as $f = \frac{|\theta_W|}{T_N} \geq 380$.

The magnetic materials under discussion in this chapter, $\text{Ba}_2\text{CuTeO}_6$ and $\text{Ba}_2\text{NiTeO}_6$, are also expected to show evidence of competing magnetic interactions. The general parent structure of these compounds is the 12$L$ ‘$\text{Ba}_2\text{NiTeO}_6$-type’ structure shown in figure 4.2 [83]. This is formed from corner-shared triplets of face-shared octahedra. The magnetic ions form a triangular lattice in the ab-plane and these triangular planes are linked alternately by corner-shared and face-shared TeO$_6$ trigonally distorted octahedra.

The B$^{2+}$ magnetic ions in the $\text{Ba}_2\text{NiTeO}_6$-type structure are always separated by a TeO$_6$ trigonally distorted octahedron, either corner- or face-shared. This means that, considering the B=Ni case, rather than the usual Ni-O-Ni superexchange interactions which can be predicted using the Kanamori-Goodenough-Anderson rules [84–87], Ni-O···O-Ni super-supersuperexchange (SSE) must be taken into account, as shown in figure 4.3. The Kanamori-Goodenough-Anderson rules apply only to single-anion linkages between magnetic ions but some qualitative rules for super-supersuperexchange have been developed recently [88, 89]. They suggest that the interactions between the Ni ions linked by the corner-sharing TeO$_6$ polyhedra will
be the strongest antiferromagnetic couplings present as the Ni-O···O angle is the largest and the O···O distances the shortest (exchange path $J_2$ in figure 4.3b). The interactions between the ions along the $c$-axis in the face-sharing columns would be expected to be more weakly antiferromagnetic and may even be ferromagnetic ($J_3$ in figure 4.3b).

Having introduced the general structure of the materials we will now turn to their physical properties. Due to the lack of previous studies of these compounds, the basic properties determined during this study are tabulated in table 4.1 to provide context for the detailed discussions to follow. Ba$_2$ZnTeO$_6$ is non-magnetic and can be seen as a benchmark material against which to compare the influence of magnetism. Ba$_2$CuTeO$_6$ has spin-$\frac{1}{2}$ Cu$^{2+}$ ions on the B-site. This compound shows no evidence of a phase transition down to 2.5 K in specific heat but hints of competing interactions in magnetic susceptibility. Finally, Ba$_2$NiTeO$_6$ is a $S = 1$ system, ordering antiferromagnetically at 8.5 K.

The crystal growth and measurements were carried out over a 10 month period involving a stay in the group of Prof. H. Takagi at RIKEN in Wako, Japan. This included a 6 week visit to the Max-Planck Institut für Festkörperforschung.
Figure 4.3: The exchange paths for the Ba$_2$NiTeO$_6$-type structure, (a) shows the in-plane exchange in the triangular lattice formed by the Ni ions in the $ab$-plane and (b) the out-of-plane exchange paths. Each B-site ion will have six equal paths ($J_1$) in the $ab$-plane, three equal paths through the corner-sharing TeO$_6$ polyhedra ($J_2$) and one in the $c$-axis direction ($J_3$).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Structure</th>
<th>TM spin state</th>
<th>Colour</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba$_2$NiTeO$_6$</td>
<td>$R3m^\dagger$ 12$L$</td>
<td>$S = 1$</td>
<td>orange</td>
<td>$T_N = 8.5$ K</td>
</tr>
<tr>
<td>Ba$_2$CuTeO$_6$</td>
<td>$C2/c$ 6$L$</td>
<td>$S = 1/2$</td>
<td>yellow</td>
<td>$T^* = 16$ K</td>
</tr>
<tr>
<td>Ba$_2$ZnTeO$_6$</td>
<td>$R3m^\dagger$ 12$L$</td>
<td>$S = 0$</td>
<td>white</td>
<td>$T_S = 165$ K, non-mag</td>
</tr>
</tbody>
</table>

$^\dagger$ These are the space groups originally reported in the 1970s by Köhl et al. [80, 83].

Table 4.1: The basic properties of the barium orthotellurate materials investigated. $T^*$ indicates the temperature of an anomaly in the magnetic susceptibility of Ba$_2$CuTeO$_6$. $T_S$ is the temperature of a feature in the specific heat of Ba$_2$ZnTeO$_6$ which is likely due to a structural transition.

in Stuttgart, hosted by the group of Prof. B. Keimer.
4.2 Material Details and Development of Crystal Growth Methods

4.2.1 Previous Synthesis Work

The crystal growth methods used for these compounds were developed based upon those described by Köhl et al. in the 1970s [80, 83]. Their original method had involved flux growth of single crystals from pre-synthesised polycrystalline Ba$_2$BTeO$_6$ (synthesised using nitrates under flowing oxygen) and BaCl$_2$ flux. They used a 5:2 flux:Ba$_2$BTeO$_6$ ratio by weight in Pt crucibles with flowing oxygen. The heating profile used was 1150 $^\circ$C for Ba$_2$NiTeO$_6$ [83] or 1050 $^\circ$C for Ba$_2$CuTeO$_6$ [80] for 24h followed by cooling at 5 $^\circ$C/h to 800 $^\circ$C, then quick cooling to room temperature.

New methods for single crystal growth and polycrystal synthesis were developed to increase the size and yield of single crystals and to make polycrystalline samples available for physical property measurements.

4.2.2 Materials Used

The TeO$_2$ used was prepared by the oxidation of high-purity Te metal. Metallic Te is easily oxidised in air. Finely ground Te was placed in a high-purity alumina crucible and heated at 600 $^\circ$C for 91/2h. The finely ground metal is transformed to an extremely fine powder of the white oxide. The completion of oxidation was confirmed by x-ray diffraction. As shown in figure 4.4, the oxidised product is the binary oxide TeO$_2$ with no indication of impurity phases. The commercially obtained BaCO$_3$ was dried at 300 $^\circ$C and weighed straight after removal from the furnace. The BaCl$_2$ was stored and weighed out in a glove box before use in the crystal growth process.

The crystal growth was performed in air in platinum crucibles with platinum lids. Platinum crucibles were used to prevent contamination by reaction of the alumina with the flux/reactant mixture. The platinum crucibles were then enclosed in an outer alumina crucible to contain any BaCl$_2$ escaping from the platinum crucible as BaCl$_2$ is known to be volatile and susceptible to creeping. The volatility of the
flux can be useful in some cases where it leads to supersaturation of the growth solution. The growth was carried out in a muffle furnace which was enclosed in a fume cupboard to ensure safe extraction of any TeO$_2$ vapours produced as TeO$_2$ is volatile above $\approx$ 700°C and toxic.

4.2.3 Polycrystalline Sample Synthesis

Polycrystalline samples of all materials were obtained by standard solid state synthesis under flowing oxygen. All three materials have similar synthesis characteristics and the same process was found to work for all of them. The previously reported solid state synthesis method used nitrates of the barium (Ba(NO$_3$)$_2$) and the transition metals (Ni(NO$_3$)$_2$, Cu(NO$_3$)$_2$ and Zn(NO$_3$)$_2$) [80, 83]. These were initially in solution form and were evaporated to dryness before the reaction commenced. For ease of handling and accuracy in weighing it was decided to try synthesis using oxides instead. The starting materials were weighed out in the stoichiometric ratio for the reaction:

$$2\text{BaCO}_3 + \text{BO} + \text{TeO}_2 \rightarrow \text{Ba}_2\text{BTeO}_6 + \text{CO} + \text{CO}_2,$$

and then thoroughly ground and pelleted. The pellets were placed in a high purity alumina boat and then in a quartz tube with flowing oxygen in a tube furnace.

Initial synthesis of Ba$_2$CuTeO$_6$ involved heating to 600°C for four hours and then to progressively higher temperatures in steps of 100°C with examination
of the colour of the pellet every four hours to determine the reaction progress (the reactant mixture is grey whereas Ba$_2$CuTeO$_6$ is a bright yellow colour). For temperatures up to 800 °C there was no clear colour change but for 900 °C a colour change was observed and so this temperature was used for further synthesis of Ba$_2$CuTeO$_6$.

The final procedure for polycrystalline samples of Ba$_2$CuTeO$_6$ and Ba$_2$ZnTeO$_6$ was slow heating to 900 °C over 5 h and then holding at this temperature for 8-12 h before cooling to room temperature, grinding and checking phase purity using x-ray diffraction. This process was repeated until the x-ray diffraction indicated that phase-pure samples had been obtained. Examples of Ba$_2$NiTeO$_6$ and Ba$_2$CuTeO$_6$ polycrystalline samples are shown in figure 4.5. The Ba$_2$CuTeO$_6$ sample is bright yellow and the Ba$_2$NiTeO$_6$ sample bright orange. The Ba$_2$ZnTeO$_6$ samples are white as would be expected due to the filled $d$-orbitals of Zn$^{2+}$.

The x-ray diffraction patterns for the polycrystalline samples of all three materials are shown in figure 4.6. It can be seen that the materials are structurally very similar as expected from previous reports. Again, in line with previous reports, the Ba$_2$CuTeO$_6$ sample can be seen to have a more complex diffraction pattern than Ba$_2$NiTeO$_6$ and Ba$_2$ZnTeO$_6$ indicating that it has a different but related structure. The Ba$_2$NiTeO$_6$ and Ba$_2$ZnTeO$_6$ patterns are almost identical aside from a difference in the lattice parameters. Consequently, the compounds can be expected to have similar if not identical structures. The peak positions of all three materials were in agreement with those predicted from the structures originally reported by Köhl et al. [80, 83, 90] with no additional peaks detected.

All samples were phase pure within the limitations of laboratory x-ray diffraction. The presence of the heavy elements barium and tellurium leads to problems of detection for the light transition metal-based oxides such as NiO, CuO and ZnO.

![Figure 4.5: Polycrystalline samples of Ba$_2$NiTeO$_6$ (left) and Ba$_2$CuTeO$_6$ (right). Polycrystalline Ba$_2$ZnTeO$_6$ is white (not shown).](image)
Figure 4.6: The powder x-ray diffraction patterns of polycrystalline samples of Ba$_2$ZnTeO$_6$ (top, red), Ba$_2$CuTeO$_6$ (middle, green) and Ba$_2$NiTeO$_6$ (bottom, blue).

Long scans over specific regions where the main binary oxide or other potential impurity peaks would be expected showed no evidence of these phases. However, as mentioned, it is possible that small impurity phases are present but not visible due to the high Ba and Te concentrations in the sample. The phase purity will be further investigated in future experiments such as neutron scattering and with other analytical techniques such as Electron Probe Micro Analysis (EPMA).

One interesting point may be made regarding the Ba$_2$NiTeO$_6$ samples. The polycrystalline samples are bright orange (and the single crystals discussed shortly are orange-brown) whereas six-fold coordinated Ni$^{2+}$ containing materials are generally expected to have a green colour. However, it has been reported that when Ni$^{2+}$ in a trigonally distorted coordination (rather than ideal octahedral coordination) is present, compounds tend to be yellow/orange in colour [91]. Since the Ni ions are in a trigonally distorted coordination in this case this would seem to explain the unusual colour of Ba$_2$NiTeO$_6$.

4.2.4 Single Crystal Growth Development

In order to check the space group assignments of the materials and measure their expected anisotropic physical properties single crystals were required. For the
structure determination small crystals would be adequate but for the physical property measurements such as specific heat and magnetization larger crystals are preferred as these reduce the need for arrays of aligned crystals (and also the uncertainties in alignment for measurements) and also improve the signal-to-noise ratio.

All three materials have similar growth characteristics and the same growth process was found to work for all of them. Initially, following the published method exactly, most of the crystals were \( \approx 100 \, \mu\text{m} \) across and \( \approx 20 \, \mu\text{m} \) thick; an example can be seen in figure 4.7a. The use of the reactant materials BaCO\(_3\), BO and TeO\(_2\) instead of pre-synthesised starting materials was tried. This gave a noticeable improvement in the yield of crystals and also the maximum size obtained. A variety of flux/starting material ratios and temperature profiles were explored to try to increase the size of the crystals obtained. The maximum starting material to flux ratio was limited by the size of the platinum crucibles to 1 g reactants:3 g flux for a typical total weight of starting reactants of 5 g. With this ratio and the optimised heating profile the crystals completely filled the lower half of the crucible after the growth and were extremely tightly packed. Growth seemed to occur both on the surface of the melt and also at the flux/Pt interface. Initial growth runs gave planar hexagonal crystals with width to thickness ratios typically \( \approx 1 : 0.2 \). The optimised process described below gave ratios closer to 1 : 0.5 and substantially larger crystals up to \( \approx 3 \, \text{mm} \) across. An example of the larger, thicker crystals from an intermediate stage of the development is shown in figure 4.7b. A larger and/or lower-form (i.e. larger diameter to height ratio) crucible should allow further improvements in crystal size.

![Figure 4.7: Examples of (a) a single crystal of Ba\(_2\)CuTeO\(_6\) from an early growth run and (b) a single crystal array built from larger, thicker crystals of Ba\(_2\)NiTeO\(_6\) during crystal growth process development.](image)
The final process developed is as follows. The starting materials were ground together in the stoichiometric ratio for the reaction:

\[ 2\text{BaCO}_3 + \text{BO} + \text{TeO}_2 \rightarrow \text{Ba}_2\text{BTeO}_6 + \text{CO} + \text{CO}_2. \]  

(4.2)

The ground reactants were mixed with BaCl\(_2\) flux in a ratio of 1 g reactants:3 g flux. The resulting mixture was placed in a platinum crucible and covered with a platinum lid. This was then placed inside an alumina crucible and lid. The mixture was heated to 1050 °C over 8 h and then held at 1050 °C for 36 h. The temperature was then decreased to 1010 °C over 10 h. This was followed by cooling to 800 °C over 4 h and then the furnace heater was switched off and the crucibles were allowed to cool to ambient temperature. The crystals were then separated from the flux using hot water.

### 4.2.5 Crystal Structure Solution Results

The room temperature structure of \(\text{Ba}_2\text{CuTeO}_6\) was solved by Daisuke Hashizume of the Materials Characterization Team at RIKEN using single crystal x-ray diffraction data taken on one of the samples grown during this investigation with a Mo \(k_\alpha\) rotating anode machine. The space group was determined as monoclinic \(C2/m\) (No. 12) with 4 formula units per cell and unit cell parameters \(a = 10.2444(3)\) Å, \(b = 5.7315(2)\) Å, \(c = 10.1055(5)\) Å and \(\beta = 108.019(3)^\circ\). The structure is shown in figure 4.8 and details of the crystal structure are tabulated in table 4.2.

This structure is different to that reported by Köhl et al. in 1974 [80] which was a triclinic version of the 12L \(\text{Ba}_2\text{NiTeO}_6\) structure. However, \(P\bar{1}\) is a maximal subgroup of \(C2/m\) (related by the matrix \([1/2, -1/2, 0][1/2, 1/2, 0][0, 0, 1]\)) and therefore the structure originally proposed can be described as a triclinically distorted form of the structure reported here. The true ambient temperature structure is a 6-layer type unit cell with the CuO\(_6\) trigonally distorted octahedra further distorted by the Jahn-Teller effect even at room temperature.

The data collected on the crystals of \(\text{Ba}_2\text{NiTeO}_6\) and \(\text{Ba}_2\text{ZnTeO}_6\) have not yet been fully analysed but initial analysis indicates the unit cell of \(\text{Ba}_2\text{NiTeO}_6\) to be trigonal in contrast to the \(R\bar{3}m\) structure previously reported [83].
Figure 4.8: The crystal structure of $\text{Ba}_2\text{CuTeO}_6$ determined by single crystal x-ray diffraction. The CuO$_6$ polyhedra are shown in green, the TeO$_6$ polyhedra in blue and the barium ions in grey.

Space Group: $C2/m$, No. 12

$R_1=0.0435$, $wR_2=0.1271$, $\chi^2=1.193$, 58 var.

$a = 10.2444(3)$ Å, $b = 5.7315(2)$ Å, $c = 10.1055(5)$ Å, $\beta = 108.019(3)^\circ$

<table>
<thead>
<tr>
<th>Site</th>
<th>Wyckoff Position</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>$U_{iso}$ (Å$^2$)</th>
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<tbody>
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<td>0</td>
<td>0.37910(3)</td>
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<td>0.84996(4)</td>
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<tr>
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<td>0</td>
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</table>

Table 4.2: The crystal structure details from the structure solution of $\text{Ba}_2\text{CuTeO}_6$. 
4.3 Novel Physical Properties of Orthotellurate Materials

In this section the results of magnetic susceptibility and specific heat measurements carried out on polycrystalline and single crystal samples of $\text{Ba}_2\text{NiTeO}_6$, $\text{Ba}_2\text{CuTeO}_6$ and $\text{Ba}_2\text{ZnTeO}_6$ are reported. The magnetic susceptibility measurements were carried out in a 1 T Quantum Design MPMS system by measuring the d.c. magnetization in applied fields between 10 Oe and 10 kOe. The specific heat measurements were carried out in a 9 T Quantum Design PPMS system using the relaxation time method. Experimental details of both methods and the additional data analysis procedures necessary due to the small single crystal sample sizes are described in detail in section 3.2.

4.3.1 $\text{Ba}_2\text{ZnTeO}_6$

Due to $\text{Ba}_2\text{ZnTeO}_6$ being an entirely closed-shell system and therefore non-magnetic it makes a useful comparison material for the magnetic materials $\text{Ba}_2\text{NiTeO}_6$ and $\text{Ba}_2\text{CuTeO}_6$. Here we report its magnetic susceptibility and specific heat for comparison with the other materials.

Magnetic Susceptibility

$\text{Ba}_2\text{ZnTeO}_6$, consisting entirely of closed-shell ions, would be expected to be diamagnetic. The molar magnetic susceptibility $\chi = M/H$ shown in figure 4.9 confirms this prediction with a small paramagnetic contribution being seen at low temperatures. The paramagnetic signal arises from the small background from the straw and Al foil used for sample mounting and isolated impurities in either the aluminium foil or the sample itself.

$^1$The $\chi = M/H$ data shown in this chapter are typically for $H = 10 \text{kOe}$. Data was also taken for all samples at lower fields down to $H = 10 \text{Oe}$. Whenever conclusions regarding the susceptibility were drawn only those temperature regimes where magnetisation had a linear field dependence, or where the 10 Oe data showed qualitatively the same signatures as the higher field data, were taken into account. In other words we ensured that our deductions were valid in the low-field limit at 10 Oe.
Figure 4.9: The molar magnetic susceptibility of polycrystalline Ba$_2$ZnTeO$_6$ for $H = 10$ kOe.

The high temperature value of $\chi = -1.44 \times 10^{-4}$ emu mol$^{-1}$ agrees well with the estimated diamagnetic susceptibility of Ba$_2$ZnTeO$_6$ of

$$\chi_D = 2 \chi_D(Ba^{2+}) + \chi_D(Zn^{2+}) + 6 \chi_D(Te^{6+}) + 6 \chi_D(O^{2-}) = -1.52 \times 10^{-4} \text{ emu mol}^{-1},$$

with $\chi_D(Ba^{2+}) = -26.5 \times 10^{-6} \text{ emu mol}^{-1}$, $\chi_D(Zn^{2+}) = -15 \times 10^{-6} \text{ emu mol}^{-1}$, $\chi_D(Te^{6+}) = -12 \times 10^{-6} \text{ emu mol}^{-1}$ and $\chi_D(O^{2-}) = -12 \times 10^{-6} \text{ emu mol}^{-1}$ [92].

**Specific Heat**

The zero-field specific heat of Ba$_2$ZnTeO$_6$ shows only one weak anomaly at $\approx 165$ K as can be seen in figure 4.10. This is seen in both polycrystalline and single crystal samples reproducibly and is presumably a sign of a structural transition, particularly since there is no signature in susceptibility and the system is non-magnetic. This will be investigated further during upcoming neutron diffraction experiments.

Ba$_2$ZnTeO$_6$ is also a valuable non-magnetic comparison material for Ba$_2$NiTeO$_6$ and Ba$_2$CuTeO$_6$ as its specific heat should be very similar to the lattice specific heat of both compounds. However, the detailed structures of all three materials must be determined for the suitability to be evaluated thoroughly, especially
in view of the evidence for a structural transition seen in the specific heat of Ba$_2$ZnTeO$_6$.

### 4.3.2 Ba$_2$NiTeO$_6$

Ba$_2$NiTeO$_6$ would be expected to show magnetic ordering due to the presence of $S = 1$ Ni$^{2+}$ ions. Both polycrystalline and single crystal samples were synthesised to investigate the physical properties.

#### Magnetic Susceptibility

The susceptibility of a polycrystalline sample of Ba$_2$NiTeO$_6$ is shown in figure 4.11. It can be seen that a somewhat broadened antiferromagnetic transition is observed at $\approx 8$ K. This was confirmed in single crystal measurements. The susceptibility of a 0.12 mg single crystal of Ba$_2$NiTeO$_6$ is shown in figure 4.12 with the magnetic field applied parallel to the $ab$-plane and to the $c$-axis. This confirms the transition seen in the polycrystalline sample. As can be expected, the single crystals show a much sharper transition. The anisotropy ratio below $T_N$ of $\frac{\chi_{ab}}{\chi_c} \geq 1$ indicates antiferromagnetic ordering in the $c$-axis direction [93].
Chapter 4. Barium Orthotelurates

Figure 4.11: The d.c. susceptibility of polycrystalline $\text{Ba}_2\text{NiTeO}_6$ for $H = 10\text{kOe}$.

Figure 4.12: The d.c. susceptibility of single crystal $\text{Ba}_2\text{NiTeO}_6$ for $H = 10\text{kOe}$. 
The magnetization of an array of 11 single crystals with total mass 1.4 mg was also measured. The Weiss constants and effective magnetic moments extracted from Curie-Weiss fits above 100 K are tabulated in table 4.3. The fits for the polycrystalline sample and the single crystal sample with field applied parallel to the c-axis are shown in figure 4.13. Some of the variation in $\theta_W$ and $\mu_{\text{eff}}$ is most likely to be due to the sample quality difference between the polycrystalline material and single crystals\(^2\), larger relative errors in the weights of the smaller samples and the subtraction of the background for the single crystal array.

\(^2\)with the possibility of a small fraction of NiO in the polycrystalline samples due to the difficulties of detecting light phases using x-ray diffraction in the presence of the heavier Ba and Te.

### Table 4.3: The Weiss constants ($\theta_W$) and magnetic moments determined from d.c. magnetization measurements for various Ba$_2$NiTeO$_6$ samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Magnetic Moment ($\mu_B$/Ni$^{2+}$)</th>
<th>$\theta_W$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>polycrystalline</td>
<td>3.439(4)</td>
<td>-154.1(7)</td>
</tr>
<tr>
<td>single crystal 0.12 mg $H_{</td>
<td></td>
<td>c}$</td>
</tr>
<tr>
<td>single crystal 0.12 mg $H_{</td>
<td></td>
<td>ab}$</td>
</tr>
<tr>
<td>single crystal array 1.4 mg $H_{</td>
<td></td>
<td>c}$</td>
</tr>
</tbody>
</table>

Figure 4.13: The inverse susceptibility for $H = 10$ kOe of polycrystalline (green) and single crystal with $H_{||c}$ (red) Ba$_2$NiTeO$_6$ with the fits to the high temperature susceptibility (dark blue lines).
The fits to the high-temperature part of the inverse susceptibility give a magnetic moment of $\approx 3.44 \mu_B/\text{Ni}^{2+}$. This is larger than the spin-only predicted $S = 1$ value of $2.83 \mu_B/\text{Ni}^{2+}$ but a non-negligible orbital contribution to the moment for $\text{Ni}^{2+}$ is not uncommon and depending upon the coordination the moment can be in excess of $3.5 \mu_B/\text{Ni}^{2+}$ [94]. For example, $\text{Ba}_3\text{NiSb}_2\text{O}_9$ with very similar Ni coordination geometry the moment has been reported as $3.54 \mu_B/\text{Ni}^{2+}$ [95]. The Weiss constant obtained from the fits is $\theta_W \approx -145$ K. This is large given the Néel temperature of 9 K for single crystals and results in a large frustration parameter $f = |\theta_W|/T_N \approx 16$.

The magnetic order in $\text{Ba}_2\text{NiTeO}_6$ was expected to be antiferromagnetic in nature, as discussed in section 4.1, from consideration of the super-supersuperexchange interactions suggested by the crystal structure. The reasonably large frustration parameter is also not unexpected. If the super-supersuperexchange in the $ab$-plane is dominant as previously predicted then the system will to first order behave as a 2D triangular lattice antiferromagnet which is a frustrated system. As a preliminary observation, the clear antiferromagnetic transition at $T_N \approx 9$ K showing anisotropic behaviour seems to confirm that the in-plane SSE is dominant and that the out-of-plane interactions are negligible in comparison. However, further detailed studies will be necessary to fully investigate this.

The field dependence of the magnetization was also investigated. Figure 4.14

![Figure 4.14: $M(H)$ for polycrystalline $\text{Ba}_2\text{NiTeO}_6$ at 5K as a function of applied magnetic field.](image)
shows $M/H$ at 5 K for polycrystalline $\text{Ba}_2\text{NiTeO}_6$. The field dependence between -1 T and 1 T is linear except for a small hysteretic contribution at low field, shown in figure 4.15, which is of the same order of magnitude as that from the sample holder, and hence may not be intrinsic. Future measurements of the magnetization at higher fields are planned since changes to the magnetic structure may be expected when the field energy scale is of the same order of magnitude as $T_N$. This roughly corresponds to a field of 10 T.

![Figure 4.15: $M/H$ for polycrystalline $\text{Ba}_2\text{NiTeO}_6$ at 5K as a function of applied magnetic field.](image)

**Specific Heat**

The zero-field specific heat of 36.91 mg of polycrystalline $\text{Ba}_2\text{NiTeO}_6$ is shown in figure 4.16 and $C/T$ as a function of $T^2$ in figure 4.17. The antiferromagnetic transition seen in the magnetic measurements is also seen in the specific heat as a lambda-type peak at $\approx 8.5$ K. The inset shows a comparison of the low-temperature part of the specific heat for the polycrystalline sample and for a 1.4 mg array of single crystals. Aside from compositional differences, the addenda for the heat capacity measurement on the single crystal array is significantly larger compared to the heat capacity of the crystals themselves, leading to relatively larger errors. For example, for the single crystal array at 5 K the sample heat capacity is only twice that of the addenda heat capacity (and for $T > 11$ K the addenda heat capacity is larger than the sample heat capacity). For the polycrystalline sample at the same temperature, the sample heat capacity is 30 times that of the addenda. The specific heats of both samples show a clear transition, with a peak at $\approx 8.5$ K. No further anomalies suggesting further structural or other transitions are seen between 2.5 K
Chapter 4. *Barium Orthotelurates*

and 300 K. The fact that a $\lambda$-type transition is observed places some constraints on the universality class of the transition with further experiments desirable to classify its nature.

