

Magnetism of the columnar ordered quadruple perovskite manganites

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Abstract

This thesis studies the magnetism of the $A'_2A''A'''Mn_4O_{12}$ columnar ordered quadruple perovskite manganites. The magnetic structures of five distinct members of this family of manganite perovskites has been determined using neutron scattering and magnetometry measurements. Point charge calculations of the crystal electric field, percolation calculations and a symmetry and group theoretical based approach to data analysis has been used to motivate the microscopic origins of the determined magnetic phases, and the physical mechanisms driving the observed magnetic phase transitions. Four regions of the magnetic phase diagram have been observed; a collinear ferrimagnetic phase, a Γ -point canted ferrimagnetic phase, a Z-point canted ferrimagnetic phase, and a magnetic phase characterised by well correlated collinear ferrimagnetic order punctuated by randomly dispersed clusters of antiferromagnetic order. We show that competing superexchange interactions and disorder can tune these manganites into different magnetically ordered phases.

In these systems we observe two mechanisms for driving spin reorientation phase transitions. In $Tm_2MnMnMn_4O_{12}$ the competition between rare-earth (Tm^{3+}) and transition metal (Mn) anisotropies coupled via $f-d$ exchange drives the spin reorientation, as is typical for distorted perovskites. In $R_2CuMnMn_4O_{12}$ ($R = Y$ or Dy) an alternative paradigm for spin reorientation was observed, which originated in frustrated Heisenberg exchange interactions, and the competition between Dzyaloshinskii-Moriya and single-ion anisotropies. Our studies on magnetic dilution in the $Sm_2MnMnMn_{4-x}Ti_xO_{12}$ systems have shown that they demonstrate an unusual variation in transition temperature, suggesting a departure from mean field physics. We observed a spin doped Griffiths phase in $Y_2MnMnMn_4O_{12}$, and the coexistence of two magnetically distinct phases below T_c .

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For me, science has involved the pursuit of new knowledge by using experimentation, logic and a little imagination. I am incredibly grateful to have grown up in the UK, where an education and a creative mindset is valued, and where I have been given the opportunity to follow my interests. Science has provided an interest that at times has consumed me, and for that I am grateful. I am thankful that there is so much yet to be discovered, and that our universe has many complexities that go beyond our present understanding.

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All I knew of Oxford were the cute pubs and narrow lanes. Meeting people who study the philosophy of jazz, glancing up to see Jocelyn Bell Burnell walking past, or bumping into former Australian prime ministers creates an environment like none other. I am incredibly proud to be part of a university committed to academic excellence. I have been inspired by all the brilliant, powerful and confident women that I have met in Oxford, something I had never come across on a daily basis before. It has been a complete adventure, I am not the same as when I started and I am thankful for the way it has shaped me.

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for my mum and dad

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*It is not knowledge, but the act of learning, not possession, but the act of getting there,
which grants the greatest enjoyment.*

Johann Carl Friedrich Gauss

Chapter 1

Introduction

In this chapter a brief overview of the topics in magnetism that are relevant to the $A'_2A''Mn_4O_{12}$ columnar ordered quadruple perovskites is given. All systems presented in this thesis are insulating, and therefore I shall exclusively discuss the magnetism of systems with well localised electronic wavefunctions. In the second half of the introduction, an overview of the magnetism of the related family of manganese perovskites, $AMnO_3$ and $AA'_3Mn_4O_{12}$ is given. Finally an introduction to the $A'_2A''B_4O_{12}$ columnar ordered quadruple perovskites is made.

1.1 Magnetism

The response of an atom to an externally applied magnetic field varies according to the electronic configuration of the atom. For atoms in which the ground state electronic configuration has finite angular momentum, a paramagnetic response to an applied magnetic field is observed, which is characterised by a rapid increase of the magnetisation as the temperature is lowered and a gradual saturation of the magnetisation as the temperature tends to 0 K. Curie's law, derived by obtaining the expression for the expected value of the magnetic moment after applying Boltzmann statistics over the $2J + 1$ manifold of angular momentum states of the atom, successfully models the variation of the magnetisation with field and temperature using a Brillouin function [1] (see Sec. 9.1 of the Appendix for further details). The

temperature dependence of the magnetisation originates in the statistical population of the energy levels in the atom, such that as the temperature is lowered, the ground state tends towards maximum occupation, and the magnetic moment towards its maximum moment value, as shown in Fig. 1.1. There are two distinct regions in the paramagnetic dependence of the magnetisation with applied field. A region in which the response of magnetisation with applied field is almost linear, from which one can obtain the effective moment of the atom (the gradient of the slope), and a saturated regime, in which the magnetic moments tend to a maximum $g_J J$ value, where g_J is the Landé g -value (defined in Sec. 9.1 of the Appendix).

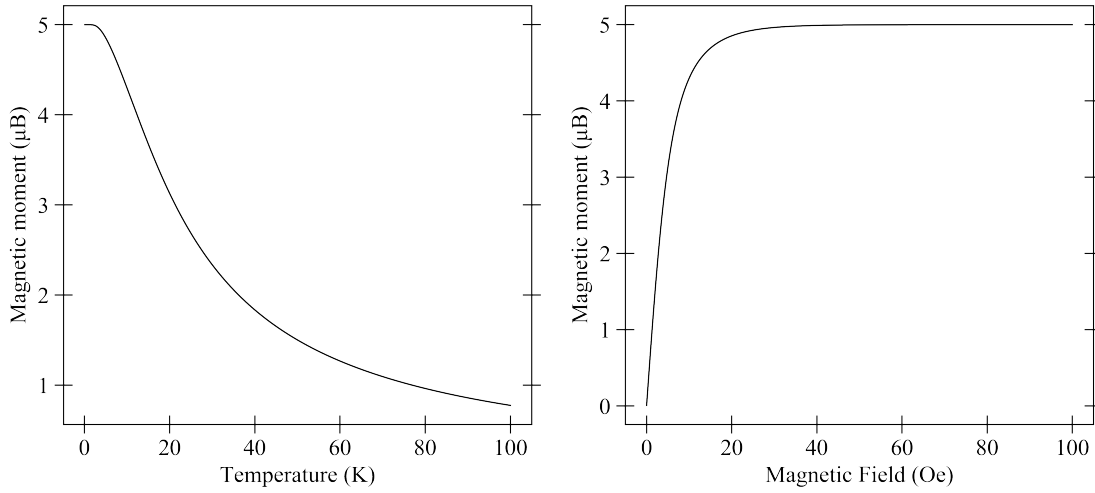


Figure 1.1: Paramagnetic dependence of the magnetic moment of an atom with $J, L, S = 5/2, 0, 5/2$ as a function of (a) temperature and (b) applied magnetic field.

A more rigorous treatment of the response of an atom under an applied magnetic field will bring about additional terms besides the Langevin paramagnetism described above. Treating the effect of the magnetic field as a perturbation to the system, one can obtain first and second order changes to the energy, known as diamagnetism and Van Vleck paramagnetism. The diamagnetic term corresponds to a shift in the ground state energy and contributes a negative term in the susceptibility that opposes the direction of the applied field. Van Vleck paramagnetism originates in the mixing of higher energy levels with the ground state due to the finite magnetic field, and is only significant when the separation between the ground and excited J states is small [2]. Both terms are typically quite small and temperature independent, and so are only experimentally observable in the absence of Langevin paramagnetism.

In strongly correlated electron systems, such as the ones studied in this thesis, there are many atoms, on

the order of at least 10^{23} atoms in a given system. And, if there exist interactions between these atoms, then at a certain temperature, T_c , these interactions will dominate over thermal effects and give rise to an ordered phase. The interactions of greatest strength are those that originate in the exchange of electrons between different atomic sites and are known as exchange interactions. Electrons are fermions and thus are required to have antisymmetric wavefunctions under exchange symmetry, as set by the Pauli exclusion principle. The antisymmetric symmetry requirement of the wavefunction restricts the allowed spin and spatial configurations that the electrons can adopt. For instance consider direct exchange between two electrons occupying nearest neighbour atomic sites. If one assumes that the orbital angular momentum of the electron is quenched, so that the spatial and spin parts of the wavefunction describing the two electron state can be separated [3], then the symmetry requirements impose that of the two spatial and spin functions one must be symmetric, and the other antisymmetric. This requirement establishes two sets of wavefunctions, one the product of the antisymmetric spatial function and symmetric spin function and the other the product of the symmetric spatial function and antisymmetric spin function. Physically the two wavefunctions correspond to spin functions with a quantum number S of either 0 or 1, and have degeneracy of one and three respectively so are known as the singlet and triplet states. The systems discussed in this thesis have many electrons, and thus an analysis of the allowed spin configurations is not as straightforward to determine. Other methods can be used to determine the possible spin configurations, such as the Goodenough Kanamori Anderson (GKA) rules, which are discussed later in Sec. 3.2.1. Besides the symmetry requirements of the wavefunction, there exist two contending energy terms that govern the interaction process; kinetic energy, t , is gained through the process of electron hopping which drives the system to adopt delocalised electronic wavefunctions, whilst the coulomb repulsion, U , from the electron-electron interaction localises the electronic wavefunctions. In insulating systems it is typical for $U \gg t$, and as such the ions in the system form weak bonds which increases the space the electron can hop whilst minimising its Coulomb repulsion.

1.1.1 Magnetic interactions

Superexchange interactions dominate the magnetic interactions in insulating systems, and occur between two magnetic ions separated by a non-magnetic ion. The systems studied in this thesis are made up of both transition metal (TM) and rare earth (RE) magnetic cations separated by non magnetic oxygen anions. Two forms of superexchange interactions are considered, the symmetric Heisenberg exchange and antisymmetric Dzyaloshinskii Moriya (DM) exchange.

Heisenberg exchange is maximised when spins on neighbouring magnetic atoms are collinear, while DM exchange is maximised when the spins are aligned perpendicular with respect to the other. The energy contribution of the exchange interactions are given by Eqns. 1.1 and 1.2 respectively, where $\mathbf{S}_i$ is the spin on the i^{th} atom, $\mathbf{S}_j$ the spin on the j^{th} atom, $\mathcal{J}_{ij}$ is the exchange integral (assumed to be isotropic) and $\mathbf{D}_{ij}$ is the DM vector. The two exchange interactions arise from different physical mechanisms. Symmetric exchange originates in spin-spin coupling, and antisymmetric exchange arises due to a spin-orbit coupling (a relativistic effect) and as such the two are not equally responsible for the magnetism in insulating compounds. Rather symmetric exchange interactions tend to dominate, while antisymmetric DM interactions play a smaller role and typically gives rise to canting or incommensurate modulations of otherwise collinear structures.

$$\mathcal{H}_{\text{sym}} = \sum_{i>j} \mathcal{J}_{ij} (\mathbf{S}_i \cdot \mathbf{S}_j) \quad (1.1)$$

$$\mathcal{H}_{\text{asym}} = \sum_{i>j} \mathbf{D}_{ij} \cdot (\mathbf{S}_i \times \mathbf{S}_j) \quad (1.2)$$

The dot product between two spins is a scalar, and therefore to ensure the superexchange energy is scalar, $\mathcal{J}_{ij}$ must also be a scalar. In this thesis I adopt the convention that the ground state of a system is obtained when the energy of a system is minimised, as such a positive $\mathcal{J}_{ij}$ value corresponds to antiferromagnetic exchange and a negative value to ferromagnetic exchange. Unlike direct exchange, which involves the hopping of an electron between two magnetic sites, symmetric superexchange involves the transfer of

an electron from one site to another via an intermediary ligand (oxygen anions for the columnar ordered quadruple perovskites). The transfer of the electron between the p -orbital of the oxygen anion and an occupied d -orbital of the transition metal ion, involves a charge-transfer energy, which must also be taken into account when evaluating the magnitude of the exchange integral, in addition to the hopping and kinetic energy terms. By mapping the Hubbard model to a spin 1/2 Heisenberg system in the limit that $U \gg t$ with one electron per site, one can show that the exchange constant $\mathcal{J}$, is equal to $4t^2/U$ [4].

The GKA rules have been successfully used to predict whether a TM-O-TM¹ symmetric superexchange interaction is antiferromagnetic or ferromagnetic by using the oxidation state, crystal electric field environment and orbital orientation of the transitional metal ions [5, 6, 7, 8, 9]. The GKA rules can largely be summarised as follows; for 180° TM-O-TM bonds the exchange between two half occupied d orbitals gives rise to antiferromagnetism, while exchange between a half occupied and empty d orbital will give rise to ferromagnetism. If the TM-O-TM is 90° the former interaction becomes ferromagnetic and the latter antiferromagnetic [6]. The exchange is classified into two types, $p\sigma$ superexchange if the overlap is along the bond axis, and $p\pi$ superexchange if the orbital overlap occurs above and below the bond axis, with the latter weaker in strength. Despite the simplicity of the rules, they are remarkably successful in explaining the majority of the magnetic structures of the manganite perovskites as shown in Sec. 1.2.

Dzyaloshinskii showed that there is a macroscopic property of a system, defined as the Dzyaloshinskii vector, that is energetically favourable when two magnetic sublattices are arranged perpendicular to one another [10]. Moriya related this microscopically as arising from a perpendicular arrangement of two nearest neighbour spins [11]. As the spin of each ion transforms as a time reversal odd axial vector, $\mathbf{D}_{ij}$, the local DM vector, must transform as a time reversal even axial vector that is antisymmetric under exchange, to ensure the energy is a scalar quantity. Therefore $\mathbf{D}_{ij}$ can only exist on bonds that do not have inversion symmetry. Further conditions are imposed on $\mathbf{D}_{ij}$ depending on the symmetry of the bond. In general a uniform DM interaction (i.e. when the DM interaction points in the same direction across nearest neighbour bonds) will give rise to incommensurate modulations of the magnetic structure, while a staggered DM interaction will give rise to spin canting.

¹This is true for TM with no large spin orbit coupling.

Besides exchange interactions, it is also possible to give rise to ordered magnetic states through the long range dipole-dipole interaction, although these are only expected to contribute at very low temperatures, on the order of ~ 0.1 K. The contribution to the energy of the system due to the interaction between two dipoles, $\boldsymbol{\mu}_1$ and $\boldsymbol{\mu}_2$ with vector $\mathbf{r}$ separating the dipoles, is given by Eqn. 1.3 [12].

$$\mathcal{H}_{\text{dip}} = \frac{\mu_0}{4\pi r^3} [\boldsymbol{\mu}_1 \times \boldsymbol{\mu}_2 - \frac{3}{r^2} (\boldsymbol{\mu}_1 \times \mathbf{r})(\boldsymbol{\mu}_2 \times \mathbf{r})] \quad (1.3)$$

1.1.2 Mean field theory

Phase transitions are activated by correlations between the electrons of the system, and the temperature at which the system transitions from the paramagnetic phase to an ordered magnetic phase is determined by the strength of the exchange interactions, the degree of magnetic frustration in the system, the dimensionality of the system and other interactions that may be present. Below T_c the evolution of the magnetisation with temperature can be modelled by mean field theory, which assumes all magnetic interactions of the system can be lumped into a single mean field that affects all magnetic ions equally. Despite a lack of details about the nature of the interaction, mean field theory correctly predicts a number of macroscopic behaviours of a system such as the paramagnetic temperature dependence of systems with ferromagnetic and antiferromagnetic exchange interactions. One can derive an expression for the temperature dependence of the magnetisation for magnetically ordered systems (Sec. 9.1 of the Appendix), in a similar way to the derivation of Curie's law, with the exception that the total field now includes a term that is proportional to the magnetisation (the mean field), which gives a pair of simultaneous equations that can only be solved graphically. From this derivation it can be shown that the extrapolated value of the x-intercept of the inverse susceptibility (Weiss constant), is negative for antiferromagnets, positive for ferromagnets and 0 for paramagnets [12], and its absolute value provides an estimate for the transition temperature. Mean field theory has been shown to correctly predict critical exponents of parameters and universality classes quite exactly. Nevertheless it does have its limitations and for instance, does not work well in the presence of fluctuations.

1.2 Manganite perovskites

The arisotype perovskite has cubic symmetry of space group $Pm\bar{3}m$. The lower symmetry perovskite structures (the hettotypes), of which there are fifteen distinct families [13], are structural distortions of the arisotype such that each family freezes in a different normal structural mode corresponding to a distinct octahedral tilting pattern. Common to the manganite perovskites is the establishment of a cooperative Jahn Teller (JT) effect in the presence of JT active Mn^{3+} ions, which also corresponds to a freezing in of a unique structural mode of the high symmetry parent perovskite structure. The Jahn Teller effect lifts the degeneracy of orbitals through a geometrical distortion of the electron density, and gives rise to unique and complex forms of orbital order in the manganite perovskites, which are ultimately responsible for their rich and varied magnetic phase diagrams.

1.2.1 Simple $AMnO_3$ manganite perovskites

The ABO_3 ($B = Mn$) manganite perovskites have an octahedral tilting pattern of $a^+b^-b^-$ (in Glazer notation [14]), which gives rise to a crystal structure with orthorhombic $Pbnm$ symmetry, as shown in Fig. 1.2(a). A great wealth of different magnetic phases are observed corresponding to changes in the oxidation state of the B-site Mn ions, which can be tuned by choice of A-site cation. In the case where the A-site is occupied by a trivalent cation such as La^{3+} , the B-site sublattice is occupied by Mn^{3+} , and an L-type antiferromagnetic (AFM) structure is observed (Fig. 1.3)^{2 3}. The orientation of the e_g orbitals in the ab plane rotate by 90° between nearest neighbour ions [17], as shown in Fig. 1.4(b) and Fig. 1.4(c), to optimise the packing of the orbitals and therefore minimise the lattice strain. The consequence of this orbital ordering is that $p\sigma$ superexchange is mediated in the ab plane by half occupied $d_{3z^2-r^2}$, Fig. 1.4(b), and empty $d_{x^2-y^2}$ orbitals, Fig. 1.4(c), giving rise to ferromagnetic exchange. Exchange between

²Note in the literature [15] the L-type structure is referred to as A-type. However to avoid confusion with labelling of magnetic modes adopted later in the thesis, this structure is referred to as L-type.

³Note that for $A = Ho$ to Yb E-type antiferromagnetic order is observed owing to a competition between the antiferromagnetic exchange mediated by the half occupied orbitals in the ab plane and the ferromagnetic exchange mediated by the e_g orbitals [16].

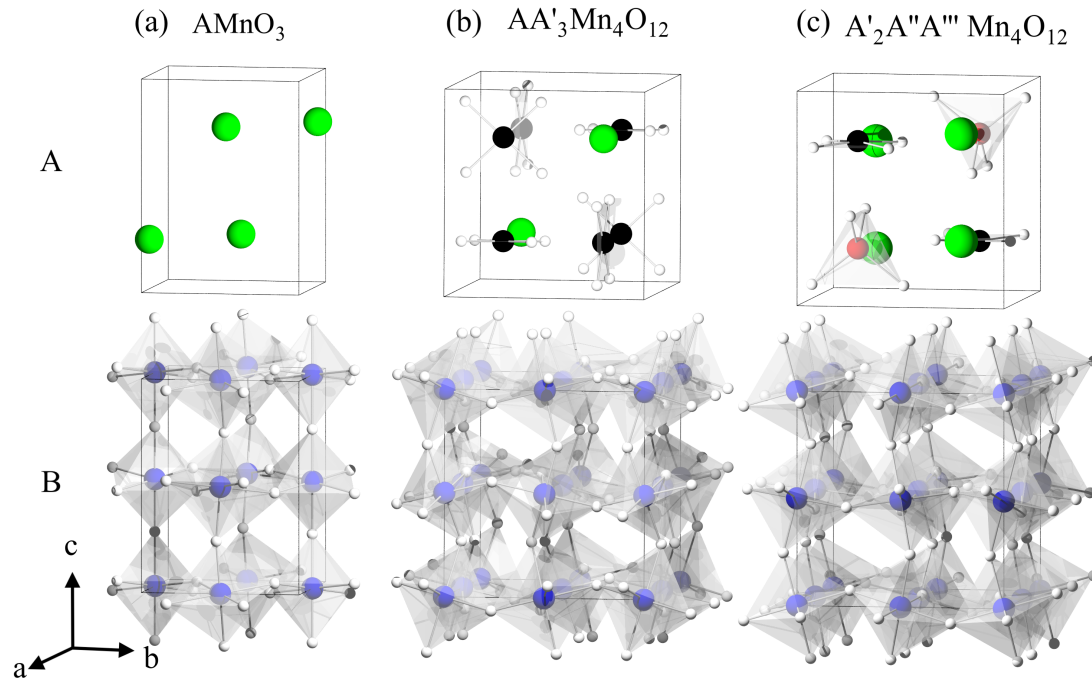


Figure 1.2: Crystal structure of the (a) $AMnO_3$ manganite perovskites in the $Pbnm$ orthorhombic symmetry showing the A-sites in green, the Mn B-sites in blue and O²⁻ anions in white. (b) The $AA'_3Mn_4O_{12}$ manganite perovskites in the $I2/m$ monoclinic symmetry with an origin shift of $(1/4, 1/4, 1/4)$ showing the A-sites in green, the square planar coordinated Mn A' sites in black, the Mn B-sites in blue and the O²⁻ anions in white. (c) The $A'_2A''A'''Mn_4O_{12}$ perovskites in the $P4_2/nmc$ tetragonal symmetry showing the A' sites in green, the square planar A'' sites in black, the tetrahedrally coordinated A''' sites in red, the Mn B sites in blue and O²⁻ anions in white. The BO₆ octahedra are shaded in grey.

the ab layers is antiferromagnetic due to the $p\pi$ superexchange interactions between the half occupied t_{2g} orbitals, Fig. 1.4(d) and Fig. 1.4(e). If the B-site are composed of only Mn^{4+} instead of Mn^{3+} , which can be achieved by the substitution of divalent cations on the A-sites, both B-site e_g orbitals are empty and superexchange in the ab plane is mediated via the half occupied t_{2g} orbitals, Fig. 1.4(f) to Fig. 1.4(j), giving rise to AFM coupling between nearest neighbour spins and a G-type antiferromagnetic structure, as observed experimentally in $CaMnO_3$ [15].

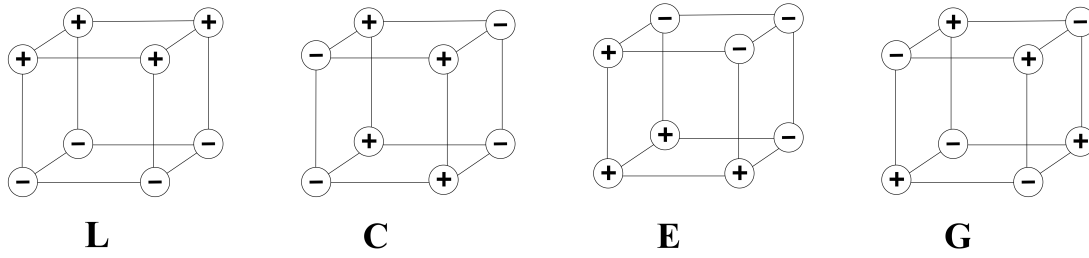
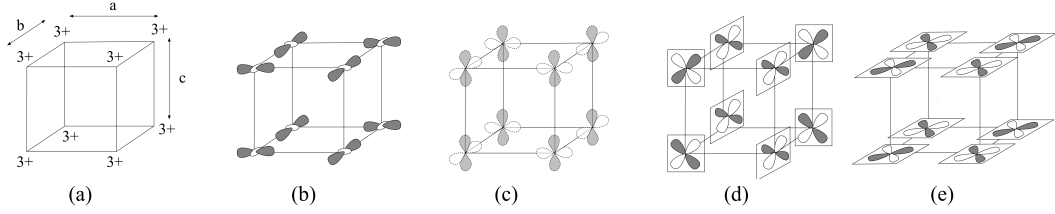


Figure 1.3: Common magnetic structures of the manganite perovskites. The circles represent Mn ions and the plus and minus signs indicate the amplitude of the magnetic moment on a given Mn ion.

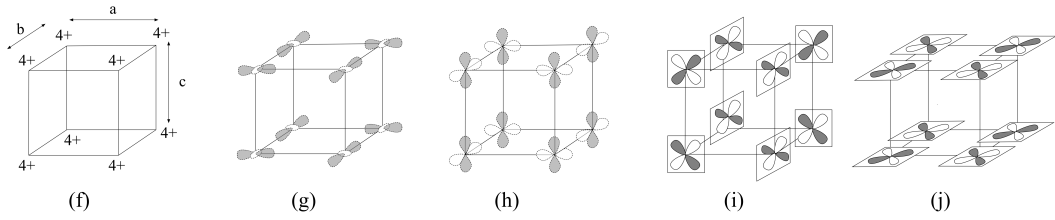
When there is 50% Mn^{3+} and 50% Mn^{4+} on the B-sites a checkerboard arrangement of charge and orbital ordering is stabilised [5, 18] that minimises the coulomb repulsion between the sites, giving rise to zig-zag spin chains of the CE-type magnetic structure as shown in Fig. 1.4(l). Once again the GKA rules can explain the appearance of CE-type structure; along the chains exchange is mediated via half occupied $d_{3z^2-r^2}$ on the Mn^{3+} and empty e_g orbitals of the Mn^{4+} making the interaction ferromagnetic, while exchange between half occupied t_{2g} orbitals give rise to antiferromagnetic coupling between zig-zag spin chains. Along c the interaction is antiferromagnetic, because exchange is mediated between half occupied t_{2g} orbitals. Note that the $d_{x^2-y^2}$ orbitals pointing along c are empty and therefore do not mediate exchange. There exists a ferromagnetic ordering of the B-site sublattice for compositions of $La_xM(II)_{1-x}MnO_3$ where $0.2 < x < 0.4$. This cannot be explained by the GKA rules as the system is metallic in this composition range and the assumptions of localised electronic wavefunctions are no longer valid. Instead ferromagnetic exchange is mediated by the e_g electron of the Mn^{3+} hopping directly to the Mn^{4+} ion via the ferromagnetic double exchange mechanism [19]. For $Pr_{1-x}Ca_xMnO_3$, the insulating state is retained at all values of x , and for $Pr_{0.7}Ca_{0.3}MnO_3$ a pseudo CE phase is stabilised, Fig. 1.4. The pseudo CE phase has the same CE charge, orbital and spin order in the ab plane but with a fer-

romagnetic interlayer coupling along c . This is because in this system any additional electron density is randomly placed into the $d_{x^2-y^2}$ orbitals oriented along the c axis, as opposed to disrupting the CE order in the ab plane, and so some of the exchange interactions along c are mediated between half occupied and empty d orbitals giving rise to a net ferromagnetic exchange along c [20].

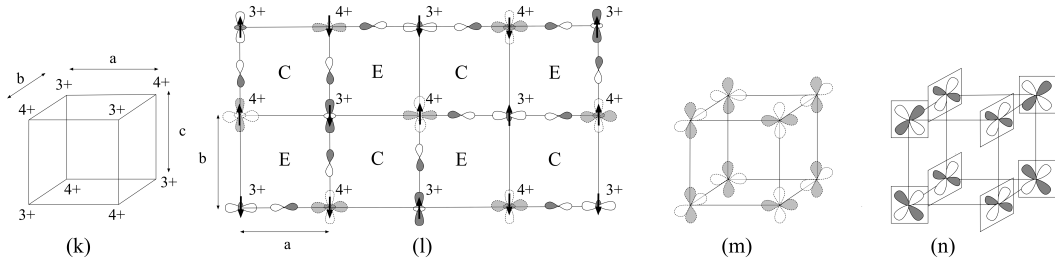
LaMnO₃



CaMnO₃



La_{0.5}Ca_{0.5}MnO₃



Pr_{0.7}Ca_{0.3}MnO₃

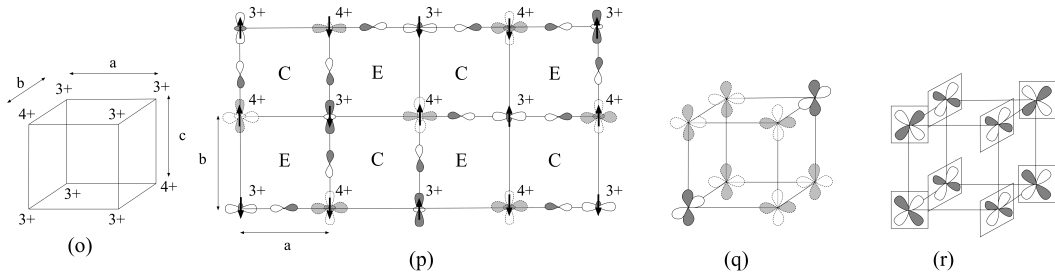


Figure 1.4: Charge and orbital structures (showing only the $3d e_g$ and t_{2g} orbitals) of the B-site Mn ions in (a) - (e) LaMnO₃ (f) - (j) CaMnO₃ (k) - (n) La_{0.5}Ca_{0.5}MnO₃ (o) - (r) Pr_{0.7}Ca_{0.3}MnO₃. Half-filled orbitals are drawn with solid lines and empty orbitals with dotted lines.

1.2.2 The $AA'_3B_4O_{12}$ quadruple perovskite manganites

The $AA'_3B_4O_{12}$ quadruple perovskites have an $a^+a^+a^+$ octahedral tilting pattern, which accommodates Mn on the A sites in a square planar coordination (Fig. 1.2(b)) and introduces A-B superexchange interactions that are mediated between two d orbitals (d - d A-B exchange) to the perovskite framework. In comparison for the simple $AMnO_3$ perovskite manganites, A-B exchange interactions are only mediated between the d -orbital of the Mn and the f -orbital of the rare-earth (RE) ion. A common magnetic ordering observed in a number of the $AA'_3B_4O_{12}$ quadruple manganites is that of C-type antiferromagnetic order on the B-site sublattice, and a collinear ferrimagnetic A-site sublattice, as shown for $A = La^{3+}$, Ce^{3+} , Sm^{3+} , Eu^{3+} and Y^{3+} [21, 22, 23]. Once again the GKA rules can largely explain the observed magnetic structures. For A occupied by a trivalent cation all B-site ions are Mn^{3+} and the half occupied $d_{3z^2-r^2}$ orbitals lie in the ac plane rotating by 90° between nearest neighbour Mn B sites lowering the symmetry to monoclinic $I2/m$ such that the octahedral tilts are now $a^+b^+c^+$ [24]. This orbital ordering is analogous to the ordering found in the simple perovskite manganites. If the B-site Mn-O-Mn bonds were 180° this would then give rise to ferromagnetic order in the ac plane and antiferromagnetic order along b , an L-type antiferromagnetic structure. However the Mn-O-Mn bond angles are between 135 - 140° , closer to the 90° Mn-O-Mn bond, and so it could be therefore argued that one should expect antiferromagnetic order in the ac plane and ferromagnetic order along b - the C-type antiferromagnetic sublattice, which is exactly the experimental observation! The Mn A sites are arranged in chains of square planar coordinated Mn ions that run parallel to the a axis, such that the square planar coordination rotates by 90° from one ion to the next in the chain, Fig. 1.5. There are no direct superexchange pathways between the A' sites, and it is unclear what gives rise to the ferromagnetic exchange observed experimentally. One of the Mn A' sites does not form part of these chains, and instead is sandwiched between the trivalent A sites, Fig. 1.5, and adopts a ferromagnetic sublattice, but which is antiferromagnetic with respect to the rest of the Mn A' sites such that a net ferrimagnetic A' site sublattice is observed, perhaps a consequence of f - d exchange interactions.

In $NaMn_7O_{12}$ the A' Mn ions are still in the +3 oxidation state, however the B-site ions are equally

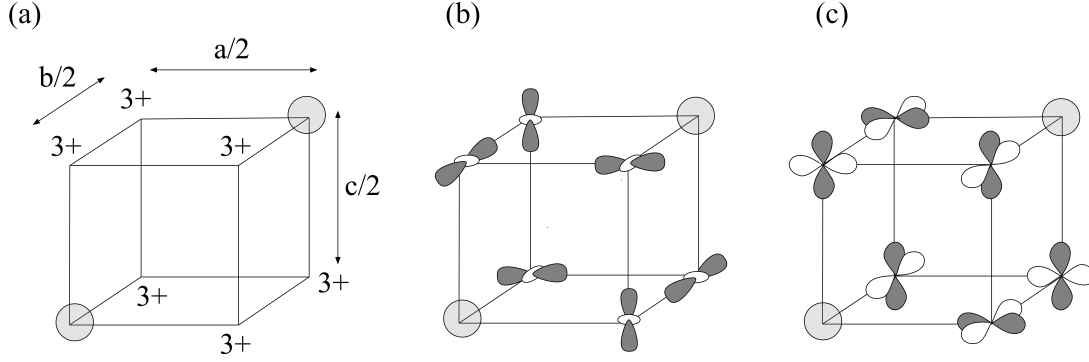


Figure 1.5: Proposed charge and orbital structure of the $R^{3+}\text{Mn}_3\text{Mn}_4\text{O}_{12}$ Mn A' sites showing the (b) half occupied $d_{3z^2-r^2}$ orbitals and (c) the half occupied t_{2g} orbitals. The circles represent the R^{3+} ions.

occupied by Mn^{3+} and Mn^{4+} , giving an average oxidation state of +3.5. The mixed valence B sites give rise to the same checkerboard arrangement of charge, orbital and magnetic order as seen in the CE phase of $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ [25]. If the B sites are doped with electrons, for instance in $\text{Na}_{1-x}\text{Ca}_x\text{Mn}_7\text{O}_{12}$, one obtains an incommensurate pseudo CE (ipCE) phase. The extra electron density moves onto the $d_{x^2-y^2}$ orbital oriented parallel to c , in analogy to the pseudo CE phase of $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$, giving rise to ferromagnetic coupling between the B site layers. The incommensurate order is driven by the magnetic coupling of the B sites to the A sites, which is unique to the quadruple perovskite manganites as in these systems both sites order by the same propagation vector and can give rise to a phenomenological coupling term that is quadratic in the spins, which is not true for the simple perovskite manganites [26]. In $\text{CaMn}_7\text{O}_{12}$, the Mn A' sites continue to remain in the +3 oxidation state, however the B-sites have an average oxidation state of +3.25 which corresponds to 75% Mn^{3+} and 25% Mn^{4+} . The occupation of the B site Mn^{3+} $d_{x^2-r^2}$ and $d_{y^2-r^2}$ orbitals alternates according to an orbital density wave that emerges below 250 K [27] and gives rise to a nearly-constant-moment magnetic helix but with a modulated spin helicity [28].

1.2.3 The $A'_2A''A'''Mn_4O_{12}$ columnar ordered quadruple perovskite manganites

By rotating the BO_6 octahedra of the arisotype perovskite structure, according to an $a^+a^+c^-$ tilting pattern, a tetragonally distorted perovskite structure of symmetry $P4_2/nmc$ with three crystallographically distinct A sites (labelled A' , A'' and A''' ⁴) and with a stoichiometry of $A'_2A''A'''B_4O_{12}$ was created. The first such perovskite with this structure and stoichiometry, $CaFe_3Ti_4O_{12}$, was synthesised in 1995 [30]. Since then a number of perovskites with the same structure and stoichiometry have been synthesised [31], which have been shown to have ferroelectric properties [32], and spin-reorientation phase transitions [33, 34]. In the last four years it has been possible to synthesise the $A'_2A''A'''B_4O_{12}$ perovskites where the entire B site is occupied by Mn [29]. This has been achieved through a high pressure high temperature synthesis technique that creates powder samples of between $\sim 80 - 100$ mg in mass [35]. The oxidation state of the B-site Mn ions are once again determined by the oxidation state of the A sites, however in comparison to the simple perovskite manganites, the octahedral tilts are rigid and create a fixed coordination environment, limiting the choice of cations that can be substituted into the A-sites. Half of the A-sites are occupied by A' , a quarter by A'' and the remaining quarter by A''' . The A' sites are 10 fold coordinated and have accommodated all rare earth ions (except Ce, Yb, Pm and Lu), Y^{3+} and Ca^{2+} [29]. The A'' sites are square planar coordinated and have accommodated Mn^{3+} , Mn^{2+} , Cu^{2+} and Fe^{2+} . The A''' sites are tetrahedrally coordinated and have accommodated Mn^{2+} , Cu^{2+} and Fe^{2+} . The A' sites form columns along c , where nearest neighbour ions rotate through the 4_2 screw that relates the two sites, as shown in Fig. 1.2(c). The Mn A' and A'' sites form c -axis chains alternating between square planar and tetrahedral oxygen coordinations, as shown in Fig. 1.2(c). When the entire B-site sublattice is occupied by Mn, the B-site ions charge and orbital order, which has the effect of lowering the symmetry to orthorhombic $Pmnn$ [29]. The B-sites are composed of alternating ab layers of Mn in the +3 and +3.5 (50% Mn^{4+} and 50% Mn^{3+}) oxidation states, stacked along c [35]. The Jahn-Teller active, octahedral oxygen coordinations of the B-site Mn^{3+} ions are elongated along z , lifting the degeneracy of

⁴Note that a slightly different labelling scheme is used in the literature [29]. In this thesis 'A-sites' is used to collectively refer to all three A' , A'' and A''' sites.

the e_g states and giving preferential electronic occupation of the $d_{3z^2-r^2}$ orbitals - a ferro-orbital order.

The presence of several crystallographically distinct sites occupied by magnetic atoms, affords the possibility of charge and spin doping strategies, which has been used to probe the magnetism in this family of manganites. In Chapter 4, the magnetic structures of $\text{Tm}_2\text{MnMnMn}_4\text{O}_{12}$ is reported. Here the inclusion of Tm^{3+} on the A' sites allowed the possibility of exploring the role of rare earth magnetism in the columnar ordered quadruple perovskite manganites. In Chapter 5, the magnetic structures of $R_2\text{CuMnMn}_4\text{O}_{12}$ ($R = \text{Y}$ or Dy) is presented, where the Cu^{2+} that is substituted onto the nominally Mn A" sites was used to weaken A"-B exchange interactions. In Chapter 6, the effects of tuning magnetic exchange interactions in the $\text{Sm}_2\text{MnMnMn}_{4-x}\text{Ti}_x\text{O}_{12}$ columnar ordered quadruple perovskite manganites by chemical substitution of nonmagnetic Ti^{4+} for B-site Mn^{3+} for $x = 1$, $x = 2$, and $x = 3$ is demonstrated. Finally in Chapter 7, the effects of 'spin doping', which was achieved by the replacement of magnetic Mn for non magnetic Y^{3+} , on the magnetism of $[\text{Y}_{2-x}\text{Mn}_x]\text{MnMn}_4\text{O}_{12}$ for $x = 0.21$ and $x = 0.16$ is explored.

Chapter 2

Experimental Methods

Neutron scattering is the primary experimental technique used to probe the magnetism in the $A'_2A''A'''Mn_4O_{12}$ columnar ordered quadruple perovskite manganites, and thus in this chapter an overview of neutron scattering, specifically discussing diffraction and small angle neutron scattering is given in Sec. 2.1. In Sec. 2.2 and Sec. 2.3, a brief description of magnetometry and electron paramagnetic resonance (EPR) is given as these are also used to probe the magnetic order in these systems.

2.1 Neutron scattering

By bombarding a sample with a beam of neutrons and subsequently observing the trajectory and energy of the scattered neutrons one can determine an enormous amount of information about both the nuclear and magnetic structure of a sample. Neutrons are spin 1/2 fermions and interact with nuclei via the strong force. Neutrons also possess a finite magnetic moment, which allows them to interact with the unpaired electrons of atoms via the magnetic dipole interaction. Because neutrons are electrically neutral they pass through the majority of the sample without interacting, which is ideal for probing the entire volume of a sample. In contrast x-rays interact strongly with the electronic density of each ion and thus typically only penetrate the surface of a material.

Experimentally it is the partial differential cross section that is measured in a neutron scattering experi-

ment, which is the proportion of the incident flux of a specific energy to be scattered into a solid angle Ω . To relate the partial differential cross section to the properties of the sample, which ultimately enables us to determine the results and significance of the experimental observations, a number of assumptions are made regarding the scattering process. It is assumed that the wavelength of the incident neutron is much larger than the range of the nuclear forces so that the neutron scattering is spherically symmetric. This is a good assumption for the neutrons used in scattering experiments, where the neutron wavelength is on the order of between 10^{-10} and 10^{-11} m, in comparison to the range of the nuclear force of approx. 10^{-14} to 10^{-15} m [36]. With this assumption one can describe the incident neutron by a plane wave characterised by its wavevector $\mathbf{k}$, and the scattered neutron by $-\frac{b}{r} \exp(i\mathbf{k} \cdot \mathbf{r})$, where b is the scattering length and $\mathbf{r}$ is the position vector of the atom [36]. Another significant assumption is that of the Born approximation, which assumes that the scattering events do not change the internal structure of the nuclei and as such the state of the system before and after the event can be considered to be the same. While the potential of the strong force is known, and well studied in nuclear physics, it is of no significance to the description of scattering as it only operates on short length scales and would not be able to describe the form of the neutron wavefunction once it reaches the detector. Thus the interaction potential between the neutron and nuclei is assumed to take the form of the Fermi pseudopotential $V(\mathbf{r}) = \frac{2\pi\hbar^2}{m} b\delta(\mathbf{r})$ (m is the mass of the neutron), which correctly gives an isotropic scattered neutron wavefunction, and allows the potential to be treated as a perturbation enabling the use of Fermi's golden rule to calculate the transition probability of the scattering event.

The scattering length, b , is dependent on the internal structure of the nucleus and does not change in a predictable way with the atomic number. It is a complex number where the imaginary component is related to the absorption cross section for the sample and its sign determines the phase change between the incident and scattered neutron [37]. For a given element the scattering length will vary across the sites according to both the spin state of the nuclei and the isotope number. It is therefore typical to use the average scattering length (coherent scattering length) in the expression for the cross section, calculated by weighting the cross sections of the individual isotopes by their relative abundances in nature. The coherent scattering length can be divided further into a part that corresponds to the $i + \frac{1}{2}$ spin state

of the combined neutron (spin $\frac{1}{2}$) and nuclei (spin i) and another part that describes the $i - \frac{1}{2}$ spin state. Deviations from the coherent scattering length give rise to incoherent scattering that is isotropic across all scattering angles and neutron wavevectors. The random variation of the scattering length with atomic number and for different isotopes is incredibly useful for providing contrast in neutron scattering experiments.

2.1.1 Crystallography

Scattering experiments are described in reciprocal space, which is a vector space containing the set of all wavevectors, $\mathbf{k}$. A crystal structure, which is the convolution of an atomic basis with a geometric lattice, is defined in reciprocal space by the set of wavevectors, $\mathbf{G}$, describing plane waves that have the periodicity of the direct lattice. The relationship between the direct space of a crystal, containing the set of all position vectors, $\mathbf{R}$, describing lattice points, and its reciprocal space is $\mathbf{G} \cdot \mathbf{R} = 2\pi n$. The relationships to convert between the bases of the two spaces are given by Eqns. 2.1, where $\mathbf{a}$, $\mathbf{b}$ and $\mathbf{c}$ are the direct lattice basis vectors and those with a $*$ are reciprocal lattice basis vectors.

$$\mathbf{a}^* = 2\pi \frac{\mathbf{b} \times \mathbf{c}}{\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})} \quad \mathbf{b}^* = 2\pi \frac{\mathbf{c} \times \mathbf{a}}{\mathbf{b} \cdot (\mathbf{c} \times \mathbf{a})} \quad \mathbf{c}^* = 2\pi \frac{\mathbf{a} \times \mathbf{b}}{\mathbf{c} \cdot (\mathbf{a} \times \mathbf{b})} \quad (2.1)$$

When working in reciprocal spaces, the metric tensor, $\mathbf{M}$, together with the form of the dot product in Eqn. 2.2, can be used to quickly compute the relationships between crystallographic directions, and is especially useful when working in non-orthonormal crystallographic settings. For computations in reciprocal space, $\mathbf{M}$, is replaced in the dot product between two reciprocal vectors by $(2\pi)^2 \mathbf{M}^{-1}$.

$$\mathbf{M} = \begin{pmatrix} \mathbf{a} \cdot \mathbf{a} & \mathbf{a} \cdot \mathbf{b} & \mathbf{a} \cdot \mathbf{c} \\ \mathbf{b} \cdot \mathbf{a} & \mathbf{b} \cdot \mathbf{b} & \mathbf{b} \cdot \mathbf{c} \\ \mathbf{c} \cdot \mathbf{a} & \mathbf{c} \cdot \mathbf{b} & \mathbf{c} \cdot \mathbf{c} \end{pmatrix} \quad \mathbf{p} \cdot \mathbf{q} = \begin{pmatrix} p_i \\ p_j \\ p_k \end{pmatrix} \mathbf{M} \begin{pmatrix} q_i & q_j & q_k \end{pmatrix} \quad (2.2)$$

Crystal structures are periodic and it is therefore typical to define a unit cell that when repeated in each of the three crystallographic directions can generate the full crystal structure. The choice of unit cell is often made to reflect the full symmetry of the crystal structure.

2.1.2 Diffraction

In this thesis I do not probe the full $\mathbf{w}$ and $\mathbf{k}$ space of a sample, rather the focus is on elastic and coherent scattering (diffraction), which involves integrating over the energy of the scattered neutrons to measure the differential cross section and probe $\mathbf{k}$ space. The differential cross section for elastic scattering from a fixed assembly of nuclei is given by Eqn. 2.3, where $\mathbf{Q}$ is the scattering wavevector (the difference between the incident and scattered wavevectors of the neutron), $\bar{b}_j$ is the coherent scattering length of atom j , $\mathbf{r}_j$ represents the position vector of atom j and the sum is taken over all atoms in the system [38].

$$\frac{d\sigma}{d\Omega} = \left| \sum_j \bar{b}_j \exp(i \mathbf{Q} \cdot \mathbf{r}_j) \right|^2 \quad (2.3)$$

The square root of the differential cross section (the scattering amplitude) is mathematically equivalent to the Fourier transform of the crystal structure. The periodicity of a crystal structure means that it is sufficient to consider diffraction from a single unit cell to determine the geometric conditions that would give rise to a diffraction peak. In doing so the scattering amplitude, $F(\mathbf{Q})$ can be separated into a part that sums over all the atoms in a unit cell, m , which is known as the structure factor $SF(\mathbf{Q})$, and a second part that sums over all the unit cells in the crystal structure, n , known as the lattice sum, as shown by Eqn. 2.4. The lattice sum over all position vectors will average to zero, unless $\mathbf{Q}$ is equal to a reciprocal lattice

vector $\mathbf{G}$, given the dot product between $\mathbf{G}$ and $\mathbf{R}$ is defined to be $2\pi n$. Thus a condition for diffraction is that $\mathbf{Q} = \mathbf{G}$. From the structure factor, Eqn. 2.5, it is possible to determine the conditions imposed on the h , k and l values that would give rise to a Bragg peak.

$$F(\mathbf{Q}) = \sum_m \bar{b}_m \exp(i \mathbf{Q} \cdot \mathbf{r}_m) \sum_n \exp(i \mathbf{Q} \cdot \mathbf{R}_n) \quad (2.4)$$

$$SF(\mathbf{Q}) = \sum_m \bar{b}_m \exp(i \mathbf{Q} \cdot \mathbf{r}_m) = \sum_m \bar{b}_m \exp(2\pi i (hx_m + ky_m + lz_m)) \quad (2.5)$$

In a diffraction experiment the condition for coherent scattering from equivalent crystallographic planes is given by Bragg's law, Eqn. 2.6, where λ is wavelength of the incident neutrons, θ is the angle of the scattered neutron beam, n is the order of the reflection and d is the distance between crystallographically equivalent planes.

$$n\lambda = 2d \sin \theta \quad (2.6)$$

Magnetic diffraction

The form of the potential describing the magnetic interactions between nuclei and neutrons is given by Eqn. 2.7; μ_n represents the neutron dipole moment and $\mathbf{B}(\mathbf{r})$ is the local magnetic flux, originating from the spin and orbital motion of the unpaired localised electrons.

$$V_M = -\mu_n \cdot \mathbf{B}(\mathbf{r}) \quad (2.7)$$

Once again Fermi's golden rule may be used to calculate the transition probability as the potential can be treated as a perturbation to the system. It can be shown [39] that the magnetic differential cross section for elastic scattering from crystalline systems with commensurate propagation vectors is given by Eqn. 2.8,

where N_m is the number of magnetic unit cells in the crystal, v_m represents the volume of the magnetic unit cell, $\mathbf{G}_m$ is a reciprocal lattice vector, $\mathbf{Q}$ is the scattering vector, $\bar{\mathbf{Q}}$ is the normalised scattering vector, and $F_M(\mathbf{Q})$ is the magnetic structure factor defined by Eqn. 2.9 and Eqn. 2.10.

$$\left(\frac{d\sigma}{d\Omega}\right) = N_m \frac{(2\pi)^3}{v_m} \sum_{\mathbf{G}_m} |F_{M\perp}(\mathbf{Q})|^2 \delta(\mathbf{Q} - \mathbf{G}_m) \quad (2.8)$$

$$F_{M\perp}(\mathbf{Q}) = \bar{\mathbf{Q}} \times (F_M(\mathbf{Q}) \times \bar{\mathbf{Q}}) \quad (2.9)$$

$$F_M(\mathbf{Q}) = \frac{\gamma r_0}{2\mu_B} \sum_m \boldsymbol{\mu}_m f_m(\mathbf{Q}) \exp(i\mathbf{Q} \cdot \mathbf{r}_m) \quad (2.10)$$

In the expression for the magnetic structure factor γ is 1.913, $r_0 = \frac{\mu_0 e^2}{4\pi m_e}$, μ_B is the Bohr magneton, $\boldsymbol{\mu}_m$ is the magnetic moment of an atom at position $\mathbf{r}_m$, $f_m(\mathbf{Q})$ is the magnetic form factor, and $\mathbf{m}$ is the position vector of an atom, where the sum is taken over all the magnetic atoms in the magnetic unit cell.

Unlike nuclear scattering, which is independent of $\mathbf{Q}$, the magnetic form factor rapidly diminishes with increasing $\mathbf{Q}$, as shown in Fig. 2.1. The magnetic form factor represents the Fourier transform of the unpaired electron density. When the neutrons pass straight through the sample, i.e $\mathbf{Q} \rightarrow 0$, the electron density scatters in phase and the magnetic form factor is maximal. As $\mathbf{Q}$ increases the electron density scatters out of phase and the magnetic form tends to zero, as is the case for the x-ray form factor [40] except that it falls off much more rapidly as it only scatters from unpaired electron density. To fully account for the magnetic interaction between the neutrons and nuclei one would need to consider all the terms in the multipole expansion of the charge density. However it is found that considering only the dipole term of this expansion is usually sufficient to describe the magnetic form factor. The expression for the magnetic form factor in the dipole approximation is given by 2.11 [41].

$$f(\mathbf{Q}) = \langle j_0(\mathbf{Q}) \rangle + \left(\frac{g_J - 2}{g_J} \right) \langle j_2(\mathbf{Q}) \rangle \quad (2.11)$$

Here the $\langle j_n(\mathbf{Q}) \rangle$ terms are the integral over the product of the spherical Bessel function for the angular momentum state in consideration together with the radial integral. P. J. Brown was able to calculate an analytic approximation for the $\langle j_n(\mathbf{Q}) \rangle$ terms by allocating electrons to each atom in a solid and by approximating the form factors as spherically symmetric [42, 41]. In Fig. 2.1 a plot of the magnetic form factors as a function of Q is given for the TM and RE ions that form the systems studied in this thesis. For TM ions the j_2 term is weighted by the deviation of the g factor from 2, which is typically very small and hence the magnetic form factor is dominated by the j_0 term. For instance for Mn ions the j_2 term will typically only contribute 1-2% towards the magnetic form factor [43] and for the case of Cu^{2+} [44] upto 15%. As such the j_0 is typically a good approximation for the magnetic form factor of the transition metal ions. This is not the case for the RE ions, as the j_2 term is weighted by the deviation of the g_J value from 2, which can vary quite significantly between different rare earth ions. For instance for Sm^{3+} there is a significant contribution from the j_2 term, which can be seen in the peak of the form factor at Q values of approx 5 nm^{-1} .

