

Neutron-Scattering Studies of Frustrated Magnetic Materials



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Declaration

This dissertation is the result of my own original work, and where it draws on the work of others, this is acknowledged at appropriate points in the text. Some introductory material contained in pages 1–5 and 62–64 in this dissertation is reproduced with modifications from my undergraduate (Part II) dissertation, which was accepted for the degree of MChem at Oxford in Trinity 2011. Some initial results, shown in Figures 2.1 to 2.7, were also originally presented in my undergraduate dissertation. The remainder of this dissertation has not previously been submitted for a degree at Oxford or any other institution.

Joseph Paddison

Abstract

Frustrated spin systems exhibit a very large number of low-energy states which can lead to the suppression of conventional magnetic order. They are nevertheless distinguished from classical paramagnets by the presence of unconventional spin correlations or “local rules”. These local correlations have been linked to systems of fundamental importance, including high-temperature superconductors and multiferroics, and are widely studied using neutron-scattering experiments. Whereas the neutron-scattering pattern of a periodic spin structure shows sharp reflections (Bragg peaks), scattering patterns of frustrated systems show only broad diffuse features. Consequently, conventional crystallographic methods cannot be used to solve these systems. Instead, the neutron scattering pattern anticipated from a predetermined interaction model is typically compared with experimental single-crystal neutron-scattering data. This approach relies on anticipating the nature of the magnetic interactions; it is also inherently unfeasible for the many interesting materials for which large single crystal samples do not exist.

In this thesis I examine whether these two problems can be addressed using reverse Monte Carlo (RMC) refinement, a method in which the orientations of spins in a large configuration are refined to match experimental diffuse-scattering data. I first assess whether RMC refinement to magnetic powder diffuse-scattering data can allow three-dimensional (3D) information to be recovered. I show that the information lost during powder averaging of the full 3D diffuse-scattering pattern is actually surprisingly minimal, and the complete 3D scattering pattern can be recovered from RMC refinement to simulated powder data. In addition, information is obtained about the presence and type of magnetic anisotropy and (in favourable cases) about higher-order correlations. I go on to develop a fast RMC algorithm to refine to large 3D diffuse-scattering datasets ($\sim 10^6$ data points) in reasonable time ($\sim$ days). These results show that RMC refinement represents a successful alternative to traditional methods of interaction modelling, allowing quantitative refinement of disordered spin structures in complex magnetic materials.

I use the RMC approach to refine to experimental diffuse-scattering data for five frustrated magnetic materials. I first consider the interplay of frustration and low-dimensional magnetism in the paramagnetic phase of the spin-chain compound $\text{Ca}_3\text{Co}_2\text{O}_6$, in which Ising-like spin chains are arranged on a triangular lattice. Both intra-chain and inter-chain correlations persist above the magnetic ordering temperature T_N , but are essentially decoupled. Intra-chain correlations resemble the ferromagnetic (FM) Ising model, while inter-chain correlations resemble the frustrated triangular-lattice antiferromagnet (AFM). Using previously-published bulk property measurements in addition to powder neutron-scattering data, I obtain values of the FM and AFM exchange interactions and the single-ion anisotropy, which provide the first consistent explanation of thermodynamic anomalies observed above T_N .

I next use powder diffuse-scattering data to obtain an atomic-scale model of the spin-liquid state in the canonical frustrated magnet $\text{Gd}_3\text{Ga}_5\text{O}_{12}$. I show that this state exhibits a hidden (non-dipolar) order which has three unusual properties. First, it is a collective phenomenon, in which multipoles are formed from ten-spin loops. Second, it is long-range, with a diverging correlation length. Third, it is a consequence of the interplay between AFM spin correlations and local magnetic anisotropy, which allows it to be indirectly observed in neutron-scattering experiments.

In a final study using powder data, I consider the partially-ordered low-temperature

magnetic structure of the frustrated AFM $\text{Gd}_2\text{Ti}_2\text{O}_7$. This structure is currently believed to involve multiple magnetic propagation vectors in a so-called $4\mathbf{k}$ model, based on analysis of powder diffuse-scattering data. I present three pieces of evidence against this $4\mathbf{k}$ structure. First, I use single-crystal neutron-diffraction measurements to observe a redistribution of magnetic intensity between Bragg peaks when a small magnetic field is applied. This result is consistent with the selective population of magnetic domains for the alternative $1\mathbf{k}$ structure, but is inconsistent with the $4\mathbf{k}$ structure unless a field-induced phase transition occurs which is silent in thermodynamic measurements. Second, I find evidence from high-resolution neutron powder-diffraction measurements that short-range rhombohedral strains are present at low temperature, which may be generated by magneto-elastic coupling only for the $1\mathbf{k}$ structure. Third, I demonstrate that the powder diffuse-scattering intensity can be modelled quantitatively by a $1\mathbf{k}$ structure.

I then present two studies of RMC refinement to single-crystal magnetic diffuse-scattering data. First, I consider the paramagnetic (PM) phase of the canonical AFM, MnO , which is only weakly frustrated. I compare the local magnetic structure in the PM phase with the well-known ordered AFM structure of MnO , and find significant differences between the two over short length-scales. This result indicates that the spin correlations of weakly-frustrated paramagnets do not necessarily resemble the incipient ordered magnetic structure over short length-scales. This result may have implications for other weakly-frustrated systems (e.g., high-temperature superconductors such as $\text{La}_{1-x}\text{Sr}_x\text{CuO}_4$).

Finally, I identify the presence of emergent spin structures in Co-doped $\beta\text{-Mn}$, a metal which has a crystal structure noted for its complexity. Single-crystal polarised-neutron scattering experiments on $\beta\text{-Mn}_{0.8}\text{Co}_{0.2}$ reveal the persistence of highly-structured magnetic diffuse scattering and the absence of magnetic order to $T = 0.05\text{ K}$. I employ RMC refinements and mean-field theory calculations to construct an effective Hamiltonian which accounts for the magnetic diffuse scattering. The interactions I identify describe an emergent spin structure which mimics the triangular-lattice AFM, one of the canonical models of frustrated magnetism.

Publications

1. Spin correlations in $\text{Ca}_3\text{Co}_2\text{O}_6$: Polarized-Neutron Diffraction and Monte Carlo Study
J. A. M. Paddison, S. Agrestini, M. R. Lees, C. L. Fleck, P. P. Deen, A. L. Goodwin, J. R. Stewart and O. A. Petrenko
Phys. Rev. B, **90**, 014411 (2014)
2. Liquidlike Correlations in Single-Crystalline $\text{Y}_2\text{Mo}_2\text{O}_7$: An Unconventional Spin Glass
H. J. Silverstein, K. Fritsch, F. Flicker, A. M. Hallas, J. S. Gardner, Y. Qiu, G. Ehlers, A. T. Savici, Z. Yamani, K. A. Ross, B. D. Gaulin, M. J. P. Gingras, J. A. M. Paddison, K. Foyevtsova, R. Valenti, F. Hawthorne, C. R. Wiebe and H. D. Zhou
Phys. Rev. B **89**, 054433 (2014)
3. Spinvert: A Program for Refinement of Paramagnetic Diffuse Scattering Data
J. A. M. Paddison, J. R. Stewart and A. L. Goodwin
J. Phys.: Condens. Matter **25**, 454220 (2013)
4. Emergent Frustration in Co-doped β -Mn
J. A. M. Paddison, J. R. Stewart, P. Manuel, P. Courtois, G. J. McIntyre, B. D. Rainford and A. L. Goodwin
Phys. Rev. Lett **110**, 267207 (2013)
5. Statics and Dynamics of the Highly Correlated Spin Ice $\text{Ho}_2\text{Ge}_2\text{O}_7$
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6. Empirical Magnetic Structure Solution of Frustrated Spin Systems
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Phys. Rev. Lett **108**, 017204 (2012)

Abbreviations and Notational Conventions

Abbreviations

PM	paramagnet(ic)
FM	ferromagnet(ic)
AFM	antiferromagnet(ic)
MC	Monte Carlo
RMC	reverse Monte Carlo
1D	one-dimensional
3D	three-dimensional
ILL	Institut Laue-Langevin
GGG	gadolinium gallium garnet
NMR	nuclear magnetic resonance
μ SR	muon-spin rotation
<i>a</i> -Si	amorphous silicon
SDW	spin-density wave
d-IPA	deuterated isopropyl alcohol
FWHM	full width at half-maximum

Notational Conventions

1. Vectors and matrices are written in bold type.
2. The magnitude of a vector is written in italics (e.g., $r = |\mathbf{r}|$).
3. Crystallographic bracket notation is used in the following way:
 - Square brackets $[\]$ denote a vector.
 - Angle brackets $\langle \rangle$ denote a set of vectors which are equivalent by symmetry.
 - Parentheses $()$ denote a plane.
 - Curly brackets $\{ \}$ denote a set of planes which are equivalent by symmetry.
 - To denote a quantity in reciprocal space, the above brackets are modified by adding an asterisk, e.g. $(100)^*$ denotes a reciprocal-space plane.

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Chapter 1

Introduction

1.1 Order, Disorder, and Frustration

Cool most substances to a sufficiently low temperature, and eventually they become solids. A similar situation holds for magnetism in magnetic materials: at some temperature the magnetic moments (“spins”) which decorate each atom change from being randomly oriented (paramagnetism), and form a magnetic structure that shows long-range magnetic order [1]. The nature of the ordering may be simple (such as ferromagnetism or antiferromagnetism) or more exotic (such as helical and cycloidal order), but the principle remains the same: a periodic arrangement of spins, which can usually be described in terms of a repeated magnetic unit cell.

It has, however, been known for a long time that there are several effects which can inhibit the formation of long-range magnetic order [1–3]. One such effect—anthropomorphically called “frustration” [4, 5]—forms the main subject of this thesis. The term refers to the inability of a system of spins to minimise the energy of all its interactions simultaneously, a situation which arises when there is an incompatibility between the atomic lattice the spins occupy and the magnetic interactions between them [6]. Probably the simplest example considers spins arranged on a triangle [Fig. 1.1(a)]. The spins are allowed to point only either up or down, and the interaction between neighbouring spins is antiferromagnetic (AFM); that is, it is energetically favourable for adjacent spins to be aligned antiparallel. However, the geometry of the system does not allow this to happen: while

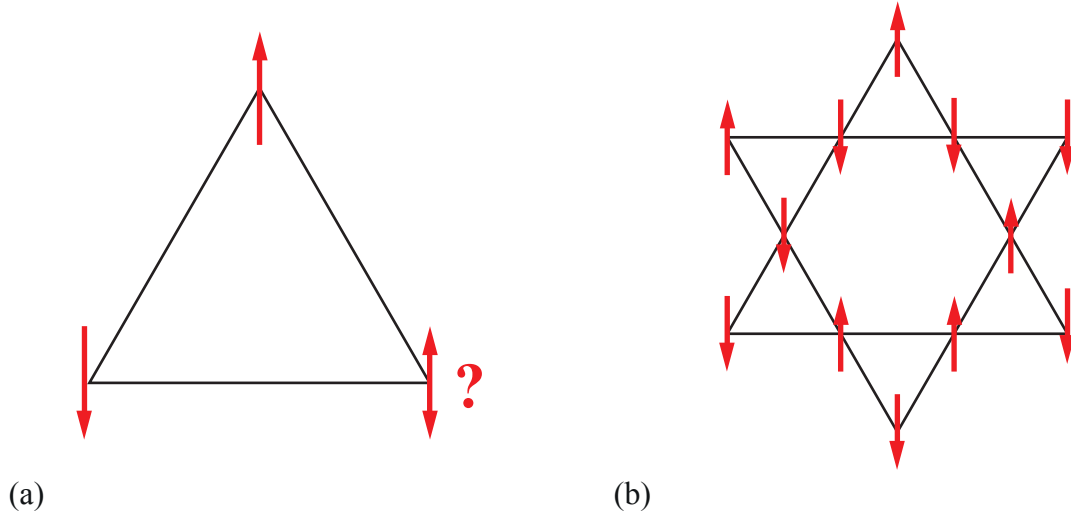


Figure 1.1: (a) Frustration on a triangle; (b) frustration on a kagome lattice. Spins are shown as red arrows.

any two spins can be antiparallel, the third has no choice but to align parallel with one of the first two. There are six possible ways of achieving such an arrangement, but none is energetically favourable compared to the others [2].

Although real systems tend not to involve separated triangles of atoms, forming a periodic atomic lattice does not necessarily relieve frustration. Fig. 1.1(b) shows the kagome lattice formed by joining triangles at their corners, with the same AFM interaction between spins. The number of equivalent spin arrangements increases with the number of triangles, leading to a total degeneracy of magnetic ground states that is very large indeed [5]. The consequence of this is that the whole magnetic structure cannot be described by repeating any smaller part of it: there is no long-range magnetic order. There is, however, a rule: each triangle has two spins “up” and one “down”, or *vice versa*. The presence of such “local rules” in the absence of long-range magnetic order is a key feature that distinguishes frustrated magnets both from classical paramagnets and ordered magnets, and has led to their being described as “spin liquids” or “cooperative paramagnets” [5, 7].

Interest in these local spin correlations has two main motivations. First, frustration often leads to states with interesting and unexpected properties; for example, in spin ice [8, 9], excitations out of the degenerate ground states are magnetic monopoles [Section 2.3] [10, 11]. Second, frustration is implicated in phenomena of practical as well as theoretical interest, including complex magnetic orderings in multiferroics [12] and the evolution

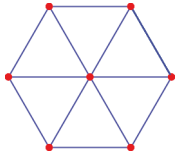
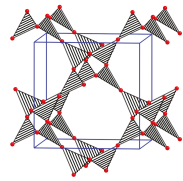
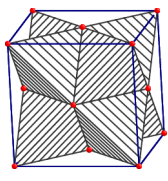
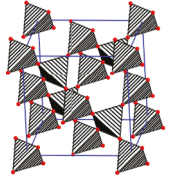
Lattice	Triangular [17]	Hyperkagome	Face-centred cubic	Pyrochlore [18]
Geometry	Edge-sharing triangles	Corner-sharing triangles	Edge-sharing tetrahedra	Corner-sharing tetrahedra
Structures	hexagonal perovskite, ABO_3 delafossite, ABO_2 Cs_2AlCl_4	garnet, $\text{A}_3\text{Ga}_5\text{O}_{12}$ $\beta\text{-Mn}$ $\text{Na}_4\text{A}_3\text{O}_8$	rock salt, AB double perovskite, Sr_2ABO_6 pyrite, AS_2	pyrochlore, AB_2O_7 spinel, BA_2O_4 cubic Laves phase, LnMn_2
Materials	$\text{Ca}_3\text{Co}_2\text{O}_6$ [Chapter 3] YMnO_3 [19] Cs_2CuCl_4 [21] NaCrO_2 [25]	$\text{Gd}_3\text{Ga}_5\text{O}_{12}$ [Chapter 4] $\beta\text{-Mn}$ [Chapter 8] $\text{Na}_4\text{Ir}_3\text{O}_8$ [22]	MnO [Chapter 7] Sr_2YRuO_6 [20] NiS_2 [23]	spin ice [Chapter 2] $\text{Gd}_2\text{Ti}_2\text{O}_7$ [Chapter 5] $\text{NaCaCo}_2\text{F}_7$ [24] ZnCr_2O_4 [26] $\text{Y}_{1-x}\text{Sc}_x\text{Mn}_2$ [27]
				

Table 1.1: Lattices on which nearest-neighbour AFM interactions are frustrated, structure types where magnetic ions can occupy these lattices, and examples of frustrated magnetic materials.

of high-temperature superconductivity from spin liquid states [13, 14]. In the following sections, I introduce materials which show frustration, and discuss how the nature of frustrated states can be investigated experimentally.

1.1.1 Materials

Most frustrated magnets are crystalline transition-metal oxides, although molecular and organic examples also exist [15, 16]. Their structures generally contain triangles or tetrahedra of magnetic atoms connected either by their corners or their edges. The materials studied in this thesis are classified by their geometry in Table 1.1.

Frustrated materials are often Mott insulators, in which repulsion between electrons on neighbouring atoms leads to electrons being localised [1]. The magnetic moment of each atom results from the angular momentum of these electrons, so spins are also localised. In these materials, the most significant magnetic interactions are usually between spins which are near neighbours. However, frustrated magnetic metals are also known [27–29], although less well-understood than their insulating counterparts.

1.1.2 Experimental Methods

The presence of frustration can be identified by measuring the temperature-dependence of the magnetic susceptibility [1], which is the ratio of the magnetisation M induced by a small applied magnetic field $H \approx B/\mu_0$, where μ_0 is the permeability of free space:

$$\chi = \left(\frac{\partial M}{\partial H} \right)_T. \quad (1.1)$$

This measurement is performed using a magnetometer (e.g., a superconducting quantum interference device, a SQUID). It indicates both the average strength of magnetic interactions in the system (the Curie-Weiss constant) and the temperature T_c at which long-range magnetic order develops (shown as a sudden change in χ). Frustration results in an ordering temperature much lower than the strength of magnetic interactions [30]. A large density of low-energy magnetic states can also be apparent as an unusually large magnetic contribution to the low-temperature specific heat [31], and in some cases leads to entropy remaining as $T \rightarrow 0$ [Chapter 2] [32].

While such observations are useful in identifying frustrated materials, they provide little information on how spins are actually arranged in spin-liquid states. A number of methods can provide more detailed information, including magnetic-resonance techniques such as NMR, μ SR, and Mössbauer spectroscopy [33, 34]. Probably the most direct information about magnetic structure is obtained from neutron-scattering experiments [Section 1.3]. The neutron-scattering intensity measures the Fourier transform $S(\mathbf{Q})$ of the spin correlation function, where $\mathbf{Q}$ is a vector in reciprocal space [35]. If the magnetic structure shows long-range order, $S(\mathbf{Q})$ contains sharp peaks known as magnetic Bragg peaks [Fig. 1.2(a)]. Measurement of the positions and intensities of the magnetic Bragg peaks usually allows the ordered magnetic structure to be determined using conventional crystallographic methods [36, 37]. In the absence of frustration, thermal fluctuations destroy long-range magnetic order, leading to a paramagnetic (PM) state above T_c . For a conventional PM, $S(\mathbf{Q})$ contains broad peaks centred at the same positions as the Bragg peaks of the incipient ordered phase [Fig. 1.2(b)]. By contrast, in frustrated systems,

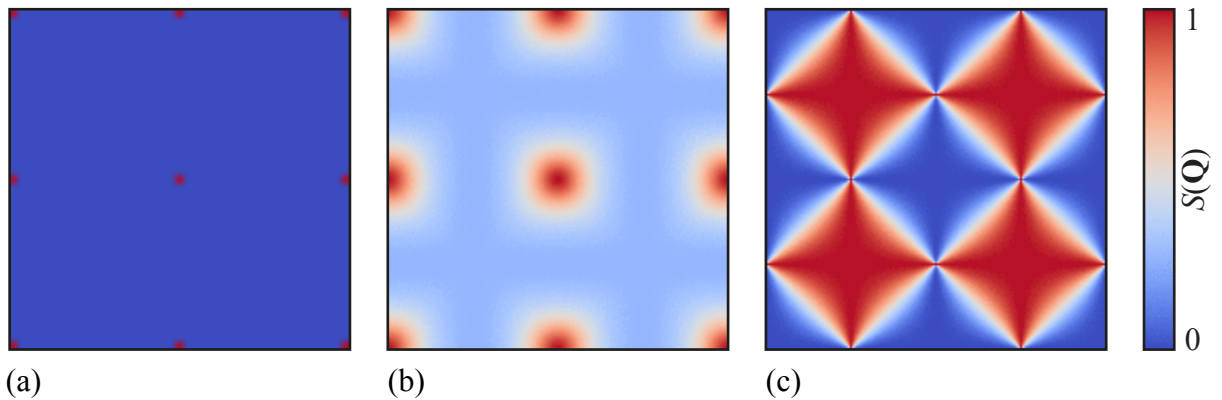


Figure 1.2: (a) Example calculation of the magnetic neutron-scattering function $S(\mathbf{Q})$ for a system without frustration below its magnetic ordering temperature T_c . (b) $S(\mathbf{Q})$ for the same system shown in (a) above T_c . (c) $S(\mathbf{Q})$ for a highly-frustrated system at low temperature. Figure based on Bramwell [38].

long-range magnetic order is suppressed primarily by the lattice geometry instead of by thermal fluctuations, leading to a spin-liquid state [5]. For a spin liquid, $S(\mathbf{Q})$ does not contain well-defined peaks; instead, it is a continuous (“diffuse”) function of $\mathbf{Q}$ which is usually highly-structured [Fig. 1.2(c)] [38]. The absence of well-defined peaks means that the conventional crystallographic methods cannot be used to analyse magnetic diffuse-scattering data for spin liquids. The development and application of methods to analyse such data is the main subject of my thesis.

1.1.3 Summary of this Chapter

The remainder of this introductory chapter is structured as follows. In Section 1.2, I present several key results from the theory of magnetism. In Section 1.3, I describe the technique of neutron scattering—the main experimental method on which the results of this thesis are built. In Section 1.4, I introduce the techniques which have been used to analyse neutron-scattering data for frustrated magnets, leading to the method of “reverse Monte Carlo” (RMC) refinement [39] which is the main approach I use in this thesis. Finally, in Section 1.5, I describe the main aims of the chapters which follow.

1.2 Models of Magnetism

In this section, I introduce some of the fundamental results of magnetism which I will use throughout this thesis, starting from isolated magnetic ions and introducing the effects of the crystal field and magnetic interactions. My treatment follows some standard texts on magnetism [1, 40].

1.2.1 Isolated Ions

Classically, magnetism originates from circulating charges: an orbiting charge carries a magnetic moment $\boldsymbol{\mu}$ which is proportional to its angular momentum $\mathbf{S}$. At the atomic scale, where the rules of quantum mechanics are followed, magnetism arises from unpaired electrons in atoms, but the proportionality between $\boldsymbol{\mu}$ and $\mathbf{S}$ remains:

$$\boldsymbol{\mu} = -g\mu_B\mathbf{S}, \quad (1.2)$$

where the negative sign arises because of the negative charge of the electron. The quantity

$$\mu_B = \frac{e\hbar}{2m_e} \quad (1.3)$$

is called the Bohr magneton; it is the natural unit for atomic magnetic moments because it is the magnetic moment of a ground-state electron in hydrogen. The g-factor g is a constant for a given material, which relates the length of the magnetic moment to the angular momentum. For an individual electron, g is very close to 2.

The introduction of quantum mechanics leads to two important differences to classical mechanics. First, in addition to angular momentum associated with orbital motion, electrons also have a source of angular momentum which is entirely quantum-mechanical in origin, called spin. Second, angular momentum is not a vector as in classical mechanics, but rather a vector operator $\hat{\mathbf{S}}$ which acts on the quantum state $|\psi\rangle$ of the system. The results of experimental measurements are given in terms of the angular-momentum quantum number S , which can only take discrete (quantised) values. The Heisenberg

uncertainty principle dictates that it is possible only to measure two quantities simultaneously and precisely: the magnitude of the angular momentum, and its projection along a single axis. These quantities are given in terms of S by

$$\hat{\mathbf{S}}^2 |\psi\rangle = S(S+1) |\psi\rangle, \quad (1.4)$$

$$\hat{S}_z |\psi\rangle = S_z |\psi\rangle, \quad (1.5)$$

where S_z is called the z -projection quantum number and can take $2S+1$ values between $-S$ and S .

Combining Eq. (1.2) and Eq. (1.4), we find an expression for the effective magnetic moment of an ion with angular-momentum quantum number S ,

$$\mu = g\mu_B \sqrt{S(S+1)}. \quad (1.6)$$

The effective magnetic moment can be determined by experimental measurements of the magnetic susceptibility. For a system of isolated magnetic moments, the non-interacting magnetic susceptibility per spin is given by Curie's law,

$$\chi_0 = \frac{\mu_0 (g\mu_B)^2 S(S+1)}{3k_B T}. \quad (1.7)$$

An alternative measurement is to apply a large magnetic field so that the spins are fully polarised along the field direction, which is taken to define the z -axis. In this case, the saturated magnetic moment is given by

$$\mu_{\text{sat}} = -g\mu_B S. \quad (1.8)$$

The effect of quantum mechanics is evident at the macroscopic scale in the difference between the magnetic moments obtained in magnetic susceptibility and saturation magnetisation: the former measures Eq. (1.4) and the latter measures Eq. (1.5) [1].

The relations above apply for a general angular momentum in quantum mechanics, regardless of its origin. For a specific ion, the value of angular momentum quantum

number is determined in the following way. Individual electrons are fermions and have spin projection quantum number $s_z = \pm\frac{1}{2}$. An electron also has an orbital projection quantum number l_z which can take $2l + 1$ values from $-l$ to l , where $l = 0, 1, 2, 3, \dots$ if the electron occupies an $s, p, d, f, \dots$ shell. For ions containing more than one electron, the total spin quantum number $S = \sum s_z$ and the total orbital angular momentum quantum number $L = \sum l_z$, where the sum is over the individual electrons. The Pauli exclusion principle dictates that the total angular momentum vanishes for filled shells. Hence, magnetism arises from partially-filled shells—in practice, usually the $3d$ shell (first transition series) or the $4f$ shell (rare earths).

If a partially-filled shell contains more than one electron, there may be many ways in which the individual s_z and l_z can be arranged, with correspondingly different S and L . Moreover, the spin and orbital angular momentum can be weakly coupled by the spin-orbit interaction, so that the total angular momentum $\hat{\mathbf{J}} = \hat{\mathbf{L}} + \hat{\mathbf{S}}$ (with quantum number J) is the relevant quantity. The values of S , L , and J can be calculated for the electronic ground state of an isolated ion using three empirical rules called Hund's rules, which are applied in sequence. First S is maximised, and second L is maximised. Finally, $J = |L - S|$ if the shell is less than half-filled, and $J = L + S$ otherwise. Hund's rules are very accurate for most rare-earth ions. In transition-metal ions, however, the effect of the local environment must be taken into account, and I consider this below.

1.2.2 Crystal-Field Theory

In a real material, the magnetic ions are not isolated, but are coordinated by other ions (ligands). The electric field due to the ligands removes the degeneracy of the $2l + 1$ electronic orbitals of the metal, because the electrostatic repulsion between the ligand and metal electrons depends on how these electrons are distributed in space, which depends in turn on which orbitals they occupy. The number of new sets of energy levels is dictated by the point symmetry of the metal-ion site, and the size of the splitting is determined by a range of factors, including the charge of the metal ion, the coordination geometry, and the identity of the ligand [41].

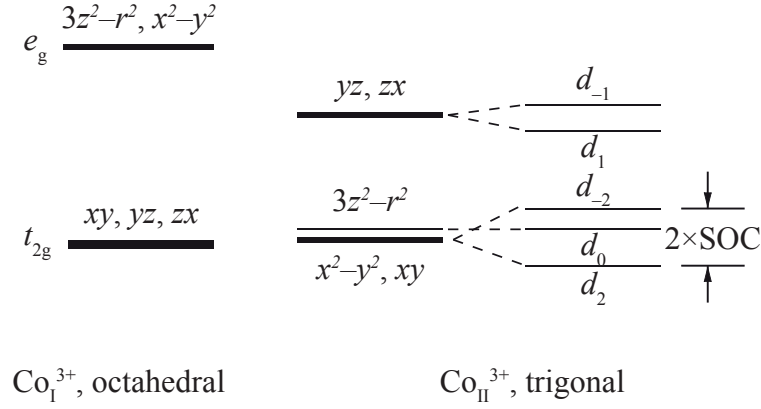


Figure 1.3: Crystal-field scheme for $\text{Ca}_3\text{Co}_2\text{O}_6$, a compound which is studied in Chapter 3. There are two crystallographically-inequivalent Co^{3+} sites, of which one is octahedrally coordinated by oxide ligands and the other has trigonal prismatic coordination. The larger crystal-field splitting for the octahedral Co^{3+} leads to a low-spin ($S = 0$) state, whereas the trigonal Co^{3+} is high-spin ($S = 2$). Figure reproduced from Wu *et al.* [43].

The crystal field has three main effects. First, in transition metal ions, the crystal-field is larger than the spin-orbit coupling. This often leads to the orbital part of the magnetic moment being partially quenched, so $\mu \approx g\mu_B\sqrt{S(S+1)}$, although in some electronic states (especially $3d^6$) a significant contribution from spin-orbit coupling may also be present [41]. Second, if the crystal field leads to a sufficiently large splitting of energy levels, then it may be energetically favourable to break Hund’s first rule and pair up spins in lower-energy crystal field energy levels (a “low-spin” state) instead of maximising the number of unpaired electron spins (a “high-spin” state). An example of this is the compound $\text{Ca}_3\text{Co}_2\text{O}_6$ which I study in Chapter 3. This system contains two crystallographically-inequivalent Co^{3+} ($3d^6$) ions with different spin states [42, 43] [Fig. 1.3].

The final important consequence of the crystal field is to generate anisotropy in the spin orientations, so that the spins prefer to point in certain directions relative to their local environment. In a PM or spin liquid, the distribution of the spin orientations is dictated by the crystallographic point symmetry of the magnetic site. At the phenomenological level, it is often possible to model the effect of the crystal field on the spin orientations

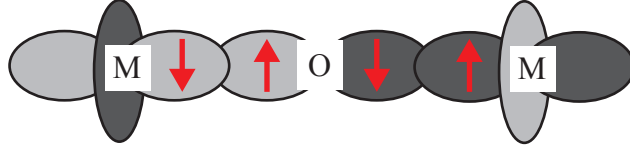


Figure 1.4: Overlap of d orbitals of transition-metal (“M”) ions with a p orbital of an oxide (“O”) ion in a M–O–M unit, leading to AFM exchange interactions. Spins are shown as red arrows.

using a single-ion term in the spin Hamiltonian,

$$H_{\text{SI}} = -\Delta \sum_i (\mathbf{S}_i \cdot \mathbf{z}_i)^2, \quad (1.9)$$

where $\mathbf{z}_i$ is a local alignment axis. If the single-ion anisotropy constant $\Delta > 0$, spins prefer to align parallel to $\mathbf{z}$ (“easy-axis anisotropy”), whereas if $\Delta < 0$ spins prefer to align perpendicular to $\mathbf{z}$ (“easy-plane anisotropy”).

1.2.3 Magnetic Interactions

In real magnetic materials, spins on different metal ions are not independent, but interact with their near neighbours. In magnetic insulators, these “exchange” interactions often do not arise from direct overlap of the atomic orbitals of the metal (“M”) ions, but are instead mediated by oxide (“O”) ions in a M–O–M unit, as shown in Fig. 1.4. Often, AFM spin alignment on neighbouring M ions is favoured, because this allows electron spins to be delocalised over the M–O–M unit without disobeying the Pauli exclusion principle, reducing the electronic kinetic energy [44].

The most common model of interactions in magnetic materials is the Heisenberg Hamiltonian. It considers spins $\mathbf{S}_i$ which are coupled by exchange interactions of strength J_{ij} ,

$$H_{\text{Heisenberg}} = -\frac{1}{2} \sum_{i,j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j, \quad (1.10)$$

where $J < 0$ denotes AFM interactions and $J > 0$ denotes FM interactions. In materials where the spin quantum number $S > 1$, it is common to approximate spins $\mathbf{S}_i$ as classical three-component vectors of length $\sqrt{S(S+1)}$. This is a good approximation in, e.g., MnO

[Chapter 7]. An important special case is if the single-ion anisotropy constant $\Delta \gg J$. Then, two possibilities exist in the temperature range $k_B T \ll \Delta$. If $\Delta < 0$, spins can be considered as two-dimensional vectors which lie within their local plane perpendicular to $\mathbf{z}$; this is called an *xy* model. Alternatively, if $\Delta > 0$, spins may be labelled simply by $\sigma = \pm 1$, depending on whether the spin is directed parallel or antiparallel to $\mathbf{z}$; this is called an Ising model. The canonical frustrated Ising model is known as “spin ice” [8, 11] and is considered in Chapter 2.

The Heisenberg, *xy*, and Ising models are very useful in understanding magnetic materials in general, and frustration in particular. The strength of J_{ij} often decreases rapidly with distance between spin pairs, so that it is often sufficient to consider interactions between only nearest-neighbour and next-nearest neighbour spins. The sign of the exchange constants can be estimated by considering the bond angles in the M–O–M exchange pathways [45] and estimates of their values can be obtained using, e.g., extended Huckel tight-binding theory [46]. Often, however, it is necessary to treat the J_{ij} as empirical parameters fitted to experimental data. Sometimes, these data are spin-wave dispersion curves collected using inelastic neutron-scattering experiments [47], but it is also possible to fit to, e.g., magnetic susceptibility data [48], NMR data [49], and magnetic diffuse-scattering data collected in the PM phase [50].

The Heisenberg Hamiltonian can be modified by including interactions of different types. While these are usually smaller than the exchange interactions, they may nevertheless have important effects in directing the magnetic ground states of frustrated systems, because the lattice geometry prevents the dominant exchange interaction from causing long-range magnetic order [51]. One of the most important of these additional interactions is the magnetic dipolar interaction,

$$H_{\text{dipolar}} = \frac{D}{2} \sum_{i,j} \frac{\mathbf{S}_i \cdot \mathbf{S}_j - 3(\mathbf{S}_i \cdot \hat{\mathbf{r}}_{ij})(\mathbf{S}_j \cdot \hat{\mathbf{r}}_{ij})}{(r_{ij}/r_1)^3}, \quad (1.11)$$

where $\hat{\mathbf{r}}_{ij} = (\mathbf{r}_j - \mathbf{r}_i)/|\mathbf{r}_j - \mathbf{r}_i|$ is the unit vector connecting spins i and j . The dipolar

interaction constant is fixed by the crystal structure and the identity of the magnetic ion:

$$D = \frac{\mu_0 (g\mu_B)^2}{4\pi r_1^3}, \quad (1.12)$$

where r_1 is the nearest-neighbour distance. Dipolar interactions can be important in rare-earth magnets because large effective magnetic moments can coexist with weak exchange interactions. There are also several other possible interactions, including biquadratic exchange ($\propto (\mathbf{S}_i \cdot \mathbf{S}_j)^2$) [52] and the Dzyaloshinsky-Moriya interaction [53, 54], but I do not consider these in this thesis.

Once the Hamiltonian $H = H_{\text{SI}} + H_{\text{Heisenberg}} + H_{\text{dipolar}} + \dots$ has been defined for a system, how can it be solved? Some exact solutions exist [55]; the earliest (and probably most famous) example is the Ising spin chain [3], which I use in Chapter 3. Usually, however, it is necessary to look for approximate solutions. Two of the most common methods are Monte Carlo (MC) simulations and analytical approximations such as mean-field theory; I consider both in Section 1.4.1. An important result from mean-field theory describes the magnetic susceptibility,

$$\chi = \frac{\mu_0 \mu^2}{3k_B(T - \theta)}, \quad (1.13)$$

which is the Curie-Weiss law. For a magnetic insulator, the Curie-Weiss temperature

$$\theta = \frac{S(S+1)}{3k_B} \sum_n Z_n J_n \quad (1.14)$$

is proportional to the average magnetic interaction strength in the material, where $n = 1, 2, \dots$ labels near-neighbour shells in order of increasing distance, and Z_n is the coordination number for shell n . The Curie-Weiss law applies at high temperature ($T > \theta$), and allows both μ and θ to be obtained by fitting Eq. (1.13) to experimental susceptibility data.

For frustrated magnetic materials, a useful quantity is the “frustration parameter” [30],

$$f = \frac{|\theta|}{T_c}, \quad (1.15)$$

where T_c is the magnetic ordering temperature of the material. A large value of f indicates that T_c is suppressed below the energy of magnetic interactions, which implies that frustration may play an important role. Generally, materials with $f \gtrsim 10$ are classified as highly frustrated, while materials with smaller f are considered as weakly frustrated [56].

1.2.4 Magnetic Order

The third law of thermodynamics dictates that the spin system should occupy a non-degenerate quantum ground state as $T \rightarrow 0$, which usually—but not necessarily—involves the formation of long-range order [57, 58]. In order to describe long-range magnetic order, it is necessary first to consider the crystal structure on which it is based. All the materials considered in this thesis are crystals, in which the time-averaged atomic positions can be described by infinite repetition of a unit cell in three dimensions. The axes of the unit cell are defined by basis vectors $\mathbf{a}, \mathbf{b}, \mathbf{c}$, having lengths a, b, c and angles $\alpha, \beta, \gamma (\geq 90^\circ)$ between the vectors. For most of the materials I will consider, the unit cell is cubic ($a = b = c, \alpha = \beta = \gamma = 90^\circ$). The exception is $\text{Ca}_3\text{Co}_2\text{O}_6$ [Chapter 3], which has a hexagonal unit cell ($a = b \neq c, \alpha = \beta = 90^\circ, \gamma = 120^\circ$) [59].

The time-averaged position of an atom in the unit cell is given by

$$\mathbf{r}_\rho = x\mathbf{a} + y\mathbf{b} + z\mathbf{c}, \quad (1.16)$$

where x, y, z are fractional coordinates which take values between zero and one, and $\rho \in \{1, n\}$ for a unit cell containing n atoms. The position of a specific unit cell in the crystal is given by a lattice vector

$$\mathbf{R} = t_1\mathbf{a} + t_2\mathbf{b} + t_3\mathbf{c}, \quad (1.17)$$

where t_1, t_2, t_3 are integers. Combining Eqs. (1.16) and (1.17), the time-averaged position of an arbitrary atom in a crystal is given by

$$\mathbf{r}_i = \mathbf{r}_\rho + \mathbf{R}. \quad (1.18)$$

Anticipating the next section, I also define the reciprocal axes,

$$\mathbf{a}^* = \frac{2\pi}{V} \mathbf{b} \times \mathbf{c}, \quad (1.19)$$

$$\mathbf{b}^* = \frac{2\pi}{V} \mathbf{c} \times \mathbf{a}, \quad (1.20)$$

$$\mathbf{c}^* = \frac{2\pi}{V} \mathbf{a} \times \mathbf{b}, \quad (1.21)$$

where $V = \mathbf{a} \cdot \mathbf{b} \times \mathbf{c}$ is the unit-cell volume [60]. For a system with orthogonal axes, $\mathbf{a}^* = (2\pi/a) \mathbf{a}$, $\mathbf{b}^* = (2\pi/b) \mathbf{b}$, and $\mathbf{c}^* = (2\pi/c) \mathbf{c}$. A reciprocal-lattice vector is given by

$$\mathbf{G} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*, \quad (1.22)$$

where h, k, l are integers called Miller indices.

The onset of magnetic order can enlarge the unit cell; an example of this is shown in Fig. 1.5. There are two common approaches to describe magnetic order [37]. The first is to define a magnetic unit cell as a multiple of the crystallographic unit cell; in Fig. 1.5, the magnetic unit cell is double the length of crystallographic unit cell along $\mathbf{a}$. In this case, h, k, l are now integers defined with respect to this new magnetic unit cell. The alternative approach is to maintain the crystallographic unit cell, but introduce a magnetic propagation vector $\mathbf{k}$ which describes how the orientations of spins in one unit cell are related to those in the next. These two approaches are equivalent provided that the magnetic structure can be described by a rational number of unit cells.

In the propagation-vector formalism, the orientation of an arbitrary spin is written in terms of Bloch waves [61]:

$$\mathbf{S}_\rho(\mathbf{t}) = \sum_{\mathbf{k}} \mathbf{S}_\rho^{\mathbf{k}}(\mathbf{0}) \exp(2\pi i \mathbf{k} \cdot \mathbf{t}), \quad (1.23)$$

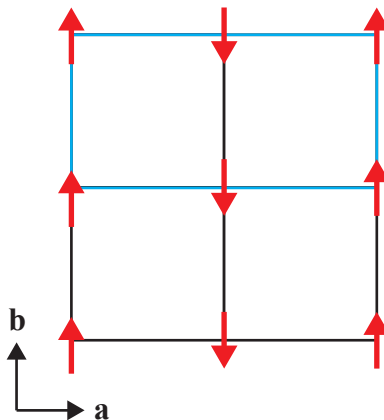


Figure 1.5: Example of enlargement of the unit cell due to magnetic ordering. Spin orientations are shown as red arrows, the crystallographic unit cell boundaries as black lines, and the magnetic unit cell as a blue rectangle.

where $\mathbf{S}_\rho^{\mathbf{k}}(\mathbf{0})$ is the basis vector for atom ρ in the crystallographic unit cell, and $\mathbf{S}_\rho(\mathbf{t})$ is the spin orientation of atom ρ in the unit cell with lattice translation $\mathbf{t} = [t_1, t_2, t_3]$ [Eq. (1.17)]. In Fig. 1.5, $\mathbf{k} = [\frac{1}{2}, 0]^*$. Usually, the magnetic order involves only a single propagation vector (so the sum in Eq. (1.23) contains one term only). So-called multi- $\mathbf{k}$ structures are also possible, but can be difficult to distinguish from single- $\mathbf{k}$ structures [37, 62]; I consider this problem in relation to the frustrated AFM $\text{Gd}_2\text{Ti}_2\text{O}_7$ in Chapter 5.

An important point is that the choice of unit cell is not unique. Usually, it is simplest to choose the smallest-possible unit cell which respects the symmetry and periodicity of the system, and has convenient (e.g., orthogonal) axes. Sometimes, however, it is useful to use a very large unit cell or “supercell”, which I discuss in Chapter 6 [63, 64].

1.3 Neutron Scattering

Neutrons have several properties that make them ideal probes of the structural and magnetic properties of materials. First, they are electrically neutral and interact weakly with matter, so that they measure the whole sample and not just its surface. Second, neutrons have spin $S = \frac{1}{2}$, so interact with the magnetic field in the sample. Third, the neutron energy can be tuned to match the energy and length scales relevant to the material being studied. Neutron scattering provides especially direct information on the correlations of spins, and is the main technique used in this thesis to probe the magnetic behaviour of

frustrated magnets.

In this section, I first introduce the theory of neutron scattering, focussing on the key results of magnetic neutron scattering [35, 65, 66]. I then discuss the experimental aspects of neutron scattering and introduce the neutron-scattering instruments which were used to collect the data of this thesis.

1.3.1 General Aspects

Neutrons are subatomic particles which are described by quantum mechanics, and therefore have both wave and particle-like properties. A beam of neutrons is a wave propagating with wavevector

$$\mathbf{k} = \frac{2\pi}{\lambda} \hat{\mathbf{k}}, \quad (1.24)$$

where the unit vector $\hat{\mathbf{k}}$ gives the direction of propagation, and the neutron wavelength is given by the de Broglie relation

$$\lambda = \frac{h}{m_n v}, \quad (1.25)$$

where m_n is the neutron mass, h is Planck's constant, and v is the neutron velocity. The geometry of a simple neutron-scattering experiment is shown in Fig. 1.6. A beam of neutrons is created with initial momentum $\hbar \mathbf{k}_i$ and initial energy $\hbar \omega_i$, where ω denotes angular frequency. This neutron beam is directed at a sample and is scattered by it. Two interactions contribute to the scattering: between the neutron and the nuclei (via the strong nuclear force), and between the neutron magnetic moment and the magnetic field due to unpaired electrons (via the magnetic dipolar interaction). The energy and momentum of the neutrons can change during the scattering process, so that a scattered neutron has final momentum $\hbar \mathbf{k}_f$ and final energy $\hbar \omega_f$. The energy transferred from neutron to sample is given by

$$\hbar \omega = \hbar (\omega_i - \omega_f) \quad (1.26)$$

and the momentum transferred from neutron to sample is given by

$$\hbar \mathbf{Q} = \hbar (\mathbf{k}_i - \mathbf{k}_f). \quad (1.27)$$

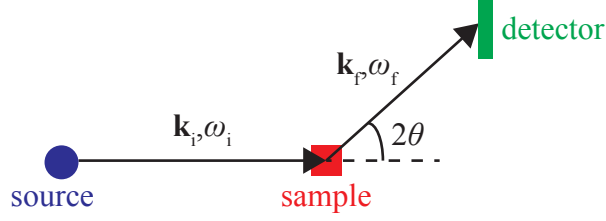


Figure 1.6: Schematic diagram of a simple neutron-scattering experiment.

Finally, a neutron detector measures the neutron-scattering intensity as a function of $\mathbf{Q}$ and ω ,

$$I(\mathbf{Q}, \omega) = \frac{\left(\begin{array}{c} \text{number of neutrons scattered per second into solid angle } d\Omega \\ \text{with final } \omega \text{ between } \omega_f \text{ and } \omega_f + d\omega_f \end{array} \right)}{N\Phi d\Omega d\omega_f},$$

where Φ is the incident neutron flux and N is the number of scattering centres in the sample.

A key distinction in neutron scattering is between elastic and inelastic scattering. The elastic scattering provides information about the time-averaged structure of the material and appears as a delta-function peak at $\omega = 0$. The inelastic scattering provides information about the dynamics of the material and is a continuous function of ω [35]:

$$I(\mathbf{Q}, \omega) = I_{\text{el}}(\mathbf{Q})\delta(\omega) + I_{\text{inel}}(\mathbf{Q}, \omega). \quad (1.28)$$

This distinction applies equally to nuclear and magnetic scattering.

In this thesis, I will often consider the “total” scattering intensity $I(\mathbf{Q})$, which provides information on the instantaneous correlations in materials. In a total-scattering (diffraction) measurement, the energy of the incoming neutron beam is chosen to be much larger than the maximum energy of dynamical processes in the material, and the energy of the scattering neutrons is not analysed [67]. Such a measurement therefore integrates $I(\mathbf{Q}, \omega)$

over ω :

$$I(\mathbf{Q}) = \frac{\text{number of neutrons scattered per second into solid angle } d\Omega}{N\Phi d\Omega} \quad (1.29)$$

$$= \int_{-\infty}^{\infty} I(\mathbf{Q}, \omega) d\omega. \quad (1.30)$$

Provided that $\hbar\omega$ is much smaller than the energy of the incoming neutrons, it is possible to assume that $|\mathbf{k}_i| \approx |\mathbf{k}_f| = k$, so that only the direction of $\mathbf{k}$ changes between the incident and scattered neutron wave; this is called the quasistatic approximation. Then, squaring Eq. (1.27) and using the definition of $\mathbf{k}$, Eq. (1.24), yields

$$Q = \frac{4\pi \sin \theta}{\lambda}, \quad (1.31)$$

which relates Q to the scattering angle and the incident neutron wavelength.

1.3.2 Nuclear Scattering

The nuclear contribution to the neutron-scattering intensity is given by the Fourier transform of the atomic positions as a function of space and time:

$$I_{\text{nuc}}(\mathbf{Q}, \omega) = \frac{k_f}{k_i} \frac{1}{2\pi N} \int \sum_{i,j} b_i b_j \langle \exp [i (\mathbf{Q} \cdot \mathbf{r}_{ij}(t) - \omega t)] \rangle dt, \quad (1.32)$$

where N is the number of atoms in the system, b_i is the neutron-scattering length of atom i , $\mathbf{r}_{ij}(t) = \mathbf{r}_j(t) - \mathbf{r}_i(0)$ is the displacement between atoms i and j as a function of time t , and angle brackets denote an average over initial times [35, 67]. In this thesis, I will only use special cases of Eq. (1.32), which I introduce below.

1.3.2.1 Coherent and incoherent scattering

The total nuclear scattering intensity defined by Eq. (1.30) can be written as a sum of two terms:

$$I_{\text{nuc}}(\mathbf{Q}) = I_{\text{incoh}} + I_{\text{coh}}(\mathbf{Q}). \quad (1.33)$$

The first term in Eq. (1.33) is called the incoherent scattering intensity and is a consequence of the fact that different atoms of the same element may have different scattering lengths, if the element exists as a mixture of isotopes or has nuclear spin $I > 0$. The incoherent scattering intensity is given by

$$I_{\text{incoh}} = \frac{1}{N} \sum_i \left(\overline{b_i^2} - \bar{b}_i^2 \right), \quad (1.34)$$

where overbars indicate that the squared scattering lengths $\overline{b_i^2}$ and $\bar{b}_i^2$ have been averaged over all atoms of the same element as atom i . Incoherent scattering contributes a flat background to the total scattering intensity and contains no information about the crystal structure.

The second term in Eq. (1.33) is called the coherent scattering intensity. For a single-crystal sample, it is given by [35, 67]

$$I_{\text{coh}}(\mathbf{Q}) = \frac{1}{N} \sum_{i,j} \bar{b}_i \bar{b}_j \langle \exp [\mathbf{i} \mathbf{Q} \cdot \mathbf{r}_{ij}(0)] \rangle, \quad (1.35)$$

where $\mathbf{r}_{ij}(0) = \mathbf{r}_j(0) - \mathbf{r}_i(0)$ is the displacement between the instantaneous positions of atoms i and j . Alternatively, if the sample is a powder (polycrystalline solid) or a liquid, then the three-dimensional (3D) scattering vector $\mathbf{Q}$ is collapsed onto a single axis $Q = |\mathbf{Q}|$. The coherent scattering intensity is then given by the Debye formula [68],

$$I_{\text{coh}}(Q) = \frac{1}{N} \sum_i \bar{b}_i^2 + \frac{1}{N} \sum_{j \neq i} \bar{b}_i \bar{b}_j \left\langle \frac{\sin [Q r_{ij}(0)]}{Q r_{ij}(0)} \right\rangle, \quad (1.36)$$

where $r_{ij}(0) = |\mathbf{r}_j(0) - \mathbf{r}_i(0)|$.

1.3.2.2 Nuclear Bragg and diffuse scattering

A structure which is ordered over a macroscopic length-scale shows sharp reflections in its scattering pattern. These sharp peaks are called Bragg peaks, after the father-son team who first described them in 1913 [69]. In a crystal, the coherent scattering is dominated by nuclear Bragg peaks at the reciprocal-lattice vectors $\mathbf{Q} = \mathbf{G}$, where $\mathbf{G}$ is defined by

Eq. (1.22). The nuclear Bragg scattering intensity is given by [35]

$$I_{\text{nuc,Bragg}}(\mathbf{Q}) = \frac{(2\pi)^3}{nV} \sum_{\mathbf{G}} |F_{\text{nuc}}(\mathbf{G})|^2 \delta(\mathbf{Q} - \mathbf{G}), \quad (1.37)$$

in which the unit-cell structure factor

$$F_{\text{nuc}}(\mathbf{G}) = \sum_{\rho=1}^n \bar{b}_{\rho} T_{\rho}(G) \exp(i\mathbf{G} \cdot \mathbf{r}_{\rho}), \quad (1.38)$$

where $\mathbf{r}_{\rho}$ is the time-averaged (crystallographic) position of atom $\rho \in \{1, n\}$ in the unit cell. The factor T_{ρ} in Eq. (1.37) is called the Debye-Waller factor, and arises because nuclei are not fixed at their average positions, but are actually “smeared” due to thermal motion and/or static disorder [70, 71]. Assuming these deviations are harmonic and isotropic,

$$T_i(Q) = \exp\left(-\frac{1}{2}U_{\text{iso},\rho}Q^2\right), \quad (1.39)$$

which reduces the scattering intensity at large values of Q [72].

For a crystalline solid, the Bragg peaks account for most—but not all—of the the coherent scattering intensity. The remaining intensity is called “diffuse scattering”, and consists of broad features lying beneath and between the Bragg peaks. Diffuse scattering arises from deviations from perfect long-range order. In a crystal, this may due to, e.g., correlated vibrational motion (phonons), static disorder, or correlated disorder in site occupancies. By contrast, in a liquid or amorphous material, there is no long-range order in atomic positions, so that $I_{\text{coh}}(Q)$ contains only diffuse scattering [73].

1.3.2.3 Crystal structure solution and refinement

The subject of crystallography is concerned with solving crystal structures by analysis of the Bragg scattering [74]. The positions of the Bragg peaks allow the dimensions of the unit cell to be determined, while the intensities of the Bragg peaks contain information about the positions of atoms within the unit cell. The key problem of crystallography is that only the magnitude (and not the phase) of $F_{\text{nuc}}(\mathbf{G})$ can be measured using con-

ventional scattering experiments [Eq. (1.37)]. Structure solution is feasible despite this because the number of possible structures is restricted by symmetry, which dictates that the structure is described by one of the 230 possible space groups [75]. This symmetry restriction means that it can be possible to solve crystal structures from powder-diffraction data. The approach is to refine an initial guess at the structure against the full diffraction pattern $I(Q)$, using a least-squares procedure to minimise the sum of squared residuals between calculated and experimental pattern [36, 76]:

$$\chi^2 = \sum_i W_i (I_i^{\text{expt}} - I_i^{\text{calc}})^2, \quad (1.40)$$

where superscript “calc” and “expt” denote calculated and experimental patterns respectively, and W_i is the weighting for data point i . The calculated pattern

$$I_i = B_i + s \sum_{\mathbf{G}} L_i A_i P_i |F_{\text{nuc}}(\mathbf{G})|^2 R_i, \quad (1.41)$$

where $|F_{\text{nuc}}(\mathbf{G})|^2$ is the structure factor given by Eq. (1.38). The other factors in Eq. (1.41) are written in terms of refined parameters: B_i is a background function, s is an overall intensity scale factor, L_i is the Lorentz factor (which depends on the geometry of the instrument), A_i takes account of neutron absorption and extinction by the sample, P_i takes account of preferred orientation of powder grains, and R_i is the peak-shape function (which includes instrumental and sample-dependent contributions) [36, 77]. This approach is known as Rietveld refinement [76], and is used in Chapter 5.

1.3.3 Magnetic Scattering

In this section, I describe the relationship between the magnetic neutron-scattering intensity $I(\mathbf{Q}, \omega)$ and the magnetic properties of the sample. To simplify the presentation, I make some assumptions, which are satisfied for all the materials studied in this thesis. First, I consider materials which contain only a single type of magnetic ion. Second, I assume that the magnetic ions exist within a crystal, and nuclei undergo only isotropic and harmonic displacements from their crystallographic positions. Third, I assume that

the unpaired electron density is distributed isotropically around the nuclear positions. Finally, I assume that the spin orientations and atomic positions are uncorrelated (i.e., that magneto-elastic coupling is negligibly small).

Within these assumptions, the $\mathbf{Q}$ and ω -dependent magnetic neutron-scattering intensity is given by [35, 66]

$$I(\mathbf{Q}, \omega) = \frac{k_f}{k_i} C T^2(Q) [gf(Q)]^2 S(\mathbf{Q}, \omega). \quad (1.42)$$

The total magnetic neutron-scattering intensity (a function of $\mathbf{Q}$ only) is given by

$$I(\mathbf{Q}) = C T^2(Q) [gf(Q)]^2 S(\mathbf{Q}). \quad (1.43)$$

In the rest of this thesis, I use $I(\mathbf{Q})$ and $S(\mathbf{Q})$ to refer to the magnetic scattering alone, rather than the combined magnetic and nuclear scattering.

For the systems I consider, the physics is contained in the magnetic scattering functions $S(\mathbf{Q}, \omega)$ or $S(\mathbf{Q})$. The other factors in Eqs. (1.42) and (1.43) are needed to make quantitative comparisons between models and experiment; I consider them each in turn. First, C is a constant with units of area, which places the intensity on an absolute scale:

$$C = \left(\frac{\mu_0 \gamma_n e^2}{4\pi 2m_e} \right)^2 \quad (1.44)$$

$$= 0.07265 \text{ barn},$$

where γ_n is neutron magnetic moment in nuclear magnetons, m_e is the mass of the electron, and e is the charge of the electron. Second, $T^2(Q)$ is the squared Debye-Waller factor of the magnetic ion [Eq (1.39)]. Finally, the magnetic form factor $f(Q)$ arises because the unpaired electron density is not localised at the positions of the nuclei; its effect is therefore to attenuate the scattering intensity at high Q , similar to the Debye-Waller factor [78]. At low temperature, the effect of the magnetic form factor is much larger than the Debye-Waller factor, which can often be neglected.

The magnetic scattering function $S(\mathbf{Q}, \omega)$ is the Fourier transform in space and time

of the correlations between spin pairs i, j [35, 66]

$$S(\mathbf{Q}, \omega) = \frac{1}{2\pi N} \int \sum_{i,j} \langle \mathbf{S}_i^\perp(0) \cdot \mathbf{S}_j^\perp(t) \rangle \exp[i(\mathbf{Q} \cdot \mathbf{r}_{ij} - \omega t)] dt, \quad (1.45)$$

where $\mathbf{r}_{ij} = \mathbf{r}_j - \mathbf{r}_i$ is the vector separation between the time-averaged positions of spins i and j [35, 66]. The selection rule for magnetic scattering is that neutrons are sensitive only to the component of spin perpendicular to $\mathbf{Q}$, given by [35, 66]

$$\mathbf{S}_i^\perp = \mathbf{S}_i - \frac{(\mathbf{S}_i \cdot \mathbf{Q}) \mathbf{Q}}{Q^2}. \quad (1.46)$$

1.3.3.1 Total, elastic, and inelastic scattering

The most important equation in this thesis is the total magnetic scattering function,

$$S(\mathbf{Q}) = \frac{1}{N} \sum_{i,j} \langle \mathbf{S}_i^\perp(0) \cdot \mathbf{S}_j^\perp(0) \rangle \exp(i\mathbf{Q} \cdot \mathbf{r}_{ij}), \quad (1.47)$$

which is the integral of $S(\mathbf{Q}, \omega)$ over energy transfer [Eq. (1.30)]. In the rest of this thesis, I suppress the angle brackets in Eq. (1.47) for the sake of simplicity of notation, and write

$$S(\mathbf{Q}) = \frac{1}{N} \sum_{i,j} \mathbf{S}_i^\perp \cdot \mathbf{S}_j^\perp \exp(i\mathbf{Q} \cdot \mathbf{r}_{ij}). \quad (1.48)$$

This formula underlies the description of all the magnetic scattering which I refer to in later chapters. It measures the correlations between instantaneous spin orientations, providing a “snapshot” picture of the magnetic structure [35, 66].

I also define the elastic magnetic scattering function,

$$S_{\text{el}}(\mathbf{Q}) = \frac{1}{N} \sum_{i,j} \langle \mathbf{S}_i \rangle^\perp \cdot \langle \mathbf{S}_j \rangle^\perp \exp(i\mathbf{Q} \cdot \mathbf{r}_{ij}), \quad (1.49)$$

which contains information about correlations of the time-average spin orientations, and describes a delta-function peak in energy transfer at $\omega = 0$ [Eq. (1.28)]. Although the formulae for $S_{\text{el}}(\mathbf{Q})$ [Eq. (1.49)] and $S(\mathbf{Q})$ [Eq. (1.47)] look similar, they have different

meanings. In a PM or spin liquid, $S_{\text{el}} = 0$ because there is no time-averaged magnetic structure [67]. By contrast, $S(\mathbf{Q}) \neq 0$ because instantaneous spin correlations are still present. While $S_{\text{el}} = 0$ means that there is no delta-function magnetic scattering at $\omega = 0$, the inelastic scattering may still have a broad maximum at $\omega = 0$. For example, it is common in paramagnets for the spins to relax in time according to an exponential decay, and in this case the inelastic scattering is a Lorentzian peak centred at $\omega = 0$ [79].

1.3.3.2 Sum rules

The magnetic scattering function obeys several sum rules [66, 79]. The most important of these in this thesis is the total-moment sum rule, which states that

$$\int S(\mathbf{Q}) d\mathbf{Q} = \frac{2}{3} S(S+1) \int d\mathbf{Q}, \quad (1.50)$$

where the integrals extend over all reciprocal space (or a smaller region of reciprocal space if $S(\mathbf{Q})$ is periodic), and the factor of $\frac{2}{3}$ arises because of the projection of spin perpendicular to $\mathbf{Q}$, Eq. (1.57). This rule applies regardless of the magnetic state of the sample, i.e., it holds for magnetically-ordered systems and paramagnets. The assumptions are that the quasistatic approximation remains satisfied at all temperatures where the rule is applied, and that the spin value S remains constant (which may be broken if, e.g., a high-spin to low-spin transition occurs).

1.3.3.3 Magnetic Bragg and diffuse scattering

Just as the long-range order of atomic positions in a crystal yields nuclear Bragg scattering, the long-range order of spins yields magnetic Bragg scattering, which is usually the dominant contribution to $S(\mathbf{Q})$ in magnetically-ordered materials. Similar to Eq. (1.37), the magnetic Bragg scattering factor is given by [35, 66]

$$S_{\text{Bragg}}(\mathbf{Q}) = \frac{(2\pi)^3}{nV} \sum_{\mathbf{G}} |\mathbf{F}(\mathbf{G})|^2 \delta(\mathbf{Q} - \mathbf{G}), \quad (1.51)$$

in which V is the volume of the magnetic unit cell, $\mathbf{G}$ is a reciprocal-lattice vector of the magnetic unit cell, and

$$\mathbf{F}(\mathbf{G}) = \sum_{\rho=1}^n \langle \mathbf{S}_{\rho} \rangle^{\perp} \exp(i\mathbf{G} \cdot \mathbf{r}_{\rho}) \quad (1.52)$$

is the magnetic structure factor, where $\langle \mathbf{S}_{\rho} \rangle$ is the time-averaged orientation of spin $\rho \in \{1, n\}$ in the magnetic unit cell. In practice, Eq. (1.51) is modified by the same experimental factors (instrumental resolution, absorption, etc.) discussed in Section 1.3.2.3.

In paramagnets and spin liquids, the absence of long-range magnetic order means that no magnetic Bragg scattering is observed, and $S(\mathbf{Q})$ consists entirely of magnetic diffuse scattering. The lack of long-range order does not, however, mean that these systems are random, because strong spin correlations can persist over short length-scales. The presence of short-range correlations means that the magnetic diffuse scattering is not flat but shows a large amount of structure [38, 80–82]. This is a signature of spin-liquid states [38] and was shown in Fig. 1.2.

Even in magnetically-ordered materials, however, the structure at microscopic length-scales will not resemble exactly the average magnetic structure. In fact, deviations from the average magnetic structure always arise, e.g., because of spin waves [63], leading to magnetic diffuse scattering in $S(\mathbf{Q})$. An example of this [64] is shown in Fig. 1.7 for MnO below its AFM ordering temperature [Chapter 7]. I now discuss how Bragg and diffuse scattering can be separated for systems where long-range and short-range spin correlations coexist, a description I will use in Chapter 5 to describe the partially-ordered magnet $\text{Gd}_2\text{Ti}_2\text{O}_7$ [62]. This approach is based on the formalism of Frey [83]. I consider a finite spin configuration containing L^3 magnetic unit cells, with n spins in each magnetic unit cell. Each spin is labelled by the origin of its particular magnetic unit cell $(\mathbf{R}, \mathbf{R}')$ and an index $\rho \in \{1, n\}$ which labels the site within the unit cell, so that the position of spin $\mathbf{S}_i \equiv \mathbf{S}_{\rho}(\mathbf{R})$ is given by $\mathbf{r}_i = \mathbf{r}_{\rho} + \mathbf{R}$. I write a spin vector at site i in the configuration as a sum of an average and a fluctuation:

$$\mathbf{S}_i \equiv \langle \mathbf{S}_i \rangle + [\mathbf{S}_i - \langle \mathbf{S}_i \rangle], \quad (1.53)$$

where $\langle \mathbf{S}_i \rangle$ is the average spin direction for site i and $\Delta \mathbf{S}_i \equiv \mathbf{S}_i - \langle \mathbf{S}_i \rangle$ is the spin fluctuation at site i . The average spin direction for each site is given by the average over all the magnetic unit cells in the configuration, $\langle \mathbf{S}_\rho \rangle \equiv (1/L^3) \sum_{\mathbf{R}} \mathbf{S}_\rho(\mathbf{R})$; this configurational average is equivalent to the time average by the ergodic principle [58]. Substituting Eq. (1.53) into Eq. (1.48) yields

$$\begin{aligned} S(\mathbf{Q}) = & \frac{1}{N} \sum_{i,j} \langle \mathbf{S}_i \rangle^\perp \cdot \langle \mathbf{S}_j \rangle^\perp \exp(i\mathbf{Q} \cdot \mathbf{r}_{ij}) \\ & + \frac{1}{N} \sum_{i,j} \Delta \mathbf{S}_i^\perp \cdot \Delta \mathbf{S}_j^\perp \exp(i\mathbf{Q} \cdot \mathbf{r}_{ij}) + \text{cross terms.} \end{aligned} \quad (1.54)$$

For a real crystal, the cross terms in Eq. (1.54) vanish, because correlations between the average magnetic structure and the short-range deviations cannot persist over an infinite range, from their definitions. Hence, the total scattering intensity can be written as a sum of Bragg and diffuse contributions,

$$S(\mathbf{Q}) = S_{\text{Bragg}}(\mathbf{Q}) + S_{\text{diffuse}}(\mathbf{Q}). \quad (1.55)$$

The Bragg scattering arises from correlations of the average spin directions and is given by Eq. (1.51), while the diffuse scattering arises from correlated fluctuations of the spins away from their average directions.