![Figure 4.16](image1.png)

**Figure 4.16:** The specific heat of polycrystalline Ba$_2$NiTeO$_6$. Inset: the low temperature part of the specific heat of the polycrystalline sample (green) and a single crystal array (blue).

![Figure 4.17](image2.png)

**Figure 4.17:** $C/T$ as a function of $T^2$ for polycrystalline (blue) and single crystal (green) Ba$_2$NiTeO$_6$. 
4.3.3 Ba$_2$CuTeO$_6$

The physical properties of Ba$_2$CuTeO$_6$ would be expected to be dominated by the magnetic interactions of the $S = 1/2$ Cu$^{2+}$ ions present. The lowered symmetry of the monoclinic structure of Ba$_2$CuTeO$_6$ compared to the rhombohedral structure of Ba$_2$NiTeO$_6$ splits the degeneracy of the exchange paths in the $ab$-plane as will be discussed in the following section. This move away from an equilateral triangular-lattice structure in the $ab$-plane would be expected to lead to a complex interplay of magnetic interactions with the nature of any ordered states depending on the relative strengths of the exchange interactions.

Magnetic Susceptibility

The d.c. molar magnetic susceptibility, $\chi = M/H$, of polycrystalline Ba$_2$CuTeO$_6$ is shown in figure 4.18. A broad maximum is apparent at $T \approx 75$ K with an upturn at temperatures below 8.5 K. The equivalent data for a single crystal with magnetic field applied in the $ab$-plane and in the $c$-axis is shown in figure 4.19. The single crystal data show the same broad maximum at $\approx 75$ K as the polycrystalline data.

![Figure 4.18: The molar susceptibility of polycrystalline Ba$_2$CuTeO$_6$ for $H = 10$ kOe.](image)
Contrary to the polycrystalline sample a clear kink is visible in the single crystal data at $\approx 16$ K for both field applied in the $ab$-plane and in the $c$-axis direction. Upon close inspection, this feature is also present in the polycrystalline data although it is not immediately obvious due to the averaging effect of the polycrystalline sample. At lower temperatures $\chi_{ab}$ increases while $\chi_c$ drops, perhaps indicating an easy-axis type behaviour where antiferromagnetic alignment in the $c$-axis direction is favoured. Below $\approx 5$ K $\chi_c$ undergoes an upturn and $\chi_{ab}$ continues to increase. Whether the upturn in $\chi_c$ is intrinsic or due to a Curie tail from orphan spins is not easy to determine since there are not enough data points in this low-temperature regime to attempt a Curie-Weiss fit.

To obtain the Weiss constant and effective magnetic moment per $\text{Cu}^{2+}$ ion for $\text{Ba}_2\text{CuTeO}_6$ a Curie-Weiss fit of the inverse susceptibility was performed. The result is shown in figure 4.20. The fit gave an effective magnetic moment of $1.79(1) \mu_B/\text{Cu}^{2+}$ in good agreement with the predicted spin-only $S = 1/2$ value of $1.73 \mu_B/\text{Cu}^{2+}$ and the experimental range $1.8$-$2.0 \mu_B/\text{Cu}^{2+}$ commonly given in reference books [96]. The Weiss constant obtained from the fit is $\theta_W = -80 \pm 1$ K. This is indicative of a reasonably strong antiferromagnetic interaction between the $\text{Cu}^{2+}$ spins at high temperature.

The magnetization as a function of field for $\text{Ba}_2\text{CuTeO}_6$ up to $H = 10^4$ Oe is shown in figure 4.21. The $M(H)$ curve is linear at $T = 40$ K but at $T = 4$ K $M(H)$
is decreased in magnitude and deviates slightly from linearity at $-4000 \text{ Oe} \geq H \geq 4000 \text{ Oe}$. This can be seen more clearly in the inset which shows the magnetization data taken at 4 K with a linear field dependence between $-4000 \text{ Oe}$ and 4000 Oe subtracted, referred to as $\Delta M$. This decrease in $M(H)$ at low temperatures could be due to short-range antiferromagnetic ordering of a fraction of the Cu$^{2+}$ ions.

**Figure 4.20:** The inverse molar susceptibility of polycrystalline Ba$_2$CuTeO$_6$ (green) and high-temperature Curie-Weiss fit (blue).

**Figure 4.21:** The molar magnetization of polycrystalline Ba$_2$CuTeO$_6$ at 4 K (green) and 40 K (blue) for $H = 10 \text{kOe}$. The inset shows the 4K magnetization with a linear term, obtained from a fit to the $-4 \text{kOe} \leq H \leq 4 \text{kOe}$ data, subtracted.
and the non-linearity to breaking of this short-range order with increasing field. Unfortunately fields above 10 kOe were not available during these experiments but future experiments under higher fields are planned.

The clear difference in the susceptibilities of the single crystal sample for $H_{\parallel c}$ and $H_{\parallel ab}$ even at high temperature are indicative of an anisotropy in the $g$-factor. This has in fact been reported as $g_{\parallel}(T = 77 \text{ K}) = 2.448$ and $g_{\perp}(T = 77 \text{ K}) = 2.081$ [80], in approximate agreement with the anisotropy seen in the current data.

The lowered symmetry of the Cu-containing compound to a monoclinic lattice due to the Jahn-Teller effect also leads to unequal Cu-Cu distances in the $ab$-plane triangular layers and unequal out-of-plane distances. This would be expected to lead to a highly non-trivial set of exchange parameters and consequently a complicated set of magnetic interactions and a high degree of frustration. A schematic diagram of possible exchange interactions is shown in figure 4.22. There are three inequivalent interactions in the $ab$-plane and two further inequivalent paths out of the plane. The angles and distances are tabulated in table 4.4. Since the general rule so far qualitatively established for SSE interactions is that the shorter the O⋯O distance and the larger the Cu-O⋯O angle the more strongly antiferromagnetic the interaction will be, the predicted strength for the interactions would

\[ J_2 > J_1 > J_3 > J_4 > J_5 \]

**Figure 4.22:** The exchange paths for Ba$_2$CuTeO$_6$ in (a) the $ab$-plane and (b) in the $c$-axis direction.
Table 4.4: The distance and angles related to interaction strength in the super-
superexchange paths in Ba$_2$CuTeO$_6$ based upon the data from the single crystal
structure solution discussed in section 4.2.5.

<table>
<thead>
<tr>
<th>Path</th>
<th>O···O distance (Å)</th>
<th>Cu-O···O angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$J_1$</td>
<td>2.72</td>
<td>144</td>
</tr>
<tr>
<td>$J_2$</td>
<td>2.75</td>
<td>140</td>
</tr>
<tr>
<td>$J_3$</td>
<td>2.72</td>
<td>134</td>
</tr>
<tr>
<td>$J_4$</td>
<td>2.72</td>
<td>130</td>
</tr>
<tr>
<td>$J_5$</td>
<td>2.85</td>
<td>120</td>
</tr>
</tbody>
</table>

be $J_1 > J_2 > J_3 > J_4 > J_5$.

The true strengths of the SSE interactions may be different to those tentatively
predicted but despite this, it seems likely that the Jahn-Teller distortion induced
lowering of the symmetry removes the frustration of the triangular lattice as seen
in Ba$_2$NiTeO$_6$. The geometry of the magnetic lattice resulting from this distortion
is unknown but the interactions can safely be expected to be strongly competing.

Specific Heat

The zero-field specific heat for a 22.4 mg polycrystalline sample of Ba$_2$CuTeO$_6$ is
shown in figure 4.23. There is no visible peak or anomaly in the specific heat, for
either polycrystalline or single crystal samples, down to 2.5 K which would indicate
a transition, contrary to susceptibility data. Examination of $C/T$ for the single
crystal and polycrystalline samples, shown in figure 4.24, also reveals a lack of any
signature of a transition. However, the specific heat of the single crystal array in
particular was extremely small compared to the addenda specific heat and it is
possible that a weak transition is present but below the resolution of the current
data. Further experiments are planned with the larger crystals now available to
ensure that reliable specific heat data is available.

The current experimental data leave two possibilities. The first is that the trans-

sition that appears as a kink in the susceptibility originates from an as-yet uniden-
tified impurity phase present in both the single crystals and the polycrystalline
samples as no ordering down to 2.5 K is indicated by $C/T$ in both the polycrys-
talline and single crystal samples. The second possibility is that the transition at
Figure 4.23: The specific heat of a 22.4 mg polycrystalline sample of Ba$_2$CuTeO$_6$.

Figure 4.24: $C/T$ vs. $T^2$ for polycrystalline (green) and single crystal (blue) Ba$_2$CuTeO$_6$.

5 K is not resolved in $C/T$ due to the small size of the signal.

Further detailed investigations including neutron scattering, lower temperature and high-field experiments are planned to clarify the details of the magnetic interactions and confirm whether any ordering is seen to lower temperatures than available so far.
4.3.4 Summary

In this chapter crystal growth development and previously unreported physical property characterisation of Ba$_2$NiTeO$_6$, Ba$_2$CuTeO$_6$ and Ba$_2$ZnTeO$_6$ has been described.

The original aim of development of crystal growth methods with the result of larger single crystals of the barium orthotellurate materials has been achieved with crystals large enough for reliable MPMS measurement of a single crystal obtained. The path to crystals large enough for single-crystal PPMS measurements is clear.

The second aim of characterising the physical properties of the compounds has also been achieved. The basic magnetic properties of all three materials have been measured with Ba$_2$ZnTeO$_6$ being diamagnetic as expected, Ba$_2$NiTeO$_6$ being a frustrated antiferromagnet with $T_N=8.5$ K and Ba$_2$CuTeO$_6$ also being a frustrated magnet with a more complicated low-temperature behaviour. The specific heats of all three materials have also been measured and are compared in figure 4.25. Ba$_2$ZnTeO$_6$ shows evidence of a previously unreported transition at $\approx 180$ K. The antiferromagnetic transition of Ba$_2$NiTeO$_6$ is seen clearly as a peak in the specific heat of polycrystalline and single crystal samples. For Ba$_2$CuTeO$_6$ the picture is more complicated with no transition being seen in specific heat for

![Figure 4.25: The molar specific heats of polycrystalline Ba$_2$NiTeO$_6$, Ba$_2$CuTeO$_6$ and Ba$_2$ZnTeO$_6$. The inset shows a close-up of the low-temperature region.](image)
either polycrystalline or single crystal samples. Whether this is due to the sample size being too small or that there is no transition at low temperature will be investigated.

Future work on this project will continue the growth of larger crystals using the methods developed as discussed in this chapter. Neutron diffraction time has also been obtained to investigate the structures in more detail (using the increased sensitivity of neutrons to oxygen positions compared to x-ray diffraction) and also examine the nature of the magnetic states in $\text{Ba}_2\text{NiTeO}_6$ and $\text{Ba}_2\text{CuTeO}_6$. The potential structural transition indicated in the specific heat of $\text{Ba}_2\text{ZnTeO}_6$ will also be investigated.
Chapter 5

BiFe$_{0.7}$Mn$_{0.3}$O$_3$ - a Multiferroic with Proper Ferroelectricity

This chapter describes work on the high temperature phases of the multiferroic BiFe$_{0.7}$Mn$_{0.3}$O$_3$. This is a Mn-substituted analogue of the pure material BiFeO$_3$ which is one of the most famous and well-studied multiferroics. The high temperature phases of BiFeO$_3$ have recently been resolved [97, 98] after many years of debate [97–112]. The highest temperature phase had been thought to have the cubic $Pm\bar{3}m$ aristotype structure but was shown to be orthorhombic in 2010 [98]. The Mn-substituted compound BiFe$_{0.7}$Mn$_{0.3}$O$_3$ had also been reported to be cubic in its highest temperature phase in 2009 by a powder x-ray diffraction study [113]. In light of the reassignment of the highest temperature phases of BiFeO$_3$ and since the high temperature phases had never been examined using neutron diffraction, a superior technique for determining oxygen ion positions and octahedral rotations, a re-examination of the high temperature phases was desirable.

The phase diagram of pure BiFeO$_3$ will be discussed first to allow comparison between the phase diagrams of the two materials. The results of the previous x-ray diffraction investigation of the BiFe$_{0.7}$Mn$_{0.3}$O$_3$ high temperature transitions will then be discussed followed by the methods and results of our high-resolution powder neutron diffraction experiments.
5.1 Introduction

BiFeO$_3$ is one of the most well-known multiferroics, partly due to the multiferroic state being stable at room temperature. Perhaps surprisingly, the crystal and magnetic structures are not yet fully understood over a wide temperature range. Given the clear importance to multiferroicity of these structures and their interplay, it is important that this be addressed. Insight from the high temperature structures may feed back into a more detailed understanding of the multiferroicity at lower temperatures. A schematic high temperature phase diagram based upon the most recent studies is shown in figure 5.1.

There are generally agreed to be three structural phases of BiFeO$_3$ at ambient pressure. The low-and ambient-temperature $\alpha$-phase is polar with space group $R3c$ (No. 167), and antiferromagnetic ordering occurring below 643 K. The non-polar $\beta$-phase, with space group $Pbnm$ (non-standard setting of $Pnma$, No. 62$^1$) only confirmed in 2009 [97], forms above 1093±5 K and, finally, the $\gamma$-phase is stable above 1198 K [97, 98, 114]. The $\gamma$-phase, however, is only stable within a small temperature window of 25 K as a peritectic$^2$ decomposition of BiFeO$_3$ to Bi$_2$Fe$_4$O$_9$ and liquid Bi$_2$O$_3$ occurs at $\approx$ 1223 K. The $\beta$-to-$\gamma$ transition has also been reported to be an insulator-to-metal transition [111, 112]. The $\gamma$-phase had been generally believed to have the cubic perovskite aristotype $Pm\bar{3}m$ structure until a high resolution powder neutron diffraction study by Arnold et al. in 2010 found

\footnotetext[1]{Space groups often have multiple ‘settings’ which are equivalent descriptions but with different choices of unit cell and/or origin. For example, the standard setting of space group $Pnma$ (No. 62) has $b$ as the largest unit cell parameter and therefore the alternative setting $Pbnm$ with the $c$-axis as the longest axis is often used as in the case of BiFeO$_3$.}

\footnotetext[2]{A peritectic reaction is one in which a liquid and a solid react to form a single solid phase with decreasing temperature.}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{phase_diagram.png}
\caption{A rough phase diagram for BiFeO$_3$. The ferroelectric $R3c$ phase is stable below $\approx$ 1093 ± 5 K with $T_N \approx$ 643 K. The transition to non-polar $Pbnm$ is first order, as is the $\beta$-to-$\gamma$ transition at $\approx$ 1198 K. The onset of peritectic decomposition to Bi$_2$Fe$_4$O$_9$ and liquid Bi$_2$O$_3$ occurs at $\approx$ 1223 K.}
\end{figure}
that the $\gamma$-phase is in fact orthorhombic and seems to have the same $Pbnm$ space group as the $\beta$-phase \[98\].

The difficulty in confirming the phase diagram of BiFeO$_3$ is largely due to metastability of BiFeO$_3$ in the range 720 K - 1090 K where the sillenite (Bi$_{25}$FeO$_{39}$) and mullite (Bi$_2$Fe$_4$O$_9$) phases are energetically favoured \[115\]. In addition, the determination of the $\gamma$-phase has been impaired by the proximity of the peritectic decomposition temperature at $\approx$ 1223 K.

It is this combination of problems that has led to a focus on the BiFe$_{0.7}$Mn$_{0.3}$O$_3$ compound in which the high temperature phases are stabilised over a larger temperature region.

### 5.2 Crystal structure

At ambient temperature, in the $\alpha$-phase, BiFeO$_3$ is a distorted perovskite-type material which adopts the polar space group $R3c$. This structure, shown in figure 5.2, has the Glazer tilt system $a^-a^-a^-$ which means that along each axis there is an antiphase tilt (i.e. alternating tilt direction in adjacent layers) and with the tilt magnitude equal in all directions (Glazer tilts are described in more detail

![Figure 5.2](image-url)

**Figure 5.2**: The ambient temperature $R3c$ structure of BiFeO$_3$ shown in the hexagonal setting. The FeO$_6$ octahedra are shown in blue and the bismuth ions in green.
in section 2.2.1). Both the Fe$^{3+}$ and Bi$^{3+}$ ions are off-centre leading to a net polarization within the unit cell.

Above approximately 1093 K there is a first order phase transition to the $\beta$-phase with the space group $Pbnm$ and the Glazer tilt system $a^-a^-b^+$ [97], this structure is shown in figure 5.3. From the Glazer tilts we can see that the tilt along the $c$-axis direction changes from antiphase to in-phase and also becomes unequal to the tilt magnitude along the $a$- and $b$-axes. This can be seen by comparing figures 5.4a and 5.4b. At this transition, the polar displacements of the Bi$^{3+}$ and Fe$^{3+}$ ions become zero as the space group $Pbnm$ is non-polar.

![Figure 5.3: The structure of BiFeO$_3$ in the $\beta$-phase with space group $Pbnm$. The FeO$_6$ octahedra are shown in blue and the bismuth ions in green.](image)

![Figure 5.4: (a) The structure of BiFeO$_3$ in the $Pbnm$ $\beta$-phase viewed down the $c$-axis and (b) the $R\bar{3}c$ $\alpha$-phase structure viewed down the equivalent direction with respect to the octahedra (none of the orthorhombic and rhombohedral unit cell axes are collinear). The FeO$_6$ octahedra are shown in blue and the bismuth ions in green.](image)
Above $\approx 720$ K, BiFeO$_3$ begins to decompose into the sillonite and mullite phases Bi$_{25}$FeO$_{39}$ and Bi$_4$Fe$_2$O$_9$ and remains metastable towards these phases up to $\approx 1090$ K. This adds difficulty both to experimental and analysis procedures but through careful experimental design and systematic analysis the $\gamma$ phase of BiFeO$_3$ has been determined to be orthorhombic, with likely $Pbnm$ symmetry [98].

Above $\approx 1223$ K [114] (although this is strongly heating rate dependent), BiFeO$_3$ decomposes peritectically to Bi$_2$Fe$_4$O$_9$ and liquid Bi$_2$O$_3$. 
5.3 The High Temperature Phase Transitions of \( \text{BiFe}_{0.7}\text{Mn}_{0.3}\text{O}_3 \)

5.3.1 Previous Work on \( \text{BiFe}_{0.7}\text{Mn}_{0.3}\text{O}_3 \)

Doped analogues of \( \text{BiFeO}_3 \) have been studied intensively in recent years [116–118]. One of the main reasons is the fact that dopants have stabilising effects on the structure and properties of \( \text{BiFeO}_3 \). \( \text{BiFe}_{0.7}\text{Mn}_{0.3}\text{O}_3 \) has been studied both at low temperature and in the high temperature regime as magnetic and dielectric properties are enhanced by the Mn substitution (the magnetization and dielectric constants are increased although \( T_C \) and \( T_N \) decrease) [116, 119, 120].

In figure 5.5 the schematic phase diagram of \( \text{BiFe}_{0.7}\text{Mn}_{0.3}\text{O}_3 \) based upon previous work is shown. The temperatures of the \( \alpha \)-to-\( \beta \) and \( \beta \)-to-\( \gamma \) transitions are suggested to decrease with Mn-substitution relative to pure \( \text{BiFeO}_3 \) (from \( T_{\alpha-\beta} \approx 1093 \text{ K} \) to \( T_{\alpha-\beta} \approx 943 \text{ K} \) for \( \text{BiFe}_{0.7}\text{Mn}_{0.3}\text{O}_3 \) and from \( T_{\beta-\gamma} \approx 1198 \text{ K} \) in \( \text{BiFeO}_3 \) to \( T_{\beta-\gamma} \approx 1160 \text{ K} \) in \( \text{BiFe}_{0.7}\text{Mn}_{0.3}\text{O}_3 \) [121]). This has the benefit of allowing a larger temperature window to investigate the high temperature phases before peritectic decomposition sets in. \( \text{BiFe}_{0.7}\text{Mn}_{0.3}\text{O}_3 \) has been reported to be metastable to formation of \( \text{Bi}_2\text{Fe}_4-x\text{Mn}_x\text{O}_9 \) and \( \text{Bi}_{25}\text{Fe}_{1-x}\text{Mn}_9\text{O}_{39} \) in the range \( \approx 873\text{-}1023 \text{ K} \) [115]. The schematic phase diagram shown in figure 5.5 is based upon the results of the x-ray diffraction, differential thermal analysis (DTA), dilatometry and conductivity measurements of Selbach \textit{et al.} [113, 121] which

![Figure 5.5: A rough phase diagram for \( \text{BiFe}_{0.7}\text{Mn}_{0.3}\text{O}_3 \) based upon transitions reported by Selbach \textit{et al.} [113, 121]. The ferroelectric R3c phase is stable below \( \approx 943 \text{ K} \) with \( T_N \approx 533 \text{ K} \). The transition to non-polar Pbnm is first order, as is the \( \beta \)-to-\( \gamma \) transition at \( \approx 1160 \text{ K} \). The onset of peritectic decomposition to \( \text{Bi}_2\text{Fe}_4\text{O}_9 \) and liquid \( \text{Bi}_2\text{O}_3 \) occurs at \( \approx 1193 \text{ K} \). The question marks indicate the phases whose structures had not been confirmed by neutron diffraction prior to our study.](image-url)
are the only investigations published to date on the high temperature phases of BiFe$_{0.7}$Mn$_{0.3}$O$_3$. They also reported the $\alpha$-to-$\beta$ transition to be an insulator-to-semiconductor transition and therefore the $\beta$- and $\gamma$-phases to be semiconducting.

In light of the recent developments regarding the pure compound, the identification of the high temperature phases has attracted renewed attention. To address this question we decided to carry out the high-resolution powder neutron diffraction study reported in the following sections.

### 5.3.2 Synthesis

The polycrystalline samples used for this investigation were synthesised by the rapid liquid phase sintering method [122]. This method uses the fact that there is a liquid phase at the sintering temperature (in our case Bi$_2$O$_3$ with melting point 820 $^\circ$C) to give a quick reaction resulting in high-density samples. Phase pure samples can be synthesised under the correct conditions. This is useful in the case of BiFeO$_3$ and BiFe$_{0.7}$Mn$_{0.3}$O$_3$ as standard solid state synthesis results in multiphase samples due to the metastability of the materials in the synthesis temperature range. The other method of obtaining pure samples involves controlled leaching of standard solid-state synthesised samples using nitric acid as the impurity phases are more soluble than BiFeO$_3$ [97, 123]. The reactants were thoroughly ground together with high-purity acetone to ensure thorough mixing and small particle size in the appropriate ratios for the reaction:

$$\text{Bi}_2\text{O}_3 + 0.7\text{Fe}_2\text{O}_3 + 0.3\text{Mn}_2\text{O}_3 \rightarrow 2\text{BiFe}_{0.7}\text{Mn}_{0.3}\text{O}_3$$ \hspace{1cm} (5.1)

The resulting powder was then compressed into small pellets and sintered at 1173 K for 10 minutes in a pre-heated furnace and then quenched to room temperature. Investigations of various temperatures, pellet sizes, heating and cooling profiles were made to identify the optimal process for minimising impurity phases which were detected using x-ray diffraction. This synthesis route was previously described by Wang et al. for BiFeO$_3$ [122] and Selbach et al. for BiFe$_{0.7}$Mn$_{0.3}$O$_3$ [113, 121]. Here we investigated the various parameters for our particular furnace setup as due to the short synthesis time, metastability to impurity phases, volatility of Bi$_2$O$_3$ at the synthesis temperature and the difference in the temperature distributions between furnaces the phase purity will be strongly dependent on small changes in
the synthesis process. The sample synthesised using the process described above was phase-pure by laboratory x-ray diffraction and the phase purity was confirmed in the later high-resolution powder neutron diffraction experiments.

5.3.3 Powder Neutron Diffraction Experiments on HRPD at ISIS

For the powder neutron diffraction experiments approximately 10 g of polycrystalline \( \text{BiFe}_{0.7}\text{Mn}_{0.3}\text{O}_3 \) was sealed in a quartz ampoule under vacuum. This was mounted in a cylindrical vanadium can for the experiment. A standard RAL (Rutherford Appleton Laboratory) furnace was used and the thermocouple for sample thermometry was attached to the vanadium can directly above the incident beam area. Approximately 15 minutes was allowed for temperature equilibration upon each setpoint change. The uncertainty in the measured temperatures is estimated to be less than 1 K.

Experimental details on neutron scattering in general, the instrument HRPD at ISIS in particular and the Rietveld refinement analysis technique are discussed in section 3.1.1. The data collection for the \( \alpha \)-phase was for 6 \( \mu \text{Ah} \) of incident proton beam at 293 K, 50 \( \mu \text{Ah} \) at 423 K and 35 \( \mu \text{Ah} \) at 473 K and 523 K. In the \( \beta \)-phase, data collection was for 15 \( \mu \text{Ah} \) except for at 913 K, 963 K, 1013 K, 1113 K and 1153 K where a total of 50 \( \mu \text{Ah} \) incident proton beam was collected. In the \( \gamma \)-phase 30 \( \mu \text{Ah} \) was collected at each temperature up to 1173 K and 8 \( \mu \text{Ah} \) at each temperature above except for 1173 K where 50 \( \mu \text{Ah} \) was collected and 1191 K where 10 \( \mu \text{Ah} \) was collected.

