

Neutron scattering studies of low-dimensional quantum magnets



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Thesis submitted for the degree of
Doctor of Philosophy

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Dedicated to my mother, Janice, my sister, Sally,
and the memory of my father, Duncan.

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This thesis presents studies of the spin dynamics in quantum magnets using inelastic neutron scattering (INS) and linear spin wave theory (LSWT). The first system considered is $\text{Ba}_2\text{CuTeO}_6$, proposed to realise weakly-coupled antiferromagnetic two-leg spin- $\frac{1}{2}$ ladders. $\text{Ba}_2\text{CuTeO}_6$ orders magnetically, but with a small Néel temperature relative to the exchange strength, suggesting that the interladder couplings are only just able to stabilise magnetic order and placing $\text{Ba}_2\text{CuTeO}_6$ close in parameter space to the critical point separating the singlet phase and Néel order. By comparing powder INS data with LSWT and quantum Monte Carlo (QMC) calculations, values are proposed for all relevant exchange parameters, which place the system on the ordered side of the phase diagram in proximity to the critical point. High-field magnetisation data are also compared with the QMC predictions. In addition, single-crystal INS measurements are presented of the spin- $\frac{1}{2}$ triangular antiferromagnet $\text{Ba}_3\text{CoSb}_2\text{O}_9$. Sharp magnons are observed throughout the Brillouin zone with a strong scattering continuum extending up to at least $4\times$ the maximum one-magnon energy. The magnon energies are strongly renormalised downwards and the intensity decreases faster upon increasing energy than predicted by LSWT, which is attributed to a transfer of spectral weight to the continuum. An empirical model of renormalisations to the LSWT dispersion is proposed that can capture quantitatively the magnon dispersions throughout the Brillouin zone. Consistent with the observation of sharp magnons throughout, it is explicitly verified that kinematic constraints disallow one $\rightarrow$ two-magnon decays for this renormalised dispersion. There is considerable structure and signal extending to much higher energies that cannot be explained by two-magnon simulations, suggesting significant quantum fluctuations beyond LSWT. The magnon dispersions have also been measured in fields up to 9 T, observing an evolution of the dispersion relations in field that is consistent with the presence of two equal-weight domains of opposite chirality.

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Chapter 1

Introduction

This thesis presents inelastic neutron scattering (INS) studies of the spin dynamics in two low-dimensional spin- $\frac{1}{2}$ systems: the coupled ladder antiferromagnet $\text{Ba}_2\text{CuTeO}_6$ and the triangular antiferromagnet $\text{Ba}_3\text{CoSb}_2\text{O}_9$. The following two chapters introduce relevant theoretical principles and experimental methods. Chapter 2 discusses key concepts in quantum magnetism, from the origin of permanent magnetic moments in insulators, to the exchange interactions between them, the resulting magnetic order, and finally, spin wave excitations. Chapter 3 then provides an overview of neutron scattering, including derivations of the nuclear and magnetic scattering cross-sections and relevant experimental techniques.

Powder INS measurements of the spin dynamics in $\text{Ba}_2\text{CuTeO}_6$ are presented in Chapter 4, showing the key features of the dynamics over the full bandwidth of the magnetic excitations, as well as high-resolution measurements of the low-energy dynamics. The linear spin wave theory (LSWT) calculation of the dispersion relations and dynamical structure factor is detailed for two-leg ladders arranged in planes stacked vertically, proposed by *ab initio* calculations to capture the magnetism of $\text{Ba}_2\text{CuTeO}_6$. Through quantitative comparison with the observed INS data, values for the intraladder and interladder couplings are extracted. In addition, the key features of the spin dynamics are compared with quantum Monte Carlo (QMC) calculations

for a plane of coupled ladders. Good agreement is found for values of interladder couplings that place the system close in parameter space to the critical point between the singlet phase and Néel order, on the ordered side of the phase diagram. As a consistency check of the overall energy scale of the interactions obtained from comparison with the LSWT and QMC models, experimental pulsed-field magnetisation data are compared with the mean-field and QMC calculations.

In Chapter 5, high-resolution single-crystal INS measurements are presented of the spin dynamics in the triangular antiferromagnet $\text{Ba}_3\text{CoSb}_2\text{O}_9$. The chapter begins with the observed magnetic excitations in the 120° spiral order ground state, showing sharp one-magnon modes throughout the Brillouin zone and strong continuum scattering up to much higher energies. The LSWT calculation is detailed for stacked triangular layers in a magnetic field applied normal to the basal plane. Compared to the LSWT predictions, the observed one-magnon energies are shown to be strongly renormalised downwards with roton-like minima in the dispersion, which motivates empirical renormalisations to the LSWT dispersions that are able to quantitatively capture the measured spin dynamics. Using this empirical parametrisation, one- and two-magnon calculations of the scattering cross-section are performed and compared to the INS data, providing evidence for a transfer of spectral weight from the one-magnon modes to the continuum states and significant high-energy continuum scattering beyond the two-magnon predictions. It is further explicitly verified that one $\rightarrow$ two-magnon decays are disallowed by kinematic constraints. INS measurements are also presented in the cone phase in a magnetic field applied normal to the layers. The evolution of the dispersion relations in an applied field is consistent with the LSWT calculation for two equal-weight domains of opposite chirality.

Finally, Chapter 6 contains concluding remarks about the studied materials presented in this thesis and outlines possible areas of interest for future research.

Chapter 2

Introduction to quantum magnetism

This chapter provides a brief overview of relevant key concepts in quantum magnetism. Firstly, the shortcomings of the classical picture of magnetism are summarised to motivate the use of quantum physics in the study of magnetic materials. After this, a brief explanation is given for the origin of the permanent magnetic moment in insulators. The effect of the crystal electric field on the magnetic ions is then discussed, including the splitting of electron energy levels, the quenching of orbital angular momentum, and the Jahn-Teller effect. The spin-orbit interaction is explained, as well as the resulting energy-level splitting and single-ion anisotropy. The following section describes the origin of exchange interactions and the form of the spin Hamiltonian, and different types of exchange interactions are discussed, including anisotropic interactions and superexchange. The phenomena of paramagnetism, ferromagnetism, antiferromagnetism and ferrimagnetism are also described, and the effects of magnetic frustration and quantum fluctuations on the ground state are discussed. Mean-field theory is then outlined as an approximate method to calculate the magnetic ground state. Finally, spin waves are introduced, with a brief discussion of the Mermin-Wagner theorem, and an overview of linear spin wave theory is provided, in particular its use in approximately calculating spin wave dispersion relations.

2.1 Classical magnetism

The classical picture of magnetic materials is able to capture many of their experimentally observed properties. By considering a simple model of the competition between the tendency of isolated magnetic moments to align with an applied magnetic field and the effect of thermal fluctuations, one can derive the $1/T$ Curie's law for paramagnetic susceptibility [1]. In the case of ions with no magnetic moment, one would expect an external magnetic field to induce a moment aligned to oppose the applied field by Lenz's law, which gives the Langevin theory of diamagnetism. Unlike the paramagnetic case, the diamagnetic susceptibility predicted by this theory is independent of temperature and scales with the area of the electron orbits [1]. Despite their crude nature, these classical models of the magnetic susceptibilities are able to account for experimentally observed properties for a wide range of materials.

However, there are significant shortcomings of a purely classical model of magnetism. Firstly, magnetic dipole interactions are very weak and cannot account for the magnetic ordering in real systems. The dipole-dipole interaction energy is given by [2]

$$E = \frac{\mu_0}{4\pi r^3} \left[\boldsymbol{\mu}_1 \cdot \boldsymbol{\mu}_2 - \frac{3}{r^2} (\boldsymbol{\mu}_1 \cdot \mathbf{r})(\boldsymbol{\mu}_2 \cdot \mathbf{r}) \right], \quad (2.1)$$

where $\boldsymbol{\mu}_{1,2}$ are the magnetic moments and $\mathbf{r}$ is their separation. In ferromagnetic iron with magnetic moment $\mu \simeq 2.1\mu_B$ and separation $r \simeq 2.55 \text{ \AA}$ [3], there is therefore an approximate interaction energy of $\mu_0\mu^2/(4\pi r^3) \sim 0.1 \text{ meV}$, which is $\sim 1 \text{ K}$. This is clearly unable to account for the Curie temperature $T_C \simeq 1043 \text{ K}$, and so the magnetism in iron (and the vast majority of magnetic materials) cannot be explained by dipoles interacting with each other's magnetic fields [3].

In addition, it can be shown generally that classical physics would predict zero thermal equilibrium magnetisation. The classical Hamiltonian for a system of N

identical particles of charge q and mass m in electric and magnetic fields can be written [3]

$$\mathcal{H}_{\text{cl}} = \frac{1}{2m} \sum_{i=1}^N [\mathbf{p}_i - q\mathbf{A}(\mathbf{r}_i)]^2 + V(\mathbf{r}_1, \dots, \mathbf{r}_N), \quad (2.2)$$

where $\mathbf{r}_i$ and $\mathbf{p}_i$ are the position and momentum of the i th particle, respectively, $\mathbf{A}$ is the magnetic vector potential and V is the sum of the electrostatic scalar potential and electron interaction energies. The corresponding partition function for this classical Hamiltonian is given by [3]

$$\mathcal{Z} = \int d\mathbf{p}_1 \dots d\mathbf{p}_N \int d\mathbf{r}_1 \dots d\mathbf{r}_N e^{-\beta\mathcal{H}_{\text{cl}}}, \quad (2.3)$$

where $\beta = 1/(k_{\text{B}}T)$. By making the substitution $\mathbf{p}'_i = \mathbf{p}_i - q\mathbf{A}(\mathbf{r}_i)$, which leaves the infinite integration limits unchanged, one can show that the partition function does not depend on the magnetic vector potential. It then follows that the magnetisation $M = k_{\text{B}}T(\partial \ln \mathcal{Z} / \partial B) = 0$ for a magnetic field B [2]. This is the Bohr-Van Leeuwen theorem and it states that classical statistical mechanics cannot explain either spontaneous or field-induced magnetisation [3]. A quantum theory of magnetism is therefore clearly needed to describe most of the interesting magnetic properties of materials.

2.2 Magnetic moments

The magnetic properties of materials arise from the magnetic moment of their electrons. All the materials considered in this thesis are insulators, in which the electrons are in localised orbitals with a limited spatial extent. The intrinsic magnetic moment of an electron is given by [4]

$$\boldsymbol{\mu}_s = -g\mu_{\text{B}}\mathbf{s}, \quad (2.4)$$

where the g factor is $g \simeq 2$ for free electrons and the intrinsic angular momentum is represented by the spin $\mathbf{s}$. The minus sign comes from the negative charge of the electron. There is also an orbital component of the magnetic moment that can be

written as [4]

$$\boldsymbol{\mu}_l = -\frac{2}{2m_e c}(\mathbf{r} \times \mathbf{p}) = -\mu_B \mathbf{l}, \quad (2.5)$$

where $\mathbf{r}$ is the position of the electron, $\mathbf{p}$ is the momentum, m_e is the mass and $\mathbf{l}$ is the orbital angular momentum.

A similar expression to Eq. (2.4) can be written for the nuclear spin, but the nuclear magneton μ_N is much smaller than the Bohr magneton μ_B ($\mu_N = \mu_B/1836$), as the mass of a proton is much greater than that of an electron [4]. Therefore, one can almost always ignore the contribution of the nuclei to the magnetic properties.

The total spin and orbital angular momenta of electrons in filled shells are zero, so only ions with a partially filled shell have a net magnetic moment. The total spin angular momentum $\mathbf{S}$ and orbital angular momentum $\mathbf{L}$ are given by [4]

$$\mathbf{S} = \sum_i \mathbf{s}_i, \quad \mathbf{L} = \sum_i \mathbf{l}_i, \quad (2.6)$$

where the sum is over all the electrons in the partially filled shell. If the spin and orbital components interact only weakly (*i.e.* the spin-orbit interaction is perturbative, to be discussed in Sec. 2.4), the total spin and orbital angular momenta are separately conserved and the eigenvalues of the corresponding operators are good quantum numbers that can be used to label the states of the ion [5]. This is known as Russell-Saunders coupling and is valid for the magnetic ions in the systems discussed in this thesis, which are 3d transition metals with weak spin-orbit interactions [5]. From hereon, $\mathbf{S}$ and $\mathbf{L}$ refer to the angular momentum quantum operators, and S and L are the associated quantum numbers.

For free magnetic ions that are well described by Russell-Saunders coupling, the angular momentum quantum numbers in the ground state can be found using Hund's rules, listed here in order of precedence: (1) the electronic configuration maximises S , then (2) it maximises L , and finally (3) the total angular momentum quantum number

$J = |S \pm L|$, where the $\pm$ corresponds to an over/under half full shell, respectively [2]. The third rule assumes that the spin-orbit effect is the most significant term in the Hamiltonian after electrostatic effects. For the case of the 3d ions considered in this thesis, the partially filled shell is the outermost electronic shell and so it feels the electric fields of the crystalline environment quite strongly. In fact, this crystal field interaction is much stronger than the spin-orbit interaction in these materials, invalidating the third Hund's rule. In this case, L and S are still good quantum numbers with values given by the first two Hund's rules, but J is no longer a good quantum number [5]. The crystal field interaction is the subject of the following section.

2.3 Crystal field effect

One can intuitively see that the electrons in the magnetic ion must be affected by the crystalline environment. Specifically, the motion of the electrons is altered by the crystal field, which is the electric field of the surrounding ions [3]. In the case of the 3d transition metal ions considered in this thesis, the partially filled electronic shell is also the outermost shell and so the magnetic properties are strongly influenced by the crystal field [5].

Clearly, the effect will depend on the symmetry of the crystal environment. In both the materials studied here, the magnetic ion is in an octahedral environment of O^{2-} ions and the crystal field effect is mainly due to the electrostatic repulsion of the electrons in the O^{2-} orbitals [2]. The crystal field perturbation depends only on spatial operators, and so it commutes with $\mathbf{S}$ but not (in general) with $\mathbf{L}$. It is therefore possible for the crystal field effect to lift the orbital degeneracy [5]. Figure 2.1(a) illustrates this crystal field effect for d orbitals in an octahedral environment, showing the orbitals split into two levels: the t_{2g} orbitals (d_{xy} , d_{xz} and d_{yz}) are reduced in

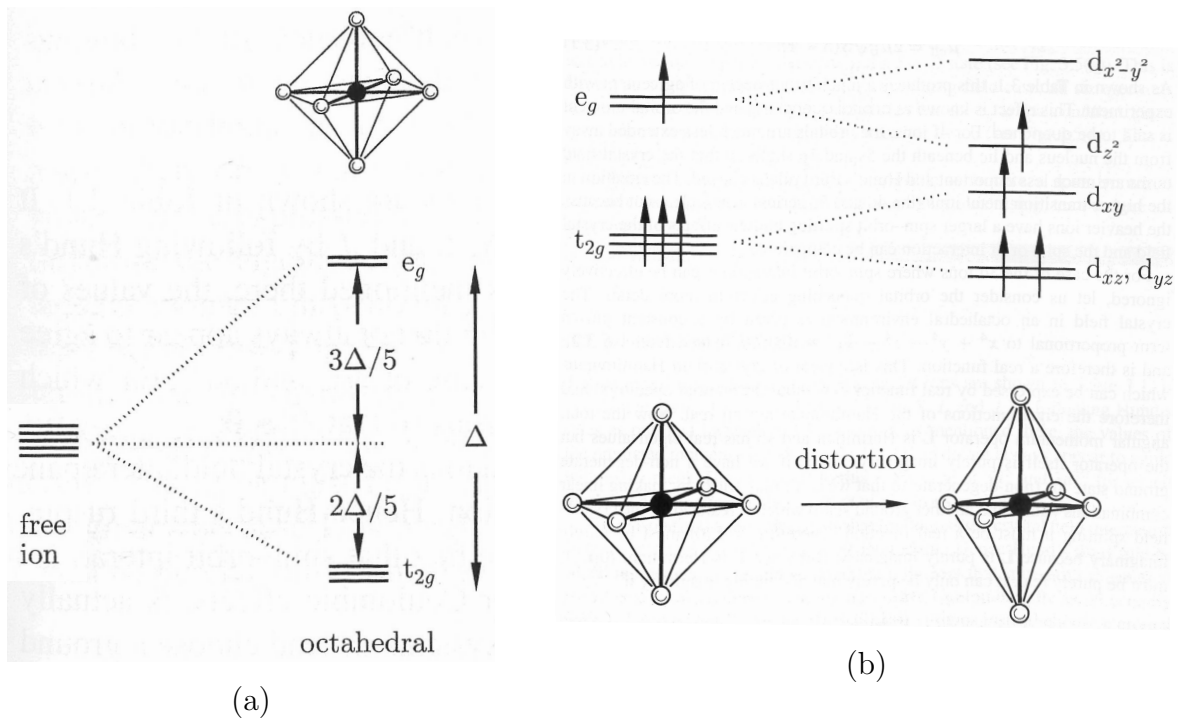


Figure 2.1: The crystal field effect for d orbitals in an octahedral environment. (a) The d orbitals split into an e_g level, which rises in energy in the crystal field, and a t_{2g} level, which lowers in energy. (b) The Jahn-Teller effect for Mn^{3+} ions in an octahedral environment. The distortion splits the e_g and t_{2g} levels, lowering the energy of the singly-occupied e_g level. Reproduced with permission of Oxford Publishing Limited through PLSclear from Ref. [2]. © Stephen Blundell, 2001

energy and the e_g orbitals (d_{z^2} and $d_{x^2-y^2}$) are increased in energy. The energy difference arises because the e_g orbitals have greater overlap with the orbitals on the neighbouring ions, resulting in an energy increase due to the stronger electrostatic repulsion [2].

As mentioned in the previous section, the significant crystal field interaction in 3d transition metal ions invalidates the third Hund's rule. Neglecting the spin-orbit interaction, which is very weak in these systems, the ground states of these ions can be represented by real functions, because the crystal field perturbation is a real function. As $\mathbf{L} = -i\mathbf{r} \times \nabla$ is pure imaginary, $\langle \mathbf{L} \rangle$ in the real ground state must be pure imaginary. But $\mathbf{L}$ is a physical observable and its eigenvalues must be real, so all the components of $\mathbf{L}$ must be zero in a non-degenerate ground state, which is known as orbital quenching [2]. One can think of this semiclassically as a precession of the orbital angular momentum in the crystal field, leaving the magnitude unchanged but with components averaging to zero [5]. The magnetic properties then arise solely from the electron spin angular momentum, which is therefore the focus of most of the discussion in this thesis. In practice, $\mathbf{L}$ may not be completely quenched because of a non-negligible spin-orbit interaction, to be discussed in the next section.

The Jahn-Teller theorem states that the crystal will tend to distort to lift any orbital degeneracy of the ground state that arises from a highly symmetric crystal field [6]. In these systems, the elastic energy cost of distorting the crystal is outweighed by the energy gain of providing a lower-energy electron ground state. The Jahn-Teller effect is shown schematically in Fig. 2.1(b) for the case of Mn^{3+} ions in an octahedral environment. In the illustrated distortion, the octahedra stretch vertically along $\hat{z}$, decreasing the overlap with neighbouring orbitals along that direction and so lowering the energy of the d_{xz} , d_{yz} and d_{z^2} orbitals. While there is no net energy gain for the filled t_{2g} level, the singly-occupied e_g level is lowered in energy, which explains why

the distortion is energetically favourable [2]. In the studied material $\text{Ba}_2\text{CuTeO}_6$ (see Sec. 4), a Jahn-Teller distortion of the CuO_6 octahedra results in ferro-orbital ordering of the $d_{x^2-y^2}$ orbitals.

Even in very low symmetry crystal fields, it is still possible to have degenerate eigenstates. This is a consequence of Kramers theorem, which states that all energy levels of a system with odd numbers of electrons are at least doubly degenerate. This holds true if the Hamiltonian is time-reversal invariant, *i.e.* in the absence of an applied magnetic field, which would split the levels by the Zeeman energy [3]. If the ground state is a Kramers doublet, the two states can be approximated by the spin-up and spin-down states of an effective spin- $\frac{1}{2}$ ion, which allows the spin Hamiltonian to be expressed in a simpler, free ion form. The g factor in Eq. (2.4) is then, in general, replaced by an effective g tensor that reflects the anisotropy of the Kramers doublet [2]. This is the principle behind the effective spin- $\frac{1}{2}$ model of $\text{Ba}_3\text{CoSb}_2\text{O}_9$ discussed in Sec. 5, as the magnetic Co^{2+} ions have a Kramers doublet ground state in the octahedral environment of O^{2-} ions.

2.4 Spin-orbit interaction

Spin-orbit coupling is a relativistic effect that arises from the interaction between the electron spin and the magnetic field generated by the motion of the nucleus in the electron's rest frame. The magnetic field experienced by the spin can be expressed as [2]

$$\mathbf{B} = \frac{\mathbf{E} \times \mathbf{v}}{c^2}, \quad (2.7)$$

where $\mathbf{v}$ is the velocity of the nucleus in the electron's rest frame. $\mathbf{E}$ is the electric field generated by the nucleus at the electron and is given by

$$\mathbf{E} = -\frac{\mathbf{r}}{r} \frac{dV(r)}{dr}, \quad (2.8)$$

where $V(r)$ is the associated potential at position $\mathbf{r}$. The Hamiltonian for the intrinsic spin-orbit interaction can then be written as [2]

$$\mathcal{H}_{\text{SO}} = -\frac{1}{2}\boldsymbol{\mu}_s \cdot \mathbf{B} \quad (2.9)$$

$$= -\frac{g\mu_B\hbar}{2m_e c^2 r} \frac{dV(r)}{dr} \mathbf{s} \cdot \mathbf{l}, \quad (2.10)$$

where the magnetic moment of the spin $\boldsymbol{\mu}_s$ is given by Eq. (2.4) and the orbital angular momentum $\hbar\mathbf{l} = m_e\mathbf{r} \times \mathbf{v}$. The factor of $\frac{1}{2}$ in Eq. (2.9) is the relativistic Thomas factor and arises when one properly accounts for the curved path of the electron upon transforming to its rest frame [4]. Note that the coefficient here is positive, as $dV(r)/dr < 0$ for the electrostatic potential of a positive charge.

Strictly speaking, once a spin-orbit interaction is included, $\mathbf{S}^2$ and $\mathbf{L}^2$ no longer commute with the Hamiltonian and so are not separately conserved. However, for the systems considered in this thesis, relativistic effects can be treated as perturbations. So Russell-Saunders coupling is still a good description and one can write [3]

$$\mathcal{H}_{\text{SO}} = \lambda \mathbf{S} \cdot \mathbf{L} \quad (2.11)$$

in terms of the total spin angular momentum $\mathbf{S}$ and the total orbital angular momentum $\mathbf{L}$ of the electrons, as given by Eq. (2.6). If the shell is less than half full, the spins must be parallel to $\mathbf{L}$ from Hund's rules in Sec. 2.2. By comparison with Eq. 2.10, one can therefore determine that the coefficient λ must be positive. If the shell is more than half full, the only electrons that contribute to $\mathbf{L}$ are those with spins antiparallel to it (as $\sum_i \mathbf{l}_i = 0$ for the parallel spins), so λ is negative [4]. As the strength of the spin-orbit interaction increases with the strength of the electric field generated by the nucleus [see Eq. (2.10)], it will be more significant in elements with a larger atomic number. So the Russell-Saunders coupling scheme breaks down for heavier elements [3].

In the Russell-Saunders coupling scheme, the energy level splitting due to the spin-orbit interaction is given by [4]

$$\lambda \langle \mathbf{S} \cdot \mathbf{L} \rangle = \frac{\lambda}{2} \langle (\mathbf{S} + \mathbf{L})^2 - \mathbf{S}^2 - \mathbf{L}^2 \rangle \quad (2.12)$$

$$= \frac{\lambda}{2} [J(J+1) - S(S+1) - L(L+1)]. \quad (2.13)$$

So if the spin-orbit interaction is significant, the energy levels are split by their total angular momentum J , which has the values

$$J = |S - L|, |S - L| + 1, \dots, S + L. \quad (2.14)$$

One therefore recovers the third Hund's rule stated in Sec. 2.2, as the energy is minimised for $J = |S - L|$ if the shell is less than half full ($\lambda > 0$) and $J = S + L$ if the shell is more than half full ($\lambda < 0$) [4].

In the case of the 3d transition metal ions, the third Hund's rule is not valid because of the strong crystal field interaction. However, the spin-orbit effect is still important in two main ways: it can restore some of the quenched orbital angular momentum and it can allow the spin to feel the anisotropy of the crystal field [3]. As the orbital angular momentum depends on the spatial distribution of the electrons, it is sensitive to the crystal field generated by the surrounding ions. The spin is not directly coupled to the lattice, but is coupled to the orbital motion through the spin-orbit interaction. In this way, the spin can couple indirectly to the crystal field, giving rise to magnetic anisotropy [3]. It can be shown that this single-ion anisotropy depends only on the square of the spin components S_i^2 [4]. For spin- $\frac{1}{2}$ systems, this term is therefore constant as S_i^2 is always $\frac{1}{4}$, and the single-ion anisotropy vanishes.

In $\text{Ba}_3\text{CoSb}_2\text{O}_9$, the spin-orbit interaction couples the spin to the uniaxial crystal field, which splits the lowest-energy orbital triplet into six Kramers doublets. At low temperatures, the magnetic properties are determined by the lowest-energy Kramers

doublet and so $\text{Ba}_3\text{CoSb}_2\text{O}_9$ can be modelled as an effective spin- $\frac{1}{2}$ system, as explained in Sec. 2.3. By coupling the spin to the lattice in $\text{Ba}_3\text{CoSb}_2\text{O}_9$, the spin-orbit interaction also results in the observed easy-plane anisotropy. Single-ion anisotropy is not present in $\text{Ba}_2\text{CuTeO}_6$, as it is a true spin- $\frac{1}{2}$ system.

2.5 Exchange interactions

Magnetic dipolar interactions are far too weak to account for observed magnetic ordering, as mentioned in Sec. 2.1. Heisenberg showed that there is a quantum mechanical explanation for the properties of magnetic materials, rooted in the electrostatic repulsion and exchange symmetry of overlapping electron orbitals [7]. This is commonly called the exchange interaction and a derivation is outlined below.

Let $\mathcal{H}$ be a Hamiltonian that describes the interaction of two electrons. If $\mathcal{H}$ is independent of spin, the eigenstates can be written as products of spin and orbital (spatial) wave functions [5]. The exchange symmetry of identical fermions requires the electron wave functions to be antisymmetric under the simultaneous interchange of the spatial and spin coordinates of the two electrons. There are four possible spin states that have well-defined exchange symmetry: the antisymmetric singlet state $(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)/\sqrt{2}$ with $S = 0$, and the symmetric triplet states $|\uparrow\uparrow\rangle$, $|\downarrow\downarrow\rangle$ and $(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle)/\sqrt{2}$ with $S = 1$ (the arrows indicate the relative orientation of the two spins). In order for the overall wave function to be antisymmetric under exchange, the spatial wave function must therefore be symmetric in the singlet state and antisymmetric in the triplet states. If the two electrons have positions $\mathbf{r}_1$ and $\mathbf{r}_2$ and can be localised at either site a or b , the spatial wave functions in the Heitler-London approximation

are [5]

$$\psi_s(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}}[\phi_a(\mathbf{r}_1)\phi_b(\mathbf{r}_2) + \phi_b(\mathbf{r}_1)\phi_a(\mathbf{r}_2)] \quad (2.15)$$

$$\psi_t(\mathbf{r}_1, \mathbf{r}_2) = \frac{1}{\sqrt{2}}[\phi_a(\mathbf{r}_1)\phi_b(\mathbf{r}_2) - \phi_b(\mathbf{r}_1)\phi_a(\mathbf{r}_2)], \quad (2.16)$$

where $\phi_i(\mathbf{r})$ is the wave function of a single electron localised at site i . It is clear that these spatial wave functions have well-defined exchange symmetry: ψ_s is symmetric under exchange of electrons and so is associated with the singlet state, and ψ_t is antisymmetric under exchange and is associated with the triplet state. Assuming the spin wave functions are properly normalised, one can then write the energies of the two states as [2]

$$E_s = \int d\mathbf{r}_1 d\mathbf{r}_2 \psi_s^* \mathcal{H} \psi_s, \quad E_t = \int d\mathbf{r}_1 d\mathbf{r}_2 \psi_t^* \mathcal{H} \psi_t. \quad (2.17)$$

In the limit of large spatial separation, the singlet-triplet splitting is $E_s - E_t = 2J$, where [2]

$$J \equiv \int d\mathbf{r}_1 d\mathbf{r}_2 \phi_a^*(\mathbf{r}_1)\phi_b^*(\mathbf{r}_2)\mathcal{H}\phi_a(\mathbf{r}_2)\phi_b(\mathbf{r}_1) \quad (2.18)$$

is the exchange integral, so-called because it is the matrix element between states that differ only in the exchange of the electrons. The interaction responsible is simply electrostatic repulsion and so drops off rapidly with increasing separation of the sites.

It is convenient to express this exchange interaction in terms of the spin operators $\mathbf{S}_1$ and $\mathbf{S}_2$ of the two electrons. Dirac observed that one can write the Hamiltonian as an effective spin Hamiltonian [8]. For a two-electron system, this has the form [5]

$$\mathcal{H} = (E_s + 3E_t)/4 - (E_s - E_t)\mathbf{S}_1 \cdot \mathbf{S}_2. \quad (2.19)$$

As $\mathbf{S}_i^2 = 3/4$ for both spins, it follows that $\mathbf{S}^2 = 3/2 + 2\mathbf{S}_1 \cdot \mathbf{S}_2$. So the singlet state ($S = 0$) has $\mathbf{S}_1 \cdot \mathbf{S}_2 = -3/4$ and the triplet state ($S = 1$) has $\mathbf{S}_1 \cdot \mathbf{S}_2 = 1/4$. The eigenenergy of the spin Hamiltonian is therefore E_s in the singlet state and E_t in the

triplet state, as required [5]. Redefining the zero of energy and using the definition of the exchange integral, one can write $\mathcal{H} = -2J\mathbf{S}_1 \cdot \mathbf{S}_2$. This simple two-electron model motivates the many-body Hamiltonian for Heisenberg exchange interactions, given by [3]

$$\mathcal{H} = \sum_{i>j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j, \quad (2.20)$$

where J_{ij} is the exchange coupling between the i th and j th spins. In many cases, one need only consider the nearest-neighbour (NN) interactions, as the exchange interaction originates from overlapping electron orbitals and so is short range.