1.3.3.4 Powder averaging

One of the main aims of this thesis is to analyse powder diffuse-scattering data for spin liquids. An exact expression for the spherical (powder) average of Eq. (1.48) was given in the 1960s by Blech and Averbach [84]; I sketch their derivation here. Taking Eq. (1.48) as the starting point, I first separate out the $i = j$ term in sum over spin pairs, which yields

$$S(\mathbf{Q}) = \frac{2}{3} |\mathbf{S}|^2 + \frac{1}{N} \sum_{j \neq i} \mathbf{S}_i^\perp \cdot \mathbf{S}_j^\perp \cos(\mathbf{Q} \cdot \mathbf{r}_{ij}), \quad (1.56)$$

where $|\mathbf{S}|^2 = S(S+1)$. I then define a local coordinate system for each pair of spins i, j , in which the local $\mathbf{z}$ axis is directed along the vector separating the pair of spins,

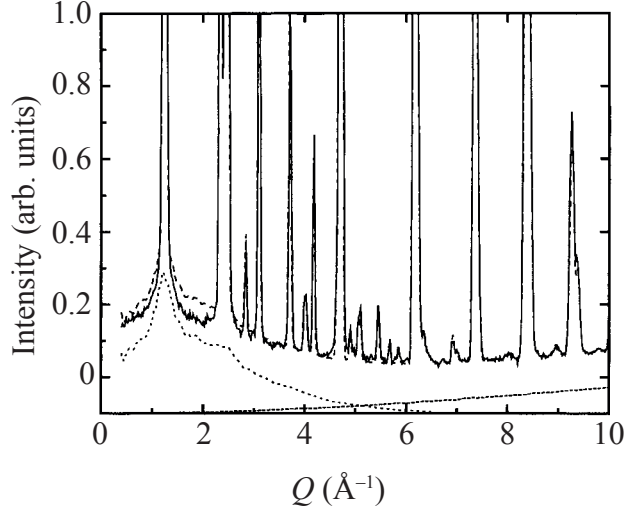


Figure 1.7: Bragg and diffuse scattering for MnO at $T = 15$ K, well below its AFM ordering temperature $T_N = 118$ K. The figure shows experimental data (solid line), the model calculation (dashed line), magnetic diffuse scattering (dotted line at lower Q), and the nuclear diffuse scattering (short-dashed line at higher Q); the latter two curves are vertically displaced by -0.1 units for clarity. Figure reproduced from Møllergård and McGreevy [64].

the local $\mathbf{x}$ axis is perpendicular to $\mathbf{z}$ and lies the plane of $\mathbf{S}_i$, and $\mathbf{y}$ is the remaining vector in a right-handed set. This gives for the coordinate axes: $\mathbf{z} = \mathbf{r}_{ij}/r_{ij}$, $\mathbf{x} = [\mathbf{S}_i - (\mathbf{S}_i \cdot \mathbf{z})\mathbf{z}] / |\mathbf{S}_i - (\mathbf{S}_i \cdot \mathbf{z})\mathbf{z}|$, and $\mathbf{y} = \mathbf{z} \times \mathbf{x}$. Within this local coordinate system, I apply the identity

$$\mathbf{S}_i^\perp \cdot \mathbf{S}_j^\perp = \sum_{\alpha, \beta} \left(\delta^{\alpha\beta} - \frac{Q^\alpha Q^\beta}{Q^2} \right) S_i^\alpha S_j^\beta, \quad (1.57)$$

which follows from Eq. (1.46). Finally, I write the components $\alpha, \beta \in \{x, y, z\}$ of $\mathbf{Q}$ in spherical polar coordinates, $\mathbf{Q} = [Q \sin \theta \cos \varphi, Q \sin \theta \sin \varphi, Q \cos \theta]$, where the angles θ and φ are defined by Fig. 1.8. Writing Eq. (1.57) in spherical polar coordinates and substituting the result into Eq. (1.56) gives an expression for $S(\mathbf{Q}) = S(Q, \theta, \varphi)$. The spherical integrals over θ and φ can then be done by hand, which gives the final result

$$S(Q) = \frac{2}{3}|\mathbf{S}|^2 + \frac{1}{N} \sum_{j \neq i} \left[A_{ij} \frac{\sin Qr_{ij}}{Qr_{ij}} + B_{ij} \left(\frac{\sin Qr_{ij}}{(Qr_{ij})^3} - \frac{\cos Qr_{ij}}{(Qr_{ij})^2} \right) \right], \quad (1.58)$$

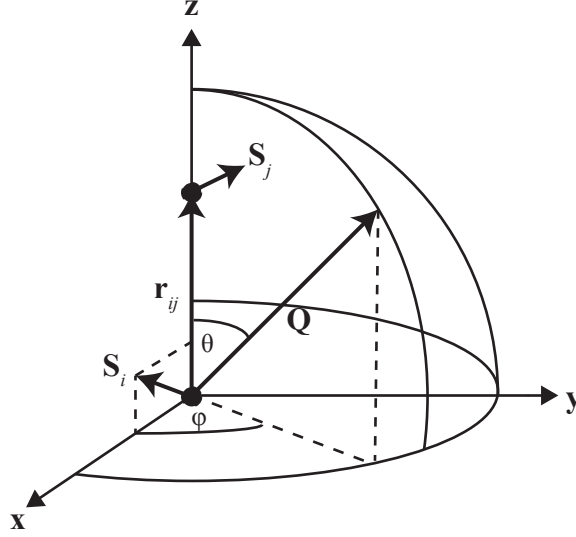


Figure 1.8: Local spherical coordinate system used to calculate the powder average of the magnetic neutron-scattering function.

where the spin correlation coefficients A_{ij} and B_{ij} are given by

$$A_{ij} = \mathbf{S}_i \cdot \mathbf{S}_j - (\mathbf{S}_i \cdot \mathbf{z})(\mathbf{S}_j \cdot \mathbf{z}), \quad (1.59)$$

$$B_{ij} = 3(\mathbf{S}_i \cdot \mathbf{z})(\mathbf{S}_j \cdot \mathbf{z}) - \mathbf{S}_i \cdot \mathbf{S}_j. \quad (1.60)$$

The double sum over spin pairs in Eq. (1.58) excludes the self-scattering terms, for which $i = j$. These terms give the additive factor of $\frac{2}{3}|\mathbf{S}|^2$ in Eq. (1.58). In an ideal PM, with zero correlation between different spins, this self-scattering is all that is measured. In a real PM, however, some degree of spin correlation is still present, often to temperatures far above the temperature of magnetic ordering [63].

The exact result for the powder scattering intensity has, in fact, been used only rarely in the literature. Instead, an approximate formula has often been used (see, e.g., [85–87]), which is valid only for isotropic spin systems—materials in which the spin orientations are uncorrelated with the local coordination geometry. In this particular case, $(\mathbf{S}_i \cdot \mathbf{z})(\mathbf{S}_j \cdot \mathbf{z}) = \langle \cos^2 \theta \rangle \mathbf{S}_i \cdot \mathbf{S}_j = \frac{1}{3} \mathbf{S}_i \cdot \mathbf{S}_j$, where angle brackets here denote a spherical average, and the powder-averaged scattering intensity is given by [88]

$$S_{\text{iso}}(Q) = \frac{2}{3} \left(|\mathbf{S}|^2 + \frac{1}{N} \sum_{j \neq i} \mathbf{S}_i \cdot \mathbf{S}_j \frac{\sin Q r_{ij}}{Q r_{ij}} \right), \quad (1.61)$$

which is analogous to the Debye formula for nuclear scattering, Eq. (1.36). This expression is not applicable for anisotropic magnets (e.g., Ising spin systems).

1.3.3.5 Magnetic susceptibility

In the final part of this section, I describe the relationship between $S(\mathbf{Q}, \omega)$ and the magnetic susceptibility, which is useful in theoretical work [Section 1.4.1]. The generalised magnetic susceptibility is a complex tensor defined by the relation

$$M^\beta(\mathbf{Q}, \omega) = \sum_{\alpha} \chi^{\alpha\beta}(\mathbf{Q}, \omega) H^\alpha(\mathbf{Q}, \omega), \quad (1.62)$$

where $\alpha, \beta \in \{x, y, z\}$ denote Cartesian components. The static $\mathbf{Q}$ -dependent susceptibility is given by $\chi(\mathbf{Q}) \equiv \chi(\mathbf{Q}, 0)$ and the bulk (thermodynamic) susceptibility measured using a magnetometer is given by $\chi \equiv \chi(0, 0)$. The real and imaginary parts of $\chi(\mathbf{Q}, \omega)$ are related by the Kramers-Kronig relation [40],

$$\text{Re} [\chi(\mathbf{Q})] = \frac{1}{\pi} \int \frac{\text{Im} [\chi(\mathbf{Q}, \omega)]}{\omega} d\omega. \quad (1.63)$$

It can be shown [79] that the imaginary part of the susceptibility is related to the inelastic neutron-scattering function [Eq. (1.28)]:

$$\text{Im} [\chi^\perp(\mathbf{Q}, \omega)] = \mu_0 (g\mu_B)^2 [1 - \exp(-\hbar\omega/k_B T)] \frac{\pi}{\hbar} S_{\text{inel}}(\mathbf{Q}, \omega). \quad (1.64)$$

This relationship is called the fluctuation-dissipation theorem, because it relates the spin fluctuations to the dissipative response to an applied field [40]. Making the assumption that $\hbar\omega \ll k_B T$, it follows from Eq. (1.63) and Eq. (1.64) that

$$\chi^\perp(\mathbf{Q}) = \frac{\mu_0 (g\mu_B)^2}{k_B T} S(\mathbf{Q}) \quad (1.65)$$

for a PM or spin liquid. Another statement of the fluctuation-dissipation theorem is

$$\chi(\mathbf{Q}) = \frac{\mu_0}{Nk_B T} \langle \mathbf{M}(-\mathbf{Q}) \cdot \mathbf{M}(\mathbf{Q}) \rangle, \quad (1.66)$$

in which $\mathbf{M}(\mathbf{Q}) = -g\mu_B \sum_i \mathbf{S}_i \exp(i\mathbf{Q} \cdot \mathbf{r}_i)$ is the Fourier transform of the sample magnetisation. This form will be useful in Section 1.4.1.

1.3.4 Neutron-Scattering Experiments

In practice, magnetic neutron scattering experiments are carried out at central facilities, such as the ISIS facility in Oxfordshire, the Institut Laue-Langevin (ILL) in Grenoble, and the SNS in Oak Ridge, Tennessee. The ILL uses a nuclear reactor to produce neutrons, which are collimated and moderated to produce a continuous neutron beam. The neutron energies follow a Maxwellian distribution with an average energy which depends on the moderator material. In a simple powder-diffraction experiment, the diffraction pattern is usually measured by fixing the incident wavelength λ using a monochromator and varying the scattering angle 2θ . By contrast, at spallation sources such as ISIS, neutrons are produced by accelerating a pulsed beam of protons in a synchrotron. The proton beam is then collided with a heavy-metal target in order to produce short pulses of neutrons by spallation, which are then moderated and collimated. At spallation sources, the diffraction pattern can be measured using a beam containing a range of neutron wavelengths, by fixing the scattering angle and measuring the time taken for neutrons to travel from source to detector (“time of flight”). Time-of-flight is related to neutron wavelength by

$$\lambda = \frac{ht}{m_n L}, \quad (1.67)$$

where t is neutron time-of-flight and L is the distance from source to detector [89].

In this section, I describe the neutron-scattering instruments used to collect data in this thesis: the D7 diffuse-scattering spectrometer at the ILL, the WISH diffractometer at ISIS, and the HRPD diffractometer at ISIS. In particular, I explain how each is optimised for the different types of neutron-scattering experiment detailed in subsequent chapters.

1.3.4.1 The D7 diffuse-scattering diffractometer at the ILL

The D7 instrument at the ILL [90] was used to collect the powder diffuse-scattering data for $\text{Ca}_3\text{Co}_2\text{O}_6$ [Chapter 3] and the single-crystal diffuse scattering data for Co-doped

β -Mn [Chapter 8]. It has several properties which make it ideal for measurement of magnetic diffuse scattering. First, its location at the ILL—the world’s highest-powered nuclear research reactor—means that the incident neutron flux is high. The combination of high flux and low background is more important than high reciprocal-space resolution for measurement of diffuse scattering, which has low intensity and varies slowly with Q . Second, the neutron detectors cover a wide angular range, which allows reciprocal-space planes to be measured on single-crystal samples [90]. Finally, the use of neutron polarisation analysis [35, 91, 92] allows the magnetic scattering to be isolated, as I now discuss.

The technique of neutron polarisation analysis involves preparing the incident neutron beam in a specific spin state (i.e., $s_z = +\frac{1}{2}$ or $s_z = -\frac{1}{2}$ with respect to a small applied magnetic field along z) and analysing the spin states of the scattered neutrons. In this way, scattering processes which flip the neutron spin (spin-flip scattering) are distinguished from those that do not (non-spin-flip scattering). The isolation of magnetic scattering relies on two rules. First, only nuclear spin-incoherent scattering and magnetic scattering can flip the neutron spin, while nuclear scattering cannot. Second, the non-spin-flip scattering is sensitive only to components of the sample magnetisation parallel to the neutron spin, whereas the spin-flip scattering is sensitive only to components of the sample magnetisation perpendicular to the neutron spin [35, 91]. On D7, the magnetic scattering is isolated using xyz polarisation analysis [92], in which the polarisation of the incident neutron beam is aligned along three orthogonal directions $\mathbf{x}, \mathbf{y}, \mathbf{z}$ in sequence. These directions are chosen such that $\mathbf{x}$ and $\mathbf{y}$ are in the plane of the neutron detector, and the sample is rotated around $\mathbf{z}$ in a single-crystal measurement. Then, the magnetic scattering can be calculated in two independent ways [92],

$$I(\mathbf{Q}) = 2 [I_{\text{sf}}^x(\mathbf{Q}) + I_{\text{sf}}^{xy}(\mathbf{Q}) - 2I_{\text{sf}}^z(\mathbf{Q})] \quad (1.68)$$

$$= 2 [2I_{\text{nsf}}^z(\mathbf{Q}) - I_{\text{nsf}}^x(\mathbf{Q}) - I_{\text{nsf}}^y(\mathbf{Q})], \quad (1.69)$$

where subscript “sf” and “nsf” denote spin-flip and non-spin-flip scattering, respectively. Eqs. (1.68) and (1.69) hold for PM (or spin-liquid) powder samples, and for single-crystal

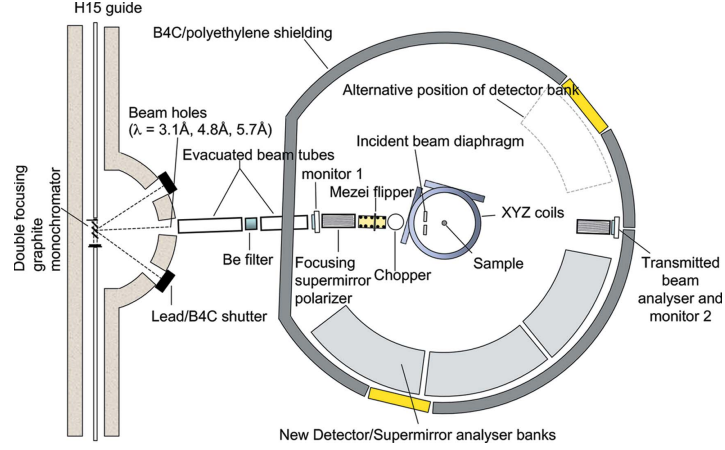
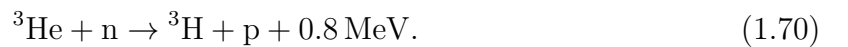


Figure 1.9: Schematic diagram of the D7 diffuse-scattering diffractometer at the ILL. Figure reproduced from Stewart *et al.* [90].

paramagnets if single-ion anisotropy is negligible.

The design of the D7 instrument [90] is shown in Fig. 1.9. A graphite monochromator allows an incident neutron wavelength of 3.1, 4.8, or 5.7 Å to be selected, by moving the rest of the instrument to match the chosen scattering angle from the monochromator. The beam is then polarised along $\mathbf{z}$ using a supermirror, a large number of layers of Co/Ti alloy which selectively reflect a single neutron spin state. The supermirror polariser uses a radially-focussing geometry which allows a wide (divergent) beam to be polarised efficiently [93]. The beam polarisation is preserved by applying a small magnetic “guide field” ($\approx 10^{-3}$ T) along $\mathbf{z}$ throughout D7. A Mezei flipper reverses the initial neutron polarisation so that both I_{nsf} (Mezei flipper off) and I_{sf} (Mezei flipper on) can be measured. The sample is surrounded by three orthogonal field coils, which are used to apply a magnetic field which adiabatically rotates the neutron polarisation along $\mathbf{x}$, $\mathbf{y}$ and $\mathbf{z}$ directions in sequence. Finally, after the incoming beam is scattered by the sample, the final neutron polarisation is analysed by a second large array of supermirrors, which are positioned in front of an array of neutron detectors covering a wide angular range (132°). The detectors are tubes of ^3He , which work by the nuclear reaction [89]



Several standard corrections are performed for polarised-neutron scattering measure-

ments [90]. First, it is necessary to correct for the fact that the incident beam is not perfectly polarised, and that the analysis of the scattered beam is not perfectly efficient. This is achieved by measuring an amorphous SiO₂ standard, which is chosen for two reasons: first, SiO₂ shows only nuclear coherent scattering (so the spin-flip intensity would be zero if the polarisation analysis were perfect); second, amorphous SiO₂ shows only diffuse scattering, so intensity is observed in all detectors at once. Next, a vanadium standard is used to correct for apparent detector efficiency (including the $d\Omega$ factor in Eq. (1.29)), because the scattering from vanadium is flat in Q . Finally, a measurement of an empty sample container is taken under identical conditions to the sample measurement, in order to subtract the background scattering. For the data reported in Chapters 3 and 8, these corrections were performed using the Large Array Manipulation Program software of the ILL [94]. Finally, it was pointed out in recent work [95] that Eq. (1.68) and Eq. (1.69) become inaccurate at low Q , because the detectors extend slightly out of the xy plane; hence data below $2\theta \approx 20^\circ$ should not be included in refinements if $I(Q)$ takes significant values at low Q .

1.3.4.2 The HRPD and WISH diffractometers at ISIS

The HRPD and WISH diffractometers at ISIS are both time-of-flight diffractometers; similar principles were therefore involved in their design, and I consider both together. In Chapter 5, single-crystal diffraction data for Gd₂Ti₂O₇ were collected on WISH, and powder-diffraction data were collected on HRPD.

The HRPD diffractometer [96] is located at Target Station One at ISIS, at which the neutron beam is pulsed with frequency 50 Hz. Its unique advantage is that it has among the highest reciprocal-space resolution of any neutron instrument, $\Delta Q/Q \approx 5 \times 10^{-5}$, which is nearly constant throughout its accessible Q -range. For a time-of-flight diffractometer, the resolution is given by differentiating Eq. (1.31), which yields

$$\left(\frac{\Delta Q}{Q}\right)^2 = \left(\frac{\Delta t}{t}\right)^2 + \left(\frac{\Delta L}{L}\right)^2 + (\cot \theta \cdot \Delta \theta)^2, \quad (1.71)$$

where Δt is the uncertainty in time-of-flight (arising from the length of the neutron pulse),

$\Delta\theta$ is the uncertainty in scattering angle (arising from the detector width and variations in the divergence of the neutron beam), and ΔL is the uncertainty in flight-path length [89]. Usually, $\Delta L/L$ is the largest term in Eq. (1.71), which arises from the width of the moderator and of the sample itself. This effect is reduced on HRPD by using an extremely long flight path, $L = 100\text{ m}$, with a supermirror guide [97]. Moreover, the term in θ is minimised by fixing the scattering angle at close to the maximum value $2\theta_{\text{max}} = 180^\circ$ (backscattering). Hence, HRPD offers unequalled ability to detect small structural distortions in powder-diffraction patterns [Chapter 5].

The WISH diffractometer [98] is located at Target Station Two at ISIS, at which the neutron beam is pulsed with frequency 10 Hz. The lower pulse frequency at Target Station Two allows a wide time-of-flight range to be measured, so that data can be collected over a wide Q -range. Moreover, WISH has a very large bank of ^3He neutron detectors, which cover nearly a full cylinder around the sample. This allows single-crystal measurements to be made of a single scattering plane, with 15° out-of-plane coverage. A range of sample environments are available on WISH, including cryostats and high-field magnets. The importance of these capabilities is demonstrated in Chapter 5.

1.4 Understanding Magnetic Diffuse-Scattering Data

In general, approaches to understanding the properties of materials can be divided into two broad classes, which I refer to as “model-dependent” and “model-independent” methods.

The starting-point for model-dependent methods is a model of the interactions between fundamental building-blocks of the system (e.g., spins, atoms, or electrons). Since a macroscopic solid contains $\sim 10^{23}$ interacting particles, each of which may have translational, electronic, and magnetic degrees of freedom, it is usually necessary to approximate the full Hamiltonian using simplified models. To calculate the ground-state ($T = 0$) properties, *ab initio* methods such as density-functional theory (DFT) are widely used [99, 100]. To calculate finite-temperature properties and to study disordered systems, common approaches include MC simulations, molecular dynamics simulations, and field theories [101–103].

Model-independent methods, by contrast, do not consider the underlying interactions of the system, but simply aim to determine its structure. In the condensed-matter sciences, crystallography is perhaps the best-known example of such a technique, and usually allows crystal structures to be determined from scattering data [74]. In disordered systems such as atomic liquids, the model-independent technique of pair-distribution function analysis can also be used to extract short-range correlations [104, 105]. Some techniques, such as empirical potential structure refinement (EPSR) for liquids and amorphous materials [106], combine aspects of both model-dependent and model-independent methods by using experimental data to augment a predefined model.

In this section, I compare the approaches which are currently used to interpret magnetic-diffuse scattering data. In Section 1.4.1, I describe the two model-dependent approaches which I use in this thesis, classical MC simulations and mean-field theory. In Section 1.4.2, I review current model-independent approaches. In Section 1.4.3, I argue that current approaches suffer from important limitations, and that a quantitative model-independent method to determine the spin correlations in frustrated magnets is needed. Finally, in Section 1.4.4, I introduce the technique of RMC refinement [39], and suggest that this approach has potential to overcome the limitations of current methods.

1.4.1 Model-Dependent Approaches

1.4.1.1 Monte Carlo simulation

The aim of MC modelling [101, 107] is to produce a series of spin configurations (or “boxes”) which are sampled from a specified statistical distribution. In scientific calculations, this distribution is usually the Boltzmann distribution, which describes a system containing a fixed number N of particles in thermal equilibrium [58]. In the Boltzmann distribution, the probability of finding the system in a state μ having energy E_μ is given by

$$p_\mu = \frac{1}{Z} \exp\left(\frac{-E_\mu}{k_B T}\right), \quad (1.72)$$

where $Z = \sum_{\mu} \exp(-E_{\mu}/k_{\text{B}}T)$ is called the partition function. The expectation value of a measurable quantity (e.g., energy or magnetisation) is calculated as

$$\langle Q \rangle = \frac{1}{Z} \sum_{\mu} Q_{\mu} \exp\left(\frac{-E_{\mu}}{k_{\text{B}}T}\right) \quad (1.73)$$

after the system has reached equilibrium [58].

One way to calculate the expectation value would be to sample the different states Q_{μ} uniformly. The problem with this approach is that there are very many states, so such a calculation would be very slow. Moreover, most of these states are unlikely to occur, and so make only a small contribution to the expectation value. A better approach is to sample the states in such a way that the probability of a state appearing in the sample is given by the Boltzmann distribution itself. The expectation value can then be calculated as a simple average of the sampled states:

$$\langle Q \rangle = \frac{1}{t} \sum_{\mu=1}^t Q_{\mu}. \quad (1.74)$$

This is known as importance sampling, and is the first key ingredient in MC algorithms [101].

The second key ingredient is the method for moving from one state to the next in the simulation, known as a “Markov chain” [108]. There are many possible Markov chains, but all must satisfy two conditions to allow the system to come to equilibrium. The first, the condition of ergodicity, states that it must be possible to move from any allowed state to any other. The second, the condition of detailed balance, dictates that the number of times the system moves from state μ to state ν should, on average, equal the number of times the reverse process occurs. This requires that

$$\frac{P(\mu \rightarrow \nu)}{P(\nu \rightarrow \mu)} = \exp\left(-\frac{E_{\nu} - E_{\mu}}{k_{\text{B}}T}\right), \quad (1.75)$$

where $P(\mu \rightarrow \nu)$ is the probability of the system moving from state μ to state ν .

The final objective is an algorithm which satisfies the conditions above, and which

allows equilibrium to be reached quickly. The most famous such algorithm—and the only one I use in this thesis—is called the Metropolis algorithm [109]. Applied to an Ising spin system, it works as follows. First, a spin is chosen at random from the configuration, and flipped (its sign is reversed). The change in energy resulting from the spin flip is calculated, and the move is accepted with probability

$$P(\mu \rightarrow \nu) = \begin{cases} \exp [-(E_\nu - E_\mu)/k_B T] & \text{if } E_\nu - E_\mu > 0 \\ 1 & \text{otherwise.} \end{cases} \quad (1.76)$$

Hence, moves which lower the energy are always accepted, and moves which increase the energy are accepted with a probability that increases as the temperature is raised.

It is straightforward to calculate $S(\mathbf{Q})$ from MC spin configurations by applying Eq. (1.48). In practice, it is necessary to average the calculated $S(\mathbf{Q})$ over many independent spin configurations in order to obtain results of good statistical quality; this configurational average is equivalent to the time average given in Eq. (1.48) by the ergodic principle [58]. In addition, Eq. (1.48) can be manipulated in order to accelerate the calculation of $S(\mathbf{Q})$, a process which I describe in detail in Chapter 6.

Thermodynamic properties can also be calculated accurately using MC simulations. In this thesis, I consider the magnetic susceptibility χ and the magnetic heat capacity C_{mag} , which are calculated from the following relations (which can be derived from the fluctuation-dissipation theorem):

$$\chi = \frac{\mu_0}{N k_B T} (\langle M_z^2 \rangle - \langle M_z \rangle^2), \quad (1.77)$$

$$C_{\text{mag}} = \frac{1}{N k_B T^2} (\langle E^2 \rangle - \langle E \rangle^2), \quad (1.78)$$

where $M_z = -g\mu_B \sum_i S_i^z$ is the total magnetisation, $E = \sum_i E_i$ the total energy, and angle brackets denote an average over configurations. Here, χ is given in SI units of $\text{m}^3 \text{spin}^{-1}$ and C_{mag} is given in units $\text{J K}^{-1} \text{spin}^{-1}$ (these units can be converted into molar quantities by multiplying by the Avogadro constant N_A). In calculations of thermodynamic properties, it is convenient to start the simulation at a large temperature $T \gg \theta$

and gradually reduce the temperature in stages, calculating thermodynamic properties at each temperature; this is known as a simulated annealing algorithm [110].

The accuracy of MC simulations is limited by two factors: the effect of finite simulation size ($\lesssim 10^4$ spins), and the effect of finite simulation time ($\lesssim 10^6$ proposed moves per spin). Both effects are often unimportant in simulations of the PM state, but become important near magnetic phase transitions [111, 112]. The finite-size effects also depend on how the edges of the system are handled. There are two options: either the system is considered as a finite cluster (“open boundary conditions”), or alternatively it is tiled periodically in space (“periodic boundary conditions”). With open boundary conditions, spins at the edges of the box have a smaller number of neighbours than spins in the bulk, which can lead to spurious edge effects. To avoid such effects, I use periodic boundary conditions for all simulations in this thesis.

The main advantages of MC simulation are that it is straightforward to implement, allows accurate calculation of thermodynamic properties and correlation functions, and imposes no restrictions of the number or type of terms in the Hamiltonian. For these reasons, it has been used in many studies of frustrated magnets (see, e.g., [81, 113, 114]). Its main disadvantage is that it is relatively slow. MC simulation may therefore be impractical when a large number of different models must be tested against experimental data, or when large or complex systems must be studied. In such cases, analytical approximations to the spin Hamiltonian are useful. The simplest such approximation is mean-field theory, which I introduce below.

1.4.1.2 Mean-field theory

Here, I introduce the mean-field approximation for $S(\mathbf{Q})$ assuming a Heisenberg Hamiltonian. The derivation is based on one given by Marshall and Lowde [79], but is extended to systems where the unit cell contains more than one atom to increase its relevance for frustrated magnets. This extension was previously derived by different methods [103, 115, 116].

The Heisenberg Hamiltonian is given by

$$H = -\frac{1}{2} \sum_{i,j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j + g\mu_B \sum_i \mathbf{B}_i \cdot \mathbf{S}_i, \quad (1.79)$$

which involves interactions between all pairs of spins, and includes a site-dependent magnetic field $\mathbf{B}_i$. The aim of the mean-field approach is to approximate the effect of interactions as an effective magnetic field at each site of the crystallographic unit cell. To achieve this, I label each spin by the origin of its particular unit cell $(\mathbf{R}, \mathbf{R}')$ and an index $\rho, \sigma \in \{1, n\}$ which labels the site within the unit cell, so that the position of spin $\mathbf{S}_i \equiv \mathbf{S}_\rho(\mathbf{R})$ is given by $\mathbf{r}_i = \mathbf{r}_\rho + \mathbf{R}$. In this notation, Eq. (1.79) becomes

$$H = -\frac{1}{2} \sum_{\mathbf{R}, \mathbf{R}'} \sum_{\rho, \sigma} J_{\rho\sigma}(\mathbf{R}' - \mathbf{R}) \mathbf{S}_\rho(\mathbf{R}) \cdot \mathbf{S}_\sigma(\mathbf{R}') + g\mu_B \sum_{\mathbf{R}, \rho} \mathbf{B}_\rho(\mathbf{R}) \cdot \mathbf{S}_\rho(\mathbf{R}). \quad (1.80)$$

The mean-field approximation proceeds by writing the spins as the sum of average and fluctuation terms, using the identity $\mathbf{S}_i \equiv \langle \mathbf{S}_i \rangle + (\mathbf{S}_i - \langle \mathbf{S}_i \rangle)$. It then neglects correlations of the spin fluctuations in Eq. (1.80). This allows the Hamiltonian to be written in the same form as a non-interacting spin system in an applied magnetic field [1],

$$H_{\text{MF}} = g\mu_B \sum_{\mathbf{R}, \rho} \mathbf{S}_\rho(\mathbf{R}) \cdot \mathbf{B}_\rho^{\text{eff}}(\mathbf{R}). \quad (1.81)$$

The effective magnetic field (“mean field”) is given by

$$\mathbf{B}_\rho^{\text{eff}}(\mathbf{R}) = \mathbf{B}_\rho(\mathbf{R}) + \frac{1}{(g\mu_B)^2} \sum_{\mathbf{R}', \sigma} J_{\rho\sigma}(\mathbf{R}' - \mathbf{R}) \mathbf{M}_\sigma(\mathbf{R}'), \quad (1.82)$$

where I have used $\mathbf{M} = -g\mu_B \langle \mathbf{S} \rangle$. Since the Heisenberg Hamiltonian contains no anisotropy terms, the induced magnetisation is always directed along the applied field, and its magnitude is independent of the field direction. I therefore drop the vector notation and substitute $\mathbf{M} \rightarrow M$ and $\mathbf{B} \rightarrow B$. Because the Hamiltonian now has the same form as for a noninteracting spin system, it is possible to write $M_\rho(\mathbf{R}) = \chi_0 B_\rho^{\text{eff}}(\mathbf{R})/\mu_0$, where χ_0 is the noninteracting spin susceptibility given by Curie’s law for an insulator,

Eq. (1.7). Taking the Fourier transform of both sides of Eq. (1.82), I obtain

$$M_\rho(\mathbf{Q}) = \frac{\chi_0}{\mu_0} \left[B_\rho(\mathbf{Q}) + \frac{1}{(g\mu_B)^2} \sum_\sigma J_{\rho\sigma}(\mathbf{Q}) M_\sigma(\mathbf{Q}) \right], \quad (1.83)$$

where

$$M_\rho(\mathbf{Q}) = \sum_{\mathbf{R}} M_\rho(\mathbf{R}) \exp(i\mathbf{Q} \cdot \mathbf{R}), \quad (1.84)$$

$$J_{\rho\sigma}(\mathbf{Q}) = \sum_{\mathbf{R}} J_{\rho\sigma}(\mathbf{R}) \exp(-i\mathbf{Q} \cdot \mathbf{R}). \quad (1.85)$$

The key step in the Fourier transform recognises that $J_{\rho\sigma}(\mathbf{R}' - \mathbf{R})$ is periodic in displacement $\mathbf{R}' - \mathbf{R}$. The sum in Eq. (1.84) is taken over spins with site index ρ in unit cell $\mathbf{R}$, and the sum in $J_{\rho\sigma}(\mathbf{Q})$ is taken over spins with site index σ at displacement $\mathbf{R}' - \mathbf{R}$ from a central spin with site index ρ (which accounts for the negative sign in the latter case).

To proceed, I require $M_\rho(\mathbf{Q})$ to appear on both sides of Eq. (1.83). This can be achieved by making a linear transformation from site labels (ρ, σ) to normal-mode variables (μ, ν) [116]:

$$M_\rho(\mathbf{Q}) = \sum_\mu m^\mu(\mathbf{Q}) U_\rho^\mu(\mathbf{Q}), \quad (1.86)$$

$$B_\rho(\mathbf{Q}) = \sum_\mu b^\mu(\mathbf{Q}) U_\rho^\mu(\mathbf{Q}), \quad (1.87)$$

where the index $\mu \in \{1, n\}$ labels the normal modes, m^μ is the amplitude of mode μ , and $U_\rho^\mu(\mathbf{Q})$ is the direction of the spin at site ρ when mode μ is populated. The $U_\rho^\mu(\mathbf{Q})$ are defined by the linear transformation

$$\lambda^\mu(\mathbf{Q}) U_\rho^\mu(\mathbf{Q}) = \sum_\sigma J_{\rho\sigma}(\mathbf{Q}) U_\sigma^\mu(\mathbf{Q}), \quad (1.88)$$

with the normalisation condition

$$\sum_\rho U_\rho^\mu(\mathbf{Q}) U_\rho^\nu(-\mathbf{Q}) = \delta^{\mu\nu}, \quad (1.89)$$

where $\delta^{\mu\nu}$ is the Kronecker delta function. Substituting Eq. (1.86)–(1.89) into Eq. (1.83) and applying the properties of the Kronecker delta function, I obtain for the mode amplitudes

$$m^\mu(\mathbf{Q}) = \frac{\chi_0}{\mu_0} \left[b^\mu(\mathbf{Q}) + \frac{1}{(g\mu_B)^2} m^\mu(\mathbf{Q}) \lambda^\mu(\mathbf{Q}) \right]. \quad (1.90)$$

The susceptibility of mode amplitudes is given by

$$\chi^{\mu\mu}(\mathbf{Q}) = \frac{\mu_0 m^\mu(\mathbf{Q})}{b^\mu(\mathbf{Q})} \quad (1.91)$$

$$= \frac{\chi_0}{1 - \frac{\chi_0}{\mu_0(g\mu_B)^2} \lambda^\mu(\mathbf{Q})}. \quad (1.92)$$

This result is related to the correlation function of mode amplitudes by the fluctuation-dissipation theorem, Eq. (1.66), which yields

$$\chi^{\mu\mu}(\mathbf{Q}) = \frac{\mu_0}{k_B T} \langle m^\mu(-\mathbf{Q}) m^\mu(\mathbf{Q}) \rangle. \quad (1.93)$$

I now apply Eq. (1.66) again to express the $\mathbf{Q}$ -dependent susceptibility $\chi(\mathbf{Q})$ in terms of the correlation function of the magnetisation, Eq. (1.84):

$$\chi(\mathbf{Q}) = \frac{\mu_0}{n k_B T} \sum_{\rho, \sigma} \langle M_\rho(-\mathbf{Q}) M_\sigma(\mathbf{Q}) \rangle \exp[i\mathbf{Q} \cdot (\mathbf{r}_\sigma - \mathbf{r}_\rho)], \quad (1.94)$$

The final result is obtained by using Eqs. (1.86), (1.92), and (1.93) in Eq. (1.94):

$$\chi(\mathbf{Q}) = \frac{1}{n} \sum_{\mu} \frac{\chi_0 |F^\mu(\mathbf{Q})|^2}{1 - \frac{\chi_0}{\mu_0(g\mu_B)^2} \lambda^\mu(\mathbf{Q})}, \quad (1.95)$$

in which

$$F^\mu(\mathbf{Q}) = \sum_{\rho} U_{\rho}^{\mu}(\mathbf{Q}) \exp(i\mathbf{Q} \cdot \mathbf{r}_{\rho}). \quad (1.96)$$

From Eqs. (1.43) and (1.65), the PM neutron-scattering intensity is proportional to Eq. (1.95) multiplied by the squared magnetic form factor, $I(\mathbf{Q}) \propto [f(Q)]^2 \chi(\mathbf{Q})$.

Mean-field theory also yields information about the ordered magnetic state which de-

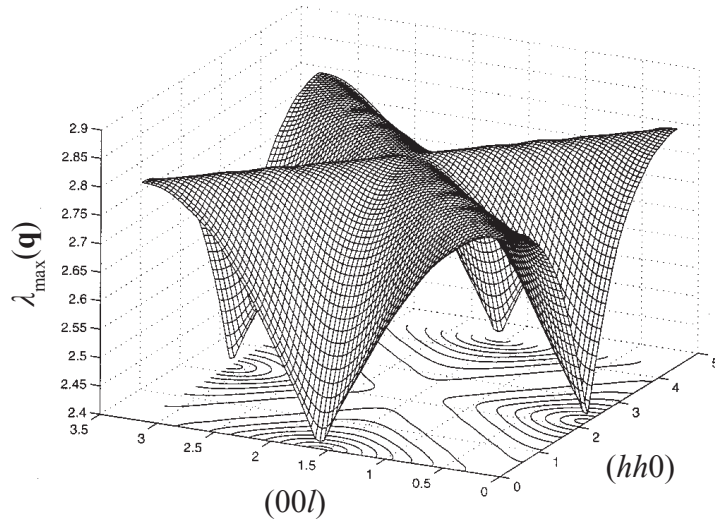


Figure 1.10: Dispersion of $\lambda_{\max}(\mathbf{q})$ (defined in the text) in the (hhl) reciprocal-space plane for the pyrochlore lattice with AFM nearest-neighbour Heisenberg exchange interactions and long-range dipolar interactions. The calculation is performed using the mean-field approximation. Figure reproduced from Raju *et al.* [116].

velops from the PM phase. I define $\lambda_{\max}(\mathbf{q})$ as the largest of the $\lambda^\mu(\mathbf{q})$ at each wavevector $\mathbf{q}$ in the first Brillouin zone, and $\lambda_{\max}(\mathbf{k})$ as the global maximum of $\lambda^\mu(\mathbf{q})$. Long-range magnetic order develops when Eq. (1.95) diverges, i.e., when $\lambda_{\max}(\mathbf{k}) = \mu_0 (g\mu_B)^2 / \chi_0$. The magnetic propagation vector of the first ordered state is then given by $\mathbf{k}$ [117]. Highly-frustrated systems are characterised by a $\lambda_{\max}(\mathbf{q})$ which is (nearly) flat throughout the first Brillouin zone, so that no single magnetic propagation vector is energetically favoured [118]. The degree of frustration can therefore be assessed by plotting $\lambda_{\max}(\mathbf{q})$ in the first Brillouin zone, an approach which I use in Chapter 8. Fig. 1.10 shows the dispersion of $\lambda_{\max}(\mathbf{q})$ for spins on the pyrochlore lattice with AFM nearest-neighbour Heisenberg exchange interactions and long-range dipolar interactions [116]. An approximately flat region occurs along the $\langle 111 \rangle^*$ directions, which indicates the presence of frustration; however, fluctuations which are not considered in mean-field theory lead to entropic selection of an ordering wavevector $\mathbf{k} = \mathbf{0}$ in more sophisticated theories [119]. This model was originally applied to the pyrochlore AFM $\text{Gd}_2\text{Ti}_2\text{O}_7$, which I consider in Chapter 5.

The mean-field approach has been widely used to calculate $I(\mathbf{Q})$ for frustrated magnets (see, e.g., [51, 103, 120, 121]). Its success here is actually quite surprising, because

the mean-field approximation neglects correlations of the spin fluctuations, which are expected to be important. Indeed, for $\mathbf{Q} = \mathbf{0}$, Eq. (1.95) reduces to the Curie-Weiss law, which is only appropriate for high temperatures $T > \theta$. There is, however, a significant amount of evidence that the mean-field approximation does not fail completely for $T \ll \theta$ in frustrated magnets. Instead, the $\mathbf{Q}$ -dependence of $\chi(\mathbf{Q})$ remains correct, but the temperature-dependence of χ_0 deviates strongly from Curie's law, Eq. (1.7) [120]. This result is fortunate, because it suggests that the relative values of different interactions in Eq. (1.10) can be determined robustly by fitting Eq. (1.95) to experimental data, if χ_0 is treated as a free parameter. The fitted interaction parameters can subsequently be placed on an absolute energy scale if the magnitude of one of the interaction parameters is already known, or by normalising to the experimentally-determined θ . This method has been used successfully in previous studies of experimental neutron-scattering data [51, 103, 120, 121]. The unexpected success of mean-field theory has been noted several times [82, 120], but no rigorous justification for it has yet been given.

The mean-field approach allows rapid calculation of $I(\mathbf{Q})$, and is therefore a useful alternative to MC simulation when many different sets of interaction parameters must be tested against experimental data; I use it for this purpose in Chapter 8. Its main disadvantages are that it does not allow accurate calculation of thermodynamic properties, and the lack of rigorous justification of Eq. (1.95) at low temperature.

1.4.2 Model-Independent Approaches

1.4.2.1 Fourier inversion

Perhaps the most straightforward method to reveal the real-space spin correlations is to Fourier transform the powder-averaged neutron-scattering pattern. The Fourier transform is given by [88, 122]

$$g_{\text{mag}}(r) = \frac{2}{\pi} \int_0^{Q_{\text{max}}} Q \bar{S}(Q) \sin(Qr) dQ \quad (1.97)$$

$$= \frac{1}{NS(S+1)} \sum_{j \neq i} \mathbf{S}_i \cdot \mathbf{S}_j \frac{\delta(r - r_{ij})}{r}, \quad (1.98)$$

where the second equality applies only for an isotropic spin system, and the normalised powder scattering factor

$$\bar{S}(Q) = \frac{3S(Q)}{2S(S+1)} - 1. \quad (1.99)$$

Hence, the Fourier transform of $\bar{S}(Q)$ is closely related to the radial spin correlation function in the simple case of an isotropic spin system. This procedure is analogous to the method of pair-distribution function (PDF) analysis of nuclear diffuse-scattering data [105], in which the Fourier transform of $(I_{\text{coh}}(Q) - \bar{b}^2)/\bar{b}^2$ [Eq. (1.36)] yields a weighted histogram of inter-atomic distances,

$$g_{\text{nuc}}(r) = \frac{1}{N} \sum_{j \neq i} \frac{\delta(r - r_{ij})}{r}, \quad (1.100)$$

for a system containing a single element.

The PDF approach has been used very widely in the analysis of nuclear diffuse scattering from liquids, glasses, and disordered solids [104, 123]; however, its magnetic analogue, Eq. (1.98), has been used relatively infrequently [88, 122, 124–126]. The likely reason for this is that the magnetic form factor restricts the upper limit Q_{max} of the integral in Eq. (1.97) to small values. For magnetic data, $Q_{\text{max}} \approx 8 \text{ \AA}^{-1}$ is the best-case scenario, compared to $Q_{\text{max}} \approx 40 \text{ \AA}^{-1}$ for modern structural diffuse-scattering measurements [104]. The effect of the restricted Q_{max} is to broaden the delta-function peaks in Eq. (1.98) and introduce truncation artifacts (“Fourier ripples” or “Gibbs phenomenon” [127]) in $g_{\text{mag}}(r)$. Fig. 1.11 shows an example of these effects for the pyrochlore magnet $\text{Y}_2\text{Mn}_2\text{O}_7$ [124]. An additional problem with the approach has been that Eq. (1.98) can only be applied to isotropic spin systems; recently, however, the exact expression for the Fourier transform of $\bar{S}(Q)$ was derived, and guidance provided on the interpretation of the resulting (more complicated) expression for $g_{\text{mag}}(r)$ [126].

1.4.2.2 Correlation-coefficient fitting

A more common approach uses least-squares fitting to estimate the spin correlations. In this method, $\bar{S}(Q)$ [Eq. (1.99)] is rewritten as a sum over shells n , where $n = 1$ corresponds

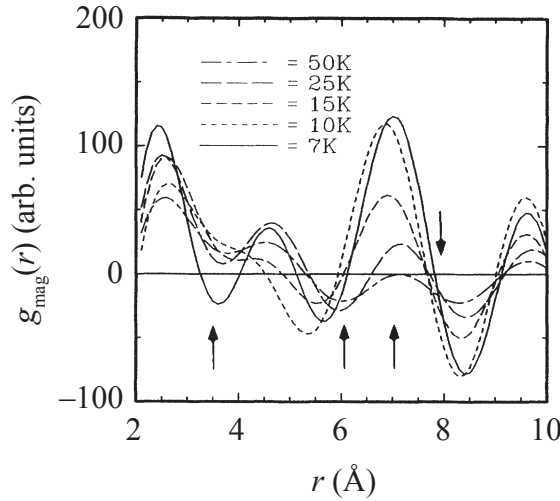


Figure 1.11: Magnetic pair-distribution function $g_{\text{mag}}(r)$ (defined in the text) for the pyrochlore magnet $\text{Y}_2\text{Mn}_2\text{O}_7$, obtained from Eq. (1.98) with $Q_{\text{max}} \approx 2.5 \text{ \AA}^{-1}$. Arrows show near-neighbour coordination distances. Figure reproduced from Reimers *et al.* [124].

to nearest-neighbours, $n = 2$ to next-nearest neighbours, and so on:

$$\bar{S}(Q) = \sum_n Z_n \langle \mathbf{S}(0) \cdot \mathbf{S}(r_n) \rangle \frac{\sin(Qr_n)}{Qr_n}. \quad (1.101)$$

Here, Z_n is the coordination number for shell n , and $\langle \mathbf{S}(0) \cdot \mathbf{S}(r_n) \rangle$ is the spin-correlation coefficient for shell n divided by $|\mathbf{S}|^2 = S(S+1)$. The values of $\langle \mathbf{S}(0) \cdot \mathbf{S}(r_n) \rangle$ are then treated as independent parameters in a linear least-squares fit to $\bar{S}(Q)$.

This approach has been widely used to interpret powder diffuse-scattering data (see, e.g., [19, 62, 85]). It is particularly useful to test whether the data can be explained solely by nearest-neighbour correlations, which may occur, for example, for valence-bond correlations [128]. However, when more than one correlation coefficient is fitted (as is usually the case in practice), unphysical values of the correlation coefficients can be obtained, because the fact that the different neighbours are connected on a lattice is not considered. For example, in a one-dimensional (1D) linear spin chain, a value $\langle \mathbf{S}(0) \cdot \mathbf{S}(r_1) \rangle = -1$ implies that the structure is AFM, so that $\langle \mathbf{S}(0) \cdot \mathbf{S}(r_2) \rangle = +1$; but there is no way of imposing such a constraint on a fit of Eq. (1.101).

1.4.2.3 Curve fitting

A final approach is to fit the most prominent features in the scattering pattern with a phenomenological peak-shape function. A Lorentzian peak-shape centred at $Q = Q_0$ may be used [129, 130]:

$$L(Q - Q_0) = \frac{1}{\pi} \frac{\gamma}{(Q - Q_0)^2 + \gamma^2}, \quad (1.102)$$

which corresponds to an exponential decay of spin correlations in real space, $\langle \mathbf{S}(0) \cdot \mathbf{S}(r) \rangle = \exp(-\gamma r)$. Unlike the previous approaches, which are essentially limited to powder data, this approach can be used to fit to single-crystal datasets [129]. It is useful for systems which are not far from conventional magnetic order, so that $I(\mathbf{Q})$ contains relatively sharp diffuse peaks, and allows the spin correlation length to be accurately determined in such cases [130]. It is, however, not appropriate for highly-frustrated systems, in which no magnetic ordering wavevector is selected and $I(\mathbf{Q})$ typically shows broad diffuse features. Moreover, if several terms are included in the fitting function, the physical meaning of each term may become unclear. An example from the recent literature [131] is shown in Fig. 1.12, in which magnetic diffuse-scattering data for $\text{Tb}_2\text{Ge}_2\text{O}_7$ were fitted by a weighted sum of two terms: a Lorentzian with $Q_0 = 0$ [Eq. (1.102)], and a term $-\sin(Qr_1)/Qr_1$ corresponding to AFM nearest-neighbour correlations [Eq. (1.101)]. The fit-to-data is excellent, but the model leads to an inconsistency: the Lorentzian term implies that the spin correlations always take positive values, while the $-\sin(Qr_1)/Qr_1$ term assumes that the spin-correlation value is negative for nearest-neighbour spins.

1.4.3 Why Do We Need Another Model-Independent Method?

Traditionally, model-independent methods have been used mostly for initial qualitative analysis of powder diffuse-scattering data (e.g., to estimate correlation length and strength), but have seldom been used for in-depth quantitative analysis. There are two main reasons for this. First, as discussed above, common model-independent methods make several assumptions: in particular, the distribution of spin orientations is usually assumed to be isotropic, and correlations are usually only considered for a small number

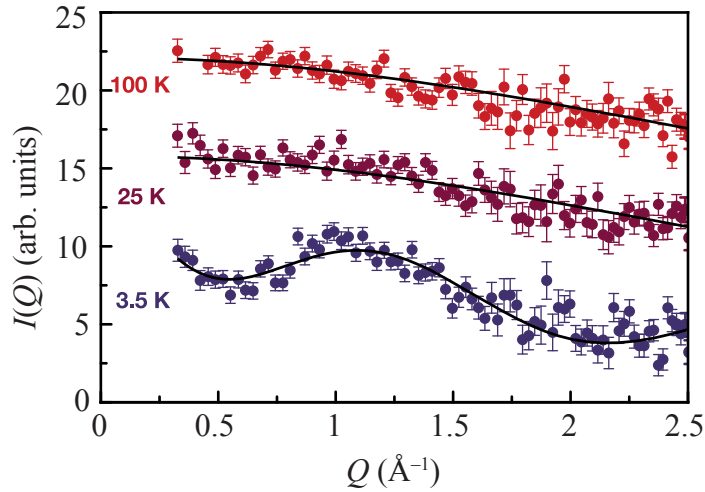


Figure 1.12: Magnetic diffuse-scattering data for $\text{Tb}_2\text{Ge}_2\text{O}_7$ [131] at three temperatures (labelled in the figure). A phenomenological model described in the text has been fitted to each dataset. Figure reproduced from Hallas *et al.* [131].

of near neighbours. Second, common model-independent methods are applicable either to powder data only, or to selected regions of single-crystal datasets. Hence, unlike model-dependent methods such as MC simulation, current model-independent methods cannot generate 3D models of disordered spin structures. This is a serious limitation, because it is the 3D crystal structure which is often responsible for frustration [Section 1.1]. For these reasons, in-depth understanding of frustrated spin systems has traditionally come from a combination of single-crystal neutron-scattering measurements and model-dependent data-analysis methods (see, e.g., [132]). In practice, interaction parameters in a spin Hamiltonian (e.g., Eq. (1.10)) are introduced one by one until satisfactory agreement is obtained with single-crystal neutron-scattering data. This approach has been very successful for several frustrated spin systems, such as the spin-ice materials $\text{Ho}_2\text{Ti}_2\text{O}_7$ and $\text{Dy}_2\text{Ti}_2\text{O}_7$ [11, 81, 113, 133].

Despite its many successes, the combination of single-crystal neutron-scattering data with model-dependent analysis has several key limitations in practice. First, it requires that large ($\sim\text{cm}^3$) single-crystal samples are available for neutron-scattering experiments. Unfortunately, however, many interesting materials cannot be prepared as single crystals. This is particularly—but by no means always—a problem for newly-synthesized compounds, which represent a significant area of frustrated-magnetism research [134, 135].

Single crystals are also usually unavailable for materials prepared by complex synthetic routes, e.g., high-pressure synthesis [136]. The lack of single crystals does not usually present a problem for magnetically-ordered materials, where magnetic Rietveld refinement often allows the magnetic structure to be solved from neutron powder-diffraction data [37]. By contrast, no approach has yet been shown to produce accurate 3D models of disordered spin structures based on neutron powder-diffraction data. An approach analogous to Rietveld refinement for spin liquids would therefore be valuable.

There are also fundamental reasons why it is important to develop model-independent data analysis methods for disordered systems. Model-independent analysis methods are, in general, more straightforward than model-dependent methods, and so are usually employed for initial data analysis. It is important that this initial analysis should be as robust as possible so that future work is directed correctly. For example, the AFM structure of MnO was determined in 1949 [137]; the magnetic interactions were determined experimentally in the 1970s [47]; and were determined by *ab initio* methods in the 2000s [138]. Throughout, the initial model-independent magnetic structure solution was used to validate the subsequent interaction models. I therefore expect that the same methodology—initial model-independent determination of the spin correlations, followed by interaction modelling—should also prove useful for disordered spin systems.

Finally, I suggest that model-independent methods may be especially well-suited to understanding spin liquids. My argument rests on the concept of emergence introduced by Anderson [139]: a large system containing many strongly-interacting particles may obey different “emergent” rules to those which describe individual particles. Frustrated magnets have been proposed as ideal systems in which to look for emergent behaviour [26, 140], because the combination of a simple crystal structure and magnetic interactions can lead to complex magnetic states. The canonical example is a system of Ising spins on a network of corner-sharing tetrahedra, which are coupled to their neighbours by ferromagnetic (FM) interactions. This model does not describe a ferromagnet, but rather spin ice, which has a macroscopically-degenerate magnetic ground state with excitations that resemble magnetic monopoles [8, 10, 11, 141]. Traditionally, the study of emergent

phenomena in frustrated systems begins by considering the interactions and proceeds to show how the resulting states obey emergent rules (e.g. the “ice rule” of spin ice). Yet it should also be possible to reverse this approach, and detect the emergent rules without first reducing the system to its underlying magnetic interactions. Indeed, as Anderson notes, this is precisely the approach followed in conventional crystallographic analysis, in which the crystal structure itself is an emergent phenomenon which breaks the fundamental symmetries obeyed by individual atoms [139]. In order to pursue such an approach, we need a model-independent method which allows 3D spin arrangements to be refined to diffuse-scattering data. This is the subject of the next section.

1.4.4 Reverse Monte Carlo Refinement

At the most basic level, RMC refinement [39] is a model-independent approach to refine a 3D configuration of atoms and/or spins to experimental data. Developed originally for the study of liquids and glasses [39, 142], it has since been applied to a range of materials including ordered magnetic structures [63, 143], flux-line lattices in unconventional superconductors [144], and spin glasses [145]. Traditionally, powder diffuse-scattering data are used to drive RMC refinements [146], but extended X-ray absorption fine-structure (EXAFS) data and single-crystal neutron, X-ray, and electron scattering data have also been used [147, 148]. The RMC method has occasionally been used to interpret powder diffuse-scattering data for frustrated magnets (see, e.g., 87, 149–151); in all cases, however, analysis was restricted to the radial spin correlation function. In this section, I introduce the RMC algorithm for the analysis of magnetic diffuse-scattering data for spin liquids, and discuss the advantages and disadvantages of this approach.

1.4.4.1 Reverse Monte Carlo algorithm

Applied to spin liquids, the RMC algorithm is used to refine a set of spin configurations to magnetic diffuse-scattering data [39, 152]. Similar to Rietveld refinement, the quality

of the fit-to-data is described by the sum of squared residuals,

$$\chi^2 = W \sum_Q \left[\frac{sI_{\text{calc}}(Q) - I_{\text{expt}}(Q)}{\sigma(Q)} \right]^2, \quad (1.103)$$

where $I(Q)$ is the powder-averaged magnetic neutron-scattering intensity given by Eq. (1.58) and Eq. (1.43), subscript “calc” and “expt” denote calculated and experimental intensities respectively, $\sigma(Q)$ is the experimental uncertainty, s is a scale factor, and W is an empirical weighting factor which determines how closely the algorithm will attempt to fit the data.

An RMC refinement proceeds in the following way. First, a periodic supercell of the crystallographic unit cell is generated, which usually contains several thousand atoms. Spins are modelled as classical vectors of unit length and are initially given random orientations. This is achieved by drawing vectors at random from the uniform distribution on the unit sphere, by setting

$$\mathbf{S} = \begin{bmatrix} \sqrt{1-u^2} \cos \phi, & \sqrt{1-u^2} \sin \phi, & u \end{bmatrix}, \quad (1.104)$$

where u and ϕ are random numbers, $u \in [-1, 1]$, and $\phi \in [0, 2\pi]$ [153]. The sum of squared residuals for this initial spin configuration is calculated by applying Eq. (1.103). Then, a spin is then chosen at random from the supercell and rotated by a small amount, forming a proposed new spin vector:

$$\mathbf{S}_\nu = \frac{\mathbf{S}_\mu + \eta \mathbf{s}}{|\mathbf{S}_\mu + \eta \mathbf{s}|}, \quad (1.105)$$

where $\mathbf{S}_\mu$ is the original spin vector, $0 < \eta \leq 1$ is the maximum spin move length, and $\mathbf{s}$ is a vector drawn at random from the uniform distribution on the unit sphere, Eq. (1.104). In practice, I have found that the results obtained are essentially independent of the value of η ; a value of $\eta = 0.2$ is used for RMC refinements in this thesis. After a spin rotation is proposed, the change in χ^2 is calculated, and the proposed move is either accepted or

rejected with probability given by the Metropolis algorithm [109]:

$$P(\mu \rightarrow \nu) = \begin{cases} \exp[-(\chi_\nu^2 - \chi_\mu^2)] & \text{if } \chi_\nu^2 - \chi_\mu^2 > 0 \\ 1 & \text{otherwise.} \end{cases} \quad (1.106)$$

This process is repeated until no further reduction in χ^2 is observed. In this way, spins are iteratively rotated into a configuration for which the spin correlations are consistent with experimental data.

It can be seen that RMC refinement is exactly analogous to conventional Metropolis MC simulation, Eq. (1.76), except the energy term $E/k_B T$ is replaced by the goodness-of-fit to data χ^2 . For this reason, RMC refinement provides direct information about the magnetic correlations of the system, but does not directly obtain the underlying magnetic interactions.

1.4.4.2 Rescaling data

In practice, it is usually necessary to multiply $I_{\text{calc}}(Q)$ by an empirically-determined scale factor s in order to match experimental data. The best-fit value of s can be calculated after each proposed move by minimising χ^2 , Eq. (1.103), with respect to s , which yields [154]

$$s = \frac{\sum_Q I_{\text{calc}}(Q) I_{\text{expt}}(Q) / [\sigma(Q)]^2}{\sum_Q [I_{\text{calc}}(Q)]^2 / [\sigma(Q)]^2}. \quad (1.107)$$

It is also possible to refine a flat or linear-in- Q background in addition to the scale factor; the relevant equations are given in Ref. 154.

1.4.4.3 Uncertainty in RMC refinement

In RMC refinement, statistical error bars on calculated quantities are estimated by repeating the refinement several times. An alternative approach would be sample a single run at time intervals which are widely-spaced compared to the autocorrelation time [101]. However, the autocorrelation time is system and data-dependent, and can be very large in strongly correlated states, so I have found it more straightforward to use independent

runs.

In addition to statistical errors, systematic errors should also be considered. There will always be some bias due to the choice of initial spin configuration, due both to the limited information contained in the experimental data and the finite time for which the refinement is run. In RMC refinement, a random initial spin configuration is often chosen [155]. The values of the correlations (or other order parameters) obtained after refinement are therefore lower bounds—the smallest values consistent with experimental data [146, 155]. As discussed in Chapter 3, the data can be relatively insensitive to changes in the overall intensity scale, so that the uncertainty in the scale is the main source of error in quantities derived from the refinement (e.g., spin correlation length). The uncertainty in derived quantities may be determined, for an assumed uncertainty in the scale, by performing separate refinements with the scale factor fixed at (say) $\pm 5\%$ of its refined value.

1.4.4.4 Advantages and disadvantages

The RMC approach has been applied to a wide range of materials, but it has also been subject to several criticisms, many of which are described in Ref. 155. At the most fundamental level, it is sometimes argued that the use of a large supercell means that the number of parameters p to be estimated greatly exceeds the number of data points d , so that the RMC model is neither unique nor physically-meaningful [156]. Since the orientation of each spin is fully defined by two angles, the number of parameters is counted as $p = 2N$ for N spins, which indeed is usually greater than d . This criticism makes the implicit assumption that the number of degrees of freedom of the RMC model is calculated using the standard expression $\nu = d - p$, which applies only when the function which is fitted to the data is linear in the parameters. Since $S(\mathbf{Q})$ actually depends on scalar products of spin-pairs [Eq. (1.48)], $\nu = d - p$ cannot be used, and the number of degrees of freedom of the RMC model is not well-defined [157]. This argument has a simple physical interpretation: counting degrees of freedom in the way described above assumes that the average orientation of every individual spin should be uniquely defined by the data. This

is false in a PM or spin liquid, because the lack of long-range magnetic order means that the average spin orientation vanishes. The quantity of interest in frustrated magnetism is not the orientations of individual spins, but their pair (and potentially higher-order) correlations. The spin orientations determined by RMC refinement are intrinsically non-unique, but the spin correlations can be both unique and physically-meaningful.

This result shows that RMC refinement is not necessarily meaningless (which is fortunate, because the rest of this thesis is based on it). However, its results are not always correct in practice; in fact, there are some well-known examples where RMC refinement fails. Perhaps the most infamous of these is amorphous Si [158], which consists of a continuous random network of Si atoms with tetrahedral coordination [Fig. 1.13(a)]. RMC refinement of PDF data for *a*-Si yields an essentially perfect fit-to-data, but fails to reproduce the expected coordination environment of each Si atom [159, 160]. Instead, as Fig. 1.13(b) shows, many Si atoms have three or five-fold coordination, which is unfeasible from a chemical standpoint and unsupported by bond-switching and electronic-structure calculations [158, 161]. The reason for this failure is that the PDF data are only directly sensitive to the average coordination number (and not to its distribution), so that an average over three- and five-fold coordination can produce a similar PDF to a configuration which is entirely four-fold coordinated. This example demonstrates a key point: RMC refinement usually fails because the information content of the data is insufficient in some respect. In such cases, RMC refinement in general overestimates the extent of disorder, so distributions are too broad and/or have multiple maxima, and the magnitudes of correlations are too small and/or too varied. This occurs for two reasons: first, RMC refinement is a stochastic process, and second, refinements are usually initialised from random starting configurations. Hence, RMC refinement produces the most disordered configurations consistent with the experimental data and any other constraints which are imposed [146, 155].

The tendency of RMC refinement to emphasise disorder can lead to results which are essentially meaningless; this is the case for *a*-Si and some other liquids and amorphous materials, unless additional constraints are applied to force the results to be chemically

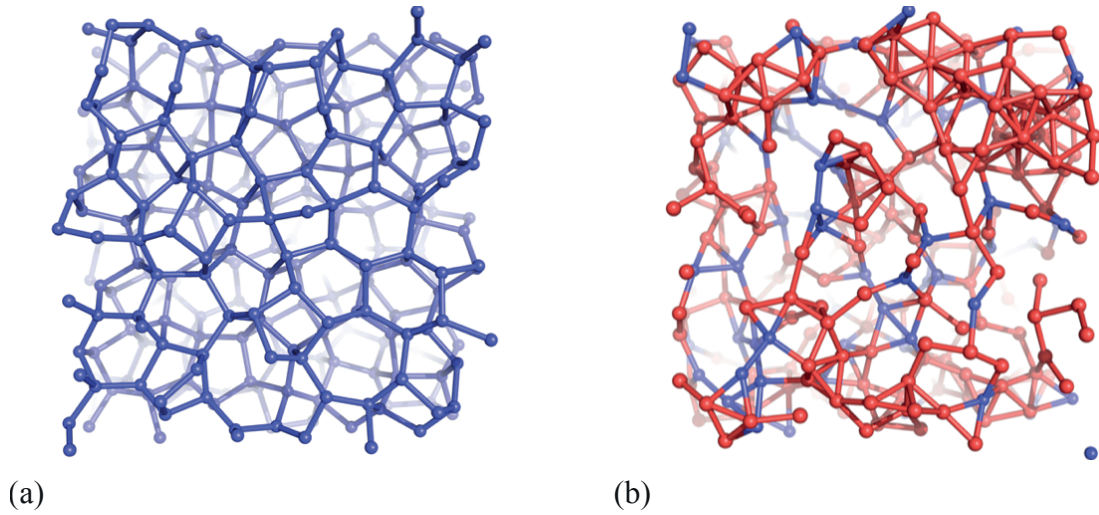


Figure 1.13: (a) Example structure of *a*-Si generated from the trusted “WWW” model [158]. (b) Structure of *a*-Si obtained from RMC refinement to pair-distribution function data. Si atoms with the correct four-fold coordination are coloured blue, and Si atoms with different coordination numbers are coloured red. Figure reproduced from Cliffe and Goodwin [162].

sensible [159]. Alternatively, RMC refinement may produce results which agree well with accepted models: this is often true in crystalline solids which contain correlated atomic displacements [104, 146]. In light of these results, can we expect that RMC refinement of magnetic diffuse-scattering data for spin liquids will be successful? There are grounds for both optimism and pessimism. A pessimist might point out that the real-space resolution of a diffraction measurement is given by $\Delta r \approx 2\pi/Q_{\max}$, and $Q_{\max}$ is limited for magnetic scattering by the effect of the magnetic form factor, so we could expect the results for spin liquids to be less successful than for atomic liquids. The optimist might counter that spin liquids differ from atomic liquids in an important respect: in an atomic liquid, three parameters are required to specify the position of each atom, but in a spin liquid only two parameters are required to specify the orientation of each spin. Hence, spin orientations for spin liquids may be more strongly constrained than atomic positions in atomic liquids. Which of these effects is more important can be determined only by experimentation, which is the subject of Chapter 2.

1.5 Outline of this Thesis

This thesis has three overall aims. First, I aim to evaluate the effectiveness of RMC refinement to magnetic diffuse-scattering data—both powder and single-crystal—to understand spin-liquid states. Second, I aim to develop new approaches to visualise disordered spin structures, in order to identify their essential characteristics without reference to the underlying magnetic interactions. Third, I aim to put these developments into practice, and use RMC refinement to understand spin-liquid states in a wide range of real materials.

This thesis is structured as follows. In Chapter 2, I investigate the information content of the powder-averaged magnetic diffuse-scattering pattern $I(Q)$. In particular, I ask whether it is possible to use RMC refinement to powder data to obtain accurate 3D information about spin-liquid states, without any knowledge of the magnetic interactions. I proceed to show that the extent of information loss during spherical averaging of $I(\mathbf{Q})$ is actually surprisingly minimal and accurate 3D information is recoverable for each frustrated system that I explore.

Having demonstrated the success of the RMC approach for simulated powder data, I apply it to experimental powder data in Chapters 3–5. In Chapter 3, I consider the interplay of frustration and low dimensionality in PM $\text{Ca}_3\text{Co}_2\text{O}_6$, in which Ising spin chains are arranged on a triangular lattice. In Chapter 4, I investigate the canonical spin liquid $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ and identify a collective non-dipolar order within the spin-liquid state. Finally, in Chapter 5 I consider the partially-ordered magnetic structure of the pyrochlore AFM $\text{Gd}_2\text{Ti}_2\text{O}_7$: I report the first experimental measurements on a single-crystal sample and attempt to reconcile these results with previous work.

In Chapter 6 I develop a fast RMC implementation to fit to large single-crystal diffuse-scattering datasets, allowing the first quantitative refinements to the full 3D $I(\mathbf{Q})$ for frustrated systems. This approach is applied to experimental data for two materials. In Chapter 7, I study the canonical AFM MnO . The spin correlations in the PM phase are compared with the local structure in its ordered AFM phase, yielding evidence that weak frustration has significant effects on the PM correlations. In Chapter 8, I study Co-doped β -Mn, identifying a signature of triangular-lattice frustration in this metallic frustrated

magnet.

I conclude in Chapter 9 with some general observations and suggestions for future work.

Chapter 2

Powder Diffuse Scattering: Proof of Principle

2.1 Chapter Summary

In this chapter, I show that the magnetic component of powder neutron-scattering data contains sufficient information to determine the 3D spin correlations in a range of frustrated systems. I demonstrate this by first simulating powder diffuse-scattering data for a number of canonical models of frustrated magnetism. Spin configurations are then refined against these simulated data using RMC refinement, as described in the previous chapter. Finally, the refined spin configurations are analysed to assess how effectively aspects of the starting models are recovered.

I consider three model systems as “test cases” in this chapter, which I choose to reflect different aspects of spin-liquid states: (i) the angular dependence of the spin correlation function which is manifest as highly-structured magnetic diffuse scattering; (ii) the single-ion magnetic anisotropy which leads to individual spins having preferred orientations with respect to their local environment; and (iii) the phenomenon of “hidden order”, in which non-dipolar correlations develop at low temperature.

2.2 Heisenberg Pyrochlore Antiferromagnet

2.2.1 Introduction

The Heisenberg Hamiltonian with AFM nearest-neighbour interactions on the pyrochlore lattice (henceforth “Heisenberg pyrochlore AFM”) is a paradigmatic model of a classical spin liquid [5, 80, 163]. If only nearest-neighbour interactions are considered, the Heisenberg Hamiltonian, Eq. (1.10), can be rewritten as a sum over tetrahedra:

$$H = -\frac{1}{4}J \sum_{\text{tet}} \left| \sum_{i=1}^4 \mathbf{S}_i \right|^2 + \text{constant}, \quad (2.1)$$

where in this chapter $\mathbf{S}_i$ denotes a classical vector of unit length. This form is useful because it shows that, for AFM interactions ($J < 0$), any state in which the vector sum of spins on each tetrahedron is zero is a state of minimum energy. For an individual tetrahedron, there is a continuous degeneracy of these states, because the four spins possess two angular degrees of freedom which can be freely varied without changing the energy [5, 163]. Moreover, the fact that individual tetrahedra share corners does not remove this degeneracy, and the Heisenberg pyrochlore AFM remains disordered at all temperatures [5, 80].