5.3.4 Results

In the following three sections (5.3.4.1, 5.3.4.2 and 5.3.4.3) the \( \alpha \)-phase structure and the \( \alpha \)-to-\( \beta \) and \( \beta \)-to-\( \gamma \) transitions observed in the experimental powder neutron diffraction data will be examined. I will also discuss the models developed for the \( \beta \)- and \( \gamma \)-phases during this investigation. In section 5.3.4.4 I will discuss the overall trends in lattice parameters and octahedral rotations and compare the present results with those of previous studies.
5.3.4.1 The $\alpha$-phase

The $\alpha$-phase of BiFe$_{0.7}$Mn$_{0.3}$O$_3$ has been reported to be isostructural to pure BiFeO$_3$ by Selbach et al. [113, 121] and Sosonowska et al. [124, 125]. Rietveld refinements, using GSAS, of an $R3c$ model for our data collected in the $\alpha$-phase at 273 K, 423 K, 473 K and 523 K showed good agreement in peak positions with no peaks unindexed (except for a few small, rather broad, peaks at approximately 1.24Å, 1.51Å and 2.15Å corresponding to the $(2,1,1)$, $(2,0,0)$ and $(1,1,0)$ reflections of vanadium from the vanadium can used to contain the sample). However, significant anisotropic broadening of some reflections manifesting itself as widely varying peak widths led to unsatisfactory fitting of peak intensities. It can be seen that in the undoped material the relative peak intensities are very different (see figure 5.6) and there is no evidence of substantial anisotropic broadening (see figure 5.7). The data shown for a pure BiFeO$_3$ sample prepared by Dr D.C. Arnold and measured as part of this thesis were taken on GEM (high-flux, medium resolution) and therefore have broader peaks than data from HRPD due to instrumental

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.6.png}
\caption{A comparison of the $\alpha$-phase data of BiFeO$_3$ at 398 K (upper, blue) taken on GEM at ISIS and BiFe$_{0.7}$Mn$_{0.3}$O$_3$ at 423 K (lower, green) taken on HRPD at ISIS. The intensities of peaks such as the $(2,0,4)$ peak at $\approx$1.98 Å and the $(2,0,2)$ peak at $\approx$2.28 Å, boxed in red, are clearly changed upon Mn substitution. The substantial anisotropic broadening seen in the BiFe$_{0.7}$Mn$_{0.3}$O$_3$ data is not present in pure BiFeO$_3$.}
\end{figure}
Figure 5.7: A comparison of the full-width half-maximums of the (2,0,-4) and (2,0,2) peaks of the α-phase of BiFeO₃ at 398 K (upper, blue) taken on GEM at ISIS and BiFe₀.₇Mn₀.₃O₃ at 423 K (lower, green) taken on HRPD at ISIS. The FWHM is effectively hkl-independent for BiFeO₃ but in BiFe₀.₇Mn₀.₃O₃ substantial anisotropy can be seen.

The Rietveld refinement of our BiFe₀.₇Mn₀.₃O₃ data for 523 K, shown in figure 5.8, with arrows indicating the vanadium peaks, gave $R_{wp}=0.0416$ and $\chi^2=3.931$ for 37 variables (including 22 parameters used to fit the background). Inclusion in the model of anisotropic broadening around the (2,0,-14) axis led to a greatly improved fit as can be seen in figure 5.9.

The results of the refinement including anisotropic broadening are tabulated in table 5.1. The anisotropic broadening was seen in all α-phase data and seems to be an intrinsic feature of Mn-substituted BiFeO₃ as it has also been reported by Sosnowska et al. [125]. Further details of the variation of the full-width half-maxima, the refined anisotropic broadening parameters and a brief investigation of the possibility of the α-phase being monoclinic are given in appendix B.

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3The GEM data were taken to investigate the possibilities of low-temperature transitions in BiFeO₃ which have been the subject of considerable debate. Unfortunately, whilst small anomalies were observed in the lattice parameters, the resolution was not high enough to see any change in the magnetic structure. As further work is needed to draw any firm conclusions, this work was not included in the main part of this thesis; a brief summary is given in appendix C.
Chapter 5. 

**BiFe_{0.7}Mn_{0.3}O_3 - a Multiferroic with Proper Ferroelectricity**

![Figure 5.8](image)

**Figure 5.8:** The Rietveld refinement results of the $R3c$ model for the $\alpha$-phase of BiFe$_{0.7}$Mn$_{0.3}$O$_3$ at 523 K with no refinement of anisotropic broadening parameters. The observed data are shown in red, the Rietveld fit in green and the difference profile in blue. The additional peaks from the vanadium sample are indicated with arrows and $(h,k,l)$ indices.

**Space Group:** $R3c$, No. 161  

$R_{wp}=0.0307$, $\chi^2=2.143$, 41 var.  

$a = 5.58833(16)\text{Å}$, $c = 13.8588(5)\text{Å}$

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff Site</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>$U_{iso} \times 100(\text{Å}^2)$</th>
<th>Occ.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi</td>
<td>6a</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1.94(7)</td>
<td>1</td>
</tr>
<tr>
<td>Fe</td>
<td>6a</td>
<td>0</td>
<td>0</td>
<td>0.22620(17)</td>
<td>1.63(10)</td>
<td>0.7</td>
</tr>
<tr>
<td>Mn</td>
<td>6a</td>
<td>0</td>
<td>0</td>
<td>0.22620(17)</td>
<td>1.63(10)</td>
<td>0.3</td>
</tr>
<tr>
<td>O1</td>
<td>18b</td>
<td>0.4504(4)</td>
<td>0.0180(4)</td>
<td>0.95600(19)</td>
<td>2.27(7)</td>
<td>1</td>
</tr>
</tbody>
</table>

**Table 5.1:** The Rietveld refinement results of the $R3c$ model (including anisotropic broadening) for the $\alpha$-phase of BiFe$_{0.7}$Mn$_{0.3}$O$_3$ at 523K.
Figure 5.9: The Rietveld refinement results of the $R3c$ model including anisotropic broadening for the $\alpha$-phase of $\text{BiFe}_{0.7}\text{Mn}_{0.3}\text{O}_3$ at 523 K.
5.3.4.2 The $\alpha$-to-$\beta$ Transition

The transition from the rhombohedral $R3c$ $\alpha$-phase to the orthorhombic $\beta$-phase can be seen clearly in the diffraction patterns. As shown in figure 5.10, the (2,0,-4) peak of the rhombohedral phase has disappeared by 963 K and the development of the orthorhombic phase, identified by the appearance of the (2,0,2) and (0,4,0) peaks, is clear at and above 913 K. The peak shift of the (2,0,-4) peak between 523 K and 913 K is due to thermal expansion as will be seen in the later analysis of lattice parameters as a function of temperature in section 5.3.4.4.

Pure BiFeO$_3$ shows a transition from $R3c$ to a $Pnma$ $\beta$-phase [97] and a previous report by Selbach et al. has identified the same transition in BiFe$_{0.7}$Mn$_{0.3}$O$_3$ [113]. Their assignment of the space group $Pnma$ for the $\beta$-phase is confirmed by analysis of the peaks based upon the cubic aristotype (as discussed below) in combination with analysis of the volume change with temperature.

![Figure 5.10: The $\alpha$-to-$\beta$ transition of BiFe$_{0.7}$Mn$_{0.3}$O$_3$. There is coexistence of the $R3c$ phase and the orthorhombic $\beta$ phase between 913 K and 953 K and the transition is completed by 963 K as shown by the disappearance of the (2,0,-4) peak of the $R3c$ structure.](image-url)
with Rietveld refinements of the possible space groups identified by the aristotype-based analysis.

Here we decided to carry out a full analysis of our high-resolution data to ensure that the structure of the \( \beta \)-phase was identified as unambiguously as possible from our data.

The diffraction pattern peaks of perovskite structures can be indexed using the peaks of the fundamental cubic aristotype structure and with ‘fractional’ reflections of this structure arising from distortions around different high symmetry points in the Brillouin zone [126, 127]. The first Brillouin zone of the \( Pm\bar{3}m \) structure and its relevant high-symmetry points (\( R = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2}) \), \( M = (\frac{1}{2}, \frac{1}{2}, 0) \) and \( X = (0, \frac{1}{2}, 0) \)) are shown in blue in figure 5.11. The first Brillouin zone of the \( Pnma \) structure is also shown in green to illustrate the folding which takes place with distortions around the \( M \) and \( R \) high-symmetry points of the \( Pm\bar{3}m \) zone.

The \( \Gamma \)-point reflections are related to polar displacements corresponding to distortion mode \( \Gamma_4^- \) (i.e. a distortion mode with symmetry corresponding to the \( \Gamma_4^- \) irreducible representation where the superscript indicates parity with respect to inversion symmetry and the subscript labels irreducible representations for the \( k \)-vector under consideration; more details are given in chapter 2) in the current case and generate no additional superlattice peaks but change the relative intensities of the fundamental peaks. The \( R \)-point superlattice reflections, with index

\[ \text{Figure 5.11: The first Brillouin zone of the aristotype cubic perovskite structure (blue) and the orthorhombic } Pnma \text{ structure (green). The } \Gamma, \text{ } R \text{ and } M \text{-high symmetry points of the cubic Brillouin zone are labelled.} \]
(h, k, l)\textsubscript{parent} ± \langle \frac{1}{2}, \frac{1}{2}, \frac{1}{2} \rangle \textsuperscript{4}, are due to \( R_4^+ \) mode out-of-phase octahedral tilts and the \( M \)-point reflections, with index (h, k, l)\textsubscript{parent} ± \langle \frac{1}{2}, \frac{1}{2}, 0 \rangle, correspond to \( M_3^+ \) mode in-phase tilts. The reflections due to distortions around the \( X \)-point from the \( X_5^+ \) mode are a consequence of the presence of both \( R_4^+ \) and \( M_3^+ \) distortions (if the \( M \)- and \( R \)-points are reciprocal lattice vectors of a phase then the vector joining the points is also a reciprocal lattice vector).

In figure 5.12 I show the diffraction pattern for \( T = 963 \) K in the \( \beta \)-phase. The peaks are labelled to indicate the index based upon the aristotype cubic parent structure with A indicating an aristotype-derived peak. M indicates \( M_3^+ \) mode-derived peaks, R indicates \( R_4^+ \) mode-derived peaks and X represents peaks due to \( X_5^+ \) mode distortions. The \( \beta \)-phase clearly shows \( R_4^+ \) and \( M_3^+ \) mode derived superlattice reflections. Stokes et al. [16, 128] have deduced the possible space groups for perovskites with different combinations of distortion modes (the distortion modes considered were those that involve ‘rigid’ octahedral tilts (\( M_3^+ \) and

\footnote{where \( \langle h, k, l \rangle \) indicates all symmetry equivalent \( h, k, l \) sets.}

![Figure 5.12](image)

**Figure 5.12:** The results of indexing the 963 K diffraction pattern in terms of cubic aristotype-derived reflections (labelled A) and peaks with fractional pseudo-cubic indices arising from \( M_3^+ \), \( R_4^+ \) and \( X_5^+ \) mode distortions (labelled M, R and X respectively).
$R^+_4$) and/or cation displacements ($\Gamma^-_4$). Based upon their investigation, the activity of $M^+_3$ and $R^+_4$ distortion modes give the 4 space groups shown in table 5.2. Peak intensity changes due to $\Gamma^-_4$ mode distortions are not easy to determine as there are many other possible causes of peak intensity changes (such as atomic displacement parameters, site occupancy, absorption and extinction effects). Consequently, space groups with $R^+_4$, $M^+_3$ and $\Gamma^-_4$ distortions as listed in table 5.3 were also investigated to allow comparison of fit quality between centrosymmetric and non-centrosymmetric models. There are 12 possible space groups for concurrent $R^+_4$, $M^+_3$ and $\Gamma^-_4$ distortions, which are tabulated in table 5.3 [128].

Of the four space groups characterised by both $R^+_4$ and $M^+_3$ distortions from the aristotype, only $Pnma$ and $P 2_1/m$ were possible candidates for the $\beta$-phase as the peak splittings clearly violated tetragonal symmetry and peaks violating the $C$-centring systematic absences were present. Finally, since there was no evidence of peak splitting suggesting monoclinic or triclinic symmetry and the peaks observed were consistent with the systematic absences of the $n$- and $a$-glide planes, $P 2_1/m$ could also be ruled out, leaving $Pnma$ as the only centrosymmetric space group.

<table>
<thead>
<tr>
<th>Space Group</th>
<th>$M^+_3$</th>
<th>$R^+_4$</th>
<th>Transform/Origin shift</th>
<th>Reason Excluded</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Cmcm$</td>
<td>(0, a, 0)</td>
<td>(0, 0, b)</td>
<td>(2,0,0)(0,0,2)(0,2,0)/(\frac{1}{2},0,\frac{1}{2})</td>
<td>C-centring violated</td>
</tr>
<tr>
<td>$Pnma$</td>
<td>(a, 0, 0)</td>
<td>(0, b, b)</td>
<td>(0,1,1)(2,0,0)(0,1,\bar{1})/(0,0,0)</td>
<td>No peak splitting</td>
</tr>
<tr>
<td>$P 2_1/m$</td>
<td>(a, 0, 0)</td>
<td>(0, b, c)</td>
<td>(0,\bar{1},1)(2,0,0)(0,1,1)/(0,0,0)</td>
<td>Tetragonal symmetry violated</td>
</tr>
<tr>
<td>$P 4_2/nmc$</td>
<td>(a, a, 0)</td>
<td>(0, 0, b)</td>
<td>(2,0,0)(0,2,0)(0,0,2)/(0,0,-1)</td>
<td></td>
</tr>
</tbody>
</table>

Table 5.2: The 4 possible space groups deduced by Stokes et al. [128] for $M^+_3$ and $R^+_4$ distortion modes. The columns labelled by the distortion mode labels $M^+_3$ and $R^+_4$ give the order parameters which are of the form $(a,b,c)$. For $M^+_3$ and $R^+_4$ the components $a$, $b$ and $c$ represent the magnitudes of the tilts around the $x$, $y$ and $z$-axes respectively. The last column lists the experimental reason for exclusion.
<table>
<thead>
<tr>
<th>Space Group</th>
<th>$\Gamma^-_4$</th>
<th>$M^+_3$</th>
<th>$R^+_4$</th>
<th>Transform/Origin shift</th>
<th>Reason Excluded</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Ama2</em></td>
<td>(0, 0, $a$)</td>
<td>(0, $b$, 0)</td>
<td>(0, 0, 0)</td>
<td>(0, 2, 0)(2, 0, 0)(0, 0, 2)/(1/2, 0, 0)</td>
<td>A-centring violated</td>
</tr>
<tr>
<td><em>Amm2</em></td>
<td>(0, 0, $a$)</td>
<td>(0, $b$, 0)</td>
<td>(0, 0, $c$)</td>
<td>(0, 2, 0)(2, 0, 0)(0, 0, 2)/(1/2, 1/2, 0)</td>
<td>A-centring violated</td>
</tr>
<tr>
<td><em>Cmc2</em></td>
<td>(0, 0, 0)</td>
<td>(0, $c$, 0)</td>
<td>(0, 0, 0)</td>
<td>(0, 2, 0)(0, 0, 2)(0, 0, 0)/(0, 0, 0)</td>
<td>C-centring violated</td>
</tr>
<tr>
<td><em>Cc</em></td>
<td>($a$, $b$, 0)</td>
<td>(0, $c$, 0)</td>
<td>(0, 0, $d$)</td>
<td>(2, 0, 0)(0, 0, 2)(0, 2, 0)/(0, 0, 1/2)</td>
<td>C-centring violated</td>
</tr>
<tr>
<td><em>P4_2mc</em></td>
<td>(0, 0, $a$)</td>
<td>($b$, $b$, 0)</td>
<td>(0, 0, $c$)</td>
<td>(0, 2, 0)(0, 0, 2)(0, 0, 0)/(1/2, 0, 0)</td>
<td>Tetragonal symmetry violated</td>
</tr>
<tr>
<td><em>Aba2</em></td>
<td>($a$, $a$, 0)</td>
<td>($b$, $b$, 0)</td>
<td>(0, 0, 0)</td>
<td>(0, 2, 0)(2, 2, 0)(2, 2, 0)/(1, 0, 1/2)</td>
<td>A-centring violated</td>
</tr>
<tr>
<td><em>Pna2</em></td>
<td>(0, 0, $a$)</td>
<td>(0, 0, $b$)</td>
<td>(0, $c$, 0)</td>
<td>(1, 1, 0)(0, 0, 0)/(0, 0, 0)</td>
<td></td>
</tr>
<tr>
<td><em>Pmc2</em></td>
<td>($a$, $a$, 0)</td>
<td>(0, 0, $b$)</td>
<td>(0, 0, $c$)</td>
<td>(0, 0, 2)(1, 1, 0)(1, 1, 0)/(1, 1, 0)</td>
<td></td>
</tr>
<tr>
<td><em>Pmn2</em></td>
<td>($\bar{a}$, $a$, $b$)</td>
<td>(0, $b$, 0)</td>
<td>(0, 0, 0)</td>
<td>(0, 0, 2)(1, 1, 0)(0, 0, 1)/(1, 0, 0)</td>
<td></td>
</tr>
<tr>
<td><em>Pc</em></td>
<td>($\bar{a}$, $a$, $b$)</td>
<td>(0, 0, 0)</td>
<td>(0, 0, 0)</td>
<td>(1, 1, 0)(1, 1, 0)(0, 0, 0)/(0, 0, 0)</td>
<td>No peak splitting</td>
</tr>
<tr>
<td><em>P2</em></td>
<td>(0, 0, $a$)</td>
<td>(0, 0, $b$)</td>
<td>(0, 0, 0)</td>
<td>(1, 1, 0)(0, 0, 2)(1, 1, 0)/(0, 0, 0)</td>
<td>No peak splitting</td>
</tr>
<tr>
<td><em>Pm</em></td>
<td>($a$, $b$, 0)</td>
<td>(0, 0, 0)</td>
<td>($d$, $e$, 0)</td>
<td>(1, 1, 0)(0, 0, 2)(1, 1, 0)/(0, 0, 0)</td>
<td>No peak splitting</td>
</tr>
</tbody>
</table>

Table 5.3: The 12 possible space groups deduced by Stokes et al. [128] for simultaneous $\Gamma^-_4$, $M^+_3$ and $R^+_4$ distortions. The columns labelled by the distortion mode labels $\Gamma^-_4$, $M^+_3$ and $R^+_4$ give the order parameters which are of the form $(a, b, c)$ for $M^+_3$ and $R^+_4$ the components $a, b$ and $c$ represent the magnitudes of the tilts around the $x, y$ and $z$-axes respectively and for $\Gamma^-_4$ they represent B-cation displacements along the parent structure $x, y$ and $z$-axes.
candidate. Using the same logic, of the 12 possible non-centrosymmetric space groups given by the aristotype-based analysis (see table 5.3), only \( Pna2_1 \), \( Pmc2_1 \) and \( Pmn2_1 \) would be consistent with our data.

Therefore, Rietveld refinements of the centrosymmetric \( Pnma \) model and the three non-centrosymmetric models were undertaken to confirm the best model for the \( \beta \)-phase. The refinements used data taken at 963 K from both the 90° and 168° detector banks (to examine as large a \( d \)-spacing range as possible, details of HRPD are given in chapter 3) with the same \( d \)-spacing range and number of background and profile parameters. The substantial contribution to the background from the quartz ampoule required the use of 22 background parameters for each bank. The three non-centrosymmetric phases all gave good refinement results, with \( Pmc2_1 \) providing the best fit with a weighted residual \( R_{wp} = 0.0253 \) and ‘goodness of fit’ \( \chi^2 = 3.117 \) for 87 variables. A comparison of the refinements of the non-centrosymmetric models can be seen in figure 5.13 and the \( R_{wp} \) and \( \chi^2 \) values along with those for \( Pnma \) in table 5.4. The results of the refinements of the centrosymmetric \( Pnma \) and non-centrosymmetric \( Pmc2_1 \) models are compared graphically in figures 5.14 and 5.15 for bank 1 and bank 2 data respectively.

The non-centrosymmetric \( Pmc2_1 \) model gives slightly better \( R_{wp} \) and \( \chi^2 \) values than centrosymmetric \( Pnma \) as can be seen from table 5.4. However, when inspected visually, the improvement is so small as to be almost indistinguishable. The comparison was extended over the whole temperature range of the \( \beta \)-phase with the same result.

Strictly speaking, it is not possible even from these high quality data to conclusively decide between the final candidate space groups. However, in the absence of data indicating the need for a non-centrosymmetric model and lack of a clear improvement from the loss of the inversion centre in \( Pmc2_1 \), \( Pnma \) seems to provide the best model to fit our data for the \( \beta \)-phase of \( \text{BiFe}_{0.7}\text{Mn}_{0.3}\text{O}_3 \), making it isostructural to the \( \beta \)-phase of \( \text{BiFeO}_3 \). The structural parameters obtained from the 963 K \( Pnma \) refinement are given in table 5.5.

\[ \text{In addition, refinement of the } Pnma \text{ model with anisotropic thermal displacement parameters for the bismuth and oxygen sites gave } R_{wp}(\text{bank 1})=0.0225 \text{ and } R_{wp}(\text{bank 2})=0.0182 \text{ and } \chi^2=2.438 \text{ for 80 variables. It also gave an improved fit by eye which is almost indistinguishable from that of the } Pmc2_1 \text{ model. Again, however, higher data quality would be needed for a reliable conclusion to be made.} \]
Figure 5.13: The results of the Rietveld refinements of the 963K data with the $Pmc_{21}$, $Pmn_{21}$ and $Pna_{21}$ models.
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### Table 5.4: The Rietveld refinement results for Pnma and Pmc2$_1$ at 963K.

<table>
<thead>
<tr>
<th>Space Group</th>
<th>Bank 1 $R_{wp}$</th>
<th>Bank 2 $R_{wp}$</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Pmc2_1$</td>
<td>0.0253</td>
<td>0.0206</td>
<td>3.117 (81 var.)</td>
</tr>
<tr>
<td>$Pmn2_1$</td>
<td>0.0253</td>
<td>0.0211</td>
<td>3.200 (81 var.)</td>
</tr>
<tr>
<td>$Pna2_1$</td>
<td>0.0283</td>
<td>0.0221</td>
<td>3.730 (76 var.)</td>
</tr>
<tr>
<td>$Pnma$</td>
<td>0.0276</td>
<td>0.0264</td>
<td>4.447 (69 var.)</td>
</tr>
</tbody>
</table>

### Table 5.5: The Rietveld refinement results of the Pnma model at 963K.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff Site</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>$U_{iso} \times 100(\text{Å}^2)$</th>
<th>Occ.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi</td>
<td>4c</td>
<td>0.9773(4)</td>
<td>0.25</td>
<td>0.5033(4)</td>
<td>8.34(9)</td>
<td>1</td>
</tr>
<tr>
<td>Fe</td>
<td>4a</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>4.16(9)</td>
<td>0.7</td>
</tr>
<tr>
<td>Mn</td>
<td>4a</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>4.16(9)</td>
<td>0.3</td>
</tr>
<tr>
<td>O1</td>
<td>4c</td>
<td>0.0165(5)</td>
<td>0.25</td>
<td>0.0660(4)</td>
<td>6.06(11)</td>
<td>1</td>
</tr>
<tr>
<td>O2</td>
<td>8d</td>
<td>0.2902(3)</td>
<td>0.9634(2)</td>
<td>0.2088(3)</td>
<td>7.68(11)</td>
<td>1</td>
</tr>
</tbody>
</table>

Space Group: Pnma, No. 62

$R_{wp}(\text{bank 1})=0.0276$, $R_{wp}(\text{bank 2})=0.0264$, $\chi^2=4.447$, 69 var.

$a=5.62738(14)$ Å, $b=7.94594(18)$ Å and $c=5.58786(14)$ Å
Figure 5.14: The results of the Rietveld refinements of bank 1 of the 963 K data with the $Pmc_2_1$ (upper) and $Pnma$ (lower) models.
Figure 5.15: The results of the Rietveld refinements of bank 2 of the 963K data with the $Pmna$ and $Pmc2_1$ models. The $Pmc2_1$ model gives $R_{wp}=0.0206$, $\chi^2=3.117$ for 87 variables (two-bank refinement). The $Pmna$ model gives $R_{wp}=0.0264$, $\chi^2=4.447$ for 69 variables (two-bank refinement).
5.3.4.3 The $\beta$–to-$\gamma$ transition

In the previous section we established based upon our data that the $\beta$-phase in BiFe$_{0.7}$Mn$_{0.3}$O$_3$ is isostructural to that of the pure compound BiFeO$_3$, consistent with previous reports. One might expect, therefore, the corresponding $\gamma$-phases to also be isostructural. Recently, however, it was discovered that the $\gamma$-phase in the pure compound is $Pbnm$ [98]. Contrary to this the current best understanding prior to our study was that the $\gamma$-phase of BiFe$_{0.7}$Mn$_{0.3}$O$_3$ is the cubic $Pm\bar{3}m$ aristotype based upon x-ray diffraction. In this section we will establish that this identification was incorrect. We will show that the space group for the $\gamma$-phase most consistent with our data is $R\bar{3}c$. Surprisingly we can confidently rule out that the $\gamma$-phase of BiFe$_{0.7}$Mn$_{0.3}$O$_3$ is $Pbnm$ and therefore it is not isostructural to the $\gamma$-phase of BiFeO$_3$ which is truly unexpected.

In this experiment, the transition to the $\gamma$-phase of BiFe$_{0.7}$Mn$_{0.3}$O$_3$ can be seen in the disappearance of the $M_3^+$ and $X_5^+$ mode superlattice reflections, also corresponding in this case to the disappearance of peaks systematically absent for body-centred cells$^6$, as shown in figure 5.16. This is in stark contrast to the pure

$^6$The reflection condition for body-centred cells is $h + k + l = 2n$. 

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure5.16.png}
\caption{The transition from $Pnma$ $\beta$-phase to the $\gamma$-phase shown by the disappearance of the peaks included in the systematic absences for body centred cells (labelled in figure).}
\end{figure}
compound and indicates that the γ-phase in BiFe₀.₇Mn₀.₃O₃ is different to that of BiFeO₃.

It is also immediately clear that this phase cannot be cubic as reported by Selbach et al. [113] due to the presence of the $R_{4}^{+}$ mode distortion superlattice peaks. It should be noted, however, that the conclusions of Selbach et al. were entirely reasonable from the x-ray data shown in their paper - it is the extra sensitivity to the oxygen positions provided by neutron diffraction that allows the $R_{4}^{+}$ mode distortion peaks to be seen in this case. This underlines the importance of neutron diffraction for reliable structure determination in such oxides where small changes to the metal-oxygen environment can have important consequences for the structure and physical properties.

Another prominent feature is that, as can be seen in figure 5.17, the intensity of the fundamental reflections are now significantly different from those expected for the aristotype (in contrast to the β-phase), indicating that either anisotropic atomic displacement parameters are playing a strong role or that $\Gamma_{-4}$ mode distortions may be involved. These are the most significant changes seen in the

![Figure 5.17](image)

**Figure 5.17:** The predicted pattern for the aristotype $Pm\bar{3}m$ structure (lower, green) and the PND diffraction data (upper, blue) for 1153 K. The arrows mark some of the $R_{4}^{+}$ mode superlattice reflections. The intensities of the fundamental reflections are also substantially different from the cubic model, the clearest differences are indicated by the dashed red boxes, indicating the possibility of $\Gamma_{-4}$ mode distortions or significantly anisotropic thermal displacement parameters as well.
diffraction data across the transition, which is complete by 1138 K in this dataset.

