Relationship of Structural and Electronic Properties in Transition Metal Oxides

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A Thesis submitted for the Degree of Doctor of Philosophy, Department of Chemistry
Abstract

This thesis is an investigation into the relationship between the structural and electronic properties of quaternary manganese oxides, of the spinel structure, with general formula $A^{+}[B_xMn^{IV}_{2-x}]O_4$ ($x = 0.5, 1$; $A = Li, Cu$; $B = Mg^{II}, Ni^{II}, Cr^{III}, Fe^{III}, Co^{III}, Rh^{III}$) and the series $Cu_{1-y}Ni_{0.5+y}Mn_{1.5}O_4$ ($0 \leq y \leq 1$). Particular emphasis is placed on the interplay between cationic distribution, and sublattice ordering, and the observed magnetic and magnetotransport properties.

Colossal magnetoresistance CMR, a large change in the electrical resistance upon application of a magnetic field, is associated with a paramagnetic-ferromagnetic transition. It is usually found in mixed valence $Mn^{(III)}/Mn^{(IV)}$ perovskites and considered with a double-exchange mechanistic framework. The mechanism was shown to be more complex by the CMR pyrochlore, $Tl_2Mn_2O_7$ which contains manganese in the integral oxidation state, four, precluding double-exchange. The array of B cations in the spinel structure $AB_2O_4$ can be described as a pyrochlore network, thus spinels with magnetic ions solely on the B sites can be considered to have a pyrochlore magnetic network.

This offers an interesting analogy with the CMR pyrochlore thallium manganate.

This thesis reports the pursuance of this analogy by the synthesis and characterisation of a series of spinels containing $Mn^{IV}$ on the octahedral sites. These materials show unusual magnetic behaviour; they undergo spontaneous magnetization below a well defined transition temperature, but the saturation magnetization is significantly smaller than predicted, and the low-field magnetization is time dependent. These observations are interpreted as being indicative of a semi-spin-glass magnetic structure, composed of an ordered ferrimagnetic component along one of the (equivalent) crystallographic axes and a disordered, glassy component perpendicular to this axis.
Acknowledgements

Firstly, I would like to thank Mark Green, who supervised this work, and was a constant source of ideas, inspiration and practical expertise. My thanks also go to Steve Bramwell, my UCL supervisor, and Richard Catlow, the director of the DFRL, for their invaluable guidance.

I could not have performed the representational analysis of the magnetic structure without the help of Andrew Wills and Tom Fennell, and would never have had to perform so foolish a task without the assistance of the experimental station managers, Dan Neumann (NIST), Richard Ibberson and Kevin Knight (RAL) and Alan Hewat (ILL). The lithium battery work was performed in collaboration with Carlo Bellitto and Fulvio Federici of the CNR, Rome. Thanks to you all.

My thanks also go to all the people at the RI, you know who you are, who made my time here so much fun, and so fulfilling. A special mention to all of Dynamo Faraday past, and, hopefully, future; it takes a special sort of football team to lose by a cricket score, and it would be a crime to let such a great name die.

Finally, and most importantly, I need to thank my family and friends for all their support and encouragement over the last three years. I couldn't have done it without you.

To all of you:

Thank you, Thank you very much\(^1\)

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\(^1\) The King
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Chapter 1

Introduction
1.1 Scientific Background

The transport properties of manganese oxides have proved a fruitful area of research in recent years. Of particular importance has been the observation of colossal magnetoresistance (CMR) in a number of perovskite and pyrochlore structures.\(^1-3\) This phenomenon, whereby a large change in the electrical resistance is observed with the application of a magnetic field, is associated with a transition from the paramagnetic to ferromagnetic state.\(^4,5\) It is extremely important in the development of new materials for the data storage industry. Most of the previous work has focussed on mixed valence Mn\(^{\text{III}}\)/Mn\(^{\text{IV}}\) oxides with the perovskite structure, where the ferromagnetism is explained within the double-exchange mechanistic framework.\(^6\) In this scheme, the ferromagnetic coupling between Mn\(^{\text{III}}\) and Mn\(^{\text{IV}}\) is mediated by electron hopping between the partially filled \(e_g\) orbitals of Mn\(^{\text{III}}\) and the empty \(e_g\) orbitals of Mn\(^{\text{IV}}\) with strong Hund's coupling. The parallel arrangement of the spins of the \(t_{2g}\) electrons reduces the energy barrier to transport in the ferromagnetic state, thus maximising the electronic kinetic energy and lowering the overall energy of the system. Application of a magnetic field drives the system to order at higher temperature, shifting the temperature of the metal-insulator transition giving CMR around the Curie temperature.\(^2\) Other mechanisms for CMR were shown to be possible with the observation of the effect in the pyrochlore, Tl\(_2\)Mn\(_2\)O\(_7\).\(^7-12\) In this material, the manganese is wholly in the integral oxidation state of 4+ and contains no \(e_g\) electrons and hence precludes double-exchange. In the pyrochlore system, the ferromagnetism is the result of a Mn-O-Mn superexchange interaction,\(^5\) whilst the conduction band is primarily of thallium 6s character.\(^13\) The CMR effect appears to derive from an indirect scattering of the
discrete ferromagnetic and conduction sublattices, resulting in hybridisation of the 
Tl(6s), Mn(3d) and O(2p) orbitals.\textsuperscript{14, 13}

Transition metal oxides with the spinel structure, particularly ferrites, such as magnetite, have long been vital components for devices used in the magnetic storage of information.\textsuperscript{15} The structure allows strong direct interactions between transition metal ions; thus many, including CoFe\textsubscript{2}O\textsubscript{4}\textsuperscript{16} and BaFe\textsubscript{12}O\textsubscript{29},\textsuperscript{17} are ferrimagnets with transition temperatures around room temperature. There are also examples of spinels exhibiting CMR, notably the chromium-based chalcogenides, FeCr\textsubscript{2}S\textsubscript{4}\textsuperscript{18}. Magnetoresistance has also been reported in magnetite,\textsuperscript{19, 20} the inverse spinel Fe\textsuperscript{3+}[Fe\textsuperscript{2+}Fe\textsuperscript{3+}]O\textsubscript{4}. In this structure, the ferromagnetic A and B sublattices, of d\textsuperscript{5} ferric ion cores, are antiparallel, giving bulk ferrimagnetism. Above the Verwey transition, the minority spin B-site electron, derived from the Fe\textsuperscript{2+} ions, occupies a spin polarised t\textsubscript{2g} band, giving poorly metallic conduction. The magnetoresistance is a result of different alignment of the ferrimagnetic moment in neighbouring grains, causing extra scattering at the grain boundaries.\textsuperscript{21}

The spinel structure, with general formula AB\textsubscript{2}O\textsubscript{4}, has many structural features common to the pyrochlore network;\textsuperscript{22} the B cation sublattice is identical to that of the pyrochlore, though the difference in the oxygen positions results in a dissimilar B-O-B bond angle. Therefore, it may be possible to produce spinel-based materials with similar electronic features to Tl\textsubscript{2}Mn\textsubscript{2}O\textsubscript{7}. That is, ferromagnetism caused by near 90\degree interactions and independent conduction from overlap between the metal ions on the tetrahedral site and the anions.
To pursue the analogy with the pyrochlore, it is necessary to have manganese (IV) ions on the B sublattice. If these octahedral sites were wholly occupied by Mn^{IV}, it can be seen clearly from charge neutrality principles that there can be no charge on the A site. This can be achieved by the delithiation of LiMn_2O_4 to form the metastable λ-MnO_2,\textsuperscript{23} though it should be noted that delithiation is never complete, and a small amount of manganese (III) remains.\textsuperscript{24} However, this material is insulating, as there is no A-site ion to form a conduction band. It is, however, possible to introduce a large amount of manganese (IV) to the B sites by balancing the charge with cations of low valency on the A site and a small proportion of the B sites. This can be achieved in a number of ways. In this thesis we investigate the series, A\textsuperscript{1}[M\textsubscript{x}Mn\textsuperscript{IV}(2-x)]O\textsubscript{4} (x = 0.5, 1; A = Li, Cu; M = Mg\textsuperscript{II}, Ni\textsuperscript{II}, Cr\textsuperscript{III}, Fe\textsuperscript{III}, Co\textsuperscript{III}, Rh\textsuperscript{III}) The AMn\textsubscript{1.5}M\textsubscript{0.5}O\textsubscript{4} (A = Li or Cu and M = Ni or Mg) are known to undergo a ferromagnetic transition at low temperatures,\textsuperscript{25,26} but there has been little investigation into other physical property measurements.

1.2 Summary of Thesis

This thesis is an investigation into the relationship between the structural and electronic properties of quaternary manganese oxides, of the spinel structure, with general formula A\textsuperscript{1}[M\textsubscript{x}Mn\textsuperscript{IV}(2-x)]O\textsubscript{4} (x = 0.5, 1; A = Li, Cu; M = Mg\textsuperscript{II}, Ni\textsuperscript{II}, Cr\textsuperscript{III}, Fe\textsuperscript{III}, Co\textsuperscript{III}, Rh\textsuperscript{III}) and the series Cu\textsubscript{1-y}Ni\textsubscript{0.5+y}Mn\textsubscript{1.5}O\textsubscript{4} (0≤y≤1); samples formulated AM\textsubscript{0.5}Mn\textsubscript{1.5}O\textsubscript{4} are discussed in chapter 4, chapter 5 reports compounds of composition AMMO\textsubscript{4}, and the series Cu\textsubscript{1-y}Ni\textsubscript{0.5+y}Mn\textsubscript{1.5}O\textsubscript{4} (0≤y≤1) is described in chapter 6. Related work, on ternary systems, A\textsubscript{1+x}Mn\textsubscript{2-x}O\textsubscript{4}, and on doping studies of LiMn\textsubscript{2}O\textsubscript{4}, is reported in chapter 7. Particular emphasis is placed on the interplay between cationic distribution, and sublattice ordering, and the observed magnetic and magnetotransport properties.
This thesis reports the pursuance of the analogy, drawn in section 1.1, between the CMR pyrochlore $\text{Tl}_2\text{Mn}_2\text{O}_7$ and manganese oxide spinels. This is performed by the synthesis and characterisation of a series of spinels containing Mn$^{IV}$ on the octahedral B sites. Samples were synthesised by solid-state methods, slow cooling was employed to induce sublattice ordering. Rietveld refinement of powder X-ray, and neutron, diffraction, using the GSAS suite of software has been employed to provide detailed structural characterization. Bulk magnetic behaviour has been investigated with a SQUID magnetometer and AC susceptometer. Low temperature neutron diffraction has been used to investigate the magnetic structure responsible for the observed magnetic phenomena. The magnetic structure is discussed by analysis of the competing superexchange interactions. The effect of magnetic ordering on the electronic transport properties has been investigated by four-probe conductivity measurement in a range of applied magnetic fields.

1.3 References


Chapter 2

*Solid State Chemistry of the Spinel Structure*
2.1 Introduction

This chapter contains an introduction to the normal crystal structure adopted by spinels, and the types of superstructure that have previously been observed. The wide variety of cation distributions over the two sublattices are discussed, with reference to the competing interactions driving this behaviour, particularly electrostatic forces and individual ion site preference. Finally, a novel form of magnetic order regularly encountered in spinels, known as ferrimagnetism,\(^1\) is introduced.

2.2 Crystal Chemistry

2.2.1 Introduction

A great body of work on the crystal chemistry of metal oxides in the spinel structure already exists.\(^2\)\(^-\)\(^4\) This section describes the basic spinel structure and introduces some key concepts employed to characterize specific spinel compounds.

2.2.2 Crystal Structure

This section introduces the basic spinel structure adopted by many compounds of empirical formula \(\text{AB}_2\text{X}_4\), where A and B are two different cations and X is an anion. The A and B cations occupy different sites with different environments, and so form two sublattices. Here, it is assumed that both the A and B sublattices are fully occupied by a single type of cation. The presence of more than one ion on a single sublattice can
result in the formation of cation ordered superstructures, which are discussed in section
2.2.3. The effect of distorting Jahn-Teller ions is covered in section 2.3.3.2.

The mineral spinel, MgAl$_2$O$_4$, gives its name to the family of oxides, MM'$^2$O$_4$, where M
and M' are different metal ions. The structure, first elucidated by Bragg,$^5$ is generated
by an almost close packed face-centred cubic (fcc) array of oxide ions with cations
occupying some of the interstices. There are two different interstitial sites, one has
tetrahedral coordination, and the other is octahedral. These are known as the A and B
sites respectively. In the unit cell of 32 oxide ions, 8 of the tetrahedral A-sites, and
sixteen of the octahedral B-sites are occupied; this represents a one-eighth, and one-half,
fractional occupation of the tetrahedral, and octahedral, interstices respectively. The
arrangement of the occupied cation sites is shown in Figure 2.1, which, for clarity,
shows only the atoms from the primitive unit cell ($a' = a$, $b' = c' = a/2$), containing two
AB$_2$O$_4$ formula units.

The symmetry is cubic and corresponds to the space group $Fd\bar{3}m$. A displacement,
defined by the parameter $u$, of the oxide ions from their ideal position, is allowed along
the body diagonal. The relative radii, r(A) and r(B), of the A and B cations, determine
the magnitude of this displacement.
The fractional atomic positions are given in Table 2.1. The symmetry operators of the space group generate the atomic coordinates. It is appropriate to note here that there is a choice of two origins in the $Fd\bar{3}m$ space group; the alternative is displaced by $(\frac{1}{8}, \frac{1}{8}, \frac{1}{8})$ from the origin used in this thesis. For the ideal close packed oxide lattice, the oxygen parameter $u = 0.25$; the anionic environment resultant from this ideal structure is illustrated in Figure 2.2 with B-O-B and A-O-B bond angles of $90^\circ$ and $125^\circ$ respectively. In real oxide systems the displacement away from the nearest tetrahedral cation along the [111] direction, as shown in Figure 2.2, causes $u$ to be greater than 0.25. At $u = 0.2625$, the octahedral and tetrahedral bond lengths are the same and the anionic coordination is closer to that of a regular tetrahedron, with B-O-B and A-O-B bond angles of $95.8^\circ$ and $121.0^\circ$ respectively. The size of the interstices in the spinel...
structure is determined by the lattice, a, and oxygen \( u \) parameters. For small deviations from the ideal lattice the interstitial radii are given by equations (2.1) and (2.2).

\[
r_a = a(u - 0.125)\sqrt{3} \tag{2.1}
\]

\[
r_b = a\sqrt{(u-0.5)^2 + 2(u-0.25)^2} \tag{2.2}
\]

In transition metal oxides studied in this thesis, typical values of a and \( u \) are 8.3 Å and 0.263 respectively.

![Figure 2.2: Anion (large, grey) environment, tetrahedrally coordinated to one A-cation (small, blue) and three B-cations (medium, purple). A displacement along the [111] direction is measured by the \( u \) parameter.](image)

<table>
<thead>
<tr>
<th>Site</th>
<th>x</th>
<th>y</th>
<th>z</th>
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<tbody>
<tr>
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<td>0.125</td>
<td>0.125</td>
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</tbody>
</table>
This crystallographic description can be difficult to visualize, hence it is often convenient to use a polyhedral description of the structure. In light of the preceding discussion it is clear that the spinel structure can be represented, as in Figure 2.3, by an array of AO₄ tetrahedra and BO₆ octahedra. The octahedra are interlinked in an edge-sharing fashion, whereas the tetrahedra are not interlinked, but separated by the octahedra; each AO₄ unit is vertex-linked to four BO₆ octahedra.

Figure 2.3: Polyhedral representation of the spinel structure with AO₄ tetrahedra (blue) and BO₆ octahedral (purple).

In many of the spinels discussed in this thesis, the cations occupying the A and B sublattices are very different. Generally, the B cations are paramagnetic transition metal ions, whilst the A cations are diamagnetic and, in the case of Li⁺, mobile. In this case it is helpful to consider the structure to be an extended framework of composition BO₂ with A cations in the tetrahedral interstices. Clearly edge-sharing octahedra is a valid
representation of this framework but, for the purposes of understanding some of the phenomena regularly encountered in spinels, such as magnetic and cationic ordering, it is not very enlightening. The building block that gives the framework its observed characteristics is the $\text{B}_4\text{O}_4$ cube, illustrated in Figure 2.4. These cubes are vertex-linked at each B position, and each anion is bonded to one A cation, in addition to the three O-B bonds within the cube, resulting in the distorted tetrahedral anionic environment discussed previously. This connectivity is illustrated in Figure 2.4 for one B-cation site and one oxide ion site. It is clear from figure 2.4 that, if only the B-sites are considered, the structure is an infinite, corner sharing, array of $\text{B}_4$ tetrahedra. In this way the spinel structure is analogous to the pyrochlore structure.

![Figure 2.4: The $\text{B}_4\text{O}_4$ cube, with B-cations small, purple and oxide ions large, grey. The octahedral B site coordination is shown for one cation, and the tetrahedral coordination shown for one anion. The neighbouring A-cation is small, blue.](image)
2.2.3 Superstructure formation

The discrete tetrahedral (A) and octahedral (B) sublattices of the spinel structure were introduced in the previous section. In a normal spinel, each sublattice contains a single type of ion, but there are many examples where these sublattices are occupied by more than one kind of cation. If different cations are present on a single sublattice then there is the possibility of long-range cation ordering. This ordering destroys some of the symmetry elements of the *Fd3m* space group and results in the formation of a superstructure. The following spinel superstructures have been observed:

a) 1:1 order on the B-sublattice. The classic example is the Verwey\(^6\) transition in Fe\(_3\)O\(_4\) (Fe\(^{3+}\)[Fe\(^{2+}\)Fe\(^{3+}\)]O\(_4\)) although this is technically electronic ordering. A number of orthorhombic space groups have been proposed, including *Imma*\(^7\) and *Pmca*\(^8\) but the exact structure remains controversial. A slightly different 1:1 ordering occurs in Zn[LiNb]O\(_4\), which crystallises in the *P41229* space group.

b) 1:3 order on the B-sublattice. This was originally observed in Fe[Li\(_0.5\)Fe\(_{1.5}\)]O\(_4\)\(^10\) that crystallises in the space group *P4332*. This is the same superstructure as that of Li[Mn\(_{1.5}\)Mg\(_{0.5}\)]O\(_4\)\(^11,12\) that investigated in this thesis.

c) 1:5 order on the B-sublattice. This has only been observed in vacancy ordered structures such as γ-Fe\(_2\)O\(_3\), Fe\(^{3+}\)[□\(_{1/3}\)Fe\(^{3+}\)\(_{5/3}\)]O\(_4\)\(^13\) which is tetragonal *P43212* with a tripled c-axis.\(^14\) This compound should probably be considered as a 1:3 ordered compound because the vacancies randomly occupy two-thirds of the octahedral 4*a* sites (there are 16 octahedral sites in total) giving a formulation of Fe\(^{3+}\)[(□\(_{2/3}\)Fe\(^{3+}\)\(_{1/3}\)]\(_{1/2}\)Fe\(^{3+}\)\(_{3/2}\)]O\(_4\). This observation can be understood by considering the spinel framework to consist of B\(_4\)O\(_4\) cubes (Section 2.2.2).
d) 1:1 order of the A-sublattice. This superstructure has been observed in $\text{Li}_{0.5}\text{Fe}_{0.5}[\text{Cr}_2]\text{O}_4$.

e) 1:2 order on the A-sublattice. This ordering has also only been observed in vacancy superstructures such as $\beta$-$\text{In}_2\text{S}_3$, formulated $\text{In}_{2/3}\Box_{1/3}[\text{In}_2]\text{O}_4$, which is also tetragonal with a tripled c-axis (space group $I4_1/amd$).

The energetic driving forces responsible for these observed superstructures are discussed in section 2.2.4.2

2.2.4 Incorporation of metal ions into the spinel lattice

The principal of electroneutrality requires that there is no overall charge on a crystal. This results in there being three basic types of spinel: $\text{M}^{2+}\text{M'}^{3+}\text{O}_4$ (2-3 spinels), $\text{M}^{4+}\text{M'}^{2+}\text{O}_4$ (4-2 spinels), and $\text{M}^{5+}\text{M'}^{1+}\text{O}_4$ (6-1 spinels). The introduction of a third cation, or the coexistence of different oxidation states in the structure yields a host of other possibilities. A spinel is referred to as normal if both the A and B sublattices contain only one type of cation; $\text{M}[\text{M'}]_2\text{O}_4$, where the metal ions on the B sites are in square brackets. An alternative cationic distribution is frequently encountered; the arrangement $\text{M'}[\text{MM'}]_4\text{O}_4$ is known as inverse spinel$^{17}$. There are also many intermediate cases. The parameter $\delta$ is used to describe the degree of inversion, giving the chemical formula defined in equation (2.3).

$$\text{M'}\delta\text{M}(1-\delta)[\text{M}(\delta)\text{M'}(2-\delta)]\text{O}_4 \quad (2.3)$$

Where $\delta = 0$ for a normal spinel, $\delta = 1$ for an inverse spinel and $\delta = \frac{2\delta}{3}$ for a completely random distribution. The presence of different cations on equivalent sites causes a perturbation of the symmetry. If the cations exhibit long range ordering on a particular site a different crystallographic space group can result. (Section 2.2.3)
2.3 Cation Distribution

2.3.1 Introduction

The great variety of cation distributions observed within the spinel structure is a particularly interesting facet of their structural chemistry. Identifying the factors determining these different distributions is clearly essential to the understanding of the observed behaviour. It is not, therefore, surprising that, over half a century, a great deal of work has been done on this problem. The first calculations were performed by Verwey et al.,\textsuperscript{6} who deemed the electrostatic term to be the controlling factor and so evaluated the variation of the Madelung constant with the $u$ parameter. They found that electrostatic effects favoured the normal distribution in 2-3 spinels, though later work by Thompson and Grimes\textsuperscript{18} found that spinels with small $u$ parameters would be more stable in the inverse configuration.

The inability of these models to predict the full range of observed distributions led both McClure\textsuperscript{19} and Dunitz and Orge}\textsuperscript{20} to speculate that octahedral site stabilisation, of certain transition metal ions by ligand field effects, was the cause of many inverse structures. This improved the model greatly, but there were still inconsistencies with experiment. More recently, a number of computational methods have been applied to the problem. These provide valuable insight because it is immediately apparent which energetic terms must be included in the model to achieve agreement with the experimental observations. Burdett et al.\textsuperscript{21} constructed a structural sorting map for spinels using pseudo-potential $s$ and $p$ orbital radii. This was able to predict the distribution with 98% accuracy despite taking no account of the $d$ orbitals, although it should be noted that a significant number of compounds fell on the boundary where
crystal field effects were required to determine the structure. Cormack et al. were able to obtain very good agreement with atomistic modelling techniques, by taking explicit account of the coordination in the potential (a measure of covalency) and including a ligand field term.

In this section the competing energetic forces responsible for the wide range of cation distributions are discussed.

### 2.3.2 Electrostatic Terms

The static lattice, or crystal, energy, $U$, is composed of Coulombic attraction and repulsion terms between charged ions and short-range repulsion terms between core electrons, as represented in equation (2.4). This equation omits relatively minor terms deriving from dipolar, and quadrupolar, van der Waals forces and the zero-point energy correction because the change in the lattice energy, with changing cation distribution, will have a tiny effect of the value of $U$.

$$U = U_c + U_r$$  \hspace{1cm} (2.4)

Where $U_c$ is the sum of the Coulombic terms and $U_r$ is the short-range (Born) repulsion. By far the most significant term in the lattice energy, $U$, is the Coulombic term, $U_c$, between the charged ions. This Coulombic attraction is a function of the Madelung constant, $M$, the relationship is presented in equation (2.5). The Madelung constant for a particular spinel is a function of both the mean ionic charge on the A-site and the deviation, $\Delta_u$, of the oxygen $u$ parameter from the ideal value. ($\Delta_u = u - 0.25$). The formula for the Madelung constant given in equation (2.6) was derived from the generalised Ewald method by Thompson and Grimes.
$$U_c = -M \frac{e^2}{a}$$  \hspace{1cm} (2.5)

$$M(q_A,u) = 139.8 + 1186\Delta_u - 6483\Delta_u^2 - (10.82 + 412.2\Delta_u - 1903\Delta_u^2)q_A + 2.609q_A^2$$  \hspace{1cm} (2.6)

Where $e$ is the electronic charge and $a$ is the lattice parameter. Throughout this section energies will be expressed in cgs units of $e^2/a$ for convenience. These values can be converted to the SI unit, Joules, putting all terms in the relevant SI unit and multiplying by a factor of $\sqrt{\frac{1}{4\pi\varepsilon_0}}$ giving the conversion factor in equation (2.7), assuming a typical value of the lattice parameter, $a$, of 8.3Å.

$$\frac{1.0 e^2}{a} = 2.778 \times 10^{-19} J$$  \hspace{1cm} (2.7)

$$= 167.3 kJ / mol$$

The stability of a spinel will increase with increasing Madelung energy, which is a function of the charge distribution. It is, therefore, natural to try to explain the cationic distribution with this term. The variation in Madelung energies, calculated from equation (2.6), with A-site charge for various values of $u$ is plotted in Figure 2.5. It is clear from this figure that although there is no simple relationship between the charge distribution and Madelung constant it is favourable to have either large cations with low charge or small cations with high charge on the A-site. Figure 2.5 also provides an explanation for the experimental observation\textsuperscript{24,25} of incomplete miscibility between spinels with low and high valent cations on the A-site, such as the Ge[Co]$_2$O$_4$ – Co[CoTi]O$_4$ system\textsuperscript{24} The pronounced minimum in the maximum Madelung energy for intermediate charge on the A-site inhibits the formation of solid solutions.
The other significant term in the lattice energy, which must be considered is the Born repulsion, $U_R$. This can be accounted for with a Born-Mayer, or Buckingham type potential, defined in equation (2.8).

$$U_R = B e^{-r/p} - C r^{-6} \tag{2.8}$$

Where $r$ is the interatomic separation and $\rho$ the polarisability correction. The parameters $B$, $C$ and $\rho$ are fitted to the properties of the binary oxides.

Combining the Coulombic and short-range terms as in equation (2.4) gives the lattice energy for a particular distribution. It is now possible to define an inversion energy, $\Delta U$ as in equation (2.9).

$$\Delta U = U(\text{inverse}) - U(\text{normal}) \tag{2.9}$$
The equilibrium cation inversion character, $\delta_{eq}$, can now be related to the free energy, $\Delta G$, as equation (2.10), by the model of Navrotsky and Kleppa\textsuperscript{26}

$$
\Delta G(\delta) = \Delta H(\delta) - T \Delta S(\delta) \tag{2.10}
$$

Where the enthalpy term, $\Delta H(\delta)$, and the entropy term, $\Delta S(\delta)$, are approximated by equations (2.11) and (2.12) respectively.

$$
\Delta H(\delta) = \delta \Delta U \tag{2.11}
$$

$$
\Delta S(\delta) = -k [\delta \ln \delta + (1-\delta) \ln(1-\delta) + \delta \ln(\delta/2) + (2-\delta) \ln(1-\delta/2)] \tag{2.12}
$$

Where $k$ is the Boltzmann constant. The following assumptions have been made in writing equations (2.11) and (2.12): (a) $\Delta H(\delta)$ is a simple linear function of $\delta$, (b) the cation distribution within each sublattice is random, (c) the nonconfigurational entropy change is negligible and (d) the volume change associated with cation inversion is negligible. An expression for the equilibrium inversion parameter $\delta_{eq}$ is now obtained by the following method. By substituting equations (2.11) and (2.12) into equation (2.10), and then differentiating with respect to $\delta$ an expression for $\frac{dG(\delta)}{d\delta}$ is obtained (equation (2.13)), then $\delta$ is replaced by $\delta_{eq}$ (therefore $\frac{dG(\delta)}{d\delta} = 0$) and equation (2.13) is rearranged to give equation (2.14).\textsuperscript{27}

$$
\frac{dG(\delta)}{d\delta} = \Delta U + kT \ln \left[ \frac{\delta^2}{(\delta^2 - 3\delta + 2)} \right] \tag{2.13}
$$

$$
\delta_{eq} = \frac{-3 + \sqrt{9 + 8(c-1)}}{2(c-1)} \tag{2.14}
$$
Where \( c = e^{\frac{\Delta U}{kT}} \).

Figure 2.6: Plot of cation inversion parameter against inversion energy divided by thermal energy.

The variation in the equilibrium inversion parameter, \( \delta_{eq} \), as a function of the normalised inversion energy, \( \Delta U/kT \), is depicted in Figure 2.6. It is clear from this plot that \( \delta_{eq} \) will deviate significantly from 0 (for normal spinels) or 1 (for inverse spinels) only when \(-5<\Delta U/kT<10\); when the inversion energy and the thermal energy are of a similar magnitude.

2.3.2.1 Electrostatic Ordering

If more than one type of cation is present on a single sublattice, then a further energy term must be considered in a purely ionic model. This is the stabilisation energy of
electrostatic ordering between the different ions on the same crystallographic site. When
the ordering is on the octahedral sites, evaluating this contribution is an interesting
problem. It was mentioned in section 2.2.2 that the B-site spinel sublattice, like that of
the pyrochlore, is an infinite array of corner sharing B₄ tetrahedra. First considering the
case of a 1:1 ratio of cations on the B-sites, then all short-range interactions will be
satisfied if each tetrahedron contains 2 cations of each type. As discussed in section 2.4,
there is no unique ground state that satisfies this requirement, hence there will be a
finite zero point entropy (this is almost identical to the zero point entropy of ice). Thus
we must consider two different energies: the electrostatic energy of short-range
interactions, \( E_{\text{self}} \), and that of long-range order, \( E_{\text{order}} \), the added stabilisation from
selecting a unique ground state.

The ordering of Fe\(^{2+}\) and Fe\(^{3+}\) ions in the low temperature form of Fe₃O₄\(^{28,7}\) viewed
down [100], is depicted in Figure 2.7. (This example has been chosen because it
involves electronic ordering, so, unlike most instances of cation ordering, the transition
is not dependent on cation mobilities.) It can be seen to be composed of rows alternating
Fe\(^{2+}\) and Fe\(^{3+}\) cations along the [011] directions (light grey bonds). The spacing between
parallel rows in the same (100) plane is twice the Fe-Fe bond distance of \( d = a/2\sqrt{2} \).
In between these rows, but not intersecting them, lie perpendicular alternating rows
along the [011] directions (dark grey bonds). In the long range ordered structure of
Figure 2.7, the two sets of rows are "in phase," i.e. Fe\(^{2+}\) is closest to Fe\(^{2+}\) (red bonds)
and Fe\(^{3+}\) is closest to Fe\(^{3+}\) (blue bonds). It can, however, be easily seen that any set of
alternating [011] and [0\(\bar{1}1\)] rows in any relative phase whatsoever is one of the short
range ordered structures.\(^{29}\) (This is the majority of the structures resulting in the zero-
point entropy, though not the full set because there is still a degree of freedom along
The Coulombic energies of this series can be calculated by the Madelung method. The self-energy for ordering of individual lines, with charges $q_1$ and $q_2$ per pair of ions is given in equation (2.15).

$$E_{self} = - \left( \frac{(q_1 - q_2)^2}{2d} \right) \ln 2$$

$$= -0.9802 \left[ \frac{(q_1 - q_2)^2}{a} \right]$$

(2.15)

The potential, $V_{opp}$, caused by an alternating line at a distance $nd$ directly opposite one of the $\text{Fe}^{3+}$ cations of the row can be approximated, by an Ewald summation, to equation (2.16).^29

$$V_{opp} = \left( \frac{4}{d} \right) K_0(n\pi)$$

(2.16)

Where $K_0$ is a cylindrical special function, known as MacDonald's function^31. Each row has 6 nearest-neighbour rows with which it can interact, two at a distance of $2d$ in its own (100) plane and four at $n = \sqrt{3}$ in the nearest-neighbour (100) planes. A maximum of four of these rows can be "out of phase"; the most favourable case is that where these are the four rows at $n = \sqrt{3}$ (this is the $\text{Fe}_3\text{O}_4$ structure in the figure.) Summing the terms of the form of equation (2.16), results in the expression of the inter-row energy, $E_{inter}$, given in equation (2.17).

$$(E_{inter})_{min} = -0.021 \left[ \frac{(q_1 - q_2)^2}{a} \right]$$

(2.17)

Summing the intra and inter-row energies $E_{self}$ and $E_{inter}$, gives a total ordering energy, $E_{tot}$ as equation (2.18).
The most unfavourable case is formed when all rows are "in phase," the maximum inter-row energy is given in equation (2.19).

\[ (E_{\text{inter}})_{\text{max}} = +0.031 \left( \frac{(q_1 - q_2)^2}{a} \right) \]  

(2.19)

This value results in a maximum total energy, given in equation (2.20).

\[ (E_{\text{tot}})_{\text{max}} = -0.949 \left( \frac{(q_1 - q_2)^2}{a} \right) \]  

(2.20)

The energies \((E_{\text{tot}})\) of all of the possible structures generated by this model lie between these two end members, hence the whole range of possible structures has an ordering energy within 5% of the minimum ordering energy, \((E_{\text{tot}})_{\text{min}}\). It is reasonable to assume that the order-disorder transition in \(\text{Fe}_2\text{O}_4\) will occur when the ordering energy and the thermal energy, \(kT\), are equal. This is expressed in equation (2.21).

\[ (E_{\text{tot}})_{\text{order}} = 2kT_{\text{order}} \]  

(2.21)

The factor 2 arises because the Coulombic potential between a pair of cations has been considered. It must, however, be noted that \((E_{\text{tot}})_{\text{order}}\) will be an overestimate, because it does not take into account polarization screening effects. If \((E_{\text{tot}})_{\text{order}}\) is taken to be the value from equation (2.18) of \(-1e^2/\alpha\), which corresponds to \(2.778 \times 10^{-19} \, J\) (equation (2.7)), then an ordering temperature of 10000K would be predicted, which clearly does not equate with the observed transition at 120K. It has, however, already been stated that the ordering transition is that between one of the many short range ordered states and the long range ordered superstructure. The energy change for this transition was shown to lie in the range of 0-5% of \((E_{\text{tot}})_{\text{min}}\) depending on which of the set of candidate
structures is the pre-transition "disordered" structure. If a median value of 2.5% were chosen, then the energy would correspond to a transition temperature of 250K. This is a much more reasonable value, considering that the starting structure is almost certainly of lower energy than the rough average, and that screening effects are not taken into account here. Thus, it can be seen that the long-range ordering energy, \( E_{\text{tot}}^{\text{order}} \), will generally be of comparable magnitude to the thermal energy and, therefore, order-disorder transitions will be expected, at accessible temperatures, in many spinels. An important result that comes out of this calculation is the high value of \( E_{\text{self}} \) in equation (2.18). This is the stabilisation achieved by fulfilling the short-range criterion, now known as the Anderson condition, that each \( B_4 \) tetrahedron (or \( B_4O_4 \) cube) has the same stoichiometry as bulk material. It has already been noted that this energy corresponds to the thermal energy at about 10000K, therefore a mixed B-sublattice is highly unlikely ever to be truly disordered. A practical consequence of the Anderson condition is that B-site cation ordered superstructures (section 2.2.3) are only likely to occur when it is possible to replicate the bulk stoichiometry on every \( B_4O_4 \) cube \( i.e. \) only 1:1 and 1:3 ratios favour long-range ordering and other ratios are likely to result in phase separation.
Figure 2.7: Ordered tetrahedral array of B-site Fe$^{2+}$ (large, red) and Fe$^{3+}$ (small, blue) cations in low temperature form of Fe$_3$O$_4$.

By a similar method\textsuperscript{29} it has been shown that the total ordering energy of 1:3 ratio B-site systems, such as Fe[Li$_{0.5}$Fe$_{1.5}$]O$_4$, is given by equation (2.22).

$$ (E_{tot})_{\text{min}} = -0.712 \left[ \frac{(q_1 - q_2)}{a} \right]^2 $$

(2.22)
In this system, like Fe$_2$O$_4$, it is impossible to select a unique ground state by considering only nearest-neighbour interactions, and, here, the problem is complicated by the dependence of the transition on cation mobilities. It does, however, seem reasonable to assume that the disordered state will satisfy the short-range Andersen condition that each B$_4$ tetrahedron (or B$_4$O$_4$ cube) will contain one lithium cation and three iron cations, because the total ordering energy of equation 22 is equivalent to about 120kJ/mol. Therefore, similarly to Fe$_2$O$_4$, the energy of the short-range-long-range order transition will be of the order of 5% of the total ordering energy. The total Coulombic ordering energies for different cation ordering schemes in the spinel structure have been tabulated$^{11,15}$ in Table 2.2

Table 2.2: Electrostatic ordering energy (in e$^2$/a units) for different charge differences

<table>
<thead>
<tr>
<th>Charge Difference between ordered ions (e)</th>
<th>1:1 B-site order (e$^2$/a)</th>
<th>3:1 B-site order (e$^2$/a)</th>
<th>1:1 A-site order (e$^2$/a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.0</td>
<td>0.7</td>
<td>0.5</td>
</tr>
<tr>
<td>2</td>
<td>4.0</td>
<td>2.8</td>
<td>2.0</td>
</tr>
<tr>
<td>3</td>
<td>9.0</td>
<td>6.4</td>
<td>4.5</td>
</tr>
<tr>
<td>4</td>
<td>16.0</td>
<td>11.2</td>
<td>-</td>
</tr>
</tbody>
</table>
2.3.3 Individual Site Preference of Certain Cations

2.3.3.1 Introduction

It has long been known that certain cations have a marked preference for a specific coordination geometry. This phenomenon will clearly exert a strong influence on the cation distribution of spinels. There are two simple models that have often been quoted to explain this observation; crystal-field stabilisation energy (CFSE) for octahedral site preference, and a covalent contribution to the bonding using hybrid orbitals for tetrahedral site preference. Whilst these models can be powerful tools in the understanding of spinels, the limitations arising from such simplifications must be understood. Both of these phenomena can be explained with a molecular orbital (MO) approach, which is known as ligand field theory.

2.3.3.2 Crystal Field Theory

McClure$^{19}$ and Dunitz and Orgel$^{20}$ simultaneously proposed, using a simple electrostatic model, that crystal field stabilisation energy (CFSE) was the cause of the octahedral site preference of many transition metal cations. For a transition metal ion in a crystal field of octahedral coordination, the d orbitals are divided into two sets, denoted $e_g$ and $t_{2g}$, according to their symmetry behaviour. The lobes (areas of maximum probability) of the $e_g$ orbitals are pointing directly towards the nearest neighbour oxide ions, whereas the $t_{2g}$ orbitals have nodal planes in these directions. The octahedral environment gives rise to a crystal-field splitting between the two sets of orbitals with an energy difference, $\Delta_0$, shown on the left of figure 2.8.
Figure 2.8: Crystal-Field splitting of d-orbitals in octahedral (left) and tetrahedral (right) field.

Similarly, a tetrahedral crystal field causes a stabilisation of the \( e \) orbitals, (the \( g \) subscript is omitted because there is no centre of symmetry) \( \Delta_T \), as depicted on the right hand side of Figure 2.8. Simple electrostatic calculations indicate that \( \Delta_T \) is \( \frac{4}{9} \Delta_O \). The greater magnitude of \( \Delta_O \) causes ions stabilised by the field splitting to have a strong preference for the octahedral site, whilst those impervious to the field (\( d^0, d^2, d^{10} \)) are often driven onto the A site. This crystal field splitting introduces the possibility of low-spin configurations for certain \( d^0 \) complexes (In first-row transition metal oxides this is limited to \( d^6 \) and occasionally \( d^7 \) ions). In the free ion, the degenerate d orbitals are filled according to the Aufbau principal, to minimise electron repulsion and maximise the intraatomic exchange energy, resulting in the high-spin configuration. In an octahedral complex these energy terms must compete with the CFSE, for example the low-spin (\( t_{2g}^6 \)) and high-spin (\( t_{2g}^4 e_g^2 \)) \( d^6 \) ions have CFSE's given by equations (2.23) and (2.24) respectively.

\[
CFSE(t_{2g}^6) = 6 \times \frac{2}{5} \Delta_O = \frac{12}{5} \Delta_O \quad (2.23)
\]

\[
CFSE(t_{2g}^4 e_g^2) = 4 \times \frac{2}{5} \Delta_O - 2 \times \frac{3}{5} \Delta_O = \frac{2}{5} \Delta_O \quad (2.24)
\]
If the difference between these two equations, $\Delta_0$, is greater than the electron repulsion energy then low-spin behaviour will be observed.

It should be noted here that if, after the octahedral (or tetrahedral) field splittings are taken into account, there are degenerate orbitals containing unequal numbers of electrons, then, according to the Jahn-Teller theorem, the structure will distort to remove this degeneracy. Tetragonal elongation, along the c-axis, of a regular octahedron causes both the $e_g$ and $t_{2g}$ level to split, although the splitting of the $e_g$ level is larger, and $d_{z^2}$ is stabilised with respect to $d_{x^2-y^2}$ as is shown in Figure 2.9, the inverse is true for a compression along the c-axis. In practice, a static, Jahn-Teller, distortion is only observed when the unequal occupancy is on the $e_g$ orbitals ($d^4$ and $d^9$ ions) whereas dynamic distortions result from uneven distribution in the $t_{2g}$ orbitals (e.g. $d^1$ and $d^3$).

Figure 2.9: Effect of tetragonal, Jahn-Teller, elongation on $e_g$ and $t_{2g}$ orbitals of an octahedral MX₆ complex.
2.3.3.3 Covalency in Highly Polarisable Cations

In marked contrast to most transition metal cations, ions that have a fully occupied set of d orbitals have a tendency to occupy tetrahedral sites. This is ascribed to a covalent contribution to the bonding via \( sp^3 \) hybrid orbitals, enabled by their high polarisability. A classic example of this is the tetrahedral coordination of \( Zn^{2+} \) in \( ZnO \), whilst \( MgO \), \( CoO \) and \( NiO \) all have the octahedral rock-salt structure. A similar tendency, albeit much less strong, is observed in \( d^5 \) ions.

2.3.3.4 Ligand Field Theory - Angular Overlap Model

Ligand field theory is based on an approximate form of molecular orbital theory, known as the angular overlap model, which concentrates on the interaction between the d orbitals of the metal ion and the ligand orbitals. The model does not account for interactions between the ligand and the metal s and p orbitals or electron-electron repulsion.

The overlap of an orbital on the metal and the ligand leads to the formation of pair of bonding and antibonding molecular orbitals. The bonding molecular orbital is the result of in phase overlap and the antibonding orbital results from out of phase overlap. The \( \sigma \)-bonding contribution to the stabilisation of the molecular orbitals, \( \Delta_{L,F(\sigma)} \), is given by equation (2.25). The anion \( \sigma \) orbitals lie on the nodal-planes of the \( t_{2g} \) orbitals, so the \( t_{2g} \) set is considered to be non-bonding in this model. The vast majority of the bonding energy in spinels comes from the \( \sigma \)-bonding contribution because the anion environment (Figure 2.2) allows each of the oxygen 2p orbitals to form a \( \sigma \)-bond with a neighbouring B-site cation. (This contrasts with the perovskite structure where the
linear anion coordination leaves the $2p_y$, $2p_z$ orbitals free for $\pi$-bonding.) In the angular overlap model to $\sigma$-bonding energy in an octahedral complex is defined by equation (2.25).

$$\Delta_{L\sigma} = \pm \frac{BS_\sigma^2}{\Delta E}$$ (2.25)

Where $S$ and $\Delta E$ are, respectively, the overlap and energy separation of the orbitals, as shown in Figure 2.10, and $B$ is the proportionality constant for perfect overlap of the metal orbital and one ligand orbital. The effect of a $\pi$-bonding contribution on Figure 2.10 is discussed later. Each ligand is a Lewis base, so its $\sigma$-orbital contains two electrons, which are transferred to the bonding MO on formation of the ML₆ complex. The metal ion has two $e_g$ orbitals, of the correct symmetry for $\sigma$-bonding, so can form two such bonding orbitals of predominantly ligand character, and two $e_g$ antibonding orbitals of predominantly metal character. The energy splitting of these orbitals from the atomic ones would be $6BS_\sigma^2/\Delta E$ (equation (2.25)) if the $e_g$ orbitals overlapped perfectly with each ligand $\sigma$-orbital, but geometrical considerations hampers this overlap and result in an observed splitting of $3BS_\sigma^2/\Delta E$. 