I simulated data for the Heisenberg pyrochlore AFM using MC simulations [Section 1.4.1.1]. A low temperature ($T/J = 0.0005$) was chosen in order to generate states which closely approximated the $\sum_{i \in \text{tet}} \mathbf{S}_i = 0$ constraint. Simulations were performed for 10^5 proposed moves per spin on periodic systems of size $6 \times 6 \times 6$ unit cells ($N = 3456$ spins), and all quantities were averaged over 64 independent spin configurations in order to produce results of high statistical quality (unless shown in the figures, all error bars are smaller than the symbol size). I set the cubic lattice parameter $a = 10.1 \text{ \AA}$, which is a typical value for rare-earth pyrochlore magnets [18]. Powder diffuse-scattering “data” were simulated from these spin configurations using Eq. (1.58). Data were generated for the reciprocal-space range $0 < Q \leq 5 \text{ \AA}^{-1}$ and binned at an interval $\Delta Q = 0.02 \text{ \AA}^{-1}$, and an arbitrary magnetic form factor (Ho^{3+}) was applied [78].

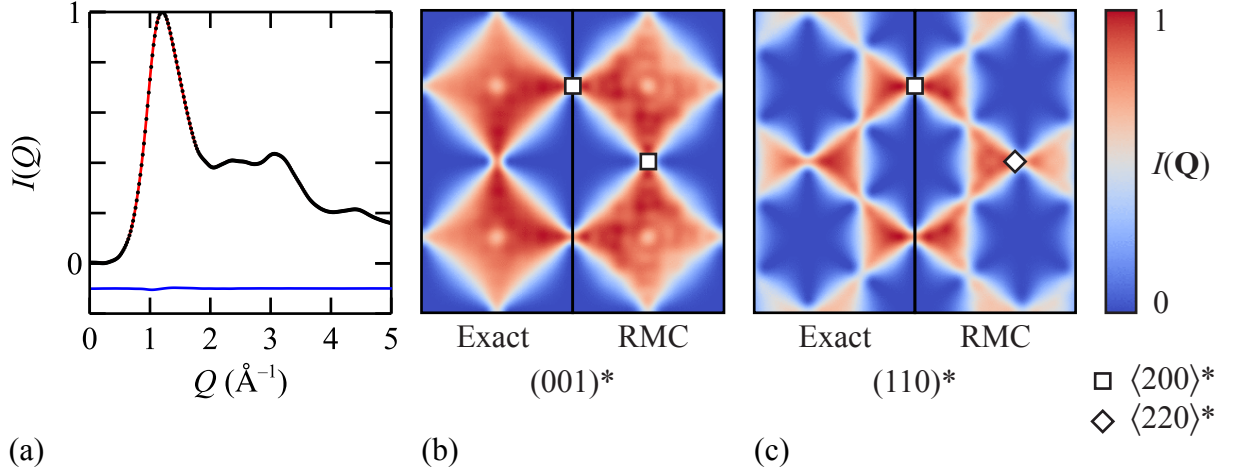


Figure 2.1: (a) Powder-averaged magnetic diffuse-scattering pattern, showing simulated data for the Heisenberg pyrochlore AFM (black circles), RMC fit (red line), and data-fit (blue line). (b) Single-crystal magnetic diffuse-scattering pattern in the $(001)^*$ reciprocal-space plane. (c) Single-crystal magnetic diffuse-scattering pattern in the $(110)^*$ reciprocal-space plane. In (b) and (c), the panels labelled “Exact” are calculated from the MC model used to generate the powder data shown in (a), and the panels labelled “RMC” are calculated from RMC refinement to these powder data.

These simulated data were then used to drive RMC refinements. As for the MC simulations, 64 separate RMC refinements were performed using configurations of size $6 \times 6 \times 6$ unit cells, which were initialised with random spin orientations. To make the test more realistic, an overall scale factor was refined to the data by applying Eq. (1.107). Each refinement was run for 200 proposed moves per spin, after which no significant improvement in goodness-of-fit was observed. A representative RMC fit is shown in Fig. 2.1(a), and shows excellent agreement with the simulated data ($R_{\text{wp}} = 0.1\%$). The overall scale factor refined to a value of 1.000036(3); the close agreement with the correct value of unity suggests that the scale factor can be refined robustly if the data are of high quality.

2.2.2 Single-Crystal Diffuse Scattering

That an RMC fit should agree with the powder data is to be expected, because this is what the refinement is designed to achieve. Hence, as I discuss in Section 1.4.4, a good fit-to-data alone does not show that the refined spin configuration is correct, or even physically-sensible: the refinement must also allow new predictions to be made.

Perhaps the most important quantity which can be calculated from the refined RMC spin configurations is the 3D magnetic diffuse-scattering pattern $I(\mathbf{Q})$. In the Heisenberg pyrochlore AFM, $I(\mathbf{Q})$ is especially interesting, because sharp singularities (known as “pinch points”) occur at reciprocal-lattice points [82, 164]. The origin of the pinch points can be understood by associating a local magnetisation $\mathbf{M}$ with the midpoint of each tetrahedron. The $\sum_{i \in \text{tet}} \mathbf{S}_i = 0$ ground-state constraint implies that $\mathbf{M}$ is divergence-free, so the magnetisation obeys a constraint $\nabla \cdot \mathbf{M} = 0$ analogous to Gauss’s law for magnetism. Fourier transforming this constraint yields $\mathbf{Q} \cdot \mathbf{M}(\mathbf{Q}) = 0$. It follows that the reciprocal-space correlation function has a dipolar form near to reciprocal-lattice positions,

$$I(\mathbf{q}) \propto \sum_{\alpha, \beta} \left(\delta^{\alpha\beta} - \frac{q^\alpha q^\beta}{q^2} \right), \quad (2.2)$$

where $\mathbf{q} = \mathbf{Q} - \mathbf{G}$, and $\mathbf{G}$ is a reciprocal-lattice vector which is not a zone centre and obeys the face-centred cubic selection rule that h, k , and l are either all odd or all even [82, 164]. This result was an important milestone in frustrated magnetism because it showed that enforcing a local rule constrains the long-range behaviour of the spin correlations. In this chapter, its relevance is that pinch points in $I(\mathbf{Q})$ are invisible in the powder average [Fig. 2.2(a)], and can only be directly measured on a single-crystal sample; hence, the ability of RMC refinement to predict pinch-point scattering from powder data would be a useful result.

Fig. 2.1(b) compares the $I(\mathbf{Q})$ calculated from the RMC spin configurations with the numerically-exact results obtained for the starting model. The RMC prediction shows very good qualitative agreement with the exact calculations, including the presence of pinch-point scattering around $\langle 200 \rangle^*$, $\langle 220 \rangle^*$, and $\langle 111 \rangle^*$ reciprocal-space positions. The pinch points, however, are not perfectly sharp. This occurs because the real-space spin correlations must be truncated at a finite distance in any atomic-scale model; hence, the blurring of pinch-points is not a specific limitation of RMC refinement, but is also present in the numerically-exact simulations.

This result shows that the combination of powder diffuse-scattering data and knowledge of the crystal structure is sufficient to recover the qualitative form of $I(\mathbf{Q})$ for the

pyrochlore Heisenberg AFM. This conclusion is not limited to this particular model system: two more examples of systems in which $I(\mathbf{Q})$ can be reconstructed from $I(Q)$ are presented in the following sections. Moreover, in a previous work [152], we considered seven separate systems, with different crystal structures and magnetic interactions, and found that the 3D scattering pattern was recoverable from powder data in each case. I do not give details of these results here, but refer instead to Fig. 2 of Ref. 152.

2.2.3 Radial Spin Correlations

So far, I have considered the reciprocal-space properties of the RMC spin configurations. The success of RMC refinement in recovering the $\sum_{i \in \text{tet}} \mathbf{S}_i = 0$ constraint can, however, be assessed more straightforwardly in real space. The $\sum_{i \in \text{tet}} \mathbf{S}_i = 0$ constraint implies that the average scalar product of a spin with its six nearest-neighbours $\langle \mathbf{S}(0) \cdot \mathbf{S}(r_1) \rangle = -1/3$ in the low-temperature limit, so the deviation of the RMC result for $\langle \mathbf{S}(0) \cdot \mathbf{S}(r_1) \rangle$ from the numerically-exact model provides a quantitative check on the refinement accuracy. I find $\langle \mathbf{S}(0) \cdot \mathbf{S}(r_1) \rangle_{\text{RMC}} = -0.329969(5)$, compared to $\langle \mathbf{S}(0) \cdot \mathbf{S}(r_1) \rangle_{\text{exact}} = -0.3332094(3)$, an error of 1%. Hence the local constraint is recovered quantitatively from RMC refinement. Fig. 2.2(a) shows that the excellent agreement between RMC refinement and the exact model is preserved at further-neighbour distances. Powder data are therefore very effective at determining the radial spin correlations. While this result is perhaps unsurprising [165], it is not necessarily the case, since $I(Q)$ and $\langle \mathbf{S}(0) \cdot \mathbf{S}(r) \rangle$ only contain equivalent information in the limit of large Q_{max} .

The RMC spin configurations not only give access to the average values of the spin correlations, but also to their distributions. Fig. 2.2(b) compares the distribution of $\mathbf{S}(0) \cdot \mathbf{S}(r_1)$ obtained from RMC refinement with the distribution obtained from the exact model. Good qualitative agreement is obtained; the main error is that the RMC distribution is slightly too flat. This result is consistent with the recognised tendency of RMC refinement to produce the most disordered spin configurations consistent with experimental data [166], described in Section 1.4.4. Despite this caveat, the results of this section show that RMC refinement is very successful at recovering spin correlations from the powder $I(Q)$:

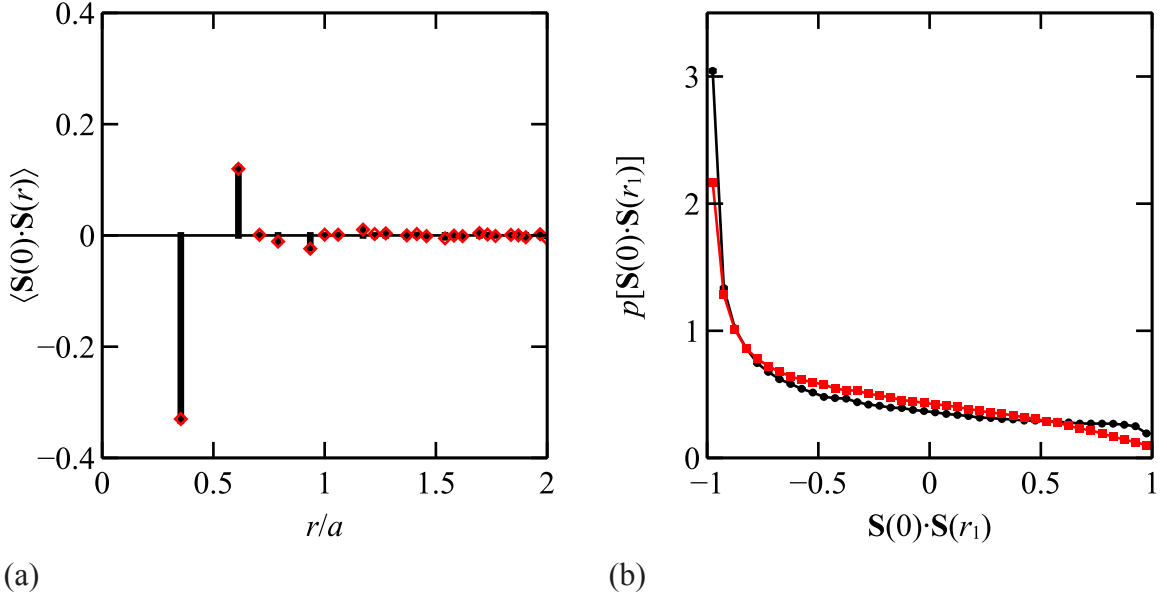


Figure 2.2: (a) Spin correlation function $\langle \mathbf{S}(0) \cdot \mathbf{S}(r) \rangle$ for the Heisenberg pyrochlore AFM. Black bars show exact results (from MC simulation) and red diamonds show results from RMC refinement to simulated powder data. (b) Probability distribution function of nearest-neighbour spin orientations for the Heisenberg pyrochlore AFM. Black circles show exact results and red squares show results from RMC refinement.

radial spin correlations are accurate to $\approx 1\%$, and very good qualitative agreement is obtained with the exact single-crystal $I(\mathbf{Q})$.

2.3 Spin Ice

2.3.1 Introduction

As a second test case I consider spin ice, which is a name for a class of rare-earth oxides $\text{Ln}_2\text{R}_2\text{O}_7$, where $\text{Ln} = \text{Ho, Dy}$ and $\text{R} = \text{Ti, Sn, Ge}$ [8, 81, 120, 133, 136, 167]. In these systems, magnetic Ln^{3+} ions are again arranged on the pyrochlore lattice. The crystal-field splitting due to the oxide ions is very large, and forces the Ln^{3+} spins to point either directly towards or directly away from the centres of the Ho_4 tetrahedra at low temperature [168]. In the spin-ice state, the spins obey the so-called “ice rule”: two spins point towards, and two spins away from, the centre of each tetrahedron [8]. This constraint does not lead to long-range magnetic order, because out of 16 ways of arranging spins on each tetrahedron, there are six that satisfy the ice rule and so are ground states. The

number of ground states N_{gs} for the entire structure containing N spins (corresponding to $N/2$ tetrahedra) can be estimated:

$$\begin{aligned}
N_{\text{gs}} &= \text{total number of spin states} \times \text{proportion that satisfy ice rule} \\
&= 2^{\# \text{ spins}} \times (\text{proportion of ice rule-satisfying states per tetrahedron})^{\# \text{ tetrahedra}} \\
&= \left(\frac{3}{2}\right)^{N/2}.
\end{aligned} \tag{2.3}$$

This macroscopic degeneracy of ground states should be reflected in a zero point entropy $S_0 = k_B \ln N_{\text{gs}} = \frac{Nk_B}{2} \ln \frac{3}{2} = 1.68 \text{ J K}^{-1} \text{ mol}^{-1}$, which has been verified experimentally using specific-heat measurements [32].

This calculation was in fact performed by Pauling in 1935 [169]—more than 60 years before the discovery of the spin ice state by Harris *et al.* in 1997 [8]—for the system which gives spin ice its name: cubic water ice. The molecular structure of water is retained in ice, so that each oxygen atom has two covalently-bonded hydrogens near to it and two hydrogen-bonded hydrogens further away, with hydrogens lying along the line connecting two oxygens. The “two in, two out” rule for spins in spin ice is exactly analogous to the “two long, two short” rule for O–H bonds in ice, and indeed an equivalent zero-point entropy has been measured for water ice [170].

The simplest Hamiltonian which explains the ice rule considers Ising spins coupled by a FM exchange interaction $J > 0$ between nearest-neighbour spins [8]. The requirement for spins to point towards or away from the centres of tetrahedra corresponds to each spin pointing either parallel or antiparallel to one of the local- $\langle 111 \rangle$ axes given in Table 2.1. Spin vectors can therefore be written as $\mathbf{S}_i = \sigma_i \mathbf{z}_i$, where $\mathbf{z}_i$ is the $\langle 111 \rangle$ axis along which the spin points, and $\sigma_i = \pm 1$ indicates whether it is parallel or antiparallel to this axis. This leads to the nearest-neighbour spin ice Hamiltonian:

$$H_{\text{NSI}} = -\frac{J}{2} \sum_{\langle i,j \rangle} (\mathbf{z}_i \cdot \mathbf{z}_j) \sigma_i \sigma_j = \frac{J}{6} \sum_{\langle i,j \rangle} \sigma_i \sigma_j, \tag{2.4}$$

where I have used the result that neighbouring spins on the pyrochlore lattice point along different $\langle 111 \rangle$ directions, so that $\mathbf{z}_i \cdot \mathbf{z}_j = -1/3$. This means that the FM exchange

Fractional coordinates	Local axes $\mathbf{x}, \mathbf{y}, \mathbf{z}$
$(0, 0, \frac{1}{2})$	$[\bar{1}\bar{1}2], [\bar{1}\bar{1}0], [\bar{1}\bar{1}1]$
$(0, \frac{1}{4}, \frac{3}{4})$	$[\bar{1}\bar{1}2], [110], [\bar{1}\bar{1}\bar{1}]$
$(\frac{1}{4}, 0, \frac{3}{4})$	$[\bar{1}\bar{1}2], [\bar{1}\bar{1}0], [\bar{1}\bar{1}\bar{1}]$
$(\frac{1}{4}, \frac{3}{4}, 0)$	$[112], [\bar{1}\bar{1}0], [\bar{1}\bar{1}1]$

Table 2.1: Table showing fractional coordinates of magnetic ions and the directions of their local $\mathbf{x}, \mathbf{y}, \mathbf{z}$ axes for the pyrochlore lattice. The crystallographic unit cell contains 16 rare-earth ions, of which 4 are listed here and the remaining 12 are related by face-centring. The point symmetry of the rare-earth site is $\bar{3}m$, which requires the spins either to lie preferentially along the local $\mathbf{z}$ -axis, or to be distributed isotropically in the plane perpendicular to $\mathbf{z}$.

constant J which couples vector spins is converted to an effective AFM exchange constant $-J/3$ between Ising pseudospins [171].

Much of the recent interest in spin ice has been due to the prediction [10]—now confirmed by experiments [11, 172, 173]—that excitations within spin ice have the properties of magnetic monopoles, the magnetic analogues of single electrical charges. The reason for this is as follows [10]: each spin is a magnetic dipole, equivalent to a pair of oppositely-charged monopoles. A tetrahedron satisfying the ice rule is neutral in terms of magnetic charges, but flipping one of the spins gives it a net magnetic charge, balanced by an opposite charge on an adjacent tetrahedron. Another spin on the adjacent tetrahedron can then flip, which moves the monopole onto a third tetrahedron. A chain of spins can be flipped in this way, forming a string of flipped dipoles with monopoles at the ends. The key part of the argument is that the degeneracy of the magnetic structure means that there is no unique way of drawing such a chain between two monopoles. The monopoles are deconfined, which is the property a “true” monopole must have in order to distinguish it from being simply one end of a dipole. I note, however, that the monopoles in the nearest-neighbour spin ice model [Eq. (2.4)] do not carry magnetic charge in the same sense as in the more accurate “dipolar spin-ice model”, which includes the long-range magnetic dipolar interaction as well as nearest-neighbour exchange interactions [81]. In particular, in the dipolar spin-ice model, magnetic monopoles interact via the (magnetic) Coulomb interaction, which is not the case for the nearest-neighbour spin ice model [174].

I simulated Eq. (2.4) using Metropolis MC simulations. These simulations were per-

formed on periodic systems of size $6 \times 6 \times 6$ unit cells, and were run until all tetrahedra were charge-neutral. Simulated powder diffuse-scattering data were averaged over 64 independent spin configurations to improve the statistics. These simulated data were then used to drive two sets of RMC refinements. In the first set, I impose the local- $\langle 111 \rangle$ Ising anisotropy as a constraint. This situation is probably realistic in many systems, because the presence and nature of single-ion anisotropy can often be inferred from measurements of the single-crystal susceptibility [175], polarised-neutron scattering [176], inelastic neutron scattering [168], or Raman spectra [177] before a study of the magnetic diffuse scattering is undertaken. In the second set of refinements, I assume no prior knowledge of the Ising anisotropy, and allow the spins to take any orientation. The aim of this second set of refinements is to assess how much information $I(Q)$ alone contains about the single-ion anisotropy.

2.3.2 Ising Refinement

In this first set of RMC refinements, I assume that the spins behave as purely Ising variables, $\mathbf{S}_i = \sigma_i \mathbf{z}_i$, where the $\mathbf{z}_i$ are given in Table 2.1. Refinements were initialised with Ising pseudospins $\sigma = \pm 1$ randomly chosen for each atom, and a single proposed move involved in flipping the sign of a randomly-chosen spin. I found that somewhat longer refinement times (1000 proposed moves per spin) were required for convergence compared to the Heisenberg refinements of the previous section. A representative fit to simulated data is shown in Fig. 2.3(a), and represents excellent agreement with experimental data ($R_{\text{wp}} = 0.09\%$). The single-crystal diffuse-scattering patterns for the Ising refinement are shown in Fig. 2.3(b) and Fig. 2.3(c). Again, excellent agreement with the numerically-exact calculations is obtained from the RMC refinements.

This excellent agreement is also found in real space. Fig. 2.4(a) shows the correlation function of Ising spins $\langle \sigma(0)\sigma(r) \rangle = -3 \langle \mathbf{S}(0) \cdot \mathbf{S}(r) \rangle$ for the exact calculation and the RMC refinement; the level of agreement is comparable to that obtained for the Heisenberg pyrochlore AFM [Section 2.2]. This is perhaps not surprising, since $\langle \sigma(0)\sigma(r) \rangle$ for the nearest-neighbour spin ice model is actually identical to $\langle \mathbf{S}(0) \cdot \mathbf{S}(r) \rangle$ for the Heisenberg

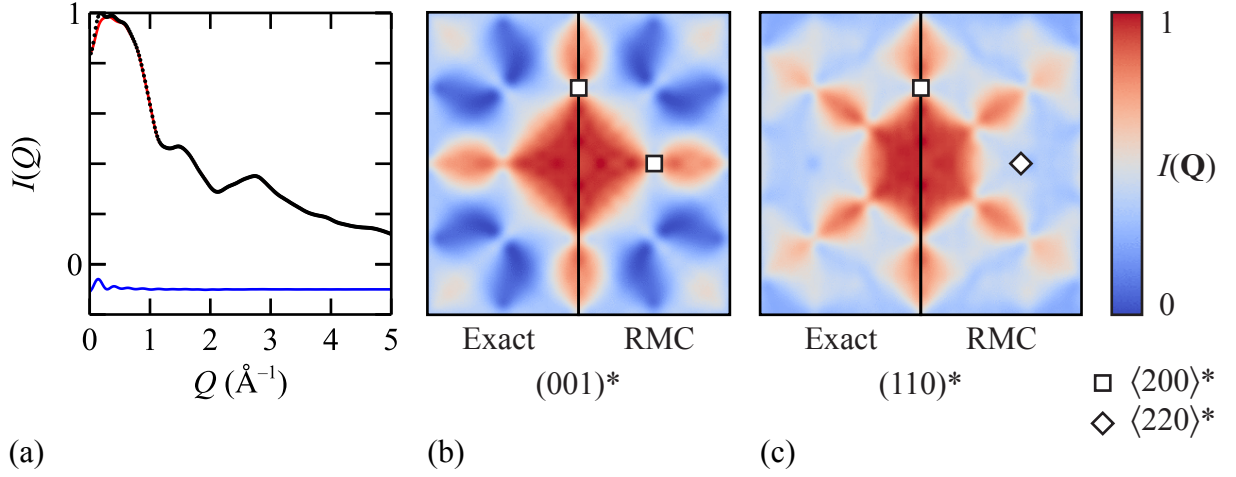


Figure 2.3: (a) Powder-averaged magnetic diffuse-scattering pattern, showing simulated data for spin ice (black circles), RMC fit assuming Ising spins (red line), and data-fit (blue line). (b) Single-crystal magnetic diffuse-scattering pattern in the $(001)^*$ reciprocal-space plane. (c) Single-crystal magnetic diffuse-scattering pattern in the $(110)^*$ reciprocal-space plane. In (b) and (c), the panels labelled “Exact” are calculated from the MC model used to generate the powder data shown in (a), and the panels labelled “RMC” are calculated from Ising RMC refinement to these powder data.

pyrochlore AFM. I also check directly whether the ice rule is satisfied in real space by counting the number of tetrahedra which are charge neutral (i.e., which obey the two-in, two-out ice rule), the number which have a single charge (i.e., three-in, one-out, or vice versa), and the remainder which are doubly charged (all-in or all-out). I find that 99% of the tetrahedra obey the ice rule in the RMC configurations, compared to 100% in the ideal spin-ice state. This result provides convincing evidence that the spin-ice state can be recovered from powder neutron-scattering data if the Ising anisotropy is assumed.

2.3.3 Unconstrained Refinement

While it may be reasonable to assume Ising spins for spin-ice materials, in other materials the extent of single-ion anisotropy may not be so easily predicted. In this section, I ask whether powder diffuse-scattering data contain enough information to recover the local- $\langle 111 \rangle$ anisotropy if its presence is not assumed. I therefore attempt to fit the same data of Section 2.3.2, but now allow the spin orientation to vary freely. This is a much more difficult task than the Ising refinement, because states in which all spins lie close to local- $\langle 111 \rangle$ directions represent a very small fraction of the phase space. Hence I do

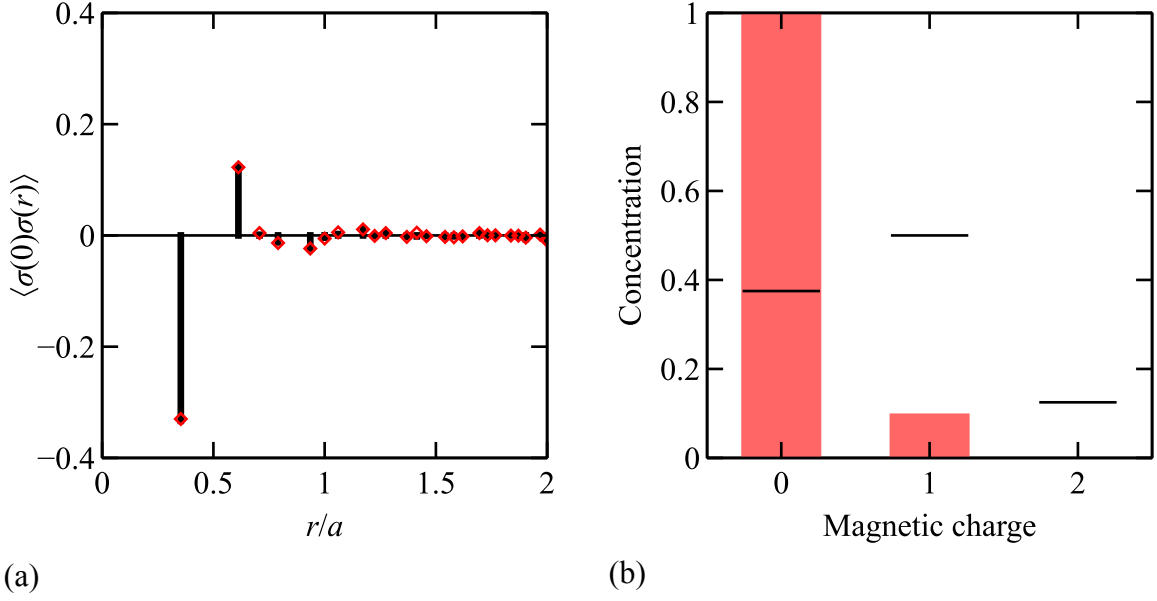


Figure 2.4: (a) Spin correlation function $\langle \sigma(0)\sigma(r) \rangle$ for spin ice. Black bars show results for the ideal spin-ice state and red diamonds show results from Ising RMC refinement to simulated powder data. (b) Fraction of tetrahedra with magnetic charge of 0, 1, and 2. Pink bars show results from Ising RMC refinement and black lines show results for entirely random spin orientations. The ideal spin-ice state corresponds to all tetrahedra having a magnetic charge of 0.

not expect a perfect result, but instead aim to determine the extent to which powder diffuse-scattering data are sensitive to local anisotropy.

That $I(Q)$ should show some sensitivity to single-ion anisotropy is anticipated from the definitions of A_{ij} and B_{ij} , Eqs. (1.59) and (1.60), which contain $\mathbf{S}_i \cdot \hat{\mathbf{r}}_{ij}$ terms. Consequently, $I(Q)$ can contain information about the single-ion anisotropy even in cubic crystals, because the point symmetry of the magnetic site may be lower than cubic. This is the case for the pyrochlore lattice, in which the rare-earth site has $\bar{3}m$ point symmetry. In practice, however, the extent of this sensitivity is difficult to predict, because it depends on the spin orientations themselves in addition to the local coordination of the magnetic ion.

Fig. 2.5 shows the fit to powder data, and compares the exact $I(\mathbf{Q})$ with the calculation from the refined RMC spin configurations. While the fit to powder data is excellent, the predicted single-crystal diffuse scattering is less convincing than the results shown in Fig. 2.3. The broad features of the single-crystal diffuse scattering are correctly recovered, but some noise and “lumpiness” is apparent in the RMC calculation. To investigate the

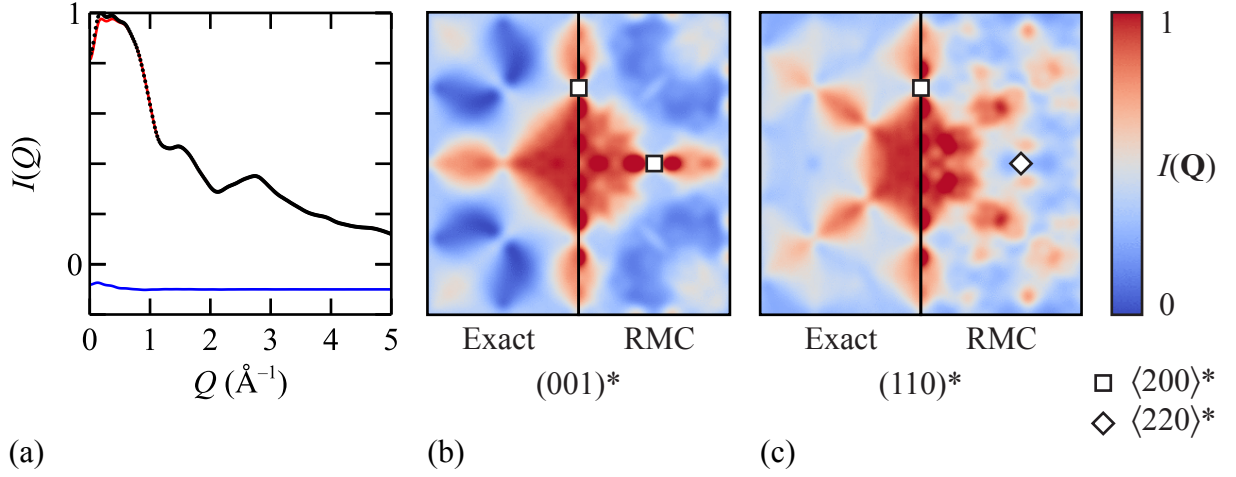


Figure 2.5: (a) Powder-averaged magnetic diffuse-scattering pattern, showing simulated data for spin ice (black circles), RMC fit with unconstrained spin orientations (red line), and data-fit (blue line). (b) Single-crystal magnetic diffuse-scattering pattern in the $(001)^*$ reciprocal-space plane. (c) Single-crystal magnetic diffuse-scattering pattern in the $(110)^*$ reciprocal-space plane. In (b) and (c), the panels labelled “Exact” are calculated from the MC model used to generate the powder data shown in (a), and the panels labelled “RMC” are calculated from unconstrained RMC refinement to these powder data.

origin of this effect, I calculate the $\langle \sigma(0)\sigma(r) \rangle$ [Fig. 2.6(a)]. The RMC refinement agrees very well with the exact $\langle \sigma(0)\sigma(r) \rangle$ at short distances, but at long distances, where a larger number of inter-atomic vectors overlap, spurious fluctuations occur. These fluctuations will produce high-frequency noise in $I(\mathbf{Q})$, which accounts for the observed features in Fig. 2.5(b) and (c). Despite this, the number of tetrahedra which satisfy the ice rule—defined by determining whether each spin lies closer to $+\mathbf{z}$ or $-\mathbf{z}$, where $\mathbf{z}$ is its local- $\langle 111 \rangle$ axis—remains high, at 88% [Fig. 2.6(b)].

Finally, I assess how effectively RMC refinement can recover the local- $\langle 111 \rangle$ spin anisotropy by calculating the distribution of individual spin orientations. Fig. 2.7(a) shows the probability distribution function $p(\mathbf{S} \cdot \mathbf{z})$ of the scalar product of spins with their local $\langle 111 \rangle$ axis, $\mathbf{z}$. For the ideal spin-ice state this function is zero for all $\mathbf{S} \cdot \mathbf{z}$ not equal to ± 1 . The RMC distribution is broader, but is nevertheless strongly peaked at $\mathbf{S} \cdot \mathbf{z} = \pm 1$. This is the key result of this section: it suggests that the RMC refinement to powder data correctly recovers the nature of single-ion anisotropy, and provides a lower bound on its magnitude.

An alternative way of visualising the spin anisotropy uses an equal-area stereographic

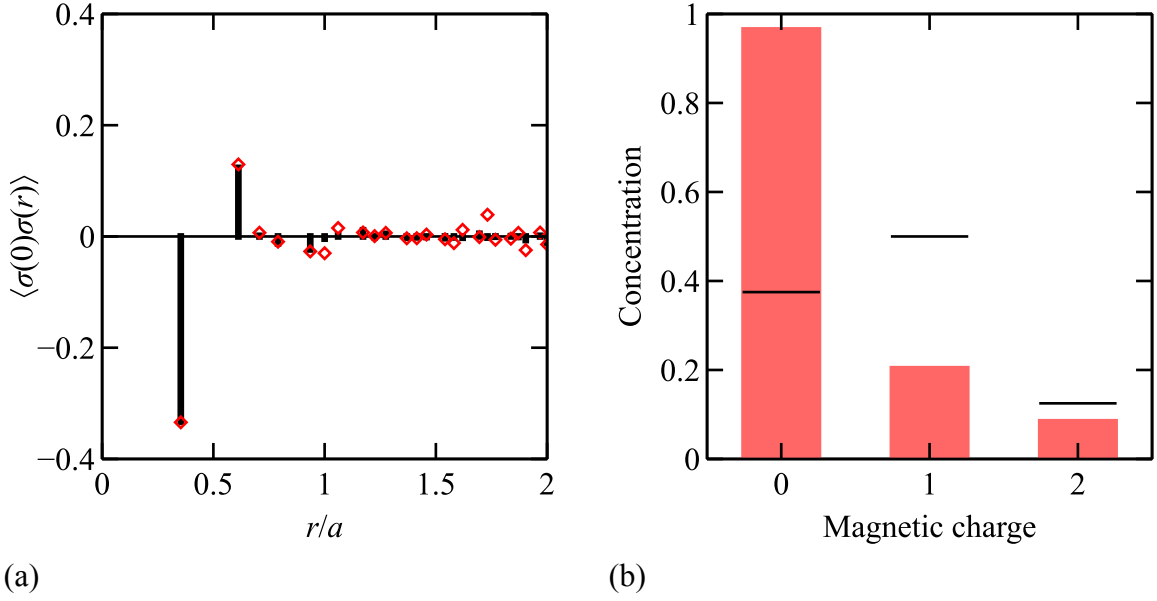


Figure 2.6: (a) Spin correlation function $\langle \sigma(0)\sigma(r) \rangle$ for spin ice. Black bars show results for the ideal spin-ice state and red diamonds show results from unconstrained RMC refinement to simulated powder data. (b) Fraction of tetrahedra with magnetic charge of 0, 1, and 2. Pink bars show results from unconstrained RMC refinement and black lines show results for entirely random spin orientations. The ideal spin-ice state corresponds to all tetrahedra having a magnetic charge of 0.

projection of the probability distribution function, which is expressed in terms of the number of spins $n(\theta, \phi)$ which lie within angular the angular range $d\theta, d(\cos \phi)$,

$$p(\theta, \phi) = \frac{n(\theta, \phi)}{N d\theta d(\cos \phi)}, \quad (2.5)$$

where N is the total number of spins. This function is conveniently shown on a logarithmic scale, so that $\ln(p) = 0$ implies that the probability of a spin having orientation in the range (θ, ϕ) to $(\theta + d\theta, \phi + d\phi)$ is equal to that expected for a random distribution, a negative value of $\ln(p)$ indicates a less-than-random probability, and a positive value a greater-than-random probability. A stereographic projection of $\ln(p)$ is shown in Fig. 2.7(b). Compared to the 1D representation shown in Fig. 2.7(a), the stereographic projection is advantageous for systems where the point symmetry is low (so that the spins may not lie along a single axis). I use it for this reason in Chapters 4 and 8.

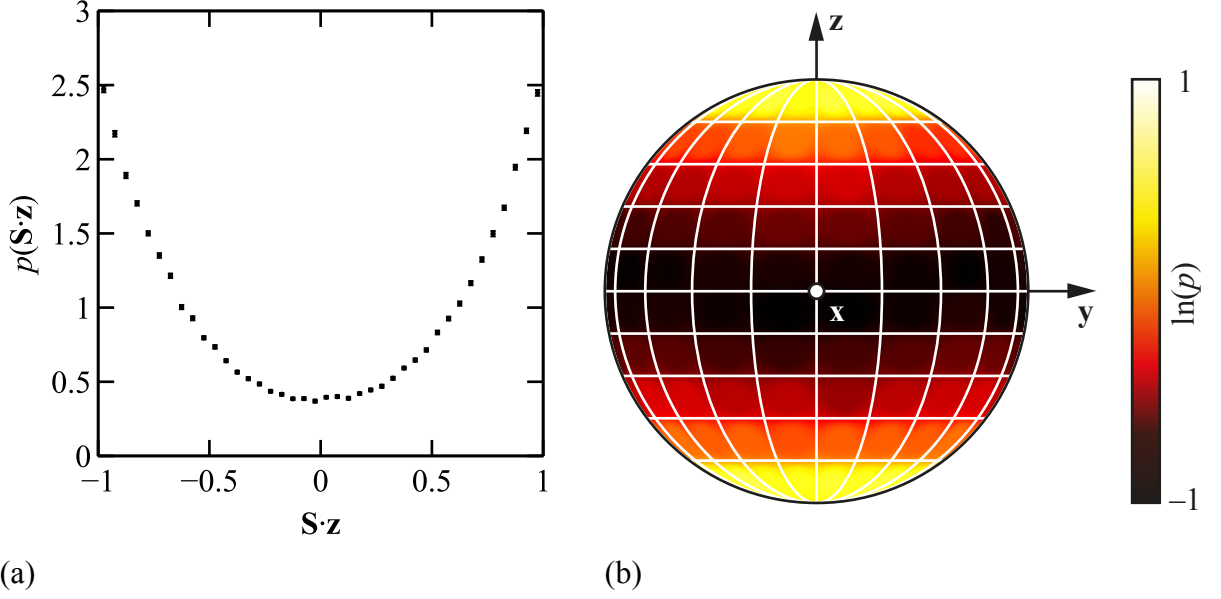


Figure 2.7: (a) Probability distribution function $p(\mathbf{S} \cdot \mathbf{z})$ of the scalar product of spins with their local $\mathbf{z}$ -axes obtained from unconstrained RMC refinement to simulated powder data for spin ice. (b) Stereographic projection of the logarithmic probability distribution $\ln(p)$ of spin orientations obtained from unconstrained RMC refinement. The local $\mathbf{x}, \mathbf{y}, \mathbf{z}$ are defined in Table 2.1.

2.4 Kagome Heisenberg Antiferromagnet

2.4.1 Introduction

As a final case study I consider the Heisenberg nearest-neighbour AFM on the kagome lattice (“Heisenberg kagome AFM”). The kagome lattice is shown in Fig. 2.8. This canonical frustrated model system was studied in detail in the early 1990s and does not show long-range magnetic order at finite temperature [178, 179]. At low temperature, spins on each triangle form a coplanar 120° arrangement, and there is a macroscopic degeneracy of ways in which these coplanar units can be arranged [178, 179]. Several real materials realise aspects of this behaviour—for example, hydronium jarosite [180, 181] and herbertsmithite [182, 183]—although in practice there is usually some subtle feature which breaks the degeneracy of ground states.

I simulated powder diffuse-scattering data for this model at a low temperature $T/J = 0.01$. MC simulations for this Hamiltonian were performed for periodic spin configurations of size $N = 3600$ spins (comprising ten stacked kagome slabs each of size 360 spins). In

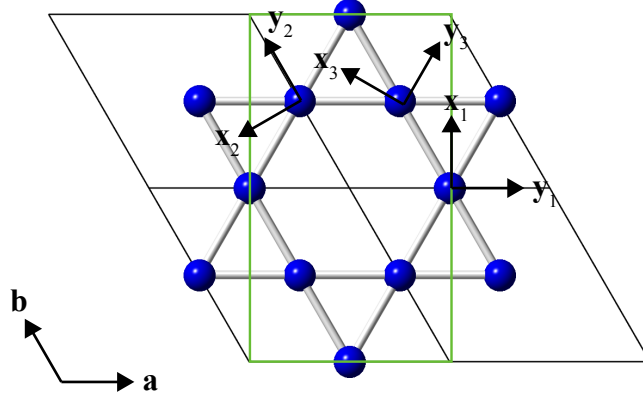


Figure 2.8: Kagome lattice. The hexagonal unit cell is shown in black and the orthorhombic cell used for RMC refinements in green. The local $\mathbf{x}$ axis for a given atom points towards the centre of one of the triangles to which the atom belongs, and the local $\mathbf{y}$ axis is a perpendicular vector. Note that due to the point symmetry $\mathbf{x}$ and $-\mathbf{x}$ are equivalent directions, as are $\mathbf{y}$ and $-\mathbf{y}$.

order to simplify the calculations, I converted the hexagonal unit cell to an orthorhombic cell containing twice as many atoms, by applying the transformation matrix

$$\begin{bmatrix} \mathbf{a}_o \\ \mathbf{b}_o \\ \mathbf{c}_o \end{bmatrix} = \begin{bmatrix} 1 & 0 & 0 \\ 1 & 2 & 0 \\ 0 & 0 & 1 \end{bmatrix} \begin{bmatrix} \mathbf{a}_h \\ \mathbf{b}_h \\ \mathbf{c}_h \end{bmatrix}. \quad (2.6)$$

Sixteen independent simulations were performed in order to obtain good statistics for the scattering calculations. The powder diffuse scattering pattern was then calculated from these spin configurations using Eq. (1.58), with an arbitrary magnetic form factor (Ho^{3+}) applied. I set the hexagonal lattice parameter $a_h = 2\pi \text{ \AA}$. Powder data were simulated in the range $0 < Q \leq 5 \text{ \AA}^{-1}$ and binned at an interval $\Delta Q = 0.02 \text{ \AA}^{-1}$. I then performed RMC refinements to these simulated data for 300 proposed moves per spin, after which time no significant improvement was observed in the goodness-of-fit.

2.4.2 Sensitivity to Nematic Order

Looking first at reciprocal space, I calculate $I(\mathbf{Q})$ from the RMC refinements and compare it with the numerically-exact result [Fig. 2.9(b)]. Both patterns were averaged over 16

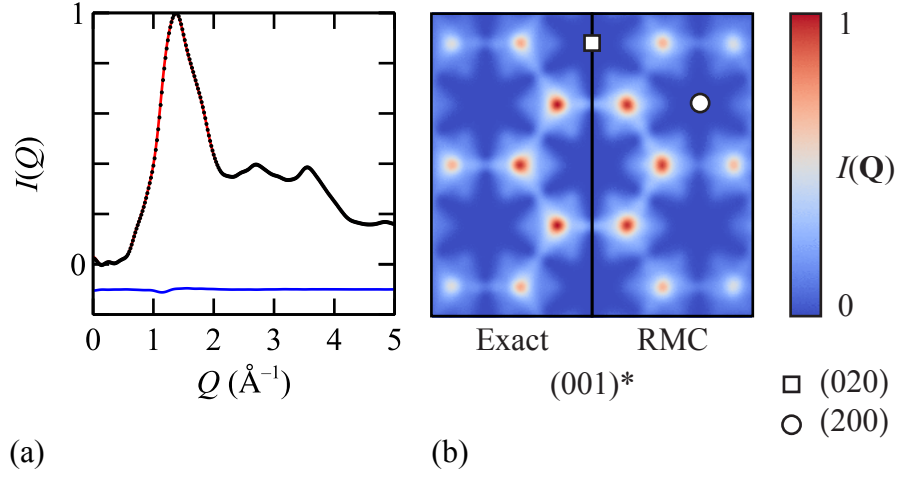


Figure 2.9: (a) Powder-averaged magnetic diffuse-scattering pattern, showing simulated data for the Heisenberg kagome AFM (black circles), RMC fit (red line), and data-fit (blue line). (b) Single-crystal magnetic diffuse-scattering pattern in the $(001)^*$ reciprocal-space plane. The panel labelled “Exact” is calculated from the MC model used to generate the input data shown in (a); the panel labelled “RMC” is calculated from the RMC refinement to these simulated powder data.

independent spin configurations. As for the previous case studies, excellent agreement is obtained, with only a slight blurring—corresponding to disordering of the spins—apparent in the RMC pattern. Both calculations also agree well with those shown in Ref. 184.

In Fig. 2.10(a) I plot the radial spin correlation function $\langle \mathbf{S}(0) \cdot \mathbf{S}(r) \rangle$ for the RMC refinements, and compare it with the exact result. Excellent agreement is again obtained. A natural question following from this is whether the RMC refinements might afford some sensitivity to higher-order spin correlations. Such correlations are indeed present in the kagome Heisenberg AFM. At low temperatures ($T/J \lesssim 0.02$), short-range spin nematic order develops, so that adjacent triangles of spins tend to lie in a common plane; the mechanism involves “order by disorder” [179, 184, 185]. Since the $\langle \mathbf{S}(0) \cdot \mathbf{S}(r) \rangle$ is insensitive to nematic order, I follow Ref. 179 and define a nematic correlation function which is equal to 1 for a coplanar state:

$$g_n(r) = \frac{3}{2} \langle (\mathbf{n}(0) \cdot \mathbf{n}(r))^2 \rangle - \frac{1}{2}, \quad (2.7)$$

where

$$\mathbf{n} = \frac{2}{3\sqrt{3}} (\mathbf{S}_1 \times \mathbf{S}_2 + \mathbf{S}_2 \times \mathbf{S}_3 + \mathbf{S}_3 \times \mathbf{S}_1) \quad (2.8)$$

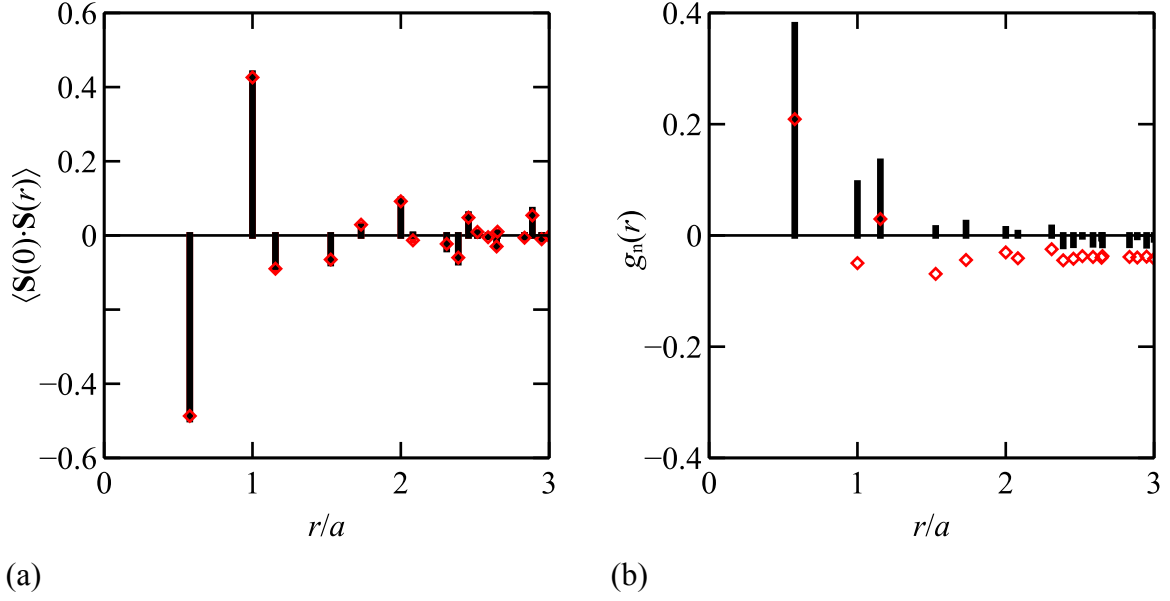


Figure 2.10: (a) Spin correlation function $\langle \mathbf{S}(0) \cdot \mathbf{S}(r) \rangle$ for the Heisenberg kagome AFM. Exact values (from MC simulations) are shown as black bars and values obtained from RMC refinement to simulated powder data are shown as red diamonds. (b) Nematic correlation function $g_n(r)$ defined in the text. Exact values are shown as black bars and values obtained from RMC refinement are shown as red diamonds.

is the vector normal to the plane formed by the three spins of a triangle. The comparison of the RMC $g_n(r)$ with the exact result is shown in Fig. 2.10(b). The RMC refinement correctly determines the trend in nematic correlations, but underestimates the magnitude at the nearest-neighbour distance by $\sim 50\%$. Thus it seems that RMC is somewhat less sensitive to higher-order spin correlations than to spin-pair correlations. Conversely, since the experimental data are only directly sensitive to spin-pair correlations, it is remarkable that RMC should show any sensitivity to higher-order correlations at all. I return to consider the sensitivity of powder diffuse-scattering data in more detail in the context of spin-liquid $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ in Chapter 4.

2.4.3 3D Spin Correlations

Finally, I consider the directional dependence of the real-space spin correlations. The correlation functions I have plotted so far are radial averages, which take no account of the geometry of the kagome lattice. However, I anticipate that this obscures a great deal of information, since it is the geometry of the lattice which usually leads to frustration

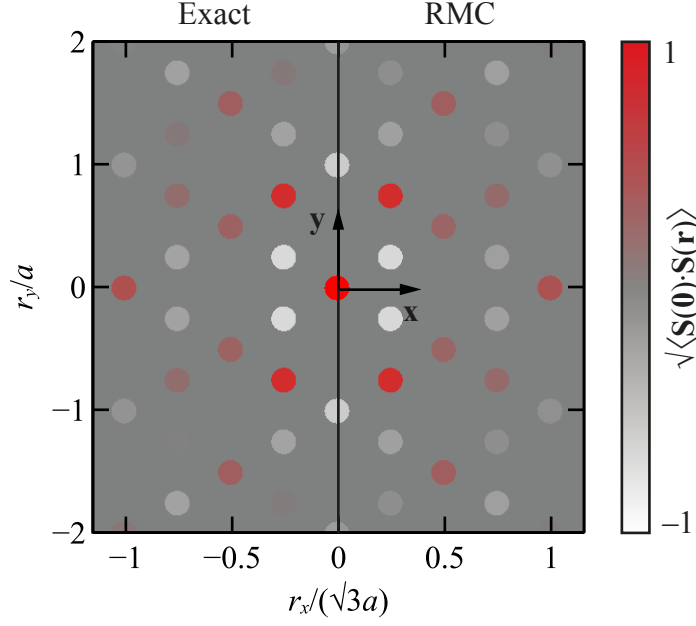


Figure 2.11: Two-dimensional spin correlation function $\langle \mathbf{S}(\mathbf{0}) \cdot \mathbf{S}(\mathbf{r}) \rangle$ for the Heisenberg kagome AFM. The left panel shows exact values and the right panel shows values obtained from RMC refinement to simulated powder data. The $\mathbf{x}$ and $\mathbf{y}$ axes are the local axes given in Fig. 2.8.

[Section 1.1]. In order to represent the directional dependence of the correlations, I consider the two-dimensional spin correlation function $\langle \mathbf{S}(\mathbf{0}) \cdot \mathbf{S}(\mathbf{r}) \rangle$. For an isotropic spin system, this is the magnetic analogue of the conditional probability plots of atomic displacements shown in Ref. 186. For a Bravais lattice, $\langle \mathbf{S}(\mathbf{0}) \cdot \mathbf{S}(\mathbf{r}) \rangle$ is straightforward to calculate: one simply calculates the scalar product of a central spin with the spin at displacement $\mathbf{r}$ away, and averages over each spin as a centre. For a non-Bravais lattice, such as kagome, the calculation is slightly more involved, because different basis atoms can be related to each other by rotational as well as translational symmetries. In such cases, it is necessary to rotate the coordinate axes when moving between basis atoms such that each atom is in an equivalent environment. For the kagome lattice, with a three-atom basis, a set of suitable local axes is shown in Fig 2.8. The directional dependence of the spin correlations is shown in Fig. 2.11. The exact spin correlations [Fig. 2.11, left panel] show a non-trivial dependence on both distance and angle, yet the result from RMC refinement reproduces all the main features of this dependence [Fig. 2.11, right panel].

2.4.4 Effect of Limited Data Quality

An obvious question which remains is: how well do these results transfer to experimental data? Compared with the simulated data used above, real data are likely to have a somewhat more limited Q -range, and to contain a certain amount of statistical noise. I now consider the effects of these limitations, and make some observations as to the kind of data which are suitable for RMC refinement.

I investigate the effect of limited Q -range on the RMC single-crystal scattering patterns by identifying two extreme scenarios. First, I attempt a refinement omitting all the data except the main diffuse peak, by setting $Q_{\max} = 2.5 \text{ \AA}^{-1}$ [Fig. 2.12(a)]. Then I consider the inverse situation, omitting all the data below $Q_{\min} = 2.5 \text{ \AA}^{-1}$ but keeping the subsequent peaks [Fig. 2.12(b)]. As anticipated, in both cases the reconstruction of $I(\mathbf{Q})$ is of lower quality than for the full refinement. What is surprising is that both refinements nevertheless reproduce the main features of the diffuse scattering. Moreover, the overall quality of both reconstructions is similar, even though the input data do not overlap in Q . This behaviour can be understood by recognising that $I(\mathbf{Q})$ is periodic in reciprocal space, and this periodicity is dictated by the crystal structure [103]. Consequently, the powder-averaged scattering from subsequent Brillouin zones contains information about the first Brillouin zone, and *vice versa*. In effect, every measured value of Q represents an average over a different selection of points in the first Brillouin zone, so that increasing $Q_{\max}$ places increasingly stronger restrictions on $I(\mathbf{Q})$.

Does this mean it is best to measure data to the highest possible $Q_{\max}$? In practice, the answer is probably only a qualified “yes”. An exception is that the behaviour of the single-crystal scattering in the limit $\mathbf{Q} \rightarrow \mathbf{0}$ is uniquely determined by the powder scattering as $Q \rightarrow 0$. This limit is generally less experimentally accessible for larger values of $Q_{\max}$. Consequently, if the data contain insufficient information to constrain the low- Q behaviour, there may be a tendency for RMC refinement to refine inaccurate values for $I(Q \rightarrow 0)$, although this problem is not very apparent in Fig. 2.12(b). Another consideration is that, as the scattering becomes weaker at higher Q , the experimental errors become proportionately larger, and fitting to errors in the high- Q data may produce

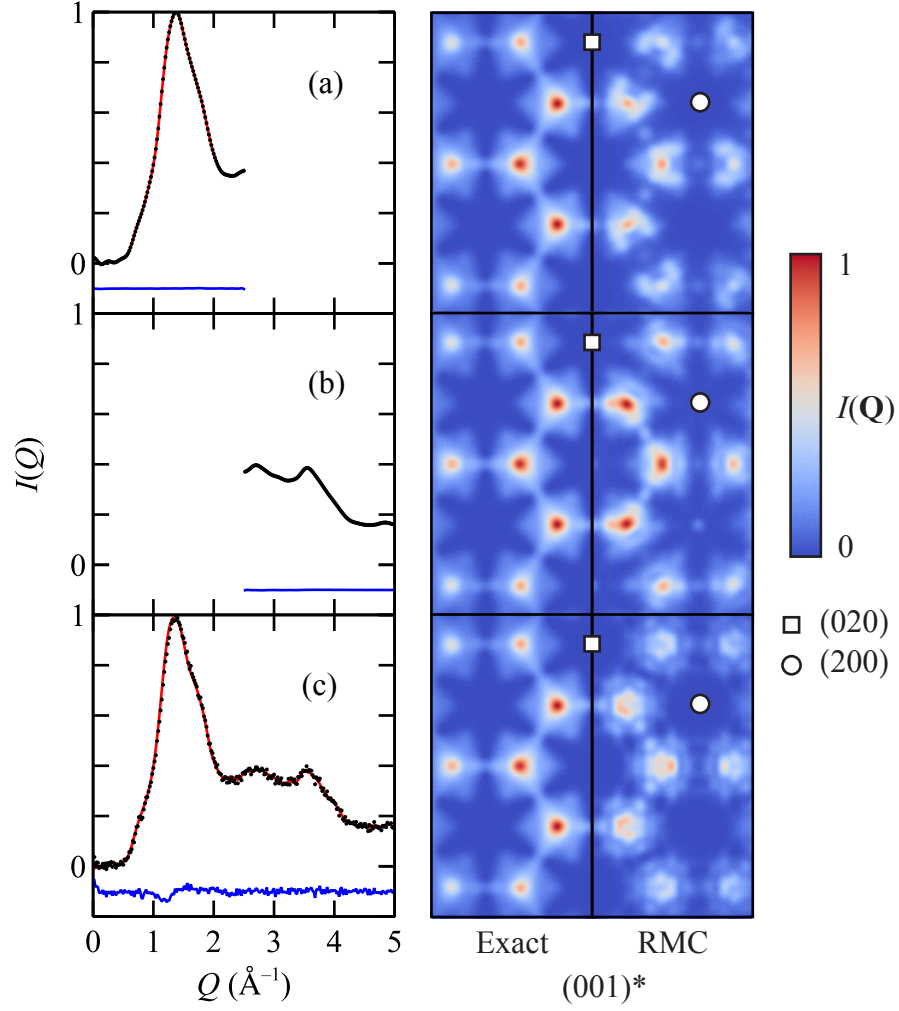


Figure 2.12: (a) RMC fit to simulated powder data with $Q_{\text{max}} = 2.5 \text{ \AA}^{-1}$ and calculated single-crystal scattering pattern from RMC refinement to these powder data. Input data are shown as black circles, fit as a red line, and data-fit as a blue line. (b) RMC fit to simulated powder data with $Q_{\text{min}} = 2.5 \text{ \AA}^{-1}$ and calculated single-crystal scattering pattern from RMC refinement to these powder data. (c) RMC fit to simulated powder data containing statistical noise and calculated single-crystal scattering pattern from RMC refinement to these powder data.

noise even at low Q in the calculated single-crystal patterns. One may therefore ask how low the statistical errors need to be. To test this, I added a small amount of statistical noise to the simulated data and repeated the RMC refinement. The noise was simulated by choosing random numbers from a Gaussian distribution with standard deviation $\sigma = 0.01$ (corresponding to an error of 1% in the most intense data point). With these relatively-small errors, I find that the single crystal pattern calculated from RMC is noticeably reduced in quality [Fig. 2.12(c)], although the main features are still recovered.

I therefore draw two main conclusions regarding the data quality which is desirable for RMC refinement. First, the differences between Fig. 2.9 and Fig. 2.12(c) suggest that it is important to measure beyond just the first peak in the scattering pattern. Second, it is essential that the statistical errors in the data are low; specifically, they should be low enough that the modulation in the powder scattering pattern is well resolved even at high Q . While these criteria may be difficult to achieve with samples that are small or very highly absorbing (particularly if the material in question also has a small spin quantum number), in most other cases they should be attainable using current-generation diffuse-scattering diffractometers such as D7 (ILL) [90] or DNS (Jülich) [187]. Refinement to experimental data using RMC is therefore likely to be both practical and informative—a point I hope to demonstrate in the following chapters.

2.5 Conclusions

The key result of this chapter is that direct investigation of magnetic correlations in frustrated spin systems which are not available as single crystals is now a realistic prospect. The RMC method allows the 3D spin correlation function and the single-crystal scattering pattern to be recovered accurately from 1D (powder) data. Moreover, it is also possible to recover qualitative information about single-ion properties (e.g., whether spins are Ising or Heisenberg-like), and about higher-order spin correlations (e.g., spin-nematic phases). Hence RMC refinement can be used to show that such effects are present; moreover, since refinements are initialised from random spin configurations, it provides a robust lower bound on their magnitude.

A key point about RMC refinement is that it is entirely independent of a spin Hamiltonian. This may be an advantage or a disadvantage: an advantage, because it is not necessary to assume a form of the Hamiltonian to model the spin correlations; a disadvantage, because it does not produce an interaction model as output. Compared to the other model-independent techniques for analysis of magnetic diffuse scattering data discussed in Section 1.4.2, the key advantage of RMC refinement is that its results are automatically compatible with the crystal structure of the system. Knowledge of the crystal structure seems to be the extra piece of information which allows RMC refinement to reconstruct 3D information from powder data. In fact, the key point here may not relate directly to RMC at all: it is simply that magnetic powder diffraction data—together with knowledge of the the crystal structure—contain a great deal of information. Other techniques exist to access this information effectively; for example, as discussed in Section 1.4.1.2, it is possible to fit interaction parameters directly to powder data within a mean-field theory model (see, e.g., [51, 188]).

There are also disadvantages to the RMC approach. Most importantly, RMC tends to produce the most disordered spin configuration compatible with experimental data [155]. In this respect, RMC resembles the maximum-entropy method (MEM), although the methods are used for different purposes: MEM is generally employed to determine spin density distributions within a unit cell [189], whereas RMC is used to determine the correlations between discrete spins in a large configuration. In my case studies, I have found that RMC overestimates disorder by only a small amount, but it is not possible to know in advance that this will be the case for any given dataset. It is important always to remember that the success of RMC depends entirely on the quality of the data with which it is provided. The data should show the whole of the first broad peak as well as some subsidiary peaks, and should ideally have excellent statistics. The lowest possible background is desirable, and for this reason polarised-neutron diffraction data have significant advantages [90]. I anticipate that RMC may be less successful for crystal structures which are complex—in the sense that they contain many radial separations between pairs of atoms which nearly overlap—since the effect of the limited real-space

resolution imposed by $Q_{\max}$ will then become more significant.

My results show that, when large single crystal samples are currently unavailable, single crystal-like information can be obtained using RMC refinement to high-quality powder data. In some cases it may be advantageous to perform experiments on powder samples, e.g., for high-throughput studies, for highly-absorbing samples [62], when only small single crystals are available, or for parametric studies as a function of temperature or pressure [190]. The technique of RMC refinement should therefore allow useful information to be obtained for a much wider range of cooperative paramagnets than is presently the case. In the remaining chapters, I apply the RMC method to a variety of topical systems. In doing so, I validate the results shown here in practice, and use them to obtain new information about frustrated spin systems.

Chapter 3

Frustration and Low Dimensionality in $\text{Ca}_3\text{Co}_2\text{O}_6$

3.1 Chapter Summary

Having shown that RMC refinement can be successfully applied to simulated data, I now apply the approach to experimental data obtained using neutron polarisation analysis. My results reveal the interplay of frustration and low-dimensional magnetism in PM $\text{Ca}_3\text{Co}_2\text{O}_6$. In this material, Ising-like spin chains are arranged on a triangular lattice. I show that both intra-chain and inter-chain correlations persist above the magnetic ordering temperature $T_N = 25$ K, but are essentially decoupled. Intra-chain correlations resemble the FM Ising model, while inter-chain correlations resemble the frustrated triangular-lattice AFM. Using previously-published bulk property measurements in addition to polarised-neutron scattering data, I obtain values of the FM and AFM exchange interactions and the single-ion anisotropy, which provide the first consistent explanation of thermodynamic anomalies observed above T_N .

3.2 Acknowledgements

This project was a collaboration with the research group of Oleg Petrenko (University of Warwick): they performed the experimental work before the start of my DPhil, and I

performed the data analysis and modelling. The $\text{Ca}_3\text{Co}_2\text{O}_6$ powder sample was prepared and characterised in the Superconductivity and Magnetism group of the Department of Physics at the University of Warwick by Oleg Petrenko, Martin Lees, Catherine Fleck, and Stefano Agrestini (now Max-Planck Institute, Dresden). This same group performed the neutron-scattering experiments at D7 (ILL). The D7 instrument scientist was Pascale Deen (now European Spallation Source and Niels Bohr Institute, University of Copenhagen). I am grateful to Oleg Petrenko for discussions and guidance concerning the data analysis.

3.3 Introduction

Conventional magnetic order can be suppressed by a number of different mechanisms. Frustration is one important example; another is if the lattice on which the spins are arranged is low dimensional (its dimensionality is less than three). In this case, the suppression of long-range order occurs because the entropy gained by spin fluctuations outweighs the energy lost by the absence of long-range order [1]. The simplest example is a 1D chain of N Ising spins, coupled by FM nearest-neighbour interactions of strength J . The argument for the absence of long-range order proceeds by first imagining the potential ordered state in which all spins are aligned parallel. Flipping M consecutive spins costs energy $2J$ (regardless of the value of M). The energy is independent of which M consecutive spins are flipped, which leads to a change in entropy $S = k_B \ln N$. For macroscopic N at any non-zero temperature, the entropy change therefore always outweighs the energy term, and long-range order does not occur [3].

Individually, frustration and low-dimensionality each have dramatic effects on magnetic properties. We therefore expect that introducing frustration within low-dimensional systems should lead to especially unusual magnetic behaviour. Canonical frustrated lattices such as kagome and triangular are, of course, two-dimensional; however, the physics of such systems is often dominated by frustration when AFM interactions are dominant [56]. The presence of next-nearest neighbour interactions within 1D chains can introduce frustration, and has been investigated in a range of quasi-1D cuprates [191, 192]. An en-

tirely different interplay of frustration and low dimensionality may however be expected when the frustration arises from interactions between chains, rather than within them. This occurs, for example, if intra-chain interactions are strong and unfrustrated and adjacent chains are coupled by frustrated interactions. In this chapter, I investigate the interplay of frustration and low-dimensional magnetism in the PM phase of the Ising-like spin-chain compound $\text{Ca}_3\text{Co}_2\text{O}_6$, which has magnetic interactions of this type.

Fig. 3.1 shows the crystal structure of $\text{Ca}_3\text{Co}_2\text{O}_6$, which is rhombohedral (space group $R\bar{3}c$) and consists of chains made up of alternating face-sharing octahedral ($\text{Co}_\text{I}^{3+}; S = 0$) and trigonal prismatic ($\text{Co}_\text{II}^{3+}; S = 2$) CoO_6 polyhedra [59, 193]. In the hexagonal setting, the unit cell parameters $a = 9.061 \text{ \AA}$ and $c = 10.367 \text{ \AA}$ at 40 K [59]. The chains are directed along the c axis and are arranged on a triangular lattice in the ab plane. The trigonal crystal field and spin-orbit coupling generate an Ising-like magnetic anisotropy at the Co_II^{3+} site, with the easy axis parallel to the chains [43, 194]. Spins are coupled by FM interactions within the chains, while much weaker AFM interactions couple adjacent chains along helical paths [195, 196]. Below the magnetic ordering temperature $T_N = 25 \text{ K}$, the magnetic structure of $\text{Ca}_3\text{Co}_2\text{O}_6$ is relatively well-understood: a longitudinal amplitude-modulated spin-density wave (SDW) propagates along the c axis with a periodicity of about $1000 \text{ \AA}$ and a phase difference of 120° between the modulation of adjacent chains [197–199]. Several unusual magnetic phenomena occur below T_N , including magnetisation steps as a function of applied magnetic field [200, 201], and an order–order transition from the SDW structure to a commensurate AFM phase which occurs over a remarkably long time-scale (several days) [202].