Inspection of the data up to 1191 K shows that there is no further transition and as can be seen in figure 5.18, the $R_4^+$ mode distortion peaks are still visible in the highest temperature data. As there were indications of melting seen in the background of the highest temperature data it would seem that the cubic aristotype phase is not reached in the stability range of BiFe$_{0.7}$Mn$_{0.3}$O$_3$.

We now turn to the question of identifying the space group of the $\gamma$-phase. Based upon the work of Stokes et al. [128], the activity of only $R_4^+$ mode distortions allow the 6 space groups shown in table 5.6 and the activity of both $R_4^+$ and $\Gamma_4^-$ mode distortions give 14 further possibilities for the space group shown in table 5.7.

![Figure 5.18:](image)

**Figure 5.18:** The highest temperature data collected still show the presence of $R$-point distortion peaks as can be seen at $\approx 2.4\,\text{Å}$ in the $d$-spacing range shown. The label refers to the index based upon the aristotype cubic parent structure.
<table>
<thead>
<tr>
<th>Space Group</th>
<th>$R^+_4$</th>
<th>Transform/Origin shift</th>
<th>Reason</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I4/mcm$</td>
<td>$(0,0,a)$</td>
<td>$(1,1,0)(\bar{1},1,0)(0,0,2)/(0,0,0)$</td>
<td>Unphysical oxygen $U_{iso}/U_{11,22}$</td>
</tr>
<tr>
<td>$Imma$</td>
<td>$(0,a,a)$</td>
<td>$(0,1,1)(2,0,0)(0,1,\bar{1})/(0,0,0)$</td>
<td></td>
</tr>
<tr>
<td>$R\bar{3}c$</td>
<td>$(a,a,a)$</td>
<td>$(\bar{1},1,0)(0,\bar{1},1)(2,2,2)/(0,0,0)$</td>
<td></td>
</tr>
<tr>
<td>$C2/m$</td>
<td>$(0,a,b)$</td>
<td>$(0,2,2)(2,0,0)(0,1,1)/(\frac{1}{2},\frac{1}{2},0)$</td>
<td>No peak splitting</td>
</tr>
<tr>
<td>$C2/c$</td>
<td>$(a,b,b)$</td>
<td>$(2,\bar{1},\bar{1})(0,1,\bar{1})(0,1,1)/(\frac{1}{2},\frac{1}{2},0)$</td>
<td>No peak splitting</td>
</tr>
<tr>
<td>$P\bar{1}$</td>
<td>$(a,b,c)$</td>
<td>$(0,1,1)(1,0,1)(1,1,0)/(0,0,0)$</td>
<td>No peak splitting</td>
</tr>
</tbody>
</table>

Table 5.6: The 6 possible space groups deduced by Stokes et al. [128] for $R^+_4$ mode distortions only. The column labelled by the distortion mode label $R^+_4$ gives the order parameter which is of the form $(a,b,c)$. For $R^+_4$ the components $a, b$ and $c$ represent the magnitudes of the tilts around the $x$, $y$ and $z$-axes respectively.
<table>
<thead>
<tr>
<th>Space Group</th>
<th>$\Gamma_4^-$</th>
<th>$R_4^+$</th>
<th>Transform/Origin shift</th>
<th>Reason/Excluded</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R3c$</td>
<td>$(a, a, a)$</td>
<td>$(b, b, b)$</td>
<td>$(0, 1, 0)(0, 1, 1)(1, 2, 2)/(0, 0, 0)$</td>
<td>No sign. polar dist. or improved fit</td>
</tr>
<tr>
<td>$Fmm2$</td>
<td>$(0, 0, a)$</td>
<td>$(b, 0, 0)$</td>
<td>$(0, 2, 0)(0, 0, 2)/(0, 1, 0)$</td>
<td>DNC</td>
</tr>
<tr>
<td>$I4cm$</td>
<td>$(0, 0, a)$</td>
<td>$(0, 0, b)$</td>
<td>$(0, 1, 0)(1, 1, 0)/(0, 0, 0)$</td>
<td>DNC</td>
</tr>
<tr>
<td>$Ima2$</td>
<td>$(a, a, 0)$</td>
<td>$(0, 0, b)$</td>
<td>$(0, 0, 2)(1, 1, 0)/(0, 0, 1/2)$</td>
<td>DNC</td>
</tr>
<tr>
<td>$Ima2$</td>
<td>$(0, 0, 0)$</td>
<td>$(b, b, 0)$</td>
<td>$(0, 0, 2)(1, 1, 0)/(0, 0, 1/2)$</td>
<td>DNC</td>
</tr>
<tr>
<td>$Ima2$</td>
<td>$(a, a, 0)$</td>
<td>$(b, b, 0)$</td>
<td>$(0, 0, 2)(1, 1, 0)/(0, 0, 1/2)$</td>
<td>DNC</td>
</tr>
<tr>
<td>$Imm2$</td>
<td>$(a, â, 0)$</td>
<td>$(b, b, 0)$</td>
<td>$(0, 0, 2)(1, 1, 0)/(0, 0, 1/2)$</td>
<td>DNC</td>
</tr>
<tr>
<td>$C2$</td>
<td>$(a, a, 0)$</td>
<td>$(b, b, c)$</td>
<td>$(1, 1, 0)(1, 1, 0)/(0, 0, 0)$</td>
<td>No peak splitting</td>
</tr>
<tr>
<td>$C2$</td>
<td>$(0, 0, a)$</td>
<td>$(b, c, 0)$</td>
<td>$(0, 0, 2)(1, 1, 0)/(1, 0, 0)$</td>
<td>No peak splitting</td>
</tr>
<tr>
<td>$Cm$</td>
<td>$(a, b, 0)$</td>
<td>$(0, 0, c)$</td>
<td>$(0, 0, 2)(1, 1, 0)/(0, 0, 0)$</td>
<td>No peak splitting</td>
</tr>
<tr>
<td>$Cm$</td>
<td>$(a, â, b)$</td>
<td>$(c, c, 0)$</td>
<td>$(1, 1, 0)(1, 1, 0)/(0, 0, 0)$</td>
<td>No peak splitting</td>
</tr>
<tr>
<td>$Cc$</td>
<td>$(a, a, b)$</td>
<td>$(c, c, d)$</td>
<td>$(1, 1, 0)(1, 1, 0)/(1, 0, 0)$</td>
<td>No peak splitting</td>
</tr>
<tr>
<td>$Cm$</td>
<td>$(a, b, 0)$</td>
<td>$(c, d, 0)$</td>
<td>$(0, 0, 2)(1, 1, 0)/(0, 0, 0)$</td>
<td>No peak splitting</td>
</tr>
<tr>
<td>$P1$</td>
<td>$(a, b, c)$</td>
<td>$(d, e, f)$</td>
<td>$(1, 1, 0)(1, 1, 0)/(0, 0, 0)$</td>
<td>No peak splitting</td>
</tr>
</tbody>
</table>

**Table 5.7:** The 14 possible space groups deduced by Stokes et al. [128] for simultaneous $R_4^+$ and $\Gamma_4^-$ mode distortions. The columns labelled by the distortion mode labels $\Gamma_4^-$ and $R_4^+$ give the order parameters as previously described. DNC indicates an unstable refinement where convergence could not be obtained.
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Of these 20 space groups, 10 were excluded based upon the fact that peak splitting or additional peaks consistent with monoclinic or triclinic symmetries were not observed (the exclusion was later confirmed by performing Rietveld refinements in case a splitting too small to be resolved was present). Of the space groups derived from only $R^+_1$ mode distortions (table 5.6) of the aristotype, three structures gave acceptable and stable Rietveld fits: $I4/mcm$, Imma and $R\bar{3}c$.

The $I4/mcm$ model, although stable and giving reasonable values of $R_{wp}=0.0319$ and $\chi^2=3.365$ (36 var.), had an unreasonably large oxygen isotropic displacement parameter for the O1 4-fold site (apical to the Fe/Mn site) of $U_{iso} = 0.377(17)$ Å$^2$. Anisotropic refinement of the O1 site gave a disk-shaped ellipsoid with $U_{11} = U_{22} = 0.203(7)$ Å$^2$. Due to these unphysically large values, $I4/mcm$ was therefore discounted as a possible model.

Contrary to this, fully isotropic refinements in both Imma and $R\bar{3}c$ gave very good results with no unindexed peaks as shown in figures 5.19 and 5.20. The $U_{iso}$ values for the oxygen sites are rather large (0.115(3) Å$^2$ for O2 in Imma and 0.0788(12) Å$^2$ for the single O-site in $R\bar{3}c$) although smaller than for the $I4/mcm$ model (0.377(17) Å$^2$). A comparison of the $R_{wp}$, $\chi^2$ and oxygen site $U_{iso}$ values for the isotropic Imma, $I4/mcm$ and $R\bar{3}c$ refinements can be seen in table 5.8.

<table>
<thead>
<tr>
<th>Space Group</th>
<th>$R_{wp}$</th>
<th>$\chi^2$</th>
<th>Oxygen Site $U_{iso}$ (Å$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I4/mcm$</td>
<td>0.0319</td>
<td>3.365 (36 var.)</td>
<td>O1: 0.377(17), O2: 0.0584(18)</td>
</tr>
<tr>
<td>Imma</td>
<td>0.0327</td>
<td>3.535 (36 var.)</td>
<td>O1: 0.069(3), O2: 0.115(3)</td>
</tr>
<tr>
<td>$R\bar{3}c$</td>
<td>0.0362</td>
<td>4.331 (33 var.)</td>
<td>O: 0.0788(12)</td>
</tr>
</tbody>
</table>

Table 5.8: The $R_{wp}$, $\chi^2$ and oxygen $U_{iso}$ values for the fully isotropic $R\bar{3}c$, $I4/mcm$ and Imma refinements.
Figure 5.19: The Rietveld refinement results of the Imma model at 1153K.
Figure 5.20: The Rietveld refinement results of the $R\overline{3}c$ model at 1153K.
It can be seen, however, in figures 5.19 and 5.20 that the fitting of the intensities of the fundamental (aristotype-derived) peaks are not optimal in either the \textit{Imma} or the \textit{R3c} fully isotropic models. Since materials involving lone-pair cations such as Bi and Pb often have structures involving off-centring of the A-site cation, refinements with anisotropic displacements of the Bi atoms only, O atoms only and the Bi and O atoms together were performed. As can be seen from figure 5.21, the anisotropic refinement of the Bi site alone cannot account for the anomalies in peak intensity and refinement of the Bi and O sites together does not improve the fit over the refinement with only O site anisotropic (in fact the O site $U_{ij}$ parameters are effectively unchanged by allowing the Bi site to displace anisotropically). The effect of anisotropic refinement of Bi and/or O sites is mirrored in the \textit{Imma} model and the $R_{wp}$ and $\chi^2$ values obtained from the refinements can be seen in table 5.9 for \textit{R3c} and table 5.10 for \textit{Imma}.

Interestingly, in both space groups setting the displacement parameter of one oxygen site to be anisotropic (the single oxygen site in \textit{R3c} and the 8-fold O2 site in the \textit{Imma} model) improves the fitting substantially\footnote{anisotropic refinement of the other oxygen site (O1) for the \textit{Imma} model gave no significant change in the refinement}. The results of the refinements are tabulated in table 5.11 and 5.12 and show that, in both cases, the anisotropic displacement parameters give quasi-2D disk-shaped ellipsoids with the short axis along the Fe/Mn-O direction. The graphical representations for both models are shown in figure 5.22.
Figure 5.21: The Rietveld refinement results of the $R\bar{3}c$ model at 1153 K with anisotropic displacement parameters refined for Bi only (top), Bi and O (middle) and O only (bottom).
<table>
<thead>
<tr>
<th>Anisotropic Site(s)</th>
<th>$R_{wp}$</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi</td>
<td>0.0484</td>
<td>7.748 (33 var.)</td>
</tr>
<tr>
<td>Bi and O</td>
<td>0.0221</td>
<td>1.612 (39 var.)</td>
</tr>
<tr>
<td>O</td>
<td>0.0222</td>
<td>1.634 (38 var.)</td>
</tr>
</tbody>
</table>

**Table 5.9:** The Rietveld refinement results for the $R\bar{3}c$ model at 1153K with different sites refined anisotropically.

<table>
<thead>
<tr>
<th>Anisotropic Site(s)</th>
<th>$R_{wp}$</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi</td>
<td>0.0445</td>
<td>6.566 (38 var.)</td>
</tr>
<tr>
<td>Bi and O</td>
<td>0.0216</td>
<td>1.522 (44 var.)</td>
</tr>
<tr>
<td>O</td>
<td>0.0218</td>
<td>1.572 (42 var.)</td>
</tr>
</tbody>
</table>

**Table 5.10:** The Rietveld refinement results for the $Imma$ model at 1153K with different sites refined anisotropically.
### Isotropic refinement: \( R_{wp}=0.0327, \chi^2=3.535 \) for 36 variables.

\[ a = 5.63999(18) \text{ Å}, \quad b = 7.97346(13) \text{ Å}, \quad c = 5.64118(19) \text{ Å}. \]

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff Position</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>100 ( \times U_{iso} ) (Å²)</th>
<th>Occ.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi</td>
<td>4e</td>
<td>0</td>
<td>0.25</td>
<td>0.5003(34)</td>
<td>9.77(18)</td>
<td>1</td>
</tr>
<tr>
<td>Fe</td>
<td>4a</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>3.57(14)</td>
<td>0.7</td>
</tr>
<tr>
<td>Mn</td>
<td>4a</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>3.57(14)</td>
<td>0.3</td>
</tr>
<tr>
<td>O1</td>
<td>4e</td>
<td>0</td>
<td>0.25</td>
<td>0.0169(28)</td>
<td>6.9(3)</td>
<td>1</td>
</tr>
<tr>
<td>O2</td>
<td>8g</td>
<td>0.25</td>
<td>0.9621(8)</td>
<td>0.25</td>
<td>11.5(3)</td>
<td>1</td>
</tr>
</tbody>
</table>

### Anisotropic refinement: \( R_{wp}=0.0218, \chi^2=1.572 \) for 42 variables.

\[ a = 5.6409(2) \text{ Å}, \quad b = 7.97308(10) \text{ Å}, \quad c = 5.64033(17) \text{ Å}. \]

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff Position</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>100 ( \times U_{iso} ) (Å²)</th>
<th>( U_{11} )</th>
<th>( U_{22} )</th>
<th>( U_{33} )</th>
<th>( U_{12} )</th>
<th>( U_{13} )</th>
<th>( U_{12,13} )</th>
<th>Occ.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi</td>
<td>4e</td>
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<td>0.25</td>
<td>0.500(3)</td>
<td>8.93(10)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>Fe</td>
<td>4a</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>3.39(9)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.7</td>
</tr>
<tr>
<td>Mn</td>
<td>4a</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>3.39(9)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
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</tr>
<tr>
<td>O1</td>
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<td>0.017(3)</td>
<td>8.4(3)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>O2</td>
<td>8g</td>
<td>0.25</td>
<td>0.9621(8)</td>
<td>0.25</td>
<td>11.80*</td>
<td>13.1(8)</td>
<td>13.7(6)</td>
<td>8.6(6)</td>
<td>-8.8(4)</td>
<td>0</td>
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</tr>
</tbody>
</table>

*equivalent \( U_{iso} \) calculated from the anisotropic parameters.

**Table 5.11**: The Rietveld refinement results of the \( Imma \) isotropic and anisotropic models at 1153 K.
### Isotropic refinement: $R_{wp}=0.0362$, $\chi^2=4.331$ for 33 variables.

$a = 5.63969(19)$ Å, $c = 13.8146(8)$ Å.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff Position</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>$100 \times U_{iso}$ (Å²)</th>
<th>Occ.</th>
</tr>
</thead>
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<td>Fe</td>
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<td>0</td>
<td>0.5</td>
<td>1.23(6)</td>
<td>0.7</td>
</tr>
<tr>
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<td>6b</td>
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<td>0.5</td>
<td>1.23(6)</td>
<td>0.3</td>
</tr>
<tr>
<td>O</td>
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<td>0.4585(5)</td>
<td>0</td>
<td>0.25</td>
<td>7.88(12)</td>
<td>1</td>
</tr>
</tbody>
</table>

### Anisotropic refinement: $R_{wp}=0.0222$, $\chi^2=1.634$ for 38 variables.

$a = 5.63973(14)$ Å, $c = 13.8145(7)$ Å.

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff Position</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>$100 \times U_{iso}$ (Å²)</th>
<th>$U_{11}$</th>
<th>$U_{22}$</th>
<th>$U_{33}$</th>
<th>$U_{12}$</th>
<th>$U_{13}$</th>
<th>$U_{23}$</th>
<th>Occ.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi</td>
<td>6a</td>
<td>0</td>
<td>0</td>
<td>0.25</td>
<td>8.88(10)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1</td>
</tr>
<tr>
<td>Fe</td>
<td>6b</td>
<td>0</td>
<td>0</td>
<td>0.5</td>
<td>3.12(8)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.7</td>
</tr>
<tr>
<td>Mn</td>
<td>6b</td>
<td>0</td>
<td>0</td>
<td>0.5</td>
<td>3.12(8)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.3</td>
</tr>
<tr>
<td>O</td>
<td>18e</td>
<td>0.4670(5)</td>
<td>0</td>
<td>0.25</td>
<td>10.01*</td>
<td>10.1(4)</td>
<td>6.2(6)</td>
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<td>-2.82(17)</td>
<td>-5.6(4)</td>
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</table>

*equivalent $U_{iso}$ calculated from the anisotropic parameters.

Table 5.12: The Rietveld refinement results of the $R\bar{3}c$ isotropic and anisotropic models at 1153K.
Figure 5.22: The structures obtained by Rietveld refinements of the 1153K data with anisotropic displacement parameters for the single oxygen site in the $R\bar{3}c$ model and for O2 in the Imma model. The Bi ions are shown in grey, the Fe/Mn ions in green and the oxygen ions in blue.
Since the large atomic displacement parameters could be due to the Bi and/or O atoms being displaced from the high symmetry positions imposed by the $R\overline{3}c$ space group, the chiral subgroup $R32$ and the polar subgroup $R3c$ of $R\overline{3}c$ were investigated for possible models. The results of the isotropic refinements can be seen in figures 5.23 and 5.24 respectively. The refinements were not significantly better than the $R\overline{3}c$ isotropic refinement and the magnitude of the isotropic displacement parameters was only slightly smaller for the $R3c$ model with $U_{iso}=6.01(11)$ and were larger for $R32$ with $O1$ $U_{iso}=9.4(5)$ and $O2$ $U_{iso}=8.4(5)$. An anisotropic refinement of the oxygen site in the $R3c$ model gave very similar ellipsoids, enlarged perpendicular to the Fe/Mn-O bond direction, to the $R\overline{3}c$ model. Since the magnitude of the polar $\Gamma_{-4}$ mode calculated using AMPLIMODES [17, 19] was only 0.11(8) Å it seems reasonable to conclude that the intensities of the aristotype-derived peaks are not being modified, in this case, by polar distortions and one can therefore conclude that the $R\overline{3}c$ model is the most appropriate rhombohedral model.

Although the $Imma$ model gives slightly better $R_{wp}$ and $\chi^2$ values, the $R\overline{3}c$ model gives smaller displacement parameters. Since the $R\overline{3}c$ phase has the higher symmetry and fewer refined parameters for a very similar quality of fit, this model

![Figure 5.23: The Rietveld refinement results of the $R32$ model at 1153K.](image)
will be used in the analysis of details of the $\gamma$-phase. The large values of the atomic displacement parameters for the Bi and O sites obtained from the refinements of our data are not so anomalous when considered in the context of oxides containing lone-pair atoms. For example, Pb perovskites have been reported with similarly large displacement parameters in paraelectric phases of a variety of materials [129–133]. Examples of such behaviour in Bi-containing perovskites are not so numerous but have still been reported [134].

In summary, our detailed analysis of the possible space groups shows that the most likely space group for the $\gamma$-phase of BiFe$_{0.7}$Mn$_{0.3}$O$_3$ is $R\bar{3}c$ with $Imma$ being the strongest alternative possibility. The previously assigned $Pm\bar{3}m$ structure is conclusively ruled out as is the possibility of a $Pbnm$ phase isostructural to BiFeO$_3$. 
5.3.4.4 Analysis of Rietveld Refinement Results

Having in the previous sections established the space groups of the $\alpha$-phase, $\beta$-phase and $\gamma$-phase phases we now concentrate on extracting physically relevant parameters from the refinements. In the first part we will present the temperature dependences of the unit cell volume and lattice parameters. This will be followed by a discussion of the temperature dependence of octahedral tilt angles and distortion modes.

The unit cell volumes for all phases were converted to an equivalent pseudo-cubic cell volume using the following relations (to allow comparison between unit cells with the same number of formula units):

- For rhombohedral unit cells with rhombohedral angle $\alpha=60^\circ$ (using the hexagonal setting$^8$):

\[
\begin{align*}
    a_a &= \frac{a_H}{\sqrt{2}} \\
    a_c &= \frac{c_H}{2\sqrt{3}} \\
    V_c &= a_a^2 \times a_c
\end{align*}
\]

- For orthorhombic cells the pseudo-cubic unit cell is monoclinic with shear angle $\beta$:

\[
\begin{align*}
    a_{ac} &= \sqrt{(a/2)^2 + (c/2)^2} \\
    a_b &= \frac{b}{2} \\
    V_c &= a_{ac}^2 \times a_b \\
    \text{shear angle } \beta &= \arccos \left( \frac{c^2 - a^2}{c^2 + a^2} \right)
\end{align*}
\]

$^8$The equations given here are correct for the case $\alpha=60^\circ$ in which the rhombohedral unit cell can be described as a double perovskite ($a \approx 8\text{Å}$) face-centered pseudo-cubic cell (although to facilitate comparison with the other phases we transform to the single perovskite aristotype cell with $a \approx 4\text{Å}$). In this case, the pseudo-cubic lattice parameters calculated from the rhombohedral $a$ and $c$ will be equal. In the case of $\alpha \neq 60^\circ$, the parameters will differ. Equations 5.2, 5.3 and 5.4 are used for all rhombohedral cells in the $\alpha$-phase and $\gamma$-phases for consistency (the largest deviation from $\alpha=60^\circ$ observed was $\alpha = 59.454(3)^\circ$. The relation between hexagonal and rhombohedral settings is $a_H = 2a_R\sin(\alpha/2)$ and $c_H = a_R\sqrt{3+6\cos\alpha}$ where $\alpha$ is the rhombohedral angle which can be calculated using the relation $\sin(\alpha/2) = 3a_H/(2\sqrt{3a_H^2+c_H^2})$. In the case of a metrically cubic cell with $\alpha = 60^\circ$ this gives $a_H = a_R$ and $c_H = \sqrt{6}a_R$. 

The calculated pseudo-cubic unit cell volumes are shown in figure 5.25 for the whole temperature range measured and in figure 5.26 enlarged for the range 913 K-1191 K. The values for both phases are shown for all temperatures in the phase

![Figure 5.25: The pseudo-cubic unit cell volume of BiFe$_{0.7}$Mn$_{0.3}$O$_3$. There is coexistence of the $\alpha$- and $\beta$- phases between 913 K and 953 K and of the $\beta$- and $\gamma$-phases at 1133 K. The areas shaded grey indicate phase coexistence.](image)

![Figure 5.26: The pseudo-cubic unit cell volume of BiFe$_{0.7}$Mn$_{0.3}$O$_3$. There is coexistence of the $\alpha$- and $\beta$- phases between 913 K and 953 K and of the $\beta$- and $\gamma$-phases at 1133 K. The areas shaded grey indicate phase coexistence.](image)
coexistence regions except for at 953 K. The changes in volume are in general agreement with those reported by Selbach et al. from dilatometry [113, 121] with a decrease in volume across the α-to-β transition and an increase across the β-to-γ transition. The first order nature of the α-to-β and β-to-γ transitions is clear from the abrupt volume changes.

Now we turn to the lattice parameters. A surprising fact we would like to point out is that in the γ-phase the R3c model lattice parameters become metrically cubic. This can be clearly seen in a comparison between the α-phase and γ-phase diffraction patterns shown in figure 5.27. The lack of peak splitting in the γ-phase corresponds to the lattice parameters being metrically cubic whereas the α-phase is clearly not. The pseudo-cubic lattice parameters of the R3c α-phase at 523 K are \( a_a = 3.9509(1) \) Å and \( a_c = 4.0000(4) \) Å and for the R3c γ-phase at 1173 K \( a_a = 3.9891(1) \) Å and \( a_c = 3.9891(7) \) Å. The meaning of this is that although the oxygen ions have moved to create the equal tilts around each axis in the R3c

\[9\] Where the fraction of the rhombohedral phase is only 6.4% according to the Rietveld refinement which combined with the peak overlap with the orthorhombic phase meant that accurate lattice parameters could not be determined at this single temperature.

---

**Figure 5.27:** A comparison of the BiFe_{0.7}Mn_{0.3}O_{3} α-phase R3c data at 523 K (lower, green) and the metrically cubic γ-phase data with no peak splitting at 1173 K (upper, blue).
phase, therefore breaking cubic symmetry, the lattice parameters have remained cubic resulting in the situation of a metrically cubic rhombohedral phase.

The lattice parameters, shown in figure 5.28 for the range 913 K-1191 K and in figure 5.29 for the γ-phase, (also including the lattice parameters extracted from the less likely Imma structure refinements for comparison) increase smoothly through the β- and γ-phases to the highest temperatures measured, remaining metrically cubic over the entire temperature range of the γ-phase.

Finally, regarding the general unit cell properties, the shear angle, β, for the metrically monoclinic pseudo-cubic representation of the orthorhombic Pnma unit cell (not shown) is β = 90.4° at 913 K and smoothly decreases to β = 90.15° at 1133 K.

Figure 5.28: The lattice parameters of BiFe$_{0.7}$Mn$_{0.3}$O$_3$ in the β- and γ-phases. The parameter $a_R$ refers to the lattice parameters extracted from refinements in R3c, since the lattice parameters are metrically cubic over the whole γ-phase $a_R = \sqrt{2}(c_R/(2\sqrt{3}))$. The labels $a_P$, $b_P = b/\sqrt{2}$ and $c_P$ refer to the β-phase $Pnma$ parameters. The area shaded grey indicates phase coexistence.
Figure 5.29: The lattice parameters of BiFe$_{0.7}$Mn$_{0.3}$O$_3$ in the $\gamma$-phase. The parameter $a_R$ refers to the lattice parameters extracted from refinements in $R\overline{3}c$, since the lattice parameters are metrically cubic over the whole $\gamma$-phase $a_R = \sqrt{2}(c_R/(2\sqrt{3}))$. The parameters extracted from the less likely Imma structure refinements with labels $a_I$, $b_I = b/\sqrt{2}$ and $c_I$ are included for comparison.
To conclude this section, we will discuss the rough magnitude of the distortion of the \( \beta \)-phase and \( \gamma \)-phases from the cubic aristotype structure as parametrized by octahedral tilt angles and distortion mode amplitudes.