![Diagram showing the energy splitting of orbitals](image-url)
Thus far the $t_{2g}$ orbitals have been treated as non-bonding, but they are able to form $\pi$-bonds with the ligand orbitals (it was mentioned earlier that this is inhibited in spinels, but there is still a small effect). Similarly to the $\sigma$-case, the $\pi$-bonding contribution is geometrically defined as $4B_\pi S_\pi^2/\Delta E$. The $t_{2g}$ orbitals become antibonding if the ligand is a $\pi$-donor, such as the oxide and chloride ions, and they become slightly bonding if the ligand is a $\pi$-acceptor, such as the cyanide and carbonyl ligands. Thus, in oxides ($\pi$-donors) the total splitting of the $t_{2g}$ and $e_g$ ions is given by equation (2.26).

$$\Delta_{t_F} = \pm \frac{3BS_\sigma^2 - 4B_\pi^2S_\pi^2}{\Delta E}$$

(2.26)

The effects of the $\pi$-bonding contribution and the mixing of the metal 4s and 4p orbitals with the ligand orbitals on the metallic orbitals are shown in the MO diagram in Figure 2.11, all bonding levels are shown to be degenerate for clarity, this is not realistic, but the stabilisation produced by the mixing, $\Delta$, can be seen to be far greater that the difference between the $t_{2g}$ and $e_g$ orbitals, $\Delta_{t_F}$. 

![MO diagram showing bonding levels and mixing effects](image-url)
The symmetry representations of the $s$, $p$ and $d$ orbitals of the cation are, respectively, $a_{1g}$, $t_{1u}$ and $e_g$ and $t_{2g}$. Linear combination of the ligand orbitals can be constructed such that those with representations $a_{1g}$, $e_g$ and $t_{1u}$ can form $\sigma$-bonds and those represented by $t_{1g}$, $t_{1u}$, $t_{2g}$ and $t_{2u}$ can be used in $\pi$-bonding.

2.4 Zero-Point Entropy on the Octahedral Sublattice

2.4.1 Introduction

It was mentioned in section 2.3.2.1 that if there is more than one type of cation on the octahedral sublattice, then there are many different configurations that can satisfy all nearest-neighbour interactions. Thus, there is a finite configurational entropy at absolute zero. This is in contradiction with the third law of thermodynamics, as formulated by Planck, which states that at absolute zero there should be only one microscopic configuration of the system, i.e. the entropy should be zero at absolute zero. This is known as the zero-point entropy. Andersen\textsuperscript{29} equated both cation distribution, and antiferromagnetic ordering, on the octahedral sublattice, with Pauling's\textsuperscript{32} explanation of the zero-point entropy of ice.

2.4.2 Zero-Point Entropy

The statistical definition of entropy, which was derived by Boltzmann, is presented in equation (2.27).
\[ S = k \ln W \quad (2.27) \]

Where \( k \) is the Boltzmann constant, and \( W \) is the weight of the system (the number of different ways in which the energy of the system can be achieved by rearranging the atoms.) Pauling defined the zero-point entropy of crystalline ice in the following manner: Each oxygen (found at the centre of corner-sharing tetrahedra) forms short covalent bonds to two hydrogen atoms and longer hydrogen bonds to the other two. For a system of \( N \) water molecules, there are a total of \( 2^{2N} \) configurations of hydrogen atoms between neighbouring oxygen atoms. There are \( 2^4 = 16 \) possible arrangements of four hydrogen atoms around the central oxygen ion. Only six of these satisfy the bonding requirement of two covalent and two hydrogen bonds. The total number of energetically equivalent configurations is given in equation (2.28), and hence, the molar residual entropy in equation (2.29).

\[ W = 2^{2N} \left( \frac{6}{16} \right)^W = \left( \frac{3}{2} \right)^W \quad (2.28) \]

\[ S = k \ln \left( \frac{3}{2} \right)^W \]

\[ = R \ln \left( \frac{3}{2} \right) \]

\[ = 3.371JK^{-1}mol^{-1} \quad (2.29) \]

Where the gas constant, \( R = N_Ak = 8.314JK^{-1}mol^{-1} \). The distribution of two types of cation over the octahedral B-sites in a spinel lattice is an almost identical problem. The B-sublattice is depicted as an infinite array of corner sharing \( B_4 \) tetrahedra in Figure 2.12. Each B-cation is shared between two tetrahedra in this model, so for \( N \) cations, with \( 2^N \) possible arrangements, there are \( \frac{N}{2} \) tetrahedra, and 6 arrangements out of a possible 16 satisfy the Anderson condition (section 2.3.2.1) that each tetrahedron has
two of each type of ion. Therefore, the weight and molar residual entropy are given by equations (2.30) and (2.31) respectively.
Where $S$ is the entropy per mole of B-cations, which corresponds to the entropy per half-mole of AB$_2$O$_4$ spinel. Equations (2.30) and (2.31) could equally apply to an Ising-type antiferromagnetic ordering on the B-site, with "spin up" and "spin down" in place of the type of cation.

The slightly different procedure must be applied to the case of a 1:3 cation ratio on the B-sites, such as Fe[Li$_{0.5}$Fe$_{1.5}$]O$_4$, because there are no longer equal numbers of the two cation types. The tetrahedra can be divided into two sets, those pointing up in Figure 2:12 and those pointing down. Every cation is in one "up" tetrahedron and one "down" tetrahedron; there are $N/4$ of each set. First, considering an "up" tetrahedron, it must have three Fe$^{3+}$ ions and one Li$^+$ cation to fulfil the Anderson condition, but the Li$^+$ cation can be in four different positions. This gives a total of $4^{N/4}$ possible configurations. This set alone creates the whole lattice, but the "down" tetrahedra must also obey the Anderson condition for the states to be energetically equivalent. The probability of any "down" tetrahedron having a 1:3 ratio is $4 \left( \frac{1}{4} \right) \left( \frac{1}{4} \right)^3 = \left( \frac{1}{4} \right)^3$. Hence we reduce the total number of configurations by this factor to calculate the number of equivalent states. Hence the weight and molar zero-point entropy are given by equations (2.32) and (2.33).

\[
W = 4^{N/4} \left[ \left( \frac{3}{4} \right)^{N/4} \right] = \left( \frac{27}{16} \right)^{N/4} \quad (2.32)
\]

\[
S = k \ln \left( \frac{27}{16} \right)^{N/4} = \frac{1}{4} R \ln \left( \frac{27}{16} \right) = 1.088 J K^{-1} mol^{-1} \quad (2.33)
\]
The type of procedure adopted to write equations (2.32) and (2.33) can also be used in the 1:1 ordering case to derive equations (2.30) and (2.31), but the derivation given in the text is the one presented in standard textbooks.

2.5 Ferrimagnetic Ordering

In 1948 Néel elaborated a new type of magnetic ordering, known as ferrimagnetism, from the study of spinels, which remains the classical example of this phenomenon. The theory of magnetic ordering will be discussed in detail in section 3. The tetrahedrally coordinated ions may be considered to constitute one magnetic sublattice (A) and the octahedral ions to similarly compose a discrete magnetic sublattice (B). It was stated in section 2.2 that these sublattices are crystallographically inequivalent, if both contain a high concentration of paramagnetic ions, ferrimagnetism can occur. To consider this bulk property, the different superexchange interactions must be considered; predictions can be made using the theory of superexchange interactions and the empirically derived rules of Goodenough and Kanamori.

If both sublattices contain magnetic ions, the strongest interaction is the A-B interaction, with an A-O-B angle of approximately 125°, which is almost always antiferromagnetic (antiparallel alignment.)

The tetrahedra are comparatively well separated by the octahedra so the A-A interaction is weak, and only important if only the A sublattice is magnetic. Thus the other important interaction is B-B, with a B-O-B bond angle of 90°. Goodenough extensively surveyed the possible combinations; the key ones for this thesis are summarised in Table 2.3. The B-B interactions are predominantly ferromagnetic (parallel ordering), and the combination of this and the antiferromagnetic A-B
interaction produce the bulk ferrimagnetism; the ions in the B sublattice magnetise ferromagnetically and the A sublattice magnetises antiparallel to B.

Table 2.3: Selected 90° B-O-B interactions.

<table>
<thead>
<tr>
<th>Exchange Path</th>
<th>Interaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn(IV)-Mn(IV) (d^3-d^3)</td>
<td>ferromagnetic *</td>
</tr>
<tr>
<td>Cr(III)-Cr(III), Mn(IV)-Cr(III)</td>
<td></td>
</tr>
<tr>
<td>Ni(II)-Ni(II) (d^8-d^8)</td>
<td>ferromagnetic</td>
</tr>
<tr>
<td>Mn(IV)-Ni(II) (d^3-d^8)</td>
<td>weak antiferromagnetic</td>
</tr>
<tr>
<td>Mn(IV)-Fe(III) (d^3-d^5)</td>
<td>weak antiferromagnetic</td>
</tr>
<tr>
<td>Mn(IV)-Co(II) (d^3-d^7)</td>
<td>weak antiferromagnetic</td>
</tr>
<tr>
<td>Fe(III)-Fe(III) (d^5-d^5)</td>
<td>weak antiferromagnetic</td>
</tr>
<tr>
<td>Co(II)-Co(II) (d^7-d^7)</td>
<td>ferromagnetic</td>
</tr>
</tbody>
</table>

*: In the case of Mn(IV)-Mn(IV) there is a direct exchange interaction between the metal t_{2g} orbitals of comparable magnitude. These orbitals are half filled, so, in accordance with the Pauli exclusion principle, this interaction is antiferromagnetic.

2.6 References


(8) M. Iizumi; T. F. Koetzle; G. Shirane; S. Chikazumi; M. Matsui; S. Todo. 


Chapter 3

Theory and Experiment
3.1 Introduction

This chapter contains an introduction to general theory pertaining to this thesis, and to the experimental techniques used in the synthesis and characterization of samples. The key investigative techniques, X-ray and neutron diffraction, magnetic, and electrical measurements, are discussed. An overview of each technique will precede a description of the theory, experimental and analytical procedures.

3.2 Synthesis

Powder samples were produced by combining stoichiometric amounts of the appropriate metal acetates, with subsequent decomposition and firing. Reaction of the acetates was found to yield a more complete mixing, and fewer impurities, than the standard solid-state technique of grinding the equivalent oxides and carbonates together, at the relatively low reaction temperature. Specifically, in the synthesis of the lithium compounds in chapters 4 and 5, when Li₂CO₃ and MnO₂ were used as starting materials, Bragg peaks assigned to the persistent impurity phase Li₂MnO₃ were identified in the product. The reaction mixture was ground thoroughly before decomposition, which was achieved by slowly heating the acetates from room temperature to 400°C (ΔT = 0.7°C/min). The substrate was then pelletised and fired at 750°C or 800°C for at least four days, with intermittent regrinding. The full heating regime for each sample will be given in the relevant chapter. The reaction was deemed to be complete when further heating brought no improvement to the XRD pattern, as measured by line width in the X-ray diffraction pattern. On completion of most of the syntheses, the reaction mixture was slow-cooled at 0.07°C per minute from 750°C to
room temperature to produce the final sample. This method was reported\textsuperscript{1} by Blasse to induce B-sublattice cation ordering in mixed spinels. It was used in this work both to ensure a thermodynamic equilibrium distribution of cations over the available sites and induce order in a particular sublattice.

To confirm the monophasicity and crystallinity of the studied material, a Siemens D500 X-ray diffractometer was used, with Cu K\textsubscript{α1} wavelength 1.54056 Å (obtained by use of a quartz monochromator) over the two theta range 5 to 100 degrees, with a scan speed of 0.12 2-theta s\textsuperscript{-1}. The materials were confirmed as single phase in the powdered form (within the noise level of the diffraction pattern) by first comparing the pattern to those of related materials with the JCPDS database contained within the diffractometer's software. No peaks additional to those expected for the desired materials were observed, though for some samples, a shoulder was observed on a subset of the Bragg peaks.

3.3 Diffraction

3.3.1 Introduction

This section contains a description of the theoretical basis of the process of diffraction. The key experimental techniques that exploit this phenomenon to provide phase identification and structure elucidation are discussed later in this chapter.

3.3.2 Theory of Diffraction

3.3.2.1 Introduction
The interaction of a monochromatic beam with a crystalline sample can result in three basic processes: absorption, refraction and scattering. Sample induced scattering can be either inelastic or elastic, that is with or without a change of energy of the incident radiation. Diffraction is the elastic scattering of waves.

### 3.3.2.2 Elastic Scattering

A good approximation of the structure of a crystalline material is an infinite three-dimensional array of lattice points, which has a basis, or motif, attached to each of these points. This basis represents the set of atoms that comprise the primitive unit cell. In this way a crystal structure is analogous to a diffraction grating. The series of light and dark areas produced when a beam of light (the wavelength of light in the visible region of the spectrum is similar to the spacing between points of the grating) passes through the grating are a result of positive and negative interference. Interference is a fundamental property of waves, thus this phenomenon can be observed in crystals if a beam of radiation, of similar wavelength to the spacing of the lattice points, is fired at the crystal. This is exploited in two of the most powerful techniques in solid-state science, x-ray and neutron diffraction.

To extract meaningful information from a diffraction experiment, the interference pattern must be interpreted in terms of properties of the crystal structure. An important concept in this analysis is that of the reciprocal lattice. The reciprocal lattice is related to the direct lattice by the following set of equations

\[
\mathbf{a}^* = \frac{\mathbf{b} \times \mathbf{c}}{V_c}; \quad \mathbf{b}^* = \frac{\mathbf{c} \times \mathbf{a}}{V_c}; \quad \mathbf{c}^* = \frac{\mathbf{a} \times \mathbf{b}}{V_c}
\]  

(3.1)

where \( V_c \) is the volume of the unit cell, hence
so that the reciprocal lattice vector $d^* = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$ is perpendicular to the direct lattice planes with Miller indices $(hkl)$. The magnitude of this vector is the reciprocal of the shortest distance between these Miller $(hkl)$ planes,

$$|d^*| = \frac{1}{d_{hkl}}$$  \hspace{1cm} (3.3)

The condition for coherent elastic scattering is expressed qualitatively by Bragg’s Law, which is expressed in equation (3.4) and depicted in figure 3.1.

For diffraction to occur, the beams diffracted from the two lattice points in figure 3.1 must interfere constructively. Therefore, the difference in the path length between the two diffracted beams must be an integral number of wavelengths. This path length difference is $\overline{AB} + \overline{BC}$; $\overline{AB} = \overline{BC} = d\sin\theta$, so the path difference is $2d\sin\theta$. Thus the condition for diffraction, or Bragg’s Law is:

$$n\lambda = 2d\sin\theta$$  \hspace{1cm} (3.4)
In Ewald’s construction, which is depicted in figure 3.2, the origin, O, is defined as the point where the incident beam, $k_0$, terminates, and C as the centre of a sphere of radius $\frac{1}{\lambda}$. The diffraction condition is met if one or more reciprocal lattice points, such as the point P, lie on the surface of the sphere, making an angle $\theta$, the Bragg Angle, such that $\angle OCP = 2\theta$.

![Ewald's Sphere Diagram](image)

Figure 3.2: Pictorial representation of Ewald's Sphere.

In the preceding section it was demonstrated that the positions of points of coherent scattering, or Bragg peaks, were determined by the distances between the Miller planes and, therefore, the lattice parameters of the crystal. Here the relative intensities of these Bragg peaks are shown to be dependent on the position of atoms within the unit cell.

Waves scattered by different atoms within the unit cell interfere with one another. The scattering power for a reflection $hkl$ is defined by the structure factor $F_{hkl}$, where the intensity, $I_{hkl}$, is the square of the amplitude of the structure factor, as equation (3.5).

$$I_{hkl} = |F_{hkl}|^2$$  \hspace{1cm} (3.5)
\[ F_{\text{hkl}} = \sum_i f_i \exp(-2\pi i(hx_i + ky_i + lz_i)) \exp(-W_i) \] \quad (X-ray) \quad (3.6)

\[ F_{\text{hkl}} = \sum_i b_i \exp(-2\pi i(hx_i + ky_i + lz_i)) \exp(-W_i) \] \quad (Neutron) \quad (3.7)

Where the structure factor is defined in equation (3.6) for X-rays, and equation (3.7) for neutron diffraction. The fractional coordinates of the \(i\)th atom are \(x_i, y_i, z_i\), \(f_i\) is the scattering amplitude for X-rays, \(b_i\) the neutron scattering length and \(W_i\) is the Debye-Waller isotropic temperature factor defined in equation (3.8). Where necessary, an anomalous dispersion contribution is included in \(f_i\) for XRD experiments, and an anomalous scattering term is included in the \(b_i\) term in neutron diffraction experiments.

\[ W_i = \frac{8\pi^2 \sin^2 \theta \langle u_i^2 \rangle}{\lambda^2} \] \quad (3.8)

where \(\langle u_i^2 \rangle\) is the mean square displacement of the \(i\)th atom.

### 3.3.2.3 Rietveld Refinement

A fundamental problem associated with powder diffraction is that the random orientation of the crystallites in the diffraction beam causes the superposition of the three crystallographic axes onto the same axis (d-spacing, or 20) of the diffraction pattern. The distances between the Miller planes are often similar, or the same, causing overlapping peaks, because the peaks in a diffraction experiment have a finite width. This peak overlap prevents accurate measurement of the intensity, and hence structure factors of individual reflections.

Rietveld\(^2,3\) developed a profile analysis method to circumvent the problem of peak overlap. An initial structural model is refined to obtain the best possible fit between the observed and calculated diffraction profiles. This process requires the accurate
description of the peak shape by a mathematical function. The procedure is given below.

At any point I in the diffraction pattern there is a measured intensity $y_i$. A function, $S_y$, composed of the observed and calculated intensity is minimised using a least squares procedure for each point on the diffraction pattern, as shown in equation (3.9).

$$S_y = \sum_i w_i |y_i - y_{ic}|^2$$  \hspace{1cm} (3.9)

Where $w_i$ is a weighting function, $w_i = \frac{1}{y_{i,obs}}$. $y_i$ and $y_{ic}$ are, respectively, the observed and calculated intensity at the $i^{th}$ step.

Observed intensity is not allocated to any particular Bragg reflection, so a relatively good starting model is required. Typically, an isostructural material, with known structure, is used to provide this starting point. When a suitable material is not available, there are many techniques used to obtain a starting model, such as direct methods and simulated annealing.

The observed intensity, $y_i$, is usually comprised from many $(d_{hkl})$ reflections. The calculated intensity $y_{ic}$ depends on the structure factor $|F_{hkl}|^2$ values obtained from the structural model. Other contributions to the intensity are parameters defining the background, a function that describes the peak-shape and the zero point, which corrects for any shift in the peak position caused by the sample not being exactly at the focus of the radiation. A typical expression for peak intensity in an XRD experiment is given in equation (3.10).

$$y_{ic} = \sum_{hkl} m_{hkl} L_{hkl} |F_{hkl}|^2 A_i G(2\theta_i - 2\theta_{hkl}) P_{hkl} T + y_{ib}$$  \hspace{1cm} (3.10)
Where:

- $s$ is the scale factor,
- $L_{hkl}$ is the Lorentz-polarisation factor for the reflection $(hkl)$,
- $m_{hkl}$ is the multiplicity factor,
- $F_{hkl}$ is the structure factor,
- $A_i$ is the asymmetry parameter,
- $G(\theta)$ is the reflection profile function,
- $2\theta_{hkl}$ is the calculated position of the Bragg peak, corrected for the zero-point shift,
- $P_{hkl}$ is the preferred orientation function,
- $T$ is the absorption correction,
- $y_{ib}$ is the background intensity at the $i$th step.

The reflection profile is a function of both the sample and instrument, and varies as a function of $2\theta$. The most common function is a combination of Lorentzian and Gaussian components and known as the pseudo-Voigt approximation. In this thesis, the profile coefficients for Simpson's rule integration of the pseudo-Voigt function[Howard, 1982 #243] were obtained from the Thompson-Cox-Hastings equation.[Thompson, 1987 #244]

It is necessary to assess the quality of the model, because the convergence of the residual to a minimum does not guarantee that the refined structure is correct; a false, or local, minimum could have been reached or a wrong starting model employed. Hence, there are several fit indices that are commonly used to calculate the goodness-of-fit. The indices, used in the Rietveld analyses in this thesis, are given in equations (3.11)-(3.15) below.
1) The Bragg R-factor, $R_B$.

$$
R_B = \frac{\sum |I_{hkl}(\text{obs}) - I_{hkl}(\text{calc})|}{\sum I_{hkl}(\text{obs})}
$$

(3.11)

2) The profile R-factor, $R_p$.

$$
R_p = \frac{\sum |y_i - y_{ic}|}{(\sum y_i)}
$$

(3.12)

3) The weighted profile R-factor, $R_{wp}$.

$$
R_{wp} = \sqrt{\frac{\sum w_i (y_i - y_{ic})^2}{\sum w_i y_i^2}}
$$

(3.13)

where $w_i$ is the weighting factor

4) The expected R-factor, $R_e$.

$$
R_e = \frac{(N - P + C)}{\sqrt{\sum w_i y_i^2}}
$$

(3.14)

where N, P and C are, respectively, the number of profile points, refined parameters and constraints.

5) The goodness of fit factor, $\chi^2$,

$$
\chi^2 = \left( \frac{R_{wp}}{R_e} \right)
$$

(3.15)

that is unity for perfect fit.

In addition to the quoted fit indices, a difference plot, which displays the difference between the observed and calculated profiles, is a key tool in discerning the quality of the refinement. Evaluation of bond lengths and angles provides an essential check to the validity of the refined structure.
In this work, the GSAS suite of programs\textsuperscript{4} was used in the refinement of the X-ray and neutron powder data. In all refinements, the background was fitted with a shifted Chebychev function and the peak shape with a pseudo-Voight function. Instrumental parameters were inserted with a Siemens d500 instrument parameter file. The first parameters to be refined were the lattice parameters, the zero point and the background function, followed by the peak shape. After convergence was reached, the atomic coordinates and thermal parameters were refined.

3.3.2.4 Magnetic Structure Solution by Representational Analysis

The Representational Analysis method uses group theory in the determination of complex magnetic structures. A phase transition, such as the onset of long-range magnetic order, corresponds to a sudden breaking of the symmetry of the system. This symmetry breaking is characterised by an order parameter $\eta$. At temperatures below the critical temperature, $T_c$, the order parameter can vary in a continuous or discontinuous manner, depending on whether it is, respectively, a second, or first, order transition. Group theory cannot be applied to first order transitions, but can be very useful for those of second order, which is the case for most magnetic transitions. According to Landau theory\textsuperscript{5}, a transition will only be second order if only one of the irreducible representations (IRs), $\Gamma_n$, of the symmetry group, $G_p$, becomes critical at $T_c$. If more than one IR were to become critical at $T_c$, the cross-terms in the free energy would be large and result in a first order transition.

There are three key steps in determining the possible magnetic structures,\textsuperscript{6} composed of linear combinations of the basis vectors $\psi_n$ associated with the irreducible representations $\Gamma_n$, of the space group $G$. Before this procedure can be applied the non-
magnetic space group must be determined, as must the propagation vector, $\vec{k}$, that related the magnetic ordering to the structural model.

1.) The transformation properties of the components of the magnetic moment under the symmetry elements of the group $G$ define a representation $\Gamma$.

2.) The representation $\Gamma$ is decomposed into the irreducible representations, $\Gamma_n$, of $G$.

3.) For each IR, the components of the basis vectors, $\psi_n$ can be determined from the matrix elements of $\Gamma_n$.

Representational analysis was performed with the SARA$h^7$ program and the quality of the various candidate structures was assessed by the Rietveld method (section 3.3.2.3) using the program SARA$h$-Refine for GSAS.
3.3.3 Diffraction Experiments

3.3.3.1 Introduction

The technique of X-ray powder diffraction is extensively used for phase identification and, more recently, structure determination. However, it is not always possible to fully determine the structure of certain materials using X-rays because scattering is a function of the number of electrons. Thus neutron diffraction has to be used for samples containing lighter elements or elements of similar atomic number. Diffraction can also be used to monitor structural transitions, which can occur upon changing physical conditions such as temperature or pressure.

3.3.3.2 Powder X-ray Diffraction

Powder XRD was initially carried out to confirm the single-phase composition of the synthesised materials and obtain the lattice parameters. The materials were finely ground to ensure random orientation of the crystallites, which is necessary for the Bragg diffraction conditions to be met in powdered samples. The samples were laid in an amorphous ceramic plate and pressed into place to ensure that all Bragg conditions are met. The XRD patterns were measured using a Siemens D500 Diffractometer, which uses Cu K-\(\alpha_1\) radiation (\(\lambda = 1.540562 \text{ Å}\)) obtained with a quartz crystal primary monochromator, operating in Bragg-Brentano geometry from a flat plate sample. In a typical experiment a two-theta range of 5-100° with a step size of 0.01° and a counting time of 5 seconds per step was used.
Laboratory based diffractometers generate X-rays by bombarding a metal target (typically copper, cobalt or molybdenum) with an electron beam emitted from a heating filament. The electron beam ionises core electrons from the K-shell (1s) of the metal target. The transition of electrons from higher, filled, electron shells into the resultant (1s) vacancies is accompanied by the simultaneous emission of X-rays of energy equal to the difference in energy between the original and final (1s) orbital. This relaxation of electrons into the vacant (1s) orbital is governed by the transition selection rule, which requires a change in orbital angular momentum of one (Δl = +/-1) thus the relaxing electron must come from the L (2p) or M (3p) orbitals. The result is two intense lines in the emission spectrum. The beam of X-rays is reflected by a crystal monochromator (typically quartz or silicon) to provide a single wavelength. The wavelength is selected according to the Bragg equation, \( n\lambda = 2d \sin \theta \) (equation (3.4)).

Laboratory based diffractometers allow convenient phase identification by comparison of the diffraction pattern with the database of known histograms. If the crystal structure is not known, indexing programs, such as TREOR,\(^8\) provide a useful tool in obtaining unit cell parameters and crystal symmetry. Once these quantities are known, full structure solution can be attempted by Rietveld refinement, as described in section 3.3.2.3. This can provide accurate atomic positions, if a reasonable starting model is available. If the quality of data obtained from a laboratory diffractometer is not sufficient to enable structure solution, a more intense beam can be used at central synchrotron facilities. The X-ray beam at a synchrotron source is of the order of a thousand times brighter than a laboratory diffractometer. This increases the signal to noise ratio, decreases collection time, and provides a well-defined peak-shape. These advantages allow Rietveld profile analysis of more complex structures. However, synchrotron radiation has not been employed in this thesis because laboratory
diffraction was adequate for initial structure refinement of these compounds, and neutron diffraction (section 3.3.3.3) was the appropriate tool for the detailed investigations undertaken in this thesis.

As discussed in section 3.3.2.2, X-rays are scattered by an interaction with electrons of the atoms and interference occurs when the X-ray beam hits the material. The scattering factor \( f_i \) (equation (3.6)) of an atom decreases with increasing scattering angle, \( 2\theta \). The scattering factor is a function of the atomic wave function, hence is determined by the summation of the contributions of \( Z \) electrons to the scattering amplitude, as in equation (3.16). The sum is across the path or phase difference between the \( Z \) scattered waves.

\[
   f_i = \frac{\text{amplitude scattered by electrons from an atom}}{\text{amplitude scattered by single electron}} \quad (3.16)
\]

It is found that \( f_i \) is proportional to the number of electrons, therefore the X-ray scattering factor is very small for light atoms, for example hydrogen or lithium. Thus, the use of X-rays in determining the precise crystal structure of compounds containing light atoms is difficult, unless using exceptional signal-noise instrumentation. Hence diffraction techniques that are not atomic number dependent, such as neutron diffraction, are used. Neutrons are scattered by nuclei, rather than the electrons. A neutron experiment allows excellent resolution and can readily distinguish elements of similar atomic number, as well as detecting light atoms, in reasonable counting times. Neutron diffraction is extremely expensive, so is only employed when other diffraction techniques are inappropriate.

3.3.3.3 Powder Neutron Diffraction
Powder Neutron diffraction experiments in this thesis were performed on two different instruments, the BT1 diffractometer at the National Institute of Standards Technology (NIST), Gaithersburg, USA, and the D1A diffractometer at the Institut Laue-Langevin (ILL), Grenoble, France. Both the ILL and NIST are reactor sources, and both D1A and BT1 are constant wavelength diffractometers, or 2-axis diffractometers.

The two standard techniques for the production of neutrons for diffraction experiments are the 'spallation' process, as implemented at Rutherford Appleton Laboratory (RAL), or by thermal methods from a nuclear reactor, as practised at the National Institute of Standards Technology (NIST) and the Institut Laue-Langevin (ILL). In a spallation source a beam of protons hits a heavy metal target, and the resulting nuclear reactions give rise to a stream of “white” neutrons. Because the protons are pulsed, so is the white beam, allowing the time-of-flight method, which provides greater resolution than monochromator based experiments, to be employed. In a reactor source, the white beam is extracted from a hole in the reactor and collimated, which limits the range of incident directions. The beam is then passed through a single crystal monochromator that selects a band of wavelengths and directs the selected neutrons, via a secondary collimator, to the sample. The beam is scattered, by the sample, into a bank of detectors. This section describes the properties of the diffractometers that were employed.

3.3.3.3.1 BT1 Diffractometer, NIST, USA

The reactor uses uranium fuel elements to produce a thermal flux of $4 \times 10^{14}$ neutrons cm$^{-2}$s$^{-1}$ at a rated power of 20MW. The reactor is D$_2$O moderated, cooled and reflected, and is run on a 7 week operating cycle.
The BT1 diffractometer is a high-resolution 32-detector instrument. Finite detector slits lead to shifting, broadening and asymmetry of the Bragg peaks.\textsuperscript{9-11} The low angle detectors are partially masked to minimise these distortions. It can be used with three different monochromators; Ge(311), Cu(311) or Si(531), with either 15\degree or 7\degree collimation. A schematic diagram of the diffractometer is shown in figure 3.3. The three monochromators are set in different positions producing different take off angles. From left to right in figure 3.3, the monochromator positions are Ge(311), Cu(311) and Si(531), with respective take off angles of 120\degree, 90\degree and 72\degree. In all measurements reported in this thesis, the Cu(311) monochromator was used, because it has the best balance between intensity and resolution over the 2\theta range of interest. The properties of the different monochromators are tabulated in table 3.1, and their relative resolution (full-width half-maximum (FWHM), measured in degrees) is plotted in figure 3.4.
Figure 3.3: Schematic of the BT1 diffractometer, NIST, USA.

Table 3.1: Monochromator Information for BT1, NIST, USA

<table>
<thead>
<tr>
<th>Monochromator</th>
<th>Collimation (arcmin)</th>
<th>Monochr. 2Theta (°)</th>
<th>Relative Bragg Intensities</th>
<th>Flux (n s^(-1) cm^-2)</th>
<th>Wavelength (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ge(311)</td>
<td>15'</td>
<td>75°</td>
<td>3.34</td>
<td>700,000</td>
<td>2.0784</td>
</tr>
<tr>
<td>Ge(311)</td>
<td>7'</td>
<td>75°</td>
<td>1.84</td>
<td>400,000</td>
<td>2.0795</td>
</tr>
<tr>
<td>Cu(311)</td>
<td>15'</td>
<td>90°</td>
<td>1.00</td>
<td>400,000</td>
<td>1.5401</td>
</tr>
<tr>
<td>Cu(311)</td>
<td>7'</td>
<td>90°</td>
<td>0.59</td>
<td>200,000</td>
<td>1.5405</td>
</tr>
<tr>
<td>Si(531)</td>
<td>15'</td>
<td>120°</td>
<td>0.47</td>
<td>200,000</td>
<td>1.5903</td>
</tr>
<tr>
<td>Si(531)</td>
<td>7'</td>
<td>120°</td>
<td>0.33</td>
<td>100,000</td>
<td>1.5904</td>
</tr>
</tbody>
</table>
Figure 3.4: Resolution as FWHM (degrees) as a function of 2theta (degrees), for BT-1 using each of the three monochromators and either 7' or 15' collimation. For comparison purposes, angles for the Ge(311) and Si(531) monochromators are extrapolated to the wavelength of the Cu(311) monochromator.
3.3.3.2 D1A diffractometer, ILL, France

The D1A diffractometer is a medium resolution instrument. The Ge(115) monochromator, which has a take-off angle of 122° and gives a wavelength of 1.911Å, focuses the 250mm high beam to 30mm at the sample. A bank of 25 high efficiency collimators and detectors, as shown in figure 3.5, detects the scattered beam. The diffraction pattern is measured up to $160^\circ 2\theta$, with a typical step size of 0.05°.

![Figure 3.5: Schematic diagram of the D1A diffractometer, ILL, France, showing the arrangement of the 25 detectors.](image)

3.3.3.3 Magnetic Scattering
The wavelength of the neutrons is determined by their energy, as shown in equation (3.17).

$$\lambda = \sqrt{\frac{h^2}{2mE}}$$  \hspace{1cm} (3.17)

where $h$ is Planck's constant, $m$ is the mass of a neutron and $E$ the energy of the neutron.

Neutron diffraction from atoms can occur by two processes:

1) Nuclear scattering, due to the interaction of the neutrons with the atomic nuclei.
2) Magnetic scattering, due to the interaction of the magnetic moments of the neutrons with permanent magnetic moments of atoms or ions.

In the absence of an applied magnetic field, the magnetic moments in a paramagnetic material are randomly arranged. Therefore, the magnetic scattering is random and only contributes a diffuse background to the sharp maxima of the Bragg peaks. In compounds with long-range magnetic order, such as ferromagnetic and antiferromagnetic materials, the magnetic moments are aligned parallel (or antiparallel) to one another, over large domains. Neutrons scattered from these ordered spins can coherently interfere with each other, giving rise to reflections associated with the magnetic structure.

The degree of scattering of the neutrons is determined by the neutron scattering cross section, $b_\nu$ (equation (3.7)) which is not a function of the atomic mass. It is for this reason that it is also possible to determine the positions of atoms that have a similar electronic structure, as long as the neutron scattering factors are dissimilar. Isotopes of the same element can have very different scattering lengths and cross-sections, hence
isotopic substitution can be used to distinguish atoms with similar cross sections. Certain isotopes, for example $^1\text{H}$, cause strong incoherent scattering, which prevents diffraction experiments so isotopic substitution (for $^2\text{H}$) is necessary for neutron diffraction experiments on materials containing these elements.

### 3.4 Theory of Magnetic Interactions

#### 3.4.1 Introduction

The magnetic behaviour of solids can be categorised within two broad categories. The first, the response to an external magnetic field, is a property of all materials. The second, spontaneous magnetisation, is much less common because it is the result of the presence of intrinsic long-range magnetic order within the material. Magnetic phenomena in solids are primarily associated with electrons; some atomic nuclei have intrinsic magnetic dipole moments but their effect is $1/1830^{th}$ of that associated with electrons. Therefore measurement of the magnetic moment of a sample, with varying temperature or applied magnetic field, provides information on the electronic configuration of the material.

#### 3.4.2 Magnetism of Individual Atoms Within Solids

When a material is placed in a magnetic field $H$, it develops a magnetization (magnetic moment per unit volume) $M$, given by equation (3.18).

$$M = \chi H$$  \hspace{2cm} (3.18)

Where $\chi$ is the magnetic susceptibility. In the cgs system of magnetic units, which has been used throughout this thesis, the flux density, $B$, is defined by equation (3.19).
\[ B = H + 4\pi M \tag{3.19} \]

The units of \( B \) and \( H \) are Gauss and Oersted respectively. The equivalent relationship in the SI system is given in equation (3.20).

\[ B = \mu_0 (H + M) \tag{3.20} \]

Where \( \mu_0 = 4\pi \times 10^{-7} \text{Tm/A} \) is the permittivity of free space. The units are Tesla for flux density and A/m for both \( H \) and \( M \). The magnetic moment, \( \mu \), is given in erg/G (also known as e.m.u.) in the cgs system and J/T in the SI convention. In this thesis, the measured sample magnetization is converted into magnetization per formula unit, and susceptibility into molar susceptibility. These values are much easier to compare to the theoretical values than the values per unit volume, and determining sample volumes is difficult for powder samples.

### 3.4.3 Magnetism in Bulk Materials

In the presence of an applied magnetic field, the motion of electrons around an atom produces a tiny magnetic field antiparallel to the applied field, according to Lenz's Law. This diamagnetism is a property of all materials, and is the dominant property of substances that only contains paired electrons. A diamagnetic material has a small, negative magnetic susceptibility, and is repelled by a magnetic field; it will tend to move towards the weakest region of the field. Materials that contain unpaired electrons are attracted to a magnetic field, and tend to move to the strongest area of field. They are termed paramagnetic and have a positive susceptibility. Paramagnetic susceptibilities are much larger in magnitude than those of diamagnetic materials. Unpaired spins in paramagnetic materials randomly fluctuate, giving zero net magnetisation in the absence of an applied field. As the temperature is reduced, the thermal excitation becomes less significant, so magnetic exchange interactions can
result in magnetically ordered states. The Hamiltonian for the magnetic exchange interaction is given in equation (3.21)

$$H = -2 \sum_{ij} J_{ij} \vec{S}_i \cdot \vec{S}_j$$  \hspace{1cm} (3.21)

The Heisenberg exchange constant between spin vectors, $J_{ij}$, is a function of the interatomic separation. A positive value of $J$ induces parallel alignment of the magnetic moments, and is known as ferromagnetic exchange. Antiparallel alignment, caused by negative $J$ values, is termed antiferromagnetic exchange. The strength of the interaction is determined by the magnitude of $J$. It was mentioned above that this exchange, which is not directly dependent on temperature (it is a function of bond distance and angle which can change with temperature), is in competition with the thermal energy, $kT$. Therefore, an exchange interaction between unpaired spins in a solid would be expected to result in a transition from a thermally randomised (paramagnetic) to a long-range ordered state at a clearly defined temperature, that is dependent on the exchange constant, $J$. This transition can be to one of a number of ordered states, which are discussed in the next section. Competing exchange interactions of opposite sign or magnetic frustration can suppress the transition temperature. The five main types of magnetically ordered state that are frequently encountered are listed below:

a) Diamagnetism (non co-operative):
A diamagnetic material has no unpaired electrons. Weak temperature independent magnetic susceptibility is observed.

b) Ideal Paramagnetism (non co-operative)
Ideal paramagnetic materials atoms have identical atomic moments and located in isotropic surroundings, sufficiently separated from one another. Few materials show this behaviour at all temperatures, but it is the high temperature state of all magnetic
materials. The temperature dependence of the susceptibility follows the Curie-Weiss law (section 3.4.5) at temperatures well above the transition temperature.

c) Ferromagnetism (co-operative)
Ferromagnetic materials have a long-range collinear array of all magnetic moments at temperatures below the Curie temperature. Domains are formed to maximise the magnetostatic energy in the absence of an applied field, which produces zero net moment. Applying an external field enlarges the domains of a favourable orientation at the expense of others.

d) Antiferromagnetism (co-operative)
Antiferromagnetic materials exhibit long-range ordering, but the moments of neighbouring atoms are exactly opposed so there is no spontaneous magnetization. Below the ordering, or Néel, temperature an antiferromagnet consists of two identical interpenetrating sublattices in which the spins of one lattice are opposed to the spin of the other. Most antiferromagnetic materials are insulating solids, such as NiO.

e) Ferrimagnetism (co-operative)
Ferrimagnetic materials occur when two or more different magnetic species are present. They occupy different kinds of lattice sites producing two sublattices (as discussed in section 2.4). The exchange interactions within each sublattice are ferromagnetic and those between the sublattices are antiferromagnetic. As the overall moments of the two sublattices are different, there is a net magnetization, the temperature dependence of which is similar to that of ferromagnetic materials.

f) Spin glass (cooperative)
A spin glass undergoes a random cooperative freezing of its magnetic moments at a well-defined temperature, $T_f$, to an irreversible metastable frozen state. For a spin glass to occur, there must be both frustration (competition between interactions of opposite sign) and geometric disorder. The disorder can be site randomness, where there is a range of nearest neighbour distances, or bond randomness, where the sign of the nearest neighbour interaction varies.

### 3.4.4 Magnetic Exchange Interactions

#### 3.4.4.1 Introduction

The origin of magnetic coupling is the Pauli exclusion principle; electrons of parallel spin have a tendency to stay away from each other. Therefore, a pair of electrons of like spin will be lower in energy than a pair with opposite spin. The energy difference between these two states is the interatomic exchange energy, or exchange coupling. The different mechanisms by which this coupling can occur are discussed in this section.

#### 3.4.4.2 Direct Exchange

Direct exchange requires direct overlap of the orbitals containing the unpaired electrons, hence it requires a short metal-metal distance with no intervening anion. If it occurs between two singly occupied orbitals, the Pauli exclusion principle requires it to be antiferromagnetic.

#### 3.4.4.3 Superexchange

3 4 2
Superexchange describes interactions between localised magnetic moments of ions through an intermediary, nonmagnetic, ion. When direct exchange is not possible, it is the dominant form of exchange in magnetic insulators. The strength of the exchange is determined by the extent of orbital overlap, i.e. bond lengths and bond angles. Localised electron states are stabilised by a mixture of excited states involving electron transfer between the cation and anion. This thesis is concerned with manganese oxide spinels, so the magnetic interactions are between 3d orbitals and superexchange is mediated by oxygen 2p orbitals.

![Diagram of orbital overlap](image)

Figure 3.6: Representation of orbital overlap of (left) \( d_{x^2-y^2} \) - \( p_z \) - \( d_{x^2-y^2} \) 90° oxygen-mediated superexchange and (right) direct \( d_{xy} : d_{xy} \) exchange between neighbouring manganese ions.

The competing interactions are illustrated in figure 3.6. A molecular orbital diagram, showing the 90° \( d_{x^2-y^2} - p_z : p_y - d_{x^2-y^2} \) superexchange interaction, is given in figure 3.7. The \( Mn^{4+} d_{x^2-y^2} \) orbital is empty, but electrons from the oxygen 2p, or 2p, orbitals (shown in blue) can \( \sigma \)-mix with this orbital and so have a probability of being found close to the manganese ion. The excited state, with the two O(2p) electrons on the
manganese ions has lowest energy when the two electrons have like spin (intraatomic exchange), and the manganese ions are most stable when all electrons have the same spin. Thus the $t_{2g}$ electrons of the two manganese ions are indirectly coupled in a collinear arrangement. The magnitude of this ferromagnetic exchange ($J_H$) is the stabilisation of the oxygen 2p, orbital resulting from this coupling.

![Figure 3.7: Superexchange mechanism of $d_{x^2-y^2}$-$p_x$-$p_y$-$d_{x^2-y^2}$ 90° interaction, mediated by two orthogonal 2p orbitals. Blue electrons are predominantly O(2p) in character.](image)

3.4.4.4 Magnetic Exchange in Metallic Systems

There are a number of magnetic exchange interactions that can occur in metallic systems. A magnetic impurity in a metallic system causes an oscillation in the susceptibility of the surrounding conduction electrons, described by the RKKY mechanism, named after Ruderman, Kittel, Kasuya and Yosida. This oscillation leads to an indirect interaction between neighbouring impurity spins, over long ranges; the sign of the exchange interaction is dependent on the distance. If the magnetic impurity ions are so dilute that they cannot be coupled by this mechanism, then it is possible to observe the Kondo effect. In this case, the coupling occurs between the localised impurity ion and the conduction electrons, below the Kondo temperature, the
conduction electrons form a cloud of oppositely polarised spin. This results in a loss of the magnetic moment, and paramagnetic behaviour.