Here, I consider the PM phase of $\text{Ca}_3\text{Co}_2\text{O}_6$, which shows an equally complex range of magnetic phenomena. The persistence of dispersive spin-wave excitations in inelastic neutron-scattering experiments indicates that strong FM correlations remain present to temperatures greater than $6T_N$ [203]; however, the resolution of these experiments did not allow the AFM exchange interaction to be extracted, leaving the rôle played by frustration unclear. Moreover, broad thermodynamic anomalies, of unknown origin, occur in both magnetic susceptibility and specific heat above T_N [201, 204–206]. Here, I therefore aim

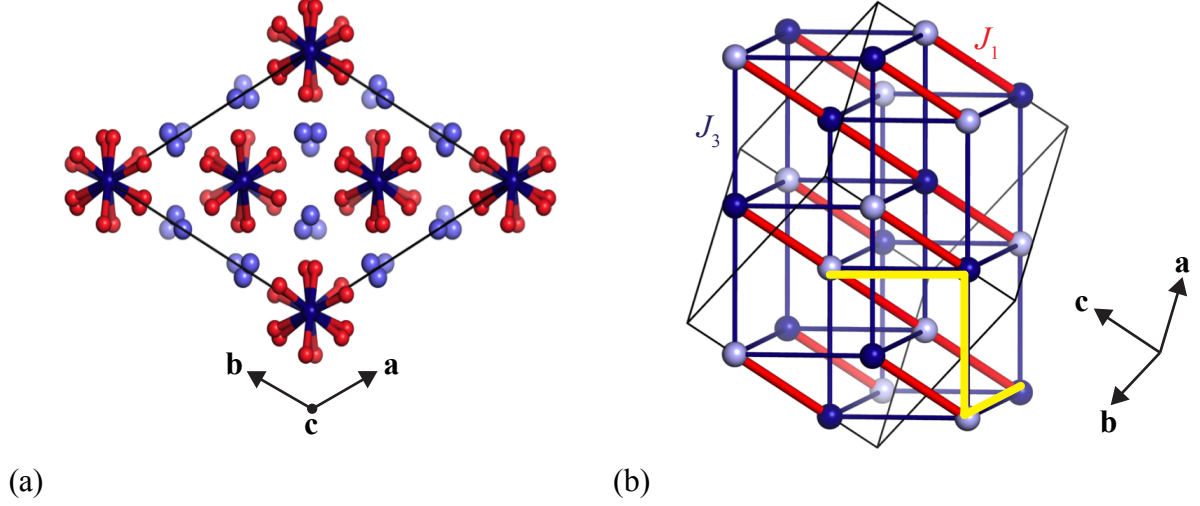


Figure 3.1: (a) Crystal structure of $\text{Ca}_3\text{Co}_2\text{O}_6$ viewed along the c axis. Magnetic $\text{Co}_{\text{II}}^{3+}$ ($S = 2$) ions are shown in dark blue, O^{2-} are shown in red, and Ca^{2+} are shown in light blue. (b) Magnetic interaction pathways in $\text{Ca}_3\text{Co}_2\text{O}_6$ (only $\text{Co}_{\text{II}}^{3+}$ ions are shown). FM intra-chain couplings J_1 are shown as red lines and AFM inter-chain couplings J_3 are shown as blue lines. Light and dark blue circles indicate one of the possible long-range magnetic orderings which would be obtained in the hypothetical case that $J_1 = 0$ with AFM J_3 . Yellow lines show the shortest path between two sites within the same Ising chain if only J_3 pathways are used.

to address three key questions. First, what is the nature of the spin correlations in the PM phase, and how are these correlations related to the expected interplay of frustration and low dimensionality? Second, what is the microscopic origin of reported anomalies in thermodynamic (bulk) measurements [201, 204–206]? Third, can the above properties be modelled in a consistent way using an effective spin Hamiltonian?

To address these questions, polarised-neutron scattering measurements were performed on a powder sample of $\text{Ca}_3\text{Co}_2\text{O}_6$ above T_N . I employ Monte Carlo methods to interpret these data above T_N and to calculate thermodynamic quantities. This chapter is structured as follows. Details of neutron-scattering experiments and analysis methods are given in Section 3.4. In Section 3.5.1, I obtain the spin correlation functions parallel and perpendicular to the chains above T_N . Finally, in Section 3.5.2 I develop a model of the magnetic interactions which is compatible with the neutron-scattering data and which explains previously-reported measurements of thermodynamic properties [201, 205, 206].

3.4 Methods

3.4.1 Experimental

A powder sample of $\text{Ca}_3\text{Co}_2\text{O}_6$ of mass 3.6 g was synthesised by a solid-state method [194, 207, 208]. The magnetic properties of the sample were checked by magnetisation measurements and found to agree with those reported previously [194, 206–209].

Polarised-neutron scattering experiments were performed using the D7 instrument at the ILL [90], which was described in Section 1.3.4. Neutrons of wavelength $4.81 \text{ \AA}$ were used, allowing the scattering to be measured in the range $0.34 < Q < 2.48 \text{ \AA}^{-1}$. In order to avoid possible complications from the influence of the out-of-plane components to forward scattering [95], data for scattering angles $2\theta < 20^\circ$ were excluded. Standard data analysis techniques, including detector efficiency normalisation from a vanadium standard and polarisation efficiency calculations from an amorphous silica standard, were used to calculate the magnetic, nuclear, and spin-incoherent scattering components from the raw data, as described in Section 1.3.4. Diffraction data obtained below T_N were refined using the FULLPROF program [36] and found to agree with previous results [197].

3.4.2 Refinement and Modelling

3.4.2.1 Reverse Monte Carlo refinements

RMC refinements were performed using periodic spin configurations of size $12 \times 7 \times 11$ orthorhombic unit cells ($N = 11\,088$ spins), where the orthorhombic cell is related to the conventional hexagonal cell by Eq. (2.6). This choice of supercell size represented a compromise between maximising the simulation size and keeping the computational time required within reasonable limits. Refinements were performed for 100 proposed flips per spin, and all calculated quantities were averaged over 10 independent spin configurations in order to minimise the statistical noise.

3.4.2.2 Monte Carlo simulations

I performed MC simulations using the classical Ising Hamiltonian,

$$H = -\frac{1}{2} \sum_{i,j} J_{ij} S_i^z S_j^z, \quad (3.1)$$

in which the z -component of spin $S^z = \pm S$, where $S = 2$, and the transverse couplings are neglected (i.e., $S_i^x S_j^x = S_i^y S_j^y = 0$). I also considered the classical anisotropic Hamiltonian,

$$H = -\frac{1}{2} \sum_{i,j} J_{ij} S_i^z S_j^z - \Delta \sum_i (S_i^z)^2, \quad (3.2)$$

in which the transverse coupling terms are again neglected and S_i^z can take now five values, $S_i^z \in \{\pm 2, \pm 1, 0\}$. For $T \ll \Delta S^2$, only the $S^z = \pm 2$ states are occupied, and Eq. (3.2) is equivalent to Eq. (3.1). I finally investigated the classical anisotropic Heisenberg Hamiltonian,

$$H = -\frac{1}{2} \sum_{i,j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j - \Delta \sum_i (S_i^z)^2, \quad (3.3)$$

in which the $\mathbf{S}_i$ are three-component vectors having length S and z -component S_i^z . In all models, J_{ij} is a general interaction between pairs of spins i, j , Δ is a single-ion anisotropy term, and the factor of $\frac{1}{2}$ corrects for the double-counting of pairwise interactions. In Section 3.5, I consider specifically interactions between nearest-neighbour and third-neighbour spins, which I label J_1 and J_3 , respectively.

MC simulations were performed using the Metropolis algorithm with simulated annealing [Section 1.4.1.1]. The initial temperature was $T = 15J_1 S^2$ for the Ising model and $T = 60J_1 S^2$ for the anisotropic models. At each temperature, 10^4 moves per spin were proposed for equilibration, followed by at least 10^5 proposed moves for calculations of the bulk properties. For the Ising model, a proposed spin move involved choosing a spin at random and flipping its orientation. For the 5-state model, a proposed spin move involved choosing one of the five possible states at random. For the anisotropic Heisenberg model, two kinds of move were alternated: randomly choosing a new spin orientation on the surface of a sphere, and a simple spin flip ($\mathbf{S}_i \rightarrow -\mathbf{S}_i$), where the latter

was used to allow the simulation to move rapidly between Ising-like states at low T [210]. To simulate diffraction patterns, I used five independent spin configurations, each of size $18 \times 10 \times 16$ orthorhombic unit cells ($N = 34\,560$ spins); an approximately cubic supercell was used because calculating powder diffraction patterns involves spherical summation of spin correlation functions in real space [84]. For bulk-properties calculations, I used a spin configuration of size of $5 \times 3 \times 64$ orthorhombic unit cells ($N = 11\,520$ spins); these dimensions were chosen since the correlation length along c is longer than in the ab plane [Section 3.5]. The magnetic susceptibility χ and specific heat C_{mag} were calculated using Eq. (1.77) and Eq. (1.78), respectively.

3.5 Results and Discussion

3.5.1 Neutron Scattering

Magnetic diffuse-scattering data were collected at six temperatures above T_N and are shown in Fig. 3.2. At $T = 25, 30$ and 35 K, $I(Q)$ is dominated by a broad peak, which decreases in intensity and shifts from $Q = 0.8$ to $0.7 \text{ \AA}^{-1}$ with increasing temperature. At $T \geq 50$ K, $I(Q)$ shows no pronounced features, but even at 100 K there are small differences between the experimental data and the PM Co^{3+} form factor which would be observed for entirely random spin orientations. I use two approaches to analyse these data. First, I fit to the data using RMC refinement. Second, I consider the extent to which the data are consistent with different sets of interactions in a simple magnetic Hamiltonian. Throughout, I assume that only the $\text{Co}_{\text{II}}^{3+}$ ($S = 2$) sites are magnetic with no magnetic moment present on the $\text{Co}_{\text{I}}^{3+}$ ($S = 0$) sites, in agreement with X-ray photoemission spectroscopy [193] and NMR [211] measurements.

Technical details of the RMC refinements were given in Section 3.4. The most important assumption is that the spins behave as Ising variables. Measurements of the magnetic entropy [205] and my own analysis in Section 3.5.2 suggest that this assumption is valid for $T \lesssim 50$ K, where the diffuse scattering shows the most pronounced features. I make the usual assumption that the magnetic form factor is given by the dipole (low- Q) formula,

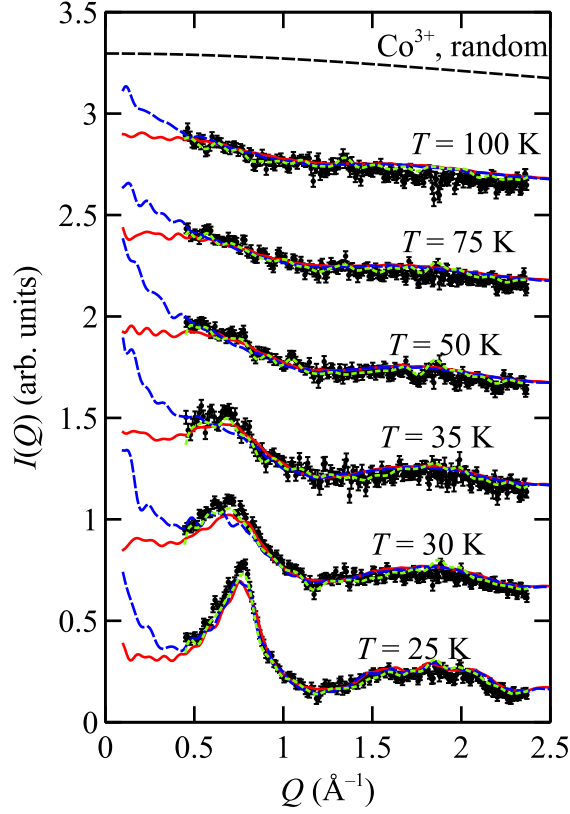


Figure 3.2: Magnetic diffuse-scattering patterns from $\text{Ca}_3\text{Co}_2\text{O}_6$ at six temperatures above T_N . The filled black symbols represent experimental data. The dotted green lines show RMC fits (see text for details). The solid red lines are calculated using MC simulations of the Ising model with exchange interactions $J_3/J_1 = -0.10$ ($J_1 S^2 = 22.9\text{ K}$), and the dashed blue lines for $J_3/J_1 = -0.02$ ($J_1 S^2 = 36.8\text{ K}$). The curves for different temperatures are consecutively offset by 0.5 units for clarity. The PM squared form factor for Co^{3+} (adjusted by the overall intensity scale determined from RMC refinement) is shown as a dashed black line for comparison.

$f(Q) = j_0(Q) + C_2 j_2(Q)$, where $j_0(Q)$ and $j_2(Q)$ are tabulated functions [78] and the factor $C_2 = L^z/(2S^z + L^z)$ accounts for the orbital contribution to the magnetic moment; I take $C_2 = 0.25$ as an average of the literature values for $\text{Ca}_3\text{Co}_2\text{O}_6$ [42, 43, 200, 201]. All fits are modified by an overall intensity scale factor in order to match the data. The optimal value of the scale factor was obtained by fitting the 25 K data and then fixed at this value when fitting the higher-temperature datasets. The RMC fits are shown in Fig. 3.2, and represent excellent agreement with the data.

The radial spin correlation function $\langle S(0)S(r) \rangle$ obtained from RMC refinement of the 25 K data is shown in Fig. 3.3(a). Correlations along the Ising spin chains $\langle S(0)S(r_z) \rangle$ are FM and decay with distance r_z along the chains. This distance dependence can be fitted by an exponential decay, $\langle S(0)S(r_z) \rangle = \exp(-r_z/\xi)$, in agreement with the theoretical calculation for the 1D FM Ising model (i.e., independent chains) [55]. By contrast, correlations between different chains are AFM, of smaller magnitude than the intra-chain correlations, and are not well described by an exponential decay; I consider them in more detail below. The temperature dependence of the FM correlation length ξ is shown in Fig. 3.3(b). The values shown were determined by fitting $\langle S(0)S(r_z) \rangle$ with an exponential for each of the six measured temperatures. The fitting range was $0 < r < 30 \text{ \AA}$ except at 100 K where the upper limit was reduced to $r = 20 \text{ \AA}$ due to the rapid decay of the correlations; in all cases, the quality of the fit was similar to that obtained at 25 K. The value of ξ falls rapidly with increasing temperature just above T_N , but decreases more slowly at higher temperatures. Here again I note a similarity with the theoretical expression for the 1D Ising model [55],

$$\xi = \frac{c}{2 \ln [\coth (J_1 S^2 / T)]}, \quad (3.4)$$

which also has a “long tail” at high temperature.

I note two qualifications regarding the RMC refinements. First, as discussed in Section 1.4.4, the values of ξ obtained from RMC represent lower bounds on the true values, since RMC refinement is a stochastic process. Second, I found that making small changes to refinement parameters (in particular the intensity scale) resulted in significant varia-

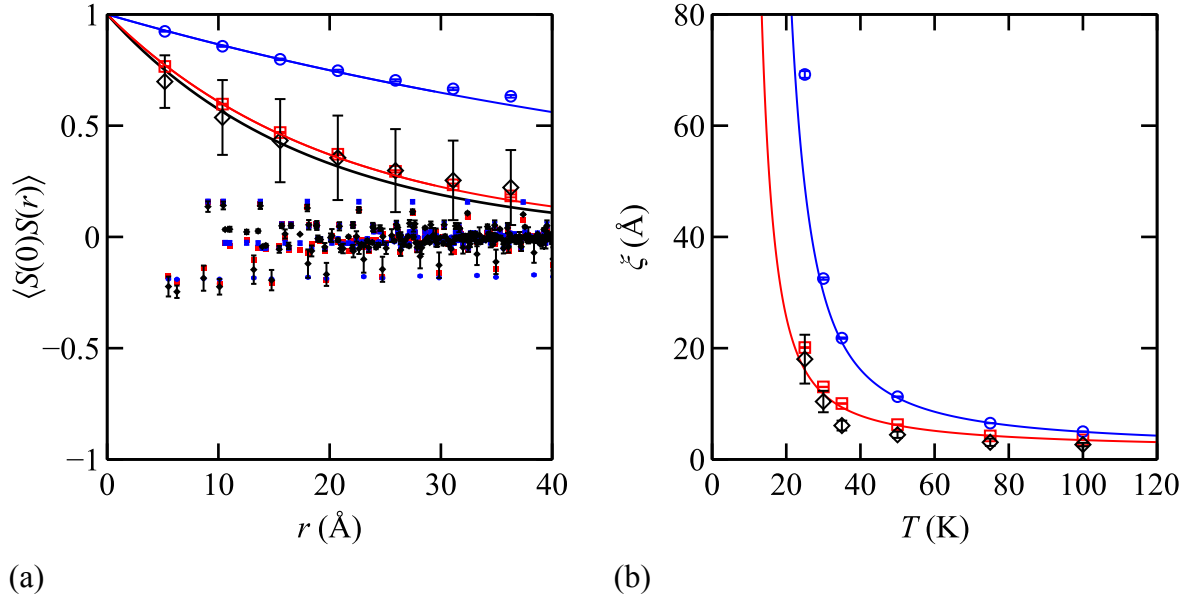


Figure 3.3: (a) Radial spin correlation function at $T = 25$ K. Results from RMC refinements to the $T = 25$ K data are shown in black. Values from MC simulations with $J_3/J_1 = -0.10$ ($J_1 S^2 = 22.9$ K) and $J_3/J_1 = -0.02$ ($J_1 S^2 = 36.8$ K) are coloured red and blue, respectively. Correlations within the Ising chains (intra-chain correlations) are shown as open symbols and correlations between different Ising chains (inter-chain correlations) are shown as closed symbols. Solid lines show fits to an exponential function $\langle S(0)S(r_z) \rangle = \exp(-r_z/\xi)$ to determine the FM intra-chain correlation length ξ (colours as above). (b) Temperature evolution of ξ (colours as above). The solid lines show the exact expression, Eq. (3.4), for independent FM Ising chains for $J_1 S^2 = 22.9$ K (red lines) and $J_1 S^2 = 36.8$ K (blue lines).

tions in the absolute values obtained for the FM correlation length. In order to estimate the uncertainties shown in Fig. 3.3 for $\langle S(0)S(r) \rangle$ and ξ , I therefore considered the effect of changing the scale by a small amount δs from its refined value s , where $\delta s = 0.1s$ was chosen as the range over which it was possible to obtain reasonable fits to the data.

I now consider the extent to which the PM diffraction data can be modelled using a magnetic Hamiltonian. Following previous work [196], I consider a model of Ising spins coupled by interactions between nearest neighbours (J_1 at 5.18 Å), next-nearest neighbours (J_2 at 5.51 Å) and third neighbours (J_3 at 6.23 Å). The J_1 and J_3 interaction pathways are shown in Fig. 3.1. Initial calculations revealed that the 25 K data can be well described by at least two different sets of parameters: either J_1 and J_3 with $J_2 = 0$, or J_1 and J_2 with $J_3 = 0$. An independent determination of both J_2 and J_3 is therefore not possible based on $I(Q)$ alone. However, it has been argued that J_3 should be of significantly greater magnitude than J_2 , based on the shorter O–O bond distance for the J_3 pathway [195] and on extended Hückel tight-binding calculations [196]. In order to proceed, I therefore assumed initially that $J_2 = 0$ and attempted to determine the values of only J_1 and J_3 . To this end, I performed DMC simulations of the Ising Hamiltonian, Eq. (3.1), as described in Section 3.4. For each ratio of J_3/J_1 that I considered, I determined the ratio $T/J_1 S^2$ for which the calculated $I(Q)$ most closely matched the 25 K data. This procedure fixes the absolute value of J_1 and hence allows model and experimental data to be compared for all the measured temperatures.

Results of these simulations are shown in Figs. 3.2 and 3.3. I present results for $J_3/J_1 = -0.02$, which is the ratio suggested in Ref. 196, and for $J_3/J_1 = -0.10$, for comparison with my analysis of thermodynamic data in Section 3.5.2. At most temperatures, both sets of interactions show good agreement with the data. There is a slight tendency for all the model calculations to lie below the data at low Q and above the data at high Q , which may indicate a small inaccuracy in the assumed magnetic form factor. The spin correlations for both models are shown in Fig. 3.3 and show the same qualitative features as the RMC results. The largest difference between the two models occurs in the region $Q \lesssim 0.5 \text{ Å}^{-1}$, with smaller values of $|J_3/J_1|$ associated with increased scattering intensity

as $Q \rightarrow 0$. Fig. 3.3(b) shows that this increased intensity at low Q is associated with a larger value of the FM correlation length ξ . Unfortunately, since this low- Q region is not accessed experimentally, the diffraction data are relatively insensitive to the values of ξ and J_3/J_1 . In order to place a stronger restriction on J_3/J_1 , it is necessary to consider thermodynamic data together with diffraction—an approach I will follow in Section 3.5.2.

Despite these limitations, it is possible to draw some general conclusions about the intra-chain correlations from Fig. 3.3(b). Most significant is that, for the values of J_3/J_1 I consider here, the values of ξ from DMC simulation agree with the exact result for *independent* FM Ising chains, Eq. (3.4), with no fitting parameters. This result suggests that the FM correlations are strongly 1D above T_N . Hence the J_3 interaction—which couples intra-chain spins by the indirect pathway shown in Fig. 3.1(b)—has negligible effect on the intra-chain correlations for small $|J_3/J_1| \lesssim 0.10$. A small J_3/J_1 ratio is a prerequisite both for 1D behaviour and frustration, since in the opposite limit $|J_3/J_1| \gg 1$ unfrustrated 3D order would occur [Fig. 3.1(b)]. Further evidence for 1D behaviour comes from the correlation strength. At the nearest-neighbour distance, I obtain $0.1 \lesssim \langle S(0)S(c/2) \rangle \lesssim 0.35$ at 100 K (lower bounds are RMC results and upper bounds are for $J_3/J_1 = -0.02$); although small in absolute terms, these values are at least double the result for a 3D Ising model at $T \approx 4T_c$ [212]. Mindful that the assumption of Ising spins may be less accurate for $T \gtrsim 50$ K, I also considered a Heisenberg model with $J_3/J_1 = -0.10$ and finite single-ion isotropy $\Delta/J_1 = 32$, which I investigate further in Section 3.5.2. This model showed the same behaviour except for slightly reduced correlation lengths at high T (ξ around 90% of the Ising result at $T = 100$ K). The presence of 1D FM correlations well above T_N has been inferred (but not modelled) using other experimental techniques: Mössbauer studies of ^{159}Eu -doped $\text{Ca}_3\text{Co}_2\text{O}_6$ indicate a progressive increase in line-width below $T \approx 150$ K [213]; μSR data indicate exponential-like relaxation to $T \approx 150$ K [214]; and inelastic neutron-scattering measurements show that dispersive magnetic excitations persist to $T \approx 150$ K [203].

I now consider the inter-chain correlations by calculating $I(\mathbf{Q})$ in the $(001)^*$ reciprocal-space plane. This calculation is of topical interest because an arrangement of single

crystals suitable for neutron-scattering measurements has recently been reported for $\text{Ca}_3\text{Co}_2\text{O}_6$ [203]. In Fig. 3.4, I show the calculated $I(\mathbf{Q})$ for three models of $\text{Ca}_3\text{Co}_2\text{O}_6$ at $T = 25\text{ K}$: the DMC model with $J_3/J_1 = -0.10$ in Fig. 3.4(a); the DMC model with $J_3/J_1 = -0.02$ in Fig. 3.4(b); and the RMC model obtained from fitting the powder data in Fig. 3.4(c). The diffuse scattering always takes the form of triangle-shaped peaks at the corners of the second Brillouin zone. The fact that similar results are obtained from both RMC refinement and a physically-sensible set of magnetic interactions suggests that my prediction of $I(\mathbf{Q})$ is robust. These calculations also indicate that a single-crystal neutron-scattering measurement of the $(001)^*$ plane would provide rather little information on the relative strength of FM and AFM interactions. Instead, it would probably be necessary to measure one of the diffuse peaks along $\mathbf{c}^*$ in order to obtain the FM correlation length as a function of temperature. Finally, in Fig. 3.4(d) I show the calculated $I(\mathbf{Q})$ for the nearest-neighbour Ising AFM on the triangular lattice [2] (henceforth “Wannier model”, after its inventor) which has previously been applied in several theoretical studies of $\text{Ca}_3\text{Co}_2\text{O}_6$ (see, e.g., Refs. 215–217). There is close agreement between Figs. 3.4(a)–3.4(c) and the Wannier model for $T \sim |J|$ (the calculation shown is for $T = 1.5|J|$). The extent of this agreement is rather surprising, since the modulation of the diffuse scattering is sensitive to small changes in the magnetic interactions [218]. Hence, although the Wannier model can provide no information on the intra-chain correlations, it provides a good qualitative description of the inter-chain spin correlations.

In conclusion, my results indicate a physical picture of PM $\text{Ca}_3\text{Co}_2\text{O}_6$ in which weak inter-chain correlations resemble the Wannier model, and the length-scale ξ over which these correlations remain coherent along the c axis can be calculated as if the chains behave independently. In this sense, above T_N , the correlations along c are effectively decoupled from those in the ab plane.

3.5.2 Bulk Properties

In this section I employ MC simulations to calculate bulk properties of $\text{Ca}_3\text{Co}_2\text{O}_6$ in the PM phase. The motivation for considering bulk properties is the strong dependence of the

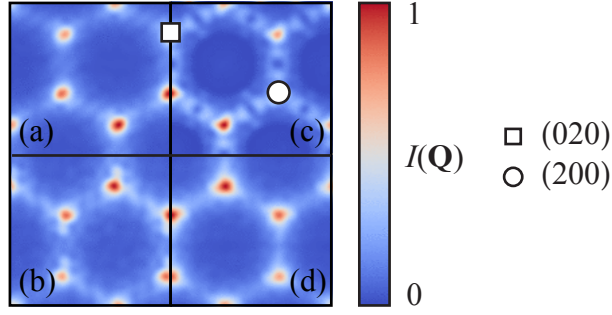


Figure 3.4: Calculated single-crystal diffuse-scattering patterns at $T = 25$ K in the $(001)^*$ reciprocal-space plane. (a) MC, $J_3/J_1 = -0.10$ ($J_1 S^2 = 22.9$ K); (b) MC, $J_3/J_1 = -0.02$ ($J_1 S^2 = 36.8$ K); (c) RMC, from fitting $T = 25$ K powder data; (d) Wannier model of Ising spins on the triangular lattice calculated using MC simulation at $T = 1.5|J|$, where J is the nearest-neighbour AFM interaction. The intensity scales are chosen so that the most intense feature in each panel is normalised to 1.

limiting value $I(Q \rightarrow 0)$ on the ratio J_3/J_1 , which suggests that the bulk susceptibility is sensitive to the strength of both FM and AFM interactions. Here, MC simulation has two important advantages over traditional approaches to fitting the susceptibility [194, 201, 219, 220]: first, it is not limited by the number or type of interactions which can be modelled; second, it is not restricted to the high-temperature limit, remaining accurate until the correlation length becomes of the order of the simulation size.

In Fig. 3.5(a) the product of the magnetic susceptibility and temperature, χT , is shown for different values of J_3/J_1 . The susceptibility is calculated parallel to the direction of the chains as described in Section 3.4. The results show two main features. First, there is an anomaly at the Néel temperature, $T_N \sim J_1 S^2$. The value of T_N decreases with decreasing $|J_3/J_1|$, as one expects, since $T_N = 0$ in the limit of independent chains [55]. (I note that a value $T_N = 0$ cannot be obtained in MC simulation due to the finite simulation size; for a model with only FM J_1 interactions, ξ approaches the size of my simulation at $T \approx 0.4J_1 S^2$, which is significantly below the transition temperatures observed for the J_1 - J_3 model.) Second, there is a broad peak at $T' > T_N$, which sharpens and moves closer to T_N as $|J_3/J_1|$ is decreased. In this respect, my simulations reproduce experimental measurements of the parallel susceptibility, which also show a broad peak at $T' \approx 40$ K ($= 1.6T_N$) [201, 204]. The experimental location of T' implies that $0.06 \lesssim |J_3/J_1| \lesssim 0.10$. These results show that the T' peak arises from the development of AFM inter-

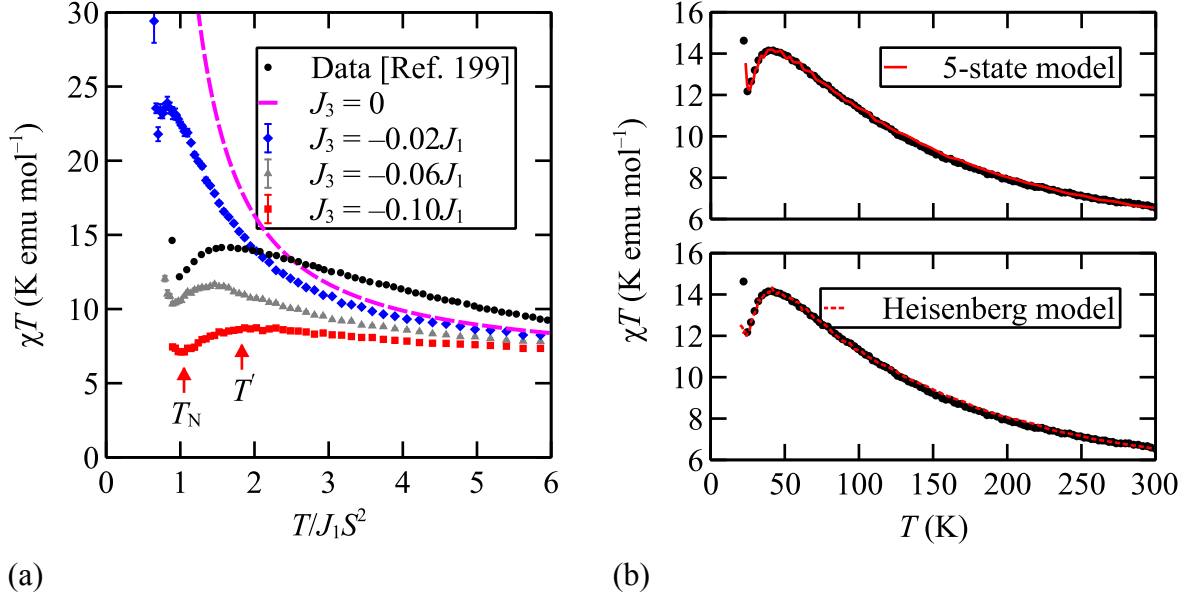


Figure 3.5: (a) Magnetic susceptibility of $\text{Ca}_3\text{Co}_2\text{O}_6$ parallel to the Ising chains. Results from MC simulations are shown for the Ising model with $J_3/J_1 = -0.02$ (blue diamonds), $J_3/J_1 = -0.06$ (grey triangles), and $J_3/J_1 = -0.10$ (red squares). The exact result [55] for FM J_1 only, $\chi T = N_A (gS\mu_B)^2 / [k_B \exp(2J_1 S^2/T)]$ in cgs units, is shown as a dashed magenta line. Experimental data (from Ref. 201) are shown as black circles. (b) Fits to magnetic susceptibility data for two anisotropic model Hamiltonians. In each panel, experimental data (from Ref. 201) are shown as black circles. The top panel shows a fit of the 5-state model, Eq. (3.2) (solid red line). The bottom panel shows a fit of the anisotropic Heisenberg model, Eq. (3.3) (dotted red line).

chain correlations, since the diffraction measurements show the development of an AFM peak close to T' [Fig. 3.2] while the intra-chain correlations remain FM throughout the measured temperature range [Fig. 3.3(b)].

Although simulations of the Ising model can qualitatively reproduce the experimental position of the T' peak, it proved impossible to obtain a satisfactory fit overall. The problem is that the gradient of the Ising curve is too shallow at higher temperatures [Fig. 3.5(a)]. To explain this observation, it is necessary to relax my previous assumption that spins behave as purely Ising variables. The Ising approximation is only valid for temperatures well below the energy scale of magnetic anisotropy ΔS^2 ; however, literature values of Δ for $\text{Ca}_3\text{Co}_2\text{O}_6$ range between $25 \leq \Delta \leq 230$ K [194, 203, 219, 220], suggesting that the Ising approximation is unlikely to be valid up to room temperature. In this case, spin fluctuations away from the c axis will cause the experimental χT to be smaller than the Ising calculation. To quantify the combined effect of J_3 and Δ , I considered the two

candidate anisotropic models introduced in Section 3.4, the 5-state model, Eq. (3.2), and the anisotropic Heisenberg model, Eq. (3.3). For each model, I used a grid search to fit the values of J_3 and Δ to the PM susceptibility data of Ref. 201. (The susceptibility data of Ref. 201 agree with Ref. 220 and with data collected powder samples, but do not appear to correspond to the data of Ref. 204 at higher temperatures; the reason for this discrepancy is unclear.) For a given set of interaction parameters, the calculated curve was first normalised horizontally by the position of T_N and a linear least-squares fit was then performed to determine the vertical scale factor. The success of this procedure relies on the fact that J_3 and Δ are weakly correlated, since the effect of J_3 is most important just above T_N , whereas the effect of finite Δ is evident at high temperature.

Fits of the two anisotropic models are shown in Fig. 3.5(b). In both cases, essentially quantitative agreement with the data is obtained throughout the PM regime. The fitted values of J_1 , J_3 and Δ are given in Table 3.1, where the interaction parameters are on an absolute scale using the value of T_N/JS^2 , taking $S = 2$. By convention, the orbital contribution to the magnetic moment is not included here, even though it represents a significant fraction of the total moment in $\text{Ca}_3\text{Co}_2\text{O}_6$. The fitted values of the exchange constants, $J_1 \approx 6 \text{ K}$ and $J_3 \approx -0.6 \text{ K}$, are nearly consistent for both anisotropic models, but the value of Δ shows a significant model dependence [Table 3.1]. This difference may be expected given that D has a different meaning in the two models. Fitted values of the effective magnetic moment $\mu_{\text{eff}} = 2S^z + L^z$ are given in Table 3.1, and are consistent with theoretical studies ($\sim 5.7 \mu_B$) [43], magnetisation measurements ($\sim 4.8 \mu_B$) [201], and an X-ray circular dichroism study ($\sim 5.3 \mu_B$) [42].

Since considering a finite anisotropy term introduces an extra parameter compared to an Ising model, it is important to ask whether this explains any measurements beyond the susceptibility. One such measurement is the magnetic specific heat, C_{mag} . In addition to the expected peak at T_N , the experimental C_{mag} shows a broad high- T peak between $80 \text{ K} \lesssim T^* \lesssim 160 \text{ K}$ [205, 206]. Although the presence of this peak is not in doubt, its intensity is uncertain due to the effect of the lattice subtraction, as a comparison of data from Ref. 205 and Ref. 206 shows [Fig. 3.6]. In Ref. 206 the high- T peak was ascribed to

Parameter	5-state model, Eq. (3.2)	Heisenberg model, Eq. (3.3)
	$J_3 = -0.08J_1, \Delta = 17J_1$	$J_3 = -0.10J_1, \Delta = 32J_1$
J_1 (K)	6.0(2)	6.3(3)
J_3 (K)	-0.60(4)	-0.50(4)
Δ (K)	110(20)	190(30)
μ_{eff}/μ_B	5.3(2)	4.8(2)

Table 3.1: Values of magnetic exchange interactions J_1 and J_3 , single-ion anisotropy term Δ , and effective magnetic moment μ_{eff} obtained by fitting the experimental magnetic susceptibility data of Ref. 201. The two models fitted are the 5-state model, Eq. (3.2), and the anisotropic Heisenberg model, Eq. (3.3). Conservative error bars were estimated from two points adjacent to the best-fit point on the grid ($\delta J_3 = 0.1J_1$, $\delta\Delta \approx 3J_1$).

the development of short-range intra-chain correlations, which release all the entropy in a fully 1D model. If this explanation is correct, then the large separation between T^* and T_N would suggest that $\text{Ca}_3\text{Co}_2\text{O}_6$ has much more 1D character than the canonical Ising spin-chain compound $\text{CoCl}_2 \cdot 2\text{NC}_5\text{H}_5$, for which the high- T peak is nearly obscured by the T_N peak [221]. In Fig. 3.6(a) I plot the magnetic specific heat from DMC simulations of the Ising model for different values of J_3/J_1 . For $J_3/J_1 = -0.10$, the broad peak at T^* is obscured by the sharp T_N peak, and even for $J_3/J_1 = -0.02$ it is only just visible as a shoulder on the T_N peak. Therefore an Ising model can only explain the existence of the high- T peak if $|J_3/J_1| \ll 0.02$. I now consider the two anisotropic models with the interaction parameters given in Table 3.1. The 5-state model shows a broad peak at $T^* \approx 140$ K ($= 1.3\Delta$), in qualitative agreement with the experimental data [Fig. 3.6(b)]. This agreement provides strong evidence that the high- T peak is actually a magnetic Schottky anomaly resulting from the temperature-dependent population of the S^z states. My results are supported by quantum calculations of the anisotropic $S = 2$ Heisenberg chain, which predict an extra peak in C_{mag} at $T^* = 1.4\Delta$ for large but finite Δ [222]. For completeness, I also show the anisotropic Heisenberg C_{mag} curve in Fig. 3.6(b). The poor agreement with the data is due to the failure of the vector-spin approximation of Eq. (3.3), which permits magnetic excitations which cost an infinitesimal amount of energy and leads to a diverging value of the magnetic entropy [223]. By contrast, the 5-state model has the correct value of the entropy for $S = 2$ spins ($\ln 5$ per spin) in the high-temperature limit.

I now present a brief comparison of my values for J_1 , J_3 and Δ with literature results.

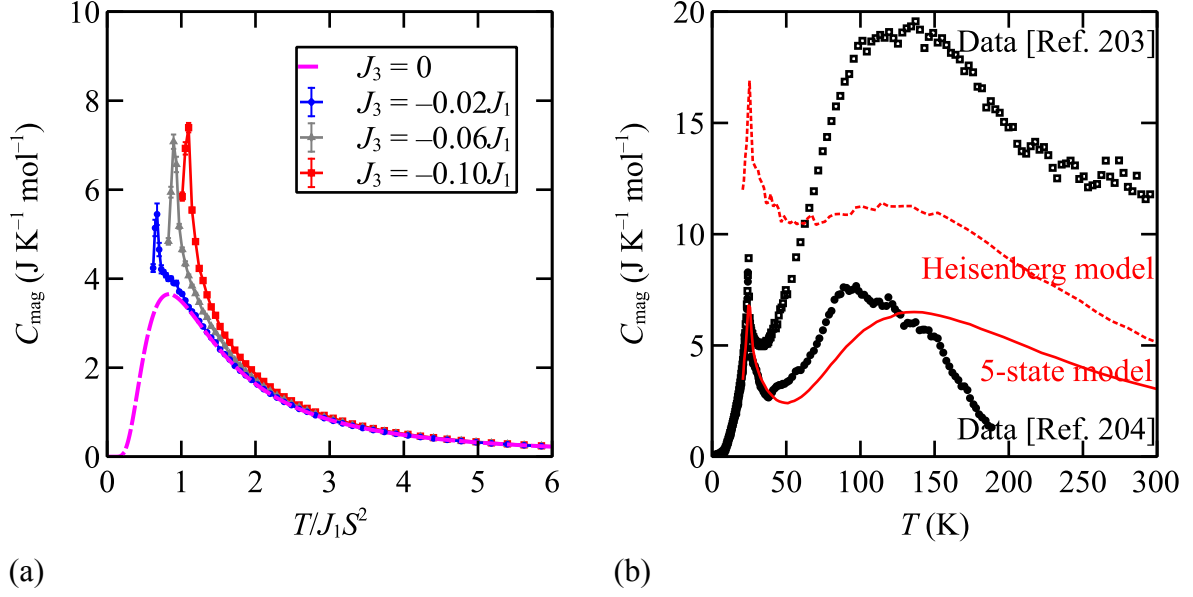


Figure 3.6: (a) Magnetic specific heat of $\text{Ca}_3\text{Co}_2\text{O}_6$. Results from MC simulations are shown for the Ising model with $J_3/J_1 = -0.02$ (blue circles), $J_3/J_1 = -0.06$ (grey triangles), and $J_3/J_1 = -0.10$ (red squares). The exact result [55] for FM J_1 only, $C_{\text{mag}} = N_A (J_1 S^2/T)^2 / [k_B \cosh^2(J_1 S^2/T)]$, is shown as a dashed magenta line. (b) Calculations of the magnetic specific heat for two anisotropic model Hamiltonians. Experimental data from Ref. 205 are shown as empty black squares and experimental data from Ref. 206 are shown as filled black circles. The calculation for the 5-state model, Eq. (3.2), is shown as a solid red line, and the calculation for the anisotropic Heisenberg model, Eq. (3.3), is shown as a dotted red line.

Values of these parameters have been reported separately, but a simultaneous fit of all three parameters has not been performed before. In Ref. 201, a fit to the single-crystal magnetic susceptibility yielded $J_1 = 13$ K; the disagreement with my results is probably due to the assumption of an Ising model up to room temperature. I find better agreement with the results of Ref. 220, in which the susceptibility was fitted to a model including both J_1 and Δ . Inelastic neutron-scattering measurements [203] show a weakly-dispersive spin wave propagating along $\mathbf{c}^*$ with a large spin gap $\omega_0 \approx 27$ meV ($= 310$ K). The dispersion was fitted using linear spin-wave theory to obtain (for isotropic exchange interactions) $J_1 = 4.9$ K and $\Delta = \omega_0/2S = 79$ K (the resolution of the data did not allow J_3 to be determined). Taking into account higher-order corrections to the spin-wave theory leads to a modified equation for the spin gap, $\Delta = \omega_0/(2S - 1)$ [222], which would yield $\Delta = 105$ K for the data of Ref. 203. These results are in reasonable agreement ($\sim 20\%$) with the 5-state model. Recently, values of the exchange interactions were obtained using ^{59}Co NMR to determine the energy cost of spin flips in the SDW phase, yielding (in my notation) $J_1 = 6.0$ K and $J_2 + J_3 = -0.58$ K [49]. The good agreement with my results is striking given the entirely different experimental technique and modelling approach considered in Ref. 49.

Finally, I consider my results in the context of the magnetic ordering identified by neutron diffraction. The first ordered state that develops at T_N is a SDW with an incommensurate magnetic propagation vector $\mathbf{k} \approx [0, 0, 1.01]^*$ [197, 198]. Assuming that J_2 is negligibly small, this propagation vector would require that $J_3/J_1 = -0.02$ [196]; however, as Fig. 3.5 shows, taking $J_3/J_1 = -0.02$ yields a much less successful description of the experimental susceptibility data than $J_3/J_1 \approx -0.1$. These results may be reconciled if J_2 is not actually negligible compared to J_3 . My simulations of the PM phase are insensitive to whether the AFM coupling is J_2 , J_3 or a combination of both; hence my value of J_3 can probably be interpreted as an overall AFM exchange interaction $J_{\text{AFM}} \approx J_2 + J_3$. By choosing J_2 and J_3 appropriately, both the overall energy of AFM interactions and the experimental propagation vector can be reproduced. For $J_{\text{AFM}} = -0.10J_1$, this occurs when $J_2 = J_3 = -0.05J_1$ [196]. I have checked that these values yield a χT curve which

is qualitatively similar to the one shown previously for $J_3/J_1 = -0.10$ ($J_2 = 0$). A similar argument was recently proposed based on NMR measurements, which also indicate that $J_2 \sim J_3$ [49].

3.6 Conclusions

I studied the PM phase of the Ising-like spin-chain compound $\text{Ca}_3\text{Co}_2\text{O}_6$ using MC modelling and RMC refinement to polarised-neutron scattering data. My results show that intra-chain spin correlations remain FM at all temperatures, decay approximately exponentially with distance along the chain, and exhibit a temperature-dependent correlation length which is well-described by the 1D Ising model over the temperature range studied ($T_N \lesssim T \lesssim 100$ K). Inter-chain correlations are weaker and AFM, and have a diffraction pattern which shows strong qualitative similarities to the nearest-neighbour AFM on the triangular lattice for $T \sim |J|$. Perhaps my most intriguing result is that important aspects of these two canonical models are simultaneously realised in PM $\text{Ca}_3\text{Co}_2\text{O}_6$, i.e., intra- and inter-chain correlations are essentially decoupled. This result is interesting for two reasons. First, it shows that the larger magnitude of the intra-chain interaction allows a spin chain to behave like a rigid, rod-like object, so that the PM correlations of these multi-spin “rods” resemble the correlations of individual spins on a triangular lattice with AFM interactions. Second, it shows that both frustration and low dimensionality have a large effect in the PM phase, despite the fact that the magnetic ordering temperature $T_N \sim JS^2$ is not strongly suppressed below the value expected for a 3D system without frustration.

I have also modelled previously-published measurements of the single-crystal magnetic susceptibility to obtain the exchange constants J_1 and J_3 and the single-ion anisotropy term Δ . Surprisingly, bulk susceptibility data are more sensitive than the magnetic diffuse-scattering data to the values of J_3 and Δ in this system. For a 5-state model, I obtain $J_1 \approx 6$ K, $J_3 \approx -0.6$ K and $\Delta \approx 110$ K (noting, however, that the value of Δ is dependent on the assumed form of the classical Hamiltonian). These values explain two anomalies in bulk measurements: (i) the high-temperature susceptibility peak at $T' \approx 40$ K, and (ii) the

broad maximum in magnetic specific heat at $T^* \sim 100$ K, which I interpret as a magnetic Schottky anomaly. This three-parameter model is the first to explain the temperature dependence of bulk measurements in $\text{Ca}_3\text{Co}_2\text{O}_6$ between T_N and room temperature. I also find that consistency with the magnetic propagation vector below T_N requires a non-negligible ratio $|J_2/J_3| \sim 1$. This conclusion (which is also reached in Ref. 49) suggests that it may be useful to re-examine the theoretical basis for the assumption that J_2 is small compared to J_3 .

Chapter 4

Hidden Order in Spin-Liquid

$\text{Gd}_3\text{Ga}_5\text{O}_{12}$

4.1 Chapter Summary

This chapter builds on two previous results. First, I showed in the previous chapter that RMC refinement to experimental powder diffuse-scattering data can reveal spin correlations in real materials. Second, the results of Section 2.4 suggest that non-dipolar correlations may in some cases also be accessed from RMC refinement. These results suggest that it may now be possible to use RMC refinement to search for states which show non-dipole (“hidden”) order. Frustrated magnetic materials are promising candidates for such states because the suppression of conventional dipole order potentially allows a hidden order to emerge in its place. An atomic-scale model of a hidden-order state has long been sought, but has proved difficult to obtain because microscopic probes are not directly sensitive to hidden order. In this chapter, I develop an atomic-scale model of the spin-liquid state in the canonical frustrated magnet $\text{Gd}_3\text{Ga}_5\text{O}_{12}$. I go on to show that this state exhibits a hidden order which has three unusual properties. First, it is a collective phenomenon, in which multipoles are formed from ten-spin loops. Second, it is long-range, with a diverging correlation length. Third, it is a consequence of the interplay between AFM spin correlations and local magnetic anisotropy, which allows it

to be indirectly observed in neutron-scattering experiments.

4.2 Acknowledgements

This project was a collaboration with the research group of Pascale Deen (Niels Bohr Institute, University of Copenhagen): they performed the experimental work while I performed the analysis and modelling. The single-crystal sample of GGG was prepared by Princeton Scientific. The single-crystal neutron-scattering measurements were performed using the D9 instrument at the ILL by Pascale Deen, Henrik Jacobsen (Niels Bohr Institute, University of Copenhagen) and Oleg Petrenko (University of Warwick), with assistance at an early stage of the project from Olga Young (University of Warwick) and Sonja Holm (University of Copenhagen). The D9 instrument scientist was Maria Teresa Fernández-Díaz and the data reduction was performed by Henrik Jacobsen. I am grateful to Henrik Jacobsen, Pascale Deen, and Oleg Petrenko for valuable advice and discussions about the data analysis.

4.3 Introduction

When a material undergoes a transition to an ordered state, its physical properties change. One of the triumphs of twentieth-century physics was to explain these macroscopic changes in terms of the microscopic ordering of atoms and spins. A canonical example is AFM order, which remained hidden until the development of neutron-scattering experiments in the 1940s [137]. Today, a similar situation exists in “hidden order” materials, where the order is likely to be non-dipolar and therefore cannot be directly probed by current experimental techniques (see, e.g., [224–226]). Hidden-order states are fascinating because they are qualitatively new states of matter. Exotic examples such as quantum spin nematics, chiral spin ices, and multipolar spin-orbital order have been theoretically proposed [227–229]. Experimentally, the hidden-order challenge is twofold. First, we wish to discover new hidden-order materials beyond the canonical example of URu_2Si_2 [224]. Second, we require an atomic-scale model of a hidden-order state which takes full advantage of the

indirect sensitivity afforded by current experimental techniques.

Frustrated magnetic materials are promising candidates for the discovery of new hidden-order states [179], because the strong spin correlations in spin-liquid states can lead to spin clusters behaving collectively. This leads to the possibility that a property of spin clusters may show non-dipolar long-range order, even though individual spins remain in a liquid-like state [230]. The experimental signature of a potential hidden order state is an anomaly in thermodynamic measurements which is not accompanied by a transition to long-range or frozen spin order [224]. This anomaly may be either sharp, as in a conventional second-order phase transition, or broad, as for the transition from the PM phase to the “Coulomb phase” in spin-ice materials [114].

The well-studied frustrated magnet $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ (gadolinium gallium garnet, GGG) exhibits thermodynamic anomalies of the second type. In GGG, a spin-liquid state is observed at temperatures above a spin-glass transition at $T_g \approx 0.14\text{ K}$ [231]. Evidence for a conventional spin liquid is the suppression of T_g to temperatures far below the AFM interaction strength of $\sim 2\text{ K}$ [51, 232], the observation of liquid-like magnetic diffuse scattering in powder neutron-scattering measurements [233], and the persistence of strong spin fluctuations to low temperature [234–236]. Yet, Fig. 4.1 shows that broad anomalies are present in both the non-linear susceptibility χ_3 and the magnetic specific heat at around 0.5 K , which do not have a well-understood microscopic origin [231, 237].

The crystal structure of GGG is shown in Fig. 4.2(a). The unit cell is cubic ($a = 12.349\text{ \AA}$) and contains 24 equivalent magnetic Gd^{3+} ions ($S = 7/2$, $L = 0$). The Gd^{3+} ions form two interpenetrating networks of opposite chirality, each of which describes a 3D hyperkagome network of corner-sharing triangles. The local coordination of the Gd^{3+} ions is shown in Fig. 4.2(b), where local axes $\mathbf{x}, \mathbf{y}, \mathbf{z}$ are defined by the three two-fold rotational axes of point symmetry, and are listed in Table 4.1. Of particular importance in the GGG structure are the ten-spin loops shown in Fig. 4.2(b), which represent the shortest path connecting a Gd^{3+} ion back to itself beyond individual triangles. Each Gd^{3+} also sits in the middle of exactly one loop; hence loop and atom share the same point symmetry and the local axes can be applied equally to loops. In a simple model

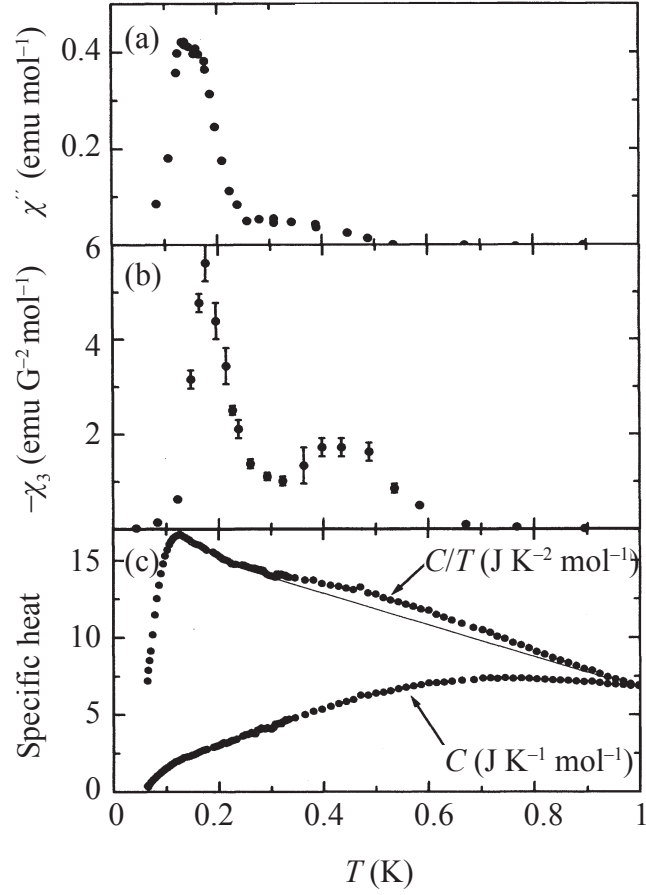


Figure 4.1: Temperature dependence of thermodynamic properties of GGG at low temperature. (a) Imaginary part of the susceptibility $\chi''(T)$. (b) Non-linear susceptibility $\chi_3(T)$. (c) Specific heat, C , and C/T . The straight line is shown to emphasise the broad peak in C/T . Figure reproduced from Schiffer *et al.* [231].

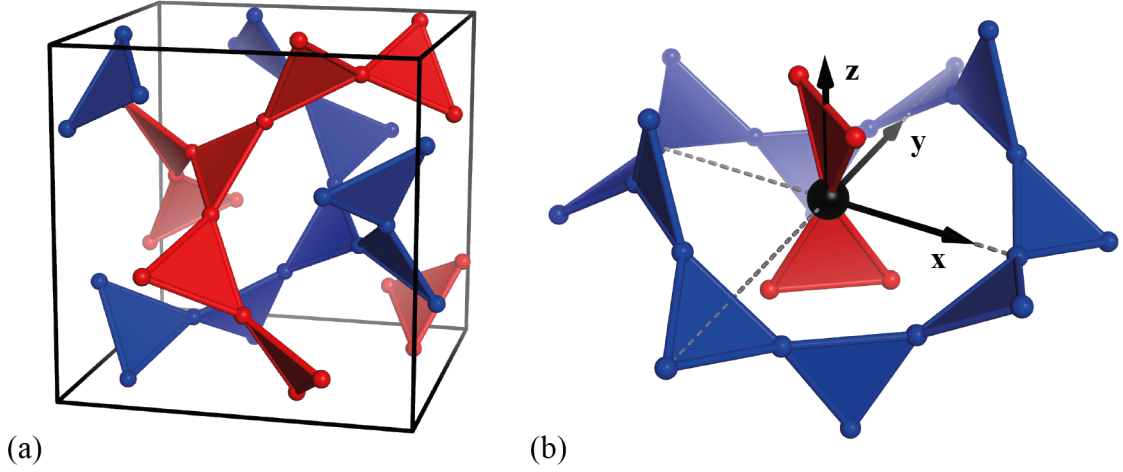


Figure 4.2: (a) Crystal structure of GGG, showing only magnetic Gd^{3+} ions. The two interpenetrating networks of corner-sharing triangles are coloured red and blue. (b) Local environment of Gd^{3+} ions. Each Gd^{3+} ion is surrounded by a loop of ten Gd^{3+} from the other network. The local axes $\mathbf{x}$, $\mathbf{y}$, $\mathbf{z}$ are given in Table 4.1 and are defined by the three two-fold axes of point symmetry of the Gd^{3+} site.

which considers only nearest-neighbour AFM interactions, collective rotations of the loop spins allow the system to move at no energy cost between its degenerate ground states [238]. It may therefore be anticipated that the ten-spin loops should play a key role in any collective behaviour present in the spin-liquid state.

4.4 Methods

4.4.1 Experimental

Neutron-scattering measurements were performed on a single crystal of GGG using the hot-neutron four-circle diffractometer D9 at the ILL. The sample was a $1 \times 1 \times 3 \text{ mm}^3$ single crystal of GGG which was grown for the laser industry by Princeton Scientific using the Czochralski method with an Ir crucible under an Ar atmosphere. The crystal was not isotope enriched and so contained large amounts of the highly neutron-absorbing isotopes ^{155}Gd and ^{157}Gd . To minimise the problem of neutron absorption, an incident neutron wavelength $\lambda = 0.512 \text{ \AA}$ was used, since neutron absorption is greatly reduced for $\lambda < 0.8 \text{ \AA}$ [239]. Data were collected over the reciprocal-space range $0.98 < Q < 3.77 \text{ \AA}^{-1}$. The sample was held in a Cu foil pocket and measured using a dilution fridge at $T = 10 \text{ K}$.

Fractional coordinates	Local axes $\mathbf{x}, \mathbf{y}, \mathbf{z}$
$\left(\frac{1}{8}, 0, \frac{1}{4}\right)$	$[100], [011], [0\bar{1}\bar{1}]$
$\left(\frac{1}{4}, \frac{1}{8}, 0\right)$	$[010], [101], [\bar{1}01]$
$\left(0, \frac{1}{4}, \frac{1}{8}\right)$	$[001], [110], [1\bar{1}0]$
$\left(\frac{3}{8}, 0, \frac{3}{4}\right)$	$[100], [0\bar{1}\bar{1}], [011]$
$\left(\frac{3}{4}, \frac{3}{8}, 0\right)$	$[010], [10\bar{1}], [101]$
$\left(0, \frac{3}{4}, \frac{3}{8}\right)$	$[001], [\bar{1}\bar{1}0], [110]$
$\left(\frac{7}{8}, 0, \frac{3}{4}\right)$	$[100], [011], [0\bar{1}\bar{1}]$
$\left(\frac{3}{4}, \frac{7}{8}, 0\right)$	$[010], [101], [10\bar{1}]$
$\left(0, \frac{3}{4}, \frac{7}{8}\right)$	$[001], [110], [1\bar{1}0]$
$\left(\frac{5}{8}, 0, \frac{1}{4}\right)$	$[100], [0\bar{1}\bar{1}], [011]$
$\left(\frac{1}{4}, \frac{5}{8}, 0\right)$	$[010], [\bar{1}01], [101]$
$\left(0, \frac{1}{4}, \frac{5}{8}\right)$	$[001], [1\bar{1}0], [110]$

Table 4.1: Table showing fractional coordinates of magnetic Gd^{3+} ions and the directions of their local $\mathbf{x}, \mathbf{y}, \mathbf{z}$ axes illustrated in Fig. 4.2. The crystallographic unit cell contains 24 Gd^{3+} ions, of which 12 are listed here and the remaining 12 are related by body-centring. The first 6 ions listed in the table (and their body-centred relations) form a single hyperkagome network, and the last 6 ions (and their body-centred relations) form the other network.

and $T = 0.175$ K. The correlated magnetic scattering intensity was isolated by taking the difference of these two datasets. The $m\bar{3}m$ diffraction symmetry appropriate for GGG was applied to the data in order to improve its apparent statistical quality.

4.4.2 Refinement and Modelling

4.4.2.1 Reverse Monte Carlo Refinements

Because the problem of Gd neutron absorption limits the statistical quality of the single-crystal data, I chose not to fit a model directly to the single-crystal data. Instead, I used RMC refinement to fit to previously-published powder diffuse-scattering data from Petrenko *et al.* [233], which were also collected at $T = 0.175$ K. The experimental single-crystal data were then used as a qualitative check on the RMC results. The magnetic component of the powder neutron-scattering data of Ref. 233 was obtained by subtraction of a higher-temperature dataset (collected at $T = 9$ K) from the $T = 0.175$ K dataset of interest. This procedure removes the non-magnetic scattering and isolates the correlated magnetic scattering. The temperature subtraction also removes the magnetic self-scattering (the additive factor of $\frac{2}{3}$ in Eq. (1.58)). Accordingly, in Eq. (1.103) I used the

following modified expression for the temperature-subtracted magnetic neutron-scattering intensity:

$$I_{\text{calc}}(Q) = C [gf(Q)]^2 \frac{1}{N} \sum_{j \neq i} \left[A_{ij} \frac{\sin Qr_{ij}}{Qr_{ij}} + B_{ij} \left(\frac{\sin Qr_{ij}}{(Qr_{ij})^3} - \frac{\cos Qr_{ij}}{(Qr_{ij})^2} \right) \right]. \quad (4.1)$$

It is necessary also to multiply Eq. (4.1) by an overall intensity scale factor s which converts normalised intensity (in barn sr⁻¹ atom⁻¹) into experimental intensity (in neutron counts). The value of s must be known before fitting to the data in order to obtain the correct magnitudes of the spin correlations, because the temperature-subtracted data oscillate around zero. The data were not placed on an absolute scale experimentally [233], so I obtained a value for s in the following way. In a frustrated AFM, the limiting value of the neutron-scattering intensity $I(Q \rightarrow 0)$ (defined by Eqs. (1.43) and (1.58)) must approach zero as $T \rightarrow 0$. Assuming this constraint holds for GGG at $T = 0.175$ K, it follows that

$$s = -\frac{3}{2} \frac{I_{\text{expt}}(Q \rightarrow 0)}{Cg^2}, \quad (4.2)$$

where $I_{\text{expt}}(Q)$ denotes the neutron-scattering intensity obtained experimentally by subtracting the $T = 9$ K data from the $T = 0.175$ K data. The variation in the experimental data at low Q implies a small uncertainty (on the order of a few per cent) in the value of s obtained from Eq. (4.2). To fine-tune the value of s within this range, I observe that fixing s at an incorrect value in an RMC refinement will tend to produce oscillations in the calculated $I(Q)$ in regions of Q -space where experimental data points are absent. The final value of s was chosen in order to eliminate such effects. The final RMC refinements were performed with a model of size $6 \times 6 \times 6$ crystallographic unit cells ($N = 5184$ spins) using periodic boundary conditions and were initialised from random starting configurations. Refinements were run for 300 proposed moves per spin, after which no significant improvement was observed in goodness-of-fit. Calculated quantities were averaged over 20 independent RMC configurations in order to minimise the statistical error.

4.4.2.2 Monte Carlo Simulations

I also performed Metropolis MC simulations [Section 1.4.1.1] of spin Hamiltonians with AFM nearest-neighbour interactions of strength J ,

$$H = -\frac{1}{2}J \sum_{\langle i,j \rangle} \mathbf{S}_i \cdot \mathbf{S}_j, \quad (4.3)$$

where the $\mathbf{S}_i$ are vectors of length $\sqrt{S(S+1)}$ which may be either isotropic (“Heisenberg model”), or alternatively confined to the local xy planes which lie perpendicular to the local $\mathbf{z}$ -axes listed in Table 4.1 (“local- xy model”). The angle brackets denote that the sum runs over nearest-neighbour spin-pairs only. The simulations were started at high temperature, $T = 5JS(S+1)$, and slowly cooled. At each temperature step, the number of proposed moves t_0 required for the system to become uncorrelated from its initial state was estimated, and $10t_0$ proposed moves were discarded to ensure equilibration. Then, $100t_0$ proposed moves were performed to calculate the magnetic specific heat from Eq. (1.78). For all simulations, a simulation size of $6 \times 6 \times 6$ crystallographic unit cells ($N = 5184$ spins) was used and periodic boundary conditions were applied.

Finally, I simulated a spin Hamiltonian containing the long-range magnetic dipolar interaction D in addition to exchange interactions,

$$H = -\frac{1}{2} \sum_{i,j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j + \frac{D}{2} \sum_{i,j} \frac{\mathbf{S}_i \cdot \mathbf{S}_j - 3(\mathbf{S}_i \cdot \hat{\mathbf{r}}_{ij})(\mathbf{S}_j \cdot \hat{\mathbf{r}}_{ij})}{(r_{ij}/r_1)^3}. \quad (4.4)$$

The dipolar term was implemented using Ewald summation [240], allowing a maximum error of 10^{-4} K in the total energy. I checked my implementation against direct summation of large periodic clusters and obtained results in exact agreement with those of Ref. 240. Following literature recommendations [241, 242], I assumed that the surrounding medium has infinite magnetic permeability (metallic boundary conditions).

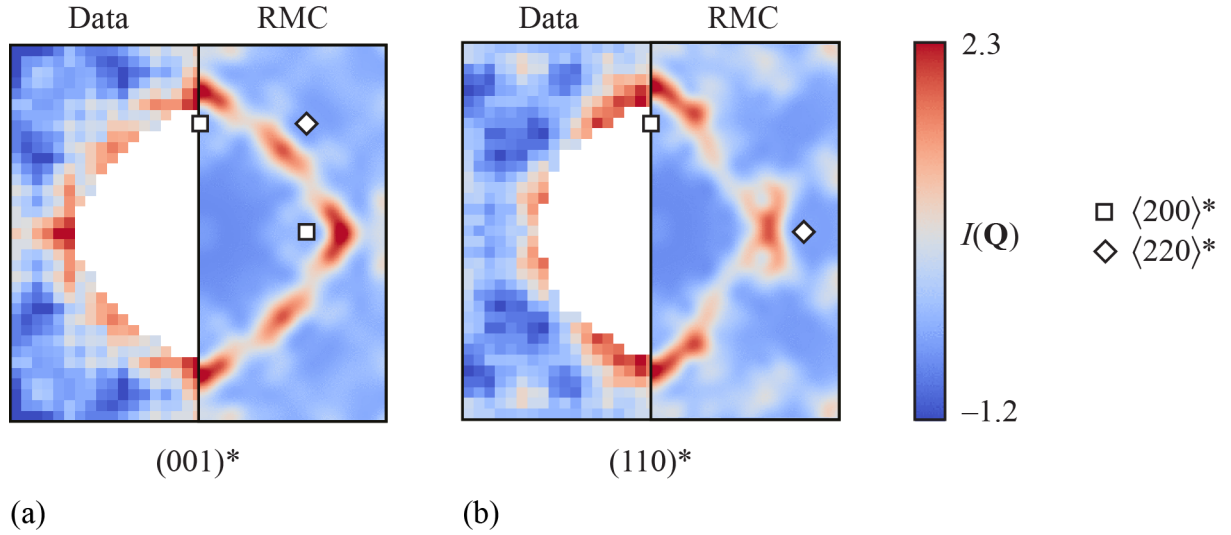


Figure 4.3: Single-crystal magnetic diffuse-scattering patterns for GGG at $T = 0.175$ K; (a) shows the $(001)^*$ reciprocal-space plane and (b) shows the $(110)^*$ reciprocal-space plane. In (a) and (b), the left-hand panel shows experimental data, and the right-hand panel shows a calculation from RMC refinement to the powder data shown in Fig. 4.4. Negative values of $I(\mathbf{Q})$ are due to the temperature subtraction.

4.5 Results and Discussion

The single-crystal neutron-scattering data measured at $T = 0.175$ K are shown in Fig. 4.3. Highly-structured magnetic diffuse scattering characteristic of a spin-liquid state is visible in both $(001)^*$ and $(110)^*$ reciprocal-space planes. In order to model these data, I used RMC refinement [39, 152] to refine to the magnetic diffuse-scattering data of Ref. 233, which were collected on a powder sample. Details of these refinements were given in Section 4.4.2. Excellent agreement between the RMC fit and the powder data is achieved at $T = 0.175$ K [Fig. 4.4]. Calculations of the single-crystal scattering from the refined RMC model [Fig. 4.3] show close qualitative agreement with the experimental single-crystal data, which provides strong evidence for the validity of the RMC model.