The octahedral tilt angles were calculated for the \( Pnma \) models using the expressions formulated by Kennedy et al. [135]:

- For the in-phase tilt around the \( b \)-axis with O2 coordinates 
  \((x, y, z) = (\frac{1}{4} + u, v, \frac{1}{4} - w)\), and average displacement from the zero-tilt position \( \delta = (u + w)/2 \), the tilt angle, \( \theta_{b^+} \), is given by:

  \[
  \theta_{b^+} = \arctan(4\delta)
  \]  
  \( (5.9) \)

- For the equal out-of-phase tilts around the \( a \)- and \( c \)-axes, the tilt angle, \( \theta_{a^-} \), is given by:

  \[
  \theta_{a^-} = \arctan(4\sqrt{2}w).
  \]  
  \( (5.10) \)

For the rhombohedral \( R\bar{3}c \) phase, the tilt angles were calculated using the method of Megaw [136]:

- For the out-of-phase tilt around all three axes, with O1 coordinates \((x, y, z) = (\frac{1}{6} - 2e, \frac{1}{3}, \frac{1}{12})\), the rhombohedral tilt angle \( \theta_R \) is defined as:

  \[
  \theta_R = \arctan(4\sqrt{3}e).
  \]  
  \( (5.11) \)

The tilt angles for the \( \beta \)- and \( \gamma \)-phases are shown in figure 5.30. Consistent with the increase of volume with temperature, the magnitude of octahedral tilting decreases with increasing temperature although the decrease through the \( \beta \)-phase is surprisingly small.

The trend of the tilt angle through the \( \gamma \)-phase implies that if the observed peritectic decomposition did not occur, a cubic phase would be reached at a temperature above 1200 K.
Figure 5.30: The octahedral tilt angles of BiFe$_{0.7}$Mn$_{0.3}$O$_3$ in the $\beta$- and $\gamma$-phases with $\theta_{b^+}$, $\theta_{a^-}$ and $\theta_R$ defined as in equations 5.9, 5.10 and 5.11. The area shaded grey indicates phase coexistence.

The amplitudes of the distortions from the $Pm\bar{3}m$ structure can be calculated using the program AMPLIMODES [17, 19] and are shown in figure 5.31 for the $\beta$- and $\gamma$-phases. The amplitudes vary only slightly through the $\beta$-phase as would be expected based upon the similar behaviour of the tilt angle. Also in agreement with the tilt angle data, the behaviour of the amplitude of the $R^+_4$ mode through the $\gamma$-phase suggests it would reach zero above 1200 K.
Figure 5.31: The distortion mode amplitudes for BiFe$_{0.7}$Mn$_{0.3}$O$_3$ in the $\beta$ and $\gamma$-phases. The area shaded grey indicates phase coexistence.
5.4 Conclusions

Based upon the above analysis of the powder neutron diffraction data, the thermal phase diagram of BiFe$_{0.7}$Mn$_{0.3}$O$_3$ may be summarised as (for a graphical representation see figure 5.32):

\[
\begin{align*}
\gamma &\mid \gtrsim 1133 \text{ K} \mid R3c (167) \mid Z = 6 \mid \text{nonferroic} \mid - \\
\beta &\mid \approx 913 \text{ K} - 1133 \text{ K} \mid Pnma (62) \mid Z = 4 \mid \text{nonferroic} \mid - \\
\alpha &\mid \lesssim 913 \text{ K} \mid R3c (161) \mid Z = 6 \mid \text{ferroelectric, ferroelastic} \mid T_N = 533 \text{ K}
\end{align*}
\]

We have confirmed the previous assignment of the most likely space group for the $\beta$-phase of BiFe$_{0.7}$Mn$_{0.3}$O$_3$ as $Pnma$ although our investigation showed that a non-centrosymmetric subgroup of $Pnma$ could not be ruled out (as discussed previously $Pbnm$ and $Pnma$ are different settings of the same space group, in figure 5.32 the setting $Pbnm$ is used for consistency with previous publications on BiFeO$_3$ and BiFe$_{0.7}$Mn$_{0.3}$O$_3$). Having shown that extrapolating from BiFeO$_3$ is not possible, it would be highly desirable to carry out physical property measurements such as second harmonic generation (SHG) or other such diagnostic measurements to confirm the centrosymmetry (or alternatively the non-centrosymmetry) of the $\beta$-phase of BiFe$_{0.7}$Mn$_{0.3}$O$_3$.

Most importantly, we conclusively showed that the $\gamma$-phase of BiFe$_{0.7}$Mn$_{0.3}$O$_3$ is neither the cubic $Pm\bar{3}m$ aristotype structure as previously assigned, nor the same $Pbnm$ structure as pure BiFeO$_3$. Our measurements were most consistent with a rhombohedral structure with space group $R3c$. This is an entirely new finding and due solely to the use of high-resolution neutron diffraction which allowed the $R_4^+$ distortion mode peaks to be resolved.

Finally, the rhombohedral $\gamma$-phase is metrically cubic through its whole range. This

![Figure 5.32](image-url)

**Figure 5.32:** The thermal phase diagram for BiFe$_{0.7}$Mn$_{0.3}$O$_3$ resolved by this study. The transition to non-polar $Pbnm$, completed by 963K, is first order, as is the $\beta$-to-$\gamma$ transition at 1133-1138K. The onset of peritecctic decomposition to Bi$_2$Fe$_4$O$_9$ and liquid Bi$_2$O$_3$ occurs at $\approx 1191$K.
explains the previous mis-assignment of the $\gamma$-phase as $Pm\bar{3}m$ based upon x-ray diffraction as this technique was not sensitive enough to the oxygen positions to resolve the $R^+_4$ distortion peaks violating the cubic symmetry. Energetically the transition to the cubic aristotype might be expected to be very close by. However, as our sample had begun to peritectically decompose and the structural parameters extracted still showed a significant distortion from the aristotype present at the highest temperatures possible to measure, it seems that an aristotype phase is not reached in the stability range of BiFe$_{0.7}$Mn$_{0.3}$O$_3$. Our results indicate that without the intervention of peritectic decomposition the aristotype phase would only be reached for $T > 1200$ K and therefore is not present in BiFe$_{0.7}$Mn$_{0.3}$O$_3$.

Though the $\beta$-to-$\gamma$ phase transition is not directly related to the multiferroicity present in the $\alpha$-phase, the fact that 30% substitution of an ion with identical ionic radius ($r = 0.645$ Å for high-spin $3d^4$ Mn$^{3+}$ and high-spin $3d^5$ Fe$^{3+}$ [137]) leads to such a clear change in the high-temperature structural properties is interesting. It indicates that factors aside from simple ionic size considerations are important at these high temperatures and requires further detailed investigation. Whether these factors are also related to the multiferroicity remains to be seen. Since Mn$^{3+}$ is a Jahn-Teller active ion it is possible that this plays a role; further local structure investigations would be desirable to clarify any contribution from Jahn-Teller effects.

In conclusion, we showed that Mn-substitution has more subtle and far-ranging structural effects on BiFeO$_3$ than previously supposed.
Chapter 6

YMnO₃ -

a Multiferroic with Improper Ferroelectricity

YMnO₃ is a magnetoelectric multiferroic with coexisting ferroelectric and antiferromagnetic orders at low temperature which has been studied since the 1950s [138]. It has attracted interest ever since due to its improper ferroelectricity and the difficulty in elucidating its exact phase diagram. The polar ambient temperature structure of YMnO₃ has been known to have the space group $P6_3cm$ since 1963 [139] but the high temperature phases have been the subject of much debate. The ferroelectric Curie temperature $T_C$, for both single crystal and polycrystalline samples, has been reported over a 400 K range from $\approx 880$K to $\approx 1275$K and various authors have reported either a single transition in this range or a pair of transitions. The high temperature phase has been generally agreed to have the aristotype $P6_3/mmc$ structure above $\approx 1300$K. The transitions and intermediate phase diagram between the ambient temperature phase and high temperature aristotype phase were sources of controversy at the outset of this study. The powder neutron diffraction experiments discussed in this chapter were designed to resolve the controversy over whether there are one or two transitions in the range 880K to 1300K and clearly identify the location of the transition to the ferroelectric state. The experiments were carried out in the group of Prof. P. Lightfoot with the neutron experiments being performed at the ISIS facility using the instrument HRPD. The experiments presented here have, we believe, resolved a major controversy over the high temperature phases of YMnO₃ and were reported in [140].

\footnote{There are a variety of definitions of ferroelectricity but here it is taken to refer to materials in which dipole moments are aligned antiparallel but do not cancel giving a net polarization.}
6.1 Crystal and Electronic Structure

YMnO$_3$ is a rare earth manganite which exists in two polymorphic forms. The rare earth manganites are A$^{3+}$B$^{3+}$O$_3$ compounds having the general formula R MnO$_3$ with R being a lanthanide or yttrium. When R is an ion with ionic radius equal to or larger than Dy$^{3+}$ the compounds adopt an orthorhombic perovskite structure. Compounds with smaller rare earth ions on the A-site crystallise in a layered hexagonal structure. Some exceptions to this general rule may be achieved with the use of low-temperature or high pressure synthesis methods [141]. YMnO$_3$ can easily be synthesised in either form but at ambient pressure, with standard solid state synthesis techniques, the hexagonal polymorph is formed. It is this hexagonal form of YMnO$_3$ that is the subject of this chapter.

The hexagonal polymorph of YMnO$_3$, first synthesised by Forrat in 1958 [138, 139], has space group $P6_3cm$ at ambient temperature [139]. This is a polar space group with point group 6mm. The layered structure, shown in figure 6.1a consists of five-fold trigonal bipyramidally oxygen coordinated Mn$^{3+}$ ions and eight-fold coordinated Y$^{3+}$ ions. In contrast to a typical perovskite structure, the layers of corner-sharing MnO$_5$ trigonal bipyramids are discrete - there is no corner-sharing in the c-axis direction. Figure 6.1b shows the high temperature undistorted structure of YMnO$_3$ which has untilted polyhedra and uncorrugated planes of Y$^{3+}$ ions.

![Figure 6.1: The YMnO$_3$ crystal structure with (a) showing the ambient temperature polar $P6_3cm$ structure and (b) the high-temperature centrosymmetric structure generally accepted to have space group $P6_3/mmc$. The blue polyhedra represent the corner-sharing MnO$_5$ trigonal bipyramids which form discrete layers in the ab-plane.](image-url)
The Mn$^{3+}$ ions are in a high-spin $3d^4$ ($S = 2$) configuration with the energy levels shown in figure 6.2 [142]. The doubly degenerate $e_{1g}$ and $e_{2g}$ levels are all half-filled which might be expected to lead to an itinerant state. Instead, strong correlations lead to a charge transfer insulating state with a large energy gap of $\approx 1$ eV. The bands just below the Fermi energy have a dominantly oxygen $2p$ character and the states above the gap dominantly Mn $3d$ in character. The band gap has been determined by optical methods to be $E_g = 1.27$ eV at room temperature [143] (this can be compared to the band-gap of silicon at 300 K $E_g = 1.1$ eV [144]).

At ambient temperature YMnO$_3$ is a ferrielectric material, showing a spontaneous polarization which is reversible upon the application of an electric field [145–148]. The dipoles in YMnO$_3$ are due to opposite but unequal displacements of the Y$^{3+}$ ions and consequential tilting and distortion of the MnO$_5$ trigonal bipyramids [149, 150]. These displacements lead to a net polarization of 6 $\mu$Ccm$^{-2}$. YMnO$_3$ is an ‘improper’ ferrielectric in which the ferrielectric transition is not driven by a structural instability to the polar state (i.e. the polarization is not the order parameter for the transition) as in $d^0$ systems such as BaTiO$_3$ or lone-pair cation ($\text{Pb}^{2+}$, $\text{Bi}^{3+}$) containing materials. It is instead a consequence of a structural transition driven by ionic size effects rather than cation displacements.

At temperatures below $T_N = 70$ K, YMnO$_3$ also displays coexisting magnetic order [151]. The Mn$^{3+}$ moments in the $ab$-plane order antiferromagnetically in a ‘120°’ state even above $T_N$. At $T_N$ the inter-plane interactions become strong enough to create ferromagnetic ordering of moments between the planes. This coexistence of antiferromagnetic and ferrielectric order makes YMnO$_3$ a magnetoelectric multiferroic below 70 K. The coupling between the two orders is rather weak in YMnO$_3$ (although it can be enhanced by doping [152]). Despite the lack of technological applications of YMnO$_3$, it provides an opportunity to study the mechanisms of coupling in a multiferroic material with improper ferrielectricity.

Figure 6.3 shows a schematic of the state of knowledge of the phase diagram of YMnO$_3$ before the study described in this chapter. The ambient temperature structure of YMnO$_3$

\begin{figure}[h]
\centering
\begin{tikzpicture}
    \node (a) at (0,0) {$a_{ig}$};
    \node (e1) at (0,-1.5) {$e_{1g}$};
    \node (e2) at (0,-3) {$e_{2g}$};
    \draw[->] (a) -- (e1);
    \draw[->] (a) -- (e2);
\end{tikzpicture}
\caption{The crystal field energy levels for the trigonal bipyramidally coordinated Mn$^{3+}$ ions in YMnO$_3$ with $S = 2$.}
\end{figure}
had been determined and there was general agreement on the symmetry of the high temperature phase but there was substantial disagreement over \( T_C \) and the number and nature of the high temperature phases. The following section will describe in detail the previous work on the high temperature phases of YMnO\(_3\) and then the results of the powder neutron diffraction study we designed to try to resolve the uncertainties in the high temperature phase diagram of this compound.

### 6.2 High Temperature Phase Transitions in YMnO\(_3\)

#### 6.2.1 Previous Work on YMnO\(_3\)

The high temperature structural properties of YMnO\(_3\) were first reported in the 1960s with a report of a ferrielectric transition with a concurrent structural transition from \( P6_3cm \) at ambient temperature to the centrosymmetric space group \( P6_3/mcm \) at high temperature [153]. However, the samples used were Bi-ux grown and the effect of impurities would be expected to affect the transition temperature and possibly introduce strain into the crystals.

There have been many investigations over the years into the high temperature phase diagram of YMnO\(_3\) using a variety of techniques. The results of these are tabulated in table 6.1. From examination of the range of transition temperatures proposed in these experiments using a wide range of methods it becomes clear that there is no general consensus beyond that there is at least one high temperature transition above 900 K.

An intermediate phase between \( P6_3/mmc \) and \( P6_3cm \) has been discussed by various authors. The first investigation, by Lonkai \textit{et al.} in 2004 [163], analysed the possible transition paths between \( P6_3/mmc \) and \( P6_3cm \) using group theoretical arguments in
Table 6.1: The transition temperatures previously reported in the literature for the ferrielectric \( T_C \) and unit-cell tripling \( T_S \) transitions of YMnO\(_3\). In the Technique column PXRD = powder x-ray diffraction, SXD = single-crystal x-ray diffraction, PND = powder neutron diffraction, DTC = differential thermal calorimetry and MEM = maximum entropy method.

<table>
<thead>
<tr>
<th>Reference</th>
<th>( T_C ) (K)</th>
<th>( T_S ) (K)</th>
<th>Technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coeuré \textit{et al.} [154]</td>
<td>913</td>
<td></td>
<td>Dielectric permittivity</td>
</tr>
<tr>
<td>Ismaïlzade and Kizhaev [153]</td>
<td>933</td>
<td></td>
<td>Pyroelectric current and SXD</td>
</tr>
<tr>
<td>Lukaszewicz and Karat-Kalicińska [155]</td>
<td></td>
<td>1275</td>
<td>SXD</td>
</tr>
<tr>
<td>Katsufuji \textit{et al.} (2002) [157]</td>
<td>( \geq 1000 )</td>
<td>( \geq 1000 )</td>
<td>PXRD</td>
</tr>
<tr>
<td>Nénert \textit{et al.} (2005) [158]</td>
<td>1020</td>
<td>1273</td>
<td>SXD</td>
</tr>
<tr>
<td>Jeong \textit{et al.} [160]</td>
<td>( \geq 1200 )</td>
<td></td>
<td>PND</td>
</tr>
<tr>
<td>Choi \textit{et al.} [161]</td>
<td>( \approx 880 )</td>
<td></td>
<td>Resistivity</td>
</tr>
<tr>
<td>Kim \textit{et al.} [162]</td>
<td>( \approx 920 )</td>
<td></td>
<td>PXRD (MEM)</td>
</tr>
</tbody>
</table>

Conjunction with neutron diffraction on the isostructural compound TmMnO\(_3\) and concluded that there was no evidence for an intermediate phase. Further studies by Nénert \textit{et al.} [158, 159], using synchrotron x-ray diffraction and differential thermal calorimetry (DTC), and a meta-analysis by Abrahams [164] were in favour of a \( P6_3/mcm \) intermediate phase. Clarifying the details of the transition is crucial for understanding the mechanism of the ferrielectricity and therefore also central to the study of the magneto-electric coupling in the multiferroic state of YMnO\(_3\).

The determination of the nature and temperature of the transition(s) is hampered by the fact that many physical property measurements are difficult at these very high temperatures. In particular the relatively small charge-transfer gap causes significant leakage currents in such measurements as dielectric permittivity. \( T_C \) would also be expected to be sensitive to impurities.

The high temperature phase of YMnO\(_3\) above 1300 K as mentioned has been generally agreed to be the \( P6_3/mmc \) structure which is the undistorted aristotype for the ambient temperature \( P6_3cm \) structure. The transition from the high temperature aristotype \( P6_3/mmc \) structure to the \( P6_3cm \) structure involves tilting of the trigonal bipyramids, corrugation of the \( Y^{3+} \) ion layer leading to tripling of the unit cell and loss of mirror symmetry perpendicular to the \( c \)-axis direction. The Y-O bond length also becomes
unequal between the two crystallographically inequivalent Y sites in the $P6_3cm$ structure. If the assumption of a second order transition between the high temperature $P6_3/mmc$ and ambient temperature $P6_3cm$ phases is used (there are no indications from previous studies of physical property discontinuities that would require a first-order transition) there are multiple possible transition paths allowed by Landau theory. The possible sequences of transitions, based upon the assumption of the transition(s) being second order in nature, are illustrated in figure 6.4. The $K_1$ mode causes tripling of the unit cell by allowing displacement of the O-Mn-O axis in the $ab$-plane and leads to the space group $P6_3/mcm$. $\Gamma^-_2$ consists of polar displacements in the $c$-axis direction and leads to space group $P6_3mc$. The $K_3$ mode leading to the space group $P6_3cm$ consists of antiferrodistortive displacements giving corrugation of the Y-ion plane, tilts of the MnO$_5$ trigonal bipyramids and unit cell tripling. The transitions all involve a unit-cell tripling $K$ mode but the order of this symmetry breaking and any polar displacement varies.

The transition, via $K$ modes, between the high temperature $P6_3/mmc$ structure and either $P6_3cm$ or $P6_3/mcm$ will be referred to as the unit cell tripling transition with transition temperature $T_S$. The ferrielectric Curie temperature, $T_C$, may be the same as or different from $T_S$ depending on the transition path taken.

Due to the differences in the order of the distortion modes acquiring non-zero amplitudes between the different possible transition paths, the best initial test of the transition path is to identify the unit cell tripling temperature, $T_S$ and any correspondence between this and the corrugation of the Y$^{3+}$ ion layer and tilting of the Mn trigonal bipyramids.

The new avenue taken in this thesis compared to previous work is that the experiments described in this chapter are high-resolution neutron diffraction experiments on polycrystalline samples. Neutron diffraction has a much greater sensitivity to the oxygen positions than x-ray diffraction and the combination of neutrons and the use of

\[ \text{Figure 6.4: The possible second order phase transition paths for YMnO}_3 \text{ between the high temperature centrosymmetric phase and the ambient temperature polar phase.} \]
HRPD at ISIS, the highest resolution beamline of its type in the world, over the entire temperature region of interest allows us to perform the most thorough study to date of the high temperature phase transitions in YMnO$_3$. Furthermore, careful synthesis of the polycrystalline samples ensured clean samples with a minimal impurity content and minimised potential problems caused by strain.

### 6.2.2 Sample Preparation

The polycrystalline sample was prepared by standard solid state synthesis from the oxides Y$_2$O$_3$ (Sigma Aldrich 99.999%) and MnO$_2$ (Sigma Aldrich 99.99+%). The stoichiometric mixture was ground under acetone and pressed into pellets. These were heated at 1473 K on sacrificial powder in an alumina boat for 140 hours with intermediate grindings every 18 hours. The phase purity was monitored using laboratory x-ray diffraction (Stoe STADI P with Cu $K_{\alpha 1}$ source in flat-plate transmission mode) throughout the synthesis to ensure that a single-phase sample was obtained. Energy dispersive x-ray (EDX) spectroscopy was also used to confirm that the sample was not contaminated by, for example, aluminium from the alumina boat.
6.2.3 Results of High Resolution Powder Neutron Diffraction Experiments

High resolution powder neutron diffraction experiments were performed on HRPD at ISIS, Didcot. The sample was contained in an evacuated quartz ampoule which was placed inside a standard cylindrical vanadium can for the experiment. A standard furnace was used and a high-temperature thermocouple was fixed to the sample can just outside the beam cross section to ensure accurate sample temperatures. Data were collected for 60 $\mu$Ah of proton beam current (approx. 2h) for all temperatures above room temperature.

6.2.3.1 The High Temperature Phase of YMnO$_3$

The transition from the aristotype $P6_3/mmc$ phase to the unit-cell tripled low temperature phase is seen in the powder neutron diffraction data most clearly by the appearance of the (202) peak which appears due to the increase in $a$ by a factor of $\sqrt{3}$. The appearance of this peak at and below 1243K is shown in figure 6.5. Due to its clear appearance in between the 1273K and 1243K data points we can therefore determine that the unit-cell tripling structural transition occurs in the range $T_S = 1258 \pm 14$K. Data above this temperature were refined using a $P6_3/mmc$ model resulting in a good fit with no peaks unindexed. From our data, in line with previous reports, the high temperature structure above 1270K is $P6_3/mmc$ with the unit cell tripling structural transition unequivocally occurring at $T_S = 1258 \pm 14$K. The refinement results are tabulated in table 6.2 and plotted in figure 6.6.

<table>
<thead>
<tr>
<th>Space Group: $P6_3/mmc$, No.194</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{wp} = 0.0331$, $\chi^2 = 6.356$, 31 var.</td>
</tr>
<tr>
<td>$a = 3.618961(15), \text{Å}$, $c = 11.34090(9), \text{Å}$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff Site</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>$U_{11}/U_{22}$ (100×Å$^2$)</th>
<th>$U_{33}$ (100×Å$^2$)</th>
<th>$U_{12}$ (100×Å$^2$)</th>
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<tr>
<td>Y</td>
<td>2a</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>2.01(3)</td>
<td>6.75(5)</td>
<td>1.004(16)</td>
</tr>
<tr>
<td>Mn</td>
<td>2c</td>
<td>$\frac{1}{3}$</td>
<td>$\frac{2}{3}$</td>
<td>$\frac{1}{4}$</td>
<td>3.97(5)</td>
<td>1.61(7)</td>
<td>1.99(2)</td>
</tr>
<tr>
<td>O1</td>
<td>2b</td>
<td>0</td>
<td>0</td>
<td>$\frac{1}{4}$</td>
<td>3.35(4)</td>
<td>6.64(8)</td>
<td>1.69(2)</td>
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<tr>
<td>O2</td>
<td>4f</td>
<td>$\frac{1}{3}$</td>
<td>$\frac{2}{3}$</td>
<td>0.08557(7)</td>
<td>3.52(3)</td>
<td>1.84(4)</td>
<td>1.760(16)</td>
</tr>
</tbody>
</table>

Table 6.2: The Rietveld refinement results from the 1303K YMnO$_3$ dataset.
Figure 6.5: The appearance of the unit cell tripling (202) peak in the powder neutron diffraction patterns of YMnO$_3$ with decreasing temperature. The black tick marks indicate the predicted peak positions for the $P6_{3}cm$ phase.

Figure 6.6: The full-range results from the Rietveld refinement of the 1303K dataset with the $P6_{3}/mmc$ model for the high temperature phase of YMnO$_3$ with the difference curve shown in red below. The black tick marks indicate the expected peak positions for the $P6_{3}/mmc$ phase.
The thermal displacement parameters and lattice parameters vary smoothly through this phase to the highest temperature measured, 1403 K, suggesting that there is no further high temperature phase close by.

The first conclusion is therefore that the unit cell tripling structural transition occurs at $T_S = 1258 \pm 14$ K. The immediate question arising is what the space group below this transition in the unit cell tripled phase is. The space group $P6_3mc$ is ruled out as this does not have a tripled cell. This leaves the possibilities $P6_3/mcm$ and $P6_3cm$. The task of identifying the space group in the unit cell tripled phase will now be discussed.

### 6.2.3.2 The Unit-Cell Tripled Phases

The data set immediately below the unit-cell tripling transition was refined for both a $P6_3cm$ model and a $P6_3/mcm$ model to investigate the possibility of an intermediate phase. The full range fit for the $P6_3cm$ model is shown in figure 6.7. The results of the two refinements for two regions of clear difference are shown in figures 6.8. The $P6_3/mcm$ refinement gave a poorer result both by eye and $R_{wp}$ and $\chi^2$ parameters. The results from the fits are tabulated in table 6.3.

There are two features of importance in the $P6_3/mcm$ refinement results. One is that the refined $O1 x$ parameter is within error of $1/3a$ which means that the displacement allowed by symmetry seems not to occur, which is not physical. The second is that the atomic displacement parameter for $O3$ is almost twice that of the other oxygen sites. When refined anisotropically this gives a large anisotropy and indicates that the

![Figure 6.7](image)

**Figure 6.7:** The full-range results from the Rietveld refinement of the 1243 K dataset with the $P6_3cm$ model for the unit cell tripled phase of YMnO$_3$ below $T_S$. The difference curve is shown in red and the black tick marks indicate the peak positions for the $P6_3cm$ phase.
imposition of mirror symmetry perpendicular to the c-axis mandated by $P_6_3/mcm$ is in contradiction to the true physical symmetry. Refinements without this constraint (i.e. in $P_6_3cm$) give significant displacements and atomic displacement parameters more consistent with the other oxygen sites.