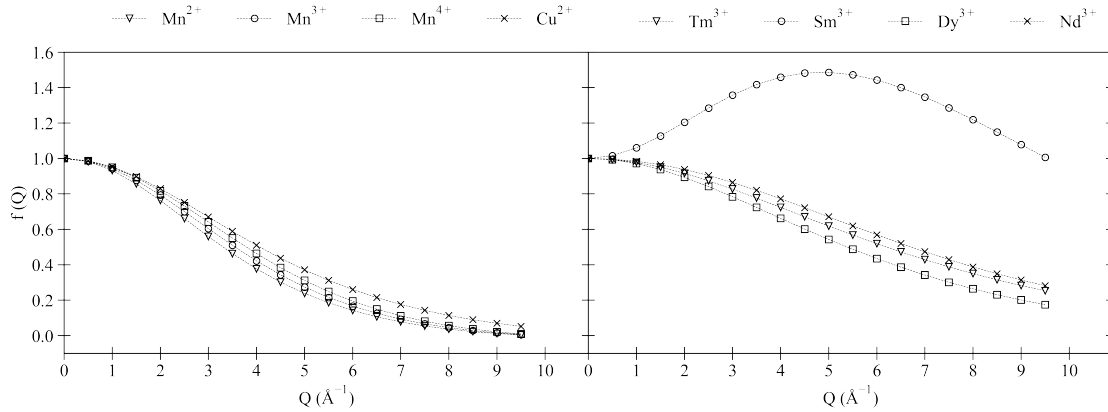


Figure 2.1: The calculated magnetic form factors using the dipole approximation, Eqn. 2.11, for the TM and RE ions studied in this thesis.

2.1.3 WISH at ISIS

The neutron diffraction experiments presented in this thesis were all conducted on powder samples using the time of flight diffractometer WISH at the ISIS neutron and muon facility [45]. In this section an overview of WISH and its key working principles is given. WISH has one of the largest bandwidth of

neutron wavelengths and provides high resolution over a wide Q range with a low background. As ISIS is a pulsed neutron source and neutrons are not continuously incident upon the sample, the incident flux is not high and it is necessary to use the entire spectrum of neutron wavelengths to perform the scattering experiment. Consequently the diffraction peaks are not measured as function of scattering angle as is the case for conventional lab based x-ray diffractometers, rather the diffraction experiment has a fixed geometry and diffraction patterns are measured at a fixed angle and as function of neutron wavelength.

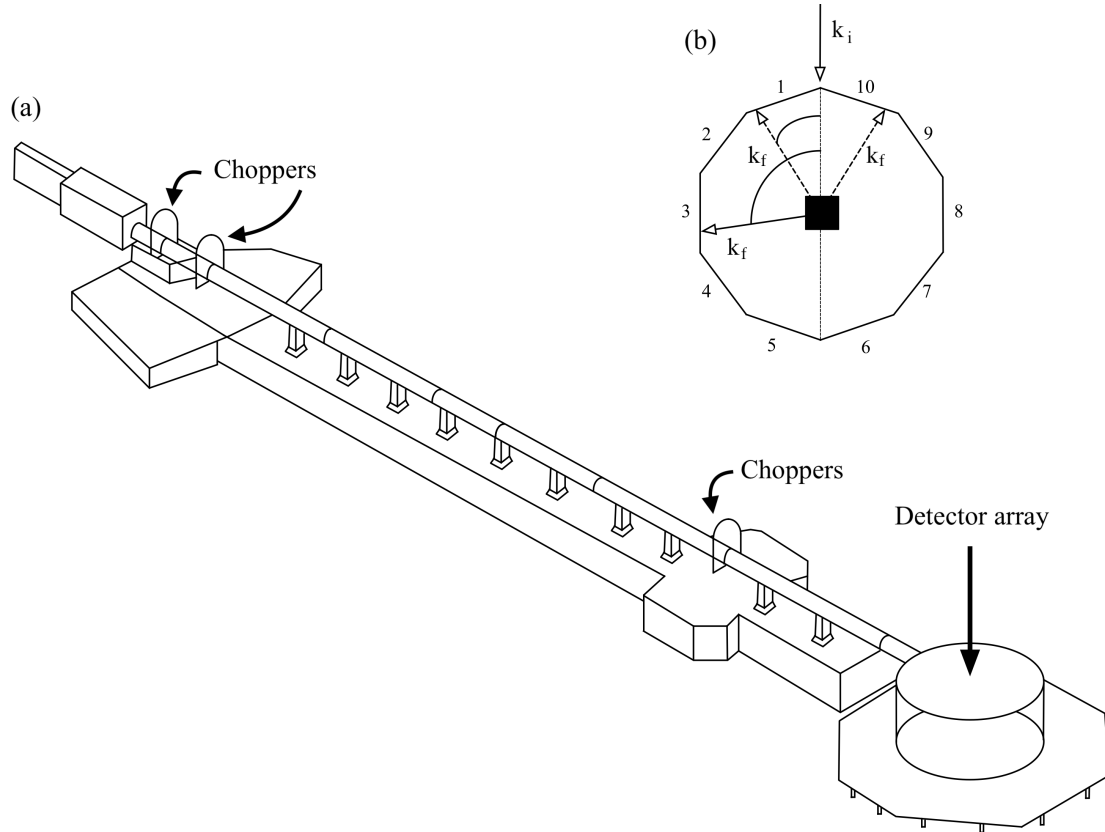


Figure 2.2: (a) Sketch of the engineering layout of the WISH diffractometer, copied from [45]. (b) Plan view of the WISH detector array showing the layout of the ten diffraction banks. Banks that are mirrored along the dotted line measure the same Q range with the same resolution. k_i denotes the incident neutron beam, and k_f is the diffracted neutron beam. The two dashed arrows representing the scattered neutron beam have the same 2θ scattering angle, but diffract into different banks.

The neutrons enter WISH after passing through a 40 K solid methane moderator. The moderator lowers the energy of the neutrons, which have been created after high energy protons are fired upon a tantalum target. In order to optimise the magnetic intensity of the scattered neutrons, it is necessary to measure at

low Q where the magnetic form factor is maximised, which requires longer wavelength (colder) neutrons. While in principle it is possible to use a colder moderator, such as pure liquid hydrogen, methane strikes a good balance between reducing the neutron wavelength and optimising the brilliance of the neutron beam [45]. The major disadvantage to using methane is that it is susceptible to radiolysis and as such the moderator has to be changed frequently. By measuring the time of flight of the neutrons t , and with the knowledge of the distance from the moderator to the sample L , it is possible to determine the neutron wavelengths using Eqn. 2.12 [38], where m_n is the mass of a neutron, v is the velocity of the neutron, h is Planck's constant and λ is the neutron wavelength. A broad spectrum of neutrons with wavelengths ranging from 1 Å to 10 Å with the intensity peaked at ~ 3.4 Å is produced [45]. The slowest neutrons from the first pulse are overtaken by the fastest neutrons of the second pulse, and so to avoid frame overlap a system of choppers are in place which cut off the fastest and slowest neutrons.

$$\frac{h}{\lambda} = m_n v = m_n \left(\frac{L}{t} \right) \quad (2.12)$$

Between 1-2 g of a powder sample is loaded into a cylindrical vanadium can, which is then lowered into a sample chamber within a cryostat. Supermirror guides are used to steer the neutron beam 40 m from the moderator to the sample. The beam has a rectangular profile of 40 mm by 20 mm after exiting the guide and can be further focused before reaching the sample. An oscillating radial collimator is used to reduce the angular divergence of the scattered beam and thus minimise the background scattering from the cryostat and other pieces of material used in constructing the sample environment. Ten detector panels made of ^3He based position sensitive detector tubes are placed around the sample to capture both forward (2θ of 10° to 90°) and back (90° - 170°) scattering events [45], covering an angular range of 320° [46]. A sketch of the detector array is given in Fig. 2.2(b) showing the arrangement of the ten different banks used in WISH. As each bank captures scattering events at fixed 2θ value for a broad spectrum of wavelengths, each bank measures a different range of Q . Banks with the largest scattering angles, 5 and 6, have the smallest Q coverage, while banks with the smallest scattering angle, 1 and 10, measure over the largest range in Q . The resolution is angular dependent and banks that are mirrored along the dotted line shown in Fig. 2.2(b) measure the same Q range, and with the same resolution, and therefore the data

collected across these banks are summed together to produce a total of five diffraction patterns.

The sample cans are made from pure Vanadium which has a small but finite coherent scattering cross section and can therefore contribute features to the diffraction pattern, but only if very small sample masses (≤ 50 mg) are used. Aluminium sample cans can also be used as they have the advantage of having a very low absorption cross section, but have the disadvantage of having a higher coherent cross section. The instrument walls and chambers are made of materials with high absorption cross sections, such as cadmium, and are therefore not expected to have a significant contribution to the diffraction pattern.

2.1.4 Corrections to the data

There are a number of corrections that must be made to the data before it can be analysed. The collected data is always normalised by the incident flux as the flux can change between each pulse of neutrons. Not all neutrons incident on a sample will give rise to scattering, instead some will be captured by the nucleus and give rise to radiative decay. The attenuation of a beam of neutrons will exponentially decay depending on the distance the neutrons have travelled through the sample according to the Beer-Lambert law, and so a correction is made to account for this, which is dependent on the sample size and shape. Multiple scattering, which is when the neutrons are rescattered after the first scattering event, can also occur and lead to an artificial increase of flux and even to artificial peaks in the data, however this is typically only relevant for single crystal experiments. Scattering from cylindrical cans (as used in the experiments conducted for this thesis) generally contributes to isotropic incoherent scattering and is unlikely to have masked any of the data, and is therefore not corrected for.

Powder samples have randomly oriented crystallites and statistically can be assumed to be oriented in every possible direction with equal probability. Therefore for a fixed orientation of the incoming neutron beam and for fixed wavelength, these randomly oriented crystallites will give rise to a cone of scattering vectors (Debye Scherrer cone) that scatter at the same 2θ and Q but in different orientations in space to produce a ring of scattering (the circumference of the base of the cone) for a given reflection. The

integrated intensity around the ring of scattering will give the total intensity for the reflection. The portion of the scattered ring captured by the detector varies with 2θ , and thus a correction is applied to account for the variation of Bragg intensity with θ . For TOF experiments, the Lorentz correction is given by Eqn. 2.13.

$$L = d^4 \sin(\theta) \quad (2.13)$$

2.1.5 Rietveld refinement

Candidate crystal structure and magnetic structure models were tested against the neutron diffraction data by Rietveld refinement using the FULLPROF Software Suite [47], and the model that best fit the data whilst maintaining the most physical sense is used as the structural or magnetic phase. There are a number of fitting parameters for modelling the data that will be discussed below.

Theoretically one would expect a diffraction peak to be modelled as a Dirac delta function, given that the condition for diffraction is when $\mathbf{Q} = \mathbf{G}$. However there are a number of factors that contribute to the broadening of a diffraction peak. For instance in TOF experiments there is an uncertainty associated with the measured wavelength, and with the determination of $\mathbf{Q}$ from the resolution of the detector pixels, contributing to a finite instrumental resolution that is not expected to vary with different systems or with temperature. This can be accounted for in the refinement of the NPD data using established instrumental resolution parameters. TOF data give rise to asymmetric peak shapes owing to the time structure of the neutron pulse, and as such cannot be modelled by a Gaussian or Lorentzian or even a weighted summation of the two (pseudovoigt). Instead it has been found that the convolution of a pseudovoigt with back to back exponential functions best models the Bragg peaks measured on WISH. Besides the instrumental resolution of TOF data, the presence of any defects and structural inhomogeneities would also contribute to a broadened peak and thus there are additional peak profile parameters that can be refined to adjust the width of the peak of each bank.

Atoms are known to vibrate about their mean position due to the presence of thermally activated phonons

and at 0 K due to zero point energy. Consequently the atoms are not fixed and this has the effect of reducing the measured scattering amplitude. The reduction is not constant with Q , but instead has a dependence given by the Debye Waller factor, Eqn. 2.14, where $\bar{u}_j$ is the mean square displacement of atom j . u_j is a parameter that can be refined, and for the purposes of this thesis is assumed to be isotropic.

Neutrons are absorbed by the sample, and the amount of absorption depends on the atoms that make up the sample and the shape of the sample holder. It has been analytically determined that absorption due to a sample in a cylindrical can has the form given by Eqn. 2.15 [47], derived in the limit that the absorption is small, and where a_1 , b_1 , a_2 and b_2 are equal to 1.7133, -0.0368, 0.0927 and 0.375 respectively, n_s and σ are the density of scattering units and the absorption cross section respectively. In the refinement of the data $n_s\sigma$ is replaced by a single parameter that is allowed to freely refine for each phase. The absorption and Debye Waller factor have almost opposite dependencies with Q . The consequence of this is that the two refinement parameters can be highly correlated, and difficult to determine exactly from powder neutron diffraction data.

$$\exp\left(-\frac{1}{2}\mathbf{Q}^2\bar{u}_j^2\right) \quad (2.14)$$

$$\exp\left((a_1 + b_1 \sin^2 \theta)n_s\sigma R + (a_2 + b_2 \sin^2 \theta)(n_s\sigma R)^2\right) \quad (2.15)$$

In the paramagnetic phase the random variation of the spin direction of the magnetic moments gives rise to incoherent magnetic scattering that contributes to the background. The dependence of the paramagnetic intensity with Q comes from the form factor and the Debye Waller factor, which have almost inverse relationships and therefore approximately varies as a constant in Q . As the system begins to order, magnetic intensity shifts from the paramagnetic background into magnetic Bragg peaks, and thus the background is allowed to freely refine with temperature.

R-factors are used to quantify how well the crystal/magnetic structure model is able to fit the diffraction

data ¹. Eqn. 2.16 and 2.17 are the profile factor and the weighted profile factor respectively, where y_i is the profile intensity, $y_{i,c}$ is the calculated profile intensity, and $w_i = \frac{1}{\sigma_i^2}$ where σ_i^2 is the variance of y_i . Eqn. 2.18, is the Bragg R-factor for nuclear scattering, where $I'_{obs,(h,k,l)}$ is the observed integrated intensity, which also contains the additional caveat that for $I_{calc,(h,k,l)} = 0$, the corresponding $I'_{obs,(h,k,l)}$ is also zero. For magnetic scattering, R_{Mag} , the same formula given in Eqn. 2.18 is used, except the nuclear intensities are replaced by magnetic ones.

$$R = 100 \frac{\sum_{1,n} |y_i - y_{c,i}|}{\sum_{1,n} y_i} \quad (2.16)$$

$$wR = 100 \left[\frac{\sum_{1,n} w_i |y_i - y_{c,i}|^2}{\sum_{1,n} w_i y_i^2} \right] \quad (2.17)$$

$$R_{Bragg} = 100 \frac{\sum_{(h,k,l)} |I'_{obs,(h,k,l)} - I_{calc,(h,k,l)}|}{\sum_{(h,k,l)} |I'_{obs,(h,k,l)}|} \quad (2.18)$$

2.1.6 Small angle neutron scattering

In the absence of any Γ -point order (e.g long-range ferromagnetic order) the scattered intensity from small-angle neutron scattering (SANS) is expected to arise from short range order in a continuous medium. Generally the differential cross section for SANS scattering is given by Eqn. 2.19 [38], where N_p is the number of identical scattering centres that have a volume of V_p . $\bar{\rho}_p^2$ is the scattering contrast, $P(\mathbf{Q})$ is the form factor (or shape factor) and $S(\mathbf{Q})$ is the structure factor. Information about the size, shape and interactions between the scattering centres can be obtained from these last three terms.

$$\frac{d\sigma(\mathbf{Q})}{d\Omega} = N_p V_p^2 \bar{\rho}_p^2 P(\mathbf{Q}) S(\mathbf{Q}) \quad (2.19)$$

¹The χ^2 statistic, typically used in regression analysis, is not a good measure of goodness of fit for Rietveld refinement as χ^2 can increase for data collected with high counting statistics [48].

The SANS measurements presented in this thesis were performed at D33 at the Institut Laue-Langevin (ILL). In general SANS instruments have long neutron flight paths and use cold neutrons as this enables measurements at smaller Q . Fig. 2.3 shows a sketch of a standard SANS instrument layout. Data is integrated radially at each value of q to produce the 1-dimensional plots of intensity as a function of Q , as shown in Sec. 7.5.

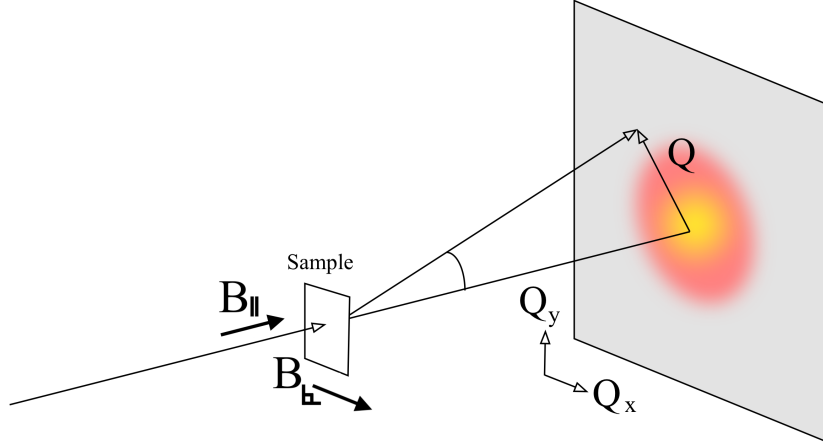


Figure 2.3: Sketch of a standard small angle neutron scattering instrument layout showing the 2-dimensional area detector and the direction of the applied magnetic field with respect to the incoming neutron beam.

Multiple scattering can be particularly problematic for SANS experiments and thus the sample mass and size is carefully chosen, which depends on the average scattering length and absorption of all elements in the sample.

2.2 Magnetometry

Magnetometers measure the magnetisation of a sample. Some of the early magnetometers relied on measuring the force on a magnetic sample in an inhomogeneous magnetic field, which can then be related to the magnetisation. In more recent magnetometers it is typical to measure an electrical signal that can be induced by sinusoidally vibrating a magnetic sample, where the electrical signal is proportional to the moment of the sample. The magnetometry measurements performed in this thesis used a supercon-

ducting quantum interference device (SQUID) magnetometer, which is made of a superconducting ring connecting two Josephson junctions. The critical current of the superconducting loop will be proportional to the magnetic flux passed through the ring, which can then be used to determine the magnetisation of the sample.

2.3 Electron paramagnetic resonance

Electron paramagnetic resonance measurements are used to quantitatively determine the electronic structure of atoms with unpaired electrons. In electron paramagnetic resonance (EPR) a sample is placed in a magnetic field to split the energy levels of atoms with unpaired electrons, according to the Zeeman effect. Radiation of a fixed frequency is then incident on the sample, and the absorption of this radiation is measured as a function of magnetic field. At certain magnetic fields, corresponding to the Zeeman splitting of the energy levels, there will be a large absorption of the incident radiation. For a single spin $1/2$ system, such as an electron, the energy levels would split into two, as shown in Fig. 2.4, corresponding to $m_s = 1/2$ and $m_s = -1/2$ states and the energy difference of the splitting would then be given by $g_e \mu_B B$ where g_e is the electron g-factor, μ_B is the Bohr magneton and B the magnetic field strength [49]. The corresponding EPR spectra would consist of a single absorption peak corresponding to the transition between the $m_s = -1/2$ state and $m_s = 1/2$ state. In practice, EPR spectra are much more complicated as systems are composed of multiple paramagnetic ions and the spectra also have absorption lines from the hyperfine structure (splittings caused by the interaction of nuclear and electron spin).

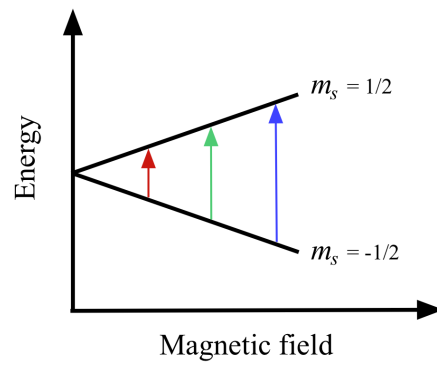


Figure 2.4: Energy level splitting of a spin 1/2 system as a function of the magnetic field. The red, green and blue arrows indicate the dependence of the splitting as a function of field (red is the lowest frequency radiation and blue the highest).

Chapter 3

Theoretical Techniques

In addition to the experimental techniques outlined in the preceding chapter, there are a number of theoretical techniques that are used to investigate the magnetism of the columnar ordered quadruple perovskites, which are outlined in this chapter. In Sec. 3.1 a description of the symmetry based approach used to analyse the results of the powder neutron diffraction is given. This is followed by a summary of the crystal field calculations used to estimate the energy level splitting for transition metal and rare earth ions in Sec. 3.2.

3.1 Symmetry

Symmetry can greatly simplify the analysis of the powder neutron diffraction data as it can establish solutions that are more likely to be observed, and also identify physical properties of the system that are protected by symmetry and are therefore unlikely to change in the course of a phase transition or when subject to external fields. The symmetry of crystals are described by space groups, where each space group contains all the symmetry operations that leaves a crystal invariant and can include rotations, translations, rotoinversions (e.g inversion and mirrors) and rototranslations (glide planes and screw axes). Every atomic site is also labelled by its symmetry through its Wyckoff position, which gives information about both the multiplicity of the site and its point group symmetry. The physical properties of crystals

are invariant with respect to at least the point group symmetry operations of the space group, according to Neumann's principle, and thus knowledge of the symmetry of a crystal structure and the local symmetry of atoms within the crystal structure can establish the symmetry constraints imposed on its physical properties.

Space groups are mathematical objects formed according to the axioms of group theory [50]. Using representation theory, every symmetry operation of a group can be represented by a linear operator. The full representation of a space group is then formed by choosing a complete set of basis functions, and determining how those basis functions transform under the point symmetry operations of the group. The full representation can be reduced into a set of irreducible representations, which represent the symmetry lowering distortions of the crystal structure for a given propagation vector. The translational symmetry of a crystal can be lowered if there occurs a modulation of the wavevector of the plane waves that describe the periodicity of the reciprocal lattice. If the modulation is given by a propagation vector that coincides with one of the high symmetry points of the Brillouin zone, the modulation is commensurate and incommensurate otherwise.

By applying the point operations of the high symmetry crystal structure to the propagation vector, one can generate the star of $\mathbf{k}$, which corresponds to the same modulation but with distinct directions in reciprocal space and where only $\mathbf{k}$ vectors that are not related by a reciprocal lattice vector are identified as unique. From powder neutron diffraction data it is not possible to distinguish between the arms of the star of $\mathbf{k}$, due to powder averaging of all different orientations of the crystal. For the systems studied in this thesis all modulations are single $\mathbf{k}$, and therefore the analysis is clear of the effects of powder averaging.

3.1.1 Magnetic space groups

The space groups are constructed with symmetry operators that transform polar vectors of the system, such as the position of an atom. To describe magnetic symmetry it is necessary to introduce another type of symmetry operator, the time reversal operator, that is able to transform the time reversal symmetry of a magnetic moment which can be described by an axial vector. A summary of how a magnetic mo-

ment changes under different symmetry operations, including primed operations, which are the combined effect of a space group operator and the time reversal operator, is illustrated in Fig. 3.1.

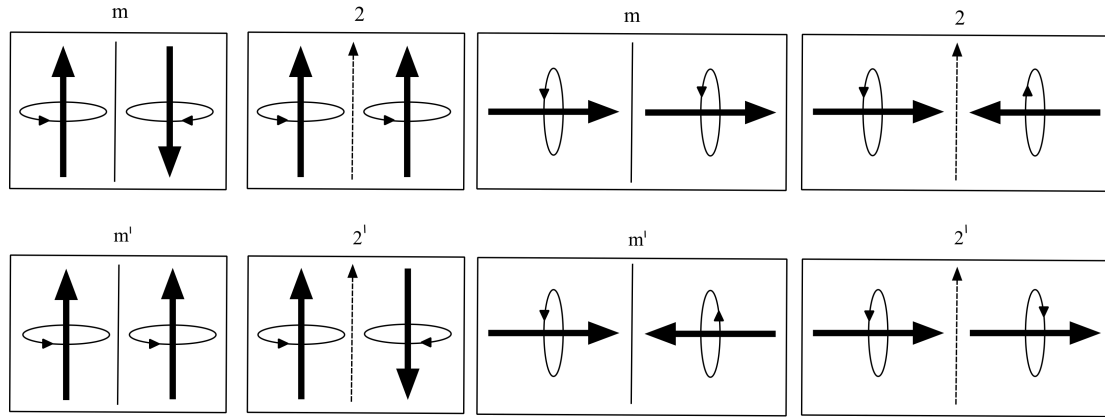


Figure 3.1: A single magnetic moment transformed under the action of a mirror (m), a 2-fold rotation (2), the combined action of the mirror with the time reversal symmetry operator (m') and the 2-fold rotation with the time reversal symmetry operator ($2'$), that are oriented both parallel and perpendicular to the magnetic moment. Note that the magnetic moment is invariant under inversion. The thick black arrow represents the magnetic moment, the oval represents the orbital of the electron, the solid black line is the mirror and the dashed arrow the 2-fold symmetry operation.

There are two sets of magnetic space groups. The black and white, and grey groups. All the symmetry operators in grey groups possess the time reversal operator, and cannot give rise to an commensurately ordered magnetic state, but instead describe paramagnetism or incommensurate magnetic order. Exactly half of the symmetry operators in the black and white groups contain the time reversal operator, as all groups must be closed by composition, and are used to describe commensurate magnetic order.

3.1.2 Phase transitions

The theory of phase transitions doesn't take into account the microscopic details of the system, rather a phase transition corresponds to a singularity in the free energy of the system and occurs when the thermodynamic potential of the two phases are equal. Phase transitions may be separated into two kinds, the second order kind feature discontinuities in the second order differential of the free energy, and give rise to a continuous change in the state variables of the system and the first order differential of the free energy. Phase transitions of the first order have discontinuous changes in the state variables of the system

and the first order differential of the free energy.

The transition between a paramagnetic and a magnetically ordered state of a system typically occurs via a second order phase transition. Rather remarkably one only needs to consider the symmetry of the crystal structure to determine the possible ordered states that the crystal adopts after undergoing a second order phase transition. In these transitions, it is always the case that one phase is of a higher symmetry than the other, such that the lower symmetry phase forms a subgroup of the high symmetry space group ¹. Furthermore the state of the system undergoes a continuous change between the phases, i.e there are no large rearrangements of the atoms or jumps in the lattice parameters and bond angles, rather there is a gradual onset of order leading to a spontaneous breaking of symmetry.

The phases either side of a second order phase transition are characterised by an order parameter, which is finite valued in the low symmetry phase and zero in the high symmetry phase. Landau was able to show that second order phase transitions are driven by the onset of a single order parameter, which represents a distortion of the high symmetry phase. The order parameter quantifies the change in the less symmetrical phase and often describes a change to a macroscopic physical observable of the system, such as the strain, magnetisation, polarisation etc. In general the order parameter is an n dimensional vector that spans the space defined by an irrep of the high symmetry space group. In the low symmetry phase and in the vicinity of the phase transition the change to the free energy of the system can be expanded as a power series of the order parameters of the system. In principle this power series contains all the possible free energy invariants of the order parameter, as well free energy terms coupling components of different order parameters. For second order phase transitions it is possible that more than one order parameter becomes finite, so long as the secondary order parameters are sufficiently small. This gives rise to non zero coupling terms between components of different order parameters in the expression for the free energy. If, however, the second parameters are large and of a comparable magnitude to the primary order parameter, a first order phase transition will occur. In general first order phase transitions can have multiple primary order parameters, and the phases either side of the transition may be unrelated by symmetry [52].

¹ Although note that second order isostructural phase transitions have been observed [51]

3.1.3 Magnetic representations

In this section the decomposition of the magnetic representations for the relevant Wyckoff positions of the $A'_2A''A'''B_4O_{12}$ manganite perovskites into its irreducible representations (irreps) in the $P4_2/nmc$ and $Pmmn$ space groups is given, and was performed using the ISOTROPY software suite [53]. The irreps of both space groups are described in terms of the symmetry adapted basis modes shown in Fig. 3.2 and Fig. 3.3. For the A sites, there are two magnetic modes, F_i and A_i , that span the symmetry equivalent ions of the A', A'' and A''' sites that are related by a n -glide symmetry. For the B sites, there are four magnetic modes, F_i , A_i , X_i and Y_i that span the symmetry equivalent ions in a single Mn B-site ab layer². The subscript $i = x, y$ or z denotes the direction of the magnetic moment component where $x||a, y||b$ and $z||c$. Each of the irreducible representations are composed of a unique combination of these symmetry adapted modes that together constitute candidate magnetic structures for the ordered phases of the system.

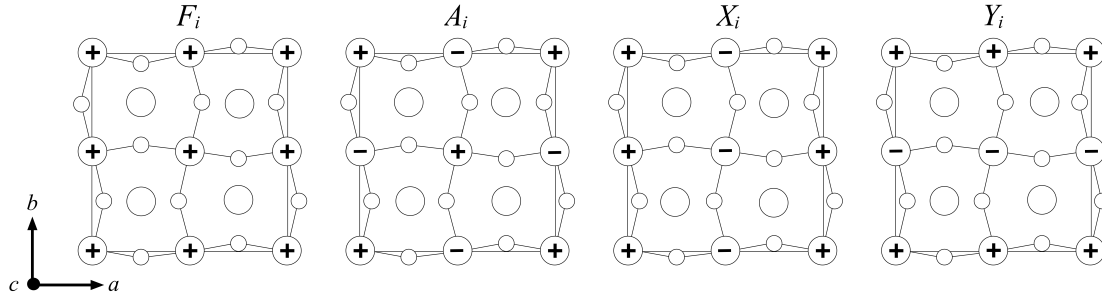


Figure 3.2: A projection of the A-sites and $z = 0$ B-site layer as seen from the c axis, illustrating the symmetry adapted magnetic modes defined in Table 9.1 of Appendix 9.2. The large circles with a + and – represent B-site ions located at $z = 0$, the small circles represent the O^{2-} ions closest to the $z = 0$ plane, and the large unfilled circles represent the A-sites. The + and – signs describe the amplitude of the magnetic moment on a given B-site ion, and the subscript i denotes the direction of the moment component.

All observed magnetic intensity that appears in the diffraction patterns collected on the systems presented in this thesis occur at Γ -point ($\mathbf{k} = 0, 0, 0$) or Z-point ($\mathbf{k} = 0, 0, 1/2$) reflections, as will be discussed in

²Note the L-type structure, illustrated in Fig. 1.3, and discussed in Sec. 1.2, would correspond to a $F_i F_i$ B-site magnetic mode in the notation adopted to describe the magnetic structures of the columnar ordered quadruple perovskites.

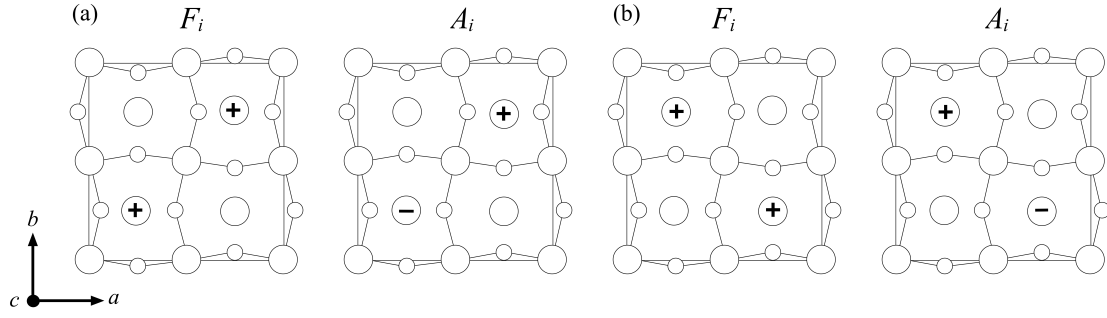


Figure 3.3: A projection of the A-sites and $z = 0$ B-site layer as seen from the c axis, illustrating the symmetry adapted modes defined in Table 9.2 of Appendix 9.2 for the A-site ions. The large circles with a + and - represent (a) the A' site ions located at $(1/4, 1/4, z)$ and $(3/4, 3/4, -z)$ and (b) the A'' and A''' site ions located at $(3/4, 1/4, z)$ and $(1/4, 3/4, -z)$. The large empty circles are the B-site ions located at $z = 0$ and the small circles represent the O^{2-} ions close to the $z = 0$ plane. The + and - signs on the A-site ions describe the amplitude of the magnetic moment on a given A-site ion and the subscript i denotes the direction of the moment component.

Chapters. 4 to 7, and hence the Γ and Z-point representations for the Wyckoff positions describing magnetic sites of the $A'_2A''A'''B_4O_{12}$ crystal structure is decomposed into its irreducible representations below.

$P4_2/nmc$

The magnetic Γ -point representation for the Wyckoff positions describing magnetic sites of the $P4_2/nmc$ crystal structure decompose into six 1-dimensional irreducible representations (irreps) ($\Gamma_1^\pm$, $\Gamma_2^\pm$, $\Gamma_3^\pm$ and $\Gamma_4^\pm$) and two 2-dimensional (2D) irreps ($\Gamma_5^\pm$), which together define a total of twelve different magnetic symmetries. Of the twelve magnetic symmetries, five do not have B-site magnetic modes and therefore would not describe the magnetic structures discussed in this thesis. The remaining seven magnetic symmetries are listed in Table. 3.1 (Miller and Love notation is used throughout).

$Pm\bar{m}n$

The magnetic Γ - and Z-point representations for the Wyckoff positions describing magnetic sites of the $Pm\bar{m}n$ crystal structure each decompose into seven irreducible representations, listed in Table 3.2.

Table 3.1: The magnetic Γ -point irreducible representations described for each of the symmetry inequivalent magnetic sites of the $P4_2/nmc$ $A'_2A''A'''B_4O_{12}$ crystal structure using the symmetry adapted basis modes defined above. Only irreps that contain B site magnetic modes are listed. The superscript 1 used for labelling the A-site modes refers to A' site ions located at $(1/4, 1/4, z)$ and $(3/4, 3/4, -z)$, and 2 for A' ions located at $(1/4, 1/4, z + 1/2)$ and $(3/4, 3/4, -z + 1/2)$. The superscript 1 and 2 used in labelling the B site magnetic modes refers to B-site ions located on the $z = 0$ and $z = 1/2$ layers respectively. Independent modes are separated by a comma, and coupled modes are listed without any space separating the modes.

Irrep.	A'	A''	A'''	B
1D irreps.				
Γ_1^+	-	-	-	$Y_x^1 X_y^2, X_y^1 Y_x^2, A_z^1 A_z^2$
Γ_2^+	-	-	-	$Y_x^1 X_y^2, X_y^1 Y_x^2, A_z^1 A_z^2$
Γ_3^+	$F_z^1 F_z^2$	F_z	F_z	$X_x^1 Y_y^2, Y_y^1 X_x^2, F_z^1 F_z^2$
Γ_4^+	$F_z^1 F_z^2$	-	-	$X_x^1 Y_y^2, Y_y^1 X_x^2, F_z^1 F_z^2$
2D irreps.				
$\Gamma_5^+(a, 0)$	F_x^1, F_x^2	F_x	F_x	F_x^1, A_y^1, X_z^1 F_x^2, A_y^2, X_z^2
$\Gamma_5^+(a, b)$	$F_x^1, F_y^1, F_x^2, F_y^2$	F_x, F_y	F_x, F_y	$F_x^1, A_x^1, A_y^1, F_y^1, X_z^1, Y_z^1$ $F_x^2, A_x^2, A_y^2, F_y^2, X_z^2, Y_z^2$
$\Gamma_5^+(a, a)$	$F_x^1 F_y^2, F_y^1 F_x^2$	F_{xy}	F_{xy}	$F_x^1 F_y^2, F_y^1 F_x^2, X_z^1 Y_z^2$ $Y_z^1 X_z^2, A_x^1 A_y^2, A_y^1 A_x^2$

Table 3.2: The magnetic Γ -point irreducible representations described for each of the symmetry inequivalent magnetic sites of the $Pmmn$ $A'_2A''A'''B_4O_{12}$ crystal structure using the symmetry adapted basis modes defined above. A1' refers to A' ions located at $(1/4, 1/4, z)$ and $(3/4, 3/4, -z)$, and A2' refers to A' ions located at $(1/4, 1/4, z + 1/2)$ and $(3/4, 3/4, -z + 1/2)$. B1 and B2 refers to the B-site ions located on the $z = 0$ and $z = 1/2$ layer respectively.

Irrep.	A1'	A2'	A''	A'''	B1	B2
$k = (0, 0, 0)$						
Γ_1^+	-	-	-	-	Y_x, X_y, A_z	Y_x, X_y, A_z
Γ_2^+	F_z	F_z	F_z	F_z	X_x, Y_y, F_z	X_x, Y_y, F_z
Γ_3^+	F_x	F_x	F_x	F_x	F_x, A_y, X_z	F_x, A_y, X_z
Γ_4^+	F_y	F_y	F_y	F_y	A_x, F_y, Y_z	A_x, F_y, Y_z
Γ_1^-	A_z	A_z	A_z	A_z	-	-
Γ_3^-	A_y	A_y	A_y	A_y	-	-
Γ_4^-	A_x	A_x	A_x	A_x	-	-
$k = (0, 0, 1/2)$						
Z_1^+	-	-	-	-	Y_x, X_y, A_z	-
Z_2^+	A_z	A_z	A_z	A_z	X_x, Y_y, F_z	-
Z_3^+	A_x	A_x	A_x	A_x	F_x, A_y, X_z	-
Z_4^+	A_y	A_y	A_y	A_y	A_x, F_y, Y_z	-
Z_1^-	F_z	F_z	F_z	F_z	-	X_x, Y_y, F_z
Z_2^-	-	-	-	-	-	Y_x, X_y, A_z
Z_3^-	F_y	F_y	F_y	F_y	-	A_x, F_y, Y_z
Z_4^-	F_x	F_x	F_x	F_x	-	F_x, A_y, X_z

3.2 Energy level splitting in magnetic ions due to the crystal electric field

The magnetic exchange between ions is strongly influenced by the shape, energy and spatial orientation of the valence orbitals that participate in the exchange process. The systems studied in this thesis are made up of both transition metal and rare earth cations, which have d and f valence orbitals respectively, and are subject to a crystal electric field created by neighbouring oxygen anions. In the presence of an electric field the degeneracy of the orbitals within each electronic subshell is reduced according to the symmetry of the field. However for ions that are described by wavefunctions with a half integer quantum number J (i.e that have an odd number of electrons), and which are not subject to a magnetic field, an electric field can at most reduce the orbital energy levels to be two fold degenerate, according to Kramers theorem.

In Sec. 3.2.1 the crystal electric field splitting of the $3d$ orbitals for the TM ions studied in this thesis is estimated. This is then used to predict the nature of symmetric exchange interactions in the $R_2\text{MnMnMn}_4\text{O}_{12}$ columnar ordered quadruple perovskite manganites using the Goodenough Kanamori Anderson rules. In Sec. 3.2.2 I outline the point charge approximation used to estimate the energy level splitting of rare earth ions due to a crystal electric field, before outlining the method used to evaluate the magnetic anisotropy of the rare earth ions.

To determine the crystal electric field (CEF) splitting, the ligands surrounding the TM/ RE cations are assumed to be point charges. This is a massive oversimplification of the spatial distribution of the electron density between the ligand and TM/ RE cation as the bonds formed are covalent in nature. Nevertheless it is found that a point charge approximation of the CEF is typically sufficient to build a qualitative picture of the CEF splitting [54].

3.2.1 Transition metal ions

Typically for the $3d$ transition metal ions the orbital angular momentum is ‘locked into’ the crystalline electric field [55] such that it does not make a contribution towards the net magnetic moment of the atom. As such the coupling between the spin and orbital degrees of freedom is negligible³ and the electronic wavefunctions are then best described by the orbital angular momentum L , and the moment by the spin angular momentum S . As L can only take integer values Kramers theorem does not apply [49].

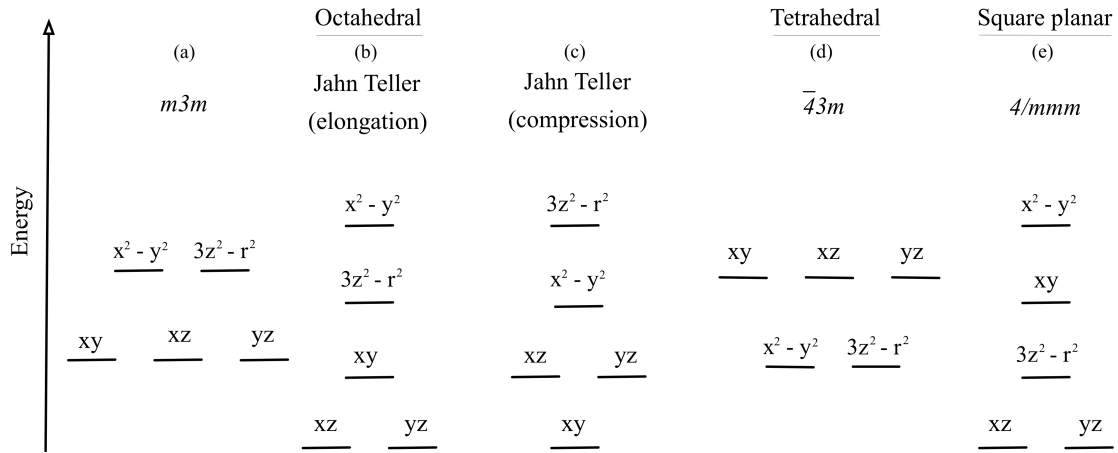


Figure 3.4: The d -orbital splitting due to (a) an $m\bar{3}m$ octahedral CEF (b) a Jahn Teller elongated octahedral CEF (c) a Jahn Teller compressed CEF, (d) a $\bar{4}3m$ tetrahedral CEF and (e) a $4/m\bar{3}m$ square planar CEF. Note the energy level splitting is not drawn to scale, and is intended only to give a qualitative indication of the relative ordering of the energy levels.

The orbitals that participate in magnetic exchange are the d -orbital angular momentum states. Fig. 3.4 shows the d -orbital splitting for TM ions in various crystal electric field symmetries. The point group symmetry will determine the minimum degeneracy of the orbital splitting, while the ordering of the energy levels will depend on the extent of the interaction of each of the orbitals with the surrounding anions. In the arisotype $Pm\bar{3}m$ structure the B-site ions have $m\bar{3}m$ octahedral site symmetry. The JT distortions and octahedral rotations present in the columnar ordered quadruple perovskites have the effect of lowering the site symmetry to $\bar{1}$ in the $P4_2/nmc$ and $Pmnn$ symmetries, so that there are three

³Well known exceptions are CoO and FeO [56].

inequivalent B-O bond lengths. If the B-sites are occupied by Mn^{3+} the JT axis is $\parallel c$ and is elongated by approx. 10%, compared with the in plane plane B-O bonds which differ by approx. 1%. As such the energy level scheme for Mn^{3+} ions can be approximated as a Jahn teller elongation shown by Fig. 3.4(b). The A'' ions have an orthorhombic site symmetry of $mm2$ in both the $P4_2/nmc$ and $Pmnn$ symmetries, but reside in a square planar coordinated environment with four equivalent A''-O bonds, and can be approximated to have an energy level ordering shown in Fig. 3.4(e). The A''' ions are tetrahedrally coordinated with tetragonal point group symmetry $\bar{4}2m$ in the $P4_2/nmc$ crystal structure with all four A'''-O bonds equivalent. In the $Pmnn$ crystal structure, the A''' sites have orthorhombic $mm2$ point group symmetry with two sets of inequivalent A'''-O bonds which differ by approx. 2%. Therefore in both the $P4_2/nmc$ and $Pmnn$ crystal structures the energy level ordering is approximated to have that of the tetrahedral cubic $\bar{4}3m$ symmetry energy level ordering show in Fig. 3.4(d).

Goodenough Kanamori Anderson rules

Given the success of the GKA rules in explaining the magnetic structures of the simple AMnO_3 and quadruple $\text{AMn}_7\text{O}_{12}$ manganite perovskites (Sec. 1.2), in this section the GKA rules are applied to qualitatively predict the nature of magnetic exchange interactions in the $Pmnn$ $R_2\text{MnMnMn}_4\text{O}_{12}$ columnar ordered manganite perovskites, using the approximation of the energy level ordering outlined in the previous section.

B-B exchange

First, the role of B-B exchange interactions is considered. In the $Pmnn$ symmetry, observed when the B-sites are entirely occupied by Mn, the structure is composed of alternating layers of Mn in the +3 and +3.5 oxidation states. The layer of $\text{Mn}^{3.5+}$ ions are expected to consist of 50% Mn^{3+} ions and 50% Mn^{4+} ions, although there is no experimental verification of this as yet. The Jahn-Teller active, octahedral oxygen coordinations of the B site Mn^{3+} ions (Mn3) are elongated along z , lifting the degeneracy of the e_g states and giving preferential electronic occupation of the $d_{3z^2-r^2}$ orbitals - a ferro-orbital order. Thus for Mn3 ions, all 3d orbitals are half occupied except for the $d_{x^2-y^2}$ orbital which is empty, as shown in

Fig. 3.5(b) and Fig. 3.5(c). This is expected to give rise to antiferromagnetic A_i modes (as defined in Sec. 3.1.2) within the Mn3 planes mediated by $p\pi$ superexchange through half occupied t_{2g} orbitals for 180° Mn-O-Mn bonds.

In comparison, the Mn4 layers are thought to be equally occupied by Mn^{3+} and Mn^{4+} . If the Mn^{3+} and Mn^{4+} were to charge order in a checkerboard pattern, it would lower the crystal symmetry to monoclinic $C2/m$, however it would not result in the appearance of any new reflections and therefore could not be distinguished experimentally by diffraction ⁴. Given the manganite perovskites have an instability to checkerboard charge ordering, as seen in the AMnO_3 and $\text{AMn}_7\text{O}_{12}$ manganite perovskites (Sec. 1.2), it is possible that they may adopt such an ordering within the Mn4 layers. Published X-ray powder diffraction data taken on $R_2\text{MnMnMn}_4\text{O}_{12}$ [35] indicate that the MnO_6 octahedra are elongated along b in the Mn4 layer, suggestive that the JT axis is parallel to b in this layer. The magnitude of the JT distortion in the Mn4 layer is approximately half of the JT distortion observed in the Mn3 layer, which is consistent with the averaging over two sites with the full JT distortion and no JT distortion. Like the Mn3 layer, antiferromagnetic A_i modes are expected to order mediated by $p\pi$ superexchange through half occupied t_{2g} orbitals for 180° Mn-O-Mn bonds. However this magnetic ordering could also be augmented by the formation of stripes of ferromagnetic order along b coupled antiferromagnetically along a (Y_i modes) in the ab layer mediated by e_g-e_g exchange.

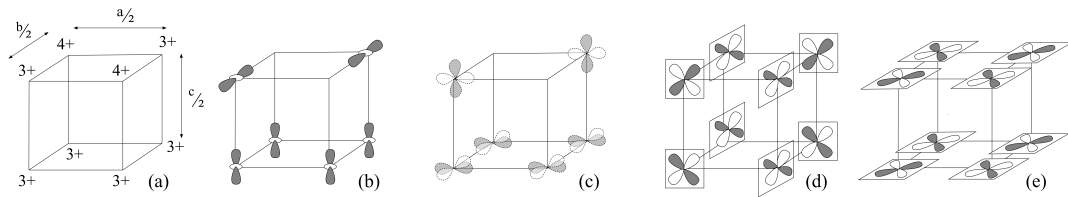


Figure 3.5: (a) Proposed charge structure of the $A'_2A''A'''Mn_4O_{12}$ manganite perovskites. Possible superexchange pathways between Mn B site ions of the $A'_2A''A'''Mn_4O_{12}$ structure decomposed into (b) the $d_{3z^2-r^2}$ (c) $d_{x^2-y^2}$ (d)-(e) t_{2g} orbitals. Half-filled orbitals are drawn with solid lines and empty orbitals with dotted lines.

⁴As the Mn^{3+} and Mn^{4+} ions are located on sites which contribute scattering to the same reflections, and as the two ions have identical neutron scattering lengths and almost the same atomic form factors a routine diffraction experiment could not be used to observe any charge ordering. Instead, one could perform a resonant x-ray scattering experiment to determine if charge ordering is present in the Mn4 layer.

The GKA rules further predict that the exchange interactions *between* the Mn3 and Mn4 layers, mediated by half-occupied and empty e_g states through $p\sigma$ superexchange will be ferromagnetic for $\sim 180^\circ$ Mn-O-Mn bonds. Therefore according to the GKA rules the B-site sublattice is expected to order with a $A_i A_i$ type antiferromagnetic structure. Note that Mn-O-Mn bonds are not exactly 180° , rather they can deviate by 40° which will significantly weaken the exchange interactions.

A-A exchange

The alternation of square planar and tetrahedral coordinations $\parallel c$ removes nearest-neighbour magnetic super exchange pathways between manganese A' and A'' sites, and therefore A-A exchange interactions are likely to be negligible. The weakness of A-A $d-d$ exchange has recently been demonstrated in $(\text{NaDy})\text{MnMnTi}_4\text{O}_{12}$ [57], where in the absence of A-B and B-B interactions ($\text{B} = \text{Ti}^{4+}$) antiferromagnetic order develops on the A-site sublattices only below ~ 12 K.

A-B exchange

Fig. 3.6 shows the possible superexchange interactions between the square planar A'' sites and the octahedrally coordinated B-sites for the systems studied in this thesis, which have $\sim 110^\circ$ bond angles (which is closer to the 90° exchange limit). In general it is important to consider both the 90° exchange interactions mediated via a single p orbital, and those mediated by two orthogonal p orbitals. However given that the latter scenario involves a reduction in the exchange constant due to Hund's coupling on the intermediary oxygen [54], and is therefore expected to be much weaker, these are not shown in Fig. 3.6. It is not possible to make a qualitative prediction regarding the nature of exchange, owing to the multiple exchange interactions present, and a lack of knowledge regarding the magnitude of exchange via different pathways. However from this analysis it is clear that the A''-B exchange interactions can differ significantly between the different columnar ordered quadruple perovskites, owing to the variation in the oxidation state of the A'' and B sites and the delicate balance between multiple exchange pathways.