I now consider the refined RMC configurations in real space, and show that here, too, they agree with results from previous studies. Consistent with simulations [243], the radial spin correlation function $\langle \mathbf{S}(0) \cdot \mathbf{S}(r) \rangle$ reveals a rapid decay of spin correlations with an exponential correlation length $\xi = 4.951(2)$ Å (similar to the nearest-neighbour distance) and a nearest-neighbour spin correlation coefficient $\langle \mathbf{S}(0) \cdot \mathbf{S}(r_1) \rangle$ close to -0.5 at $T = 0.175$ K [Fig. 4.5(a)]. The temperature dependence of $\langle \mathbf{S}(0) \cdot \mathbf{S}(r_1) \rangle$ was obtained

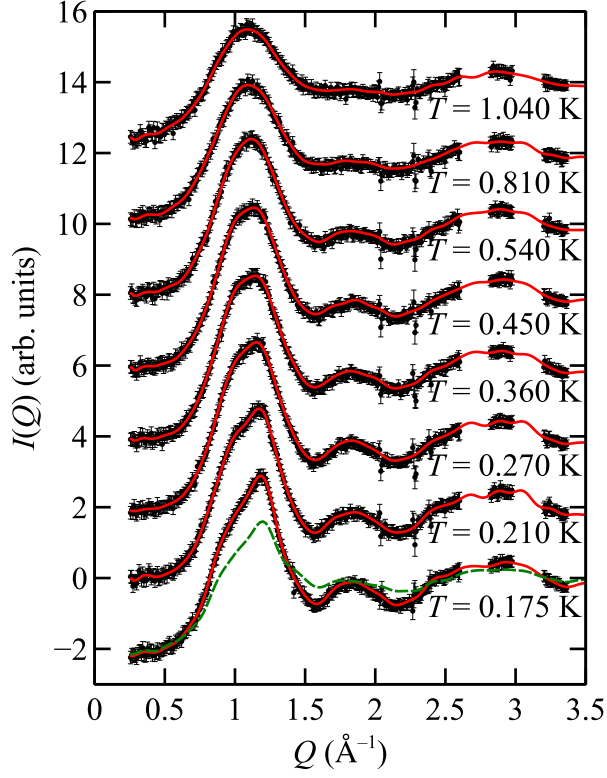


Figure 4.4: Powder-averaged magnetic diffuse-scattering patterns for GGG at eight temperatures in the spin-liquid regime (labelled on the graph), showing experimental neutron-scattering data (black circles) and RMC fits (red lines). Consecutive datasets are vertically shifted by 2 units for clarity. At $T = 0.175$ K, the green dashed line shows the calculated magnetic diffuse-scattering intensity for an isotropic model. Negative values of $I(Q)$ are due to the temperature subtraction.

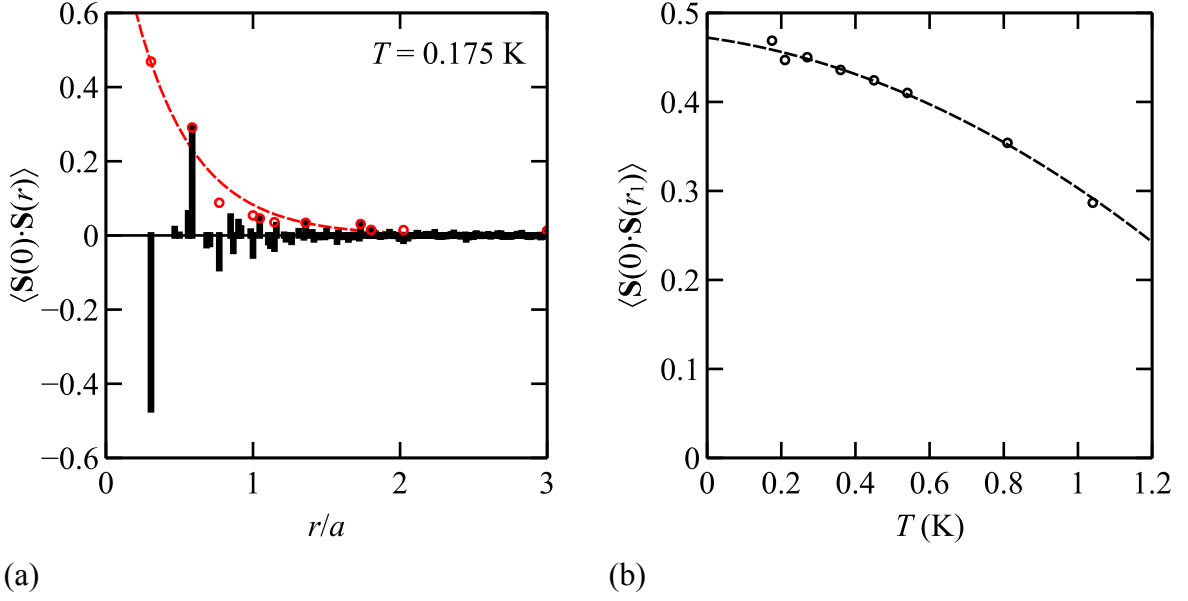


Figure 4.5: (a) Radial spin correlation function $\langle \mathbf{S}(0) \cdot \mathbf{S}(r) \rangle$ determined from RMC refinement at $T = 0.175$ K. The bars show spin correlation values and the red dashed line is a fit to an exponential envelope, $\exp(-r/\xi)$, where $\xi = 4.951(2)$ Å. (b) Temperature dependence of the nearest-neighbour spin correlation coefficient $\langle \mathbf{S}(0) \cdot \mathbf{S}(r_1) \rangle$. The dashed black line is a guide to the eye.

from the refined configurations at higher temperatures and shows a gradual decrease with increasing temperature [Fig. 4.5(b)]. I also obtain a strongly anisotropic distribution of spin orientations, with spins preferentially oriented within the local xy plane [Fig. 8.7(a)]. The magnitude of the anisotropy decreases with increasing temperature, but the spin-orientation distribution is not yet fully isotropic at $T = 1.04$ K [Fig. 8.7(b)]. Since RMC refinement is a stochastic process, and the refinements were started from entirely random spin configurations, the magnitudes of the anisotropy shown in Fig. 4.6 represent lower bounds on the true values. I also performed refinements of the $T = 0.175$ K data in which the spins were constrained to lie within their local xy planes, and found that the a good fit-to-data (not shown) is also obtained in this case; hence, the xy anisotropy is certainly large at $T = 0.175$ K, and the data are even consistent with the assumption that spins have no component perpendicular to their local- xy plane.

The presence of strong magnetic anisotropy in GGG may seem surprising, because Gd^{3+} is an S -state ion in which the crystal-field splitting is small [244]. My results are, however, consistent with Mössbauer measurements [34], which also indicate a strong pla-

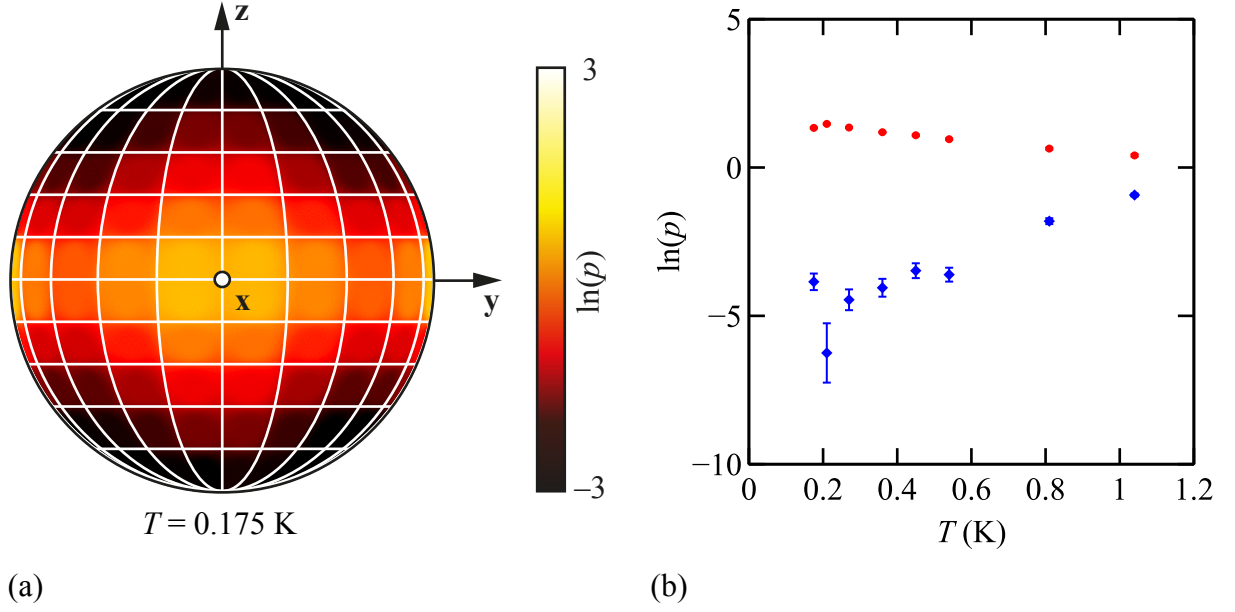


Figure 4.6: (a) Stereographic projection showing the spin-orientation distribution function $\ln(p)$ (defined by Eq. (2.5)) determined from RMC refinement at $T = 0.175$ K. Spins are aligned preferentially in the local- xy plane. (b) Temperature evolution of the maximum (red circles) and minimum (blue diamonds) values of $\ln(p)$.

nar anisotropy in the spin-liquid regime. My analysis also extends the Mössbauer results by determining which of the three possible local planes is the “easy” plane. In order to check directly that the experimental powder diffuse-scattering data are sensitive to anisotropy in GGG, as they are for spin ice [Section 2.3], I used Eq. (1.61) to calculate the $I(Q)$ which would be obtained if the anisotropy were absent. The $I(Q)$ calculated in this way disagrees strongly with the experimental data [Fig. 4.4], confirming the sensitivity of the data to anisotropy. Fig. 4.4 also shows that the effect of local- xy anisotropy is to sharpen the diffuse magnetic peaks, an effect which cannot be explained by experimental factors (e.g., background or statistical errors). Based on this analysis, I conclude that both the single-ion properties and short-range spin correlations of the RMC model are consistent with previous results.

To look for exotic behaviour beyond dipole order, I consider the ten-ion loops which are shown in Fig. 4.2(a). Adjacent spins in a loop are nearest neighbours and are therefore antiferromagnetically correlated. Surprisingly, inspection of spin configurations suggested that significant AFM alignment persists beyond nearest neighbours and throughout the loop, a result obscured by the radial average in Fig. 4.5(a). To quantify this correlation,

I calculated the average spin alignment axis of each loop,

$$\mathbf{L}(\mathbf{r}) = \frac{1}{10} \sum_{n=1}^{10} \cos(n\pi) \mathbf{S}_n(\mathbf{r}), \quad (4.5)$$

where $\mathbf{r}$ is the position of the centre of the loop and $\mathbf{S}_n$ are spins (normalised to unit length) within the loop. I refer to $\mathbf{L}(\mathbf{r})$ as the “ten-spin director” to emphasise that $\mathbf{L}$ does not transform as a vector, because the two-fold symmetry of the Gd^{3+} site requires that $\mathbf{L}(\mathbf{r})$ and $-\mathbf{L}(\mathbf{r})$ identify the same alignment axis; my use of the director here mirrors the description of nematic liquid crystals [245]. The average magnitude $\langle |\mathbf{L}(\mathbf{r})| \rangle = 0.49$ with standard deviation 0.18, which shows that AFM correlation is strong within each loop and relatively consistent between different loops. The cyclic arrangement of ten AFM spins in a ring describes an effective multipole of order 6, which contains 5 nodal planes orthogonal to the plane of the loop and a single nodal plane coincident with it [Fig. 4.7(a)]. In more precise language, a multipole expansion of the magnetic field distribution generated by such a ten-spin loop contains a large contribution from the spherical harmonic with $l = 6$ and $|m| = 1$. Viewed in these terms, the ten-spin director describes the multipole orientation associated with a given ten-ion loop. Fig. 4.7(b) shows the key result of this chapter: the distribution of ten-spin directors is strongly peaked along the local $\mathbf{z}$ direction. This result is remarkable because it shows that the fluctuations of the ten spins in a loop select a single axis on average, so the rotational degree of freedom possessed by individual xy -like spins is lost in the loop directors. Hence the ten-spin directors have no ground-state degrees of freedom, and are ordered. Moreover, since the ten-spin directors describe multipole orientations, the order is multipolar. The unit cell of this magnetic multipole crystal is shown in Fig. 4.8. The multipole order preserves the symmetry of the crystal structure but is not required by this symmetry, which only constrains the distribution of ten-spin directors to preserve the three two-fold rotation axes.

If the multipole order in GGG is long-range, a relevant correlation function should have a diverging correlation length. Fig. 4.9 shows the axial correlation function of the

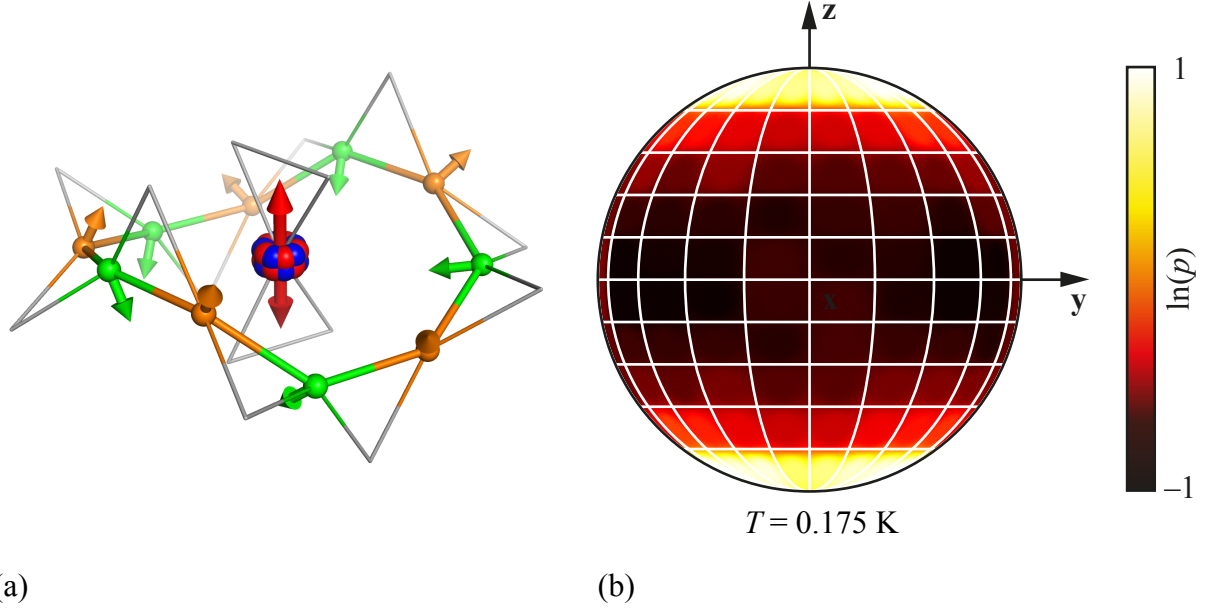


Figure 4.7: (a) Relationship between representative spin orientations and ten-spin director for a ten-spin loop. Antiferromagnetically-correlated spins are coloured alternating green and orange as the loop is traversed. The multipole formed by the ten spins is shown at the centre $\mathbf{r}$ of the loop, and the ten-spin director $\mathbf{L}(\mathbf{r})$ defined in the text is shown as a red double-headed arrow. (b) Stereographic projection showing the distribution of orientations of $\hat{\mathbf{L}}(\mathbf{r})$ determined from RMC refinement at $T = 0.175$ K.

normalised ten-spin directors,

$$g_L(r) = 2 \left\langle |\hat{\mathbf{L}}(0) \cdot \hat{\mathbf{L}}(r)| \right\rangle - 1, \quad (4.6)$$

where $\hat{\mathbf{L}} = \mathbf{L}/|\mathbf{L}|$. The $g_L(r)$ is equal to -1 if, on average, loop directors separated by distance r are normal and to $+1$ if they are collinear. No appreciable decay of $g_L(r)$ is visible at $T = 0.175$ K. I also fitted the maximum value of $g_L(r)$ with a linear function $b(r/a) + c$ over the long-distance region ($1 < r/a < 3$). The radial distances at which $g_L(r)$ has its maximum value were determined from the correlation function of the ideal multipole crystal [Fig. 4.8]. This fit yielded $b = -0.0007 \pm 0.0009$. Assuming that the correlation magnitude would decrease gradually with distance if long-range order were absent, this result shows that the axial correlation length at $T = 0.175$ K is greater than $10^3 a$ within the statistical error of the RMC refinements. Hence, the axial correlation length of ten-spin directors diverges, as is expected from the axial distribution of ten-spin directors shown in Fig. 4.7(b). To investigate the temperature evolution of multipole

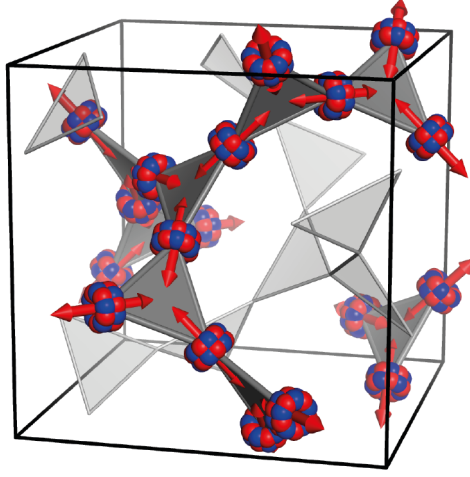


Figure 4.8: Crystal structure showing the unit cell of the magnetic multipole crystal. Multipoles and spin directors are shown as in Fig. 4.7(a) and are illustrated for only one of the two Gd^{3+} networks for clarity.

order, I then fitted the maximum value of $g_L(r)$ with a straight line at each temperature to obtain a limiting multipole correlation g_{max} [Fig. 4.9(b)]. The magnitude of g_{max} decreases with increasing temperature, but the excellent quality of the straight-line fits in Fig. 4.9(b) shows that the correlation length remains diverging.

How is my analysis sensitive to non-dipolar order, given that neutron scattering is a dipolar probe? To answer this question I note that neutron scattering is directly sensitive to two quantities: the spin anisotropy and the spin-pair correlations [Section 1.3]. If an interplay of both quantities generates hidden order, neutron scattering may be indirectly sensitive to the hidden order itself. To test whether this is the case for GGG, I performed MC simulations of the nearest-neighbour Heisenberg model and the local- xy model described in Section 4.4.2. Neither of these models is intended as an accurate representation of the spin Hamiltonian of GGG; instead, the aim is to determine the requirements for the hidden-order state. Fig. 4.10(a) shows $g_L(r)$ for the local- xy model at $T = 0.5|JS(S+1)|$. In this model, $g_L(r)$ has a diverging correlation length; hence the combination of AFM interactions and local- xy anisotropy is sufficient to generate the hidden-order state. Fig. 4.10(b) shows the Heisenberg model at $T = 0.5|JS(S+1)|$. Here, $g_L(r)$ does not diverge, showing that AFM interactions alone do not generate the hidden-order state. One might ask, then, whether local- xy anisotropy alone can explain

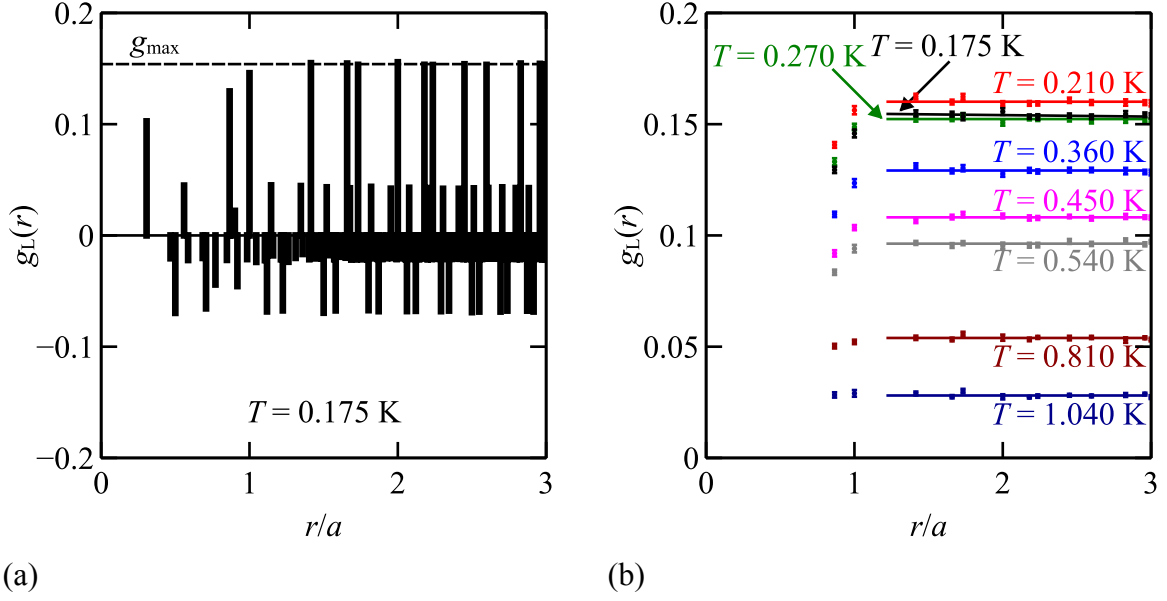


Figure 4.9: (a) Axial correlation function of ten-spin directors $g_L(r)$ at $T = 0.175$ K, showing the presence of long-range multipole order. (b) Temperature evolution of $g_L(r)$ and straight-line fits to the high- r region. Temperatures are labelled on the graph. Only points where $g_L(r)$ has its maximum value are shown.

my observations. The axial correlation function of the spins, $2 \langle |\mathbf{S}(0) \cdot \mathbf{S}(r)| \rangle - 1$, necessarily diverges in the local- xy model as a trivial consequence of the xy anisotropy. The axial correlation function of loop directors can also diverge by symmetry, but $g_{\max}$ need not be significant. Fig. 4.10(c) shows that $g_{\max}$ is indeed negligible for the local- xy model with zero interaction between spins (i.e., spins randomly oriented within their local- xy planes). This result also follows from the definition of $\mathbf{L}(\mathbf{r})$, Eq. 4.5, which shows that $\mathbf{L}(\mathbf{r})$ is zero in the absence of spin correlations. These results show that the hidden-order state is not a consequence of either AFM correlations or local- xy anisotropy alone, but instead results from an interplay of both these features.

I now argue that the development of hidden order in GGG provides a plausible explanation for broad thermodynamic anomalies which are observed in the spin-liquid state [231, 237]. To show this, I consider again the Heisenberg and local- xy models introduced above. Using MC simulations, I calculated $g_{\max}$ and the magnetic specific heat C_{mag} as a function of temperature. Fig. 4.11(a) shows that the local- xy model shows a specific-heat peak centred at $T \sim 0.5 |JS(S+1)|$ in the spin-liquid regime. I found that this model also shows a phase transition at lower temperature, which is not shown in Fig. 4.11(a). By

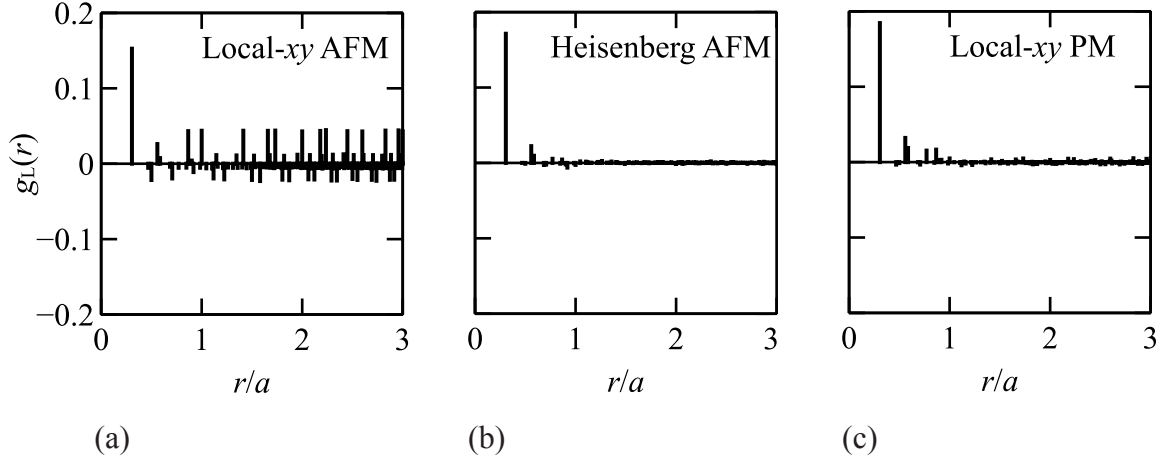


Figure 4.10: Axial correlation function of ten-spin directors $g_L(r)$ for three models discussed in the text: (a) local- xy AFM model at $T = 0.5|JS(S+1)|$, (b) Heisenberg AFM model at $T = 0.5|JS(S+1)|$, and (c) local- xy PM model.

contrast, no such peak is observed in the Heisenberg model over the relevant temperature range [Fig. 4.11(b)]. I note that the Heisenberg model does show a fluctuation-driven transition to a spin-nematic state, but this transition occurs at a much lower temperature ($T \lesssim 0.004|JS(S+1)|$) [184, 246] and is therefore not relevant to the spin-liquid regime of GGG, for which $T \gtrsim 0.1|JS(S+1)|$. In order to separate the broad peak in the local- xy model from the overall increase in C_{mag} with decreasing temperature, I fitted a quadratic polynomial to the region on either side of the broad peak and subtracted this fitted polynomial from the total C_{mag} . A similar procedure was followed to isolate the broad peak in the experimental data [231]. While the shape of the broad peak depends on the choice of fitting range and the order of the polynomial used, its presence is robust to different choices of these parameters. Finally, in order to match the temperature range over which the peak develops in the experimental data, I took $J_1S(S+1) = -1.5$ K, which agrees well with the experimental value $J_1S(S+1) = -1.7$ K [51, 231]. Fig. 4.12(a) shows g_{max} and the specific-heat peak for the local- xy model, and Fig. 4.12(b) shows g_{max} determined from RMC refinement and the experimental specific-heat data. The temperature evolution of the specific-heat peak correlates with the evolution of hidden order in a similar way for both local- xy model and experiment, suggesting that the broad specific-heat peak is a signature of loss of entropy associated with developing hidden order.

Having established the presence of local- xy anisotropy and hidden order in spin-liquid

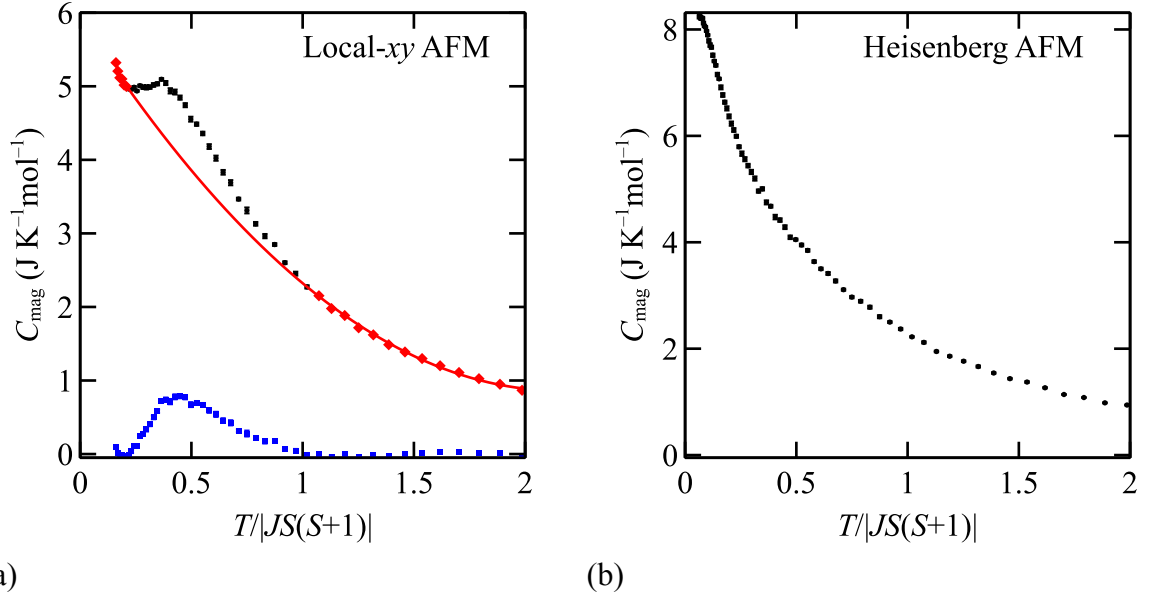


Figure 4.11: Temperature dependence of the magnetic specific heat C_{mag} (black circles) for two models discussed in the text: (a) local- xy AFM model and (b) Heisenberg AFM model. In (a), red diamonds show the points to which a quadratic background (red line) was fitted and blue squares represent the broad peak at $T \sim 0.5|JS(S+1)|$ obtained by subtraction of the fitted background from the total C_{mag} .

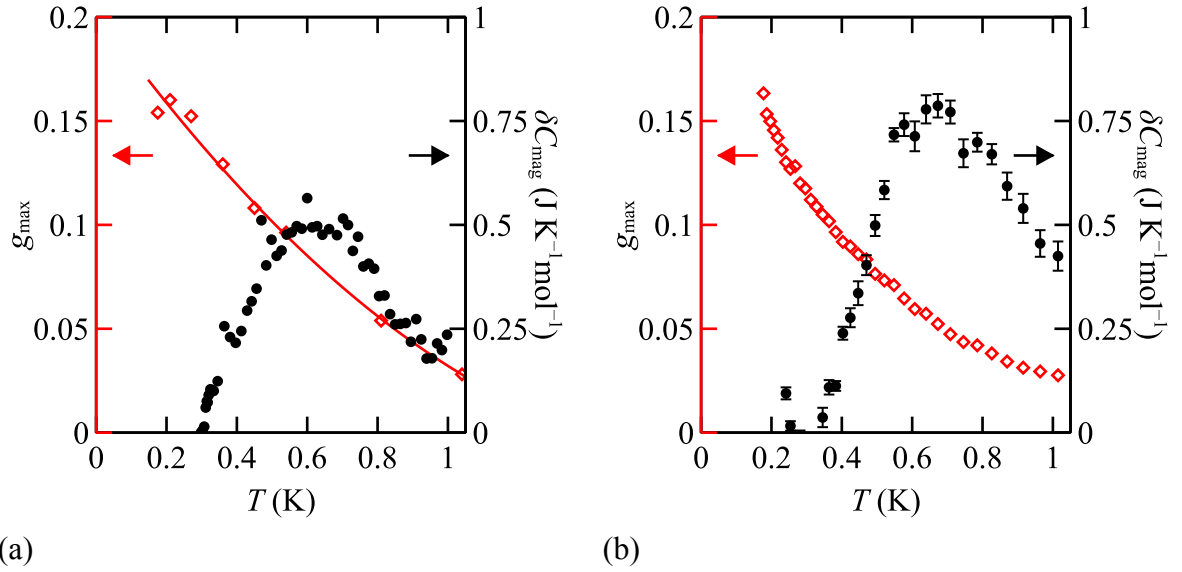


Figure 4.12: Temperature evolution of the broad peak in the magnetic specific heat δC_{mag} (black circles) compared with temperature evolution of the limiting multipolar correlation g_{max} (red diamonds). (a) shows experimental specific-heat data from Ref. 231 and g_{max} obtained from RMC refinement of experimental neutron-scattering data; (b) shows the specific heat and g_{max} calculated for the local- xy AFM model described in the text. The red line in (a) is a guide to the eye. The broad specific-heat peak has been isolated by fitting polynomial background functions to both experimental and simulated curves, as described in the text.

GGG, I now investigate the possible microscopic origin of these effects. There are two terms in the magnetic Hamiltonian which may explain the spin anisotropy. First, the long-range magnetic dipolar interaction couples spin and lattice degrees of freedom, and is of comparable strength to the nearest-neighbour exchange in GGG. Second, although Gd^{3+} is an S -state ion and hence has no crystal-field splitting at first order, the mixing of excited crystal-field states at second order generates a small crystal-field splitting which has been determined using electron-spin resonance experiments [244]. A self-consistent parameterisation of the spin Hamiltonian for GGG was obtained in Ref. 51, which includes dipolar and exchange interactions but neglects the crystal-field splitting. In Ref. 51, values for the exchange constants were obtained by fitting to $I(Q)$ in the spin-glass regime at $T = 0.043$ K using the mean-field approximation introduced in Section 1.4.1.2. The values obtained were $J_1 = -0.107$ K, $J_2 = +0.005$ K, $J_3 = -0.010$ K; the dipolar interaction strength $D = 0.0457$ K is fixed by the crystal structure. To determine whether the long-range dipolar interaction alone can explain the observed anisotropy, I performed MC simulations of the model of Ref. 51 at $T = 0.450$ K (this temperature was chosen to be sufficiently low to show the effects I wish to probe, but not so low as to require impractically-long simulation times). The dipolar summation was implemented using the standard method of Ewald summation [240] [Section 4.4.2]. Figs. 4.13(a) and 4.13(b) compare the experimental spin-orientation distribution functions obtained from RMC refinement with the model of Ref. 51. In both cases, local- xy anisotropy is observed, with an additional slight preference for spins to point along $\mathbf{x}$. The magnitude of anisotropy is, however, somewhat larger for the RMC refinements ($\ln(p_{\min}) = -3.6(2)$) compared to the model of Ref. 51 ($\ln(p_{\min}) = -2.2(1)$), which could perhaps be explained by the neglect of crystal-field effects in Ref. 51. Figs. 4.14(a) and 4.14(b) show that—as is now expected for the combination of predominantly AFM interactions and local- xy anisotropy— $g_L(r)$ diverges for both the RMC refinement and the model of Ref. 51. I therefore conclude that the observation of strong local- xy anisotropy and hidden order in GGG is consistent with the state-of-the-art in interaction modelling. Moreover, the long-range magnetic dipolar interaction appears to drive the hidden order by introducing local- xy anisotropy.

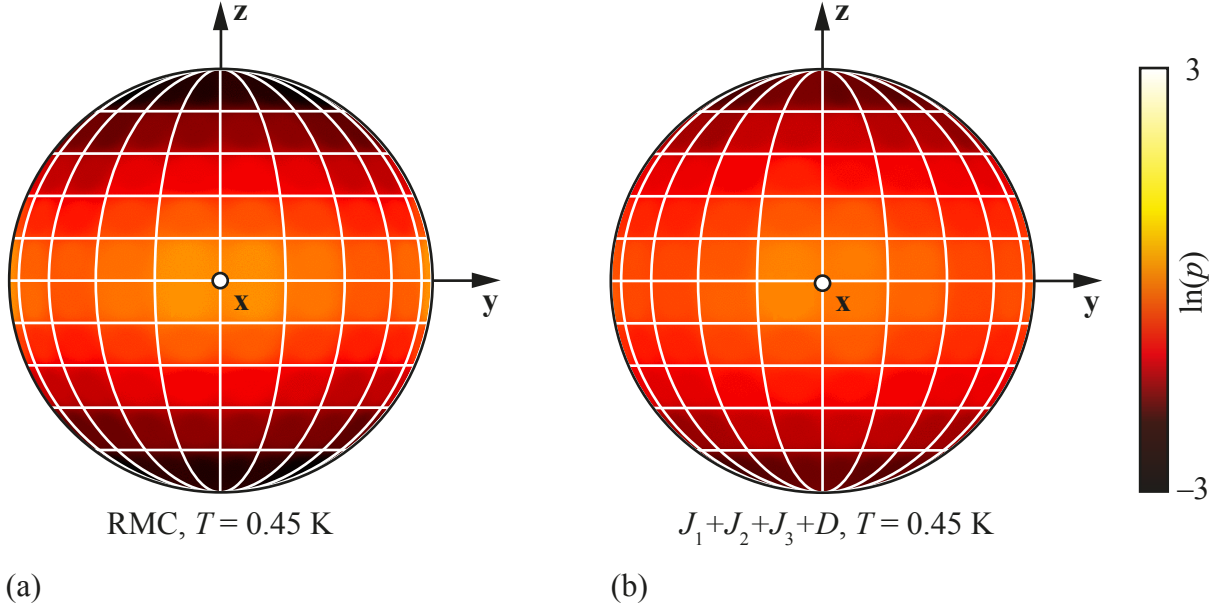


Figure 4.13: (a) Spin-orientation distribution function $\ln(p)$ (defined by Eq. (2.5)) obtained from RMC refinement at $T = 0.450$ K. (b) $\ln(p)$ obtained from MC simulation of the spin Hamiltonian proposed in Ref. 51 at $T = 0.450$ K. In both cases, the $\mathbf{x}$, $\mathbf{y}$, and $\mathbf{z}$ axes refer to the local coordinate system defined in Table 4.1.

This result suggests an interesting comparison with dipolar spin-ice physics, in which the long-range dipolar interaction is largely responsible for the development of ice-rules correlations [81, 247].

4.6 Conclusions

The hidden-order state of GGG is the only known example of a magnetic multipole crystal in a spin liquid. This hidden-order state does not break the crystal symmetry and is built from groups of spins which are individually fluctuating. It also seems likely that the multipolar order will be apparent in larger clusters than the ten-spin loops. Compared to the canonical example of URu_2Si_2 [224], the lack of symmetry breaking in GGG may broaden the specific-heat anomaly observed as the hidden-order state develops, similar to the transition to the “Coulomb phase” in spin-ice materials [114]. An interesting comparison can be drawn with frustrated spinels such as MgCr_2O_4 , in which hexagonal spin loops may form strongly-ordered (“protected”) degrees of freedom but adjacent loops are only weakly correlated [26, 248]. The hidden order in GGG represents the opposite

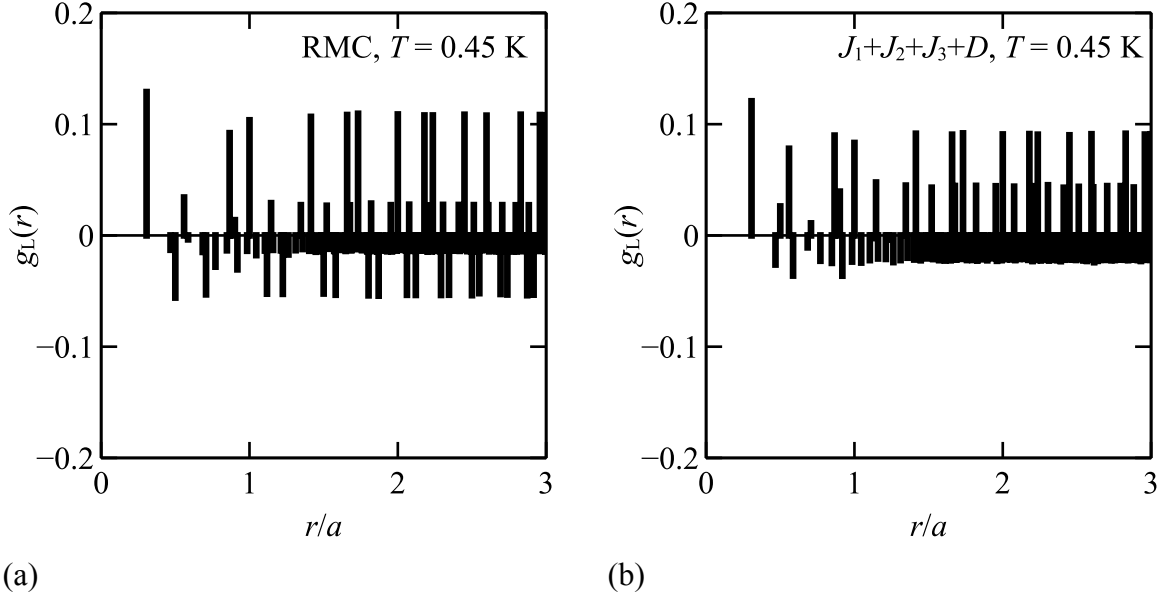


Figure 4.14: (a) Axial correlation function of the ten-spin directors $g_L(r)$ obtained from RMC refinement at $T = 0.450$ K. (b) $g_L(r)$ obtained from MC simulation of the spin Hamiltonian proposed in Ref. 51 at $T = 0.450$ K.

limit, in which the loops are long-range ordered while individual spins show only short-range correlations. The case of GGG therefore represents a new realisation of hidden order, with fundamentally-different properties to previous examples. My results suggest that RMC refinement may prove valuable to unmask hidden-order states in other materials, such as chiral spin liquids in frustrated magnetic materials [230] and spin nematics in high-temperature superconductors [249].

Chapter 5

Partial Order and Domain Formation in $\text{Gd}_2\text{Ti}_2\text{O}_7$

5.1 Chapter Summary

The magnetic states generated by geometrical frustration can often be divided into two categories. First, there are spin liquids like those studied in Chapters 3 and 4, in which frustration inhibits spin-dipole order. Second, there are conventional (though often complex) ordered magnetic phases, which eventually form due to perturbations beyond frustrated interactions. In this chapter, I study the frustrated pyrochlore AFM $\text{Gd}_2\text{Ti}_2\text{O}_7$, which defies this classification: it has an unusual *partially*-ordered magnetic structure at the lowest measurable temperatures. This structure is currently believed to involve multiple magnetic propagation vectors in a so-called $4\mathbf{k}$ model, based on analysis of powder-averaged magnetic diffuse-scattering data [62]. Here, I present three pieces of evidence against this $4\mathbf{k}$ structure. First, I report single-crystal neutron-diffraction measurements which show a redistribution of intensity between magnetic Bragg peaks when a small magnetic field is applied. This result is consistent with the selective population of magnetic domains for the alternative $1\mathbf{k}$ structure, but is inconsistent with the $4\mathbf{k}$ structure unless a field-induced phase transition occurs which is silent in thermodynamic measurements. Second, I present evidence from high-resolution neutron powder-diffraction

measurements that rhombohedral strains with finite length-scale are present at low temperature, which may be generated by magneto-elastic coupling only for the $1\text{-}\mathbf{k}$ structure. Third, I show that the argument previously used [62] to rule out the $1\text{-}\mathbf{k}$ structure is flawed, and demonstrate that the powder-averaged magnetic diffuse-scattering intensity can actually be fitted quantitatively by a $1\text{-}\mathbf{k}$ structure. The short-range spin correlations in this $1\text{-}\mathbf{k}$ structure include an important contribution from correlations between different magnetic sites which was not considered previously.

5.2 Acknowledgements

The single crystal of $\text{Gd}_2\text{Ti}_2\text{O}_7$ was prepared by H. D. Zhou (University of Tennessee and National High Magnetic Field Laboratory, Florida State University) and Jason Gardner (Neutron Group, National Synchrotron Radiation Research Center, Taiwan). I performed the in-field single-crystal neutron-diffraction experiments on the WISH diffractometer at ISIS with Ross Stewart, Georg Ehlers (Quantum Condensed Matter Division, Oak Ridge National Laboratory), and Oleg Petrenko (University of Warwick). The WISH instrument scientists were Pascal Manuel and Dmitry Khalyavin, who also supplied Fig. 5.2(b). I performed the powder neutron-diffraction experiments on the HRPD diffractometer at ISIS with the same group of people. The HRPD instrument scientist was Aziz Daoud-Aladine. Cryogenic support was provided by Oleg Kirichuk (STFC-ISIS) and his team. The Rietveld refinements of the D20 data from Ref. 62 were performed by Georg Ehlers. The Rietveld refinements of the HRPD data were performed by Andrew Cairns (University of Oxford), and we thank Josh Makepeace and Mark Senn (both University of Oxford) for assistance with the TOPAS program.

5.3 Introduction

In partially-ordered magnetic states, there are two magnetic sites, one of which shows long-range magnetic order while the other shows short-range (PM) spin correlations. The fundamental interest in partially-ordered magnets lies in understanding the interplay be-

tween order and disorder, which is inherent in the magnetic structure and may drive its formation [250, 251]. The existence of partial magnetic order in a surprisingly-large number of frustrated magnets (see, e.g., [252–257]) indicates the need for a general approach to analyse neutron-scattering data for these unusual materials. The study of partially-ordered states also has important implications beyond magnetism, where partial structural order plays a key role in determining the properties of diverse materials such as fast-ion conductors and high-pressure elemental phases [145, 258].

In this chapter, I investigate the magnetic structure of the partially-ordered pyrochlore AFM $\text{Gd}_2\text{Ti}_2\text{O}_7$. In $\text{Gd}_2\text{Ti}_2\text{O}_7$, magnetic Gd^{3+} ions ($S = 7/2$, $L = 0$) are coupled by predominantly AFM interactions ($\theta = -9.6$ K [116]). Unlike the ideal Heisenberg pyrochlore AFM discussed in Section 2.2, thermodynamic measurements show that $\text{Gd}_2\text{Ti}_2\text{O}_7$ undergoes two magnetic ordering transitions, at $T_1 = 1.1$ K and $T_2 = 0.75$ K [116, 259–262]. Neutron powder-diffraction experiments showed that both these magnetic states order with magnetic propagation vector $\mathbf{k} = [\frac{1}{2}\frac{1}{2}\frac{1}{2}]^*$ [62, 263]. In what follows, I will consider only the low-temperature state ($T < T_2$). The presence of partial magnetic order for $T < T_2$ is shown by the coexistence of magnetic Bragg peaks with a large amount of magnetic diffuse scattering, which persists to the lowest temperatures accessible experimentally ($T \approx 0.05$ K) [62]. A partially-ordered state is allowed by symmetry because application of one of the four $\mathbf{k} = \langle \frac{1}{2}\frac{1}{2}\frac{1}{2} \rangle^*$ propagation vectors splits the single crystallographic Gd^{3+} site into two inequivalent magnetic sites. The “kagome” site contains $\frac{3}{4}$ of the structure’s atomic positions which form kagome planes perpendicular to $\mathbf{k}$, and the “interstitial” site contains the remaining $\frac{1}{4}$ of atomic positions which link the planes. The magnetic Bragg peaks observed in neutron powder-diffraction experiments can be convincingly fitted by a magnetic structure involving a single propagation vector, which I refer to as the 1- $\mathbf{k}$ structure [263, 264]. In the 1- $\mathbf{k}$ structure, kagome (“K”) spins have an ordered moment close to the maximum expected for Gd^{3+} ($7.0 \mu_B$ per spin), and are arranged perpendicular to $\mathbf{k}$ and mutually at 120° on each triangle. Interstitial (“I”) spins have only a small ordered moment and hence remain mostly PM [62].

A major challenge in magnetic structure solution of high-symmetry systems is the so-

called “multi- $\mathbf{k}$ ” problem [37, 265]. Applied to $\text{Gd}_2\text{Ti}_2\text{O}_7$, this states that the 1- $\mathbf{k}$ structure is not the only possible magnetic solution, because multi- $\mathbf{k}$ (2- $\mathbf{k}$, 3- $\mathbf{k}$, or 4- $\mathbf{k}$) structures can be generated by superposing two or more different 1- $\mathbf{k}$ structures ($\mathbf{k} \in \langle \frac{1}{2} \frac{1}{2} \frac{1}{2} \rangle^*$). The multi- $\mathbf{k}$ structures give identical Bragg scattering to the 1- $\mathbf{k}$ structure in powder-diffraction experiments. However, the 2- $\mathbf{k}$ and 3- $\mathbf{k}$ structures have been ruled out on physical grounds because they would require some Gd^{3+} ions to have ordered moments much larger than $7.0 \mu_B$ [62]. The candidate 1- $\mathbf{k}$ and 4- $\mathbf{k}$ structures are shown in Figs. 5.1(a) and (b), respectively. The following similarities and differences exist between them. (i) Both structures contain ordered and PM spins in the ratio 3:1. However, in the 1- $\mathbf{k}$ structure, neighbouring PM spins are separated by $7.2 \text{ \AA}$ and occupy a face-centred cubic lattice, whereas in the 4- $\mathbf{k}$ structure they are separated by $3.6 \text{ \AA}$ and occupy isolated tetrahedra. (ii) In both structures, ordered spins are arranged perpendicular to their local $\langle 111 \rangle$ directions. However, in the 1- $\mathbf{k}$ structure, all ordered spins are also perpendicular to a single *global* $[111]$ direction. (iii) Macroscopic samples of both structures would contain magnetic domains. However, the internal symmetries of these domains (as well as the lost symmetry elements relating distinct domains of the same structure) are different for the 1- $\mathbf{k}$ and 4- $\mathbf{k}$ cases. Each 1- $\mathbf{k}$ domain has rhombohedral symmetry (magnetic space group $R\bar{1}\bar{3}m$), whereas each 4- $\mathbf{k}$ domain retains cubic symmetry (magnetic space group $F\bar{4}3m$). Importantly, this means that different 1- $\mathbf{k}$ domains have propagation vectors related by rotation symmetry elements (so-called “arm domains”) and therefore have different single-crystal neutron diffraction patterns. By contrast, different 4- $\mathbf{k}$ domains are only associated with time-reversal and translation symmetry breaking, and appear identical to neutrons.

Several experimental approaches have been used to attempt to distinguish between 1- $\mathbf{k}$ and 4- $\mathbf{k}$ structures. The authors of a previous neutron diffraction study proposed that the observed magnetic diffuse scattering is compatible only with a 4- $\mathbf{k}$ structure [62]. Other experimental results present an inconclusive picture. Mössbauer measurements are consistent with each spin being aligned perpendicular to its local $\langle 111 \rangle$ direction [260], which is the case for both 1- $\mathbf{k}$ and 4- $\mathbf{k}$ structures. An ESR study [266] reported symmetry-breaking $[111]$ anisotropy in the PM phase which was later shown to be a

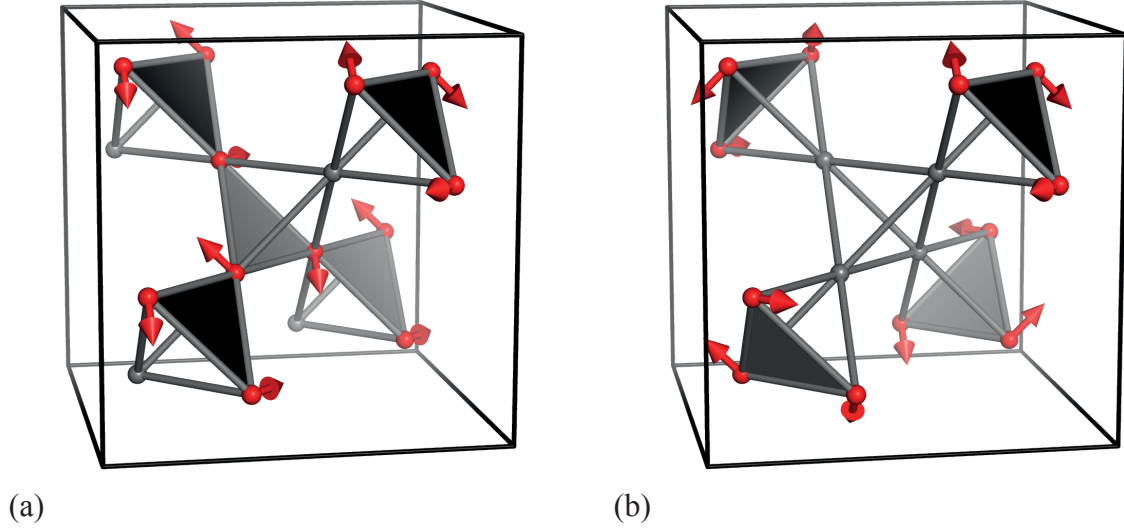


Figure 5.1: (a) 1- $\mathbf{k}$ and (b) 4- $\mathbf{k}$ magnetic structure candidates for the low-temperature magnetic structure of $\text{Gd}_2\text{Ti}_2\text{O}_7$. In both structures, the ordered site is shown in red, the disordered site is shown in grey, and average spin orientations are shown as red arrows. A single crystallographic unit cell is shown; spin orientations are reversed in adjacent unit cells.

sample-size effect [267]; subsequent ESR measurements for $T < T_2$ were consistent with the 4- $\mathbf{k}$ structure, although the 1- $\mathbf{k}$ structure was not explicitly ruled out [268]. Torque magnetometry measurements reveal the development of a transverse magnetisation for small applied magnetic fields ($B < 1$ T) along $\langle 100 \rangle$ or $\langle 112 \rangle$ directions which shows that macroscopic cubic symmetry is readily broken by an applied field [269–271].

From the theoretical perspective, models with AFM nearest-neighbour Heisenberg exchange and long-range dipolar interactions predict a ground state with $\mathbf{k} = 0$ [119, 272], in contradiction with experiment. Both 1- $\mathbf{k}$ and 4- $\mathbf{k}$ structures can be stabilised over a wide temperature range by the inclusion of various additional magnetic interactions [251, 273], but the particular interactions relevant to the real material have not yet been determined. Entirely different models of the magnetic structure have also been proposed based on theoretical considerations [274]; however, these proposals are inconsistent with the neutron powder-diffraction results [264], so I do not consider them further here. Symmetry restrictions are relevant for the phase transition at T_1 , as it is reported to be continuous [263]. According to Landau theory [275, 276], the ordered state which forms at T_1 must be either 1- $\mathbf{k}$ or 4- $\mathbf{k}$ with equal arms components. By contrast, renormalization-

group theory predicts the absence of a stable fixed point for the transition to the $1\text{-}\mathbf{k}$ structure [251, 275], requiring fluctuation-induced first-order character for this case. Importantly, however, the transition at T_2 is discontinuous [31], which means that none of these symmetry restrictions is relevant to the low-temperature state that I consider here. An unambiguous experimental solution of the multi- $\mathbf{k}$ problem at low temperature is therefore a prerequisite for detailed theoretical modelling.

An ideal probe to distinguish between $1\text{-}\mathbf{k}$ and $4\text{-}\mathbf{k}$ structures is single-crystal neutron scattering in an applied magnetic field. In zero applied field, a macroscopic sample contains an equal population of all degenerate magnetic domains. The application of a small magnetic field breaks this domain degeneracy and produces a domain imbalance. If the structure is $1\text{-}\mathbf{k}$, this leads to a redistribution of the intensity between magnetic Bragg peaks, whereas no change is observed if the structure is $4\text{-}\mathbf{k}$. The experimental challenge of such measurements is the very high neutron absorption cross-section of ^{155}Gd and ^{157}Gd , which makes diffraction experiments infeasible for samples with natural Gd abundance unless high-energy neutrons are used [277]. This problem was ameliorated by preparing a single crystal of $\text{Gd}_2\text{Ti}_2\text{O}_7$ which was 99.4% isotopically-enriched with the non-absorbing isotope ^{160}Gd .

This chapter is structured as follows. In Section 5.4, I use in-field single-crystal neutron diffraction measurements to obtain strong evidence that the low-temperature structure may not, in fact, be $4\text{-}\mathbf{k}$ as was previously proposed [62]. In Section 5.5, I investigate the possibility of non-cubic magneto-elastic strains over the magnetic domain length-scale, which may occur if the structure is not $4\text{-}\mathbf{k}$. Finally, in Section 5.6, I show the magnetic diffuse scattering observed experimentally—previously considered to be consistent only with the $4\text{-}\mathbf{k}$ structure [62]—can actually be modelled quantitatively within a $1\text{-}\mathbf{k}$ model.

5.4 In-Field Single-Crystal Diffraction Measurements

5.4.1 Experimental

In this section I describe single-crystal measurements in an applied magnetic field which allow the 1- $\mathbf{k}$ and 4- $\mathbf{k}$ structures to be distinguished. The WISH diffractometer [98] at ISIS (discussed in Section 1.3.4) was used to measure the field-dependence of magnetic Bragg reflections with an applied magnetic field along the $[1\bar{1}0]$ direction. A dilution refrigerator insert allowed a minimum temperature $T = 0.07\text{ K} \ll T_2$ to be reached. The sample was a small single crystal of volume $\sim 10\text{ mm}^3$, which was cut from a larger crystal of isotopically-enriched $^{160}\text{Gd}_2\text{Ti}_2\text{O}_7$ grown by the floating-zone image furnace method using an isotopically-natural $\text{Gd}_2\text{Ti}_2\text{O}_7$ seed crystal [278, 279]. Preliminary measurements of the larger crystal on the SPINS three-axis spectrometer at National Institute of Standards and Technology demonstrated the crystal quality, with an approximately isotropic mosaicity of FWHM $\approx 0.4^\circ$. Polarised-neutron diffraction measurements on the D7 diffractometer at the ILL determined the absorption cross-section of the larger crystal to be $\approx 300\text{ barn Gd}^{-1}$ for incident neutron wavelength $\lambda = 4.8\text{ \AA}$.

5.4.2 Results

The field-dependence of selected magnetic Bragg peaks is shown in Fig. 5.2(a). Magnetic peaks in the $(1\bar{1}0)^*$ plane disappear on the application of a magnetic field $\mu_0 H \gtrsim 0.2\text{ T}$ [left-hand panels of Fig. 5.2(a)]. This result is consistent with the 1- $\mathbf{k}$ structure, as Fig. 5.2(b) shows. The applied field makes the same angle (90°) with two of the $\mathbf{k}$ (labelled $\mathbf{k}_1$ and $\mathbf{k}_4$ in Fig. 5.2(b)) which lie within the $(1\bar{1}0)^*$ plane, and a different angle (35°) with the remaining two $\mathbf{k}$ (labelled $\mathbf{k}_2$ and $\mathbf{k}_3$ in Fig. 5.2(b)) which lie outside the $(1\bar{1}0)^*$ plane. Hence one pair of domains is populated by the application of a field and the other pair is depopulated. Our data indicate that the field depopulates domain pair $(\mathbf{k}_1, \mathbf{k}_4)$ which lies in the $(1\bar{1}0)^*$ plane. The intensity of peaks outside the $(1\bar{1}0)^*$ plane should show a corresponding increase as the other domain pair $(\mathbf{k}_2, \mathbf{k}_3)$ is simultaneously populated by the applied field. In practice these out-of-plane peaks had low intensities due

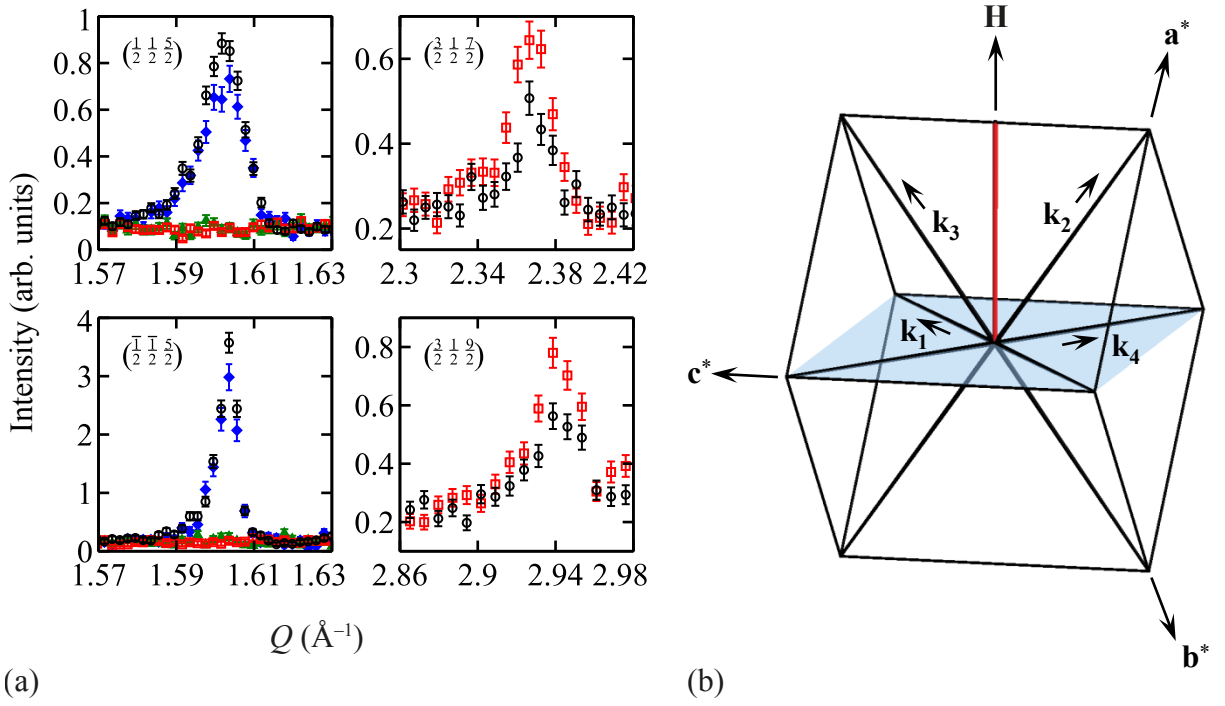


Figure 5.2: (a) Intensities of selected single-crystal magnetic Bragg peaks at different values of the applied magnetic field $\mu_0 \mathbf{H}$ parallel to $[1\bar{1}0]$ at $T = 0.07$ K. Magnetic Bragg peaks are labelled in each panel; left-hand panels show peaks within the $(1\bar{1}0)^*$ plane and right-hand panels show peaks outside the $(1\bar{1}0)^*$ plane. Points are shown as follows: $\mu_0 H = 0$ (black hollow circles), $\mu_0 H = 0.1$ T (blue filled diamonds), $\mu_0 H = 0.2$ T (green filled triangles), and $\mu_0 H = 0.5$ T (red hollow squares). Only $\mu_0 H = 0$ and $\mu_0 H = 0.5$ T are shown in the right-hand panels in order to maintain clarity. (b) Effect of applied magnetic field $\mu_0 \mathbf{H}$ parallel to the $[1\bar{1}0]$ direction on magnetic domains in a 1- $\mathbf{k}$ structure. The direction of the applied field is shown as a red line, the $(1\bar{1}0)^*$ plane is shown in blue, and the magnetic propagation vectors selected in different domains are labelled $\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3,$ and $\mathbf{k}_4$. The reciprocal axes are labelled $\mathbf{a}^*, \mathbf{b}^*,$ and $\mathbf{c}^*$.

to the effect of the magnetic form factor at higher Q and the flux profile of WISH, which significantly reduced the counting statistics. However, I was able to identify two out-of-plane magnetic peaks, all of which show increased intensity in applied field consistent with the 1- $\mathbf{k}$ structure [right-hand panels of Fig. 5.2(a)]. Two additional magnetic peaks, in-plane $\left(\frac{3}{2} \frac{3}{2} \frac{1}{2}\right)$ and out-of-plane $\left(\frac{3}{2} \frac{1}{2} \frac{5}{2}\right)$ (not shown), were also checked and showed the same trend.

5.4.3 Discussion

The observation of changes in peak intensity consistent with a domain imbalance provides strong evidence against the 4- $\mathbf{k}$ structure candidate, for which different domains have

identical single-crystal diffraction patterns. The only scenario in which our data might be consistent with a $4\text{-}\mathbf{k}$ structure were if the applied magnetic field actually caused a magnetic phase transition rather than a domain imbalance. Phase transitions in small magnetic field are known to occur in some highly-frustrated magnets [280], so this possibility cannot be excluded. However, in $\text{Gd}_2\text{Ti}_2\text{O}_7$ there is no experimental evidence of a phase transition in either specific heat [261] or torque magnetometry [270] measurements for fields along $\langle 110 \rangle$ of less than 2 T, whereas we observe changes in peak intensity for much smaller fields ($B \approx 0.2$ T). The observation of a domain imbalance does not rule out the $2\text{-}\mathbf{k}$ structure or the $3\text{-}\mathbf{k}$ structure, both of which also contain domains with different diffraction patterns. However, as previously noted, these possibilities are incompatible with the magnitude of the ordered magnetic moment determined by Rietveld refinement [62].

5.5 High-Resolution Powder Diffraction Measurements

If the magnetic structure of $\text{Gd}_2\text{Ti}_2\text{O}_7$ is not $4\text{-}\mathbf{k}$, the formation of magnetic order involves a lowering of symmetry from cubic. Hence, the magnetic ordering transition may be accompanied by a lattice distortion through a coupling to symmetry-breaking strain components (as in the well-known case of MnO [143]). In principle, such a distortion should always be present if the magnetic structure is not $4\text{-}\mathbf{k}$. In practice, however, the size of any distortion depends on the strength of the magneto-elastic coupling. Moreover, it is possible that a distortion may not persist over the entire crystal, but instead may be coherent only over the smaller length-scale which corresponds to the magnetic domain size.

5.5.1 Experimental

High-resolution powder neutron-diffraction measurements were performed to determine whether a structural distortion is present in $\text{Gd}_2\text{Ti}_2\text{O}_7$. The HRPD diffractometer at ISIS (discussed in Section 1.3.4) was used because it has among the highest reciprocal-space

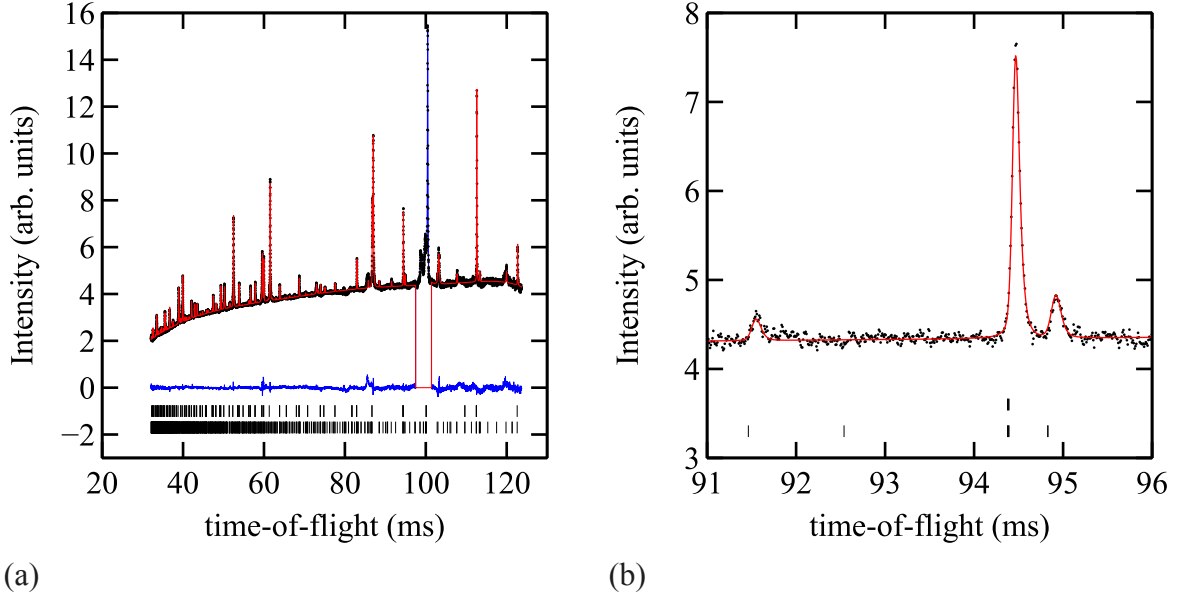


Figure 5.3: (a) High-resolution powder neutron-diffraction data for $\text{Gd}_2\text{Ti}_2\text{O}_7$ at $T = 0.03$ K. Experimental data are shown as black circles, Rietveld fit as a red line, and data-fit as a blue line. The upper line of tick marks indicates the positions of the nuclear Bragg peaks and the lower line of tick marks indicates the positions of magnetic Bragg peaks. The region around 100 ms was excluded as it contains a large background contribution from solid IPA that could not be modelled robustly. (b) Expanded region of the neutron-diffraction data and fit at high time-of-flight, showing the magnetic and nuclear peak-shapes. In (a) and (b), the Rietveld refinement was performed constraining the magnetic peak-shape to equal the nuclear peak-shape convoluted with a Gaussian domain-size broadening function, and the fits are shown for the best-fit distortion parameter $D = 0.0002$ [Fig. 5.4(b)].

resolution of any neutron instrument ($\Delta Q/Q \approx 5 \times 10^{-4}$), which would allow a much smaller distortion to be observed than previous measurements [62, 263]. Measurements were performed at $T = 1.1$ K and $T = 0.03$ K on the same powder sample used in previous studies [62, 263]. The sample was mounted in a Cu holder and deuterated isopropyl alcohol (d-IPA) was added to improve thermal contact. A ^3He cryostat with a dilution-refrigerator insert was used to reach sub-Kelvin temperatures.