### 3.4.4.5 Double-Exchange

A metal-insulator transition is sometimes accompanied by a simultaneous ferromagnetic-paramagnetic transition. This phenomenon was first explained by Zener, who proposed the double exchange mechanism. The classic example of this is the mixed valence Mn$^{3+}$/Mn$^{4+}$ perovskites, La$_{1-x}$Sr$_x$MnO$_3$. Metallic conduction, via hopping of $e_g$ electrons between Mn$^{3+}$ ions and Mn$^{4+}$ ions, can only occur, according to Hund's rules, if the $t_{2g}$ electrons are ferromagnetically aligned. This is illustrated in figure 3.8. Thus, the ferromagnetic coupling is derived from the intraatomic exchange energy, and the stabilisation brought about by the increased kinetic energy of the $e_g$ electrons.

![Diagram of the double-exchange interaction between Mn$^{3+}$ and Mn$^{4+}$](image)

Figure 3.8: Diagram of the double-exchange interaction between Mn$^{3+}$ and Mn$^{4+}$. Upon transfer of the $e_g$ electron, Hund's rules will only be satisfied if the two sets of $t_{2g}$ electrons are ferromagnetically aligned.
3.4.5 Curie-Weiss Paramagnetism

The magnetisation of a paramagnetic material is proportional to the applied field, until it reaches its saturation limit. Curie$^{19}$ found a relationship between the susceptibility and temperature for paramagnetic substances, as given in equation (3.22).

$$\chi_m = \frac{C}{T} = \frac{N\mu_{\text{eff}}^2\mu_0^3}{3kT}$$  \hspace{1cm} (3.22)

The effective moment, $\mu_{\text{eff}}$, is defined in equation (3.23), $C$ is a constant, known as the Curie constant and $N$ is the number of magnetic sites per mole.

$$\mu_{\text{eff}} = g\sqrt{J(J+1)}$$  \hspace{1cm} (3.23)

The total angular momentum, $J$, is the sum of the orbital and spin momenta ($J = L + S$) and $g$ is the gyromagnetic ratio, usually approximated to 2. The Curie law is only obeyed fully if the magnetic moments are localised and non-interacting. If magnetic exchange interactions are present, then the temperature dependence of the molar susceptibility, in the paramagnetic region, is given by the Curie-Weiss law, given in equation (3.24).

$$\chi_m = \frac{C}{T - \theta}$$  \hspace{1cm} (3.24)

The Weiss Constant, $\theta$, is positive for ferromagnetic interactions, and negative for antiferromagnetic exchange. A curve fitting routine can be used to extract values of $C$ and $\theta$ from the Curie-Weiss region of a plot of susceptibility against temperature. By using the spin-only approximation for the angular momentum ($L = 0; J = S$), which is usually good for first row transition metal ions, equations (3.22) and (3.23) can be combined to give equation (3.25).
\[ C = \frac{N_A \mu_B^2}{3k} \left( g \sqrt{S(S+1)} \right) \]  

\[ S(S+1) = \left( \frac{3k}{N_A \mu_B^2 g^2} \right) C \]  

(3.25)

In this thesis, the Curie constant, \( C \), of a particular compound, determined by curve fitting, is quoted in units of erg K^{-1} G^{-2} mol^{-1}, the constant before \( C \) in equation (3.25) is evaluated to 2.0 G^{-2} mol K^{-1} erg^{-1}, hence, for the quoted \( C \) values, the unpaired spin per formula unit it determined, from the relationship \( S(S+1) = 2C \), by the standard quadratic method. In this thesis, the number of unpaired electrons, \( n \), per formula unit is quoted instead of \( S \) (\( n = 2S \)).

3.4.6 Spin glasses

A spin glass undergoes an unusual form of magnetic transition.\(^{20,21}\) It is clearly a cooperative process to a frozen state that takes place at a well-defined temperature, \( T_f \), but there is not periodic ordering. Instead there are an infinite number of energetically equivalent ground states, where the spins become fixed in random orientations at the freezing temperature. If the material is heated above \( T_f \) and then cooled, a different ground state will be selected, influenced by the relative orientations of the spins as the freezing temperature is reached. It was mentioned in section 3.4.3 that both frustration and disorder were required for the freezing process to occur. The nature of the freezing process gives rise to some interesting magnetic properties. There is a maximum, or cusp, in the AC and DC magnetic susceptibilities at \( T_f \) and the ZFC and FC magnetic susceptibilities diverge below this temperature. The position of the cusp in the AC susceptibility shows a characteristic frequency dependence,\(^{22}\) increasing with increasing frequency. Spin glasses exhibit another property not exhibited by long-range...
ordered magnetic systems, known as the aging effect. If the sample is zero field cooled to below the freezing temperature and then held at that temperature for a waiting time, \( t_w \), before a small DC probing field is applied, then the magnetization of the sample will slowly increase with time. In a ferromagnet, or antiferromagnet, the application of the field changes the lowest energy conformation, but the system very rapidly reaches equilibrium, so the magnetisation is constant with time. In a spin glass, the freezing of spin orientations prevents this equilibration, but over time the system can gradually relax through a combination of equilibrium (short-range) and non-equilibrium (long-range) dynamic processes. The equilibrium processes follow a logarithmic decay, as represented in equation (3.26).

\[
\Delta M(t) = M(0) = SH \log_{10} t
\]  

(3.26)

\( S \) is the relaxation rate of the magnetisation, \( M \), and \( t \) the time elapsed since a field \( H \) was applied. The non-equilibrium contribution is a result of domain growth processes, which are extremely slow in the frustrated spin glass regime. These processes are highly dependent on the time the spin glass has been in the frozen state, \( t_w \), because this is the amount of time the domains in the ZFC frozen state have had to grow; the larger these domains are, the harder they are to move. These processes are described by the stretched exponential function expressed in equation (3.27).

\[
M(t) = M(0) \exp \left[ - \left( \frac{t}{t_p} \right)^{-n} \right]
\]  

(3.27)

The time constant, \( t_p \), and \( M(0) \) depend on both \( T \) and \( t_w \), but \( n \) is only a function of \( t \). The contribution described in equation (3.27) is most significant when \( t = t_w \) because at this time the new domain growth processes have been acting for the same duration as those in the previous ZFC regime, and hence have reached the same lengthscale. This results in overall relaxation behaviour which is logarithmic when \( t \ll t_w, t \gg t_w \) and has
a strong stretched exponential contribution when $t = t_w$. Thus the overall relaxation rate, $S$, as defined in equation (3.28), reaches a maximum when $t = t_w$.

$$S = \left( \frac{1}{H} \right) \left( \frac{\partial M}{\partial \log_{10} t} \right)_{H}$$

(3.28)

When $S$ is plotted against the logarithm of the elapsed time, $t$, for a range of different waiting times, $t_w$, this maximum will be shifted with varying $t_w$. This dependence is known as the aging, or memory, effect.

### 3.4.7 Semi-Spin Glasses

In 1979 Villain predicted that a very small amount of disorder on the B-sites of spinels could result in a phase with an ordered ferromagnetic component and a transverse spin glass component. He dubbed this mixed phase a semi-spin glass. There is little experimental evidence of this behaviour in the systems envisaged by Villain, but the coexistence of ferromagnetic and spin glass behaviour has been observed in a number of highly disordered systems. The situation is complicated by the difficulty in distinguishing a semi-spin glass from a cluster glass, which contains small ferromagnetic clusters. The electrons within these clusters are fully aligned but the clusters undergo a cooperative transition random spin glass-like state. There are also compounds termed reentrant spin glasses, which are spin glasses at low temperatures, and as the temperature is raised undergo subsequent spin glass-ferromagnetic and ferromagnetic-paramagnetic transitions.
A semi-spin glass can be described as the superposition of an ordered ferromagnetic component and a frozen, disordered, transverse spin glass component. If the direction of the ferromagnetic component, of magnitude \( \mu_F \), is arbitrarily assigned to be \( z \), then the spin glass component can be described as a random radius, of magnitude \( \mu_{SG} \), of a circle in the \( xy \) plane, making a random angle, \( \theta \), with the \( x \)-axis. This is illustrated in figure 3.9. The value of the angle, \( \Phi \), between the frozen moment and the ferromagnetic component, is clearly independent of the random angle, \( \theta \), and thus is the same at all magnetically equivalent sites. Thus, the magnetic moments describe an inverted cone of height \( \mu_F \) and width \( \mu_{SG} \) from each magnetic site. The absolute value of the magnitude of the magnetic moment is given by \( \mu = g\sqrt{S(S+1)} \), but zero point quantum fluctuations result in a
maximum ordered moment of $\mu = gS$, where $g = 2$. From figure 3.9, we can derive the following relations, listed in equations (3.29)-(3.31).

\begin{align*}
\mu^2 &= \mu_F^2 + \mu_{SG}^2 \\
\mu_F &= \mu \cos \Phi \\
\mu_{SG} &= \mu \sin \Phi
\end{align*}

(3.29) 

(3.30) 

(3.31) 

By taking $\mu = gS$ and calculating $\mu_F$ from saturation magnetization, or neutron diffraction measurements, values of $\mu_{SG}$ and $\Phi$ can be obtained.

### 3.5 Measurement of Magnetic Properties

#### 3.5.1 Experimental

Magnetic measurements have been carried out on two instruments. DC susceptibility was measured using a Quantum Design MPMS SQUID magnetometer and AC susceptibility using an Oxford Instruments MagLab\textsuperscript{2000} System.

#### 3.5.1.1 DC Susceptibility Measurements

DC magnetic susceptibility measurements were typically performed in the temperature range of 5-300K, with a step size of 2K below 50K, and 5K above that temperature. Where it was deemed necessary, temperatures down to 1.8K, or up to 400K, were employed. The Zero Field Cooled (ZFC), and Field Cooled (FC), magnetic susceptibility in 100Oe was measured for all samples, and where necessary the measurements were repeated in 1000Oe. Aging experiments were performed on spin glass samples. In these experiments the sample was ZFC to the target temperature.
below the freezing temperature and then held at that temperature for a waiting time, \( t_w \), before the probing field (typically 200e) was applied. The magnetisation was measured at constant temperature, with a pause of one second between measurements, as a function of time. The samples, of known weight were placed in gelatine capsules. The capsule was loaded into the sample holder packed with other empty capsules to prevent the sample moving and to provide an averaged environment. The capsules were held in place with non-magnetic tape.

### 3.5.1.2 AC Susceptibility Measurements

AC susceptibility measurements were carried out when it was deemed that dynamic measurements could elucidate observed features in the DC susceptibility measurements, particularly if frustration or irreversibility was suspected in a magnetic transition, such as spin-glass formation.

AC measurements were performed over a temperature range across the magnetic transition, typically sweeping at a rate of \( 1K\text{min}^{-1} \) over 30K with an AC driving field of 10e. This measurement was run at a number of different driving frequencies, typically 100Hz, 1kHz and 10kHz. The samples, of known weight were placed in gelatine capsules. The capsule was loaded into the sample holder packed with other empty capsules to prevent the sample moving and to provide an averaged environment. The capsules were held in place with non-magnetic tape.

### 3.5.2 SQUID Magnetometers
The Superconducting Quantum Interference Device or SQUID provides the most accurate measurements of magnetic susceptibility. A schematic diagram of a SQUID is shown in figure 3.10, the key component is a superconducting ring with two Josephson junctions, which are regions of normally conducting material small enough to allow the Cooper pairs of the superconducting current to tunnel through.

![Figure 3.10: Schematic diagram of a SQUID Magnetometer](image)

When a current is applied across the superconducting ring, to bias the SQUID, it divides between the two Josephson junctions, if this current is greater than the critical current then the ring has a finite resistance and a potential difference, or voltage, is produced across it. The magnetic flux within the ring, defined as the product of the area of the ring and the magnetic field enclosed by it, is quantised. Hence, only multiples of the flux quantum, given in equation (3.32), can be trapped within the superconducting ring.

\[
\frac{hc}{2e} = 2 \times 10^{-7} \text{Oe cm}^2
\]  

(3.32)

The ring is made of a type II superconductor, hence each flux quantum present in the ring will reduce the critical current. Furthermore, the magnetic field (which can have any value) cannot always be completely flux quantised within the area of the ring, so any excess field, too small to form a quantum in the ring, must be repelled. This repulsion is achieved by creating an equal and opposite field by means of induction of a
current around the ring. This inductive current reduces the critical current significantly, causing a large oscillation in the critical current with applied field. This is shown in figure 3.11, where moving from one maximum to the next, away from zero applied field, is the process of the absorption of one flux quanta into the ring.

![Oscillation of the critical current with applied field in a SQUID ring.](image)

Figure 3.11: Oscillation of the critical current with applied field in a SQUID ring.

In a SQUID magnetometer, the magnetic field produced by the sample is measured by means of a bridge circuit consisting of a primary coil and two secondary coils wound in opposition and connected in series. If the two secondary coils were perfectly balanced, the induced voltage would exactly cancel out. Introducing a sample in one of the secondary coils unbalances the bridge, and results in a net current. This current is used to induce a field across the SQUID, causing the critical current to fluctuate as in figure 3.11. A constant biasing current is being passed through the ring, so the voltage across the ring will fluctuate, and this is the quantity that is measured, whilst moving the sample through the pick-up coil. The field inducing the current in the pick-up loop is proportional to the magnetic moment of the sample divided by the cube of the distance between the sample and the loop. The relationship of the voltage across the SQUID and this distance allows the calculation of the dipole moment of the sample and hence, the magnetisation and susceptibility of the sample to be determined.
3.5.2 AC Susceptibility Measurements

AC susceptibility measurements\(^\text{27}\) are carried out in a similar manner to their DC counterparts. The difference is that an AC drive magnetic field is superimposed on the DC field, resulting in a time-dependent moment on the sample. The fluctuating moment on the sample induces a current in the pick-up coil, which is measured by a SQUID as described in the previous section.

When the frequency is very low, AC and DC magnetometry are essentially the same. In this case, the magnetic moment of the sample follows the magnetisation versus field curve measured in a DC experiment. For a small AC field, the induced AC moment, \(M_{AC}\), is given by equation

\[
M_{AC} = \left(\frac{dM}{dH}\right)H_{AC} \sin(\omega t) \quad (3.33)
\]

\(H_{AC}\) is the amplitude of the driving AC field, \(\omega\) is the driving frequency and \(\chi = \left(\frac{dM}{dH}\right)\) is the susceptibility, or the gradient of the magnetisation against field curve. Hence the susceptibility can be measured.

At high frequency, the AC moment of the sample no longer follows the DC magnetization curve because dynamic effects in the sample result in a time lag. The driving field is changing too quickly for the sample to keep up, so a phase shift develops between the driving field and the induced moment. This can be detected by the magnetometer, thus two quantities are measured in an AC experiment, the susceptibility, \(\chi\), and the phase shift relative to the drive field, \(\phi\). These are normally considered as the susceptibility having an in-phase, or real, component \(\chi'\) and an out of
phase, or imaginary, component, $\chi''$. These two representations are related by the expressions given in equation (3.34).

$$\begin{align*}
\chi' &= \chi \cos \varphi \\
\chi'' &= \chi \sin \varphi \\
\chi &= \sqrt{\chi'^2 + \chi''^2} \\
\varphi &= \arctan \left( \frac{\chi''}{\chi'} \right)
\end{align*}$$  

(3.34)

In the low frequency regime, where AC and DC measurements are most closely analogous, the real component, $\chi'$, is the gradient of the magnetisation versus temperature curve, or the DC susceptibility, and the imaginary, component, $\chi''$, indicates dissipative processes in the sample, such as eddy currents. Relaxation and irreversibility in spin-glasses can result in finite values of $\chi''$. AC measurements are particularly important for spin glasses because the location of the maximum in the susceptibility versus temperature curve is frequency dependent, a property not exhibited by other magnetic ordering schemes. A nonzero value of the imaginary, component, $\chi''$ can also be found in ferromagnets, if there is irreversible domain wall movement. The onset of superconductivity in a sample will result in a large, positive imaginary component, and the real component falling to $-1$, indicating a perfect diamagnet.

### 3.6 Conductivity Measurements

Conductivity measurements were performed on the electronic properties probe of the Oxford Instrument MagLab$^{2000}$ system, using the standard four probe technique, as illustrated in figure 3.12. Gold wires were affixed to a sintered pellet, of approximate dimensions, $1cm \times 0.5cm \times 0.1cm$, with gold paint. A constant current was passed across the pellet, and the potential difference was measured between the two inner wires, hence the resistance in the region of the pellet between these two wires, of path length, $l$, and
cross-sectional area, \( A \), was calculated. The bulk property of resistivity, \( \rho \), was elucidated from the sample specific property of resistance, \( R \), by the relationship in equation (3.35).

\[
\rho = \frac{RA}{l} \quad (3.35)
\]

Typical values of \( A \) and \( l \), respectively, were \( 0.5cm \times 0.1cm = 0.05cm^2 \) and \( 0.1cm \), giving the resistivity in units of \( \Omega cm \).

Figure 3.12: Arrangement of wires on pellet for four probe conductivity measurements
3.7 References


Chapter 4

Structure and Ferromagnetism in $\text{Mn}^{4+}$ spinels:

$AM_{0.5}Mn_{1.5}O_4$ (A = Li, Cu, M = Ni, Mg)
4.1 Introduction

The rich and varied solid-state chemistry of manganese oxides was introduced in chapter one. Particular emphasis was given to colossal magnetoresistance (CMR) materials, which are important in the development of new data storage devices, and spinels, formulated AB$_2$O$_4$, which are widely used in current recording devices. The observation of this phenomenon in the pyrochlore compound, thallium manganite (Tl$_2$Mn$_2$O$_7$) was highlighted because, unlike the many mixed valence perovskite-based CMR materials, the manganese ions are all in the Mn$^{4+}$ oxidation state, precluding the double-exchange mechanism. The first chapter also mentioned the equivalence of the pyrochlore lattice and the lattice of the B-sites in spinels (this is expanded upon in section 2.2.2) and drew an analogy between the pyrochlore thallium manganite and spinels containing B-site Mn$^{4+}$.

To pursue this analogy, it is necessary to have manganese (IV) ions on the B sublattice. If these octahedral sites were wholly occupied by Mn$^{IV}$, it can be seen clearly from charge neutrality principles that there can be no charge on the A site. This can be achieved by the delithiation of LiMn$_2$O$_4$ to form the metastable $\lambda$-MnO$_2$, though it should be noted that delithiation is never complete, and a small amount of manganese (III) remains. However, this material is insulating, as there is no A-site ion to form a conduction band, as in the case of the Tl-O band in Tl$_2$Mn$_2$O$_7$. It is, however, possible to introduce a large amount of manganese (IV) to the B sites by balancing the charge with cations of low valency on the A site and a small proportion of the B sites. This is achieved in the series, AMn$_{1.5}$M$_{0.5}$O$_4$ (A= Li or Cu and M= Ni or Mg), which are known to undergo a ferromagnetic transition at low temperatures but there has been little
investigation into other physical property measurements. This chapter describes the synthesis, structure, magnetic and transport properties of the spinel series, \( \text{AM}_{0.5}\text{Mn}_{1.5}\text{O}_4 \) (\( A = \text{Li or Cu} \) and \( M = \text{Ni or Mg} \)), which has a similar magnetic network to the pyrochlore \( \text{Tl}_2\text{Mn}_2\text{O}_7 \).

### 4.2 Experimental

Powder samples of composition \( \text{AB}_{0.5}\text{Mn}_{1.5}\text{O}_4 \) (\( A = \text{Li, Cu}; B = \text{Mg, Ni} \)) were produced by the method described in section 3.2. The reaction scheme is given in equation (4.1). When \( \text{Li}_2\text{CO}_3 \) and \( \text{MnO}_2 \) were used as alternative starting materials, Bragg peaks assigned to the persistent impurity phase \( \text{Li}_2\text{MnO}_3 \) were identified in the product.

\[
\text{A(CH}_3\text{CO}_2)_2\cdot\text{H}_2\text{O} + 0.5\text{B(CH}_3\text{CO}_2)_2\cdot4\text{H}_2\text{O} + 1.5\text{Mn(CH}_3\text{CO}_2)_2\cdot4\text{H}_2\text{O} \\
\rightarrow \text{AB}_{0.5}\text{Mn}_{1.5}\text{O}_4 + 12\text{CO}_2 + n\text{H}_2\text{O} \quad (A = \text{Li, Cu}; B = \text{Mg, Ni, Co})
\]

(4.1)

The reaction mixture was ground thoroughly before decomposition, which was achieved by slowly heating the acetates from room temperature to 400°C (\( \Delta T = 0.7^\circ\text{C/min} \)). The product was then pelletised and fired at 750°C for four days with intermittent regrinding. On completion of the synthesis the reaction mixture was slow-cooled at 0.07°C per minute from 750°C to room temperature to produce the final sample.\(^5\) Characterization methods are detailed in chapter 3, and those pertaining to this chapter are summarized below. X-ray diffraction data was collected on a Siemens D500 diffractometer fitted with a primary monochromator giving \( \lambda = 1.54056\text{Å} \). DC Magnetic susceptibility measurements were performed using a Quantum Design MPMS7 SQUID magnetometer. AC susceptibility and magnetoresistance measurements were performed in an Oxford Instruments Maglab 2000 system. Neutron diffraction experiments were carried out on the BT1 constant wavelength diffractometer at the National Institute of
Standards Technology using a Cu(311) monochromator (λ = 1.5401 Å). Analysis of this data was performed by the Rietveld method\textsuperscript{26} within the GSAS suite of software.\textsuperscript{19}

4.3 Results

4.3.1 Structure

The X-ray diffraction (XRD) patterns confirmed the formation of monophasic, highly crystalline spinel phases for all compositions. There were, however, shoulders on the set of peaks \{hhl\} where \(h+l = 2n\). This can be clearly seen in the XRD pattern of LiMg\(_{0.5}\)Mn\(_{1.5}\)O\(_4\), shown in figure 4.1, the reflections that have these shoulders are tabulated in table 4.1. These shoulders are discussed in section 4.4.

Table 4.1: Bragg peaks with shoulder in LiMg\(_{0.5}\)Mn\(_{1.5}\)O\(_4\).

<table>
<thead>
<tr>
<th>Reflection</th>
<th>d spacing (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(111)</td>
<td>4.723</td>
</tr>
<tr>
<td>(220)</td>
<td>2.892</td>
</tr>
<tr>
<td>(311)</td>
<td>2.466</td>
</tr>
<tr>
<td>(222)</td>
<td>2.361</td>
</tr>
<tr>
<td>(400)</td>
<td>2.045</td>
</tr>
<tr>
<td>(331)</td>
<td>1.877</td>
</tr>
<tr>
<td>(333)</td>
<td>1.574</td>
</tr>
<tr>
<td>(440)</td>
<td>1.446</td>
</tr>
<tr>
<td>(622)</td>
<td>1.233</td>
</tr>
<tr>
<td>(444)</td>
<td>1.181</td>
</tr>
</tbody>
</table>
LiMg$_{0.5}$Mn$_{1.5}$O$_4$ and CuMg$_{0.5}$Mn$_{1.5}$O$_4$ exhibited cation ordering on the octahedral sites, resulting in a superstructure refined in the $P4_332$ space group. This ordering can be monitored by the emergence of low-angle peaks, indexed (110), (210) and (211) in the XRD pattern, as shown, respectively, in figures 4.1 and 4.4. These reflections are forbidden in the more conventional spinel space group, $Fd\bar{3}m$, as face-centred symmetry results in the reflection condition $(hkl): h+k=2n$, $h+l=2n$ and $k+l=2n$. This phenomenon was not apparent in the nickel containing samples, whose X-ray diffraction patterns could be satisfactorily fitted using the $Fd\bar{3}m$ space group. The XRD pattern of LiNi$_{0.5}$Mn$_{1.5}$O$_4$ is shown in figure 4.6. However, the absence of the low angle reflections in the X-ray diffraction patterns, as observed for LiMg$_{0.5}$Mn$_{1.5}$O$_4$ in figure 4.1, is not conclusive evidence of cation disorder in the ANi$_{0.5}$Mn$_{1.5}$O$_4$ (A= Li or Cu) series of compounds, as nickel and manganese have similar numbers of electrons. Further information was obtained by neutron diffraction; the negative coherent scattering length of manganese (-3.73fm) gives strong contrast with the other metal ions, particularly nickel (10.3fm). The CuNi$_{0.5}$Mn$_{1.5}$O$_4$ powder neutron diffraction pattern was satisfactorily refined in the $Fd\bar{3}m$ space group, with manganese and nickel randomly distributed over the octahedral sites, giving an $R_{wp}$ goodness-of-fit factor of 6.97%. However, it was found that a slight improvement in the fit was achieved using a multiphase refinement using both the ordered ($P4_332$) and disordered ($Fd\bar{3}m$) structures, with respective weight fractions of 5% and 95%. This resulted in reduction of the $R_{wp}$ goodness-of-fit factor to 6.66%, the resultant fit is shown in figure 4.5. Powder neutron diffraction patterns were also collected for LiMg$_{0.5}$Mn$_{1.5}$O$_4$ and CuMg$_{0.5}$Mn$_{1.5}$O$_4$. Rietveld refinement of these patterns confirmed the long-range ordered structure. A good fit was obtained for both patterns with a single ordered ($P4_332$) phase, the fit to the room temperature pattern of CuMg$_{0.5}$Mn$_{1.5}$O$_4$, with CuO
impurity phase, is shown in figure 4.3. The structural parameters obtained in these measurements are summarized in tables 4.2 and 4.3.

Table 4.2: Structural parameters obtained from Rietveld refinement of the powder neutron diffraction pattern of LiMg$_{0.5}$Mn$_{1.5}$O$_4$ at room temperature and 10 K and CuMg$_{0.5}$Mn$_{1.5}$O$_4$ at room temperature. The space group P4$_3$32 was used with positions A (x,x,x) (A= Li or Cu), Mg(1)/Mn(1) at (0.625, 0.625, 0.625), Mg(2)/Mn(2) at (0.125,y,z), O(1) at (x,x) and O(2) at (x,y,z).

<table>
<thead>
<tr>
<th>Site</th>
<th>Li (300K)</th>
<th>Li (10K)</th>
<th>Cu (300K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(x,y,z)</td>
<td>0.0028 (11)</td>
<td>0.0048 (8)</td>
<td>0.0057 (2)</td>
</tr>
<tr>
<td>U / Å$^2$</td>
<td>0.0197(13)</td>
<td>0.0135 (13)</td>
<td>0.0105 (7)</td>
</tr>
<tr>
<td>Mg(1)</td>
<td>0.959 (10)</td>
<td>0.959 (10)</td>
<td>0.953 (9)</td>
</tr>
<tr>
<td>Occupancy</td>
<td>0.041 (10)</td>
<td>0.041 (10)</td>
<td>0.047 (9)</td>
</tr>
<tr>
<td>Mn(1)</td>
<td>0.0067(13)</td>
<td>0.0028 (13)</td>
<td>0.0083 (17)</td>
</tr>
<tr>
<td>Occupancy</td>
<td>0.3796 (5)</td>
<td>0.3783 (4)</td>
<td>0.3804 (6)</td>
</tr>
<tr>
<td>Mg(2)/Mn(2)</td>
<td>0.8704 (5)</td>
<td>0.8717 (4)</td>
<td>0.8696 (6)</td>
</tr>
<tr>
<td>y</td>
<td>0.014 (3)</td>
<td>0.014 (3)</td>
<td>0.016 (3)</td>
</tr>
<tr>
<td>z</td>
<td>0.986 (3)</td>
<td>0.986 (3)</td>
<td>0.984 (3)</td>
</tr>
<tr>
<td>Mn(2)</td>
<td>0.0028(7)</td>
<td>0.0002 (4)</td>
<td>0.0058 (10)</td>
</tr>
<tr>
<td>Occupancy</td>
<td>0.3833 (2)</td>
<td>0.3837 (2)</td>
<td>0.3850 (3)</td>
</tr>
<tr>
<td>U / Å$^2$</td>
<td>0.0073(7)</td>
<td>0.0037 (5)</td>
<td>0.0053 (7)</td>
</tr>
<tr>
<td>O(1)</td>
<td>0.1512 (2)</td>
<td>0.1505 (2)</td>
<td>0.1493 (3)</td>
</tr>
<tr>
<td>(x,y,z)</td>
<td>-0.1433 (3)</td>
<td>-0.1434 (3)</td>
<td>0.8585 (2)</td>
</tr>
<tr>
<td>O(1) U / Å$^2$</td>
<td>0.1235 (3)</td>
<td>0.1233 (3)</td>
<td>0.1271 (3)</td>
</tr>
<tr>
<td>O(2)</td>
<td>0.0066(4)</td>
<td>0.0026 (3)</td>
<td>0.0091 (5)</td>
</tr>
<tr>
<td>a=b=c</td>
<td>8.18722 (14)</td>
<td>8.18110 (9)</td>
<td>8.28179 (22)</td>
</tr>
<tr>
<td>R$_{wp}$</td>
<td>10.41 %</td>
<td>7.56 %</td>
<td>8.19 %</td>
</tr>
<tr>
<td>$\chi^2$</td>
<td>1.151</td>
<td>1.950</td>
<td>1.815</td>
</tr>
</tbody>
</table>
Table 4.3: Structural parameters obtained from Rietveld refinement of the powder neutron diffraction pattern of CuNi$_{0.5}$Mn$_{1.5}$O$_4$ at room temperature and 10K, and from powder X-ray diffraction at room temperature for LiNi$_{0.5}$Mn$_{1.5}$O$_4$. The space group $Fd\bar{3}m$ was used with positions A at (0.125,0.125,0.125) B (Mn and Ni) at (0.5,0.5,0.5) and O at (u,u,u).

<table>
<thead>
<tr>
<th>Site</th>
<th>Cu (300K)</th>
<th>Cu (15K)</th>
<th>Li (300K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A 8a</td>
<td>0.0117 (5)</td>
<td>0.0074 (3)</td>
<td>0.015 (28)</td>
</tr>
<tr>
<td>Mn 16d</td>
<td>0.748 (1)</td>
<td>0.748 (1)</td>
<td>0.75‡</td>
</tr>
<tr>
<td>Ni 16d</td>
<td>0.252 (1)</td>
<td>0.252 (1)</td>
<td>0.25‡</td>
</tr>
<tr>
<td>O 32e</td>
<td>0.0117 (5) †</td>
<td>0.0074 (3) †</td>
<td>0.070 (10)</td>
</tr>
<tr>
<td>(u,u,u)</td>
<td>0.26314 (6)</td>
<td>0.26323 (5)</td>
<td>0.2632 (7)</td>
</tr>
<tr>
<td>U / Å$^2$</td>
<td>0.01275 (9)</td>
<td>0.0066(2)</td>
<td>0.088 (29)</td>
</tr>
<tr>
<td>a(=b=c)</td>
<td>8.27858 (11)</td>
<td>8.27127 (8)</td>
<td>8.16594 (3)</td>
</tr>
<tr>
<td>R$_p^2$</td>
<td>6.66 %</td>
<td>6.10 %</td>
<td>9.32%</td>
</tr>
<tr>
<td>$\chi^2$</td>
<td>1.232</td>
<td>1.741</td>
<td>1.028</td>
</tr>
</tbody>
</table>

† Constrained to A-site value.
‡: Not refined for X-ray data.

Figure 4.1: Rietveld refinement of the X-ray diffraction pattern of LiMg$_{0.5}$Mn$_{1.5}$O$_4$ using the $P4_332$ space group, where the Mg and Mn are ordering onto crystallographically distinct sites on the B-sublattice.
Top: Figure 4.2a: Rietveld refinement of the powder neutron diffraction pattern of LiMg\textsubscript{0.5}Mn\textsubscript{1.5}O\textsubscript{4} at 10K with a ferromagnetic phase included.
Bottom: Figure 4.2b: Rietveld refinement of the powder neutron diffraction pattern of LiMg\textsubscript{0.5}Mn\textsubscript{1.5}O\textsubscript{4} at 10K without ferromagnetic phase.
The inset in both diagrams is an expanded region containing the low angle data, showing significant improvement with the inclusion of the magnetic scattering.
Top: Figure 4.3: Rietveld refinement of CuMg$_{0.5}$Mn$_{1.5}$O$_4$ from neutron diffraction, fitted with impurity phase, CuO. Inlaid: Shoulder peak (311).
Bottom: Figure 4.4: Rietveld refinement of CuMg$_{0.5}$Mn$_{1.5}$O$_4$ from X-ray diffraction. Inlaid: Shoulder peak (111).
Top: Figure 4.5  Rietveld refinement of the powder neutron diffraction pattern of CuNi₀.₅Mn₁.₅O₄, using a two-phase refinement, with the majority phase (~90%) in the \textit{Fd\textbar 3m} space group and an additional impurity phase in the ordered \textit{P4₃32} space group.

Bottom: Figure 4.6: Rietveld refinement of LiNi₀.₅Mn₁.₅O₄ from X-ray diffraction data.

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4.3.2 Magnetism

Figure 4.7 shows the temperature dependence of the magnetization of the $A'B'_{0.5}Mn'_{1.5}O_4$ ($A$ = Li, Cu; $B$ = Mg, Ni) series. Each of the materials undergoes spontaneous magnetisation from a paramagnetic state at a well-defined temperature; the minimum in the derivative of the magnetization with respect to temperature, $\frac{dT}{dM}$, as presented in figure 4.9. In the magnesium containing compounds, the manganese ions are the only magnetic species and the behaviour is ferromagnetic below the Curie temperature ($T_c$). The nickel containing compounds constitutes a more complicated set of interactions, as the Mn and Ni moments are expected to be antiferromagnetically coupled, resulting in bulk ferrimagnetism. A consequence of this ferrimagnetic ordering can be seen in figure 4.8, there is a reduction in the saturation magnetisation in the nickel containing compounds. The saturation moments of lithium and copper magnesium manganate are $2.263\mu_B/Mn$ and $2.387\mu_B/Mn$ respectively, these are significantly greater than those of the nickel compounds, respectively $1.958\mu_B/Mn$ and $1.964\mu_B/Mn$. These values are significantly below the theoretical spin-only values, ($3\mu_B/Mn$ and $2.33\mu_B/Mn$ respectively for the magnesium and nickel compounds) which is typical of many spinel systems.

The ordering temperature is both dependent on the A and B site cations. The replacement of Li by Cu on the A site causes the $T_C$ (or $T_N$) to increase by 15K, whereas replacement of Mg with Ni causes it to increase by around 100K. The variation in magnetic susceptibility above the ordering temperature provides another interesting comparison between the Mg and Ni analogues. All four compounds show close agreement with the Curie-Weiss law above their ordering temperatures, the high
temperature Curie-Weiss fits, and plots of the inverse magnetic susceptibility against
temperature, or the four compounds are given in figures 4.10-4.17. The results of this
fitting are presented in table 4.4. For the Mg containing samples, the Curie constants are
close to the predicted spin only value of 3.63ergKmol⁻¹Oe⁻². However, for the Ni
containing samples, the Curie constant of only 2.34(2)ergKmol⁻¹Oe⁻² for
CuNi₀.₅Mn₁.₅O₄, and 1.620ergKmol⁻¹Oe⁻² for LiNi₀.₅Mn₁.₅O₄, are both far smaller than
the predicted value of 5.15, assuming three unpaired electrons per manganese and two
per nickel ion.

Table 4.4: Summary of the result of Curie-Weiss fits above the ordering
temperature for the AB₀.₅Mn₁.₅O₄ (A = Li or Cu, B = Ni or Mg) series of
compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Magnetic Behaviour</th>
<th>Transition Temperature (K)</th>
<th>Curie Constant (ergKmol⁻¹Oe⁻²)</th>
<th>Weiss Constant (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiMg₀.₅Mn₁.₅O₄</td>
<td>Ferromagnetic</td>
<td>21</td>
<td>3.412(36)</td>
<td>37.6(1)</td>
</tr>
<tr>
<td>CuMg₀.₅Mn₁.₅O₄</td>
<td>Ferromagnetic</td>
<td>47</td>
<td>3.207(11)</td>
<td>61.5(1)</td>
</tr>
<tr>
<td>LiNi₀.₅Mn₁.₅O₄</td>
<td>Ferrimagnetic</td>
<td>100</td>
<td>1.620(10)</td>
<td>108.7(2)</td>
</tr>
<tr>
<td>CuNi₀.₅Mn₁.₅O₄</td>
<td>Ferrimagnetic</td>
<td>135</td>
<td>2.34(2)</td>
<td>103(1)</td>
</tr>
</tbody>
</table>

Low temperature powder neutron diffraction was used to investigate the nature of the
ferromagnetic ordering. The Rietveld refinement of LiMg₀.₅Mn₁.₅O₄ at 10K, with and
without a magnetic contribution, is presented in figures 4.2a and 4.2b. The magnetic
model is included as a second phase, with lattice parameters derived from the 10K
structural refinement, and P1 symmetry. The model that gave the best fit to the data is
ferromagnetic with the moment aligned with one of the equivalent crystallographic
axes, arbitrarily z. The refined moment on the 12d site was 2.167(50)μB, in good
agreement with the saturation magnetic moment of 2.263μB/Mn. The only significant
magnetic contribution, to the 15K powder neutron diffraction pattern of CuNi₀.₅Mn₁.₅O₄,
is an increase in intensity in the (111) peak. This cannot be accounted for with a purely
structural model, but was satisfactorily fitted with a magnetic model of collinear
moments, along z, of 1.489(40)μB on each 16d site. This gave a goodness-of-fit factor

of 6.09%. The saturation magnetisation data discussed above clearly show that antiferromagnetic coupling between the Mn$^{IV}$ and Ni$^{II}$ ions results in bulk ferrimagnetism with a saturation moment of 1.964μB/Mn, which is equivalent to 1.473μB per B-site cation. This collinear alignment in the best refinement is further indication that there is little or no cation ordering of the nickel and manganese ions on the length scale of neutron diffraction.

The discrepancy between the magnetic moment of LiMg$_{0.5}$Mn$_{1.5}$O$_4$, observed in both saturation magnetization and neutron diffraction measurements, and its spin-only theoretical value, was further investigated by the representational analysis method, described in section 3.3.2.4. The results of this analysis are presented in appendix I and summarized here. The irreducible representation of the magnetic structure that becomes critical at the Curie temperature has some associated basis vectors that have antiferromagnetic components. Thus, one could envisage a symmetry allowed combination of a ferromagnetic component along [100] and a perpendicular antiferromagnetic component, but, although it was possible to include a small antiferromagnetic component without significant reduction in the quality of the fit, there was insufficient improvement to justify the inclusion of the extra parameters. Thus there was no evidence for an antiferromagnetic component to the ordering over the length scale of neutron diffraction.
Top: Figure 4.7: Magnetisation of the $\text{AB}_{0.5}\text{Mn}_{1.5}\text{O}_4$ ($\text{A}=\text{Li, Cu}; \text{B}=\text{Mg, Ni}$) series, in an applied field of 1000e, as a function of temperature.

Bottom: Figure 4.8: Magnetisation of the $\text{AB}_{0.5}\text{Mn}_{1.5}\text{O}_4$ ($\text{A}=\text{Li, Cu}; \text{B}=\text{Mg, Ni}$) series, at 5K, as a function of applied field.
Figure 4.9: Derivative of Molar Magnetisation of the $\text{AB}_{0.5}\text{Mn}_{1.5}\text{O}_4$ ($\text{A}=\text{Li, Cu}$; $\text{B}=\text{Mg, Ni}$) series, in an applied field of 100Oe, as a function of temperature.
Top: Figure 4.10: Curie-Weiss fit to susceptibility data for LiMg$_{0.5}$Mn$_{1.5}$O$_4$.

Bottom: Figure 4.11: Inverse susceptibility data for LiMg$_{0.5}$Mn$_{1.5}$O$_4$. 

Top: Figure 4.12: Curie-Weiss fit to susceptibility data for CuMg$_{0.5}$Mn$_{1.5}$O$_4$.
Bottom: Figure 4.13: Inverse susceptibility data for CuMg$_{0.5}$Mn$_{1.5}$O$_4$. 
Top: Figure 4.14: Curie-Weiss fit to susceptibility data for LiNi$_{0.5}$Mn$_{1.5}$O$_4$.
Bottom: Figure 4.15: Inverse susceptibility data for LiNi$_{0.5}$Mn$_{1.5}$O$_4$.
Figure 4.17: Inverse susceptibility data for CuNi_0.5Mn_0.5O.

Figure 4.16: Curve-Weiss fit to susceptibility data for CuNi_0.5Mn_0.5O.
4.3.2.1 AC Susceptibility

In light of the absence of evidence for an ordered component perpendicular to the ferromagnetic component, it was hypothesized the materials show semi-spin glass behaviour. A semi-spin glass has a disordered spin glass component transverse to the ordered ferromagnetic component. To test for spin glass character, frequency dependence AC susceptibility measurements, and DC magnetization aging experiments were performed for LiMgoMn1.5O4. The AC susceptibility measurements, which are presented in figure 4.18, are inconclusive. There is no appreciable frequency shift over the measured frequency range, but it was not possible to achieve sufficient resolution at frequencies below 100Hz, and for many spin glasses a large frequency shift is only observed much below the frequency, often around 0.01-1Hz. The real part of the AC susceptibility plateaus at the Curie temperature, rather than forming a peak symmetrical around Tc, which further obscures any shift in the cusp that would be caused by spin glass behaviour.
Figure 4.18: Normalised ($\chi_N = \chi / \chi_{\text{max}}$) real ($\chi'$) and imaginary ($\chi''$) AC susceptibility of LiMg$_{0.5}$Mn$_{1.5}$O$_{4}$, in a driving field of 10e with frequency of 100Hz and 1kHz, against temperature (top) and expansion of the small ($\chi / \chi_{\text{max}}$) region (bottom).
4.3.2.2 Time Dependent Magnetization

Zero field cooled aging experiments were performed according to the scheme in section 3.5.1.1, for both LiMg$_{0.5}$Mn$_{1.5}$O$_4$ and CuNi$_{0.5}$Mn$_{1.5}$O$_4$. The evolution of the magnetization with time upon the application of a 200e field, after a waiting time of 1000s, (section 3.4.6) is shown in figure 4.19, for a number of temperatures in the range 5-60K. For clarity, this data is also presented in figure 4.20 as a change in magnetization, $\Delta M$, where $\Delta M = M(t) - M(t = 1\text{ min})$. It is clear that there is a strong increase in the constant temperature, constant field magnetization with time at 5K and 10K, whilst there is a small increase at 20K, and no change with time at 25K and above. Similar measurements for CuNi$_{0.5}$Mn$_{1.5}$O$_4$, at 5K and 130K, are presented in figures 4.21 and 4.22, which show that the ZFC magnetization of CuNi$_{0.5}$Mn$_{1.5}$O$_4$ in an applied field of 200e is also temperature dependent, at all temperatures below $T_C$. The inverse derivative of the ZFC magnetization with respect to time, $\left[\left(\frac{1}{H}\right)\left(\frac{\partial M}{\partial t}\right)_{H,J}\right]^{-1}$, of LiMg$_{0.5}$Mn$_{1.5}$O$_4$ at 10K is plotted in figure 4.23, and gives an almost straight line, indicating a close-to-logarithmic increase in magnetization with time. This data is very noisy because the derivative was calculated as the gradient between one point and the next, and at longer waiting times the change in magnetization between measurements is of similar magnitude to the error in the measurement. The near-linearity of the inverse derivative is indicative of spin glass character, to investigate the deviation from linearity, the relaxation rate, $S$ (equation (3.29)), was plotted against time in figure 4.24, and can be seen to have a clear maximum when the elapsed time is approximately equal to the waiting time, $t_w$. The maximum in the relaxation rate when $t = t_w$, is strongly indicative of spin glass behaviour. This derivative, $S = \left(\frac{1}{H}\right)\left(\frac{\partial M}{\partial \log_{10} t}\right)_{H,J}$, is similar to
that discussed above, but because the magnetization is differentiated with respect to the logarithm of the time (in seconds, seconds are used for consistency with the literature) the derivative would be constant with time if the evolution of the magnetization were purely logarithmic.