The data were also checked for reflections that would violate the $c$-glide reflection condition of both $P_6_3cm$ and $P_6_3/mcm$. There were no reflections found breaking this condition confirming the restriction used so far to space groups $P_6_3cm$ and $P_6_3/mcm$.

The conclusion from these refinements is that there is no symmetry-distinct intermediate phase in the transition from the high temperature $P_6_3/mmc$ phase to the ambient temperature $P_6_3cm$ phase as directly below the transition out of the $P_6_3/mmc$ phase the structure has already adopted the $P_6_3cm$ structure of the ambient temperature phase. This leaves only one possibility based upon Landau theory - that the transition $P_6_3/mmc \rightarrow P_6_3cm$ is direct at $T_S = 1258 \pm 14$K, through the unit cell tripling distortion mode $K_3$. Having said this, the direct transition $P_6_3/mmc \rightarrow P_6_3cm$ does allow for the possibility that the signatures seen in previous studies of a transition at $\approx 900$K are signatures of an isostructural\(^2\) transition within the $P6_3cm$ space group. Due to this possibility the lattice parameters and atomic positions were inspected for any such anomalies in the $P6_3cm$ phase. The two possibilities for the phase diagram having determined that the transition is $P6_3/mmc \rightarrow P6_3cm$ are shown in figure 6.9.

\(^2\)An isostructural transition, as defined by Christy [165], is a transition in which the space group symmetry and Wyckoff positions are unchanged.
Space Group: $P6_3cm$, No. 185

$R_{wp} = 0.0284$, $\chi^2 = 4.854$, 42 var.

$a = 6.25833(4) \text{Å}$, $c = 11.34918(12) \text{Å}$

<table>
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<tr>
<th>Atom</th>
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<th>x</th>
<th>y</th>
<th>z</th>
<th>$U_{iso} (100 \times \text{Å}^2)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Y1</td>
<td>2a</td>
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<td>0</td>
<td>0.2639(5)</td>
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</tr>
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<td>Y2</td>
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<td>$\frac{1}{3}$</td>
<td>$\frac{2}{3}$</td>
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<td>Mn</td>
<td>6c</td>
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<td>0</td>
<td>1.62(6)</td>
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<tr>
<td>O1</td>
<td>6c</td>
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<td>O3</td>
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<td>0</td>
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<td>O4</td>
<td>4b</td>
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<td>$\frac{2}{3}$</td>
<td>0.0153(5)</td>
<td>3.18(10)</td>
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Space Group: $P6_3/mcm$, No. 193

$R_{wp} = 0.0335$, $\chi^2 = 6.750$, 35 var.

$a = 6.25834(5) \text{Å}$, $c = 11.34917(15) \text{Å}$

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<th>Atom</th>
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<td>Y1</td>
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<td>O3</td>
<td>4c</td>
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<td>$\frac{1}{4}$</td>
<td>4.79(12)</td>
</tr>
</tbody>
</table>

Table 6.3: The Rietveld refinement results from the 1243K YMnO$_3$ dataset for $P6_3cm$ (top) and $P6_3/mcm$ (bottom).

$P6_3/mmc$ \(\approx 1260 \text{K} \rightarrow K_3 \rightarrow P6_3cm \approx 900 \text{K}$ isomorphic \(\rightarrow P6_3cm$.

Figure 6.9: The possible transition paths for YMnO$_3$ after ruling out symmetry-distinct intermediate phases.
6.2.3.3 Temperature Dependences of Parameters through Phase Diagram

All datasets below the unit-cell tripling transition were refined using the $P6_3cm$ model and all above using space group $P6_3/mmc$. The structure parameters from the refinement of the room temperature dataset, tabulated in table 6.4, are in good agreement with the previously reported values.

<table>
<thead>
<tr>
<th>Space Group: $P6_3cm$, No. 185</th>
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<tr>
<td>$R_{wp}=0.0330$, $\chi^2=5.885$, 39 var.</td>
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<td>1.16(7)</td>
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<td>Y2</td>
<td>4b</td>
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<td>$\frac{2}{3}$</td>
<td>0.2325(4)</td>
<td>1.30(5)</td>
</tr>
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<td>0</td>
<td>0.80(5)</td>
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<td>6c</td>
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<td>1.55(7)</td>
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<td>1.05(6)</td>
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<td>0.4744(6)</td>
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</tr>
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<td>4b</td>
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<td>$\frac{2}{3}$</td>
<td>0.0169(5)</td>
<td>1.42(7)</td>
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</table>

Table 6.4: The Rietveld refinement results from the 293K dataset for YMnO$_3$.

Lattice Parameters

The temperature dependences of the lattice parameters and unit cell volume are shown in figure 6.10. The $a$-axis parameter is plotted as $\sqrt{3}a$ in the high-temperature phase to facilitate comparison. Around 1270 K there is a sharp decrease in the gradient. The unit cell volume shows a similar trend. The $c$-axis parameter decreases until 1270 K; above this temperature it is roughly constant. All of this is consistent with the transition described in the previous section. The standard deviation errors for these lattice parameters are of the order $1.5 \times 10^{-5}$ Å for the $a$-axis and $4 \times 10^{-5}$ Å for the $c$-axis.

To better visualise these trends, a linear temperature dependence was subtracted from the $a$-axis and volume parameters. A simple linear fit was performed to the highest temperature data and this was subtracted. Subsequent to this, the 1403 K value was subtracted from all data (this normalisation step was also used for the $c$-axis data). The resulting quantities are plotted in figure 6.11. The change in behaviour around 1270 K is clear for all quantities. Further confirmation of this can be obtained by inspection of
Figure 6.10: The temperature dependences of the lattice parameters and unit cell volume of YMnO$_3$ from the powder neutron diffraction data.

Figure 6.11: The temperature dependences of the detrended and normalised lattice parameters and unit cell volume of YMnO$_3$ from the powder neutron diffraction data.
the temperature derivatives of the \( a \)-axis and \( c \)-axis parameters and the unit cell volume in figure 6.12.

The temperature dependence of the Y layer corrugation is shown in figure 6.13. The high temperature phase has just one Y site which gives a plane of \( Y^{3+} \) ions parallel to the \( ab \)-plane and zero corrugation. As the temperature is lowered and the polar \( P6_3/mmc \) phase

\[ \times 10^{-4} \]

\[ 2 \]

\[ 0 \]

\[ -1 \]

\[ -2 \]

\[ 400 \]

\[ 600 \]

\[ 800 \]

\[ 1000 \]

\[ 1200 \]

\[ 1400 \]

\[ \Delta \text{Y (Å)} \]

\[ 0 \]

\[ 0.1 \]

\[ 0.2 \]

\[ 0.3 \]

\[ 0.4 \]

\[ 0.5 \]

\[ 400 \]

\[ 600 \]

\[ 800 \]

\[ 1000 \]

\[ 1200 \]

\[ 1400 \]

\[ \text{Temperature (K)} \]

\[ \text{Temperature (K)} \]

\[ \text{Temperature derivative of } c \]

\[ \text{Temperature derivative of } a \]

\[ \text{Derivative of Lattice Parameter (Å/K)} \]

**Figure 6.12:** The temperature derivatives of the lattice parameters of YMnO\(_3\).

**Figure 6.13:** The magnitude of the \( Y^{3+} \) ion layer corrugation as a function of temperature for YMnO\(_3\). In the high temperature \( P6_3/mmc \) phase, the corrugation is zero as the \( Y^{3+} \) ions, occupying a single site, are constrained by symmetry to lie in a plane perpendicular to the \( c \)-axis.
is entered the mirror symmetry perpendicular to the c-axis in $P6_3/mmc$ is lost and the Y site splits leading to a corrugation of the Y plane. This corrugation increases sharply from zero to $\approx 0.27\,\text{Å}$ upon entering the $P6_3cm$ phase and then increases smoothly with decreasing temperature.

As can be seen there is no strong anomaly in the lattice parameters below the unit cell tripling transition at $T_S = 1258 \pm 14\,\text{K}$. We will now turn our attention to the intra-unit-cell atomic positions.

**Atomic Positions**

As in the case of the Y$^{3+}$ ion plane, the MnO$_5$ trigonal pyramids also displace with the loss of mirror symmetry with the transition $P6_3/mmc \rightarrow P6_3cm$. This can, for example, be seen in the apical oxygen tilt (here defined as the angle of O1-O2 to the c-axis direction) shown in figure 6.14.

The true surprise comes on inspecting the O3 and O4 positions. The $z$-coordinates of O3 and O4 also displace in the $P6_3cm$ phase as can be seen in figure 6.15a. But most importantly, another feature is also seen in these displacements between 973 K and 913 K where the $z$-coordinate of both sites decreases sharply. For temperatures below $T = 853\,\text{K}$, the O3 ion is displaced below the $z$-coordinate of the Mn ion. Examination of the equatorial plane tilt (the angle of O3-O4 to the $ab$-plane) in figure 6.15b reveals the sharp increase in this parameter at the same temperature of $913\,\text{K} < T < 973\,\text{K}$.

![Figure 6.14: The temperature dependence of the apical oxygen tilts in YMnO$_3$.](image-url)
These changes in the O3 and O4 displacements and equatorial plane tilt would, based upon a simple ionic model, correspond to a sharp decrease in polarization with decreasing temperature in YMnO$_3$ at $T^* \approx 920$K$^3$. At first sight this is extremely surprising. However, the polarization is not the primary order parameter as the mode driving the unit cell tripling high temperature structural transition is antiferrodistortive. This decrease could account for the pyroelectric current peak seen by Ismailzade and Kizhaev [153] as pyroelectric current (for a constant rate of heating) is only proportional to $\frac{\partial P}{\partial T}$ and does not measure the absolute value of polarization unless parameters such as the contact area and the magnitude and sign of the polarization at at least one temperature are known. A crossover in the temperature dependence of resistivity has also previously been reported by two groups in this region [156, 161].

The bond lengths for Y1-O bonds are shown in figure 6.16 and in general show smooth variation with temperature except for the Y1-O3 bond length which decreases sharply around $T^*$. The coordination of the Y1 site by O1, O2 and O3 can be seen in figure 6.17. The O1 and O2 sites coordinate the Y$^{3+}$ ion equatorially whereas the O3 site is in an apical position. This decrease in the Y1-O3 apical bond length is consistent with a hybridization of Y1 and O3 observed using the maximum entropy method (MEM) with synchrotron x-ray data by Kim et al. [162]. The Y1-O3 hybridization they observed was at $T^* = 910 - 930$K.

$^3$The changes in the O3 and O4 displacements occur between our 913K and 973K datasets. We can therefore deduce that $T^* = 943K \pm 30K$. Due to the correlation with observations in previous studies of anomalies at $T \approx 920$K we refer to this transition temperature as $T^* \approx 920$K.
Chapter 6. YMnO$_3$ - a Multiferroic with Improper Ferrielectricity

Figure 6.16: The temperature dependence of the Y-O bond lengths in YMnO$_3$.

Figure 6.17: The Y$^{3+}$ ion coordination in the polar $P6_3cm$ phase of YMnO$_3$. At room temperature, the Y-O bond lengths given by the Rietveld refinement are Y1-O1 = 2.267(4) Å, Y1-O2 = 2.308(2) Å and Y1-O3 = 2.298(8) Å. The distance between Y1 and the lower O3 ion, shown by a dotted line, is 3.402(8) Å.

Overall one can deduce from our experiments that at $T^* \approx 920$K an isostructural transition occurs that is ultimately responsible for the anomalies previously observed in MEM by Kim et al. as well as those seen in resistivity and pyroelectric current [153, 156, 161].

To gain a more complete understanding of these transitions, the magnitudes of the distortion modes from the $P6_3/mmc$ structure were investigated using AMPLIMODES [17, 19]. The relevant distortion modes are $\Gamma_1^+$, $\Gamma_2^-$, $K_1$ and $K_3$. $\Gamma_1^+$ is a symmetric
breathing mode distortion with the change in the $z$-coordinate of the Mn apical oxygen O1 being the order parameter. $\Gamma^-_2$ consists of polar ionic displacements in the $c$-axis direction and leads to space group $P6_3mc$. The $K_1$ mode triples the unit cell by allowing displacement of the O-Mn-O axis in the $ab$-plane and leads to the space group $P6_3/mcm$. The $K_3$ mode leads to the space group $P6_3cm$ by antiferrodistortive displacements giving corrugation of the Y$^{3+}$ ion plane, tilts of the MnO$_5$ trigonal bipyramids and unit cell tripling. The results of the analysis are shown in figure 6.18. The $K_3$ mode is dominant as would be expected following our confirmation of the transition pathway to $P6_3cm$. The sharp decrease in $\Gamma^-_2$ at $T^*$ is consistent with our observation of a decrease in polarization at this temperature$^4$.

A critical exponent can tentatively be extracted from the $K_3$ mode data using a weighted power law fit of the form $K_3 = A(T_C - T)^\beta$. The fit was performed over the range $913 \text{K} \leq T \leq 1273 \text{K}$ with the result shown in figure 6.19 giving $\beta = 0.271 \pm 0.003$, $T_C = 1271.5 \pm 0.1 \text{K}$ and $A = 0.135 \pm 0.002$. This exponent could be interpreted as suggesting an order-disorder-type transition but the lack of a high density of data points in our data close to the critical temperature makes reliable conclusions impossible.

That our results were reproducible could be tested by performing the same distortion

$^4$That the $K_1$ mode is the largest for the 1243 K dataset is possibly an artefact of the fact that this is largely due to the Mn $z$-coordinate displacement and Mn has the smallest neutron scattering length of the elements present and so is the least well-determined parameter in the analysis. The better fit of the $P6_3cm$ model at this temperature indicates that the $K_3$ mode is probably also dominant in reality at this temperature.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure618.png}
\caption{The temperature dependence of the displacement modes in YMnO$_3$.}
\end{figure}
mode analysis on the data tabulated by Jeong et al. [160]. They performed powder neutron diffraction experiments at 1000K, 1050K, 1100K and 1200K. The structural parameters they obtained were used by us with AMPLIMODES in a treatment identical to that of our data. The results, shown in figure 6.20, agree well with our data. The reproducibility of the analysis results on independently obtained data on independently prepared samples is a good indication of the intrinsic nature of the behaviour observed.

**Figure 6.19:** The fit of the temperature dependence of the $K_3$ order parameter in YMnO$_3$.

**Figure 6.20:** The temperature dependence of the displacement modes in YMnO$_3$ from our data (open symbols) and the data of Jeong et al. [160] (closed symbols).
However, the detailed conclusions about the two transitions presented here could not have been reached based on data with the limited temperature range measured by Jeong et al.

That the decrease in $\Gamma_2^-$ at $T^*$ leads to a decrease in polarization is confirmed by the calculation of the polarization, $P$. This was performed using a simple ionic model of the form

$$P = \sum_i \frac{\Delta c_i Q_i e m_i}{V},$$

(6.1)

with $c_i$ being the site displacement from the centrosymmetric position in Å, $Q_i$ the ionic charge, $e$ the electron charge, $m_i$ the site multiplicity and $V$ the unit cell volume. The resulting estimate of the temperature dependence of the polarization is shown in figure 6.21. This can be compared with the expected temperature dependence of polarization estimated by integrating the pyroelectric current data reported by Ismailzade and Kizhaev [153] shown in the inset. The pyroelectric current, $I_p$, is related to the time derivative of the polarization by

$$I_p = A \left( \frac{\partial P}{\partial T} \right) \left( \frac{\partial T}{\partial t} \right)$$

(6.2)

where $A$ is the area of the contacts attached to the sample for measurement. It can therefore be used to obtain the temperature dependence of the polarization if the relevant experimental parameters are known. In the case of the data of Ismailzade and Kizhaev, the contact area is not reported meaning that the absolute magnitude of the polarization cannot be calculated. Furthermore, the magnitude and sign of the polarization is not specified for any temperature and therefore it is equally possible that the data could correspond to an increase in polarization with decreasing temperature which would in fact be the expected behaviour for a ferroelectric material.

Despite the uncertainty with regard to the pyroelectric current data of Ismailzade and Kizhaev, the polarization calculated from our neutron diffraction data using the simple ionic model along with the fact that the space group immediately at and below the unit cell tripling transition is $P6_3cm$ indicates that $T_C$ is the same as $T_S$. 
Figure 6.21: The temperature dependence of the polarization in YMnO$_3$ calculated from the atomic positions from the Rietveld refinements. The dotted line is a guide to the eye. The inset shows pyroelectric current data from Ismailzade and Kizhaev [153] integrated to give an estimation of the temperature dependence of the polarization.
6.3 Conclusions

We have successfully managed to resolve the high temperature phases of YMnO$_3$ and the transition path from the aristotype centrosymmetric structure to the polar ambient temperature phase. The resulting phase diagram summarising our results is shown in figure 6.22.

We have identified a potential isostructural phase transition at $T^* \approx 920$K. This scenario is consistent with all reports on anomalies on physical properties around this temperature and may be related to Y-O hybridisation as has been previously suggested from electron density studies.

Our results seem to indicate that the polarization in the $P6_3cm$ phase above $T^*$ is greater than that at ambient temperature below $T^*$. One important avenue of future research resulting from this would be investigation of the possibility of stabilising this higher polarization state over a wider temperature range.

Since publication of our results [140], further work on YMnO$_3$ has been performed. An AFM and TEM study by Chae et al. [166] of vortex-antivortex pairs saw trimerization-ferroelectric domains below $T_S$ and no change in the patterns upon crossing $T^*$ which they took to indicate that $T_S = T_C$ and that $T^*$ is consistent with an isosymmetric transition rather than this being the ferroelectric $T_C$. A study involving dielectric permittivity measurements [167] did not show any anomaly at $T^*$ but the authors ascribe this to the conductivity of YMnO$_3$ being too high at these temperatures [167].

![Figure 6.22: A rough schematic of the thermal phase diagram of YMnO$_3$ determined by our experiment.](image)
Chapter 7

PdCoO$_2$ and PdCrO$_2$ - Itinerant Electron Systems

7.1 Introduction

The two materials investigated in this chapter, PdCoO$_2$ and PdCrO$_2$, have recently attracted interest due to their high conductivities. PdCoO$_2$ is the highest conductivity oxide known at low temperature with an $ab$-plane residual resistivity as low as 0.007 $\mu\Omega$cm [168]. PdCrO$_2$, despite being an antiferromagnet at low temperature, has an in-plane residual resistivity as low as 0.038 $\mu\Omega$cm (this study). The next highest conductivity oxides to date are ReO$_3$ with $\rho_0=0.125 \mu\Omega$cm [169] and SrMoO$_3$ with $\rho_0=0.35 \mu\Omega$cm [170]. These structures are both cubic and therefore structurally and electronically 3D in character in contrast to PdCoO$_2$ and PdCrO$_2$ which are quasi-2D delafossites. The implied anomalously low electron-impurity scattering rates are truly surprising.

The high temperature conductivities of these materials (electron-phonon scattering dominated) are also exceptional. At room temperature they both have lower resistivities than elemental Pd and that of PdCoO$_2$ is only 1.5 times greater than that of Cu. Again these are the lowest resistivities known for an oxide at this temperature. That these materials have such high conductivity in both the high temperature electron-phonon scattering regime and the low-temperature electron-electron/electron-impurity scattering regime is highly unusual.

The fact that both regimes have exceptionally low scattering rates implies that the relevant physics is a property of the quasiparticles themselves. We have therefore set out to investigate the Fermi surface properties of PdCoO$_2$ and PdCrO$_2$. 

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The investigation of the Fermi surfaces of PdCoO$_2$ and PdCrO$_2$ described in this chapter were undertaken by a team including myself, Dr Edward Yelland (University of St Andrews and Edinburgh University) and Dr Clifford Hicks (University of St Andrews). The experiments described, unless otherwise specified, were performed by the whole team. The crystals were provided by Dr Hiroshi Takatsu (Kyoto University, now Tokyo Metropolitan University).

In this chapter I will first introduce the delafossite structure and the context of the study through a discussion of the known properties of both systems. The results of the investigation will then be discussed in turn for PdCoO$_2$ and PdCrO$_2$, with an outlook for possible future measurements.
7.2 The ABO$_2$ Delafossite Family

The delafossite family are ternary oxides with the general formula ABO$_2$. They are named after the mineral CuFeO$_2$ which was first reported by Friedel who named it in honour of the famous crystallographer Gabriel Delafosse [171]. The A-site may be occupied by Cu, Pd, Ag or Pt and the B-site by Al, Sc, Fe, Cr, Co, Ni, Rh, In or a lanthanide ion. The term ‘delafossite structure’ is often used when referring to either of two different polymorphs of ABO$_2$ materials, both of which are shown in figure 7.1. These two polymorphs share the same coordination geometries of A- and B-site ions but the stacking arrangements differ. In both cases the A-site is a 1+ valence ion which is linearly coordinated by oxygen. The B-site ion has valence 3+ and has a distorted octahedral oxygen coordination. A bilayer consisting of a triangular lattice layer of A-site ions and a BO$_6$ edge-sharing layer forms the building block for both structures (see figure 7.1a). The first polymorph, shown in figure 7.1b, is that which is isostructural to the archetype delafossite CuFeO$_2$. This structure has a stacking based upon three such subunits with the A-site ion sheets offset, but unrotated, relative to each other. This is often referred to as the 3$R$ polymorph due to its rhombohedral space group, $R3m$ and the three-layered stacking system. The second polymorph, shown in figure 7.1c, has the A-site sheets rotated 180° to each other with no offset and only two such layers in the stacking pattern. This polymorph is referred to as the 2$H$ structure and has hexagonal space group $P6_3/mmc$. The distribution of the delafossite-type compounds between the two polymorphic structures is shown in figure 7.2. The Pd and Pt delafossite compounds

![Figure 7.1: (a) The delafossite stacking subunit, (b) the 3$R$ and (c) the 2$H$ polymorphs.](image-url)
under study have so far only been synthesised as the 3$R$ polymorph. They are also all metallic [172, 173]. This would be expected as the Pd and Pt electronic configurations for 1+ ions would be predicted as $4d^95s^0$ and $5d^96s^0$ respectively\(^1\). In contrast, the Cu and Ag 1+ ions would be predicted to have $3d^{10}4s^0$ and $4d^{10}5s^0$ configurations leading to a tendency for Cu- and Ag-based delafossites to be insulating or semiconducting\(^2\).

The synthesis of delafossites with $A = \text{Pt, Pd, Ag, and Cu}$ and $B = \text{Cr, Fe, Co, Rh, Al, Ga, Sc, In, and Ti}$ was first reported in 1971 by Shannon et al. [180]. A hydrothermal reaction method was used for all but the Pd-based compounds, which were synthesised by metathesis, and AgCrO$_2$ and AgRhO$_2$ which were flux-grown [181]. Metathetical reactions involve the exchange of constituent parts of two or more chemical species. In the case of the reaction used to synthesise PdCrO$_2$, polycrystalline LiCrO$_2$ which is easily synthesised in air is mixed with Pd powder and PdCl$_2$, sealed in a quartz ampoule and heated at 800 °C for 96h [180, 182]. The reaction occurring is:

$$2\text{LiCrO}_2 + \text{Pd} + \text{PdCl}_2 \rightarrow 2\text{PdCrO}_2 + 2\text{LiCl}$$

\(^1\)The configuration in reality seems to be better represented as $4d^{9-\delta}5s^0$ for Pd due to non-negligible $s-d$ hybridization. This will be discussed in more detail in section 7.3.

\(^2\)Notable exceptions are AgNiO$_2$ which is a semimetal [174-177], CuRh$_{1-x}$Mg$_y$O$_2$ ($0.04 \leq y \leq 0.20$) and Cu$_{1-x}$Ag$_x$Rh$_{1-y}$Mg$_y$O$_2$ ($0.0 \leq x \leq 0.20, 0.04 \leq y \leq 0.20$) which are metallic [178, 179].
Single crystals have only recently been synthesised [182] by following this step with flux growth using NaCl flux and polycrystalline PdCrO₂ powder (obtained by the above metathetical reaction) in an evacuated quartz tube. Crystals of up to $2 \times 3.5 \times 0.3 \text{mm}^3$ have been obtained by using small crystals as seeds for further flux growth.

PdCoO₂ is also synthesised by a metathetical route [181] with the reaction

$$ \text{PdCl}_2 + 2\text{CoO}_2 \rightarrow \text{PdCoO}_2 + \text{CoCl}_2. $$

The reactant powders are ground together and sealed in an evacuated quartz tube. They are then slowly heated to $1000 \, ^\circ\text{C}$ followed by quick cooling to $580 \, ^\circ\text{C}$ [183]. After this, the tube is heated to $700 \, ^\circ\text{C}$ and kept at this temperature for 40h followed by cooling at $40 \, ^\circ\text{C}/\text{h}$ to room temperature. The crystals can be separated from the flux using hot ethanol [184]. An excess of PdCl₂ can be used to obtain larger crystals of up to $2.8 \times 1.3 \times 0.3 \text{mm}^3$ [183].

The resistivities at room temperature of the metallic Pt and Pd-based delafossites are shown in table 7.1 along with those of CuRh₀.₈Mg₀.₂O₂, AgNiO₂, Pd, Cu, Ag and Au for comparison. At room temperature, PdCoO₂ is the most conductive oxide known and the only elemental metals with lower resistivities are Au, Cu and Ag. Both PdCoO₂ and PdCrO₂ have higher conductivities than elemental Pd at room temperature.

As mentioned, both materials investigated in this study, PdCoO₂ and PdCrO₂ belong to the 3R polymorphic group. They are both highly conductive and show a large transport anisotropy. This high anisotropy coupled with such high conductivities is unusual and since no detailed Fermi surface structure was known for these compounds, we performed a de Haas-van Alphen study of both metals.
## Table 7.1: The room temperature resistivities of the Pt and Pd containing delafossites and the highest conductivity elemental metals. The metallic CuRh$_{0.8}$Mg$_{0.2}$O$_2$ and semimetallic AgNiO$_2$ are also included for comparison.