5.5.2 Results

Experimental data are shown for $T = 0.03$ K in Fig. 5.3. Inspection of the nuclear Bragg peaks at low time-of-flight showed no obvious sign of any peak splitting. To perform a quantitative test, Rietveld refinements of these data were performed using the program TOPAS Academic (version 5) [281]. Two models were tested against the data: the cubic

parent space group $Fd\bar{3}m$ which would be obtained for a 4-**k** structure and the rhombohedral space group $R\bar{3}m$ which would be obtained for a 1-**k** structure. The software ISODISTORT was used to generate structural models for both the rhombohedral nuclear and magnetic structures [275, 276]. In each case background Bragg peaks arising due to the Cu and V sample environments were fitted by Pawley refinement; peak shapes were modelled by a convolution of fixed instrumental and refined sample-dependent contributions. It was found that the contribution from solid d-IPA could not be robustly modelled in this way but was consistent with the recently-reported solid structure (space group $P2_1/c$) [282]. Instead, the region of the data containing a strong contribution from d-IPA (overlapping with sample and other background peaks) was excluded from the refinement.

The degree of distortion was quantified by defining a distortion parameter

$$D = \frac{c_h}{\sqrt{6}a_h} - 1,$$

where a_h and c_h are lattice parameters of the crystallographic unit cell in the hexagonal setting of the rhombohedral space group $R\bar{3}m$. For the undistorted cubic structure, $D = 0$ as $c_h = \sqrt{6}a_h$ in this case.

Because the distortion is expected to be subtle, if present at all, several sets of refinements were performed. First, the crystal structure was refined to the PM ($T = 1.1$ K) data. A series of refinements were performed where D was systematically varied in the range $-0.0006 \leq D \leq 0.0006$; for each refinement, the cell volume, sample peak-shape and background parameters were refined. Fig. 5.4(a) shows that the minimum R_{wp} is symmetric around $D = 0$ at $T = 1.1$ K; hence a distortion is absent in the PM phase within the resolution of HRPD.

Second, the crystal and magnetic structures were refined to the low-temperature ($T = 0.03$ K) data. Initially, the magnetic and nuclear sample peak-shapes were allowed to refine separately. The magnetic structure was fixed as the 1-**k** structure; this does not bias the results, since the 1-**k** structure has identical powder-averaged magnetic Bragg scattering to the 4-**k** structure for $D = 0$. The small ordered magnetic moment on the interstitial site

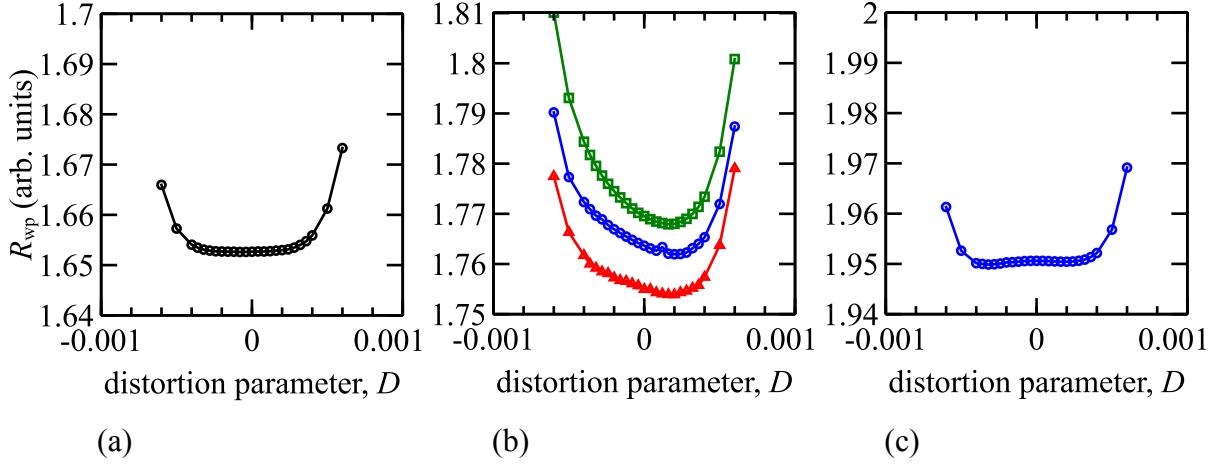


Figure 5.4: (a) Dependence of goodness-of-fit R_{wp} on the distortion parameter D (defined in the text) for Rietveld refinement to HRPD data collected at $T = 1.1$ K (in the PM phase). (b) Dependence of R_{wp} on D for Rietveld refinement to HRPD data collected at $T = 0.03$ K (in the low-temperature ordered phase). Green squares correspond to refinements where the magnetic peak-shape is constrained to be equal to the nuclear peak-shape; blue squares correspond to refinements where the magnetic peak-shape is constrained to equal the nuclear peak-shape convoluted with a Gaussian domain-size broadening function; and red triangles correspond to refinements where the magnetic peak-shape is refined independently of the nuclear peak-shape. (c) Dependence of R_{wp} on the distortion parameter for Rietveld refinement to HRPD data collected at $T = 0.03$ K where the magnetic peaks were not fitted in the refinement.

was not refined because it is essentially determined by a single peak at low Q which lies outside the range of our data. Fig. 5.4(b) shows that R_{wp} now has a minimum for $D > 0$ when D is systematically varied. This result suggests that a rhombohedral distortion exists in the low-temperature phase. There were two reasons to be cautious about this initial result, however. First, when a_{h} and c_{h} were refined independently, the refinement converged to the undistorted structure within error, although with a R_{wp} greater than the lowest value obtained in the systematic variation of D . Second, the refined value for the ordered magnetic moment for Gd^{3+} was unphysically large ($\mu_{\text{ord}} = 7.8(1) \mu_{\text{B}}$). These results suggested that the number of refined parameters for the magnetic phase was too great.

A second set of refinements to the low-temperature data was therefore attempted, in which the sample magnetic peak-shape was constrained to equal the (resolution-limited) nuclear peak-shape, convoluted with a Gaussian domain-size broadening function. This single extra peak-broadening parameter for the magnetic phase can be related to the mag-

netic domain size: we obtain $\xi_{\text{domain}} = 2.4(2) \times 10^3 \text{ \AA}$. Repeating the systematic variation of D showed that the best fit was again obtained for $D > 0$ [Fig. 5.4(b)]. The fit-to-data obtained for the optimal value of D is shown in Fig. 5.3. Moreover, refining a_h and c_h yielded a statistically-significant value of $D = 0.00022(4)$, and the ordered magnetic moment was no longer unphysically large ($\mu_{\text{ord}} = 6.7(1) \mu_B$, within the range obtained in previous studies [62, 263]). The lattice parameters $a_h = 7.19352(9) \text{ \AA}$ and $c_h = 17.6244(6) \text{ \AA}$. These values can be compared to $a_h^0 = 7.19406(1) \text{ \AA}$ and $c_h^0 = 17.62177(3) \text{ \AA}$ which are obtained for refinement of the low-temperature data with the cubic constraint that $c_h = \sqrt{6}a_h$. As a final check, a model was refined to the data where magnetic and nuclear phases were forced to have the same peak-shape, which yielded the same evidence for a distortion [Fig. 5.4(b)].

Finally, I attempted to determine whether the sensitivity to the distortion is due primarily to either the nuclear or the magnetic peaks. To investigate this, refinements to the low-temperature data were performed where the magnetic phase was not included. Since the magnetic peaks were still present in the data, this procedure resulted in a poorer fit, although the refinements still converged robustly. Fig. 5.4(c) shows that, surprisingly, evidence for a distortion is very much weaker when the magnetic peaks are excluded. Hence, there is no evidence for symmetry lowering from cubic over the nuclear coherence length-scale. By contrast, there is evidence for rhombohedral symmetry-lowering over the magnetic coherence length-scale, ξ_{domain} . These results may be explained if the magneto-elastic coupling distorts the lattice within each $1\text{-}\mathbf{k}$ magnetic domain, but these distortions vanish over the nuclear coherence length-scale. Interestingly, a similar effect has been reported for the small monoclinic distortion in the AFM phase of MnO [125, 143].

5.5.3 Discussion

I conclude that there is evidence from neutron powder-diffraction measurements for a rhombohedral distortion in $\text{Gd}_2\text{Ti}_2\text{O}_7$ in the low-temperature phase, but not in the PM phase. This distortion may be driven by magneto-elastic strains within magnetic domains, and persists over a length-scale $\xi_{\text{domain}} = 2.4(2) \times 10^3 \text{ \AA}$. This result suggests that the low-

temperature magnetic structure of $\text{Gd}_2\text{Ti}_2\text{O}_7$ is $1\text{-}\mathbf{k}$, in agreement with the single-crystal diffraction results in applied magnetic field. I stress that this distortion is subtle, and this analysis operates close to both the resolution limit of HRPD and to the noise level in the data. Notwithstanding this, the result is statistically significant: $|c_h - c_h^0|/\sigma_{c_h} = 4$ for the magnetic refinement with Gaussian-broadened magnetic peaks, and the the same result is obtained consistently regardless of the details of the refinement (e.g., choice of magnetic peak shape).

5.6 Magnetic Total-Scattering Analysis

I now develop a model of the short-range magnetic correlations in $\text{Gd}_2\text{Ti}_2\text{O}_7$ which is consistent with the key result of Sections 5.4 and 5.5—that the average magnetic structure is probably not $4\text{-}\mathbf{k}$. This result apparently contradicts a previous analysis of magnetic diffuse scattering [62], which concluded that the $4\text{-}\mathbf{k}$ structure was the best candidate. The single-crystal data shown in Section 5.4 do not address this problem because they do not have sufficient statistics to observe a diffuse-scattering signal. I therefore present a new analysis of published powder diffuse-scattering data from Ref. 62, which avoids a key assumption (discussed below) made in the original analysis. I show that these diffuse-scattering data are actually fully consistent with the $1\text{-}\mathbf{k}$ structure, and investigate the spin correlations in this model.

5.6.1 Theory

In Ref. 62, fits to powder-averaged magnetic diffuse scattering data were attempted for both the $1\text{-}\mathbf{k}$ and $4\text{-}\mathbf{k}$ structures using a model which included only the disordered site in each case. The $4\text{-}\mathbf{k}$ model gave a significantly better fit-to-data, which was explained by the much smaller nearest-neighbour distance between disordered spins in the $4\text{-}\mathbf{k}$ structure [Fig. 5.1]. Hence a key assumption was that the ordered site does not give rise to diffuse scattering. However, this assumption lacks theoretical justification, as the following argument shows. The total-moment sum rule, Eq. (1.50), states that the integral

of the magnetic scattering intensity over all Q and energy is proportional to the total squared moment, $\mu^2 = (g\mu_B)^2 S(S+1)$, which is constant for a given magnetic ion and does not depend on the extent of magnetic order [283]. For a site that shows conventional long-range order, with excitations described by linear spin-wave theory, one component of spin is aligned along a local axis with maximum projection $\pm S$ at low temperature. This projection gives rise to Bragg scattering with intensity proportional to $\mu_{\text{ord}}^2 = (g\mu_B)^2 S^2$. The transverse spin components remain fluctuating and contribute the rest of the total integrated intensity, proportional to $\mu^2 - \mu_{\text{ord}}^2 = (g\mu_B)^2 S$ [35, 284]. In a diffraction experiment, an integral over magnetic excitations is performed. Consequently, magnetic diffuse scattering is present even in conventionally-ordered magnets at low temperature [63, 64], as I discuss in Section 1.4. In $\text{Gd}_2\text{Ti}_2\text{O}_7$, it is possible to make a rough estimate of the proportion of the diffuse scattering that arises from the “ordered” and “disordered” sites at low temperature by taking $\mu = 7.94 \mu_B$ for both sites and assuming that the ordered site has the maximum ordered moment $\mu_{\text{ord}} = 7.0 \mu_B$ whereas the disordered site has $\mu_{\text{ord}} = 0$. Then, 25% of the total integrated scattering intensity will be diffuse scattering from the disordered site and $3/[4(S+1)] = 17\%$ of the total integrated intensity will be diffuse scattering from the ordered site. The net contribution to the diffuse scattering from ordered and disordered sites is therefore expected to be similar. This conclusion holds if the incident neutron energy (~ 100 K for thermal neutrons) is much greater than the largest magnetic excitation energy of the system. This is certainly the case for $\text{Gd}_2\text{Ti}_2\text{O}_7$, in which both the exchange interaction and the single-ion anisotropy are on the order of a few K [285].

5.6.2 Methods

I now develop a new method to model the diffuse scattering in $\text{Gd}_2\text{Ti}_2\text{O}_7$ which takes the above considerations into account. I require that my model satisfies three conditions. (i) A single model is consistent with the total (Bragg+diffuse) magnetic scattering data. (ii) Each Gd^{3+} ion has a fixed total magnetic moment. (iii) The average magnetic structure is the $1\text{-}\mathbf{k}$ structure. I use RMC refinement to determine whether spin configurations

exist which are consistent with these constraints. Spin configurations containing $N = 16\,000$ classical spins were initialised so that kagome spins were fully ordered in the $1\text{-}\mathbf{k}$ structure and interstitial spins were assigned random orientations. The cost function contains two terms: the sum of squared residuals which quantifies the level of agreement with experimental data, and a term that constrains the average structure to be $1\text{-}\mathbf{k}$:

$$\chi^2 = \chi_{\text{data}}^2 + \chi_{1\text{-}\mathbf{k}}^2, \quad (5.1)$$

in which

$$\chi_{\text{data}}^2 = W_{\text{data}} \sum_Q [I_{\text{expt}}(Q) - sI_{\text{calc}}(Q)]^2, \quad (5.2)$$

$$\chi_{1\text{-}\mathbf{k}}^2 = W_{1\text{-}\mathbf{k}} \sum_i |\langle \mathbf{S}_i \rangle - t_i \mathbf{e}_i^{1\text{-}\mathbf{k}}|^2. \quad (5.3)$$

Here, $I(Q)$ is the powder-averaged magnetic total-scattering intensity (subscript “calc” and “expt” denote calculated and experimental patterns respectively), $\langle \mathbf{S}_i \rangle$ is the average spin vector at atomic position i , and $\mathbf{e}_i^{1\text{-}\mathbf{k}}$ is a unit vector giving the spin orientation in the $1\text{-}\mathbf{k}$ structure. The scale factors s and t_i are determined by least-squares fitting at each stage of the refinement: s scales the calculated diffraction pattern to the experimental data and $t_i = \mu_{\text{ord},i}/\mu$ scales the ordered moment of site i in the $1\text{-}\mathbf{k}$ structure to the RMC model. The values of the weighting factors W_{data} and $W_{1\text{-}\mathbf{k}}$ are chosen to obtain a good fit-to-data while maintaining very close agreement between the RMC model and the $1\text{-}\mathbf{k}$ structure. The scattering intensity is also constrained to equal zero as $Q \rightarrow 0$, as is appropriate for an AFM state.

The total magnetic scattering intensity was calculated as the sum of Bragg and diffuse contributions using the approach outlined in Section 1.3.3.3 [83]. This approach has some practical advantages over alternative approaches to calculating the total scattering [64, 146]. In particular, finite-size effects can be minimised by calculating the Bragg scattering for an infinite periodic structure, and the diffuse scattering can be calculated quickly from radial spin correlation functions instead of by numerical powder averaging. The powder diffuse-scattering intensity is calculated using Eqs. (1.58)–(1.60), where $\mathbf{S}_i$ is

replaced with $\Delta\mathbf{S}_i$ everywhere. The powder Bragg scattering intensity is calculated from the average magnetic structure by powder-averaging Eq. (1.51), which yields

$$I_{\text{Bragg}}(Q) = C [gf(Q)]^2 \frac{2\pi^2}{nV} \sum_{\mathbf{G}} \frac{|\mathbf{F}(\mathbf{G})|^2}{G^2} \mathcal{R}(Q - G), \quad (5.4)$$

in which $V = 8a_{\text{cubic}}^3$ is the volume of the magnetic unit cell and other symbols have the same meaning as in Eq. (1.51). The instrumental resolution function for D20 has an approximately Gaussian form over the limited Q -range considered here:

$$\mathcal{R}(Q - G) = \sqrt{\frac{D}{\pi}} \frac{1}{H(G)} \exp \left[-D \left(\frac{Q - G}{H(G)} \right)^2 \right], \quad (5.5)$$

where the constant $D = 4 \ln 2$. $H(G)$ is the full width at half-maximum (in units of $\text{\AA}^{-1}$) of a peak centred at $\mathbf{G}$, and is given by Caglioti's formula [89],

$$H(G) = \frac{2\pi \cos \theta}{\lambda} \sqrt{U \tan^2 \theta + V \tan \theta + W}, \quad (5.6)$$

where θ is given by Eq. (1.31), and U, V, W are parameters (with units of rad^2) determined by an initial Rietveld refinement of the magnetic phase using the FULLPROF program [36]. The factor $G^2 \cos \theta$ ($\propto \sin^2 \theta \cos \theta$) which appears in the denominator of Eq. (5.4) is the Lorentz factor for constant-wavelength neutrons. In my implementation, I neglect the effect of instrumental resolution on the diffuse scattering. This is valid provided the diffuse features are broader than the FWHM of the resolution function. The finite box size also unavoidably limits the resolution of the calculated diffuse scattering (with an effective $H \sim 4\pi/R$, where R is side length of the RMC supercell), and this effect is usually larger than the effect of the instrumental resolution.

A particular issue in the refinements concerns the direction of the small ordered moment on the interstitial site. The ordered moments are parallel within the crystallographic unit cell shown in Fig. 5.1(a). By symmetry, their orientation may either be parallel to $\mathbf{k}$ or in the plane perpendicular to $\mathbf{k}$, and both possibilities give very similar powder Bragg scattering. I therefore attempted three separate sets of refinements where the ordered

interstitial moment was constrained to lie along either $[1\bar{1}0]$, $[11\bar{2}]$, or $[111]$. The results I show are for the interstitial ordered moment along $[1\bar{1}0]$; however, I found that all three possibilities yielded equivalent results in Figs. 5.6 and 5.7.

5.6.3 Data Processing

I use published powder diffraction data from Ref. 62 for my total-scattering analysis. In Ref. 62, data were collected on two instruments: the polarised-neutron diffractometer D7 [90] and the medium-resolution diffractometer D20 [286] (both at the ILL). Data were collected at $T \ll T_2$ and at $T = 1.4 \text{ K}$ ($> T_N$) using each instrument. The $T = 1.4 \text{ K}$ data from D7 and D20 are compared in Fig. 5.5. I chose to refine against the unpolarised D20 data because they have much better reciprocal-space resolution and counting statistics than the D7 data. To remove the nuclear scattering from the D20 data, a Rietveld refinement to the nuclear Bragg peaks at $T = 1.4 \text{ K}$ was first performed, and the refined nuclear Bragg intensities were then subtracted from the $T \ll T_2$ data. To estimate the extent of additional non-magnetic background, I fitted an overall scale factor and flat background to match the D20 data to the D7 data at $T = 1.4 \text{ K}$. This procedure was found to yield good agreement in the range $0.5 \leq Q \leq 2.5 \text{ \AA}^{-1}$ [Fig. 5.5]. Having performed these corrections, the D20 data for $T \ll T_2$ were used as input for the RMC refinement.

5.6.4 Results and Discussion

The total-scattering fit obtained using RMC is shown in Fig. 5.6(a). Very good agreement is obtained between the fit and the experimental data. Of particular relevance is the excellent fit obtained to the diffuse scattering component [Fig. 5.6(b)], which proves that the observed diffuse scattering is consistent with a 1-**k** model. The diffuse scattering shows two distinct features. First, beneath the Bragg peaks there is a broad diffuse feature centred at $Q \approx 1.1 \text{ \AA}^{-1}$. The broadness of this peak indicates that it is due to short-range spin correlations within a crystallographic unit cell, and its position suggests that these correlations are AFM at the nearest-neighbour distance ($3.6 \text{ \AA}$) [62]. Second, sharper diffuse peaks are observed at the base of the magnetic Bragg peaks. These

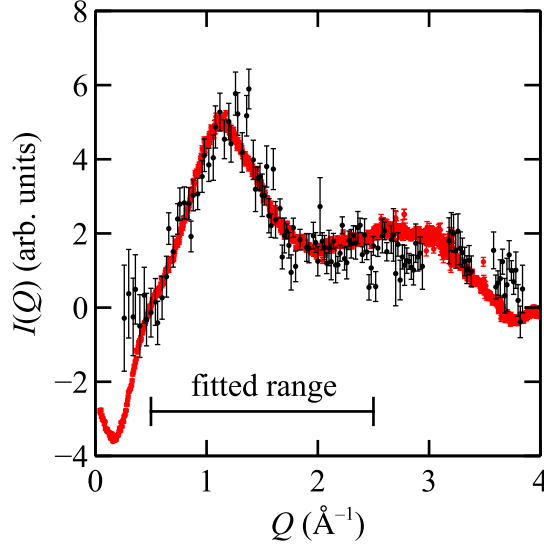


Figure 5.5: Scaling of the D20 diffuse-scattering data (red circles) to the D7 diffuse-scattering data (black circles) at $T = 1.4$ K. A scale factor and flat background was fitted to match the two datasets. The D20 data for RMC refinements described in the text used the reciprocal-space range $0.5 \leq Q \leq 2.5 \text{ \AA}^{-1}$ (marked in the figure), where good agreement is obtained between D20 and D7 data.

relatively sharp diffuse features were not resolved in Ref. 62 due to the lower resolution of the D7 data. They indicate that medium-range correlations are also present, and are qualitatively similar both to thermal diffuse scattering in atomic systems and to energy-integrated spin-wave scattering in magnetic systems [64].

I analysed the refined RMC spin configurations to understand the real-space origin of these diffuse features. I obtain an ordered moment $\mu_{\text{ord}} = 6.4 \mu_{\text{B}}$ for the kagome site and $\mu_{\text{ord}} = 1.9 \mu_{\text{B}}$ for the interstitial site. These values are in fair agreement with Rietveld refinements ($6.7\text{--}7.0 \mu_{\text{B}}$ and $\approx 1.9 \mu_{\text{B}}$ for kagome and interstitial sites, respectively [62, 263]); small discrepancies may arise because μ_{ord} is determined from the ratio of Bragg to diffuse scattering in RMC refinement, but by comparison of magnetic and nuclear Bragg intensities in Rietveld refinement. Importantly, the ordered moments on both sites are significantly smaller than the total moment, which shows that the magnetic disorder is present on both sites. To elucidate the nature of the spin correlations, I calculated partial spin correlation functions,

$$\langle \mathbf{S}(0) \cdot \mathbf{S}(r) \rangle_{\rho\sigma} = \frac{1}{N_{\rho} Z_{\rho\sigma}(r)} \sum_{\rho}^{N_{\rho}} \sum_{\sigma}^{Z_{\rho\sigma}(r)} \mathbf{S}_i^{\rho} \cdot \mathbf{S}_j^{\sigma}, \quad (5.7)$$

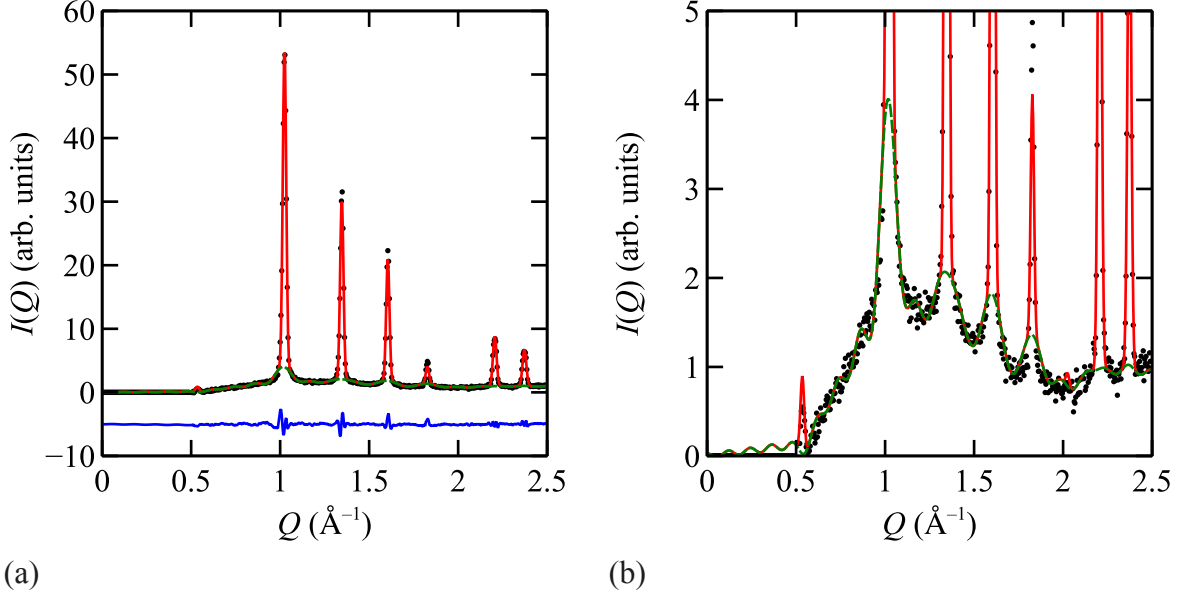


Figure 5.6: (a) RMC fit to experimental magnetic total-scattering data (from Ref. 62) at $T = 0.25$ K. Experimental data are shown as black circles, RMC fit as a red line, and data–fit as a blue line. (b) Fit with expanded vertical scale to highlight the magnetic diffuse scattering, shown as a green dashed line.

where ρ, σ denote either interstitial or kagome spins, N_ρ is the number of spins of type ρ , and $Z_{\rho\sigma}(r)$ is the number of spins of type σ which coordinate a spin of type ρ at distance r . Following Eq. (1.53), I split the calculated $\langle \mathbf{S}(0) \cdot \mathbf{S}(r) \rangle_{\rho\sigma}$ into two parts: the average-structure correlation function $\langle \mathbf{S}(0) \rangle \cdot \langle \mathbf{S}(r) \rangle_{\rho\sigma}$, which does not decay with distance and gives rise to Bragg scattering, and the spin fluctuation correlation function $\langle \Delta \mathbf{S}(0) \cdot \Delta \mathbf{S}(r) \rangle_{\rho\sigma}$, which decays with distance and gives rise to diffuse scattering. These quantities are shown in Fig. 5.7. The kagome-kagome correlations [Fig. 5.7(a)] are dominated by the average structure, as anticipated from the relatively large value of μ_{ord} for this site. The spin fluctuations enhance the average structure and persist over several crystallographic unit cells, which is consistent with a superposition of low-energy spin waves. By contrast, the interstitial-interstitial correlations [Fig. 5.7(b)] are much weaker. There is vanishing correlation within the first crystallographic unit cell because each ordered moment has an equal number of parallel and antiparallel neighbours. Spin fluctuations are mostly uncorrelated, although they slightly enhance the average structure beyond a single crystallographic unit cell.

The intra-site correlations discussed above account for the relatively sharp diffuse

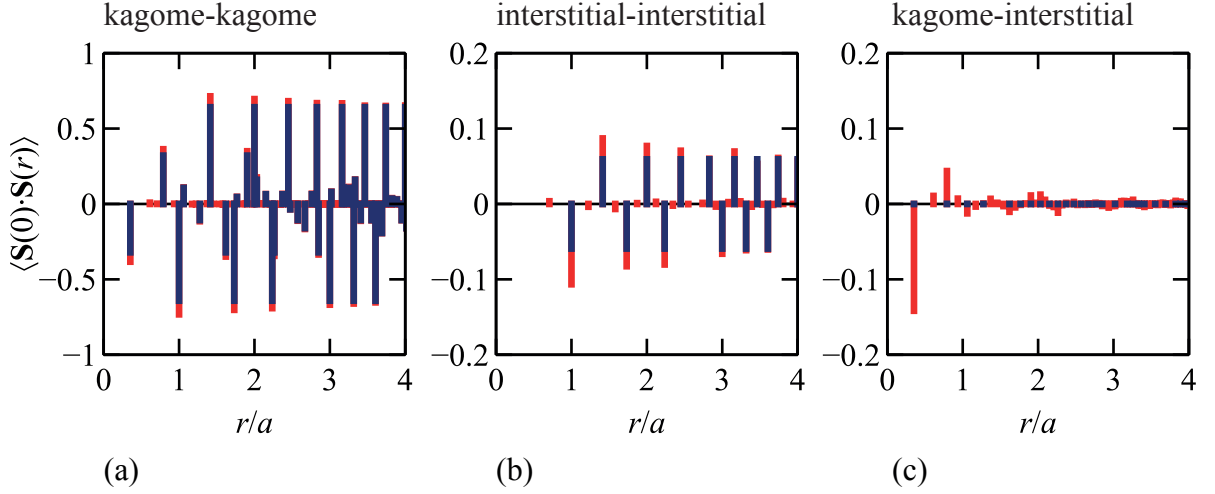


Figure 5.7: Partial spin correlation functions defined in the text for the kagome and interstitial sites shown in Fig. 5.1(a): (a) kagome-kagome correlations, (b) interstitial-interstitial correlations, and (c) kagome-interstitial correlations. In each panel, average-structure correlations are shown as blue bars and spin-fluctuation correlations are shown as red bars. Note the different vertical scale in (a) compared to (b) and (c).

scattering at the base of the magnetic Bragg peaks [Fig. 5.6(b)], but do not account for the broad diffuse peak at $Q \approx 1.1 \text{ \AA}^{-1}$. Fig. 5.7(c) shows the inter-site (kagome-interstitial) correlation function. The three-fold site symmetry constrains the average-structure inter-site correlations to equal zero. However, the spin-fluctuation correlation function shows a significant AFM peak at the nearest-neighbour distance and is negligible beyond a single unit cell. I therefore suggest that the broad diffuse peak arises from correlations of the spin fluctuations *between* the kagome and interstitial sites of the $1\text{-}\mathbf{k}$ structure, rather than spin correlations within the disordered site of the $4\text{-}\mathbf{k}$ structure as was previously proposed [62]. This result is perhaps surprising, because the two sites order at different temperatures and with different ordered moments, and it might be expected that spin waves on the kagome site cannot strongly interact with the much more localised spin fluctuations on the interstitial site. A possible explanation may be that, since the average-structure inter-site correlations are zero by symmetry, interactions of the form $\mathbf{S}_i \cdot \mathbf{S}_j$ can only occur via the fluctuations. The energy-integrated data I consider here do not directly determine the timescale of these fluctuations, but instead reveal spin correlations at an instant of time. However, neutron spin echo [287] and muon-spin rotation measurements [31, 288] have shown that low-energy spin dynamics persist at $T \ll T_2$, suggesting that the observed

correlations are dynamic.

Finally, I also performed refinements constraining the average structure to be $4\mathbf{k}$ instead of $1\mathbf{k}$. These refinements produced a fit to the diffuse scattering which was indistinguishable from the $1\mathbf{k}$ model (not shown). I therefore draw three main conclusions from the total-scattering analysis. First, the diffuse scattering data alone cannot distinguish between $1\mathbf{k}$ and $4\mathbf{k}$ models; however, they provide no reason to doubt the $1\mathbf{k}$ structure which is suggested by the results of Sections 5.4 and 5.5. Second, if the magnetic structure is $4\mathbf{k}$, correlations between the kagome and interstitial site are mostly responsible for the broad peak at $Q \approx 1.1 \text{ \AA}^{-1}$. Third, regardless of the details of the magnetic structure, both magnetic sites must make a significant contribution to the magnetic diffuse scattering.

5.7 Conclusions

I have used a combination of powder and single-crystal neutron diffraction to investigate the partially-ordered state of $\text{Gd}_2\text{Ti}_2\text{O}_7$ at low temperature ($T \ll T_2$). The intensities of single-crystal magnetic Bragg peaks change in a small applied magnetic field, which is consistent with the formation of a domain imbalance. This result suggests that the magnetic structure of $\text{Gd}_2\text{Ti}_2\text{O}_7$ is unlikely to be $4\mathbf{k}$ (in contradiction with previous results [62]). This result is supported by Rietveld refinement to high-resolution neutron powder-diffraction data, which obtains statistically-significant evidence that a rhombohedral distortion exists over a length-scale comparable to the magnetic domain size in the low-temperature phase (but not in the PM phase). The main evidence for the $4\mathbf{k}$ structure has previously come from analysis of the magnetic diffuse scattering. However, I find that a good fit to the magnetic diffuse scattering data can also be obtained assuming a $1\mathbf{k}$ model. In this model, medium-range spin correlations between spins on the kagome site lead to relatively-sharp diffuse features beneath magnetic Bragg peaks, while short-range AFM correlations between spins on different sites contribute to a broad diffuse peak at $Q \approx 1.1 \text{ \AA}^{-1}$. My results show that the magnetic disorder in $\text{Gd}_2\text{Ti}_2\text{O}_7$ is not limited to one site, as was previously proposed [62], and highlight the importance of self-consistently

modelling all contributions to the diffraction pattern in partially-ordered systems.

The results of this chapter suggest several avenues for future research. From the theoretical perspective, prediction of the magnetic ground state requires detailed knowledge of the magnetic interactions. Single-crystal inelastic neutron scattering measurements would allow the magnetic interactions to be determined, and would clearly distinguish between $1\text{-}\mathbf{k}$ and $4\text{-}\mathbf{k}$ structures. Such measurements were attempted on the CNCS spectrometer at the SNS, but no inelastic scattering was observed, probably because of the relatively large absorption cross-section of our sample (≈ 300 barn Gd^{-1} at $\lambda = 4.8$ Å for 99.4% isotopic substitution). From a methodological perspective, my results suggest that previous claims that diffuse-scattering data can distinguish between $1\text{-}\mathbf{k}$ and $4\text{-}\mathbf{k}$ structures [62] are not borne out in the case of $\text{Gd}_2\text{Ti}_2\text{O}_7$. I have not considered the $2\text{-}\mathbf{k}$ and $3\text{-}\mathbf{k}$ structures in my analysis because they have been shown to be incompatible with the size of the ordered magnetic moment [62]. However, further experiments to test this assumption would be valuable, especially given recent modelling results which suggest a $2\text{-}\mathbf{k}$ structure may exist at low temperature [251]. Perhaps most importantly, while I have considered only the low-temperature ($T \ll T_2$) phase, the possibility of a different structure for $T_2 < T < T_1$ cannot be ruled out, and this possibility requires further investigation [251].

Chapter 6

Single-Crystal Diffuse Scattering: Proof of Principle

6.1 Chapter Summary

In the previous chapters, I have obtained new information about emergent phenomena in frustrated systems using RMC refinement to powder diffuse-scattering data. There are, however, several reasons why RMC refinement to single-crystal data would be valuable, too. First, the information content of single-crystal data is in principle greater than for powder data, provided other factors (e.g., statistical quality, background level, and coverage of Q -space) are kept equal. Hence the success of the RMC refinement for powder data indicates that even better results should be obtained for single-crystal data. Second, recent developments in neutron-scattering instrumentation—for example, the instruments SXD and MERLIN at the ISIS neutron source [289, 290]—now allow large volumes of reciprocal-space to be collected rapidly. No general approach currently exists to analyse such large datasets; instead, current methods typically focus on small regions which are deemed to contain the most interesting features (see, e.g., [291, 292]).

In this chapter, I introduce the method of RMC refinement to 3D magnetic diffuse-scattering data. While the basic RMC algorithm is unchanged compared to powder refinements, the key difference is that single-crystal refinement is a problem on a much

larger scale: compared to a powder dataset, the size of a 3D single-crystal dataset is typically greater by three to four orders of magnitude. For this reason, previous RMC refinements of structural diffuse scattering [147, 154, 156, 293–295] were restricted to fitting a small number of reciprocal-space planes. Here, I first develop a new algorithm which allows magnetic diffuse scattering to be calculated more rapidly than previous approaches. I go on to demonstrate the effectiveness of the approach by fitting to a large volume of simulated diffuse-scattering data for the Heisenberg pyrochlore AFM introduced in Chapter 2.

6.2 Computational Aspects

In this section, I compare possible approaches to calculate $S(\mathbf{Q})$ from a spin configuration. This is the slowest step in an RMC algorithm and must be performed at each iteration. An important consideration here is that each iteration of the RMC algorithm changes only a single spin. The fastest overall method is therefore the one which allows $S(\mathbf{Q})$ to be *updated* the fastest. In this section, I compare different approaches according to two criteria: the speed at which $S(\mathbf{Q})$ is updated, and the accuracy of the calculation.

6.2.1 $S(\mathbf{Q})$ from Real-Space Correlation Functions

Probably the most straightforward method to calculate $S(\mathbf{Q})$ is first to calculate the spin correlation function in real space and then calculate its Fourier transform:

$$S(\mathbf{Q}) = \frac{1}{N} \sum_{\alpha, \beta} \left(\delta^{\alpha\beta} - \frac{Q^\alpha Q^\beta}{Q^2} \right) \sum_{\mathbf{r}} \langle S^\alpha(\mathbf{0}) S^\beta(\mathbf{r}) \rangle \exp(i\mathbf{Q} \cdot \mathbf{r}). \quad (6.1)$$

Here, $\alpha, \beta \in \{x, y, z\}$ represent Cartesian components, and the projection of spin perpendicular to $\mathbf{Q}$ is achieved by applying Eq. (1.57). Assuming periodic boundary conditions, the sum is carried out to a maximum distance $r_{\max} = R/2$ along each Cartesian direction. This method is entirely analogous to the calculation of the powder $S(Q)$, Eq. (1.58).

The main advantage of this approach is that $S(\mathbf{Q})$ is a smoothly-varying function of $\mathbf{Q}$. Its main disadvantage is that it is very slow. To show this, I consider a configuration con-

taining N spins and ask how many operations are needed to update $N_{\mathbf{Q}}$ diffuse-scattering points after a single spin is rotated. The limiting step here is the Fourier transform, which requires $\mathcal{O}(NN_{\mathbf{Q}})$ multiplications (where $\mathcal{O}$ is shorthand for “on the order of”). This indicates that, whereas a powder refinement may take minutes or hours ($N_Q \sim 10^2$), an analogous single-crystal refinement ($N_{\mathbf{Q}} \sim 10^6$) is expected to take months or years—which is clearly impractical.

A possible solution to this problem would be to use the “fast Fourier transform” (FFT) algorithm to calculate the Fourier transform. For many applications, the FFT allows Fourier transforms to be computed much more rapidly than the direct calculation considered above, in $\mathcal{O}[(N + N_{\mathbf{Q}}) \log(N + N_{\mathbf{Q}})]$ operations [296]. Indeed, this possibility was considered in early work on diffuse-scattering calculations [297]. Unfortunately, however, FFT algorithms require that both the spin-correlation function and $S(\mathbf{Q})$ be sampled on uniform grids, which may be too restrictive when fitting to experimental data [297]. Moreover, as I discuss below, there is an alternative method which allows $S(\mathbf{Q})$ to be updated in fewer operations than the FFT.

6.2.2 $S(\mathbf{Q})$ from Reciprocal-Space Structure Factor

An alternative approach starts from the expression for magnetic Bragg scattering [63, 64]. The key point here is that it is possible to choose the magnetic unit cell to be the entire spin configuration (supercell), because the use of periodic boundary conditions means the supercell is itself periodic. Then, the Bragg peaks of the supercell occur at reciprocal-lattice vectors $\mathbf{G} = \frac{2\pi}{R} [h, k, l]^*$, where h, k, l are integers and R is the side length of supercell with volume $V = R^3$ (I assume a cubic system for simplicity). The Bragg scattering of the supercell is given by [35, 64, 66]

$$S_{\text{Bragg}}(\mathbf{Q}) = \frac{(2\pi)^3}{NV} \sum_{\mathbf{G}} |\mathbf{F}(\mathbf{G})|^2 \delta(\mathbf{Q} - \mathbf{G}), \quad (6.2)$$

where the magnetic structure factor

$$\mathbf{F}(\mathbf{G}) = \sum_{i=1}^N \mathbf{S}_i^\perp \exp(i\mathbf{G} \cdot \mathbf{r}_i). \quad (6.3)$$

If a larger supercell is used, the Bragg peaks become more closely spaced, and in the limit of an infinite supercell the Bragg peaks are continuous. In this way, the Bragg peaks of the supercell are used to approximate the diffuse scattering [63, 64].

In this approach, the structure factor is stored in memory, and after each proposed spin rotation a factor $(\mathbf{S}_i^{\text{new}} - \mathbf{S}_i^{\text{old}}) \exp(i\mathbf{G} \cdot \mathbf{r}_i)$ is simply added to Eq. (6.3). Hence the update is performed in $\mathcal{O}(N_{\mathbf{G}})$ multiplications; for typical spin configuration sizes ($N \sim 10^4$), this represents an improvement of several orders of magnitude on the approach of Section 6.2.1.

There are two disadvantages with a simple application of Eq. (6.2), however. First, $S_{\text{Bragg}}(\mathbf{Q})$ is not a smoothly-varying function, but a series of delta-function peaks at the reciprocal-lattice vectors of the supercell. Large supercells are therefore required to obtain sufficiently closely-spaced peaks, which increases computational expense. The second disadvantage follows from this: if the dimensions of the supercell greatly exceed the correlation length of the system, the calculated $S_{\text{Bragg}}(\mathbf{Q})$ appears very noisy [297, 298]. This result may appear counterintuitive, but can be justified as follows. Consider a system of linear dimension R containing N spins, with an isotropic spin correlation length $\xi \ll R$. The number of “correlated” spin pairs is $\sim \frac{4}{3}\pi\xi^3 N$. When periodic boundary conditions are applied, correlations are calculated up to a maximum distance $R/2$, so the ratio of “correlated” to “uncorrelated” spin pairs is $\sim (2\xi/R)^3$. Hence, the signal-to-noise ratio decreases with increasing system size $\propto 1/N$. This presents a significant problem for spin liquids, where spin correlations are often negligible beyond a few unit cells, so $S(\mathbf{Q})$ may be dominated by noise due to random spin fluctuations at large distances.

6.2.3 $S(\mathbf{Q})$ by Method of Sub-Boxes

The difficulties of the two approaches discussed above led to a modified method being proposed in Ref. 297. In this approach, the periodic spin configuration is divided into

a set of smaller overlapping regions, called “sub-boxes” or “lots”, each of which has open boundary conditions. The size of the sub-box must be chosen to be greater than ξ but smaller than $R/2$ along each Cartesian direction (in order to avoid spurious contributions from the periodicity of the spin configuration itself). The square modulus of the structure factor for each sub-box is calculated separately and the results averaged to obtain $S(\mathbf{Q})$.

The method of sub-boxes has been used successfully in a number of diffuse-scattering studies (see, e.g., [275, 299–302]). This approach has two advantages. First, the use of open boundary conditions for each sub-box means that the calculation is not restricted to the Bragg positions of the supercell. Second, the size of the sub-box can be tuned to match ξ in order to reduce noise in the calculated $S(\mathbf{Q})$. These factors mean that the method produces qualitatively-correct and subjectively-pleasing calculations of $S(\mathbf{Q})$ [297, 298].

Despite these advantages, there are two reasons why the method of sub-boxes may not represent the optimal approach for RMC refinement. First, a sub-box would ideally be placed at each site, so that every spin is sampled the same number of times. In practice, however, this would be too slow, since the calculation time scales linearly with the number of sub-boxes. Instead, the number of sub-boxes is typically chosen such that every spin is contained within at least one sub-box on average, and the positions of the sub-boxes are distributed randomly throughout the configuration [297, 298]. Hence, choosing different random sets of sub-boxes within the same spin configuration yields quantitatively-different results.

The second disadvantage of this method is that it leads to significant blurring of $S(\mathbf{Q})$, because the use of open boundary conditions means that fewer spin-pairs are separated by larger distances (there are N self-correlations at zero distance, but no correlations which are separated by the sub-box size along a Cartesian direction). Formally, the correlation function for an open system of side $r_{\max}$ is equal to the correlation function for the infinite system multiplied by a triangular “response function” which is unity at $r = 1$ and zero at $r = \pm r_{\max}$. If the size of the sub-box is 5 unit cells in each direction, this effect reduces the correlations by 20% within the first unit cell. This may result in inaccurate estimates

for, e.g., spin correlation lengths in RMC refinement.

None of these disadvantages affects the qualitative features of the calculated $S(\mathbf{Q})$, and so should not affect the trends identified in previous studies. However, a more accurate approach may be desirable for quantitative refinement. I attempt to develop such an approach below.

6.2.4 A New Approach: $S(\mathbf{Q})$ by Resampling

Of the methods discussed above, the method of Section 6.2.2 is fastest, but has the key disadvantage that $S_{\text{Bragg}}(\mathbf{Q})$ is not a smoothly-varying function of $\mathbf{Q}$. In this section, I show that this problem can be solved using well-understood signal-processing techniques, allowing this fast method to be used in practice.

The Nyquist-Shannon sampling theorem states that, provided $S(Q)$ contains no Fourier components with periodicities $\geq R/2$, then $S(Q)$ can be determined for all Q by giving its values at intervals of $\Delta Q \leq 2\pi/R$ [303]. The importance of this result is that $S(\mathbf{Q})$ can in principle be calculated at arbitrary $\mathbf{Q}$ given only its values at the reciprocal-lattice points; hence, $S(\mathbf{Q})$ is fully determined by $S_{\text{Bragg}}(\mathbf{G})$. The relationship between $S(\mathbf{Q})$ and $S_{\text{Bragg}}(\mathbf{G})$ is as follows. In the calculation of $S(\mathbf{Q})$ for a periodic system, spin correlations are cut off at a maximum distance r_{max} along each Cartesian direction, which is equivalent to multiplying the correlation function for an infinite periodic system with a rectangular response function. Hence, by the convolution theorem, $S(\mathbf{Q})$ is equal to $S_{\text{Bragg}}(\mathbf{G})$ convoluted with the Fourier transform of the response function, which is called the “weight function” [304]. In 3D, this yields

$$S(\mathbf{Q}) = \frac{(2\pi)^3}{NV} \sum_{\mathbf{G}=-\infty}^{\infty} |\mathbf{F}(\mathbf{G})|^2 \mathcal{W}(\mathbf{Q} - \mathbf{G}), \quad (6.4)$$

where the weight function

$$\mathcal{W}(\mathbf{Q}) = \left(\frac{r_{\text{max}}}{\pi}\right)^3 \prod_{\alpha=1}^3 \frac{\sin(Q^{\alpha} r_{\text{max}})}{Q^{\alpha} r_{\text{max}}}, \quad (6.5)$$

is a product of sinc functions along each Cartesian direction. This formula was originally

given by Whittaker and Shannon [303, 305]. Alternatively, the spin correlations may be calculated up to a maximum radial distance $r_{\max}$, so that the cutoff is spherical rather than cubic in real space; then, the weight function is given by [306]

$$\mathcal{W}(Q) = \frac{r_{\max}^3}{2\pi^2} \left[\frac{\sin(Qr_{\max})}{(Qr_{\max})^3} - \frac{\cos(Qr_{\max})}{(Qr_{\max})^2} \right]. \quad (6.6)$$

The advantage of this approach is that Eq. (6.4) is a smoothly-varying function of $\mathbf{Q}$, which is mathematically equivalent to Eq. (6.1). In practice, however, it is not possible to calculate Eq. (6.4) exactly, because the sum over reciprocal lattice vectors extends to $\pm\infty$. An obvious solution would be simply to truncate the sum, but this procedure leads to spurious oscillations (“Gibbs phenomenon” or “Fourier ripples”) in the real-space spin correlation function [127]. A better solution is to multiply $\mathcal{W}(\mathbf{Q})$ with a so-called “window” function that decays smoothly to zero [307]. Two common choices are the central lobe of a sinc function (known as a Lanczos window) or the central lobe of a cosine function:

$$W_{\text{Lanczos}}(\mathbf{Q}) = W(\mathbf{Q}) \prod_{\alpha=1}^3 \frac{\sin(Q^\alpha R/2m)}{Q^\alpha R/2m}, \quad (6.7)$$

$$W_{\text{Cosine}}(\mathbf{Q}) = W(\mathbf{Q}) \prod_{\alpha=1}^3 \cos(Q^\alpha R/2m), \quad (6.8)$$

where m is an integer which determines the width of the central lobe [304]. The sum in Eq. (6.4) now extends from $[Q_\alpha R/2\pi] - m + 1$ to $[Q_\alpha R/2\pi] + m$ along each Cartesian direction, where square brackets denote the floor function. This approach, known as windowed-sinc filtering, has not previously been applied to diffuse-scattering calculations, but is very widely used in image filtering and digital-signal processing, which present similar challenges [306].

Because the sum in Eq. (6.4) is now taken over a finite range, the response function is no longer a rectangular function. In Fig. 6.1, the response function (calculated by numerically Fourier transforming the weight function) is shown for different choices of m for the Lanczos and cosine windows. Fig. 6.1 shows that, by choosing the value of m appropriately, it is possible to ensure that the response function is essentially flat over

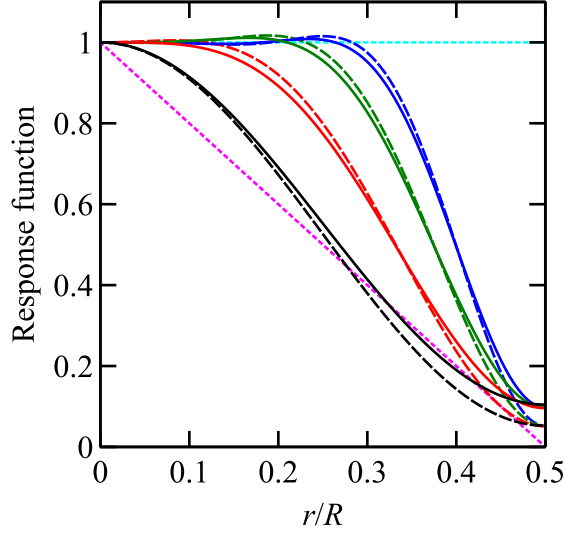


Figure 6.1: Real-space response function for different reciprocal-space window functions described in the text. Solid lines show response functions for the Lanczos window and dashed lines show response functions for the cosine window. Different values of the window length m are shown in different colours: $m = 2$ (black), $m = 3$ (red), $m = 4$ (green), and $m = 5$ (blue). The cyan dotted line shows the response function for direct calculation of the correlation function for a periodic system [Section 6.2.1], and the magenta dotted line shows the response function for the method of sub-boxes [Section 6.2.3].

the length-scale for which spin correlations are significant, allowing $S(\mathbf{Q})$ to be calculated accurately. By contrast, the triangular response function inherent to the method of sub-boxes is never flat, so always leads to some loss of accuracy in $S(\mathbf{Q})$.

The time taken using this resampling approach is the sum of two contributions. The first contribution is the time to update the $N_{\mathbf{G}}$ supercell Bragg intensities after a single spin is rotated, which takes $\mathcal{O}(N_{\mathbf{G}})$ operations. The second contribution is the time to resample the intensity at the $N_{\mathbf{Q}}$ experimental data points. This is a convolution, which in general takes $\mathcal{O}(m^3 N_{\mathbf{Q}})$ operations. Hence, for large m and/or $N_{\mathbf{Q}} > N_{\mathbf{G}}$, the second contribution may dominate. However, the resample time can be greatly reduced if the data points are arranged on an orthogonal grid with axes parallel to the supercell axes. In this case, Eq. (6.5) can be calculated along each Cartesian direction in sequence, reducing the resample time to $\mathcal{O}(m N_{\mathbf{Q}})$ [308]. This optimisation should usually be practical for 3D single-crystal datasets. Moreover, the resampling could be parallelised straightforwardly, with potential to accelerate the calculation further [309].

The calculation of single-crystal diffuse scattering patterns involves some compromises

in practice. In particular, it is not always ideal to choose m as large as possible in order to yield a flat response over the largest possible distance, because inclusion of longer-range correlations increases the level of noise and other artifacts in $S(\mathbf{Q})$ [Section 6.2.2]. It is also necessary to trade off increasing m against the consequential increase in computer time. For all the $S(\mathbf{Q})$ calculations shown in this thesis, I used either a cosine window with $m = 3$ (which has a flat response to within $\pm 1\%$ for $0 \leq r/R \leq 0.14$) or a Lanczos window with $m = 4$ (which has a flat response to within $\pm 1\%$ for $0 \leq r/R \leq 0.22$). Finally, to check my implementation, I compared the calculation of $S(\mathbf{Q})$ using Eq. (6.4) with a calculation using the exact formula, Eq. (6.1), in which the spin correlation function was multiplied by the response function. Exact agreement between these two calculations was obtained, confirming that the implementation of Eq. (6.4) was correct.

6.3 Heisenberg Pyrochlore Antiferromagnet, Revisited

In this section I show that RMC refinement to large 3D magnetic diffuse-scattering datasets is viable. To do this, I simulate a volume of single-crystal diffuse scattering for the Heisenberg pyrochlore AFM (the same system considered in Section 2.2). I then refine spin configurations to these simulated data using the RMC method, and assess how effectively these refined spin configurations recover the starting model.

For all the refinements I discuss, magnetic diffuse-scattering “data” were simulated using the spin configurations described in Section 2.2. The calculated $I(\mathbf{Q})$ was averaged over 64 independent spin configurations, each of size $6 \times 6 \times 6$ unit cells ($N = 3456$ spins). Data were simulated in the range $-4 \leq h, k, l \leq 4$ in each direction and binned in intervals of 0.1 reciprocal-lattice units. This generated a cube containing $\sim 5 \times 10^5$ data points; however, only half of these needed to be included in the fit because $I(\mathbf{Q}) = I(-\mathbf{Q})$. All $I(\mathbf{Q})$ calculations were performed using the resampling method using the cosine window with $m = 3$ and cubic summation [Section 6.2.4].

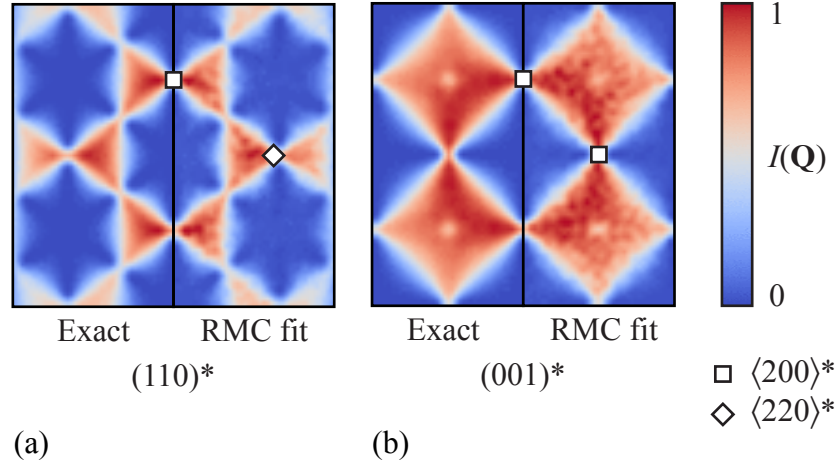


Figure 6.2: Comparison of simulated diffuse-scattering data for the ideal Heisenberg pyrochlore AFM (labelled “Exact”) with an RMC fit to a volume of simulated diffuse-scattering data (labelled “RMC fit”). (a) shows the $(110)^*$ reciprocal-space plane and (b) shows the $(001)^*$ reciprocal-space plane. The RMC fits were performed using a single spin configuration.

6.3.1 Individual Spin Configurations

First, I consider the simplest-possible case: refining a single spin configuration to simulated single-crystal data. A spin configuration of size $6 \times 6 \times 6$ unit cells ($N = 3456$ spins) was refined to the 3D simulated data for 200 proposed moves per spin. Eight independent refinements were performed in order to obtain uncertainties. Each refinement took ~ 13 hours of CPU time on a 3.07 GHz Intel Xeon processor, proving that the approach is practical for large 3D datasets.

Fig. 6.2 shows the simulated data and RMC fit in two reciprocal-space planes. A good fit-to-data is obtained; the only noticeable problem is that the fitted $I(\mathbf{Q})$ is somewhat more noisy than the simulated data. This is unsurprising, because the simulated data were obtained by averaging the intensity from 64 independent spin configurations, but only a single spin configuration is used in the RMC refinement. Accordingly, I obtain a best-case goodness-of-fit $R_{\text{wp}} \approx 5\%$ for these single-crystal refinements, compared to $R_{\text{wp}} \ll 1\%$ for the powder refinements of Chapter 2. It is perhaps not obvious why the lack of statistical averaging should have a greater effect in the single-crystal than powder refinement, since a single spin configuration is refined in both cases; the most likely explanation is that the spherical (powder) average improves the statistical quality of the calculated powder $I(Q)$.

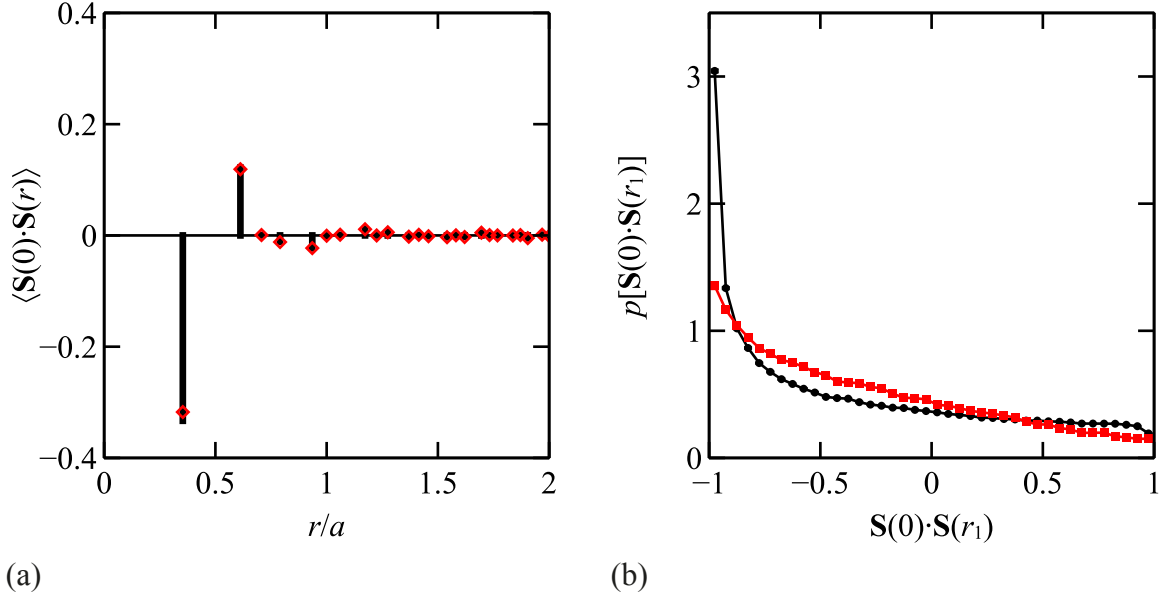


Figure 6.3: (a) Spin correlation function $\langle \mathbf{S}(0) \cdot \mathbf{S}(r) \rangle$ for the Heisenberg pyrochlore AFM. Black bars show exact results (from MC simulation) and red diamonds show results from RMC refinement of a single spin configuration to a volume of simulated diffuse-scattering data. (b) Probability distribution function of nearest-neighbour spin orientations. Black circles show exact results and red squares show results from RMC refinement of a single spin configuration to a volume of simulated diffuse-scattering data.

I now ask whether the real-space properties of the refined spin configurations are correct. Fig. 6.3 shows the spin correlation function and distribution of nearest-neighbour spin correlations. Good overall agreement is obtained between the RMC results and the starting model. However, I find that the nearest-neighbour spin-correlation coefficient $\langle \mathbf{S}(0) \cdot \mathbf{S}(r_1) \rangle$ obtained from RMC refinement is underestimated by around 5%, and the distribution of spin orientations is markedly too flat. As noted in Section 1.4.4, a similar effect is observed in RMC refinements for α -Si [160, 162]: the average properties are relatively well-recovered by RMC refinement but their distributions are too broad. These errors are relatively small in absolute terms, but nevertheless are of greater magnitude than for refinements to simulated powder data [Chapter 2]. These results suggest that—withstanding the general success of the approach—the limited statistical quality of the fit indeed has some adverse effects on the results.

The limitation of statistical quality of the fit was also identified in early RMC studies of single-crystal structural diffuse scattering [154, 156, 293], but no effective solution has yet been proposed. There are two possible approaches to improve the results. First, powder

data may be included in the fit in addition to single-crystal data. Second, the RMC algorithm itself can be adjusted to improve the statistical quality. The first approach is straightforward; I discuss the second in the following section.

6.3.2 Ensemble Reverse Monte Carlo Refinement

The main difficulty identified in the previous section—a lack of sufficient statistical averaging in $I(\mathbf{Q})$ —cannot be addressed simply by using larger spin configurations, because this increases the number of long-range correlations which add to the noise [Section 6.2.2]. Instead, it is necessary to increase the number of spins included in the calculation without also increasing the length-scale. There are two ways in which this might be achieved. First, a larger spin configuration could be used, but the value of $r_{\max}$ in Eq. (6.5) restricted to less than its maximum value of $R/2$. Second, the size of the spin configuration could be maintained, but an ensemble of spin configurations refined simultaneously. These different spin configurations might be visualised as different regions of a macroscopic crystal which are separated by a distance much greater than ξ .

Both approaches are possible; however, the second is less computationally-expensive than the first. This is because the number of supercell Bragg peaks scales as L^3 , where L is the side length of the supercell. Hence, increasing L rapidly increases the time per move (in effect, time is wasted calculating long-range spin correlations which then must be filtered out of $I(\mathbf{Q})$). I therefore focus on the second approach, which I term “ensemble RMC refinement”. The algorithm is as follows. First, an ensemble of N_{configs} spin configurations is created (here $N_{\text{configs}} = 8$). A single iteration of the algorithm involves choosing a spin configuration at random from the ensemble and rotating a randomly-chosen spin within this configuration, so the computer time is proportional to N_{configs} . I calculate $I_i(\mathbf{Q})$ for each configuration in the ensemble separately; the total $I(\mathbf{Q}) = \frac{1}{N_{\text{configs}}} \sum_i I_i(\mathbf{Q})$ is fitted to the single-crystal data. In all other respects, the RMC algorithm remains the same as in the previous section.

Fig. 6.4 shows the fit to simulated single-crystal data obtained using ensemble RMC refinement. Better agreement is obtained than for the single spin configurations ($R_{\text{wp}} <$

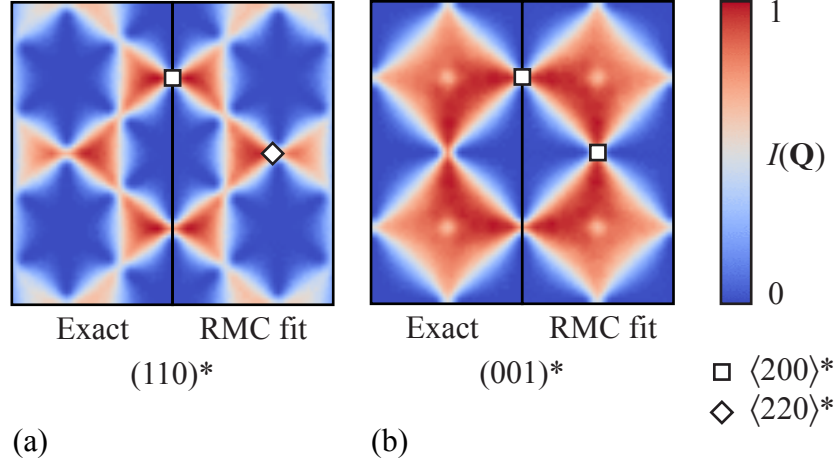


Figure 6.4: Comparison of simulated diffuse-scattering data for the ideal Heisenberg pyrochlore AFM (labelled “Exact”) with an RMC fit to a volume of simulated diffuse-scattering data (labelled “RMC fit”). (a) shows the $(110)^*$ reciprocal-space plane and (b) shows the $(001)^*$ reciprocal-space plane. The RMC fits were performed using the “ensemble RMC” algorithm described in the text to fit eight spin configurations to data simultaneously.

1%), with no statistical noise now visible in the fits. This improvement is also apparent in Fig. 6.5, which shows that the ensemble RMC fit now underestimates $\langle \mathbf{S}(0) \cdot \mathbf{S}(r_1) \rangle$ by only $\approx 1\%$, and the distribution of $\mathbf{S}(0) \cdot \mathbf{S}(r_1)$ is more strongly peaked at -1 . Perhaps the most surprising result of this chapter is that these best-case results are essentially equal to those obtained by refinement to powder data [Section 2.2]. Hence, in this system, the information loss involved in powder averaging seems to be negligible. This result cannot be general, and future work to determine the circumstances in which single-crystal data contain more information would be valuable.

6.3.3 Effect of Limited Data Extent

While it is increasingly common to measure large volumes of reciprocal space in neutron-scattering experiments, this is by no means routine; nor is it even practical on most constant-wavelength diffractometers. Frequently, therefore, models are fitted to individual planes or lines of experimental diffuse-scattering data (see, e.g., [50, 132, 291]). In this section, I consider the effect of refining to the $\{110\}^*$ reciprocal-space planes only. It is not clear in advance whether this approach will be successful. On the one hand,

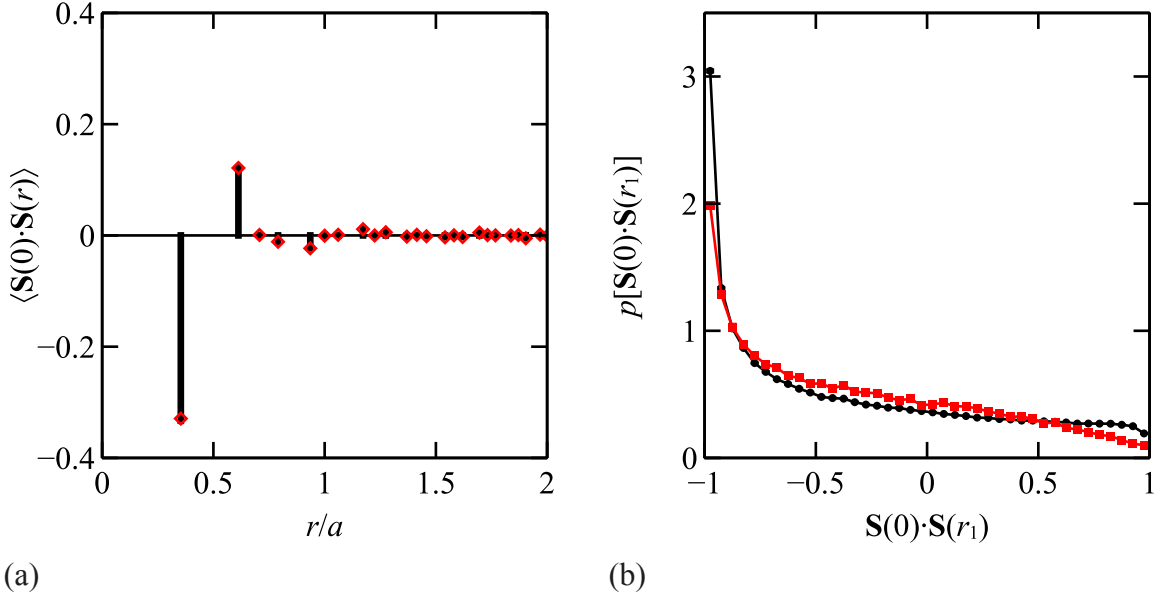


Figure 6.5: (a) Spin correlation function $\langle \mathbf{S}(0) \cdot \mathbf{S}(r) \rangle$ for the Heisenberg pyrochlore AFM. Black bars show exact results (from MC simulation) and red diamonds show results from ensemble RMC refinement of eight spin configurations to a volume of simulated diffuse-scattering data. (b) Probability distribution function of nearest-neighbour spin orientations. Black circles show exact results and red squares show results from ensemble RMC refinement to a volume of simulated diffuse-scattering data.

spin Hamiltonians have been successfully parameterised based on fitting to individual planes of diffuse scattering (see, e.g., [113, 291]). On the other hand, RMC refinement is fundamentally different to those approaches, since it is entirely data-driven. Moreover, the absence of any data in some regions of reciprocal space has been shown to have a significant effect for RMC refinement to structural diffuse-scattering data [147, 154]. To investigate this point, I simulated single-crystal data for the six symmetry-equivalent $\{110\}^*$ planes for the pyrochlore Heisenberg AFM and refined a single spin configuration to these simulated data.