If the magnetic structure is represented by the model shown in figure 3.9, then the relative sizes of the ferromagnetic and spin glass components can be approximated according to the method in section 3.4.7 (equations (3.30)-(3.32)). If the magnitude of the ferromagnetic component is taken to be the 5K, 50kOe saturation magnetization, which was in excellent agreement with the ordered moment derived from the neutron diffraction pattern of LiMg$_{0.5}$Mn$_{1.5}$O$_4$, then the ferromagnetic component divided by the theoretical moment gives the cosine of the canting angle, $\Phi$, defined, in figure 3.9, as the angle between the moments on individual ions and the direction of ferromagnetic ordering (one of the crystallographic axes, arbitrarily $z$). The values obtained from this treatment are presented in table 4.5.

Table 4.5: Magnitudes of the ferromagnetic and spin glass components of the magnetic structure, and the canting angle, $\Phi$, calculated from the model in figure 3.9.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Theoretical Saturation Moment ($\mu_B / Mn$)</th>
<th>Ferromagnetic Component ($\mu_B / Mn$)</th>
<th>Spin Glass Component ($\mu_B / Mn$)</th>
<th>Canting Angle, $\Phi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiMg$<em>{0.5}$Mn$</em>{1.5}$O$_4$</td>
<td>3</td>
<td>2.263</td>
<td>1.97</td>
<td>41°</td>
</tr>
<tr>
<td>CuMg$<em>{0.5}$Mn$</em>{1.5}$O$_4$</td>
<td>3</td>
<td>2.387</td>
<td>1.82</td>
<td>37°</td>
</tr>
<tr>
<td>LiNi$<em>{0.5}$Mn$</em>{1.5}$O$_4$</td>
<td>2.33</td>
<td>1.958</td>
<td>1.26</td>
<td>33°</td>
</tr>
<tr>
<td>CuNi$<em>{0.5}$Mn$</em>{1.5}$O$_4$</td>
<td>2.33</td>
<td>1.964</td>
<td>1.25</td>
<td>33°</td>
</tr>
</tbody>
</table>
Figure 4.19: Aging of ZFC Magnetization (in 200e) for LiMg$_{0.5}$Mn$_{1.5}$O$_4$. 
Figure 4.20: Change in ZFC Magnetization with time (in 20Oe) for LiMg$_{0.5}$Mn$_{1.5}$O$_4$ at selected temperatures (top), and expansion of the small $\Delta M$ region (bottom).
Top: Figure 4.21: Aging of ZFC Magnetization (in 200e) for CuNi0.5Mn1.5O4 at selected temperatures.
Bottom: Figure 4.22: Change in ZFC Magnetization with time (in an applied field of 200e) for CuNi0.5Mn1.5O4 at selected temperatures.
Top: Figure 4.23: Inverse derivative of the ZFC Magnetization (M/H, in 20Oe), with respect to time in minutes, for LiMg$_{0.5}$Mn$_{1.5}$O$_4$ at 10K.

Bottom: Figure 4.24: Relaxation rate, S (section 3.4.6) derivative of the ZFC Magnetization (M/H, in 20Oe), with respect to log$_{10}$(time) in seconds, for LiMg$_{0.5}$Mn$_{1.5}$O$_4$ at 10K.
4.3.3 Conductivity

The plot of the natural logarithm of the resistance against $1/T$ for LiNi$_{0.5}$Mn$_{1.5}$O$_4$ is shown in figure 4.25. The linear dependence of $\ln(\rho)$ with $1/T$ in the region 270K - 350K is consistent with a thermally activated semiconductor. This contrasts with the non-linear dependence of $\ln(\rho)$ with $1/T$ for CuNi$_{0.5}$Mn$_{1.5}$O$_4$ (figure 6.27) both above, and below, the Curie temperature, which is discussed further in chapter 6. The poor conductivity of this sample prevented measurement of the resistance at low temperature due to a low carrier density, precluding measurement around the Curie temperature.

![Graph: Natural logarithm of resistivity against inverse temperature for LiNi$_{0.5}$Mn$_{1.5}$O$_4$ in zero field, the straight line shows the fits to a semi-conductive activation energy model of the resistance.](image)

Figure 4.25: Natural logarithm of resistivity against inverse temperature for LiNi$_{0.5}$Mn$_{1.5}$O$_4$ in zero field, the straight line shows the fits to a semi-conductive activation energy model of the resistance.
Above the ordering temperatures, the resultant activation energies were determined to be 0.78(1)eV for LiNi$_{0.5}$Mn$_{1.5}$O$_4$, which is large compared to the approximation of the activation energy for CuNi$_{0.5}$Mn$_{1.5}$O$_4$ of 0.20(1)eV. Figure 4.26 shows the dependence of the resistivity of CuNi$_{0.5}$Mn$_{1.5}$O$_4$ with temperature in an applied magnetic field of 0Oe, 100000Oe and 250000Oe. The plots are almost overlapping with only small deviations at high temperature and a magnetoresistance effect, defined by $\rho(h)/\rho(0)$, of around 2%. The temperature dependence of the resistivity changes dramatically at the Curie point of 150K.

![Figure 4.26: Natural logarithm of resistivity against temperature for CuNi$_{0.5}$Mn$_{1.5}$O$_4$ in three different applied magnetic fields, of 0Oe, 1*10^4 Oe and 2.5*10^4 Oe.](image)
4.4 Discussion

The slow cooling sample preparation was first reported by Blasse\textsuperscript{5} and allows the formation of the cation ordered form of LiMg\(_{0.5}\)Mn\(_{1.5}\)O\(_4\), with crystallographically distinct manganese and magnesium sites. It also resulted in the shoulder features on a set of the Bragg peaks, \{hhl\} where \(h+l=2n\), becoming more prominent than in the diffraction patterns of the quenched compounds. These shoulders could be the result of an unidentified second phase in the material, or Warren peaks caused by the ordering of the stacking faults in the material. The shoulder peaks could not be matched to any plausible phase in the database of the Siemens D500 diffractometer, and neither could they be fitted, as a second spinel phase in the Rietveld refinement. Further experiments (section 8.4.1) are required to resolve this question. The following mechanism has been proposed for stacking fault formation in the cubic close packed (ccp) oxide lattice. Stacking faults are caused by the occurrence of a single layer of energetically similar hexagonal close packed (hcp) oxide. The ABCABCA stacking of anion layers in the ccp system is perturbed to give an ABCABABCA defect. The slow cooling has allowed these defects to order themselves over domains of the lengthscale of the diffraction experiments. This phenomenon has been previously reported in other \(Fd\bar{3}m\) systems, such as diamond\textsuperscript{3,29} and C\(_{70}\).\textsuperscript{4}

The Rietveld refinements of the neutron diffraction data show that, as expected from crystal field theory, the A-sites are fully occupied by the monovalent ions, lithium or copper, and the cations with higher valency, magnesium, nickel and manganese, occupy the octahedral B-sites. Feng et al\textsuperscript{9} demonstrated that Zn[Li\(_{0.5}\)Mn\(_{1.5}\)]O\(_4\) does not follow this trend because \(d^{10}\) Zn\(^{2+}\) has a strong tetrahedral site preference (section 2.3.3). The lattice parameters obtained were in good agreement (±0.01 Å) with previous reports for
It is worth noting here that electroneutrality could be satisfied with Cu$^{2+}$ and an equal number of Mn$^{3+}$ ions replacing Cu$^{+}$ and Mn$^{4+}$. These are both Jahn-Teller ions, and the lack of a distortion to tetragonal symmetry coupled with the similarity of the magnetisation measurements (figures 4.7 and 4.8) for copper and lithium analogues indicate that copper is present in the +1 oxidation state. This is also borne out by the Cu-O bond lengths, 1.9808(8)Å in CuNi$_{0.5}$Mn$_{1.5}$O$_4$ and a mean distance of 1.992(6)Å in CuMg$_{0.5}$Mn$_{1.5}$O$_4$. Taking a Shannon$^{28}$ ionic radius for tetrahedral O$^{2-}$ of 1.24Å, the radii of the copper ions in the two samples are approximately 0.74Å and 0.75Å respectively. The tetrahedral Shannon ionic radii for Cu$^{+}$ and Cu$^{2+}$ are, respectively, 0.74Å and 0.71Å. The small energy difference between Cu$^{2+}$/Mn$^{3+}$ and Cu$^{+}$/Mn$^{4+}$ is highlighted by the observation of both Cu$^{+}$ and Cu$^{2+}$ by Elbadraoui et al$^8$ in CuMn$_2$O$_4$ by X-ray photoelectron spectroscopy (XPS). The compound CuFe$_{0.5}$Mn$_{1.5}$O$_4$, which was shown by Lenglet et al$^{21}$ to be Cu$^{2+}_{0.18}$Mn$^{2+}_{0.5}$Fe$^{3+}_{0.32}$[Cu$^{2+}_{0.16}$Mn$^{2+}_{0.5}$Fe$^{3+}_{0.34}$]O$_4$ by Mössbauer spectroscopy. The dissimilarity of this material and those described in this chapter is highlighted by the lattice parameter of 8.52Å, compared to 8.27Å and 8.28Å for CuNi$_{0.5}$Mn$_{1.5}$O$_4$ and CuMg$_{0.5}$Mn$_{1.5}$O$_4$ respectively.

It is somewhat surprising that the cation ordered superstructure, observed for the Mg containing compounds, is only observed as a minority phase in the neutron diffraction of CuNi$_{0.5}$Mn$_{1.5}$O$_4$. Lagrange et al$^{18}$ reported no long-range cation order in a LiNi$_{0.5}$Mn$_{1.5}$O$_4$ sample with a very similar (8.17Å) lattice parameter from *** measurements. However, Lee et al$^{20}$ employed $^6$Li magic angle spinning (MAS) NMR to show that all the Li ions had an identical local environment, and Gryffroy et al$^{15}$ reported the presence of long-range order in LiNi$_{0.5}$Mn$_{1.5}$O$_4$, and only short-range cation...
ordering in CuNi$_{0.5}$Mn$_{1.5}$O$_4$, which was expressed as a modulation of the background in
the powder neutron diffraction pattern. This therefore implies that presence of Li on the
A site is more conducive to cation ordering than Cu. This might be due to the smaller
lattice parameter in the lithium system. Though there is, clearly, some tendency to order
in the Ni-Mn system, the ordering occurs far more readily in the Mg-Mn array, as is
evidenced by the clear observation of superstructure in CuMg$_{0.5}$Mn$_{1.5}$O$_4$. For the
ordered phase to be energetically favourable, the enthalpic gain must outweigh the
entropic loss of the system. There are two potential driving forces for cation ordering on
the B sublattice, size mismatch and charge difference. Electrostatic ordering is
discussed in section 2.3.2.1 and the electrostatic ordering energy (equation 2.18) is a
function of the square of the charge difference. These electrostatic ordering energies are
of the order of 100kJmol$^{-1}$, and so ordering would always be expected, but that the
tetrahedral lattice of B-sites, of a spinel, is analogous to Pauling's
c "ice rules" (section 2.4) because the electrostatic term only requires that each tetrahedron has the same
composition as the bulk, and there are many different states that satisfy this
requirement. Long-range cation order involves the selection of a unique ground state,
and the energy difference between the most, and least, favourable states that satisfy the
ice-rules criterion, is only about 5% (section 2.3.2.1) of the electrostatic energy. Hence,
it is almost certain that CuNi$_{0.5}$Mn$_{1.5}$O$_4$ features short-range B-site cation ordering, with
each B$_4$ tetrahedron containing three Mn$^{4+}$ cations and one Ni$^{2+}$ cation. The disparity in
charge is significant, because an ordered scheme prevents regions with a non-zero net
close occurring. This is probably the most important factor, but the Ni and Mg ions
both have a +2 charge, so it does not explain the change in behaviour. Thus we must
consider the relative sizes of the cations in question. Mn$^{(IV)}$ is small, with an ionic radius
of 67pm. Both Ni$^{(II)}$ and Mg$^{(II)}$ are significantly larger than the Mn, at 83pm and 86pm
respectively, but are of similar magnitude, therefore not explaining the difference
ordering behaviour. However, the Ni^{II} is susceptible to oxidation to Ni(III), which is also stable in an octahedral environment. Therefore, the more likely cause of the reduced degree of cation ordering in the Ni containing compound, in contrast to those containing Mg, is that some degree of charge transfer is occurring. This reduces the difference in charge between ions on the same B site and therefore the susceptibility to cation order. The principal structural unit of the octahedral sublattice is the B\textsubscript{4}O\textsubscript{4} cube, shown in figure 2.4, which will be distorted from an ideal cube if the B cations are not all identical in size. These units are interlinked at the B-cation vertices, and every unit will, if possible, have the same composition, known as the Anderson condition.\textsuperscript{1} These building blocks can only pack together in the most efficient manner if the large, low-valent, distortion inducing cation is in the same position on each one. This is the origin of the cation ordering, and the reason that superstructures derived from ordering on the octahedral sites in the spinel structure are only observed when the stoichiometry can be represented with just four sites, that is in a 1:1 and 1:3 ratios only.

The magnetic behaviour of both the spinel/pyrochlore system in general, and these compounds in particular, is complex. Goodenough\textsuperscript{11} gave a qualitative interpretation of the various exchange interactions expected for a given exchange pathway and electronic configuration. However, there are often competing interactions of opposite sign, caused by the direct and superexchange pathways.\textsuperscript{22} This makes it difficult to predict the overall sign of the exchange integral, and causes superficially similar systems to exhibit markedly different magnetic properties. These compounds, AB\textsubscript{0.5}Mn\textsubscript{1.5}O\textsubscript{4}, are considered with reference to the closely related compounds \(\lambda\)-MnO\textsubscript{2},\textsuperscript{14} and Y\textsubscript{2}Mn\textsubscript{2}O\textsubscript{7}.\textsuperscript{25,24} Both of these analogous compounds have a pyrochlorous magnetic lattice containing only manganese ions, yet their bulk magnetic behaviour is very different. At low temperatures LiMg\textsubscript{0.5}Mn\textsubscript{1.5}O\textsubscript{4} is a ferromagnet, \(\lambda\)-MnO\textsubscript{2} is an
antiferromagnet and \( Y_2Mn_2O_7 \) is a spin glass with predominantly ferromagnetic interactions, as indicated by the positive Weiss constant \( (\theta = +41K) \). It is appropriate to consider the magnetic trends within the series \( AB_{0.5}Mn_{1.5}O_4 \) before drawing conclusions about other structure types. The large variation in transition temperature within the series is indicative of a large change in superexchange energy between \( LiMg_{0.5}Mn_{1.5}O_4 \) \( (T_C= 40K) \) and \( CuNi_{0.5}Mn_{1.5}O_4 \) \( (T_N= 150K) \). In all cases the A cations are diamagnetic, so only B-B interactions need to be considered. The edge-sharing array of \( BO_6 \) octahedra results in a direct superexchange interaction of the \( d_{xy} \) (or \( d_{xz} \) or \( d_{yz} \)) orbitals of neighbouring cations. In an ideal spinel the nearest-neighbour B-O-B angle is 90°, but a distortion is often observed. For example, the \( B_4O_4 \) parallelepiped in \( LiMg_{0.5}Mn_{1.5}O_4 \) at 10K has Mn-O-Mn angles of 94.91(15)° and 99.25(22)° and an average Mn-O bond length of 1.907(4)Å. The magnesium (II) ion is also diamagnetic, therefore, in \( LiMg_{0.5}Mn_{1.5}O_4 \), the only exchange interaction is Mn(IV)-Mn(IV). The bulk magnetic properties make it clear that ferromagnetic oxygen-mediated superexchange overrides the antiferromagnetic direct exchange between \( t_{2g} \) orbitals. The most significant oxygen mediated interaction is probably the nearest neighbour \( t_{2g}-p_x:p_y-t_{2g} \) superexchange, though in \( Y_2Mn_2O_7 \) Reimers et al demonstrated that the coupling between nearest neighbours was negative (antiferromagnetic), but frustrated by ferromagnetic second and third neighbour interactions. It is immediately apparent from Figure 4.7 that substitution of magnesium with nickel has a large effect on the Curie temperature. This can be rationalised as there are now three superexchange interactions. The ferromagnetic Mn(IV)-Mn(IV) and Ni(II)-Ni(II) (not expected to be strong as the cation ordering results in all of a nickel ions nearest neighbours being manganese ions) and the antiferromagnetic Ni(II)-Mn(IV), giving ferrimagnetic order on the B sublattice. The strength of the superexchange interaction is dependent on the length of the B-O-B pathway; the B-O bond distance decreases with decreasing lattice parameter, and
increasing oxygen u parameter. It can be seen from the structural data in Table 1 and 2, that in both the lithium and the copper analogues, the substitution of nickel for magnesium both decreases the lattice parameter and increases the u parameter. Thus the great increase in $T_C$ upon introduction of nickel can be wholly rationalised. A comparison of the copper and lithium compounds is less straightforward. Both are diamagnetic, so there are no new interactions, and a comparison of the structural parameters in Tables 4.2 and 4.3 shows the substitution of lithium for copper to have very little effect on the u parameter, and expand the lattice parameter, thus the B-O distance is increased. This decreases the B-O-B overlap and hence the strength of the ferromagnetic superexchange interaction whereas the Curie temperature increases. It is now appropriate to consider the magnetic behaviour of $\lambda$-$\text{MnO}_2$, it was mentioned earlier that it possesses an identical B-lattice, which is wholly occupied by manganese (IV) ions. Thus it would be reasonable to expect similar behaviour with a significantly higher transition temperature because there are no diamagnetic magnesium holes in the magnetic sublattice. It is, however, observed to be an antiferromagnet, the dominant interaction being the direct exchange between metal $t_{2g}$ orbitals. Thus in this system the magnitude of the direct interaction is greater than that of the competing ferromagnetic exchange. If the effect of the magnesium "holes" is assumed to have a similar effect on both magnetic ordering schemes, then the key difference must be the Mn-Mn separation. The direct exchange interaction is extremely sensitive to this parameter, which determines the degree of $t_{2g}$-$t_{2g}$ overlap, whilst the strength of the oxygen mediated coupling is effective over larger distances. It should, however, be noted that the Mn-O-Mn bond angle is also highly significant. In LiMg$_{0.5}$Mn$_{1.5}$O$_4$ the Mn-Mn contact is between 2.867(4)Å and 2.923(4)Å, and the Mn-O-Mn angle varies between 94.25(22)$^\circ$ and 98.6(4)$^\circ$, which is a slightly greater manganese separation than quoted$^{14}$.
for λ-MnO₂ (2.84Å) and a similar angle (96°). It is remarkable that a difference of only
1% in the Mn-Mn separation can result in such different magnetic behaviour.

The preceding discussion sought to explain the observed bulk magnetic behaviour. The
standard measurements used to characterize magnetic materials, magnetization against
both temperature and applied field and neutron diffraction, suggested that these
compounds were simply ferromagnetic and ferrimagnetic. The only clue to be found in
these experiments that the magnetic structure might be more complex, was the large
discrepancy between the ordered moment on the manganese ions, observed in both the
saturation magnetization and neutron diffraction measurements, and the spin-only
theoretical value for a ferromagnet. The spin-only approximation should be very good
for a d³ first-row transition metal because crystal field effects quench the, already small,
orbital contribution. The fine balance between competing ferromagnetic and
antiferromagnetic interactions has already been discussed. This first led to the
hypothesis that there was an antiferromagnetically ordered component, perpendicular to
the ferromagnetic component. This was investigated by further analysis of the neutron
diffraction data using the Representational Analysis method. This method showed that a
transverse antiferromagnetic component was symmetry allowed, but found no evidence
for long-range antiferromagnetic order. In light of the fact that the neutron diffraction
measurements indicate that the B-site lattice is about 98.5% (table 4.2) cation ordered in
the magnesium containing compounds, and disordered in the nickel compounds (table
4.3), the observation of semi-spin glass behaviour in these compounds is consistent with
the prediction (section 3.4.7) of Villain. The observation of a nearly logarithmic time
dependence in the ZFC low-field magnetization for both LiMg₀.5Mn₁.₅O₄ and
CuNi₀.₅Mn₁.₅O₄, with the maximum deviation from the logarithmic coming when the
elapsed time, t, is approximately equal to the waiting time, tₘ, is strong evidence of
some form of spin glass character. Upon application of a small magnetic field, a Heisenberg ferromagnet quickly reaches equilibrium between the tendency of the domains to align with the field and the interdomain dipole interactions, hence the magnetization is only a function of temperature and field. The alternative cluster glass model (section 3.4.7) is discounted because the applied field of 50kOe in the saturation measurements would force the parallel alignment of the ferromagnetic clusters, giving the theoretical saturation magnetization. There is also the possibility that these compounds are reentrant spin glasses, undergoing first a paramagnetic-ferromagnetic (PM-FM) and then a subsequent ferromagnetic-spin glass (FM-SG) transition. To investigate this, the time dependence measurements were performed close to the Curie temperature. In LiMg_{0.5}Mn_{1.5}O_{4} (T_{C} = 21K) there was discernible time dependence at 20K, and none at 25K indicating that the onset of ferromagnetism and spin glass character is simultaneous. This is reinforced by the measurements for CuNi_{0.5}Mn_{1.5}O_{4} (T_{C} = 135K) showing time dependence at 5K and 130K. The representational analysis of the structure of LiMg_{0.5}Mn_{1.5}O_{4} showed that the irreducible representation of the symmetry group that goes critical at the Curie temperature (section 3.3.2.4) contains basis vectors with antiferromagnetic components. The magnetic structure is composed of a linear combination of these vectors (listed in appendix I, table I.3), so a single second-order transition from a paramagnetic to a semi-spin glass (PM-SSG) state is symmetry allowed. There is no evidence to suggest that there are two separate transitions competing with each other, although reentrant spin glasses with very similar transition temperatures have been reported.\textsuperscript{13}

If the magnetic structure is represented by the model shown in figure 3.9, then the relative sizes of the ferromagnetic and spin glass components can be approximated according to the method in section 3.4.7 (equations (3.30)-(3.32)). If the magnitude of
the ferromagnetic component is taken to be the 5K, 50kOe saturation magnetization, which was in excellent agreement with the ordered moment derived from the neutron diffraction pattern of LiMg0.5Mn1.5O4, then the ferromagnetic component divided by the theoretical moment gives the cosine of the angle Φ, defined in figure 3.9.

The non-linear dependence of ln(ρ) with 1/T for CuNi0.5Mn1.5O4, both above, and below, the Curie temperature, is discussed within a variable range hopping mechanism in chapter 6. The conduction properties of these compounds are likely to be derived from a primarily Mn-O valence band and a Li/Cu-O conduction band. The high energy and small dispersion of this latter band results in no overlap with the Mn-O energy states, in contrast to the situation with the Tl-O and Mn-O bands of Tl2Mn2O7, resulting in semi-conducting properties. The Mn-O valence band also explains the different temperature variation of the resistance below Tc as long range magnetic ordering would increase the localization and the energy barrier for the conduction process to take place.
4.5 Conclusion

The series of compounds AM$_{0.5}$Mn$_{1.5}$O$_4$ (A = Li or Cu and M = Ni or Mg) has been synthesized. The compounds AMg$_{0.5}$Mn$_{1.5}$O$_4$ show long-range cation ordering of the B-sites whereas there is only short-range B-site order in CuNi$_{0.5}$Mn$_{1.5}$O$_4$. All the compounds undergo spontaneous magnetization with critical temperatures between 21K and 135K, the nickel containing compounds show ferrimagnetic behaviour, with the manganese and nickel sublattices ordering antiparallel to each other. The magnetic structure of these compounds is shown to be complex by the observation of an aging effect in the low field ZFC magnetization, a phenomenon characteristic of spin glasses. A semi-spin-glass structure is proposed, consisting of a ferromagnetic (or ferrimagnetic component along [100] and a transverse spin glass component.

4.6 References


Chapter 5

*Structure and Ferromagnetism in Mn$^{4+}$ spinels: AMMnO$_4$*

($A = \text{Li, Cu}; \ M = \text{Cr, Fe, Co and Rh}$)
5.1 Introduction

Some interesting aspects of the solid-state chemistry of manganese oxides, particularly the colossal magnetoresistance (CMR) behaviour of the pyrochlore compound, thallium manganite (Tl$_2$Mn$_2$O$_7$), were introduced in chapter one. Chapter 4 reported the successful synthesis of the series of spinels, AM$_{0.5}$Mn$_{1.5}$O$_4$ (A= Li or Cu and M= Ni or Mg) that have interesting magnetic and transport properties. It was envisaged (section 4.1) that these compounds would be analogous to thallium manganite, but they were semiconducting, rather than metallic. This chapter describes the synthesis, structure, magnetic and transport properties of the spinel series, A$^1$M$^{III}$Mn$^{IV}$O$_4$ (A = Li, Cu; M = Cr, Fe, Co and Rh), which has a similar magnetic network to the pyrochlore Tl$_2$Mn$_2$O$_7$. The zinc-doped compound, Cu$_{0.5}$Zn$_{0.5}$[RhMn]O$_4$ was also prepared to investigate whether metallicity could be induced by mixed valence Mn$^{3+}$/Mn$^{4+}$ B-site manganese.

5.2 Experimental

Powder samples of composition AMMnO$_4$ (A = Li$^I$, Cu$^I$ and Zn$^{II}$; M$^{III}$ = Cr, Fe, Co and Rh) were produced by the method described in section 3.2. The reaction scheme is given in equation (5.1). When Li$_2$CO$_3$ and MnO$_2$ were used as alternative starting materials, Bragg peaks assigned to the persistent impurity phase Li$_2$MnO$_3$ were identified in the product.

\[
\text{A(CH}_3\text{CO}_2)_2.\text{H}_2\text{O} + \text{M(CH}_3\text{CO}_2)_2.4\text{H}_2\text{O} + \text{Mn(CH}_3\text{CO}_2)_2.4\text{H}_2\text{O} \\
\rightarrow \text{AMMnO}_4 + 12\text{CO}_2 + n\text{H}_2\text{O} \quad \text{(A = Li, Cu; M = Cr, Fe, Co, Rh.)} 
\]

(5.1)

Iron acetate is only available with low (95%) purity, and rhodium acetate is extremely expensive, so Fe$_2$O$_3$ and Rh$_2$O$_3$ were used in their stead. Zinc acetate,
$\text{Zn(CH}_2\text{CO}_2)_2\cdot\text{H}_2\text{O}$, was also used in the synthesis of $\text{Cu}_{0.5}\text{Zn}_{0.5}[\text{RhMn}]\text{O}_4$. The reaction mixture was ground thoroughly before decomposition, which was achieved by slowly heating the acetates from room temperature to 400°C ($\Delta T= 0.7^\circ\text{C/min}$). The product was then pelletised and initially fired at 750°C for one day, with further heating, with intermittent regrinding, of each compound, until the reaction was deemed complete. The heating regime, for each of the samples that were used in the characterization experiments presented here, is given in table 5.1; both air-quenched and slow-cooled samples are presented for $\text{LiMnFeO}_4$. On completion of the synthesis the reaction mixture was slow-cooled at 0.07°C per minute from 750°C to room temperature to produce the final sample.\textsuperscript{1} Characterization methods are detailed in chapter 3, and those pertaining to this chapter are summarized below. X-ray diffraction data was collected on a Siemens D500 diffractometer fitted with a primary monochromator giving $\lambda= 1.54056\text{Å}$. DC Magnetic susceptibility measurements were performed using a Quantum Design MPMS7 SQUID magnetometer. Magnetoresistance measurements were performed on the electronic properties probe of an Oxford Instruments Maglab 2000 system. AC susceptibility measurements were performed on the magnetic properties probe of an Oxford Instruments Maglab 2000 system, in a driving field of 10e. Neutron diffraction experiments were carried out on the BT1 constant wavelength diffractometer at the National Institute of Standards Technology using a Cu(311) monochromator ($\lambda= 1.5401 \text{Å}$). Analysis of this data was performed by the Rietveld method\textsuperscript{2} within the GSAS suite of software.\textsuperscript{3}
### Table 5.1: Heating regimes for attempted syntheses of ABMnO₄ compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Days at 800°C</th>
<th>Days at 850°C</th>
<th>Days at 900°C</th>
<th>Days at 950°C</th>
<th>Cooling Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCrMnO₄</td>
<td>4</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>Quenched</td>
</tr>
<tr>
<td>CuCrMnO₄</td>
<td>4</td>
<td>3</td>
<td>0</td>
<td>0</td>
<td>Quenched</td>
</tr>
<tr>
<td>LiFeMnO₄</td>
<td>4</td>
<td>3</td>
<td>0</td>
<td>0</td>
<td>Quenched and slow-cooled</td>
</tr>
<tr>
<td>CuMnFeO₄</td>
<td>4</td>
<td>1</td>
<td>1</td>
<td>4</td>
<td>Slow-cooled</td>
</tr>
<tr>
<td>LiCoMnO₄</td>
<td>4</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>Slow-cooled</td>
</tr>
<tr>
<td>CuCoMnO₄</td>
<td>4</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>Slow-cooled</td>
</tr>
<tr>
<td>CuRhMnO₄</td>
<td>9</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>Quenched</td>
</tr>
<tr>
<td>Cu₀.₅Zn₀.₅RhMnO₄</td>
<td>9</td>
<td>2</td>
<td>0</td>
<td>0</td>
<td>Quenched</td>
</tr>
</tbody>
</table>

### 5.3 Results

#### 5.3.1 Structure

The X-ray diffraction (XRD) patterns indicated the formation of monophasic, highly crystalline spinel phases for all compositions, although the Cu Kα₁ radiation caused fluorescence in the Fe³⁺/Mn⁴⁺ systems, giving a high background and poor signal-noise ratio for those compounds. This problem, which is illustrated in figures 5.3 and 5.4, the XRD patterns of the quenched and slow-cooled samples of LiFeMnO₄, made it difficult to detect the presence of minority impurity phases. It was, however, clear from the relative intensities of the two main peaks that there was a significant amount of iron on the A-sites in both samples, refined to be 43(1)% in the quenched sample and 19(2)% in the slow-cooled compound. The Rietveld refinement of the neutron diffraction pattern of CuFeMnO₄ is shown in Figure 5.5, the top set of tick marks correspond to the impurity CuO, with a refined phase fraction of 7.0(2)%, which was not detected in the XRD pattern. The XRD patterns of all of the samples were refined in the conventional spinel space group, \( Fd\bar{3}m \), the resulting fits are shown, for the compounds that neutron
diffraction patterns are not available, in figures 5.1-5.4 and 5.7-5.8. The structural parameters obtained in all the presented refinements are summarized in table 5.2, the oxygen $u$ parameter is discussed in section 2.2.2 and the quoted thermal parameters are the isotropic $U$ values from the GSAS suite of programs. It should be noted that the lack of low-angle superstructure peaks similar to those exhibited by LiMg$_{0.5}$Mn$_{1.5}$O$_4$ and CuMg$_{0.5}$Mn$_{1.5}$O$_4$ (chapter 4) does not preclude long range cation order on the octahedral sites, because chromium, iron, cobalt and manganese all have similar numbers of electrons. Further information was obtained by neutron diffraction; the negative coherent scattering length of manganese (-3.73fm) gives strong contrast with most other metal ions. The refinements of the powder neutron diffraction patterns of CuRhMnO$_4$ and Cu$_{0.5}$Zn$_{0.5}$[RhMn]O$_4$ in the $Fd\bar{3}m$ space group are shown in figures 5.9 and 5.10 respectively. In both cases the fit to the data is reasonable, considering the width of the peaks, with respective $R_{wp}$ fit indices of 8.56% and 9.63%, though there are shoulders on a subset of the peaks, similar to those attributed to stacking faults in LiMg$_{0.5}$Mn$_{1.5}$O$_4$ (chapter 4) and the peaks at high angle are broad, which is indicative of small particle size or strain due to size mismatch of cations. The CuFeMnO$_4$ powder neutron diffraction pattern was satisfactorily refined in the $Fd\bar{3}m$ space group (giving a $\chi^2$ goodness-of-fit factor of 1.131, with CuO included as a second phase) except that the fit gave no intensity in the (111) peak, whereas it can be seen in figure 5.5 to have a large intensity. The (111) Bragg reflection is allowed, but the refined fractional occupancies (table 5.2) give no intensity. The intensity of this peak can be correctly fitted by the inclusion of a large amount of manganese (scattering length = -3.73fm) on the A-site, but this affects the relative intensities of many other peaks, and results in a significantly inferior overall fit. The full pattern can be fitted with the inclusion of a cation ordered second phase with the cation ordered superstructure observed for Zn[LiNb]O$_4$ with space group ($P4_322$). The fit to this multiphase model is shown in figure 5.6 to
demonstrate that this is a possible solution, but the refinement is not sensitive to the 
structure of this phase because only one peak is poorly fitted in the \( Fd\bar{3}m \) phase, so it
was not possible to obtain physically realistic thermal parameters for this phase, and
there are other possible 1:1 B-site ordering schemes (section 2.2.3) such as that of
orthorhombic low temperature \( \text{Fe}_3\text{O}_4 \)\(^6,7 \) that could account for an intense (111)
reflection.

Table 5.2: Summary of key structural data for compounds \( \text{AMMnO}_4 \).

<table>
<thead>
<tr>
<th>Compound</th>
<th>Lattice Parameter ( \text{A} )</th>
<th>Oxygen ( u ) parameter</th>
<th>A-site occupancy ( \dagger )</th>
<th>A-site ( U ) / 100( \text{Å}^2 )</th>
<th>B-site occupancy ( \dagger )</th>
<th>B-site ( U ) / 100( \text{Å}^2 )</th>
<th>O-site ( U ) / 100( \text{Å}^2 )</th>
<th>( \chi^2 )</th>
<th>( R_{wp} ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{LiCrMnO}_4 )</td>
<td>8.2024(4)</td>
<td>0.2628(7)</td>
<td>Li=0.970(8)</td>
<td>1.1(6)</td>
<td>Cr=0.5</td>
<td>Mn=0.485(5)</td>
<td>Li=0.015(5)</td>
<td>0.72(8)</td>
<td>1.7(2)</td>
</tr>
<tr>
<td>( \text{CuCrMnO}_4 )</td>
<td>8.3242(2)</td>
<td>0.2603(4)</td>
<td>Cu=1.0</td>
<td>1.52(9)</td>
<td>Mn=0.5</td>
<td>Cr=0.5</td>
<td>Mn=0.5</td>
<td>1.38(29)</td>
<td>3.9(4)</td>
</tr>
<tr>
<td>( \text{LiFeMnO}_4 ) Quenched</td>
<td>8.3636(8)</td>
<td>0.2594(9)</td>
<td>Li=0.573(13)</td>
<td>0.92(68)</td>
<td>Fe=0.427(13)</td>
<td>Li=0.213(6)</td>
<td>Fe=0.287(6)</td>
<td>2.19(40)</td>
<td>4.2(4)</td>
</tr>
<tr>
<td>( \text{LiFeMnO}_4 ) Slow-cooled</td>
<td>8.2870(10)</td>
<td>0.2651(9)</td>
<td>Li=0.805(16)</td>
<td>1.4(13)</td>
<td>Fe=0.195(16)</td>
<td>Mn=0.5</td>
<td>Li=0.098(8)</td>
<td>0.72(8)</td>
<td>1.7(2)</td>
</tr>
<tr>
<td>( \text{CuFeMnO}_4 ) *</td>
<td>8.40271(34)</td>
<td>0.26120(15)</td>
<td>Cu=0.707(14)</td>
<td>1.94(14)</td>
<td>Mn=0.566(5)</td>
<td>Fe=0.434(5)</td>
<td>Mn=0.453(5)</td>
<td>1.31(21)</td>
<td>2.5(7)</td>
</tr>
<tr>
<td>( \text{LiCoMnO}_4 )</td>
<td>8.05595(21)</td>
<td>0.2629(5)</td>
<td>Li=0.906(11)</td>
<td>4(1)</td>
<td>Cr=0.094(11)</td>
<td>Mn=0.5</td>
<td>Co=0.457(5)</td>
<td>0.5(1)</td>
<td>0.9(2)</td>
</tr>
<tr>
<td>( \text{CuCoMnO}_4 )</td>
<td>8.1998(12)</td>
<td>0.2653(14)</td>
<td>Cu=1.0</td>
<td>1.4(6)</td>
<td>Mn=0.5</td>
<td>Cr=0.047(5)</td>
<td>Mn=0.457(5)</td>
<td>0.2(6)</td>
<td>0.8(10)</td>
</tr>
<tr>
<td>( \text{CuRhMnO}_4 ) *</td>
<td>3.89683(33)</td>
<td>0.26271(13)</td>
<td>Cu=0.953(7)</td>
<td>1.64(12)</td>
<td>Mn=0.047(7)</td>
<td>Rh=0.5</td>
<td>Cu=0.024(4)</td>
<td>1.21(29)</td>
<td>1.2(4)</td>
</tr>
<tr>
<td>( \text{Zn}<em>{0.5}\text{Cu}</em>{0.5}\text{RhMnO}_4 ) *</td>
<td>8.4288(11)</td>
<td>0.26195(11)</td>
<td>Zn=0.5</td>
<td>1.38(11)</td>
<td>Cu=0.440(6)</td>
<td>Rh=0.5</td>
<td>Cu=0.030(3)</td>
<td>0.1(2)</td>
<td>1.17(5)</td>
</tr>
</tbody>
</table>

*: Parameters obtained from neutron diffraction; data for other sample from X-ray diffraction.
\( \dagger \): Constrained to total unity; values without quoted standard deviation were not refined.
Top: Figure 5.1: Rietveld refinement of the powder X-ray diffraction pattern of quenched LiCrMnO$_4$.
Bottom: Figure 5.2: Rietveld refinement of the powder X-ray diffraction pattern of quenched CuCrMnO$_4$. 

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Top: Figure 5.3: Rietveld refinement of the powder X-ray diffraction pattern of quenched LiFeMnO₄.
Bottom: Figure 5.4: Rietveld refinement of the powder X-ray diffraction pattern of slow-cooled LiFeMnO₄.
Top: Figure 5.5: Rietveld refinement of the powder neutron diffraction pattern of CuFeMnO$_4$ in the $Fd\bar{3}m$ space group. Top row of tick marks corresponds to the impurity phase, CuO, with refined phase fraction of 7.0(2)$\%$. 

Bottom: Figure 5.6: Rietveld refinement of the powder neutron diffraction pattern of CuFeMnO$_4$, using a two phase refinement, with the majority phase (~80%) in the $Fd\bar{3}m$ space group and an additional phase in the ordered $P4_322$ space group.
Top: Figure 5.7: Rietveld refinement of the powder X-ray diffraction pattern of LiCoMnO₄ in the $Fd\bar{3}m$ space group.
Bottom: Figure 5.8: Rietveld refinement of the powder X-ray diffraction pattern of CuCoMnO₄ in the $Fd\bar{3}m$ space group.
Top: Figure 5.9: Rietveld refinement of the powder neutron diffraction pattern of CuRhMnO$_4$ in the $Fd\bar{3}m$ space group.

Bottom: Figure 5.10: Rietveld refinement of the powder neutron diffraction pattern of Cu$_{0.5}$Zn$_{0.5}$RhMnO$_4$ in the $Fd\bar{3}m$ space group.
5.3.2 Magnetism

The magnetic susceptibility of the series $\text{A}^\text{i}M^{\text{III}}\text{Mn}^{\text{IV}}\text{O}_4$ ($\text{A} = \text{Li}^\text{i}$, $\text{Cu}^\text{i}$ and $\text{Zn}^{\text{II}}$; $M^{\text{III}} = \text{Cr, Fe, Co and Rh}$) is much more varied than that of the compounds, $\text{A}^\text{i}M^{\text{II}}_{0.5}\text{Mn}^{\text{IV}}_{1.5}\text{O}_4$ in chapter 4. The magnetic susceptibility of the zero field cooled, (ZFC) and field cooled, (FC) measurements, in an applied field of 1000e, are presented in figures 5.11-5.18; susceptibility (magnetization/applied field) units of ergs per Gauss per mole are used for the compounds that do not undergo a spontaneous magnetization, namely $\text{LiCrMnO}_4$ (figure 5.11) and $\text{LiCoMnO}_4$ (figure 5.15), which show a divergence of the ZFC and FC magnetization below a cusp in the ZFC susceptibility, characteristic of a spin glass freezing. Magnetization in Bohr magnetons per manganese ion is presented for the spontaneously magnetized compounds, namely $\text{CuCrMnO}_4$ (figure 5.12), $\text{LiFeMnO}_4$ (figure 5.13), $\text{CuFeMnO}_4$ (figure 5.14), $\text{CuCoMnO}_4$ (figure 5.16) and $\text{CuRhMnO}_4$ (figure 5.17) and $\text{Cu}_{0.5}\text{Zn}_{0.5}\text{RhMnO}_4$ (figure 5.18), because the approximation of susceptibility $\frac{dM}{dH}$ as $\frac{M}{H}$ requires $M$ to be a linear function of $H$, and therefore breaks down at the Curie temperature. Relative values can be obtained by multiplying the magnetization by $\frac{\mu_B N_A}{H} = 55.86 \text{erg Oe}^{-1} \text{mol}^{-1}$. The ZFC and FC susceptibilities of $\text{Cu}_{0.5}\text{Zn}_{0.5}\text{RhMnO}_4$ do not show a marked discontinuity at any point, until they diverge at 8K, in a spin glass-like manner, but the 10K susceptibility of $\text{Cu}_{0.5}\text{Zn}_{0.5}\text{RhMnO}_4$ is five times greater than that of $\text{LiCoMnO}_4$ and $\text{LiCrMnO}_4$, despite its having fewer unpaired electrons, and the plot of inverse susceptibility against temperature, figure 5.42, deviates from linear at about 70K in a manner suggesting weak ferromagnetism, or superparamagnetism, the 1kOe (figure 5.28) and 50kOe (figure 5.21) hysteresis.
measurements indicate a small hysteresis effect and show signs of saturation, so it is
deemed to have some ferromagnetic character. The freezing temperature, $T_f$, of the spin
glass materials was deemed to be the cusp in the ZFC susceptibility, the low
temperature region of the susceptibility data for LiCoMn$_2$O$_4$ is shown in figure 5.19, and
additional experiments on Cu$_{0.5}$Zn$_{0.5}$RhMnO$_4$ in the temperature range 1.8-20K in
applied fields of 1000e and 10000e are presented in figure 5.20. The data in figure 5.20
is flawed because both ZFC susceptibilities show a discontinuity at 4.2K caused by a
warming of the sample when the SQUID magnetometer changed cooling mode, the
ZFC data above this point are really FC because the temperature has risen above $T_f$ and
then been cooled below it again. It does, however, show both a strong divergence of the
ZFC and FC susceptibilities below 4.2K and a divergence in the 1000e and 10000e
susceptibilities at about 20K, the freezing temperature is taken to be 8K from the AC
measurement in figure 5.61, but the magnetization becomes non-linear with respect to
temperature at about 20K, which is consistent with ferromagnetism. The critical
temperatures of the materials undergoing spontaneous magnetisation were determined
by taking the minimum in the derivative of the magnetization with respect to
temperature, $\frac{dM}{dT}$, as presented in figure 5.22. The bulk magnetic behaviour of the
series is summarized in table 5.3. Saturation magnetization measurements on the series
AM$_{0.5}$Mn$_{1.5}$O$_4$ ($A = $ Li, Cu; $B = $ Mg, Ni) demonstrated both a reduction in the saturation
magnetization of the nickel compounds, caused by the antiparallel ordering of the nickel
moments, and a general discrepancy in the observed values and the theoretical
prediction for a normal ferromagnet. Saturation magnetization measurements at 5K for
the compounds, AMMnO$_4$, are presented in figure 5.22, and the saturation
magnetization values at 50kOe are listed in table 5.3, although, unfortunately, data is
only available up to 6kOe for CuCoMnO$_4$, and only the 1kOe hysteresis measurement
(figure 5.24) is available for CuFeMnO$_4$. It is also more difficult to determine what the
Theoretical saturation moment is likely to be, because there is no evidence of long-range B-site order in these compounds, and a significant amount of cation inversion in the LiFeMnO₄ compounds. The relevant 90° B-O-B Kanamori-Goodenough interactions are listed in table 2.3, (Rh⁺³ and Co⁺³ are assumed to be low-spin d⁶) and indicate that the Mn and Fe sublattices are likely to align ferrimagnetically, though this could be complicated by the magnetic A-site cations in LiFeMnO₄ (the 135° Fe(A)-O-Mn/Fe(B) superexchange interaction is strongly antiferromagnetic) and, in CuCrMnO₄, either ferromagnetic or ferrimagnetic order is possible, though the frustration in the spin glass LiCrMnO₄ strongly suggests that the antiferromagnetic direct exchange is stronger than the ferromagnetic superexchange for Cr⁺³- Cr⁺³ and Cr⁺³- Mn⁺⁴. The saturation magnetization values in table 5.3 are clearly below the expected values for ferromagnetic ordering of both sublattices, whilst the theoretical moment for ferrimagnetic ordering of CuCrMnO₄ is zero, so these experiments indicate that a ferromagnetic semi-spin-glass behaviour, similar to AMg₀.₅Mn₁.₅O₄ rather than the ferrimagnetic semi-spin-glass observed for ANi₀.₅Mn₁.₅O₄ in chapter 4 is the most likely structure. Certainly, neither simple ferromagnetism, nor simple ferrimagnetism can account for the data.