In the convention of Eq. (2.20), pairs of spins minimise their energy by aligning parallel (ferromagnetically) for $J_{ij} < 0$ and aligning antiparallel (antiferromagnetically) for $J_{ij} > 0$. In the case of electrons on the same site, the exchange is normally ferromagnetic to minimise the electrostatic repulsion, as parallel spins are prevented from occupying the same space by the Pauli exclusion principle [2]. An antiferromagnetic exchange is more common for electrons on different sites, which can be explained using a particle-in-a-box model: parallel spin are constrained to their respective ions by the Pauli exclusion principle, but antiparallel spins can ‘spread out’ their wave function between the ions by virtual hopping, reducing their kinetic energy [2].

The spin Hamiltonian in Eq. (2.20) depends only on the relative alignment of the spins and not on their absolute orientation, which is a characteristic feature of the isotropic Heisenberg model and arises from the spin independence of the original Hamiltonian [5]. As mentioned in Sec. 2.4, the addition of the spin-orbit interaction can result in magnetic anisotropy. This motivates the definition of an anisotropic spin Hamiltonian, which can be expressed for NN interactions as [9]

$$\mathcal{H}_{\text{NN}} = \sum_{\langle ij \rangle} (J_x S_i^x S_j^x + J_y S_i^y S_j^y + J_z S_i^z S_j^z), \quad (2.21)$$

where the standard $\langle ij \rangle$ notation has been used to indicate a sum over NN sites. The

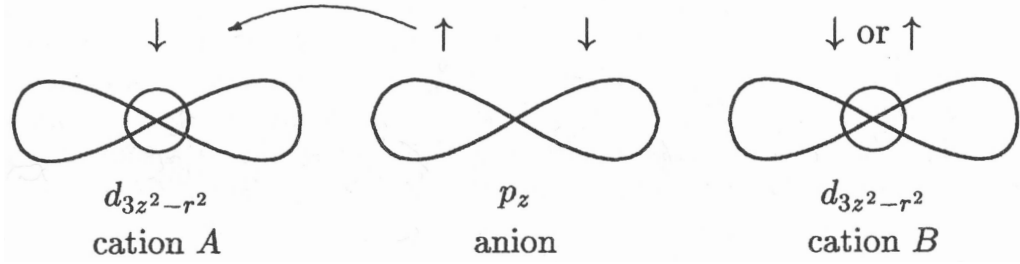


Figure 2.2: Superexchange between magnetic cations via a non-magnetic anion. This interaction favours an antiferromagnetic alignment of the site A and B spins, which allows both the electrons in the anion orbital to reduce their kinetic energy by hopping to the neighbouring cations. Reproduced with permission of World Scientific Publishing Co. Pte. Ltd. (WSP) from Ref. [3]. © 1999 by WSP

Heisenberg model is recovered in the isotropic case when $J_x = J_y = J_z$. If easy-axis anisotropy is present, alignment is favoured along a single direction (chosen here to be $\hat{z}$) and so $|J_z| > |J_x|$ and $|J_z| > |J_y|$. In the limit of very strong easy-axis anisotropy, the spins are constrained to lie along the easy axis and one can use the Ising model with $J_x = J_y = 0$. If easy-plane anisotropy is present, alignment is favoured in a plane (chosen here to be the xy plane) and so $|J_z| < |J_x|$ and $|J_z| < |J_y|$. In the limit of very strong easy-plane anisotropy, the spins are constrained to lie in the easy plane and one can use the XY model with $J_z = 0$. Although the Heisenberg model is suitable for the studied material $\text{Ba}_2\text{CuTeO}_6$, it does not give the complete picture for $\text{Ba}_3\text{CoSb}_2\text{O}_9$. The latter has a weak easy-plane anisotropy and the relevant spin Hamiltonian is given by the XXZ model, in which $J_x = J_y \neq J_z$.

The interaction derived using the Heitler-London model above is a direct exchange interaction, so-called because it arises from the direct electrostatic interaction of the electrons at the two sites [5]. If the interaction is instead mediated by a common non-magnetic neighbour, it is known as a superexchange [10, 11]. Figure 2.2 illustrates schematically the superexchange between electrons in the d orbitals of cations A and B via the p orbital of a neighbouring anion [3]. If the A and B spins are ferromagnetically aligned, only one of the p electrons can reduce its kinetic energy by hopping to

a neighbouring site due to the Pauli exclusion principle. However, if they are antiferromagnetically aligned, both p electrons can hop to a neighbour. Antiferromagnetic alignment also allows the electron at A to reduce its kinetic energy by hopping to B via the anion and vice versa. So it is energetically favourable for the spins to be aligned antiparallel and there is an antiferromagnetic superexchange interaction between spins A and B [3]. For this reason, superexchange is normally (but not always) antiferromagnetic. In both studied materials $\text{Ba}_2\text{CuTeO}_6$ and $\text{Ba}_3\text{CoSb}_2\text{O}_9$, the main magnetic interaction is superexchange via the O^{2-} 2p orbitals.

Dzyaloshinsky predicted the existence of an anisotropic exchange interaction, based on a symmetry analysis [12]. Moriya later derived the form of this interaction by considering the exchange interaction between an ion in its ground state and an ion excited by the spin-orbit interaction [4, 13]. This introduces a term in the Hamiltonian given by

$$\mathcal{H}_{\text{DM}} = \mathbf{D} \cdot (\mathbf{S}_1 \times \mathbf{S}_2), \quad (2.22)$$

where $\mathbf{D}$ is a constant vector. This is commonly called the Dzyaloshinsky-Moriya (D-M) interaction and often has the effect of slightly canting the spins [2]. If there is an inversion symmetry at the midpoint between the two ions, then clearly $\mathbf{S}_1 \times \mathbf{S}_2 = -\mathbf{S}_2 \times \mathbf{S}_1 = \mathbf{S}_2 \times \mathbf{S}_1 = \mathbf{0}$ and the D-M interaction vanishes. In this way, the high symmetry of $\text{Ba}_3\text{CoSb}_2\text{O}_9$ forbids D-M interactions between NN spins. They are however allowed in $\text{Ba}_2\text{CuTeO}_6$ and there is evidence of an anisotropic exchange interaction in magnetisation measurements.

2.6 Magnetic order

At high temperatures, when thermal fluctuations have greater energy than the magnetic interactions, spin systems are disordered and there are no long-range spin correlations. This is the paramagnetic phase, in which spins behave like decoupled

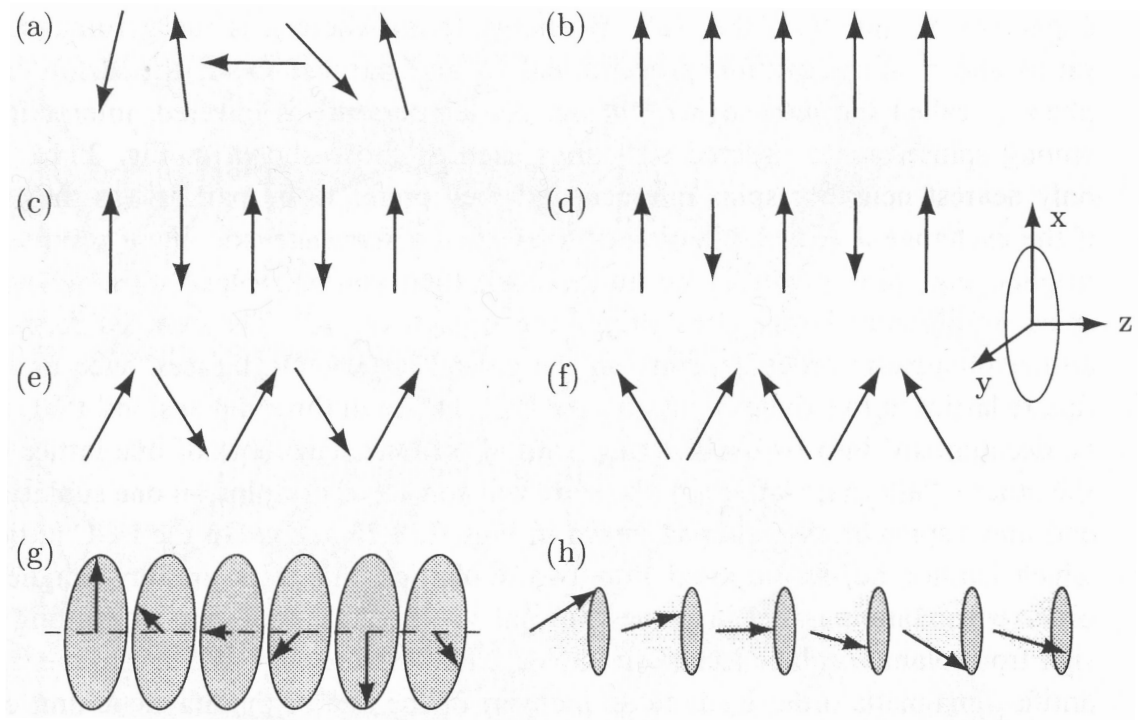


Figure 2.3: Illustration of the spin configuration along one dimension in (a) a para-magnet, (b) a ferromagnet, (c) an antiferromagnet, (d) a ferrimagnet, (e) a canted antiferromagnet, (f) a fan structure, (g) a helical structure and (h) a cone structure. Reproduced with permission of Cambridge University Press (CUP) through PLSclear from Ref. [9]. © CUP 1995

moments and tend to align with an applied magnetic field [9], as shown schematically in Fig. 2.3(a). Below a critical temperature, the system may become magnetically ordered with a structure that depends on the nature of the interactions and the crystal geometry.

It can be shown that classical spins on a Bravais lattice will, in general, order in a helical structure at low temperatures [4]. For spins rotating in the xy plane, this can be represented by

$$S_i^x = S \cos(\mathbf{Q} \cdot \mathbf{r}_i + \phi) \quad (2.23)$$

$$S_i^y = S \sin(\mathbf{Q} \cdot \mathbf{r}_i + \phi) \quad (2.24)$$

$$S_i^z = 0, \quad (2.25)$$

where ϕ is the phase of the spin at the origin, $\mathbf{r}_i$ is the position of the i th spin, and $\mathbf{Q}$ is called the “ordering wave vector”. The ordering wave vector quantifies the rotation of spins from one site to the next and is a useful way of describing magnetic structures, in part because it can be directly measured using neutron scattering (see Sec. 3). Note that the spins are aligned parallel in planes perpendicular to $\mathbf{Q}$, and rotate between the planes. In general, the ordering wave vector can take any value in the Brillouin zone. If the components of the ordering wave vector are rational in reciprocal lattice units of the underlying crystal structure, the magnetic order is said to be “commensurate”, otherwise it is “incommensurate” [9].

In ferromagnets, the spins are aligned parallel along a single direction (in a given domain), as illustrated in Fig. 2.3(b). There can therefore be a finite magnetisation in the absence of an applied magnetic field, called a “spontaneous magnetisation” [2]. The magnetisation can be used as the order parameter, as it vanishes upon heating to the critical temperature [3]. The simplest ferromagnetic (FM) structure has an ordering wave vector at the Brillouin zone centre and all the spins have the same

magnitude and direction.

In antiferromagnets, the magnetic interactions favour an antiparallel alignment of spins, but whether this is achievable depends on the geometry of the system and any competing interactions [2]. The resulting order is known as Néel order, after Louis Néel who first proposed this model [14], and the corresponding ordering temperature is called the Néel temperature. The simplest antiferromagnetic (AFM) structure has an ordering wave vector at the Brillouin zone boundary and consists of two interpenetrating sublattices of oppositely aligned spins [9], shown schematically for one dimension in Fig. 2.3(c). There is therefore no spontaneous magnetisation, although the sublattices taken separately do have a finite magnetisation. This sublattice magnetisation vanishes at the Néel temperature, allowing it to be used as an order parameter [3]. Both systems presented in this thesis are antiferromagnets with magnetic ordering that is commensurate with the crystal lattice.

If the oppositely aligned spins have different magnitudes, it is possible to have a finite spontaneous magnetisation. This type of magnetic ordering is called ferrimagnetism [9] and is shown schematically in Fig. 2.3(d). The first magnetic material to be studied about 3000 years ago was lodestone, a naturally-occurring magnetised iron ore, which is ferrimagnetic [2]. Also depicted in Fig. 2.3 are (e) the canted phase and (f) the “fan” phase, which can arise from the competition between the exchange interactions and the local crystal fields or an applied magnetic field [9].

The discussion of magnetic order thus far has assumed classical spins. This model works quite well for ferromagnets, because both classical and quantum physics predict the same ground state of spins aligned along a common direction [3]. For antiferromagnets, the reality is more complicated. As discussed in Sec. 2.5, the electron spin wave function must have well-defined exchange symmetry in the absence of the spin-orbit interaction. For a pair of spins, this results in singlet and triplet states. When

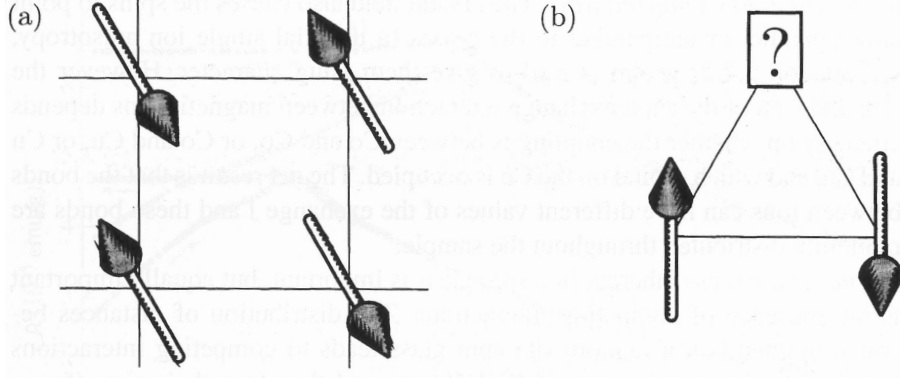


Figure 2.4: AFM ordering of spins (arrows) for NN interactions (black lines) on (a) a square lattice and (b) a triangular plaquette. The “?” represents the inability of the third spin to satisfy both NN interactions in the triangular system, resulting in frustration. Reproduced with permission of Oxford Publishing Limited through PLSclear from Ref. [2]. © Stephen Blundell, 2001

the spins are AFM coupled, their energy is minimised when the total spin is minimised, *i.e.* the ground state is a singlet. So rather than having a Néel order of $|\uparrow\downarrow\rangle$ or $|\downarrow\uparrow\rangle$, the quantum mechanical ground state is actually a superposition $(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)/\sqrt{2}$ that preserves the symmetry of the Hamiltonian. In the classical model, strict antiparallel alignment along z allows the system to gain energy only from the z term of the spin Hamiltonian in Eq. (2.21). By allowing the spins to fluctuate, the system is able to gain energy from the x and y terms as well. The resulting singlet ground state has energy $-JS(S+1)$ for an isotropic exchange J , which is an energy saving of JS compared to the classical energy $-JS^2$ [3]. It turns out that Néel order is a good description of the ground state for systems of dimension $d \geq 2$, but the ground state exhibits zero-point quantum fluctuations that lower its energy and reduce the sublattice magnetisation [3]. Quantum fluctuations are expected to be strongest in $S = \frac{1}{2}$ systems; classical physics is recovered in the large S limit, as predicted by the correspondence principle.

2.6.1 Magnetic frustration

If it is not possible for a system to simultaneously satisfy all the magnetic interactions, it is said to be “frustrated” (a term coined by Toulouse [15]). In the case of a square-lattice antiferromagnet, illustrated in Fig. 2.4(a), it is possible to select a ground state in which the spins are oppositely aligned to their neighbours and all the NN interactions are satisfied. However, the triangular antiferromagnet in Fig. 2.4(b) is frustrated, because the third spin on the triangular plaquette cannot minimise its exchange interaction with both of its neighbours [2]. This is an example of geometric frustration, in which interactions are frustrated by the geometry of the lattice. It is also possible for frustration to arise from competing interactions on different length scales. For example, the square-lattice AFM in Fig. 2.4(a) would be frustrated if there was also a next-nearest-neighbour (NNN) AFM interaction, *i.e.* an interaction that favours antiparallel spins along the diagonals of the squares. In the presence of this competing interaction, there is no magnetic ground state that simultaneously minimises all the exchange interactions [2].

In the case of the triangular plaquette in Fig. 2.4(b), the ground state of the Ising Hamiltonian has a six-fold degeneracy of equally unsatisfied configurations. A macroscopic system is therefore highly degenerate and remains disordered down to zero temperature with finite zero-point entropy, a state known as cooperative paramagnetism [2, 3]. In the Heisenberg model, the interaction between the in-plane spin components lifts the degeneracy and there is a helical ground state that reflects a compromise between the competing interactions [3]. This is the ground state observed in $\text{Ba}_3\text{CoSb}_2\text{O}_9$, a near-Heisenberg triangular antiferromagnet with 120° spiral order in the basal plane.

Frustration often results in incommensurate spin structures. Competing interactions can stabilise a helical structure of the form described by Eqs. (2.23)–(2.25),

where the ordering wave vector $\mathbf{Q}$ depends only on the ratio of the exchange couplings [2]. In other words, the helical structure need not share the periodicity of the crystal lattice and the order is in general incommensurate. An example of helical order is illustrated in Fig. 2.3(g) and “cone” order in Fig. 2.3(h). The latter occurs when the spins have helical structure in the plane and a spin component perpendicular to the plane, for example due to an applied magnetic field or easy-axis anisotropy, which could be represented by Eqs. (2.23)–(2.25) with $S^z \neq 0$ [2]. This type of order is observed in $\text{Ba}_3\text{CoSb}_2\text{O}_9$ in a magnetic field applied normal to the spiral order.

Exchange interactions are expected to be less effective and quantum fluctuations more significant in frustrated systems [3]. As previously mentioned, quantum fluctuations result in a reduction of the sublattice magnetisation and this can be described by an effective spin reduction ΔS . The spin reduction is considerably larger in the triangular antiferromagnet ($\Delta S \simeq 0.261$) than the square antiferromagnet ($\Delta S \simeq 0.197$), because quantum fluctuations are more significant in the frustrated system [3].

2.6.2 Mean-field theory

The simplest and most common way of approximately calculating the classical magnetic ground state and phase transitions is mean-field theory (MFT). The exchange interaction is modelled by an effective “molecular field” (or “mean field”) $\mathbf{B}_{\text{MF}}$, reducing the Hamiltonian to the paramagnetic form [2]

$$\mathcal{H} = g\mu_{\text{B}} \sum_i \mathbf{S}_i \cdot (\mathbf{B} + \mathbf{B}_{\text{MF}}), \quad (2.26)$$

where $\mathbf{B}$ is an external magnetic field. The benefit of this approach is that it simplifies the calculation to a one-body problem [4]. The zero-temperature mean-field state is the lowest-energy configuration of the spins. The first step is to find an expression for a single spin moment in the average field of the others. One can then solve self-consistently for a general site, assuming the spins all experience the same effective

field [9]. When applied to a ferromagnetic transition, this is known as the “Weiss model of ferromagnetism” [2]. MFT is a quite general technique, but this section is just concerned with its application to spin systems.

As MFT assumes that all sites experience the same average field, it neglects the effects of fluctuations. MFT provides a good description for high dimensions and long-range interactions, because the field experienced by a spin approaches the average value as the number of contributing interactions increases. At low dimensions (normally below four), fluctuations are important and MFT cannot describe the system close to a critical point, where fluctuations are particularly pronounced [9]. MFT ignores the possibility of quantum fluctuations, as it assumes there are only weak thermal fluctuations, and so always predicts a finite ordering temperature. It is also unable in general to describe strongly frustrated systems, in which quantum fluctuations are expected to be significant.

MFT is used in this thesis to calculate the classical ground states for both studied materials. In the spin ladder system $\text{Ba}_2\text{CuTeO}_6$, the interladder and interlayer couplings result in a three-dimensional (3D) character at low temperatures, stabilising the long-range Néel order predicted by MFT. Assuming a spin-flop state in an applied magnetic field, MFT is then used to calculate the classical magnetisation curve. In the triangular lattice antiferromagnet $\text{Ba}_3\text{CoSb}_2\text{O}_9$, the magnetic structure in the ground state is the same as predicted by MFT, which was used to calculate the cone phase in an applied magnetic field for the spin wave calculation (see Sec. 2.7.1).

2.7 Spin waves

Magnetically ordered systems can be excited by quantised spin deviations at finite temperatures, which propagate through the lattice as “spin waves” [3]. Figure 2.5 illustrates schematically the classical picture of a spin wave, which is a collective pre-

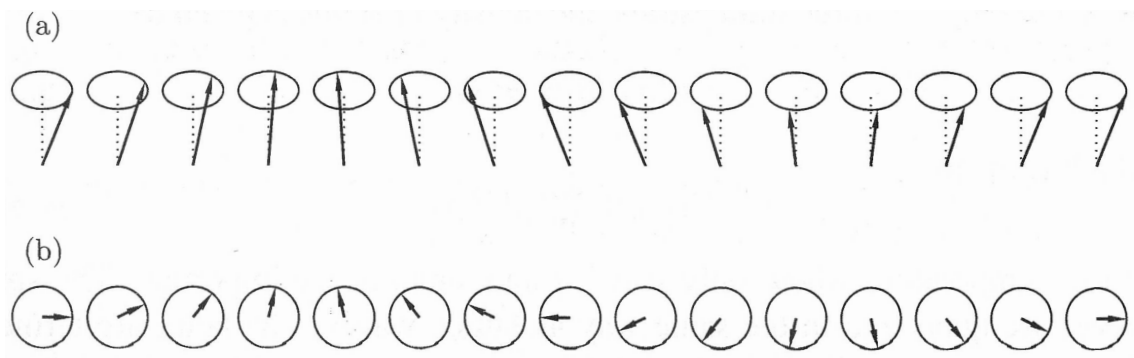


Figure 2.5: Schematic diagram of a spin wave in a one-dimensional ferromagnet. (a) Spins (arrows) precessing about the ordered spin direction (dotted line). (b) View from above showing the direction of spin rotation. Reproduced with permission of Oxford Publishing Limited through PLSclear from Ref. [2]. © Stephen Blundell, 2001

cession of the spins about their equilibrium position, for the case of a one-dimensional (1D) ferromagnet [5]. Spin waves can be modelled as “magnons” in quantum mechanics, which are bosonic quasiparticles with $S_z = \pm 1$, corresponding to a single quantised spin deviation [3]. Spin waves are polarised transverse to the ordered spin direction, as they correspond to deviations from the equilibrium position [5].

In the absence of magnetic anisotropy, a small deviation of the spins from their equilibrium position costs infinitesimal energy, as long as the deviation has the same periodicity as the magnetic structure [3]. For the 1D ferromagnet in Fig. 2.4, this would mean an identical small deviation at every site that leaves the spins parallel and so costs no energy. In other words, magnons are Goldstone modes that arise from the magnetic order breaking the continuous rotational symmetry of the spin lattice, and therefore emanate from the magnetic ordering wave vector [3]. This is analogous to phonons that arise from translational symmetry breaking in crystal lattices.

In Heisenberg systems at low temperatures, one therefore expects an acoustic mode with zero energy at the magnetic ordering wave vector and the Brillouin zone centre (the large wavelength limit). In systems with more than one magnetic sublattice

tice, there can also be optical modes with finite energy in the large wavelength limit [5]. It is possible for acoustic magnons to cost energy at the ordering wave vector in the presence of a magnetic anisotropy, if the ordering no longer breaks a continuous rotational symmetry; the mode is then said to be “gapped” and the energy cost of creating a magnon there is the “spin gap” [2]. For the studied material $\text{Ba}_2\text{CuTeO}_6$, the observed gapless magnon mode is consistent with isotropic Heisenberg interactions. In $\text{Ba}_3\text{CoSb}_2\text{O}_9$, the in-plane modes are Goldstone modes that correspond to a breaking of the in-plane rotational symmetry, but the out-of-plane mode is gapped due to the easy-plane anisotropy.

In isotropic 1D and 2D Heisenberg systems, the spin waves are strong enough to completely prevent magnetic order at finite temperatures, which is known as the Mermin-Wagner theorem [16]. This theorem supports the earlier statement in Sec. 2.6.2 that MFT is less accurate at low dimensions, where fluctuations are more significant. Long-range order can be stabilised in low-dimensional systems with significant anisotropy, as the resulting energy gap suppresses the spin wave excitations [2]. In 3D systems, magnetic order can survive the destabilising effect of spin waves, as there are more paths connecting the different sites that allow long-range spin correlations [9]. For example, $\text{Ba}_2\text{CuTeO}_6$ is an isotropic quasi-2D spin system with long-range order stabilised at low finite temperatures by the weak interlayer coupling.

2.7.1 Linear spin wave theory

Linear spin wave theory provides a semiclassical way of calculating the magnon dispersion relations and spin correlation functions. It is therefore frequently used in simulations of inelastic neutron scattering experiments, which directly probe magnetic excitations and are discussed in Sec. 3. The calculation assumes long-range order from mean-field theory (see Sec. 2.6.2) and only small deviations of the spins

from their equilibrium positions, which are valid assumptions for many systems at low temperatures. The magnetic excitations therefore form a dilute gas of magnons, allowing magnon interactions to be neglected. In this thesis, the calculations were performed analytically using the method outlined below and were checked against the numerical predictions of SPINW [17].

Firstly, the spin Hamiltonian can be simplified by observing that the three spin component operators S_j^x , S_j^y and S_j^z are not independent, but are related by $(S_j^x)^2 + (S_j^y)^2 + (S_j^z)^2 = S(S+1)$ [18]. One can therefore rewrite the Hamiltonian in terms of two independent operators: the boson creation operator $a_j^\dagger$ and annihilation operator a_j , which correspond to creating and annihilating a spin deviation at the j th site, respectively. This is performed by the Holstein-Primakoff transformation [19]:

$$S_j^+ = S_j^x + iS_j^y = \sqrt{2S} \sqrt{1 - \frac{a_j^\dagger a_j}{2S}} a_j \quad (2.27)$$

$$S_j^- = S_j^x - iS_j^y = \sqrt{2S} a_j^\dagger \sqrt{1 - \frac{a_j^\dagger a_j}{2S}} \quad (2.28)$$

$$S_j^z = S - a_j^\dagger a_j, \quad (2.29)$$

where z is the ordered spin direction, S_j^+ (S_j^-) is the spin raising (lowering) operator at the j th site, and the new operators satisfy the boson commutation relations $[a_j, a_l^\dagger] = \delta_{jl}$. The form of Eqs. (2.27) and (2.28) ensures the maximum number of spin deviations is $2S$, as required for the allowed states $\langle S_j^z \rangle = S, S-1, \dots, -S$ [18]. The spin component S_j^z in Eq. (2.29) can be derived from the two preceding transformations; note that it equals the maximum spin component S minus the number of spin deviations $\langle a_j^\dagger a_j \rangle$, as expected. One can extend this approach to multiple magnetic sublattices by defining separate operators for boson creation and annihilation on each sublattice [18].

The next step is to expand the square roots in Eqs. (2.27) and (2.28), assuming the temperature is low enough that the average number of spin deviations $\langle a_j^\dagger a_j \rangle$ is

much smaller than $2S$, the maximum number allowed on a given site. One can then expand in powers of $a_j^\dagger a_j/2S$, giving [18]

$$S_j^+ = \sqrt{2S} \left(1 - \frac{a_j^\dagger a_j}{4S} + \dots \right) a_j \quad (2.30)$$

$$S_j^- = \sqrt{2S} a_j^\dagger \left(1 - \frac{a_j^\dagger a_j}{4S} + \dots \right) \quad (2.31)$$

Using the harmonic approximation, terms in the Hamiltonian up to bilinear order in the boson operators are kept and higher order terms are discarded (hence the name, “*linear* spin wave theory”), which is equivalent to neglecting magnon interactions [18]. (Note that first order terms must vanish at equilibrium, because they correspond to the torque.)

It is useful to then substitute the boson operators $a_j^\dagger$ and a_j with their Fourier transforms $a_{\mathbf{k}}^\dagger$ and $a_{\mathbf{k}}$, respectively, which are defined as [18]

$$a_j = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} e^{-i\mathbf{k} \cdot \mathbf{r}_j} a_{\mathbf{k}} \quad (2.32)$$

$$a_j^\dagger = \frac{1}{\sqrt{N}} \sum_{\mathbf{k}} e^{i\mathbf{k} \cdot \mathbf{r}_j} a_{\mathbf{k}}^\dagger, \quad (2.33)$$

where $\mathbf{r}_j$ is the position of the j th site, N is the total number of unit cells, and the sum is over all wave vectors in the first Brillouin zone (with N discrete values specified by periodic boundary conditions). Note that the boson commutation relations are unchanged by the Fourier transformation. The Hamiltonian can then be written as [3]

$$\mathcal{H} = \left(1 + \frac{1}{S} \right) E_{\text{MF}} + \frac{1}{2} \sum_{\mathbf{k}} \mathbf{X}^\dagger \mathbf{H} \mathbf{X}, \quad (2.34)$$

where $\mathbf{X}$ is a basis of the boson operators, $\mathbf{H}$ is the Hamiltonian matrix describing one-magnon excitations, and E_{MF} is the classical mean-field energy of the ground state. For example, one could choose $\mathbf{X}^\dagger = (a_{\mathbf{k}}^\dagger \ a_{-\mathbf{k}})$ if there is only one magnetic sublattice. This reframes the problem in terms of delocalised spin deviations that are spread out across the spin lattice [2].