Results of these refinements are shown in Figs. 6.6 and 6.7. An excellent fit to simulated data is obtained [Fig. 6.6(a)]. However, in order to be useful, the refinement must also allow accurate predictions to be made. To check whether this is the case, I calculated $I(\mathbf{Q})$ in the $(001)^*$ plane, which was not included in the fit. Disappointingly, only very approximate agreement is obtained with the exact calculation [Fig. 6.6(b)]. Hence, RMC refinement to individual single-crystal plane(s) does not allow other planes (not included in the refinement) to be reconstructed. This result agrees with previous RMC studies

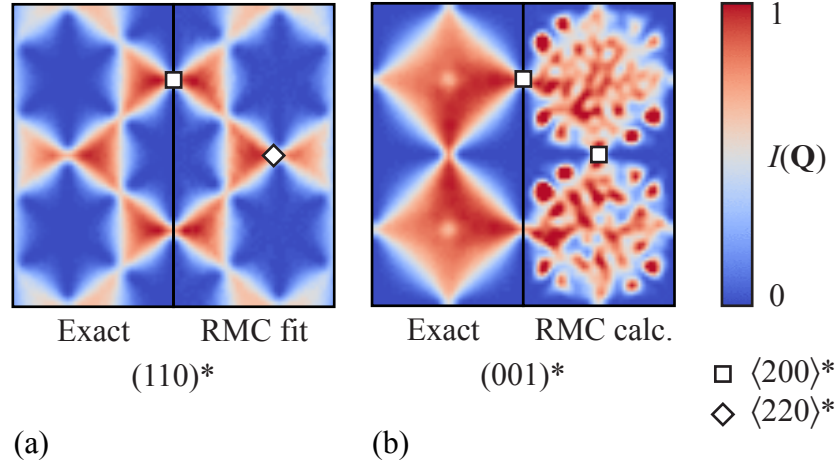


Figure 6.6: (a) Simulated diffuse-scattering data for the ideal Heisenberg pyrochlore AFM in the $(110)^*$ reciprocal-space plane (left panel) and RMC fit to this plane (right panel). (b) Simulated diffuse-scattering data in the $(001)^*$ reciprocal-space plane (left panel) and the corresponding pattern calculated from RMC refinement to the $(110)^*$ plane (right panel).

of structural single-crystal diffuse scattering [147, 154]. It is, however, in marked contrast to RMC refinement of powder data, which determines the full $I(\mathbf{Q})$ for this system [Section 2.2].

Fig. 6.7 shows that the comparative failure of RMC refinement to individual single-crystal planes is also apparent in real space. The magnitudes of the spin correlations are underestimated by $\approx 30\%$ and the distribution of nearest-neighbour spin orientations is only broadly correct.

The main implication of these results is that RMC refinement of individual single-crystal planes is not a useful approach. The results obtained compare badly with refinements to either the powder $I(Q)$ or to the full 3D $I(\mathbf{Q})$. The obvious practical conclusion is that powder data should always be included in RMC refinements, unless the full 3D $I(\mathbf{Q})$ has been measured. Moreover, because RMC refinement is entirely data-driven, these results allow some conclusions to be drawn about the relative information content of different types of dataset. Perhaps surprisingly, my results suggest that powder data can be more information-rich than individual single-crystal planes, provided that the data are in both cases of high quality. While I have only demonstrated this result for the Heisenberg pyrochlore AFM, I anticipate that it may hold more generally, because powder

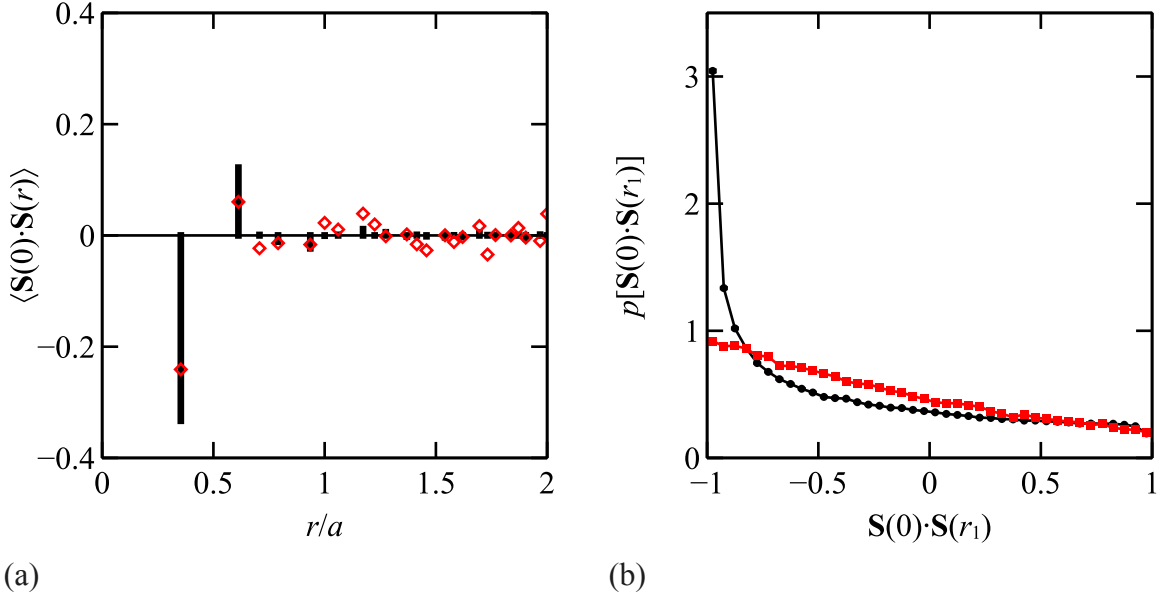


Figure 6.7: (a) Spin correlation function $\langle \mathbf{S}(0) \cdot \mathbf{S}(r) \rangle$ for the Heisenberg pyrochlore AFM. Black bars show exact results (from MC simulation) and red diamonds show results from RMC refinement to simulated diffuse-scattering data in the $(110)^*$ reciprocal-space plane. (b) Probability distribution function of nearest-neighbour spin orientations. Black circles show exact results and red squares show results from RMC refinement to simulated diffuse-scattering data in the $(110)^*$ plane.

data contain some information about all points in the Brillouin zone, whereas individual single-crystal planes contain no information about large regions of reciprocal space.

6.4 Conclusions

In this chapter, I have demonstrated that RMC refinement is a viable approach for quantitative refinement of large 3D datasets. This work significantly extends previous studies of structural diffuse scattering [147, 154, 156, 293–295], which considered only individual reciprocal-space planes. The key development is a new approach to calculate the single-crystal diffuse scattering function $I(\mathbf{Q})$, which builds on well-understood principles of digital signal processing. This method retains accuracy of the short-range spin correlations, is faster than previous approaches, and is easily parallelisable. Using this approach, it is possible to refine $\gtrsim 10^3$ spin orientations to $\gtrsim 10^5$ data points in a matter of hours.

I tested this method using simulated data for the Heisenberg pyrochlore AFM. Good results ($\sim 5\%$ accuracy) are obtained when refining individual spin configurations to simu-

lated 3D single-crystal data; the limiting factor is the lack of sufficient statistical averaging from individual spin configurations. To overcome this problem, a new “ensemble RMC” algorithm was developed, which fits multiple spin configurations to data simultaneously.

Finally, I showed that fitting to data which are limited in extent—e.g., individual reciprocal-space planes for a 3D system—drastically reduces the accuracy of the results. This problem can be effectively avoided either by fitting to powder data in addition to individual single-crystal planes, or by fitting to 3D single-crystal datasets.

Chapter 7

The Paramagnetic Structure of MnO

7.1 Chapter Summary

Having shown in the previous chapter that RMC refinement to 3D diffuse-scattering data is feasible, I now apply this new technique to a canonical AFM material, manganese(II) oxide (MnO). MnO undergoes a transition to long-range AFM order occurs at $T_N = 118$ K. In the PM phase above T_N , weak frustration arises due to AFM nearest-neighbour interactions on the face-centred cubic lattice. Here I compare the spin correlations in PM MnO at $T = 160$ K to the ordered AFM state, using RMC refinement to refine to a complete 3D experimental neutron-scattering dataset. The magnetic short-range order is visualised using the 3D spin correlation function. I find that the directional dependence of PM spin correlations in MnO differs significantly from the incipient ordered AFM state. This result shows that, even in weakly-frustrated paramagnets, the PM correlations do not simply resemble the incipient ordered state multiplied by a damping function of distance.

7.2 Acknowledgements

The single-crystal neutron-scattering data were collected using the SXD instrument at ISIS by David Keen, Matthias Gutmann, and Matthew Tucker (all STFC-ISIS, Rutherford Appleton Laboratory) before the start of my DPhil. The crystal of MnO was supplied by Steve Hull (also STFC-ISIS). It is thought to have been prepared in the 1960s, but

our attempts to establish the identity of the crystal grower have been unsuccessful. I am grateful to Matthias Gutmann and Martin Dove (Queen Mary, University of London) for valuable discussions concerning the data analysis.

7.3 Introduction

Phase transitions between ordered and disordered states encompass diverse phenomena including the melting of solids, dopant ordering in alloys, and (A)FM–PM transitions [310, 311]. In conventional magnets, order–disorder transitions show two basic properties: the transition temperature T_c is similar to the Curie–Weiss temperature θ , and the correlations of the disordered phase resemble those of the ordered phase multiplied by a damping function of distance [312–314]. Highly-frustrated magnets are widely studied because they show fundamentally-different behaviour. The transition temperature is suppressed far below the energy scale of the magnetic interactions ($\theta/T_c \gtrsim 10$), and a “cooperative PM” regime exists over a wide temperature range $T_c < T < \theta$ in which magnetic order is suppressed by geometrical frustration instead of thermal fluctuations [6].

By contrast, weakly-frustrated magnets—in which unfrustrated interactions are larger than frustrated interactions—have received relatively little attention. Spin-disordered states in weakly-frustrated systems have usually been modelled in a similar way to conventional paramagnets: as a collection of small domains within which the spin arrangement resembles the incipient ordered state [315]. The best-known systems in which this assumption has been widely applied are the cuprate superconductors, in which “fluctuating spin-stripe” phases are assumed to resemble well-characterised ordered spin-stripe phases over short length-scales [316, 317]. Given the wide application of this assumption, it is important to test whether it holds in simple systems. In this chapter, I identify the prototypical AFM MnO as a counter-example, in which the spin correlations in the PM state are qualitatively *different* to the incipient AFM state. These results show that weak frustration has non-trivial effects on PM spin correlations, which are not well-described by models based on a proximal long-range ordered state.

Above its AFM ordering temperature $T_N = 118$ K, MnO has the cubic rock-salt struc-

ture, in which magnetic Mn^{2+} ions ($S = 5/2$, $L = 0$) occupy a face-centred cubic lattice. Below T_N , the onset of AFM order with magnetic propagation vector $\mathbf{k} = [\frac{1}{2}\frac{1}{2}\frac{1}{2}]^*$ is accompanied by a rhombohedral lattice distortion [137, 143, 318]. The presence of weak frustration in MnO is indicated by a modest value of the frustration parameter $|\theta|/T_N \approx 5$ [319], which occurs because the frustrated AFM coupling between nearest neighbours is smaller than the unfrustrated next-nearest neighbour coupling [47]. Previous neutron-scattering studies have shown that structured magnetic diffuse scattering is present above T_N and short-range spin correlations persist to $T \gtrsim 1100$ K [50, 63, 64, 84, 315, 320]. These measurements were, however, restricted to either the powder average or individual reciprocal-space planes. In this chapter, I present the first atomic-scale refinement of the 3D $I(\mathbf{Q})$, which I use to determine the relationship between ordered AFM and PM correlations in MnO.

7.4 Methods

7.4.1 Experimental

Neutron-scattering data were collected at $T = 160$ K ($> T_N$) using the SXD time-of-flight Laue diffractometer at ISIS [289]. The sample was a single crystal of MnO prepared by the floating-zone method. Standard corrections were performed using the SXD2001 software; in particular, the data were corrected for instrumental background scattering by subtracting the scattering intensity from an empty sample holder, and were normalised using the incoherent scattering from a vanadium standard. The crystal structure (space group $Fm\bar{3}m$) was refined to the nuclear Bragg intensities using the JANA software package [321]. Selected crystallographic data and lattice parameters are given in Table 7.1; refined variables and derived quantities are given in Table 7.2.

7.4.2 Refinement and Modelling

The 3D RMC algorithm described in Chapter 6 was used to refine to the $T = 160$ K data. The data described a cube in reciprocal space extending between $-3 \leq h, k, l \leq 3$

Empirical formula	MnO
Formula weight (g mol ⁻¹)	70.93744
Crystal system	Cubic
Space group	$Fm\bar{3}m$ (No. 225)
Radiation	neutron (time-of-flight)
Temperature (K)	160
a (Å)	4.4344(7)
No. of unique reflns ($I > 3\sigma(I)$)	940
R (F_o)	0.0743
R_w (F_o)	0.2242
GOF	10.25

Table 7.1: Crystallographic details for MnO determined by single-crystal neutron diffraction.

Atom	Wyckoff site	Fractional coordinates	Occupancy	U_{iso} (Å ²)
Mn1	$4a$	(0, 0, 0)	Mn _{1.0}	0.00509(9)
O1	$4b$	$(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$	O _{1.0}	0.00434(9)

Table 7.2: Crystallographic data for MnO determined by single-crystal neutron diffraction.

reciprocal-lattice units in each Cartesian direction, and were binned in intervals of 0.04 reciprocal-lattice units. The $m\bar{3}m$ diffraction symmetry appropriate for MnO was applied to the data and nuclear Bragg peaks were removed by excising regions where the intensity exceeded a threshold value (plus a small surrounding volume). The total number of data points included in the refinement was $\approx 1.5 \times 10^6$.

The RMC refinements were performed using single spin configurations of size $12 \times 12 \times 12$ conventional unit cells ($N = 6912$ spins), with periodic boundary conditions. The resampling approach described in Section 6.2.4 was used to calculate $I(\mathbf{Q})$. The formula for cubic summation, Eq. (6.5), was used with Lanczos resampling, Eq. (6.7), with window length $m = 4$. This choice of parameters allows the spin correlations to be calculated accurately (within $\pm 1\%$) for radial distances $0 \leq r \leq 12 \text{ Å}$, beyond which the spin correlations were found to take negligibly small values [Fig. 6.1]. The scattering intensity was multiplied by the squared magnetic form factor for Mn^{2+} [78] and by the Debye-Waller factor $\exp(-U_{\text{iso}}Q^2)$, where the isotropic atomic displacement factor U_{iso} for Mn^{2+} at $T = 160 \text{ K}$ is given in Table 7.2. In addition, an overall intensity scale factor and constant-in- Q background term were refined to match the experimental data at each iteration of the refinement using the least-squares equations given in Ref. 154.

The constant-in- Q background was included in order to compensate for the considerable incoherent scattering intensity present for Mn ($b_{\text{coh}}/b_{\text{inc}} \approx 4$ [277, 322]). Refinements were initialised with random spin orientations and run for 100 proposed moves per spin, which required a total CPU time of ~ 3 days on a 3.07 GHz Intel Xeon processor. Four separate refinements were performed in order to estimate statistical errors on calculated quantities; unless shown in the figures, the errors are smaller than the symbol size in the plots.

7.5 Results

A 3D representation of the experimental single-crystal data and the RMC fit is shown in Fig. 7.1. Excellent agreement is achieved between data and fit ($R_{\text{wp}} = 8.3\%$). These results represent the first time that an atomic-scale model has been refined to a full 3D diffuse-scattering pattern. The spin Hamiltonian of MnO has, however, previously been characterised using two approaches: inelastic neutron-scattering measurements in the low-temperature AFM phase [47], and magnetic diffuse-scattering measurements of the (110)* plane in the PM phase [50]. In Ref. 50, good agreement with diffuse-scattering data was obtained for a Heisenberg model with AFM nearest and next-nearest neighbour exchange constants, $J_1 = -3.3$ K and $J_2 = -4.6$ K at $T \approx 160$ K, which also agreed well with extrapolated values from the spin-wave measurements [50]. To test whether our RMC refinement is consistent with the literature results, I simulated the J_1 - J_2 model using MC simulations at $T = 160$ K. Fig. 7.2 compares the radial spin correlation function $\langle \mathbf{S}(0) \cdot \mathbf{S}(r) \rangle$ obtained from RMC with the results for the J_1 - J_2 model. The trend in the correlations is identical between the two calculations; quantitatively, the difference in magnitude of the next-nearest neighbour correlation value is 7%. The spin correlation length $\xi = 2.258(1)$ Å was obtained by fitting an exponential envelope, $\exp(-r/\xi)$, to $|\langle \mathbf{S}(0) \cdot \mathbf{S}(r) \rangle|$. I also calculated the spin-orientation distribution from the RMC refinements, but found no statistically-significant anisotropy in the spin orientations. The results from RMC refinement therefore agree closely with the Heisenberg model—validating both the methodology of the RMC refinement and the accuracy of the MnO spin Hamiltonian.

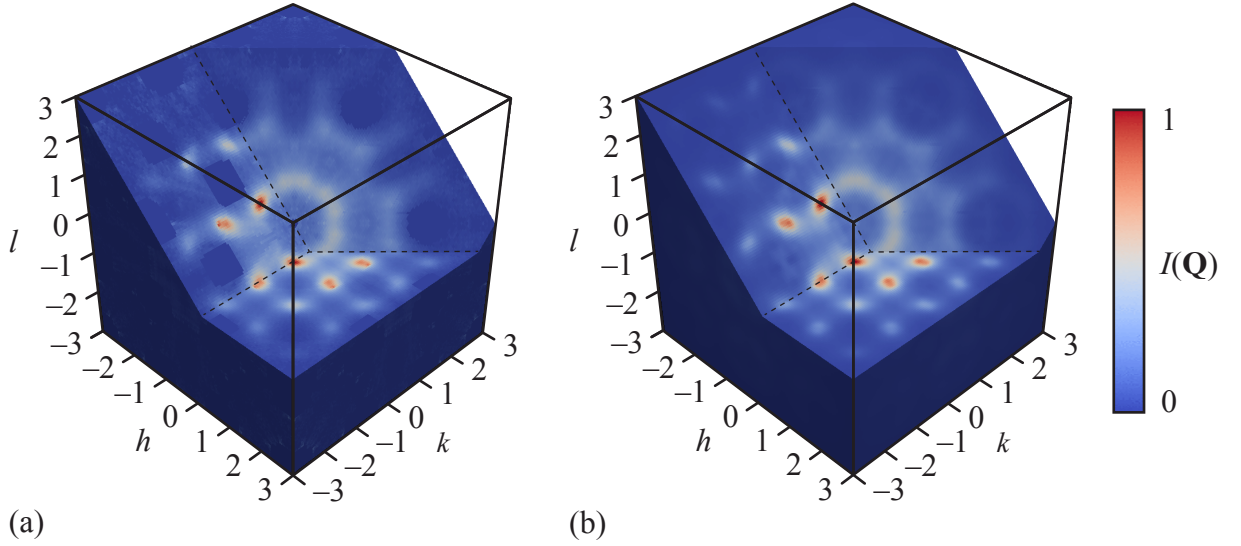


Figure 7.1: (a) Experimental magnetic diffuse-scattering data for PM MnO at $T = 160$ K. Nuclear Bragg peaks have been removed from the experimental data. (b) RMC fit to the data shown in (a). In (a) and (b), sections of three reciprocal-space planes are shown: $(101)^*$, $(1\bar{1}1)^*$, and $(001)^*$. The $(001)^*$ plane is shifted by -0.5 reciprocal-lattice units along the $[001]^*$ direction.

I now turn to the main question of this chapter: the relationship between the spin correlations of the PM phase and the low-temperature AFM phase. The $\langle \mathbf{S}(0) \cdot \mathbf{S}(r) \rangle$ shown in Fig. 7.2(a) already hints that the PM correlations do not simply resemble the AFM correlations multiplied by a decreasing function of distance. As expected from the relative magnitudes of J_1 and J_2 , the strongest correlation is between next-nearest neighbours, for which AFM interactions are not frustrated. However, significant AFM correlation is present at the nearest-neighbour distance in the PM phase, whereas this correlation is exactly zero for the ordered AFM state. This result implies that the absence of long-range order allows frustrated nearest-neighbour interactions to be partially satisfied in the PM phase. In order to assess the influence of the frustrated geometry on the spin correlations, I consider the 3D spin correlation function $\langle \mathbf{S}(\mathbf{0}) \cdot \mathbf{S}(\mathbf{r}) \rangle$ introduced in Section 2.4. Fig. 7.2(b) shows that a distinctive pattern—hidden in the radial correlation function—emerges in $\langle \mathbf{S}(\mathbf{0}) \cdot \mathbf{S}(\mathbf{r}) \rangle$. The $\langle \mathbf{S}(\mathbf{0}) \cdot \mathbf{S}(\mathbf{r}) \rangle$ can be described as a set of nested octahedral shells, with the sign of the spin correlations alternating between FM and AFM for successive shells as distance is increased [Fig. 7.2(c)]. This pattern extends over length-scales much greater than the radial correlation length $\xi = 2.258(1)$ Å. Hence,

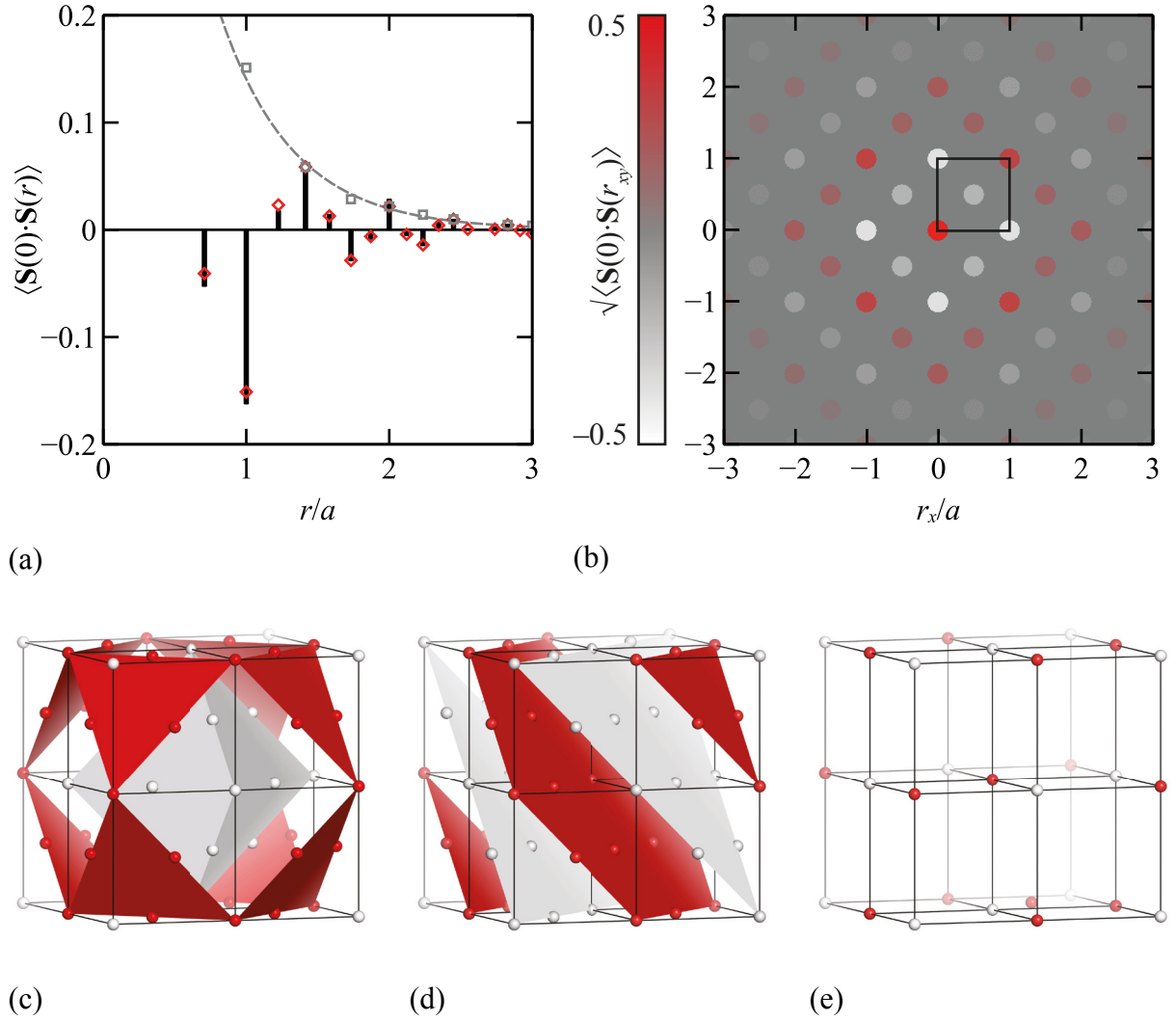


Figure 7.2: (a) Radial spin correlation function $\langle \mathbf{S}(0) \cdot \mathbf{S}(r) \rangle$ of MnO at $T = 160$ K. Black bars show results from MC simulations described in the text and red diamonds show results from RMC refinement to single-crystal magnetic diffuse-scattering data. The dashed grey line shows the fit of an exponential envelope to the RMC $\langle \mathbf{S}(0) \cdot \mathbf{S}(r) \rangle$, which yields spin correlation length $\xi = 2.258(1)$ Å. (b) 3D spin correlation function $\langle \mathbf{S}(0) \cdot \mathbf{S}(\mathbf{r}) \rangle$ obtained from RMC refinement. The crystallographic unit cell is shown as a black box. (c) Schematic representation of $\langle \mathbf{S}(0) \cdot \mathbf{S}(\mathbf{r}) \rangle$ for MnO in the PM phase. Red areas indicate FM correlations and grey areas AFM correlations. (d) Schematic representation of $\langle \mathbf{S}(0) \cdot \mathbf{S}(\mathbf{r}) \rangle$ for a single domain of the ordered low-temperature AFM structure of MnO. (e) Schematic representation of $\langle \mathbf{S}(0) \cdot \mathbf{S}(\mathbf{r}) \rangle$ obtained for a superposition of domains of the low-temperature AFM structure.

taking any Mn atom as the origin, its Mn neighbours at coordinates $\mathbf{r}/a = [x, y, z]$ are ferromagnetically correlated if $x + y + z = 2n$, and antiferromagnetically correlated if $x + y + z = 2n + 1$, for integer n . The parity of $\langle \mathbf{S}(\mathbf{0}) \cdot \mathbf{S}(\mathbf{r}) \rangle$ is consistent with the fact that J_1 and J_2 interactions are both AFM, and the smallest number of exchange pathways which connects two Mn^{2+} ions is equal to $x + y + z$.

The description of the PM spin structure of MnO as a set of nested octahedral shells [Fig. 7.2(c)] is compared with a single domain of the AFM structure and a superposition of AFM domains in Figs. 7.2(d) and 7.2(e), respectively. In a single domain of the AFM structure [Fig. 7.2(d)], spins are ferromagnetically aligned within (111) planes, and the direction of spin alignment reverses between adjacent planes [318]; hence, the PM correlations resemble the AFM structure viewed along the [111] direction. However, a superposition of AFM domains [Fig. 7.2(e)] does not fully describe the PM correlations, because $\langle \mathbf{S}(\mathbf{0}) \cdot \mathbf{S}(\mathbf{r}) \rangle$ would vanish for nearest-neighbour spins in this case. The RMC results [Fig. 7.2(b)] are intermediate between Fig. 7.2(c) and Fig. 7.2(e): the signs of the spin correlations are described by Fig. 7.2(c), but the magnitudes of the spin correlations are largest at the positions shown in Fig. 7.2(e).

These results suggest that the traditional interpretation of the PM phase as a collection of small AFM domains is oversimplified. Might it, however, still be partially correct? In the traditional interpretation, the spins order with one of the four symmetry-equivalent $\mathbf{k} \in \langle \frac{1}{2} \frac{1}{2} \frac{1}{2} \rangle^*$ within domains of length-scale $\sim \xi$ [312, 315]. Different $\mathbf{k}$ are selected within different domains, so that the cubic symmetry of the PM phase is preserved. To look for such domain structure in the RMC spin configurations, I calculate the a local version of the magnetic structure factor,

$$S_{\mathbf{k}}(\mathbf{r}) = \left| \sum_i \mathbf{S}_i \exp \left(\frac{2\pi i}{a} \mathbf{k} \cdot \mathbf{r}_i \right) \exp \left(-\frac{|\mathbf{r} - \mathbf{r}_i|}{2\xi} \right) \right|^2,$$

where $\mathbf{k} \in \langle \frac{1}{2} \frac{1}{2} \frac{1}{2} \rangle^*$, ξ is the spin correlation length, $\mathbf{r}_i$ is the position of spin $\mathbf{S}_i$ within the configuration, and $\mathbf{r}$ is a continuous variable defined at all positions within the configuration. The quantity $S_{\mathbf{k}}(\mathbf{r})$ is sensitive to local periodicity within radius $\sim \xi$ of position $\mathbf{r}$.

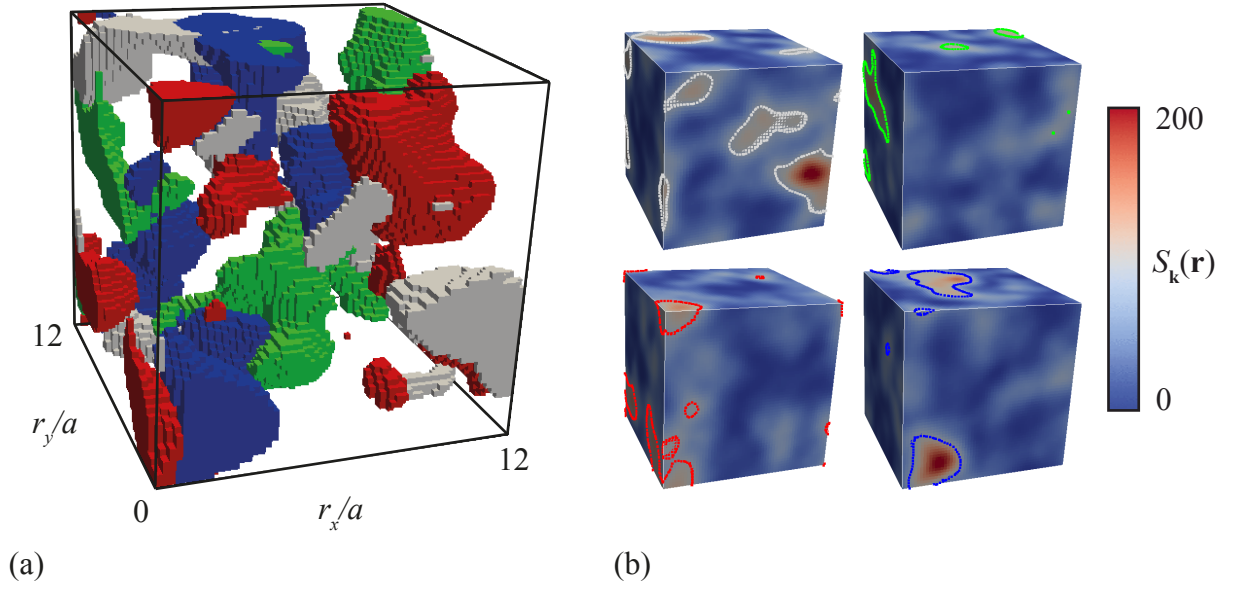


Figure 7.3: Magnetic domain structure of MnO at $T = 160$ K obtained as described in the text. In (a), different domains with local periodicity $\mathbf{k} \in \langle \frac{1}{2} \frac{1}{2} \frac{1}{2} \rangle^*$ are shown in different colours. The coloured regions show the threshold where $S_{\mathbf{k}}(\mathbf{r}) = 85$ (the range of $S_{\mathbf{k}}(\mathbf{r})$ is between approximately zero and 200). In (b), the four images show different $\mathbf{k} \in \langle \frac{1}{2} \frac{1}{2} \frac{1}{2} \rangle^*$, and the value of $S_{\mathbf{k}}(\mathbf{r})$ in each image is shown using a blue-to-red colourmap. Coloured points indicate the threshold where $S_{\mathbf{k}}(\mathbf{r}) = 85$, using the same colours as (a). All images are shown in the same orientation.

Fig. 7.3(a) shows that the spin configurations consist of many small regions within which a single $\mathbf{k}$ dominates. These regions are of variable size but are largely non-overlapping, suggesting that domain structure is indeed present in the PM phase of MnO. Interestingly, there are several regions visible in Fig. (7.3)(b) where domain structure persists over a length-scale significantly larger than ξ , which may be balanced by regions where the degree of local order is weaker.

7.6 Conclusions

The chapter contains two key results. First, refinement to large single-crystal magnetic diffuse-scattering datasets is practical using the approach of Chapter 6, and the results agree with accepted models of MnO. Second, the PM structure of MnO, a weakly-frustrated magnet, is not simply described as a collection of small domains within which the spin arrangement resembles the ordered magnetic phase over small length-scales. Despite this, there is evidence for a modified domain structure. This result may have impli-

cations for the interpretation of spin disorder in other materials in which frustration may play a role, e.g., “fluctuating spin stripes” in high-temperature superconductors, in which the spin-disordered state is often assumed to resemble an ordered spin-stripe phase over short length-scales [317].

Chapter 8

Emergent Frustration in Co-doped β -Mn

8.1 Chapter Summary

In this final results chapter, I apply the 3D RMC method to obtain new information about spin correlations in a poorly-understood spin liquid, Co-doped β -Mn. Typically, investigations of spin-liquid states have focused on insulating materials in which magnetic ions occupy a frustrated lattice such as kagome or triangular [6]. In such cases, emergent states can arise from a simple geometry and magnetic interactions between nearest-neighbour spins. Here, I demonstrate a reversal of this paradigm: the presence of emergent spin structures in Co-doped β -Mn, a metal which has a crystal structure noted for its complexity [323]. Single-crystal polarised-neutron scattering experiments on β -Mn_{0.8}Co_{0.2} reveal the persistence of highly-structured magnetic diffuse scattering and the absence of magnetic order to $T = 0.05$ K. I employ RMC refinements and mean-field theory calculations to construct an effective Hamiltonian which accounts for the magnetic diffuse scattering. The interactions I identify describe an emergent spin structure which mimics the triangular-lattice AFM, one of the canonical models of frustrated magnetism.

8.2 Acknowledgements

Single crystals of β -Mn_{0.8}Co_{0.2} and β -Mn_{0.88}Co_{0.12} were prepared by Pierre Courtois at the ILL. Neutron-diffraction measurements using the D15 four-circle neutron diffractometer at the ILL were performed by Garry McIntyre (now Australian Nuclear Science and Technology Organisation) and Ross Stewart. The crystal-structure refinement was performed by Garry McIntyre. The following people used the D7 instrument at the ILL to measure the diffuse scattering for the two crystals. For the β -Mn_{0.8}Co_{0.2} crystal, the (001)* and (110)* planes were measured at temperatures between 1.5 and 300 K by Ross Stewart and Brian Rainford. The (110)* plane was measured at 0.05 K, and the (111)* and (11 $\bar{2}$)* planes were measured at 1.5 K, by Ross Stewart, Pascal Manuel, Giovanni Pasquino, and myself. For the β -Mn_{0.8}Co_{0.2} crystal, I measured the (001)* and (110)* planes with Brian Rainford and Ross Stewart. The instrument scientists were Pascale Deen, Ken Andersen, Gøran Nilsen, and Andrew Wildes. Cryogenic support was provided by Xavier Tonon and his team at the ILL. I am grateful to Brian Rainford for insightful advice on the data analysis.

8.3 Introduction

The metallic elements of the 3d transition series might be considered simple systems. The low-temperature crystal structures of all the 3d elements (except Mn) contain only a single atom in the primitive unit cell. The magnetic ground states, too, are well-understood: Sc, Ti, V, and Cu are Pauli paramagnets; Fe, Co, and Ni have FM ground states; and Cr has an AFM spin-density-wave ground state [324]. By contrast, the central 3d element Mn shows very complex behaviour. Four structural polymorphs of Mn are known: of these, α -Mn is stable at low temperature, while β -Mn is stable between 1025 K and 1393 K and metastable if quenched to low temperature [325]. The crystal structure of α -Mn contains four inequivalent crystallographic sites with 58 atoms in the unit cell; a complex AFM order forms below 95 K in which all four sites have different magnetic moment lengths [325, 326].

The magnetic behaviour of β -Mn is even more unusual: it is the unique example of an elemental spin liquid. No long-range magnetic order is observed in β -Mn to $T < 1.4$ K, but the observation of magnetic diffuse scattering (centred at $Q \approx 1.6 \text{ \AA}^{-1}$) shows that antiferromagnetically-correlated magnetic moments nevertheless exist in the PM state [28]. Inelastic neutron-scattering studies show that spin fluctuations have a wide distribution of energies indicative of non-Fermi-liquid behaviour [327], and these fluctuations persist to very high energies (> 100 meV) [28]. The temperature-dependence of the electrical resistivity [327] and spin-lattice relaxation rate [328] for pure β -Mn correspond to theoretical predictions for a metal on the verge of AFM order at $T = 0$ [329], and a strongly enhanced electronic (T -linear) specific heat coefficient suggests that longitudinal spin fluctuations are important [330]. The β -Mn structure is primitive cubic (space group $P4_132$), with a unit cell containing 20 Mn atoms divided over two inequivalent crystallographic sites, $8c$ and $12d$ [331]. Nuclear quadrupole resonance experiments find the spin-lattice relaxation rate to be ~ 20 times greater for $12d$ site than the $8c$ site, suggesting that only the $12d$ possesses a significant magnetic moment [28, 332]. Calculations using spin-polarised density-functional theory also find a larger moment on the $12d$ site, although the moment on the $8c$ is not always found to be negligible [323, 333]. The Mn atoms of the $12d$ site form a three-dimensional “hyperkagome” network of corner-sharing triangles [Fig. 8.1(a)]—an arrangement which has led several authors to suggest that the spin-liquid behaviour in β -Mn may result from geometrical frustration [28, 323, 334].

Neutron-scattering measurements represent an ideal approach to identify the rôle of frustration in β -Mn. In practice, however, there are two difficulties associated with performing such experiments on *elemental* β -Mn. First, the presence of high-energy spin fluctuations means that the quasistatic approximation is not satisfied for conventional neutron-diffraction measurements; instead, it is necessary to perform inelastic neutron scattering measurements and manually integrate over energy transfer to obtain $I(\mathbf{Q})$ [28]. Second, because elemental β -Mn is metastable at low temperature, single-crystal samples cannot be prepared. Both of these problems can be solved by doping β -Mn with small amounts of other elements. Doping with Ir, Ru, or Os fundamentally changes the mag-

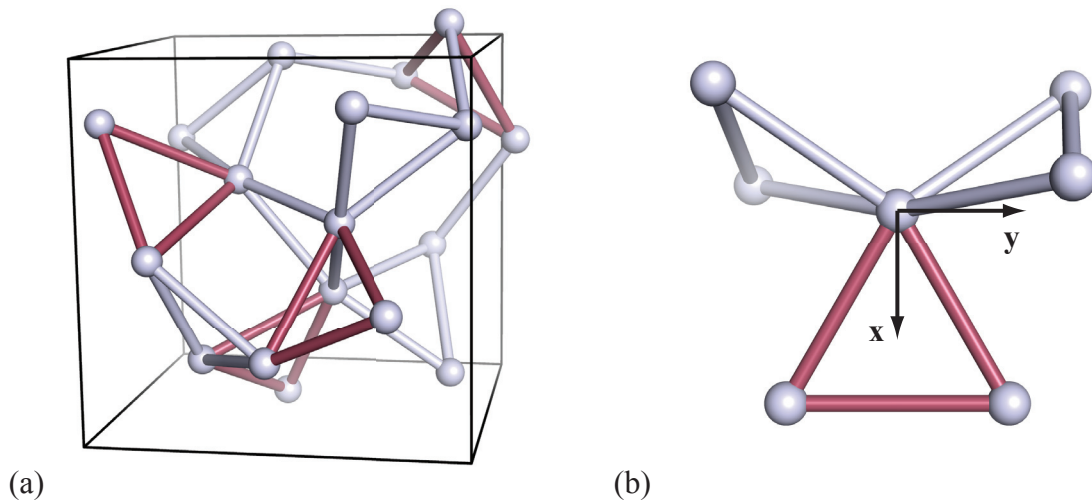


Figure 8.1: (a) The β -Mn crystal structure (space group $P4_132$), showing magnetic Mn atoms (12d site) only. Frustrated nearest-neighbour connections are shown as grey or burgundy lines. While all connections shown are of identical length to within 1%, only connections shown the same colour can be brought into coincidence by symmetry. (b) Local Mn environment. The six nearest neighbours of each Mn are arranged in a “windmill” geometry, with each triangular “blade” perpendicular to a $\langle 111 \rangle$ axis. The local $\mathbf{x}$, $\mathbf{y}$, and $\mathbf{z}$ (out of the page) axes are defined for each Mn atom relative to the burgundy-coloured triangle. This choice of coordinates aligns the $\mathbf{x}$ axis with the two-fold rotation axis which is the only point symmetry element of the 12d site.

netism of pure β -Mn, leading to the development of incommensurate long-range magnetic order together with a large increase in the lattice constant [335, 336]. By contrast, doping with Al, In, or Co does not lead to the development of long-range magnetic order, and the magnetic diffuse-scattering peak at $Q \approx 1.6 \text{ \AA}^{-1}$ remains similar to the pure element [149, 150, 337, 338]. However, the spin-fluctuation rate in these alloys is greatly reduced, as is shown by muon-spin rotation experiments [338, 339], a smaller enhancement of the electronic specific-heat [330], and inelastic neutron-scattering measurements [28]. β -Mn can also be doped with V, Fe and Ni, but these alloys have not been studied with neutron diffraction [330, 340]. Compared to the other alloys, doping with Co (unlike In) leads to negligible change in the lattice parameter, and Co (unlike Al) substitutes almost entirely onto the non-magnetic 12d site [341, 342]. Importantly, it is also possible to prepare large single crystals of Co-doped β -Mn [342]. These results suggest that Co-doped β -Mn may represent an experimentally-tractable system with strong similarities to pure β -Mn.

In this chapter, I use polarised-neutron scattering experiments, RMC refinement, and interaction modelling to investigate two large single crystals of β -Mn, doped with 12%

and 20% Co. The chapter is structured as follows. In Section 8.4, I describe the neutron-scattering experiments which form my new experimental results, and the RMC and mean-field methods which I used to refine to these data. In Section 8.5, I discuss the spin correlations and a possible interaction model for Co-doped β -Mn. The spin correlations are shown to describe an emergent spin structure which mimics the triangular lattice AFM and helps to explain the absence of long-range magnetic order in β -Mn.

8.4 Methods

8.4.1 Experimental

8.4.1.1 Magnetic diffuse-scattering measurements

The low-temperature magnetic diffuse scattering of β -Mn_{1-x}Co_x was measured using the D7 polarised-neutron diffractometer at the ILL [90] introduced in Section 1.3.4. Neutron *xyz* polarisation analysis [92] was used to separate the magnetic scattering from the nuclear scattering and the nuclear spin-incoherent scattering. The incident neutron wavelength $\lambda = 3.1 \text{ \AA}$. The β -Mn_{0.8}Co_{0.2} sample was a 17.2 g single crystal prepared using the Bridgman technique. This sample was measured in four reciprocal-space planes at $T = 1.5 \text{ K}$: $(100)^*$, $(110)^*$, $(11\bar{2})^*$, and $(111)^*$. In addition, the $(110)^*$ plane was measured over a larger temperature range: $T = 0.05, 10, 30, 50, 100, 150$, and 200 K . A second, smaller, sample of β -Mn_{0.88}Co_{0.12} was also measured at $T = 1.5 \text{ K}$ in the $(110)^*$ and $(111)^*$ reciprocal-space planes. All data were corrected using standard calibration measurements for detector efficiency (vanadium), finite beam polarisation, and analysing power (amorphous silica) [Section 1.3.4].

8.4.1.2 Crystal-structure determination

The crystal structure of β -Mn_{0.8}Co_{0.2} was characterised using the D15 four-circle neutron diffractometer at the ILL. The incident neutron wavelength $\lambda = 1.176 \text{ \AA}$. The sample was a small ($\sim 1 \text{ mm}^3$) fragment of the same β -Mn_{0.8}Co_{0.2} crystal used for the polarised-neutron measurements on D7. D15 was calibrated prior to the experiment using a standard NaCl

sample. A total of 1095 Bragg reflections were collected from β -Mn_{0.8}Co_{0.2} at ambient temperature. Background corrections following the minimum $\sigma(I)/I$ algorithm [343] and Lorentz corrections were applied to all data.

8.4.2 Refinement and Modelling

8.4.2.1 Reverse Monte Carlo refinements

The RMC refinements were performed using single spin configurations of size $10 \times 10 \times 10$ conventional unit cells ($N = 12\,000$ spins), with periodic boundary conditions. Only the magnetic $12d$ site was included in the refinements. The magnetic diffuse-scattering intensity $I(\mathbf{Q})$ was calculated using the resampling approach described in Section 6.2.4. The formula for spherical summation was used with cosine resampling, Eq. (6.8), with window length $m = 3$. The scattering intensity included the squared magnetic form factor for Mn²⁺ [78].

The sum of squared residuals was given by

$$\chi^2 = \sum_{d,\mathbf{Q}} W_d \left[\frac{s_d I_d^{\text{calc}}(\mathbf{Q}) - I_d^{\text{expt}}(\mathbf{Q})}{\sigma_d(\mathbf{Q})} \right]^2, \quad (8.1)$$

where $I(\mathbf{Q})$ represents the magnetic scattering intensity at position $\mathbf{Q}$ in reciprocal space, superscript “calc” and “expt” denote calculated and experimental values, subscript d denotes different datasets, and s_d are scale factors for each dataset (determined as described below). The datasets include powder data from Stewart *et al.* [150], the four symmetrised single-crystal reciprocal-space planes and their symmetry-equivalent copies (namely, three $\{100\}^*$, six $\{110\}^*$, twelve $\{112\}^*$, and four $\{111\}^*$, i.e., 25 planes in total). I include symmetry-equivalent copies of each plane in the fit because RMC refinement does not automatically reproduce the required $m\bar{3}m$ Laue symmetry of the diffraction pattern. In addition, an overall intensity scale factor was refined to match each dataset separately at each iteration of the refinement, using the least-squares equations given in Ref. 154. Refinements were initialised from random spin orientations and run for 200 proposed moves per spin.

8.4.2.2 Mean-field modelling

In order to determine an effective Heisenberg Hamiltonian consistent with the magnetic diffuse-scattering data, I apply the mean-field approach detailed in Section 1.4.1.2. In the mean-field approximation, the magnetic-diffuse scattering intensity is given by

$$I(\mathbf{Q}) = \frac{s [f(Q)]^2}{k_B T} \chi(\mathbf{Q}), \quad (8.2)$$

where $\chi(\mathbf{Q})$ is calculated from Eqs. (1.95) and (1.96) and s is a refined intensity scale factor calculated from Eq. (1.107). As I discuss in Section 1.4.1.2, the mean-field approach allows rapid calculation of $I(\mathbf{Q})$ for a given set of interaction parameters $\{J_n\}$, which means that it is computationally feasible to fit the $\{J_n\}$ directly to the experimental data.

The Gauss-Newton algorithm [344] was used to perform nonlinear least-squares fits of $\{J_n\}$. This is a standard approach which has been previously been applied to fit diffuse-scattering data [300], so I give only brief details here. The residuals are first written as a vector, $\mathbf{D} = [D_1, D_2, \dots, D_{N_d}]$, with elements

$$D_i = \frac{\sqrt{W_i}}{\sigma_i} (I_i^{\text{expt}} - I_i^{\text{calc}}),$$

where I_i is a (powder or single-crystal) magnetic neutron scattering data point, σ_i an experimental error, and W_i a user-determined weighting. At each iteration of the Gauss-Newton algorithm, the change Δ in the interaction parameters is determined by solving the linearised least-squares matrix equation

$$(\mathbf{A}^T \mathbf{A}) \Delta = -\mathbf{A}^T \mathbf{D}.$$

Here, superscript “T” denotes the matrix transpose, and $\mathbf{A}$ is a matrix (the Jacobian) with $N_d \times N_J$ elements, which are given by

$$\begin{aligned} A_{ij} &= \frac{\partial R_i}{\partial J_j} \\ &\approx \frac{D_i^{j+} - D_i^{j-}}{2\delta}, \end{aligned}$$

where D_i^{j+} is the residual for data-point i , calculated using the set of interaction constants $\mathbf{J}^{j+} = (J_1, J_2, \dots, J_j + \delta, \dots, J_{N_J})$, and D_i^{j-} is the residual calculated using $\mathbf{J}^{j-} = (J_1, J_2, \dots, J_j - \delta, \dots, J_{N_J})$. The increment δ is a small number (I take $\delta = 0.0001$). The Gauss-Newton algorithm guarantees that Δ is in a direction that will reduce χ^2 . However, the size of the increment may be too large, so that $\mathbf{J}^{\text{new}} = \mathbf{J} + \Delta$ overshoots the mark, and χ^2 actually increases. When this problem occurs, it is solved by replacing Δ by a fraction $f\Delta$ of its original value ($0 < f \leq 1$) until χ^2 decreases [344].

In the mean-field fits, the four single-crystal datasets and the powder data were included with the same relative weightings as for the RMC refinement. The powder $I(Q)$ was obtained by numerical powder averaging of Eq. (8.2) using a cubic grid containing 50^3 points in the Brillouin zone. These calculations were accelerated by using the fact that the mean-field $I(\mathbf{Q})$ automatically possesses the diffraction symmetry of the crystal. For β -Mn, with $m\bar{3}m$ diffraction symmetry, this implies that only a reciprocal-space wedge containing $1/48$ of a cube needs to be calculated to obtain the powder average. Mean-field refinements were initialised with all interaction parameters set to zero, which was found to lead to reasonably rapid convergence (typically 10 to 20 iterations) for the models considered here.

8.4.2.3 Triangular antiferromagnet simulation

In order to calculate the $\langle \mathbf{S}(\mathbf{0}) \cdot \mathbf{S}(\mathbf{r}) \rangle$ for the triangular-lattice AFM, I performed MC simulations using the Heisenberg Hamiltonian [218, 345–347],

$$H = -\frac{1}{2} \left(J_{\text{nn}} \sum_{\langle i,j \rangle} \mathbf{S}_i \cdot \mathbf{S}_j - J_{\text{nnn}} \sum_{\langle\langle i,j \rangle\rangle} \mathbf{S}_i \cdot \mathbf{S}_j \right),$$

where J_{nn} and J_{nnn} denote nearest-neighbour and next-nearest-neighbour couplings, respectively. The ratio $J_{\text{nnn}}/J_{\text{nn}} = 0.125$ and the simulation temperature was $T = 0.375|J_{\text{nn}}|$. MC simulations were run for 10^4 proposed moves per spin with periodic boundary conditions applied. The configuration size was $N = 16\,000$ spins and results were averaged over 10 independent configurations.

Empirical formula	Mn _{0.81} Co _{0.19}
Formula weight (g mol ⁻¹)	55.694
Crystal system	Cubic
Space group	$P4_132$ (No. 213)
Radiation	neutron $\lambda = 1.176$ Å
Temperature (K)	300
a (Å)	6.3160(25)
No. of unique reflns ($I > 3\sigma(I)$)	134
R (F_o)	0.03003
R_w (F_o)	0.01359
GOF	1.72

Table 8.1: Crystallographic details for β -Mn_{0.8}Co_{0.2} determined by single-crystal neutron diffraction.

Atom	Wyckoff site	Fractional coordinates	Occupancy	$B_{\text{iso}}/B_{\text{eq}}$ (Å ²)
Mn1	8c	(x, x, x)	Mn _{0.5271(15)} Co _{0.4729(15)}	0.45(5)
Mn2	12d	$(\frac{1}{8}, y, \frac{1}{4} + y)$	Mn _{1.0}	0.769(21)

Table 8.2: Crystallographic data for β -Mn_{0.8}Co_{0.2} determined by single-crystal neutron diffraction. In the table, the refined parameters $x = 0.06171(14)$ and $y = 0.20243(3)$.

8.5 Results and Discussion

8.5.1 Crystal-Structure Refinement

The crystal structure of β -Mn_{0.8}Co_{0.2} was refined to the D15 diffraction data using the program CCSL [348]. Selected crystallographic data and lattice parameters are given in Table 8.1; refined variables and derived quantities are given in Table 8.2. Any 12d Mn atom has six near-neighbours, of which two are at a slightly different distance to the remaining four. The distances become equal if the parameter $y = (9 - \sqrt{33})/16 \approx 0.2035$ [331]. The experimentally-determined value $y = 0.20243(3)$ in β -Mn_{0.8}Co_{0.2} differs by less than 1% from this idealised value. The overall Mn/Co composition and 8c/12d site occupancy by Co are fully correlated, and cannot be refined simultaneously; the 12d occupancy was therefore fixed at Mn_{1.0} and the composition was refined. The close agreement between the refined composition (β -Mn_{0.81}Co_{0.19}) and nominal composition (β -Mn_{0.80}Co_{0.20}) suggests that Co substitutes almost entirely on the 12d site, in agreement with previous results [341, 342].

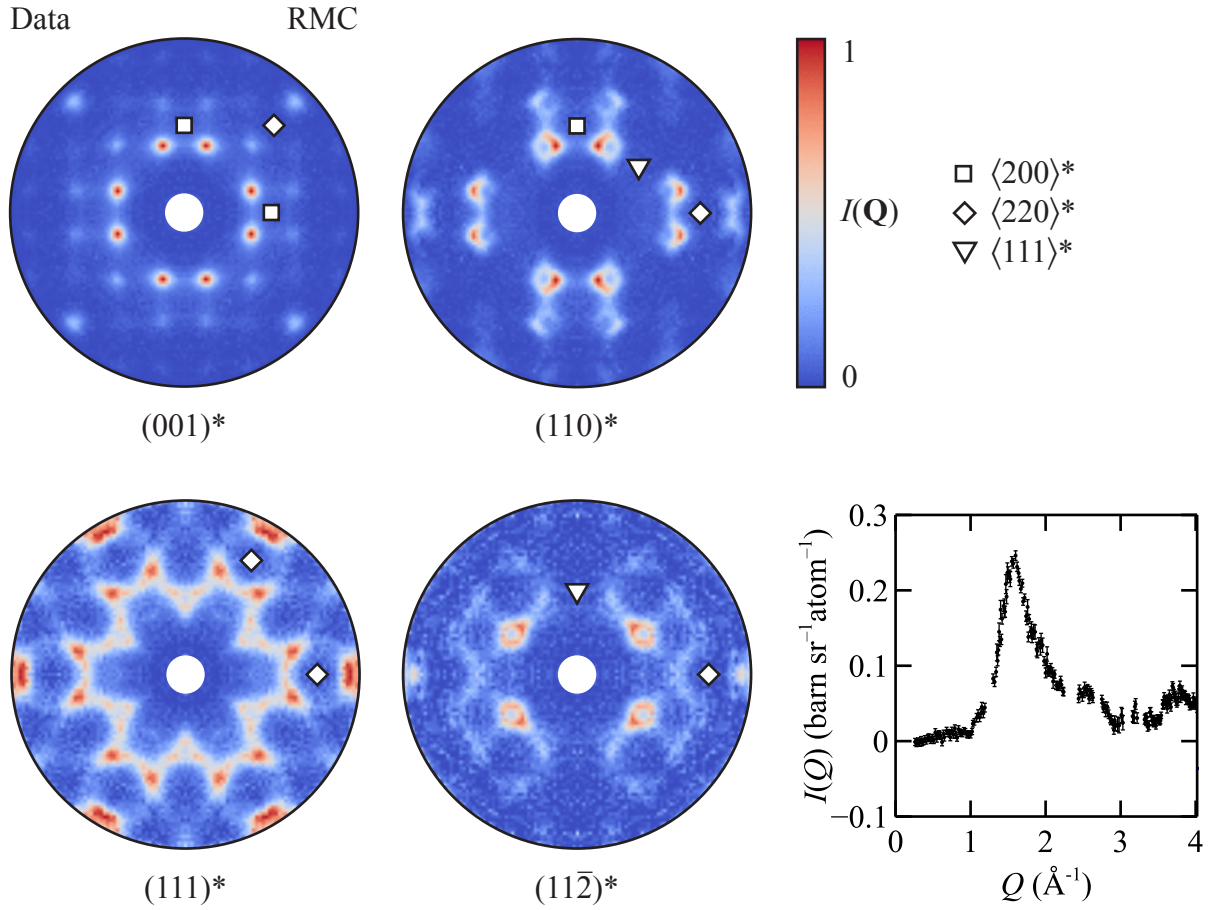


Figure 8.2: Magnetic diffuse-scattering data for $\beta\text{-Mn}_{0.8}\text{Co}_{0.2}$. Experimental single-crystal data are shown in four reciprocal-space planes at $T = 1.5$ K, clockwise from top left $(001)^*$, $(110)^*$, $(112)^*$, and $(111)^*$. The $m\bar{3}m$ diffraction symmetry has been applied to the data and intensity scales are chosen such that the maximum value of $I(\mathbf{Q})$ in each plane is equal to 1. Experimental powder data at $T = 2$ K are shown bottom right.

8.5.2 Magnetic Diffuse-Scattering Data

The neutron-scattering experiments described in Section 8.4.1 provide strong evidence that frustration plays a central role in $\beta\text{-Mn}_{1-x}\text{Co}_x$. Measurements of the $\beta\text{-Mn}_{1-x}\text{Co}_x$ sample at temperature $T = 1.5$ K are shown in four reciprocal-space planes in Fig. 8.2. These data reveal highly-structured magnetic diffuse-scattering patterns, a hallmark of frustrated magnetism [38].

Fig. 8.3 shows the temperature evolution of the magnetic diffuse scattering for the $\beta\text{-Mn}_{0.8}\text{Co}_{0.2}$ sample in the $(110)^*$ plane. Remarkably, the diffuse scattering remains essentially unchanged between 0.05 and 50 K, with no sign of long-range magnetic order at 0.05 K. Preliminary inelastic neutron-scattering measurements [349] indicate the presence

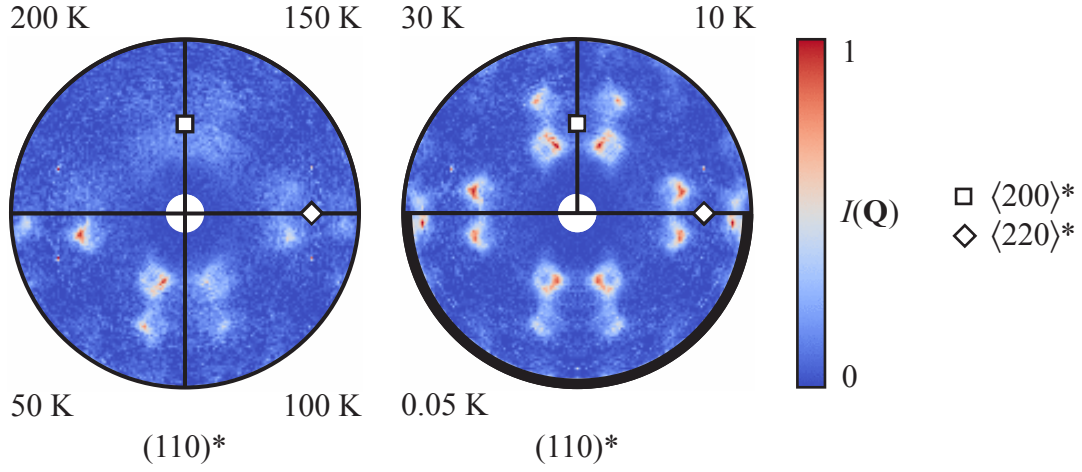


Figure 8.3: Temperature evolution of magnetic diffuse-scattering data for $\beta\text{-Mn}_{0.8}\text{Co}_{0.2}$ in the $(110)^*$ reciprocal-space plane. Temperatures are labelled in the figure. All data except $T = 0.05$ K are shown on the same intensity scale and the $m\bar{3}m$ diffraction symmetry has been applied to the data.

of high-frequency spin fluctuations in $\beta\text{-Mn}_{0.8}\text{Co}_{0.2}$ with significant intensity beyond the energy range of the D7 measurements (~ 3.5 meV) for $T > 50$ K. The presence of a significant inelastic contribution to the scattering means that the quasistatic approximation breaks down at higher temperatures, so it is not possible to perform quantitative fits to the $T > 50$ K data. Qualitatively, however, the presence of broad diffuse features at $T = 200$ K suggests that antiferromagnetically-correlated magnetic moments begin to develop near this temperature, indicating that the energy scale of the magnetic interactions is on the order of a few hundred K.

Single-crystal diffuse-scattering measurements of the $\beta\text{-Mn}_{0.88}\text{Co}_{0.12}$ sample in the $(110)^*$ and $(111)^*$ reciprocal-space planes are shown in Fig. 8.4. Importantly, these measurements show that the form of the diffuse scattering is robust to Co concentration, indicating that the magnetic short-range order is unlikely to result from Co-doping, but is instead an inherent property of $\beta\text{-Mn}$.

8.6 Nearest-Neighbour Model

The results of the previous section suggest two key questions. First, what is the microscopic origin of the persistent magnetic disorder in $\beta\text{-Mn}_{1-x}\text{Co}_x$? Second, what is

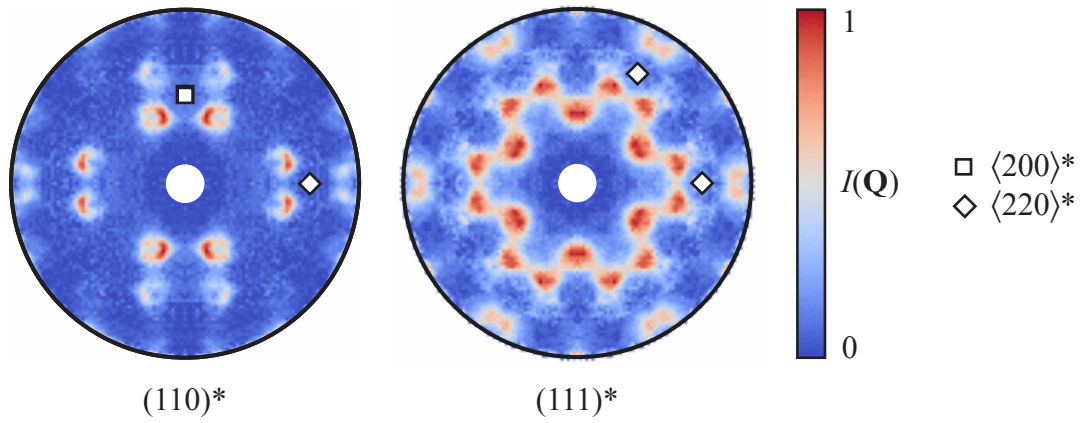


Figure 8.4: Magnetic diffuse-scattering data for $\beta\text{-Mn}_{0.88}\text{Co}_{0.12}$ in the $(110)^*$ and $(111)^*$ reciprocal-space planes. The $m\bar{3}m$ diffraction symmetry has been applied to the data and intensity scales are chosen such that the maximum value of $I(\mathbf{Q})$ in each plane is equal to 1.

the nature of the real-space spin correlations which give rise to the structured diffuse scattering?

The simplest model which might address these points considers only AFM interactions between nearest-neighbour spins of the $12d$ site [334]. At the mean-field level, these interactions lead to a macroscopic degeneracy of magnetic ground states [334]. Fig. 8.5 shows the magnetic diffuse-scattering intensity for this model, calculated in the mean-field approximation [Section 1.4.1.2]. It is clear that the diffuse scattering calculated from the nearest-neighbour model disagrees markedly with the experimental data.

8.7 Reverse Monte Carlo Refinement

In order to develop a more sophisticated model, I used RMC refinement to fit simultaneously to the four single-crystal reciprocal-space planes shown in Fig. 8.5 and the powder neutron-scattering data of Ref. 150. Details of these refinements were given in Section 8.4.2. The refinements make two important assumptions. First, I assume that the spin correlations in $\beta\text{-Mn}_{0.8}\text{Co}_{0.2}$ can be represented by a disordered arrangement of fixed-length spins. This is known as the “effective local moment” approximation [350, 351]. Second, I assume that only the $12d$ site is magnetic; $8c$ spins are not included in the refinement. Nuclear quadrupole resonance experiments provide evidence for the absence

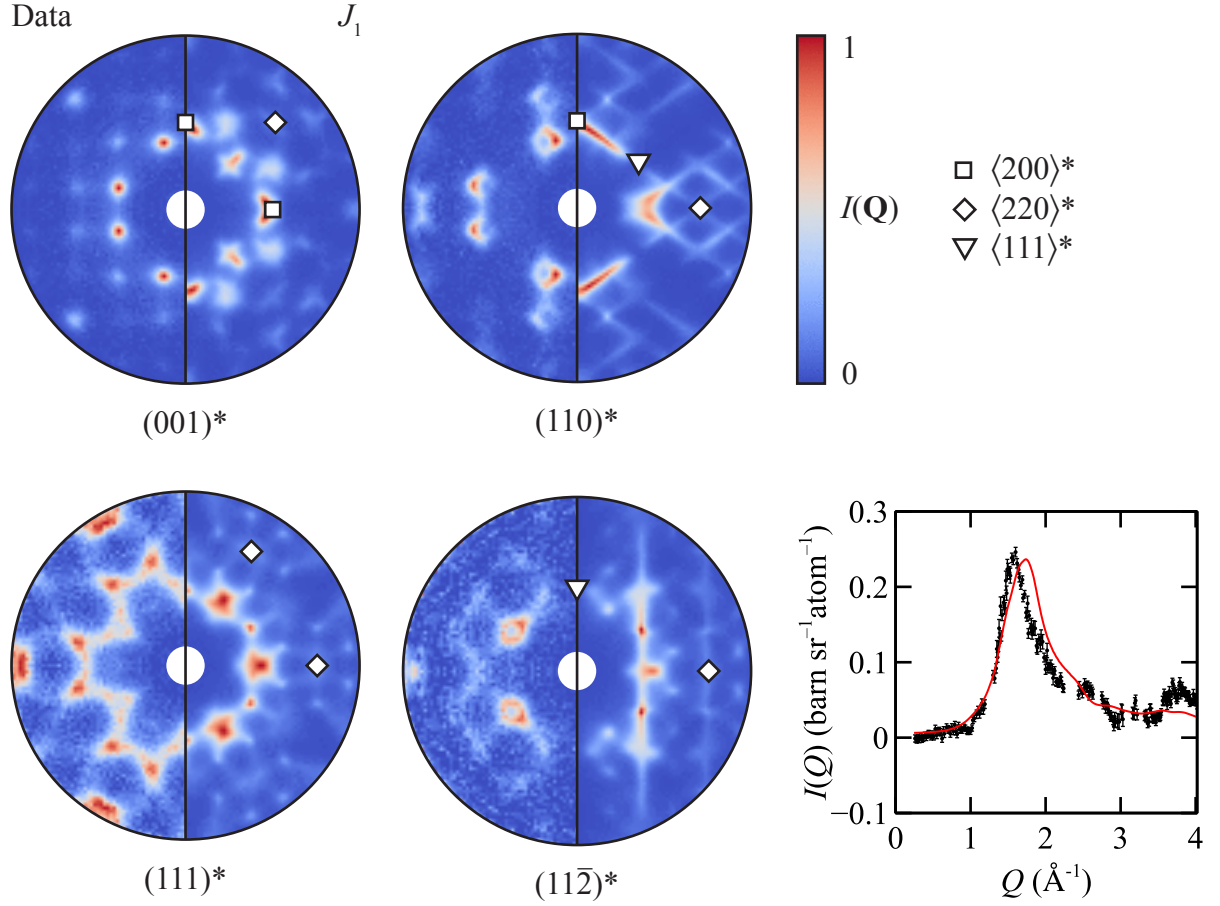


Figure 8.5: Magnetic diffuse-scattering patterns for β -Mn_{0.8}Co_{0.2}. Single-crystal patterns are shown in four reciprocal-space planes, clockwise from top left (001)*, (110)*, (11 $\bar{2}$)*, and (111)*. In each plane, the left panel shows $T = 1.5$ K experimental neutron scattering data and the right panel shows the model with AFM nearest-neighbour interactions J_1 only. The $m\bar{3}m$ diffraction symmetry has been applied to the data and intensity scales are chosen such that the maximum value of $I(\mathbf{Q})$ in each plane is equal to 1. The $T = 2$ K powder pattern is shown bottom right; experimental data are shown as black circles and J_1 model as a red line.

of 8c magnetic moments for both pure β -Mn and Al-doped β -Mn [28, 332]. While these experiments have not been performed for Co-doped β -Mn, the similarity of the powder $I(Q)$ for all three systems suggests that a reasonable starting-point is to assume that the 8c site is non-magnetic in Co-doped β -Mn. I show below that this assumption is compatible with the experimental data, and rule out possible alternative models involving both magnetic sites.