The spontaneously magnetized samples were further investigated by measuring the low-field hysteresis. In all these measurements, which are shown in figures 5.23-5.28, the sample was zero field cooled to 5K, then the magnetization was measured as the field was stepped from 0Oe → 1000Oe → -1000Oe → 0Oe, in 500e steps. In hindsight, it would have been better for the final run to have gone from -1000Oe → 1000Oe, as it did for CuFeMnO₄ in figure 5.24, because the samples show a strong memory effect, and the first is zero field cooled, so there is some asymmetry between the positive and negative segments. The coercive field is taken to be the distance between the ZFC point
and the FC intercept of $M=0$. Quenched LiFeMnO$_4$ and CuFeMnO$_4$ show almost identical low field hysteresis. The respective plots are shown in figures 5.23 and 5.24, they are both a broad S-shape, with a magnetization of 0.8-0.9\(\mu_B/Mn\) and coercive field of about 50Oe. It was earlier suggested that the cobalt ions might be low-spin Co$^{3+}$, if this were the case, then the hysteresis of CuCoMnO$_4$ and CuRhMnO$_4$ would be expected to look very similar because Rh$^{3+}$ is well known$^8$ to be low-spin in oxide spinels. In fact, CuRhMnO$_4$ show almost no hysteresis, with a coercive field of less than 100e, and a high magnetization of 1.6\(\mu_B/Mn\) in 10000e, whereas CuCoMnO$_4$ and CuCrMnO$_4$ have a large hysteresis effect with a very fat S-shape, a coercive field of about 1500e, and a small magnetization, of 0.3\(\mu_B/Mn\).

The electronic configurations, and exchange interactions were further investigated by fitting the high temperature susceptibilities to the Curie-Weiss law. The temperature range, over which it was appropriate to perform this fitting, was determined by plotting the inverse molar susceptibility against temperature; this function is linear in the Curie-Weiss region. The Curie-Weiss fits, and inverse susceptibility plots for the series AMMnO$_4$, are presented in figures 5.29-5.42 and the derived Curie ($C$) and Weiss ($\theta$) constants, and the number of unpaired electrons per formula unit, $n$, determined from $C$ by equation (3.26) are presented in table 5.3. For a simple ferromagnet, the plot of inverse susceptibility against temperature is linear above $T_C$ with a gradient of $1/C$, and intercepts the T-axis at $\theta$ ($T_C = \theta$). Similarly for a simple antiferromagnet, the slope is $1/C$ and the intercept is ($\theta = -T_N$). This behaviour was observed for the compounds, AM$_{0.5}$Mn$_{1.5}$O$_4$ (chapter 4) despite the fact that the magnetic structure was later shown to be much more complex, because the magnetic interactions are predominantly ferromagnetic. It can be seen from the data in table 5.3 that the Weiss constants of CuRhMnO$_4$, 21(2)K, is positive and corresponds almost exactly with the $T_C$ determined
earlier. For all the other compounds, the Weiss constant is negative. The magnitude of the negative Weiss constant is larger than the freezing temperature for both of the spin glass compounds, \( \theta = -55.9(7)K, T_f = 14K \) for LiCrMn\(_{0.4}\) and \( \theta = -12.5(5)K, T_f = 7K \) for LiCoMn\(_{0.4}\), which is consistent with a large degree of frustration in the predominantly antiferromagnetic interactions. A similar situation is observed, despite the observation of spontaneous magnetization, for CuCoMn\(_{0.4}\), \( \theta = -36(4)K, T_f = 21K \), and Cu\(_{0.5}\)Zn\(_{0.5}\)RhMnO\(_4\), \( \theta = -38(2)K, T_f = 8K \), which is consistent with the assignment of these compounds as semi-spin-glasses with predominantly antiferromagnetic interactions, and the ferromagnetic component resulting from canting. In CuCrMnO\(_4\) and CuFeMnO\(_4\), the Weiss constants are negative, but very small; \( \theta = -4(2)K, T_f = 26K \) for CuCrMnO\(_4\) and \( \theta = -5(3)K, T_f = 49K \) for CuCrMnO\(_4\). This indicates that there are a similar number of ferromagnetic and antiferromagnetic interactions at high temperature, and the ferromagnetism is due to a canting of the spin glass state. The contrasting behaviour is best illustrated by the plots of the inverse molar susceptibility against temperature for CuCrMnO\(_4\) (figure 5.32), CuFeMnO\(_4\) (figure 5.34) CuCoMnO\(_4\) (figure 5.38) and Cu\(_{0.5}\)Zn\(_{0.5}\)RhMnO\(_4\) (figure 5.42); all of these plots are linear at high temperatures, heading for a negative intercept with the T-axis, but at some temperature, well above the transition temperature, they curve towards the T-axis to meet it at a positive value. This contrasts with the typical ferromagnetic behaviour seen for CuRhMnO\(_4\) (figure 5.40). The number of unpaired electrons per formula unit, calculated from the Curie constant, (table 5.3) corresponds well with the expected values for CuRhMnO\(_4\) \( n = 3.1 \) and Cu\(_{0.5}\)Zn\(_{0.5}\)RhMnO\(_4\) \( n = 3.6 \), which are, respectively expected to contain Mn\(^{4+}\) (d\(^3\)) ions and a 1:1 ratio of Mn\(^{3+}\) (d\(^4\)) and Mn\(^{4+}\) (d\(^3\)) as the only magnetic ions, giving theoretical values of \( n_{exp} = 3.0 \) and \( n_{exp} = 3.5 \). However, for the remaining samples, the value derived from the Curie constant is below the theoretical value; although the \( n \) values for the cobalt samples could be explained if
its electronic configuration were low-spin $d^6$, none of the magnetic measurements on these samples indicate that cobalt and rhodium are analogous, and, as discussed above, high-spin $d^6$ is the likely configuration. The compounds $\text{ACrMn}_4$ and $\text{AFeMn}_4$ have respective theoretical values of $n_{\text{exp}} = 6$ and $n_{\text{exp}} = 8$. The systematic reduction of the Curie constants, from the expected values, indicates that over the temperature range studied (5-300K), strong antiferromagnetic interactions persist, and that higher temperatures are required to investigate the Curie-Weiss region.

### Table 5.3: Summary of the result of Curie-Weiss fits above the ordering temperature for the AMMnO$_4$ series of compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Magnetic Behaviour</th>
<th>Transition Temp. (K)</th>
<th>Curie Constant (ergKmol$^{-1}$Oe$^2$)</th>
<th>Weiss Constant (K)</th>
<th>Unpaired electrons / formula unit</th>
<th>Saturation Magnetization ($\mu_B$/Mn)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiCrMnO$_4$</td>
<td>Spin glass</td>
<td>14</td>
<td>2.516(7)</td>
<td>-55.9(7)</td>
<td>3.6</td>
<td>N/A</td>
</tr>
<tr>
<td>CuCrMnO$_4$</td>
<td>FM-SG</td>
<td>26</td>
<td>3.48(6)</td>
<td>-4(2)</td>
<td>4.4</td>
<td>1.34</td>
</tr>
<tr>
<td>LiFeMnO$_4$</td>
<td>FM-SG</td>
<td>375</td>
<td>†</td>
<td>†</td>
<td>†</td>
<td>1.65</td>
</tr>
<tr>
<td>CuFeMnO$_4$</td>
<td>FM-SG</td>
<td>375</td>
<td>†</td>
<td>†</td>
<td>†</td>
<td>0.82</td>
</tr>
<tr>
<td>CuCoMnO$_4$</td>
<td>Spin glass</td>
<td>7</td>
<td>2.52(1)</td>
<td>-12.4(5)</td>
<td>3.6</td>
<td>N/A</td>
</tr>
<tr>
<td>CuCoMnO$_4$</td>
<td>FM-SG</td>
<td>21</td>
<td>2.25(3)</td>
<td>-36(4)</td>
<td>3.4</td>
<td>0.76†</td>
</tr>
<tr>
<td>CuRhMnO$_4$</td>
<td>FM-SG</td>
<td>19</td>
<td>2.048(4)</td>
<td>20.2(1)</td>
<td>3.1</td>
<td>2.22</td>
</tr>
<tr>
<td>Cu$<em>{0.5}$Zn$</em>{0.5}$MnO$_4$</td>
<td>FM-SG</td>
<td>8</td>
<td>2.57(2)</td>
<td>-38(2)</td>
<td>3.6</td>
<td>0.86†</td>
</tr>
</tbody>
</table>

†: 1kOe value because 50kOe data is not available.
††: 6kOe value because 50kOe data is not available.
‡: No data is available in the Curie-Weiss region.
Top: Figure 5.11: ZFC and FC susceptibility of LiCrMnO$_4$.  
Bottom: Figure 5.12: ZFC and FC susceptibility of CuCrMnO$_4$. 
Top: Figure 5.13: ZFC and FC susceptibility of LiFeMnO$_4$
Bottom: Figure 5.14: FC susceptibility of CuFeMnO$_4$
Top: Figure 5.15: ZFC and FC susceptibility of LiCoMnO$_4$.
Bottom: Figure 5.16: ZFC and FC susceptibility of CuCoMnO$_4$. 
Top: Figure 5.17: ZFC and FC susceptibility of CuRhMnO₄.
Bottom: Figure 5.18: ZFC and FC susceptibility of Zn₀.₅Cu₀.₅RhMnO₄.
Top: Figure 5.19: ZFC and FC susceptibility of LiCoMnO$_4$.
Bottom: Figure 5.20: ZFC and FC susceptibility (in 100G and 1000G) of Zn$_{0.5}$Cu$_{0.5}$RhMnO$_4$. 
Top: Figure 5.21: Saturation magnetization measurements at 5K for selected ABMnO$_4$ compounds. Both quenched (Q) and slow-cooled (SC) samples of LiMnFeO$_4$ are shown.

Bottom: Figure 5.22: Differential of FC magnetization for selected ABMnO$_4$ compounds.
Top: Figure 5.23: Hysteresis Loop at 5K (0G → 1000G → -1000G → 0G) for quenched LiFeMnO₄.
Bottom: Figure 5.24: Hysteresis Loop at 5K (0G → 1000G → -1000G → 0G) for CuFeMnO₄
Top: Figure 5.25: Hysteresis Loop at 5K (0G → 1000G → -1000G → 0G) for CuCoMnO$_4$.
Bottom: Figure 5.26: Hysteresis Loop at 5K (0G → 1000G → -1000G → 0G) for CuCrMnO$_4$. 
Top:  Figure 5.27: Hysteresis Loop at 5K (0G → 1000G → -1000G → 0G) for CuRhMnO$_4$.
Bottom: Figure 5.28: Hysteresis Loop at 5K (0G → 1000G → -1000G → 0G) for Cu$_{0.5}$Zn$_{0.5}$RhMnO$_4$
Top: Figure 5.29: Curie-Weiss fit to susceptibility data for LiCrMnO$_4$.
Bottom: Figure 5.30: Inverse susceptibility data for LiCrMnO$_4$. 
Top: Figure 5.31: Curie-Weiss fit to susceptibility data for CuCrMnO₄.

Bottom: Figure 5.32: Inverse susceptibility data for CuCrMnO₄.
Top: Figure 5.33: Curie-Weiss fit to susceptibility data for CuFeMnO₄.
Bottom: Figure 5.34: Inverse susceptibility data for CuFeMnO₄.
Top: Figure 5.35: Curie-Weiss fit to susceptibility data for LiCoMnO$_4$.
Bottom: Figure 5.36: Inverse susceptibility data for LiCoMnO$_4$. 
Top: Figure 5.37: Curie-Weiss fit to susceptibility data for CuCoMnO₄.
Bottom: Figure 5.38: Inverse susceptibility data for CuCoMnO₄.
Top: Figure 5.39: Curie-Weiss fit to susceptibility data for CuRhMnO₄.

Bottom: Figure 5.40: Inverse susceptibility data for CuRhMnO₄.
Top: Figure 5.41: Curie-Weiss fit to susceptibility data for Cu$_{0.5}$Zn$_{0.5}$RhMnO$_4$.
Bottom: Figure 5.42: Inverse susceptibility data for Cu$_{0.5}$Zn$_{0.5}$RhMnO$_4$. 
5.3.2.1 AC Susceptibility

AC susceptibility measurements were performed to confirm that LiCrMnO₄ and Cu₀.₅Zn₀.₅RhMnO₄ are spin glasses, and to test the hypothesis that the compounds CuMMnO₄ are ferromagnetic semi-spin-glasses. A semi-spin glass has a disordered, frozen, spin glass component transverse to the ordered ferromagnetic component. The AC susceptibility measurements of LiCrMnO₄, which are presented in figure 5.43, show a cusp in the real part of the susceptibility, $\chi'$, at about 14K, with a clear frequency dependence in the range of 1-10kHz; this region is expanded in figure 5.44. The imaginary part of the susceptibility, $\chi''$, is expanded around 14K in figure 5.45. It shows a sharp maximum at the same temperature as the cusp in $\chi'$, with a tailing off to a non-zero plateau below that temperature; the height of both the maximum, and the plateau also show a frequency dependence. The AC susceptibility behaviour of LiCrMnO₄ is that expected of a spin glass undergoing a sharp cooperative freezing at a freezing temperature, $T_f$, of 14K. Inspection of the DC susceptibility measurements of Cu₀.₅Zn₀.₅RhMnO₄, in figures 5.18 and 5.20 suggest that it behaves in a very similar way to LiCrMnO₄, and so a similar set of AC susceptibility measurements might be expected. In fact the AC behaviour of Cu₀.₅Zn₀.₅RhMnO₄, shown in figure 5.49, is completely different. The real part of the susceptibility, $\chi'$, shows a broad maximum around 8K, expanded in figure 5.50, with a slight frequency dependence in the range of 0.25-10kHz, unfortunately sufficient resolution could not be achieved below 250Hz, where most spin glasses display a large frequency shift. The imaginary part of the susceptibility, $\chi''$, is expanded in figure 5.51, it can be seen to be non-zero, with frequency dependent magnitude over the entire measured temperature range, 5-20K, though the maximum does correspond with the maximum in $\chi'$, at 8K. The AC susceptibility behaviour of Cu₀.₅Zn₀.₅RhMnO₄ does show features consistent with a spin
glass undergoing a cooperative freezing at a freezing temperature, $T_f$, of 8K, but the
cusp is very broad and there is clear evidence of non-paramagnetic behaviour up to
20K. The DC measurements in figure 5.20 revealed a divergence of the 100Oe and
1000Oe DC susceptibilities in the same temperature range, indicating that the
magnetization is not a linear function of the applied field below 20K, and the frequency
dependence of $\chi''$ indicate some sort of spin glass character in this region. The data
could be interpreted as the emergence of spin glass clusters at around 20K, with a
gradual growth of these domains with decreasing temperature until they go critical at
8K. The AC susceptibility of CuCrMnO$_4$, which is spontaneously magnetized below
29K, is shown in figure 5.46, performed in zero biasing field (as were the previous AC
measurements), and also with a biasing field of 100Oe superimposed on the 1Oe driving
field. The real part of the susceptibility, $\chi'$, shows a broad maximum around 26K, which
is expanded in figure 5.47, with a slight frequency dependence in the range of 0.25-
10kHz, although, once again, low frequency data is required to confirm the frequency
shift and characterize the frequency dependence. The imaginary part of the
susceptibility, which is expanded in figure 5.48, also shows a broad maximum at 26K of

$$\frac{\chi''}{\chi'_{\text{max}}}=0.13$$

in the 10kHz data, but at 0.25kHz and 1kHz the maximum is
shifted to 24K and the magnitude is reduced by a factor of three, to
$$\frac{\chi''}{\chi'_{\text{max}}}=0.04.$$ It can
be seen in figures 5.46 and 5.48 that the application of a 100Oe biasing field suppresses
the maximum in both the real and imaginary parts of the susceptibility. A more
surprising observation is that the biased, 10kHz $\chi''$, figure 5.48, becomes non-zero at
about 60K, with a very similar shape to that of the real part of the susceptibility, whilst
the biased, 1kHz data, like the zero biasing field imaginary susceptibilities, only
becomes non-zero close to $T_C$, at around 40K. The AC susceptibility behaviour of
CuCrMnO$_4$ is consistent with a ferromagnetic semi-spin-glass undergoing a cooperative
freezing at a freezing temperature, $T_f$ of 26K. Both the DC magnetization (figure 5.16), and the real part of the AC susceptibility, start to rise rapidly from about 60K, indicating the formation of clusters with a ferromagnetic component at this temperature. Below 40K, these clusters are sufficiently large that there is an emergence of a finite imaginary susceptibility. It appears that, in the range 40-60K, in the presence of a 100Oe biasing field, the domains can precess with the driving field at 1kHz without significant energy loss, but at 10kHz the domains are unable to "keep up" with the field, indicating a relaxation time in the region of $10^{-3}$-$10^{-4}$s.
Top: Figure 5.43: Normalised \( \chi_N = \chi / \chi_{\text{max}} \) real (\( \chi' \)) and imaginary (\( \chi'' \)) AC susceptibility of LiCrMnO₄, in a driving field of 10e with selected frequencies, against temperature.

Bottom: Figure 5.44: Expansion of the cusp in the real part of the AC susceptibility of LiCrMnO₄, in a driving field of 10e with selected frequencies, against temperature.
Top: Figure 5.45: Expansion of the cusp in the imaginary part of the AC susceptibility of LiCrMnO$_4$, in a driving field of 10e with selected frequencies, against temperature.

Top: Figure 5.46: Normalised ($\chi' = \chi / \chi'_{\text{max}}$) real ($\chi'$) and imaginary ($\chi''$) AC susceptibility of CuCrMnO$_4$, in a driving field of 10e with selected frequencies, against temperature, with and without an applied DC field of 1000e.
Top: Figure 5.47: Expansion of the cusp in the real part of the AC susceptibility of CuCrMnO₄, in a driving field of 10e with selected frequencies, against temperature.
Bottom: Figure 5.48: Expansion of the imaginary part of the AC susceptibility of CuCrMnO₄, in a driving field of 10e with selected frequencies, against temperature with and without an applied DC field of 100Oe.
Figure 5.49: Normalised ($\chi'_N = \chi / \chi_{max}'$) real ($\chi'$) and imaginary ($\chi''$) AC susceptibility of Cu$_{0.5}$Zn$_{0.5}$RhMnO$_4$, in a driving field of 10e with selected frequencies, against temperature.
Top: Figure 5.50: Expansion of the cusp in the real part of the AC susceptibility of Cu$_{0.5}$Zn$_{0.5}$RhMnO$_4$, in a driving field of 10e with selected frequencies, against temperature.
Bottom: Figure 5.51: Expansion of the imaginary part of the AC susceptibility of Cu$_{0.5}$Zn$_{0.5}$RhMnO$_4$, in a driving field of 10e with selected frequencies, against temperature.
5.3.2.2 Time Dependent Magnetization

Zero field cooled aging experiments were performed according to the scheme in section 3.5.1.1, for CuCrMnO$_4$, CuRhMnO$_4$ and Cu$_{0.5}$Zn$_{0.5}$RhMnO$_4$. The evolution of the magnetization of CuCrMnO$_4$ with time, upon the application of a 200e field, after a waiting time of 1000s, (section 3.4.6) is shown in figure 5.52, for selected temperatures in the range 5-60K. For clarity, this data is also presented in figure 5.53 as a change in magnetization, $\Delta M$, where $\Delta M = M(t) - M(t=1 \text{ min})$. It is clear that there is a strong increase in the constant temperature, constant field magnetization with time at 5K, 10K and 20K, and it can be seen from the expansion at the bottom of figure 5.53 that there are smaller, but significant, increases at 30K and 40K, whilst there seems to be a tiny increase at 50K and 60K, but it is difficult to be sure that this is a real effect. Similarly, the time dependence of the magnetization of CuRhMnO$_4$, in the temperature range 5-40K, is shown in figure 5.60. The change in magnetization during these measurements is presented in figure 5.61. There is a smooth increase, with time at 5K and 7K, and although the 10K and 15K data sets contain discontinuities, possibly caused by the movement of the sample in the sample holder, they do indicate a strong increase. Interestingly, the 20K data shows a small decrease with time, the expected behaviour for a normal ferromagnet, and the measurements from 25K and above show no change. This seems to indicate that the spin glass behaviour emerges at the Curie temperature (19K), but that significant ferromagnetic interactions persist above $T_C$ without spin glass behaviour. Similar measurements for Cu$_{0.5}$Zn$_{0.5}$RhMnO$_4$, at 1.8K and 5K, are presented in figures 5.56 and 5.57, which show that the ZFC magnetization of Cu$_{0.5}$Zn$_{0.5}$RhMnO$_4$ in an applied field of 200e is also temperature dependent at temperatures below the observed transition at 8K. The inverse derivative of the ZFC
magnetization with respect to time, $\left[\left(\frac{1}{H}\right)\frac{\partial M}{\partial t}_{r,H}\right]^{-1}$, of CuCrMn$_{0.4}$ at 20K, with waiting time, $t_w$, of 100s and 1000s, is plotted in figure 5.54, and though both waiting times give an almost straight line, indicating a close-to-logarithmic increase in magnetization with time, it is clear that the time dependence of the magnetization is a function of $t_w$. This data is very noisy because the derivative was calculated as the gradient between one point and the next, and at longer waiting times the change in magnetization between measurements is of similar magnitude to the error in the measurement. The near-linearity of the inverse derivative is indicative of spin glass character, to investigate the deviation from linearity, the relaxation rate, $S$ (equation (3.29)), after waiting times of 100s and 1000s, was plotted against time in figure 5.55, and both data sets can be seen to have a clear maximum when the elapsed time is approximately equal to the waiting time, $t_w$. Similarly the inverse derivative of the magnetization of CuRhMn$_{0.4}$ at 5K after a waiting time of 1000s, is shown to be near-linear in figure 5.62, and the maximum in the 5K relaxation rate, shown in figure 5.63, corresponds with the waiting time for $t_w = 100$ and 1000s, and no clear maximum is observed up over the experimental time of 8000s, for the $t_w = 10000$s data. The same aging behaviour is observed in the inverse derivative (figure 5.58) and relaxation rate (figure 5.59) of Cu$_{0.5}$Zn$_{0.5}$RhMn$_{0.4}$ at 1.8K and 5K, with waiting time of 1000s. The maximum in the relaxation rate when $t = t_w$, is strongly indicative of spin glass behaviour. This derivative, $S = \left(\frac{1}{H}\right)\frac{\partial M}{\partial \log_{10} t}_{r,H}$, is similar to that discussed above, but because the magnetization is differentiated with respect to the logarithm of the time (in seconds; seconds are used for consistency with the literature) the derivative would be constant with time if the evolution of the magnetization were purely logarithmic.
Table 5.4: Magnitudes of the ferromagnetic and spin glass components of the magnetic structure, and the canting angle, $\Phi$, calculated from the model in figure 3.9.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Theoretical Saturation Moment ($\mu_B$/magnetic ion)</th>
<th>Ferromagnetic Component ($\mu_B$/magnetic ion)</th>
<th>Spin Glass Component ($\mu_B$/magnetic ion)</th>
<th>Canting Angle, $\Phi$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuCrMnO$_4$</td>
<td>3</td>
<td>0.67</td>
<td>2.92</td>
<td>77°</td>
</tr>
<tr>
<td>CuRhMnO$_4$</td>
<td>3</td>
<td>2.22</td>
<td>2.02</td>
<td>42°</td>
</tr>
<tr>
<td>Cu$<em>{0.5}$Zn$</em>{0.5}$RhMnO$_4$</td>
<td>3.5</td>
<td>0.86</td>
<td>3.39</td>
<td>76°</td>
</tr>
</tbody>
</table>

If the magnetic structure is represented by the model shown in figure 3.9, then the relative sizes of the ferromagnetic and spin glass components can be approximated according to the method in section 3.4.7 (equations (3.30)-(3.32)). The iron compounds are not included, because there is uncertainty as to whether the B-site iron and manganese are ferromagnetically or ferrimagnetically coupled, and there is a strong degree of cation inversion. No saturation moment is available for CuCoMnO$_4$, and again, there is uncertainty over the electronic configuration of the cobalt ions, so this compound has not been included either. In CuCrMnO$_4$, the Mn$^{4+}$ and Cr$^{3+}$ ions are both d$^3$, and are treated equally, giving a theoretical maximum saturation magnetization of $gS = 6\mu_B$/Mn. Ferrimagnetic ordering would give zero net moment, so is discounted. In the rhodium compounds, the manganese ions are treated as the only magnetic species, giving theoretical maximum saturation magnetization values of 3$\mu_B$/Mn and 3.5$\mu_B$/Mn for CuRhMnO$_4$ and Cu$_{0.5}$Zn$_{0.5}$RhMnO$_4$ respectively. Unfortunately, there is no 50kOe data for Cu$_{0.5}$Zn$_{0.5}$RhMnO$_4$, but as the 1kOe magnetization is only 0.14$\mu_B$/Mn, the saturation value is unlikely to be much greater, so this value will be used. If the magnitude of the ferromagnetic component is taken to be the 5K, 50kOe saturation magnetization, which was in excellent agreement with the ordered moment derived from the neutron diffraction pattern of LiMg$_{0.5}$Mn$_{1.5}$O$_4$, then the ferromagnetic component divided by the theoretical moment gives the cosine of the canting angle, $\Phi$, defined, in figure 3.9, as the angle between the moments on individual ions and the
direction of ferromagnetic ordering (one of the crystallographic axes, arbitrarily \( z \)). The values obtained from this treatment are presented in table 5.4.

Figure 5.52: Aging of ZFC Magnetization (in 20Oe) for CuCrMnO\(_4\)
Figure 5.53: (Top) Change in ZFC Magnetization with time (in 200e) for CuCrMnO$_4$ at selected temperatures, and (bottom) expansion of the small $\Delta M$ region.
Top: Figure 5.54: Inverse derivative of the ZFC Magnetization (M/H, in 20Oe), with respect to time in minutes, for CuCrMnO₄ at 20K, with waiting times, tₜ, of 100s and 1000s.

Bottom: Figure 5.55: Relaxation rate, S (section 3.4.6) derivative of the ZFC Magnetization (M/H, in 20Oe), with respect to log₁₀(time) in seconds, for CuCrMnO₄ at 20K, with waiting times, tₜ, of 100s and 1000s.
Top: Figure 5.56: Aging of ZFC Magnetization (in 20Oe) for Zn$_{0.5}$Cu$_{0.5}$RhMnO$_4$ at selected temperatures.

Bottom: Figure 5.57: Change in ZFC Magnetization (in 20Oe) for Zn$_{0.5}$Cu$_{0.5}$RhMnO$_4$ at selected temperatures.
Top: Figure 5.58: Inverse derivative of the ZFC Magnetization \((M/H, \text{in 20Oe})\), with respect to time, in minutes, for \(\text{Zn}_{0.5}\text{Cu}_{0.5}\text{RhMnO}_4\) at 5K, with waiting time, \(t_w\), of 1000s.

Bottom: Figure 5.59: Relaxation rate, \(S\) (section 3.4.6) derivative of the ZFC Magnetization \((M/H, \text{in 20Oe})\), with respect to \(\log_{10}(\text{time})\) in seconds, for \(\text{Zn}_{0.5}\text{Cu}_{0.5}\text{RhMnO}_4\) at 1.8K, and 5K, with waiting time, \(t_w\), of 1000s.
Top: Figure 5.60: Aging of ZFC Magnetization (in 200e) for CuRhMnO₄ at selected temperatures.
Bottom: Figure 5.61: Change in ZFC Magnetization (in 200e) for CuRhMnO₄ at selected temperatures.
Top: Figure 5.62: Inverse derivative of the ZFC Magnetization (M/H, in 20Oe), with respect to time, in minutes, for CuRhMnO$_4$ at 5K, with waiting time, $t_w$, of 1000s.

Bottom: Figure 5.63: Relaxation rate, $S$ (section 3.4.6) derivative of the ZFC Magnetization (M/H, in 20Oe), with respect to $\log_{10}$(time) in seconds, for CuRhMnO$_4$ at 5K, with waiting times, $t_w$, of 100s, 1000s and 10000s.
5.3.3 Conductivity

The plot of the natural logarithm of the resistance against \(1/T\) for quenched LiFeMnO\(_4\), CuRhMnO\(_4\) and Cu\(_{0.5}\)Zn\(_{0.5}\)RhMnO\(_4\) is shown in figure 5.64. The linear dependence of \(\ln(\rho)\) with \(1/T\) in the region 200K-400K is consistent with a thermally activated semiconductor. The poor conductivity of these samples prevented measurement of the resistance at low temperature due a low carrier density, precluding measurement around the Curie temperature. Above the ordering temperatures, the resultant activation energies were determined to be 0.10(1)eV for CuRhMnO\(_4\), 0.50(1)eV for Cu\(_{0.5}\)Zn\(_{0.5}\)RhMnO\(_4\) and 0.70(1)eV for LiFeMnO\(_4\). Figures 5.65 and 5.66 show the dependence of the resistivity with temperature of, respectively, Cu\(_{0.5}\)Zn\(_{0.5}\)RhMnO\(_4\) and CuRhMnO\(_4\) in an applied magnetic field of 0Oe, 10000Oe and 25000Oe. Cu\(_{0.5}\)Zn\(_{0.5}\)RhMnO\(_4\) shows an increase in resistivity with increasing field over the entire temperature range studied, with a positive magnetoresistance effect, defined by \(\rho(h)-\rho(0)/\rho(0)\), of around 25% at 150K, and 2% at 300K. Conversely, CuRhMnO\(_4\) shows a decrease in resistivity with increasing field over the entire temperature range studied, with a negative magnetoresistance effect, defined by \(\rho(h)-\rho(0)/\rho(0)\), of around 20% at 100K, and 5% at 300K. These measurements were repeated on second batches of sintered pellets, and the same results were obtained. Measurements of conductivity and a function of applied magnetic field were attempted. The first measurements were unsatisfactory because the temperature control was inadequate, and later experiments failed because the signal-noise ratio in the instrument had become poor.
Figure 5.64: Plot of the natural log of the resistivity (in Ωcm) against inverse temperature for CuRhMnO₄ (red), Cu₀.₅Zn₀.₅RhMnO₄ (black) and quenched LiFeMnO₄ (blue).
Top: Figure 5.65: Plot of resistivity of Cu$_{0.5}$Zn$_{0.5}$MnO$_4$ against temperature in applied magnetic fields of 0 Oe (red), 10 kOe (blue) and 50 kOe (black). Inset: expansions of the regions around 150K and 300K.

Bottom: Figure 5.66: Plot of resistivity of CuRhMnO$_4$ against temperature in applied magnetic fields of 0 Oe (red), 10 kOe (blue) and 50 kOe (black). Inset: expansions of the regions around 100K and 300K.
5.4 Discussion

The slow cooling sample preparation was first reported by Basse$^1$ and was shown in chapter 4 to induce the formation of the cation ordered form of LiMg$_{0.5}$Mn$_{1.5}$O$_4$, with crystallographically distinct manganese and magnesium sites. The same method was tried for all the compositions reported in this chapter, but no conclusive evidence of cation ordering was found, and the XRD patterns of certain compositions showed a deterioration (peak broadening) after the slow-cooling, so characterization measurements were performed on the quenched samples. This deterioration is probably linked to the observation in chapter 4 that the slow-cooling also appears to favour the occurrence of shoulders on a number of the Bragg reflections in LiMg$_{0.5}$Mn$_{1.5}$O$_4$. The fluorescence in the iron and cobalt samples in the copper K$_{a1}$ beam caused difficulty in determining the purity of those samples by XRD, Kawai et al$^9$ encountered a similar problem in the XRD of LiCo$_{0.5}$Mn$_{1.5}$O$_4$.

The lattice parameters obtained by Rietveld refinement were in good agreement (±0.01 Å) with previously reported values for LiCrMnO$_4$$^{10}$ and CuCrMnO$_4$$^{11}$. The Rietveld refinements of the neutron diffraction data of the rhodium containing compounds show that, as expected from crystal field theory, the A-sites are almost fully occupied by the copper and zinc ions, with the manganese and rhodium cations on the B-sites, although there was 2.4(4)\% cation inversion in CuRhMnO$_4$ and 3.0(3)\% inversion in Cu$_{0.5}$Zn$_{0.5}$RhMnO$_4$, in both cases it was copper and manganese ions interchanging, because these ions have alternative oxidations states that favour the inversion, Cu$^{2+}$ and Mn$^{3+}$. The neutron diffraction pattern of CuFeMnO$_4$ revealed the presence of the impurity phase CuO, with a phase fraction of 7\% by weight, corresponding to 15\% of the copper atoms in the synthetic mixture. The true
composition of the spinel phase is likely to be approximately Cu$_{0.9}$Mn$_{1.05}$Fe$_{1.05}$O$_4$. This implies that there will be a significant number of magnetic A-site cations, and that the average oxidation state of either manganese or iron must be slightly reduced from the nominal oxidation state of $+4$ and $+3$ respectively. This reduction is the likely explanation for the surprisingly large lattice parameter of CuFeMnO$_4$, which is greater than that of CuRhMnO$_4$ (respectively 8.4027(3)Å and 8.3968(3)Å) despite octahedral Fe$^{3+}$ (high-spin) and Rh$^{3+}$ having respective Shannon ionic radii of 0.785Å and 0.805Å. It was noted in chapter 4 that in the compounds, CuM$_{0.5}$Mn$_{1.5}$O$_4$, electroneutrality could be satisfied with Cu$^{2+}$ and an equal number of Mn$^{3+}$ ions replacing Cu$^+$ and Mn$^{4+}$, but this was discounted because of the striking similarity in the magnetic properties of the lithium and cooper compounds, the lack of a tetragonal distortion, and the Cu-O bond lengths. With these materials there are a wide range of combinations of available oxidation states that would satisfy charge neutrality, electron energy loss spectroscopy (EELS) (these methods are reviewed in chapter 8) has been used by Suzuki et al$^{13}$ to verify that LiM$^{3+}$Mn$^{4+}$O$_4$ is the correct description for (M=Cr, Mn, Co), similarly Sigala et al$^{14}$ employed EELS to monitor the oxidation states of Cr and Mn in LiCr$_y$Mn$_{2-y}$O$_4$ ($0 \leq y \leq 1$) before and after lithium deintercalation. They found the as prepared samples to contain Cr$^{3+}$ and Mn$^{3+/4+}$, and found the fully deintercalated material to be Cr$^{4+y}$Mn$^{4+}_{2-y}$O$_4$.

With the exception of LiFeMnO$_4$, which has strong cation inversion, there is a systematic difference in the magnetic properties of LiMMnO$_4$ (spin glass) and CuMMnO$_4$ (spontaneous magnetization), hence the oxidation state of the copper requires careful consideration, though the aging measurements indicate that the copper compounds are semi-spin-glasses, so the magnetic structures are not as different as might first appear. The refined Cu-O bond length, from the neutron diffraction pattern,
in CuRhMnO₄ is 2.003(2)Å, taking a Shannon ionic radius for tetrahedral O²⁻ of 1.24Å, the radii of the copper ions are approximately 0.76Å, indicating that Cu⁺ is present. The tetrahedral Shannon ionic radii for Cu⁺ and Cu²⁺ are, respectively, 0.74Å and 0.71Å. The A-site radii, determined by X-ray diffraction, of CuCrMnO₄ and CuCoMnO₄ are respectively 0.71Å and 0.75Å. This distance is a function of the oxygen position parameter, \( u \), (equation 2.1) and the difference between these two values is likely to indicate that the determination of the oxygen position by XRD is not sufficiently accurate to differentiate between Cu⁺ and Cu²⁺ by bond distance.

The refinement of the neutron diffraction pattern of CuFeMnO₄ was problematic. The loss of 15% of the copper to CuO made the A-site occupancy uncertain, because manganese, iron or vacancies could fill the remaining sites, and the neutron diffraction technique only provides information on the average scattering length at the site. Models of all possible cation distributions with the cubic \( Fd\bar{3}m \) structure, but none could account for the strong intensity observed in the (111) peak while correctly fitting the relative intensities of the remaining peaks. It was hypothesized that the intensity of (111) was caused by 1:1 cation ordering on the B-sites, but none of the cation ordering models in the literature could fit all of the peaks. Therefore a multiphase refinement of the most promising ordered model, with the normal spinel phase (and copper oxide) was tried. It was possible to fit the whole pattern with this model, but, because only one peak was poorly fitted in the disordered refinement, any extra phase that allowed intensity in the (111) peak could have fit the pattern, so this is only proposed as a possible solution. The quoted crystallographic data are those obtained from the single-phase refinement in the \( Fd\bar{3}m \) structure, with the fractional occupancy of the copper allowed to refine freely. The total B-site occupancy was constrained to total unity, and suggests that the B-sites are manganese rich, so there is likely to be some Fe³⁺ on the A-sites.
It is not surprising that there is no clear evidence of a cation ordered superstructure in the compounds, $A[M^{III}Mn^{IV}]O_4$, because a cation ordered superstructure was only observed as a minority phase in the neutron diffraction pattern of $Cu[Ni^{II}\cdot 0.5Mn^{IV\cdot 1.5}]O_4$ in chapter 4, and the electrostatic ordering energy (equation 2.18) is a function of the square of the charge difference. When the different Mn:M ratios are taken into account, the electrostatic ordering energy of the compounds $A[M^{II\cdot 0.5}Mn^{IV\cdot 1.5}]O_4$ is calculated to be a factor of 2.8 greater, (table 2.2) than the term for $A[M^{III}Mn^{IV}]O_4$. It was noted in section 2.4, that these electrostatic ordering energies are of the order of 100kJmol$^{-1}$, as so ordering would always be expected, but that the tetrahedral lattice of B-sites, of a spinel, is analogous to Pauling's $^{15}$ "ice rules" because the electrostatic term only requires that each tetrahedron has the same composition as the bulk, and there are many different states that satisfy this requirement. Long-range cation order involves the selection of an unique ground state, and the energy difference between the most, and least, favourable states that satisfy the ice-rules criterion, is only about 5% (section 2.3.2.1) of the electrostatic energy. Hence, it is almost certain that each of the compounds, formulated $A[M^{III}Mn^{IV}]O_4$ features short-range B-site cation ordering, with each $B_4$ tetrahedron containing two $M^{3+}$ cations and two $Mn^{4+}$, though this is complicated by the cation inversion seen for LiFeMnO$_4$, without the selection of an unique ground state. The observation that each $B_4$ tetrahedron will be representative of the bulk has been termed the Andersen condition.$^{16}$

The complexity of the magnetic behaviour exhibited in the spinel/pyrochlore system was discussed in chapter 4. In particular, the bulk ferromagnetism of the series $AM_{0.5}Mn_{1.5}O_4$ was contrasted with the observation of antiferromagnetism and spin glass behaviour respectively, in the closely related compounds $\lambda$-MnO$_2$$^{17}$ and
Goodenough\textsuperscript{20} gave a qualitative interpretation of the various exchange interactions expected for a given exchange pathway and electronic configuration; those relevant to this thesis are presented in table 2.3. However, there are often competing interactions of opposite sign, caused by the direct and superexchange pathways.\textsuperscript{21} This makes it difficult to predict the overall sign of the exchange integral, and causes superficially similar systems to exhibit markedly different magnetic properties. Measurements of the temperature dependence of the ZFC and FC susceptibility in the compounds, AM\textsubscript{0.5}Mn\textsubscript{1.5}O\textsubscript{4}, highlight the stark difference in the bulk properties of superficially similar materials. LiCrMn\textsubscript{0.4}, LiCoMn\textsubscript{0.4} and Cu\textsubscript{0.5}Zn\textsubscript{0.5}RhMn\textsubscript{0.4}, show a cusp in the susceptibility with a divergence of the ZFC and FC susceptibilities below that temperature, consistent with spin glass behaviour, whilst CuCrMn\textsubscript{0.4}, CuFeMn\textsubscript{0.4}, CuCoMn\textsubscript{0.4} and CuRhMn\textsubscript{0.4} show low temperature (19-50K) spontaneous magnetization and LiMnFeO\textsubscript{4} is spontaneously magnetized up to 375K. This diversity can be rationalised by considering the model proposed to explain the observation of the aging effect in the compounds, AM\textsubscript{0.5}Mn\textsubscript{1.5}O\textsubscript{4}, in section 4.4; the spontaneous magnetization is the result of the ferromagnetic component (along [100]) of a semi-spin-glass phase. The aging experiments, performed on a number of these compounds, confirm this model to be correct. The anomalous behaviour of LiFeMn\textsubscript{0.4} is explained by the observation of a large amount of Fe\textsuperscript{3+} ions on the A-sites in the XRD pattern. The presence of magnetic A-site cations greatly strengthens the magnetic lattice, because the antiferromagnetic 135° A-O-B superexchange interaction is much stronger than the 90° B-O-B interaction. Antiferromagnetic alignment of the A and B sublattices, results in bulk ferrimagnetism because there are a greater number of B cations. Cu\textsubscript{0.5}Zn\textsubscript{0.5}RhMn\textsubscript{0.4} is also different from the remainder of the series because the manganese ions are mixed valence Mn\textsuperscript{3+/4+} and all the other cations are diamagnetic, so the magnetic lattice is more closely related to the antiferromagnetic LiMn\textsubscript{2}O\textsubscript{4}. Thus,
those compounds that can be formulated Li[MMn]O₄ are spin glasses, whilst those formulated Cu[MMn]O₄ are semi-spin-glasses with a ferromagnetic component. It is surprising to observe a systematic difference in the magnetic properties of the lithium and copper containing compounds in light of the striking similarity (chapter 4.4) in the magnetic structures of the compounds Li[M₀.₅Mn₁.₅]O₄ and Cu[M₀.₅Mn₁.₅]O₄.