Finally, the Hamiltonian matrix $\mathbf{H}$ in Eq. (2.34) can often be diagonalised using a Bogolyubov transformation [20]:

$$\alpha_{\mathbf{k}} = u_{\mathbf{k}} a_{\mathbf{k}} + v_{\mathbf{k}} a_{-\mathbf{k}}^{\dagger} \quad (2.35)$$

$$\alpha_{-\mathbf{k}}^{\dagger} = v_{\mathbf{k}} a_{\mathbf{k}} + u_{\mathbf{k}} a_{-\mathbf{k}}^{\dagger}, \quad (2.36)$$

where $u_{\mathbf{k}}^2 - v_{\mathbf{k}}^2 = 1$ to preserve the boson commutation relations. This requirement motivates the choice $u_{\mathbf{k}} = \cosh \theta_{\mathbf{k}}$ and $v_{\mathbf{k}} = \sinh \theta_{\mathbf{k}}$, where $\theta_{\mathbf{k}}$ is chosen to diagonalise the Hamiltonian. An equivalent approach is to diagonalise the matrix $\mathbf{gH}$, where $\mathbf{g} = [\mathbf{X}, \mathbf{X}^{\dagger}]$ is a metric tensor that ensures the commutation relations are preserved [21]. The Hamiltonian can then be expressed in the familiar form of a quantum harmonic oscillator [18]:

$$\mathcal{H} = \left(1 + \frac{1}{S}\right) E_{\text{MF}} + \sum_{\mathbf{k}} \hbar \omega_{\mathbf{k}} \left(\alpha_{\mathbf{k}}^{\dagger} \alpha_{\mathbf{k}} + \frac{1}{2} \right), \quad (2.37)$$

where $\alpha_{\mathbf{k}}^{\dagger}$ ($\alpha_{\mathbf{k}}$) creates (annihilates) a magnon with wave vector $\mathbf{k}$ and energy $\hbar \omega_{\mathbf{k}}$, and the $\frac{1}{2} \sum_{\mathbf{k}} \hbar \omega_{\mathbf{k}}$ term introduces a zero-point correction to the ground state energy. In general, there will be a magnon mode for each magnetic sublattice. Using this transformation, it is then straightforward to calculate the spin correlation functions in the ground state, which is the magnon vacuum state.

The sublattice magnetisation can also be calculated using this formalism. Summing Eq. (2.29) over the spin sites, the total z component of the spin in the ground state is given by [18]

$$\sum_j \langle S_j^z \rangle = NS - \sum_{\mathbf{k}} \langle a_{\mathbf{k}}^{\dagger} a_{\mathbf{k}} \rangle = N(S - \Delta S), \quad (2.38)$$

where the Fourier transforms are defined in Eqs. (2.32) and (2.33). Applying the Bogolyubov transformation in Eqs. (2.35) and (2.36), the “spin reduction” ΔS is derived as

$$\Delta S = \frac{1}{N} \sum_{\mathbf{k}} v_{\mathbf{k}}^2, \quad (2.39)$$

which gives the average reduction in the ordered moment due to zero-point quantum fluctuations. Whereas this correction vanishes for a ferromagnet, it is in general finite for an antiferromagnet and depends on the interactions present and the lattice geometry [3], as discussed in Sec. 2.6.1.

Linear spin wave theory (LSWT) was used to simulate neutron scattering data for both of the studied materials presented in this thesis. For the coupled ladder antiferromagnet $\text{Ba}_2\text{CuTeO}_6$, long-range Néel order is stabilised by interladder and interlayer interactions and there is only weak frustration. LSWT is therefore able to describe qualitatively all the key features of the data. However, the triangular antiferromagnet $\text{Ba}_3\text{CoSb}_2\text{O}_9$ displays magnetic excitations that deviate greatly from the LSWT calculation, suggesting that quantum fluctuations are much more significant in this highly frustrated system. A strong and extended scattering continuum also indicates that multi-magnon processes, which are beyond the predictions of LSWT, are important to understanding the spin dynamics.

Chapter 3

Introduction to neutron scattering

An overview of neutron scattering is presented here, including the underlying theory and relevant experimental techniques. Firstly, the physical properties of neutrons are described, to elucidate their suitability as a probe of condensed matter. The following section introduces the neutron scattering cross-section, the measured quantity in these experiments, and derives a general expression for the cross-section in terms of the scattering potential, using the Born approximation. The cross-section for nuclear scattering is then derived, introducing the concepts of coherent and incoherent scattering and the Debye-Waller factor. The coherent cross-section is written in terms of the scattering function using the van Hove formulation. The derivation of the magnetic scattering cross-section is then outlined, assuming a spin-only moment and localised electrons, in terms of the magnetic form factor and the dynamical structure factor. The neutron sum rules that constrain the total integrated intensity are stated for reference. This is followed by a brief discussion of one- and two-magnon scattering, including magnon decay and lifetime broadening. The final section provides details about the experimental method, starting with the production of neutrons by spallation at the ISIS neutron source. There is then a brief discussion of the difference between single-crystal and powder scattering experiments and the effect of the instrument resolution. The technique of time-of-flight spectroscopy is explained,

for both direct and indirect geometries, and the MERLIN and LET instruments at ISIS are described and compared. Finally, there is a general discussion of sample environments, including goniometers, shielding, refrigeration and cryomagnets.

3.1 Properties of neutrons

Neutron scattering is a powerful and widely-used technique for measuring condensed matter systems. The usefulness of neutrons as an experimental probe arises from their physical properties, which are outlined below.

Firstly, neutrons have no electrical charge, allowing them to penetrate samples and measure the bulk properties. The lack of charge also means neutrons are principally scattered by the strong nuclear force and the strength of this interaction varies dramatically with atomic number; neutrons can therefore be used to measure samples which would be transparent to X-rays [22].

In addition, neutrons are spin- $\frac{1}{2}$ particles with magnetic moment

$$\boldsymbol{\mu}_n = -\gamma\mu_N\boldsymbol{\sigma}, \quad (3.1)$$

where

$$\mu_N = \frac{e\hbar}{2m_p} \quad (3.2)$$

is the nuclear magneton, e is the elementary charge, m_p is the proton mass, $\gamma = 1.913$ is a constant and $\boldsymbol{\sigma}$ is the Pauli spin operator. (The Pauli spin operator is related to the neutron spin operator $\boldsymbol{S}_n$ by $\boldsymbol{\sigma} = 2\boldsymbol{S}_n$.) The magnetic moment of the neutron allows it to couple to electron spins in partially filled shells. Neutron scattering measurements are therefore sensitive to the magnetic structure and dynamics of spin systems, and so are frequently used in the study of quantum magnets.

Furthermore, neutrons are readily produced at energy scales that are convenient for probing quasiparticle excitations in condensed matter. Neutron scattering experi-

ments typically use thermal neutrons, which are neutrons that have thermalised with a room temperature ($T \sim 300$ K) moderator. Thermal neutrons therefore have energy $k_{\text{B}}T \sim 25$ meV, which is similar to the energy scale of crystal lattice vibrations and spin wave excitations [23].

Finally, the de Broglie wavelength of thermal neutrons is $\lambda = h/\sqrt{2m_{\text{n}}E} \sim 1.8$ Å, which is the same order of magnitude as typical interatomic distances in solids and liquids [22]. Consequently, neutrons scattered from condensed matter are expected to give interference patterns that contain information about the atomic structure.

3.2 Scattering cross-section

Figure 3.1 illustrates the geometry of a neutron scattering event: a neutron with incident wave vector $\mathbf{k}$ and energy E hits the target and scatters off with wave vector $\mathbf{k}'$ and energy E' at polar coordinates (θ, ϕ) , where the polar axis is chosen to be the incident beam direction [23]. In a scattering experiment, a beam of monochromatic neutrons hits a sample and the scattered neutrons are counted at position-sensitive detectors. For inelastic scattering experiments, it is also important to measure the energy of the scattered neutrons, for example from the neutron time-of-flight (as described in Sec. 3.3.1). The resulting measured quantity is the partial differential cross-section $d^2\sigma/d\Omega dE'$, defined as the number of neutrons per unit time scattered into a small solid angle $d\Omega$ between energies E' and $E' + dE'$, divided by the incident neutron flux Φ [22]. Commonly, this is simply called the “intensity”. The normalisation by the neutron flux ensures that the intensity is not dependent on the incident beam. Integrating over the energy E' gives the differential cross-section $d\sigma/d\Omega$, and further integrating over the solid angle Ω gives the total scattering cross-section σ_{tot} [22].

Following the derivations in Refs. [22, 23], consider a target that has an initial

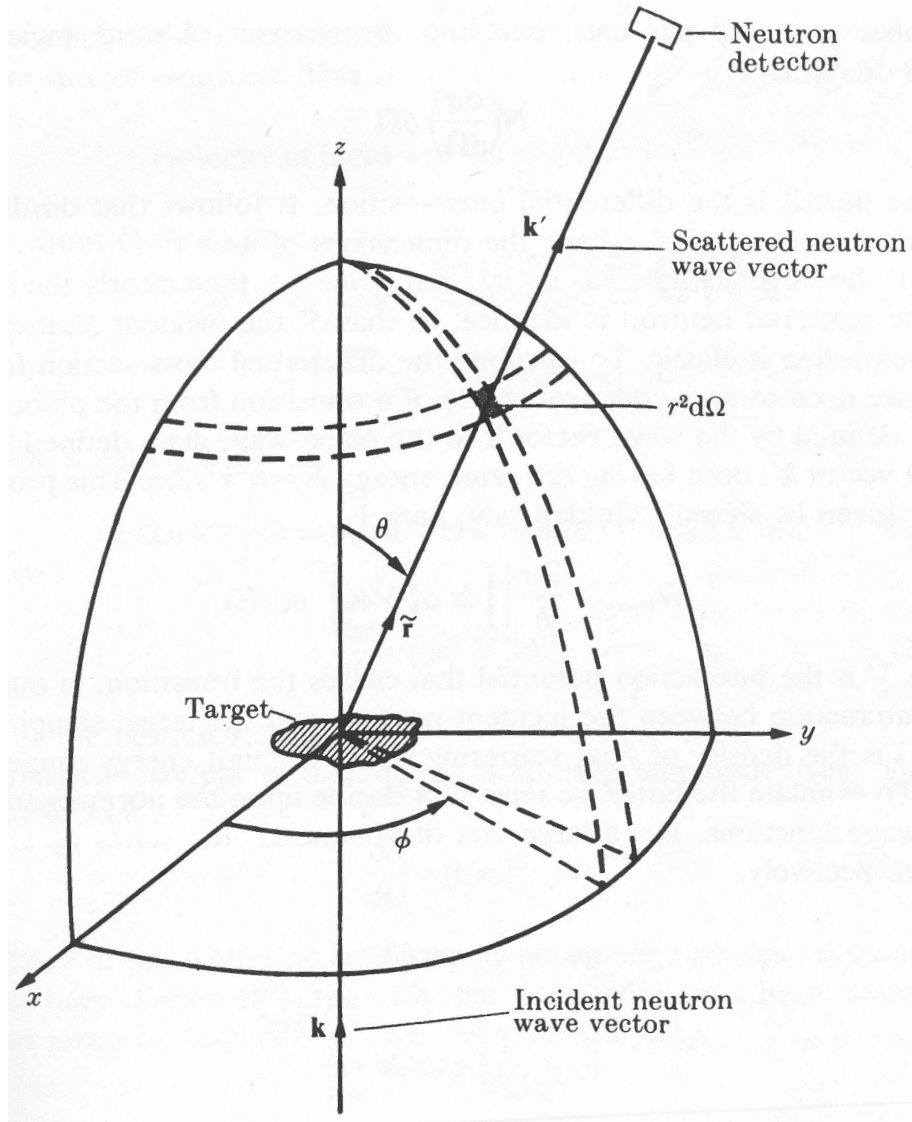


Figure 3.1: Geometry of a neutron scattering experiment. A neutron with wave vector $\mathbf{k}$ is scattered by the target into an area $r^2 d\Omega$ in the direction (θ, ϕ) with final wave vector $\mathbf{k}'$. The neutron is then measured at the detector. Reproduced with permission of Oxford Publishing Limited through PLSclear from Ref. [23]. © Stephen Lovesey 1984

state labelled by λ and a final state λ' . The differential cross-section for this transition is given by [23]

$$\left(\frac{d\sigma}{d\Omega}\right)_{\lambda'}^{\lambda} = \frac{1}{\Phi} \frac{1}{d\Omega} W(\mathbf{k}, \lambda \rightarrow \mathbf{k}', \lambda'), \quad (3.3)$$

where Φ is the incident neutron flux and $W(\mathbf{k}, \lambda \rightarrow \mathbf{k}', \lambda')$ is the transition rate from the initial neutron and target state $\mathbf{k}, \lambda$ to the final state $\mathbf{k}', \lambda'$. Using the Born approximation, the scattering potential V is assumed to only weakly perturb the incident neutron wave. The transition rate is then given by Fermi's golden rule [23]:

$$W(\mathbf{k}, \lambda \rightarrow \mathbf{k}', \lambda') = \frac{2\pi}{\hbar} \left| \int d\mathbf{r} d\mathbf{R} \psi_{\mathbf{k}'}^* \chi_{\lambda'}^* V \psi_{\mathbf{k}} \chi_{\lambda} \right|^2 \rho_{\mathbf{k}'}(E), \quad (3.4)$$

where $\mathbf{r}$ is the position of the neutron, $\mathbf{R}$ is the position of the target, $\psi_{\mathbf{k}}$ ($\psi_{\mathbf{k}'}$) is the initial (final) neutron wave function, χ_{λ} ($\chi_{\lambda'}$) is the initial (final) target wave function, and $\rho_{\mathbf{k}'}(E)$ is the density of final states. Substituting Eq. 3.4 into Eq. 3.3 and summing over the initial and final states, the differential cross-section is derived as [23]

$$\frac{d\sigma}{d\Omega} = \frac{k'}{k} \sum_{\lambda, \lambda'} P_{\lambda} |\langle \mathbf{k}' \lambda' | V | \mathbf{k} \lambda \rangle|^2, \quad (3.5)$$

where P_{λ} is the probability that the target is initially in state λ . Treating the neutron as a plane wave and choosing a convenient normalisation, the matrix element can be written as [24]

$$\langle \mathbf{k}' \lambda' | V | \mathbf{k} \lambda \rangle \equiv \frac{m_n}{2\pi\hbar^2} \int d\mathbf{r} d\mathbf{R} e^{-i\mathbf{k}' \cdot \mathbf{r}} \chi_{\lambda'}^* V e^{i\mathbf{k} \cdot \mathbf{r}} \chi_{\lambda}, \quad (3.6)$$

where m_n is the mass of a neutron. The k'/k prefactor in Eq. (3.5) arises from normalising the incident and scattered neutron flux.

The partial differential cross-section can now be found by including an energy dependence. For this system, conservation of energy requires that [23]

$$\hbar\omega = E - E' = E_{\lambda'} - E_{\lambda} = \frac{\hbar^2}{2m_n} [k^2 - (k')^2], \quad (3.7)$$

where $\hbar\omega$ is the energy transferred to the target and E_λ ($E_{\lambda'}$) is the energy of the target in the initial (final) state. The partial differential cross-section is then given by [23]

$$\frac{d^2\sigma}{d\Omega dE'} = \frac{k'}{k} \sum_{\lambda, \lambda'} P_\lambda |\langle \mathbf{k}'\lambda' | V | \mathbf{k}\lambda \rangle|^2 \delta(\hbar\omega + E_\lambda - E_{\lambda'}), \quad (3.8)$$

which expresses the fraction of neutrons with initial wave vector $\mathbf{k}$ and energy E that are scattered by a potential V into a solid angle $d\Omega$ with final wave vector $\mathbf{k}'$ and energy E' ; it is therefore a measurable quantity in a scattering experiment.

The important variables in a neutron scattering experiment are the energy transfer $\hbar\omega$ in Eq. (3.7) and the scattering vector

$$\boldsymbol{\kappa} = \mathbf{k} - \mathbf{k}', \quad (3.9)$$

which gives the momentum transferred to the target. In the following section, it will be shown that the scattering amplitude depends only on $\boldsymbol{\kappa}$ and not the individual neutron wave vectors, which is a consequence of the Born approximation [23].

3.2.1 Nuclear scattering

Neutrons scatter from the target nuclei mainly due to the short-range strong nuclear force. As the interaction range is much smaller than typical neutron wavelengths, the scattering is approximately isotropic. This motivates using the “Fermi pseudopotential”, which for the j th nucleus has the form [23]

$$V_j(\mathbf{r}) = \frac{2\pi\hbar^2}{m_n} b_j \delta(\mathbf{r} - \mathbf{R}_j), \quad (3.10)$$

where $\mathbf{R}_j$ is the position of the j th nucleus and b_j is its “scattering length”. The scattering length is a measure of the strength of the nuclear interaction and its value depends on the nuclide and the relative alignment of the nuclear and neutron spins. A positive scattering length corresponds to a repulsive force [22].

Substituting Eq. (3.10) into Eq. (3.8), one arrives at the following expression for the partial differential cross-section [22]:

$$\frac{d^2\sigma}{d\Omega dE'} = \frac{k'}{k} \sum_{\lambda, \lambda'} P_\lambda \left| \sum_j b_j \langle \lambda' | e^{i\boldsymbol{\kappa} \cdot \mathbf{R}_j} | \lambda \rangle \right|^2 \delta(\hbar\omega + E_\lambda - E_{\lambda'}), \quad (3.11)$$

where the matrix element in Eq. (3.6) has been simplified, because the Fourier transform of the pseudopotential has no wave vector dependence. Assuming P_λ is given by the Boltzmann distribution, the thermal average of an operator A is denoted by $\langle A \rangle = \sum_\lambda P_\lambda \langle \lambda | A | \lambda \rangle$. Using this notation, writing the Dirac delta as an integral over time, and using time-dependent Heisenberg operators, the partial differential cross-section further simplifies to [22]

$$\frac{d^2\sigma}{d\Omega dE'} = \frac{k'}{k} \frac{1}{2\pi\hbar} \sum_{j, j'} b_j b_{j'} \int_{-\infty}^{\infty} dt \langle e^{-i\boldsymbol{\kappa} \cdot \mathbf{R}_{j'}(0)} e^{i\boldsymbol{\kappa} \cdot \mathbf{R}_j(t)} \rangle e^{-i\omega t}, \quad (3.12)$$

where $\mathbf{R}_j(t)$ is the position of the j th nucleus at time t .

If the target contains a large number of nuclei, the measured cross-section is close to the average over all possible distributions of the scattering lengths b_j , given by Eq. (3.12) with $b_j b_{j'}$ replaced by $\overline{b_j b_{j'}}$ to denote the mean [22]. Assuming the scattering lengths are independent of one another, $\overline{b_j b_{j'}} = (\bar{b})^2$ for $j' \neq j$ and $\overline{b_j b_{j'}} = \bar{b}^2$ for $j' = j$, which allows the partial differential cross-section to be expressed as the sum of coherent (“coh”) and incoherent (“inc”) cross-sections [22]:

$$\frac{d^2\sigma}{d\Omega dE'} = \left(\frac{d^2\sigma}{d\Omega dE'} \right)_{\text{coh}} + \left(\frac{d^2\sigma}{d\Omega dE'} \right)_{\text{inc}}, \quad (3.13)$$

where

$$\left(\frac{d^2\sigma}{d\Omega dE'} \right)_{\text{coh}} = \frac{\sigma_{\text{coh}}}{4\pi} \frac{k'}{k} \frac{1}{2\pi\hbar} \sum_{j, j'} \int_{-\infty}^{\infty} dt \langle e^{-i\boldsymbol{\kappa} \cdot \mathbf{R}_{j'}(0)} e^{i\boldsymbol{\kappa} \cdot \mathbf{R}_j(t)} \rangle e^{-i\omega t}, \quad (3.14)$$

$$\left(\frac{d^2\sigma}{d\Omega dE'} \right)_{\text{inc}} = \frac{\sigma_{\text{inc}}}{4\pi} \frac{k'}{k} \frac{1}{2\pi\hbar} \sum_j \int_{-\infty}^{\infty} dt \langle e^{-i\boldsymbol{\kappa} \cdot \mathbf{R}_j(0)} e^{i\boldsymbol{\kappa} \cdot \mathbf{R}_j(t)} \rangle e^{-i\omega t}, \quad (3.15)$$

and

$$\sigma_{\text{coh}} = 4\pi(\bar{b})^2, \quad \sigma_{\text{inc}} = 4\pi[\bar{b}^2 - (\bar{b})^2]. \quad (3.16)$$

It is clear that only the coherent scattering cross-section can exhibit interference effects, as it is the only part that depends on the correlation between the positions of different nuclei; one would therefore expect this term to contain information about the crystal structure. Physically, the coherent contribution is equivalent to the scattering from a system of identical nuclei with the average scattering length $\bar{b}$ and the incoherent contribution arises due to deviations from the average [see Eq. (3.16)], for example because of different neutron-nucleus spin alignments or the presence of different isotopes [22].

In the case of a Bravais lattice, one can write the nuclear position $\mathbf{R}_l(t)$ as the sum of the equilibrium position $\mathbf{l}$ and the displacement $\mathbf{u}_l(t)$. As the lattice sites are equivalent, Eqs. 3.14 and 3.15 become [22]

$$\left(\frac{d^2\sigma}{d\Omega dE'} \right)_{\text{coh}} = \frac{\sigma_{\text{coh}}}{4\pi} \frac{k'}{k} \frac{N}{2\pi\hbar} \sum_l \int_{-\infty}^{\infty} dt e^{i\boldsymbol{\kappa} \cdot \mathbf{l}} \langle e^{-i\boldsymbol{\kappa} \cdot \mathbf{u}_0(0)} e^{i\boldsymbol{\kappa} \cdot \mathbf{u}_l(t)} \rangle e^{-i\omega t}, \quad (3.17)$$

$$\left(\frac{d^2\sigma}{d\Omega dE'} \right)_{\text{inc}} = \frac{\sigma_{\text{inc}}}{4\pi} \frac{k'}{k} \frac{N}{2\pi\hbar} \int_{-\infty}^{\infty} dt \langle e^{-i\boldsymbol{\kappa} \cdot \mathbf{u}_0(0)} e^{i\boldsymbol{\kappa} \cdot \mathbf{u}_0(t)} \rangle e^{-i\omega t}, \quad (3.18)$$

where N is the total number of nuclei, assuming one nucleus in each unit cell.

The elastic scattering cross-section can be obtained by considering correlations in the large time limit $t \rightarrow \infty$. In this limit, the correlation between $\mathbf{u}_0(0)$ and $\mathbf{u}_l(t)$ is independent of time and the integral becomes simply $\int_{-\infty}^{\infty} dt e^{-i\omega t} = 2\pi\hbar\delta(\hbar\omega)$ [22]. Elastic scattering also requires $k = k'$, by conservation of energy in Eq. (3.7). The thermal average can then be simplified using a result proven by Bloch: the probability function of a harmonic oscillator is a Gaussian function of the displacement variable Q [25]; it follows that $\langle e^Q \rangle = e^{\langle Q^2 \rangle/2}$. Finally, the coherent cross-section is more usefully expressed as a sum over the reciprocal lattice vectors $\boldsymbol{\tau}$ of the structural unit cell, using [22]

$$\sum_l e^{i\boldsymbol{\kappa} \cdot \mathbf{l}} = \frac{(2\pi)^3}{v_0} \sum_{\boldsymbol{\tau}} \delta(\boldsymbol{\kappa} - \boldsymbol{\tau}), \quad (3.19)$$

where v_0 is the volume of the unit cell. The elastic partial differential cross-sections

can then be written as [22]

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\text{coh el}} = \frac{\sigma_{\text{coh}}}{4\pi} N \frac{(2\pi)^3}{v_0} e^{-2W} \sum_{\boldsymbol{\tau}} \delta(\boldsymbol{\kappa} - \boldsymbol{\tau}) \delta(\hbar\omega), \quad (3.20)$$

$$\left(\frac{d^2\sigma}{d\Omega dE'}\right)_{\text{inc el}} = \frac{\sigma_{\text{inc}}}{4\pi} N e^{-2W} \delta(\hbar\omega), \quad (3.21)$$

where $2W = \langle [\boldsymbol{\kappa} \cdot \mathbf{u}_0(0)]^2 \rangle$. The factor e^{-2W} therefore reduces the intensity by an amount that increases with the scattering vector and with the average deviation of the nuclei from their equilibrium positions, which amounts to an intensity correction due to thermal fluctuations and is known as the Debye-Waller factor. The experiments presented in this thesis were conducted at low temperatures, allowing this factor to be ignored. These equations can be generalised to a non-Bravais crystal using a nuclear unit cell structure factor [22].

An inspection of Eq. (3.20) reveals that the coherent cross-section has sharp peaks where the scattering vector equals a reciprocal lattice vector, which is a statement of the Laue condition and the peaks are structural Bragg peaks. In contrast, the incoherent cross-section described by Eq. (3.21) is almost isotropic at low temperatures, giving a flat background in the intensity. In the case of vanadium, the incoherent cross-section is much larger than the coherent cross-section, which results in featureless neutron scattering that can be used to calibrate the neutron flux [26].

The inelastic contribution to the cross-sections in Eqs. (3.17) and (3.18) corresponds to neutrons exciting vibrational modes of the target system. These excitations are quantised as phonons, which are Goldstone bosons arising from the crystal lattice breaking the continuous translational symmetry, and therefore emanate from the structural Bragg peaks. The intensity increases rapidly with increasing temperature, as more vibrational modes are excited [22]. A detailed discussion of the inelastic nuclear scattering cross-sections is omitted here, because phonon excitations are not the focus of the studies presented in this thesis.

The scattering cross-sections can be better understood by adopting the van Hove formulation, which expresses the thermal averages in terms of correlation functions [27]. The coherent cross-section in Eq. (3.14) can equivalently be written as [22]

$$\left(\frac{d^2\sigma}{d\Omega dE'} \right)_{\text{coh}} = \frac{\sigma_{\text{coh}}}{4\pi} \frac{k'}{k} NS(\boldsymbol{\kappa}, \omega), \quad (3.22)$$

where

$$S(\boldsymbol{\kappa}, \omega) = \frac{1}{N} \frac{1}{2\pi\hbar} \sum_{j,j'} \int dt \langle e^{-i\boldsymbol{\kappa} \cdot \mathbf{R}_{j'}(0)} e^{i\boldsymbol{\kappa} \cdot \mathbf{R}_j(t)} \rangle e^{-i\omega t} \quad (3.23)$$

is called the “scattering function” and is the Fourier transform in space and time of the pair correlation function. The cross-section can therefore be expressed as a product of two factors: one that depends on how the neutron interacts with the target, σ_{coh} , and one that only depends on the properties of the target system, $S(\boldsymbol{\kappa}, \omega)$. The latter is typically the focus of a neutron scattering experiment.

3.2.2 Magnetic scattering

The cross-sections for magnetic scattering can be similarly derived by considering the interaction between the neutron and the magnetic moment of the electrons in the partially filled shell. Only the spin moment will be considered here, as the orbital component is quenched in both the systems presented in this thesis. The magnetic field at a point $\mathbf{R}$ due to an electron’s spin is given by [22]

$$\mathbf{B}_s = \nabla \times \mathbf{A}, \quad \mathbf{A} = \frac{\mu_0}{4\pi} \frac{\boldsymbol{\mu}_s \times \hat{\mathbf{R}}}{R^2}, \quad (3.24)$$

where $\mathbf{A}$ is the vector potential and $\boldsymbol{\mu}_s$ is the intrinsic magnetic moment of an electron, given by Eq. (2.4). Recalling the form of the neutron magnetic moment $\boldsymbol{\mu}_n$ in Eq. (3.1), the potential of a neutron in this magnetic field is [22]

$$V_m = -\boldsymbol{\mu}_n \cdot \mathbf{B}_s = -\frac{\mu_0}{4\pi} \gamma \mu_N g \mu_B \boldsymbol{\sigma} \cdot \left(\nabla \times \frac{\mathbf{s} \times \hat{\mathbf{R}}}{R^2} \right). \quad (3.25)$$

As the magnetic potential depends explicitly on the neutron spin operator $\boldsymbol{\sigma}$, it is important to consider the spin state σ of the neutron when calculating the cross-section. The partial differential cross-section in Eq. (3.8) can be rewritten [22]

$$\frac{d^2\sigma}{d\Omega dE'} = \frac{k'}{k} \sum_{\lambda, \lambda'} P_\lambda \sum_{\sigma, \sigma'} P_\sigma |\langle \mathbf{k}' \sigma' \lambda' | V_m | \mathbf{k} \sigma \lambda \rangle|^2 \delta(\hbar\omega + E_\lambda - E_{\lambda'}), \quad (3.26)$$

where the sum is over all initial spin states σ and final spin states σ' of the neutron, and P_σ is the probability that the neutron is initially in state σ . Integrating over the spatial coordinates of the neutron, the matrix element is found to be [22]

$$\langle \mathbf{k}' \sigma' \lambda' | V_m | \mathbf{k} \sigma \lambda \rangle = -\gamma r_0 \frac{g}{2} \sum_j \langle \sigma' \lambda' | \boldsymbol{\sigma} \cdot [\hat{\mathbf{k}} \times (\mathbf{s}_j \times \hat{\mathbf{k}})] e^{i\boldsymbol{\kappa} \cdot \mathbf{r}_j} | \sigma \lambda \rangle, \quad (3.27)$$

where the j th electron has position $\mathbf{r}_j$ and spin $\mathbf{s}_j$, and the sum is over all unpaired electrons. r_0 is called the “classical radius of the electron”, given by

$$r_0 = \frac{\mu_0}{4\pi} \frac{e^2}{m_e}, \quad (3.28)$$

where m_e is the mass of an electron.