<table>
<thead>
<tr>
<th>Metal</th>
<th>$\rho$ (295 K) ($\mu\Omega$ cm)</th>
<th>$\rho_0$ ($\mu\Omega$ cm)</th>
<th>State</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd*</td>
<td>10.53</td>
<td>0.0200</td>
<td>crystal</td>
<td>[185]</td>
</tr>
<tr>
<td>Cu*</td>
<td>1.69</td>
<td>0.0002</td>
<td>crystal</td>
<td>[185]</td>
</tr>
<tr>
<td>Ag*</td>
<td>1.60</td>
<td>0.0200</td>
<td>crystal</td>
<td>[185]</td>
</tr>
<tr>
<td>Au*</td>
<td>2.21</td>
<td>0.001</td>
<td>crystal</td>
<td>[185]</td>
</tr>
<tr>
<td>PdCoO$_2$</td>
<td>2.6(2)</td>
<td>0.007</td>
<td>crystal (ab-plane)</td>
<td>[168]</td>
</tr>
<tr>
<td>PtCoO$_2$</td>
<td>200</td>
<td>63</td>
<td>sputtered thin film</td>
<td>[173]</td>
</tr>
<tr>
<td>PdCrO$_2$</td>
<td>110</td>
<td>55</td>
<td>sputtered thin film</td>
<td>[173]</td>
</tr>
<tr>
<td>PdRhO$_2$</td>
<td>130</td>
<td>105</td>
<td>sputtered thin film</td>
<td>[173]</td>
</tr>
<tr>
<td>PtCoO$_2$</td>
<td>105</td>
<td>87</td>
<td>sputtered thin film</td>
<td>[173]</td>
</tr>
<tr>
<td>CuRh$<em>{0.8}$Mg$</em>{0.2}$O$_2$</td>
<td>3000</td>
<td>polycrystalline</td>
<td>[179]</td>
<td></td>
</tr>
<tr>
<td>AgNiO$_2$</td>
<td>10000</td>
<td>6500</td>
<td>polycrystalline</td>
<td>[174]</td>
</tr>
</tbody>
</table>

$^*$The $\rho_0$ values quoted are indicative of the values obtained for pure samples of these metals.
7.3 Physical Properties of PdCoO$_2$ and PdCrO$_2$

The extremely high conductivity of PdCoO$_2$ is interesting both from an applications perspective and at the same time conceptually challenging. An oxide with effectively insulating CoO$_2$ layers [187] and a reasonably low conduction electron density of $n \approx 1.62 \times 10^{22}$ cm$^{-3}$ [188] is simply not expected to display such high conductivity. The value of the conductivity is especially surprising when considered in the context of elemental Pd which has an electron density more than four times that of PdCoO$_2$ (for Pd $n \approx 6.8 \times 10^{22}$ cm$^{-3}$) yet a conductivity almost four times smaller. The same general argument holds for PdCrO$_2$ which, despite being magnetic, also has a higher conductivity than elemental Pd. The Fermi surfaces of the highest conductivity elemental metals and those of the oxides SrMoO$_3$ and ReO$_3$ are truly 3D (those of Pd, Ag and ReO$_3$ are shown in figure 7.3 for illustration). The quasi-2D nature of the Fermi surfaces of the non-magnetic metallic delafossites (and the lack of knowledge of the Fermi surface of the antiferromagnetic PdCrO$_2$) hampers comparison between these types of high conductivity material. However, detailed knowledge of the Fermi surfaces should give an increased understanding of the reasons for their exceptional conductivity. The high conductivity has previously been ascribed to the combination of Pd-Pd metallic bonding involving $s-d$ hybridization in the $ab$-plane combined with a high $v_F$ across a large Fermi surface and a long quasiparticle lifetime [187]. However, details of the $k_z$-dependence will be essential for a complete understanding of the highly anisotropic conductivity displayed by both PdCoO$_2$ and PdCrO$_2$.

The basic physical properties of PdCoO$_2$ and PdCrO$_2$ are tabulated in table 7.2. It can be seen that the values for the transport properties are rather similar. Even at low temperature where PdCrO$_2$ is antiferromagnetically ordered the difference in

\textbf{Figure 7.3:} The Fermi surfaces of (a) Pd, (b) Ag and (c) ReO$_3$ calculated using the \textsc{Quantum ESPRESSO} package. The Fermi surfaces of Cu, Au and SrMoO$_3$ are also highly 3D.
conductivity with the non-magnetic PdCoO$_2$ is little more than a factor of five. The resistivities of both compounds in the $ab$-plane and $c$-axis directions are shown in figure 7.4. PdCoO$_2$ has an almost temperature-independent resistivity below 1 K and the low-temperature part of the resistivity does not obey the expected $T^2$ dependence for a Fermi liquid. The low temperature resistivity of PdCrO$_2$, shown in figure 7.5, also deviates from $T^2$ behaviour at low temperature, as may be expected for a magnetically ordered material. Deviation from the $T^2$ temperature dependence does not necessarily indicate non-Fermi liquid behaviour but does indicate a non-trivial suppression or enhancement of one or more scattering channels in the low-temperature limit.

The linear coefficients of the electronic specific heat, $\gamma$, for these two materials are also very similar indicating relatively low effective masses for both compounds. The total specific heats for PdCoO$_2$ and PdCrO$_2$ are shown in figure 7.6, in which the antiferromagnetic transition in PdCrO$_2$ can be seen clearly.
Figure 7.4: The resistivities of single crystal (a) PdCoO$_2$ [183] and (b) PdCrO$_2$ [186].

Figure 7.5: The resistivity of a sample from the batch of PdCrO$_2$ crystals used in the torque experiments. A fit of the data below $T_N$ of the form $\rho = \rho_0 + AT^\alpha$ gives an exponent of $\alpha = 2.89$. 

\[ \rho_{300}/\rho_0 = 244.7 \] 
\[ \rho = \rho_0 + AT^\alpha \] 
\[ \alpha = 2.89 \]
In order to consider the general orbital character of the band structure at the Fermi energy it is instructive to start with the effective ionic valencies from a tight-binding point of view. The Co ions in PdCoO$_2$ have been confirmed by x-ray absorption spectroscopy (XAS) to be in the 3+ valence low-spin ($S = 0$) state [190]. The Cr ions in PdCrO$_2$ are in the 3+ high-spin $d^5$ configuration giving $S = 3/2$ and in both compounds the Pd ion is in a monovalent configuration. The Co/Cr environment is trigonally distorted from the ideal 6-fold octahedral oxygen coordination. This modifies the energy level diagrams due to a changed crystal field, as shown in figure 7.7. The low-spin configuration of the Co ions in PdCoO$_2$ means that the low-lying $a_{1g}$ and $e'_g$ levels are fully filled and therefore the CoO$_2$ layers are effectively insulating. In the case of PdCrO$_2$, the crystal field levels are all half-filled and give ‘local moments’ of $3.95 \pm 0.15 \mu_B$ per Cr$^{3+}$ [189, 191]. The exact magnetic structure is yet to be determined (see section 7.3.1).

Most reports from electronic structure calculations and photoemission experiments have so far reported a dominantly Pd $d$-orbital dominated density of states near the Fermi energy for PdCoO$_2$ [187, 192–196] and PdCrO$_2$ [197]. However, some reports have identified a Pd 5$s$ contribution and discussed the possible occurrence of the 4$d$-5$s$ hybridisation originally predicted by Orgel [198] for 4$d^{10}$ ions [172, 199–203]. This would lead
to the linearly coordinated monovalent Pd ion having an electron configuration approximating to $4d^{9-5}s^{\delta}$ rather than the expected (un-hybridized) $4d^{9}5s^{0}$. The theoretical studies of this hybridization are impeded by the fact that much of the $5s$ orbital contribution would be expected to be found in the interstitial spaces and therefore outside the muffin tin radii used in DFT calculations which again confirms the need for further experimental study of this aspect of the electronic structure of PdCoO$_2$.

The Fermi surface of PdCoO$_2$ has been studied by ARPES [190, 201] and electronic structure calculations [193, 196, 200] but experimental studies probing the entire Fermi surface including the $k_{z}$-dependence have not yet been reported. Only electronic structure calculations and no experimental Fermi surface determinations are available for PdCrO$_2$ and these are limited by the lack of firm knowledge of the magnetic structure.

The first Brillouin zone for the primitive cell of the $R\bar{3}m$ delafossites is shown in figure 7.8. The relevant high symmetry points are labelled. The DFT Fermi surfaces for PdCoO$_2$ and non-magnetic PdCrO$_2$ are shown in figure 7.9. I used the QUANTUM ESPRESSO package.

**Figure 7.8:** The first Brillouin zone of space group $R\bar{3}m$. The relevant high symmetry points $\Gamma=(0,0,0)$, $Z=(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, $F=(0,\frac{1}{2},\frac{1}{2})$, $L=(0,\frac{1}{2},0)$ are labelled using the notation of Bradley and Cracknell [204].

(a) PdCoO$_2$  
(b) PdCrO$_2$

**Figure 7.9:** The Fermi surfaces of (a) PdCoO$_2$ and (b) the non-magnetic chemical unit cell of PdCrO$_2$ calculated using the QUANTUM ESPRESSO package. The inner two sheets are dominantly Cr-based whilst the outer sheet is mainly of Pd-character.
ESPRESSO package [205] to carry out these calculations. PdCoO$_2$ is predicted to have a strongly quasi-2D Fermi surface formed from a single band crossing the Fermi energy. The Fermi surface is large with an area of $\approx 50\%$ of the first Brillouin zone. PdCrO$_2$ on the other hand, ignoring the magnetic order known to exist, is predicted to have a much more 3D Fermi surface composed of three sheets. Two of these sheets are highly 3D whilst one is more quasi-2D in nature although not to the same extent as the single sheet of PdCoO$_2$. It is interesting that even ignoring the reconstruction due to magnetic order that the predicted Fermi surface for PdCrO$_2$ is more 3D whilst that of PdCoO$_2$ is effectively 2D. A DFT calculation of the Fermi surface for a non-collinear magnetic structure of PdCrO$_2$ has been performed by Ong and Singh [197] and the result is shown in figure 7.10. The true magnetic structure is likely more complicated than this (see discussion in section 7.3.1) but even though this calculated Fermi surface is likely to be further reconstructed it can be seen that the Fermi surface of PdCrO$_2$ will have a complicated topology very different from that of PdCoO$_2$.

Figure 7.11 shows the DFT band structure of PdCoO$_2$ calculated using the QUANTUM ESPRESSO suite of codes [205]. This is the basis for the Fermi surface shown in figure 7.9.a). It can be seen that this predicts only one band crossing the Fermi level. It is clear, however, that the two crossing points appear to give rather different effective masses. The density of states for PdCoO$_2$ from the calculations is shown in figure 7.12. The Fermi energy is near a minimum between two peaks in the density of states. This is in agreement with experimental data from photoemission and inverse photoemission (PES/IPES) spectra [194]. The Fermi surface calculated in the same manner, shown in figure 7.9, is very 2D-like and has a rounded hexagonal cross-section in the $ab$-plane. This is in qualitative agreement with the ARPES data reported by Noh et al. [187] shown in figure 7.13 although the edges of the hexagonal shape are noticeably more concave in the electronic structure calculation.

![Figure 7.10: The PdCrO$_2$ Fermi surface calculated by Ong and Singh for the non-collinear $\sqrt{3} \times \sqrt{3}$ magnetic structure [197].](image)

One further detail of note is that although PdCoO$_2$ has been shown to have no superconducting phase down to 15mK [183], there has been a prediction that doping of an additional 0.3 electrons per formula unit will enlarge the Fermi surface to the point that a Van Hove singularity (a non-analyticity in the density of states [206]) will occur and potentially lead to superconductivity [193]. However, based upon the interpretation of our dHvA results the details of this prediction may be in some doubt as will be discussed later.

**Figure 7.11:** The band structure of PdCoO$_2$ from electronic structure calculations.

**Figure 7.12:** The density of states of PdCoO$_2$ from electronic structure calculations.
Chapter 7. PdCoO$_2$ and PdCrO$_2$ - Itinerant Electron Systems

Figure 7.13: The Fermi surface of PdCoO$_2$ from ARPES reported by Noh et al. [187].

7.3.1 The Magnetic Properties of PdCrO$_2$.

Following the first reports of synthesis, crystal structure and electronic properties by Shannon, Prewitt and Rodgers in 1970-1971 [172, 180, 181, 207] and of magnetic properties by Doumerc et al. in 1986 [191], Mekata et al. performed the first investigation of the magnetic structure of PdCrO$_2$ in 1995 [208]. PdCrO$_2$ was almost unstudied after this until the last few years in which significant progress has been made in investigating and understanding the complex and interesting properties of this material including unusual critical behaviour and the unconventional anomalous Hall effect.

For insulators, ignoring the complication of coupling to a charge reservoir, frustrated triangular lattices have been well studied theoretically since the original paper on the Ising-type system by Wannier in 1950 [209]. The 2D Heisenberg system was first investigated by Anderson in 1973 when the ground state was proposed to be of the resonating valence bond (RVB) type [210]. This was followed by the study of phase transitions and proposal of the existence of $Z_2$ vortices by Miyashita and Shiba [211] and Kawamura and Miyashita in the 1984 [212]. The Hamiltonian under consideration (for an insulator) was of the form:

$$\mathcal{H} = J \sum_{(i,j)} \mathbf{S}_i \cdot \mathbf{S}_j, \text{ with } J > 0,$$

(7.1)

with the positive sign of $J$ giving antiferromagnetic exchange interactions. The classical ground state of this system is a 120° ordered structure on three sublattices and theoretical treatment of quantum models by Monte-Carlo simulations give strong evidence that this is the true ground state for this model Hamiltonian [213].
The Hamiltonian for the rhombohedral Heisenberg triangular antiferromagnet is [214]:

\[ H = |J| \sum_{i,\delta} \mathbf{S}_i \cdot \mathbf{S}_{i+\delta} + |J'| \sum_{i,\delta'} \mathbf{S}_i \cdot \mathbf{S}_{i+\delta'} + D \sum_i (S^z_i)^2, \]  
(7.2)

with \(i\) being the site label, \(\delta\) and \(\delta'\) being the translation vector to in-plane and out-of-plane nearest neighbours respectively, \(J\) and \(J'\) denoting the in-plane and inter-plane exchange couplings and \(D\) being the anisotropy constant (here \(D > 0\)).

For a material with \(D = 0\), there is no single-ion anisotropy and so the system is a pure Heisenberg system. For real materials, \(D\) will be non-zero but if it is much smaller than \(J\) and \(J'\) the system will appear Heisenberg-like to low temperatures. Under zero-field conditions, for a positive value of \(D\), the spins are confined to the xy-plane and for negative \(D\) a plane perpendicular to the xy-plane is energetically favoured.

The main interest in PdCrO\(_2\) to date has been in relation to its magnetic structure and properties. The Cr\(^{3+}\) ions in PdCrO\(_2\) are \(S = 3/2\) and occupy a triangular lattice in the \(ab\)-plane. These triangular layers are stacked along the \(c\)-axis in a staggered configuration relative to each other as can be seen in figure 7.14. The spins are presumed to be localised, behaving in a Heisenberg-type manner and are frustrated due to the geometry of their triangular lattice [208]. The Heisenberg nature of the spins is confirmed by the isotropic susceptibility above \(T_N\), shown in figure 7.15. Below \(T_N\), anisotropy is present with \(\chi_{ab} > \chi_c\) and strong frustration is indicated by the magnitude of the frustration parameter \(f = |\theta_W|/T_N = 13\) with \(\theta_W\) being the Weiss temperature obtained by fitting the high-temperature part of the susceptibility [189]. The anisotropy in such a triangular-lattice system indicates a 120° antiferromagnetic ordering with easy-axis anisotropy.

Below \(T_N = 37.5\,\text{K}\), the spins order in a 120° antiferromagnetic structure as shown in figure 7.16. The exact alignment of the spins has not yet been determined but seems...
Figure 7.15: The magnetic susceptibility of single crystal PdCrO$_2$ [182].

Figure 7.16: The spin structure with three Cr$^{3+}$ sublattices of the Heisenberg triangular antiferromagnet with easy-axis anisotropy leading to spins aligning in a plane containing the $c$-axis. The spins on the green sublattice Cr ions are pointing out of the page. The dotted line shows the outline of the chemical unit cell and the solid line the magnetic unit cell. The different colours indicate the three magnetic sublattices.

to be within a plane parallel to the $c$-axis [188]. The 120° structure causes a $\sqrt{3} \times \sqrt{3}$ reconstruction of the unit cell with a 30° rotation. The magnetic unit cell for this ordering and the corresponding Brillouin zone are shown in figure 7.17.

Recently, Takatsu et al. have suggested the existence of a secondary magnetic transition at $\approx 20$ K based upon signatures seen in specific heat and powder neutron diffraction [189]. They also propose that the magnetic structure is somewhat more complicated than
that proposed by Mekata et al. [208] due to the appearance of additional peaks in their spectra with half-integer $l$.

PdCrO$_2$ is a highly conductive but also highly anisotropic material. As discussed previously, the $c$-axis resistivity is always at least 190 times greater than the $ab$-plane resistivity. At the transition into the antiferromagnetic state a clear kink the resistivity is seen and below $T_N$ the resistivity, both of polycrystals and single crystals measured in the $ab$-plane, is of the form $\rho_0 + AT^\alpha$ with $\alpha \approx 3$. This large exponent for the temperature dependence is within the expected range for a magnetic metallic system [215].
7.4 Micro-Cantilever Torque Magnetometry Experiments on PdCoO$_2$ and PdCrO$_2$

The experiments described in this chapter were performed using a custom-designed single-axis rotation probe in a standard Kelvinox-25 dilution refrigerator with a base temperature of $\approx 25$ mK in combination with a 17 T magnet. The samples were mounted on piezo-resistive cantilevers. The cantilevers, commercially available from Seiko with part number PRC120, consist of a pair of levers, one of which holds the sample while the other has an identical resistance to allow its use as a reference lever in the measurement circuit. The angle between the samples and the direction of the applied magnetic field were measured using an angle sensing coil mounted at right angles to the sample platform as shown in figure 7.18. The measurement circuit is based on a Wheatstone bridge. This was balanced prior to measurements and with use of the reference lever allows the collection of extremely high resolution data. More details on the measurement technique are given in chapter 3.

The samples used for this project were grown by Dr Hiroshi Takatsu at Kyoto University using the methods outlined in section 7.2. They are extremely high quality crystals. The best residual resistivities measured by us are 0.007 $\mu\Omega$cm for PdCoO$_2$ and 0.037 $\mu\Omega$cm for PdCrO$_2$ and are significantly lower than the literature values. The PdCoO$_2$ samples had in-plane resistivities of 2.6(2) $\mu\Omega$cm at room temperature and therefore residual resistivity ratios of $\approx 250$ [168]. An example crystal of PdCrO$_2$ can be seen mounted in figure 7.18.

Figure 7.18: Left: The piezo-resistive cantilever and PdCrO$_2$ sample used in the quantum oscillation experiments. The upper lever holds the sample and the lower lever is a reference lever for the measurement. Right: the angle-sensing coil mounted perpendicular to the sample platform.
7.4.1 Micro-Cantilever Torque Results for PdCoO₂

The measurements were carried out over a field range of 4 T to 15 T with a temperature range of 100 mK to 30 K and an angular range of 5.6° to +185° relative to the c-axis.

The PdCoO₂ sample displayed large amplitude quantum oscillations over a large field range. An example raw dataset for 160° is shown in figure 7.19. The inset to this figure shows the high frequency oscillations which are present. Due to the use of the micro-cantilever torque technique, zero angle measurements are not possible. Datasets as a function of temperature and angle were taken. The resulting traces from the angle study are shown in figure 7.20.

The Fourier transform of the θ = 5.6° data as a function of 1/B, shown in figure 7.21 gives three distinct frequencies at 1.2 kT, 29.5 kT and 30.7 kT. The FFTs as a function of angle are shown in figure 7.22 and the FFT peak positions in figure 7.23. The two larger frequencies show a roughly \( \frac{1}{\cos \theta} \) dependence with no oscillations resolvable above \( \approx 60° \). This is consistent with a quasi-2D Fermi surface with the form of open ‘cylinder(s)’ around the c-axis direction. The frequencies at 29.5 kT and 30.7 kT are both likely to come from the single hexagonal cylinder seen by ARPES and predicted by DFT calculations. Since the ARPES data for PdCoO₂ has shown only a single pocket and there is no evidence of additional small pockets from electronic structure calculations, the 1.2 kT frequency is likely to be due to magnetic interaction as it corresponds to the difference between the two larger frequencies\(^3\). This is particularly obvious when comparing the angular dependencies in figure 7.23. We believe this therefore to be the

\[^3\]That the frequency is not due to torque interaction was demonstrated by the measurement of Shubnikov-de Haas oscillations by EAY. The 1.2 kT frequency was still present in these oscillations and therefore is not due to torque interaction.

\[\text{Figure 7.19: An example of the raw quantum oscillation data for PdCoO}_2\]
\[\text{obtained at } \theta = 160^\circ. \text{ The inset is an enlargement of the main curve.}\]
most probable interpretation, especially since the electronic specific heat is already fully accounted for by the masses of the 29.5kT and 30.7kT frequencies as will be discussed below.

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure7.20}
\caption{The raw quantum oscillation data for the angular-dependent dataset for PdCoO$_2$.}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure7.21}
\caption{The Fourier transform of the $\theta = 5.6^\circ$ data for PdCoO$_2$.}
\end{figure}
Figure 7.22: The angle dependence of the Fourier transform of the PdCoO$_2$ quantum oscillations. Traces are offset such that the 0kT intercept corresponds to the measured angle.

Figure 7.23: The angle dependence of the PdCoO$_2$ quantum oscillation frequencies. It can be seen that the 1.2kT frequency has the angular dependence expected for a difference frequency.
The cyclotron masses of the quasiparticles in the different orbits can be extracted from the temperature dependence of the quantum oscillation amplitudes by fitting to the Lifshitz-Kosevich formula for the temperature dependence of the amplitude, $R_{LK}$, shown in equation 7.3 (details in chapter 2). In the equation $n$ is the harmonic index, $m^*$ is the cyclotron mass in units of $m_e$ and all other variables and constants have their usual meaning.

$$R_{LK} = \frac{C n m^* T / B}{\sinh \left( C n m^* T / B \right)}, \quad C = \frac{2\pi^2 k_B m_e}{\hbar e} \approx 14.69 \, \text{T/K}$$  \hspace{1cm} (7.3)

The fitting of the three frequencies, shown in figure 7.24, gives effective masses of $2.21(8) \, m_e$, $1.29(4) \, m_e$ and $1.41(6) \, m_e$ for the $1.2 \, \text{kT}$, $29.5 \, \text{kT}$ and $30.7 \, \text{kT}$ frequencies respectively. For a sum/difference frequency the mass obtained from the temperature dependence of the amplitude would be expected to be approximately the sum of the masses of the component frequencies and the mass for the $1.2 \, \text{kT}$ frequency is in rough agreement with this expectation. For a quasi-2D system the Lifshitz-Kosevich fit also allows calculation of the Sommerfeld coefficient, $\gamma$:

$$\gamma = \frac{\pi N_A k_B^2 A}{3 \hbar^2} m^*, \quad (7.4)$$

where $A$ is the cross-sectional area of the unit cell in the hexagonal setting and all other symbols have their standard meanings. This equation gives $\gamma \approx 1 \, \text{mJmol}^{-1}\text{K}^{-2}$ assuming
a single Fermi surface sheet with effective mass \( m^* = (m_{29.5kT} + m_{30.7kT})/2 \). This compares very well with the experimentally determined value of \( 1.28(20) \text{mJmol}^{-1}\text{K}^{-2} \).
Fermi Surface Parameterization

Comparison with the extremal orbit predictions of the electronic structure calculations gave good general agreement with our data at very low angle but unsatisfactory agreement at higher angle. This indicated that the $k_z$ dependence of the Fermi surface topology given by the calculation was not a good match for the true dependence. To try to resolve this, two forms of Fermi surface parameterization were investigated for the PdCoO$_2$ data. These will be discussed in turn.

Tight-binding Method

The first method is a band structure based tight-binding model fit to the data. A basic tight-binding model is used to fit the experimental data to try to resolve the discrepancy between the DFT Fermi surface and the experimentally derived areas. The model is of the form

$$
\epsilon(k) = - \left[ \sum_{nn} t_{nn} \cos(k.r) + \sum_{nnn} t_{nnn} \cos(k.r) + \sum_{z} t_{z} \cos(k.r) + \sum_{zz} t_{zz} \cos(k.r) \right].
$$

(7.5)

In this model, the dispersion $\epsilon(k)$ is described by a sum of cosines with transfer integrals $t_{nn}$, $t_{nnn}$, $t_{z}$, $t_{zz}$ for the nearest neighbour in-plane, next-nearest-neighbour in-plane, nearest neighbour out-of-plane and next-nearest-neighbour out-of-plane hopping respectively. The intersite distances are denoted by $r$ with $k$ representing the wavevector in momentum space. Since the observed Fermi surface shape (at half filling) was fitted and not the Fermi velocities only the relative values of the transfer integrals are important. $t_{nn}$ was therefore fixed to 1. In order to carry out the fitting procedure, using Matlab, a single step consisted of calculating the tight-binding Fermi surface for half-filling, extracting the extremal orbits (using a Matlab code by Dr E A Yelland) and then iterating this. The process is illustrated in figure 7.25. The parameters for the converged fit were $t_{nnn} = 0.3531$, $t_{z} = 0.1237$, $t_{zz} = 0.1369$. The resulting Fermi surface is shown in figure 7.26. It can be seen that the general shape is qualitatively very similar to that obtained from electronic structure calculations. The converged fit results for the angle dependence of the frequencies are shown in comparison to the experimental data in figure 7.27. It can be seen that the general angle dependence and frequency multiplicities are reasonably well reproduced.
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Figure 7.25: The tight-binding model fitting procedure for PdCoO$_2$.

Figure 7.26: The Fermi surface given by the tight-binding model fit for PdCoO$_2$.

Figure 7.27: The angle dependence of the quantum oscillation frequencies of PdCoO$_2$ for the FFT range 12.5T to 15T (blue circles) and those obtained from the tight-binding model (black dots).
Cylindrical Harmonics Method

The second method is not band structure based but a geometric parameterization in terms of cylindrical harmonics. This uses a set of symmetry-allowed cylindrical harmonics to describe a quasi-2D Fermi surface. The harmonics are of the form

$$k_F(\phi, k_z) = \sum_{\mu, \nu} k_{\mu, \nu} \cos \nu \phi \cos \nu dk_z$$  \hspace{1cm} (7.6)

with $\phi$ being the azimuthal angle, $k_z$ the $z$-component of the wavevector and $d$ being the interlayer distance. The magnitudes of the $k_z$-independent warpings $k_{00} = 0.040(3) \text{Å}^{-1}$ and $k_{12,0} = 0.007(2) \text{Å}^{-1}$ were estimated from ARPES data [187] as these are not obtainable from dHvA. Adjustment by eye of the remaining terms $k_{00}$, $k_{01}$, $k_{02}$ and $k_{31}$ to give the best agreement with the experimental data was used by Dr C. W. Hicks [168]. The values obtained for the parameters were $k_{00} = 0.9538(3) \text{Å}^{-1}$, $k_{01} = 0.0107(3) \text{Å}^{-1}$, $k_{02} = -0.0009(3) \text{Å}^{-1}$ and $k_{31} = 0.0010(3) \text{Å}^{-1}$.