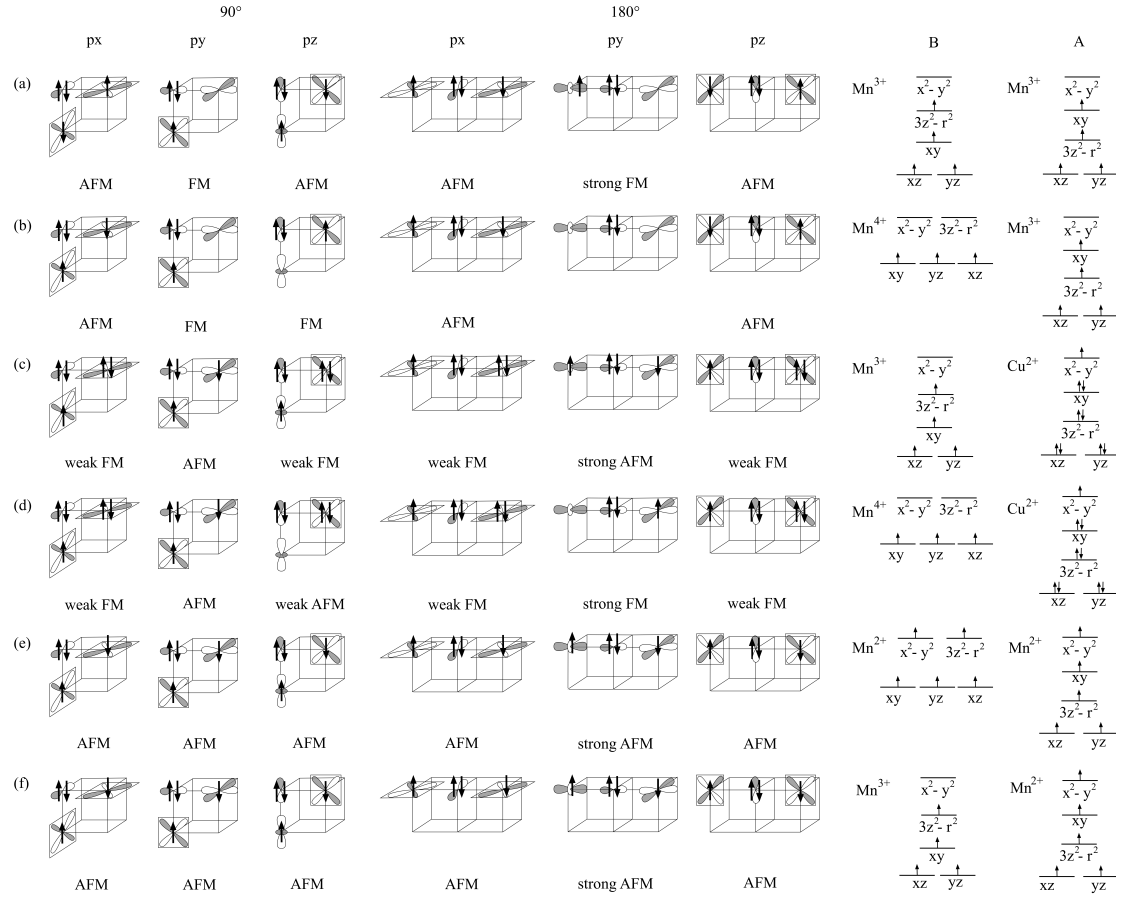


Figure 3.6: Superexchange pathways between various A'' and B site ions of the $A'_2A''A'''B_4O_{12}$ crystal structure mediated via a single p orbital are shown. For the $A'_2A''A'''B_4O_{12}$ manganites the A'' -O-B bond is $\sim 110^\circ$, closer to the 90° limit, nevertheless exchange pathways for both 90° and 180° bonds are given, to demonstrate how the exchange interactions may change between these limits. Exchange is considered between (a) a JT active Mn^{3+} ion on the B-site and a square planar coordinated Mn^{3+} ion on the A-site (observed in $Tm_2MnMnMn_4O_{12}$ and $Sm_2MnMnMn_3TiO_{12}$) (b) a Mn^{4+} ion on the B-site and a square planar coordinated Mn^{3+} ion on the A-site (observed in $Tm_2MnMnMn_4O_{12}$) (c) a JT active Mn^{3+} ion on the B-site and a square planar coordinated Cu^{2+} ion on the A-site (observed in $R_2CuMnMnMn_4O_{12}$) (d) a Mn^{4+} ion on the B-site and a square planar coordinated Cu^{2+} ion on the A-site (observed in $R_2CuMnMnMn_4O_{12}$) (e) Mn^{2+} ion on the B-site and a square planar coordinated Mn^{2+} ion on the A-site (observed in $Sm_2MnMnMnTi_3O_{12}$) and (f) JT active Mn^{3+} ion on the B-site and a square planar coordinated Mn^{2+} ion on the A-site (observed in $Sm_2MnMnMn_2Ti_2O_{12}$). The label of 'strong' and 'weak' is given according to whether the exchange is mediated via empty/ half/ fully occupied orbitals and if mediated via a $p\sigma$ or $p\pi$ bond. In general exchange mediated via a $p\sigma$ bond will be stronger than $p\pi$, and exchange between half occupied orbitals will be stronger than exchange mediated by empty or fully occupied orbitals.

3.2.2 Rare earth ions

Spin orbit coupling is a relativistic effect and therefore becomes more significant for the heavier elements, such as the rare earth ions. So long as the spin orbit coupling is weak and not negligible, the Russell Saunders coupling scheme is used to evaluate J , and Hund's rules are used to determine the filling of the $4f$ shells of the free ion. In the Russell Saunders coupling scheme the sum over all the individual spins of the $4f$ shell is taken to get the spin angular momentum S , and the sum over the orbital angular momentum states that are occupied by spins is taken to get the total orbital angular momentum L . The total ground state angular momentum is then evaluated as $|L + S|$ if the $4f$ orbitals are more than half filled and $|L - S|$ for when the $4f$ orbitals are less than half filled. Even though the properties of lanthanide ions are not always accurately described by the Russell Saunders coupling scheme, due to admixtures of levels with the same J , it has been shown that this will only give rise to a small departure to the results of the CEF calculations and can therefore be neglected [58]. The effects of the crystal electric field are small in comparison to the spin orbit coupling and as such can be treated as a perturbation to the free ion wavefunctions described by J .

Point charge approximation of crystal electric field

The eigenvalues and eigenfunctions of the ion are evaluated by diagonalising the crystal electric field Hamiltonian, where the interaction potential between the crystal electric field and the RE ion is given by the classical coulomb potential, and which can be expressed in terms of the spherical and tesseral harmonics [59]. Owing to an equivalence in the transformation properties of the spherical/ tesseral harmonics and the angular momentum operators, $\hat{J}_x$, $\hat{J}_y$ and $\hat{J}_z$, Stevens showed it is possible to reexpress the coulomb potential in terms of the angular momentum operators with an additional multiplicative factor, making it much easier to evaluate the action of the potential energy on the free ion wavefunctions [60]. Thus the potential can be expressed as a sum over the product of the crystal electric field parameters, B_n^m , with the Stevens operator equivalents, O_n^m , as tabulated in Ref. [59], and is given by Eqn. 3.1. In general the point group symmetry of the RE ion will determine the allowed values of n and m , as the

potential function must be invariant with respect to the operations of the point group symmetry of the RE Wyckoff position. For given l , no odd n terms will appear in the summation if the ion site has inversion symmetry, and for all terms $n \leq 2l$, no terms higher than $n = 6$ are finite for $4f$ electrons [59].

$$\mathcal{H}_{\text{cef}} = \sum_n \sum_{m=-n}^n B_n^m O_n^m \quad (3.1)$$

The crystal electric field parameters are the product of the multiplicative factors used in converting between the spherical harmonics and the Stevens factors (θ_n), the description of the local crystal electric field specific to the given system (A_n^m), and the expectation value of the n^{th} power of the radial distance of the $4f$ electrons of the RE ion ($\langle r^n \rangle$), as shown by Eqn. 3.2.

$$B_n^m = A_n^m \langle r^n \rangle \theta_n \quad (3.2)$$

A point charge ionic model is used to evaluate the local CEF potential A_n^m between the unfilled orbitals of the free RE ion (the $4f$ subshell) and the surrounding anions and is given by Eqn. 3.3, where for each value of n and m , the crystal electric field is determined by taking the sum over all nearest neighbour anions surrounding the RE ion. q_i is the charge of each anion in units of e (charge of an electron), the position of the i^{th} ion is given in spherical coordinations by r_i , θ_i and ϕ_i , Z_n^m is the corresponding tesseral harmonic, C_n^m is the numerical factor occurring in Z_n^m and ϵ_0 is the permittivity of free space. In this model all charges are assumed to be point like and the interaction between ions is assumed to be entirely ionic with no covalent character, and is therefore not an accurate representation of the CEF but is useful as a first approximation.

$$A_n^m = \frac{|e^2|}{(2n+1)\epsilon_0} \sum_i \frac{q_i}{r_i^{n+1}} C_n^m Z_n^m(\theta_i, \phi_i) \quad (3.3)$$

Magnetic Anisotropy

As a consequence of the coupling between the spin and orbital angular momenta, the orientation of the magnetic moment will no longer be isotropic in space, but rather can couple to the crystallographic structure and may preferentially align along certain crystallographic directions. The $4f$ orbitals are highly anisotropic and give rise to a large magnetic anisotropy, which can be estimated using the results of the point charge approximation of the crystal electric field as described below.

The A' sites have point site symmetry $2mm$ therefore for even electron ions, the effect of the crystalline electric field is to split all levels into singlet states. A singlet state is non magnetic, but under an applied magnetic field can admix energy levels and develop a polarised magnetic moment. The components of the magnetic moment, m_i ($i = x, y, z$) can be calculated for each eigenfunction of the perturbed Hamiltonian, $|\Psi\rangle$ using Eqn. 3.4, where $\hat{J}_i$ is the angular momentum operator. The expected moment, $\langle m_i \rangle$, is then calculated by summing the moments over all eigenfunctions of the perturbed wavefunctions weighted by Boltzmann statistics evaluated at a specific temperature. By calculating the magnetic moments in every possible direction over a full hemisphere, it is possible to map the susceptibility of the RE ion and hence determine its anisotropy.

$$m_i = \langle \Psi | \hat{J}_i | \Psi \rangle g_J \quad (3.4)$$

For A' sites with odd electron ions, the CEF splits all levels into Kramers doublets. If the energy of the splitting between the lowest lying Kramers doublets and the next excited state is much larger than $k_B T$ (the thermal energy required to excite an electron between the energy levels), the ground state doublets alone can be used to provide a good approximation of the $4f$ electronic states. The doublets can then be mapped onto a $J_{\text{eff}} = 1/2$ basis, which can be used to calculate the g-tensor anisotropy of the ion.

Chapter 4

Magnetic structure and spin-reorientation phase transition in $\text{Tm}_2\text{MnMnMn}_4\text{O}_{12}$

This chapter details the neutron powder diffraction study performed on $\text{Tm}_2\text{MnMnMn}_4\text{O}_{12}$ (TMO), the first such study performed on any of the $R_2\text{MnMnMn}_4\text{O}_{12}$ columnar ordered quadruple perovskite manganites. Long-range magnetic order develops below 74 K, and at 28 K a spin-flop transition occurs. A point charge approximation of the crystal electric field is used to estimate the electronic energy level splitting of the Tm^{3+} ions. A prediction of the anisotropy and moment magnitudes is made for each of the Tm sublattices, taking into account the effects of f - d and f - f exchange interactions. A comparison of the experimentally determined magnetic structure is then made to the theoretically derived magnetic structure based on the GKA rules. The observed magnetic structures can be understood to arise due to ferro-orbital order, the A'' and A''' site point symmetry, $mm2$, and the dominance of A-B exchange over both A-A and B-B exchange.

Acknowledgements

The powder samples of $\text{Tm}_2\text{MnMnMn}_4\text{O}_{12}$ were synthesised and characterised by L. Zhang, K. Yamaura and A. A. Belik. Magnetometry measurements were collected by L. Zhang, K. Yamaura and A. A. Belik.

Neutron powder diffraction experiments were performed by D. D. Khalyavin and P. Manuel. I analysed the neutron powder diffraction data, performed the symmetry analysis, performed the calculations to estimate the anisotropy and moment magnitudes of the Tm^{3+} ions together with R. D. Johnson. P. G. Radaelli helped with the interpretation of the magnetometry data. This work was published in Ref. [61].

4.1 Introduction

Tm^{3+} ions occupy the two 10-fold coordinated symmetry inequivalent A' sites, which are labelled Tm1 and Tm2, Fig. 4.1(a). The square planar A'' sites are occupied Mn^{3+} , labelled Mn1, and the A'' by Mn^{2+} , labelled Mn2, as determined by bond valence calculations [35]. This leaves the Mn B sites to have an average oxidation state of +3.25, such that three quarters of the B site Mn ions are in the +3 oxidation state, and the remaining quarter are in the +4 oxidation state. Experimentally the crystal structure of $\text{Tm}_2\text{MnMnMn}_4\text{O}_{12}$ is determined to have orthorhombic symmetry with space group $Pmmn$, which contains all the generators of the higher symmetry $P4_2/nmc$ parent structure apart from a 4_2 screw rotation that is broken due to charge ordering of the B-site Mn ions. The B-sites consist of alternating layers of Mn in the +3 and +3.5 oxidation states, which are labelled Mn3 and Mn4, respectively. The Mn4 layer could consist of 50% Mn^{3+} ions and 50% Mn^{4+} ions as discussed in Sec. 3.2.1. However given that this has not been experimentally verified the following analysis has been performed under the assumption that all Mn4 ions have an average oxidation state of +3.5. These layers are stacked along the c axis, as shown in Fig. 4.1, and give rise to a novel form of ferro-orbital order, where the half filled $d_{3z^2-r^2}$ of the JT distorted Mn3 ions are all aligned approximately parallel to c [62], mediated by the cooperative Jahn-Teller effect. Magnetometry and specific heat data collected on samples of $\text{Tm}_2\text{MnMnMn}_4\text{O}_{12}$, and published in Ref. [35], suggest the presence of two magnetic phase transitions at 75 K and 20 K.

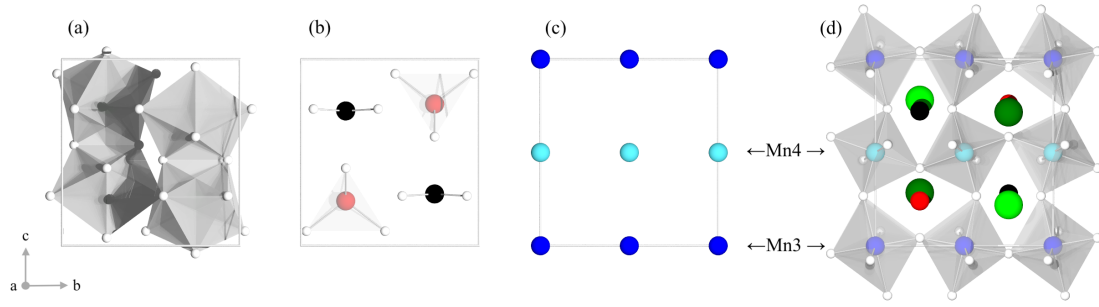


Figure 4.1: A projection of the crystal structure of $\text{Tm}_2\text{MnMnMn}_4\text{O}_{12}$ in the $Pmmn$ space group as seen from the a axis showing (a) the 10-fold coordinated R^{3+} sites (b) the square planar coordinated Mn1 (A') sites in black and the tetrahedrally coordinated Mn2 (A'') sites in red (c) the Mn3 and Mn4 (B) sites in dark and light blue respectively and (d) the entire crystal structure with the MnO_6 octahedra shaded in grey and the Tm1 and Tm2 sites in light and dark green respectively. The O^{2-} anions are given in white.

4.2 Experimental details

Polycrystalline samples with nominal composition $\text{Tm}_{0.91}\text{Mn}_{3.09}\text{O}_6$ (hereafter referred to as $\text{Tm}_2\text{MnMnMn}_4\text{O}_{12}$) were prepared from stoichiometric mixtures of Mn_2O_3 and Tm_2O_3 (99.9%). Single-phase Mn_2O_3 was prepared from commercial MnO_2 (99.99%) by heating in air at 923 K for 24 h. The mixtures were placed in Pt capsules and treated at 6 GPa and ~ 1670 K for 2 h (the time required to heat the sample to the desired temperature was 10 min) in a belt-type high-pressure apparatus. After the heat treatments, the samples were quenched to room temperature, the pressure was slowly released, and a black pellet of loosely packed powder was obtained. The temperature of the high-pressure apparatus was controlled by the heating power with a calibrated relationship between power and temperature. A sample with nominal composition $\text{Tm}_2\text{MnMnMn}_4\text{O}_{12}$ contained a large amount of $\text{Tm}_{1-x}\text{Mn}_x\text{MnO}_3$ impurity (approximately 28 wt. %). Shifting the nominal composition to $\text{Tm}_{0.91}\text{Mn}_{3.09}\text{MnO}_6$ was found to significantly reduce the impurity content.

DC magnetisation measurements were performed using a SQUID magnetometer (Quantum Design, MPMS-XL-7T) between 2 and 400 K in different applied fields under both zero-field-cooled (ZFC) and field-cooled on cooling (FCC) conditions.

Neutron diffraction measurements were performed using WISH. A 1.5 g powder sample of $\text{Tm}_2\text{MnMnMn}_4\text{O}_{12}$ was loaded into a 6 mm diameter vanadium can, and mounted within a ^4He cryostat. The sample was cooled to 1.5 K and diffraction data with good counting statistics were collected upon warming at 5 K intervals, except between 70 and 80 K where measurements were taken every 2 K. Data were also collected with high counting statistics within each magnetic phase including the paramagnetic phase for reference (85 K, 40 K and 1.5 K). The diffraction data were fit using the FULLPROF software suite [47].

4.3 Neutron powder diffraction study

4.3.1 Crystal structure

A $Pmmn$ crystal structure model based upon the published structure of $\text{Dy}_2\text{MnMnMn}_4\text{O}_{12}$ [35] was refined against neutron powder diffraction data measured in the paramagnetic phase at 85 K (Fig. 4.2(a)). The occupation of all atomic sites was set to one, but Mn was free to substitute Tm — as expected for the $R_2\text{MnMnMn}_4\text{O}_{12}$ phases [29]. An excellent fit was achieved ($R = 3.32\%$, $wR = 2.68\%$, $R_{\text{Bragg}} = 4.57\%$), and the refined crystal structure parameters are given in Table 9.5. Also tabulated are the cation bond valence sums, calculated using bond lengths given in Tables 9.8 and 9.9 of Appendix 9.3.1, which correspond well to the cited oxidation states. Approximately 15% of the Tm sites were found to be randomly substituted by Mn, giving the chemical formula $[\text{Tm}_{1.70(2)}\text{Mn}_{0.30(2)}]\text{MnMnMn}_4\text{O}_{12}$. Five weak diffraction peaks, labelled by asterisks in Fig. 4.2(a), could not be accounted for using the $Pmmn$ crystal structure model of $\text{Tm}_2\text{MnMnMn}_4\text{O}_{12}$. Instead, they were found to originate in two impurity phases, a TmMnO_3 -related phase (8.1(7) wt%) and MnCO_3 (0.5(1) wt%). The TmMnO_3 related impurity phase was determined to have composition $\text{Tm}_{0.59}\text{Mn}_{0.41}\text{MnO}_3$.

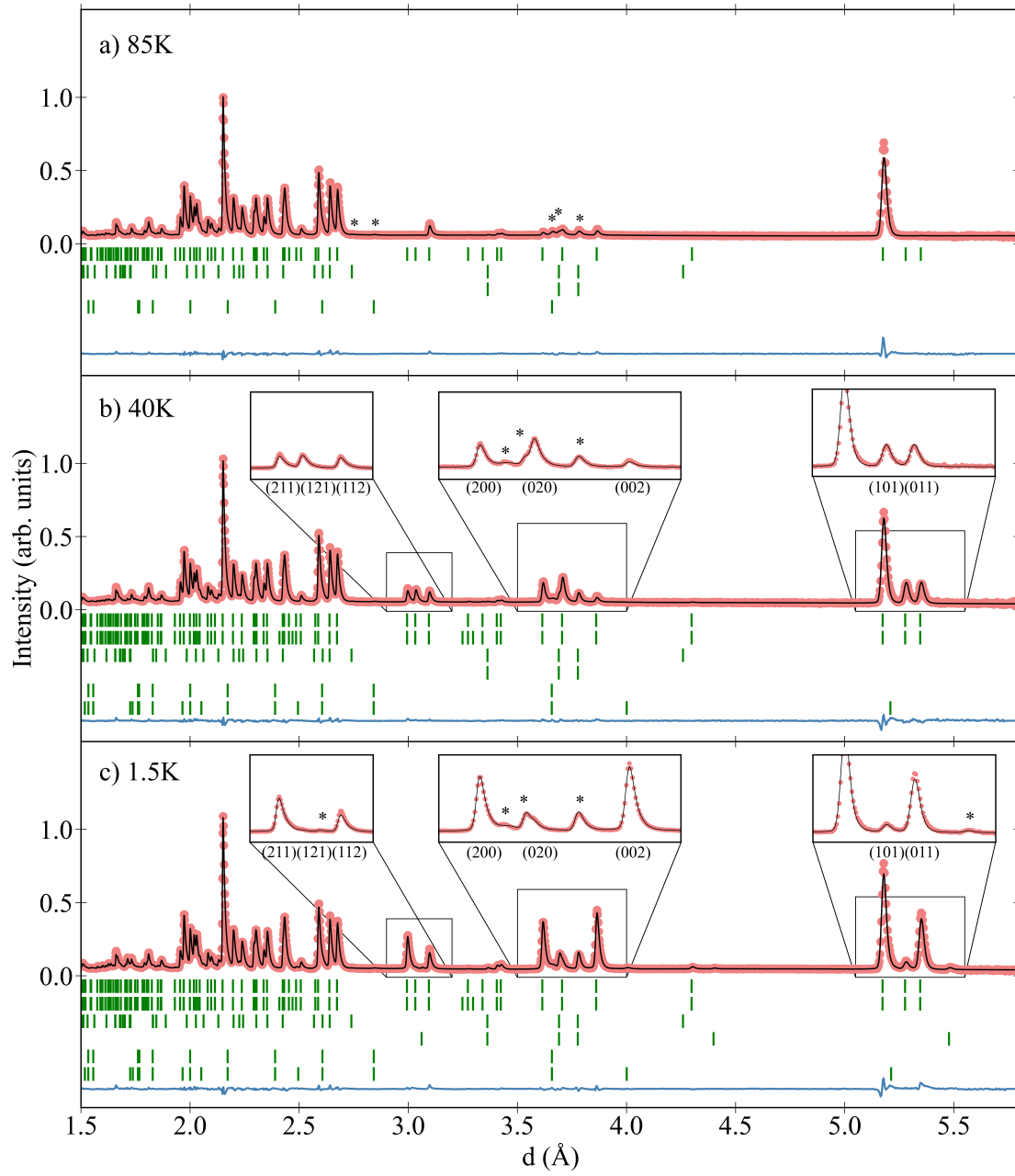


Figure 4.2: Neutron powder diffraction data taken on WISH at temperatures of a) 85 K b) 40 K and c) 1.5 K. The refinement is given by the black line and the raw data by the red circles, peaks labelled with an asterisk are from the impurity phases. The green tick marks indicate, from top to bottom, the nuclear and magnetic reflections from $\text{Tm}_2\text{MnMnMn}_4\text{O}_{12}$, labelled (1), the TmMnO_3 -related impurity, labelled (2), and the MnCO_3 impurity, labelled (3).

4.3.2 Magnetic structure

Below $T_c = 74$ K four new diffraction peaks appeared as shown in Fig. 4.2(b), which could be indexed as (011), (101), (121) and (211) with respect to the parent, $Pmmn$ crystal structure refined above, concomitant with changes in the sample's magnetisation and hence magnetic in origin. The intensities of the (002), (020) and (200) diffraction peaks, already present in the paramagnetic phase, were observed to grow below 74 K. These additional diffraction intensities were also determined to be magnetic, as their temperature dependence was the same as the first family of purely magnetic intensities listed above. All observed magnetic diffraction intensities are uniquely consistent with a $\mathbf{k}=(0,0,0)$, Γ -point magnetic propagation vector.

Magnetic structure models constructed from linear combinations of the tabulated symmetry adapted basis functions, Table 3.2, were systematically tested against neutron powder diffraction data measured at 40 K. It was determined that between 74 K and 28 K a magnetic structure involving A', A'' and B manganese moments, which transformed by the Γ_2^+ representation, was uniquely consistent with the diffraction data. Specifically, a model in which all Mn sublattices ordered with F_z modes (defined in Sec. 3.1.3) such that the Mn1, Mn3 and Mn4 sublattices are ferromagnetically aligned, and the Mn2 sublattice moments antialigned (a net ferrimagnetic structure), Fig. 4.3(b), had the best fit to the 40 K data shown in Fig. 4.2(b) ($R = 3.90\%$, $wR = 3.09\%$, $R_{\text{Mag}} = 4.90\%$). The refined moment magnitudes are given in Table 4.1. The fit was found to be insensitive to interchanging the Mn1 (Mn3) and Mn2 (Mn4) moments, and a model most consistent with the respective oxidation states is presented. It is noteworthy that the magnetic structure factor of the Mn B sites is exactly zero for the ($h11$) and ($1k1$) reflections, which therefore only have magnetic scattering contributions from the Mn A' and A'' sites.

Atom	Tm1	Tm2	Mn1	Mn2	Mn3	Mn4
40 K ($m z$ (μ_B))	0	0	1.957(9)	-3.10(1)	1.89(1)	1.58(1)
1.5 K ($m y$ (μ_B))	-0.77(2)	-3.70(3)	2.003(9)	-3.17(1)	1.91(1)	1.59(1)

Table 4.1: Magnetic moments of $\text{Tm}_2\text{MnMnMn}_4\text{O}_{12}$ refined at 1.5 and 40 K. Symmetry equivalent atoms have the same magnetic moment.

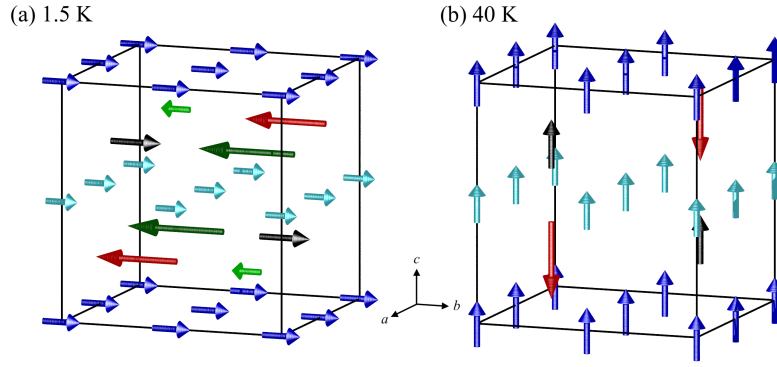


Figure 4.3: The refined magnetic structure of $\text{Tm}_2\text{MnMnMn}_4\text{O}_{12}$ at a) 1.5 K and b) 40 K. The crystallographic unit cell is drawn in black. The Tm1 and Tm2 ions are given light and dark green respectively, the Mn1 ions in red, the Mn2 ions in black, the Mn3 ions in dark blue and Mn4 ions in light blue.

On cooling below 28 K, the magnetic diffraction peaks undergo an approximately discontinuous change in their relative intensities. For example, the magnetic contribution to the (020) peak disappears, a large (002) magnetic intensity appears, and the (200) magnetic peak remains approximately the same. Given that the magnetic neutron diffraction intensity is proportional to the component of the spin perpendicular to the scattering vector, as discussed in Sec. 2.1, these changes are qualitatively consistent with a 90° flop of magnetic moments from the c axis to the b axis. Indeed, testing each of the irreducible representations against the neutron powder diffraction data conclusively revealed that the magnetic structure below $T_{\text{flop}} = 28$ K transformed by Γ_4^+ . This single irreducible representation solution for the low temperature magnetic structure comprises the same ferrimagnetic structure found above T_{flop} , but with moments aligned parallel to y (b axis) instead of z (c axis), as shown in Fig. 4.3(a). In order to accurately fit the 1.5 K diffraction data shown in Fig. 4.2(c), ($R = 3.82\%$, $wR = 3.53\%$, $R_{\text{Mag}} = 5.37\%$), it was necessary to include a finite, symmetry allowed moment on the Tm1 and Tm2 sublattices, both aligned antiparallel to the net magnetisation. The thulium contribution to the diffraction pattern is particularly apparent at d -spacings of 1.70-1.72 Å. Here the magnetic form factor of manganese is greatly reduced, as shown in Fig. 2.1, and thus the observed growth in magnetic intensity below T_{flop} is principally representative of the evolution of magnetic moments on the Tm1 and Tm2 ions. The moment magnitudes for all symmetry inequivalent cations refined at 1.5 K are given in Table 4.1. Again, the ratios between the Mn1 (Mn3) and Mn2 (Mn4) moments were chosen to be consistent with their oxidation states (these ratios were fixed

in the variable temperature data analysis presented below). Note that the Tm1 and Tm2 moments were found to be significantly smaller than their theoretical free ion values ($7\mu_B$), which is consistent with a polarised singlet ground state as discussed in Sec. 4.5.

As shown in Table 3.2 of Sec. 3.1.3, both the Γ_2^+ and Γ_4^+ irreducible representations allow for a canted magnetic structure of the B sites, *i.e.* the orthogonal superposition of antiferromagnetism onto the nominally ferromagnetic sublattice. However, the inclusion of these additional degrees of freedom into the refined magnetic structure model did not improve the fit to the neutron powder diffraction data, thus the collinear ferrimagnetic structures can be considered minimal models of $\text{Tm}_2\text{MnMnMn}_4\text{O}_{12}$.

Both impurity phases adopt long range magnetic order at low temperatures. Tm deficient TmMnO_3 undergoes three magnetic phase transitions at ~ 110 K, ~ 50 K and ~ 20 K [63], and MnCO_3 magnetically orders below 34.5 K [64]. The Tm-poor TmMnO_3 magnetic structures are yet to be fully determined, so the respective intensities were fit using the Le Bail method. The MnCO_3 magnetic diffraction peaks were fit using a G-type antiferromagnetic structure that well reproduced the diffraction intensities.

The temperature dependence of all symmetry inequivalent moment magnitudes was evaluated by fitting the above magnetic structure models to variable temperature neutron powder diffraction data, and is plotted in Fig. 4.4(b). Critical behaviour is observed at T_c that is consistent with a second order phase transition. To reliably extract the Tm moment dependences the magnitudes of the Mn moments were assumed to remain constant below 30 K. Fig. 4.4(c) shows the direction of the net magnetisation (moment axis) as a function of temperature, where Ω describes a rotation from the c axis towards the b axis. Ω was allowed to freely vary close to the spin-flop reorientation transition, but was fixed to the directions of the single irreducible representation magnetic structures deep into their respective phases.

4.4 Magnetometry

In this section, the ZFC and FCC DC M/H measurements shown in Fig. 4.4(a) are analysed in the context of the determined magnetic structure, and demonstrate that they are in full agreement with the

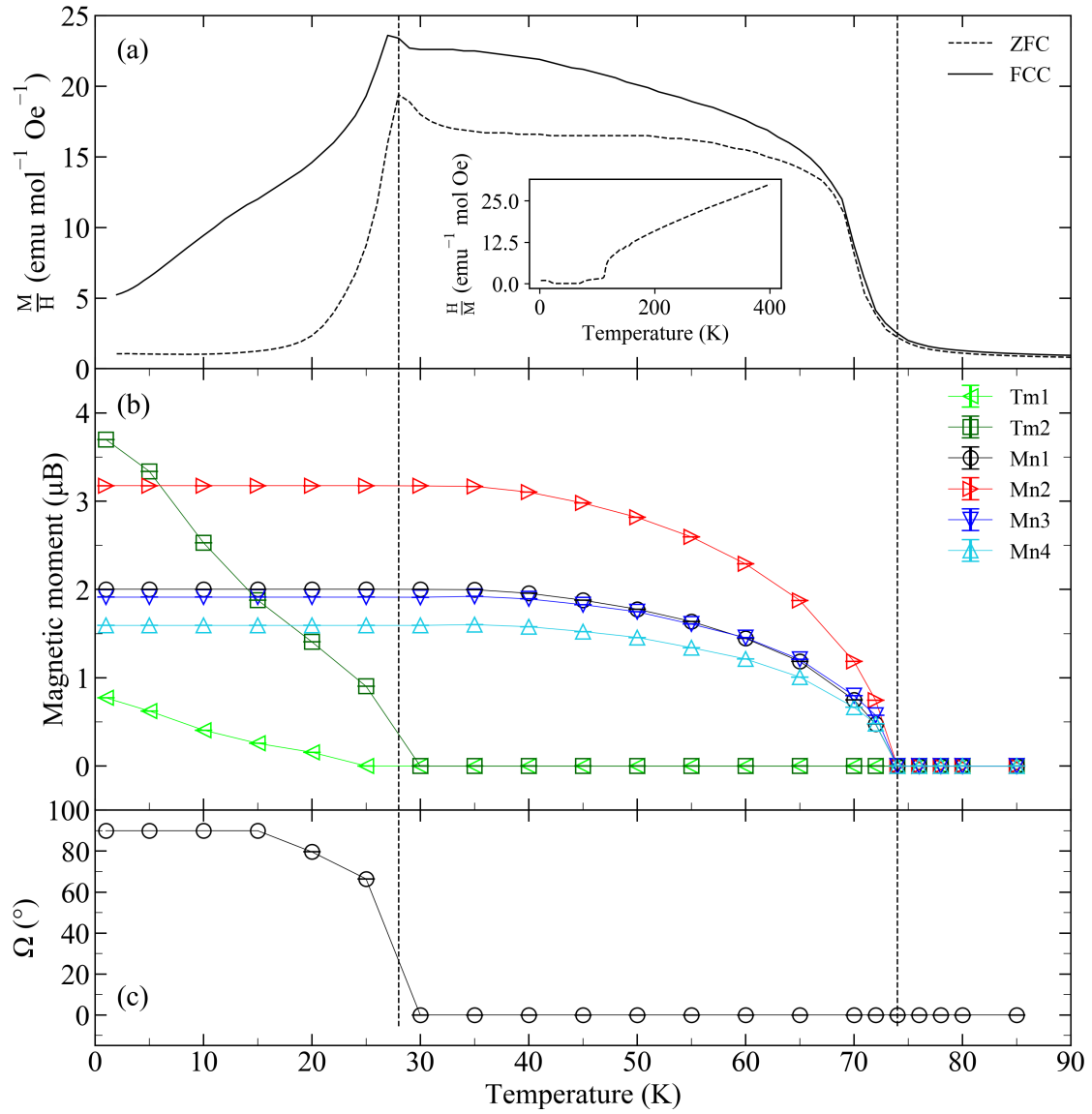


Figure 4.4: Temperature dependence of a) ZFC and FCC magnetisation measurements under an applied DC field of 100 Oe, b) single ion moment magnitudes given for each of the magnetic sublattices, and c) the direction of magnetisation, where Ω is the angle that describes a rotation from the c axis to the b axis. The black dashed lines are drawn at $T_c = 74$ K, and at $T_{\text{flop}} = 28$ K. The inset in a) shows the temperature dependence of H/M up to 400K.

results of the neutron powder diffraction data analysis. One can consider three primary contributions to the temperature dependence of M/H ; i) changes in the magnetic susceptibility of the manganese ions, which is peaked at the two phase transitions [35], ii) the Van-Vleck magnetic susceptibility of the thulium ions, which is small at all temperatures, and iii) the saturated magnetisation, domain effects, and powder averaging. Having ZFC to the lowest measured temperature both manganese and thulium susceptibilities are small, and approximately equal populations of ferrimagnetic domains cancel the sample's net magnetisation. As T_{flop} is approached on warming, the coercive field reduces [35] allowing for an increasing imbalance in ferrimagnetic domains induced by the small measuring field, giving rise to an increase in the sample's net magnetisation that is further enhanced by the reduction in the Tm1 and Tm2 moments aligned antiparallel to the net magnetisation. At the spin-flop transition the system becomes magnetically isotropic and the susceptibility is peaked, giving rise to a cusp in the powder averaged magnetisation. On further warming the sample maintains a net magnetisation, which decreases as T_c is approached, in accordance with the temperature dependence of the ordered magnetic moments (Fig. 4.4(b)). Above T_c the susceptibility follows a Curie-Weiss-like dependence of a paramagnet as shown in the inset of Fig. 4.4(a).

4.5 Rare earth magnetism

4.5.1 Tm^{3+} crystal electric field calculations

The CEF parameters, B_n^m , were calculated for Tm1 and Tm2 using atomic fractional coordinates and lattice parameters determined at 1.5 K, using the methods outlined in Sec. 3.2.2. The obtained values are given in Table 4.2. Similar magnitudes were obtained for the CEF parameters of the two Tm sites, but the sign of B_2^2 , B_4^2 , B_6^2 , and B_6^6 are opposite, which can be understood based on the presence of a 4_2 screw relating the two Tm sites that is present in the absence of B-site charge ordering. The eigenvalues and eigenfunctions of the crystal electric field Hamiltonian are given in Tables 4.3 and 4.4. The Tm^{3+} multiplets split into 13 singlet states.

Table 4.2: Crystal electric field parameters for Tm1 and Tm2, evaluated by the point charge model, and given in units μeV . Note that no estimate for the uncertainty has been provided for these values as they are only intended to provide a qualitative estimate for the crystal electric field splitting.

Atom	B_2^0	B_2^2	B_4^0	B_4^2	B_4^4	B_6^0	B_6^2	B_6^4	B_6^6
Tm1	1250	-915	-0.445	-3.70	2.53	0.00299	-0.0185	-0.0522	0.0495
Tm2	1252	741	-0.391	3.12	3.12	0.00353	0.0254	-0.0521	-0.0468

Table 4.3: Energy and eigenfunctions of the 13 singlet states of Tm1, as calculated using the crystal electric field Hamiltonian. The eigenfunctions are given as a linear superposition of $|J, mJ\rangle$ states. Note that no estimate for the uncertainty has been provided for these values as they are only intended to provide a qualitative estimate for the energy and eigenfunctions of the 13 singlet states.

Atom	Energy (meV)	Eigenfunction
Tm1	0	$0.005 6, \pm 6\rangle + 0.056 6, \pm 4\rangle + 0.390 6, \pm 2\rangle + 0.831 6, 0\rangle$
	0.20	$0.018 6, \pm 5\rangle + 0.167 6, \pm 3\rangle + 0.687 6, \pm 1\rangle$
	22.90	$\mp 0.076 6, \pm 5\rangle \mp 0.405 6, \pm 3\rangle \mp 0.574 6, \pm 1\rangle$
	24.52	$\mp 0.027 6, \pm 6\rangle \mp 0.211 6, \pm 4\rangle \mp 0.674 6, \pm 2\rangle$
	46.79	$-0.040 6, \pm 6\rangle - 0.262 6, \pm 4\rangle - 0.535 6, \pm 2\rangle + 0.537 6, 0\rangle$
	55.42	$0.176 6, \pm 5\rangle + 0.665 6, \pm 3\rangle - 0.166 6, \pm 1\rangle$
	63.20	$\mp 0.156 6, \pm 5\rangle \mp 0.554 6, \pm 3\rangle \pm 0.411 6, \pm 1\rangle$
	84.42	$\pm 0.118 6, \pm 6\rangle \pm 0.664 6, \pm 4\rangle \mp 0.212 6, \pm 2\rangle$
	84.88	$0.113 6, \pm 6\rangle + 0.643 6, \pm 4\rangle - 0.250 6, \pm 2\rangle + 0.147 6, 0\rangle$
	116.24	$\pm 0.685 6, \pm 5\rangle \mp 0.171 6, \pm 3\rangle \pm 0.030 6, \pm 1\rangle$
	116.40	$0.685 6, \pm 5\rangle - 0.175 6, \pm 3\rangle + 0.024 6, \pm 1\rangle$
	153.17	$0.697 6, \pm 6\rangle - 0.120 6, \pm 4\rangle + 0.007 6, \pm 2\rangle + 0.001 6, 0\rangle$
	153.18	$\mp 0.697 6, \pm 6\rangle \pm 0.121 6, \pm 4\rangle \mp 0.010 6, \pm 2\rangle$

Table 4.4: Energy and eigenfunctions of the 13 singlet states of Tm2, as calculated using the crystal electric field Hamiltonian. The eigenfunctions are given as a linear superposition of $|J, mJ\rangle$ states. Note that no estimate for the uncertainty has been provided for these values as they are only intended to provide a qualitative estimate for the energy and eigenfunctions of the 13 singlet states.

Atom	Energy (meV)	Eigenfunction
Tm2	0	$-0.002 6, \pm 6\rangle + 0.032 6, \pm 4\rangle - 0.357 6, \pm 2\rangle + 0.862 6, 0\rangle$
	0.32	$\pm 0.009 6, \pm 5\rangle \mp 0.130 6, \pm 3\rangle \pm 0.695 6, \pm 1\rangle$
	19.49	$0.057 6, \pm 5\rangle - 0.363 6, \pm 3\rangle + 0.604 6, \pm 1\rangle$
	21.65	$\pm 0.021 6, \pm 6\rangle \mp 0.176 6, \pm 4\rangle \pm 0.685 6, \pm 2\rangle$
	40.91	$0.029 6, \pm 6\rangle - 0.215 6, \pm 4\rangle + 0.576 6, \pm 2\rangle + 0.493 6, 0\rangle$
	50.91	$\pm 0.146 6, \pm 5\rangle \mp 0.680 6, \pm 3\rangle \mp 0.129 6, \pm 1\rangle$
	56.45	$-0.131 6, \pm 5\rangle + 0.590 6, \pm 3\rangle + 0.367 6, \pm 1\rangle$
	78.69	$\mp 0.100 6, \pm 6\rangle \pm 0.677 6, \pm 4\rangle \pm 0.177 6, \pm 2\rangle$
	78.84	$-0.097 6, \pm 6\rangle + 0.665 6, \pm 4\rangle + 0.203 6, \pm 2\rangle + 0.118 6, 0\rangle$
	110.48	$0.693 6, \pm 5\rangle + 0.141 6, \pm 3\rangle + 0.020 6, \pm 1\rangle$
	110.60	$\mp 0.692 6, \pm 5\rangle \mp 0.145 6, \pm 3\rangle \mp 0.018 6, \pm 1\rangle$
	149.07	$0.700 6, \pm 6\rangle + 0.102 6, \pm 4\rangle + 0.003 6, \pm 2\rangle - 0.002 6, 0\rangle$
	149.08	$\pm 0.700 6, \pm 6\rangle \pm 0.102 6, \pm 4\rangle \pm 0.005 6, \pm 2\rangle$

4.5.2 Polarised magnetic ground state

The 0 K singlet ground state is non-magnetic. However, there does exist an instability towards a polarised magnetic state when under a magnetic field, $\mathbf{B}$ [65]. The polarising field may originate in f - d magnetic exchange interactions between the Tm and the Mn sublattice. The single ion Hamiltonian is therefore written as follows;

$$\mathcal{H} = \mathcal{H}_{\text{cef}} + g_J \mu_B \mathbf{J} \cdot \mathbf{B}_{fd} \quad (4.1)$$

where $\mathbf{B}_{fd}$ represents an effective f - d exchange field. The sum of expectation values, $\langle J_x \rangle$, $\langle J_y \rangle$, and $\langle J_z \rangle$, for all eigenstates weighted by the Boltzmann distribution ($T = 10$ K), was evaluated for numerous magnetic field directions covering a full hemisphere, and in the limit of small $\mathbf{B}_{fd}$. A strong Ising-like anisotropy was found for both Tm ions, with the Ising directions of Tm1 and Tm2 parallel to the crystallographic a and b axes, respectively, as illustrated by the stereographic projections shown in Fig. 4.5. Note that the 90° rotation of the Ising axis from Tm1 to Tm2 is consistent with the tetragonal 4_2 screw pseudo-symmetry discussed above.

The sign of B_2^0 determines the single ion anisotropy to be Ising-like parallel to z (negative), or easy plane perpendicular to z (positive). In the latter case, large B_2^2 then imposes Ising-like anisotropy in the xy plane, the direction of which is determined by the sign of B_2^2 (negative makes it parallel to x and positive parallel to y). Given the dominance of these terms (Table 4.2) in the approximation of the CEF, any perturbation away from this model will not affect the qualitative determination of the Ising-like anisotropy and its direction.

4.5.3 How can Tm1 develop a moment perpendicular to its Ising axis?

The experimentally determined Mn magnetic structure $||b$ at low temperature provides a uniaxial polarising magnetic field for both Tm ions via f - d exchange. In this case one would expect a sizeable moment

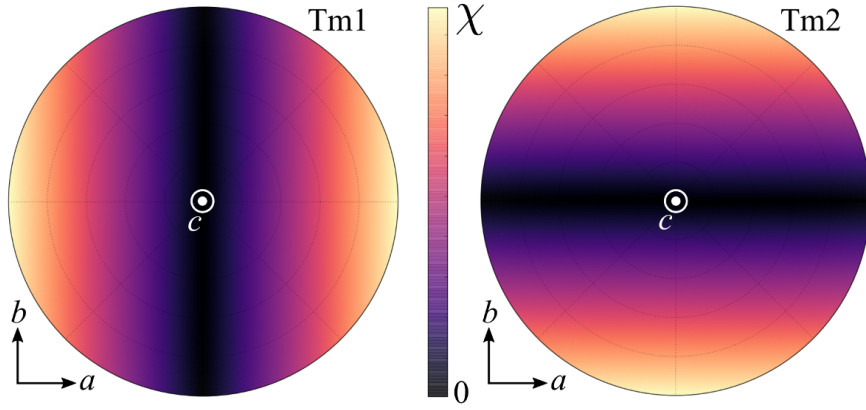


Figure 4.5: Stereographic projections of the Tm1 and Tm2 magnetic susceptibility calculated in the limit of small applied magnetic fields. The crystal electric field induced Ising-like single ion anisotropy of Tm1 and Tm2 lies parallel to a and b , respectively.

to be induced on Tm2 $\parallel b$, and a very small moment ($\leq 0.05 \mu_B$) to be induced on Tm1 $\parallel b$, as detailed in Sec. 4.5.2 and shown in Fig. 4.5. While the experimentally determined moment on the Tm2 sublattice ($3.7\mu_B$) is consistent with these results, the observation of a sizeable moment ($0.7\mu_B$) on the Tm1 sublattice aligned parallel to b was surprising. In this section it is shown that finite ferromagnetic f - f exchange interactions can give rise to the sizeable moment observed on the Tm1 sublattice.

To evaluate the effects of a finite ferromagnetic f - f exchange interactions on the magnetic moments on each of the Tm sublattices, a two ion spin Hamiltonian, Eqn. 4.2, composed of a term describing the crystal electric field, effective f - d exchange field and the f - f exchange field between Tm ions (separated along the c axis) was solved. The first and second terms are summed over both Tm1 and Tm2 sublattices. In the third term $\mathbf{J1}$ and $\mathbf{J2}$ refer to the angular momentum operators of the Tm1 and Tm2 sublattices respectively.

$$\mathcal{H} = \sum_{i=1,2} \mathcal{H}_{\text{cef},i} + g_J \mu_B \sum_{i=1,2} \mathbf{J}_i \cdot \mathbf{B}_i + \mathcal{J}_{f-f} (\mathbf{J1}_x \cdot \mathbf{J2}_x + \mathbf{J1}_y \cdot \mathbf{J2}_y + \mathbf{J1}_z \cdot \mathbf{J2}_z) \quad (4.2)$$

The magnetic field, $\mathbf{B}_i$ at each Tm site is expressed in terms of a Mn polarising field, ϕ_{Mn} , which describes a right handed rotation from the a axis within the ab plane. The polarising field was assumed to be uniaxial, in accordance with the experimentally determined Mn magnetic structure, and the polarising

fields at each Tm site was allowed to be different and is parametrised by the field at the Tm2 site, B_2 , and the ratio of the Mn polarising fields at the Tm1 and Tm2 sites, B_1/B_2 , as shown below.

$$\mathbf{B}_1 = \frac{B_1}{B_2} B_2 (\cos \phi_{\text{Mn}}, \sin \phi_{\text{Mn}}, 0) \quad (4.3)$$

$$\mathbf{B}_2 = B_2 (\cos \phi_{\text{Mn}}, \sin \phi_{\text{Mn}}, 0) \quad (4.4)$$

Experimentally the Tm1 and Tm2 sublattices are ferromagnetically coupled, therefore the f - f exchange, $\mathcal{J}_{f-f}$ was assumed to be ferromagnetic and has a negative sign. The moments on both Tm sublattices was evaluated using Eqn. 4.2 for different values of B_1/B_2 , $\mathcal{J}_{f-f}$ and ϕ_{Mn} , and is shown in Fig. 4.6. In general changing the ratio of B_1/B_2 , changes the ratio between the moments on the Tm1 and Tm2 sites, whilst changing the magnitude of B_2 principally changes the magnitude of the calculated moments, but also has the effect of changing the ratio of the moments between the two Tm sites. Rotating the Mn polarising field in the ab plane has the effect of moving between a ground state magnetic structure that orders by the Γ_4^+ irrep ($\phi_{\text{Mn}} = 90^\circ$), to a magnetic structure that orders by the Γ_3^+ irrep ($\phi_{\text{Mn}} = 0^\circ$). In between these limits a mixed irrep solution, using a combination of the Γ_3^+ and Γ_4^+ irreps is necessary to describe the magnetic structure.

B_2 was chosen to be 1.56 T so that a region of the phase diagram was consistent with the experimentally determined Tm magnetic moment magnitudes (dashed circles in Fig. 4.6). From Fig. 4.6 one can see that in the absence of any f - f exchange, the moments on the Tm1 site have almost zero moment when the Mn polarising field is oriented parallel to b , but can gain a finite moment $\parallel a$ when the Mn polarising field is $\parallel a$, consistent with Fig. 4.5. When the Mn polarising field is $\parallel b$ only finite f - f exchange interactions can stabilise a moment $\parallel b$ on the Tm1 site.

In $\text{Tm}_2\text{MnMnMn}_4\text{O}_{12}$ the Tm2 moment dominates below T_{flop} , imposing its b axis anisotropy on the system. Hence it is likely that the f - d exchange field in $\text{Tm}_2\text{MnMnMn}_4\text{O}_{12}$ is significantly larger at the Tm2 site than at the Tm1 site. In $\text{Tm}_2\text{MnMnMn}_4\text{O}_{12}$ the 4_2 screw symmetry is broken by charge and

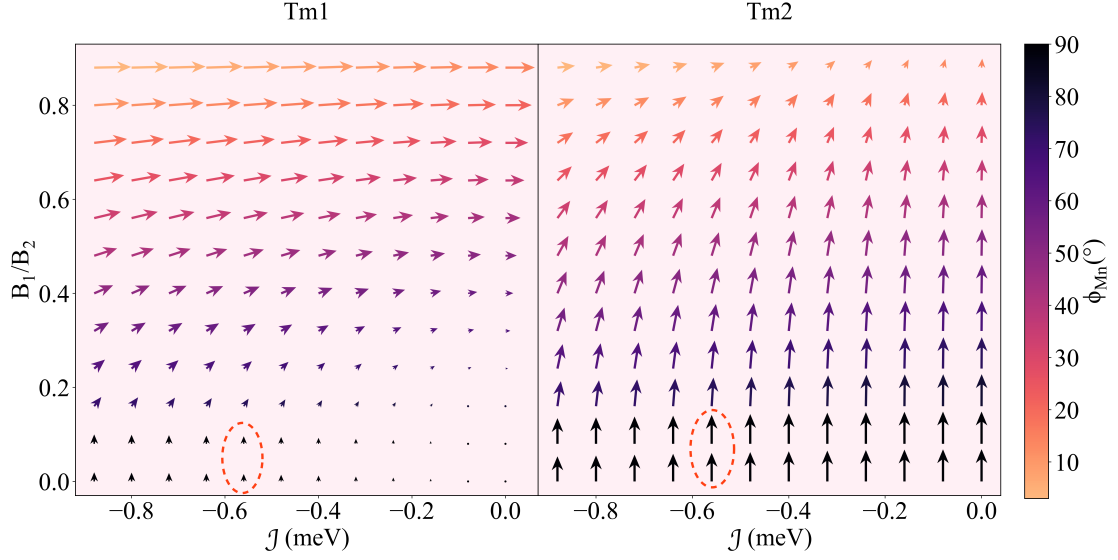


Figure 4.6: The Tm1 and Tm2 sublattice moments evaluated as a function of $\mathcal{J}_{f-f}$, B_1/B_2 , and the global in-plane magnetisation direction field from the Mn sublattice, ϕ_{Mn} . B_2 was set to 1.56 T. The moments consistent with the experimentally determined values are circled in red. A ϕ_{Mn} angle of 0° corresponds to the polarising field oriented parallel to the a axis, and a ϕ_{Mn} angle of 90° corresponds to the polarising field aligned along the b axis.

orbital order [35] that gives rise to different nearest neighbour Tm-O-Mn bonding conditions for Tm1 and Tm2, resulting in different f - d exchange fields at the two sites, and hence allowing a collinear ground state ferrimagnetic structure. For a 90° polarising field only finite f - f exchange interactions can give rise to a moment on Tm1 oriented perpendicular to its Ising axis, and hence it is feasible that the larger than expected Tm1 moment could naturally occur due to finite, ferromagnetic f - f exchange interactions.

4.6 Discussion

4.6.1 GKA revisited

As a direct consequence of the A-site $mm2$ point symmetry, all four nearest neighbour A-B exchange interactions must be equivalent, as shown in Fig. 4.7, and hence can only lower the energy of the system if ferromagnetism resides in the B site layers. To the contrary, the antiferromagnetic order favoured by B-B exchange, as discussed in Sec. 3.2.1, exactly frustrates the A-B exchange. Given the experimentally

determined ferrimagnetic structure, it is apparent that in $\text{Tm}_2\text{MnMnMn}_4\text{O}_{12}$ A-B exchange dominates B-B exchange - a scenario that is emerging in the study of quadruple perovskites [22], where large deviations from 180° B-O-B bond angles significantly weaken the respective superexchange interactions (in $\text{Tm}_2\text{MnMnMn}_4\text{O}_{12}$ these bond angles are $\sim 140^\circ$, as given in Table 9.9 of Appendix 9.3.1). One might expect that the $\text{R}_2\text{MnMnMn}_4\text{O}_{12}$ system could be tuned from ferrimagnetic to antiferromagnetic by modifying the critical balance between A-B and B-B exchange. In the absence of significant A-A exchange the stability of these two magnetic structures does not, in principle, depend upon long range magnetic order of the A-site ions. Hence this tuning can be achieved at the local level, where individual spins contribute on average to a net A-B exchange interaction.