Assuming the electrons are localised at the lattice sites, the electron position $\mathbf{r}_i$ can be replaced with the sum of the nuclear position $\mathbf{R}_{ld}$ and the electron position relative to the nucleus $\mathbf{r}$. The matrix element in Eq. (3.27) can then be written as [22]

$$\langle \mathbf{k}' \sigma' \lambda' | V_m | \mathbf{k} \sigma \lambda \rangle = -\gamma r_0 \frac{g_d}{2} F_d(\boldsymbol{\kappa}) \sum_{l,d} \langle \sigma' \lambda' | \boldsymbol{\sigma} \cdot [\hat{\mathbf{k}} \times (\mathbf{S}_{ld} \times \hat{\mathbf{k}})] e^{i\boldsymbol{\kappa} \cdot \mathbf{R}_{ld}} | \sigma \lambda \rangle, \quad (3.29)$$

where l labels the unit cell, d labels the ions within the unit cell, g_d is the g factor of the d th ion, and $\mathbf{S}_{ld}$ is the total spin operator for the ld ion. $F_d(\boldsymbol{\kappa})$ is the magnetic form factor of the d th ion, given by [22]

$$F_d(\boldsymbol{\kappa}) \equiv \int d\mathbf{r} \rho_d(\mathbf{r}) e^{i\boldsymbol{\kappa} \cdot \mathbf{r}}, \quad (3.30)$$

where $\rho_d(\mathbf{r})$ is the normalised density of unpaired electrons in the d th ion. Unlike the short-range nuclear interaction, the neutron can ‘see’ the spatial distribution of

the electrons; the resulting magnetic form factor drops off rapidly with increasing $|\boldsymbol{\kappa}|$, which necessitates measuring magnetic neutron scattering at small scattering vectors.

The matrix element in Eq. (3.29) can be simplified by recognising that $\boldsymbol{\sigma}$ depends only on neutron coordinates and the cross-product expression $\hat{\boldsymbol{\kappa}} \times (\mathbf{S}_{ld} \times \hat{\boldsymbol{\kappa}})$ depends only on electron coordinates. Substituting Eq. (3.29) into Eq. (3.26), the partial differential cross-section is then derived as [22]

$$\begin{aligned} \frac{d^2\sigma}{d\Omega dE'} = & (\gamma r_0)^2 \frac{k'}{k} \sum_{\alpha,\beta} (\delta_{\alpha\beta} - \hat{\kappa}_\alpha \hat{\kappa}_\beta) \sum_{l',d'} \sum_{l,d} \frac{1}{4} g_{d'} g_d F_{d'}^*(\boldsymbol{\kappa}) F_d(\boldsymbol{\kappa}) \\ & \times \sum_{\lambda,\lambda'} P_\lambda \langle \lambda | e^{-i\boldsymbol{\kappa} \cdot \mathbf{R}_{l'd'}} S_{l'd'}^\alpha | \lambda' \rangle \langle \lambda' | e^{i\boldsymbol{\kappa} \cdot \mathbf{R}_{ld}} S_{ld}^\beta | \lambda \rangle \delta(\hbar\omega + E_\lambda - E_{\lambda'}), \end{aligned} \quad (3.31)$$

where the α, β summations are over components x, y, z , and S_{ld}^α is the α spin component operator for the ld ion. The orientation factor $(\delta_{\alpha\beta} - \hat{\kappa}_\alpha \hat{\kappa}_\beta)$ makes it clear that a neutron can only couple to components of the moment that are perpendicular to the scattering vector $\boldsymbol{\kappa}$, and arises from considering the cross-product expression in Eq. (3.29) as the projection of $\mathbf{S}_{ld}$ onto the plane perpendicular to $\hat{\boldsymbol{\kappa}}$. Writing the Dirac delta as an integral over time and converting to time-dependent Heisenberg operators, the partial differential cross-section is alternatively expressed as [22]

$$\begin{aligned} \frac{d^2\sigma}{d\Omega dE'} = & \frac{(\gamma r_0)^2}{2\pi\hbar} \frac{k'}{k} \sum_{\alpha,\beta} (\delta_{\alpha\beta} - \hat{\kappa}_\alpha \hat{\kappa}_\beta) \sum_{l',d'} \sum_{l,d} \frac{1}{4} g_{d'} g_d F_{d'}^*(\boldsymbol{\kappa}) F_d(\boldsymbol{\kappa}) \\ & \times \int_{-\infty}^{\infty} dt \langle e^{-i\boldsymbol{\kappa} \cdot \mathbf{R}_{l'd'}(0)} e^{i\boldsymbol{\kappa} \cdot \mathbf{R}_{ld}(t)} \rangle \langle S_{l'd'}^\alpha(0) S_{ld}^\beta(t) \rangle e^{-i\omega t}, \end{aligned} \quad (3.32)$$

where $\langle \dots \rangle$ is again used to indicate a thermal average. For a Bravais lattice with one magnetic ion per unit cell, the cross-section reduces to [22]

$$\begin{aligned} \frac{d^2\sigma}{d\Omega dE'} = & N \frac{(\gamma r_0)^2}{2\pi\hbar} \frac{k'}{k} \left[\frac{1}{2} g F(\boldsymbol{\kappa}) \right]^2 \sum_{\alpha,\beta} (\delta_{\alpha\beta} - \hat{\kappa}_\alpha \hat{\kappa}_\beta) \sum_l e^{i\boldsymbol{\kappa} \cdot \mathbf{l}} \\ & \times \int_{-\infty}^{\infty} dt \langle e^{-i\boldsymbol{\kappa} \cdot \mathbf{u}_0(0)} e^{i\boldsymbol{\kappa} \cdot \mathbf{u}_l(t)} \rangle \langle S_0^\alpha(0) S_l^\beta(t) \rangle e^{-i\omega t}, \end{aligned} \quad (3.33)$$

where $\mathbf{u}_l(t)$ is the displacement of the l th nucleus from its equilibrium position at time t .

The partial differential cross-section can be rewritten using the van Hove formulation introduced in Eq. (3.22) [23]:

$$\frac{d^2\sigma}{d\Omega dE'} = N(\gamma r_0)^2 \frac{k'}{k} \left[\frac{1}{2} g F(\boldsymbol{\kappa}) \right]^2 e^{-2W} \sum_{\alpha, \beta} (\delta_{\alpha\beta} - \hat{\kappa}_\alpha \hat{\kappa}_\beta) S^{\alpha\beta}(\boldsymbol{\kappa}, \omega), \quad (3.34)$$

where $S^{\alpha\beta}(\boldsymbol{\kappa}, \omega)$ is the Fourier transform in space and time of the spin correlation function [*cf.* Eq. (3.23)], commonly called the “dynamical structure factor”. Converting back to time-independent Schrödinger operators, as in Eq. (3.31), one can derive the following convenient form [23]:

$$S^{\alpha\beta}(\boldsymbol{\kappa}, \omega) = \sum_{\lambda, \lambda'} P_\lambda \langle \lambda | S_{-\boldsymbol{\kappa}}^\alpha | \lambda' \rangle \langle \lambda' | S_{\boldsymbol{\kappa}}^\beta | \lambda \rangle \delta(\hbar\omega + E_\lambda - E_{\lambda'}), \quad (3.35)$$

where $S_{\boldsymbol{\kappa}}^\alpha$ is the Fourier transform of the α spin component operator, defined as

$$S_{\boldsymbol{\kappa}}^\alpha = \frac{1}{\sqrt{N}} \sum_{l,d} e^{i\boldsymbol{\kappa} \cdot \mathbf{R}_{ld}} S_{ld}^\alpha. \quad (3.36)$$

When the correlation functions are calculated using LSWT, as outlined in Sec. 2.7.1, one assumes a temperature $T = 0$ and the dynamical structure factor is written as

$$S^{\alpha\beta}(\boldsymbol{\kappa}, \omega) = \sum_{\lambda'} \langle 0 | S_{-\boldsymbol{\kappa}}^\alpha | \lambda' \rangle \langle \lambda' | S_{\boldsymbol{\kappa}}^\beta | 0 \rangle \delta(\hbar\omega + E_0 - E_{\lambda'}), \quad (3.37)$$

where $|0\rangle$ is the ground state with energy E_0 . Neutron scattering therefore offers a way to directly probe the spin correlations in a magnetic material and so provides information on the magnetic structure and dynamics.

A simple case to consider is a paramagnet in zero applied magnetic field, as the spins are uncorrelated in space and time. The spin correlation function can therefore be written $\langle S_{ld}^\alpha(0) S_{l'd'}^\beta(t) \rangle = \langle S_{ld}^\alpha S_{l'd'}^\beta \rangle = \delta_{ll'} \delta_{dd'} \delta_{\alpha\beta} \langle (S_{ld}^\alpha)^2 \rangle = \frac{1}{3} \delta_{ll'} \delta_{dd'} \delta_{\alpha\beta} S_d(S_d + 1)$, where S_d is the spin of the d th ion in the unit cell. The partial differential cross-section in Eq. (3.31) then simplifies to [22]

$$\frac{d^2\sigma}{d\Omega dE'} = \frac{2}{3} N_0 (\gamma r_0)^2 e^{-2W} \sum_d \left[\frac{1}{2} g_d F_d(\boldsymbol{\kappa}) \right]^2 S_d(S_d + 1) \delta(\hbar\omega), \quad (3.38)$$

where N_0 is the total number of unit cells. A paramagnet therefore exhibits diffuse scattering on the elastic line.

A significant simplification of the cross-section in Eq. (3.34) is possible when S^z is a good quantum number (*i.e.* it is conserved), for example in the case of the Heisenberg model. It can be shown that only the diagonal $\alpha = \beta$ terms contribute to the intensity and $S^{xx} = S^{yy}$ by symmetry [23]. The x and y orientation factors can then be combined using $(1 - \hat{\kappa}_x^2) + (1 - \hat{\kappa}_y^2) = 1 + \hat{\kappa}_z^2$. The resulting scattering cross-section is given by [23]

$$\frac{d^2\sigma}{d\Omega dE'} = N(\gamma r_0)^2 \frac{k'}{k} \left[\frac{1}{2} g F(\boldsymbol{\kappa}) \right]^2 e^{-2W} [(1 + \hat{\kappa}_z^2) S^{xx}(\boldsymbol{\kappa}, \omega) + (1 - \hat{\kappa}_z^2) S^{zz}(\boldsymbol{\kappa}, \omega)]. \quad (3.39)$$

This simplified form is appropriate for the studied material $\text{Ba}_2\text{CuTeO}_6$, which comprises coupled spin ladders with Heisenberg interactions.

In magnetic neutron scattering, the total integrated intensity is constrained by the so-called “sum rules”. Independent of the Hamiltonian, the dynamical structure factor for a spin S must satisfy [28]

$$\frac{1}{N} \sum_{\alpha, \boldsymbol{\kappa}} \int_{-\infty}^{\infty} d(\hbar\omega) S^{\alpha\alpha}(\boldsymbol{\kappa}, \omega) = S(S + 1), \quad (3.40)$$

where N is the total number of spins and the off-diagonal components of $S^{\alpha\beta}$ cancel. More restrictive rules apply for $S = \frac{1}{2}$, which specify each component of the dynamical structure factor [28]:

$$\frac{1}{N} \sum_{\boldsymbol{\kappa}} \int_{-\infty}^{\infty} d(\hbar\omega) S^{\alpha\beta}(\boldsymbol{\kappa}, \omega) = \frac{1}{4} \delta_{\alpha\beta}. \quad (3.41)$$

If a reference frame is chosen such that the spins are ferromagnetically aligned along the z axis, the S^{xx} and S^{yy} components correspond to one-magnon excitations and the S^{zz} component contains the elastic Bragg peaks and two-magnon scattering. The total integrated intensity of the Bragg peaks is $(S - \Delta S)^2$, where the spin reduction ΔS can be estimated using LSWT [see Sec. 2.7.1, in particular Eq. (2.39)]. LSWT

does not automatically obey these sum rules, but a normalisation factor can be introduced to impose them, assuming LSWT correctly predicts the energy and wave vector dependence of the dynamical structure factor. This approach was used in the analysis of the $\text{Ba}_3\text{CoSb}_2\text{O}_9$ data to set the total integrated intensity of the simulated two-magnon continuum.

The elastic magnetic cross-section can be extracted by considering correlations in the large time limit $t \rightarrow \infty$, as explained previously for the nuclear scattering cross-section in Sec. 3.2.1. The same method can be used for magnetic scattering from a Bravais crystal to derive the elastic component of the cross-section in Eq. (3.33) [22]:

$$\left(\frac{d^2\sigma}{d\Omega dE'} \right)_{\text{el}} = N(\gamma r_0)^2 \left[\frac{1}{2} gF(\boldsymbol{\kappa}) \right]^2 e^{-2W} \sum_{\alpha, \beta} (\delta_{\alpha\beta} - \hat{\kappa}_\alpha \hat{\kappa}_\beta) \sum_l e^{i\boldsymbol{\kappa} \cdot \mathbf{l}} \langle S_0^\alpha \rangle \langle S_l^\beta \rangle \delta(\hbar\omega). \quad (3.42)$$

For the case of a helical spin structure in the xy plane with ordering wave vector $\mathbf{Q}$, as described by Eqs. (2.23)–(2.25), the elastic cross-section is given by [22]

$$\begin{aligned} \left(\frac{d^2\sigma}{d\Omega dE'} \right)_{\text{el}} &= \frac{N (2\pi)^3}{4 v_0} (\gamma r_0)^2 \left[\frac{1}{2} gF(\boldsymbol{\kappa}) \right]^2 e^{-2W} (1 + \hat{\kappa}_z^2) \langle S \rangle^2 \\ &\times \sum_{\boldsymbol{\tau}} [\delta(\boldsymbol{\kappa} + \mathbf{Q} - \boldsymbol{\tau}) + \delta(\boldsymbol{\kappa} - \mathbf{Q} - \boldsymbol{\tau})] \delta(\hbar\omega), \end{aligned} \quad (3.43)$$

where $\boldsymbol{\tau}$ is a reciprocal lattice vector of the structural unit cell and v_0 is the volume of the unit cell. It is clear by inspection that the intensity is strongly peaked about scattering vectors $\boldsymbol{\kappa} = \boldsymbol{\tau} \pm \mathbf{Q}$, *i.e.* there are magnetic Bragg peaks at plus/minus the ordering wave vector and symmetry-equivalent points in reciprocal space. These $\pm \mathbf{Q}$ Bragg peaks are observed in the studied material $\text{Ba}_3\text{CoSb}_2\text{O}_9$, which has a 120° ordered ground state. Note that collinear order is simply a special case of helical order, in which the $\boldsymbol{\tau} \pm \mathbf{Q}$ peaks are not uniquely defined. So neutron diffraction is able to measure the magnetic ordering wave vector and thereby directly probes the magnetic structure.

Neutrons can also scatter inelastically from spin waves, which are described in

Sec. 2.7. As magnetic neutron scattering experiments are typically conducted at very low temperatures, to a good approximation the sample is initially in the vacuum state with no magnons excited [26]. An incident neutron can then create a magnon, losing energy in the process. The magnon energies and wave vectors are measured by the change in the neutron energy and wave vector, applying appropriate conservation laws. The one-magnon modes have a well-defined dispersion relation, broadened by the resolution of the instrument and any finite-lifetime effects (see the following discussion). The dispersion relations and spin correlation functions can be calculated approximately using LSWT, as outlined in Sec. 2.7.1.

It is also possible for neutrons to lose energy by creating multiple magnons. The change in neutron energy and wave vector must equal the sum of the energies and wave vectors of the magnons created, by energy and momentum conservation; for a two-magnon scattering event, this gives a scattering vector $\boldsymbol{\kappa} = \mathbf{k}_1 + \mathbf{k}_2$ and energy transfer $\hbar\omega_{2\mathcal{M}} = \hbar\omega_{1\mathcal{M}}(\mathbf{k}_1) + \hbar\omega_{1\mathcal{M}}(\mathbf{k}_2)$, where $\hbar\omega_{2\mathcal{M}}$ is the total two-magnon energy and $\hbar\omega_{1\mathcal{M}}(\mathbf{k})$ is the one-magnon dispersion relation. As the dispersions are smooth functions, it is possible to continuously tune the energy of the magnon pair by making small deviations in the individual magnon wave vectors. Consider a small deviation $\delta\mathbf{k}$ such that $\mathbf{k}_1 \rightarrow \mathbf{k}_1 + \delta\mathbf{k}$ and $\mathbf{k}_2 \rightarrow \mathbf{k}_2 - \delta\mathbf{k}$, leaving $\boldsymbol{\kappa}$ unchanged. The two-magnon energy is then $E(\mathbf{k}_1 + \delta\mathbf{k}) + E(\mathbf{k}_2 - \delta\mathbf{k}) = \hbar\omega_{2\mathcal{M}} + \delta E$, where in general $\delta E \neq 0$. Two-magnon scattering is therefore expected to cover a continuum of energies, and the same reasoning applies to higher-order scattering events. If there are magnon pairs with energies below the one-magnon modes, *i.e.* $\hbar\omega_{2\mathcal{M}} < \hbar\omega_{1\mathcal{M}}$ at a given $\boldsymbol{\kappa}$, then it is kinematically allowed for a magnon to decay into two magnons. If the Hamiltonian also has a finite matrix element between the initial and final states, magnons at these wave vectors are expected to decay. The resulting finite magnon lifetime manifests in neutron scattering data as a finite broadening of the one-magnon modes in en-

ergy, due to the Heisenberg uncertainty principle ($\Delta E \Delta t \geq \frac{\hbar}{2}$). There is evidence of such lifetime broadening in the studied material $\text{Ba}_2\text{CuTeO}_6$, where the simulated two-magnon continuum drops below the one-magnon modes. However, there is no evidence of this broadening in $\text{Ba}_3\text{CoSb}_2\text{O}_9$, which is consistent with simulations that place the two-magnon continuum above the one-magnon modes throughout reciprocal space.

3.3 Neutron scattering experiments

The experiments presented in this thesis were performed at the ISIS neutron and muon source, which generates a pulsed beam of neutrons using a particle accelerator. Nuclear reactors can also be used to produce neutrons by fission [26], but this overview will only cover techniques that are directly relevant.

A schematic diagram of the ISIS neutron source is shown in Fig. 3.2. At the ion source, H^- ions are produced from hydrogen plasma by electrical discharge and are extracted in pulses. Radio-frequency electric fields are used to focus and bunch the ions, which are then fed into a linear accelerator (“linac”). In the linac, high-intensity radio-frequency electric fields further accelerate the ions, before feeding them into the synchrotron. The injected H^- ions are stripped of their electrons and enter a 52 m diameter circular orbit, guided round by dipole magnets and focussed by quadrupole magnets [26]. After injection, the protons are accelerated in two bunches using radio-frequency cavities, which are synchronised with the dipole magnets to maintain the orbit (hence the name “synchrotron”). The pulses are then ejected by kicker magnets into the extracted proton beam lines, which are evacuated tubes with quadrupole magnets to focus the beam. The whole process is repeated 50 times per second with an average current of $200 \mu\text{A}$ [26].

The extracted proton beam lines lead to target stations, where the proton hits a

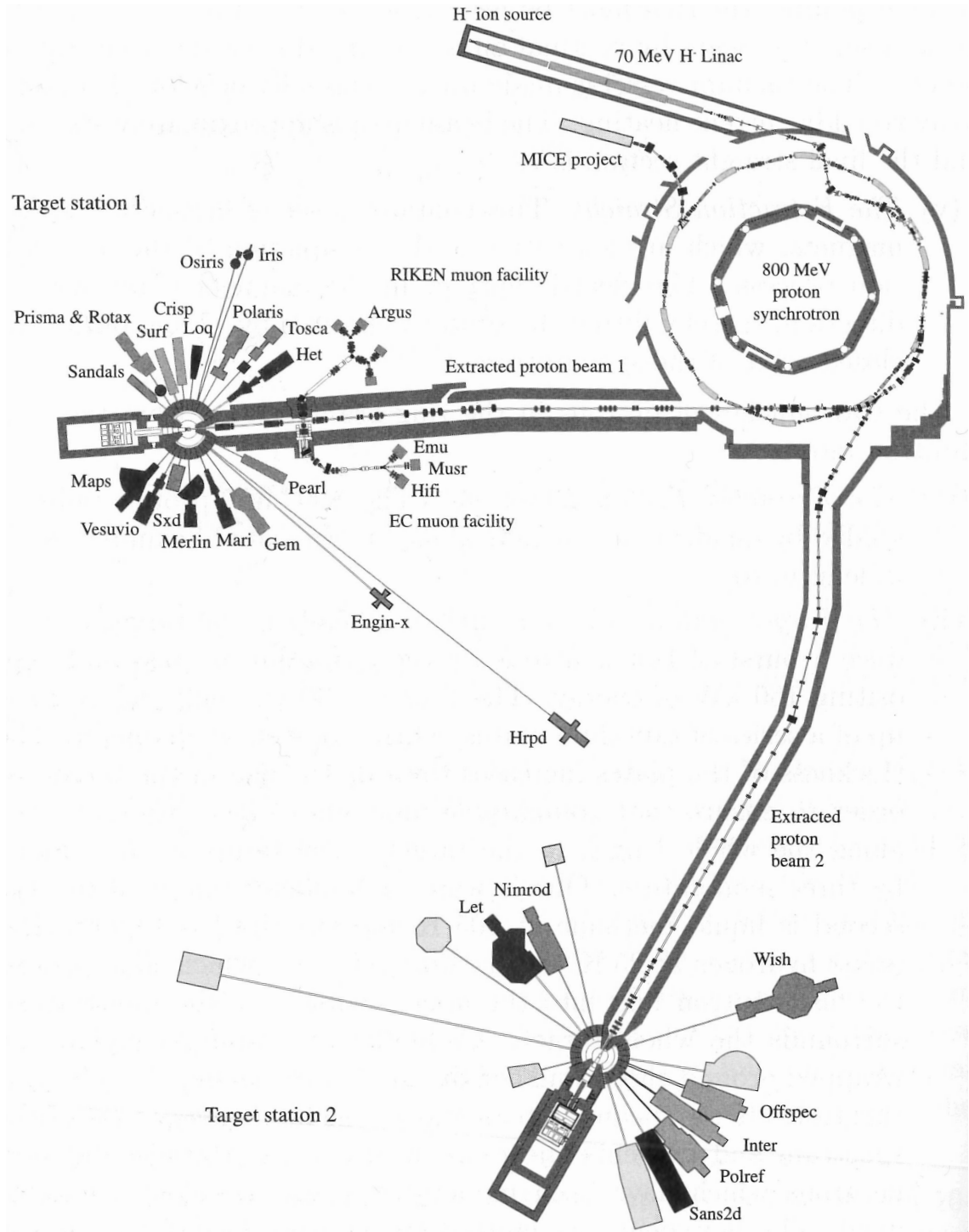


Figure 3.2: Layout of ISIS neutron source, including the H^- ion source, the linear accelerator (“Linac”), the proton synchrotron, the target stations and the neutron instruments. The experiments presented in this thesis were conducted at the MERLIN spectrometer at Target Station 1 and the LET spectrometer at Target Station 2. Reproduced with permission of Oxford Publishing Limited through PLSclear from Ref. [26]. © Oxford University Press, 2009

tantalum target and produces neutrons by spallation [26]. In this process, incident high-energy protons are absorbed by the target nuclei, triggering a cascade of high-energy particles, which eventually results in the de-excitation of the nuclei and the emission of lower-energy neutrons. The target is surrounded by beryllium reflectors that focus the neutrons onto moderators, which are bodies of light molecules that cool neutrons to useful energy ranges for experiments. The neutrons thermalise with the moderator as they pass through it and the resulting energy distribution depends on the type of moderator and its temperature. Target Station 1 has three types of moderators to produce neutrons of different energies: two water moderators at room temperature, a liquid methane moderator at 105 K and a liquid hydrogen moderator at 25 K [26]. Target Station 2 is optimised for long-wavelength neutrons, with a solid methane moderator at 40 K [29] and a composite hydrogen/solid methane moderator at 17 K [30]. The neutrons are then directed towards the instruments by total reflection in nickel-coated supermirror guides. Finally, the neutron beam is collimated by steel and concrete shutters [26].

Recall the definition of the differential cross-section in Eq. (3.3), which includes a normalisation by the incident neutron flux Φ . In neutron scattering instruments, this normalisation is performed by dividing the count rate at the detectors by the count rate measured at a monitor in the incident beam. The beam monitor can also be used to correct for the spectrum of the incident beam, *i.e.* to account for some neutron energies being more common than others [26]. The final intensity is therefore independent of any changes in the neutron flux supplied to the instrument.

The target sample is typically either a single crystal (or multiple, co-aligned single crystals) or a powder. A single-crystal measurement is able to directly measure the cross-section in Eq. (3.34), as the sample has a well-defined orientation that is determined by X-ray or neutron diffraction. Powder samples comprise many randomly-

oriented grains, so the experiment measures a spherical average of the cross-section, integrated over all directions of $\boldsymbol{\kappa}$; the resulting two-dimensional data set is a function of $|\boldsymbol{\kappa}|$ and ω [26]. Although single-crystal scattering yields more information than powder scattering, there is often considerable difficulty in growing sizeable single-crystal samples, making the powder method more experimentally accessible.

As mentioned in the previous section, neutron scattering measurements are limited by the instrument resolution, which broadens the observed features. There will in general be an energy-dependent spread of both neutron energies and wave vectors, due to the finite neutron pulse width, the spatial extent of the sample, the angular divergence of the beam, the finite size of the detector elements, the spatial extent of the moderator, and the sample mosaic [26]. A common approximation is adopted throughout this thesis, which models the resolution as a constant spread in energy, found by fitting to scans through the incoherent scattering at the elastic line. The instrument resolution can then be included explicitly in the dynamical structure factor in Eq. (3.37) as

$$S^{\alpha\beta}(\boldsymbol{\kappa}, \omega) = \sum_{\lambda'} \langle 0 | S_{-\boldsymbol{\kappa}}^{\alpha} | \lambda' \rangle \langle \lambda' | S_{\boldsymbol{\kappa}}^{\beta} | 0 \rangle R(\hbar\omega + E_0 - E_{\lambda'}), \quad (3.44)$$

where $R(\hbar\omega + E_0 - E_{\lambda'})$ is the lineshape of the mode with excitation energy $E_{\lambda'} - E_0$.

Figure 3.2 indicates the wide range of neutron instruments at the two target stations, most of which are beyond the scope of this brief introduction. All the experiments presented in this thesis were conducted at the MERLIN and LET instruments, which are time-of-flight spectrometers.

3.3.1 Time-of-flight spectroscopy

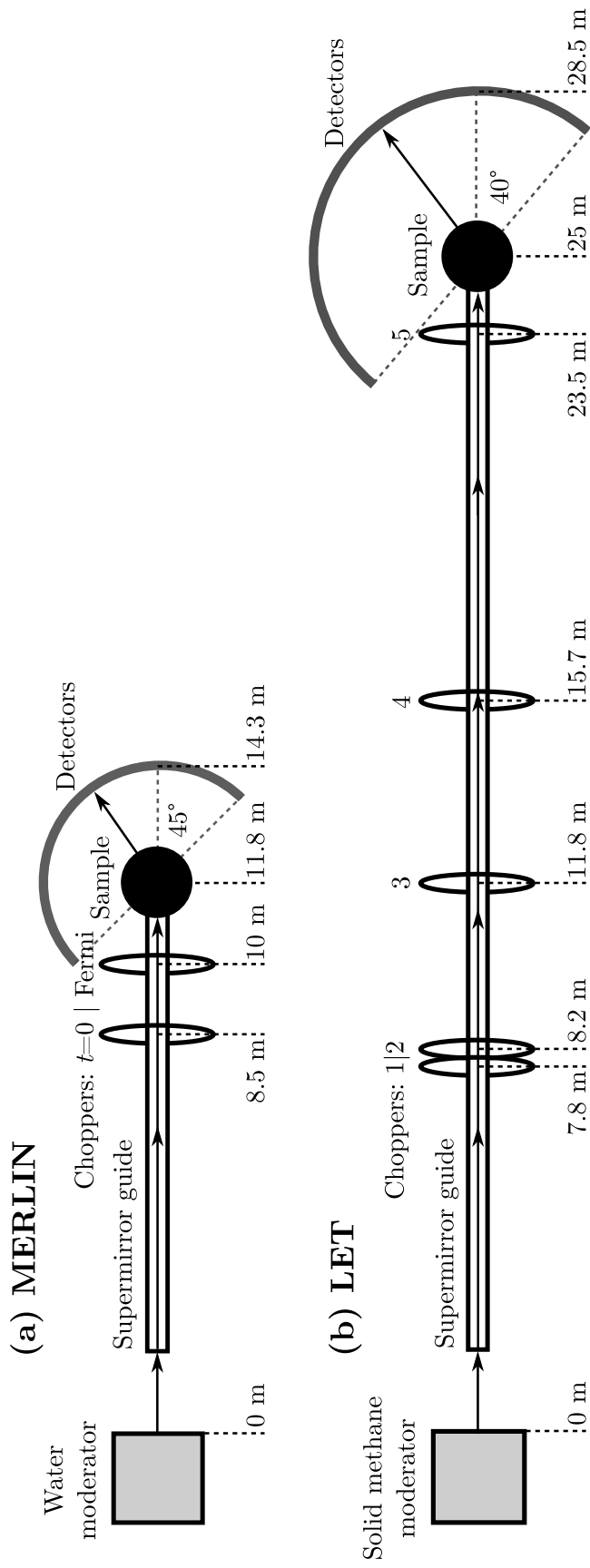


Figure 3.3: Schematic diagram of the (a) MERLIN [31] and (b) LET [32] spectrometers at ISIS neutron source in plan view, indicating the positions of the moderator (shaded square), supermirror guide (rectangle), choppers (ovals), sample (filled circle) and detectors (semicircle), and the flight path of a neutron (arrows). LET's longer flight path and more sophisticated system of choppers contribute to its higher energy resolution. LET's detectors also have a higher wave vector resolution for the same angular range, achieved by using a larger detector array positioned farther from the sample [32].

Time-of-flight spectrometers calculate the energy transfer by measuring how long it takes the neutron to arrive at the detector from entering the instrument [26]. The scattered neutrons are observed at an array of position-sensitive detectors, allowing the scattering vector to be determined from the neutron energy and the scattering angle. Time-of-flight measurements require bursts of neutrons with well-defined start times, *i.e.* a pulsed beam, normally produced by an accelerator source. The key advantage of time-of-flight spectroscopy over other techniques, for instance a triple-axis spectrometer, is its ability to simultaneously probe a wide region of (κ, ω) reciprocal space [26].