A comparison between the angle dependencies of the frequencies from the model and the experimental data is shown in figure 7.28. The resulting Fermi surface from these parameters is shown in figure 7.29.

Interestingly, the Fermi surface obtained from this parameterization shows a $k_{01}$-dominated shape with almost no visible contribution from $k_{31}$. This is in contrast to previous LDA studies (and also the tight-binding parameterization) which show clear bulges near the $F$-points of the Brillouin zone. This dominant $k_{01}$ warping contribution would be consistent with a significant $5s$ contribution from Pd to the hopping.

The analysis in terms of cylindrical harmonics indicates that overall the Fermi surface is less warped as a function of $k_z$ and has a much higher Pd $5s$ contribution that previously

**Figure 7.28:** The cylindrical harmonics comparison to the dHvA data by Dr C.W. Hicks for PdCoO$_2$ [168]. The data point shading indicates the relative amplitudes of the frequencies.
thought. Further investigation by Dr. E. A. Yelland led to the discovery that an on-site potential for the Co ions of $\approx 5\text{eV}$ gave a reduction in the $k_{31}/k_{01}$ ratio and the effective masses leading to much improved agreement between the LDA Fermi surface and that derived from the experimental data [168].
7.4.2 Results for PdCrO$_2$

The torque measurements on PdCrO$_2$ show very large amplitude quantum oscillations to surprisingly high temperature. An example trace for $\theta = 5.6^\circ$ is shown in figure 7.30 with the high frequency oscillations shown in the inset. The oscillations can be seen at fields as low as 4T and clearly have multiple frequency components.

During the experiment at certain angles a previously unknown first order phase transition with large field hysteresis was found. The known boundary and characteristics of this phase transition will be discussed in the following section with a full analysis of the quantum oscillation data as a function of temperature and field being described in section 7.4.2.2.

![Figure 7.30](image)

**Figure 7.30:** An example of the raw quantum oscillation data for PdCrO$_2$ at 0.5K, $\theta = 5.6^\circ$. The inset is an enlargement of the main curve.

7.4.2.1 First Order Phase Transition

A phase transition was seen at certain angles during the experiments which had not previously been reported. In figure 7.31, the up-sweep and down-sweep raw data for $\theta = 69.6^\circ$ is shown with a $B^2$ background intrinsic to the torque technique subtracted. The clear hysteresis between the up- and down-sweep is indicative of a first order phase transition. At this angle, the hysteresis extends over more than 7T. Figure 7.32 shows the transition in the raw data (with no background subtraction) at various angles measured. The transition is seen for applied field angles above 50$^\circ$ and below $\approx 130^\circ$ relative to the $c$-axis (with 0$^\circ$ being $H \parallel [001]$ and 180$^\circ$ being $H \parallel [00\bar{1}])$, corresponding to angles within $\pm 40^\circ$ of the $ab$-plane at 0.7K. There is a large hysteresis in torque associated with the transition although the hysteresis in magnetization would be expected to be
small. Without knowledge of the magnetic structure and therefore spin orientation, reliable extraction of the magnetization from the measurements is not possible. Since the magnetic structure is thought to be almost coplanar in a plane containing the c-axis in PdCrO$_2$, this transition may be associated with a rotation of the majority-spin plane or a small change in the orientation of the $ab$-plane component. A schematic diagram of the phase transition as a function of angle is shown in figure 7.33. The transition field has been estimated by the position of the maximum difference in the torque between the up-sweep and down-sweep.
Intriguingly, the transition field seems to go towards 0 T at $\approx 130^\circ$ although the size of the hysteresis is very difficult to measure as the magnitude decreases. It is possible that the transition does not approach zero but curves round at higher angles and starts moving to higher fields again. In the case that the transition field did go to zero tesla, the low-field phase and high-field phase would be the same phase (with no intrinsic symmetry difference), since at 0 T all angles are identical. Furthermore, it has to be conjectured that the latent heat of the transition has to go to zero when $H_C$ approaches 0 T at $\theta \approx 130^\circ$. The relation to a quantum critical endpoint is the subject of ongoing research. In particular a detailed study of the low-field region which is shaded grey in figure 7.33 is necessary in order to determine the exact evolution of the phase transition. Two central observations would be the behaviour of the associated latent heat and the transition temperature approaching $H = 0$ T. The detailed thermodynamic study of this phase transition would be an ideal project for the 3-axis vector magnet system available in the group of Prof. A. P. Mackenzie.

The existence of this transition has crucial consequences for the quantum oscillation measurements. It can be seen in figure 7.33 that data taken above $\approx 80^\circ$ will be in the high field state for a large field range and so FFTs over appropriate ranges for $\theta \gtrsim 80^\circ$ would give details of the high-field state. Conversely, below $\approx 50^\circ$ the transition field is greater than 15 T therefore allowing investigation of the low-field state for $\theta \lesssim 50^\circ$. 

Figure 7.33: A schematic of the transition field of the first order phase transition seen in PdCrO$_2$ as a function of angle. The low-field area shaded grey requires further detailed measurements to determine exactly how the phase transition evolves.
For angles between 53° and 78° the datasets have a large enough field range on either side of the transition to allow comparison of the FFTs in the high- and low-field states. The details of the FFTs will be analysed in section 7.4.2.2, in the current section general similarities/differences between the frequencies in the low-field and high-field states will be discussed.

The FFTs for the low- and high-field states are shown in figure 7.34 for the down-sweep and 7.35 for the up-sweep datasets for angles where both are accessible. Between the down-sweep and up-sweep data there is good qualitative agreement in the change in the frequencies on going from the low-field to the high-field state and vice versa. The differences in sweep rate (0.15-0.4 T/min for the up-sweep and 0.012-0.024 T/min for the down-sweep) will account for some of the quantitative differences. The frequencies, and therefore extremal orbits, on the high field side are slightly larger in general than on the low-field side. A greater number of frequencies are also seen on the high-field side although it is possible that this is largely due to effects such as enhanced amplitudes of frequencies which are below the noise level on the low-field side or enhanced

![Figure 7.34](image-url)
Figure 7.35: The difference, for the up-sweep datasets, between the FFTs for the high-field state (blue) and low-field state (green) of PdCrO$_2$ for various angles.

torque/magnetic interaction effects at the higher fields.

Whilst it is not possible to reach firm conclusions based upon the limited data available, it seems that there is no dramatic Fermi surface reconstruction at the transition. The small quantitative changes in the frequencies near 1.5 kT at 53.8° could either be due to a small change in the shape/size of the small pockets that these frequencies derive from or to a non-linear change in magnetization. Without further detailed knowledge of $M$ it is impossible to tell. Overall the fact that the Fermi surface does not change substantially is consistent with the previous observation that the high-field state and low-field state should have the same symmetry (i.e. Brillouin zone).

The FFTs as a function of angle from the low-field state in this intermediate angle range are shown in figure 7.36 and those from the high-field state in figure 7.37. The frequencies follow an angle dependence which shows small but increasing deviations from a quasi-2D $\frac{1}{\cos \theta}$ dependence with $\theta$ tending towards $\theta = 90^\circ$. In particular the presence of quantum oscillations at 78° shows a less strongly quasi-2D character than for PdCoO$_2$. 
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**Figure 7.36:** The FFTs in the low-field state of PdCrO$_2$ as a function of angle.

**Figure 7.37:** The FFTs in the high-field state of PdCrO$_2$ as a function of angle.
7.4.2.2 Quantum Oscillation Analysis

The temperature dependence of the raw oscillation data for $\theta = 5.6^\circ$ is shown in figure 7.38 and the angle dependence in the high-field and low-field states at $T=0.7$ K in figure 7.39 (the intermediate angle range where quantum oscillations in both states are seen have been discussed previously in section 7.4.2.1.

Figure 7.40 shows one particular Fourier transform of the $\theta = 5.6^\circ$, 0.1 K data. It can be seen that there are a large number of peaks with very close spacing. Harmonics of the fundamentals are seen up to $\approx 60kT$ (not shown). The Fermi surface would be expected to be more complicated than that of PdCoO$_2$ from the results of the electronic structure calculations and due to the magnetic structure. However, a large number of the observed frequencies in the spectra are most likely due to sum/difference frequencies from magnetic and torque interaction rather than the complicated Fermi surface structure.

![Figure 7.38: The temperature dependence of the quantum oscillations seen in PdCrO$_2$ at $\theta = 5.6^\circ$.](image)
The main peaks in figure 7.40 are labelled with those identified as fundamental frequencies being $\alpha, \beta, \gamma, \delta, \epsilon$ and $\zeta$. The $\alpha$ and $\beta$ frequencies at 0.81kT and 0.87kT are very closely spaced and correspond to small extremal areas of $\approx 4.4\%$ and $4.7\%$ of the maximum Brillouin zone area possible with a 120° antiferromagnet-based magnetic structure (discussed in section 7.3.1 and shown in figure 7.17). The $\gamma$ and $\delta$ frequencies at 3.5kT and 10.4kT correspond to $\approx 19\%$ and $\approx 56\%$ of the Brillouin zone area respectively. The frequencies labelled $\epsilon$ and $\zeta$ are tentatively assigned as magnetic breakdown orbits as the areas corresponding to these frequencies are approximately 1.5 times that of the largest possible magnetic Brillouin zone ($\approx 1.78 \text{ Å}^{-2}$, which is $1/3$ the cross sectional area of the non-magnetic Brillouin zone$^4$).

The angle dependence of the Fourier transforms of the oscillations in the high-field and low-field states is shown in figure 7.41. The deviations from a $\frac{1}{\cos \theta}$ dependence

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$^4$The more complicated magnetic structure indicated by neutron diffraction would back-fold this Brillouin zone and therefore lead only to a decrease of the Brillouin zone area.
Figure 7.40: The Fourier transform of the quantum oscillations seen in PdCrO$_2$ at $\theta = 5.6^\circ$, 0.1 K. The fundamental and sum/difference frequencies are labelled.

(a) High-field state

(b) Low-field state

Figure 7.41: The FFT of data from the torque measurements of PdCrO$_2$ at 0.7 K. The angle labels refer to the angle from the $c$-axis.
can be seen more clearly when the amplitudes are plotted as a function of $F \times \cos \theta$ as in figure 7.42 although the large number of closely spaced frequencies make the trends difficult to follow. The angle dependence of the PdCrO$_2$ frequencies deviates further from the $F/\cos \theta$ form than the angle dependence of PdCoO$_2$. This, combined with the observation of quantum oscillations to higher angles indicates that PdCrO$_2$ is less strongly quasi-2D than PdCoO$_2$. The lower frequencies are seen to angles as high as $78^\circ$ which is a clear indication that the Fermi surface is not strongly quasi-2D. Though the anisotropy in the resistivity is still extremely large for PdCrO$_2$, the fact that the CrO$_2$ layers sandwiched in between the Pd layers are not expected to be insulating could account for the less strongly quasi-2D nature of the Fermi surface of PdCrO$_2$ compared to PdCoO$_2$.

The identification of peaks as sum/difference frequencies due to torque/magnetic interaction can be supported by examination of the effective masses obtained from Lifshitz-Kosevich fits of the temperature dependences of the amplitudes of the peaks with temperature. The results of the fits of the main frequencies are presented in figure 7.43. The fundamental and sum/difference frequencies along with the effective masses determined from the LK fits are tabulated in table 7.3. It can be seen from this table that the interaction frequencies have masses which are of the order of the sum of the masses of the component frequencies as expected for torque/magnetic interaction frequencies.

![Figure 7.42: The FFT of data from the torque measurements of PdCrO$_2$ at 0.7 K plotted as a function of $F \times \cos \theta$. For a quasi-2D Fermi surface the peaks would be angle-independent using this representation. It can be seen that for PdCrO$_2$ there is a deviation from linearity which is largest near $\theta = 90^\circ$. The angle labels refer to the angle from the c-axis.](image-url)
Chapter 7. PdCoO$_2$ and PdCrO$_2$ - Itinerant Electron Systems

Figure 7.43: The temperature dependence of the quantum oscillations with Lifshitz-Kosevich formula fits seen in PdCrO$_2$ at 5.6°.

<table>
<thead>
<tr>
<th>Fundamental Frequency</th>
<th>Frequency (kT)</th>
<th>$m^*(m_e)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$</td>
<td>0.81</td>
<td>0.28(1)</td>
</tr>
<tr>
<td>$\beta$</td>
<td>0.87</td>
<td>0.32(1)</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>3.5</td>
<td>0.65(2)</td>
</tr>
<tr>
<td>$\delta$</td>
<td>10.4</td>
<td>1.10(1)</td>
</tr>
<tr>
<td>$\epsilon$ (MB)</td>
<td>26.6</td>
<td>1.18(5)</td>
</tr>
<tr>
<td>$\zeta$ (MB)</td>
<td>27.3</td>
<td>1.13(3)</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Interaction Frequency</th>
<th>Frequency (kT)</th>
<th>$m^*(m_e)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha + \gamma$</td>
<td>4.3</td>
<td>0.96(4)</td>
</tr>
<tr>
<td>$\delta - \alpha$</td>
<td>9.7</td>
<td>1.23(2)</td>
</tr>
<tr>
<td>$\delta + \alpha$</td>
<td>11.3</td>
<td>1.16(4)</td>
</tr>
<tr>
<td>$\delta + \beta$</td>
<td>11.4</td>
<td>1.17(5)</td>
</tr>
</tbody>
</table>

Table 7.3: The main frequencies and the effective masses obtained from LK fits for PdCrO$_2$. The label MB denotes the frequency being assigned as a probable magnetic breakdown frequency.
The effective masses are relatively light and are lighter than those of the non-magnetic PdCoO₂.
7.5 Conclusions and Further Work

High quality data has been obtained over a large angular range for both PdCoO$_2$ and PdCrO$_2$. The Fermi surface of PdCoO$_2$ has been successfully parameterized. Insight into the high conductivity and anisotropy seen in this material has been gained by the resolution of the details of the $k_z$-dependent warping. Information about the electronic structure of PdCrO$_2$ has been extracted from the data showing a complex Fermi surface with a more 3D character than that of PdCoO$_2$. Furthermore, an as-yet unreported first-order transition in PdCrO$_2$ has been discovered.

The Fermi surface of PdCoO$_2$ has been resolved and although it is quasi-2D as expected, the experimentally determined $k_z$-dependent warping shows interesting differences in detail to that predicted by electronic structure calculations. The results of the angular-dependent quantum oscillation study indicate that the Pd 5$s$ states play a more important role than has generally been assumed in the transport properties of PdCoO$_2$. This work therefore provides the basis and motivation for more detailed investigations of the Pd 5$s$ contribution to these materials.

The quantum oscillation data for PdCrO$_2$ show a different picture to the data for PdCoO$_2$. Whilst the exact Fermi surface has not yet been determined for PdCrO$_2$ the data show that it is more 3D in character than that of PdCoO$_2$. This is unsurprising considering that the CrO$_2$ layers are not expected to be insulating. This is in contrast to PdCoO$_2$ in which there are effectively insulating CoO$_2$ layers sandwiched between the metallic Pd layers. Intriguingly the data indicate that the first order transition discovered in PdCrO$_2$ as a function of angle and field does not involve a significant Fermi surface reconstruction. This leaves open the possibility that the transition is isostructural with respect to crystal structure and due to a subtle change in the magnetic structure. This work is therefore a starting point for more thorough investigations of the nature of this transition and more detailed mapping of the phase boundary. Due to the complex angular dependence the 3-axis vector magnet system in St Andrews would be uniquely suited for the latter part of this investigation. Additionally, a full determination of the Fermi surface of PdCrO$_2$ should be attainable with the combination of magnetic neutron diffraction, electronic structure calculations and further quantum oscillation measurements.

Further work in the directions outlined above along with a determination of the electronic and thermal transport properties of these materials is ongoing in the group of Prof. Mackenzie. Further angular quantum oscillation studies of PdCrO$_2$ are currently being performed by Dr E. A. Yelland.
Chapter 8

Conclusions and Further Work

In this thesis four materials (or classes of materials) have been investigated in various degrees of detail. The studies have also provided a variety of results. Some old problems have been solved such as the resolution of the nature of the high-temperature phase transitions of YMnO$_3$. Surprising results have been uncovered in the high-temperature phases of BiFe$_{0.7}$Mn$_{0.3}$O$_3$ and also in the details of the Fermi surface of PdCoO$_2$ and the discovery of a first-order phase transition of PdCrO$_2$. Progress has been made in materials synthesis development and the discovery of new phases in the quaternary barium orthotellurates.

Overall these projects have given a good overview of some of the important areas of materials science and have also provided a firm foundation for future work. The techniques used are essential for the understanding of known systems and also for the synthesis and investigation of novel materials. Further studies of the possible isostructural transition of YMnO$_3$ will hopefully include physical property measurements to clarify the exact nature of the transition. Local structure measurements such as XANES (x-ray absorption near edge structure) and neutron PDF (pair distribution analysis) would be most helpful both in this case and in the high-temperature phases of BiFe$_{0.7}$Mn$_{0.3}$O$_3$. Further investigation by Dr C. W. Hicks and Dr E. A. Yelland of the delafossite materials PdCoO$_2$ and PdCrO$_2$ is currently ongoing and will hopefully give more understanding of the electronic structure of these materials and the first-order phase transition discovered in PdCrO$_2$. The main project that I will carry forward is that on the quaternary barium orthotellurates. The high-resolution neutron diffraction measurements and low-temperature investigations shortly to be performed should take the project to the next stage of understanding. The neutron diffraction will clarify the details of the structures and confirm their space groups and also give information on the local coordination geometries of the magnetic ions. The low-temperature magnetic measurements will extend
the phase diagram to high field and also give further information about the anisotropy present. These studies would not be possible without the knowledge of the techniques gained during the work described in this thesis.
Appendix A

Appendix: Symmetry and Space Group Notation

Here the basic nomenclature of space groups will be briefly discussed to allow clarification of the various space groups discussed in this thesis. More detailed discussions of space group symmetry and nomenclature can be found in, for example, Burns and Glazer [7].

Space group symbols are composed of a combination of a symbol indicating the type of lattice centring followed by symmetry labels indicating symmetry elements occurring for certain directions (or planes perpendicular to these directions) dependent upon the crystal system. The lattice centring symbols are $P$ for primitive (i.e. non-centred), $A$ for $A$-centred (centred on the face perpendicular to the $a$-axis), $B$ for $B$-centred, $C$ for $C$-centred, $F$ for face-centred, $I$ for body-centred and $R$ for rhombohedral centring.

The symmetry elements are written in Hermann-Mauguin notation as discussed in section 2.3.2 for the case of point groups. The operations in table 2.1 are also relevant for space groups. However, space groups have additional translational symmetry elements: glide planes and screw axes. A glide plane is a combination of a reflection and a translation, and a screw axis a combination of a rotation and translation.

Glide planes are represented by the symbols $a$, $b$ and $c$ for glides along the respective crystallographic axes, $n$ for a diagonal glide across a unit cell face and $d$ for a glide along the body diagonal of the unit cell. Screw axes are represented by $N_n$ where $N$ is the order of the axis (i.e. 2 for a 2-fold rotation axis) and the fraction $n/N$ gives the fraction of the unit cell vector translated for every fraction of a rotation.

As an example, $Pbnm$ is an orthorhombic space group (an alternative setting of $Pnma$, no. 62). The symbol indicates that the unit cell is primitive ($P$) with a $b$-glide plane...
perpendicular to the $x$-axis, a $n$-glide plane perpendicular to the $y$-axis and a mirror plane perpendicular to the $z$-axis.

An example of a tetragonal space group is $I4/mmm$. This is body-centred ($I$) with a mirror plane perpendicular to the four-fold axis ($4/m$), and two further mirror planes perpendicular to $[1,0,0]/[0,1,0]$ and $[110]$.

Finally, an example of a space group containing a screw axis is the hexagonal space group $P6_3cm$. This is primitive with a $6_3$ screw axis along the $z$-axis, a $c$-glide plane perpendicular to the $x$-axis and a mirror plane perpendicular to the long diagonal of the $ab$-plane.
Appendix B

Appendix: Anisotropic Peak Broadening in the α-phase of BiFe$_{0.7}$Mn$_{0.3}$O$_3$

![Graph showing FWHM vs. d-spacing for different phases and samples.]

**Figure B.1:** The full-width half-maximum for the α-phase of BiFe$_{0.7}$Mn$_{0.3}$O$_3$ (red) showing the variation for different reflections. This is indicative of anisotropic broadening. The pure BiFeO$_3$ refinement with anisotropic broadening terms refined is shown in purple and it can be seen that there is negligible anisotropic broadening in this case. The full-width half-maxima for the β-phase of BiFe$_{0.7}$Mn$_{0.3}$O$_3$ (blue, pink) and YMnO$_3$ (green) are also shown to illustrate the t-dependence for samples with negligible anisotropic broadening.
Appendix B. Appendix: Anisotropic Peak Broadening in the \(\alpha\)-phase of \(\text{BiFe}_{0.7}\text{Mn}_{0.3}\text{O}_3\)

The effect of what is assumed to be anisotropic strain in the \(\alpha\)-phase can be seen in the variation of the FWHM of reflections. The FWHM values from Rietveld refinements can be seen in figure B.1. Since the sample was quenched after synthesis the appearance of some strain would be expected. The FWHM values from the refinements are dependent, however, on the structural parameters and so model-independent single-peak fits of the (2,0,-4) and (2,0,2) peaks were performed using the software package CMPR [216] to obtain an accurate FWHM. These are shown in figures B.2 and B.3. The fits gave FWHM(2,0,4)=0.01142(11) Å and FWHM(2,0,2)=0.00470(7) Å for BiFe\(_{0.7}\)Mn\(_{0.3}\)O\(_3\) at 423K.

A refinement in space group \(R3c\) using the empirical tensor representation for strain gave a much improved fit with \(R_{wp}=0.0286\), \(\chi^2=1.867\) for 42 variables. The refined values for the anisotropic broadening parameters were \(\gamma_{1c}=181(11)\), \(L_{11}=1.66(36)\), \(L_{12}=2.08(32)\), \(L_{13}=-0.093(63)\) and \(L_{23}=1.674(78)\). However, when using the better-founded Stephens formalism a satisfactory fit was not obtained. This may imply that the broadening is not consistent with rhombohedral symmetry or it may simply be that the \(hkl\)-dependent broadening is not due to microstrain but some other parameter such as compositional

![Figure B.2: The single-peak fit for the (2,0,-4) peak of the \(\alpha\)-phase of BiFe\(_{0.7}\)Mn\(_{0.3}\)O\(_3\) at 423K. The FWHM obtained is 0.01142(11) Å.](image-url)
Appendix B. Appendix: Anisotropic Peak Broadening in the α-phase of BiFe$_{0.7}$Mn$_{0.3}$O$_3$

variation. A refinement in Cc, the monoclinic subgroup of R3c was performed to investigate the possibility that the anisotropic broadening was due to unresolved peak splitting. This resulted in a satisfactory refinement with the Stephens model giving $R_{wp}=0.0248$, $\chi^2=1.412$ for 56 variables. The refined values for the Stephens parameters were $S_{400}=193(12)$, $S_{040}=12(1)$, $S_{202}=68(5)$, $S_{022}=40(2)$, $S_{301}=176(12)$, $S_{103}=18(2)$, $S_{121}=31(1)$ with mixing parameter $\eta = 0.772(15)$. A comparison of the refinements can be seen in figure B.4 and the structural parameters of the Cc model are tabulated in table B.1.

It is not possible to conclude based upon this evidence whether the true symmetry is monoclinic or rhombohedral without further detailed study.
Appendix B. Appendix: Anisotropic Peak Broadening in the α-phase of BiFe$_{0.7}$Mn$_{0.3}$O$_3$

Figure B.4: A comparison between the $R3c$ model with the empirical tensor description of the anisotropic microstrain (blue) and the $Cc$ model (green) with the Stephens description of the anisotropic microstrain.

Space Group: $Cc$, No. 9

$R_{wp}=0.0248$, $\chi^2=1.412$, 57 var.

$a = 9.7881(4)$ Å, $b = 5.5869(3)$ Å, $c = 13.8582(4)$ Å

$\beta = 160.7478(2)^\circ$

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<tr>
<th>Site</th>
<th>Wyckoff Position</th>
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<th>y</th>
<th>z</th>
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<th>Occ.</th>
</tr>
</thead>
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<td>0.001(3)</td>
<td>0</td>
<td>0.0220(7)</td>
<td>1</td>
</tr>
<tr>
<td>Fe</td>
<td>4a</td>
<td>0.005(6)</td>
<td>0.003(4)</td>
<td>0.230(4)</td>
<td>0.0166(10)</td>
<td>0.7</td>
</tr>
<tr>
<td>Mn</td>
<td>4a</td>
<td>0.005(6)</td>
<td>0.003(4)</td>
<td>0.230(4)</td>
<td>0.0166(10)</td>
<td>0.3</td>
</tr>
<tr>
<td>O1</td>
<td>4a</td>
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<td>0.769(2)</td>
<td>0.523(4)</td>
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Table B.1: The structural details from the refinement of BiFe$_{0.7}$Mn$_{0.3}$O$_3$ in space group $Cc$ at 523 K.
Appendix C

Appendix: Low Temperature Structural Study of BiFeO$_3$ by Powder Neutron Diffraction

The data in this appendix were collected between room temperature and 7 K on GEM at ISIS to investigate the low-temperature crystal and magnetic structures of BiFeO$_3$.

The lattice parameters of the $R3c$ structure as a function of temperature are plotted in figures C.1 and C.2. The error bars from the Rietveld refinements are within the size of the data points. Small anomalies may be identified at $T \approx 35$ K and $T \approx 170$ K. These anomalies are also visible in the unit cell volume plotted in figure C.3.

Unfortunately, the instrumental resolution was not high enough to see any change in the magnetic structure. Further work will be required to investigate these anomalies in more detail.
Figure C.1: The temperature dependence of the $a$-axis parameter of BiFeO$_3$.

Figure C.2: The temperature dependence of the $c$-axis parameter of BiFeO$_3$. 
Figure C.3: The temperature dependence of the unit cell volume of BiFeO$_3$. 
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