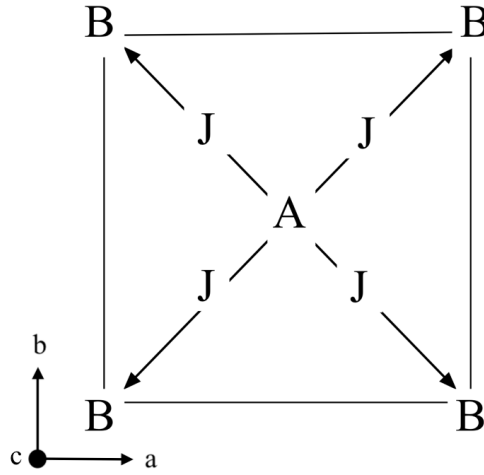


Figure 4.7: A representation of the nearest neighbour A-B exchange interactions below an A-site ion as viewed from the c axis. The four A-B exchange interactions, with magnitude J , are equivalent by the $mm2$ symmetry of the A site.

4.6.2 Spin reorientation phase transition

The microscopic origin of the spin-flop transition is now considered. Above T_{flop} the direction of the magnetic moments is determined by the average Mn single ion anisotropy, which is likely dominated by the electronic configuration of the Jahn-Teller active Mn3 ions placing the moments along c [66]. However, the c axis is a magnetically hard axis for both Tm1 and Tm2, whose Ising-like anisotropy was calculated to be along the a and b axes, respectively (Sec. 4.5). Hence, as the system temperature reaches

the energy scale of the f - d exchange field [67, 68], it becomes energetically favourable for the manganese magnetic moments to flop into the ab -plane such that the Tm ions adopt a polarised magnetic moment (at the expense of the weaker manganese SIA).

4.7 Conclusions

In $\text{Tm}_2\text{MnMnMn}_4\text{O}_{12}$, the A', A'' and B site manganese ions develop a collinear ferrimagnetic structure below 74 K, with moments oriented along the c axis. Remarkably, the ferrimagnetic order is in contradiction to that predicted by Goodenough-Kanamori-Anderson rules, whereby orbital order favours C-type antiferromagnetism (Fig. 1.3) instead. In $\text{Tm}_2\text{MnMnMn}_4\text{O}_{12}$, the average A-B exchange, together with the $mm2$ A- site symmetry, wins over B-B exchange and gives rise to ferrimagnetism. This offers the possibility of tuning the magnetic structure of $R_2\text{MnMnMn}_4\text{O}_{12}$ oxides from ferrimagnetic to antiferromagnetic through a modification of the competition between A-B and B-B exchange, for instance through doping of the A sites. Below 28 K, the Mn moments flop through a spin reorientation transition, retaining the higher temperature ferrimagnetic structure but with moments aligned along the b axis, and with a finite moment developing on both Tm sublattices aligned antiparallel to the net Mn magnetisation. Point charge calculations show that the Tm1 and Tm2 sublattices can adopt a polarised magnetic moment lying within the ab -plane, induced by a uniaxial f - d exchange field created by the ordered Mn B site sublattice, which motivates the spin flop transition at low temperature. The magnetic behaviour of $\text{Tm}_2\text{MnMnMn}_4\text{O}_{12}$ is strikingly similar to that of the rare-earth (RE) orthoferrites (REFeO_3), which crystallise in the orthorhombic $Pnma$ space group, and feature spin reorientation transitions driven by the single ion anisotropy of the rare earth ions [69].

Chapter 5

Spontaneous rotation of ferrimagnetism driven by antiferromagnetic spin canting

Spin-reorientation phase transitions that involve the rotation of a crystal's magnetisation have been well characterised in distorted perovskite oxides such as the orthoferrites. In these systems spin reorientation occurs due to competing rare earth and transition metal anisotropies coupled via f - d exchange. Here an alternative paradigm for spin reorientation in distorted perovskites is demonstrated. It is shown that the $R_2\text{CuMnMn}_4\text{O}_{12}$ ($R = \text{Y}$ or Dy) triple A-site columnar ordered quadruple perovskites have three ordered magnetic phases and up to two spin reorientation phase transitions. Unlike the spin reorientation phenomena in other distorted perovskites, these transitions are independent of rare earth magnetism, but are instead driven by an instability towards antiferromagnetic spin canting likely originating in frustrated Heisenberg exchange interactions, and the competition between Dzyaloshinskii-Moriya and single-ion anisotropies.

Acknowledgements

The powder samples of $R_2\text{CuMnMn}_4\text{O}_{12}$ ($R = \text{Y}$ and Dy) were synthesised, and magnetometry measurements were collected by L. Zhang and A. A. Belik. I performed the neutron powder diffraction

experiments together with D. D. Khalyavin and P. Manuel. J. Liu, R. D. Johnson and I collected the EPR data on $\text{Y}_2\text{CuMnMn}_4\text{O}_{12}$, and J. Liu assisted with the interpretation of the data. I refined the neutron powder diffraction data, performed the symmetry analysis, determined the g-tensor anisotropy of Dy^{3+} and modelled the mean field spin Hamiltonian, together with R. D. Johnson. This work was published in Ref. [70].

5.1 Introduction

Temperature induced spin-reorientation (SR) phase transitions occur between two long-range ordered magnetic phases [71, 72, 73], and can involve the rotation of the staggered magnetisation in antiferromagnets [74, 75, 76, 77], the net magnetisation in ferromagnets and ferrimagnets [78, 79], or both coupled together [80]. The discovery of SR transitions and the establishment of their microscopic origin has attracted substantial attention within the condensed matter physics community both in the fundamental study of order and dynamics in quantum magnetism, and in more applied directions where magnetisation switching is an essential ingredient for realising nanoscale components that form the building blocks of spintronic based technology [81], such as those used in spin-torque devices [82].

SR-based devices lend themselves to operating in the ultrafast regime when there exist two antialigned magnetic sublattices in, for example antiferromagnets or ferrimagnets [83], which is critical to achieving operational speeds that are comparable to those of charge-based devices [84]. The rare-earth (RE) orthoferrite [85, 86] distorted-perovskite oxides (generic chemical formula ABO_3 , $\text{A} = \text{RE}$ and $\text{B} = \text{Fe}$) are archetypal examples of materials that host ultrafast SR phase transitions [87]. Antiferromagnetic (AFM) order resides on the transition metal (TM) sublattice at all temperatures below T_N , and in certain symmetries a weak ferromagnetic (FM) moment appears through spin canting, which is coupled to the primary AFM order via the Dzyaloshinskii-Moriya interaction [88]. For compounds with a magnetic RE species, f - d exchange interactions have been found to couple either the weak FM moment or the staggered magnetisation of the TM sublattice to the RE sublattice. A temperature induced SR transition can then result if the RE and TM ions have competing magnetic anisotropies [69], as was observed in

$\text{Tm}_2\text{MnMnMn}_4\text{O}_{12}$ (Chapter. 4).

Here a new paradigm for SR transitions in distorted perovskites is demonstrated. It is shown that both $\text{Y}_2\text{CuMnMn}_4\text{O}_{12}$ (YCMO) and $\text{Dy}_2\text{CuMnMn}_4\text{O}_{12}$ (DCMO) columnar-ordered quadruple perovskites adopt a canted FIM structure ($m||b$) below $T_1 = 175$ K and 159 K, and undergo a SR transition to a collinear FIM ($m||c$) at $T_2 = 115$ K and 125 K, respectively. Both materials undergo another phase transition at $T_3 = 17$ K, to a canted FIM ground state with a doubled magnetic unit cell. In YCMO, this transition is accompanied by a rotation of the magnetisation back to $m||b$. In DCMO SR does not occur at T_3 , owing to an additional Ising-like anisotropy of the polarised Dy^{3+} crystal electric field (CEF) ground state. Unlike other distorted perovskites, the observed SR phenomena in YCMO and DCMO is independent of RE magnetism, but can instead be driven by an instability towards AFM spin canting combined with Dzyaloshinskii-Moriya and single-ion anisotropies.

5.2 Experimental details

A 2.06g polycrystalline sample of YCMO was prepared from a stoichiometric mixture of h-YMnO_3 , Mn_2O_3 , CuO and $\text{MnO}_{1.839}$. The mixture was annealed in small batches at 6 GPa and ~ 1670 K for 2 h in Pt capsules in a belt-type high-pressure apparatus, before the mixture was quenched to room temperature. A 1.32g polycrystalline sample of DCMO was prepared in the same way, using Dy_2O_3 instead of the h-YMnO_3 precursor [62]. DC magnetisation measurements were performed using a SQUID magnetometer (Quantum Design, MPMS-XL-7T) between 2 and 400 K under both zero-field-cooled (ZFC) and field-cooled on cooling (FCC) conditions. Neutron powder diffraction measurements were performed on WISH, and are discussed in Sec. 5.3.

5.3 Neutron powder diffraction study

Both samples were cooled to 1.5 K and neutron diffraction data were collected on warming through all magnetic phases in 5 K steps (2 K steps were used close to T_1 and also close to T_3 for YCMO). In

addition, data were collected with high counting statistics at temperatures representative of each magnetic phase. The crystal structure for both samples was refined against data collected in the paramagnetic phase using the published $Pmmn$ structure [62], which gave an excellent fit. The crystal structure parameters are detailed in Sec. 9.3 of the Appendix.

To determine the antisite cation disorder, which is common in these systems, each of the cations present in the sample was systematically substituted for the primary cation expected to occupy the site, and the model was refined. The refinement was constrained such that the total occupation of each site was not allowed to exceed the expected occupation (as determined by the Wyckoff position). The two A' sites (labelled $R1$ and $R2$) were found to be fully occupied by Y^{3+} and Dy^{3+} in each of the samples. The A'' sites (labelled Cu1) were occupied by 79.6(4)% Cu^{2+} and 20.4(4)% Mn^{3+} in YCMO, and 69.6(4)% Cu^{2+} and 30.4(4)% Mn^{3+} in DCMO. The A''' sites (Mn2) were occupied by 73.6(4)% Mn^{2+} and 26.4(4)% Y^{3+} in YCMO, and 78.4(4)% Mn^{2+} and 21.6(4)% Dy^{3+} in DCMO. The two symmetry inequivalent B sites form layers stacked alternately along c , labelled Mn3 and Mn4. The Mn3 layers were fully occupied by Mn^{3+} in YCMO, but had a 8(1)% occupation of Cu^{2+} in DCMO. The Mn4 layers were fully occupied by Mn^{4+} in both samples. Here the substitution of Cu^{2+} on the site has enabled complete occupation of the Mn4 layer by a single cation, unlike in $Tm_2MnMnMn_4O_{12}$ where the Mn4 layer is proposed to contain 50% Mn^{3+} and 50% Mn^{4+} .

To determine the magnetic structure of each magnetically ordered phase, first the magnetic propagation vector of each phase was identified. Subsequently all possible linear combinations of the magnetic modes for the given magnetic propagation vector, as tabulated in Table 3.2, were used to construct candidate magnetic structure models, under the assumption that all modes must transform by a single irreducible representation. The neutron powder diffraction data is analysed in terms of symmetry-adapted magnetic modes, F_i , A_i , X_i , and Y_i defined in Sec. 3.1.3. These candidate magnetic structure models were tested against the neutron diffraction data using the FULLPROF Software Suite [47], and the model that best fit the data while maintaining physical magnetic moment values, was identified as the magnetic structure of the phase.

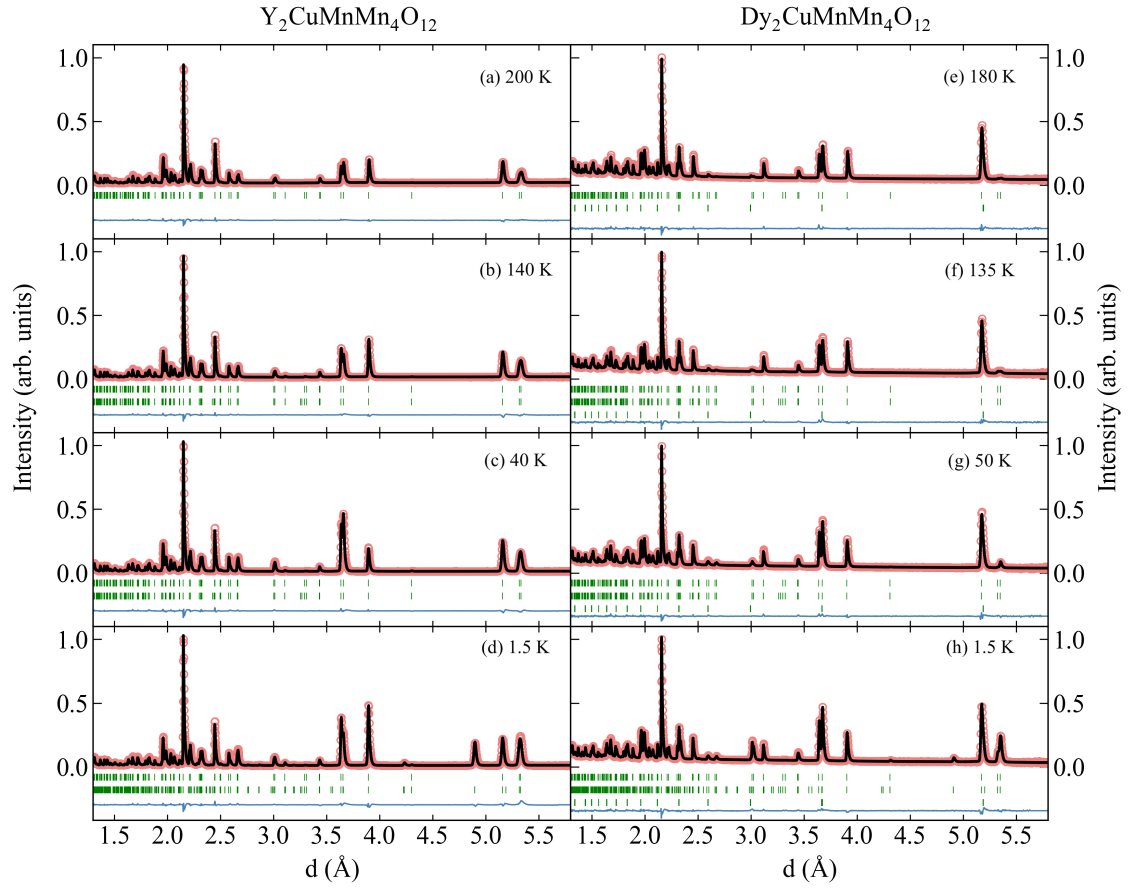


Figure 5.1: Neutron powder diffraction data taken on WISH for (a)-(d) YCMO and (e)-(h) DCMO. The refinement is given by the black line and the raw data by the red circles. The green tick marks indicate, from top to bottom, the nuclear and magnetic reflections. The reflections from DCMO are labelled (1) and the reflections from the $\text{DyMn}_7\text{O}_{12}$ impurity are labelled (2).

5.3.1 $\text{Y}_2\text{CuMnMn}_4\text{O}_{12}$

Below $T_1 = 175$ K new Γ -point intensities appeared in the diffraction pattern for YCMO (Fig. 5.1 and Fig. 5.2(a)) that occurred concomitantly with a rapid increase in the DC magnetic susceptibility shown in Fig. 5.3(a), which together indicate the development of long range FM sublattices. Rietveld refinement of the diffraction data showed that in this first magnetic phase (labelled CFI') Mn2 and Mn4 sites order with F_y modes, and the Mn3 sites order with A_x, F_y, Y_z modes (Fig. 5.5(c), all of which transform by the single irreducible representation (irrep) Γ_4^+ . This magnetic structure model gave an excellent fit to the data ($R_{\text{Mag}} = 3.57\%$ at 140 K). It was possible to obtain an equally good fit with additional A_x, Y_z AFM canting on the Mn4 sublattices, which is allowed by symmetry within the Γ_4^+ irrep. However given that the introduction of canted Mn4 layers did not significantly change the fit to the data, a minimal model in which only the Mn3 layers are canted, consistent with the low temperature CFI magnetic phase (see below) is presented. Key features of the magnetic structure can be directly observed in the diffraction pattern. For example the $\{200\}$ family of magnetic reflections, Fig. 5.2(a)-(c), originate in scattering from A- and B-site F_i modes only, and their relative intensities provide a direct measure of the direction, i , of the respective moments, as shown through structure factor calculations detailed in Sec. 9.2 of the Appendix. Zero magnetic intensity at (020) and equal magnetic intensities at (200) and (002), as shown in Fig. 5.2(a), is uniquely consistent with F_y modes. The $\{110\}$ family of magnetic intensities shown in Fig. 5.2(d)-(f) are also sensitive to F_i modes at the A-sites, and AFM A_i, X_i, Y_i modes (instead of F_i modes) at the B-sites. In this phase zero magnetic intensity at (110), and equal magnetic intensities at (011) and (101), Fig. 5.2(d), can only be accounted for by the presence of A_x, Y_z modes on Mn3 layers in addition to the Mn2 F_y mode. The F_y -modes combine to give a FIM structure with a net magnetisation parallel to y , and the A_x and Y_z modes give rise to spin canting of the Mn3 layers with the same amplitude in every Mn3 layer. The temperature dependence of the net magnetisation arising from the F_y modes, and the perpendicular moment magnitude of the A_x and Y_z canting are given in Fig. 5.3(c) and Fig. 5.3(e), respectively. As the temperature is lowered the magnetisation increases, in agreement with the temperature dependence of all symmetry inequivalent magnetic moments (Fig. 5.6). Note no moment was refined on the Cu1 sites, as discussed at the end of this section.

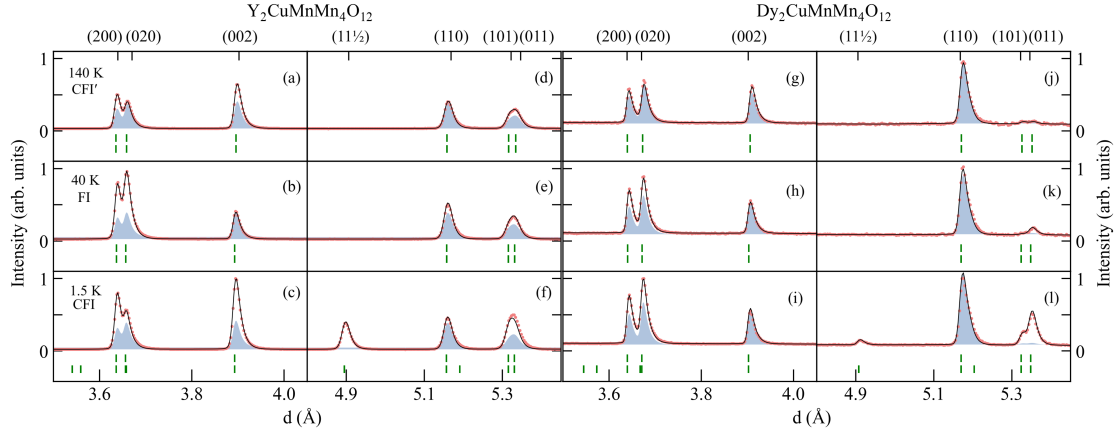


Figure 5.2: Neutron powder diffraction data taken on WISH; (a), (d), (g) and (j) were collected at 140 K; (b), (e), (h) and (k) at 40 K and (c), (f), (i) and (l) at 1.5 K. (a)-(c) $\{200\}$ and (d)-(f) $\{110\}$ reflections from YCMO, and (g)-(i) $\{200\}$ and (j)-(l) $\{110\}$ reflections from DCMO. The data are shown by the red circles, the fit by the solid black line and the blue shading represents the nuclear contribution to scattered intensity, including an impurity phase for DCMO. The green tick marks indicate, from top to bottom, the nuclear and magnetic reflections.

At $T_2 = 115$ K the shift of magnetic intensity from the (002) to the (020) reflection, whilst the (200) intensity remains the same (Fig. 5.2(b), indicates that the F_i mode, and therefore the net magnetisation, rotated from the b axis to the c axis. This SR transition is also apparent in magnetometry measurements shown in Fig. 5.3(a), that feature a characteristic cusplike increase in the magnetisation [61]. Rietveld refinement of data measured at 40 K showed that this second magnetic phase (labelled FI) has a collinear FIM structure where the Mn2, Mn3 and Mn4 sublattices order with F_z modes (Fig. 5.5), that transform by the single Γ_2^+ irrep, achieving an excellent fit to the data ($R_{\text{Mag}} = 2.935\%$ at 40 K). Note the relative phase of the modes on the different magnetic sites stays the same above and below the spin reorientation phase transition, and it is the entire magnetic structure that undergoes a rotation from $\parallel b$ to $\parallel c$, accompanied by a reduction of the AFM canting modes on the Mn3 sites. The SR transition at T_2 was found to occur over a 20 K interval, as shown in Fig. 5.3(a) and Fig. 5.3(c). The collinear phase then persists on cooling to a second SR transition at $T_3 = 17$ K.

Below T_3 , two significant changes to the diffraction pattern were observed. Firstly, eight new magnetic peaks appeared that could be indexed with a $\mathbf{k} = (0,0,0.5)$ propagation vector (Z-point). Secondly, intensity shifted from the (020) to the (002) reflection, showing that the F_i modes rotated back to the b axis.

In this third magnetic phase (labelled CFI), Mn2, Mn3 and Mn4 F_y modes, which all transform by the single Γ_4^+ irrep, accounted for all Γ -point magnetic intensities apart from a small intensity close to (011) that is likely due to the presence of an unidentified magnetic impurity. Testing each of the seven Z-point irreps, Table 3.2, against the eight new Z-point reflections that appeared in the diffraction pattern, showed that ordering of Z-point Y_x, A_z modes on either the Mn3 layers, described by the Z_1^+ irrep, or on the Mn4 layers, described by the Z_2^- irrep gave the best fit to this new family of reflections. The amplitude of the Y_x, A_z AFM canting modes on the Mn3 layers changes sign from one Mn3 layer to the next, in accordance with the propagation vector (Fig. 5.5(a). The two possible solutions could be differentiated, as in the latter case the Mn4 moment magnitudes were greater than the theoretically allowed maximum, making the Z_1^+ the only physical solution, and an excellent fit to the data was achieved ($R_{\text{Mag}} = 5.81\%$ at 1.5 K).

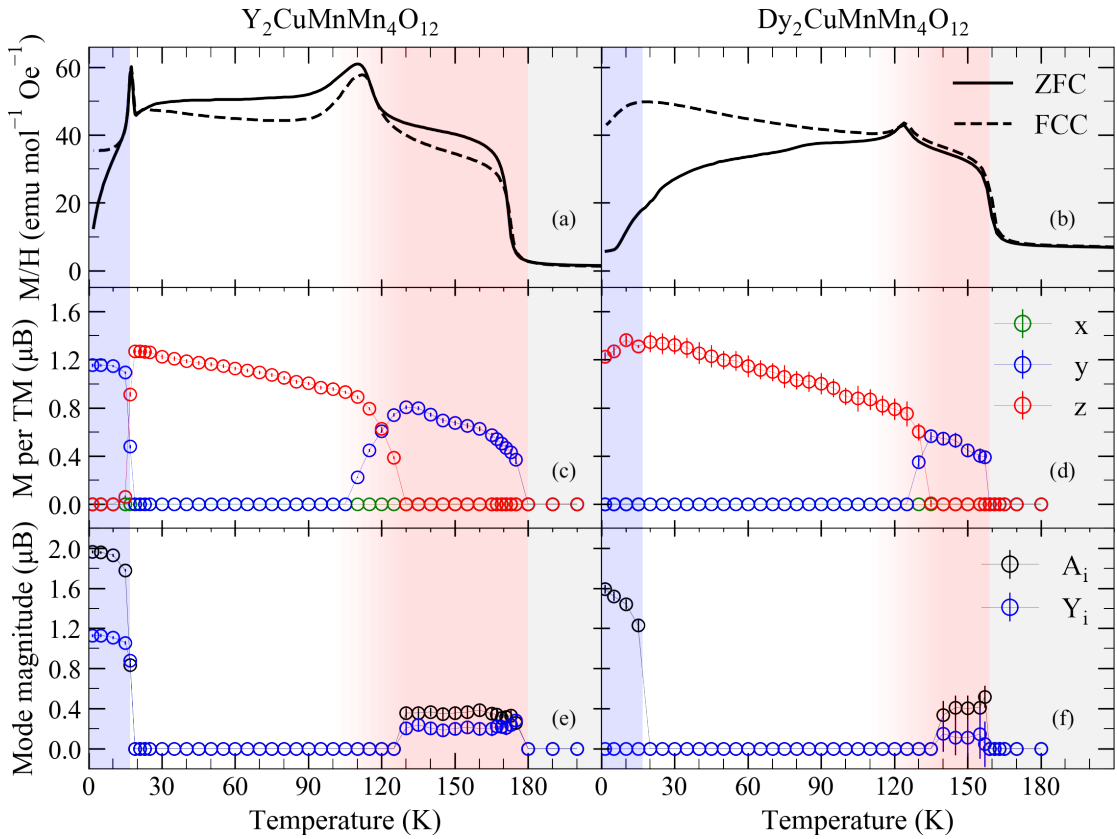


Figure 5.3: Temperature dependence of (a)-(b) ZFC and FCC magnetisation measurements under an applied DC field of 100 Oe (c)-(d) the net magnetisation per TM, and (e)-(f) the Mn3 moment magnitudes for each AFM spin canting mode. The net magnetisation was calculated by taking the sum over all magnetic sites in the unit cell (Cu1 had a contribution of zero to the net magnetisation).

The temperature dependence of all symmetry-inequivalent moment magnitudes and spin canting angles were evaluated by fitting the proposed magnetic structure models to variable temperature neutron powder diffraction data, and is shown in Fig. 5.6(a), 5.6(c), 5.6(e) and 5.6(g). Note that throughout the data analysis the moment magnitudes of symmetry inequivalent magnetic sublattices were refined independently. In all magnetic phases the analysis indicated zero moment on the Cu1 sites, despite strong exchange coupling of Cu demonstrated by ESR measurements (see Fig. 5.7 of Sec. 5.4). This effect could occur if the minority Mn^{3+} and majority Cu^{2+} ions, randomly located on the Cu1 site, had antiparallel moments, giving an average moment lower than the sensitivity of the experiment ¹. Note the sudden increase in the Mn2 site and Mn3 site moments below T_3 , Fig. 5.6(k), could indicate the softening of a low energy magnon mode, as discussed in the Conclusions (Chapter. 8).

The temperature dependence of the lattice parameters and unit cell volume, with respect to the 200 K crystal structure, were evaluated by fitting the crystal structure to variable temperature neutron powder diffraction data, and is shown in Fig. 5.4(a) and Fig. 5.4(b). A discontinuous change in the lattice parameters is observed at the onset of the CFI phase in YCMO, Fig. 5.4, which may indicate a first order magnetostructural phase transition.

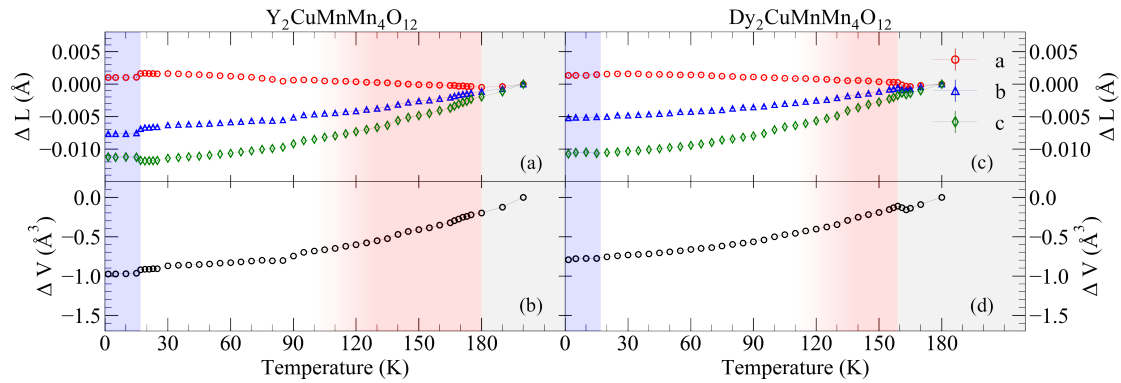


Figure 5.4: The temperature dependence of (a) the change in lattice parameters, a , b and c (b) the change in the unit cell volume V , for YCMO taken with respect to the 200 K crystal structure. The temperature dependence of (c) the change in lattice parameters, a , b and c (d) the change in the unit cell volume V , for DCMO taken with respect to the 180 K crystal structure.

¹This scenario is akin to alloys of niobium-vanadium and compounds with a mixture of deuterium and hydrogen, that give zero nuclear scattering length.

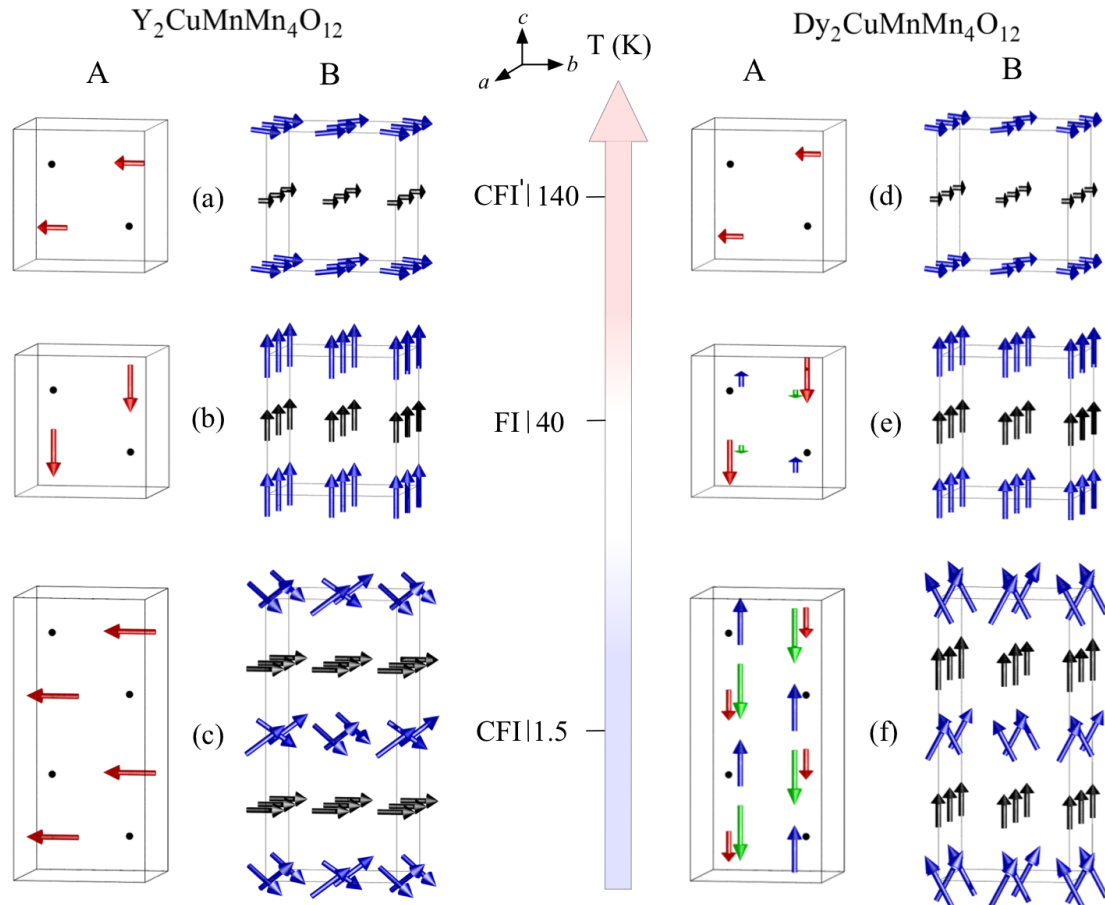


Figure 5.5: The refined magnetic structures, separated into the A and B sites, of (a)-(c) YCMO and (d)-(f) DCMO at temperatures of 1.5 K, 40 K and 140 K. For the A sites, $R1$ is shown in blue, $R2$ in green, $\text{Cu}1$ in black and $\text{Mn}2$ in red. For the B sites $\text{Mn}3$ is shown in blue and $\text{Mn}4$ in black. The crystallographic unit cell is drawn in black.

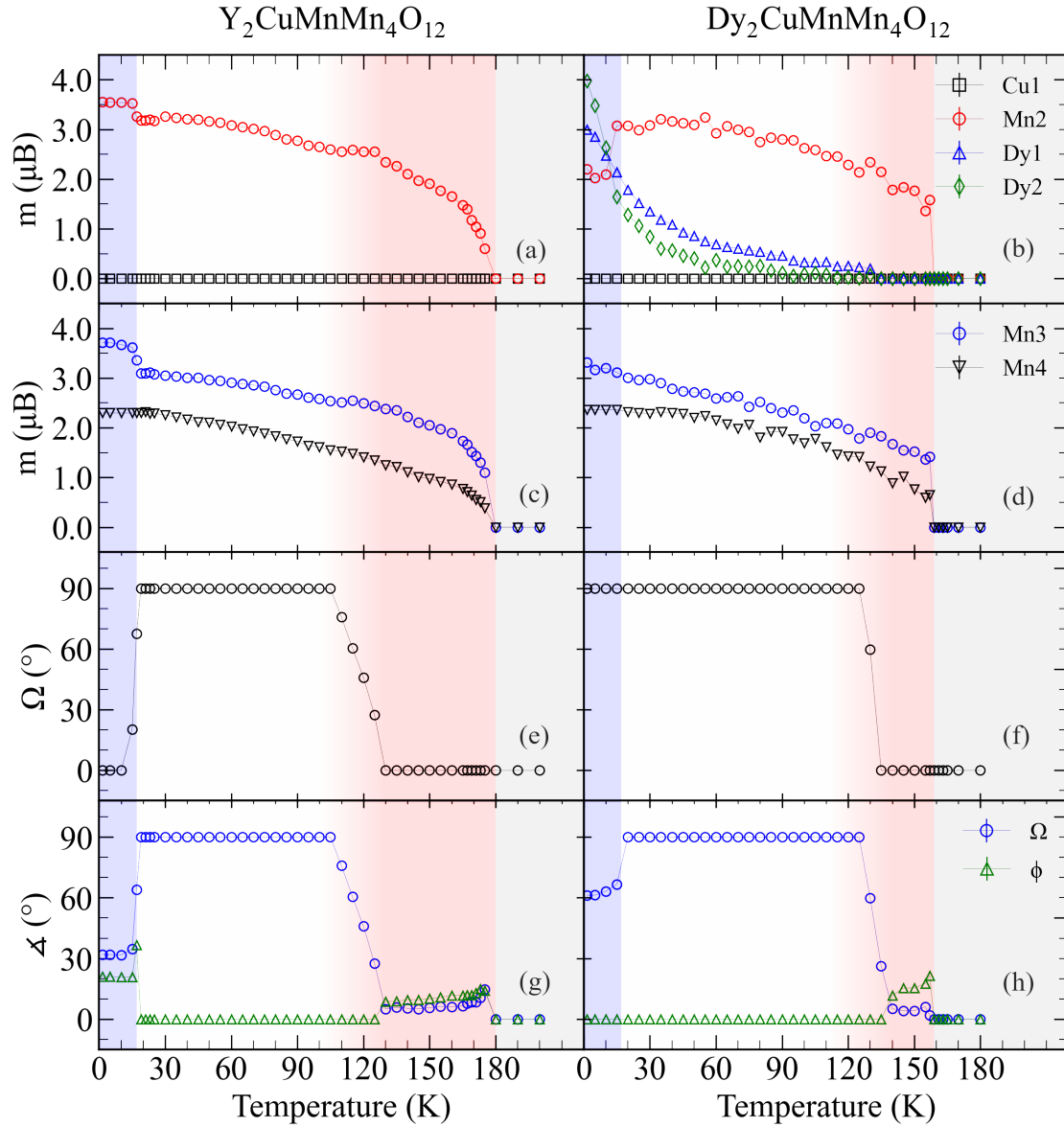


Figure 5.6: The temperature dependence of (a)-(b) the A' , A'' and A'' site magnetic moment magnitudes and (c)-(d) the B site magnetic moment magnitudes. (e)-(f) the spin canting angle Ω plotted for all magnetic sites with the exception of Mn3 (g)-(h) the Mn3 spin canting angles Ω and Φ . The magnetic moment components can be obtained from the total moment, m , and the spin canting angles Ω and Φ by the following expressions $x = m \cos \Omega \sin \Phi$, $y = m \cos \Omega \cos \Phi$ and $z = m \cos \Omega$ (defined for the Mn3 moment at $[0,0,0]$).

5.3.2 Dy₂CuMnMn₄O₁₂

In DCMO, the first two magnetic phases, CFI' and FI (Fig. 5.5(c) and Fig. 5.5(b)), were found to be identical to YCMO, except that in the FI phase an additional polarised moment developed on the Dy1 and Dy2 sublattices with $m \parallel c$. The two phases, CFI' and FI, transformed by the single Γ_4^+ and Γ_2^+ irreps respectively, and good fits to the data were obtained $R_{\text{Mag}} = 7.09\%$ at 135 K and $R_{\text{Mag}} = 4.08\%$ at 50 K, respectively. Note that the R_{Mag} values are considerably higher for the fits of the DCMO data compared with YCMO, because of the strong absorption from Dy which resulted in much weaker diffracted magnetic intensity. CEF calculations (Sec. 5.6.2) showed that the lowest lying Kramers doublet of both Dy1 and Dy2 is well separated from excited states, and has a strong Ising like g-tensor anisotropy $\parallel z$, which is consistent with the onset of a Dy1 and Dy2 moment only below the SR transition at $T_2 = 125$ K. Evidence for the polarised Dy1 and Dy2 moments was found at the (011) and (101) reflections (Fig. 5.2(k)), which are expected to be of equal intensity in the absence of a moment on the RE sites, determined by structure factor calculations given in Sec. 9.2 of the Appendix, as was the case for the YCMO magnetic structure refined at 40 K (Figure 5.2(e)). Instead the (011) and (101) reflections had unequal intensities consistent with a finite moment on the Dy sublattices. By comparison with YCMO, it is apparent that the additional Dy magnetism had two significant effects on the behaviour of the system. Firstly the SR transition between CFI' and FI became sharper, Fig. 5.3(b) and Fig. 5.3(d), and secondly at $T_3 = 17$ K it prevented the SR between phases FI and CFI (as indicated by the absence of any changes at the $\{200\}$ family of reflections (Fig. 5.2(i), and the absence of a cusp in the magnetic susceptibility, Fig. 5.3(b). Instead the CFI phase of DCMO had Γ -point F_z modes across all sites that maintained the FIM structure with magnetisation $\parallel c$ (Fig. 5.5(d). A single Z-point peak also appeared in the CFI phase, which could be fit by a single AFM canting mode on the Mn3 layer (either A_x or A_y), corresponding to the Z_4^+ and Z_3^+ irreps respectively. The moment direction of the A_i mode could not be robustly distinguished, given that the mode fitted a single statistically significant peak, the $(11\frac{1}{2})$ reflection, and was equally well fit with moments along a or b (at 1.5 K $R_{\text{Mag}} = 5.34\%$). Below T_3 there is a gradual increase in the magnetic intensity at the (101), which is best accounted for if the 22% Dy on the Mn2 sublattice gains an antiparallel moment to the Mn ions already ordered on that sublattice. This leads to a gradual reduction

in the net Mn2 sublattice magnetisation on cooling below T_3 as shown in Fig. 5.3(b). Another piece of experimental evidence that supports this observation is the small enhancement in the magnetisation apparent on cooling through T_3 , shown in Fig. 5.6(b), which would occur if the Dy moments align parallel to the net magnetisation. The temperature dependence of all symmetry-inequivalent moment magnitudes and spin canting angles were evaluated by fitting the proposed magnetic structure models to variable temperature neutron powder diffraction data, and is shown in Fig. 5.6(a), Fig. 5.6(c), Fig. 5.6(e) and Fig. 5.6(g). Throughout the data analysis the moment magnitudes of symmetry inequivalent magnetic sublattices were refined independently. Note that once again in all magnetic phases the analysis indicated zero moment on the Cu1 sites.

The temperature dependence of the change in lattice parameters and the change in unit cell volume, with respect to the 180 K crystal structure, were evaluated by fitting the crystal structure to variable temperature neutron powder diffraction data, and is shown in Fig. 5.4(c) and Fig. 5.4(d).

5.4 Electron paramagnetic resonance measurements

To determine if the Cu^{2+} ions are magnetically ordered below T_1 electron paramagnetic resonance (EPR) measurements were performed on YCMO at 300 K and 3 K using both X- (9.472 GHz) and Q-band (34 GHz) EPR spectrometers equipped with a ^4He flow cryostat. In the paramagnetic phase, and in the absence of any coupling between the ions, one would expect to observe three sets of peaks arising from the Cu^{2+} , Mn^{2+} and Mn^{4+} ions (Jahn-Teller active Mn^{3+} is expected to be absent in the range of the field sweep). Instead a single broad peak is observed, centred at $g = 1.99$ with a half width at half maximum of 0.051 T. The observation of a single peak indicates strong exchange coupling between all sites. The broadened linewidth can occur in the presence of antisymmetric Dzyaloshinsky-Moriya (DM) interactions, as observed in the simple orthorhombic manganites [89], and which is consistent with the observations from the neutron diffraction data of canting modes that give rise to DM interactions. The EPR experiment was repeated at 3 K, where the paramagnetic Cu^{2+} resonance is expected to be an order of magnitude larger than the signal at 300 K, and no significant feature was observed as shown by the

blue dashed line in Fig. 5.7, which conclusively rules out the presence of paramagnetic Cu^{2+} at low temperature.

Hence this confirms that even though the NPD data (which is sensitive to the average structure) did not detect any moment on the Cu1 sublattice, the ESR measurements (which is sensitive to local ordering) suggests the Cu^{2+} ions are ordered. The NPD data can be insensitive to an ordered moment on the Cu1 sublattice if the Mn^{3+} and Cu^{2+} ions randomly located on the Cu1 sublattice, due to the antisite disorder, have antiparallel moments.

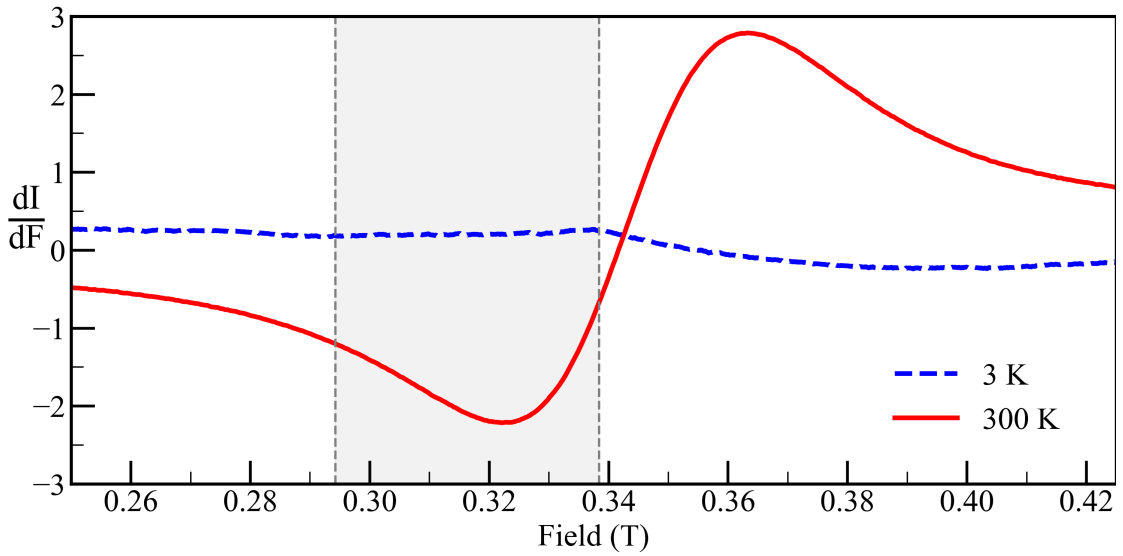


Figure 5.7: X-band EPR spectrum of YCMO showing the derivative of the absorption as a function of field at 300 K and 3 K. The shaded region in grey shows the range in magnetic field where one may expect to observe paramagnetic Cu^{2+} (corresponding to g values of 2 to 2.3 [44]).

5.5 Origin of canting

Spin canting typically arises when the Dzyaloshinskii-Moriya (DM) interaction is allowed by symmetry (*e.g.* in the orthoferrite YFeO_3 DM exchange induces a $\sim 0.3^\circ$ canting of Fe spins [90], which is small due to the DM interaction being approximately thirty times weaker than Heisenberg exchange [91]). By comparison, Mn3 spins in $R_2\text{CuMnMn}_4\text{O}_{12}$ exhibit canting angles of up to $\sim 30^\circ$ (Fig. 5.6), which are improbably large for DM-induced spin canting. Furthermore, the symmetry of spin canting found in the

CFI phase of DCMO is incompatible with DM exchange, as explained in the next section. Instead, large spin canting in $R_2\text{CuMnMn}_4\text{O}_{12}$ can be established by the competition between effective FM (Mn3-O-A-O-Mn3) and AFM (Mn3-O-Mn3) isotropic Heisenberg exchange between NN Mn3 spins in a given layer, as described in reference [61]. The former interactions favour F_i modes, whereas the latter primarily favour an A_i mode, which can be augmented by X_i or Y_i modes in the case of inequivalent exchange along x and y . In the mean field approximation one can show that this competition leads to two separate orders for the Mn3 sublattice; collinear FM or canted FM, which can be selected by tuning the ratio of the effective FM and AFM interaction strengths. This tuning is apparent when comparing the magnetic structures of $R_2\text{CuMnMn}_4\text{O}_{12}$ and $\text{Tm}_2\text{MnMnMn}_4\text{O}_{12}$ [61]. In $\text{Tm}_2\text{MnMnMn}_4\text{O}_{12}$ every A' site was occupied by Mn^{3+} and spin canting was not observed [61]. In $R_2\text{CuMnMn}_4\text{O}_{12}$ the magnetic moment on the A' sites was considerably reduced by the substitution of Mn^{3+} for Cu^{2+} , giving a smaller effective FM exchange and prevalent spin canting.

Whilst competing Heisenberg exchange can establish spin canting, it cannot alone determine the orientation of the magnetic moments with respect to the crystal structure. However, once the canted structure exists, DM interactions can play a dominant role in determining the spin anisotropy, as they will be optimized when the moment components of the primary B-site magnetic modes (F_i , A_i , Y_i)² are placed along specific crystallographic directions [92, 93]. This is discussed in detail in the following section, in which the trilinear free energy invariants are derived.

5.6 Magnetic anisotropy

5.6.1 Trilinear free energy invariants

Formally the DM interactions couple orthogonal moment components from two magnetic modes of different type (*e.g.* A_x , F_y) and only exist on bonds that do not have inversion symmetry. In the perovskite

²Note that B-site A_i and Y_i modes are expected to arise according to the GKA rules (Sec. 3.2.1). The F_i mode are expected to arise if A-B exchange dominates over B-B exchange (Sec. 4.6.1).

oxides the breaking of inversion symmetry between neighbouring B site Mn atoms is due to a polar displacement of an oxygen anion away from the inversion centre. The displacements of oxygen anions are primarily due to the octahedral rotations of the MnO_6 octahedra and therefore it is possible that the two magnetic modes giving rise to the DM interactions would couple to a structural distortion giving rise to the octahedral rotations, and form trilinear coupling invariants.

By doing a modal decomposition of the crystal structure with a higher symmetry space group, that preserves the inversion symmetry on the B-site Mn-O-Mn bonds, one can determine the irreps that give rise to the magnetic modes and structural distortions, and therefore the possible trilinear free energy invariants that give rise to DM interactions. The invariants with the largest mode amplitudes are more likely to be observed given that they would have a higher contribution to the free energy.

A hypothetical manganite structure with $P4/mmm$ tetragonal space group symmetry that retains the inequivalent Mn3 and Mn4 B site ions present in the lower symmetry $Pmmn$ crystal structure, whilst also preserving the centrosymmetric B site Mn bonds, was used to perform the modal decomposition. The crystal structure parameters for the hypothetical parent structure are given in Table 5.1. ISODISTORT was used to perform the mode decomposition of the distorted structure using a basis transformation of (2,0,0), (0,2,0), (0,0,1) with an origin of (0,0,0) between the undistorted $P4/mmm$ and the distorted $Pmmn$ crystal structures.

Table 5.1: Crystal structure parameters of hypothetical $P4/mmm$ parent crystal structure of . The lattice parameters were set to be $a = 3.635\text{\AA}$, $b = 3.635\text{\AA}$, and $c = 7.79621(9)\text{\AA}$.

Atom	Site	Sym.	x	y	z
Mn1	1a	$4/mmm$	0.00	0.00	0.00
Mn2	1b	$4/mmm$	0.00	0.00	0.50
O1	2f	mmm	0.50	0.00	0.00
O2	2e	mmm	0.50	0.00	0.50
O3	2g	$4mm$	0.00	0.00	0.25

From the mode decomposition three structural modes, labelled Λ_x , Λ_y and Λ_z , were identified, which correspond to the $(a^+, 0, 0)$, $(0, b^+, 0)$ and $(0, 0, c^-)$ octahedral tilts respectively. These modes are

Table 5.2: The octahedral tilt modes for the Wyckoff positions of the hypothetical $P4/mmm$ manganite crystal structure. These tilt modes give rise to the $Pmmn$ crystal structure of $R_2\text{MnMnMn}_4\text{O}_{12}$ and are listed with the corresponding propagation vector, order parameter and mode amplitude.

Mode	Propagation vector	O.P.	Amplitude
Λ_x	(0.0, 0.5, 0.0)	(a, 0)	1.94533
Λ_y	(0.5, 0.0, 0.0)	(0, a)	1.87089
Λ_z	(0.5, 0.5, 0.0)	(a)	1.38944

listed in Table 5.2 together with the corresponding propagation vector and order parameter. For each magnetic mode the propagation vector, order parameter and mode amplitude are listed with the respect to the $P4/mmm$ structure in Table 5.3.

Table 5.3: The propagation vector and order parameter of the F_i , A_i , X_i , Y_i magnetic modes listed with the respect to the hypothetical $P4/mmm$ structure for each of the three polarisation modes. $k_z = 0$ for the Γ -point magnetic modes, and $k_z = 1/2$ for the Z-point magnetic modes.

Mode	Polarisation	Propagation vector	O.P.
F_i	x	(0.0, 0.0, k_z)	(a, 0)
	y	(0.0, 0.0, k_z)	(0, a)
	z	(0.0, 0.0, k_z)	(a)
A_i	x	(0.5, 0.5, k_z)	(a, -a)
	y	(0.5, 0.5, k_z)	(a, a)
	z	(0.5, 0.5, k_z)	(a)
X_i	x	(0.5, 0.0, k_z)	(0, a)
	y	(0.5, 0.0, k_z)	(0, a)
	z	(0.5, 0.0, k_z)	(0, a)
Y_i	x	(0.0, 0.5, k_z)	(a, 0)
	y	(0.0, 0.5, k_z)	(a, 0)
	z	(0.0, 0.5, k_z)	(a, 0)

The ISOTROPY software suite [53] was used to form the trilinear free energy invariants that could give rise to the DM interaction by coupling two magnetic order parameters to an octahedral tilt structural order parameter, so that the combined action of all three modes are invariant by all operators of the $P4/mmm$ parent space group and is translationally invariant. The symmetry of these order parameters

are characterised in terms of the $P4/mmm$ parent, and their invariance will be judged by the $P4/mmm$ parent. Only a finite number of combinations are therefore allowed, and are listed in Table 5.4.

Table 5.4: Dzyaloshinskii-Moriya coupling invariants listed according to the irreducible representations of their magnetic modes defined with respect to the true $Pmmn$ parent. The magnetic mode not coupled by DM but which transforms by the same irreducible representation is given in brackets.