There are two possible geometries for time-of-flight measurements: direct geometry, in which the incident energy is fixed and the final energy is measured; and indirect geometry, in which the incident energy is measured and the final energy is fixed [26]. The fixed energy is set by Bragg scattering from a single-crystal analyser and/or by choppers, which are mechanical devices that only allow the neutrons to pass through in specified time intervals. Choppers are often rotating, neutron-absorbing discs with small windows to allow neutrons through. The measured part of the energy is found from the neutron time of flight, as described above. Both MERLIN and LET are direct-geometry time-of-flight spectrometers.

A simple direct-geometry neutron instrument, such as MERLIN, uses a Fermi chopper with rotating slits to select a monochromatic pulse. The LET instrument has a more complex system, consisting of several choppers with frequencies that can be independently varied to allow multiple energy ranges of neutrons through in the same time frame [33]; this is known as repetition rate multiplication (RRM) [32]. It is a powerful technique that allows excitations to be measured at multiple energy scales simultaneously.

The MERLIN instrument is designed to provide a high neutron flux with medium

energy resolution [31] and is shown schematically in Fig. 3.3(a). MERLIN has a dedicated room-temperature water moderator at Target Station 1. The neutrons leaving the moderator pass down a supermirror guide, which maximises the flux at the sample. A $t = 0$ chopper blocks the high-energy neutrons and sets the start time for the time-of-flight measurement. The Fermi chopper then fixes the incident energy of the neutrons. After the neutrons are scattered by the sample, they are measured by an array of 3 m long ^3He detector tubes, covering an angular range of -45° to 135° in the horizontal plane and $\pm 30^\circ$ in the vertical direction [31]. MERLIN was used to probe key features of the full energy spectrum of spin wave excitations in the studied material $\text{Ba}_2\text{CuTeO}_6$.

The LET instrument is a cold-neutron spectrometer, providing high energy resolution measurements with a very low background [32]. The layout is illustrated schematically in Fig. 3.3(b). The neutrons are cooled by the 17 K composite hydrogen/solid methane moderator at Target Station 2, before passing down a supermirror guide to a series of five choppers: the first and last choppers set the incident energy and the energy resolution, the second chopper filters out slow neutrons from the previous time frame, the third chopper removes pulses to prevent the time-of-flight measurements overlapping, and the fourth chopper removes slow neutrons from the long tail of the moderator distribution [32]. The scattered neutrons are then measured at an array of 4 m long ^3He detector tubes, covering -40° to 140° in the horizontal plane and $\pm 30^\circ$ in the vertical direction [32]. LET was used to perform high-resolution measurements of the low-energy spin dynamics in $\text{Ba}_2\text{CuTeO}_6$ and $\text{Ba}_3\text{CoSb}_2\text{O}_9$.

A few key similarities and differences are evident when comparing MERLIN and LET in Fig. 3.3. They are both direct-geometry time-of-flight spectrometers with the same basic principle of operation: first, the neutrons thermalise with a moderator;

they then travel down a supermirror guide to a series of choppers that fix the incident energy; and finally, they scatter off the sample and are measured at a 180° array of position-sensitive detectors [32, 31]. However, there are also significant differences: LET uses a solid methane moderator that is more suitable for producing low-energy neutrons; the primary flight path in LET is more than double that in MERLIN, allowing a more sophisticated system of choppers and higher-resolution time-of-flight measurements; and LET uses larger detectors positioned farther from the sample, giving it a greater wave vector resolution for the same angular range [32, 31]. These differences make LET a superior instrument for measuring low-energy excitations.

The position-sensitive detectors in MERLIN and LET are long tubes containing ^3He gas [32, 31]. When an incident neutron is absorbed by the ^3He , a nuclear reaction produces energetic particles that ionise the surrounding gas. The metal tube acts as a cathode and a thin metal wire running axially down the centre acts as an anode. When a voltage is applied across the electrodes, they attract the charged particles produced by the ionisation. The resulting discharge is measured as a current pulse at either ends of the wire anode, and the time difference depends on the position of the neutron absorption event. The detector tube is therefore sensitive to the position of the captured neutron along its length, and stacking tubes in a space-filling array creates a two-dimensional position-sensitive detector bank [26].

It is possible to completely map the four-dimensional (4D) Brillouin zone in $(\boldsymbol{\kappa}, \omega)$ reciprocal space by combining single-crystal data sets collected over a range of crystal orientations in small angular steps; at ISIS, this is known as a ‘‘Horace scan’’. As the four $(\boldsymbol{\kappa}, \omega)$ variables are independent of one another, one can visualise the data along any chosen direction in reciprocal space [32]. This technique was used to measure several Brillouin zones in $\text{Ba}_3\text{CoSb}_2\text{O}_9$, providing a complete picture of the wave vector and energy dependence of the one-magnon modes and much of the continuum

scattering. The time-of-flight neutron data processing, including the packaging of data sets in Horace scans, was performed throughout using the MANTID [34] and HORACE [35] data analysis packages.

3.3.2 Sample environment

Single-crystal samples are normally mounted on a goniometer, which allows the crystal to be aligned and for data collection over a range of sample orientations. Oxygen-free high-conductivity (OFHC) copper is commonly used for this sample mount, to ensure good thermal contact with the refrigerator/cryostat. Powder samples must be contained in a holder, which is often made of aluminium as it has a small neutron absorption cross-section. If a cylindrical can is used, the sample can then be rotated without changing the scattering geometry, which minimises the effect of any preferred orientation in the powder [26]. To reduce the spurious signal that can arise due to scattering from the sample environment, as much of the apparatus as possible is shielded using a material with a high neutron absorption cross-section, such as cadmium or gadolinium [26].

Magnetic neutron scattering experiments are often performed at very low temperatures to ensure the system is in its magnetic ground state. Depending on the temperatures required for the experiment, there are different refrigeration options available. A closed-cycle refrigerator (CCR) is a closed system that can cool down to $\simeq 4$ K through the cyclic compression and expansion of helium gas [26]. CCRs are generally more reliable and cheaper to run than cryostats, making them the natural choice for systems that are ordered within the accessible temperature range. A CCR was therefore suitable for the experiments on $\text{Ba}_2\text{CuTeO}_6$, which has an ordering temperature $T_N \simeq 14.1$ K [36].

For systems with lower ordering temperatures, a cryostat could be used. A

variable-temperature cryostat can cool down to $\simeq 1.2$ K by pumping on liquid helium [26]. In the “Orange Cryostat” design, a helium exchange gas is used to cool a sample at the end of a 1 m long probe. The temperature inside the closed volume varies from the set sample temperature at the bottom to room temperature at the top [26]. An Orange Cryostat was sufficient for the initial zero-field measurements of $\text{Ba}_3\text{CoSb}_2\text{O}_9$, which orders below $T_N \simeq 3.8$ K [37].

Even lower temperatures are achievable using a ^3He - ^4He dilution refrigerator. The first stages of cooling are similar to a conventional cryostat, using liquid nitrogen and liquid helium. The final stage is a mixing chamber containing two phases of ^3He - ^4He in equilibrium: a concentrated phase (mainly ^3He) and a dilute phase (mainly ^4He). ^3He flows from the concentrated phase to the dilute phase, which is an endothermic process that cools the chamber environment [38]. In this way, dilution refrigerators can cool a sample down to $\simeq 30$ mK [26]. The in-field $\text{Ba}_3\text{CoSb}_2\text{O}_9$ experiment used a dilution refrigerator insert to take measurements at $\simeq 100$ mK.

A cryomagnet is sometimes used to perform neutron scattering experiments in an applied magnetic field, for example to measure the evolution of the magnetic structure and spin dynamics. The LET cryomagnet applies a magnetic field of up to 9 T, using a split pair of solenoids with a gap to allow neutrons through. Despite the gap, the magnet blocks a lot of the scattered neutrons, restricting the angular range to 90° in the horizontal plane and $\pm 15^\circ$ in the vertical direction [32]. This cryomagnet was used to measure the spin dynamics in the “cone” phase of $\text{Ba}_3\text{CoSb}_2\text{O}_9$, with the spins canted along a magnetic field applied normal to the spiral order.

Chapter 4

Coupled spin ladders in $\text{Ba}_2\text{CuTeO}_6$

This chapter presents neutron scattering measurements of the magnetic excitations in $\text{Ba}_2\text{CuTeO}_6$, proposed by *ab initio* calculations to magnetically realise weakly-coupled antiferromagnetic two-leg spin- $\frac{1}{2}$ ladders. Isolated ladders are expected to have a singlet ground state protected by a spin gap. $\text{Ba}_2\text{CuTeO}_6$ orders magnetically, but with a small Néel temperature relative to the exchange strength, suggesting that the interladder couplings are relatively small and only just able to stabilise magnetic order, placing $\text{Ba}_2\text{CuTeO}_6$ close in parameter space to the critical point separating the gapped phase and Néel order. Through comparison of the observed spin dynamics with linear spin wave theory and quantum Monte Carlo calculations, values are proposed for all relevant intraladder and interladder exchange parameters, which place the system on the ordered side of the phase diagram in proximity to the critical point. High-field magnetisation data are also compared with quantum Monte Carlo predictions for the proposed model of coupled ladders. The chapter follows closely the published results in Ref. [39].

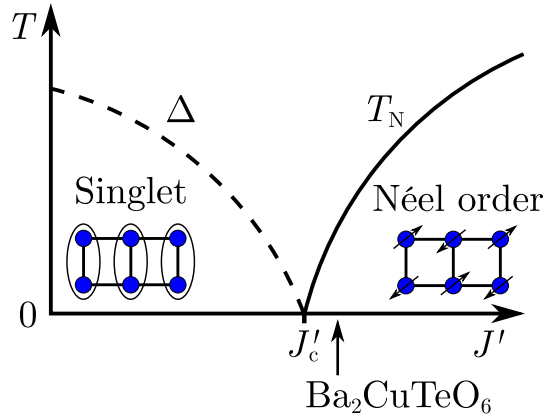


Figure 4.1: Schematic phase diagram of two-leg spin- $\frac{1}{2}$ AFM ladders as a function of the in-plane interladder exchange coupling J' [see Fig. 4.2(b)]. Below a critical coupling J'_c , the ground state is an overall singlet with a spin gap Δ . The $J' = 0$ state is schematically illustrated in the inset in the strong rung limit ($J_{\text{rung}} \gg J_{\text{leg}}$), showing the Cu^{2+} ions (blue circles) and spin singlet bonds (black ovals). For $J' > J'_c$, AFM Néel order is expected below a finite temperature T_N for non-zero interplane coupling J_{3D} . $\text{Ba}_2\text{CuTeO}_6$ has been proposed to be located close to the quantum critical point, on the ordered side of the phase diagram [40, 36].

4.1 Introduction

Spin ladder systems have attracted considerable interest in the study of high-temperature superconductivity [41, 42, 43], Bose-Einstein condensation [44], spinon confinement [45], and Tomonaga-Luttinger liquids [46, 47, 48], and are known to exhibit interesting quantum critical behaviour. For a two-leg spin- $\frac{1}{2}$ antiferromagnetic (AFM) ladder system, a quantum phase transition is expected to occur as the interladder exchange coupling J' is varied, as shown in the schematic phase diagram in Fig. 4.1. When J' is lower than a critical value J'_c , for non-zero leg and rung couplings, the ground state is a quantum paramagnet with a spin gap Δ to triplet excitations [49, 50, 51]. For larger J' the ground state has long-range Néel order with spin wave excitations. [52, 51, 50, 53] The value of the critical interladder coupling is dependent on the ratio of the leg and rung couplings and the geometry of the interladder coupling, with $J'_c = 0.314J$ for in-plane coupled ladders with $J_{\text{leg}} = J_{\text{rung}} = J$ [54].

Few candidate systems of coupled spin ladders have been found that are close to

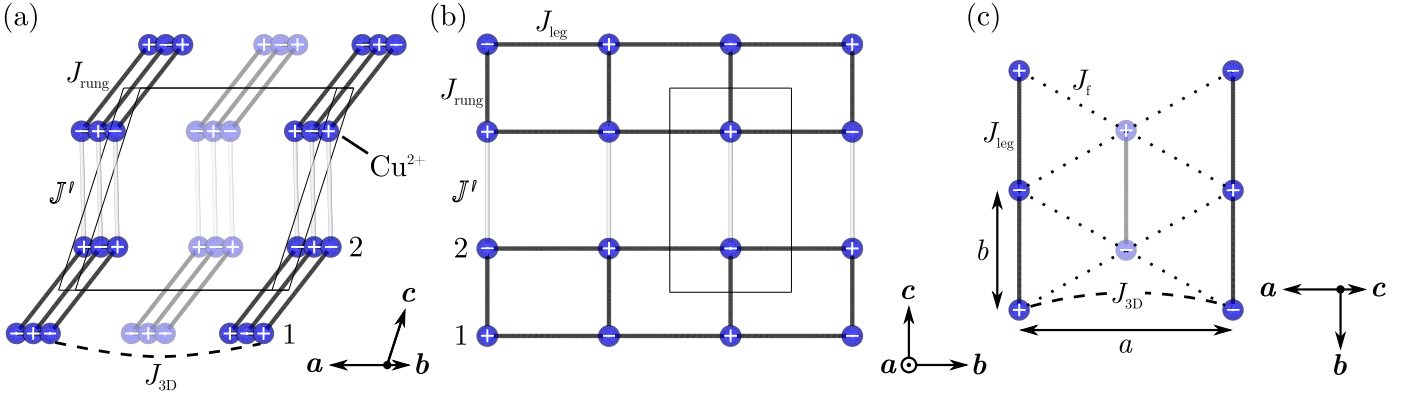


Figure 4.2: Crystal structure of $\text{Ba}_2\text{CuTeO}_6$ showing Cu^{2+} ions (blue circles) arranged in two-leg ladders running along $\mathbf{b}$, with intraladder exchanges J_{leg} and J_{rung} (thick black lines), interladder coupling J' along $\mathbf{c}$ (gray lines), next-nearest-neighbour interplane interaction J_{3D} along $\mathbf{a}$ (dashed line), frustrated interplane interaction J_f in the ab plane (dotted lines), the structural monoclinic unit cell (thin black outline), and the arrangement of up (+) and down (-) spins in the magnetic ground state of the minimal Hamiltonian used in the analysis. The diagrams were produced using VESTA. [59] (a) Three buckled planes of coupled ladders stacked along $\mathbf{a}$ with adjacent planes shifted by $(\mathbf{a} + \mathbf{b})/2$. (b) View along $\mathbf{a}$ with the $\mathbf{c}$ axis slightly into the page, showing a single plane of coupled ladders. (c) Projection of the structure on the ab plane, showing the interplane interactions J_f (dotted lines, frustrated) and J_{3D} (dashed line, unfrustrated).

the quantum critical region. (dimethylammonium)(3,5-dimethylpyridinium) CuBr_4 has a small Néel temperature $T_N = 2$ K relative to the nearly-equal leg and rung couplings $J = 7$ K and has a sizeable in-plane interladder coupling $J' = 0.32J$ [55], which suggest that it lies very close to the critical point on the ordered side of the phase diagram in Fig. 4.1. $\text{LaCuO}_{2.5}$ has also been proposed as a possible realisation of a nearly-critical system of coupled ladders [56], with magnetic ordering observed below $T_N = 125$ K by muon spin rotation [57] (μSR), and a much larger intraladder coupling $J = 1340$ K extracted from magnetic susceptibility data [51]. This has been supported by tight-binding calculations that predict an interladder coupling $J' = 0.25J$ [58], close to the critical value $J'_c = 0.115J$ found from quantum Monte Carlo calculations of the susceptibility for the proposed three-dimensional (3D) spin ladder system [50].

$\text{Ba}_2\text{CuTeO}_6$ crystallises in an ordered hexagonal perovskite-type structure with space group $C2/m$ at room temperature [60]. It has been proposed that the Cu^{2+} ions are arranged in weakly-coupled two-leg spin- $\frac{1}{2}$ ladders [61, 40, 36]. Figure 4.2(b) presents a view of the structure along $\mathbf{a}$, showing a single plane of Cu^{2+} ions (blue circles) forming coupled spin ladders (thick black lines) running along $\mathbf{b}$. The planes of spin ladders are stacked along the a axis, as shown in Fig. 4.2(a), with adjacent planes shifted by $(\mathbf{a} + \mathbf{b})/2$ relative to one another. Magnetic susceptibility measurements show an anomaly near 16 K that has been attributed to a magnetic ordering transition [40], with μSR providing direct evidence for long-range magnetic ordering below $T_N = 14.1$ K. This temperature is much smaller than the estimated intraladder exchange strength $J \simeq 90$ K [40, 36]. It has been suggested that the lack of clear signatures of long-range order in NMR, specific heat, and initial neutron diffraction measurements is evidence of strong quantum fluctuations and a large suppression of the ordered moment, which would be expected close to the critical point [40].

Inelastic neutron scattering (INS) measurements are presented here that directly probe the magnetic excitations in wave vector and energy. There is good agreement between the observed spin dynamics over the full bandwidth of the excitations and theoretical predictions for a system of two-leg ladders with sufficiently strong interladder couplings to stabilise a Néel-ordered ground state, and values are proposed for the intraladder and interladder couplings that are consistent with the observed spin dynamics and previous high field magnetisation data.

The rest of this chapter is organised as follows. Section 4.2 describes the experimental set-up used for the powder INS measurements. The key features of the dynamics over the full bandwidth of the magnetic excitations are presented in Sec. 4.3.1 and high-resolution measurements of the low-energy dynamics are reported in Sec. 4.3.2. The following Sec. 4.4.1 outlines the linear spin wave theory (LSWT) calculation

of the dispersion relations and scattering cross-section for two-leg ladders arranged in planes stacked vertically, proposed by *ab initio* calculations to capture the magnetism of $\text{Ba}_2\text{CuTeO}_6$, and reviews its predictions. Through quantitative comparison with the observed INS data, values for the intraladder and interladder couplings are extracted, first considering a plane of parallel coupled ladders (Sec. 4.4.1.1), which already accounts for most features of the spin dynamics. One discrepancy is an apparent broadening of the line shape of the highest-energy excitations and Sec. 4.4.1.2 proposes a possible parametrisation of this effect. Section 4.4.1.3 shows that the observed suppression of the inelastic magnetic signal at the lowest energies can be naturally understood as arising from a very weak interaction between parallel ladder planes; this gives the lowest energy dispersion a 3D character, in turn leading to a gradual suppression of the spectral weight at the lowest energies. Sec 4.4.1.4 presents fits of the LSWT model for unequal leg and rung couplings to the measured spin wave spectrum, which indicate that the previous assumption of equal leg and rung couplings was valid. In Sec. 4.4.2, the key features of the spin dynamics are compared with quantum Monte Carlo (QMC) calculations for a plane of coupled ladders and good agreement is found for values of interladder couplings that are sufficiently strong to put the system on the ordered side of the phase diagram. Furthermore, similarities and differences between the observed spin dynamics and that expected for ladders precisely at the critical interladder coupling strength are discussed in Sec. 4.4.2.1. As a consistency check of the overall energy scale of the interactions obtained from comparison with the LSWT and QMC models, Sec. 4.5 compares experimental pulsed field magnetisation data with mean-field and QMC calculations. Finally, the conclusions are summarised in Sec. 4.6.

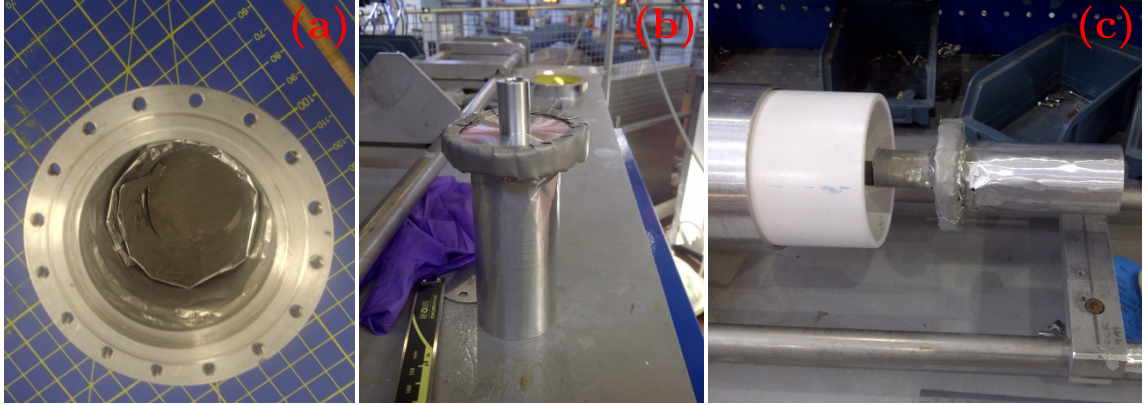


Figure 4.3: $\text{Ba}_2\text{CuTeO}_6$ sample mounting in an aluminium can for the INS experiments. (a) Interior of the can, showing the powder sample wrapped in aluminium foil. (b) Exterior of the can, including cadmium shielding on the can lid. (c) Sample can mounted on the CCR probe with additional cadmium shielding on the can lid and temperature sensor. Photographs courtesy of A. S. Gibbs (ISIS neutron source).

4.2 Experimental details

The 16 g powder sample of $\text{Ba}_2\text{CuTeO}_6$ used was part of a batch of polycrystalline material previously found to be single phase using X-ray and neutron diffraction, with spin susceptibility measurements suggesting less than 0.1% spin- $\frac{1}{2}$ impurities [40]. The sample was first wrapped in a flat envelope of aluminium foil, which was rolled to line an aluminium can, as shown in Fig. 4.3(a), to ensure an even distribution of powder and minimise the effect of any preferred direction. The can lid and temperature sensor were shielded using cadmium, which can be seen in Figs. 4.2(b) and (c), the latter showing the can mounted on the probe. The can lid and base were also shielded internally using cadmium discs, which are not visible in the photographs.

The spin dynamics was measured using the direct-geometry time-of-flight neutron spectrometer MERLIN at the ISIS neutron source in the UK [31]. An incident neutron energy $E_i = 30$ meV gave an energy resolution on the elastic line of 1.24(2) meV [full width at half maximum (FWHM)]. The scale of the magnetic excitations was found to extend up to $E \simeq 16$ meV [see Fig. 4.4(a)], so this experimental configuration provided

a suitable energy transfer range with sufficient resolution to probe key features of the full spectrum. Repetition rate multiplication (RRM) also allowed data to be collected simultaneously for incident neutrons with $E_i = 12, 18, 62$, and 185 meV, although these measurements did not reveal additional features in the spectrum. A closed cycle refrigerator (CCR) was used to cool the sample to a base temperature $T = 5.8$ K (well below the magnetic ordering transition at $T_N = 14.1$ K) and up to $T = 152$ K in the paramagnetic phase. Typical counting times for each temperature setting were around 9 h at an average proton current of $152 \mu\text{A}$. The raw neutron counts were converted into absolute cross-section units of $\text{mb sr}^{-1} \text{meV}^{-1} \text{Cu}^{-1}$ using the measured scattering intensities from a vanadium standard.

Additional higher-resolution measurements were performed using the direct-geometry time-of-flight neutron spectrometer LET at ISIS [32]. INS data were collected for incident energies $E_i = 1.96, 3.58$, and 21 meV, with energy resolutions on the elastic line of $0.044(1)$, $0.105(1)$, and $1.25(1)$ meV (FWHM), respectively, and a CCR was again used to provide temperature control. Counting times ranged between 7 h at low temperatures in the magnetically-ordered phase to 2.5 h in the paramagnetic phase at high temperatures, at an average proton current of $40 \mu\text{A}$. The measured integrated incoherent scattering on the elastic line was used to scale the data collected at the various incident energies to the same arbitrary units, assuming that the relative intensity scale factor arises only from the different incident neutron fluxes. All neutron data were processed using the MANTID data analysis package [34].

4.3 Measurements and results

4.3.1 Overview of the spin dynamics

The powder INS spectrum observed at base temperature is shown in Fig. 4.4(a). The key features are a flat ‘mode’ near $E \simeq 16$ meV and a V-shaped dispersive feature

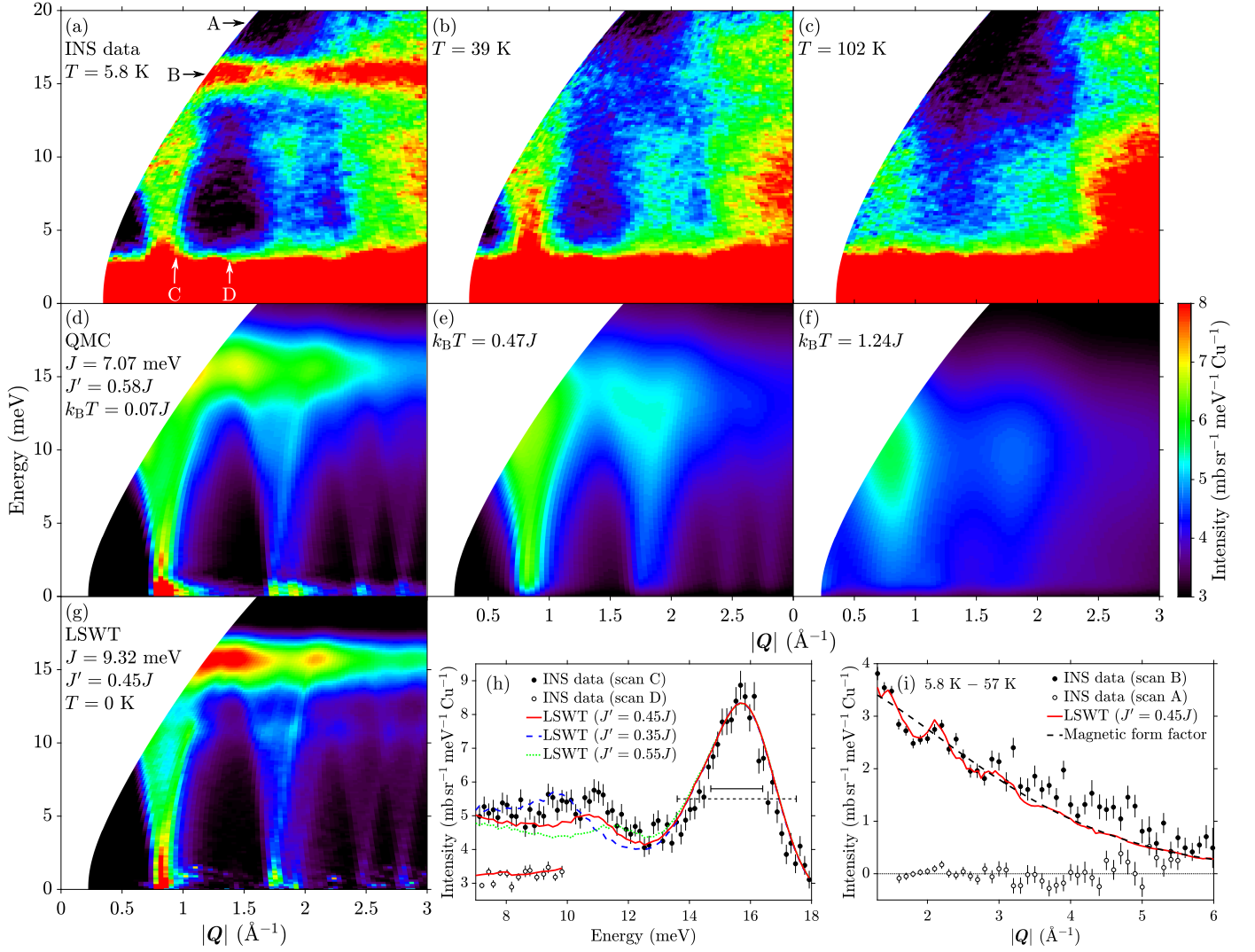


Figure 4.4: INS powder data at various temperatures (top row, MERLIN, $E_i = 30$ meV) compared with QMC (middle row) and LSWT predictions (bottom row) for no interactions between ladder planes shown in Fig. 4.2(b). The colour scale gives the intensities in absolute units. (h) Energy scan C in (a) (solid symbols), observing a clear intensity dip in the range 12–14 meV between the V-shaped signal and the higher energy flat mode. This dip is sensitive to the J'/J ratio, as shown by contrasting the model prediction for the best-fit value (upper red solid line) with lower/higher values (dashed blue/dotted green traces) that over-/underestimate the range of the intensity dip region. The peak centred near 16 meV is broader than expected based on experimental energy resolution effects (solid horizontal bar). The dashed horizontal bar indicates the FWHM of the flat mode in the QMC calculation in (d). (i) Wave vector scan B in (a) through the high-energy flat mode, compared with the LSWT model (solid red line) and the squared magnetic form factor of Cu^{2+} ions [scaled $f^2(|\mathbf{Q}|)$, dashed black line]. The higher-temperature $T = 57$ K data have been subtracted from the $T = 5.8$ K data to remove the non-magnetic background; open symbols in (i) indicate the quality of this background subtraction in regions where little magnetic scattering is expected. Scans were performed along the following directions: A, constant energy $E = [18, 21]$ meV; B, constant energy $E = [14.5, 17]$ meV; C, constant scattering angle $2\theta = [13^\circ, 16^\circ]$; and D, constant wave vector $|\mathbf{Q}| = [1.3, 1.5] \text{ \AA}^{-1}$.

centred near $|\mathbf{Q}| \simeq 0.8 \text{ \AA}^{-1}$. The magnetic character of both inelastic features is confirmed by their temperature dependence shown in Figs. 4.4(b) and 4.4(c); the flat mode has disappeared at 39 K, and the V-shaped feature has become overdamped at 102 K in the paramagnetic phase. The flat mode intensity as a function of $|\mathbf{Q}|$ at base temperature also follows the squared magnetic form factor of Cu^{2+} ions [shown in Fig. 4.4(i)], further confirming its magnetic character. The measured magnetic excitations in $\text{Ba}_2\text{CuTeO}_6$ are proposed to behave like spin waves, as the interladder coupling is sufficient to stabilise magnetic order at the base temperature of the experiments. In the limit of decoupled ladders, there is a singlet ground state with a spin gap to a band of triplet excitations, whose bandwidth depends on the intrachain coupling [49]. It is possible that the observed flat mode may contain some triplon character.