The fit-to-data obtained by RMC refinement is shown in Fig. 8.6. The excellent agreement between data and fit indicates that the spin correlations can be well described within the effective local-moment approximation. The agreement also shows that the data are consistent with the assumption that the 8c site is non-magnetic. This result is, however, in conflict with the conclusions of a previous RMC study using powder data, in which a slightly improved fit-to-data was found when both 8c and 12d spins were included in the refinement [150]. It is important to note that the inclusion of the 8c spins cannot make the fit worse, since it introduces extra degrees of freedom into the model. More importantly, however, I discovered computer-programming errors in the RMC program used in this previous study, which I describe in detail in Appendix A. Once these errors are corrected, the powder data no longer provide any evidence to prefer a model in which both sites are magnetic.

Having obtained spin configurations consistent with experiment, I consider first the radial spin correlation function $\langle \mathbf{S}(0) \cdot \mathbf{S}(r) \rangle$ shown in Fig. 8.7(a). As anticipated from the absence of neutron-scattering intensity near $\mathbf{Q} = \mathbf{0}$, strongly AFM nearest-neighbour correlations are present. However, I find that FM further-neighbour correlations are prominent, and note that FM correlations between fifth-nearest-neighbours are as strong as nearest-neighbour AFM correlations. This finding is perhaps unexpected given conventional descriptions of β -Mn as a frustrated AFM [28], but may nonetheless show some consistency with spin-polarised density-functional theory studies, which predict FM correlations within the 12d Mn sublattice [323].

To investigate the possibility of magnetic anisotropy, I calculated the spin-orientation distribution function from the RMC spin configurations [Fig. 8.7(b)]. Since this function

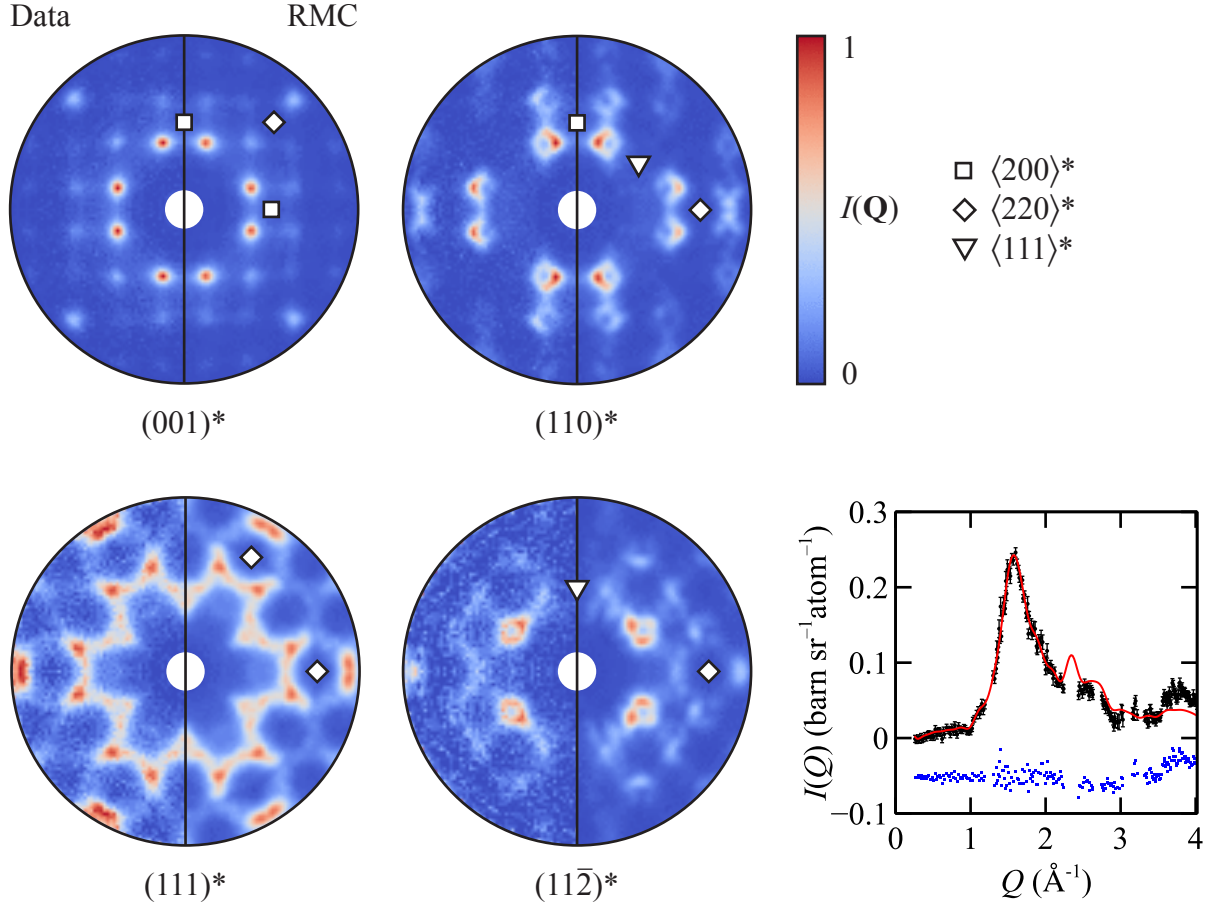


Figure 8.6: Magnetic diffuse-scattering patterns for $\beta\text{-Mn}_{0.8}\text{Co}_{0.2}$. Single-crystal patterns are shown in four reciprocal-space planes, clockwise from top left $(001)^*$, $(110)^*$, $(11\bar{2})^*$, and $(111)^*$. In each plane, the left panel shows $T = 1.5$ K experimental neutron scattering data and the right panel shows the RMC fit to data. The $m\bar{3}m$ diffraction symmetry has been applied to experimental data and RMC fits, and intensity scales are chosen such that the maximum value of $I(\mathbf{Q})$ in each plane is equal to 1. The powder pattern at $T = 2$ K is shown bottom right; experimental data are shown as black circles, RMC fit as a red line, and difference (data–fit) as blue squares.

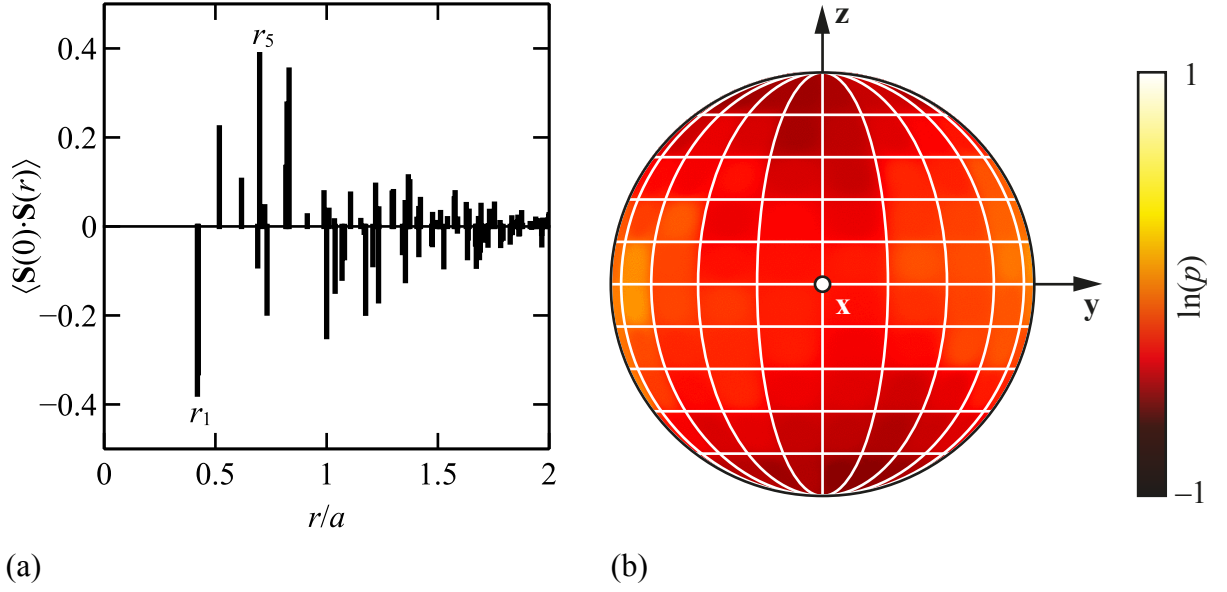


Figure 8.7: (a) Radial spin correlation function $\langle \mathbf{S}(0) \cdot \mathbf{S}(r) \rangle$ calculated from RMC spin configurations. (b) Stereographic projection of the spin-orientation distribution function $\ln(p)$ (defined by Eq. (2.5)) calculated from RMC spin configurations. The coordinate axes are the local axes shown in Fig. 8.1(b).

is expected to have the same twofold point symmetry as the $12d$ site, I make use of the local axes illustrated in Fig. 8.1(b) and listed in Table 8.3, which respect the $12d$ site symmetry. I find a statistically-significant preference for spins to point along the local $\mathbf{y}$ axis, with a reduced spin density along the local $\mathbf{z}$ axis. The magnitude of the anisotropy is rather small: $\ln(p_{\max}) = 0.40(2)$ and $\ln(p_{\min}) = -0.59(6)$, corresponding to an average spin being 2-3 times more likely to align close to the local $\mathbf{y}$ axis compared to the local $\mathbf{z}$ axis (for comparison, the same calculation for GGG yields a factor of several hundred [Section 4.5]). I therefore draw two main conclusions from the initial RMC analysis. First, the presence of strong FM correlations beyond nearest-neighbours suggests that longer-range interactions may well be significant in $\beta\text{-Mn}_{0.8}\text{Co}_{0.2}$. Second, the relatively small magnitude of local magnetic anisotropy suggests that the an effective Heisenberg model may be a reasonable first approximation.

Fractional coordinates	Local axes $\mathbf{x}, \mathbf{y}, \mathbf{z}$
$\left(\frac{1}{8}, y, \frac{1}{4} + y\right)$	$[011], [211], [\bar{1}\bar{1}\bar{1}]$
$\left(\frac{1}{4} + y, \frac{1}{8}, y\right)$	$[101], [\bar{1}21], [\bar{1}\bar{1}\bar{1}]$
$\left(y, \frac{1}{4} + y, \frac{1}{8}\right)$	$[110], [1\bar{1}2], [1\bar{1}\bar{1}]$
$\left(\frac{3}{8}, 1 - y, \frac{3}{4} + y\right)$	$[0\bar{1}\bar{1}], [211], [\bar{1}\bar{1}\bar{1}]$
$\left(\frac{3}{4} + y, \frac{3}{8}, 1 - y\right)$	$[10\bar{1}], [121], [1\bar{1}\bar{1}]$
$\left(1 - y, \frac{3}{4} + y, \frac{3}{8}\right)$	$[\bar{1}10], [112], [11\bar{1}]$
$\left(\frac{5}{8}, \frac{1}{2} - y, \frac{3}{4} - y\right)$	$[0\bar{1}\bar{1}], [2\bar{1}1], [\bar{1}\bar{1}\bar{1}]$
$\left(\frac{3}{4} - y, \frac{5}{8}, \frac{1}{2} - y\right)$	$[\bar{1}0\bar{1}], [12\bar{1}], [1\bar{1}\bar{1}]$
$\left(\frac{1}{2} - y, \frac{3}{4} - y, \frac{5}{8}\right)$	$[\bar{1}\bar{1}0], [\bar{1}\bar{1}2], [\bar{1}\bar{1}\bar{1}]$
$\left(\frac{7}{8}, \frac{1}{2} + y, \frac{1}{4} - y\right)$	$[01\bar{1}], [\bar{2}11], [111]$
$\left(\frac{1}{4} - y, \frac{7}{8}, \frac{1}{2} + y\right)$	$[\bar{1}01], [1\bar{2}1], [111]$
$\left(\frac{1}{2} + y, \frac{1}{4} - y, \frac{7}{8}\right)$	$[1\bar{1}0], [11\bar{2}], [111]$

Table 8.3: Fractional coordinates of $12d$ (Mn2) atoms in the crystallographic unit cell, and their corresponding local axes $\mathbf{x}, \mathbf{y}, \mathbf{z}$ shown in Fig. 8.1(b).

8.8 Interaction Modelling

To complement the RMC refinements described above, I now seek to develop an effective Heisenberg Hamiltonian for $\beta\text{-Mn}_{0.8}\text{Co}_{0.2}$ that captures the key magnetic interactions. The application of a Heisenberg model does not deny the itinerant nature of the magnetism in $\beta\text{-Mn}_{0.8}\text{Co}_{0.2}$; instead, I use the Heisenberg Hamiltonian as a phenomenological model, in which the effects of the Fermi surface geometry and magnetic interactions are mapped onto a small number of effective interaction parameters. A similar effective local-moment approach has been successfully applied in first-principles studies of, e.g., other first-row transition metals [352, 353] and pnictide superconductors [52]. I use the mean-field theory introduced in Section 1.4.1.2 to calculate $I(\mathbf{Q})$ for a given set of J_n [103], and fit the $\{J_n\}$ to experimental data using the least-squares approach described in Section 8.4.2.

A number of different interaction models were tested against the data. I first assumed that only the $12d$ site is magnetic, as for the RMC refinements. In order to minimise the number of parameters, I also constrained the two symmetry-inequivalent J_1 to be equal, since the relevant spin-correlation coefficients obtained from RMC refinement ($-0.3768(2)$ and $-0.3287(5)$) were relatively similar. In order to determine the minimum number of J_n sufficient to describe the data, I plot the dependence of the sum of squared residuals χ^2 on the number of J_n allowed to vary. The results of this procedure are surprising

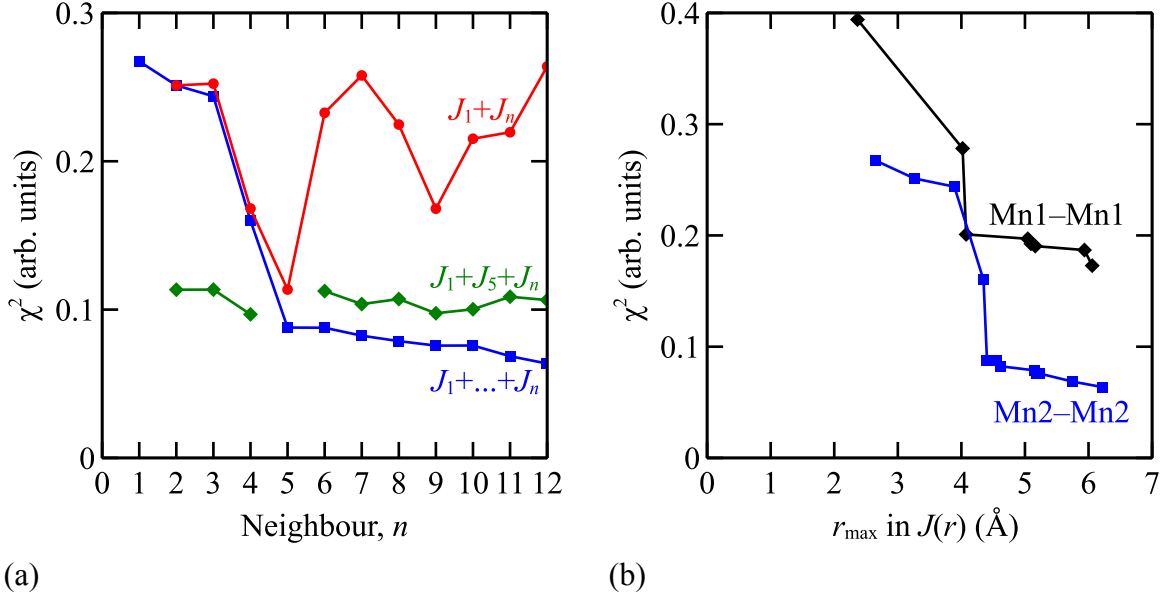


Figure 8.8: (a) Variation of the sum of squared residuals χ^2 as a function of the number of interaction parameters J_n allowed to vary when fitting a Heisenberg model to the data, assuming that only the $12d$ (Mn2) site is magnetic. The χ^2 minimum for $J_1 + J_n$ (red line) at $n = 5$ indicates a good fit to data, which is not significantly improved by allowing a third parameter to vary (green line) or by including all J_n up to $n = 12$ (blue line). (b) Variation of the sum of squared residuals χ^2 as a function of the maximum range of magnetic interactions. The black line (labelled Mn1-Mn1) shows results for interactions within the $8c$ sublattice only, and the blue line (labelled Mn2-Mn2) shows results for interactions within the $12d$ sublattice only.

yet unambiguous [Fig. 8.8(a)]: only two interaction parameters are necessary to obtain qualitative agreement with the data, with the inclusion of up to 10 further parameters leading only to small additional improvements in the fit. I also attempted refinements where the symmetry-inequivalent J_1 were allowed to vary independently, which again resulted in only minor improvements. The two essential parameters are AFM J_1 and FM J_5 , corresponding to the two largest magnitudes of $\langle \mathbf{S}(0) \cdot \mathbf{S}(r) \rangle$ in Fig. 8.7(a). Fig. 8.9 shows calculated magnetic-diffuse scattering patterns for the best-fit ratio $J_5/J_1 = -0.65$. The calculation is for $\lambda_{\max} = 0.991\chi_0$, consistent with previous descriptions of β -Mn as being on the verge of AFM order [327, 328, 354]. The overall agreement with experimental data is remarkable given that the model contains only two interaction parameters.

In order to test my previous assumption of a non-magnetic $8c$ site, Fig. 8.8(b) shows the dependence of χ^2 on the maximum range of the exchange interactions when interactions within either the $8c$ or $12d$ sublattice are included. The fit-to-data is always better in the

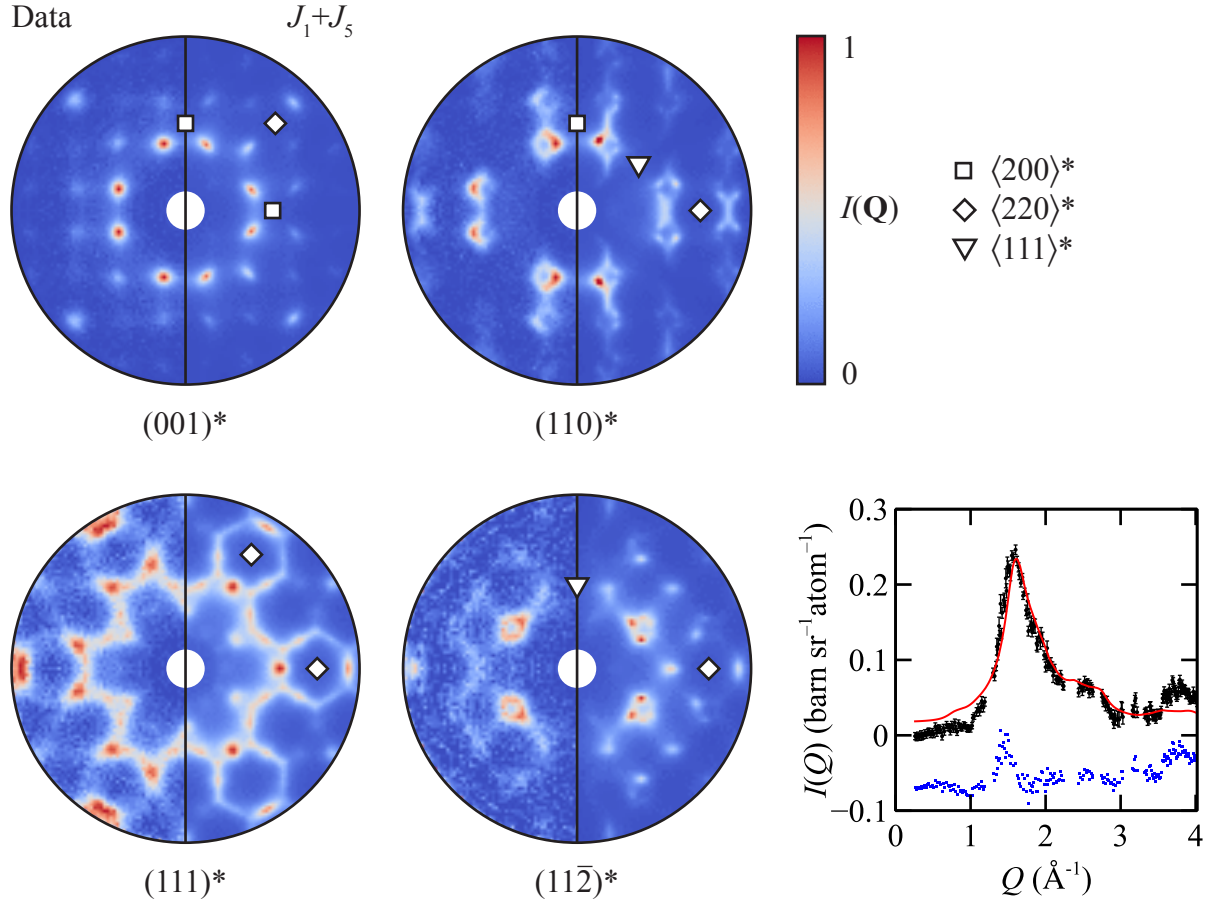


Figure 8.9: Magnetic diffuse-scattering patterns for β -Mn_{0.8}Co_{0.2}. Single-crystal patterns are shown in four reciprocal-space planes, clockwise from top left (001)*, (110)*, (11 $\bar{2}$)*, and (111)*. In each plane, the left panel shows $T = 1.5$ K experimental neutron scattering data and the right panel shows the J_1 - J_5 model described in the text. Intensity scales are chosen such that the maximum value of $I(\mathbf{Q})$ in each plane is equal to 1. The powder pattern at $T = 2$ K is shown bottom right; experimental data are shown as black circles, J_1 - J_5 model as a red line, and difference (data-fit) as blue squares.

latter case, consistent with the dominant contribution to the magnetism arising from the $12d$ site. This does not, however, exclude the possibility that both sites are significantly magnetic—a situation which has been proposed based on spin-polarised density-functional theory calculations, which find FM within each sublattice but AFM coupling between sublattices (i.e., a ferrimagnetic ground state) [323]. If both sites are magnetic, there are six symmetry-inequivalent couplings at short distances (between 2.36 Å and 2.68 Å). I attempted to fit a model to the data in which all six couplings were allowed to vary, but found that the resulting fit was significantly worse ($\chi^2 = 0.17$) than the J_1 - J_5 model despite its much larger number of parameters. I therefore conclude that the experimental data are explained neither by a model in which the $8c$ site dominates the magnetism, nor by short-range ferrimagnetic order.

In principle, it would be desirable to place the interaction parameters J_1 and J_5 on an absolute scale. Unfortunately, this has not proved possible for β - $\text{Mn}_{1-x}\text{Co}_x$. In magnetic insulators, the energy of the magnetic interactions can be obtained using several methods, e.g., by measurement of spin-wave dispersion curves in a magnetically-ordered phase [47], from the temperature-dependence of the magnetic susceptibility [48], or by fitting to the magnetic diffuse scattering [50]. In β - $\text{Mn}_{1-x}\text{Co}_x$, the absence of long-range magnetic order rules out the first approach. The other two approaches both require a model for the non-interacting spin susceptibility, χ_0 . In an insulator, this is given by Curie's law, Eq. (1.7), which is proportional to the squared magnitude of the magnetic moment. In the effective local-moment approach for metals, it is proportional to the mean-squared magnitude of the local moment; unlike in an insulator, however, this quantity may be temperature-dependent, because of longitudinal spin fluctuations [355]. This temperature-dependence could be determined by high-energy inelastic neutron-scattering measurements, but these have not yet been performed for β - $\text{Mn}_{1-x}\text{Co}_x$. At present, the best qualitative indication of the strength of the magnetic interactions is the temperature ~ 200 K at which magnetic diffuse scattering begins to develop [Fig. 8.3].

The J_1 - J_5 Hamiltonian nevertheless helps explain the absence of magnetic order in β - $\text{Mn}_{1-x}\text{Co}_x$. In a conventional magnet, $\lambda_{\max}(\mathbf{q})$ (defined in Section 1.4.1.2) has a global

maximum at some wavevector $\mathbf{k}$ in the first Brillouin zone, and, at the mean-field level, $\mathbf{k}$ is the propagation vector of the first ordered state [117]. By contrast, in a frustrated magnet, $\lambda_{\max}(\mathbf{q})$ is flat in $\mathbf{q}$, preventing the formation of an ordered state [118]. Fig. 8.10 shows the dispersion of the eigenvalues of the interaction matrix $\lambda_{\mu}(\mathbf{q})$ for the J_1 - J_5 model. Three views are shown: a “degeneracy isosurface” showing the $\lambda_{\mu}(\mathbf{q})$ which differ by 2% from the global maximum $\lambda_{\max}(\mathbf{k})$ [Fig. 8.10(a)]; a two-dimensional cut showing the dispersion in the $(hk\frac{1}{2})$ plane [Fig. 8.10(b)]; and the dispersion along high-symmetry directions [Fig. 8.10(c)]. In Fig. 8.10(a), the presence of a large surface close to $\lambda_{\max}(\mathbf{k})$ indicates a large near-degeneracy of ordering wavevectors. This degeneracy is greatest in the $(hk\frac{1}{2})$ reciprocal-space plane shown in Fig. 8.10(b), and is also apparent as a flat region of the maximum eigenvalue between M and R points in Fig. 8.10(c). These results show that $\lambda_{\max}(\mathbf{q})$ in β -Mn_{1-x}Co_x is nearly flat across a large surface in reciprocal space, indicating that frustration of the J_1 - J_5 Hamiltonian is an important factor contributing to the lack of order in β -Mn_{1-x}Co_x. However, the degree of dispersion is greater than for other highly-frustrated magnets (e.g., spin-ice materials [356]), so it is still possible that longitudinal spin fluctuations (not included in this model) may play an additional rôle in suppressing magnetic order. In the mean-field J_1 - J_5 model, the propagation vector of the incipient ordered state has an incommensurate $\mathbf{k} = [k, k, k]^*$, where $k = 0.36(1)$; interestingly, β -Mn_{1-x}Ru_x with $x \geq 0.12$ also orders with $\mathbf{k} = [k, k, k]^*$, where $k = 0.278$ [335].

The form of the degeneracy isosurface in Fig. 8.10(a) is particularly intriguing. When tiled in 3D space, it resembles a tessellation known as a truncated cubic honeycomb—an arrangement of cubes with their corners (located at the R point) truncated by octahedra [357]. The PM susceptibility $\chi(\mathbf{Q})$ may take large values at reciprocal-space positions where $\lambda_{\max}(\mathbf{q})$ approaches $\lambda_{\max}(\mathbf{k})$, so the experimental neutron-scattering patterns [Fig. 8.2] can be seen as projections of the surface shown in Fig. 8.10(a), modulated by the structure factor of the crystal. In the Stoner model of a metal, the locations of peaks in $\chi(\mathbf{Q})$ correspond to nesting vectors of the Fermi surface [40]. It would therefore be useful to perform Fermi-surface measurements of β -Mn_{1-x}Co_x (using, e.g., angle-resolved

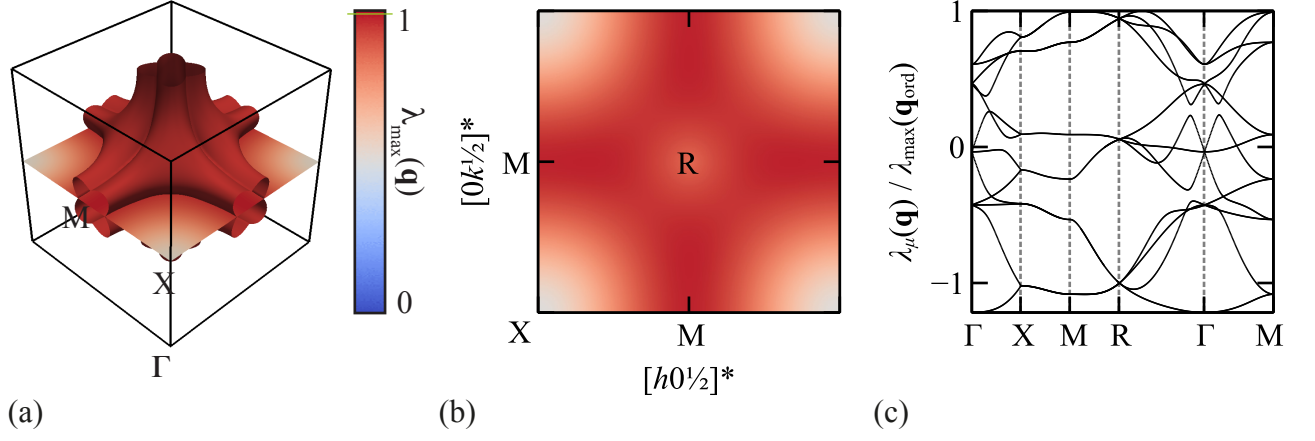


Figure 8.10: (a) Surface in $\mathbf{q}$ -space for which $\lambda_{\max}(\mathbf{q})$ (defined in the text) differs by 2% from the global maximum, $\lambda_{\max}(\mathbf{k})$. (b) Nearly-dispersionless behaviour of $\lambda_{\max}(\mathbf{q})$ in the $(hk\frac{1}{2})$ plane. The scale is chosen such that the maximum and minimum values of $\lambda_{\max}(\mathbf{q})$ in the first Brillouin zone are equal to 1 and 0 respectively. The thin green horizontal line on the scale bar indicates the level at which the isosurface in (a) is plotted. (c) Dispersion of the 12 eigenvalues $\lambda_{\mu}(\mathbf{q})$ of the interaction matrix $\mathbf{J}(\mathbf{q})$ along high-symmetry directions in reciprocal space. The values are scaled relative to the maximum eigenvalue in the Brillouin zone, $\lambda_{\max}(\mathbf{k})$.

photoemission spectroscopy) in order to investigate whether the shape of the degeneracy isosurface is reflected in the Fermi surface [358].

8.9 Emergent Frustration

Having obtained a credible interaction model, I proceed to determine how these interactions are manifest in the spin correlations obtained from RMC refinement. The $\langle \mathbf{S}(0) \cdot \mathbf{S}(r) \rangle$ shown in Fig. 8.7(a) does not suffice for this purpose, because the radial average obscures the relationship of the crystal structure to the spin correlations. I therefore consider the 3D spin correlation function $\langle \mathbf{S}(\mathbf{0}) \cdot \mathbf{S}(\mathbf{r}) \rangle$. To do so, I note first that the J_5 interactions form four sets of helical chains directed along the cubic $\langle 111 \rangle$ directions, of which one set is shown in Fig. 8.11(a). Representing these chains as rods oriented along the helical axis maps a set of helices onto a triangular rod lattice. In this picture, the entire structure is described as four such rod lattices oriented along the cubic $\langle 111 \rangle$ directions, as shown in Fig. 8.11(b). This mapping follows a similar procedure to the one described in Ref. 331.

Fig. 8.11 shows the arrangement of rods relative to the global unit-cell axes; however,

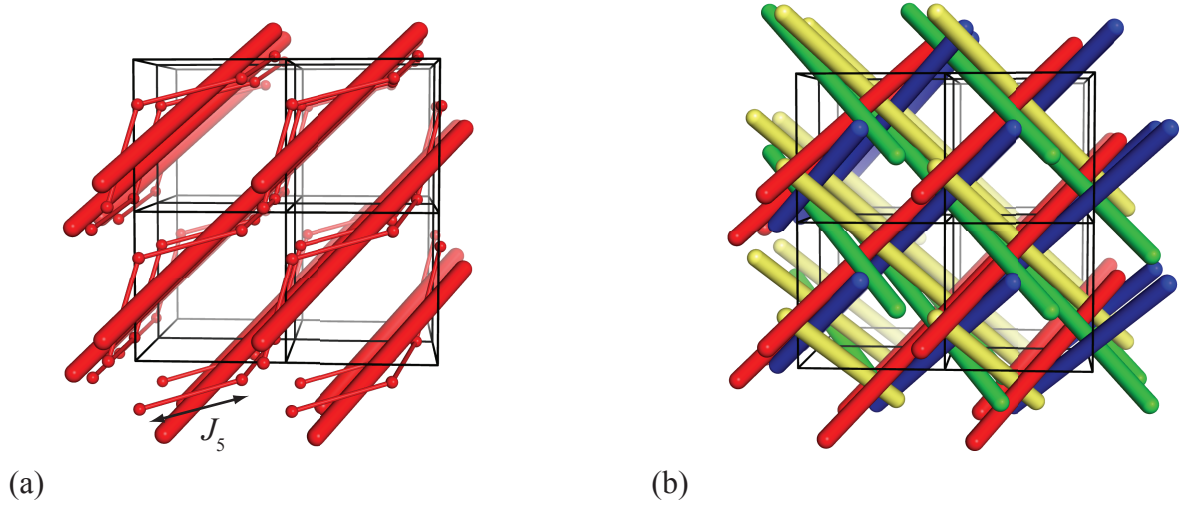


Figure 8.11: Relationship of FM J_5 interactions to unit-cell axes. (a) J_5 interactions couple spins along helical chains, shown as thin red lines. Unit-cell boundaries are shown as black lines. The direction of propagation of each helix is shown as a thick red rod. A set of rods forms a triangular rod lattice directed along one of the four cubic $\langle 111 \rangle$ directions; for clarity, only one of these four sublattices is shown. (b) All four $\langle 111 \rangle$ rod sublattices are now included, with rods parallel to different $\langle 111 \rangle$ directions shown in different colours.

the calculation $\langle \mathbf{S}(\mathbf{0}) \cdot \mathbf{S}(\mathbf{r}) \rangle$ requires a local viewpoint, because $\mathbf{r}$ is defined relative to the position of an arbitrary central atom. I therefore take account of the crystal symmetry by using the local axes $\mathbf{x}, \mathbf{y}, \mathbf{z}$ defined in Table 8.3 and shown in Fig. 8.1(b). The relationship between J_1 and J_5 interactions is shown in local coordinates in Fig. 8.12. In the local coordinate system, the FM J_5 rods propagate parallel to the local $\mathbf{z}$ axis [Fig. 8.12(a)]. The central Mn is coupled by AFM J_1 to two atoms within the same rod sublattice; its four other nearest neighbours belong to the other three rod sublattices [Fig. 8.12(c)].

The mapping of the β -Mn structure onto a rod packing suggests considering the spin correlations in two different orientations: along the J_5 rods, and in the plane perpendicular to them. I consider first the spin correlations along J_5 rods, denoted $\langle \mathbf{S}(\mathbf{0}) \cdot \mathbf{S}(r_z) \rangle$. This quantity represents the correlation of a central Mn spin with its neighbours at distance r_z within the central rod in Fig. 8.12(a). Values of $\langle \mathbf{S}(\mathbf{0}) \cdot \mathbf{S}(r_z) \rangle$ are shown in Fig. 8.12(b): they are always FM, and show an approximately exponential decay as a function of r_z with correlation length $\xi_z = 3.510(5) \text{ \AA}$. This trivial r_z dependence means that it is possible to interpret a rod as behaving like a single collective object, and to calculate the summed spin correlation value $\langle \boldsymbol{\sigma}(\mathbf{0}) \cdot \boldsymbol{\sigma}(\mathbf{r}_{xy}) \rangle = \sum_{\mathbf{r} \in \text{rod}} \langle \mathbf{S}(\mathbf{0}) \cdot \mathbf{S}(\mathbf{r}) \rangle$, where the sum is over all

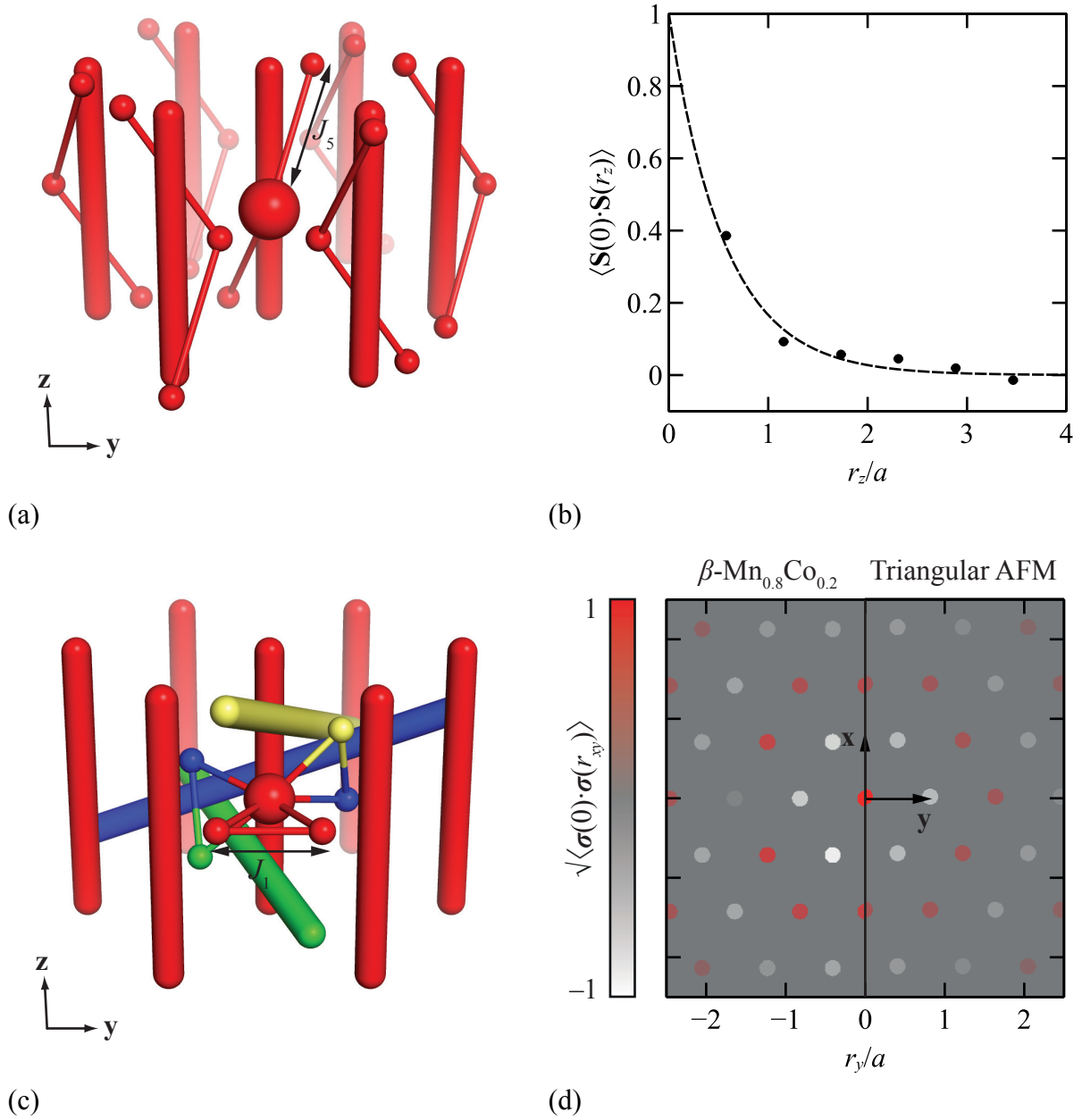


Figure 8.12: (a) FM J_5 interactions couple spins along helical chains, shown as thin red lines. The direction of propagation of each chain is shown as a thick red rod. The complete crystal structure can be described as four rod sublattices, each of which describes a triangular rod lattice. For clarity, only a single rod sublattice is shown. (b) Spin correlations $\langle \mathbf{S}(0) \cdot \mathbf{S}(r_z) \rangle$ along J_5 rods are FM and decay exponentially with distance r_z along the rod. (c) AFM J_1 interactions, shown as thin lines, couple spins from adjacent rods. An arbitrary central Mn atom, shown as a large red sphere, is coupled to two atoms within the same rod sublattice (coloured red); its four other nearest neighbours belong to the other three rod sublattices (coloured green, blue and yellow). (d) The left panel shows spin correlations $\langle \sigma(0) \cdot \sigma(r_{xy}) \rangle$ perpendicular to J_5 rods. Values shown represent a sum along each rod, as described in the text, and are normalised by $\langle |\sigma(0)|^2 \rangle$. The spin correlations alternate between AFM and FM throughout the triangular rod lattice. The right panel shows spin correlations $\langle \sigma(0) \cdot \sigma(r_{xy}) \rangle$ for a frustrated AFM Heisenberg model on the triangular lattice (described in the text).

correlations within the helical chain centred at $\mathbf{r}_{xy}$ and directed along z . These sums do not diverge because the FM correlations have finite length. Values of $\langle \boldsymbol{\sigma}(\mathbf{0}) \cdot \boldsymbol{\sigma}(\mathbf{r}_{xy}) \rangle$ are shown in Fig. 8.12(d) (left panel). The sign of $\langle \boldsymbol{\sigma}(\mathbf{0}) \cdot \boldsymbol{\sigma}(\mathbf{r}_{xy}) \rangle$ alternates throughout the triangular rod packing, because adjacent rods are coupled by J_1 . This pattern strongly resembles the $\langle \boldsymbol{\sigma}(\mathbf{0}) \cdot \boldsymbol{\sigma}(\mathbf{r}_{xy}) \rangle$ calculated for an AFM Heisenberg model on the triangular lattice [2, 218, 346], shown in Fig. 8.12(d) (right panel). The triangular-lattice calculation (described in Section 8.4.2) uses a ratio of next-nearest-neighbour to nearest-neighbour interactions $J_{\text{nnn}}/J_{\text{nn}} = 0.125$ at $T = 0.375|J_{\text{nn}}|$. I therefore suggest that the comparable strength of J_1 and J_5 leads, over short length scales, to frustration of multi-spin rods on a triangular lattice. This emergent behaviour contrasts with the frustration of single spins on a hyperkagome lattice which would result from a J_1 -only model [334].

It follows from the definition of the local coordinate axes that the spin correlations shown in Fig. 8.12(d) represent the correlations within any one of the four triangular rod sublattices. All four sublattices are shown in cartoon form in Fig. 8.13(a); the relative orientation of arrows indicates the alternation of FM and AFM correlations within a sublattice. Considering now correlations between different sublattices, a trend is for adjacent rod sublattices to be antiferromagnetically correlated, due to J_1 couplings between different sublattices. I speculate that this results in an additional contribution to frustration, since it is easy to identify sets of three rods from different sublattices which are connected by AFM J_1 ; an example of such an arrangement is shown in Fig. 8.13(b).

8.10 Conclusions

The identification of strong magnetic frustration and emergent spin structures in the compositionally-simple system $\beta\text{-Mn}_{1-x}\text{Co}_x$ provides a valuable experimental reference-point against which to benchmark developments in the theory of unconventional metals [354, 359]. My results may provide a tantalising glimpse at the behaviour of elemental $\beta\text{-Mn}$ itself: the magnetic diffuse scattering is robust to Co concentration in the range for which single crystals can be prepared, and the Q -dependence of the diffuse scattering from powder samples remains essentially unchanged for the entire range of Co concentration

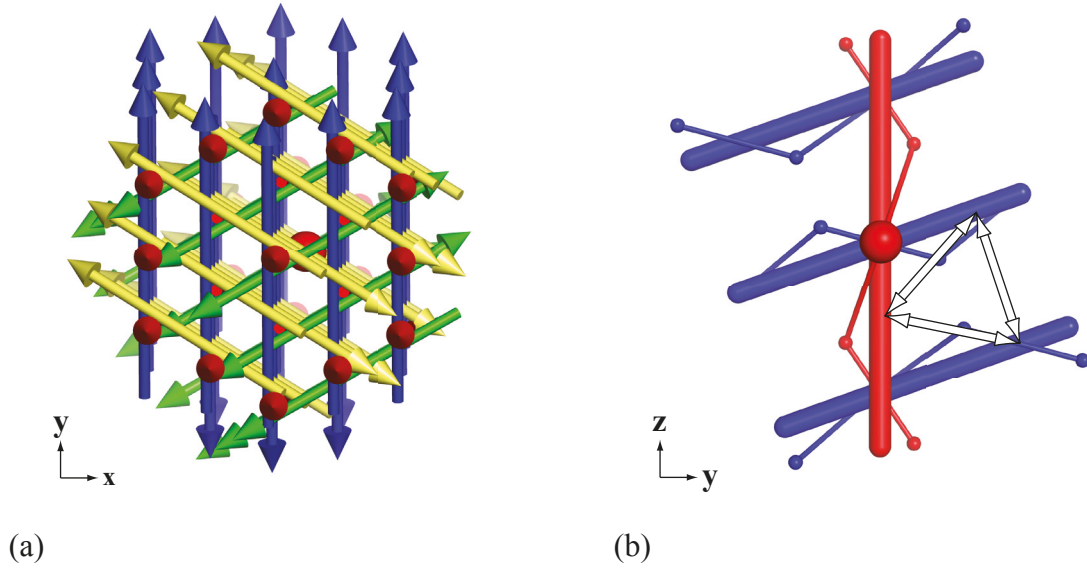


Figure 8.13: (a) Pictorial representation of the spin correlation function in $\beta\text{-Mn}_{0.8}\text{Co}_{0.2}$. Helices along different $\langle 111 \rangle$ directions are shown as parallel rods of different colours. The sign of the spin correlations within each helix is indicated by the orientation of its rod, showing alternating shells of FM/AFM correlations along each direction. (b) Rods from different sublattices are coupled by AFM J_1 in a frustrated manner.

from zero to 20%, with only an increase in the static magnetic moment evident on doping [28, 150]. The observation of spin structures resembling the canonical triangular AFM in $\beta\text{-Mn}_{1-x}\text{Co}_x$ reverses a paradigm of frustrated magnetism exemplified by the metallic pyrochlore YMn_2 [27, 80]—namely, that emergent states tend to be found in materials with simple frustrated crystal structures. There are hints here of a more general phenomenon: the emergence of collective states within complex networks has also been observed in fields as diverse as neural signalling [360] and the dynamics of amorphous materials [361]. Hence a focus on structural complexity may prove an important experimental strategy for realising new states of correlated matter [362].

Chapter 9

Conclusion and Outlook

9.1 Concluding Remarks

In Section 1.5, I identified three key aims for this thesis: (i) to evaluate the effectiveness of RMC refinement to magnetic diffuse-scattering data (both powder and single-crystal) for spin liquids; (ii) to develop new approaches to visualise spin-liquid states; and (iii) to use these developments to identify unexpected collective phenomena in a wide range of frustrated spin systems. In this concluding chapter, I assess the success with which these aims have been met, and suggest some possible directions in which the work of this thesis could be extended.

First, I conclude that RMC refinement is very successful in recovering magnetic information from powder diffuse-scattering data. In all the cases I considered, RMC refinement allowed essentially-quantitative recovery of the radial spin correlation function from powder diffuse-scattering data. More surprisingly, the method also allows the 3D spin correlation function and the single-crystal scattering pattern to be qualitatively recovered. Moreover, I recover qualitative information about the anisotropy of spin orientations, and about higher-order spin correlations. These results are demonstrated for simulated diffuse-scattering data in Chapter 2 and Ref. 152, and borne out in practice by the excellent agreement between RMC results and calculations using traditional (model-dependent) methods for both $\text{Ca}_3\text{Co}_2\text{O}_6$ [Chapter 3] and GGG [Chapter 4]. Good results are also obtained for RMC refinement to single-crystal diffuse-scattering data, provided

that the data cover a large volume of reciprocal space; however, refinement to restricted regions of reciprocal space leads to disappointing results [Chapter 6].

My second conclusion is that PM spin correlations can be successfully visualised in real space using several approaches. The presence of single-ion spin anisotropy can be shown using stereographic projections of the spin-orientation distribution function. The spin-pair correlations are completely characterised by the 3D spin correlation function $\langle \mathbf{S}(\mathbf{0}) \cdot \mathbf{S}(\mathbf{r}) \rangle$. Together, these quantities provide a fairly complete description of PM spin structures, although higher-order correlations may also be important in some cases [Chapter 4].

Finally, I aimed to use RMC refinement, combined with real-space visualisation techniques, to understand real materials. These results form the main part of this thesis, and specific conclusions are given for each system at the end of chapters 3–5, 7 and 8. Here, I therefore make some general observations. First, a key benefit of calculating real-space functions is to allow connections to be made between the real-space spin structures and the scattering pattern. In this way, similarities can be recognised between apparently-disparate materials. For example, I find that the frustration of FM “rods” on a triangular lattice, with AFM coupling between different rods, is key to the behaviour of both $\text{Ca}_3\text{Co}_2\text{O}_6$ and Co-doped β -Mn. Second, I observe that the $\langle \mathbf{S}(\mathbf{0}) \cdot \mathbf{S}(\mathbf{r}) \rangle$ often shows a strong directional dependence at distances much greater than the radial spin correlation length, even for weakly-frustrated spin systems such as MnO [Chapter 7]. Finally, a close examination of real-space structure can allow emergent phenomena, such as “hidden order” in GGG, to be identified [Chapter 4].

9.2 Future Possibilities

In this section, I suggest some possible avenues for future work which draws on the results of this thesis.

9.2.1 RMC Refinement to Powder Data

There are several systems in which RMC refinement to powder diffuse-scattering data may prove useful. For example, the $S = \frac{1}{2}$ kagome system kapellasite was recently synthesised [363], with bulk properties and inelastic neutron scattering measurements suggesting a quantum spin-liquid phase [364]. In the absence of single-crystal samples, RMC refinement of powder data would allow detailed characterisation of these spin-liquid correlations. Second, the “metallic spin ice” $\text{Pr}_2\text{Ir}_2\text{O}_7$ [29] exhibits a range of seemingly-unique properties, including a spontaneous Hall effect in the PM phase suggestive of chiral order [230]. While powder diffuse-scattering data are not directly sensitive to such effects, the results of Chapter 4 suggest that RMC refinement could possess some indirect sensitivity to chiral order (or identify a different explanation for the observed phenomena). Only small single crystals ($\sim 1 \text{ mm}^3$) are reported [365], so RMC refinement to powder-diffraction data would allow a valuable comparison of the calculated $I(\mathbf{Q})$ with microscopic models [366]. Furthermore, the ability of RMC refinement to use a structural model containing non-magnetic impurities would allow studies of canonical frustrated spin glasses such as $\text{SrCr}_{9x}\text{Ga}_{12-9x}\text{O}_{19}$ (SCGO) (see, e.g., [367, 368]) and $\text{Ba}_2\text{Sn}_2\text{ZnGa}_{10-7x}\text{Cr}_{7x}\text{O}_{22}$ (BSZCGO) [369]: a model of the structural disorder could be produced using, e.g., pair-distribution function techniques [104, 123], and this structural model used as a starting-point for RMC refinement of magnetic diffraction data. In this way, the impact of the structural disorder on the magnetic correlations could be compared with theoretical models [370].

9.2.2 Application to Structural Disorder

The results of Section 6.2 are given for RMC refinement of single-crystal magnetic diffuse-scattering data. They are, however, straightforwardly modified to allow refinement of correlated *structural* disorder in non-magnetic materials. The modification essentially involves mapping spin orientations onto atomic displacements by making the substitution

$$\mathbf{S}_i^\perp \rightarrow \exp(i\mathbf{Q} \cdot \mathbf{d}_i),$$

where $\mathbf{d}_i$ is the displacement of atom i from its average position. Such RMC refinements could potentially be driven by single-crystal X-ray diffuse-scattering data collected on lab-based single-crystal diffractometers [299].

It is also possible to modify the mean-field equations given in Section 1.4.1.2 in order to allow the structural diffuse-scattering pattern to be rapidly calculated for a set of effective pairwise interaction potentials. The calculation proceeds by expanding the nuclear scattering factor as a power series in $\langle \exp[\mathbf{i}\mathbf{Q} \cdot (\mathbf{d}_j - \mathbf{d}_i)] \rangle$ and keeping terms up to first order [60]. For isotropic displacements of atoms of a single element, this yields

$$I_{\text{coh}}(\mathbf{Q}) = b_{\text{coh}}^2 \exp(-U_{\text{iso}}Q^2) \sum_{i,j} \langle \mathbf{Q} \cdot \mathbf{d}_i \rangle \langle \mathbf{Q} \cdot \mathbf{d}_j \rangle \exp(\mathbf{i}\mathbf{Q} \cdot \mathbf{r}_{ij}),$$

where $\mathbf{r}_{ij} = \mathbf{r}_j - \mathbf{r}_i$ is the displacement between the average positions of atoms i and j . Proceeding by analogy with Section 1.4.1.2, I obtain for isotropic displacements

$$I_{\text{coh}}(\mathbf{Q}) \propto \sum_{\mu} \frac{|F_{\text{nuc}}^{\mu}(\mathbf{Q})|^2}{1 - D\lambda^{\mu}(\mathbf{Q})},$$

where

$$F_{\text{nuc}}^{\mu}(\mathbf{Q}) = \sum_{\rho} Q U_{\rho}^{\mu}(\mathbf{Q}) \exp(\mathbf{i}\mathbf{Q} \cdot \mathbf{r}_{\rho}),$$

and D is constant at fixed temperature. A similar result can be obtained for displacements along specified directions, analogous to an Ising spin system. These results (which do not appear to have been given in the literature) could be used to refine effective pairwise interaction constants to diffuse-scattering data for systems such as charge ices [299, 371] and to revisit canonical disordered crystals such as stabilised zirconias [372, 373].

9.2.3 RMC Refinement to Inelastic Neutron-Scattering Data

A third natural extension of the methodology developed in this thesis would be to refine to inelastic neutron-scattering data. Conventional refinement to the total-scattering intensity $I(\mathbf{Q})$ produces spin configuration which represent an instantaneous “snapshot” of spin correlations [Section 1.3.3]. If the refinement is driven instead by $I(\mathbf{Q}, \omega)$, where ω

is kept fixed, then the refined spin configurations will provide a real-space image of spin fluctuations with energy ω . In practice, the measured $I(\mathbf{Q}, \omega)$ could be separated into a series of constant- ω slices, and each slice refined using RMC. Such a process would allow the “dynamical spin correlation function” $\langle \mathbf{S}(0, \omega) \cdot \mathbf{S}(r, \omega) \rangle$ to be determined: this function is the magnetic analogue of the “dynamical pair-distribution function” introduced in recent work [374, 375], and describes short-range spin fluctuations of a given energy. This function may contain important information in systems such as high-temperature superconductors, in which long-range magnetic order is often absent, but disordered “spin stripes” are nevertheless believed to exist as fluctuations over a limited energy range [317].

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Appendix A

Supporting Information for Chapter 8

In Chapter 8, I obtained good fits to both powder and single-crystal neutron-scattering data on $\beta\text{-Mn}_{1-x}\text{Co}_x$ using a model in which only the $12d$ (Mn2) site is magnetic. This result is inconsistent with a previous experimental study of $\beta\text{-Mn}_{1-x}\text{Co}_x$ using powder neutron diffraction, Ref. A.1 In that study, the authors reported a somewhat better fit-to-data if moments were present on both sites. In order to understand this apparent contradiction with the new results presented here, I re-analysed the data of Ref. A.1 During this process I identified errors in Ref. A.1 which affect the conclusions drawn in that work.

I begin by summarising the analysis of Ref. A.1. There, RMC refinement was used to fit to powder diffuse-scattering data for $\beta\text{-Mn}_{1-x}\text{Co}_x$. Various Co concentrations were analysed, but particular attention was given to the 20% alloy which was also the main subject of Chapter 8. I therefore restrict my discussion to $\beta\text{-Mn}_{0.8}\text{Co}_{0.2}$ [Figs. 4 and 6, and top panel of Fig. 5, in Ref. A.1]. In Ref. A.1, RMC refinements were attempted using two different models. Initially, it was assumed that magnetic moments existed only on the $12d$ site, with the $8c$ site non-magnetic. This model was found to give a relatively poor fit to data, with $\chi^2 = 6.52$ [dashed line in Fig. 4 in Ref. A.1]. The authors then considered a model with equal magnetic moments on both the $8c$ and $12d$ sites. This model gave an improved fit to data, with $\chi^2 = 3.08$ [solid line in Fig. 4 in Ref. A.1]. On this basis, it was concluded in Ref. A.1 that the both the $8c$ and $12d$ sites are likely to be magnetic.

In order to make clear the nature of the errors in Ref. A.1, I first present the main equations. In the $12d$ -only model considered initially in Ref. A.1, the magnetic atoms occupy a single crystallographic site. In this case the spin correlation function is given by

$$\langle \mathbf{S}(0) \cdot \mathbf{S}(r) \rangle = \frac{1}{NZ(r)} \sum_i^N \sum_j^{Z(r)} \mathbf{S}_i \cdot \mathbf{S}_j, \quad (\text{A.1})$$

where the coordination number $Z(r)$ is the number of spins $\mathbf{S}_j$ at radial distance r from a spin $\mathbf{S}_i$ at the origin. The sum over j runs over the coordination number, and the sum over i runs over all N spins. The normalisation factor $NZ(r) \equiv n(r)$ is then the total number of radial distances of length r between pairs of spins in the RMC supercell. (I note that, unlike Ref. A.1 here I write spins as unit vectors, so that the factors of $\sqrt{S(S+1)}$ which are present in Ref. A.1 are absorbed into the $\mathbf{S}_i$.)

In the $8c+12d$ model considered in Ref. A.1, the magnetic atoms occupy two inequivalent crystallographic sites ($N_s = 2$), each with a different number of atoms in the RMC supercell: $N_1 = 8L^3$, $N_2 = 12L^3$, where L^3 is the number of unit cells in the RMC supercell. In Ref. A.1 partial spin correlation functions were defined for each pair of spin-types

$\rho, \sigma \in \{1, 2\}$:

$$\langle \mathbf{S}(0) \cdot \mathbf{S}(r) \rangle_{\rho\sigma} = \frac{1}{N_\rho Z_{\rho\sigma}(r)} \sum_i^{N_\rho} \sum_j^{Z_{\rho\sigma}(r)} \mathbf{S}_i^\rho \cdot \mathbf{S}_j^\sigma. \quad (\text{A.2})$$

Here, N_ρ is the number of spins of type ρ . The coordination number $Z_{\rho\sigma}(r)$ is the number of spins of type σ at radial distance r from a spin of type ρ at the origin. Accordingly, the normalisation factor $N_\rho Z_{\rho\sigma}(r) \equiv n_{\rho\sigma}(r)$ is the number of equivalent distances between spin-type ρ and spin-type σ . We have that

$$N_\rho Z_{\rho\sigma}(r) = N_\sigma Z_{\sigma\rho}(r), \quad (\text{A.3})$$

so for the β -Mn structure $Z_{12}(r) = \frac{3}{2}Z_{21}(r)$, i.e., the coordination number is not uniquely defined for $8c$ - $12d$ distances. It is also possible to define a total spin correlation function as the average over partial spin correlation functions:

$$\begin{aligned} \langle \mathbf{S}(0) \cdot \mathbf{S}(r) \rangle &= \frac{1}{n(r)} \sum_\rho^{N_s} \sum_\sigma^{N_s} n_{\rho\sigma}(r) \langle \mathbf{S}(0) \cdot \mathbf{S}(r) \rangle_{\rho\sigma}, \\ n(r) &= \sum_\rho^{N_s} \sum_\sigma^{N_s} N_\rho Z_{\rho\sigma}(r). \end{aligned} \quad (\text{A.4})$$

In the $8c+12d$ model of Ref. A.1, it was assumed that the two crystallographic sites have identical magnetic properties (magnetic form factors and magnetic moments). In this case, the powder magnetic scattering intensity $I(Q)$ for an isotropic magnet can be written in terms of the total spin correlation function:

$$I(Q) \propto [f(Q)]^2 \left[1 + \frac{1}{N} \sum_r n(r) \langle \mathbf{S}(0) \cdot \mathbf{S}(r) \rangle \frac{\sin(Qr)}{Qr} \right]. \quad (\text{A.5})$$

This is the form which should have been fitted to data in Ref. A.1. However, the equation which was actually fitted to the data (given on page 3 of Ref. A.1) further assumes that the magnetic atoms occupy only a single crystallographic site. In this particular case, we have that $n(r) = NZ(r)$, and Eq. (A.5) simplifies to

$$I(Q) \propto [f(Q)]^2 \left[1 + \sum_r Z(r) \langle \mathbf{S}(0) \cdot \mathbf{S}(r) \rangle \frac{\sin(Qr)}{Qr} \right]. \quad (\text{A.6})$$

This equation is appropriate for the $12d$ -only model, but is not correct for the $8c+12d$ model to which it was applied in Ref. A.1. For example, Eq. (A.6) fails to recognise that the $12d$ site will make a greater total contribution to the magnetic scattering intensity, since there are more $12d$ spins than $8c$ spins. It also fails to take into account that $Z(r)$ is not uniquely defined for $8c$ - $12d$ distances, for which $Z_{12}(r) = \frac{3}{2}Z_{21}(r)$. For these distances, Ref. A.1 assumed that $Z(r) = Z_{12}(r)$.

I consider the implications of this error by calculating the powder diffuse-scattering pattern from the RMC spin configuration of Ref. A.1 in two ways: first, replicating the error of Ref. A.1 by using Eq. (A.6); second, using the correct formula, Eq. (A.5). These calculations are compared with the experimental powder data in Fig. A.1(a). The two calculated curves are very different, indicating that the error has a major effect. Therefore, I conclude that the correlation functions which are derived from the RMC spin

configuration [Figs. 5 and 6 in Ref. A.1] do not accurately reflect the spin correlations in the real material.

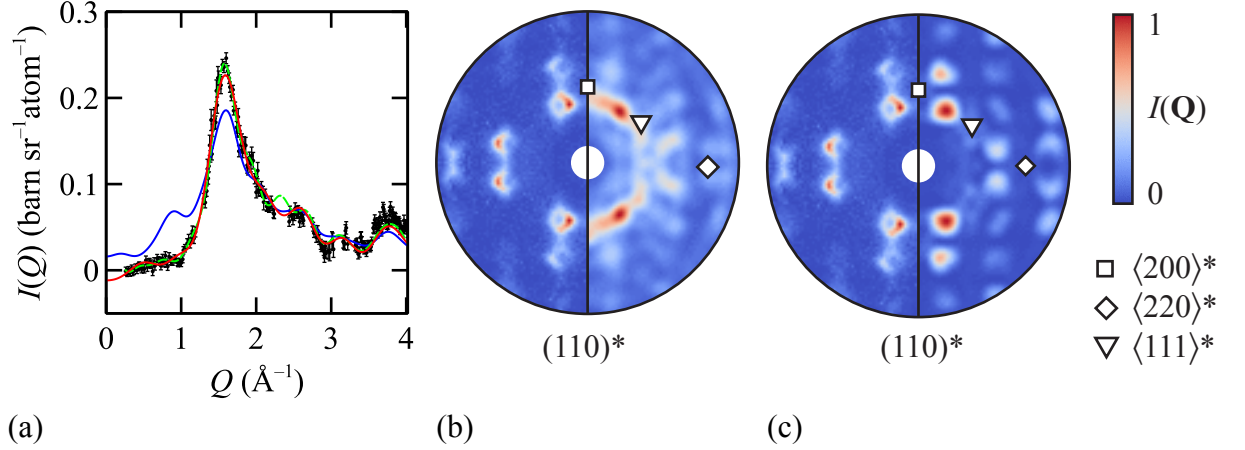


Figure A.1: (a) Comparison of the fit to powder data calculated from the RMC spin configuration for the $8c+12d$ refinement of Ref. A.1. Black circles are experimental data points. The red line is the original fit shown in the paper, which was calculated using an incorrect equation for the scattering intensity, Eq. A.6. The blue line is the fit calculated from the same spin configuration using the correct equation for the scattering intensity, Eq. A.5. The green line shows a new fit using the code of this thesis. (b) Calculated single-crystal scattering pattern in the $(110)^*$ plane from the $8c+12d$ RMC spin configuration of Ref. A.1 (right panel) compared with experimental data (left panel). (c) Calculated single-crystal scattering pattern in the $(110)^*$ plane from new $12d$ -only RMC refinement (right panel) compared with experimental data (left panel).

The error discussed above relates only to the $8c+12d$ refinement in Ref. A.1, and has no effect on the $12d$ -only refinement which was first attempted. However, I also found that an unrelated computer-programming error was present for the $12d$ -only refinement alone, which meant the spins were incorrectly normalised to have length $[S(S+1)]^{-1/2}$, rather than unit length. Since errors were present in both RMC refinements, it is not possible to draw any conclusions from the relative goodness-of-fit about the $12d$ -only *vs.* $8c+12d$ models. In particular, the poor fit-to-data of the initial $12d$ -only model may have been due to errors in the RMC program. To test this, I repeated the initial RMC refinement of Ref. A.1 with the refinement program used in the previous chapters of this thesis, again assuming that only the $12d$ site is magnetic. The fit to data I now obtain is shown in Fig. A.1(a). This new fit shows essentially perfect agreement with the data, with $\chi^2 = 2.1$ —a value significantly lower than for either of the refinements given in Ref. A.1. As a second check, I also corrected the errors in the original code of Ref. A.1 and repeated the refinements: the results obtained (not shown) now agree with the code used in this thesis. As a final check, I calculated the single-crystal diffuse scattering from the spin configurations for the original $8c+12d$ refinement of Ref. A.1, and the spin configurations for the new $12d$ -only refinement. These calculations are shown in Fig. A.1(b) and Fig. A.1(c), respectively. The single-crystal diffuse scattering for the refinement of Ref. A.1 does not agree with the experimental data, but the single-crystal diffuse scattering for the new refinement shows much better agreement. This provides further evidence that the refinements of Ref. A.1 do not reproduce the spin correlations of the real material.

I therefore conclude that the poor fits obtained in Ref. A.1 arise from errors in the computer code used for the original RMC refinements. Once these errors are corrected, the data of Ref. A.1 provide no reason to prefer a model with magnetic moments on both $12d$ and $8c$ sites over the $12d$ -only model.

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