Magnetic Irrep.	Coupling to Λ_x	Coupling to Λ_y	Coupling to Λ_z
$\Gamma_1^+, Z_1^\pm$	$X_y : A_z (Y_x)$	$Y_x : A_z (A_z)$	-
$\Gamma_2^+, Z_2^\pm$	$Y_y : F_z (X_x)$	$X_x : F_z (Y_y)$	-
$\Gamma_3^+, Z_3^\pm$	$A_y : X_z (F_x)$	$F_x : X_z (A_y)$	$F_x : A_y (X_z)$
$\Gamma_4^+, Z_4^\pm$	$F_y : Y_z (A_x)$	$A_x : Y_z (F_y)$	$A_x : F_y (Y_z)$

The A_x , F_y , and Y_z combination (Γ_4^+ irrep), as found in the CFI' phase of both YCMO and DCMO, presents a unique combination of all three primary modes mutually coupled by DM interactions, and places the net magnetisation parallel to b . The intermediate FI phase of both YCMO and DCMO has an approximately collinear magnetic structure (within the sensitivity of the experiment), which drastically reduces the DM interactions. The F_i modes then follow the weak easy axis single-ion-anisotropy of Mn^{3+} , which is parallel to the c axis on average [66]. This suggests a SR phase transition driven by the competition between DM and single ion anisotropies. In the CFI phase of YCMO, symmetry prohibits DM interactions between the Γ -point F_y and the Z-point A_i, Y_i modes. However the latter modes can couple via DM exchange in two symmetries: the Z_1^+ irrep (Y_x, A_z) and the Z_4^+ irrep (A_x, Y_z). Symmetry alone cannot determine which scenario is realised (the former was observed), but both involve moment components along x and z meaning that the net magnetisation from the Γ -point F_i mode will be placed parallel to b (y) to establish a constant moment ground state. To the contrary, in the CFI phase of DCMO the net magnetisation lies parallel to c (F_z modes). For A_i or Y_i modes to be included in a constant moment ground state they must have moment components perpendicular to z . However, there is no single irrep that transforms (couples) A_x, Y_y or Y_x, A_y . Accordingly, the canted ground state of DCMO does not optimise antisymmetric exchange but is instead predominantly selected by the dominant, Ising-like anisotropy of Dy^{3+} as shown in Sec. 5.6.2.

5.6.2 Dy³⁺ crystal electric field calculations

The electronic configuration of Dy³⁺ is [Xe] 4f⁹, and for the free ion Hunds rules give $S = 5/2$, $L = 5$, and $J = 15/2$ for the lowest energy 16-fold multiplet of states. Dy³⁺ is a Kramers ion, and in DCMO its crystal electric field (CEF), which transforms by the abelian point group $mm2$ (C_{2v}), can lift the multiplet degeneracy to form 8 doublet states.

The point charge calculations were performed for Dy1 and Dy2 using atomic fractional coordinates refined in the paramagnetic phase (Table 9.14), and lattice parameters measured at 1.5 K, and the obtained values of B_n^m are given in Table 5.5. Similar magnitudes were obtained for the CEF parameters of the two Dy sites, but the sign of B_2^2 , B_4^2 , B_6^2 , and B_6^6 are opposite, which can be understood based on the presence of a 4_2 screw pseudosymmetry relating the two Dy sites, as found in $\text{Tm}_2\text{MnMnMn}_4\text{O}_{12}$.

Table 5.5: Crystal electric field parameters for Dy1 and Dy2, evaluated by the point charge model, given in units μeV and to 3.s.f. Note that no estimate for the uncertainty has been provided for these values as they are only intended to provide a qualitative estimate for the crystal electric field splitting.

Atom	B_2^0	B_2^2	B_4^0	B_4^2	B_4^4	B_6^0	B_6^2	B_6^4	B_6^6
Dy1	-883	647	0.213	1.90	-0.810	-0.000774	0.00420	0.0130	-0.0117
Dy2	-764	-563	0.153	-1.88	-0.811	-0.000883	-0.00531	0.0132	0.0119

The CEF Hamiltonian, $\mathcal{H}_{\text{cef}}$, was diagonalised giving 8 doublet states, as expected. For Dy1 and Dy2 the first excited doublet was found to be 32.4107 meV and 29.1728 meV higher than the ground state, respectively. Hence, the ground state doublets alone provided an adequate description of the Dy1 and Dy2 4f electronic states throughout the magnetically ordered phases of DCMO. The degenerate ground state doublet wavefunctions for Dy1 were, to good approximation;

$$\Psi_{\pm}^{(1)} = 0.98|15/2, \pm 15/2\rangle - 0.18|15/2, \pm 11/2\rangle + 0.02|15/2, \pm 7/2\rangle \quad (5.1)$$

and for Dy2:

$$\Psi_{\pm}^{(2)} = 0.98|15/2, \pm 15/2\rangle - 0.19|15/2, \pm 11/2\rangle + 0.02|15/2, \pm 7/2\rangle \quad (5.2)$$

given in terms of the $|J, m_J\rangle$ basis.

The ground state doublets could be mapped onto a $J = 1/2$ basis such that,

$$\mathbf{g}^{(1)}\langle\pm|\hat{S}|\pm\rangle = g_J\langle\Psi_{\pm}^{(1)}|\hat{J}|\Psi_{\pm}^{(1)}\rangle, \text{ and} \quad (5.3)$$

$$\mathbf{g}^{(2)}\langle\pm|\hat{S}|\pm\rangle = g_J\langle\Psi_{\pm}^{(2)}|\hat{J}|\Psi_{\pm}^{(2)}\rangle \quad (5.4)$$

where $\mathbf{g}^{(1)}$ and $\mathbf{g}^{(2)}$ are the g-tensors for Dy1 and Dy2, and $|+\rangle$ and $|-\rangle$ are the $m_J = +1/2$ and $m_J = -1/2$ states of the $J_{\text{eff}} = 1/2$ basis, respectively. Using these expressions one can show that $g_{zz}^{(1)} = 19.82$, $g_{zz}^{(2)} = 19.80$, g_{xx} and g_{yy} are zero to good approximation, and all other components equal zero by symmetry. Therefore the g-tensors for Dy1 and Dy2 are uniaxial, parallel to the crystallographic c axis of DCMO.

5.7 Microscopic Dzyaloshinskii Moriya interactions

In this section the DM interactions in the CFI' phase is considered, and a spin Hamiltonian is derived to explore the optimum canting angle of the spins in the ab plane of the Mn3 and Mn4 layers. In the absence of chirality, which is the case for the RCMO systems, it is possible to evaluate local DM vectors, $\mathbf{D}_{ij}$, as the cross product between the bond, $\mathbf{r}_{ij}$, and the displacement of the ion from the centre of the bond, $\mathbf{P}_{ij}$, as given by Eqn. 5.5. [54].

$$\mathbf{D}_{ij} = \mathbf{P}_{ij} \times \mathbf{r}_{ij} \quad (5.5)$$

Fig. 5.8 shows a projection of the $Pmmn$ $R_2\text{CuMnMn}_4\text{O}_{12}$ unit cell from each of the crystallographic directions, with the experimentally determined A_x, F_y, Y_z spin configuration of the CFI' phase. The direction of the DM vector of every bond in a single $Pmmn$ unit cell of the $R_2\text{CuMnMn}_4\text{O}_{12}$ crystal structure was determined according to Eqn. 5.5 and shown in Fig. 5.8 labelled as D. The direction of the cross product between the two spins either side of each bond is also shown in Fig. 5.8 and labelled S. If

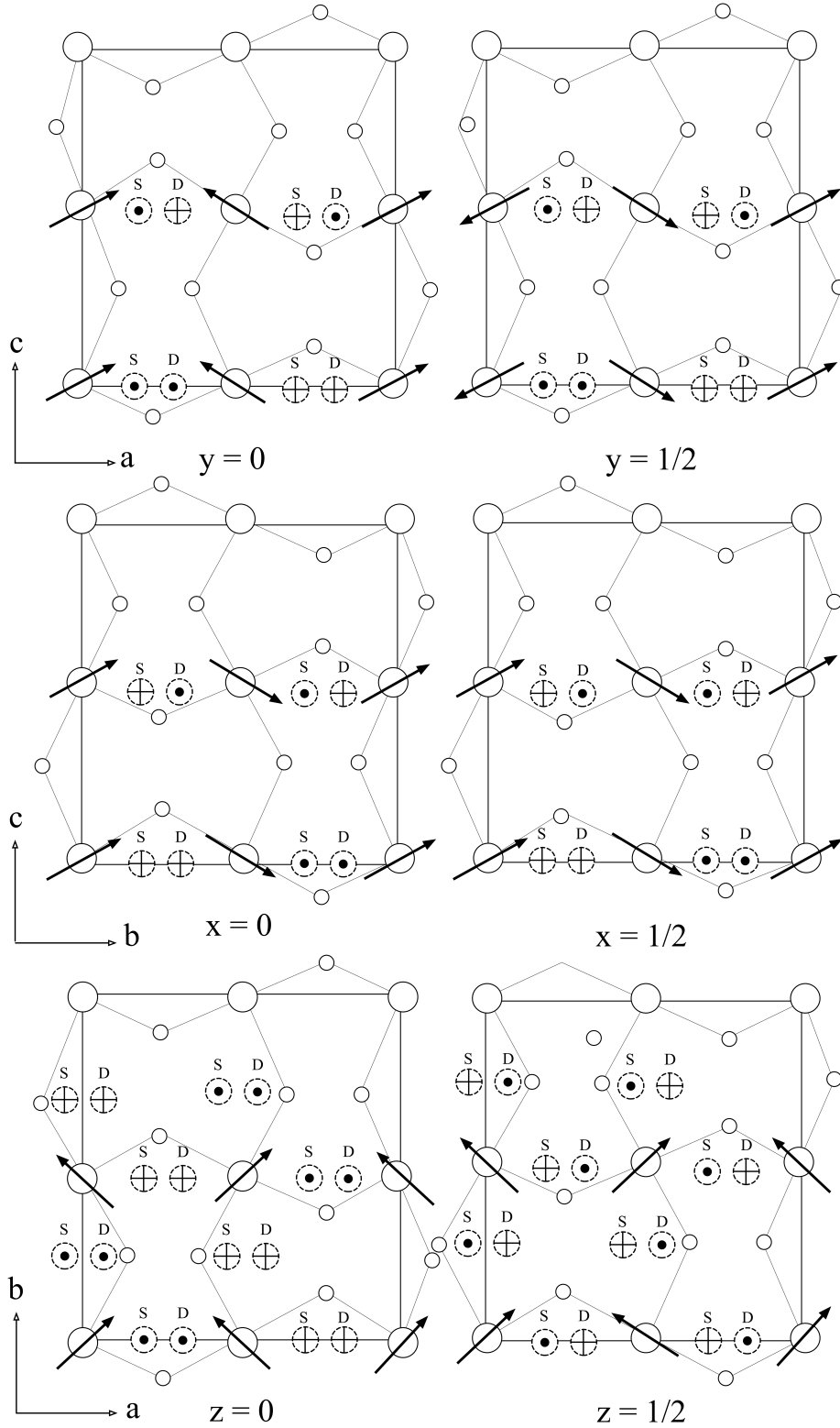


Figure 5.8: A projection of the $R_2\text{CuMnMn}_4\text{O}_{12}$ crystal structure shown from each of the crystallographic directions showing the B-site ions (large circles), the O^{2-} ions (small circles) with the Γ_4^+ A_x, F_y, Y_z magnetic modes illustrated by the solid black arrows superimposed onto the B-site ions. The direction of the local DM vector across each bond, labelled D, and the cross product of the spins across each bond, labelled S is also shown.

S and D are aligned parallel to each other, then a positive contribution to the free energy is obtained, and a negative contribution if antialigned. Note that the magnitude of the DM interaction will vary between bonds along different crystallographic directions, given that the amplitude of the spins and the degree of displacement of the oxygen anion from the centrosymmetric position varies. It is apparent that for the spin configuration shown in Fig. 5.8, the DM interactions in the Mn3 and Mn4 layers have opposite signs and the energy gain from DM is almost cancelled. In contrast if the spins in the Mn4 layers were aligned antiparallel to the spins in the Mn3 layers then DM exchange would be maximised as the sign of the Mn4 DM interactions would reverse, but at a cost to the Heisenberg exchange energy along c .

As the canting of the Mn4 layers was undetermined from neutron powder diffraction data, in this section the spin Hamiltonian of the Heisenberg and DM exchange energies for a single $Pmmn$ unit cell adopting the A_x, F_y spin configuration, Eqn. 5.6, was evaluated as a function of the Mn3 and Mn4 canting angles in the ab plane, Ω_3 and Ω_4 respectively. The canting angles for which the spin Hamiltonian is minimised was determined for a given set of exchange parameters, and evaluated with the ground state theoretical moments $g\langle J_z \rangle \mu_B$ (for simplicity both A-site Mn ions were taken to have an oxidation state of +3).

$$\begin{aligned} \mathcal{H} = & \mathcal{J}_C(\mathbf{S}_{3_1} \cdot \mathbf{S}_{4_1}) + \mathcal{J}_{AB}(\mathbf{S}_{3_1} \cdot \mathbf{S}_A + \mathbf{S}_{4_1} \cdot \mathbf{S}_A) + \mathcal{J}_{BB}(\mathbf{S}_{3_1} \cdot \mathbf{S}_{3_2} + \mathbf{S}_{4_1} \cdot \mathbf{S}_{4_2}) \\ & + \mathbf{D}_3 \cdot (\mathbf{S}_{3_1} \times \mathbf{S}_{3_2}) + \mathbf{D}_4 \cdot (\mathbf{S}_{4_1} \times \mathbf{S}_{4_2}) \end{aligned} \quad (5.6)$$

Each term in the spin Hamiltonian represents the exchange between two spins across a bond, weighted by the multiplicity of the bond in a unit cell. The first term is the symmetric Heisenberg exchange between nearest neighbour Mn3 and Mn4 spins, $\mathbf{S}_3$ and $\mathbf{S}_4$, with exchange constant $\mathcal{J}_C$, the second term is the symmetric exchange between A-site spins, $\mathbf{S}_A$, and nearest neighbour B-site Mn3 and Mn4 spins with exchange constant $\mathcal{J}_{AB}$. The third term is the symmetric exchange between nearest neighbour B-site Mn ions with exchange constant $\mathcal{J}_{BB}$, and the fourth and fifth are the antisymmetric exchange interactions between the B-site Mn ions in the Mn3 and Mn4 layers respectively, where $\mathbf{D}_3$ is $(0, 0, D)$ and $\mathbf{D}_4$ is $(0, 0, -D)$ as determined from Fig. 5.8. Fig. 5.9 shows the exchange pathways described above in a single $Pmmn$ unit cell. To simplify the calculation the exchange constants $\mathcal{J}_{AB}$ and $\mathcal{J}_{BB}$ are assumed

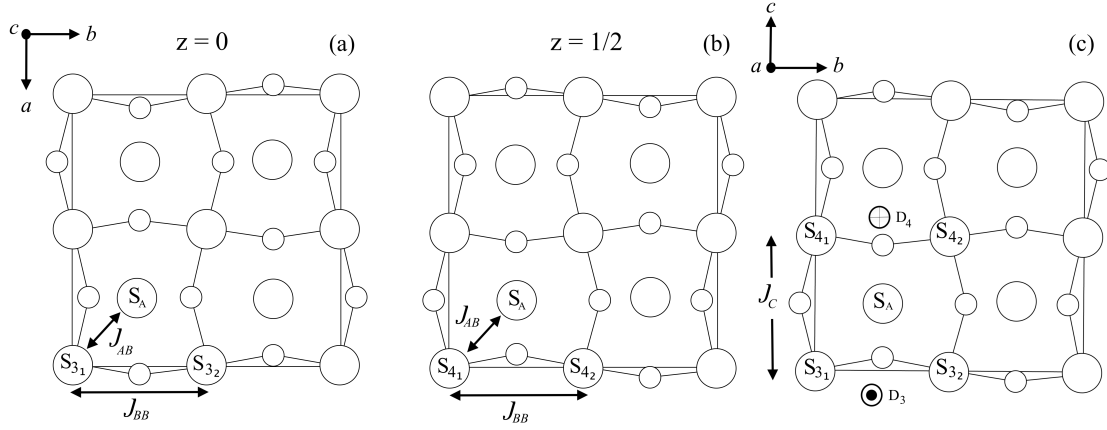


Figure 5.9: A projection of the $R_2\text{CuMnMn}_4\text{O}_{12}$ crystal structure shown from the c axis showing the $\mathcal{J}_{AB}$ and $\mathcal{J}_{BB}$ exchange interactions for (a) the $z = 0$ layer and (b) the $z = 1/2$ layer. (c) A projection of the $R_2\text{CuMnMn}_4\text{O}_{12}$ crystal structure shown from the a axis showing $\mathcal{J}_C$ and the $\mathbf{D}_3$ and $\mathbf{D}_4$ vectors. The large circles represent the B-site ions and the small circles represent the O^{2-} ions.

to be the same for both the Mn3 and Mn4 ions, which are not expected to vary significantly in the real system and therefore this is a adequate approximation to make.

The subscript 1 and 2 is used to distinguish between the B-site Mn spins located at $(0, 0, z)$ and $(0, 0.5, z)$ respectively, where $z = 0$ for Mn3 ions and $z = 0.5$ for Mn4 ions (see Fig. 5.9). The moments on the spins are defined according to Eqns. 5.7, such that they represent the A_x, F_y spin configuration, where Ω represents a right handed rotation from the a axis within the ab plane. If $\Omega = 0^\circ$ then spins adopt the A_x configuration, and if $\Omega = 90^\circ$ the spins adopt the F_y configuration.

$$\begin{aligned} \mathbf{S}_{31} &= (\cos \Omega_3, \sin \Omega_3, 0) & \mathbf{S}_{32} &= (-\cos \Omega_3, \sin \Omega_3, 0) \\ \mathbf{S}_{41} &= (\cos \Omega_4, \sin \Omega_4, 0) & \mathbf{S}_{42} &= (-\cos \Omega_4, \sin \Omega_4, 0) \end{aligned} \quad (5.7)$$

Fig. 5.10 shows the variation in the energy of the spin Hamiltonian as a function of the Ω_3 and Ω_4 canting angles evaluated for different exchange parameters, with the minimum in the energy marked by a white cross. The collinear ferrimagnetic structure corresponds to $\Omega_3 = \Omega_4 = 90^\circ$, the intersection of the two dashed lines in each of the subfigures in Fig. 5.10. $\mathcal{J}_C$ is assumed to be ferromagnetic (negative) as observed experimentally (see magnetic structures of $\text{Tm}_2\text{MnMnMn}_4\text{O}_{12}$ and $R_2\text{CuMnMn}_4\text{O}_{12}$), and

predicted by the GKA rules (Sec. 3.2.1), $\mathcal{J}_{AB}$ is assumed to be ferromagnetic owing to the $mm2$ point site symmetry of the Mn A' and A'' sites and $\mathcal{J}_{BB}$ is assumed to be antiferromagnetic according to the GKA rules (Sec. 3.2.1).

In the presence of only $\mathcal{J}_{AB}$ and $\mathcal{J}_{BB}$ exchange, a canted structure occurs if $\mathcal{J}_{BB}/\mathcal{J}_{AB} > 1/4$ for the Mn3 layer and $\mathcal{J}_{BB}/\mathcal{J}_{AB} > 1/3$ for the Mn4 layer, as demonstrated in Fig. 5.10 (a)-(c). Introducing a finite ferromagnetic $\mathcal{J}_C$ exchange, causes the two B-site layers to cant in the same direction, Fig. 5.10 (d), and for a sufficiently large D the spins cant in the opposite direction. Fig. 5.10 (e).

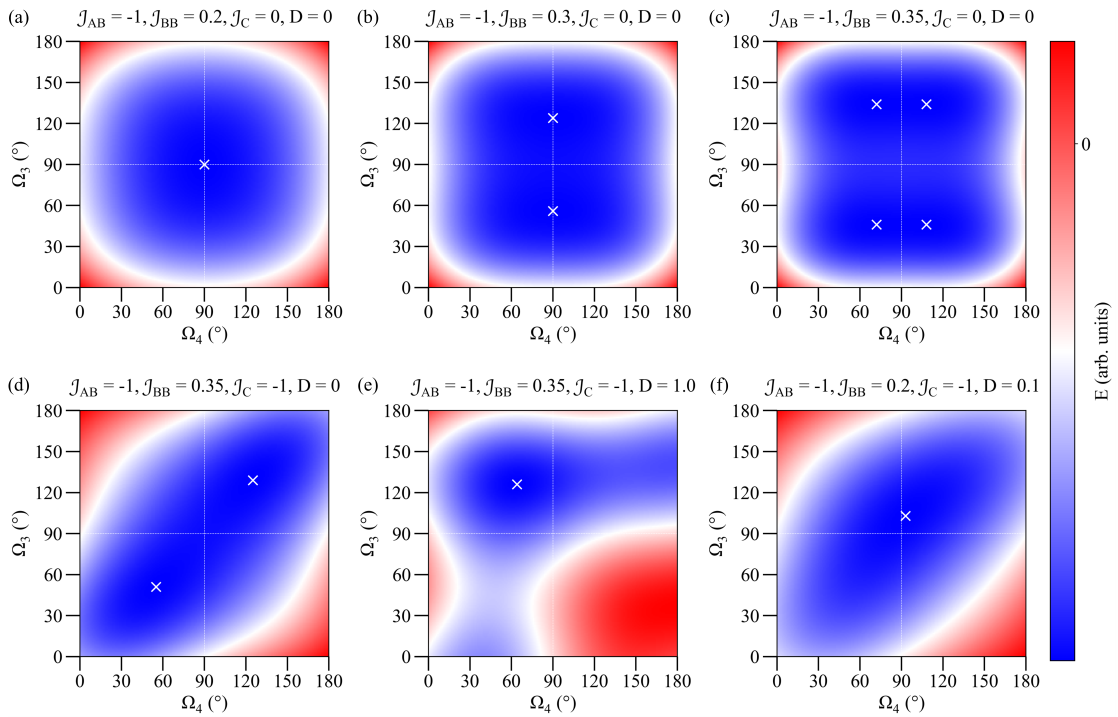


Figure 5.10: The spin Hamiltonian, Eqn. 5.6, of the Heisenberg and DM exchange energies of a single $R_2\text{MnMnMn}_4\text{O}_{12}$ $Pmmn$ unit cell, evaluated as a function of both the Mn3 and Mn4 canting angles, Ω_3 and Ω_4 , and for different sets of exchange constants. The white cross corresponds to the minimum in the exchange energy, and the intersection of the white dashed lines represents the energy of the collinear ferrimagnetic structure. If $\Omega = 0^\circ$ then spins adopt the A_x configuration, and if $\Omega = 90^\circ$ the spins adopt the F_y configuration.

Fig. 5.10(f) is the energy calculated for a set of exchange constants that gives rise to a minimum in the energy consistent with the experimentally determined canting angles in the CFI' phase of YCMO (see Fig. 5.6). D was set to be an order of magnitude smaller than the symmetric exchange interactions,

as observed in the simple orthorhombic manganites [89]. From this analysis it is apparent that in the presence of only $\mathcal{J}_{AB}$, $\mathcal{J}_{BB}$ and $\mathcal{J}_C$ exchange interactions the degree of canting in the two layers is almost equivalent Fig. 5.10(d). However in the presence of small finite DM exchange, the canting is suppressed in the layer with a smaller moment, in agreement with the experimental observation. For large values of D , the spins in the Mn4 layer cant in the opposite direction to the spins in the Mn3 layer, Fig. 5.10.

5.8 Conclusions

In summary, $\text{Y}_2\text{CuMnMn}_4\text{O}_{12}$ and $\text{Dy}_2\text{CuMnMn}_4\text{O}_{12}$ host magnetic phase transitions between canted and collinear structures that are accompanied by spin reorientation from $m||b$ (favoured by DM in the canted phases) to $m||c$ (favoured by single ion anisotropy in the collinear phase), with the exception of the $\text{Dy}_2\text{CuMnMn}_4\text{O}_{12}$ canted ground state where Dy^{3+} Ising like anisotropy imposes $m||c$. The results are in complete contrast to well established SR phenomena in other distorted perovskites, but instead demonstrate a mechanism for spin reorientation originating in spin canting instabilities. Importantly, these triple A-site columnar ordered quadruple perovskites have the potential to host ultrafast spin reorientation transitions whilst boasting a large $1\mu_B$ moment per TM, making them candidate materials to realise novel spin based technology. In future studies it would be interesting to investigate modification of the SR phenomena through further chemical substitution and doping on this triple A site columnar ordered perovskite framework.

Chapter 6

Effects of magnetic dilution in



In this chapter the effects of site-selective magnetic dilution in the $\text{Sm}_2\text{MnMnMn}_{4-x}\text{Ti}_x\text{O}_{12}$ A-site columnar ordered quadruple perovskite manganites ($x = 1$, $x = 2$ and $x = 3$) is investigated. It is shown that in all three compositions the Mn ions adopt a collinear ferrimagnetic structure below 27 K, 62 K and 34 K, respectively. An unexpected increase in the ordering temperature was observed between the $x = 1$ and $x = 2$ samples, which indicates a considerable departure from mean field behaviour. This result is corroborated by large reductions in the theoretical ground state magnetic moments observed across the series, which indicate the presence of spin fluctuations and or disorder. Long range magnetic order in the $x = 3$ sample, which occurs below the percolation threshold for B-B exchange, can only be understood to arise if magnetic order in $\text{Sm}_2\text{MnMnMn}_{4-x}\text{Ti}_x\text{O}_{12}$ is mediated via *both* A-B and B-B exchange, hence confirming the importance of A-B exchange interactions in these materials as discussed in previous chapters. Finally it is observed that site-selective magnetic dilution enables the tuning of a ferrimagnetic compensation point and the introduction of temperature-induced magnetisation reversal.

Acknowledgements

The powder samples of $\text{Sm}_2\text{MnMnMn}_{4-x}\text{Ti}_x\text{O}_{12}$ for $x = 1, 2, 3$ were synthesised and characterised by R. Liu, K. Yamaura and A. A. Belik. I performed neutron powder diffraction experiments together with D. D. Khalyavin and P. Manuel. I analysed the neutron powder diffraction data, performed the symmetry analysis, modelled the effects of the crystal electric field and performed the percolation calculations together with R. D. Johnson. This work was published in Ref. [94]

6.1 Introduction

In this chapter, the tuning of magnetic exchange interactions in the $\text{Sm}_2\text{MnMnMn}_{4-x}\text{Ti}_x\text{O}_{12}$ A-site columnar ordered quadruple perovskite manganites is investigated by chemical substitution of non-magnetic Ti^{4+} for B-site Mn^{3+} for $x = 1$, $x = 2$ and $x = 3$. This series interpolates between the A-site only, antiferromagnetic structure of $(\text{NaDy})\text{MnMnTi}_4\text{O}_{12}$ [57], and the full ferrimagnetic structure of $\text{Tm}_2\text{MnMnMn}_4\text{O}_{12}$ (Chapter. 4). $\text{Sm}_2\text{MnMnMn}_{4-x}\text{Ti}_x\text{O}_{12}$ has a tetragonal crystal structure with space group $P4_2/nmc$, where the charge and orbital order responsible for the lower orthorhombic symmetry of the $R_2\text{MnMnMn}_4\text{O}_{12}$ manganites [35, 61] has been suppressed by the B-site chemical disorder [95]. The three symmetry inequivalent A sites, are occupied by 10-fold coordinated Sm^{3+} (Sm1), square planar coordinated Mn^{2+} or Mn^{3+} (Mn1), depending on the amount of Ti^{4+} substituted on the B sites, and by tetrahedrally coordinated Mn^{2+} (Mn2) respectively. The B sites, labelled Mn3/Ti1, are octahedrally coordinated and occupied by 75% Mn^{3+} and 25% Ti^{4+} for the $x = 1$ sample, 50% Mn^{3+} and 50% Ti^{4+} for the $x = 2$ sample and 25% Mn^{2+} and 75% Ti^{4+} for the $x = 3$ sample. The two cations are disordered across the B sites with an average oxidation state of between +3.25 and +3.5. Published DC magnetometry measurements show that samples with $x = 1$, $x = 2$ and $x = 3$ undergo a single magnetic phase transition at temperatures of $T_c = 27$ K, 62 K and 40 K respectively [95]. Here a quantitative neutron diffraction study shows that all compositions undergo a transition to a long range ordered magnetic phase below T_c in which the Mn ions adopt a collinear ferrimagnetic structure. These results demonstrate an

unusual increase in the ordering temperature between the $x = 1$ and $x = 2$ samples, despite an increase in the amount of non-magnetic Ti^{4+} on the B-site sublattice – contrary to what is observed in numerous other magnetically dilute systems [96] and is suggestive of a departure from mean field physics. In the $x = 2$ sample it is demonstrated that site-selective magnetic dilution has enabled the tuning of ferrimagnetic compensation and the introduction of temperature-induced magnetisation reversal. It is shown that in the $x = 3$ sample, long-range B-site magnetic order must percolate via *both* A-B and B-B exchange, demonstrating the importance of A-B exchange in mediating magnetism in the A-site columnar ordered quadruple perovskites.

6.2 Experimental Details

Polycrystalline samples of $\text{Sm}_2\text{MnMnMn}_{4-x}\text{Ti}_x\text{O}_{12}$ were synthesised under high-temperature and high-pressure conditions from stoichiometric mixtures of Mn_2O_3 , Mn_3O_4 , TiO_2 and Sm_2O_3 for $x = 1$, from Mn_2O_3 , MnO , TiO_2 and Sm_2O_3 for $x = 2$, and MnO , TiO_2 and Sm_2O_3 for $x = 3$, as detailed in Ref. [95]. Neutron powder diffraction experiments were performed using the time of flight diffractometer, WISH at ISIS [45]. $x = 1$, $x = 2$ and $x = 3$ samples of mass 0.8 g, 0.9 g, and 0.7 g, respectively, were loaded into 3 mm vanadium cans and cooled to 1.5 K. Diffraction data with good counting statistics were collected on warming from a base temperature of 1.5 K up to 35 K in 5 K steps for the $x = 1$ sample, up to 78 K in 6 K steps for the $x = 2$ sample, and up to 60 K in 6 K steps for the $x = 3$ sample. Measurements with high counting statistics were made in the paramagnetic phase (80 K for $x = 1$ and $x = 3$, 90 K for $x = 2$) and at 1.5 K for all three samples. Symmetry analysis was performed using the ISOTROPY software suite [53], and the diffraction data were fit using FULLPROF [47]. Magnetic measurements were performed on a SQUID magnetometer (Quantum Design, MPMS-XL-7T) between 2 and 400 K in 100 Oe under both zero-field-cooled (ZFC) and field-cooled on cooling (FCC) conditions. Isothermal magnetisation measurements were performed between -70 and 70 kOe at 5 K.

6.3 Neutron powder diffraction study

The $P4_2/nmc$ crystal structure model previously reported for $\text{Sm}_2\text{MnMnMn}_{4-x}\text{Ti}_x\text{O}_{12}$ [95] was refined against the neutron powder diffraction data measured in the paramagnetic phase of each of the samples. For the $x = 1$ and $x = 3$ samples weak diffraction peaks that could not be indexed by the $P4_2/nmc$ model were found to originate in an MnCO_3 impurity phase (0.11 wt. %) and $\text{Sm}_2\text{Ti}_2\text{O}_7$ impurity phase (0.25 wt. %) respectively. For all three samples the atomic displacement parameter of Mn1 refined to unphysically large values when the ion was constrained to the centre of the square planar coordination (Wyckoff position 2a). Hence, a split-atom model, in which the z coordinate of the Mn1 was allowed to freely refine (Wyckoff position 4c) as employed in Ref. [95], is adopted, representative of site disorder above and below the square planar coordination, which reduced the atomic displacement parameter to physical values as shown in Tables 9.18, 9.19 and 9.20.

Sm was free to substitute Mn on the A'' and A''' sites and Mn was free to substitute Sm on the A' sites, while imposing full site occupations. An excellent fit was achieved in all samples and the refined stoichiometries were as follows: $\text{Sm}_2\text{Mn}(\text{Mn}_{0.848(4)}\text{Sm}_{0.152(4)})\text{Mn}_3\text{TiO}_{12}$ ($R = 2.72\%$, $wR = 2.90\%$, $R_{\text{Bragg}} = 4.06\%$ at 80 K), $\text{Sm}_2\text{Mn}(\text{Mn}_{0.94(2)}\text{Sm}_{0.06(2)})\text{Mn}_2\text{Ti}_2\text{O}_{12}$ ($R = 2.71\%$, $wR = 2.87\%$, $R_{\text{Bragg}} = 5.05\%$ at 90 K) and $\text{Sm}_2\text{MnMnMnTi}_3\text{O}_{12}$ ($R = 2.03\%$, $wR = 2.20\%$, $R_{\text{Bragg}} = 5.69\%$ at 80 K). Refinement details are given in Sec. 9.3.3 of the Appendix. Note that the R_{Bragg} values are large in all samples due to strong absorption from Sm^{3+} which results in much weaker diffracted intensities.

A gradual growth of the (200), (002), (112) and (110) reflections was observed for all three samples below T_c , as shown in Fig. 6.1, in accordance with changes in the sample's magnetisation (Fig. 6.4), and hence these peaks were identified as magnetic in origin. For all three samples, the magnetic peaks are sharp and of a similar width to the nuclear peaks, indicating that the magnetic structure is well correlated. The above peak positions were consistent with a Γ -point, $\mathbf{k} = (0, 0, 0)$, magnetic propagation vector. The magnetic Γ -point representation for the Wyckoff positions of the Sm and Mn sublattices decomposes into six 1-dimensional irreducible representations (irreps) ($\Gamma_1^\pm$, $\Gamma_2^\pm$, Γ_3^+ and Γ_4^+) and two 2-dimensional

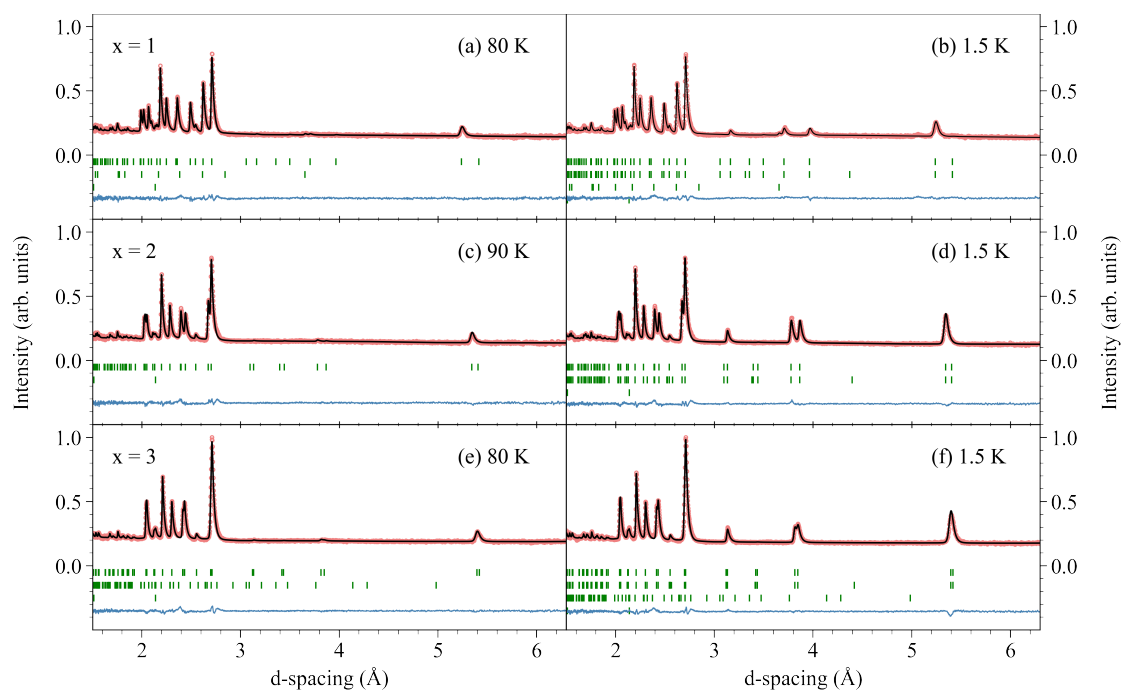


Figure 6.1: (Neutron powder diffraction data collected on the time of flight diffractometer WISH at ISIS of (a)-(b) the $x = 1$ sample (c)-(d) the $x = 2$ sample and (e)-(f) the $x = 3$ sample, at temperatures representative of the paramagnetic phase and at 1.5 K. The data are given by the red circles, the fit of the data by the solid black line, and their difference as a blue line. The green tick marks are the nuclear and magnetic reflections from top to bottom of $\text{Sm}_2\text{MnMnMn}_{4-x}\text{Ti}_x\text{O}_{12}$ labelled (1) and an impurity phase labelled (2).

(2D) irreps ($\Gamma_5^\pm$), which together define a total of 12 different magnetic symmetries, Sec. 3.1.3. The rapid increase of the magnetic susceptibility below T_c (Fig. 6.4) indicated the presence of ferromagnetic sublattices, which are only consistent with the Γ_3^+ or Γ_5^+ irreps. Furthermore, the observation of finite magnetic intensity on the (002) reflection indicates that the magnetic moments are not aligned parallel to the c -axis, which uniquely identifies that the magnetic structure transforms by the Γ_5^+ irrep.

The Γ_5^+ symmetry adapted basis functions for the A and B sites are summarised in Table 3.1. Magnetic structure models constructed from linear combinations of these basis functions were exhaustively tested by refinement against the neutron diffraction data measured at 1.5 K from all samples. A model in which the B-sites moments were oriented collinearly in the ab plane and ferromagnetically coupled, and the A' and A'' sites collinear but anti-aligned with respect to the B site sublattice, gave the best fit to the data ($R_{\text{Mag}} = 17.0\%$ for $x = 1$, 5.39% for $x = 2$ and 4.34% for $x = 3$), and is shown in Fig. 6.2(a). The A site Sm^{3+} moments refined to values lower than the sensitivity of the measurement ($\sim 0.1\mu\text{B}$), hence they were fixed to zero.

Table 6.1: Absolute values of the 1.5 K experimental (Exp.) and theoretical (Calc.) magnetic moments of $\text{Sm}_2\text{MnMnMn}_{4-x}\text{Ti}_x\text{O}_{12}$. The net magnetisation, M , per formula unit is determined from the experimental moment values, where the A sites align antiparallel to the B sites. The remnant magnetisation, M_r , extrapolated from magnetometry data was scaled by a factor of 2 to account for powder averaging. All moments are given in units of μB .

	$x = 1$		$x = 2$		$x = 3$	
	Exp.	Calc.	Exp.	Calc.	Exp.	Calc.
Sm1	0.00	0.71	0.00	0.71	0.00	0.71
Mn1	1.70(7)	4.0	3.72(7)	5.0	4.09(8)	5.0
Mn2	2.03(9)	5.0	3.72(7)	5.0	4.09(8)	5.0
Mn3	0.82(6)	4.0	2.54(6)	4.0	2.1(1)	5.0
M per f.u	1.3(1)		2.4(1)		6.0(2)	
M_r per f.u	1.006(7)		1.05(1)		5.68(3)	
T_c	27 K		62 K		34 K	

The refined magnetic structure is consistent with the collinear ferrimagnetic phase found in $\text{Tm}_2\text{MnMnMn}_4\text{O}_{12}$ [61] and $\text{R}_2\text{CuMnMn}_4\text{O}_{12}$ [70]. Moment orientations of $m||[x, 0, 0]$, $m||[x, x, 0]$

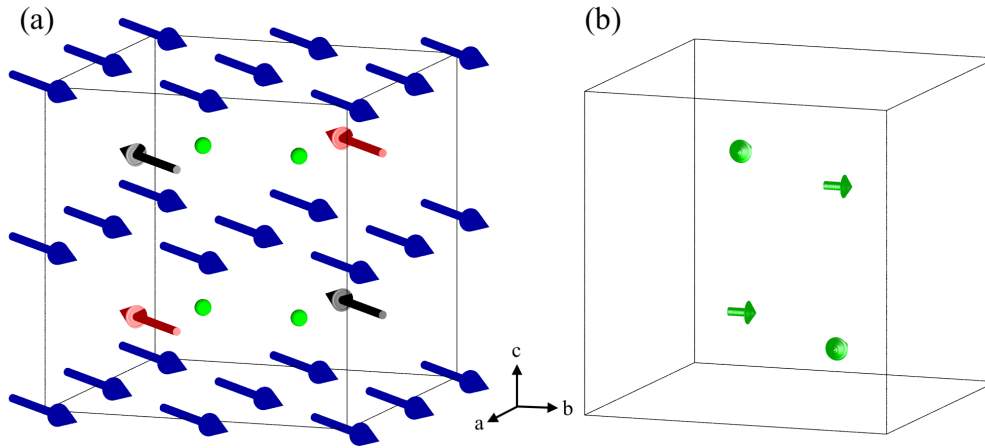


Figure 6.2: (a) Experimentally determined magnetic structure of $\text{Sm}_2\text{MnMnMn}_{4-x}\text{Ti}_x\text{O}_{12}$ upto a direction in the ab plane. (b) Theoretically proposed spin configuration of the Sm sites as determined by point charge calculations. The A' sites are coloured in green, the A'' sites in black, and the A''' sites in red. The B sites are coloured in blue, and for clarity a scenario in which all B-site ions of a magnetic unit cell are Mn3 is shown – a more accurate depiction of the unit cell would consist of statistically disordered Ti1 and Mn3 ions on the B-sites. The magnetic space group is $\text{Ccc}'a'$ (No. 68.516) with basis vectors $(1,1,0), (-1,1,0), (0,0,1)$ and an origin of $(1,1/2,1)$ with respect to the paramagnetic space group.

or $m \parallel [x, y, 0]$ correspond to different magnetic symmetries described by the three distinct order parameter directions of the Γ_5^+ irrep (see Table 3.1), however these three cases cannot be differentiated by the neutron diffraction data due to powder averaging in the tetragonal crystal symmetry. In the following a model with $m \parallel [x, x, 0]$ is adopted, which is consistent with Sm^{3+} crystal electric field calculations (Sec. 6.4).

6.4 Magnetic Anisotropy

The Jahn-Teller active Mn^{3+} ions present in the $x = 1$ and $x = 2$ samples are expected to impose an average weak single-ion anisotropy $\parallel c$ [66, 61], while all other Mn ions are isotropic Mn^{2+} . The three $\text{Sm}_2\text{MnMnMn}_{4-x}\text{Ti}_x\text{O}_{12}$ samples have a magnetisation direction in the ab plane, perpendicular to the easy axis of the Mn^{3+} ions, suggesting that the magnetic anisotropy of Sm^{3+} may instead play an important role despite the data being insensitive to an ordered moment on the Sm sites. Note that in $\text{Tm}_2\text{MnMnMn}_4\text{O}_{12}$ the competition between the Mn^{3+} and RE magnetic anisotropies was found to result

in a spin reorientation phase transition. If the magnetic anisotropy is indeed determined by Sm^{3+} , then the absence of a spin-reorientation phase transition in the $\text{Sm}_2\text{MnMnMn}_{4-x}\text{Ti}_x\text{O}_{12}$ compounds implies significant f - d exchange coupling immediately below T_c (note in the orthoferrites strong f - d exchange coupling is also present in SmFeO_3 and leads to a phase transition approx. 300 K - 400 K above all other rare-earth orthoferrites [69]).

Point charge approximations to the Sm^{3+} crystal electric field (CEF) were used to calculate the ground state magnetic anisotropy of Sm^{3+} , and hence establish whether f - d exchange coupling of rare-earth moments to the manganese sublattices might be responsible for the ab plane magnetisation direction observed in $\text{Sm}_2\text{MnMnMn}_{4-x}\text{Ti}_x\text{O}_{12}$. Sm^{3+} has electronic configuration $[\text{Xe}]4f^5$, and Hunds rules give $S = 5/2$, $L = 5$ and $J = 5/2$ for the lowest-energy 6-fold multiplet of states. The local crystal electric field of Sm^{3+} has the point group symmetry $2mm$, which lifts the multiplet degeneracy to form 3 Kramers doublets. All non-zero crystal electric field parameters, B_n^m [59], were calculated for Sm^{3+} in its two atomic positions, $(\frac{1}{4}, \frac{1}{4}, z)$ and $(\frac{1}{4}, \frac{1}{4}, z + \frac{1}{2})$, labelled Sm11 and Sm12 respectively (Table 6.2). Atomic positions refined for the $x = 2$ compound at 1.5 K were used for reference, and similar values were obtained using the atomic positions of the $x = 1$ and $x = 3$ samples. Sm11 and Sm12 are symmetry equivalent, and related by a 4_2 screw, therefore all values of B_n^m are the same across the two sites, except the B_2^2 and B_4^2 terms which change sign upon 90° rotation about c .

Table 6.2: Non-zero crystal electric field parameters for Sm^{3+} in $\text{Sm}_2\text{MnMnMn}_2\text{Ti}_2\text{O}_{12}$ evaluated by the point charge model, and given in units μeV . Note that no estimate for the uncertainty has been provided for these values as they are only intended to provide a qualitative estimate for the crystal electric field splitting.

Ion	Frac. coords.	B_2^0	B_2^2	B_4^0	B_4^2	B_4^4
Sm11	0.25, 0.25, 0.209	2430	5204	-11.65	40.94	41.85
Sm12	0.25, 0.25, 0.709	2430	-5204	-11.65	-40.94	41.85

Consider the following Hamiltonian for a single Sm^{3+} ion;

$$\mathcal{H} = \sum_n \sum_{m=-n}^n B_n^m O_n^m + g_J \mu_B \mathbf{J} \cdot \mathbf{B}_{\text{ex}} \quad (6.1)$$

where O_n^m are the Stevens operators [59], g_J is the Landé g -factor, $\mathbf{J} = (J_x, J_y, J_z)$ is the vector total angular momentum operator, and $\mathbf{B}_{\text{ex}}$ is an effective exchange field originating in f - d exchange interactions with the manganese sublattices.

The magnetic anisotropy of Sm11 and Sm12 was determined by repeatedly solving Equation 6.1 for a 1 T field applied in different directions over a full hemisphere. The eigenfunctions were determined by diagonalising of $\mathcal{H}$, and magnetic moment components m_x , m_y , and m_z were calculated by summing the expectation values of $\langle J_x \rangle$, $\langle J_y \rangle$ and $\langle J_z \rangle$ over all eigenfunctions, multiplied by g_J , and weighted by Boltzmann statistics evaluated at $T = 10$ K, as explained in Sec. 3.2.

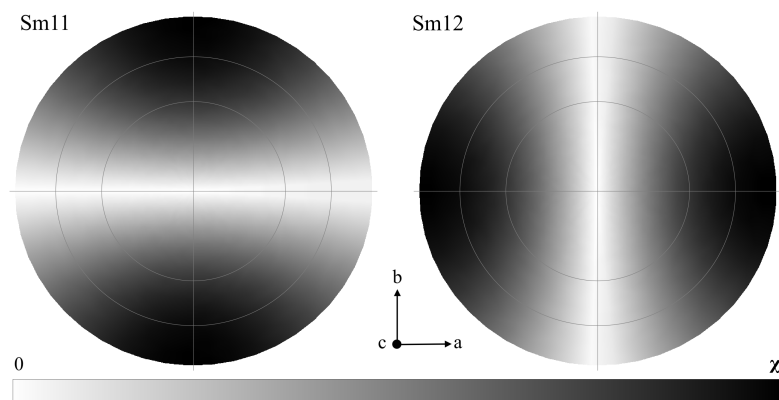


Figure 6.3: The magnetic susceptibility of Sm11 and Sm12 plotted as a stereographic projection over a full hemisphere under an applied field of 1T.

The total Sm11 and Sm12 moments for the different field directions are shown in Fig. 6.3 as a stereographic projection. A strong Ising like anisotropy was found $\parallel y$ for Sm11 and $\parallel x$ for Sm12. The easy axis rotates between x and y for Sm^{3+} sites in accordance with the 4_2 screw symmetry that relates the two sites. Note that this perpendicular alignment of Sm11 and Sm12 moments parallel to y and x , respectively, is described by the A site $F_y F_x$ mode associated with the (a, a) order parameter direction of Γ_5^+ (see Table 3.1). Within this symmetry, the Sm moments maximally couple to the Mn collinear ferrimagnetic structure if the Mn moments lie $\parallel [x, x, 0]$. Hence, not only can the Sm ions impose an ab -plane magnetic anisotropy, they can also determine the direction of the magnetisation in the plane (as shown in Fig. 6.2(b)).

6.5 Ferrimagnetic compensation point

The refined moment magnitudes are given in Table 6.1, which also lists the net ferrimagnetic moment per formula unit. The strong dependence of the net ferrimagnetic moment on composition, x , is reflected in the remnant magnetisation, M_r , evaluated by extrapolating the powder-averaged bulk magnetisation to zero field (see Fig. 6.5). Scaled extrapolated values are listed in Table 6.1, and their relative magnitudes correspond well to the net ferrimagnetic moment per formula unit obtained from neutron diffraction, except for the $x = 2$ sample. A scale factor was used as the magnetometry data is powder averaged, and an arbitrary scale factor is therefore necessary to compare the magnetometry and neutron powder diffraction data. This discrepancy cannot be explained by the proposed magnetic structure model.

The temperature dependences of all symmetry-inequivalent moment magnitudes, plotted in Fig. 6.4, were evaluated by fitting the magnetic structure model to variable temperature neutron powder diffraction data measured from all three samples. The refinements were constrained such that each magnetic ion had a moment no larger than its theoretically predicted maximum, given in Table 6.1, and with the ratio of the Mn1:Mn2 moments chosen to be consistent with their nominal oxidation states. The refinement was insensitive to a Sm1 moment at all temperatures, so it was set to zero. For the $x = 2$ sample the B-site moments grow rapidly as the temperature decreases, but quickly saturate in comparison to the A-site moments which steadily grow with decreasing temperature. As a result, the net magnetisation (the sum over all magnetic moments in the unit cell with the A sublattices antialigned with respect to the B sublattice) reverses direction with decreasing temperature, giving rise to a compensation point at 45 ± 3 K. Magnetisation reversal was also observed in the temperature dependent magnetic susceptibility FCC data of the $x = 2$ sample, as shown in the inset of Fig 6.4(e), for which the compensation temperature was determined to be 46 ± 1 K in excellent agreement with the neutron diffraction results. Note that the absolute value of the negative, low temperature magnetic susceptibility is not reflective of the full net ferrimagnetic moment, as the coercive field of the sample may come close to the 100 Oe applied field.