The nature of the ferromagnetic component was investigated with low field hysteresis measurements. The great similarity between the hysteresis of LiFeMnO₄ and CuFeMnO₄ indicates that there is probably also some cation inversion in CuFeMnO₄, as was suggested by the (incomplete) refinement of the neutron diffraction pattern. The striking similarity of the hysteresis of CuCoMnO₄ to CuCrMnO₄, rather than CuRhMnO₄ with low-spin d⁶ rhodium, suggests that the cobalt ions are not low-spin d⁶. The cobalt is probably high-spin d⁶ Co³⁺; although it is possible that the difference from the rhodium sample is caused by a small amount of Co²⁺, this would not explain the similarity to the chromium sample. Rh³⁺ is known to facilitate long range superexchange interactions between magnetic ions despite its diamagnetism, for example Cu⁺⁺[Rh⁺⁺]₂O₄ is antiferromagnetic, whilst Cu⁺⁺[Al⁺⁺]₂O₄ is paramagnetic.⁸

Another potential explanation for the difference between the cobalt and rhodium samples, is that this ability of the rhodium, to strengthen the Mn-O-Mn superexchange interaction relative to the Mn-Mn direct exchange, cannot be matched by low-spin Co³⁺. However, high-spin d⁶ seems the most likely electronic configuration.

The AC susceptibility measurements confirm that LiCrMnO₄ is a spin glasses and strongly suggests that CuCrMnO₄ is a ferromagnetic semi-spin-glass, although it would be preferable to have data in the low frequency range, where large frequency shifts are often observed in spin glasses. It is interesting to note that the AC measurements of
Cu$_{0.5}$Zn$_{0.5}$RhMnO$_4$ are much more similar to those of CuCrMnO$_4$ than LiCrMnO$_4$. The sharp spin glass transition in LiCrMnO$_4$ is in contrast with the broad transition observed in Cu$_{0.5}$Zn$_{0.5}$RhMnO$_4$, this difference might just be a consequence of there being twice as many magnetic ions in LiCrMnO$_4$, and is also complicated by the presence of Mn$^{3+}$. Each B$_4$ tetrahedron in Cu$_{0.5}$Zn$_{0.5}$RhMnO$_4$ almost certainly contains (section 2.3.2.1) one Mn$^{4+}$ and one Mn$^{3+}$, though there is no long-range order. This leads to non-linear chains, in random directions, of alternating Mn$^{3+}$ and Mn$^{4+}$. The Mn$^{3+}$-O-Mn$^{4+}$ superexchange interaction is antiferromagnetic, so the deviation from linearity, observed in both the inverse DC susceptibility, and the relationship of the magnetization with respect to the applied field, is probably due to ordering within these chains. In the absence of defects, this ordering would be antiferromagnetic or spin glass in nature, but a small concentration of defects allows a ferromagnetic component to emerge, by the Villain$^{22}$ mechanism. The interchain interactions are random in terms of both distance and sign, the Mn$^{4+}$-O-Mn$^{4+}$ superexchange interaction is ferromagnetic whilst both Mn$^{3+}$-O-Mn$^{4+}$ and Mn$^{3+}$-O-Mn$^{3+}$ are antiferromagnetic. The sharp transition at 8K is assigned to the cooperative freezing of all the chains into a single spin glass ground state. It is interesting to compare the zero biasing field susceptibility of CuCrMnO$_4$, with that of LiMg$_{0.5}$Mn$_{1.5}$O$_4$, which is also spontaneously magnetized. Both $\chi'$ and $\chi''$ of LiMg$_{0.5}$Mn$_{1.5}$O$_4$ rise to a maximum as the temperature is decreased to $T_C$, and then plateau below $T_C$, whereas for CuCrMnO$_4$, both the real and imaginary part of the susceptibility show a broad, nearly symmetrical peak around $T_C$. The behaviour of CuCrMnO$_4$ is that predicted by a simple model of ferromagnetism, whilst the plateau shown by LiMg$_{0.5}$Mn$_{1.5}$O$_4$ is frequently observed in ferromagnets with strong interdomain dipole interactions.
In chapter 4, the observation of a nearly logarithmic time dependence in the ZFC low-field magnetization for both LiMg$_{0.5}$Mn$_{1.5}$O$_4$ and CuNi$_{0.5}$Mn$_{1.5}$O$_4$, with the maximum deviation from the logarithmic coming when the elapsed time, $t$, approximately equal to the waiting time, $t_w$, was ascribed to spin glass character. For the compounds, AMMnO$_4$, a larger amount of time dependence data has been collected, allowing the assignment of semi-spin-glass behaviour to be more confident. The observation of a shift in the maximum of the relaxation rate, with a change in the waiting time (section 3.5.1.1) before the field was applied, in the measurements of ZFC magnetization against time, for both CuCrMnO$_4$ and CuRhMnO$_4$ is particularly significant. In chapter 4, the alternative magnetic models that could account for some of the observed properties were ruled out for the following reasons: the ZFC magnetization of a ferromagnet does not increase with time because it reaches a rapid equilibrium between the tendency of the domains to align with the field and the interdomain dipole interactions, and the cluster glass model (section 3.4.7) could not prevent the applied field of 50kOe from forcing the parallel alignment of the ferromagnetic clusters in the saturation measurements. The possibility that reentrant spin glass behaviour, comprising of subsequent paramagnetic-ferromagnetic (PM-FM) and ferromagnetic-spin glass (FM-SG) transitions, was also mooted. To investigate this, the time dependence measurements were performed across the Curie temperatures of CuCrMnO$_4$ and CuRhMnO$_4$. In CuRhMnO$_4$ ($T_C = 19K$), a clear increase is observed in the region 5-15K, and no increase is observed over the range 20-40K, which is consistent with the emergence of ferromagnetism and spin glass character in a single transition. There seems to be a slight decrease with time at 20K, which is often seen in normal ferromagnets, because thermal fluctuations can result in the breaking up of domains. The ferromagnetic transition in CuCrMnO$_4$ is much less sharp than that of CuRhMnO$_4$, with a Curie temperature, determined by AC susceptibility, of 26K, but there is still a
clear increase in the magnetization with time at 30K, and progressively smaller increases are seen at 40K, 50K and 60K, though the increases at 50K and 60K are barely within the error in the measurements. This data is consistent with the derivative of the DC magnetization measurement, which showed a broad peak, beginning at around 40K, and demonstrates that spin glass character is present well above the Curie temperature. These measurements appear to rule out reentrant spin glass behaviour, where the spin glass transition takes place at a lower temperature than the ferromagnetic transition. There is no evidence to suggest that there are two separate transitions competing with each other, although reentrant spin glasses with very similar ferromagnetic and spin glass transition temperatures have been reported.23

The conduction properties of these compounds are likely to be derived from a primarily Mn-O valence band and a Li/Cu-O conduction band. The high energy and small dispersion of this latter band results in no overlap with the Mn-O energy states, in contrast to the situation with the Ti-O and Mn-O bands of Ti$_2$Mn$_2$O$_7$, resulting in semiconducting properties. The observation of a much higher activation energy in the mixed valence Mn$^{3+}$/Mn$^{4+}$ compound Cu$_{0.5}$Zn$_{0.5}$RhMnO$_4$ than CuRhMnO$_4$ shows that the conduction electrons are largely derived from manganese, and that these electrons are highly localised, whereas it had been hoped that the Mn-O band would cross one of the broad Rh-O bands, giving metallic character, in a similar manner to Ti$_2$Mn$_2$O$_7$. The magnetoresistance measurements of Cu$_{0.5}$Zn$_{0.5}$RhMnO$_4$ than CuRhMnO$_4$ are highly surprising, with conductivity against temperature measurements at different applied field indicating fairly large magnetoresistance effects of opposite sign. CuRhMnO$_4$ showed a negative magnetoresistance effect, defined by $\rho(h) - \rho(0)/\rho(0)$, of around 20% at 100K, and 5% at 300K. Conversely, Cu$_{0.5}$Zn$_{0.5}$RhMnO$_4$ shows an increase in resistivity with increasing field over the entire temperature range studied, with a
positive magnetoresistance effect of around 25% at 150K, and 2% at 300K. The negative MR effect of CuRhMnO₄ was the hoped for result of the introduction of rhodium into the lattice, despite the absence of the metallic properties of Tl₂Mn₂O₇. The positive MR shown by Cu₀.₅Zn₀.₅RhMnO₄ is extremely difficult to explain, many materials show very small (1-2%) positive magnetoresistance, but the measurements taken indicate an effect of 25% at 150K.

5.5 Conclusion

The series of compounds AMMnO₄ (A = Li, Cu or Zn) and M = Cr, Fe, Co or Rh) has been synthesized. There is no clear evidence for long-range cation ordering of the B-sites in any of the compounds. The high temperature (375K) spontaneous magnetization of LiFeMnO₄ was shown to be caused by a large degree of cation inversion, giving strong A-O-B interactions. The remaining compounds LiMMnO₄ (M = Cr, Co) are spin glasses with respective freezing temperatures of 14K and 7K. In contrast, the compounds, CuMMnO₄ (M = Cr, Fe, Co, Rh) undergo spontaneous magnetization, with critical temperatures between 19K and 49K. These compounds were also shown to have spin glass character by the observation of an aging effect in the low field ZFC magnetization, a phenomenon characteristic of spin glasses. A semi-spin-glass structure is proposed, consisting of a ferromagnetic (or ferrimagnetic component along [100] and a transverse spin glass component. The rhodium compounds showed surprising magnetotransport properties; CuRhMnO₄ and Cu₀.₅Zn₀.₅RhMnO₄ showed, respectively negative and positive magnetoresistance.
5.6 References


Chapter 6

*Synthesis, Structure and Electronic Properties of the series Cu$_{1-x}$Ni$_{0.5+x}$Mn$_{1.5}$O$_4$* (*0*<*x*<*1*)
6.1 Introduction

Some interesting aspects of the solid-state chemistry of manganese oxides, particularly the colossal magnetoresistance (CMR) behaviour of the pyrochlore compound, thallium manganite (Tl₂Mn₂O₇), were introduced in the first chapter. Chapter 4 reported the successful synthesis of the series of spinels, AM₀.₅Mn₁.₅O₄ (A = Li or Cu and M = Ni or Mg) that show interesting magnetic and transport properties. The introduction of nickel into the lattice resulted in a large increase in the Curie temperature, and the presence of magnetic ions on the A-sites in LiMnFeO₄ (chapter 5) caused a spectacular increase in the Curie temperature (T_C = 375K.). It was envisaged that the introduction of more nickel into the lattice would further increase the Curie temperature, by introducing magnetic A-B interactions. This chapter describes the synthesis, structure, magnetic and transport properties of the spinel series, Cu₁₋ₓNi₀.₅₊ₓMn₁.₅O₄ (0 < x < 1). The end member of this series, Ni₁.₅Mn₁.₅O₄, is discussed in chapter 7. This series represents the part of the series Cu₁.₅₋ₓNiₓMn₁.₅O₄ (0 < x < 1.5) that Jarrige and Mexmain¹ were unable to prepare as phase pure samples.

6.2 Experimental

Powder samples of composition Cu₁₋ₓNi₀.₅₊ₓMn₁.₅O₄ (0 < x < 1) were produced by the method described in section 3.2. The reaction scheme is given in equation (6.1). The series was originally formulated Cu₁₋₂ₓNi₀.₅₊₃ₓMn₁.₅₋₂ₓO₄, because in CuNi₀.₅Mn₁.₅O₄, the oxidation states of the metal ions were shown by bond length analysis to be Cu(I), Ni(II) and Mn(IV), so, to preserve charge neutrality, two copper ions and one manganese ion were replaced by three nickel ions. In the z > 0.2 members of this series,
it was apparent from the XRD patterns that there was a significant amount of nickel oxide (NiO) impurity. The neutron diffraction patterns of the \( z \leq 0.2 \) compounds revealed a small amount of NiO, which was explained by the presence of manganese (presumably Mn\(^{2+}\)) ions on the A-sites. The partial reduction of Mn\(^{4+}\) to Mn\(^{2+}\) prevents the incorporation of some of the nickel into the lattice. Thus the series was reformulated, assuming that there is a statistical distribution of Mn\(^{2+}\) and Ni\(^{2+}\) on the A-sites, not occupied by Cu\(^{+}\) ions, giving a formulation, Cu\(^{+}\)\(_{2y}\)Ni\(^{2+}\)\(_{y}\)Mn\(^{2+}\)\(_{y}\)[Ni\(^{2+}\)\(_{0.5+\gamma}\)Mn\(^{4+}\)\(_{1.5-\gamma}\)]O\(_4\) or Cu\(_{1-x}\)Ni\(_{0.5+x}\)Mn\(_{1.5}\)O\(_4\), where \( x = 2y \).

\[ \begin{align*}
(1-x)\text{Cu(CH}_3\text{CO}_2)_2\cdot\text{H}_2\text{O} + (0.5+x)\text{Ni(CH}_3\text{CO}_2)_2\cdot4\text{H}_2\text{O} \\
+1.5\text{Mn(CH}_3\text{CO}_2)_2\cdot4\text{H}_2\text{O} & \rightarrow \text{Cu}_{(1-x)}\text{Ni}_{(0.5+x)}\text{Mn}_{(1.5)}\text{O}_4 + 12\text{CO}_2 + n\text{H}_2\text{O} \quad (6.1) \\
(0<x<1)
\end{align*} \]

The reaction mixture was ground thoroughly and the acetates decomposed by slowly heating from room temperature to 400°C (\( \Delta T = 0.7^\circ C/\text{min} \)). The product was then pelletised and initially fired at 750°C for one day, with further heating at 750°C for 4 days, with intermittent regrinding, until the reaction was deemed complete. On completion of the synthesis the reaction mixture was slow-cooled at 0.07°C per minute from 750°C to room temperature to produce the final product. Characterisation methods are detailed in chapter 3, and those pertaining to this chapter are summarized below. X-ray diffraction data was collected on a Siemens D500 diffractometer fitted with a primary monochromator giving \( \lambda = 1.54056\text{Å} \). DC Magnetic susceptibility measurements were performed using a Quantum Design MPMS7 SQUID magnetometer. Magnetoresistance measurements were performed on the electronic properties probe of an Oxford Instruments Maglab 2000 system. Neutron diffraction experiments were carried out on the BT1 constant wavelength diffractometer at the National Institute of Standards Technology using a Cu(311) monochromator (\( \lambda = 1.5401 \)).
Å). Analysis of this data was performed by the Rietveld method\textsuperscript{3} within the GSAS suite of software.\textsuperscript{4}
6.3 Results

6.3.1 Structure

The X-ray diffraction (XRD) patterns of the original series, formulated $\text{Cu}_{1-2z}\text{Ni}_{0.5+3z}\text{Mn}_{1.5-2z}\text{O}_4$ indicated the formation of increasing amounts of the impurity phase, NiO, with increasing $z$ for $z > 0.2$. The neutron diffraction patterns of $\text{Cu}_{0.8}\text{Ni}_{1.1}\text{Mn}_{1.3}\text{O}_4$ and $\text{Cu}_{0.8}\text{Ni}_{0.8}\text{Mn}_{1.4}\text{O}_4$ depicted in figures 6.1 and 6.2 respectively, show that there is a small amount of nickel oxide present in these samples too. The cause of the incomplete mixing of the samples was revealed by refinement of the A-site fractions of these compounds, presented in table 6.1; when the series was formulated, it had been assumed that the nickel ions would be $\text{Ni}^{2+}$ and the manganese, $\text{Mn}^{4+}$, and therefore that the excess $\text{Ni}^{2+}$ ions would be forced onto the A-sites because $\text{Mn}^{4+}$ has the greater crystal field stabilisation energy (section 2.3.3.2). It can be seen from table 6.1 that there is a significant amount of manganese on the A-sites of both the $z = 0.1$ and $z = 0.2$ samples; neutron diffraction is very sensitive to the composition due to the contrasting coherent scattering lengths. The A-site manganese is almost certainly $\text{Mn}^{2+}$ ($d^5$), which favours tetrahedral coordination (section 2.3.3.3).

### Table 6.1: Refined A-site fractional occupancies from the neutron diffraction patterns of $\text{Cu}_{0.8}\text{Ni}_{1.1}\text{Mn}_{1.3}\text{O}_4$ and $\text{Cu}_{0.8}\text{Ni}_{0.8}\text{Mn}_{1.4}\text{O}_4$.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\text{Cu}^\dagger$</th>
<th>$\text{Ni}$</th>
<th>$\text{Mn}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Cu}<em>{0.8}\text{Ni}</em>{0.8}\text{Mn}_{1.4}\text{O}_4$</td>
<td>0.8</td>
<td>0.073(4)</td>
<td>0.127(4)</td>
</tr>
<tr>
<td>$\text{Cu}<em>{0.8}\text{Ni}</em>{1.1}\text{Mn}_{1.3}\text{O}_4$</td>
<td>0.6</td>
<td>0.255(4)</td>
<td>0.145(4)</td>
</tr>
</tbody>
</table>

$\dagger$: The A-site fraction of copper was fixed to the stoichiometric value, and the total A-site fraction was constrained to unity.
Top: Figure 6.1: Rietveld refinement of the neutron diffraction pattern of Cu$_{0.6}$Ni$_{1.1}$Mn$_{1.3}$O$_4$ (bottom tick marks) with NiO impurity phase (top marks).
Bottom: Figure 6.2: Rietveld refinement of the neutron diffraction pattern of Cu$_{0.8}$Ni$_{0.8}$Mn$_{1.4}$O$_4$ (bottom tick marks) with NiO impurity phase (top marks).
In light of this observation, the series was reformulated as \( \text{Cu}_{1-2y}\text{Ni}_y\text{Mn}_y[\text{Ni}_{0.5+y}\text{Mn}_{1.5-y}]\text{O}_4 \) or \( \text{Cu}_{1-x}\text{Ni}_{0.5+x}\text{Mn}_{1.5}\text{O}_4 \), where \( x = 2y \). The XRD patterns of all compositions of this series were consistent with monophasic, highly crystalline, spinels. The XRD patterns of all of the samples were refined in the conventional spinel space group, \( Fd\bar{3}m \).

Although the relative occupancies of copper and nickel could not be refined, due to the similar number of electrons, the changing composition was monitored by the evolution of the lattice parameter, illustrated in figure 6.3. The XRD patterns for this series are extremely similar, so only those of the end members (\( x = 0.1 \) and \( x = 0.9 \)) are shown, in figures 6.4 and 6.5 respectively. To investigate the cationic distribution in the series, neutron diffraction patterns of the \( x = 0.4 \) and \( x = 0.6 \) compounds were collected. The Rietveld refinements (section 3.3.2.3) of these patterns are presented in figures 6.6 and 6.7 respectively, and the structural parameters obtained in these fits are tabulated in table 6.2, the oxygen \( u \) parameter is discussed in section 2.2.2 and the quoted thermal parameters are the isotropic \( U \) values from the GSAS suite of programs. These samples were also found to have a small amount (3% weight fraction of NiO), this is because the A-site fractional occupancy of Mn\(^{2+}\) is greater than that of Ni\(^{2+}\) for both \( x = 0.4 \) (Mn = 0.288(3), Ni = 0.112(3)) and \( x = 0.6 \) (Mn = 0.367(3), Ni = 0.233(3)).
### Table 6.2: Summary of key structural data for compounds \( \text{Cu}_{1-x}\text{Ni}_{0.5+x}\text{Mn}_{1.5}\text{O}_4 \).  

<table>
<thead>
<tr>
<th>Substitution Parameter, ( x )</th>
<th>Lattice Oxygen Parameter, ( u ) parameter (Å)</th>
<th>A-site ( f ) occupancy</th>
<th>A-site ( U ) / 100(^4)</th>
<th>B-site ( f ) occupancy</th>
<th>B-site ( U ) / 100(^4)</th>
<th>O-site ( r ) occupancy</th>
<th>( \chi^2 )</th>
<th>( R_{wp} ) (%)</th>
</tr>
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<td>( \text{Cu}=0.9)</td>
<td>1.13(8)</td>
<td>( \text{Ni}=0.3)</td>
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<td>1.512</td>
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<tr>
<td>0.4</td>
<td>8.3038(1) 0.26324(4)</td>
<td>( \text{Cu}=0.6)</td>
<td>1.24(6)</td>
<td>( \text{Mn}=0.606(2))</td>
<td>0.64(10)</td>
<td>1.21(2)</td>
<td>1.092</td>
<td>5.48</td>
</tr>
<tr>
<td>0.6</td>
<td>8.3185(2) 0.26300(5)</td>
<td>( \text{Cu}=0.4)</td>
<td>1.86(9)</td>
<td>( \text{Ni}=0.233(3))</td>
<td>0.88(7)</td>
<td>1.08(2)</td>
<td>1.046</td>
<td>6.23</td>
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<tr>
<td>0.90000</td>
<td>8.3384(2) 0.2617(3)</td>
<td>( \text{Cu}=0.1)</td>
<td>1.8(1)</td>
<td>( \text{Mn}=0.871(6))</td>
<td>0.28(7)</td>
<td>1.2(1)</td>
<td>1.225</td>
<td>4.60</td>
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<td></td>
</tr>
</tbody>
</table>

†: Constrained to total unity; values without quoted standard deviation were not refined.

![Figure 6.3: Variation of lattice parameter with increasing nickel content in series \( \text{Cu}_{1-x}\text{Ni}_{0.5+x}\text{Mn}_{1.5}\text{O}_4 \). Line is a guide to the eye.](image-url)
Top: Figure 6.4: Rietveld refinement of the X-ray diffraction pattern of Cu$_{0.1}$Ni$_{1.4}$Mn$_{1.5}$O$_4$.
Bottom: Figure 6.5: Rietveld refinement of the X-ray diffraction pattern of Cu$_{0.9}$Ni$_{0.6}$Mn$_{1.5}$O$_4$. 
Top: Figure 6.6: Rietveld refinement of the neutron diffraction pattern of Cu$_{0.4}$Ni$_{1.1}$Mn$_{1.5}$O$_4$ (bottom tick marks) with NiO impurity phase (top marks).

Bottom: Figure 6.7: Rietveld refinement of the neutron diffraction pattern of Cu$_{0.6}$Ni$_{0.9}$Mn$_{1.5}$O$_4$ (bottom tick marks) with NiO impurity phase (top marks).
6.3.2 Magnetism

The field cooled (FC) magnetic susceptibilities, in an applied field of 100 Oe, of the series $\text{Cu}_{1-x}\text{Ni}_{0.5+x}\text{Mn}_{1.5}\text{O}_4$ are presented in figure 6.8. Each of the materials undergoes spontaneous magnetisation from a paramagnetic state at a well-defined temperature; the minimum in the derivative of the magnetization with respect to temperature, $\frac{dM}{dT}$, as presented in figure 6.9.

![Figure 6.8: Variation of Field Cooled (in 100 Oe) Magnetization against Temperature in the spinel series $\text{Cu}_{1-x}\text{Ni}_{0.5+x}\text{Mn}_{1.5}\text{O}_4$.](image-url)
In chapter 4, CuNi_{0.5}Mn_{1.5}O_{4} was shown to be ferrimagnetically ordered on the B-sites, with the manganese and nickel sublattices aligned antiparallel to one another. The saturation magnetization measurements, shown in figure 6.10, confirm that similar behaviour is seen throughout this series. The 50kOe saturation magnetizations are tabulated in table 6.3, and can be seen to decrease with increasing nickel content, confirming that the nickel B-sublattice is ordering antiparallel to that of manganese. It is interesting to note that the 100 Oe magnetizations (figure 6.8) do not follow the same trend as the 50kOe values, with Cu_{0.9}Ni_{0.6}Mn_{1.5}O_{4} having a markedly higher magnetization than CuNi_{0.5}Mn_{1.5}O_{4} in these conditions. The Néel temperature (table...
6.3) is constant for \( x = 0 \) and \( x = 0.1 \), and decreases steadily with increasing \( x \) for \( x > 0.1 \). This is the opposite of the expected trend, because the value of \( x \) is an indication of the fraction of magnetic cations on the A-sites, and the high Curie temperature of \( \text{LiMnFeO}_4 \) (chapter 5) was attributed to the presence of 40% Fe on the A-sites. The increase in the number of magnetic ions was intended to strengthen the magnetic lattice and raise the transition temperature. The fact that a lowering of the \( T_C \) is observed is probably a consequence of additional magnetic frustration in the lattice.

The fits to the Curie-Weiss law above the ordering temperatures, and plots of the inverse magnetic susceptibility against temperature, which are shown in figures 6.11-6.22, provide further evidence of frustration. The Curie (\( C \)) and Weiss (\( \theta \)) constants derived from this fitting, and the number of unpaired electrons per formula unit, \( n \), determined from \( C \) by equation (3.25) are presented in table 6.3. For the samples up to, and including, \( x = 0.2 \), the Weiss constant are positive and close to the value of the

<table>
<thead>
<tr>
<th>Substitution Parameter, ( x )</th>
<th>Magnetic Behaviour</th>
<th>Transition Temp. ((K))</th>
<th>Curie Constant ((\text{ergKmolt}^{-1}\text{Oe}^2))</th>
<th>Weiss Constant ((K))</th>
<th>Unpaired electrons / formula unit</th>
<th>Saturation Magnetization ((\mu_B/\text{Mn}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>FM-SG</td>
<td>135.00</td>
<td>2.34(2)</td>
<td>103(1)</td>
<td>3.5</td>
<td>1.9643</td>
</tr>
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<td>0.1</td>
<td>FM-SG</td>
<td>135.00</td>
<td>2.07(2)</td>
<td>128(2)</td>
<td>3.2</td>
<td>1.6574</td>
</tr>
<tr>
<td>0.2</td>
<td>FM-SG</td>
<td>120.00</td>
<td>2.14(2)</td>
<td>101(2)</td>
<td>3.3</td>
<td>1.4399</td>
</tr>
<tr>
<td>0.3</td>
<td>FM-SG</td>
<td>110.00</td>
<td>2.5(1)</td>
<td>65(9)</td>
<td>3.6</td>
<td>1.1969</td>
</tr>
<tr>
<td>0.4</td>
<td>FM-SG</td>
<td>†</td>
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<td>0.6</td>
<td>FM-SG</td>
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<td>3.03(3)</td>
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<td>0.8</td>
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<td>†</td>
<td>†</td>
<td>†</td>
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</tr>
<tr>
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<td>FM-SG</td>
<td>85.000</td>
<td>3.31(8)</td>
<td>-121(9)</td>
<td>4.2</td>
<td>0.62860</td>
</tr>
</tbody>
</table>

\( \dagger \): Data is not available.
transition temperature, indicating predominantly ferromagnetic interactions, and the inverse susceptibility plots of these compounds (figures 6.12, 6.14, 6.16) are fairly straight and cross the T-axis at the transition temperature. The Weiss constant of Cu$_{0.7}$Ni$_{0.8}$Mn$_{1.5}$O$_4$ (+65(9)K) is significantly below the Néel temperature (110K), and the Weiss constants obtained for Cu$_{0.4}$Ni$_{1.1}$Mn$_{1.5}$O$_4$ and Cu$_{0.1}$Ni$_{1.4}$Mn$_{1.5}$O$_4$ are strongly negative, respectively $-27(3)$K and $-121(9)$K. Similarly, the inverse susceptibility plots of these compounds, respectively figures 6.18, 6.20, and 6.22 show a straight line at high temperature, heading to a negative intercept, which begins to curve towards the T-axis at temperatures far above $T_N$. This shows that the antiferromagnetic interactions are getting progressively stronger, and dominate the ferromagnetic interactions for $x > 0.5$. The Curie-Weiss fit is only valid in the straight-line region of the inverse susceptibility plots, and the Curie constants obtained (table 6.3) are systematically below the expected values, giving between 3.2 and 4.2 unpaired electrons per formula unit, whereas CuNi$_{0.5}$Mn$_{1.5}$O$_4$ has 4.5 unpaired electrons per formula unit, and this number will increase with $x$. This implies that higher temperature measurements are required to investigate the true Curie-Weiss region.
Figure 6.10: Variation of magnetization against applied field in spinel series $\text{Cu}_{1-x}\text{Ni}_{0.5+x}\text{Mn}_{1.5}\text{O}_4$. 
Top: Figure 6.11: Curie-Weiss fit to magnetic susceptibility data for CuNi$_{0.5}$Mn$_{1.5}$O$_4$.
Bottom: Figure 6.12: Inverse magnetic susceptibility data for CuNi$_{0.5}$Mn$_{1.5}$O$_4$. 
Top: Figure 6.13: Curie-Weiss fit to magnetic susceptibility data for Cu$_{0.9}$Ni$_{0.6}$Mn$_{1.5}$O$_4$.
Bottom: Figure 6.14: Inverse magnetic susceptibility data for Cu$_{0.9}$Ni$_{0.6}$Mn$_{1.5}$O$_4$. 
Figure 6.15: Curve-Wiess fit to magnetic susceptibility data for CuO$_2$Ni$^{2+}$Mn$^{3+}$O$_4$. 

Figure 6.16: Inverse magnetic susceptibility data for CuO$_2$Ni$^{2+}$Mn$^{3+}$O$_4$. 

Figure 6.17: Inverse molar susceptibility / G mol$^{-1}$ vs. temperature / K.
Top: Figure 6.17: Curie-Weiss fit to magnetic susceptibility data for Cu$_{0.7}$Ni$_{0.8}$Mn$_{1.5}$O$_4$.

Bottom: Figure 6.18: Inverse magnetic susceptibility data for Cu$_{0.7}$Ni$_{0.8}$Mn$_{1.5}$O$_4$. 
Top: Figure 6.19: Curie-Weiss fit to magnetic susceptibility data for Cu$_{0.4}$Ni$_{1.1}$Mn$_{1.5}$O$_4$.
Bottom: Figure 6.20: Inverse magnetic susceptibility data with, and without temperature independent paramagnetism correction, for Cu$_{0.4}$Ni$_{1.1}$Mn$_{1.5}$O$_4$
Top: Figure 6.21: Curie-Weiss fit to magnetic susceptibility data for Cu$_{0.3}$Ni$_{1.4}$Mn$_{1.5}$O$_4$.
Bottom: Figure 6.22: Inverse magnetic susceptibility data with, and without temperature independent paramagnetism correction, for Cu$_{0.3}$Ni$_{1.4}$Mn$_{1.5}$O$_4$. 
Zero field cooled aging experiments were performed according to the scheme in section 3.5.1.1, for Cu$_{0.4}$Ni$_{1.1}$Mn$_{1.5}$O$_4$. The evolution of the magnetization of Cu$_{0.4}$Ni$_{1.1}$Mn$_{1.5}$O$_4$ with time, upon the application of a 200e field, after a waiting time of 1000s, (section 3.4.6) is shown in figure 6.23, for selected temperatures in the range 5-120K. For clarity, this data is also presented in figure 6.24 as a change in magnetization, $\Delta M$, where $\Delta M = M(t) - M(t=1\text{ min})$. It is clear that there is a strong increase in the constant temperature, constant field magnetization with time at 5K, 20K and 50K, and it seems that there is a smaller increase at 100K, though there is a poor signal-noise ratio at this temperature. The data at 110K and 120K appear to be straight lines with no aging effect. The inverse derivative of the ZFC magnetization with respect to time, 
\[
\left[\frac{1}{H} \frac{\partial M}{\partial t} \right]^{-1},
\] (section 3.4.6) of Cu$_{0.4}$Ni$_{1.1}$Mn$_{1.5}$O$_4$ at 5K, with waiting time, $t_w$, of 100s, 1000s and 10000s, is plotted in figure 6.25, and all waiting times give a nearly linear relation between this derivative and time almost straight line, indicating a close-to-logarithmic increase in magnetization with time. It is clear that the time dependence of the magnetization is a function of $t_w$. The near-linearity of the inverse derivative is indicative of spin glass character, to investigate the deviation from linearity, the relaxation rate, $S$ (equation (3.28)), after waiting times of 100s, 1000s and 10000s, was plotted against time in figure 6.26, the 100s has a maximum at an elapsed time of about 2000s and the other two data sets have no clear maximum. The expected behaviour is that the maximum occurs when the elapsed time is approximately equal to the waiting time, $t_w$. This derivative, $S = \left(\frac{1}{H} \frac{\partial M}{\partial \log_{10} t} \right)_{t,H}$, is similar to that discussed above, but because the magnetization is differentiated with respect to the logarithm of the time (in seconds; seconds are used for consistency with the literature) the derivative would be constant with time if the evolution of the magnetization were purely logarithmic.
Despite the poor correspondence between the waiting times and the maxima in the relaxation rates, it seems clear that Cu$_{0.4}$Ni$_{1.1}$Mn$_{1.5}$O$_4$ shows spin glass character, and is a semi-spin-glass, as CuNi$_{0.5}$Mn$_{1.5}$O$_4$ was shown to be in chapter 4. It therefore seems likely that all the members of this series are semi-spin-glasses, as they all show spontaneous magnetization, and the frustration is increasing with increasing $x$. 
Top: Figure 6.23: Aging of ZFC Magnetization (in 200e) for Cu$_{0.4}$Ni$_{1.1}$Mn$_{1.5}$O$_4$ at selected temperatures.

Bottom: Figure 6.24: Change in ZFC Magnetization (in 200e) for Cu$_{0.4}$Ni$_{1.1}$Mn$_{1.5}$O$_4$ at selected temperatures.
Top: Figure 6.25: Inverse derivative of the ZFC Magnetization (M/H, in 200e), with respect to time, in minutes, for Cu$_{0.4}$Ni$_{1.1}$Mn$_{1.5}$O$_4$ at 5K, with waiting times, $t_w$, of 100s, 1000s and 10000s.

Bottom: Figure 6.26: Relaxation rate, $S(t) = (1/H)(dM/dt)$, derivative of the ZFC Magnetization (M/H, in 200e), with respect to $\log_{10}$(time) in seconds, for Cu$_{0.4}$Ni$_{1.1}$Mn$_{1.5}$O$_4$ at 5K, with waiting times, $t_w$, of 100s, 1000s and 10000s.
6.3.3 Conductivity

The conductivity of CuNi$_{0.5}$Mn$_{1.5}$O$_4$ was discussed in section 4.3.3; the dependence of the natural logarithm of the resistance against inverse temperature was shown to be non-linear both above and below $T_C$ (figure 4.25) but the mechanism appears to change at the Curie temperature. The plot of the natural logarithm of the resistance against $1/T$ for the series Cu$_{1-x}$Ni$_{0.5+y}$Mn$_{1.5}$O$_4$ is shown in figure 6.27, for the temperature range 70K-400K. A clear curvature can be seen for all the samples, indicating that a simple activated semiconductor model cannot account for the temperature dependence of the resistivity either above or below the Curie temperature for the $x > 0$ compounds. Attempts were made to fit a number of transport models to the experimental data, a polaronic model$^5$ gave an improved fit, compared to the simple activated model. However, the power indices obtained were not the characteristic values for polaronic transport. As these compounds are disordered, a variable range hopping (VRH) model was proposed. To test this model, the natural logarithms of the resistivities were plotted against $1/T^{(1/4)}$ (figure 6.28) the characteristic temperature dependence of this model.$^5,6$

If the resistivity is defined as in equation (6.2), then it follows that the natural logarithm of the resistivity is given in equation (6.3), and that the gradient and intercept of the lines in figure 6.28 are, respectively, ln $\rho_0$ and $D$. The values obtained from this fitting are presented in table 6.4

$$\rho = \rho_0 \exp \left( \frac{D}{T^{\gamma}} \right)$$  \hspace{1cm} (6.2)

$$\ln \rho = \ln \rho_0 + \frac{D}{T^{\gamma}}$$  \hspace{1cm} (6.3)

$D$ and $\rho_0$ are constants; $\rho_0$ is the infinite temperature resistivity.
Figure 6.27: Variation of the natural logarithm of the resistivity against inverse temperature for different values of the substitution parameter, x, in spinel series Cu$_{1-x}$Ni$_{0.5+x}$Mn$_{1.5}$O$_4$. One large marker represents 500 data points.

It can be seen from figure 6.28, that the natural logarithm or the resistivity against $1/T^{(1/4)}$ of the $x = 0$ compound is only linear below $T_C$, indicating that the variable range hopping mechanism is only appropriate in this region. It appears that the VRH is applicable to the $x > 0$ compounds over the entire measured temperature range, both above and below $T_C$. The resistivity can be seen to drop dramatically, over all temperatures, between $x = 0$ and $x = 0.1$, and this is due to a large fall in the infinite temperature resistivity between $x = 0$ ($\rho_0 = 2 \times 10^{-5} \Omega \text{cm}$) and $x = 0.1$ ($\rho_0 = 2 \times 10^{-7} \Omega \text{cm}$). It is important to note that $\rho_0$ is dependent on the grain boundaries and not necessarily representative of the bulk material. When $x > 0.1$ the resistivity starts to rise again, and
in the range $0.1 \leq x \leq 0.4$ this is predominantly caused by a small increase in the infinite temperature resistivity, with similar gradient, whereas in the range $0.6 \leq x \leq 0.8$, the gradient becomes more steep, which at real temperatures is more significant than the decrease in the infinite temperature resistivity (to $2 \times 10^{-10} \Omega \text{cm}$ for Cu$_{0.2}$Ni$_{1.3}$Mn$_{1.5}$O$_4$) that is observed.

Table 6.4: Results of the fitting of the natural logarithm of the resistivity to the variable range hopping model, for the series Cu$_{1-x}$Ni$_{0.5+y}$Mn$_{1.5}$O$_4$.

<table>
<thead>
<tr>
<th>Substitution Parameter, $x$</th>
<th>$D$ ($K^{(1/a)}$)</th>
<th>ln $\rho_0$</th>
<th>$\rho_0$ ($\Omega \text{cm}$)</th>
</tr>
</thead>
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<tr>
<td>0†</td>
<td>53</td>
<td>-8.4</td>
<td>$2 \times 10^{-4}$</td>
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<td>0.1</td>
<td>58</td>
<td>-15.4</td>
<td>$2 \times 10^{-7}$</td>
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<td>$4 \times 10^{-7}$</td>
</tr>
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<td>$7 \times 10^{-7}$</td>
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<tr>
<td>0.6</td>
<td>77</td>
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<td>$5 \times 10^{-9}$</td>
</tr>
<tr>
<td>0.8</td>
<td>107</td>
<td>-22.5</td>
<td>$2 \times 10^{-10}$</td>
</tr>
<tr>
<td>0.9</td>
<td>†</td>
<td>†</td>
<td>†</td>
</tr>
</tbody>
</table>

†: Data is not available.
‡: Fitted only below $T_c$, the VRH model breaks down at $T_c$ for the $x = 0$ compound.
Figure 6.28: Variation of the natural logarithm of the resistivity against $1/T^{(1/4)}$ for different values of the substitution parameter, $x$, in spinel series $\text{Cu}_1\cdot_5\text{Ni}_{0.5-x}\text{Mn}_{1.5}\text{O}_4$. Lines show all data points; one large marker every 500 points.
The change in conduction mechanism in CuNi$_{0.5}$Mn$_{1.5}$O$_4$ at the Curie temperature was discussed in section 4.3.3, but it can be seen in figure 6.29 that there is no concomitant change in the magnetoresistance. To investigate whether there was a magnetoresistance effect, defined by $\rho(h) - \rho(0)/\rho(0)$, in this series, the resistivity was measured as a function of temperature, in an applied field of 10kOe, as well as zero field, for the $x = 0.1$ (figure 6.30), $x = 0.2$ (figure 6.31), $x = 0.3$ (figure 6.32) and $x = 0.6$ (figure 6.33). All of these compounds showed no magnetoresistance effect above the respective Curie temperatures (table 6.3), but there seemed to be a slight deviation of the zero field and applied field measurements at the transition temperature. The $x = 0.3$ data (figure 6.32) seems strange, because the resistance increases in the applied field, whereas it decreases in the other measurements, and the divergence (145K) is not exactly at $T_C$ (110K). The divergence of the zero field and applied field measurements is probably caused by a lag in the temperature sweep rate, rather than a real effect.

Bottom: Figure 6.29: Magnetoresistance across $T_N$ (135K) for CuNi$_{0.5}$Mn$_{1.5}$O$_4$.
Top: Figure 6.30: Magnetoresistance across $T_N$ (135K) for Cu$_{0.9}$Ni$_{0.6}$Mn$_{1.5}$O$_4$.
Bottom: Figure 6.31: Magnetoresistance across $T_N$ (120K) for Cu$_{0.8}$Ni$_{0.7}$Mn$_{1.5}$O$_4$.

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Top: Figure 6.32: Magnetoresistance across $T_N$ (110K) for $\text{Cu}_{0.7}\text{Ni}_{0.8}\text{Mn}_{1.5}\text{O}_4$.

Bottom: Figure 6.33: Magnetoresistance across $T_N$ (65K) for $\text{Cu}_{0.4}\text{Ni}_{1.1}\text{Mn}_{1.5}\text{O}_4$. 
6.4 Discussion

The slow cooling sample preparation was first reported by Blasser\textsuperscript{2} and was shown in chapter 4 to induce the formation of the cation ordered form of LiMg\textsubscript{0.5}Mn\textsubscript{1.5}O\textsubscript{4}, with crystallographically distinct manganese and magnesium sites. The same method was employed for all the compositions reported in this chapter, though long-range B-site cation ordering was not expected, to try to achieve a thermodynamic (as opposed to a kinetically trapped) cationic distribution. In chapter 5, the XRD patterns of certain compositions showed a deterioration (peak broadening) after the slow-cooling, this phenomenon was not observed for any of these samples.

The reasonably smooth increase in the lattice parameter with increasing \( x \) is a good indication that a progressively larger amount of nickel is being taken up into the lattice. Jarrige and Mexmain\textsuperscript{1} saw a similar trend, and interpreted the increasing lattice parameter as evidence that a mixture of phases were forming, because in the first part of their series, \( \text{Cu}_{1.5-x}\text{Ni}_x\text{Mn}_{1.5}\text{O}_4 \) \((0 < x < 0.5)\), the lattice parameter had smoothly decreased with increasing \( x \). Jarrige and Mexmain formulated \( \text{Cu}_{1.5}\text{Mn}_{1.5}\text{O}_4 \) as \( \text{Cu}^+[\text{Cu}^{2+}_{0.5}\text{Mn}_{1.5}]\text{O}_4 \),\textsuperscript{7,1} and yet did not consider that substituting Ni\textsuperscript{2+}, which has a strong octahedral site preference (section 2.3) for tetrahedral Cu\textsuperscript{+} might have a different effect on the lattice parameter to replacing octahedral Cu\textsuperscript{2+}. In fact, the increase in the lattice parameter is almost certainly a result of the decrease in the average manganese valence upon replacement of Cu\textsuperscript{+} by Ni\textsuperscript{2+}, and the breakdown of the 1:3 B-site cation ordering of the parent compound, \( \text{CuNi}_{0.5}\text{Mn}_{1.5}\text{O}_4 \), as competition for octahedral sites forces some of the manganese onto tetrahedral sites, almost certainly as Mn\textsuperscript{2+}, but is also affected by complex cation ordering over the A and B sites. Elbadraoui \textit{et al.}\textsuperscript{8} studied the cationic distribution of the spinels \( \text{Cu}_x\text{Ni}_{0.67}\text{Mn}_{2.33-x}\text{O}_4 \) \((0 < x < 0.5)\) with X-ray photoelectron spectroscopy (XPS) and observed Cu\textsuperscript{+}, Cu\textsuperscript{2+}, Mn\textsuperscript{2+} and Ni\textsuperscript{2+} on the
tetrahedral sites and Cu$^{2+}$, Mn$^{3+}$, Mn$^{4+}$ and Ni$^{2+}$ on the octahedral sites. In these materials copper is being substituted for tetrahedral Mn$^{2+}$, at low doping levels isovalent substitution (Cu$^{2+}$) seems to be favoured, for example Gillot et al$^{9}$ determined the oxidation state of copper in Cu$_{x}$Ni$_{0.67}$Mn$_{2.33-x}$O$_{4}$ to be +2 by thermoelectric measurements and lattice parameter calculations. Hashemi$^{10}$ reported from XPS measurements that CuNiMnO$_{4}$ contains both Cu$^{+}$ and Cu$^{2+}$. There is clearly a very small energy difference between Cu$^{+}$/Mn$^{4+}$ and Cu$^{2+}$/Mn$^{3+}$.