The V-shaped scattering is physically attributed to dispersive spin waves emanating from a magnetic Bragg peak. The experimentally-observed V-shaped wave vector magnitude is close to that of the first magnetic Bragg peak $(h_m, \frac{1}{2}, 1)$ of Néel-ordered ladders in each bc plane [shown in Fig. 4.2(b)], with parallel ($h_m = 0$) or alternating ($h_m = -\frac{1}{2}$) stacking between next-nearest-neighbour ladder planes along $\mathbf{a}$ being essentially indistinguishable within the resolution of the present experiment. The intense flat mode is attributed to magnetic excitations with a high density of states, non-dispersive along at least one crystallographic direction. In the present system, these excitations are magnons near the maximum of the two-dimensional (2D) dispersion surface for a plane of coupled ladders, which are non-dispersing in the direction normal to the ladder planes for weak interplane interactions. Note that the strong signal at $|\mathbf{Q}| > 2.2 \text{ \AA}^{-1}$ in Figs. 4.4(a)–4.4(c) intensifies with increasing temperature, consistent with it originating from phonon scattering.

4.3.2 Low energy excitations

High-resolution measurements focussing on the low-energy excitations are presented in Fig. 4.5(a). The three narrow V shapes near $|\mathbf{Q}| = 0.81, 1.76, \text{ and } 1.94 \text{ \AA}^{-1}$ correspond to regions where V-shaped dispersive features were also observed in the lower-resolution data in Fig. 4.4(a) and are identified with spin wave dispersions coming out of the magnetic Bragg peaks $(h_m, \frac{1}{2}, 1)$, $(h_m, \frac{3}{2}, 1)$, and $(h_m, \frac{1}{2}, 3)$, respectively. These features are again confirmed to be magnetic as they are not present at high T in Fig. 4.5(b) ($T = 154 \text{ K}$). Focussing on the low-energy region, one can observe a clear intensity decrease upon decreasing energy below $\simeq 0.55 \text{ meV}$, see Figs. 4.5(a) and 4.5(e) (solid points). This is a gradual decrease, rather than a sharp cut-off, with a clear inelastic signal observed down to the lowest resolvable energies. Figure 4.5(c) presents even higher resolution INS data, which show that a spin gap, if present, is smaller than an upper bound of $\simeq 0.15 \text{ meV}$.

4.4 Analysis

4.4.1 Linear spin wave theory for coupled ladders

This section outlines the LSWT calculation of the dispersion relation and dynamical structure factor for neutron scattering from two-leg ladders arranged in planes with monoclinic stacking, as shown in Fig. 4.2(a). Following *ab initio* calculations [40], AFM Heisenberg exchange interactions are assumed along the legs (J_{leg}), along the rungs (J_{rung}), between the ladders in the bc plane (J'), and between next-nearest-neighbour planes shifted by $\mathbf{a}$ (J_{3D}). The exchange paths and the relative spin alignments in the mean-field ground state are shown in Fig. 4.2. The coupling J_f between offset adjacent planes is neglected as it is frustrated [see Fig. 4.2(c)], leading to decoupled adjacent ladder planes at the mean-field level. So at this level of the approximation, the light and dark blue Cu^{2+} sites in Fig. 4.2 form two magnetically-

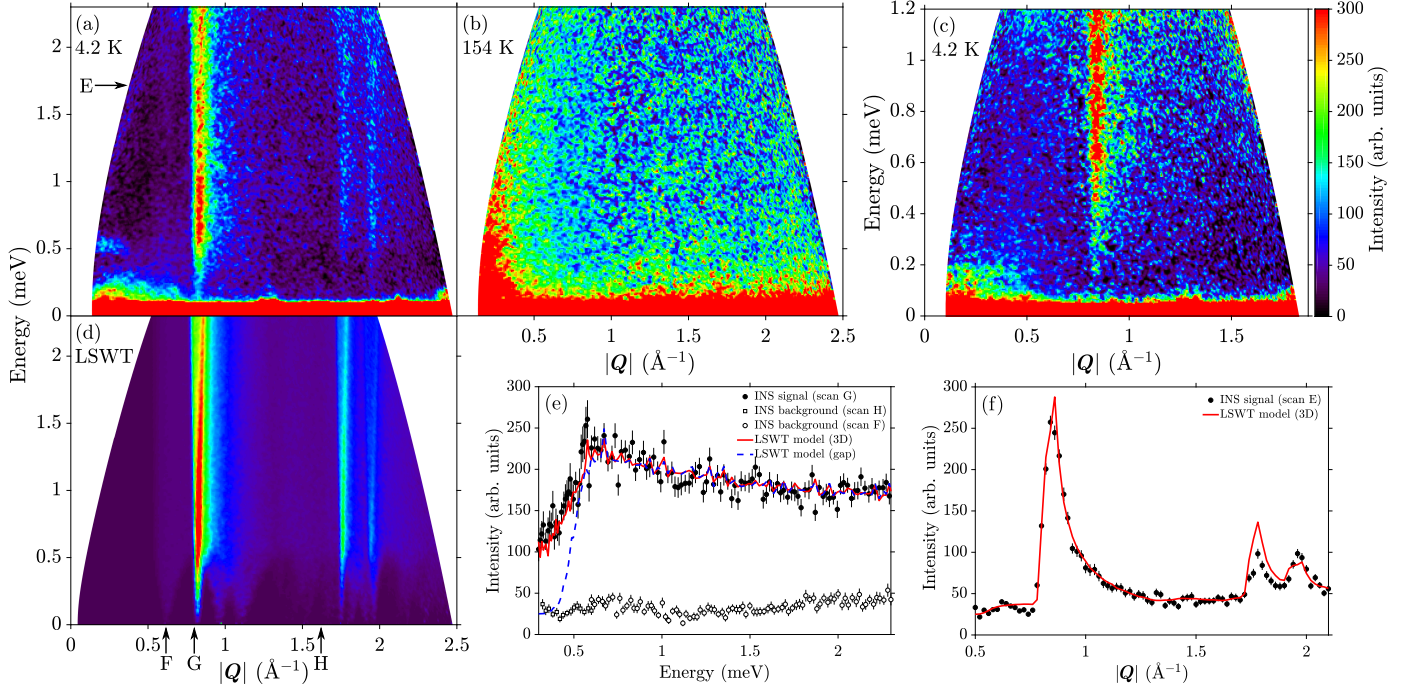


Figure 4.5: (a) INS powder data observing a suppression of the magnetic inelastic signal at low energies compared in (d) with the LSWT predictions for the case of finite interplane interactions as described in the text. The gradual intensity suppression at low energies is further confirmed by higher-resolution data in (c), and the magnetic character of the signal is established by its disappearance in the paramagnetic phase at high temperature in (b). (e), (f) Energy and wave vector scans [labelled “G” in (d) and “E” in (a), respectively] compared with the LSWT model including interplane couplings (solid red lines). Dashed blue line in (e) shows predictions for the alternative finite gap model described in the text, which does not account for the gradual intensity suppression below the maximum. Open symbols [scans F and H in (d)] indicate the non-magnetic background. Data were collected on LET using $E_i = 3.58$ meV for (a), (b), (e), and (f), and $E_i = 1.96$ meV for (c). Scans were performed along the following directions: E, constant energy $E = [1.5, 1.9]$ meV; F, constant wave vector $|Q| = [0.56, 0.64]$ $\text{\AA}^{-1}$; G, constant wave vector $|Q| = [0.6, 1.2]$ $\text{\AA}^{-1}$; and H, constant wave vector $|Q| = [1.5, 1.7]$ $\text{\AA}^{-1}$.

decoupled subsystems. The calculation focusses on the dark blue sites with two Cu^{2+} ions per primitive structural unit cell, labelled “1” and “2” in Figs. 4.2(a) and 4.2(b).

In the mean-field ground state, the spins are AFM aligned in the ladder planes, and parallel planes displaced by $\mathbf{a}$ are oppositely aligned, as shown by the alternation of $+$ and $-$ signs in Fig. 4.2 (dark blue sites). To describe the spin axes, a Cartesian coordinate system (x, y, z) is used with $\hat{\mathbf{z}}$ along the direction of the ordered moments in the ground state (b axis). The analytic calculation is simplified by performing a rotation of the local spin axes in the xz plane by an angle $\alpha(\mathbf{r}) = \mathbf{Q}_{\text{rot}} \cdot \mathbf{r}$, where $\mathbf{r}$ is the spin position and $\mathbf{Q}_{\text{rot}} = \frac{1}{2}\mathbf{a}^* + \frac{1}{2}\mathbf{b}^*$. In this rotating frame, the magnetic unit cell then reduces to the same size as the primitive structural cell, with two sublattices labelled “1” and “2” in Figs. 4.2(a) and 4.2(b).

Using the Holstein-Primakoff transformation introduced in Sec. 2.7.1, the spin component operators for the first sublattice S_{1j}^x , S_{1j}^y and S_{1j}^z can be expressed in terms of boson creation and annihilation operators $a_j^\dagger$ and a_j , respectively, as given by Eqs. (2.27)–(2.29). This approach can be extended to the second sublattice by defining the transformation [18]

$$S_{2j}^+ = S_{2j}^x + iS_{2j}^y = \sqrt{2S}b_j^\dagger \sqrt{1 - \frac{b_j^\dagger b_j}{2S}} \approx \sqrt{2S}b_j^\dagger \quad (4.1)$$

$$S_{2j}^- = S_{2j}^x - iS_{2j}^y = \sqrt{2S} \sqrt{1 - \frac{b_j^\dagger b_j}{2S}} b_j \approx \sqrt{2S}b_j \quad (4.2)$$

$$S_{2j}^z = -S + b_j^\dagger b_j, \quad (4.3)$$

where the subscript “2” labels spin operators on sublattice 2, and $b_j^\dagger$ (b_j) is the boson creation (annihilation) operator for deviations of the oppositely-aligned spins on the second sublattice.

Defining the Fourier transformations using Eqs. (2.32) and (2.33), and neglecting terms higher than quadratic order in the boson operators, the spin Hamiltonian in

this rotated frame is obtained as

$$\mathcal{H} = \frac{1}{2} \sum_{\mathbf{k}} \mathbf{X}^\dagger \mathbf{H} \mathbf{X} - N(S+1) \frac{A}{2}, \quad (4.4)$$

where N is the total number of spin sites, A is a parameter defined below, and the sum is over all wave vectors $\mathbf{k}$ in the first Brillouin zone of the primitive structural unit cell. The operator basis is chosen to be $\mathbf{X}^\dagger = (a_{\mathbf{k}}^\dagger \ b_{\mathbf{k}}^\dagger \ a_{-\mathbf{k}} \ b_{-\mathbf{k}})$, such that $a_{\mathbf{k}}^\dagger$ ($a_{\mathbf{k}}$) creates (annihilates) a plane-wave magnon on the first sublattice and likewise for b on the second sublattice. The Hamiltonian matrix has the form

$$\mathbf{H} = \begin{pmatrix} A & 0 & C & D^* \\ 0 & A & D & C \\ C & D^* & A & 0 \\ D & C & 0 & A \end{pmatrix}, \quad (4.5)$$

where, at a general wave vector $\mathbf{Q} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$ [expressed as (h, k, l) in reciprocal lattice units of the monoclinic $C2/m$ structural cell],

$$\begin{aligned} A &= 2S \left(J_{\text{leg}} + \frac{J_{\text{rung}}}{2} + \frac{J'}{2} + J_{3\text{D}} \right) \\ C &= -2S (J_{\text{leg}} \cos \mathbf{Q} \cdot \mathbf{b} + J_{3\text{D}} \cos \mathbf{Q} \cdot \mathbf{a}) \\ D &= S (J_{\text{rung}} + J' e^{-2\pi i l}) e^{2\pi i (h\xi + l\zeta)} \\ &\equiv D_0 e^{i\phi}, \quad D_0 = |D|. \end{aligned} \quad (4.6)$$

Here $\xi = -0.1866(1)$ and $\zeta = 0.4299(1)$ define the separation between the two spins on each rung $\mathbf{r}_2 - \mathbf{r}_1 = \xi\mathbf{a} + \zeta\mathbf{c}$ [40], where the subscripts “1” and “2” refer to the numbered positions in Figs. 4.2(a) and 4.2(b).

The dispersion relations for a 4×4 Hamiltonian matrix of this form are given in Ref. [62] (Appendix A). Using this result and rotating back to the fixed laboratory frame gives two distinct spin wave branches with dispersion relations

$$\hbar\omega_{\mathbf{Q}}^\pm = \sqrt{A^2 - (C \mp D_0)^2}, \quad (4.7)$$

which by periodicity hold for a general wave vector $\mathbf{Q}$ in reciprocal space. The upper (lower) label corresponds to excitations with even (odd) parity with respect to

swapping sites 1 and 2 in the primitive cell. There are two dispersion branches as there are two sites in the magnetic cell; each branch is doubly degenerate, corresponding to magnons with spin component $S_z = \pm 1$.

Following Ref. [62], the dynamical structure factor (per spin in the laboratory frame) for spin fluctuations along the x direction is obtained as

$$S^{xx}(\mathbf{Q}, \omega) = \frac{S}{4}(1 + \cos \phi) \frac{A + C - D_0}{\hbar\omega_{\mathbf{Q}}^+} [n(\hbar\omega_{\mathbf{Q}}^+) + 1] \mathcal{N}(\hbar\omega_{\mathbf{Q}}^+, \sigma) \\ + \frac{S}{4}(1 - \cos \phi) \frac{A + C + D_0}{\hbar\omega_{\mathbf{Q}}^-} [n(\hbar\omega_{\mathbf{Q}}^-) + 1] \mathcal{N}(\hbar\omega_{\mathbf{Q}}^-, \sigma), \quad (4.8)$$

where $\mathcal{N}(\hbar\omega, \sigma)$ is a Gaussian function with the centre at $\hbar\omega$ and standard deviation σ , used to model the instrumental energy resolution ($\text{FWHM} = 2\sqrt{2\ln 2}\sigma$). Note that the finite-temperature Bose factor $n(\hbar\omega) + 1$, where $n(\hbar\omega) = 1/(e^{\hbar\omega/k_B T} - 1)$, has been included in the definition of the dynamical structure factor for consistency with the notation used in the QMC calculations. The above analytic expressions for the dispersion and dynamical structure factor were checked explicitly against the numerical predictions of SPINW [17].

The one-magnon neutron scattering cross-section, using the simplified form in Eq. (3.39) that includes the orientation factor and magnetic form factor, is then

$$I(\mathbf{Q}, \omega) = (\gamma r_0)^2 \left(1 + \frac{Q_z^2}{|\mathbf{Q}|^2}\right) \left[\frac{g}{2} f(|\mathbf{Q}|)\right]^2 S^{xx}(\mathbf{Q}, \omega), \quad (4.9)$$

where $(\gamma r_0)^2 = 290.6 \text{ mb sr}^{-1}$ allows the intensity to be written in absolute units of $\text{mb sr}^{-1} \text{ meV}^{-1} \text{ Cu}^{-1}$, $f(|\mathbf{Q}|)$ is the spherical magnetic form factor for Cu^{2+} ions, Q_z is the component of the wave vector $\mathbf{Q}$ along the z direction (b axis), and the g factor is assumed equal to 2. Equation (4.9) was spherically averaged to produce Figs. 4.4(g) and 4.5(d) for direct comparison with the powder INS data. The spherically-averaged INS spectrum is very similar for different spin directions in the ground state with only slight changes in intensity modulations, which cannot be reliably differentiated using

the experimental INS data. For concreteness, the ordered moments are therefore assumed to be aligned along $\mathbf{b} \parallel \hat{\mathbf{z}}$ and the corresponding orientation factor has been used in all calculations of the INS intensity.

4.4.1.1 Plane of parallel coupled ladders

First consider the limit of no interactions between spins in different ladder planes ($J_{3D} = 0$), for which there is no dispersion along h . Figure 4.6(a) plots the corresponding spin wave dispersion relations along a path of high-symmetry directions in reciprocal space for the case of equal rung and leg couplings ($J_{\text{rung}} = J_{\text{leg}} = J$) and finite interladder exchange J' . The $\hbar\omega^-$ dispersion surface is gapless at the $(0, \frac{1}{2}, 1)$ wave vector corresponding to in-plane Néel order and disperses linearly along both in-plane directions (where the dispersion along $\mathbf{b}^*$ is due to J_{leg} and along $\mathbf{c}^*$ is due to the interladder coupling J'), forming an elliptical cone at low energies. Note that magnons at the highest energies have extended regions with very little dispersion along $\mathbf{b}^*$ or $\mathbf{c}^*$, which would lead to a large density of states at those energies upon spherical averaging of the spectrum.

To compare with the experimental INS powder data, the spherical average of the LSWT one-magnon spectrum was performed, including the full wave vector and energy dependence of the one-magnon neutron scattering cross-section, the neutron orientation factor, the Bose temperature factor, the spherical magnetic form factor for Cu^{2+} ions, and the convolution with the estimated instrumental resolution. The best fit to the data assuming equal leg and rung couplings ($J_{\text{leg}} = J_{\text{rung}} = J$), as predicted by *ab initio* calculations [40], is shown in Fig. 4.4(g) (a more refined analysis for $J_{\text{leg}} \neq J_{\text{rung}}$ will be presented in Sec. 4.4.1.4). In the fit, both the intra- and interladder exchanges J and J' were varied, as well as an overall intensity scale factor, and the best-fit parameter values are listed in Fig. 4.4(g). As explained before, the region above $|\mathbf{Q}| \simeq 2.2 \text{ \AA}^{-1}$ is dominated by phonon scattering and will not be discussed

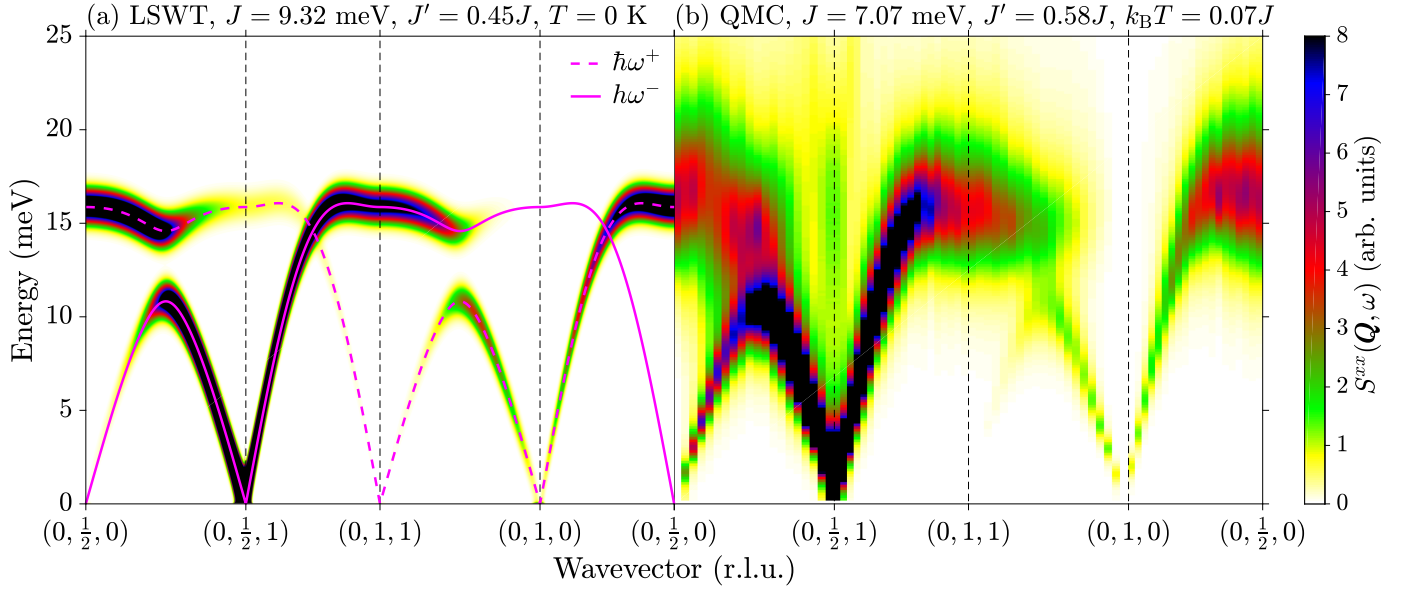


Figure 4.6: Colour map representation of the dynamical structure factor $S^{xx}(\mathbf{Q}, \omega)$ along high-symmetry directions in reciprocal space for a plane of coupled ladders [shown in Fig. 4.2(b)] with intraladder coupling $J_{\text{rung}} = J_{\text{leg}} = J$ and interladder coupling J' . (a) LSWT spectrum using Eq. (4.8) with a constant $\sigma = 0.53$ meV to match the observed FWHM of the elastic line in the INS MERLIN data. Solid and dashed lines indicate the magnon dispersion relations given in Eq. (4.7). (b) QMC spectrum at temperature $k_B T = 0.07J$. The exchange parameters used in each case are those corresponding to the best fit of each model to the powder INS data in Fig. 4.4(a). Wave vectors (h, k, l) are given in reciprocal lattice units (r.l.u.) of the structural monoclinic unit cell in Fig. 4.2, and the colour scale is in arbitrary units.

further.

The model reproduces well the key features of the observed magnetic inelastic signal in Fig. 4.4(a); in particular, the primary V-shaped feature is attributed to the $\hbar\omega^-$ spin wave cone emanating from the magnetic Bragg rod at $(h, \frac{1}{2}, 1)$, and the flat mode near $E \simeq 16$ meV is attributed to the almost dispersionless magnons near the top of the 2D dispersion in Fig. 4.6(a), which are also dispersionless in the third direction for decoupled ladder planes. The feature in the INS data in Fig. 4.4(a) that is most sensitive to the strength of the interladder coupling J' is an apparent narrowing of the V-shaped signal before it merges with the higher-energy flat mode, with a clear intensity dip in this intermediate energy region. This is most clearly seen in the energy scan in Fig. 4.4(h), which reveals an intensity dip in the range 12–14 meV between the top of the V shape and the flat mode at higher energies. The energy dependence of the intensity in this scan is best described for $J' = 0.45J$ (upper red solid line); for weaker couplings the intensity dip region is significantly wider than observed, as illustrated for $J' = 0.35J$ (blue dashed line), whereas for stronger couplings the dip region narrows and becomes less distinct, as illustrated for $J' = 0.55J$ (green dotted line). For ease of comparison, the value of the intraladder coupling J was adjusted to keep the energy of the higher-energy flat mode unchanged in all the above cases. Additional INS measurements, shown in Fig. 4.7(a) with the LSWT calculation in Fig. 4.7(b) and an energy scan in Fig. 4.7(c), provide further confirmation that the LSWT model for decoupled ladder planes captures well the key features of the magnetic inelastic response.

4.4.1.2 Width of high-energy flat mode

A notable feature of the energy scan in Fig. 4.4(h) is that the strong peak centred around $E \simeq 16$ meV appears broader than expected based on the estimated instrumental resolution and powder averaging (combined expected FWHM represented by

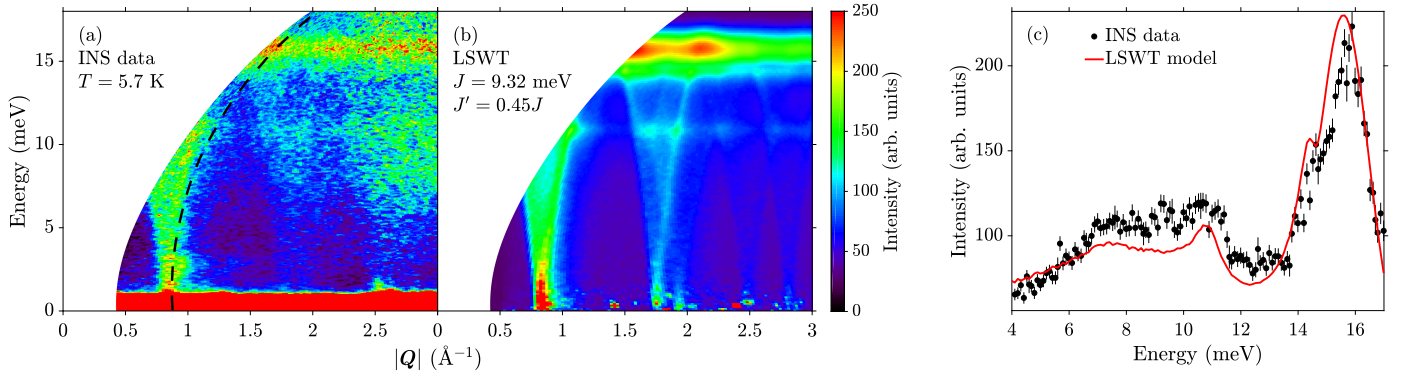


Figure 4.7: (a) Additional INS powder data (LET, $E_i = 21$ meV, $T = 5.7$ K) compared in (b) with the LSWT model for decoupled ladder planes [same exchange parameters as in Fig. 4.4(g)]. The colour scale gives the intensities in arbitrary units. (c) Energy scan at constant scattering angle ($2\theta = [7^\circ, 25^\circ]$) through the INS data (black circles) and the LSWT calculation (red line), probing the V-shaped feature, the intensity dip region, and the high-energy mode. The centre of the scan is indicated by the dashed line in (a).

the solid horizontal bar at the peak's half-maximum), and this observed broadening cannot be accounted for by using moderately different leg and rung couplings. The width of the flat mode and its relative intensity compared to the V-shaped feature are best reproduced [solid red line in Fig. 4.4(h)] if a Gaussian broadening (of empirical FWHM 2.1 meV) is assumed for high-energy magnons. Finite one-magnon lifetime effects are generally associated with one $\rightarrow$ two-magnon decay processes and Fig. 4.8 illustrates the phase space (shaded area) for two-magnon processes; the one-magnon dispersions overlap with this region above an energy threshold of 14.5 meV, so in all comparisons with the LSWT model an intrinsic lifetime has been assumed for magnons above this energy threshold and this seems to provide a good empirical parametrisation of the data.

4.4.1.3 Low-energy excitations and couplings between planes

The observed non-monotonic energy dependence of the magnetic intensity at low energies, with a gradual suppression of the signal below $\simeq 0.55$ meV [shown in Figs. 4.5(a) and 4.5(e)], cannot be explained by the above model of isolated ladder planes with

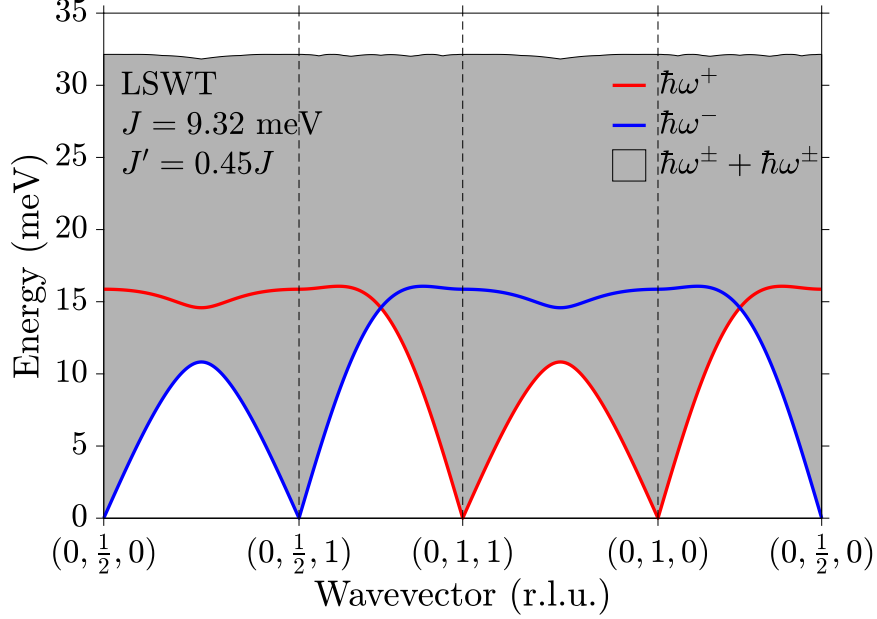


Figure 4.8: Phase space for two-magnon excitations (grey shaded area), calculated using LSWT for isolated ladder planes. The one-magnon dispersions [red and blue solid lines, Eq. (4.7)] overlap with the continuum above an energy threshold. The exchange parameters are as in Fig. 4.6(a).

Heisenberg exchanges. This model would predict a gapless, elliptical spin wave cone at the lowest energies with a constant spectral density of states in a wide energy range above zero energy. To identify the possible origin of the observed loss of spectral weight at low energies, two possible extensions of the previous model have been separately considered: (i) addition of a finite interaction between parallel ladder planes, which gives the lowest-energy magnons a 3D dispersion with a suppressed density of states, and (ii) presence of a finite spin gap, still assuming isolated ladder planes. Such a spin gap may physically originate from Dzyaloshinskii-Moriya couplings (symmetry-allowed as the Cu-Cu bonds are not centrosymmetric) or other anisotropic exchanges.