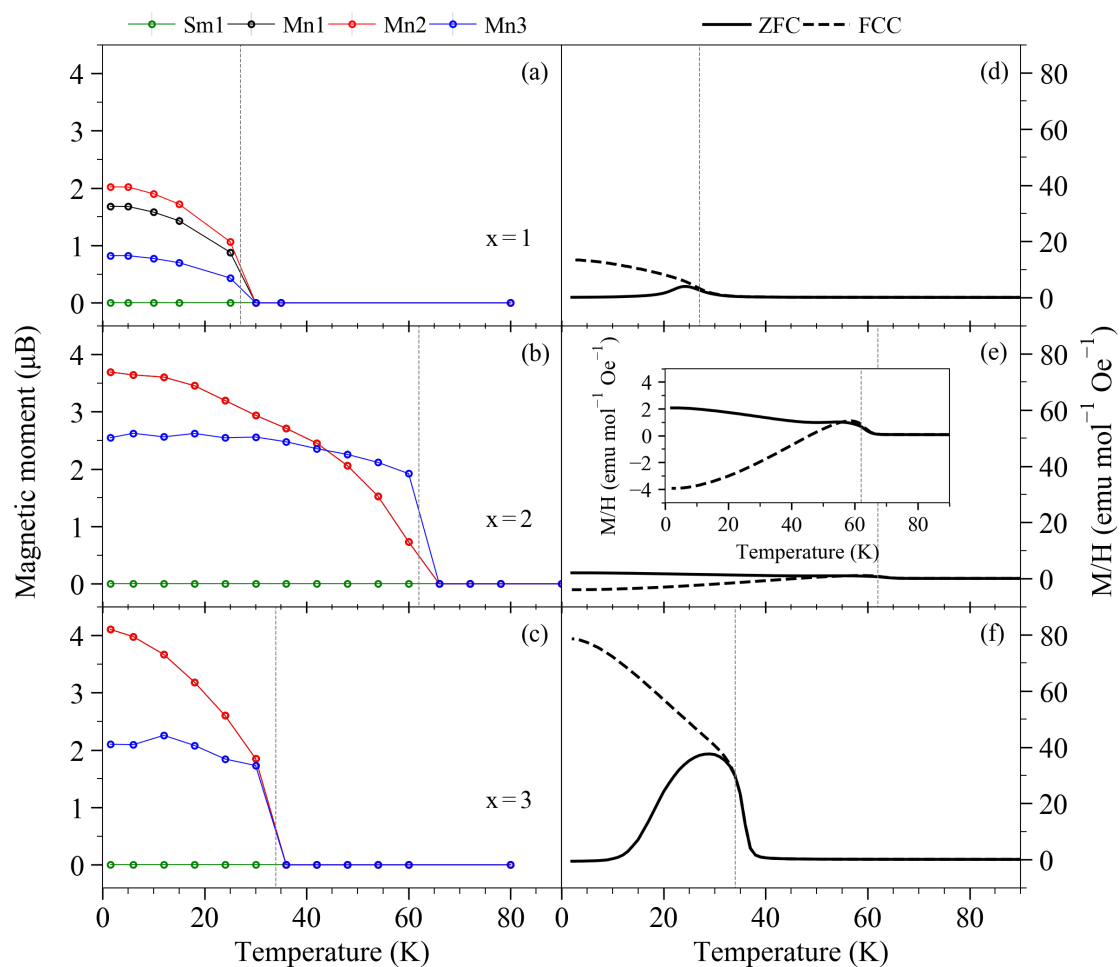


Figure 6.4: (a)-(c) The temperature dependence of moment magnitudes given for each of the symmetry inequivalent magnetic ions. The moments of Mn1 and Mn2 were fixed to be the same in the $x = 2$ and $x = 3$ samples to be consistent with their equivalent nominal oxidation states. (d)-(f) ZFC and FCC magnetisation measurements under an applied DC field of 100 Oe. The inset in (e) shows the ZFC and FCC measurements for the $x = 2$ sample on a reduced scale.

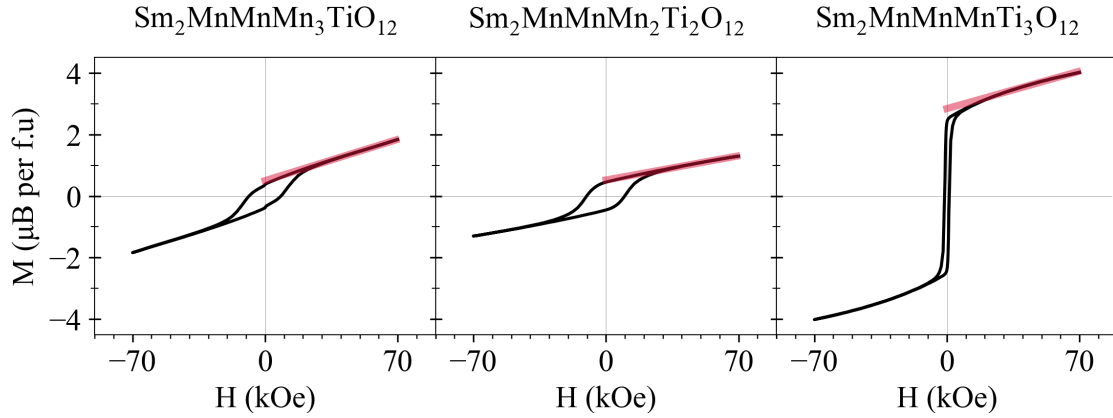


Figure 6.5: Plots of the magnetisation, M , as a function of applied field, H , taken at a temperature of 5 K for each of the samples. A magnetic field range of 22.5 to 70 kOe was used to extrapolate the magnetisation to zero field and the extrapolated remnant magnetisation is shown by the red line.

6.6 Percolation calculations

First, the percolation of long-range magnetic order via B-B exchange alone is considered. In $\text{Sm}_2\text{MnMnMn}_{4-x}\text{Ti}_x\text{O}_{12}$ B-B exchange pathways span a three dimensional framework. Each B site has six nearest-neighbour B sites, such that for every non magnetic Ti^{4+} ion substituted onto this sublattice, six nearest neighbour magnetic B-B exchange pathways are removed. The site-percolation threshold (the probability, p , of Mn B site occupation required to establish a percolating cluster that spans the entire lattice between two opposing faces) for a simple cubic lattice representative of the B-B framework is 31.16% [97]. Hence, B-B exchange is expected to play no role in establishing long-range magnetic order in the $x = 3$ sample, for which the B site Mn occupation is 25%.

To explore the origin of long range magnetic order in the $x = 3$ sample the percolation threshold was calculated if magnetic order were to percolate via both A-B and B-B exchange. Two interpenetrating simple cubic lattices were used to represent the $\text{A}'_2\text{A}''\text{A}'''\text{B}_4\text{O}_{12}$ unit cell, where the Mn A' and A''' sites were set to be fully occupied, and the Sm A'-sites were set to be unoccupied to exclude interactions with the RE ions. Mn ions were randomly placed on the B sites according to a probability of occupation, p . For a given p , the sites were sorted into clusters, where a cluster is composed of a continuous network of nearest neighbour Mn ions, separated from other clusters by Ti ions. The percolation threshold was

evaluated as the minimum value of p for which there exists a cluster that percolates through the entire lattice along the c -axis. In this case the percolation threshold was reduced from 31.16% to 12.4(1)%, as shown in Fig. 6.6, demonstrating that A-B exchange is crucial to mediating long range magnetic order in the $x = 3$ sample.

Note that A-A exchange could also percolate long range magnetic order, however measurements of $(\text{NaDy})\text{Mn}_2\text{Ti}_4\text{O}_{12}$ demonstrated that it does so at temperatures of ~ 12 K [57] which is significantly below the ordering temperatures of all measured $\text{Sm}_2\text{MnMnMn}_{4-x}\text{Ti}_x\text{O}_{12}$ samples.

6.7 Departures from mean field theory

Diluting a magnetic sublattice with non magnetic ions is predicted to decrease the magnetic ordering temperature [96, 98], and at the mean field level one expects an approximately linear dependence in the transition temperature on magnetic ion concentration [99, 100, 101]. Remarkably, the ordering temperature of the $\text{Sm}_2\text{MnMnMn}_{4-x}\text{Ti}_x\text{O}_{12}$ solid solution does not smoothly decrease upon increasing x (Fig. 6.7(a)), which indicates a significant departure from mean field physics in this system [102] that is also reflected in the moment magnitudes. In insulating materials the magnetic moment of a given ion should reach its full $g\langle J_z \rangle \mu_B$ value in the ground state. The ground state magnetic moments refined for $\text{Sm}_2\text{MnMnMn}_{4-x}\text{Ti}_x\text{O}_{12}$ are compared to their theoretical values in Table 6.1, and plotted in terms of a relative reduction factor in Fig. 6.7(b). A considerable departure from the full moment is observed for all $\text{Sm}_2\text{MnMnMn}_{4-x}\text{Ti}_x\text{O}_{12}$ samples, and the relative reduction in moment magnitude (Fig. 6.7(b)) correlates well with the non-linear variation observed in T_c (Fig. 6.7(a)). In diffraction the time-averaged correlated moment is measured and therefore a reduction in the ground state moment magnitudes could originate from strong spin fluctuations and or static disorder.

Ideally one would perform the same analysis on a $x = 0$ sample, which has a fully magnetic B-site sublattice, and a $x = 4$ sample, which has a non-magnetic B-site sublattice. However, the former can only be grown in very small quantities [35], and the latter requires the A-site Mn ions to adopt an unfeasible +1 oxidation state. Instead, the moment magnitudes and ordering temperature for $\text{Tm}_2\text{MnMnMn}_4\text{O}_{12}$

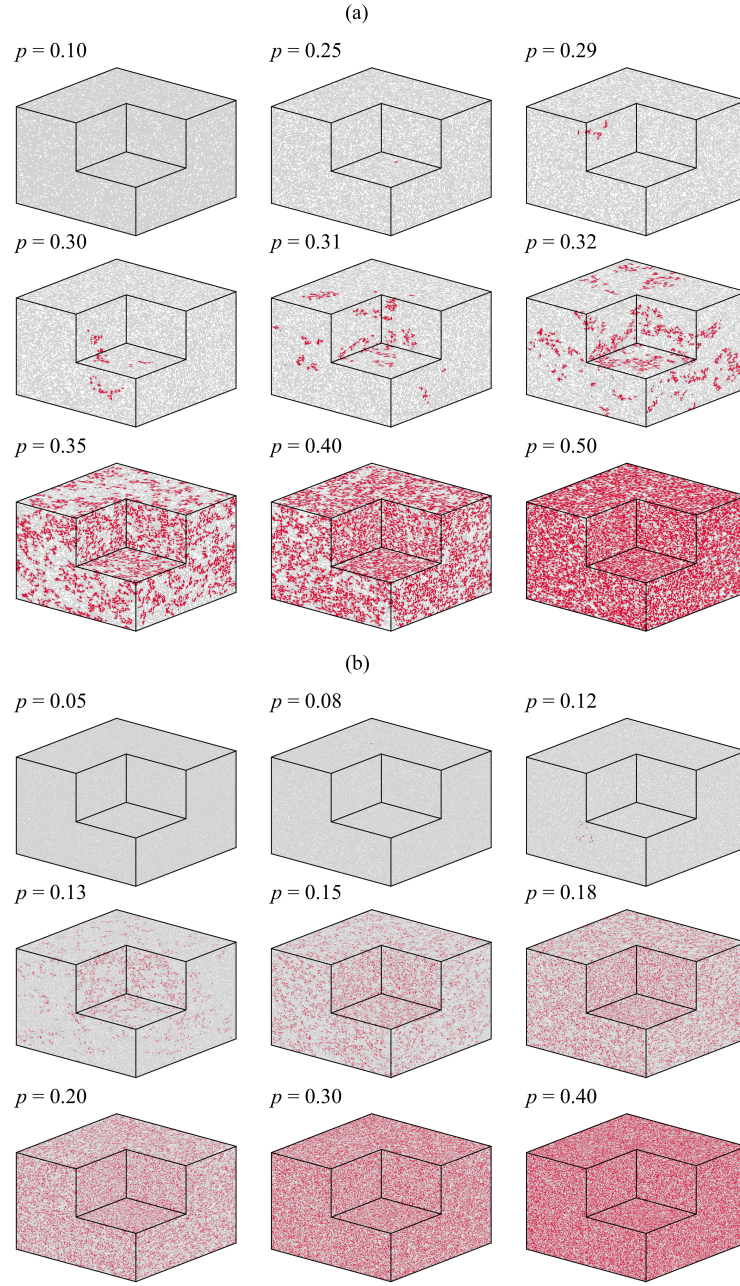


Figure 6.6: Three dimensional illustration of (a) simple cubic lattices representative of the ABO_3 framework spanning a hundred unit cells in each of the three Cartesian directions showing clusters of B-site ions where magnetic order is percolated via B-B exchange and (b) cubic lattices representative of the $\text{A}'_2\text{A}''\text{A}'''\text{B}_4\text{O}_{12}$ framework spanning a hundred unit cells in each of the three Cartesian directions showing only clusters of B-site ions when magnetic order is percolated by both A-B and B-B exchange. For each lattice framework nine different values of the lattice occupation, p , are given. In each figure, only voxels that intersect the surface are shown, and a quarter of the cubic lattice has been removed to reveal the interior. The largest Mn cluster is given in red, all other sites occupied by Mn are given in white and sites occupied by Ti^{4+} are in grey.

have been used, as indicative of the $x = 0$ sample, and the ordering temperature and moment magnitude of $(\text{NaDy})\text{MnMnTi}_4\text{O}_{12}$ as indicative of the $x = 4$ sample, plotted in Fig. 6.7 as unfilled circles. Importantly, these data further support the correlation between the reduction in the relative moment magnitudes and the ordering temperature - an effect that appears to be prevalent in the broader family of materials.

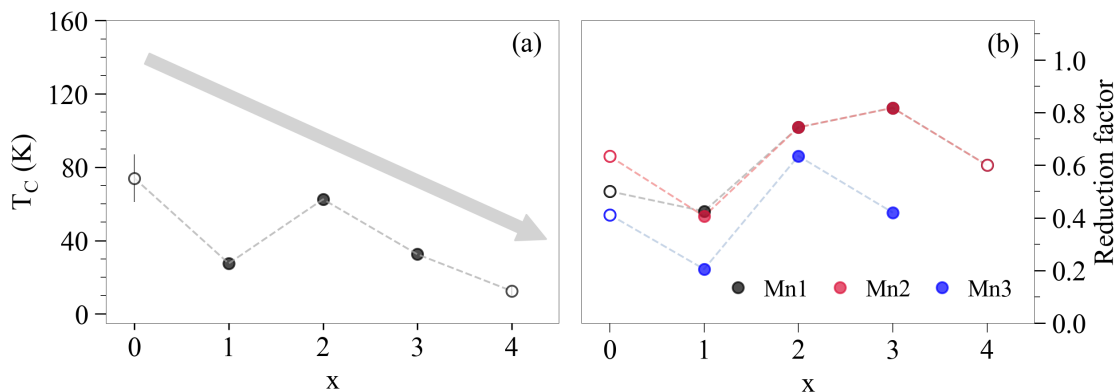


Figure 6.7: The dependence of (a) the ordering temperature T_c and (b) the reduction in magnetic moment relative to the full $g_J \langle J_z \rangle \mu_B$ ground state value, on the concentration of non-magnetic Ti^{4+} (labelled by x). The data for the $x = 0$ and $x = 4$ samples are from $\text{Tm}_2\text{MnMnMn}_4\text{O}_{12}$ [61] and $(\text{NaDy})\text{MnMnTi}_4\text{O}_{12}$ [57]. The grey arrow in (a) is used to illustrate the trend of the mean field dependence of the ordering temperature with x .

In $\text{Sm}_2\text{MnMnMn}_{4-x}\text{Ti}_x\text{O}_{12}$ static disorder of the magnetic structure may originate in at least one of two forms of crystallographic disorder inherent to these compounds; i) mixed cation occupation and ii) displacements of Mn1 ions above and below their coordination plane. All nuclear neutron diffraction peaks were found to be sharp and limited by the instrumental resolution, indicating that either form of crystallographic disorder statistically effected every unit cell equally, giving a crystal structure that is well correlated on average. The magnetic diffraction peaks had widths similar to those of the nuclear peaks, indicating that the magnetic structures were also well correlated on average, such that any static disorder of the magnetic structure must be statistical in nature (i.e. extensive inhomogeneities are not prevalent). Static disorder is therefore unlikely to lead to a departure from mean field behaviour, as mean field theory is based on an average exchange field that affects all magnetic ions equally.

By comparison, spin fluctuations can coexist with well correlated magnetic order [103], have been shown to reduce moment magnitudes even at low temperature [104], and could naturally gives rise to non-mean

field behaviour that may be prevalent in the $x = 1$ and $x = 3$ samples, and weakened in the $x = 2$ sample. The prevalence of spin fluctuations is emerging in the wider family of A-site columnar ordered quadruple perovskites that support competing exchange pathways. For example, in $R_2\text{CuMnMn}_4\text{O}_{12}$ ($R = \text{Y}$ or Dy), B site Mn^{3+} moments appear to saturate at $\frac{3}{4}$ of their theoretical value, and only on cooling through a low temperature phase transition, proposed to originate in the softening of low energy magnons, do they recover their full moment [70].

6.8 Conclusion

All three magnetically dilute $x = 1$, $x = 2$ and $x = 3$ $\text{Sm}_2\text{MnMnMn}_{4-x}\text{Ti}_x\text{O}_{12}$ samples adopt long range magnetically ordered phases below 27 K, 62 K and 34 K, respectively. The Mn ions were empirically found to adopt a collinear ferrimagnetic structure upto a direction in the ab plane, and it is proposed that the moment direction within the plane is likely determined by $f-d$ exchange interactions between the Mn and Sm sublattices. It is shown that the introduction of 50% magnetic dilution onto the B-site sublattice gives rise to a ferrimagnetic compensation point and magnetisation reversal. Percolation calculations demonstrated that long range magnetic order in the $x = 3$ sample can only occur if it percolates via *both* A-B and B-B exchange, hence demonstrating the importance of A-B exchange in the A-site columnar ordered quadruple perovskite manganites. Finally it was demonstrated that the unusual variation in transition temperature that occurred upon magnetic dilution was reflected in the reduction of ground state magnetic moments observed on all Mn sites and in all samples. Together, these results suggest the presence of spin fluctuations and or disorder leading to a departure from mean field physics. In future studies it would be interesting to perform inelastic neutron scattering experiments to measure the Sm^{3+} CEF energy levels and further refine the model of the magnetic anisotropy, as well as probe the presence of spin fluctuations at the lowest measured temperatures.

Chapter 7

Observation of an antiferromagnetic spin-doped Griffiths phase

The competition between the effective FM B-B exchange (favoured by A-B exchange interactions) and the AFM B-B exchange causes the $[\text{Y}_{2-x}\text{Mn}_x]\text{MnMnMn}_4\text{O}_{12}$ $x = 0.21$ and $x = 0.16$ columnar ordered quadruple perovskite manganites to separate into two distinct magnetic phases, as evidenced from neutron powder diffraction data. Below $T_g = 111$ K, the system undergoes a transition from a paramagnetic phase to a Griffiths phase, which is characterised by short range antiferromagnetic clusters contained in a paramagnetic matrix. Below $T_c = 64$ K, the system is composed of well correlated long range collinear ferrimagnetic order, punctuated by short range antiferromagnetic clusters. A sharp increase in the antiferromagnetic phase fraction is observed below ~ 35 K, concomitant with a decrease in the ferrimagnetic phase fraction. Small angle neutron scattering measurements show that the experimental signature of a Griffiths phase, a sharp downturn in the inverse susceptibility with a susceptibility exponent less than unity, cannot be explained by the formation of short range ferromagnetic clusters, as is typical for the majority of observed Griffiths phases. Instead it is demonstrated that this feature could occur due to a change in the paramagnetic properties of the Mn A-site ions.

Acknowledgements

The powder samples of $\text{Y}_{1.79}\text{Mn}_{0.21}\text{MnMnMn}_4\text{O}_{12}$ and $\text{Y}_{1.84}\text{Mn}_{0.16}\text{MnMnMn}_4\text{O}_{12}$ were synthesised and characterised by L. Zhang, K. Yamaura and A. A. Belik. I performed the neutron powder diffraction experiments together with D. D. Khalyavin, P. Manuel and R. D. Johnson. I collected the magnetometry data together with R. D. Johnson. N. J. Steinke set up the SANS experiments. I collected the SANS data remotely and performed the analysis together with N. J. Steinke and R. D. Johnson. Thanks to P. G. Radaelli for helpful discussions on Griffiths phases in the simple perovskite manganites.

7.1 Introduction

In the preceding chapters, we have seen that the competition between the effective FM B-B exchange, favoured by A-B exchange interactions owing to the $mm2$ A-site point symmetry (Sec. 4.6.1), and the AFM B-B exchange, favoured by the GKA rules (Sec. 3.2.1), has given rise to a number of microscopically distinct phases in the $\text{A}'_2\text{A}''\text{Mn}_4\text{O}_{12}$ manganites. The competition between these exchange interactions have thus far affected all unit cells equally, giving rise to well correlated magnetic structures on average. For instance in $\text{Tm}_2\text{MnMnMn}_4\text{O}_{12}$ and $\text{Sm}_2\text{MnMnMn}_{4-x}\text{Ti}_x\text{O}_{12}$ a single collinear ferromagnetic phase was observed. It was suggested that owing to the dominance of A-B exchange over B-B exchange, the system ordered on average to favour the exchange interactions of the greatest strength (A-B exchange), while the competing exchange interactions (AFM B-B exchange) manifested as spin fluctuations. Likewise in $\text{R}_2\text{CuMnMn}_4\text{O}_{12}$ ($\text{R} = \text{Y}$ or Dy) a single well correlated magnetic phase is observed at all temperatures, however owing to a reduction in the average A-B exchange interactions (due to the replacement of Cu^{2+} for Mn^{3+}) the competing exchange interactions are now accommodated by the introduction of spin canting onto the B-site layers. In this chapter it is shown that in $[\text{Y}_{2-x}\text{Mn}_x]\text{MnMnMn}_4\text{O}_{12}$ $x = 0.21$ and $x = 0.16$, the competing effective FM and AFM B-B exchange interactions are distributed unevenly across the system, causing the system to segregate into two distinct magnetic phases. Below $T_g = 111$ K, the system undergoes a transition from a paramagnetic phase to a phase characterised by short

range antiferromagnetic clusters contained in a paramagnetic matrix. Below $T_c = 64$ K, a phase transition to well correlated long range collinear ferrimagnetic (FIM) order is observed. The antiferromagnetic clusters continue to grow below T_c , with a sharp increase in the antiferromagnetic phase fraction below ~ 30 K, which is concomitant with a decrease in the FIM phase fraction.

In the AMnO_3 simple perovskite manganites, first discussed in Sec. 1.2, the introduction of hole doping (Mn^{4+}) through the substitution of a divalent cation on the A sites gives rise to an electronic texture that is inhomogeneous on the nanoscale. In general for $\text{A(III)}_x\text{A''(II)}_{1-x}\text{MnO}_3$ $x < 0.5$ an insulator to metal phase transition is observed below T_c , and the system is observed to order ferromagnetically in the metallic phase owing to the double exchange mechanism [19]. Numerous studies have found that there is a finite temperature interval that precedes the phase transition to ferromagnetic order, where the system is characterised by coexistence of paramagnetic insulating and ferromagnetic metallic regions [105, 106] (a Griffiths phase). For certain compositions of the mixed valence manganites [107], such as in $\text{Pr}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ [108], the randomly dispersed Mn^{4+} on the B-site sublattice give rise to short range metallic and insulating charge ordered regions below T_c , which order ferromagnetically and antiferromagnetically respectively. The localisation of the charge in the insulating regions, and the corresponding orbital order give rise to antiferromagnetism as understood through the context of the GKA rules (Sec. 1.2).

Griffiths phases were first theoretically predicted to exist in random Ising ferromagnets that had a degree of magnetic dilution [109], such that a fraction of the magnetic sites which were nominally occupied by an Ising spin were depleted. In this case it was predicted that there exists a finite temperature interval between the transition to long range ferromagnetic order, T_c , and the temperature at which the pure (magnetically undilute) system would order, T_g , where the free energy is non analytical. Bray extended these arguments to any magnetic system that had a random bond probability distribution, and showed a Griffiths phase occurs when there are clusters of magnetic order that are sufficiently large to produce a singularity in the free energy [110, 111]. Since the predictions by Griffiths and Bray, a number of systems have been shown to have Griffiths phases [112, 113, 114, 115], and a characteristic signature of such a phase has now widely been identified as a susceptibility exponent, $1 - \lambda$, less than unity, such

that $\chi^{-1} \propto (T - T_c)^{1-\lambda}$ [112, 116] as shown in Fig. 7.1 for $\text{Tb}_5\text{Si}_2\text{Ge}_2$. Microscopically this feature in the susceptibility has been assumed to arise from the formation of short range ferromagnetic clusters [115, 117]. In the $\text{A(III)}_x\text{A''(II)}_{1-x}\text{MnO}_3$ $x < 0.5$ simple perovskite manganites it is charge doping that causes these systems to separate into two distinct electronic phases, giving rise to two magnetic phases and the establishment of a Griffiths phase. The coexistence of the two electronically and magnetically distinct phases in these manganites is argued to be directly responsible for establishing colossal magnetoresistance [107, 118, 119, 120, 116], although this has yet to be proven [121, 122].

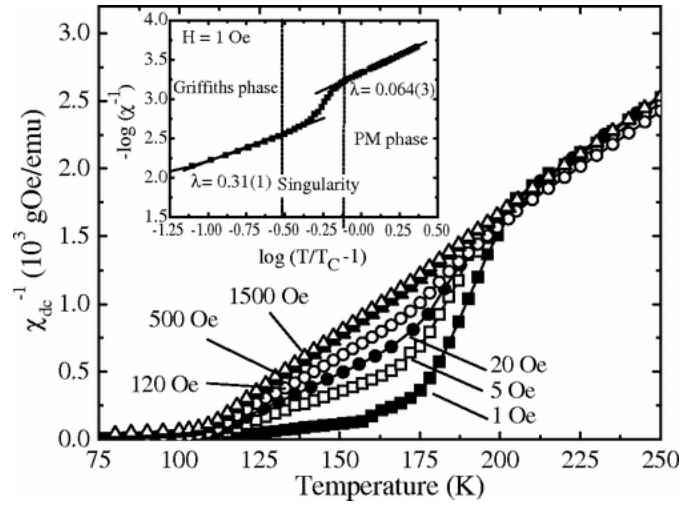


Figure 7.1: Temperature dependence of the inverse susceptibility χ^{-1} of $\text{Tb}_5\text{Si}_2\text{Ge}_2$. The inset shows fits at 1 Oe in the Griffiths and PM phases, respectively. Reproduced with permission of American Physical Society through SciPris from Ref. [115].

In analogy to the simple perovskite manganites, the introduction of spin doping through the substitution of magnetic Mn ions for non magnetic Y^{3+} A' ions in $[\text{Y}_{2-x}\text{Mn}_x]\text{MnMnMn}_4\text{O}_{12}$, gives rise to a spin texture that is inhomogeneous on the nanoscale. In these systems we have observed a Griffiths phase between T_c and T_g , and contrary to the majority of observed Griffiths phases, is characterised by the formation of short range antiferromagnetic clusters. Here it is shown that the experimental signature of a Griffiths phase, a sharp downturn in the inverse susceptibility before the system cools to the Curie temperature with a susceptibility exponent less than unity [116], can be explained by the change to the paramagnetic properties of the A-site ions. This has important consequences for the interpretation of systems that feature this anomaly in the susceptibility, which is often assumed to arise from the formation of

short range ferro/ferri magnetic clusters. Below $T_c = 64$ K the system orders into two distinct magnetic phases, a ferrimagnetic (FIM) and antiferromagnetic (AFM) phase. Unlike the simple perovskite manganites, where charge doping gives rise an inhomogeneous electronic texture and the resulting Griffiths phase, in the $[Y_{2-x}Mn_x]MnMnMn_4O_{12}$ systems it is ‘spin doping’ that gives rise to an inhomogeneous spin texture and the resulting Griffiths phase. This is a result of significance given recent trends to replace established electronic paradigms with spin-only functionality in future spintronic devices.

7.2 Experimental details

Powder samples of $Y_{1-\delta}Mn_{3+\delta}O_6$ were made from stoichiometric mixtures of Mn_2O_3 and Y_2O_3 (99.9%) using a high-temperature high-pressure synthesis method as detailed in Ref. [35].

Neutron powder diffraction measurements were performed on a 1.93 g sample of $Y_{1.79}Mn_{0.21}MnMnMn_4O_{12}$ and a 1.51 g sample of $Y_{1.84}Mn_{0.16}MnMnMn_4O_{12}$. Data with high counting statistics were collected at temperatures representative of each of the magnetically ordered phases, 85 K and 1.5K for both $[Y_{2-x}Mn_x]MnMnMn_4O_{12}$ samples. Data with lower counting statistics were collected on warming from 1.5 K to 50 K (60 K) in 5 K temperature steps, between 50 K (60 K) and 70 K in 2 K temperature steps, between 70 to 85 K in 5 K temperature steps for $Y_{1.84}Mn_{0.16}MnMnMn_4O_{12}$ ($Y_{1.79}Mn_{0.21}MnMnMn_4O_{12}$). A second set of neutron powder diffraction experiments were performed at a later date to collect data at 250 K, 200 K and between 140 K and 50 K in 10 K steps on both samples.

Magnetometry measurements were performed on a SQUID-VSM magnetometer (Quantum Design, MPMS3) between 2 and 400 K. Each sample was cooled to 2 K under zero applied magnetic field, a field was applied at 2 K and data was collected on warming from 2 K to 400 K (ZFC). Data was then collected on cooling (FCC) and then upon warming (FCW). The field was zeroed and the procedure was performed again, each time with a different applied magnetic field.

Small angle neutron scattering measurements were performed on D33 at the Institute Laue Langevin

(ILL) on both samples listed above, pressed into a flat disc like pellet, and placed in an aluminium sample mount. The magnetic field can be applied in a direction perpendicular or parallel to the incoming neutron beam, the former orientation was used for the SANS measurements performed on the $Y_{1.84}Mn_{0.16}MnMnMn_4O_{12}$ sample and the latter for the $Y_{1.79}Mn_{0.21}MnMnMn_4O_{12}$ sample. The orientation of the magnetic field perpendicular to the neutron beam enables one to investigate anisotropy in the system, but also causes a reduction to the scattered intensity. Background SANS data was collected at 295 K at the beginning of the experiment, and at the end of the experiment at 295 K under a 1 T field for both samples. For the $Y_{1.84}Mn_{0.16}MnMnMn_4O_{12}$ sample, data was collected in a single detector setting using a Q range of $0.003 \text{ \AA}^{-1}$ to $0.2 \text{ \AA}^{-1}$ in steps of $0.0005 \text{ \AA}^{-1}$, at 130 K, between 90 K and 60 K in 10 K steps and between 60 K and 1.5 K in 15 K steps under no applied magnetic field. Field dependent data was then collected using fields of 0.01, 0.1, 1.0 and 2.0 T at 1.5 K, and fields of 0.01, 0.1, and 1.0 T at 90 K, and fields of 1.0 T, 0.002 T, 0.01 T, 0.05 T and 0.1 T at 130 K. For the $Y_{1.79}Mn_{0.21}MnMnMn_4O_{12}$ sample SANS data was collected using a Q range of $0.003 \text{ \AA}^{-1}$ to $0.1 \text{ \AA}^{-1}$ in steps of $0.0005 \text{ \AA}^{-1}$ at 130 K and 90 K under applied fields of 0 T, 0.002 T, 0.01 T, 0.05 T, 0.1 T, 0.5 T and 1 T. SANS data was then collected under zero applied field between 80 K and 5 K in 5 K steps. Finally at 5 K data field dependent data was collected using applied fields of 0.01 T, 0.1 T, 1 T and 1.5 T.

7.3 Neutron powder diffraction

The published $Pm\bar{m}n$ crystal structure model [35] was used to refine the neutron powder diffraction data collected in the paramagnetic phase of both samples, as shown in Fig. 7.2(a) and Fig. 7.2(d). The A' sites (Y1 and Y2) were predominately occupied by non magnetic Y^{3+} and a small amount of magnetic Mn ions, the A'' sites by Mn^{3+} and the A''' sites by Mn^{2+} . The two symmetry inequivalent B sites, labelled Mn3 and Mn4, were occupied by Mn^{3+} and $Mn^{3.5+}$ ions respectively. The refined stoichiometries of the two $Y_2MnMnMn_4O_{12}$ samples were $Y_{1.768(9)}Mn_{0.232(9)}MnMnMn_4O_{12}$ and $Y_{1.840(7)}Mn_{0.160(8)}MnMnMn_4O_{12}$. In the $Y_{1.79}Mn_{0.21}MnMnMn_4O_{12}$ sample 13.2(4)% of Y1 sites and 10.0(4)% of Y2 sites were occupied by Mn ions, and in the $Y_{1.84}Mn_{0.16}MnMnMn_4O_{12}$ sample 10.0(4)% of Y1 sites and 6.0(4)% of Y2 sites were occupied by Mn ions. Both samples con-

tained a YMn_2O_5 impurity, with a weight fraction of 1.26 wt. % and 1.32 wt. % respectively. The $\text{Y}_{1.84}\text{Mn}_{0.16}\text{MnMnMn}_4\text{O}_{12}$ sample also contained a YMnO_3 impurity, with a weight fraction of 0.37 wt.%. An excellent fit was achieved for both samples, $R = 3.30\%$, $wR = 3.30\%$, $R_{\text{Bragg}} = 3.04\%$ for the $\text{Y}_{1.79}\text{Mn}_{0.21}\text{MnMnMn}_4\text{O}_{12}$ sample at 250 K and $R = 3.36\%$, $wR = 3.71\%$, $R_{\text{Bragg}} = 3.02\%$ for the $\text{Y}_{1.84}\text{Mn}_{0.16}\text{MnMnMn}_4\text{O}_{12}$ sample at 255 K. The refined crystal structure parameters for each sample are given in Tables 9.24 and 9.27 of Sec. 9.3.4 of the Appendix.

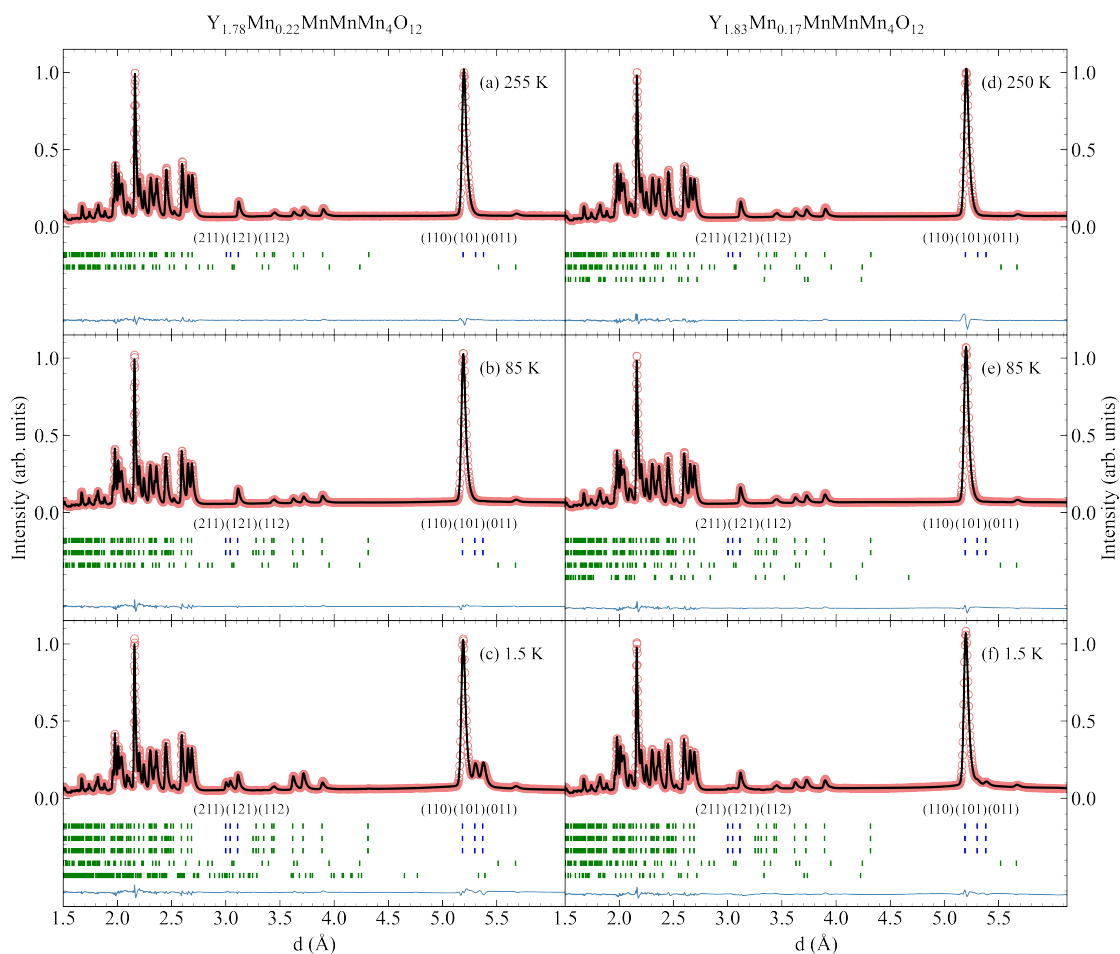


Figure 7.2: Neutron powder diffraction data taken on WISH at temperatures of (a) 255 K, (b) 85 K, and (c) 1.5 K for $\text{Y}_{1.79}\text{Mn}_{0.21}\text{MnMnMn}_4\text{O}_{12}$ and (d) 250 K, (e) 85 K, (f) 1.5 K for $\text{Y}_{1.84}\text{Mn}_{0.16}\text{MnMnMn}_4\text{O}_{12}$. The refinement is given by the black line and the raw data by the red circles; peaks labelled with an asterisk are from the impurity phases. The green tick marks indicate, from top to bottom, the nuclear and magnetic reflections from $\text{Y}_2\text{MnMnMn}_4\text{O}_{12}$, labelled (1), the YMn_2O_5 impurity labelled (2), and the YMnO_3 impurity, labelled (3). The $\{112\}$ and $\{110\}$ family of reflections have been highlighted by the blue tick marks.

Below 200 K a gradual decrease in the paramagnetic background is observed in both samples, which is accompanied by changes in the samples' magnetisation, there is a slight curvature in the inverse susceptibility between 200 K and 120 K, see insets of Fig. 7.3(a) and Fig. 7.3(d). Below $T_g = 111$ K the appearance of broad diffuse intensity centred about the $\{110\}$ and $\{112\}$ family of reflections is observed in both samples, which is concomitant with a sharp drop in the inverse susceptibility, Fig. 7.3(b) and Fig. 7.3(e), and hence this scattered intensity is identified as magnetic in origin. The diffuse scattering grows till the lowest measured temperatures with a sharp increase in intensity below 35 K for the $Y_{1.79}Mn_{0.21}MnMnMn_4O_{12}$ sample and below 30 K for the $Y_{1.84}Mn_{0.16}MnMnMn_4O_{12}$ sample. Below $T_c = 64$ K the appearance of four new Γ -point reflections, the (011), (101), (121) and (211), and the growth of the (020), (200) reflections was observed. This occurred at the same temperature a plateau was reached in the inverse susceptibility (corresponding to a large increase in the magnetisation of the sample), Fig. 7.3(c) and Fig. 7.3(f), and hence this intensity was also identified as magnetic. The intensity on top of the sharp magnetic Bragg peaks increases till 35 K for $Y_{1.79}Mn_{0.21}MnMnMn_4O_{12}$ and till 30 K for $Y_{1.84}Mn_{0.16}MnMnMn_4O_{12}$, before steadily decreasing till the lowest measured temperatures, as shown for the (101) and (011) reflections.

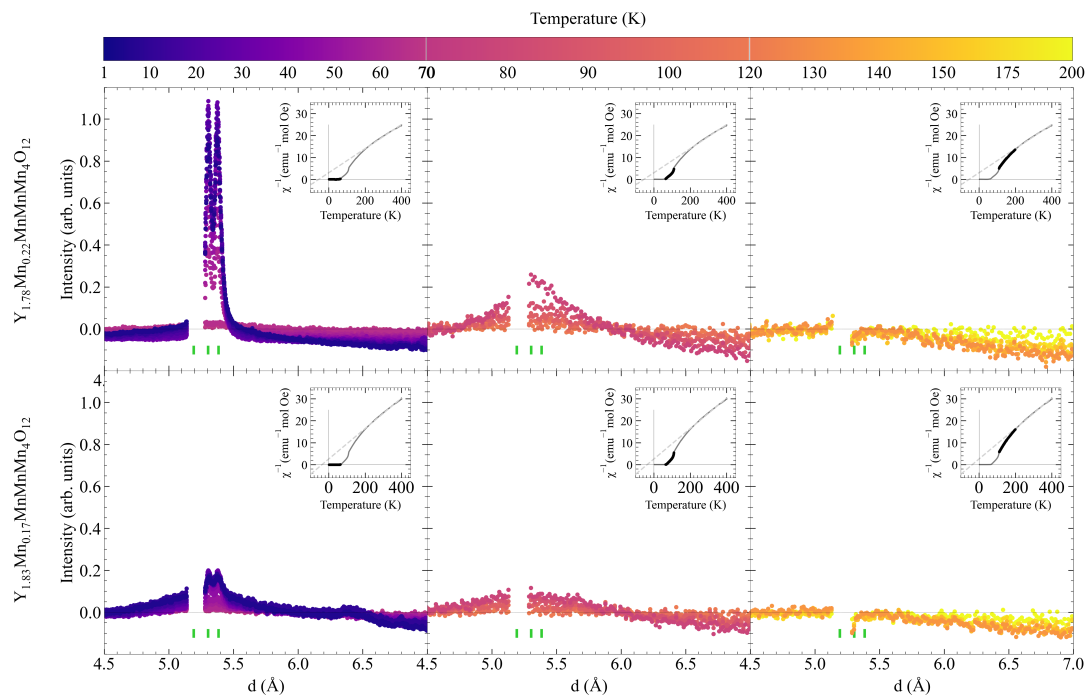


Figure 7.3: Neutron powder diffraction patterns collected on WISH centred about the $\{110\}$ family of reflections. Data collected on the $Y_{1.78}Mn_{0.21}MnMnMn_4O_{12}$ sample between (a) 120 K to 200 K subtracted from 250 K data (b) 70 K to 110 K subtracted from 120 K data and (c) 1.5 K to 75 K subtracted from 85 K data. Data collected on the $Y_{1.84}Mn_{0.16}MnMnMn_4O_{12}$ sample between (d) 120 K to 200 K subtracted from 255 K data (e) 70 K to 110 K subtracted from 120 K data and (f) 1.5 K to 75 K subtracted from 100 K data. The insets show the temperature dependence of FCC magnetisation measurements under an applied DC field of 100 Oe for each of the samples, with the temperature range of the corresponding neutron powder diffraction data emphasised in bold. A Curie Weiss fit of the inverse susceptibility between 400-200 K data is given by the dashed line.

The origin of the broad diffuse intensity that onsets below 110 K, and the sharp magnetic Bragg peaks that grow below 70 K, are investigated in the following two sections.

7.3.1 AFM phase

Broad diffuse intensity is observed about the $\{110\}$ and $\{112\}$ family of reflections, with the scattering on the latter reflection significantly weaker in intensity. Magnetic scattering at the $\{110\}$ and $\{112\}$ families of reflections can originate from either Γ -point AFM B-site modes or Γ -point F_i A-site modes,

as determined from structure factor calculations, in Sec. 9.2 of the Appendix. F_i A-site modes are inconsistent with the results of the small angle neutron scattering measurements detailed in Sec. 7.5, and hence it was determined that the diffuse scattering originates from AFM B-site modes. Table 7.1 summarises the reflection conditions for scattering from all B-site modes, taking into account the phase between the Mn3 and Mn4 layers. Scattering at these two families of reflections can occur from $A_i A_i$, $X_i X_i^-$ and $Y_i Y_i^-$ modes, as shown in Table 7.1¹. Here the notation $A_i A_i$ represents the spins of the Mn3 ions transforming by an A_i mode, and the spins of the Mn4 ions transforming by an A_i mode.

Each of these three B-site antiferromagnetic mode combinations was tested against the neutron powder diffraction data, and the best fit to the diffraction pattern, shown in Fig. 7.2, was using a magnetic structure model in which the B-site magnetic structure transforms by an $A_z A_z$ mode ($R_{\text{Mag}} = 0.87\%$ for the $\text{Y}_{1.79}\text{Mn}_{0.21}\text{MnMnMn}_4\text{O}_{12}$ sample and $R_{\text{Mag}} = 0.75\%$ for the $\text{Y}_{1.84}\text{Mn}_{0.16}\text{MnMnMn}_4\text{O}_{12}$ sample at 1.5 K), shown in Fig. 7.5(a), corresponding to the Γ_1^+ irrep.

If the moments were oriented along x or y one would observe a larger magnetic intensity on the (112) reflection in comparison to the (110) reflection. For moments oriented along z the (112) is expected to be weaker in intensity, which is exactly the experimental observation. The Γ_1^+ irrep allows for a canted magnetic structure of the B sites, by inclusion of X_i and Y_i modes. However the inclusion of these additional degrees of freedom into the refined magnetic structure could not reliably be determined to improve the fit, given the broadness of the diffuse scattering, and hence a minimal magnetic structure model of the AFM order is presented.²

A least squares regression using a Lorentzian profile of the form, $I = I_0(1/\xi)^2/[Q^2 + (1/\xi)^2]$, centred about $Q = 1.21 \text{ \AA}^{-1}$ (where the $A_z A_z$ mode is expected to scatter), was used to fit the diffuse scattering, as in Ref. [123], and extract a correlation length. The fits and temperature dependence of the correlation length is shown in Fig. 7.4.

¹ A single A_i mode, i.e on a single B site layer, could also give rise to scattering on the (110) and (112), however significant intensity is also expected on the (111) reflection which was not observed.

² The inclusion of either the X_i and Y_i modes in the magnetic structure would not change the analysis presented in Sec. 7.6 and Sec. 7.7, or the conclusions drawn from this work.

Table 7.1: Reflection conditions for B-site F_i , A_i , X_i , Y_i symmetry adapted basis modes as determined by structure factor calculations shown in Sec. 9.2. When two B-site modes are listed, the first mode corresponds to the magnetic structure of the Mn3 layer, and the second mode to the magnetic structure of the Mn4 layer. For instance the notation $A_i A_{\bar{i}}$ corresponds to the magnetic structure of the Mn3 ions transforming by an A_i mode and the magnetic structure of the Mn4 ions transforming by an $A_{\bar{i}}$ mode. f_m is the magnetic form factor, which is approximated to be same for the Mn3 and Mn4 ions. Note that the magnetic moment direction has not been taken into account when calculating the structure factors.

Mode	(001)	{200}	(010)	(100)	(011)	(101)	(110)	(111)	(012)	(102)	(112)	(121)	(211)
$F_i F_i$	0	$8f_m$	0	0	0	0	0	0	0	0	0	0	0
$F_i F_{\bar{i}}$	$8f_m$	0	0	0	0	0	0	0	0	0	0	0	0
F_i	$4f_m$	$4f_m$	0	0	0	0	0	0	0	0	0	0	0
$A_i A_i$	0	0	0	0	0	0	$8f_m$	0	0	0	$8f_m$	0	0
$A_i A_{\bar{i}}$	0	0	0	0	0	0	0	$8f_m$	0	0	0	0	0
A_i	0	0	0	0	0	0	$4f_m$	$4f_m$	0	0	$4f_m$	0	0
$X_i X_i$	0	0	0	$8f_m$	0	0	0	0	0	$8f_m$	0	0	0
$X_i X_{\bar{i}}$	0	0	0	0	0	$8f_m$	0	0	0	0	0	$8f_m$	0
X_i	0	0	0	$4f_m$	0	$4f_m$	0	0	0	$4f_m$	0	$4f_m$	0
$Y_i Y_i$	0	0	$8f_m$	0	0	0	0	0	$8f_m$	0	0	0	0
$Y_i Y_{\bar{i}}$	0	0	0	0	$8f_m$	0	0	0	0	0	0	0	$8f_m$
Y_i	0	0	$4f_m$	0	$4f_m$	0	0	0	$4f_m$	0	0	0	$4f_m$

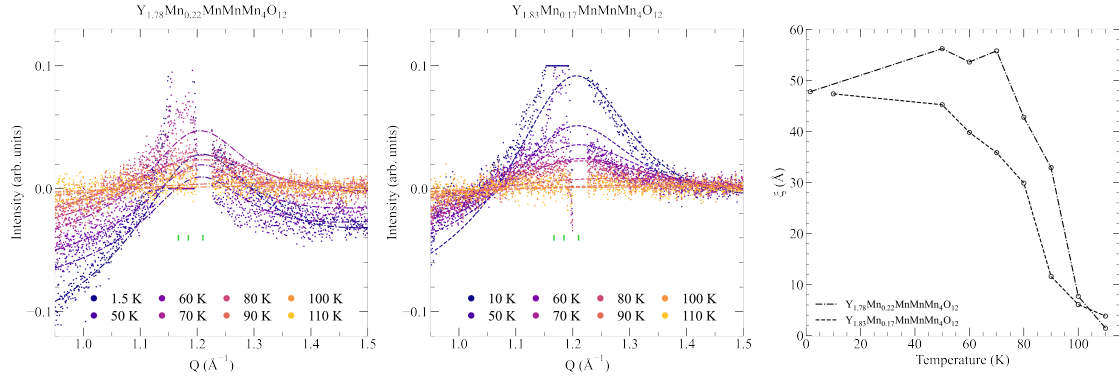


Figure 7.4: Neutron powder diffraction patterns collected on WISH centred about the $\{110\}$ family of reflections. Data collected on (a) the $Y_{1.79}Mn_{0.21}MnMnMn_4O_{12}$ sample between 1.5 K and 110 K subtracted from 120 K data (b) between 10 K to 110 K subtracted from 120 K data. The raw data is given by the circles and the fits to the data by the solid line. The data was fit using a Lorentzian distribution of the form, $I = I_0(1/\xi)^2/[Q^2 + (1/\xi)^2]$, centred about $Q = 1.21 \text{ \AA}^{-1}$ (the peak position of the (110) reflection)) using a second order polynomial as background. (c) The temperature dependence of the correlation length, extracted from the Lorentzian fits of the data, for both $[Y_{2-x}Mn_x]MnMnMn_4O_{12}$ samples.

7.3.2 FIM phase

The sharp magnetic Bragg peaks that appear below $T_c = 64$ K index with a Γ -point propagation vector. From structure factor calculations, outlined in Sec. 9.2 of the Appendix, one can deduce that the Bragg magnetic scattering on the (020) and (200) reflections originate from either A or B-site Γ -point F_i modes. The observation of equal amounts of magnetic intensity on the (200) and (020), and zero magnetic intensity on the (002) reflections are consistent with the ordering of F_z modes, which transform by the Γ_2^+ irrep. Magnetic structure models were constructed by taking linear combinations of the symmetry adapted basis functions of the Γ_2^+ irrep, and each of these models was used to refine the neutron powder diffraction data using the FULLPROF software suite. The magnetic structure model that gave the best fit to the data at 40 K, was one in which the Mn1, Mn2, Mn3 and Mn4 sublattices order with F_z modes, such that the Mn2 sublattice moments are oriented antiparallel to the Mn1, Mn3 and Mn4 sublattice moments to give a net collinear ferrimagnetic structure ($R_{\text{Mag}} = 3.14\%$ for the $Y_{1.79}Mn_{0.21}MnMnMn_4O_{12}$ sample and $R_{\text{Mag}} = 5.17\%$ for the $Y_{1.84}Mn_{0.16}MnMnMn_4O_{12}$ sample at 40 K), as shown in Fig. 7.5(b). This is

similar to both magnetically ordered phases of $\text{Tm}_2\text{MnMnMn}_4\text{O}_{12}$ and the FI phase of $\text{R}_2\text{CuMnMn}_4\text{O}_{12}$.

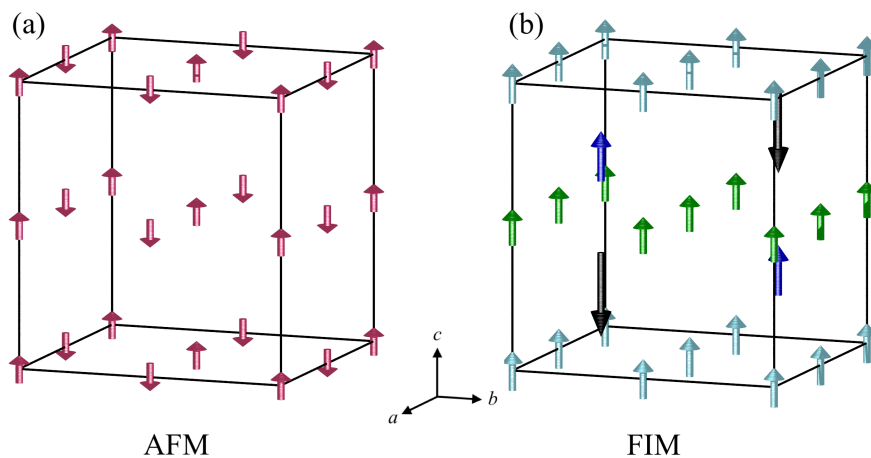


Figure 7.5: The refined magnetic structure of the (a) AFM phase and (b) FIM phase of $\text{Y}_2\text{MnMnMn}_4\text{O}_{12}$ at 40 K. The crystallographic unit cell is drawn in black. For the AFM phase the Mn3 and Mn4 ions are crimson, and in the FIM phase the Mn1 ions are blue, the Mn2 ions black, the Mn3 ions green and Mn4 ions skyblue.