The observation of a small amount (weight fraction ~ 3%) of nickel oxide in the powder neutron diffraction patterns of the $x = 0.4$ and $x = 0.6$ compounds demonstrates that the problems encountered in the original formulation (Cu$_{1.2}$Ni$_{0.5+x}$Mn$_{1.5-x}$O$_{4}$) have not been completely solved in the final series. The difficulty of the XRD Bragg peaks of NiO overlying with those of the spinels reported in this thesis is discussed further in section 7a.3.1. If this impurity phase had been detected in the XRD measurements, further heating, and higher reaction temperatures, could have been employed.

The difficulty in producing phase pure samples in this series can be readily understood in terms of crystal field theory (section 2.3.3) and electroneutrality. The parent compound Cu[Ni$_{0.5}$Mn$_{1.5}$]O$_{4}$ has a high crystal field stabilization energy (CFSE) because both Ni$^{2+}$ (d$^{8}$) and Mn$^{4+}$ (d$^{3}$) have large octahedral CFSEs and Cu$^{+}$ (d$^{10}$) has no CFSE, so has no octahedral site preference (OSP), in fact the highly polarisable d$^{10}$ shell favours a covalent contribution to the bonding, resulting in a tetrahedral site preference (TSP). Thus all the cations are located in the most favourable sites, and the degree of cation inversion (section 2.3.2) is minimal (section 4.3.1). However, when $x > 0$, the ratio of cations with OSP:TSP is $(2 + x): (1 - x)$, whilst the ratio of octahedral sites: tetrahedral sites remains 2:1. Thus, the cationic distribution is frustrated, and there is
competition for octahedral sites between Ni\(^{2+}\) and Mn\(^{4+}\). This situation is partially mitigated by the availability of an oxidation state of manganese that favours tetrahedral coordination, namely Mn\(^{2+}\). The great improvement in the quality of samples in the final formulation supports the presence of Mn\(^{2+}\) on the tetrahedral site. There are numerous examples of A-site Mn\(^{2+}\) spinels,\(^{11-13}\) such as MnCr\(_2\)O\(_4\), as well as other structures containing tetrahedral Mn\(^{2+}\). However, it is clear from the great body of research into manganese oxide, that, in the reaction conditions (high temperature in air) that tetrahedral Mn\(^{2+}\) is not the energetically favoured valency. The equilibrium between octahedral Mn\(^{4+}\) and tetrahedral Mn\(^{2+}\) clearly has electroneutrality implications, which are particularly important in the spinel structure as it cannot readily accommodate oxygen vacancies in contrast to the perovskite structure for example. This is due to the spinel structure being composed of a cubic close packed oxide array; in all the Rietveld refinements of PND patterns reported in this thesis, the fractional occupancies of the oxide ions were freely refined and remained (within one standard deviation) unity.

From the refinement, in the powder neutron diffraction patterns of the \(x = 0.4\) and \(x = 0.6\) compounds, of the A-site fraction, and the observation of impurity NiO, it appears that the equilibrium distribution, in the reaction conditions, has a greater amount of Mn\(^{2+}\) than Ni\(^{2+}\) on the A-sites (table 6.2). The formulation of the series assumed an equal amount of each. This unequal distribution could be statistical (there is more manganese than nickel in the reaction mixture) but it seems that there is a slight preference for A-site manganese. It is not clear whether this is a thermodynamic or kinetic effect, but it is clearly not significant enough to induce long-range cation order.

It is interesting to note that the lattice parameter of Ni\(_{1.5}\)Mn\(_{1.5}\)O\(_4\) (nominally the other end member of the series) is far smaller than would be expected by extrapolation of
figure 6.3. The PND refinement of Ni_{1.5}Mn_{1.5}O_4 (chapter 7a.3) strongly indicates some form of intrasublattice cation ordering, though its exact nature is not clear. This gives very different behaviour to the rest of the series, so this compound is not included here.

In light of the complexity of the magnetic behaviour exhibited in the spinel/pyrochlore system in general, and in chapters 4 and 5 (particularly the effect of magnetic A-site cations on the ferrimagnetic Néel temperature (375K) of LiFeMnO_4), the smooth decrease in the ferrimagnetic Néel temperature, with increasing $x$, is disappointing. It had been hoped that the introduction of magnetic A-site cations would greatly strengthen the magnetic lattice, increasing $T_N$. The 50kOe saturation magnetization shows the expected smooth decrease with increasing $x$, but there is an interesting feature in the value of the low field (100 Oe) field cooled magnetization; there is a great increase from $x = 0$ to $x = 0.1$ (0.20 to 0.35$\mu_B$/Mn at 5K) followed by a smooth decrease for $x > 0.1$. This increase in the low field magnetization indicates that it has become easier to rotate, and more favourable to align, magnetic domains, though it is possible that the magnetic A-site cations are increasing the degree of colinearity of the B-site manganese moments within individual domains.

Though all of the samples exhibit bulk ferrimagnetism, the plots of inverse susceptibility against temperature reveal a crossover in the sign of the Weiss constant, $\theta$, and between $x = 0.3$ ($\theta = +65$K) and $x = 0.6$ ($\theta = -27$K). Therefore implying that the dominant magnetic interaction changes from ferromagnetic to antiferromagnetic across this composition. For the $x = 0$, $x = 0.1$ and $x = 0.2$ compounds, the inverse susceptibility against temperature is linear, with a T-axis intercept at $T_N$, which is classic ferromagnetic behaviour, whereas at $x = 0.3$, $\theta$ is positive (65K), but much less than $T_N$ (110K) and for $x \geq 0.6$, $\theta$ is negative. Goodenough$^{14}$ gave a qualitative
interpretation of the various exchange interactions expected for a given exchange pathway and electronic configuration; those relevant to this thesis are presented in table 2.3. It seems clear from these rules, and the observations of chapters 4 and 5, that the 90° Mn-O-Mn (B-B) interactions are ferromagnetic, the 90° Ni-O-Mn interactions are antiferromagnetic and all 135° A-O-B interactions are antiferromagnetic. When this model is considered, the crossover is expected, in fact it is quite surprising that the parent compound, Cu[Ni_{0.5}Mn_{1.5}]O_4 shows such model ferromagnetic behaviour. Each B_4O_4 unit (section 2.2.2) in this material contains one nickel ion and three manganese ions, therefore each B_4 tetrahedron contains three Ni-Mn and three Mn-Mn nearest neighbour (NN) interactions, so it might be expected that the ferromagnetic and antiferromagnetic interactions would be of comparable strength, and that the Weiss constant would be significantly reduced, though they are critically dependent on bond distances and angles. Ferromagnetic behaviour is seen in the \( x = 0.2 \) compound, which would be expected to have a greater number of AFM than FM B-site NN interactions, plus a number of AFM A-B interactions. Therefore, either the B-B FM interactions are much stronger than the B-B AFM interactions, or that there are FM further neighbour interactions that play a significant role.

In chapters 4 and 5, the observation of a nearly logarithmic time dependence of the ZFC low-field magnetization for both LiMg_{0.5}Mn_{1.5}O_4 and CuNi_{0.5}Mn_{1.5}O_4, with the maximum deviation from the logarithmic coming when the elapsed time, \( t \), approximately equal to the waiting time, \( t_w \), was ascribed to spin glass character. Unfortunately, for the compounds, Cu_{1-x}Ni_{0.5+x}Mn_{1.5}O_4, data of this type has been collected only for the \( x = 0.6 \) compound, and there is no confirmatory AC susceptibility data. In this compound, the same nearly-logarithmic behaviour is observed, strongly
suggesting semi-spin-glass character. A shift in the maximum of the relaxation rate, with a change in the waiting time (section 3.5.1.1) before the field was applied, in the measurements of ZFC magnetization against time, is also seen, giving strong evidence of the aging effect (section 3.4.6) and, hence, spin glass behaviour, although it should be noted that in this case the maximum in the relaxation rate, \( S \), (equation 3.28) does not correspond well with the waiting time, \( t_w \). In chapters 4 and 5, the alternative magnetic models that could have accounted for some of the observed properties were ruled out for the following reasons: the ZFC magnetization of a ferromagnet does not increase with time because it reaches a rapid equilibrium between the tendency of the domains to align with the field, and the interdomain dipole interactions, the cluster glass model (section 3.4.7) could not prevent the applied field of 50kOe from forcing the parallel alignment of the ferromagnetic clusters in the saturation measurements, and the coincident onset of ferromagnetism and spin glass character appeared to rule out reentrant spin glass behaviour. However, reentrant spin glasses with very similar ferromagnetic and spin glass transition temperatures have previously been reported.\(^{15}\)

In light of all the aging measurements in chapters 4 and 5 and the observation of ferrimagnetism and spin glass character in both Cu\(_{0.4}\)Ni\(_{1.1}\)Mn\(_{1.5}\)O\(_4\) and CuNi\(_{0.5}\)Mn\(_{1.5}\)O\(_4\), it seems very likely that all of the series, Cu\(_{1-x}\)Ni\(_{0.5+x}\)Mn\(_{1.5}\)O\(_4\), follow the semi-spin-glass model proposed by Villain.\(^{16}\)

An interesting feature of the constant temperature magnetization data, which can be seen much more clearly in the change in magnetization plot (figure 6.24) is that the noise in the 100K data is, at least, an order of magnitude greater (\(~1\times10^{-4}\mu_B/Mn\)) than in any of the other measurements of this compound, where the error is approximately 5x10\(^{-6}\)\(\mu_B/Mn\). The Néel temperature was determined, by taking the maximum in the derivative of the magnetization with respect to temperature, to be 110K. From the low
field time dependent magnetization measurements (figure 6.23) it can be seen that at 110K, the ferromagnetism is just emerging, and there is no evidence of non-equilibrium (spin glass) behaviour, the 20 Oe magnetization has the largest value of any of the temperatures measured, and though the data is very noisy, seems to show some spin glass behaviour. This is interpreted as the presence of small discrete magnetic clusters with a ferromagnetic component at 110K, and a magnetically ordered structure composed of interacting domains at 100K.

The non-linear dependence of the natural logarithm of the resistivity and inverse temperature shows that an Arrhenius-like activated transport model cannot account for the observed data. However, the variable range hopping model (the natural logarithm of the resistivity against $1/T^{(1/4)}$) gives a linear dependence for all the $x > 0$ compositions, and also fits the $x = 0$ data below the Curie temperature. In light of the disordered structure, a random hopping mechanism is not surprising, and implies transport between localized states, randomly occupying a fraction of crystallographically indistinguishable sites, (probably the A-site Mn$^{2+}$ or Ni$^{2+}$) which is beyond the scope of a simple, band theory, approach.

In all of the compounds studied, there was, within errors, zero magnetoresistance, defined by $\rho(h) - \rho(0)/\rho(0)$, above the respective Curie temperatures. There is a magnetoresistance effect below the transition temperatures, but it is limited to a few percent.
6.5 Conclusion

The series of compounds Cu$_{1-x}$Ni$_{0.5+x}$Mn$_{1.5}$O$_4$ (0 < x < 1) has been synthesized. Although a small amount of nickel oxide impurity is present, there is a smooth increase in the lattice parameter with increasing x. All of the compounds are ferrimagnetic, both the saturation magnetization and the Néel temperature decrease with increasing nickel content. The x = 0 and x = 0.6 compounds were also shown to have spin glass character by the observation of an aging effect in the low field ZFC magnetization, a phenomenon characteristic of spin glasses. A semi-spin-glass structure is proposed, consisting of a ferromagnetic (or ferrimagnetic component along [100] and a transverse spin glass component. The transport properties were consistent with a variable range hopping model, both above and below, the Néel temperature. The compounds showed little, or no, magnetoresistance.
6.6 References


(6) P. V. E. McLintock; D. J. Meredith; J. K. Wigmore *Matter at low temperatures*; Blackie: Glasgow, 1984.


Chapter 7

Synthesis, Structure and Magnetism of Selected Ternary Manganese Oxide Spinels
This chapter is concerned with ternary manganese oxide spinels, which are closely related to the quaternary phases discussed in chapters 4, 5 and 6, and it is split into two discrete sections. The first part, section 7a, reports the synthesis and characterization of compounds of composition $\text{Cu}_{1+x}\text{Mn}_{2-x}\text{O}_4$ and $\text{Ni}_{1+x}\text{Mn}_{2-x}\text{O}_4$, which was performed to provide greater insight into the quaternary Cu-Ni-Mn-O systems described in chapters 4 and 6. The second segment, section 7b, reports the results of a structural study into the role of dopant ions in the enhancement of the electrochemical performance of the lithium battery material, LiMn$_2$O$_4$. This work was performed in collaboration with Dr. C. Bellitto of the C. N. R., Rome. The author was not involved in the synthesis, or electrochemical studies, which are presented elsewhere.1-3

The synthesis of a range of quaternary manganese (IV) oxide spinels, with interest electronic properties, has been reported in the three preceding chapters. Particular emphasis has been placed on the copper-nickel-manganese oxide system, because CuNi$_{0.5}$Mn$_{1.5}$O$_4$ was shown in chapter 4 to have the highest Curie temperature in the AM$_{0.5}$Mn$_{1.5}$O$_4$ series. This system was further investigated by the synthesis and characterization of the series Cu$_{1-x}$Ni$_{0.5+x}$Mn$_{1.5}$O$_4$, described in chapter 6, which highlighted the difficulty in predicting the cationic distribution and oxidation states in the complex systems. To shed further light on the quaternary systems previously discussed, the synthesis of a number of copper, and nickel, ternary manganites of composition Cu$_{1+x}$Mn$_{2-x}$O$_4$ and Ni$_{1+x}$Mn$_{2-x}$O$_4$ was attempted, to gain information on the
manner in which the ordering of the cations, the valence state of the manganese, and the variation in the lattice, and oxygen 'u,' parameters influence the magnetism.

7a.2 Experimental

Powder samples of composition $A_{1+x}Mn_{2-x}O_4$ ($A = Ni; x = 0, 0.5, 1 \text{ and } A = Cu; x = 0, 0.4, 0.5$) were produced by the method described in section 3.2. The reaction scheme is given in equation (7.1).

$$
(1+x)A(CH_3CO_2)_2\cdot H_2O + (2-x)Mn(CH_3CO_2)_2\cdot 4H_2O \\
\rightarrow A_{1+x}Mn_{2-x}O_4 + 12CO_2 + nH_2O \quad (A = Ni, Cu; x = 0, 0.4, 0.5, 1.)
$$

(7.1)

The reaction mixture was ground thoroughly before decomposition, which was achieved by slowly heating the acetates from room temperature to 400°C ($\Delta T = 0.7^\circ C/min$). The product was then pelletised and initially fired at 750°C for one day, with further heating, with intermittent regrinding, of each compound, until the reaction was deemed complete. The heating regime, for each of the samples that were used in the characterization experiments presented here, is given in table 7.1. On completion of the synthesis the reaction mixture was slow-cooled at 0.07°C per minute from 800°C to room temperature to produce the final sample. Characterization methods are detailed in chapter 3, and those pertaining to this chapter are summarized below. X-ray diffraction data was collected on a Siemens D500 diffractometer fitted with a primary monochromator giving $\lambda = 1.54056\AA$. Neutron diffraction experiments were carried out on the BT1 constant wavelength diffractometer at the National Institute of Standards Technology using a Cu(311) monochromator ($\lambda = 1.5401 \AA$). Analysis of this data was performed by the Rietveld method within the GSAS suite of software. DC Magnetic
susceptibility measurements were performed using a Quantum Design MPMS7 SQUID magnetometer.

### Table 7.1: Heating regime of ternary manganite compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>Days at 800°C</th>
<th>Days at 850°C</th>
<th>Days at 900°C</th>
<th>Days at 950°C</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuMn$_2$O$_4$</td>
<td>4</td>
<td>1</td>
<td>1</td>
<td></td>
<td>$4\text{Cu}<em>{1.4}\text{Mn}</em>{1.6}\text{O}_4 + \text{Mn}_2\text{O}_3$†</td>
</tr>
<tr>
<td>Cu$<em>{1.3}$Mn$</em>{1.5}$O$_4$</td>
<td>4</td>
<td>1</td>
<td>1</td>
<td></td>
<td>$4\text{Cu}<em>{1.4}\text{Mn}</em>{1.6}\text{O}_4 + \text{CuO}$†</td>
</tr>
<tr>
<td>Cu$<em>{1.4}$Mn$</em>{1.6}$O$_4$</td>
<td>4</td>
<td>0</td>
<td>0</td>
<td></td>
<td>0 Appeared pure from XRD pattern</td>
</tr>
<tr>
<td>NiMn$_2$O$_4$</td>
<td>4</td>
<td>0</td>
<td>0</td>
<td></td>
<td>0 Appeared pure from XRD pattern</td>
</tr>
<tr>
<td>Ni$<em>{1.3}$Mn$</em>{1.5}$O$_4$</td>
<td>4</td>
<td>0</td>
<td>0</td>
<td></td>
<td>0 Appeared pure from XRD pattern</td>
</tr>
<tr>
<td>Ni$_2$MnO$_4$</td>
<td>4</td>
<td>0</td>
<td>0</td>
<td></td>
<td>0 Initial XRD inconclusive</td>
</tr>
</tbody>
</table>

†: Composition determined by comparison of XRD pattern to standard patterns database on Siemens d500 diffractometer.

### 7a.3 Results

#### 7a.3.1 Structure

It was clear from the XRD patterns, that the reaction mixtures for both CuMn$_2$O$_4$, and Cu$_{1.3}$Mn$_{1.5}$O$_4$, disproportionated to Cu$_{1.4}$Mn$_{1.6}$O$_4$\(^7\), with Mn$_2$O$_3$ and CuO the respective by-products. Cu$_{1.4}$Mn$_{1.6}$O$_4$ seems to be the stable phase at the reaction temperature in ambient pressure. CuMn$_2$O$_4$ is found as a rock, and its synthesis, both as a tetragonal\(^8\), and a cubic\(^7\), phase has been reported in sealed-tube experiments, and has that of Cu$_{1.5}$Mn$_{1.5}$O$_4$\(^9,10\). These results could not be reproduced. The XRD patterns of Cu$_{1.4}$Mn$_{1.6}$O$_4$, NiMn$_2$O$_4$ and Ni$_{1.3}$Mn$_{1.5}$O$_4$ were consistent with the formation of monophasic, highly crystalline spinel phases, though the lattice parameter of Cu$_{1.4}$Mn$_{1.6}$O$_4$ (8.2843(6)Å) was slightly smaller than that reported by Beley et al\(^7\) (8.305(3)Å), and the lattice parameter of Ni$_{1.3}$Mn$_{1.5}$O$_4$ (8.3376(2)Å) was significantly smaller than that found by Jarrige and Mexmain\(^11\) (=8.39Å), though it was stated that

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this material was not phase pure, and this result look quite out of place with the rest of their Cu$_{1.5}$Ni$_x$Mn$_{1.5}$O$_4$ series. The lattice parameter of NiMn$_2$O$_4$ (8.3863(5) Å) was in good agreement with that obtained by Asbrink et al.$^{12}$ (8.379(1) Å). Small differences are expected due to different cation ordering. The Rietveld refinement of the X-ray diffraction patterns of Cu$_{1.4}$Mn$_{1.6}$O$_4$ and NiMn$_2$O$_4$ are shown in figures 7.1 and 7.2. The X-ray diffraction pattern for Ni$_2$MnO$_4$, was deceptive, because all the peaks could be indexed in the Fd-3m space group, but their relative intensities could not be reproduced in the Rietveld analysis. When nickel oxide was introduced as an impurity phase, with a refined weight fraction of 48%, the pattern was accurately reproduced, as shown in Figure 7.5. All of the Bragg reflections from nickel oxide overly with peaks generated by the spinel, because the cubic lattice parameter (4.178 Å) is, coincidentally, half the value of that of these spinels. The XRD does, however, indicate that a spinel phase, formulated Ni$_{2-y}$Mn$_{1+y}$O$_4$, where the amount of NiO indicates that $y > 0.5$, has been produced. Thus, a simple indexation of the pattern cannot provide proof that a monophasic sample has been made. The XRD patterns of all of the samples were refined in the conventional spinel space group, Fd$\bar{3}$m, the resulting fits are shown, for the compounds that neutron diffraction patterns are not available, in figures 7.1-7.2 and 7.5. The structural parameters obtained in all the presented refinements are summarized in table 7.2, the oxygen $u$ parameter is discussed in section 2.2.2 and the quoted thermal parameters are the isotropic U values from the GSAS suite of programs. The quoted values for Ni$_{1.5}$Mn$_{1.5}$O$_4$ are those obtained from the refinement of the neutron diffraction pattern in the normal spinel Fd$\bar{3}$m space group, the fractional occupancies were not refined for XRD data. It should be noted that the lack of low-angle superstructure peaks similar to those exhibited by LiMg$_{0.5}$Mn$_{1.5}$O$_4$ and CuMg$_{0.5}$Mn$_{1.5}$O$_4$ (chapter 4) does not preclude long range cation order on either the octahedral or tetrahedral sites, because nickel, copper and manganese all have similar numbers of electrons. Further
information was obtained by neutron diffraction of Ni$_{1.5}$Mn$_{1.5}$O$_4$; the negative coherent scattering length of manganese (-3.73 fm) gives strong contrast with nickel (+10.3 fm). The Rietveld refinement of the room temperature powder neutron diffraction pattern of Ni$_{1.5}$Mn$_{1.5}$O$_4$ in the space group $Fd\bar{3}m$ is shown in figure 7.3, most of the peaks are well fitted (giving a $\chi^2$ goodness-of-fit factor of 2.999 and a weighted profile coefficient, $r_{wp}$, of 9.53%), but the (200) and (420) peaks, that are forbidden in the $Fd\bar{3}m$ space group, are observed. It is also interesting to note that that (442) peak is not fitted at all, and that this peak overlies with the forbidden (600) reflection. Thus, it seems that the extra reflection conditions in the $Fd\bar{3}m$ space group, resultant from the $d$ glide plane, ($h00$: $h = 4n$ and $0kl$: $k + l = 4n$) do not apply to the neutron diffraction, and that this glide plane is not observed. The formation of a cation ordered superstructure (section 2.2.3) is the obvious candidate for the destruction of the glide plane symmetry, because it is not observed in the XRD and takes place above the magnetic transition temperature. A similar problem was found in the neutron diffraction of CuMnFe$_4$ (section 5.3.1), which was attributed to cation ordering. None of the B-site cation ordering models (section 2.2.3) that were tried for CuMnFe$_4$, such as the Zn[LiNb]O$_4$ $^{13,14}$ and low temperature Fe$_3$O$_4$ models, $^{15,16}$ could account for the (200) reflection. A 1:1 A-site cation ordering model, such as that found in Li$_{0.5}$Fe$_{0.5}$[Cr$_2$]O$_4$, $^{17,18}$ with the $F4\bar{3}m$ space group was tried. The observed extra peaks are allowed reflections in this superstructure, but, as in the CuMnFe$_4$ refinement, a single-phase superstructure model could not account for the relative intensities of all the peaks. The fit to this multiphase model is shown in figure 7.4, (giving fit indices of $\chi^2 = 2.173$ and $R_{wp} = 8.13\%$) to demonstrate that this is a possible solution, but the refinement is not sensitive to the structure of this phase because two or three peaks are poorly fitted in the $Fd\bar{3}m$ phase, so it was not possible to obtain physically realistic thermal parameters for this phase.
Top: Figure 7.1: Rietveld refinement of Cu$_{1.4}$Mn$_{1.6}$O$_4$ from X-ray diffraction data.
Bottom: Figure 7.2: Rietveld refinement of NiMn$_2$O$_4$ from X-ray diffraction data.
Top: Figure 7.3: Rietveld refinement of the neutron diffraction pattern of Ni$_{1.5}$Mn$_{1.5}$O$_4$ in the $Fd\bar{3}m$ space group.

Bottom: Figure 7.4: Rietveld refinement of the neutron diffraction pattern of Ni$_{1.5}$Mn$_{1.5}$O$_4$ in the $Fd\bar{3}m$ space group + 30% $F4\bar{3}m$ superstructure.
Figure 7.5: Rietveld refinement of NiMn$_2$O$_4$ from X-ray diffraction data.

Table 7.2: Summary of key structural data for compounds A$_{1+x}$Mn$_{2-x}$O$_4$.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Lattice Parameter (Å)</th>
<th>Oxygen u parameter</th>
<th>A-site occupancy</th>
<th>A-site U / 100Å$^2$</th>
<th>B-site occupancy</th>
<th>B-site U / 100Å$^2$</th>
<th>O-site U / 100Å$^2$</th>
<th>$\chi^2$</th>
<th>$R_{wp}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$<em>{1.4}$Mn$</em>{1.6}$O$_4$</td>
<td>8.2843(6)</td>
<td>0.2613(3)</td>
<td>Cu=1.0</td>
<td>1.15(10)</td>
<td>Cr=0.2</td>
<td>0.56(7)</td>
<td>1.3(3)</td>
<td>1.195</td>
<td>3.48</td>
</tr>
<tr>
<td>NiMn$_2$O$_4$</td>
<td>8.3863(5)</td>
<td>0.2640(6)</td>
<td>Ni=0.134</td>
<td>1.9(3)</td>
<td>Mn=0.87</td>
<td>Ni=0.435(4)</td>
<td>0.4(2)</td>
<td>0.9(4)</td>
<td>1.100 8.19</td>
</tr>
<tr>
<td>Ni$<em>{1.5}$Mn$</em>{1.5}$O$_4$</td>
<td>8.3376(2)</td>
<td>0.26180(9)</td>
<td>Ni=0.465(5)</td>
<td>2.4(2)</td>
<td>Ni=0.518(3)</td>
<td>Mn=0.482(3)</td>
<td>0.66(8)</td>
<td>1.35(4)</td>
<td>2.999 9.53</td>
</tr>
<tr>
<td>Ni$_2$MnO$_4$</td>
<td>8.3718(9)</td>
<td>0.2593(10)</td>
<td>Ni=1.0</td>
<td>1.2(4)</td>
<td>Mn=0.5</td>
<td>Ni=0.5</td>
<td>0.2(5)</td>
<td>1.0(9)</td>
<td>1.143 8.93</td>
</tr>
</tbody>
</table>

†: Constrained to total unity; values without quoted standard deviation were not refined.
‡: Fixed to the values obtained by Asbrink et al by neutron diffraction.\(^{12}\)
7a.3.2 Magnetism

The magnetic susceptibility of the series $A_{1-x}Mn_{2-x}O_4$ ($A = Cu, Ni; x = 0, 0.4, 0.5, 1$) is, mostly, very similar to that observed for $CuNi_{0.5}Mn_{1.5}O_4$ in chapter 4, and the series of compounds in chapter 6, formulated $Cu_{1-x}Ni_{0.5+x}Mn_{1.5}O_4$. The exception to this is the striking magnetic behaviour (figure 7.9) of the sample nominally $Ni_2MnO_4$, which is discussed below. The XRD pattern indicated the formation of a spinel phase, formulated $Ni_{2-y}Mn_{1+y}O_4$, and an impurity phase, NiO, with a weight fraction of 48%. The zero field cooled, (ZFC) and field cooled, (FC) in an applied field of 1000e, magnetizations are presented in figures 7.6-7.9 and show that $Cu_{1.4}Mn_{1.6}O_4$, $NiMn_{2}O_4$ and $Ni_{1.5}Mn_{1.5}O_4$ all undergo a paramagnetic to ferromagnetic (ferrimagnetic in the case of the nickel compounds) transition, in the temperature range 100K-120K. This similarity is not surprising for the nickel compounds, and their correspondence to the copper sample is superficial; the fits to the Curie-Weiss law in the paramagnetic region, and plots of inverse susceptibility against temperature, given in figures 7.10-7.17, show there is a markedly different variation of susceptibility with temperature. $Cu_{1.4}Mn_{1.6}O_4$ shows typical ferromagnetic behaviour, having a positive Weiss constant, in good agreement with the Curie temperature, whilst the nickel compounds have strongly negative Weiss constants, indicating that the interactions are predominantly antiferromagnetic, and that the spontaneous magnetization is caused by ferrimagnetic ordering. The parameters extracted from these fits are tabulated in table 7.3. The number of unpaired electrons per formula unit, calculated from the Curie constant, (table 7.3) are consistently lower than the expected values; $Cu_{1.4}Mn_{1.6}O_4$ ($n = 3.5$) is expected to contain $Mn^{4+}$ ($d^3$) ions and, presumably, a small amount of $Cu^{2+}$ ($d^9$) ions giving a theoretical value of ($n_{exp} = 5.0$). It is difficult to predict the exact theoretical value for $NiMn_{2}O_4$ and $Ni_{1.5}Mn_{1.5}O_4$, because the oxidation state of the manganese is not clear, but assuming mostly $Mn^{2+}$ ($d^5$) on the
A-sites and Mn$^{4+}$ ($d^3$) ions on the B-sites, with Ni$^{2+}$ ($d^8$) ions, about 10 unpaired spins per formula unit ($n_{exp} = 10$) would be expected. The systematic reduction of the Curie constants, from the expected values, indicates that over the measured temperature range (5-300K), strong interactions persist, and that higher temperatures are required to investigate the Curie-Weiss region.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Magnetic Behaviour</th>
<th>Transition Temp. (K)</th>
<th>Curie Constant (ergKmol$^{-1}$Oe$^2$)</th>
<th>Weiss Constant (K)</th>
<th>Unpaired electrons / formula unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiMn$_2$O$_4$</td>
<td>Ferrimagnetic</td>
<td>100</td>
<td>4.7(1)</td>
<td>-79(7)</td>
<td>5.2</td>
</tr>
<tr>
<td>Ni$<em>{1.5}$Mn$</em>{1.5}$O$_4$</td>
<td>Ferrimagnetic</td>
<td>120</td>
<td>4.42(6)</td>
<td>-187(6)</td>
<td>5.0</td>
</tr>
<tr>
<td>Cu$<em>{1.4}$Mn$</em>{1.6}$O$_4$</td>
<td>Ferromagnetic</td>
<td>100</td>
<td>2.451(3)</td>
<td>99.1(2)</td>
<td>3.5</td>
</tr>
</tbody>
</table>

The magnetic behaviour of the compound originally formulated Ni$_2$MnO$_4$, is shown in figure 7.5. It shows a very interesting phenomenon called compensation, where, in a certain temperature range, the magnetisation is negative i.e. the net magnetisation of the sample is aligned antiparallel to the applied field. The exact formulation of the spinel phase Ni$_{2-y}$Mn$_{1+y}$O$_4$ is not known, and a pure phase of its composition has not been synthesised. The same results were obtained when the synthesis and magnetic measurements were repeated.

### 7a.4 Discussion

To investigate the cationic distribution, a neutron diffraction pattern was taken for Ni$_{1.5}$Mn$_{1.5}$O$_4$, and a similar one was collected by Asbrink et al$^{12}$ for NiMn$_2$O$_4$ which they formulated Ni$^{(II)}_{0.12}$Mn$^{(II)}_{0.87}$[Ni$^{(II)}_{0.87}$Mn$^{(IV)}_{0.87}$Mn$^{(III)}_{0.26}$]O$_4$. The pattern for
Ni$_{1.5}$Mn$_{1.5}$O$_4$ contained peaks forbidden in the normal spinel $Fd\bar{3}m$ symmetry, indexed (200) and (420). These peaks are allowed in the 1:1 A-site cation ordered $F4\bar{3}m$ model, such as that found in Li$_{0.5}$Fe$_{0.5}$[Cr$_2$]O$_4$,$^{17,18}$ and the refinement in the $Fd\bar{3}m$ structure indicated a composition close to Ni$^{II}_{0.5}$Mn$^{II}_{0.5}$[Ni$^{II}$Mn$^{IV}$]O$_4$, which would be predicted in light of Asbrink et al. Though the single-phase refinement in the $F4\bar{3}m$ space group could not account for the pattern, the multiphase refinement with a long-range ordered model, and the normal, disordered, model, gave a good fit. Unfortunately, there is not enough information on the ordered phase in the diffraction pattern to fully characterize the minority, ordered, phase. A similar problem was encountered as in the refinement of the neutron diffraction pattern of CuMnFe$_2$O$_4$, (section 5.3.1) though in this case, it was the intensity of the (111) peak that could not be fitted in a disordered spinel model, and 1:1 B-site order was suspected. Using these estimations of the cationic distribution and oxidation, the magnetic exchange interactions can be considered. The cations are mutually separated by larger anions, so exchange interactions must be mediated by the oxygen p orbitals, thus the strength and sign of the interaction is dependent on both the geometry and distance of the M-O-M path. The sign, and approximate strength, of these interactions are discussed in section 2.5. In the nickel compounds, all the cations are magnetic, and so the A-O-B 125° interactions will dominate, the tetrahedral d$^5$ Mn(II) and d$^8$ Ni(II) ions both couple antiferromagnetically with the octahedral d$^3$ Mn(IV) and d$^8$ Ni(II) ions. This will probably force the collinear arrangement of both the A and B sublattices, despite the antiferromagnetic nature of the 90° Ni-O-Mn. The neutron diffraction measurements suggest that there is no long-range order on the B-sites, so there is both randomness and frustration in the B-site magnetic lattice. It is therefore, likely that these compounds are semi-spin-glasses, like the compounds in the preceding three chapters, but there is no AC susceptibility or aging data to verify this hypothesis. The copper manganite case is
much more straightforward. The $d^{10}$ Cu(I) ion is highly polarisable, with a strong covalent contribution to its bonding, therefore there is a strong driving force (section 2.3.3) for it to occupy the tetrahedral site. As this is a diamagnetic ion, there is no A-B interaction, and only B-B interactions, principally the ferromagnetic Mn(IV)-Mn(IV), must be considered. The B-B coupling alone does not give a perfectly aligned ferromagnet, though this often results from the antiparallel AB coupling. When the A site is diamagnetic the moments on the B cations are tilted away from perfect alignment, the extent of the tilting is known as the Yaffet-Kittel angle. This could not be investigated further for this compound without information from a neutron scattering experiment.

The magnetic behaviour of the compound originally formulated Ni$_2$MnO$_4$, is very surprising. It shows a phenomenon called compensation, where, in a certain temperature range, the magnetisation is negative i.e. the net magnetisation of the sample is aligned antiparallel to the applied field. It is not clear why this phenomenon should occur for this compound and not the related pure phases, although it has been observed in spinels. It is a result of one sublattice magnetising, parallel to the applied field, at a high temperature. As the temperature is lowered, another sublattice, coupled antiparallel to the first becoming ferromagnetic. This second sublattice is thus aligned against the applied field, and if is has a larger ordered moment, results in a negative magnetisation. The impurity phase, nickel oxide, is known to be antiferromagnetic over the entire measured temperature range and is not directly responsible for this behaviour, though it is possible that the coupling of the strongly antiferromagnetic NiO magnetic lattice to that of the spinel phase causes the compensation. The exact formulation of the spinel phase, Ni$_x$Mn$_{3-x}$O$_4$ is not known, and a pure phase of its composition has not been synthesised.
7a.5 Conclusion

The ferromagnetic Cu$_{1.4}$Mn$_{1.6}$O$_4$, and the ferrimagnetic NiMn$_2$O$_4$ and Ni$_{1.5}$Mn$_{1.5}$O$_4$ have been synthesised. Semi-spin-glass behaviour, like that observed in the preceding three chapters is likely, but verifying measurements are not available. CuMn$_2$O$_4$ and Cu$_{1.5}$Mn$_{1.5}$O$_4$ could not be synthesised under atmospheric conditions, but have been claimed\textsuperscript{19,10} by Jarrige \textit{et al} in sealed tube experiments. These could not be reproduced. The attempt to produce Ni$_2$MnO$_4$ was also unsuccessful, but the resultant spinel phase, which has yet to be synthesised pure, showed extremely interesting compensation magnetisation behaviour.
Top: Figure 7.6: ZFC and FC susceptibility of Cu$_{1.4}$Mn$_{1.6}$O$_4$.

Bottom: Figure 7.7: ZFC and FC susceptibility of NiMn$_2$O$_4$. 
Top: Figure 7.8: ZFC and FC susceptibility of Ni$_{1.5}$Mn$_{1.5}$O$_4$.
Bottom: Figure 7.9: ZFC and FC susceptibility of Ni$_2$MnO$_4$.
Top: Figure 7.10: Curie-Weiss fit to susceptibility data for Cu$_{1.4}$Mn$_{1.6}$O$_4$.
Bottom: Figure 7.11: Inverse susceptibility data for Cu$_{1.4}$Mn$_{1.6}$O$_4$. 
Top: Figure 7.12: Curie-Weiss fit to susceptibility data for NiMn$_2$O$_4$.
Bottom: Figure 7.13: Inverse susceptibility data for NiMn$_2$O$_4$. 
Top: Figure 7.14: Curie-Weiss fit to susceptibility data for Ni$_{1.5}$Mn$_{1.5}$O$_4$.

Bottom: Figure 7.15: Inverse susceptibility data for Ni$_{1.5}$Mn$_{1.5}$O$_4$. 

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Top: Figure 7.16: Curie-Weiss fit to susceptibility data for Ni$_2$MnO$_4$.
Bottom: Figure 7.17: Inverse susceptibility data for Ni$_2$MnO$_4$. 
7b.1 Introduction

Lithium manganese oxide, $\text{Li}_{1+y} \text{Mn}_x \text{O}_4$, with a cubic spinel structure has been found to be a potential cathode material in rechargeable lithium ion batteries, due to its environmental friendliness and low cost in comparison to $\text{LiCoO}_2$.\textsuperscript{20} Despite its structural robustness, and the ability to expand and contract isotropically over the compositional range $0<x<1$ at $\sim$4V vs. Li, the lithium ion cells with $\text{Li}[\text{Mn}]_2\text{O}_4$ electrodes show a slow fade at ambient temperature. This deterioration increases as the operating temperature of the cell is increased to 50°C, a temperature easily reached in a device. We have recently found that both $\text{Ga}^{3+}$ and $\text{Cr}^{3+}$-doped $\text{LiMn}_2\text{O}_4$ could be prepared as a single-cubic phase and that they offer a much better electrochemical performance in the $\sim$4V region, at both room temperature and 55°C, than the undoped material.\textsuperscript{1,2} The reason that the partial substitution of Mn ions with another trivalent metal ion improves these characteristics is still unclear.\textsuperscript{21} In an attempt to understand the origin of the problem of capacity and cyclability fading, a neutron diffraction study of these doped materials was undertaken. Further, our recent neutron studies showed that $\text{Ga}^{3+}$ ions selectively occupy the octahedral (16d) sites of the cubic spinel lattice.\textsuperscript{3}

To further investigate the relationship between the site occupancy of the dopant ion, and the profound improvement in the electrochemical performance, the series of compounds, $\text{Li}_{1+y} \text{M}_x \text{Mn}_{2-x} \text{O}_4$, ($\text{M} = \text{Co}, \text{Ni}, \text{Zn}, \text{Ti}; x<0.05; y=0.02$) has been prepared and characterized. The stability with respect to charge-discharge cycling in these compounds has been measured, and it is correlated with the site occupancy and valence state of the various dopant ions, as determined by Rietveld\textsuperscript{5} refinement of powder neutron diffraction data, collected on the D1A diffractometer. The strong contrast between the negative scattering lengths of manganese and lithium (respectively $-3.73\text{fm}$
and \(-1.90\text{fm}\), and the large positive scattering lengths of all the dopant ions, except titanium, allows accurate location of low concentrations of dopant, and makes neutron diffraction the ideal tool for this study.