First consider the case of a finite AFM interaction J_{3D} between parallel ladder planes displaced along $\mathbf{a}$, for which the LSWT dispersion relations are given in Eq. (4.7). (The spherically-averaged spin wave spectrum for ferromagnetic J_{3D} has also been numerically calculated, and the results are rather similar with only small

differences at the very lowest energies; the data are not sensitive enough to distinguish between these two scenarios, so in the following only the AFM J_{3D} case is considered for concreteness.) The spherically-averaged spin wave spectrum for the best-fit value $J_{3D} \simeq 5 \times 10^{-4}J$, with J and J' fixed at the values determined previously, is shown in Fig. 4.5(d) and compares well with the INS data in Fig. 4.5(a). In particular, the model reproduces well the positions and relative intensities of the three visible V-shaped features and their intensity drop-off at low energies. This is more clearly seen in the energy scan through the centre of the primary V-shaped feature in Fig. 4.5(e), where the observed intensity profile is well captured by the model calculation (solid red line). The only fitted parameters for this energy scan are J_{3D} and an overall intensity scale factor. In this model, the non-monotonic intensity profile arises from the cross-over from a 3D to a 2D spectral density of states upon increasing energy above the interplane zone boundary energy $E_{3D} = 2S\sqrt{2J_{3D}(2J_{\text{leg}} + J_{\text{rung}} + J')} = 0.54 \text{ meV}$ [which occurs at $(0, \frac{1}{2}, 1)$]. Below this energy, the magnons have a 3D dispersion, linear in all directions at the lowest energies, for which the spectral density of states has an $\hbar\omega$ dependence [as the density of states varies as $(\hbar\omega)^2$ and the dynamical structure factor for AFM magnons varies as $1/\hbar\omega$]. Above the saddle-point energy E_{3D} , the magnon dispersion is predominantly in the plane of the ladders and the spectral density of states is constant for linearly-dispersing magnons in 2D (as the density of states varies as $\hbar\omega$ and the structure factor as $1/\hbar\omega$), explaining the near-constant intensity at these energies. The shape of the intensity profile in wave vector scans at energies above E_{3D} in Fig. 4.5(f), showing an asymmetric tail towards higher wave vectors, is also well explained by quasi-2D linearly-dispersing magnons (red line).

In the alternative parametrisation of isolated ladder planes ($J_{3D} = 0$) with a finite gap Δ , the dispersion relations are assumed to have the modified form

$$\hbar\tilde{\omega}_{\mathbf{Q}}^{\pm} = \sqrt{(\hbar\omega_{\mathbf{Q}}^{\pm})^2 + \Delta^2}, \quad (4.10)$$

with the dynamical correlations as given in Eq. (4.8), but with $\hbar\omega_{\mathbf{Q}}$ replaced by $\hbar\tilde{\omega}_{\mathbf{Q}}$. The dashed blue line in Fig. 4.5(e) shows the calculation for $\Delta = 0.5$ meV; such a model clearly predicts a much more abrupt intensity drop-off than is actually observed. Note that this analysis does not preclude the existence of a much smaller spin gap with an upper bound of $\simeq 0.15$ meV, the resolution of the experiments. (A spin gap of order 0.2 meV may be expected since measurements in applied field show a transition near a critical field of 15 kOe, associated with a spin-flop transition) [61]. A similar intensity suppression has been reported in a spin chain material, in which doping with non-magnetic impurities opens a pseudo-gap [63]. In that case, the measured intensity decreases monotonically at low energies, whereas here a non-monotonic dependence is observed with a peak at $\simeq 0.55$ meV, which is better described by a saddle-point in the dispersion at the interplane zone boundary. Furthermore, the pseudo-gap was reported for a 1% doping and there is estimated to be only 0.1% non-magnetic impurities in the present system [40]. Based on the above two parametrisations, it is therefore concluded that the finite interplane couplings are the most likely origin for the observed signal suppression at low energies, and the intensity maximum near 0.55 meV is attributed to the interplane magnetic zone boundary energy.

4.4.1.4 Unequal leg and rung couplings

The assumption that $J_{\text{leg}} = J_{\text{rung}}$ was tested by comparing the data to the LSWT model for isolated ladder planes ($J_{3D} = 0$) with variable J' and J_{rung} relative to J_{leg} and calculating a corresponding goodness of fit χ^2 , defined as

$$\chi^2 = \frac{(\hbar\hat{\omega}^+ - \hbar\omega^+)^2}{(\sigma^+)^2} + \frac{(\hbar\hat{\omega}^- - \hbar\omega^-)^2}{(\sigma^-)^2}, \quad (4.11)$$

where $\hbar\omega^+ = 2S\sqrt{J_{\text{rung}}(2J_{\text{leg}} + J')}$ and $\hbar\omega^- = 2S\sqrt{J'(2J_{\text{leg}} + J_{\text{rung}})}$ are the energies at $(0, \frac{1}{2}, \frac{1}{2})$ of the even and odd magnon modes [using Eq. (4.7)], respectively, and

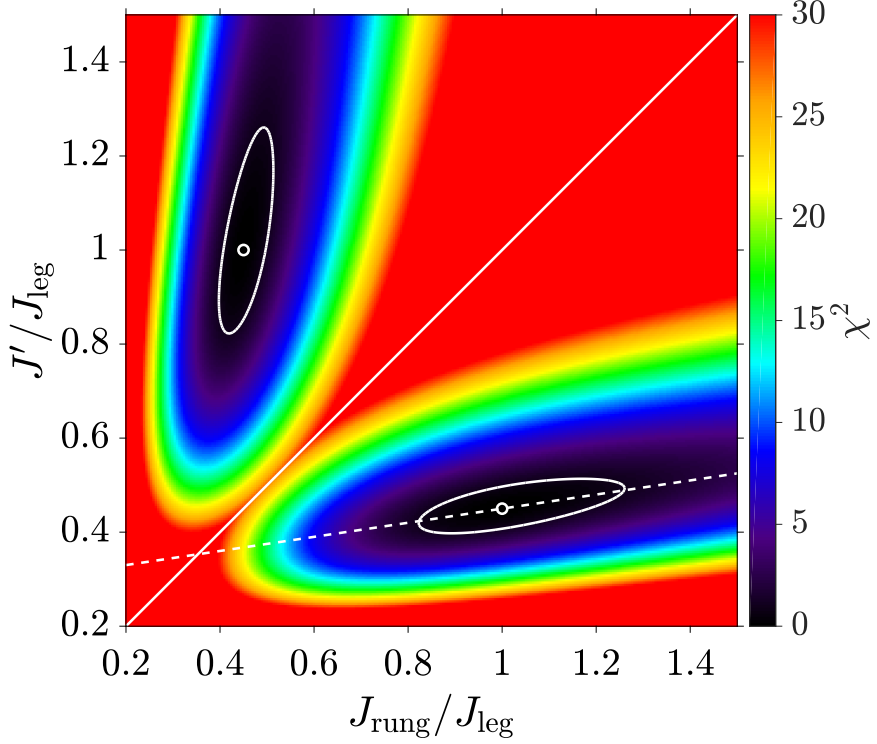


Figure 4.9: χ^2 as a function of J'/J_{leg} and $J_{\text{rung}}/J_{\text{leg}}$ for the LSWT model of coupled two-leg spin- $\frac{1}{2}$ ladders, quantifying the deviation from the calculation for the best-fit parameters [see Eq. (4.11)]. The solid white line represents $J_{\text{rung}} = J'$. Below this line is the physically-expected case of weakly-coupled ladders, as shown in Fig. 4.2(b). J_{leg} was chosen to match the flat mode energy to the experimentally-observed value. The parameter values for the fitted model ($J_{\text{rung}} = J_{\text{leg}}$ and $J' = 0.45J_{\text{leg}}$) are indicated by white circles (including the equivalent model with $J' \leftrightarrow J_{\text{rung}}$). The dashed white line is a plot of Eq. (4.12), discussed in the text. The white ovals are the $\chi^2 = 1$ (1σ) contours.

$\hbar\omega^+$ and $\hbar\omega^-$ are these energies for the best-fit parameters $\hat{J}_{\text{leg}} = \hat{J}_{\text{rung}} = 9.32$ meV and $\hat{J}' = 0.45\hat{J}_{\text{leg}}$. For each (J_{rung}, J') pair, J_{leg} was chosen to keep the energy of the flat mode in the spherically-averaged spectrum fixed at the best-fit value [fixing A in Eq. (4.6)]. $\sigma^+ = 0.6$ meV and $\sigma^- = 0.4$ meV are the uncertainties in the fitted positions of the even and odd modes at $(0, \frac{1}{2}, \frac{1}{2})$, respectively, estimated by comparing the energy scan in Fig. 4.4(h) to models with variable $\hbar\omega^+$ and $\hbar\omega^-$ at a constant flat mode energy. χ^2 for a range of J'/J_{leg} and $J_{\text{rung}}/J_{\text{leg}}$ values is plotted as a colour map in Fig. 4.9. The mirror symmetry about $J_{\text{rung}} = J'$ (solid white line) is to be expected, as the system is invariant under interchange of rung and interladder couplings [for $J' > J_{\text{rung}}$, the J_{rung} exchange acts as an interladder coupling for ladders with rung coupling J' , see Fig. 4.2(b)]. Assuming $J' < J_{\text{rung}}$ and fixing the energy of the flat mode and the (lower energy) odd mode at $(0, \frac{1}{2}, \frac{1}{2})$, the following relationship is found between J' and J_{rung} using Eq. (4.7):

$$J' = \frac{\hat{J}'(2J_{\text{leg}} + J_{\text{rung}})}{2\hat{J}_{\text{leg}} + \hat{J}_{\text{rung}}}, \quad (4.12)$$

which is plotted as a dashed white line in Fig. 4.9. Starting from the best-fit parameters (white circle) and moving along the line with increasing $J_{\text{rung}}/J_{\text{leg}}$, the even mode at $(0, \frac{1}{2}, \frac{1}{2})$ increases in energy and the gap in signal near 13 meV in Fig. 4.4(h) widens. If $J_{\text{rung}}/J_{\text{leg}}$ is decreased from the fitted value, the even mode decreases in energy and the gap between the even and odd modes [shown in Fig. 4.6(a)] closes and disappears on the $J_{\text{rung}} = J'$ line, at which point the system consists of a rectangular lattice of anisotropic couplings (J along $\mathbf{b}$ and J' along $\mathbf{c}$). The $\chi^2 = 1$ contour lines in Fig. 4.9 (white ovals), which correspond to a 1σ deviation from the best-fit parameter values, show that there is a finite range of $J_{\text{rung}}/J_{\text{leg}}$ values for which the LSWT model could provide a good fit to the INS data. This suggests that the ratio of rung and leg couplings $J_{\text{rung}}/J_{\text{leg}}$ is likely to be between 0.8 (weaker rungs) and 1.3 (stronger rungs), with J'/J_{leg} adjusted accordingly (J' reduced on the weak rung

side).

4.4.2 Quantum Monte Carlo calculations for a plane of coupled ladders

The LSWT description used so far in the analysis relies on the assumption that the system is located deep in the ordered side of the schematic phase diagram in Fig. 4.1, where zero-point quantum fluctuations are relatively small. However, this is not the case for values of the interladder coupling J' that put the system still in the ordered phase, but close to the critical point separating it from the gapped singlet phase at low J' . Since the estimated J'/J value is close to the expected critical threshold for the onset of magnetic order, it is insightful to compare the INS results with more elaborate theories that better capture quantum fluctuation effects. For this purpose, quantum Monte Carlo (QMC) calculations have been performed for a plane of coupled ladders with intraladder coupling $J_{\text{leg}} = J_{\text{rung}} = J$ and interladder coupling J' . The obtained dynamical correlations along high-symmetry directions in reciprocal space are shown in Fig. 4.6(b) for the best-fit parameter values as listed in the figure title. The calculation qualitatively resembles many features already captured at the LSWT level [Fig. 4.6(a)], such as how the strongest scattering weight disperses in the Brillouin zone, the spin wave cone emerging out of the Néel order Bragg peak, and the extended regions with little dispersion at the top of the excitation bandwidth. The dynamical correlations appear significantly broadened, in particular at high energies, and this effect may be interpreted as being partly due to multimagnon contributions. This intrinsic broadening is illustrated by the horizontal dashed bar plotted near the main peak's half-maximum in Fig. 4.4(h); the width is of a comparable extent to the lineshape width observed experimentally.

The best-fit values for the intra- and interladder exchanges were again obtained by fitting the calculated spherically-averaged dynamical correlations (including all the

relevant neutron scattering intensity prefactors and instrumental resolution effects) to the measured low-temperature magnetic INS signal, with the aim of reproducing the high-energy flat mode and the V-shaped signal. The overall intensity scale factor was determined by fitting to a cut through the high-energy flat mode. The best-fit result is shown in Fig. 4.4(d) for comparison with the data in Fig. 4.4(a). The level of agreement is similar to the LSWT parametrisation shown in Fig. 4.4(g); the only difference is that, in the QMC case, the large broadening of the linewidths at high energies makes the intensity dip between the top of the V shape and the high-energy flat mode less prominent. The disappearance of the flat high-energy mode and broadening of the V-shaped feature with increasing temperature in the paramagnetic phase, shown in Figs. 4.4(a)–4.4(c), also seem to be qualitatively captured by QMC calculations at the corresponding temperatures, see Figs. 4.4(d)–4.4(f). The best-fit value for the intraladder exchange $J = 7.07$ meV is close to the range of previous estimates determined from fits to temperature-dependent susceptibility data (7.3–8.1 meV) [40, 36]. The extracted interladder exchange $J' = 0.58J$ is larger than the theoretically-predicted critical value $J'_c = 0.314J$ for a 2D model of coupled ladders [54], placing $\text{Ba}_2\text{CuTeO}_6$ in the Néel-ordered state beyond the quantum critical point (as indicated in Fig. 4.1), consistent with the experimental observations of a finite T_N [40, 36, 61]. Note that the best-fit value for the exchange J differs between the LSWT and QMC calculations, as the latter includes the effects of higher-order quantum fluctuations. One would therefore expect the values found from comparison with the QMC calculation to be closer to the actual exchange parameters in the material.

4.4.2.1 Spin dynamics for ladders at criticality

For a system of coupled two-leg spin- $\frac{1}{2}$ ladders with equal leg and rung couplings, the quantum critical point occurs at $J'_c = 0.314J$ [54]. For completeness, the QMC

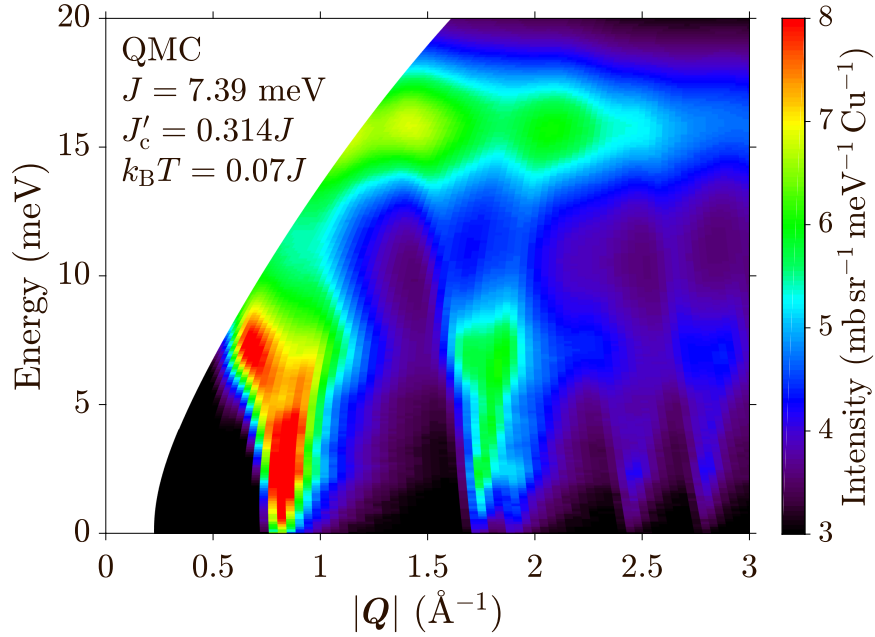


Figure 4.10: Spherically-averaged spin dynamics for ladders at the quantum critical coupling $J'_c = 0.314J$, calculated using QMC, to be contrasted with the measured powder INS data in Fig. 4.4(a). The scale $J = 7.39$ meV was chosen to best reproduce the location of the flat mode in the data, and T corresponds to the base temperature of the experiment $k_B T = 0.07J$.

calculation for this critical coupling is shown in Fig. 4.10, to be compared with the data in Fig. 4.4(a). The value of J in this calculation was chosen to reproduce the measured energy of the flat mode in the data. A notable difference compared to the data is that the narrowing at the top of the V-shaped dispersion, used previously to determine the J' value, is clearly larger than experimentally observed, confirming that $\text{Ba}_2\text{CuTeO}_6$ has a stronger J' and is therefore located deeper in the ordered side of the phase diagram in Fig. 4.1.

4.5 High-field magnetisation

As a consistency check of the overall energy scale of the interactions deduced from fits to the LSWT and QMC calculations, the magnetisation curve as a function of applied magnetic field was compared with the predictions of the two theoretical models. Fig-

ure 4.11 shows the previously-measured high-field magnetisation data for magnetic fields applied parallel and perpendicular to the ab plane (red and blue solid lines, respectively), where the horizontal scale is the renormalised magnetic field $\frac{1}{2}gB$, assuming $g_{\parallel ab} = 2.080$ and $g_{\perp ab} = 2.289$ [40]. The slight difference between the two curves is consistent with the assumption that the system is almost isotropic, with only rather small Dzyaloshinskii-Moriya or other exchange anisotropy terms. Neglecting such small anisotropies, which are beyond the scope of the present analysis, the mean-field prediction assuming a spin-flop phase is shown as the upper dashed green line and the QMC calculation as a dashed black line. The experimental magnetisation data (average of the two solid lines) is significantly reduced compared to the mean-field prediction (which neglects entirely zero-point quantum fluctuations) and is quite close to the QMC calculation. This agreement acts as a consistency check of the sum of the exchanges [given by term A in Eq. (4.6)] deduced by comparing the observed spin dynamics with the QMC calculations.

4.6 Conclusion

To summarise, inelastic neutron scattering measurements of the spin dynamics in $\text{Ba}_2\text{CuTeO}_6$ have been presented over the full bandwidth of magnetic excitations. The observed spectrum is consistent with that expected for two-leg antiferromagnetic ladders with finite interladder couplings in the bc plane and almost negligible couplings between planes. Through quantitative comparison with both linear spin wave theory and quantum Monte Carlo calculations, values have been proposed for all relevant exchange parameters, both intraladder as well as interladder. The deduced values put the system on the ordered side of the phase diagram for coupled two-leg ladders, in proximity to the critical point where the magnetic order is suppressed.

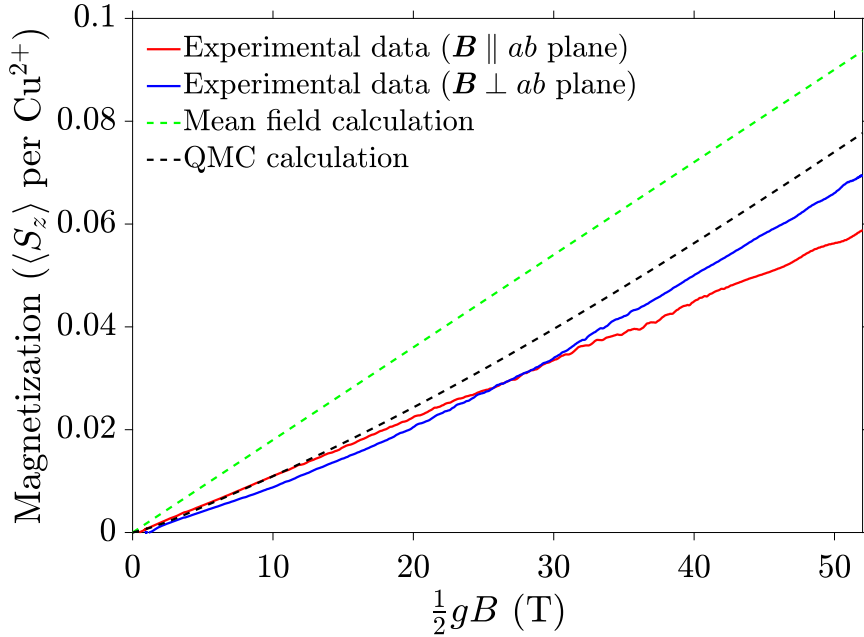


Figure 4.11: Longitudinal magnetisation curve in single crystals of $\text{Ba}_2\text{CuTeO}_6$ as a function of the applied field, for $\mathbf{B} \parallel ab$ plane (red line) and $\mathbf{B} \perp ab$ plane (blue line) [40]. The mean-field theory prediction assuming a spin-flop phase is shown by the green dashed line [exchange parameters as in Fig. 4.6(a)] and the QMC calculation by the black dashed line [exchange parameters as in Fig. 4.6(b)].

4.7 Acknowledgements

The $\text{Ba}_2\text{CuTeO}_6$ sample was synthesised and characterised by A. S. Gibbs at MPI Stuttgart under the supervision of H. Takagi. A. S. Gibbs also prepared the sample for the experiments. I am grateful to the Science and Technology Facilities Council for the beamtime allocations that enabled our measurements at the ISIS Neutron and Muon Source. I helped to perform the measurements at MERLIN, together with A. S. Gibbs (ISIS), R. Coldea and H. C. Walker (ISIS), and the measurements at LET were conducted by D. Voneshen (ISIS). I performed the data processing and analysis, including the MFT and LSWT calculations and the data fitting, with the assistance of R. Coldea. The QMC calculations were performed by T. Ying (Harbin and Aachen) and S. Wessel (Aachen), and I fitted them to the experimental data. I would also like to acknowledge useful discussions with F. Mila (EPFL) and H. Takagi.

Chapter 5

Near-Heisenberg triangular antiferromagnet $\text{Ba}_3\text{CoSb}_2\text{O}_9$

This chapter explores the magnetic excitations of the spin- $\frac{1}{2}$ triangular antiferromagnet $\text{Ba}_3\text{CoSb}_2\text{O}_9$ in the 120° ordered phase using single-crystal high-resolution inelastic neutron scattering. Sharp magnons are observed throughout the Brillouin zone with a strong scattering continuum at higher energies extending up to at least $4\times$ the maximum one-magnon energy, with sixfold-symmetric intensity patterns of rings, triangles and hexagons becoming apparent at various energies. The magnon energies are strongly renormalised downwards and the intensity decreases much faster upon increasing energy than predicted by linear spin wave theory (LSWT), attributed to a transfer of spectral weight to the higher-energy continuum states, which push down the one-magnon dispersions. An empirical model is proposed of momentum and energy-dependent renormalisations on the LSWT dispersion for a spin Hamiltonian with nearest-neighbour and next-nearest-neighbour exchanges and weak easy-plane anisotropy that can capture quantitatively the complete magnon dispersions throughout the Brillouin zone, including the soft modes at the zone boundary and near half the ordering wave vector. Consistent with the experimental observation of sharp magnons throughout, it is explicitly verified that this strongly-renormalised dispersion ensures magnons remain well-defined quasiparticles, as kinematic constraints disallow

one→two-magnon decays. While some low-energy features of the continuum could be captured by simulating two-magnon excitations, there is considerable structure and signal extending to much higher energies that cannot be accounted for, suggesting significant quantum fluctuations beyond the spin wave approximation. The dispersion relations of opposite chirality 120° structures are degenerate in zero field, but are expected to split for a cone structure stabilised in a magnetic field applied normal to the spiral order. The magnon dispersions have been measured in fields up to 9 T, observing a splitting of the magnon modes and evolution of the dispersion relations in field that are consistent with the presence of two equal-weight domains of opposite chirality, as expected in the absence of Dzyaloshinskii-Moriya interactions.

5.1 Introduction

Triangular-lattice quantum antiferromagnets have been much studied theoretically as potential hosts for frustration-enhanced cooperative quantum effects, from the one-third magnetisation plateau phase in applied field protected by a zero-point quantum gap [64, 65, 66, 67], to strongly-renormalised magnon dispersions from non-linear effects [68, 69], to conceptual models of quantum spin liquid phases [70, 71, 72]. While it is well established that the nearest-neighbour triangular-lattice Heisenberg antiferromagnet (TLHAF) has a non-collinear 120° magnetic order in the ground state [73, 74, 75, 76, 77], as expected at the mean-field level but with a reduced ordered moment, less is known about the full energy spectrum. In particular, a perturbative ($1/S$) spin wave expansion predicts strong downward renormalisation of the magnon dispersions and soft roton-like minima near the M points (mid-edges of the Brillouin zone) [69, 68, 78], with magnons expected to decay over extended regions of reciprocal space for the extreme quantum limit of $S = \frac{1}{2}$ [78, 79]. The expected roton-like minima and lifetime broadening of the magnon dispersion were

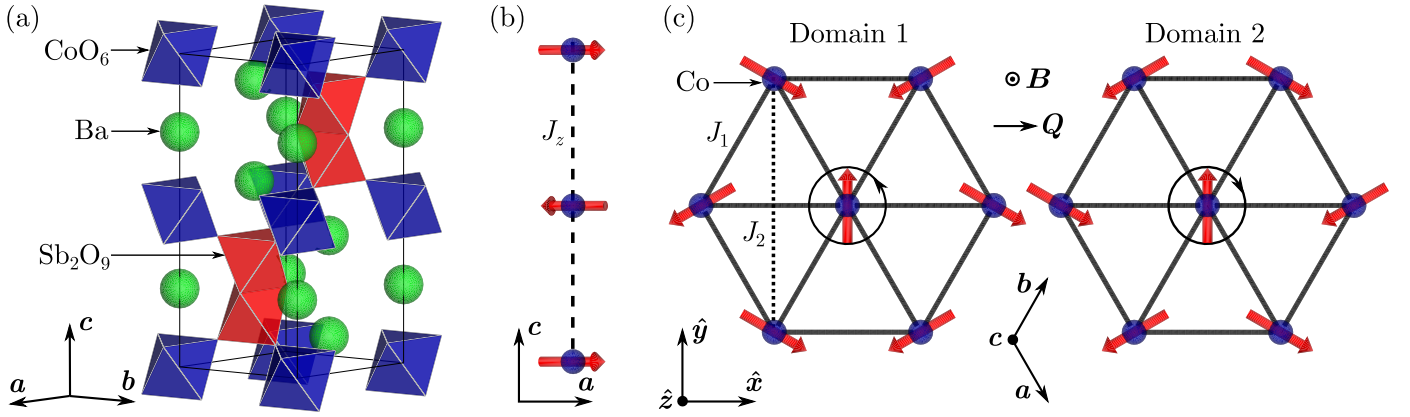


Figure 5.1: Crystal structure of $\text{Ba}_3\text{CoSb}_2\text{O}_9$ showing triangular lattices of CoO_6 octahedra (blue) in the ab plane separated by Ba^{2+} ions (green) and Sb_2O_9 double octahedra (red), with NN intralayer coupling J_1 (thick lines), NNN intralayer coupling J_2 (dotted line), interlayer coupling J_z (dashed line), the structural hexagonal unit cell (thin lines) and the alignment of the spins (red arrows) in the 120° spiral order ground state of the magnetic Hamiltonian in Eq. (5.1). The diagrams were produced using VESTA [59]. (a) A single hexagonal unit cell showing three triangular layers of CoO_6 octahedra stacked along c . (b) Projection of the structure on the ac plane, showing adjacent Co^{2+} sites in three different layers, the interlayer coupling J_z and the resulting antiferromagnetic interlayer order. (c) View along c of the hexagonal structure, illustrating the two possible chiralities of the magnetic ground state: domain 1 corresponds to an anticlockwise rotation of the spin about c traversing left to right along the ordering wave vector $\mathbf{Q}$, and domain 2 corresponds to a clockwise rotation. The relative alignment of the applied magnetic field $\mathbf{B}$ is also shown.

observed experimentally in the spatially-anisotropic $S = 2$ TLHAF LuMnO_3 [80].

Alternative theoretical approaches propose that instead the spectrum is better understood in terms of underlying spin- $\frac{1}{2}$ spinon excitations [83, 84]. This is inspired by theoretical studies of the spatially-anisotropic TLHAF with dominant coupling J between spins along one of the three lattice directions (“chains”) and a smaller coupling $J' < J$ along the other two lattice directions, which interpolates between the spatially-isotropic triangular lattice ($J' = J$) and decoupled chains ($J' = 0$). In the latter limit, it is well established that excitations are spin- $\frac{1}{2}$ spinons. This remains a good description for some range of finite interchain couplings J' [85], exemplified by experiments on Cs_2CuCl_4 ($J' \sim J/3$) that observed excitations dominated by a broad continuum and spin waves carrying relatively little scattering weight [86]. Recent

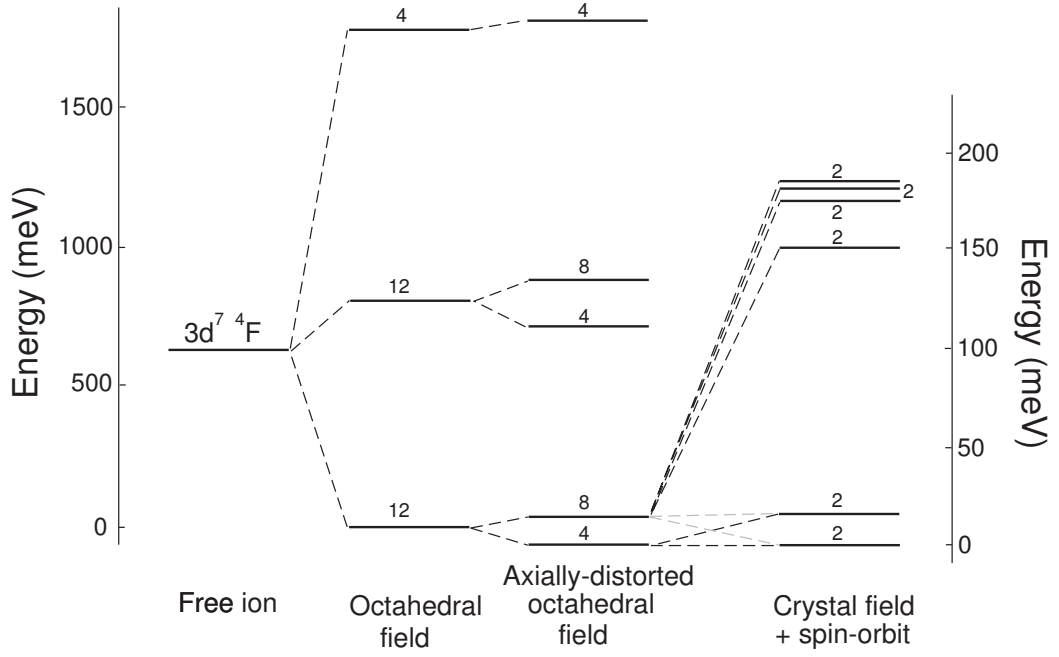


Figure 5.2: Single-ion energy levels of Co^{2+} ions in $\text{La}_{1.5}\text{Sr}_{0.5}\text{CoO}_4$, illustrating the ground state in an axially-distorted octahedral crystal field with spin-orbit interactions, a qualitatively similar configuration to $\text{Ba}_3\text{CoSb}_2\text{O}_9$. The relative energy scales of the interactions are shown, with an expanded vertical scale on the right for the splitting due to the spin-orbit interaction. In $\text{Ba}_3\text{CoSb}_2\text{O}_9$, the $J_{\text{eff}} = \frac{1}{2}$ Kramers doublet ground state is well separated from the $J_{\text{eff}} = \frac{3}{2}$ doublet [81], allowing it to be treated as an effective spin- $\frac{1}{2}$ system. Reproduced with permission from Ref. [82].

theories suggest that starting from a picture of underlying spinon excitations may provide a useful way of capturing some properties of the spatially-isotropic $S = \frac{1}{2}$ TLHAF [87].