7.3.3 Temperature dependence

The above magnetic structure models; the Mn3 and Mn4 layers ordering with A_z modes to fit the diffuse, and the collinear ferrimagnetic structure to fit the sharp magnetic Bragg peaks, was used to fit variable temperature powder neutron diffraction data. The Mn1, Mn2, Mn3 and Mn4 moments in the FIM phase are freely refining. The moment magnitudes across the Mn3 and Mn4 layers in the AFM phase could not be independently be refined, so they were fixed to be the same (one would expect them to have a dependence in line with the ratio of the oxidation states). As the phase fractions and moment magnitudes are correlated, it was not possible to extract a temperature dependence of the sublattice moment magnitudes or the phase fractions. Instead the phase fractions of each magnetic phase was fixed to be a 100%, as if each magnetic phase was perfectly correlated, and the moment magnitudes across each sublattice were allowed to freely refine, enabling the *average* magnetic moment of each sublattice to be extracted as a function of temperature, which is shown in Fig. 7.6(a) and Fig. 7.6(b). Below 30 K for the $\text{Y}_{1.79}\text{Mn}_{0.21}\text{MnMnMn}_4\text{O}_{12}$ sample and 35 K for the $\text{Y}_{1.84}\text{Mn}_{0.16}\text{MnMnMn}_4\text{O}_{12}$ sample, the average

moment on each of the magnetic sublattices in the FIM phase begins to decrease, which occurs concomitantly with a sharp increase in the average refined magnetic moments of the AFM phase, Fig. 7.6. The total moment across the Mn3 and Mn4 sublattices, determined by summing the moments across the AFM and FIM phases, is plotted in Fig. 7.6(c), and grows steadily to the lowest measured temperatures.

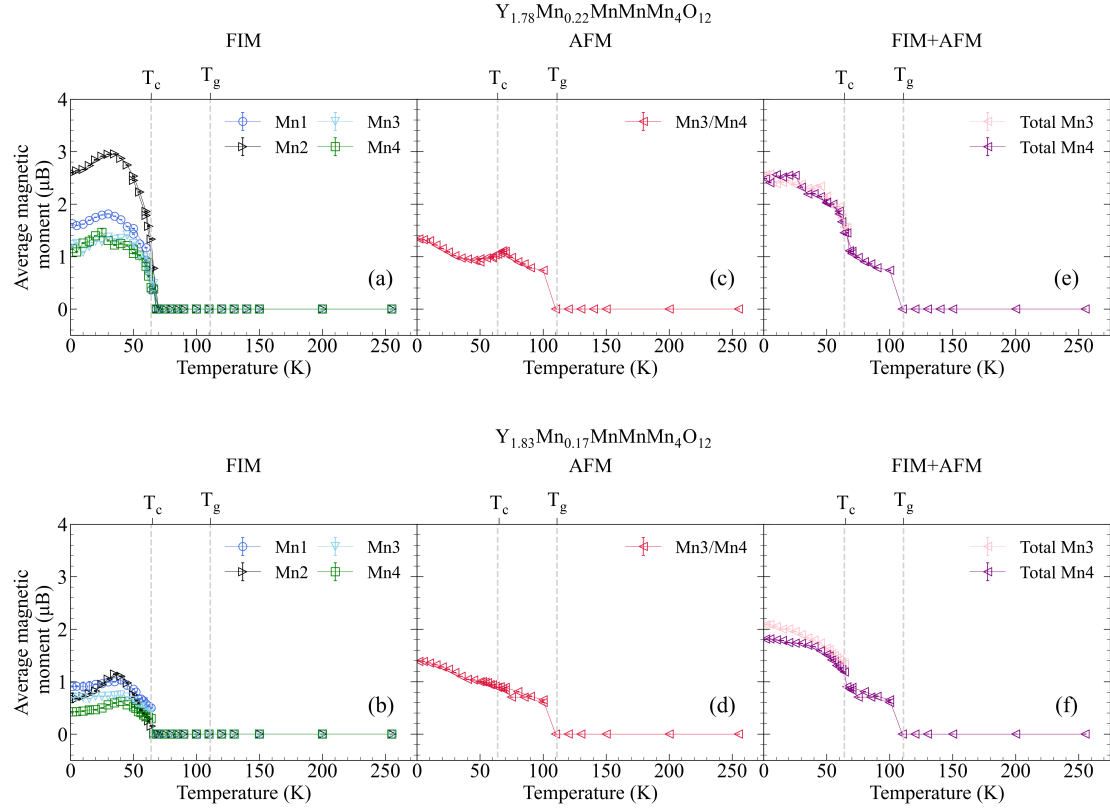


Figure 7.6: Variable temperature neutron powder diffraction data showing the average refined moment magnitudes for each of the symmetry inequivalent magnetic sites for (a)-(b) the collinear ferrimagnetic phase (FIM), (c)-(d) the short range antiferromagnetic clusters (AFM) and (e)-(f) the combined FIM and AFM moment for the $Y_{1.79}Mn_{0.21}MnMnMn_4O_{12}$ and $Y_{1.84}Mn_{0.16}MnMnMn_4O_{12}$ samples.

7.4 Magnetometry

In this section, the ZFC and FCC DC magnetometry measurements are discussed in the context of the determined magnetic phases. A plot of the susceptibility and inverse susceptibility for different applied fields is shown in Fig. 7.7 for both samples. A number of observations were made from these data. From 400 K to 200 K the inverse susceptibility can be fit well with a Curie Weiss like temperature

dependence of the magnetometry. This is consistent with the absence of any changes to the diffraction pattern between 400 K and 250 K, indicating no change to the magnetic properties of the sample. A fit of the inverse susceptibility data between 400 K and 200 K gives a Curie Weiss temperatures of -46 K for the $Y_{1.79}Mn_{0.21}MnMnMn_4O_{12}$ sample and -67 K for $Y_{1.84}Mn_{0.16}MnMnMn_4O_{12}$ sample, as shown in Fig. 7.7(b) and Fig. 7.7(d), suggesting the onset of antiferromagnetic order below T_c .

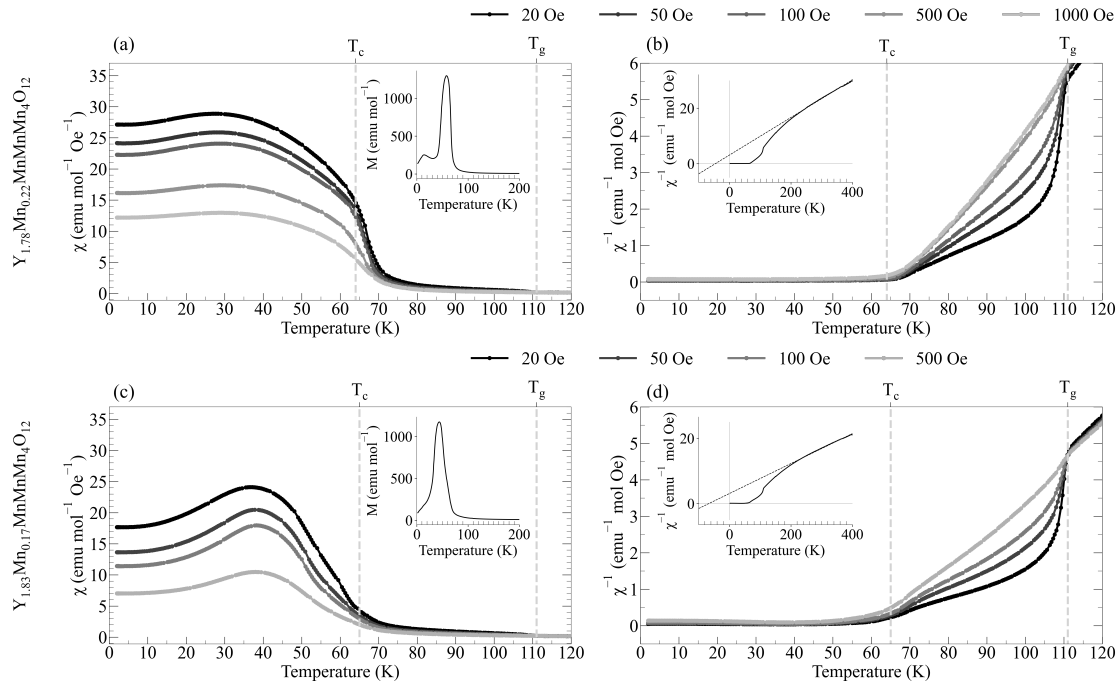


Figure 7.7: Temperature dependence of FCC magnetisation measurements under different applied DC fields showing (a) the susceptibility (b) the inverse susceptibility for the $Y_{1.79}Mn_{0.21}MnMnMn_4O_{12}$ sample under different applied DC fields. The inset in (a) and (c) is the temperature dependence of the ZFC magnetisation, and in (b) and (d) it is the inverse susceptibility collected at 100 Oe, with a Curie Weiss fit of the 400-200 K data shown by the dashed line.

Below ~ 200 K a departure from Curie Weiss like behaviour was observed in the inverse susceptibility, (see inset of Fig 7.7(b) and Fig. 7.7(d)), and a gradual decrease to the paramagnetic background in the NPD data. These observations are consistent with the onset of magnetic ordering with a correlation length too small to give rise to any diffraction peaks, or alternatively may indicate a change in the spin fluctuations of the sample.

Between a 111 K and T_c there is a small and sharp decrease to the inverse susceptibility, which is sup-

pressed upon application of a magnetic field, Fig. 7.7(b) and Fig. 7.7(d). A ferromagnetic impurity could cause a sharp decrease to the inverse susceptibility, however no evidence of any ferromagnetic impurity peaks were found in the diffraction data. Furthermore the suppression of this feature upon application of a magnetic field would not be consistent with the behaviour of a ferromagnetic impurity. This feature in the magnetometry is qualitatively very similar to features observed in the Griffiths phases of other systems, as shown in Fig. 7.1. Indeed fitting $\chi^{-1} \propto (T - T_c)^{1-\lambda}$ to the 50 Oe data in this temperature interval, gives a susceptibility exponent, $1 - \lambda$, of less than 1, 0.92 for $\text{Y}_{1.79}\text{Mn}_{0.21}\text{MnMnMn}_4\text{O}_{12}$ sample, and 0.85 for the $\text{Y}_{1.84}\text{Mn}_{0.16}\text{MnMnMn}_4\text{O}_{12}$ sample. Microscopically this feature in the magnetometry has often been argued to arise due to the presence of short range ferromagnetic clusters [116, 115, 117]. For the $[\text{Y}_{2-x}\text{Mn}_x]\text{MnMnMn}_4\text{O}_{12}$ systems, concomitant with the sharp decrease in the inverse susceptibility is the observation of broad diffuse intensity in the NPD that scatters from antiferromagnetic clusters. No evidence of B-site ferromagnetic order is observed from the NPD data in this temperature region, however it is feasible that the system did contain short range A-site ferro/ferrimagnetic clusters, but they were too small to be measured using neutron powder diffraction. Thus small angle neutron scattering measurements were performed to determine if any short range ferromagnetic order was present in the Griffiths phases of these systems, and is presented in Sec 7.5.

Below $T_c = 64$ K there is a rapid increase in the susceptibility of both samples, Fig. 7.7(a) and Fig. 7.7(c), indicating the onset of long range ferro/ferrimagnetic order. This is consistent with the appearance of magnetic Bragg peaks in the NPD data, which originates from a collinear ferrimagnetic structure. The susceptibility is significantly lower in the $\text{Y}_{1.84}\text{Mn}_{0.16}\text{MnMnMn}_4\text{O}_{12}$ sample, consistent with the smaller average moment refined across all magnetic sites from the NPD data for this sample, see Fig. 7.6(d).

7.5 Small angle neutron scattering

Small angle neutron scattering (SANS) measurements were performed to probe whether any short range ferromagnetic order is present in the Griffiths phase. The transmitted intensity from the full beam and the scattered intensity from an empty sample cell was used to normalise each SANS pattern, so that any

contributions from the transmitted beam and aluminium sample holder were subtracted away. For the temperature dependent data collected under zero applied field, each pattern was also normalised by the SANS pattern collected at high temperature, to subtract away the nuclear contribution to the scattered intensity.

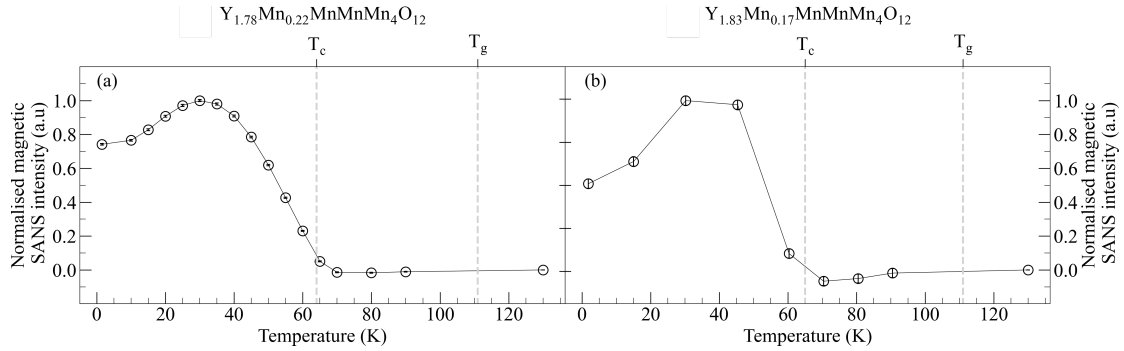


Figure 7.8: Temperature dependence of the normalised magnetic SANS intensity of the $Q = 0.0028 \text{ \AA}^{-1}$ peak as a function of temperature for the (a) $Y_{1.79}Mn_{0.21}MnMnMn_4O_{12}$ and (b) $Y_{1.84}Mn_{0.16}MnMnMn_4O_{12}$ samples.

Fig. 7.8 shows the variation in the magnetic intensity summed over the collected Q range, and plotted as a function of temperature for both samples. No statistically significant change to the magnetic intensity was observed in the Griffiths phase of either sample, indicating the absence of any ferro/ferri magnetic clusters in this temperature region. Further measurements were performed to observe the change to the SANS intensity as a function of magnetic field for the $Y_{1.79}Mn_{0.21}MnMnMn_4O_{12}$ sample. In the presence of any ferro/ferri magnetic clusters, one would expect the field to couple to the net magnetisation of the cluster and cause a change to the observed magnetic SANS intensity, as has been observed in other systems [115]. No statistically significant change to the SANS intensity was observed in the Griffiths phase as a function of magnetic field, as shown in Fig. 7.9(b), conclusively ruling out the presence of any ferromagnetic order ³.

Magnetic SANS intensity begins to appear below T_c in both samples. To fit this intensity, a number of

³The scattering length density is calculated by determining the average neutron scattering lengths in a unit cell, while the magnetic scattering length density is the average magnetic moment in a unit cell, which is zero for antiferromagnetic order, and hence SANS is only sensitive to the presence of ferromagnetism.

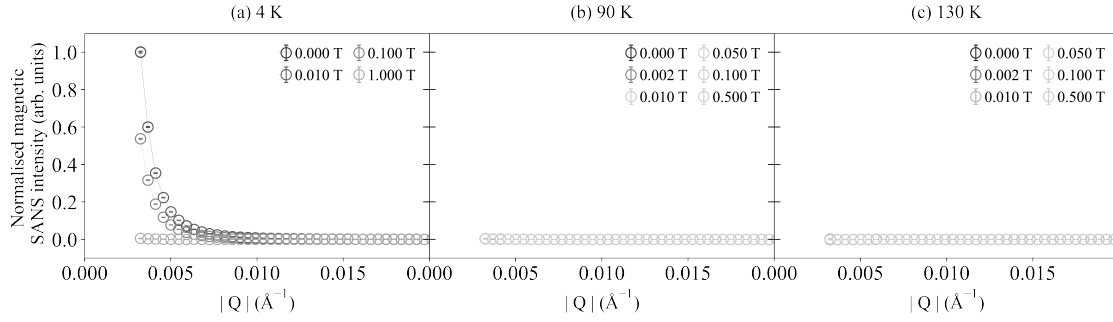


Figure 7.9: Normalised magnetic SANS intensity under different applied magnetic fields at (a) 4 K (b) 90 K and (c) 130 K for $Y_{1.79}Mn_{0.21}MnMnMn_4O_{12}$.

standard expressions for the form factor were tested⁴, and a Lorentzian squared, centred about $Q = 0$, gave the best fit to the data. However there was a high degree of correlation between the fit parameters (the amplitude and half-width half maximum), and it is therefore likely that the SANS measurements had only captured the tail of the peak, and as a consequence the amplitude and half width half maximum could not be decorrelated. The variation in the peak intensity as a function of temperature, shown in Fig. 7.8, reproduces the observed variation in intensity of the Bragg peaks measured from NPD, and thus this intensity was identified as scattering from the $(0, 0, 0)$ reflection of the FIM phase. Upon application of a magnetic field, the $(0, 0, 0)$ reflection appears to sharpen at 4 K, Fig. 7.9(a), which would imply that the magnetic field suppress the antiferromagnetic clusters and favours the FIM phase.

7.6 Discussion

The AFM phase is predicted to arise in the presence of dominant B-B exchange interactions, and the FIM phase in the presence of dominant A-B exchange. Below T_c both magnetic phases coexist, indicating that the distribution of exchange interactions across the system is inhomogeneous, so that in some regions of the system A-B exchange dominates over B-B exchange, while in other regions of the system the converse

⁴The scattered SANS intensity is proportional to the product of the structure factor, the contrast factor and the form factor, as shown in Sec. 2.1.6. The observation of a single peak in the measured Q range at all temperatures implies that the structure factor does not need to be taken into account, as it typically gives rise to a series of peaks in the SANS data. The contrast factor is the difference in the scattering length density between the different phases, and is constant in Q . Therefore in this analysis the magnetic SANS intensity can be modelled entirely by the form factor.

is true. Locally, exchange interactions can be tuned by cation disorder. In one sample 13.2(4)% of the Y sites are occupied by Mn and in the other 10.0(4)% of the Y sites are occupied by Mn. The occupation of a Y site by Mn, gives rise to A-B exchange interactions on a site that was otherwise magnetically inert, thus substitution of Mn for Y is equivalent to spin doping. In regions of the system where there is appreciable spin doping the FIM phase will be favoured, while in regions of the system where the nominal stoichiometric composition is retained, the AFM phase will be stabilised. This is consistent with the greater suppression of the FIM phase in the sample with less cation disorder, $\text{Y}_{1.84}\text{Mn}_{0.16}\text{MnMnMn}_4\text{O}_{12}$.

The FIM phase that orders below $T_c = 64$ K is fairly well correlated, as it gives rise to magnetic Bragg peaks with similar widths to that of the nuclear Bragg peaks. Surprisingly the average magnetic moment of the magnetic sublattices in the FIM phase begins to decrease below ~ 30 K. Given that it would be rather unphysical for the moment magnitude on a site to decrease as the temperature is lowered, the decrease in the average moment can be explained by a decrease in the FIM phase fraction. Certainly the concomitant sharp increase in the average B-site moments of the AFM phase below 30 K supports the picture of an increase of the AFM phase fraction at the expense of the FIM phase fraction. Microscopically the phase fractions of the two phases can change if the relative A-B and B-B exchange interactions in a given region change with temperature. Consider for instance a region of the crystal structure in which the magnetic order is on the cusp of becoming FIM or AFM. From Fig. 7.6 one can see that in the FIM phase the average Mn1 and Mn2 sublattice moments grow rapidly below T_c , while the Mn3 and Mn4 B-sites moments increase more gradually. Therefore it is feasible that at high temperature, where the Mn A-site moments are larger than the Mn B-site moments, A-B exchange interactions dominate and FIM order is stabilised. While below 30 K it is possible that the B-site moments have grown sufficiently such that B-B exchange dominates and the region flips from being FIM to AFM.

Finally it is noted that the direction of the magnetic moments in both the AFM and FIM phases are $\parallel c$, consistent with the presence of the weak easy axis single ion anisotropy of the JT active Mn^{3+} ions $\parallel c$, and the absence of any other sources of anisotropy in the system.

7.7 What gives rise to the small increase in susceptibility below T_g ?

The sharp increase in the magnetic susceptibility below T_g is not due to the presence of ferromagnetic clusters, as has been observed in the Griffiths phases of other systems, and what one may intuitively predict if an increase to the susceptibility is observed. In this section a change to the paramagnetic properties of the A-sites is shown to give a rise to the magnetic susceptibility, and is therefore presented as a possible scenario to explain the observed feature characteristic of a Griffiths phase.

In the ZFC data of both samples, see insets of Fig. 7.7(a) and Fig. 7.7(c), there is a small increase to the susceptibility below both ~ 30 K and $T_g = 111$ K, concomitant with the growth of the AFM phase fraction. The formation of an AFM cluster cannot increase the susceptibility as the net moment of an AFM cluster will sum to zero, however a change to the magnetism of the A-site ions contained within the AFM clusters could increase the susceptibility.

The $A_z A_z$ modes transform by the Γ_1^+ irrep in which the B-sites are decoupled from the A-sites, as shown in Table 3.2. Given the absence of any experimental signatures of A-site ordering in the neutron data ⁵, and with an A-A exchange ordering temperature of ~ 15 K [57], it is feasible the Mn A-sites remain paramagnetic till ~ 15 K. Below 15 K a small decrease to the ZFC susceptibility is observed, see inset of Fig. 7.7(a), which may be representative of the A-site ordering.

Instead of accessing all possible paramagnetic states of the ion, the Mn A-sites may instead continuously flip between two states oriented parallel or antiparallel to a given B-site. If this was the case then an increase to the susceptibility would be observed! Fig. 7.10 plots the susceptibility of a paramagnetic Mn^{2+} ion that access all six possible m_J states (+5/2, +3/2, +1/2, -1/2, -3/2, -5/2) and the susceptibility of the same ion that only access two of the six m_J states, +5/2 and -5/2; a clear increase to the susceptibility is observed in the latter scenario. The A-sites are more likely to orient parallel or antiparallel to a given B-site as this will maximise the symmetric A-B exchange. However instead of choosing a single orien-

⁵If the Mn A-sites transform by the F_i modes this would be inconsistent with the results of the SANS measurements, and if the Mn A-sites were to transform by the A_i modes this would be inconsistent with the results of the NPD measurements.

tation, which would frustrate half of the nearest neighbour A-B exchange interactions when the B-sites transform with A_i modes as discussed in Sec. 4.6.1, the Mn A-sites could continuously flip between a moment oriented parallel and antiparallel to the B sites, thus equally satisfying and frustrating all nearest neighbour A-B exchange interactions over time.

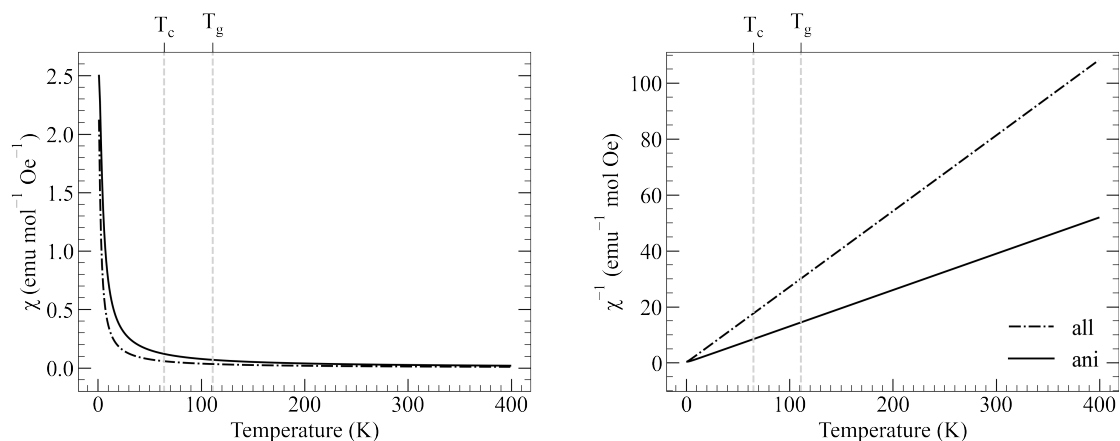


Figure 7.10: The (a) susceptibility and (b) the inverse susceptibility of paramagnetic Mn^{2+} ion that access all six possible m_J states, $+5/2$, $+3/2$, $+1/2$, $-1/2$, $-3/2$, $-5/2$, (dotted and dashed line) and the susceptibility of the same ion that only access two of the six m_J states, $+5/2$ and $-5/2$ (solid line).

The suppression of the feature in the magnetometry with application of magnetic field can then be explained in this model in one of two ways. The magnetic field could suppress the antiferromagnetic clusters, thereby restoring the Mn A-site to the normal paramagnetic dependence. Alternatively the magnetic field could prevent the Mn A-sites from continuously flipping and favour one of the two states. The SANS measurements support the former scenario given that it appears as if the magnetic SANS intensity measured at 4 K, Fig. 7.9, representative of the FIM phase, is sharpening with magnetic field indicating the FIM phase is becoming more correlated, and the AFM clusters are suppressed. Although whether the field dependence of the system at low temperature is representative of the field dependence in the Griffiths phase is not yet clear. Furthermore if the magnetic field favoured a single state of the Mn A-site, one may expect an increase to the observed SANS intensity as a function of magnetic field at 90 K, which was not observed.

7.8 Conclusions

To conclude, magnetometry data collected on the $x = 0.21$ and $x = 0.16$ samples of $[\text{Y}_{2-x}\text{Mn}_x]\text{MnMnMn}_4\text{O}_{12}$ indicated that short range ferromagnetic clusters were stabilised between 111 K and 64 K. However, this is not supported by the results of the small angle neutron scattering experiments, nor by the neutron powder diffraction experiments. The absence of any SANS intensity between 64 K and 111 K, and which does not change as a function of magnetic field, indicates the absence of ferromagnetic clusters. Between 64 K and 111 K neutron powder diffraction data shows broad intensity that scatters about the $\{110\}$ and $\{112\}$ family of reflections that could either be consistent with B-site AFM modes or A-site FM modes. Below 64 K long range ferrimagnetic order develops where the A and B-sites transform by FM modes, which scatter into sharp magnetic Bragg peaks. If the broad diffuse intensity originated in A-site FM modes, one may expect that as the long range ferrimagnetic order develops, the broad diffuse intensity should shift into the sharp magnetic Bragg peaks. However, the broad diffuse intensity *grows* below T_c , and at the expense of the sharp magnetic Bragg peaks below 30 K, indicating that the diffuse scattering originates in a competing magnetic phase. An AFM G-type structure (Fig. 1.3), predicted by the GKA rules in the presence of dominant B-B exchange over A-B exchange, can explain the results of the small angle neutron scattering and the neutron powder diffraction measurements. The amount of magnetic Mn that replaces the non-magnetic Y^{3+} on the A' sites, tunes the strength of B-B exchange to A-B exchange, such that as the amount of magnetic Mn on the A-sites increases (i.e., for larger values of x) the strength of A-B exchange increases. Therefore, the greater suppression of the FIM phase in the $x = 0.16$ sample is entirely consistent with the above model.

The downturn in the inverse susceptibility that was observed between 64 K and 111 K, and which is suppressed upon application of a magnetic field, is widely regarded in the literature to be characteristic of a Griffiths phase consisting of ferromagnetic clusters. However, since the neutron scattering results and the predictions by the GKA rules are suggestive of antiferromagnetic clusters in this temperature region, a different model was sought to explain this feature in the magnetometry data. It is shown that a change to the paramagnetic properties of the Mn A-site ions could also cause a downturn in the inverse

susceptibility.

Nevertheless, given that there has not yet been any other observation of an antiferromagnetic Griffith's phase, and as no rigorous theoretical work has been performed to suggest what the change to the susceptibility may look like in the presence of antiferromagnetic clusters, it is hard to confirm what the anomaly in the inverse susceptibility corresponds to. A review of the literature on the Griffiths phases show that in other systems where the predominant interactions are antiferromagnetic, the anomaly in the susceptibility is still attributed to ferromagnetic clusters [117][124] with no further experimental evidence to corroborate this. This supports a picture in which the drop in the inverse susceptibility may be suggestive of a Griffiths phase, but not ferromagnetic clusters. However further theoretical work would need to be performed to confirm this.

Chapter 8

Conclusions

To conclude, the body of work presented in this thesis represents a comprehensive study of the magnetic structures of the columnar ordered quadruple perovskite manganites. An analysis of the proposed charge and orbital order establishes four primary superexchange interactions that are relevant to the magnetic ordering in these systems, as follows. Firstly there are eight nearest neighbour symmetry equivalent A-B exchange interactions for a given A site ion that imposes an effective FM B-B exchange in the Mn B-site layers. Secondly there are antiferromagnetic B-B exchange interactions that are mediated between half occupied t_{2g} orbitals of the Mn B-site ions via $p\sigma$ superexchange, which is in direct competition with the effective FM B-B exchange interactions. The exchange mediated via half filled and empty e_g orbitals between nearest neighbour Mn B-site ions that are separated along c imposes ferromagnetic exchange between the Mn B-site ab layers. Finally the $a^+a^+c^-$ octahedral tilting breaks the inversion symmetry between Mn B-site ions, allowing for finite DM exchange interactions that can stabilise a canted antiferromagnetic Mn B-site magnetic structure.

Four distinct regions of the magnetic phase diagram of these family of manganite perovskites has been explored by performing neutron powder diffraction experiments; a collinear ferrimagnetic phase, a Γ -point canted ferrimagnetic phase, a Z-point canted ferrimagnetic phase, and a magnetic phase characterised by well correlated collinear ferrimagnetic order punctuated by randomly dispersed clusters of antiferromagnetic order. In Chapter 4 it was shown that $\text{Tm}_2\text{MnMnMn}_4\text{O}_{12}$ adopts a collinear ferrimagnetic

structure with moments aligned along the c axis below 74 K, as favoured by effective ferromagnetic B-B exchange. In Chapter 5, it is shown that the replacement of Cu^{2+} for Mn^{3+} on the A" site, which has a smaller magnetic moment and therefore reduces the average A-B exchange interactions, thereby reducing the effective FM B-B exchange, gives rise to a canted FIM phase. In Chapter 6, it is shown that the systematic reduction of the average B-B exchange interactions by the replacement of magnetic Mn ions for non-magnetic Ti^{4+} ions in $\text{Sm}_2\text{MnMnMn}_{4-x}\text{Ti}_x\text{O}_{12}$ ($x = 1, x = 2, x = 3$), gives rise to a collinear ferrimagnetic phase, but with significantly reduced moments across all magnetic sublattices, suggesting the presence of spin fluctuations. Finally in Chapter 7 it is shown that 'spin doping', achieved by the replacement of magnetic Mn for non magnetic Y^{3+} , establishes regions in the crystal structure in which the AFM B-B exchange interactions dominate and stabilise short range antiferromagnetic clusters.

Rare earth magnetism has a significant role in determining the magnetisation direction of the observed magnetic structures, and can drive or suppress spin reorientation phase transitions in these systems. In $\text{Tm}_2\text{MnMnMn}_4\text{O}_{12}$, the Mn moments flop through a spin reorientation transition below 28 K, retaining the higher temperature collinear ferrimagnetic structure but with moments aligned along the b axis, and with a finite moment developing on both Tm sublattices aligned antiparallel to the net Mn magnetisation. Point charge calculations show that the Tm1 and Tm2 sublattices can adopt a polarised magnetic moment lying within the ab -plane, induced by a uniaxial f - d exchange field created by the ordered Mn B site sublattice. The competition between the magnetic anisotropy of the Tm2 ions and JT active Mn^{3+} ions drives the spin reorientation transition at low temperature. In $\text{Dy}_2\text{CuMnMn}_4\text{O}_{12}$ the Dy^{3+} ions are shown to have a large g-tensor anisotropy imposing $m||c$ in the FI and CFI phases. A spin reorientation phase transition is observed at T_2 , and is driven by the competition between the DM anisotropy and the Ising like g-tensor anisotropy of the Dy^{3+} ions. At T_3 the spin reorientation phase transition that is observed in the related compound $\text{Y}_2\text{CuMnMn}_4\text{O}_{12}$ is suppressed owing to the large g-tensor anisotropy of the Dy^{3+} ions. The absence of spin-reorientation phase transitions in the $\text{Sm}_2\text{MnMnMn}_{4-x}\text{Ti}_x\text{O}_{12}$ compounds, which might be expected to occur due to the competition between the ab -plane Sm^{3+} anisotropy and the JT active Mn^{3+} weak easy axis anisotropy $||c$, implies significant f - d exchange coupling immediately below T_c .

These columnar ordered quadruple perovskites have the potential to host ultrafast spin reorientation transitions whilst boasting a large $1\mu_B$ moment per TM, making them candidate materials to realise novel spin based technology. However, at present, they can only be synthesised as powders, and the transition temperatures at which they magnetically order is substantially below room temperature, and thus it is not yet possible to utilise the technologically relevant properties of these systems.

We have identified the primary exchange interactions that govern the magnetic order in these systems, and shown that competing exchange and disorder can tune these manganites into different magnetically ordered phases. We have demonstrated an alternative mechanism for driving spin reorientation phase transitions in complex oxides, that originate in spin canting instabilities. This has the potential to substantially broaden the range of strongly correlated electron systems in which magnetisation switching via spin reorientation might occur. In comparison to the simple AMnO_3 simple perovskite manganites, the inclusion of transition metal ions onto the A-sites establishes a new 3-dimensional network of A-B exchange interactions that can percolate long range magnetic order in the columnar ordered quadruple perovskite manganites as demonstrated for $\text{Sm}_2\text{MnMnMn}_{4-x}\text{Ti}_x\text{O}_{12}$. Antisite cation disorder on the A'-sites in $[\text{Y}_{2-x}\text{Mn}_x]\text{MnMnMn}_4\text{O}_{12}$ creates an inhomogeneous spin texture, which establishes a Griffiths phase and causes these systems to separate into two distinct magnetic phases below T_c . Taken together, these results demonstrate the significance of A-B exchange interactions in dominating the physics of the columnar ordered quadruple perovskites. This is in contrast to the simple AMnO_3 and $\text{AA}'_3\text{Mn}_4\text{O}_{12}$ manganites, where B-B exchange determines the magnetic ordering of these systems. Demonstrating that the characteristic experimental signature of a Griffiths phase, a sharp down turn in the inverse susceptibility with a susceptibility exponent less than unity, cannot be explained by the formation of ferromagnetic clusters, but instead can occur due to a change in the paramagnetic properties of the A-site ions could have important consequences for the interpretation of magnetic order in other systems that feature this anomaly in the susceptibility, and which is often assumed to arise from the formation of short range ferromagnetic clusters.

While our studies have gained significant insights into the magnetism of the columnar ordered quadruple perovskites, there are also many questions that have been raised, and which only further experimental

and or theoretical studies could answer. Firstly our predictions regarding the nature of the different exchange interactions has not been experimentally verified, and it would therefore be of interest to perform inelastic scattering experiments to determine the exact magnitude and sign of the A-B, B-B and A-A exchange interactions. Likewise our point charge calculations only provide an estimate for the crystal electric field splitting of the rare earth ions, and inelastic scattering measurements could be used to experimentally verify the validity of the point charge calculations in determining the magnetic anisotropy of these systems. The sensitivity of our neutron powder diffraction measurements would not be able to deduce the presence of small canting angles of less than $\sim 0.3^\circ$, and which are predicted to arise from DM interactions. Determining whether there is a small degree of canting in what is nominally the collinear ferrimagnetic phase would also be of interest to investigate.

In all systems, the magnetic moments that are refined across all magnetically ordered sublattices are reduced in comparison to their expected ground state theoretical moment, which is particularly pronounced in the $\text{Sm}_2\text{MnMnMn}_{4-x}\text{Ti}_x\text{O}_{12}$ systems. Given that these systems are insulating one would expect them to be close to adopting their full ground state theoretical moment at the lowest measured temperatures. As the majority of these systems have well correlated magnetic phases, it is feasible that the reduced moment measured through diffraction is due to the presence of spin fluctuations. The reduction in the ground state moment is particularly striking for the rare earth ions. Dy^{3+} has the potential to host a ground state moment of $\sim 10\mu_B$, which was significantly lower than the refined moment of $3.5\mu_B$. It may therefore be of interest to perform inelastic scattering measurements to probe the spin excitations within these systems.

In the $R_2\text{CuMnMnMn}_4\text{O}_{12}$ systems the microscopic origin of the collinear to canted phase transitions is unclear, as is the development of Z-point canting at low temperature. Signs of a jump in the lattice parameters in the low temperature phase transition of the $\text{Y}_2\text{CuMnMn}_4\text{O}_{12}$ system, indicates a magnetostructural coupling that may be relevant in the development of the Z-point canting at low temperature. The recovery of the Mn2 and Mn3 moments in $\text{Y}_2\text{CuMnMn}_4\text{O}_{12}$ below T_3 , may indicate a reduction to the spin fluctuations, as this could increase the moment measured through diffraction, and which may be driven by the softening of a low energy magnon mode. All of the above would be interesting to

investigate further.

The A" site ions develop a moment oriented parallel or antiparallel to the B-site F_i modes, depending on the local A-B exchange interactions. For instance in $\text{Tm}_2\text{MnMnMn}_4\text{O}_{12}$ and $\text{Y}_2\text{MnMnMn}_4\text{O}_{12}$ the A" site moments are antiparallel to the B-site F_i modes, while in the $\text{Sm}_2\text{MnMnMn}_{4-x}\text{Ti}_x\text{O}_{12}$ compounds the A" site moments are parallel to the B-site F_i modes. In the $R_2\text{CuMnMnMn}_4\text{O}_{12}$ systems, the A" sites have an average net moment of ~ 0 , which could occur if the minority Mn^{3+} and majority Cu^{2+} ions, randomly located on the A" site, have antiparallel moments. An analysis of the A-B exchange interactions in the context of the Goodenough Kanamori Anderson rules shows that there are multiple exchange interactions present (Sec. 3.2.1). It would be interesting to know if there is a dominant A-B exchange pathway that changes the moment orientation of the ions on A" sites with respect to the B-site moments.

Finally, theoretical studies to map out the full magnetic phase diagram of these systems maybe of interest given the sensitivity of the magnetic phases to small perturbations to the system, such as cation disorder. For instance given that the FIM phase is thought to be stabilised in the presence of cation disorder, perhaps a well correlated AFM phase can be stabilised in the absence of any cation disorder, i.e. in the ideal stoichiometric samples.

Chapter 9

Appendix

The Appendix is organised as follows. The Curie law and Curie-Weiss law is given in Sec. 9.1. Details of the symmetry adapted modes and structure factor calculations are listed in Sec. 9.2. The refined structure parameters for all $A'_2A''A'''B_4O_{12}$ studied in this thesis are listed in Section 9.3.

9.1 Curie and Curie-Weiss law

In this section the magnetisation of a paramagnetic system is given, Eqn. 9.1. M is the magnetisation, N is the number of magnetic ions per unit volume, g_J is the Landé g -value, defined by Eqn. 9.3, μ_B is the Bohr magneton, μ_0 is the permeability of free space, $B_J(x)$ is the Brillouin function, defined by Eqn. 9.4 and given in terms of x (Eqn. 9.2), B is the applied magnetic field, T is the temperature, k_B is the Boltzmann constant and J is the total angular momentum. Extensive derivations of these equations are given in numerous textbooks, see for instance Ref. [12].

$$M = Ng_J\mu_B JB_J(x) \quad (9.1)$$

$$x = \frac{g_J\mu_B JB}{k_B T} \quad (9.2)$$

$$g_J = \frac{3}{2} + \frac{S(S+1) - L(L+1)}{2J(J+1)} \quad (9.3)$$

$$B_J(x) = \frac{2J+1}{2J} \coth\left(\frac{2J+1}{2J}x\right) - \frac{1}{2J} \coth\left(\frac{1}{2J}x\right) \quad (9.4)$$

In the limit that B tends to zero, so that M can be approximated to be proportional to H (Fig. 1.1) it can be shown that the susceptibility can be written as follows (see Ref. [12] for a derivation), which is Curie's law.

$$\chi = \frac{N\mu_0\mu_B^2 g_J^2 J(J+1)}{3k_B T} = \frac{N\mu_0\mu_{eff}^2}{3k_B T} \quad (9.5)$$

The effective moment, defined in Eqn. 9.6, can then be obtained by fitting the temperature dependence

of the inverse paramagnetic susceptibility. The effective moment provides a temperature and field independent measure of the magnetic properties of a system.

$$\mu_{eff} = gJ\sqrt{J(J+1)}\mu_B \quad (9.6)$$

The Curie-Weiss law, which describes the paramagnetic susceptibility for systems that develop magnetic order, is given by Eqn. 9.7, see Ref. [12] for a derivation, where T_C is the Weiss constant.

$$\chi = \frac{N\mu_0\mu_{eff}^2}{3k_B(T - T_C)} \quad (9.7)$$

9.2 Symmetry adapted magnetic modes and structure factor calculations

In this section the symmetry adapted B-site magnetic modes, F_i , A_i , X_i and Y_i are defined in Table 9.1, and the A-site magnetic modes, F_i and A_i , are defined in Table 9.2.

Table 9.1: Magnetic modes that span the symmetry equivalent ions in a given Mn B site ab layer where z can take values of 0 or 1/2. The subscript i denotes the direction of the moment component.

Frac. coords.	F_i	A_i	X_i	Y_i
0.0, 0.0, z	+	+	+	+
0.5, 0.0, z	+	-	-	+
0.0, 0.5, z	+	-	+	-
0.5, 0.5, z	+	+	-	-

Table 9.2: Magnetic modes that span the symmetry equivalent A' -sites that are related by a 4_2 screw, where z can take values of $1/4$ or $3/4$. The subscript i denotes the direction of the moment component.

Frac. coords.	F_i	A_i
A' sites		
0.25, 0.25, z	+	+
0.75, 0.75, $-z$	+	-
A'' and A''' sites		
0.75, 0.25, z	+	+
0.25, 0.75, $-z$	+	-

The structure factors for each of the symmetry adapted B-site ion basis modes was calculated using Eqn. 2.5, and is shown below. The corresponding reflection conditions is given in Table 9.3.

B-sites

F_i

$$SF_{(h,k,l)} = f_m(1 + \exp^{\pi i h} + \exp^{\pi i k} + \exp^{\pi i(h+k)}) \quad (9.8)$$

A_i

$$SF_{(h,k,l)} = f_m(1 - \exp^{\pi i h} - \exp^{\pi i k} + \exp^{\pi i(h+k)}) \quad (9.9)$$

X_i

$$SF_{(h,k,l)} = f_m(1 - \exp^{\pi i h} + \exp^{\pi i k} - \exp^{\pi i(h+k)}) \quad (9.10)$$

Y_i

$$SF_{(h,k,l)} = f_m(1 + \exp^{\pi i h} - \exp^{\pi i k} - \exp^{\pi i(h+k)}) \quad (9.11)$$

Structure factor calculations for two B-site magnetic modes that describe the magnetic structure of the B-sites on the $z = 0$ layer (the first mode listed) and the $z = 1/2$ layer (the second mode listed) is shown below. The corresponding reflection conditions are given in Table 7.1 of Chapter 7.

Table 9.3: Reflection conditions for the B-site F_i , A_i , X_i , Y_i symmetry adapted basis modes as determined by structure factor calculations.

Mode	F_i	A_i	X_i	Y_i
h	$2n$	$2n + 1$	$2n + 1$	$2n$
k	$2n$	$2n + 1$	$2n$	$2n + 1$

$F_i F_i$

$$SF_{(h,k,l)} = f_m(1 + \exp^{\pi i h} + \exp^{\pi i k} + \exp^{\pi i(h+k)} + \exp^{\pi i l} + \exp^{\pi i(h+l)} + \exp^{\pi i(k+l)} + \exp^{\pi i(h+k+l)}) \quad (9.12)$$

$F_i F_{\bar{i}}$

$$SF_{(h,k,l)} = f_m(1 + \exp^{\pi i h} + \exp^{\pi i k} + \exp^{\pi i(h+k)} - \exp^{\pi i l} - \exp^{\pi i(h+l)} - \exp^{\pi i(k+l)} - \exp^{\pi i(h+k+l)}) \quad (9.13)$$

$A_i A_i$

$$SF_{(h,k,l)} = f_m(1 - \exp^{\pi i h} - \exp^{\pi i k} + \exp^{\pi i(h+k)} + \exp^{\pi i l} - \exp^{\pi i(h+l)} - \exp^{\pi i(k+l)} + \exp^{\pi i(h+k+l)}) \quad (9.14)$$

$A_i A_{\bar{i}}$

$$SF_{(h,k,l)} = f_m(1 - \exp^{\pi i h} - \exp^{\pi i k} + \exp^{\pi i(h+k)} - \exp^{\pi i l} + \exp^{\pi i(h+l)} + \exp^{\pi i(k+l)} - \exp^{\pi i(h+k+l)}) \quad (9.15)$$

$X_i X_i$

$$SF_{(h,k,l)} = f_m(1 - \exp^{\pi i h} + \exp^{\pi i k} - \exp^{\pi i(h+k)} + \exp^{\pi i l} - \exp^{\pi i(h+l)} + \exp^{\pi i(k+l)} - \exp^{\pi i(h+k+l)}) \quad (9.16)$$

$$\underline{X_i X_{\bar{i}}}$$

$$SF_{(h,k,l)} = f_m(1 - \exp^{\pi i h} + \exp^{\pi i k} - \exp^{\pi i(h+k)} - \exp^{\pi i l} + \exp^{\pi i(h+l)} - \exp^{\pi i(k+l)} + \exp^{\pi i(h+k+l)}) \quad (9.17)$$

$$\underline{Y_i Y_{\bar{i}}}$$

$$SF_{(h,k,l)} = f_m(1 + \exp^{\pi i h} - \exp^{\pi i k} - \exp^{\pi i(h+k)} + \exp^{\pi i l} + \exp^{\pi i(h+l)} - \exp^{\pi i(k+l)} - \exp^{\pi i(h+k+l)}) \quad (9.18)$$

$$\underline{Y_i Y_{\bar{i}}}$$

$$SF_{(h,k,l)} = f_m(1 + \exp^{\pi i h} - \exp^{\pi i k} - \exp^{\pi i(h+k)} - \exp^{\pi i l} - \exp^{\pi i(h+l)} + \exp^{\pi i(k+l)} + \exp^{\pi i(h+k+l)}) \quad (9.19)$$

A-sites

To simplify the structure factor calculations of the A-sites, they are approximated to have a z fractional coordinates of exactly 1/4 or 3/4. The reflection conditions for the A-site F_i and A_i symmetry adapted basis modes are given in Table 9.4.

Table 9.4: Reflection conditions for the A" and A'" F_i and A_i magnetic modes as determined by structure factor calculations.

Mode	F_i	A_i
$h + k + l$	$2n$	$2n + 1$

In the absence of any Γ -point B-site canting the scattering on the (101) and (011) reflections originate from A-site magnetic modes only, and hence to determine the contributions of the different A-sites to each reflection in the collinear magnetic phases, l was set to 1. The structure factor calculations for the A-site scattering to the (101) and (011) reflections is given by Eqn. 9.20 and Eqn. 9.21 respectively. This was used in the analysis of $R_2\text{CuMnMn}_4\text{O}_{12}$, and hence the magnetic form factors are labelled

accordingly by the atomic species present in $R_2\text{CuMnMn}_4\text{O}_{12}$, i.e the magnetic form factor of the Mn2 ion is represented by ‘Mn₂’

$$|SF_{(0,1,1)}|^2 = 4(R_2 - R_1)^2 + 4(\text{Mn}_2 - \text{Cu}_1)^2 + 8(R_2 - R_1)(\text{Mn}_2 - \text{Cu}_1) \quad (9.20)$$

$$|SF_{(1,0,1)}|^2 = 4(R_2 - R_1)^2 + 4(\text{Mn}_2 - \text{Cu}_1)^2 - 8(R_2 - R_1)(\text{Mn}_2 - \text{Cu}_1) \quad (9.21)$$

9.3 Crystal structure parameters

9.3.1 $\text{Tm}_2\text{MnMnMn}_4\text{O}_{12}$

The crystal structural parameters of $\text{Tm}_2\text{MnMnMn}_4\text{O}_{12}$ refined at 85 K against neutron powder diffraction data ($R = 3.32\%$, $wR = 2.68\%$, $R_{\text{Bragg}} = 4.57\%$) are tabulated in Table 9.5. The cation bond valence sums (BVS), also listed in Table 9.5, match well with the cited oxidation states [35]. To determine the antisite cation disorder, which is common in these systems, each of the cations present in the sample was systematically substituted for the primary cation expected to occupy the site, and the model was refined. The refinement was constrained such that the total occupation of each site was not allowed to exceed the expected occupation (as determined by the Wyckoff position). The Tm1 site was found to be occupied by 84.4(4)% Tm and 15.6(4)% Mn and the Tm2 site was found to be occupied by 85.2(4)% Tm and 14.8(4)% Mn. All other sites were found to fully occupied by the nominal ions on that site. The occupations were not expected to change as a function of temperature, and thus the occupations were only refined in the paramagnetic phase.

The crystal structural parameters of $\text{Tm}_2\text{MnMnMn}_4\text{O}_{12}$ refined at 40 K against neutron powder diffraction data ($R = 3.32\%$, $wR = 2.68\%$, $R_{\text{Bragg}} = 4.57\%$) are tabulated in Table 9.6.

The crystal structural parameters of $\text{Tm}_2\text{MnMnMn}_4\text{O}_{12}$ refined at 1.5 K against neutron powder diffraction data ($R = 3.32\%$, $wR = 2.68\%$, $R_{\text{Bragg}} = 4.57\%$) are tabulated in Table 9.7.

Table 9.5: Crystal structure parameters of $\text{Tm}_2\text{MnMnMn}_4\text{O}_{12}$ ($Z = 4$, space group $Pmmn$) refined at 85 K. The lattice parameters were determined to be $a = 7.22944(7)$ Å, $b = 7.41079(7)$ Å, and $c = 7.72580(9)$ Å. Excellent reliability parameters of $R = 3.32\%$, $wR = 2.68\%$, $R_{\text{Bragg}} = 4.57\%$ were achieved in the refinement. Bond valence sums (BVS) were calculated using the bond valence parameters, $R_0(\text{Mn}^{2+}) = 1.79(5)$, $R_0(\text{Mn}^{3+}) = 1.76(5)$ and $B = 0.37$ [125].

Atom	Site	Sym.	x	y	z	U_{iso} (Å ²)	B.v.s. ($ e $)	Occ.
Tm1	2a	$mm2$	0.25	0.25	0.7844(5)	0.0082(7)	2.98(5)	
Tm2	2a	$mm2$	0.25	0.25	0.2859(5)	0.0082(7)	2.94(5)	
Mn1	2b	$mm2$	0.75	0.25	0.7226(7)	0.0098(9)	2.72(6)	
Mn2	2b	$mm2$	0.75	0.25	0.2375(7)	0.0098(9)	1.97(6)	
Mn3	4c	$\bar{1}$	0	0	0	0.008(1)	3.21(9)	
Mn4	4d	$\bar{1}$	0	0	0.5	0.006(1)	3.7(1)	
O1	8g	1	0.4355(2)	-0.0681(2)	0.2671(2)	0.0131(4)	-	
O2	4f	$.m.$	0.0581(3)	0.25	0.0450(3)	0.0129(6)	-	
O3	4e	$m..$	0.25	0.5281(3)	0.9202(3)	0.0087(6)	-	
O4	4f	$.m.$	0.5402(3)	0.25	0.4177(3)	0.0147(7)	-	
O5	4e	$m..$	0.25	0.4308(3)	0.5409(3)	0.0110(6)	-	

The cation-anion bond lengths for the A-site cations is given in Table 9.8 and selected cation-anion bond lengths and cation-anion-cation bond angles for the B-site cations in Table 9.9.

Table 9.6: Crystal structure parameters of $\text{Tm}_2\text{MnMnMn}_4\text{O}_{12}$ ($Z = 4$, space group $Pmmn$) refined at 40 K. The lattice parameters were determined to be $a = 7.23081(8)$ Å, $b = 7.41094(8)$ Å, and $c = 7.7238(1)$ Å. Excellent reliability parameters of $R = 3.90\%$, $wR = 3.09\%$, $R_{\text{Bragg}} = 4.90\%$ were achieved in the refinement. Bond valence sums (BVS) were calculated using the bond valence parameters, $R_0(\text{Mn}^{2+}) = 1.79(5)$, $R_0(\text{Mn}^{3+}) = 1.76(5)$ and $B = 0.37$ [125].