### 7b.2 Results

The room temperature neutron diffraction patterns of nine compositions of doped \(\text{Li}_{1.02}\text{Mn}_{2-x}\text{M}_x\text{O}_4\) (\(M' = \text{Cr(III)}, \text{Co(III)}, \text{Ni(III)}, \text{Ga(III)}, \text{Zn(II)}, \text{and Ti(IV)}; x = 0.05, 0.07, 0.10\)), and an undoped sample, were collected on the D1A diffractometer, at the ILL, France (section 3.3.3.3.2). The diffraction pattern of \(\text{Li}_{1.02}\text{Mn}_{1.95}\text{Ga}_{0.05}\text{O}_4\) was collected on the BT1 diffractometer (section 3.3.3.3.1), NIST, U.S.A, and the results of its refinement have already been published elsewhere.\(^3\) At such low levels of doping, the diffraction patterns are indistinguishable to the eye, so a representative selection of fits to the data is presented in figures 7.18-7.20; the undoped sample in figure 7.18, an A-site doped compound (\(M = \text{Zn}\)) in figure 7.19 and a B-site doped compound (\(M = \text{Ga}\)) in figure 7.20. All structures were refined in the cubic \(Fd\bar{3}m\) space group, by the Rietveld method (section 3.3.2.3), using the GSAS suite of programmes. The cubic spinel lattice (section 2.2.2), with the atomic positions given in table 2.1, is defined by the lattice parameter, \(a\), and the oxygen position parameter, \(u\). Refined crystallographic data is presented in table 7.4. The fractional occupancy of the lithium ions refined to values well below unity for all samples, including \(x=0\), and is strongly correlated with the isotropic thermal factor, \(U_{\text{iso}}\). In the undoped sample, all the metal ions present have negative neutron scattering lengths, so this is not due to cation inversion, and is probably caused by a small amount of the lithium sitting on alternative sites, such as the octahedral 16e site at the origin and the tetrahedral (8c) site with fractional coordinates...
the difference Fourier plot indicated a peak at the (8c) site, but the inclusion of lithium at this site in the refinement did not improve the fit, which is presented in figure 7.18. It is not possible to refine the fractional occupancy of the dopant ions at the A-site unless the scattering length resultant from the lithium ions can be correctly accounted for, therefore in all refinements the A-site thermal factor, $U_{iso}$, was set to 0.02 (a typical value from other Li-spinels) and the fractional occupancy was allowed to refine freely. For all data sets, when the A-site temperature factors were freely refined, physically reasonable values in the range $(0.015/\AA^2 < U_{iso} < 0.025/\AA^2)$ were obtained, but the constraint was imposed to allow direct comparison of the site fractions. If any of the dopant ions (except Ti) were on the A-sites, the refined fraction of the lithium ions would be greatly below the value of the undoped sample (0.877(11)) because all of these dopant ions have large, positive, scattering lengths. It can be seen from table 7.4, that, within standard deviations, all the samples except zinc-doped have lithium fractions equal to, or greater than, the undoped sample. The quoted lithium site fractions for the zinc-doped samples are the refined values after the nominal value for zinc was also placed on the A-site, the zinc fraction was not refined and the lithium fraction is, as would be expected, similar to and slightly lower than that of the undoped sample. It is clear from the crystallographic data that all the dopant ions occupy the Mn (B) site, except in the case of the zinc-doped materials, where the dopant is predominantly found on the A-site. In the case of $\text{Li}_{1.02}\text{Mn}_{1.95}\text{Ti}_{0.05}\text{O}_4$, the fractional occupancy was not refined because Ti and Mn have very similar neutron scattering lengths (respectively $-3.43\text{fm}$ and $-3.93\text{fm}$); hence there is very poor contrast in powder neutron diffraction experiments. Neutron diffraction does, however, allow very accurate determination of the lattice and oxygen $u$ parameters, and it can be seen from table 2, that the values of the titanium-doped sample (respectively $8.2249(2)$ and $0.26311(3)$) are very similar to those of the undoped and chromium doped materials, and markedly
different to the values found for the zinc-substituted compound. This indicates that the
titanium ions are also located on the B-sites. The lattice parameter found for all the
doped spinels is lower than that observed for the pure LiMn$_2$O$_4$ spinel (~8.24Å). The
averaged value is ~8.22Å, and it does not vary greatly with the type and valence of B-
site doping metal ions. The zinc-doped samples show a smaller lattice parameter (8.20-
8.21Å), although this is probably due to the increase in the average oxidation state of
the manganese (average oxidation state ~ 3.5) upon substitution of some Mn ions with
Zn$^{2+}$ ions; the ionic radii of tetrahedral Li$^+$ and Zn$^{2+}$ are very similar, respectively 0.73Å
and 0.74Å. The reduction of the Mn$^{3+}$: Mn$^{4+}$ ratio also reduces the local Jahn-Teller
distortions allowing the lattice to relax. The lattice relaxation is also helped by the
increase in the average charge on the A-sites, with concomitant reduction of the valence
of the B-sites, because the uneven charge distribution around the oxide ions causes
strong anion polarization; each oxide ion is coordinated to one A cation and three B
cations, forming a distorted tetrahedron. The same factors probably account for the
reduction of the lattice parameter of the series Li$_{1.02}$Mn$_{2-x}$M$_x$O$_4$ compared to LiMn$_2$O$_4$,
the excess lithium results in the partial replacement of the manganese with Li$^+$ ions at
the (16d) sites, which suppresses the charge ordering transition observed when the
manganese oxidation state is exactly +3.5. Different models for the metal distribution
were applied in the refinements: the metal ion, M, was located, respectively, solely in
the octahedral (16d) sites, and solely in tetrahedral (8d) sites, in the first two models,
and then distributed over both the octahedral and tetrahedral sites in the third one. The
inspection of the fit indices revealed that the doping ions Ni(III), Co(III), Cr(III),
occupy the (16d) octahedral sites, as would be expected for their electronic
configurations, which give a greater crystal field stabilisation energy in the octahedral
coordination, as does the Ti(IV) ion. Identical site occupancy behaviour has been found
for the double ion doped material, Li$_{1.02}$Mn$_{1.95}$Ga$_{0.04}$Cr$_{0.01}$O$_4$. The refined dopant B-site
fractions are close to the nominal value of x/2 for all these compounds, except Li$_{1.02}$Mn$_{1.93}$Ni$_{0.07}$O$_4$, which has the same refined site fraction as Li$_{1.02}$Mn$_{1.95}$Ni$_{0.05}$O$_4$; there is also an unindexed peak at 1.47Å in the diffraction pattern of Li$_{1.02}$Mn$_{1.93}$Ni$_{0.07}$O$_4$, so it is likely that the solid solution of nickel in Li$_{1.02}$Mn$_2$O$_4$ ends at y=0.05. The diffraction pattern of Li$_{1.02}$Mn$_{1.95}$Co$_{0.05}$O$_4$ contains weak unindexed peaks at 1.43Å and 1.56Å, and very small peaks at 1.13Å, 1.48Å, and 1.49Å, these peaks are not seen for any of the other samples, and it is clear that not all of the cobalt has been taken into the lattice, but the lattice parameter (8.2165(4)) is significantly different from the undoped sample, demonstrating that some cobalt has been substituted into the lattice. Two nominal compositions of the zinc-doped materials were examined: x=0.05 and 0.10. The same three models were applied for the zinc distribution with the overall zinc content constrained to the nominal composition. The model with the Zn in the tetrahedral (δa) site gave a significantly better fit to the observed data than the solely octahedral model. The correlation of these experimental findings with the electrochemical data is in progress, but it is interesting to note that doping the lattice with zinc, which has been found to occupy the A-sites, produces materials with an inferior electrochemical performance.

Table 7.4: Summary of key structural data for compounds AMMnO$_4$.

<table>
<thead>
<tr>
<th>Dopant</th>
<th>Lattice Parameter, a/Å</th>
<th>Oxygen Parameter, u</th>
<th>A-site occupancy†</th>
<th>B-site Mn occupancy</th>
<th>B-site U$_{iso}$/Å$^2$</th>
<th>O-site U$_{iso}$/Å$^2$</th>
<th>r_m (%)</th>
<th>χ²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Undoped</td>
<td>8.2211(3) 8.2170(3)</td>
<td>0.26320(5) 0.26314(4)</td>
<td>Li=0.88(1) Li=0.88(1)</td>
<td>Mn=0.991(9) Mn=0.964(4) Cr=0.036(4) Cr=0.04</td>
<td>1.30(9) 0.94(7) 1.00(6) 1.55(3)</td>
<td>1.82(3) 1.62(3) 4.73 2.321</td>
<td>6.12 4.88 4.73 2.321</td>
<td>2.696 2.114 2.114 2.114</td>
</tr>
<tr>
<td>Cr=0.05 Ga=0.01</td>
<td>8.2302(1) 8.2325(4)</td>
<td>0.26325(4) Li=0.97(1)</td>
<td>Mn=0.988(2) Ga=0.007(2) Cr=0.04</td>
<td>1.22(9) 1.66(2) 1.14(8) 1.71(1) 1.19(5) 1.77(2)</td>
<td>2.03(4) 1.12(4) 1.89(4) 1.71(1) 1.17(5) 1.77(2)</td>
<td>7.44 6.78 6.78 7.06 4.49 4.49</td>
<td>3.997 3.348 3.348 3.733 1.465 1.465</td>
<td></td>
</tr>
<tr>
<td>Co=0.05</td>
<td>8.2165(4) 8.2155(1)</td>
<td>0.26327(6) 0.26321(5)</td>
<td>Li=0.84(1) Li=0.86(1)</td>
<td>Mn=0.966(6) Co=0.034(6) Mn=0.980(2) Ni=0.020(2) Ni=0.020(2) Ni=0.020(2)</td>
<td>1.22(9) 1.66(2) 1.14(8) 1.71(1) 1.19(5) 1.77(2)</td>
<td>2.03(4) 1.12(4) 1.89(4) 1.71(1) 1.17(5) 1.77(2)</td>
<td>7.44 6.78 6.78 7.06 4.49 4.49</td>
<td>3.997 3.348 3.348 3.733 1.465 1.465</td>
</tr>
<tr>
<td>Ni=0.05</td>
<td>8.2139(4) 8.2139(4)</td>
<td>0.26318(5) 0.26318(5)</td>
<td>Li=0.88(1) Li=0.88(1)</td>
<td>Mn=0.980(2) Ni=0.020(2) Ni=0.020(2) Ni=0.020(2)</td>
<td>1.22(9) 1.66(2) 1.14(8) 1.71(1) 1.19(5) 1.77(2)</td>
<td>2.03(4) 1.12(4) 1.89(4) 1.71(1) 1.17(5) 1.77(2)</td>
<td>7.44 6.78 6.78 7.06 4.49 4.49</td>
<td>3.997 3.348 3.348 3.733 1.465 1.465</td>
</tr>
<tr>
<td>Ni=0.07</td>
<td>8.2249(2) 8.2249(2)</td>
<td>0.26311(3) 0.26311(3)</td>
<td>Li=0.89(1) Li=0.89(1)</td>
<td>Mn=0.982(6) Ti=(0.025) $</td>
<td>1.19(5) 1.77(2) 1.19(5) 1.77(2)</td>
<td>1.59(2) 1.59(2) 4.49 4.49</td>
<td>4.52 4.52</td>
<td>1.727 1.727</td>
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<tr>
<td>Ti=0.05</td>
<td>8.2105(3) 8.2105(3)</td>
<td>0.26323(4) 0.26323(4)</td>
<td>Li=0.84(1) Li=0.84(1)</td>
<td>Mn=0.970(6) Zn=0.05 Zn=0.05</td>
<td>1.06(6) 1.59(2) 1.06(6) 1.59(2)</td>
<td>1.59(5) 1.59(5) 6.90 6.90</td>
<td>3.823 3.823</td>
<td>3.823 3.823</td>
</tr>
<tr>
<td>Zn=0.05</td>
<td>8.2043(2) 8.2043(2)</td>
<td>0.26311(6) 0.26311(6)</td>
<td>Li=0.81(1) Li=0.81(1)</td>
<td>Mn=0.96(1) Zn=0.10</td>
<td>1.03(9) 1.59(5) 1.03(9) 1.59(5)</td>
<td>1.59(5) 1.59(5) 6.90 6.90</td>
<td>3.823 3.823</td>
<td>3.823 3.823</td>
</tr>
</tbody>
</table>

† A-site isotropic thermal parameter (U$_{iso}$) constrained to be 0.02/Å$^2$. 

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Top: Figure 7.18: Rietveld refinement of the powder neutron diffraction pattern of Li$_{1.02}$Mn$_2$O$_4$.
Bottom: Figure 7.19: Rietveld refinement of the powder neutron diffraction pattern of Zn$_{0.05}$Li$_{1.05}$Mn$_{1.95}$O$_4$. 

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Figure 7.20: Rietveld refinement of the powder neutron diffraction pattern of Li_{1.02}Ga_{0.05}Mn_{1.95}O_{4}.
7b.3 Discussion

The lattice parameters and cation ordering schemes determined in this study (Table 7.4) are in good agreement with those reported elsewhere. Berg et al.\textsuperscript{22} studied LiNi\textsubscript{0.18}Mn\textsubscript{1.82}O\textsubscript{4}, and found the nickel ions to be octahedral Ni\textsuperscript{2+}, and the lattice parameter to be 8.219(3)Å, in good agreement with the values obtained for Li\textsubscript{1.02}Ni\textsubscript{0.05}Mn\textsubscript{1.95}O\textsubscript{4} and Li\textsubscript{1.02}Ni\textsubscript{0.07}Mn\textsubscript{1.93}O\textsubscript{4}, respectively 8.2155(1)Å and 8.2139(1)Å. Kwang et al.\textsuperscript{23} found LiTi\textsubscript{0.05}Mn\textsubscript{1.95}O\textsubscript{4} to contain octahedral Ti\textsuperscript{4+} though the lattice parameter of 8.2459Å is significant larger than that found here (8.2249(2)Å). The lattice parameter obtained for Li\textsubscript{1.02}Cr\textsubscript{0.05}Mn\textsubscript{1.95}O\textsubscript{4} (8.2170(3)Å) is also significantly smaller than reported elsewhere; Oikawa et al.\textsuperscript{24} found a lattice parameter of 8.2374(1)Å from a neutron diffraction study of LiCr\textsubscript{0.11}Mn\textsubscript{1.89}O\textsubscript{4}. These differences of approximately 0.02Å are almost certainly a result of the lithium content of the samples. These materials were deliberately synthesized slightly lithium rich to avoid the Mn\textsuperscript{3+}/Mn\textsuperscript{4+} charge ordering observed in Li\textsubscript{1.00}Mn\textsubscript{2}O\textsubscript{4}\textsuperscript{25,26}, and the lattice parameter of the undoped material Li\textsubscript{1.02}Mn\textsubscript{2}O\textsubscript{4} (8.2211(3)Å) is approximately 0.02Å smaller than that reported elsewhere for LiMn\textsubscript{2}O\textsubscript{4} by Cho et al. and Kwang et al.,\textsuperscript{27,23} though almost identical to that reported by Berg et al. Sigala et al.\textsuperscript{28} used electron energy loss spectroscopy (EELS) to monitor the oxidation states of Cr and Mn in LiCr\textsubscript{y}Mn\textsubscript{2-y}O\textsubscript{4} (0 ≤ y ≤ 1) before and after lithium deintercalation. They found the as prepared samples to contain Cr\textsuperscript{3+} and Mn\textsuperscript{3+/4+}. Suzuki et al.\textsuperscript{29} used (EELS) to study the oxidation states of Mn and M in LiMnM\textsubscript{O} (M = Ti, Cr, Mn, Co), which they assigned Li\textsuperscript{+}Mn\textsuperscript{4+}Ti\textsuperscript{4+}O\textsubscript{4}, Li\textsuperscript{+}Mn\textsuperscript{3+}Mn\textsuperscript{4+}O\textsubscript{4}, Li\textsuperscript{+}Cr\textsuperscript{3+}Mn\textsuperscript{4+}O\textsubscript{4}, and Li\textsuperscript{+}Co\textsuperscript{3+}Mn\textsuperscript{4+}O\textsubscript{4}. These results are consistent with the assignation of the dopant titanium as octahedral Ti\textsuperscript{4+}, and chromium and cobalt as octahedral Cr\textsuperscript{3+} and Co\textsuperscript{3+}. The assignment of the zinc ions as tetrahedral Zn\textsuperscript{2+} is in agreement with Lee et al.,\textsuperscript{30} who studied the cationic distribution in the system LiZn\textsubscript{x}Mn\textsubscript{2-x}O\textsubscript{4} with \textsuperscript{6}Li magic
angle spinning (MAS) NMR, and showed that the zinc preferentially occupies the tetrahedral A-sites, driving the lithium onto the octahedral B-sites.

7b.4 Conclusion

The series of compounds \( \text{Li}_{1.02}\text{Mn}_{2-x}\text{M}_x\text{O}_4 \) (\( M = \text{Cr(III)}, \text{Co(III)}, \text{Ni(III)}, \text{Ga(III)}, \text{Zn(II)}, \) and \( \text{Ti(IV)}; x = 0.05 \)), has been characterized. The deterioration in the electrochemical properties upon zinc doping has been correlated with the A-site occupancy of the zinc ions. Similarly, the improvement, observed in some of the other doped compounds, such as the gallium and chromium doped materials, is related to the B-site occupancy of those ions.

7.4 References


Chapter 8

Discussion
8.1 Introduction

This chapter contains a critical assessment of the research undertaken in this thesis, and a discussion of future work that could build on this research. Additional experimental techniques that could provide independent verification of certain parameters, particularly cationic distributions and oxidation states, which were obtained by model dependent data analysis in this thesis. There is also a discussion of possible experiments that would build on the results obtained and further illuminate the novel magnetic properties that have been observed in these systems.

8.2 Summary of Key Results

This thesis is an investigation of the structural and electronic properties oxide spinels containing octahedrally coordinated manganese (IV) ions. These spinels can be described with the general formula $A^xB_xMn^{IV}(2-x)O_4$ ($x = 0.5, 1; A = Li, Cu; B = Mg^{II}, Ni^{II}, Cr^{III}, Fe^{III}, Co^{III}, Rh^{III}$) and $Cu_{1+y}Ni_{0.5+y}Mn_{1.5}O_4$ ($0 \leq y \leq 1$). Particular emphasis is placed on the interplay between cationic distribution, and sublattice ordering, and the observed magnetic and magnetotransport properties. The primary motivation for this study was the analogy with the CMR pyrochlore, $Tl_2Mn_2O_7$, which contains a similar array of manganese (IV) ions. Unfortunately, the remarkable low-field magnetoresistance properties of $Tl_2Mn_2O_7$ were not reproduced in this system, but some unusual, and very interesting magnetic properties were observed. In particular, the majority of these compounds were described as semi-spin-glasses; a hybrid magnetic...
structure composed of a ferromagnetic component and a spin glass component. The observation of significantly reduced saturation magnetic moments for all these compounds cast doubt on the simple ferromagnetic structure that was originally proposed, and non-equilibrium behaviour of the magnetic properties was demonstrated by the time dependent low field magnetization.

8.3 Experimental Techniques

The electronic properties of these compounds were discussed within a framework of the crystallographic structure and the cationic oxidation states. These parameters were determined primarily by Rietveld refinement of powder X-ray, and neutron, diffraction patterns, using the GSAS suite of software, and SQUID magnetometry. Bulk magnetic behaviour has been investigated with a SQUID magnetometer and AC susceptometer. Low temperature neutron diffraction, including the use of the representational analysis technique, has been used to investigate the magnetic structure responsible for the observed magnetic phenomena. The magnetic structure is discussed by analysis of the competing superexchange interactions. The effect of magnetic ordering on the electronic transport properties has been investigated by four-probe conductivity measurement in a range of applied magnetic fields.

8.4 Critical Assessment of Results

8.4.1 Structural Characterization
The structural characterization is almost entirely diffraction based. Access to microscopy facilities would allow the study of the structural morphology\textsuperscript{9} by scanning electron microscopy (SEM) and spot energy dispersive X-ray analysis (EDX) could be used to confirm that the composition of individual crystallites is the same as that of the bulk. Lattice imaging could be used to investigate the occurrence of stacking faults in the structure, which were suspected to have caused shoulder peaks on the main peaks in some of the diffraction patterns. The GSAS correlation matrix showed that there was a strong correlation between the thermal parameters and the site occupation in the refinement of the XRD patterns with a poor signal/noise ratio, particularly those affected by fluorescence (discussed below). In all cases where a noisy XRD pattern was refined, high quality diffraction data was available for a closely analogous compound, so spurious results were easily identified. In some cases the thermal parameters had to be fixed because their refinement did not yield physically meaningful values.

The cationic distribution was determined largely by Rietveld\textsuperscript{6} refinement of neutron diffraction patterns. This is a model dependent technique and yields only an average neutron scattering factor at each site. There was a problem in the refinement of some X-ray diffraction (XRD) patterns, particularly Mn-Fe and Mn-Co systems, because fluorescence gave a high background intensity. It would be interesting to compare the results obtained to these fits, with fits to data collected on the Siemens D500 in its current configuration; the primary monochromator has been removed and a graphite secondary monochromator installed, this setup give a lower resolution, but removes most of the fluorescence contribution to the signal. Oxidation states were assigned largely by analysis of the magnetization measurements, with confirmation by metal-oxygen bond length analysis and comparison with Shannon\textsuperscript{10} ionic radii. The oxidation state of certain transition metal ions were assigned by comparison with analogous
materials containing a cation with a known oxidation state in place of that cation. For example, the similarity of the structural and magnetic properties of CuMgO.5Mn1.5O4 and LiMgO.5Mn1.5O4 11-13 is strong evidence that CuMgO.5Mn1.5O4 contains Cu⁺ and Mn⁴⁺, rather than Cu²⁺ and Mn³⁺/⁴⁺.

In recent years a number of novel techniques have been used to study the cationic distribution and oxidation states in transition metal oxide spinels. Sigala et al 14 used electron energy loss spectroscopy (EELS) to monitor the oxidation states of Cr and Mn in LiCrₓMn₂₋ₓO₄ (0 ≤ y ≤ 1) before and after lithium deintercalation. They found the as-prepared samples to contain Cr⁴⁺ and Mn³⁺/⁴⁺, and found the fully deintercalated material to be Cr⁴⁺Mn⁴⁺₂₋ₓO₄. Suzuki et al 15 used (EELS) to study the oxidation states of Mn and M in LiMnM₀₄ (M = Ti, Cr, Mn, Co), which they assigned Li⁺Mn³⁺Ti⁴⁺O₄, Li⁺Mn³⁺Mn⁴⁺O₄, Li⁺Cr³⁺Mn⁴⁺O₄, and Li⁺Co³⁺Mn⁴⁺O₄. This study, which is completely consistent with the oxidation states used in this thesis, was partly motivated by a report by Kanzaki et al 16 that concluded (contradicted by a number of later diffraction studies, for example Wills et al 17 and Rodriguez-Carvajal et al 18) from nuclear magnetic resonance (NMR) experiments that LiMn₂O₄ should be described Li⁶Mn⁴⁺₂O₄. The result is also contradicted by the X-ray absorbance spectroscopy measurements, used by Yamaguchi et al 19 to study the Jahn-Teller distortions in LiMn₂O₄. X-ray absorbance spectroscopy fine structure (XAFS) has been employed by Ammundsen et al 20, 21 to study the local structure around the transition metal ions in LiCrₓMn₂₋ₓO₄, and similarly by Aitchison et al 22 in the study of LiCoₓMn₂₋ₓO₄. Lee et al 23 studied the cationic distribution in the system LiZnₓMn₂₋ₓO₄ with ⁶Li magic angle spinning (MAS) NMR, and showed that the zinc preferentially occupies the tetrahedral A-sites, driving the lithium onto the octahedral B-sites. Similar studies were performed on LiCrₓMn₂.
LiCoMnO$_4$ with electron paramagnetic resonance (EPR), and used the same technique to study the Mn$^{4+}$ ordering in Li[Li$_{0.33}$Mn$_{1.67}$]O$_4$ spinels.$^{26}$

8.4.2 Magnetic Characterization

The low field magnetization measurements (section 3.5.1.1) were performed with a SQUID magnetometer, operating in its standard set-up, averaging four measurements. Each measurement, which is collected by sweeping the sample through the pick-up coil, takes about fifteen seconds. This is not ideal for a time dependent measurement, because only one data point is collected per minute; the logarithmic nature of the time dependence means that much important informant is contained in the first ten seconds, and by one hundred seconds, half of the time axis has been traversed in a typical experiment ($10^0$-$10^4$s), yet in the setup used the second data point was being collected at 100s. Also, non-equivalent measurements are being averaged together. These measurements would be improved if the data were not averaged in this way, giving a measurement every fifteen seconds. The use of a vibrating sample magnetometer (VSM) instead of a SQUID would allow many measurements per second to be collected. Alternatively, it might be possible to write software to allow the SQUID to be operated in a manner analogous to a VSM, by carefully centring the sample at the start of the measurement and then leaving the sample stationary at the maximum point and measuring the evolution of this maximum with time. This method would lose some accuracy in the absolute value of the measured signal, but would allow almost instantaneous data collection. Another problem with the experimental setup is that zero field and one milliTesla measurements were performed in a five Tesla magnet. These high field magnets are not designed for accurately setting very small field and finding
true zero field is difficult. An auxiliary power supply could be fitted to give more precise control of the magnet at low fields.

The low field magnetization measurements demonstrated that the majority of the materials in this thesis show some spin glass character. There was not time to fully characterize the nature of this semi-spin-glass state. It would have been interesting to see if the thermoremanent magnetization showed a logarithmic plus stretched exponential time decay, and a field dependence, and then to check whether the parameters obtained in the two relaxation experiments were the same. It would also be desirable to characterize the memory or aging properties of these materials. Similarly, the AC susceptibility measurements, performed on a probe in the Oxford Instruments MagLab 2000 system, demonstrated a frequency dependence, but did not provide enough information to characterize this dependence, because resolution was lost at low frequencies (<100Hz). Measurements in the range 1-10000Hz would reveal the full frequency dependence, and allow the use of dynamical scaling analysis to extract dynamic critical exponents.

8.4.3 Transport Measurements

Transport measurements were performed by a standard four point method, on sintered pellets, in an Oxford Instruments Maglab 2000 system. Resistivity measurements of this type can be dominated by the grain boundaries, rather than giving a measure of the bulk properties. Measurements on single crystals avoid this problem, and comparison of single crystal and sintered pellet data can reveal both the intergrain and intragrain transport properties. If single crystals are not available, a similar study can be performed
with microwave spectroscopy, for example Yates et al.\textsuperscript{37,38} combined these techniques in the investigation of La\textsubscript{0.67}Ca\textsubscript{0.33}MnO\textsubscript{3}\textsuperscript{38} and La\textsubscript{0.7-x}Y\textsubscript{x}Ca\textsubscript{0.33}MnO\textsubscript{3}.\textsuperscript{37}
8.5 References


Appendix I

Representational Analysis of LiMg$_{0.5}$Mn$_{1.5}$O$_4$
I.1 Introduction

LiMg$_{0.5}$Mn$_{1.5}$O$_4$ crystallises in the $P4_332$ space group (#212). Bulk ferromagnetic behaviour is observed below 25K, with a 5K saturation moment of 2.3$\mu_B$/Mn in an applied field of 5x10$^4$Oe; the predicted saturation moment is $gS = 2 \times \gamma = 3 \mu_B / Mn$, for Mn$^{4+}$ ($d^3$). The fit of the susceptibility to the Curie-Weiss law in the paramagnetic (120K<T<300K) region gives $C = 3.41(3)$ergKmol$^{-1}$Oe$^{-2}$ and $\theta = +37.6(1)$K. The A spin-only treatment of the Curie constant confirms that there are 3 unpaired electrons per Mn ($gS = 2.9 \mu_B / Mn$). The positive Weiss constant shows that the interactions are predominantly ferromagnetic. Neutron diffraction at 10K reveals no new Bragg peaks, but additional intensity was observed on some of the nuclear reflections. Hence it is assumed that the magnetic ordering has a propagation vector $\vec{k} = 0$. This data was refined with a ferromagnetic 2$^{nd}$ phase aligned along [100], which gave a reasonable fit, with a refined moment of 2.3$\mu_B$/Mn. This does not explain the smaller than predicted moment, but the data was not of sufficiently high resolution to go further with this method.

The lattice parameter, $a$, at 10K is 8.18110(9)Å and the manganese position (12d) is ($\zeta$, 0.3783, 0.8717). The twelve equivalent manganese positions in the unit cell are given in Table 1. These generate a lattice of corner-linked equilateral triangles, shown in Figure 1. The vertices are linked to give Mn-Mn-Mn angles of 180° and 120° giving the propeller like structure shown in Figure 2. All the triangles are interlinked, which contrasts with gadolinium gallium garnet (GGG) that has two non-intersecting arrays, as shown in Figure 3.
Table 1.1: Fractional coordinates of equivalent manganese positions in LiMg$_{0.5}$Mn$_{1.5}$O$_4$ at 10K

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<td>Mn(12)</td>
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Representational analysis of this $\vec{k} = 0$ magnetic structure was performed with the SARAh program. There are five irreducible representations (IRs) labelled $\Gamma_n$, in the decomposition of the magnetic structure, given in Table 2. There are a total of 36 basis vectors associated with the five IRs (the number of basis vectors under an IR is the multiplicity times the order) Correspondingly there are 36 degrees of freedom in the magnetic structure. (12 manganese atoms * 3 dimensions.) Of these five IRs, only one, $\Gamma_3$, contains basis vectors which could result in ferromagnetism; all the basis vectors in the first four IRs are antiferromagnetic i.e. they have zero net moment.
Table 1.2: Multiplicity and order of the IRs of the Mn sublattice of LiMg$_{0.5}$Mn$_{1.5}$O$_4$

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The ferromagnetic phase transition is second order, therefore, according to Landau theory$^2$, all the basis vectors involved in the transition belong to the same IR, which must be $\Gamma_2$ to have a ferromagnetic component. The set of 15 basis vectors, numbered 22-36 and labelled $\psi_{22}$-$\psi_{36}$, are listed in Table 3. Each vector represents a component (that can be zero) along $x$, $y$ and $z$ on all of the magnetic ions, and is shown, in Table 3, as a matrix. The twelve rows of the matrix represent (in order) the 12 manganese ions (Table 1), and the 1$^{st}$, 2$^{nd}$ and 3$^{rd}$ columns indicates the moment along $x$, $y$ and $z$, respectively.
Table I.3: Basis vectors of $\Gamma_5$ of RA of LiMg$_{0.5}$Mn$_{1.5}$O$_4$.

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Figure I.1: Magnetic lattice in LiMg$_{0.5}$Mn$_{1.5}$O$_4$, viewed down [111].

Figure I.2: Propeller structure of magnetic lattice of LiMg$_{0.5}$Mn$_{1.5}$O$_4$, viewed down [111].
1.2 Method

1.2.1 Candidate Structures

Candidate ordered structures are generated by linear combination of these basis vectors, labelled $\psi_n$. It is clear from table 3 that the atoms are divided into three groups of four, Mn(1)-Mn(4), Mn(5)-Mn(8) and Mn(9)-Mn(12), and that these groups are not always coupled to each other. Without constraint, there are clearly an infinite number of
possibilities, but it is possible to impose some physical constraints on this group theory treatment. The following constraints have been used in this investigation:

- The magnitude of the moment on each atom is assumed to be the same.
- The structure must be able to account for a saturation moment of $2.3\mu_B/$Mn, i.e. there must be a ferromagnetic component on at least eight of the twelve manganese ions, and the relative angles of the moments are also taken into account.

First, the combinations composed solely of the ferromagnetic basis vectors, ($\psi_{22}$, $\psi_{27}$ and $\psi_{32}$) and ($\psi_{25}$, $\psi_{30}$ and $\psi_{35}$) are considered. Ferromagnetic combinations are labelled $\Psi_{(xyz)}$ where $(xyz)$ is the direction of the moments. For example, a combination of $\Psi_{22}$ and $\psi_{25}$ gives a simple ferromagnet along [100] as shown in equation (I.1).

$$c_1\psi_{25} + \frac{c_1}{2}\psi_{22} = \Psi_{(100)} \quad (I.1)$$

Similarly, ferromagnets along [010] and [001] are generated in equations (I.2) and (I.3)

$$c_1\psi_{30} + \frac{c_1}{2}\psi_{27} = \Psi_{(010)} \quad (I.2)$$

$$c_1\psi_{35} + \frac{c_1}{2}\psi_{32} = \Psi_{(001)} \quad (I.3)$$

All three of these simple ferromagnetic functions are equivalent because the symmetry is cubic. They fulfil the physical criteria, and so do any of their linear combinations.

Thus we can write equation (I.4)

$$p\Psi_{(100)} + q\Psi_{(010)} + r\Psi_{(001)} = \Psi_{(pqr)} \quad (I.4)$$

Thus a Heisenberg ferromagnet, with ferromagnetic order pointing in any direction is a candidate structure. It is, however, important to note that $\Psi_{(pqr)} \quad p, q, r \neq 0$ cannot be mixed with any of the nine antiferromagnetic basis vectors because combining ferromagnetic and antiferromagnetic components in the same direction on the same set of atoms violates the criterion that each atom must have the same moment. In fact,
because all of the antiferromagnetic basis vectors have components in more than one
direction, $\Psi_{(001)}$ cannot be mixed with anything other than $\Psi_{(001)}$. Thus the only simple
ferromagnet that can mix with some of the antiferromagnetic components (which would
account for the reduced saturation moment) is $\Psi_{(100)}$.

It is also possible to make more complex (canted) ferromagnets from the ferromagnetic
basis vectors. For example, whilst combining $\psi_{22}$ and $\psi_{27}$ does not fulfil the criterion of
all atoms having the same moment, mixing $\psi_{22}$, $\psi_{27}$ and $\psi_{32}$ in equal amounts is allowed.
Because the moments in a given direction on different atoms are no longer equal, a
more complex notation is required, as in equation (1.5)

$$c_1 (\psi_{22} + \psi_{27} + \psi_{32}) = \Psi_{\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}}$$  \hspace{1cm} (1.5)

The notation $\Psi_{\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}}$ represents a canted ferromagnet with the moments on
manganese atoms 1-4 aligned along [100], 5-8 along [010], and 9-12 along [001]. This
structure would give a predicted moment of $\sqrt{3} = 1.73 \mu_B / \text{Mn}$, which is too small to
account for the observed saturation moment. However, equation (1.6) can be similarly
written.

$$c_1 (\psi_{25} + \psi_{30} + \psi_{35}) = \Psi_{\begin{bmatrix} 0 & 1 & 1 \\ 0 & 1 & 1 \\ 0 & 1 & 1 \end{bmatrix}}$$  \hspace{1cm} (1.6)

In $\Psi_{\begin{bmatrix} 0 & 1 & 1 \\ 0 & 1 & 1 \\ 1 & 1 & 0 \end{bmatrix}}$, the moments are aligned along [011], [101] and [110], resulting in a
predicted moment of $\sqrt{6} = 2.45 \mu_B / \text{Mn}$, in good agreement with the observed value.
Clearly, this is a good candidate structure, although there is no reason that it should not
be further mixed, for example equations (1.5) and (1.6) can be combined to give (1.7).

$$p\Psi_{\begin{bmatrix} 0 & 1 & 1 \\ 0 & 1 & 1 \\ 1 & 1 & 0 \end{bmatrix}} + q\Psi_{\begin{bmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}} = \Psi_{\begin{bmatrix} q & p & p \\ p & q & p \\ p & p & q \end{bmatrix}}$$  \hspace{1cm} (1.7)
Whilst $\Psi\left(\begin{array}{ccc} p & p & p \\ p & p & p \\ p & p & q \end{array}\right); p, q \neq 0$ is a candidate structure, it cannot be mixed with any of the antiferromagnetic basis vectors and when $p = q$, it is equivalent to $\Psi_{(111)}$. Hence this structure would be expected to saturate fully in $5 \times 10^4$ Oe. It is, however, possible to mix $\Psi\left(\begin{array}{ccc} 0 & 1 & 1 \\ 1 & 0 & 1 \\ 1 & 1 & 0 \end{array}\right)$ with one of $\Psi_{24}, \Psi_{29}$ and $\Psi_{32}$, which are antiferromagnetic components, that could "lock in" the canting, by preventing the combination with $\Psi\left(\begin{array}{ccc} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{array}\right)$. $\Psi_{24}, \Psi_{29}$ and $\Psi_{34}$, cannot mix with each other, but can, respectively, mix with $\Psi_{22}, \Psi_{27}$ and $\Psi_{32}$, as shown in equation (1.8).

$$q\Psi_{24} + \frac{q}{2}\Psi_{22} = \Psi\left(\begin{array}{ccc} q & 0 & 0 \\ 0 & 0 & 0 \\ 0 & Q & 0 \end{array}\right)$$

(1.8)

The notation $\Psi\left(\begin{array}{ccc} q & 0 & 0 \\ 0 & Q & 0 \\ 0 & 0 & Q \end{array}\right)$ indicates a combination of ferromagnetic ordering of magnitude $q$ on the sites indicated by the $q$ in the matrix, and antiferromagnetic ordering of magnitude $q$ on the sites and directions indicated by the $Q$'s in the matrix. Equivalent linear combinations of both $\Psi_{27}$ and $\Psi_{29}$, and $\Psi_{32}$ and $\Psi_{34}$, are also possible. Clearly it is possible to form a linear combination of $\Psi\left(\begin{array}{ccc} q & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & Q \end{array}\right)$ and $\Psi\left(\begin{array}{ccc} 0 & 1 & 1 \\ 1 & 0 & 1 \\ 1 & 1 & 0 \end{array}\right)$, as in equation (1.9)

$$p\Psi\left(\begin{array}{ccc} 0 & 1 & 1 \\ 1 & 0 & 1 \\ 1 & 1 & 0 \end{array}\right) + \Psi\left(\begin{array}{ccc} q & 0 & 0 \\ 0 & Q & 0 \\ 0 & 0 & Q \end{array}\right) = \Psi\left(\begin{array}{ccc} q & p & p \\ p & Q & p \\ p & p & Q \end{array}\right)$$

(1.9)

In $\Psi\left(\begin{array}{ccc} q & p & p \\ p & Q & p \\ p & p & Q \end{array}\right)$, all of the manganese atoms have a ferromagnetic component along [100], with a mixture of ferromagnetic and antiferromagnetic components along [010] and [001], resulting in a ferromagnet canted around [100]. This is clearly a good candidate structure, which could explain the observed properties, including the good fit with the FM[100] model in the initial Rietveld refinement. It is possible to form a similar
combination, with ferromagnetic components along [100] only, and antiferromagnetic components on all of the atoms along [010] and [001], as in equation (1.10).

$$p \psi_{25} + \frac{q}{2} \psi_{22} + p (\psi_{23} + \psi_{24}) + q \psi_{26} = \Psi \begin{pmatrix} q & p & p \\ p & p & q \\ p & q & p \end{pmatrix}$$  \hspace{1cm} (I.10)

1.2.2 Rietveld Refinement of the Candidate Structures

The combinations of basis vectors used to produce the above candidate structures were inserted into the SARAh Refine program,\(^1\) with the best structural fit from the earlier Rietveld\(^3\) refinement. The resulting goodness-of-fit and basis vector coefficients of the best fit, obtained after a large number of cycles (1000-2000 for the structures with 5 or 6 basis vectors) had been run, are presented in Table 4. The individual coefficients of the basis vectors were not constrained to be equal, as they have been in some of the candidate structures, but instead, the overall magnitude of the moments of all atoms were constrained to be within 2% of each other.

1.3 Results

The simple model \(\psi_{(100)}\), defined in equation (I.1), of ferromagnetic order along [100] (equivalent to [010] or [001]) provides a very good fit to the data, with a resultant goodness-of-fit index of \(\chi^2 = 1.115\). This makes it difficult for more complex models to offer significant improvement. This model cannot, however, account for the significantly reduced saturation moment, in applied fields up to 5\(\times\)10\(^5\)Oe. Importantly, the simple canted ferromagnetic candidate structures, which could have explained the reduced moment, \(\Psi \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}\) (equation (I.5)) and \(\Psi \begin{pmatrix} 0 & 1 & 1 \\ 0 & 1 & 0 \\ 1 & 0 & 1 \end{pmatrix}\) (equation (I.6)) give very poor fits to the data, with respective resulting goodness-of-fit indices of \(\chi^2 = 1.733\) and \(\chi^2 = 1.425\). Thus, these structures can be discounted.
The inclusion of all six ferromagnetic basis vectors in the refined model, based on the candidate structures $\psi_{\text{spin}}$ (equation (1.4)) and $\Psi \begin{pmatrix} y & x & x \\ x & x & y \\ x & y & y \end{pmatrix}$ (equation (1.7)) did not significantly improve the quality of fit ($\chi^2 = 1.111$) despite the increased number of variables, and there were many different solutions with indistinguishable goodness-of-fit indices ($1.111 \leq \chi^2 \leq 1.115$). This model also fails to account for the reduced saturation moment in large applied field; although the spins are not collinear in the best fit, there appears to be nothing preventing their alignment in a field.

The refinement of the coefficients of the basis vectors from the model $\Psi \begin{pmatrix} y & x & x \\ x & x & y \\ x & y & y \end{pmatrix}$, (equation (1.10)) could not produce as good a fit as $\psi_{(100)}$ after 2000 cycles ($\chi^2 = 1.173$). This model is based on a ferromagnetic component along [100] and antiferromagnetic components along [010] and [001]. Clearly, setting $c_{23}, c_{24}$ and $c_{26}$ to zero would result in the markedly better goodness-of-fit found for $\psi_{(100)}$ ($\chi^2 = 1.115$). Therefore $\psi_{(100)}$ is the best solution for this model, and $\Psi \begin{pmatrix} y & x & x \\ x & x & y \\ x & y & y \end{pmatrix}$ can be ruled out.

The refinement of the coefficients of the basis vectors from the model $\Psi \begin{pmatrix} y & x & x \\ x & y & x \\ x & x & y \end{pmatrix}$ (equation (1.9)) did produce a fit that was at least as good ($\chi^2 = 1.106$) as that of $\psi_{(100)}$. This model is based on a ferromagnetic component along [100] and a mixture of ferromagnetic and antiferromagnetic components along [010] and [001]. The presence of an antiferromagnetic component in the $y$ direction on the atoms Mn(5) to Mn(8) and
in the z direction on atoms Mn(9) to Mn(12) would explain the reduced saturation moment.

Table I.4: Parameters from best refinements of basis vector sets of candidate structures

<table>
<thead>
<tr>
<th>Basis Vectors</th>
<th>Best $\chi^2$</th>
<th>Coefficients</th>
<th>Relationship to Candidate Structure</th>
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| $\Psi_{22}, \Psi_{25}$ | 1.115 | $c_{22} = 0.33$  
$c_{25} = 0.67$ | $\Psi^{(100)}$ equation (I.1) |
| $\Psi_{22}, \Psi_{27}, \Psi_{32}$ | 1.733 | $c_{22} = 0.33$  
$c_{27} = 0.33$  
$c_{32} = 0.34$ | $\Psi^{\left( \begin{array}{ccc} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{array} \right)}$ equation (I.5) |
| $\Psi_{25}, \Psi_{30}, \Psi_{35}$ | 1.425 | $c_{25} = 0.33$  
$c_{30} = 0.34$  
$c_{35} = 0.33$ | $\Psi^{\left( \begin{array}{ccc} 0 & 1 & 1 \\ 1 & 0 & 1 \\ 1 & 1 & 0 \end{array} \right)}$ equation (I.6) |
| $\Psi_{22}, \Psi_{27}, \Psi_{32}$  
$\Psi_{25}, \Psi_{30}, \Psi_{35}$ | 1.111 | $c_{22} = 0.158$  
$c_{27} = 0.102$  
$c_{32} = -0.009$  
$c_{25} = 0.349$  
$c_{30} = 0.246$  
$c_{35} = -0.134$ | Based on $\Psi_{(xyz)}$ equation (I.4)  
(or $\Psi^{\left( \begin{array}{ccc} y & x & x \\ x & y & x \\ x & x & y \end{array} \right)}$ equation (I.7)) |
| $\Psi_{22}, \Psi_{25}$  
$\Psi_{23}, \Psi_{24}, \Psi_{26}$ | 1.173 | $c_{22} = 0.238$  
$c_{25} = 0.414$  
$c_{23} = 0.098$  
$c_{24} = -0.142$  
$c_{26} = 0.108$ | Based on $\Psi^{\left( \begin{array}{ccc} y & x & x \\ x & y & x \\ x & x & y \end{array} \right)}$ equation (I.10) |
| $\Psi_{22}, \Psi_{25}$  
$\Psi_{30}, \Psi_{35}, \Psi_{24}$ | 1.106 | $c_{22} = 0.285$  
$c_{25} = 0.569$  
$c_{30} = 0.001$  
$c_{35} = -0.079$  
$c_{24} = 0.065$ | Based on $\Psi^{\left( \begin{array}{ccc} y & x & x \\ x & y & x \\ x & x & y \end{array} \right)}$ equation (I.9) |

I.4 Conclusions

At 30K LiMg$_{0.5}$Mn$_{1.5}$O$_4$ undergoes a second order transition to a magnetically ordered state with a ferromagnetically ordered component equivalent to 2.3$\mu_B$ per manganese ion in $5 \times 10^4$Oe. This is significantly less than the expected value of 3$\mu_B$/Mn. Landau theory requires that all of the basis vectors involved in such a transition must belong to the same irreducible representation (IR). Representational analysis found that the magnetic structure was composed of 36 basis vectors in 5 IRs; only $\Gamma_5$ contains basis vectors with non-zero net moments, thus the basis vectors involved in the ferromagnetic
transition must belong to this IR. Candidate structures, generated by linear combination of these basis vectors, which could account for the observed saturation moment and that also fulfil the physical criterion of having moments of the same magnitude on each manganese ion, have been specified. The candidate structures were then tested by Rietveld refinement, with the SARAh refine program, of the coefficients of each of the basis vectors employed in each candidate structure. A simple model of ferromagnetic ordering along \([100]\), annotated \(\psi_{(100)}\), gave a very good fit to the data, and none of the other, more complex, structures was demonstrably superior in terms of the goodness-of-fit index, \(\chi^2\). This model cannot, however, explain the reduced saturation moment. Many of the candidate structures that could account for the observed saturation moment were ruled out because they gave a very poor fit to the diffraction pattern. There was one candidate structure, annotated \(\Psi_{y\ X\ X\ Y\ X\ X\ Y}\), comprising of a ferromagnetic component along \([100]\) and a mixture of ferromagnetic and antiferromagnetic components along \([010]\) and \([001]\), which both gave a slightly better fit and offered an explanation for the reduced moment. The resolution of the available diffraction data is not sufficient to distinguish between the \(\psi_{(100)}\) and \(\Psi_{y\ X\ X\ Y\ X\ X\ Y}\) models, but the combination of representational analysis and Rietveld refinement has ruled out all the other alternatives that were previously specified.

I.5 References