Atom	Site	Sym.	x	y	z	$U_{\text{iso}} (\text{\AA}^2)$	B.v.s. ($ e $)
Tm1	2a	$mm2$	0.25	0.25	0.7843(5)	0.0061(8)	2.96(5)
Tm2	2a	$mm2$	0.25	0.25	0.2867(5)	0.0061(8)	2.94(5)
Mn1	2b	$mm2$	0.75	0.25	0.7222(8)	0.008(1)	2.71(6)
Mn2	2b	$mm2$	0.75	0.25	0.2367(8)	0.008(1)	1.98(6)
Mn3	4c	$\bar{1}$	0	0	0	0.007(1)	3.21(9)
Mn4	4d	$\bar{1}$	0	0	0.5	0.006(1)	3.7(1)
O1	8g	1	0.4357(3)	-0.0682(2)	0.2667(2)	0.0100(5)	-
O2	4f	$.m.$	0.0575(4)	0.25	0.0452(3)	0.0102(6)	-
O3	4e	$m..$	0.25	0.5286(3)	0.9200(4)	0.0070(7)	-
O4	4f	$.m.$	0.5409(4)	0.25	0.4183(3)	0.0113(7)	-
O5	4e	$m..$	0.25	0.4308(3)	0.5400(3)	0.0089(7)	-

Table 9.7: Crystal structure parameters of $\text{Tm}_2\text{MnMnMn}_4\text{O}_{12}$ ($Z = 4$, space group $Pm\bar{m}n$) refined at 1.5 K. The lattice parameters were determined to be $a = 7.22976(8)$ Å, $b = 7.41107(8)$ Å, and $c = 7.72381(9)$ Å. Excellent reliability parameters of $R = 3.82\%$, $wR = 3.53\%$, $R_{\text{Bragg}} = 5.37\%$ were achieved in the refinement. Bond valence sums (BVS) were calculated using the bond valence parameters, $R_0(\text{Mn}^{2+}) = 1.79(5)$, $R_0(\text{Mn}^{3+}) = 1.76(5)$ and $B = 0.37$ [125].

Atom	Site	Sym.	x	y	z	U_{iso} (Å ²)	B.v.s. ($ e $)
Tm1	2a	$mm2$	0.25	0.25	0.7850(5)	0.0058(8)	2.96(5)
Tm2	2a	$mm2$	0.25	0.25	0.2875(4)	0.0058(8)	2.94(5)
Mn1	2b	$mm2$	0.75	0.25	0.7239(7)	0.002(1)	2.88(6)
Mn2	2b	$mm2$	0.75	0.25	0.2372(8)	0.002(1)	2.26(6)
Mn3	4c	$\bar{1}$	0	0	0	0.010(1)	3.21(9)
Mn4	4d	$\bar{1}$	0	0	0.5	0.009(1)	3.7(1)
O1	8g	1	0.4364(3)	-0.0688(2)	0.2669(3)	0.0106(5)	-
O2	4f	$m.$	0.0576(4)	0.25	0.0435(4)	0.0106(7)	-
O3	4e	$m..$	0.25	0.5279(3)	0.9208(4)	0.0068(8)	-
O4	4f	$m.$	0.5399(4)	0.25	0.4200(4)	0.0125(8)	-
O5	4e	$m..$	0.25	0.4306(3)	0.5399(4)	0.0103(8)	-

Table 9.8: Bond lengths for the A sites refined at 85K, for $\text{Tm}_2\text{MnMnMn}_4\text{O}_{12}$ in the $Pm\bar{m}n$ space group.

Tm1-O1 ($\times 4$)	2.672(2) Å	Tm2-O1 ($\times 4$)	2.716(2) Å	Mn1-O1 ($\times 4$)	1.903(2) Å
Tm1-O2 ($\times 2$)	2.445(4) Å	Tm2-O2 ($\times 2$)	2.320(4) Å		
Tm1-O3 ($\times 2$)	2.313(3) Å	Tm2-O4 ($\times 2$)	2.333(3) Å	Mn2-O2 ($\times 2$)	2.678(4) Å
Tm1-O5 ($\times 2$)	2.310(4) Å	Tm2-O5 ($\times 2$)	2.381(4) Å	Mn2-O4 ($\times 2$)	2.058(5) Å

Table 9.9: Bond lengths and selected bond angles for the B-sites refined at 85K, for $\text{Tm}_2\text{MnMnMn}_4\text{O}_{12}$ in the $Pm\bar{m}n$ space group.

Mn3-O1 ($\times 2$)	2.1748(2) Å	Mn4-O1 ($\times 2$)	1.9259(2) Å	Mn3-O2-Mn3 ($\times 2$)	147.1(1)°
Mn3-O2 ($\times 2$)	1.9316(7) Å	Mn4-O4 ($\times 2$)	1.9803(9) Å	Mn3-O3-Mn3 ($\times 2$)	140.4(1)°
Mn3-O3 ($\times 2$)	1.9209(8) Å	Mn4-O5 ($\times 2$)	1.9052(8) Å	Mn3-O1-Mn4 ($\times 2$)	140.7(8)°
				Mn4-O4-Mn4 ($\times 2$)	138.6(1)°
				Mn4-O5-Mn4 ($\times 2$)	143.1(1)°

9.3.2 $R_2\text{CuMnMn}_4\text{O}_{12}$

The crystal structural parameters of $\text{Y}_2\text{CuMnMn}_4\text{O}_{12}$ (YCMO) refined at 200 K, 140 K, 40 K and 1.5 K against neutron powder diffraction data are tabulated in Tables 9.10, 9.11, 9.12 and 9.13 respectively. The cation bond valence sums (BVS) also listed match well with the cited oxidation states [62]. The refined cation disorder can be summarised by the chemical formula $\text{Y}_2[\text{Mn}_{0.204(4)}\text{Cu}_{0.796(4)}][\text{Mn}_{0.736(4)}\text{Y}_{0.264(4)}]\text{Mn}_4\text{O}_{12}$. Note that this formula does not charge balance using integer oxidation states (cited in the main text), but would if the B site Mn4 ions had a fractional oxidation state (as seen in $\text{Tm}_2\text{MnMnMn}_4\text{O}_{12}$ [35]) of +3.77, consistent with the calculated BVS and corresponding to a 77% occupation of Mn^{4+} and 23% occupation of Mn^{3+} on the B-sites. The occupations were not expected to change as a function of temperature, and thus the occupations were only refined in the paramagnetic phase.

Table 9.10: Crystal structure parameters of $\text{Y}_2\text{CuMnMn}_4\text{O}_{12}$ ($Z = 4$, space group $Pmmn$) refined at 200 K. The lattice parameters were determined to be $a = 7.27072(9)$ Å, $b = 7.3192(1)$ Å, and $c = 7.79621(9)$ Å. Excellent reliability parameters of $R = 3.96\%$, $wR = 4.49\%$, $R_{\text{Bragg}} = 4.52\%$ were achieved in the refinement. Bond valence sums (BVS) were calculated using the bond valence parameters, $R_0(\text{Y}^{3+}) = 2.01(1)$, $R_0(\text{Cu}^{2+}) = 1.68(1)$, $R_0(\text{Mn}^{2+}) = 1.79(1)$, $R_0(\text{Mn}^{3+}) = 1.76(1)$, $R_0(\text{Mn}^{4+}) = 1.75(1)$, $B = 0.37$ [125].

Atom	Site	Sym.	x	y	z	$U_{\text{iso}} (\text{\AA}^2)$	B.v.s. ($ e $)
Y1	$2a$	$mm2$	0.25	0.25	0.7802(6)	0.015(1)	3.0(1)
Y2	$2a$	$mm2$	0.25	0.25	0.2794(6)	0.009(1)	2.97(7)
Cu1	$2b$	$mm2$	0.75	0.25	0.7313(7)	0.004(1)	2.02(2)
Mn2	$2b$	$mm2$	0.75	0.25	0.286(4)	0.004(1)	2.2(4)
Mn3	$4c$	$\bar{1}$	0	0	0	0.011(2)	3.3(1)
Mn4	$4d$	$\bar{1}$	0	0	0.5	0.0003(2)	3.7(1)
O1	$8g$	1	0.4382(2)	-0.0636(2)	0.2676(3)	0.0062(6)	-
O2	$4f$	$.m.$	0.0586(4)	0.25	0.0396(4)	0.0075(9)	-
O3	$4e$	$m..$	0.25	0.5338(4)	0.9225(4)	0.0029(9)	-
O4	$4f$	$.m.$	0.5352(4)	0.25	0.4167(4)	0.005(1)	-
O5	$4e$	$m..$	0.25	0.4366(4)	0.5418(4)	0.0079(9)	-

Table 9.11: Crystal structure parameters of $\text{Y}_2\text{CuMnMn}_4\text{O}_{12}$ ($Z = 4$, space group $Pmmn$) refined at 140 K. The lattice parameters were determined to be $a = 7.27071(8)$ Å, $b = 7.31603(9)$ Å, and $c = 7.79049(8)$ Å. Excellent reliability parameters of $R = 4.38\%$, $wR = 4.42\%$, $R_{\text{Bragg}} = 4.56\%$ were achieved in the refinement. Bond valence sums (BVS) were calculated using the bond valence parameters, $R_0(\text{Y}^{3+}) = 2.01(1)$, $R_0(\text{Cu}^{2+}) = 1.68(1)$, $R_0(\text{Mn}^{2+}) = 1.79(1)$, $R_0(\text{Mn}^{3+}) = 1.76(1)$, $R_0(\text{Mn}^{4+}) = 1.75(1)$, $B = 0.37$ [125].

Atom	Site	Sym.	x	y	z	U_{iso} (Å ²)	B.v.s. ($ e $)
Y1	2a	$mm2$	0.25	0.25	0.7787(6)	0.014(1)	3.0(1)
Y2	2a	$mm2$	0.25	0.25	0.2806(6)	0.010(1)	2.9(1)
Cu1	2b	$mm2$	0.75	0.25	0.7315(8)	0.004(1)	2.0(1)
Mn2	2b	$mm2$	0.75	0.25	0.286(4)	0.004(1)	2.2(7)
Mn3	4c	$\bar{1}$	0	0	0	0.0070(6)	3.3(2)
Mn4	4d	$\bar{1}$	0	0	0.5	0.0070(6)	3.7(2)
O1	8g	1	0.4386(3)	-0.0642(3)	0.2668(3)	0.0079(5)	-
O2	4f	$.m.$	0.0581(4)	0.25	0.0390(4)	0.0078(9)	-
O3	4e	$m..$	0.25	0.5339(4)	0.9231(4)	0.0046(8)	-
O4	4f	$.m.$	0.5357(4)	0.25	0.4168(4)	0.0061(1)	-
O5	4e	$m..$	0.25	0.4365(4)	0.5422(4)	0.0095(9)	-

Table 9.12: Crystal structure parameters of $\text{Y}_2\text{CuMnMn}_4\text{O}_{12}$ ($Z = 4$, space group $Pmmn$) refined at 40 K. The lattice parameters were determined to be $a = 7.2724(1)$ Å, $b = 7.3132(1)$ Å, and $c = 7.7852(1)$ Å. Excellent reliability parameters of $R = 4.75\%$, $wR = 4.68\%$, $R_{\text{Bragg}} = 4.52\%$ were achieved in the refinement. Bond valence sums (BVS) were calculated using the bond valence parameters, $R_0(\text{Y}^{3+}) = 2.01(1)$, $R_0(\text{Cu}^{2+}) = 1.68(1)$, $R_0(\text{Mn}^{2+}) = 1.79(1)$, $R_0(\text{Mn}^{3+}) = 1.76(1)$, $R_0(\text{Mn}^{4+}) = 1.75(1)$, $B = 0.37$ [125].

Atom	Site	Sym.	x	y	z	U_{iso} (Å ²)	B.v.s. ($ e $)
Y1	2a	$mm2$	0.25	0.25	0.7802(6)	0.015(1)	3.0(4)
Y2	2a	$mm2$	0.25	0.25	0.2794(6)	0.009(1)	3.0(1)
Cu1	2b	$mm2$	0.75	0.25	0.7313(7)	0.004(1)	2.0(1)
Mn2	2b	$mm2$	0.75	0.25	0.286(4)	0.004(1)	2.1(4)
Mn3	4c	$\bar{1}$	0	0	0	0.011(2)	3.3(2)
Mn4	4d	$\bar{1}$	0	0	0.5	0.0003(2)	3.7(3)
O1	8g	1	0.4382(2)	-0.0636(2)	0.2676(3)	0.0062(6)	-
O2	4f	$.m.$	0.0586(4)	0.25	0.0396(4)	0.0075(9)	-
O3	4e	$m..$	0.25	0.5338(4)	0.9225(4)	0.0029(9)	-
O4	4f	$.m.$	0.5352(4)	0.25	0.4167(4)	0.005(1)	-
O5	4e	$m..$	0.25	0.4366(4)	0.5418(4)	0.0079(9)	-

Table 9.13: Crystal structure parameters of $\text{Y}_2\text{CuMnMn}_4\text{O}_{12}$ ($Z = 4$, space group $Pmmn$) refined at 1.5 K. The lattice parameters were determined to be $a = 7.2720(1)$ Å, $b = 7.3118(1)$ Å, and $c = 7.7853(9)$ Å. Excellent reliability parameters of $R = 5.30\%$, $wR = 5.03\%$, $R_{\text{Bragg}} = 5.31\%$ were achieved in the refinement. Bond valence sums (BVS) were calculated using the bond valence parameters, $R_0(\text{Y}^{3+}) = 2.01(1)$, $R_0(\text{Cu}^{2+}) = 1.68(1)$, $R_0(\text{Mn}^{2+}) = 1.79(1)$, $R_0(\text{Mn}^{3+}) = 1.76(1)$, $R_0(\text{Mn}^{4+}) = 1.75(1)$, $B = 0.37$ [125].

Atom	Site	Sym.	x	y	z	U_{iso} (Å ²)	B.v.s. ($ e $)
Y1	2a	$mm2$	0.25	0.25	0.7791(7)	0.012(1)	3.1(1)
Y2	2a	$mm2$	0.25	0.25	0.28912(7)	0.010(1)	3.0(1)
Cu1	2b	$mm2$	0.75	0.25	0.7328(9)	0.004(1)	2.0(1)
Mn2	2b	$mm2$	0.75	0.25	0.281(4)	0.004(1)	2.1(3)
Mn3	4c	$\bar{1}$	0	0	0	0.005(5)	3.3(2)
Mn4	4d	$\bar{1}$	0	0	0.5	0.005(5)	3.7(3)
O1	8g	1	0.4394(3)	-0.0648(3)	0.2663(3)	0.0063(4)	-
O2	4f	$.m.$	0.0590(5)	0.25	0.0386(5)	0.005(1)	-
O3	4e	$m..$	0.25	0.5331(4)	0.9238(5)	0.0040(9)	-
O4	4f	$.m.$	0.5352(5)	0.25	0.4162(5)	0.004(1)	-
O5	4e	$m..$	0.25	0.4361(5)	0.5423(5)	0.006(1)	-

The tabulated crystal structure parameters of $\text{Dy}_2\text{CuMnMn}_4\text{O}_{12}$ (DCMO) refined at 180 K, 135 K, 50 K and 1.5 K against the neutron powder diffraction data is given in Tables 9.14 9.15, 9.16 and 9.17 respectively. The cation bond valence sums (BVS), also listed, match well with the cited oxidation states [62]. The refined cation disorder can be summarised by the chemical formula $\text{Dy}_2[\text{Mn}_{0.304(4)}\text{Cu}_{0.696(4)}][\text{Mn}_{0.784(4)}\text{Dy}_{0.216(4)}][\text{Mn}_{1.83(2)}\text{Cu}_{0.16(2)}]\text{Mn}_2\text{O}_{12}$. Note that this formula does not charge balance using integer oxidation states (but would if the B site Mn4 ions had a fractional oxidation state (as seen in $\text{Tm}_2\text{MnMnMn}_4\text{O}_{12}$ [35]) of +3.83, consistent with the calculated BVS and would correspond to a 83% occupation of Mn^{4+} and 17% occupation of Mn^{3+} on the B-sites. The U_{iso} of all ions, except O^{2-} , refined with negative values due to correlations with strong absorption from Dy. Even though the negative U_{iso} values are unphysical, they do not alter the results of the magnetic structure refinements.

Table 9.14: Crystal structure parameters of $\text{Dy}_2\text{CuMnMn}_4\text{O}_{12}$ ($Z = 4$, space group $Pmmn$) refined at 180 K. The lattice parameters were determined to be $a = 7.2796(2)$ Å, $b = 7.3486(2)$ Å, and $c = 7.8165(2)$ Å. Excellent reliability parameters of $R = 2.76\%$, $wR = 2.64\%$, $R_{\text{Bragg}} = 4.69\%$ were achieved in the refinement. Bond valence sums (BVS) were calculated using the bond valence parameters, $R_0(\text{Dy}^{3+}) = 2.04(1)$, $R_0(\text{Cu}^{2+}) = 1.68(1)$, $R_0(\text{Mn}^{2+}) = 1.79(1)$, $R_0(\text{Mn}^{3+}) = 1.76(1)$, $R_0(\text{Mn}^{4+}) = 1.75(1)$, $B = 0.37$ [125].

Atom	Site	Sym.	x	y	z	U_{iso} (Å ²)	B.v.s. ($ e $)
Dy1	2a	$mm2$	0.25	0.25	0.7807(7)	-0.0040(9)	3.1(2)
Dy2	2a	$mm2$	0.25	0.25	0.2797(7)	-0.0040(9)	3.0(1)
Cu1	2b	$mm2$	0.75	0.25	0.736(3)	-0.006(6)	2.0(1)
Mn2	2b	$mm2$	0.75	0.25	0.218(1)	-0.01(3)	2.0(8)
Mn3	4c	$\bar{1}$	0	0	0	-0.006(9)	3.2(2)
Mn4	4d	$\bar{1}$	0	0	0.5	-0.007(6)	3.7(3)
O1	8g	1	0.4378(6)	-0.0635(7)	0.2678(8)	0.0002(9)	-
O2	4f	$.m.$	0.0589(9)	0.25	0.041(1)	0.0002(9)	-
O3	4e	$m..$	0.25	0.534(1)	0.921(1)	0.0002(9)	-
O4	4f	$.m.$	0.5392(9)	0.25	0.421(1)	0.0002(9)	-
O5	4e	$m..$	0.25	0.4354(9)	0.542(1)	0.0002(9)	-

Table 9.15: Crystal structure parameters of $\text{Dy}_2\text{CuMnMn}_4\text{O}_{12}$ ($Z = 4$, space group $Pm\bar{m}n$) refined at 135 K. The lattice parameters were determined to be $a = 7.2795(1)$ Å, $b = 7.3460(1)$ Å, and $c = 7.8118(1)$ Å. Excellent reliability parameters of $R = 2.85\%$, $wR = 2.79\%$, $R_{\text{Bragg}} = 5.51\%$ were achieved in the refinement. Bond valence sums (BVS) were calculated using the bond valence parameters, $R_0(\text{Dy}^{3+}) = 2.04(1)$, $R_0(\text{Cu}^{2+}) = 1.68(1)$, $R_0(\text{Mn}^{2+}) = 1.79(1)$, $R_0(\text{Mn}^{3+}) = 1.76(1)$, $R_0(\text{Mn}^{4+}) = 1.75(1)$, $B = 0.37$ [125].

Atom	Site	Sym.	x	y	z	$U_{\text{iso}} (\text{\AA}^2)$	B.v.s. ($ e $)
Dy1	2a	$mm2$	0.25	0.25	0.7799(5)	-0.0064(5)	3.1(1)
Dy2	2a	$mm2$	0.25	0.25	0.2807(6)	-0.0064(5)	3.1(1)
Cu1	2b	$mm2$	0.75	0.25	0.737(2)	-0.010(3)	2.0(1)
Mn2	2b	$mm2$	0.75	0.25	0.24(1)	-0.03(1)	1.9(4)
Mn3	4c	$\bar{1}$	0	0	0	-0.009(5)	3.2(2)
Mn4	4d	$\bar{1}$	0	0	0.5	-0.012(4)	3.7(3)
O1	8g	1	0.4378(6)	-0.0635(7)	0.2678(8)	-0.0037(6)	-
O2	4f	$.m.$	0.0589(9)	0.25	0.041(1)	-0.0037(6)	-
O3	4e	$m..$	0.25	0.534(1)	0.921(1)	-0.0037(6)	-
O4	4f	$.m.$	0.5392(9)	0.25	0.421(1)	-0.0037(6)	-
O5	4e	$m..$	0.25	0.4354(9)	0.542(1)	-0.0037(6)	-

Table 9.16: Crystal structure parameters of $\text{Dy}_2\text{CuMnMn}_4\text{O}_{12}$ ($Z = 4$, space group $Pmmn$) refined at 50 K. The lattice parameters were determined to be $a = 7.2801(1)$ Å, $b = 7.3431(1)$ Å, and $c = 7.8058(1)$ Å. Excellent reliability parameters of $R = 2.83\%$, $wR = 2.82\%$, $R_{\text{Bragg}} = 5.35\%$ were achieved in the refinement. Bond valence sums (BVS) were calculated using the bond valence parameters, $R_0(\text{Dy}^{3+}) = 2.04(1)$, $R_0(\text{Cu}^{2+}) = 1.68(1)$, $R_0(\text{Mn}^{2+}) = 1.79(1)$, $R_0(\text{Mn}^{3+}) = 1.76(1)$, $R_0(\text{Mn}^{4+}) = 1.75(1)$, $B = 0.37$ [125].

Atom	Site	Sym.	x	y	z	$U_{\text{iso}} (\text{\AA}^2)$	B.v.s. ($ e $)
Dy1	2a	$mm2$	0.25	0.25	0.7795(5)	-0.0068(5)	3.1(1)
Dy2	2a	$mm2$	0.25	0.25	0.2814(5)	-0.0068(5)	3.1(1)
Cu1	2b	$mm2$	0.75	0.25	0.734(2)	-0.007(3)	2.0(1)
Mn2	2b	$mm2$	0.75	0.25	0.24(1)	-0.02(1)	1.9(4)
Mn3	4c	$\bar{1}$	0	0	0	-0.007(6)	3.2(2)
Mn4	4d	$\bar{1}$	0	0	0.5	-0.013(4)	3.7(3)
O1	8g	1	0.4394(5)	-0.0638(5)	0.2679(6)	-0.0025(6)	-
O2	4f	$.m.$	0.0583(7)	0.25	0.0414(9)	-0.0025(6)	-
O3	4e	$m..$	0.25	0.5354(7)	0.9232(8)	-0.0025(6)	-
O4	4f	$.m.$	0.5392(7)	0.25	0.4211(9)	-0.0025(6)	-
O5	4e	$m..$	0.25	0.4334(7)	0.5402(8)	-0.0025(6)	-

Table 9.17: Crystal structure parameters of $\text{Dy}_2\text{CuMnMn}_4\text{O}_{12}$ ($Z = 4$, space group $Pmmn$) refined at 1.5 K. The lattice parameters were determined to be $a = 7.2801(1)$ Å, $b = 7.3431(1)$ Å, and $c = 7.8058(1)$ Å. Excellent reliability parameters of $R = 2.76\%$, $wR = 2.64\%$, $R_{\text{Bragg}} = 4.69\%$ were achieved in the refinement. Bond valence sums (BVS) were calculated using the bond valence parameters, $R_0(\text{Dy}^{3+}) = 2.04(1)$, $R_0(\text{Cu}^{2+}) = 1.68(1)$, $R_0(\text{Mn}^{2+}) = 1.79(1)$, $R_0(\text{Mn}^{3+}) = 1.76(1)$, $R_0(\text{Mn}^{4+}) = 1.75(1)$, $B = 0.37$ [125].

Atom	Site	Sym.	x	y	z	U_{iso} (Å ²)	B.v.s. ($ e $)
Dy1	2a	$mm2$	0.25	0.25	0.7795(5)	-0.0068(5)	3.1(1)
Dy2	2a	$mm2$	0.25	0.25	0.2811(6)	-0.0068(5)	3.1(1)
Cu1	2b	$mm2$	0.75	0.25	0.735(2)	-0.007(3)	2.0(1)
Mn2	2b	$mm2$	0.75	0.25	0.235(6)	-0.02(1)	2.0(3)
Mn3	4c	$\bar{1}$	0	0	0	-0.007(6)	3.2(1)
Mn4	4d	$\bar{1}$	0	0	0.5	-0.013(4)	3.7(3)
O1	8g	1	0.4393(5)	-0.0646(5)	0.2671(7)	-0.0025(6)	-
O2	4f	$.m.$	0.0603(7)	0.25	0.0418(9)	-0.0025(6)	-
O3	4e	$m..$	0.25	0.5358(7)	0.9220(8)	-0.0025(6)	-
O4	4f	$.m.$	0.5391(7)	0.25	0.4229(9)	-0.0025(6)	-
O5	4e	$m..$	0.25	0.4336(8)	0.5394(9)	-0.0025(6)	-

9.3.3 $\text{Sm}_2\text{MnMnMn}_{4-x}\text{Ti}_x\text{O}_{12}$

The crystal structure parameters of $\text{Sm}_2\text{MnMnMn}_{4-x}\text{Ti}_x\text{O}_{12}$ for $x = 1$, $x = 2$ and $x = 3$ refined in the paramagnetic phase are given in Tables 9.18, 9.19 and 9.20 respectively. The occupations were not expected to change as a function of temperature, and thus the occupations were only refined in the paramagnetic phase.

Table 9.18: Crystal structure parameters of $\text{Sm}_2\text{Mn}(\text{Mn}_{0.848(4)}\text{Sm}_{0.152(4)})\text{Mn}_3\text{TiO}_{12}$ ($Z = 2$, space group $P4_2/nmc$) refined at 80 K. The lattice parameters were determined to be $a = 7.4072(1)$ Å and $c = 7.9304(3)$ Å. Excellent reliability parameters of $R = 2.72\%$, $wR = 2.85\%$, $R_{\text{Bragg}} = 3.97\%$ were achieved in the refinement. Bond valence sums (BVS) were calculated using the bond valence parameters, $R_0(\text{Sm}^{3+}) = 2.01(1)$, $R_0(\text{Mn}^{3+}) = 1.76(1)$, $R_0(\text{Mn}^{2+}) = 1.79(1)$, $R_0(\text{Ti}^{4+}) = 1.82(1)$, $B = 0.37$ [125]. N.B the Wyckoff position of the Mn1 ions is listed for the split site with an occupation of 0.5, and the high symmetry position is given in square brackets with an occupation of 1.

Ion	Site	Sym.	x	y	z	$U_{\text{iso}} (\text{\AA}^2)$	B.v.s. ($ e $)
Sm1	$4d$	$2mm.$	0.25	0.25	0.211(4)	0.009(9)	3.2(2)
Mn1	$4c[2a]$	$2mm.$	0.75	0.25	0.722(3)	0.009(9)	2.34(4)
Mn2	$2b$	$\bar{4}m2$	0.75	0.25	0.250	0.008(5)	1.74(4)
Mn3/Ti1	$8e$	$\bar{1}$	0	0	0	0.023(2)	3.7(1)/3.23(9)
O1	$8g$	$.m.$	0.25	0.0594(6)	-0.0371(5)	0.028(2)	-
O2	$8g$	$.m.$	0.25	0.5359(7)	0.5772(6)	0.029(2)	-
O3	$8f$	$..2$	0.4358(4)	-0.4358(4)	0.25	0.030(2)	-

The crystal structure parameters of $\text{Sm}_2\text{MnMnMn}_{4-x}\text{Ti}_x\text{O}_{12}$ for $x = 1$, $x = 2$ and $x = 3$ refined at 1.5 K are given in Tables 9.21, 9.22 and 9.23 respectively.

Table 9.19: Crystal structure parameters of $\text{Sm}_2\text{Mn}(\text{Mn}_{0.94(2)}\text{Sm}_{0.06(2)})\text{Mn}_2\text{Ti}_2\text{O}_{12}$ ($Z = 2$, space group $P4_2/nmc$) refined at 90 K. The lattice parameters were determined to be $a = 7.5506(1)$ Å and $c = 7.7273(3)$ Å. Excellent reliability parameters of $R = 2.71\%$, $wR = 2.85\%$, $R_{\text{Bragg}} = 4.9\%$ were achieved in the refinement. Bond valence sums (BVS) were calculated using the bond valence parameters, $R_0(\text{Sm}^{3+}) = 2.01(1)$, $R_0(\text{Mn}^{2+}) = 1.79(1)$, $R_0(\text{Mn}^{3+}) = 1.76(1)$, $R_0(\text{Ti}^{4+}) = 1.82(1)$, $B = 0.37$ [125]. N.B the Wyckoff position of the Mn1 ions is listed for the split site with an occupation of 0.5, and the high symmetry position is given in square brackets with an occupation of 1.

Ion	Site	Sym.	x	y	z	$U_{\text{iso}} (\text{\AA}^2)$	B.v.s. ($ e $)
Sm1	4d	$2mm.$	0.25	0.25	0.200(5)	0.022(4)	3.2(6)
Mn1	4c[2a]	$2mm.$	0.75	0.25	0.787(2)	0.022(4)	1.78(8)
Mn2	2b	$\bar{4}m2$	0.75	0.25	0.250	0.022(4)	1.71(7)
Mn3/Ti1	8e	$\bar{1}$	0	0	0	0.016(2)	3.7(3)/ 3.2(2)
O1	8g	$.m.$	0.25	0.0607(6)	-0.0341(3)	0.019(2)	-
O2	8g	$.m.$	0.25	0.5409(6)	0.5700(5)	0.022(2)	-
O3	8f	$..2$	0.4438(3)	-0.4438(3)	0.25	0.023(2)	-

Table 9.20: Crystal structure parameters of $\text{Sm}_2\text{MnMnMnTi}_3\text{O}_{12}$ ($Z = 2$, space group $P4_2/nmc$) refined at 80 K. The lattice parameters were determined to be $a = 7.6290(1)$ Å and $c = 7.6932(2)$ Å. Excellent reliability parameters of $R = 2.03\%$, $wR = 2.19\%$, $R_{\text{Bragg}} = 4.14\%$ were achieved in the refinement. Bond valence sums (BVS) were calculated using the bond valence parameters, $R_0(\text{Sm}^{3+}) = 2.01(1)$, $R_0(\text{Mn}^{2+}) = 1.79(1)$, $R_0(\text{Mn}^{3+}) = 1.76(1)$, $R_0(\text{Ti}^{4+}) = 1.82(1)$, $B = 0.37$ [125]. N.B the Wyckoff position of the Mn1 ions is listed for the split site with an occupation of 0.5, and the high symmetry position is given in brackets with an occupation of 1.

Ion	Site	Sym.	x	y	z	$U_{\text{iso}} (\text{\AA}^2)$	B.v.s. ($ e $)
Sm1	4d	$2mm.$	0.25	0.25	0.202(5)	0.027(3)	3.2(7)
Mn1	4c[2a]	$2mm.$	0.75	0.25	0.797(2)	0.027(3)	1.57(6)
Mn2	2b	$\bar{4}m2$	0.75	0.25	0.250	0.027(3)	1.80(9)
Mn3/Ti1	8e	$\bar{1}$	0	0	0	0.020(2)	3.6(2)/3.1(2)
O1	8g	$.m.$	0.25	0.0642(5)	-0.0333(6)	0.027(2)	-
O2	8g	$.m.$	0.25	0.5439(5)	0.5719(5)	0.025(2)	-
O3	8f	$..2$	0.4451(4)	-0.4451(4)	0.25	0.028(1)	-

Table 9.21: Crystal structure parameters of $\text{Sm}_2\text{Mn}(\text{Mn}_{0.848(4)}\text{Sm}_{0.152(4)})\text{Mn}_3\text{TiO}_{12}$ ($Z = 2$, space group $P4_2/nmc$) refined at 1.5 K. The lattice parameters were determined to be $a = 7.4068(1)$ Å and $c = 7.9275(2)$ Å. Excellent reliability parameters of $R = 2.39\%$, $wR = 2.65\%$, $R_{\text{Bragg}} = 3.90\%$ were achieved in the refinement. Bond valence sums (BVS) were calculated using the bond valence parameters, $R_0(\text{Sm}^{3+}) = 2.01(1)$, $R_0(\text{Mn}^{3+}) = 1.76(1)$, $R_0(\text{Mn}^{2+}) = 1.79(1)$, $R_0(\text{Ti}^{4+}) = 1.82(1)$, $B = 0.37$ [125]. N.B the Wyckoff position of the Mn1 ions is listed for the split site with an occupation of 0.5, and the high symmetry position is given in square brackets with an occupation of 1.

Ion	Site	Sym.	x	y	z	$U_{\text{iso}} (\text{\AA}^2)$	B.v.s. ($ e $)
Sm1	4d	$2mm.$	0.25	0.25	0.212(3)	0.008(3)	3.2(6)
Mn1	4c[2a]	$2mm.$	0.75	0.25	0.719(2)	0.008(3)	2.3(2)
Mn2	2b	$\bar{4}m2$	0.75	0.25	0.250	0.008(3)	1.73(8)
Mn3/Ti1	8e	$\bar{1}$	0	0	0	0.024(2)	3.7(3)/3.2(2)
O1	8g	$.m.$	0.25	0.0599(5)	-0.0369(4)	0.028(2)	-
O2	8g	$.m.$	0.25	0.5354(5)	0.5769(4)	0.029(2)	-
O3	8f	$..2$	0.4356(2)	-0.4356(2)	0.25	0.029(2)	-

Table 9.22: Crystal structure parameters of $\text{Sm}_2\text{Mn}(\text{Mn}_{0.94(2)}\text{Sm}_{0.06(2)})\text{Mn}_2\text{Ti}_2\text{O}_{12}$ ($Z = 2$, space group $P4_2/nmc$) refined at 1.5 K. The lattice parameters were determined to be $a = 7.6374(1)$ Å and $c = 7.8133(3)$ Å. Excellent reliability parameters of $R = 2.71\%$, $wR = 2.87\%$, $R_{\text{Bragg}} = 5.05\%$ were achieved in the refinement. Bond valence sums (BVS) were calculated using the bond valence parameters, $R_0(\text{Sm}^{3+}) = 2.01(1)$, $R_0(\text{Mn}^{2+}) = 1.79(1)$, $R_0(\text{Mn}^{3+}) = 1.76(1)$, $R_0(\text{Ti}^{4+}) = 1.82(1)$, $B = 0.37$ [125]. N.B the Wyckoff position of the Mn1 ions is listed for the split site with an occupation of 0.5, and the high symmetry position is given in square brackets with an occupation of 1.

Ion	Site	Sym.	x	y	z	$U_{\text{iso}} (\text{\AA}^2)$	B.v.s. ($ e $)
Sm1	4d	$2mm.$	0.25	0.25	0.214(3)	0.017(3)	2.9(5)
Mn1	4c[2a]	$2mm.$	0.75	0.25	0.790(1)	0.017(3)	1.78(8)
Mn2	2b	$\bar{4}m2$	0.75	0.25	0.250	0.017(3)	1.62(6)
Mn3/Ti1	8e	$\bar{1}$	0	0	0	0.018(2)	3.5(2)/ 3.1(2)
O1	8g	$.m.$	0.25	0.0614(5)	-0.0344(4)	0.022(2)	-
O2	8g	$.m.$	0.25	0.5403(5)	0.5709(4)	0.025(2)	-
O3	8f	$..2$	0.4434(3)	-0.4434(3)	0.25	0.024(2)	-

Table 9.23: Crystal structure parameters of $\text{Sm}_2\text{MnMnMnTi}_3\text{O}_{12}$ ($Z = 2$, space group $P4_2/nmc$) refined at 1.5 K. The lattice parameters were determined to be $a = 7.6276(1)$ Å and $c = 7.6918(2)$ Å. Excellent reliability parameters of $R = 2.15\%$, $wR = 2.34\%$, $R_{\text{Bragg}} = 3.59\%$ were achieved in the refinement. Bond valence sums (BVS) were calculated using the bond valence parameters, $R_0(\text{Sm}^{3+}) = 2.01(1)$, $R_0(\text{Mn}^{2+}) = 1.79(1)$, $R_0(\text{Mn}^{3+}) = 1.76(1)$, $R_0(\text{Ti}^{4+}) = 1.82(1)$, $B = 0.37$ [125]. N.B the Wyckoff position of the Mn1 ions is listed for the split site with an occupation of 0.5, and the high symmetry position is given in brackets with an occupation of 1.

Ion	Site	Sym.	x	y	z	$U_{\text{iso}} (\text{\AA}^2)$	B.v.s. ($ e $)
Sm1	4d	$2mm.$	0.25	0.25	0.220(4)	0.024(3)	3.0(2)
Mn1	4c[2a]	$2mm.$	0.75	0.25	0.796(2)	0.024(3)	1.58(2)
Mn2	2b	$\bar{4}m2$	0.75	0.25	0.250	0.024(3)	1.81(2)
Mn3/Ti1	8e	$\bar{1}$	0	0	0	0.022(2)	3.6(1)/3.36(9)
O1	8g	$.m.$	0.25	0.0638(5)	-0.0344(6)	0.026(2)	-
O2	8g	$.m.$	0.25	0.5442(5)	0.5719(4)	0.023(2)	-
O3	8f	$..2$	0.4445(4)	-0.4445(4)	0.25	0.026(1)	-

9.3.4 $[\text{Y}_{2-x}\text{Mn}_x]\text{MnMn}_4\text{O}_{12}$

The crystal structural parameters of $\text{Y}_{1.79}\text{Mn}_{0.21}\text{MnMnMn}_4\text{O}_{12}$ refined at 255 K, 40 K and 1.5 K against neutron powder diffraction data are tabulated in Tables 9.24, 9.25 and 9.26 respectively. To determine the antisite cation disorder, each of the cations present in the sample was systematically substituted for the primary cation expected to occupy the site, and the model was refined. The refinement was constrained such that the total occupation of each site was not allowed to exceed the expected occupation (as determined by the Wyckoff position). The Y1 site was found to be occupied by 86.8(4)% Y and 13.2(4)% Mn and the Y2 site was found to be occupied by 90.0(4)% Y and 10.0(4)% Mn. All other sites were found to fully occupied by the nominal ions on that site. The occupations were not expected to change as a function of temperature, and thus the occupations were only refined in the paramagnetic phase.

The crystal structural parameters of $\text{Y}_{1.84}\text{Mn}_{0.16}\text{MnMnMn}_4\text{O}_{12}$ refined at 250 K, 40 K and 1.5 K against neutron powder diffraction data are tabulated in Tables 9.27, 9.28 and 9.29 respectively. To determine

Table 9.24: Crystal structure parameters of $\text{Y}_{1.79}\text{Mn}_{0.21}\text{MnMnMn}_4\text{O}_{12}$ ($Z = 4$, space group $Pm\bar{m}n$) refined at 255 K. The lattice parameters were determined to be $a = 7.24742(7)$ Å, $b = 7.43400(2)$ Å, and $c = 7.78894(9)$ Å. Excellent reliability parameters of $R = 3.30\%$, $wR = 3.30\%$, $R_{\text{Bragg}} = 3.04\%$ were achieved in the refinement. Bond valence sums (BVS) were calculated using the bond valence parameters, $R_0(\text{Y}^{3+}) = 2.01(1)$, $R_0(\text{Mn}^{3+}) = 1.76(1)$, $R_0(\text{Mn}^{2+}) = 1.79(1)$, $R_0(\text{Mn}^{3+}) = 1.76(1)$, $R_0(\text{Mn}^{4+}) = 1.75(1)$, $B = 0.37$ [125].

Atom	Site	Sym.	x	y	z	U_{iso} (Å ²)	B.v.s. ($ e $)
Y1	2a	$mm2$	0.25	0.25	0.7816(4)	0.0067(1)	2.92(5)
Y2	2a	$mm2$	0.25	0.25	0.2839(4)	0.011(2)	2.88(8)
Mn1	2b	$mm2$	0.75	0.25	0.7227(6)	0.002(1)	2.70(5)
Mn2	2b	$mm2$	0.75	0.25	0.2393(8)	0.019(5)	1.96(6)
Mn3	4c	$\bar{1}$	0	0	0	0.002(1)	3.16(9)
Mn4	4d	$\bar{1}$	0	0	0.5	0.09(1)	3.6(1)
O1	8g	1	0.4349(2)	-0.0682(2)	0.2673(2)	0.0111(6)	-
O2	4f	$.m.$	0.0568(3)	0.25	0.0422(3)	0.0105(7)	-
O3	4e	$m..$	0.25	0.5296(3)	0.9220(3)	0.0087(7)	-
O4	4f	$.m.$	0.5417(3)	0.25	0.4159(3)	0.0109(7)	-
O5	4e	$m..$	0.25	0.4338(3)	0.5403(3)	0.0095(7)	-

Table 9.25: Crystal structure parameters of $\text{Y}_{1.79}\text{Mn}_{0.21}\text{MnMnMn}_4\text{O}_{12}$ ($Z = 4$, space group $Pm\bar{m}n$) refined at 85 K. The lattice parameters were determined to be $a = 7.24135(7)$ Å, $b = 7.43224(8)$ Å, and $c = 7.78107(9)$ Å. Excellent reliability parameters of $R = 3.38\%$, $wR = 4.03\%$, $R_{\text{Bragg}} = 3.61\%$ were achieved in the refinement. Bond valence sums (BVS) were calculated using the bond valence parameters, $R_0(\text{Y}^{3+}) = 2.01(1)$, $R_0(\text{Mn}^{3+}) = 1.76(1)$, $R_0(\text{Mn}^{2+}) = 1.79(1)$, $R_0(\text{Mn}^{3+}) = 1.76(1)$, $R_0(\text{Mn}^{4+}) = 1.75(1)$, $B = 0.37$ [125].

Atom	Site	Sym.	x	y	z	U_{iso} (Å ²)	B.v.s. ($ e $)
Y1	2a	$mm2$	0.25	0.25	0.7815(5)	0.014(1)	2.99(9)
Y2	2a	$mm2$	0.25	0.25	0.2846(4)	0.011(1)	2.91(5)
Mn1	2b	$mm2$	0.75	0.25	0.7230(7)	0.002(2)	2.7(1)
Mn2	2b	$mm2$	0.75	0.25	0.2402(9)	0.018(2)	1.95(6)
Mn3	4c	$\bar{1}$	0	0	0	0.008(1)	3.18(9)
Mn4	4d	$\bar{1}$	0	0	0.5	0.0029(1)	3.6(2)
O1	8g	1	0.4357(3)	-0.0679(2)	0.2668(3)	0.0125(5)	-
O2	4f	$.m.$	0.0578(4)	0.25	0.0417(3)	0.0110(7)	-
O3	4e	$m..$	0.25	0.5285(3)	0.9218(3)	0.0090(8)	-
O4	4f	$.m.$	0.5415(3)	0.25	0.4160(3)	0.0122(8)	-
O5	4e	$m..$	0.25	0.4322(3)	0.5403(3)	0.0108(7)	-

Table 9.26: Crystal structure parameters of $\text{Y}_{1.79}\text{Mn}_{0.21}\text{MnMnMn}_4\text{O}_{12}$ ($Z = 4$, space group $Pm\bar{m}n$) refined at 1.5 K. The lattice parameters were determined to be $a = 7.24102(8)$ Å, $b = 7.42975(8)$ Å, and $c = 7.7810(1)$ Å. Excellent reliability parameters of $R = 4.33\%$, $wR = 4.42\%$, $R_{\text{Bragg}} = 3.54\%$ were achieved in the refinement. Bond valence sums (BVS) were calculated using the bond valence parameters, $R_0(\text{Y}^{3+}) = 2.01(1)$, $R_0(\text{Mn}^{3+}) = 1.76(1)$, $R_0(\text{Mn}^{2+}) = 1.79(1)$, $R_0(\text{Mn}^{3+}) = 1.76(1)$, $R_0(\text{Mn}^{4+}) = 1.75(1)$, $B = 0.37$ [125].

Atom	Site	Sym.	x	y	z	U_{iso} (Å ²)	B.v.s. ($ e $)
Y1	2a	$mm2$	0.25	0.25	0.7810(5)	0.019(1)	3.00(5)
Y2	2a	$mm2$	0.25	0.25	0.2840(5)	0.009(1)	2.94(5)
Mn1	2b	$mm2$	0.75	0.25	0.7212(8)	0.005(2)	2.7(2)
Mn2	2b	$mm2$	0.75	0.25	0.241(1)	0.018(2)	1.95(6)
Mn3	4c	$\bar{1}$	0	0	0	0.009(2)	3.2(1)
Mn4	4d	$\bar{1}$	0	0	0.5	0.0033(1)	3.6(1)
O1	8g	1	0.4356(3)	-0.0677(3)	0.2665(3)	0.0116(6)	-
O2	4f	$.m.$	0.0584(4)	0.25	0.0423(4)	0.0114(8)	-
O3	4e	$m..$	0.25	0.5282(3)	0.9215(4)	0.0087(8)	-
O4	4f	$.m.$	0.5412(4)	0.25	0.4160(4)	0.0122(9)	-
O5	4e	$m..$	0.25	0.4320(4)	0.5401(4)	0.0098(8)	-

the antisite cation disorder, each of the cations present in the sample was systematically substituted for the primary cation expected to occupy the site, and the model was refined. The refinement was constrained such that the total occupation of each site was not allowed to exceed the expected occupation (as determined by the Wyckoff position). The Y1 site was found to be occupied by 90.0(4)% Y and 10.0(4)% Mn and the Y2 site was found to be occupied by 94.0(4)% Y and 6.0(4)% Mn. All other sites were found to be fully occupied by the nominal ions on that site. The occupations were not expected to change as a function of temperature, and thus the occupations were only refined in the paramagnetic phase.

Table 9.27: Crystal structure parameters of $\text{Y}_{1.84}\text{Mn}_{0.16}\text{MnMnMn}_4\text{O}_{12}$ ($Z = 4$, space group $Pm\bar{m}n$) refined at 250 K. The lattice parameters were determined to be $a = 7.25284(8)$ Å, $b = 7.44842(8)$ Å, and $c = 7.7963(1)$ Å. Excellent reliability parameters of $R = 3.49\%$, $wR = 3.79\%$, $R_{\text{Bragg}} = 3.14\%$ were achieved in the refinement. Bond valence sums (BVS) were calculated using the bond valence parameters, $R_0(\text{Y}^{3+}) = 2.01(1)$, $R_0(\text{Mn}^{3+}) = 1.76(1)$, $R_0(\text{Mn}^{2+}) = 1.79(1)$, $R_0(\text{Mn}^{3+}) = 1.76(1)$, $R_0(\text{Mn}^{4+}) = 1.75(1)$, $B = 0.37$ [125].

Atom	Site	Sym.	x	y	z	U_{iso} (Å ²)	B.v.s. ($ e $)
Y1	2a	$mm2$	0.25	0.25	0.7814(4)	0.0120(9)	2.91(5)
Y2	2a	$mm2$	0.25	0.25	0.284(4)	0.0081(9)	2.89(5)
Mn1	2b	$mm2$	0.75	0.25	0.7246(7)	0.004(1)	2.66(5)
Mn2	2b	$mm2$	0.75	0.25	0.2402(1)	0.033(2)	1.93(6)
Mn3	4c	$\bar{1}$	0	0	0	0.0076(1)	3.2(1)
Mn4	4d	$\bar{1}$	0	0	0.5	0.0074(1)	3.5(1)
O1	8g	1	0.4352(2)	-0.0677(2)	0.2667(2)	0.0126(6)	-
O2	4f	$.m.$	0.0570(3)	0.25	0.0415(3)	0.0111(7)	-
O3	4e	$m..$	0.25	0.5291(3)	0.9223(3)	0.0089(8)	-
O4	4f	$.m.$	0.5401(3)	0.25	0.4148(3)	0.0126(8)	-
O5	4e	$m..$	0.25	0.4334(3)	0.5399(3)	0.0097(7)	-

Table 9.28: Crystal structure parameters of $\text{Y}_{1.84}\text{Mn}_{0.16}\text{MnMnMn}_4\text{O}_{12}$ ($Z = 4$, space group $Pmmn$) refined at 85 K. The lattice parameters were determined to be $a = 7.24352(7)$ Å, $b = 7.45028(7)$ Å, and $c = 7.78826(9)$ Å. Excellent reliability parameters of $R = 3.32\%$, $wR = 3.36\%$, $R_{\text{Bragg}} = 3.34\%$ were achieved in the refinement. Bond valence sums (BVS) were calculated using the bond valence parameters, $R_0(\text{Y}^{3+}) = 2.01(1)$, $R_0(\text{Mn}^{3+}) = 1.76(1)$, $R_0(\text{Mn}^{2+}) = 1.79(1)$, $R_0(\text{Mn}^{3+}) = 1.76(1)$, $R_0(\text{Mn}^{4+}) = 1.75(1)$, $B = 0.37$ [125].

Atom	Site	Sym.	x	y	z	U_{iso} (Å ²)	B.v.s. ($ e $)
Y1	2a	$mm2$	0.25	0.25	0.7816(4)	0.0081(7)	2.95(5)
Y2	2a	$mm2$	0.25	0.25	0.2840(3)	0.0082(8)	2.91(5)
Mn1	2b	$mm2$	0.75	0.25	0.7235(6)	0.004(1)	2.66(5)
Mn2	2b	$mm2$	0.75	0.25	0.2407(8)	0.027(2)	1.94(6)
Mn3	4c	$\bar{1}$	0	0	0	0.008(1)	3.16(9)
Mn4	4d	$\bar{1}$	0	0	0.5	0.005(1)	3.6(1)
O1	8g	1	0.4355(2)	-0.0678(2)	0.2669(2)	0.0118(4)	-
O2	4f	$.m.$	0.0577(3)	0.25	0.0418(3)	0.0104(5)	-
O3	4e	$m..$	0.25	0.5288(2)	0.9224(3)	0.0075(6)	-
O4	4f	$.m.$	0.5411(3)	0.25	0.4152(3)	0.0123(6)	-
O5	4e	$m..$	0.25	0.4322(3)	0.5398(3)	0.0101(6)	-

Table 9.29: Crystal structure parameters of $\text{Y}_{1.84}\text{Mn}_{0.16}\text{MnMnMn}_4\text{O}_{12}$ ($Z = 4$, space group $Pm\bar{m}n$) refined at 1.5 K. The lattice parameters were determined to be $a = 7.24095(7)$ Å, $b = 7.44771(7)$ Å, and $c = 7.79047(9)$ Å. Excellent reliability parameters of $R = 3.72\%$, $wR = 3.76\%$, $R_{\text{Bragg}} = 2.86\%$ were achieved in the refinement. Bond valence sums (BVS) were calculated using the bond valence parameters, $R_0(\text{Y}^{3+}) = 2.01(1)$, $R_0(\text{Mn}^{3+}) = 1.76(1)$, $R_0(\text{Mn}^{2+}) = 1.79(1)$, $R_0(\text{Mn}^{3+}) = 1.76(1)$, $R_0(\text{Mn}^{4+}) = 1.75(1)$, $B = 0.37$ [125].

Atom	Site	Sym.	x	y	z	U_{iso} (Å ²)	B.v.s. ($ e $)
Y1	2a	$mm2$	0.25	0.25	0.7815(4)	0.0076(8)	2.94(7)
Y2	2a	$mm2$	0.25	0.25	0.2843(4)	0.0067(8)	2.93(5)
Mn1	2b	$mm2$	0.75	0.25	0.7244(7)	0.0051(1)	2.66(5)
Mn2	2b	$mm2$	0.75	0.25	0.2395(8)	0.024(2)	1.93(5)
Mn3	4c	$\bar{1}$	0	0	0	0.0076(1)	3.17(9)
Mn4	4d	$\bar{1}$	0	0	0.5	0.0074(1)	3.6(1)
O1	8g	1	0.4354(2)	-0.0676(2)	0.2665(2)	0.0111(5)	-
O2	4f	$.m.$	0.0579(3)	0.25	0.0419(3)	0.0103(6)	-
O3	4e	$m..$	0.25	0.5286(2)	0.9224(3)	0.0075(6)	-
O4	4f	$.m.$	0.5405(3)	0.25	0.4152(3)	0.0122(7)	-
O5	4e	$m..$	0.25	0.4323(3)	0.5394(3)	0.0095(6)	-

Chapter 10

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