$\text{Ba}_3\text{CoSb}_2\text{O}_9$ has been proposed as a near-ideal realisation of the spatially-isotropic spin- $\frac{1}{2}$ TLHAF [88, 89, 90]. The magnetic Co^{2+} ions are arranged in stacked hexagonal layers with space group $P6_3/mmc$, as per Fig. 5.1(a). The highly-symmetric structure forbids anisotropic Dzyaloshinskii-Moriya (D-M) interactions for up to third nearest neighbours (NN) in the plane and for all pairs between planes [89]. Figure 5.2 shows the single-ion energy level diagram for the qualitatively similar case of Co^{2+} ions in $\text{La}_{1.5}\text{Sr}_{0.5}\text{CoO}_4$ [82]. Free Co^{2+} ions have an electronic configuration $[\text{Ar}]3d^7$ with $L = 3$ and $S = \frac{3}{2}$ from Hund's rules. There are therefore 28 degenerate levels in the ground state, which are split into Kramers doublets by the axially-distorted octahedral crystal field and the spin-orbit interaction. In the case of $\text{Ba}_3\text{CoSb}_2\text{O}_9$, the octahedra are distorted along the c axis [81]. Previous inelastic neutron scattering measurements have shown that the lowest-energy $J_{\text{eff}} = \frac{1}{2}$ doublet is well separated from the $J_{\text{eff}} = \frac{3}{2}$ doublet, with an excitation energy ~ 40 meV [81]; $\text{Ba}_3\text{CoSb}_2\text{O}_9$ can therefore be modelled as an effective spin- $\frac{1}{2}$ system at low temperatures. The magnetic ground state is a 120° spiral order in the basal plane, depicted in Fig. 5.1(b)–(c), due to a small easy-plane exchange anisotropy [91, 92, 93, 94]. Magnetisation measurements observed a clear one-third plateau for magnetic fields applied in the basal plane [89, 91], a direct experimental realisation of the up-up-down phase stabilised by quantum fluctuations [64], which has also been observed in the spatially-anisotropic system Cs_2CuBr_4 [95]. Previous INS measurements in $\text{Ba}_3\text{CoSb}_2\text{O}_9$ revealed a strong downwards renormalisation of the magnon dispersion, a pronounced roton-like minimum at the M points, and an extended scattering continuum at higher energies [90, 94, 96]. While linear spin wave theory (LSWT) can account for INS measure-

ments in the up-up-down phase [97], it has been unable to quantitatively capture the observed dispersion relations in the zero-field helical phase [94, 96], even when magnon interactions are included by a $1/S$ correction [94]. The measured spin dynamics therefore suggests the presence of strong quantum effects beyond the perturbative level.

A quantitative parametrisation of the dispersion relations and knowledge of the energy and momentum dependence of the continuum scattering are essential in order to test the ability of theoretical models to describe the magnetic excitations. Motivated by this, extensive studies are presented of the magnetic excitations in large single crystals of $\text{Ba}_3\text{CoSb}_2\text{O}_9$ [37] with high-resolution INS measurements spanning multiple Brillouin zones, which reveal that the high-energy excitation continuum displays highly-structured intensity modulations with rings, hexagons and triangles apparent at various energies. Below the energy threshold of the continuum scattering, sharp, resolution-limited magnons are also observed throughout reciprocal space with no decay. Empirical dispersion renormalisations are proposed that allow the quantitative parametrisation of all modulations of the experimentally-observed magnon dispersion relations in the full three-dimensional Brillouin zone, including all soft modes and a strongly energy-dependent dispersion renormalisation. Detailed knowledge of the dispersion relations is essential in order to test if any regions exist where magnon decays can in principle occur. For the observed strongly-renormalised dispersion, it is shown here that magnon decays are in fact disallowed throughout the Brillouin zone (*i.e.* one- and two-magnon phase spaces in energy and momentum never overlap), consistent with the experimental observation of sharp magnons throughout the probed reciprocal space. Note that adding an easy-plane exchange anisotropy to the TLHAF model gaps out the primary one-magnon dispersion at the ordering wave vector and reduces the overlap phase space, with magnons becoming stable throughout recipro-

cal space for $\Delta \lesssim 0.92$ [94]. However, the renormalised magnon dispersions in that case are not compatible with the experimentally-observed dispersions. This suggests that quantum interaction effects between one-magnon and higher-energy continuum states in the actual material are significantly stronger than can be captured perturbatively at the $1/S$ level, consistent with recent density matrix renormalisation group (DMRG) calculations observing avoided quasiparticle decay in spin- $\frac{1}{2}$ models even relatively close to the TLHAF limit [98]. Direct evidence is also observed for a transfer of spectral weight from the one-magnon states to the higher-energy continuum, a further consequence of such strong interactions. Finally, INS measurements are presented of $\text{Ba}_3\text{CoSb}_2\text{O}_9$ in a magnetic field applied normal to the spiral order, which provide a direct probe of the spin dynamics in the cone phase. By comparing the evolution of the magnon dispersions with applied field to the LSWT predictions, the presence of two domains of opposite chirality is confirmed, as expected in the absence of D-M interactions.

The rest of this chapter is organised as follows. Section 5.2 describes the experimental set-up used for the single-crystal INS measurements in zero applied magnetic field and for a field normal to the basal plane. Section 5.3 discusses the spin dynamics for the 120° spiral order ground state in zero applied magnetic field. The zero-field section begins by outlining the key features of the observed magnetic excitations and their physical origin in Sec. 5.3.1. The following Sec. 5.3.2 details the one- and two-magnon simulations: Sec. 5.3.2.1 outlines the LSWT calculation and Sec. 5.3.2.2 summarises its predictions and shortcomings; Sec. 5.3.2.3 describes the proposed parametrisation of the data using empirical renormalisations of the LSWT calculation and Sec. 5.3.2.4 presents the best-fit to the data; and Sec. 5.3.2.5 compares the numerical simulation of the two-magnon continuum using this parametrisation to the data. Section 5.4 presents the INS measurements of the spin dynamics in the

cone phase in a magnetic field applied normal to the plane, and compares the results to the LSWT calculations. Finally, the conclusions are summarised in Sec. 5.5.

5.2 Experimental details

Two large $\text{Ba}_3\text{CoSb}_2\text{O}_9$ single crystals of total mass 4 g were used in the INS experiments, grown by the floating-zone technique in an image furnace [37] and co-aligned using X-ray Laue diffraction. In Fig. 5.3(a), the black crystals are shown mounted on individual oxygen-free high-conductivity (OFHC) copper goniometers, which can be independently tilted using screws in the brass cylindrical supports to accommodate small corrections to the alignments. The copper foil and wires wrapped around the crystals improve the thermal contact with the refrigerator. The sample mount is shown from a different angle in Fig. 5.3(b), with cadmium shielding secured to the base using copper wire.

The samples were aligned with $\mathbf{c}^*$ vertical to probe the hk scattering plane, expected to contain the interesting physics in this quasi-2D system. A remaining misalignment of 2.8° from the vertical axis of the instrument was determined by analysing the neutron Bragg peak positions; an appropriate correction was applied in the data processing using HORACE [35]. A small sample mosaic of 2° (FWHM) was calculated from the width of the nuclear Bragg peaks.

The sample was measured using the direct geometry time-of-flight neutron spectrometer LET at the ISIS neutron source in the UK [32]. Repetition rate multiplication (RRM) allowed data to be collected simultaneously for incident neutrons with energies $E_i = 3.53$ and 7.01 meV, with energy resolutions on the elastic line of $0.0620(1)$ and $0.159(4)$ meV (full width at half maximum, FWHM), respectively. The magnetic excitations were found to extend up to $E \simeq 1.6$ meV, so this experimental configuration allowed high-resolution measurements of the one-magnon dispersion

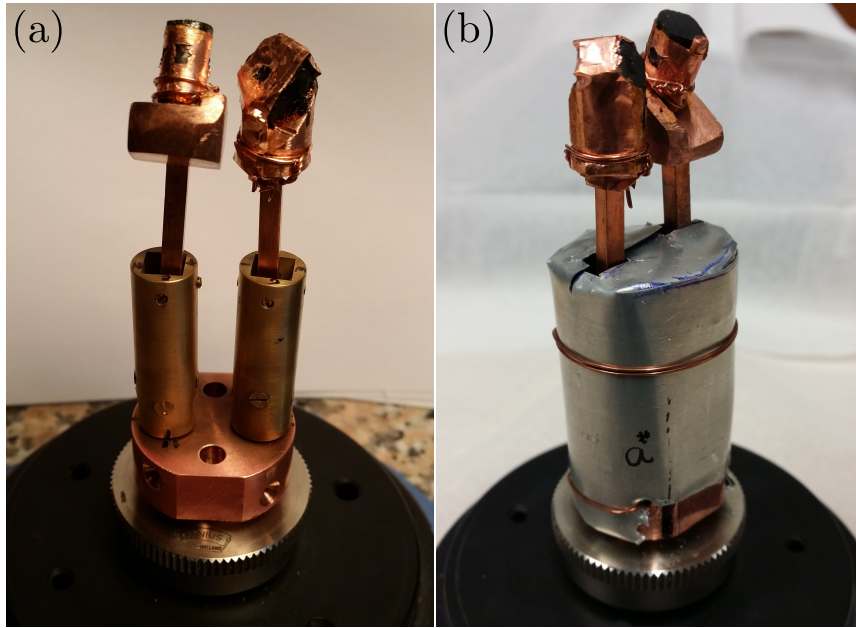


Figure 5.3: Two co-aligned $\text{Ba}_3\text{CoSb}_2\text{O}_9$ single crystals on the sample mount for the INS experiments. (a) Sample mount consisting of two individually-adjustable oxygen-free high-conductivity (OFHC) copper goniometers in brass cylindrical supports. OFHC copper foil hoods and copper wires are wrapped around the crystals to improve thermal contact with the refrigerator. (b) Sample mount from a different angle, including the cadmium shielding of the base, held in place with copper wire. Photographs courtesy of S. Williams (Oxford).

and the multi-magnon continuum scattering. The data collected at $E_i = 7.01$ meV have been scaled throughout to match the intensity of the magnetic scattering in the $E_i = 3.53$ meV data. A variable-temperature insert with a He exchange gas was used to cool the sample to a base temperature $T = 1.7$ K, below the magnetic ordering transition at $T_N \simeq 3.8$ K [88, 37], and up to $T = 32$ K in the paramagnetic phase. The sample was rotated through an angle of 140° in the scattering plane, allowing data to be collected across several Brillouin zones in the hk plane and a full Brillouin zone along the l direction. The typical counting time at each orientation was 15 minutes (7 minutes) for a total of 70 h (32 h) at $T = 1.7$ K (32 K), with an average proton current of $40 \mu\text{A}$.

Additional measurements were performed on the same sample in an applied magnetic field using the LET spectrometer [32] to probe the spin wave excitations in the “cone” phase, where the ground state is the 120° spiral order in the ab plane with the spins canted in the direction of a magnetic field applied along c . INS data were collected for incident energies $E_i = 2.24, 3.81$, and 7.83 meV, with energy resolutions on the elastic line of $0.0300(3)$, $0.064(1)$, and $0.179(8)$ meV (FWHM), respectively. A ^3He - ^4He dilution refrigerator allowed measurements at a base temperature $T = 0.1$ K in the AFM ordered phase and at $T = 30$ K in the paramagnetic phase. Measurements were performed at the base temperature for applied fields $B = 3, 6$ and 9 T, and the paramagnetic background was measured in zero field. The sample was again rotated through 140° in the ab plane, counting for 14 minutes at each orientation in $B = 6$ and 9 T, for 10 minutes in $B = 3$ T and 7 minutes in zero field, with an average proton current of $40 \mu\text{A}$ for a total of 32 h, 48 h and 16 h, respectively.

The counting statistics of all the plotted data have been improved as much as possible using point-group symmetry operations that leave $|\mathbf{k}|$ unchanged, so as not to mix different values of the magnetic form factor. All time-of-flight neutron data

were processed using the MANTID [34] and HORACE [35] data analysis packages.

5.3 Spin dynamics in zero applied magnetic field

5.3.1 Measurements and results

In this section, INS measurements are presented of $\text{Ba}_3\text{CoSb}_2\text{O}_9$ in zero applied magnetic field, with a 120° spiral order ground state confirmed by previous experiments [91, 92, 93, 94]. The following labelling convention is used throughout: for some high-symmetry point X, this form indicates $l = 0$ and X' indicates $l = 1$; X_1 and X_2 label different symmetry-equivalent points in the Brillouin zone; and $\mathbf{k}_X = (h, k, l)$ is the corresponding wave vector, where $(h, k, l) = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$ in reciprocal lattice units of the structural unit cell in Fig. 5.1(a). Figures 5.4 and 5.5 show the INS data collected in zero applied magnetic field. Figures 5.5(e)–(h) correspond to incident neutron energy $E_i = 3.53$ meV, Figs. 5.5(i)–(l) correspond to $E_i = 7.01$ meV, and Fig. 5.4 combines data collected at both incident energies. The l integration range in Fig. 5.4 increases with energy transfer to improve the signal strength, which is possible because the l dispersion becomes less significant at higher energies. At base temperature $T = 1.7$ K, the key magnetic features are a sharp gapless mode emanating from the K' point [$\mathbf{k}_{K'_1} = (\frac{1}{3}, \frac{1}{3}, 1)$], a sharp mode with a spin gap $\Delta E \simeq 0.8$ meV, a small interlayer dispersion, minima in the dispersion at the M point [$\mathbf{k}_{M_1} = (\frac{1}{2}, \frac{1}{2}, 0)$] and $K/2$ point [$\mathbf{k}_{K_1}/2 = (\frac{1}{3}, \frac{1}{3}, 0)/2$], a drop-off in intensity at the Γ point [$\mathbf{k}_\Gamma = (0, 1, 0)$], and strong continuum scattering centred on the K' point. The continuum scattering extends up to > 6 meV, giving it an energy scale at least $4\times$ greater than that of the one-magnon modes, which have a maximum energy of $\simeq 1.6$ meV. These features become overdamped in the higher temperature $T = 32$ K measurements, confirming their magnetic character.

Figure 5.5 shows how the hexagonal patterns in the hk plane develop with in-

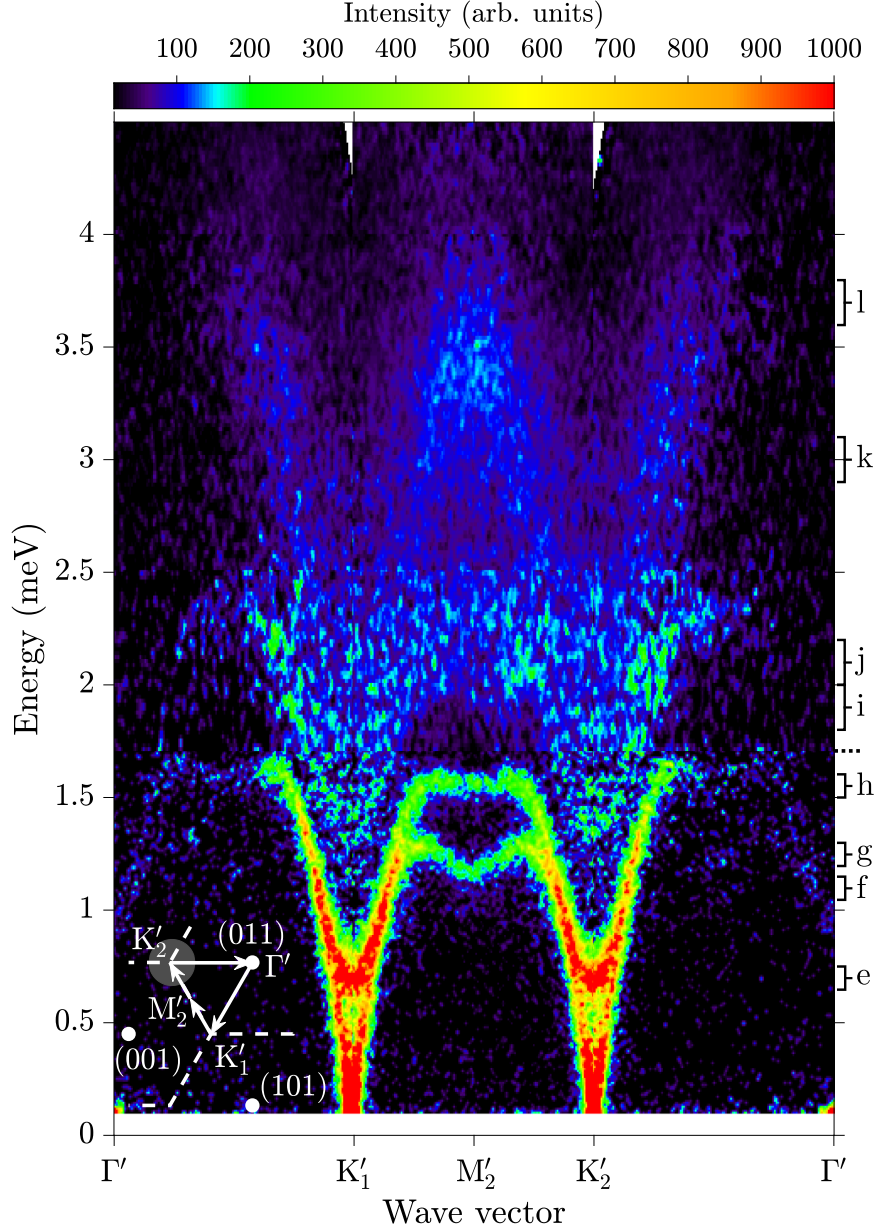


Figure 5.4: INS data along high-symmetry directions in reciprocal space showing the full range of one-magnon excitations up to $\simeq 1.6$ meV and a broad continuum up to > 4.5 meV, collected at $T = 1.7$ K. The colour map shows the intensity in arbitrary units as a function of wave vector and energy. The wave vector path is $\Gamma' (0, 1, 1) \rightarrow K'_1 (\frac{1}{3}, \frac{1}{3}, 1) \rightarrow M'_2 (0, \frac{1}{2}, 1) \rightarrow K'_2 (-\frac{1}{3}, \frac{2}{3}, 1) \rightarrow \Gamma'$, illustrated by arrows in the white bottom-left inset with the Brillouin zone boundaries represented by dashed lines. The dotted line at 1.7 meV on the right indicates the cross-over from incident energy $E_i = 3.53$ meV data (below) to $E_i = 7.01$ meV data (above). The integration width in the hk plane is $\pm 0.05 \text{ \AA}^{-1}$, and along l is $\pm 0.05 \text{ \AA}^{-1}$ for energies $E \leq 2$ meV, $\pm 0.1 \text{ \AA}^{-1}$ for $2 < E \leq 4$ meV and $\pm 0.2 \text{ \AA}^{-1}$ for $E > 4$ meV. The quasielastic scattering below 0.1 meV has been omitted. The labelled brackets on the right indicate the energy bands of the hk slices with the same panel letters in Fig. 5.5.

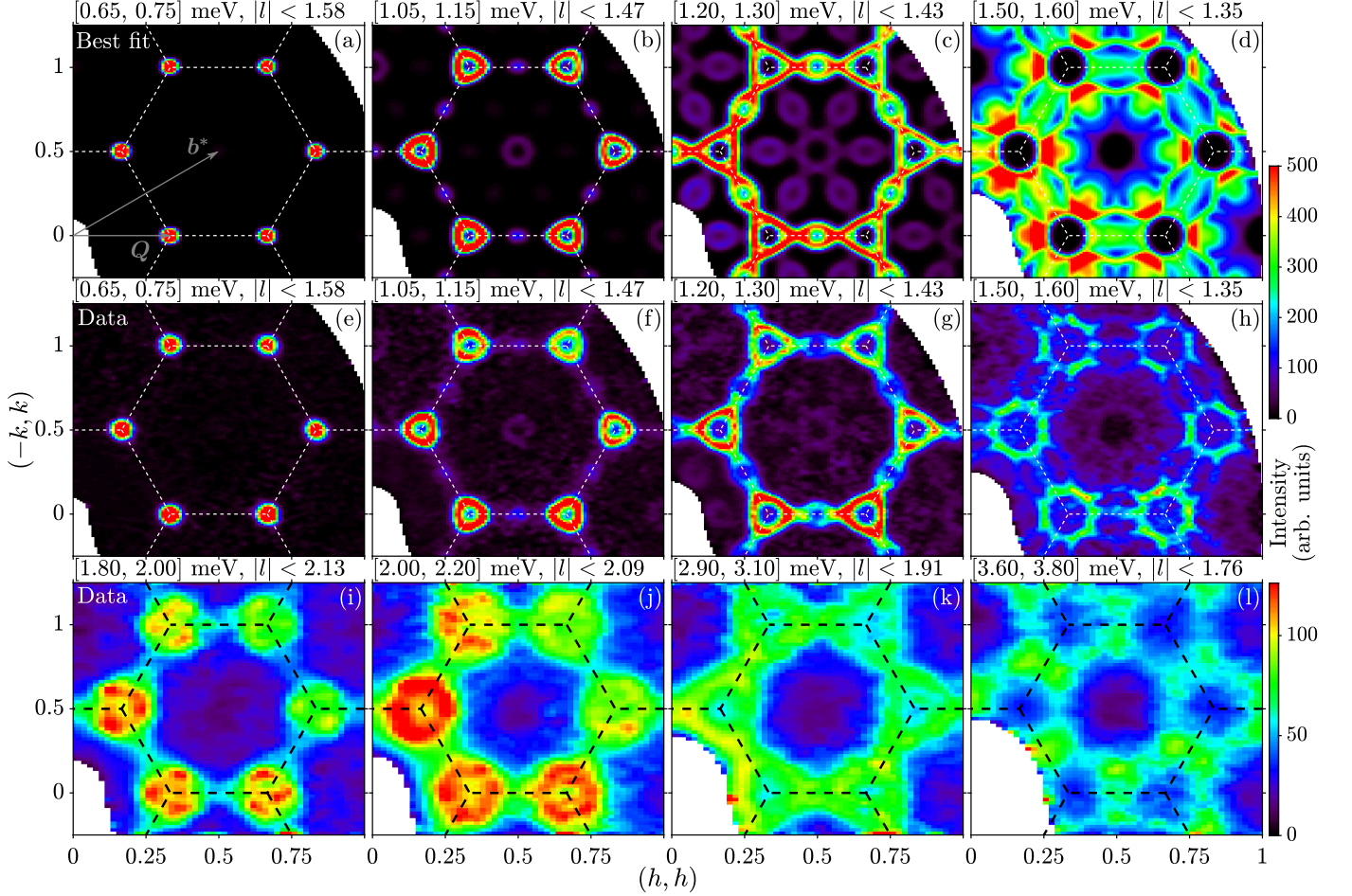


Figure 5.5: INS data and calculations for constant energy slices in the hk plane. The integration ranges are given in the panel titles (above). The data were collected at $T = 1.7$ K. The Brillouin zone boundary is indicated with dashed lines, and $\mathbf{b}^*$ and $\mathbf{Q}$ are shown for reference as grey arrows in (a). The colour map gives the intensity in arbitrary units. The energy integration ranges of the panels are indicated by the brackets on the right of Fig. 5.4. (e)–(h) Data showing the sharp one-magnon modes, for incident energy $E_i = 3.53$ meV. (a)–(b) The corresponding calculations using the best-fit empirical parametrisation discussed in Sec. 5.3.2.3, including the magnetic form factor for Co^{2+} ions, the neutron orientation factor, the finite temperature Bose factor and convolution with the instrument resolution. (i)–(l) Slices through the continuum scattering at higher energies ($E_i = 7.01$ meV).

creasing energy, consistent with the six-fold symmetry of the triangular lattice. Spin wave cones emanate from the K' points at low energies [Fig. 5.5(e)], which become triangular at $\simeq 1.1$ meV [Fig. 5.5(f)]. At $\simeq 1.25$ meV [Fig. 5.5(g)], a cone has opened up at the M points where the first roton-like minimum has been intersected. At $\simeq 1.55$ meV [Fig. 5.5(h)], the spin wave cones have expanded and the second roton-like minimum is visible at the M points. Figures 5.5(i)–(l) show the structure of the continuum scattering, which consists of two intense cones centred at the K' points (cf. Fig. 5.4). These cones expand with increasing energy, becoming triangular at $\simeq 3$ meV [Fig. 5.5(k)], before losing intensity above $\simeq 4$ meV [Fig. 5.5(l)].

The Goldstone mode is physically attributed to spin waves polarised in the ab plane, which arise from the spiral order ground state breaking the continuous rotational symmetry and therefore emanate from the magnetic ordering wave vector. The other mode, corresponding to out-of-plane spin waves, is gapped due to the small easy-plane anisotropy in this system [91, 92, 93, 94]. Three modes are expected in total, corresponding to the three sublattices of the magnetic ground state in Figs. 5.1(b)–(c), but only two carry significant weight at any given wave vector. No lifetime broadening effects associated with one→two-magnon decay processes are observed, as the FWHM of the high-energy modes is consistent with the instrument resolution measured on the elastic line, suggesting that the magnons are long-lived. The lack of intensity at the Γ point is expected for an AFM system and the overall decrease in magnetic signal with increasing wave vector in Fig. 5.5 is attributed to the magnetic form factor of the Co^{2+} ions. As predicted for a spin- $\frac{1}{2}$ TLHAF [69, 68, 78, 83, 79, 84], there is evidence of significant quantum fluctuations, including mode softening and roton-like minima at the M and $K/2$ points, which flatten the top of the dispersion, and strong continuum scattering at high energies, well beyond the extent expected for purely two-magnon processes.

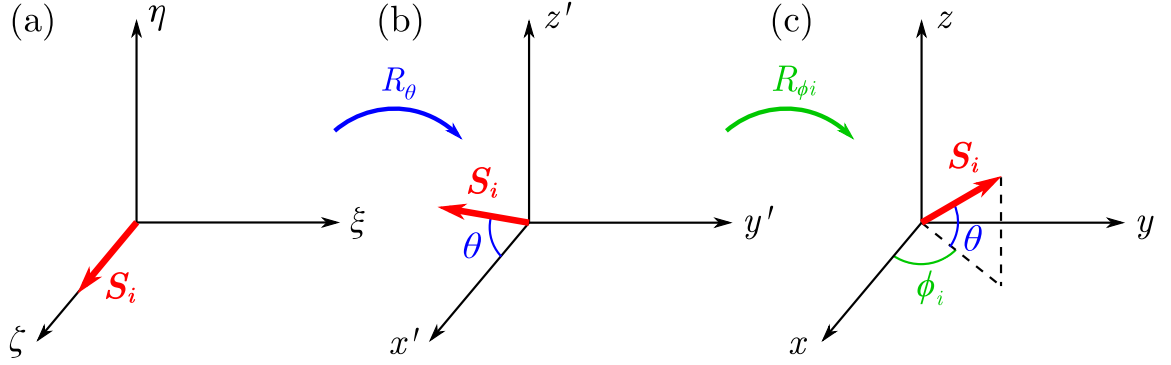


Figure 5.6: Transformation between the Cartesian coordinates used in the LSWT calculation, from the rotating frame of reference (ζ, ξ, η) to the laboratory frame (x, y, z) . Note that only the coordinate system changes; the spin $\mathbf{S}_i$ is unaffected by the transformation. (a) The rotating frame, in which all spins are aligned along the ζ direction. The LSWT calculation was performed in this frame for simplicity. (b) An intermediate frame (x', y', z') , with spins aligned along the x' direction in the $x'y'$ plane and canted by an angle θ out of the plane, after applying a rotation R_θ . This accounts for the effect of a magnetic field applied along z'/z . (c) The laboratory frame, obtained by applying a further rotation R_{ϕ_i} . The spins are again canted along the z direction, and also have a helical order in the xy plane, with the i th spin rotated by an angle ϕ_i about the z axis. This is the cone phase of a triangular antiferromagnet in a magnetic field applied normal to the spiral order.

5.3.2 Analysis

5.3.2.1 Linear spin wave theory calculation

This section outlines the LSWT calculation of the dispersion relation and dynamical structure factor for neutron scattering from a triangular antiferromagnet. Based on previous electron spin resonance, [91], nuclear magnetic resonance [92], ultrasound velocity [93] and neutron diffraction [94] measurements of $\text{Ba}_3\text{CoSb}_2\text{O}_9$, the following spin Hamiltonian with XXZ interactions is assumed:

$$\begin{aligned}
\mathcal{H} = & J_1 \sum_{\langle ij \rangle}^{\text{NN}} (S_i^x S_j^x + S_i^y S_j^y + \Delta S_i^z S_j^z) \\
& + J_2 \sum_{\langle kl \rangle_2}^{\text{NNN}} (S_k^x S_l^x + S_k^y S_l^y + \Delta S_k^z S_l^z) \\
& + J_z \sum_{\langle mn \rangle}^{\text{interlayer}} (S_m^x S_n^x + S_m^y S_n^y + \Delta S_m^z S_n^z) - g\mu_B B \sum_i S_i^z,
\end{aligned} \tag{5.1}$$

where the nearest-neighbour (NN) intralayer exchange J_1 , the next-nearest-neighbour (NNN) intralayer exchange J_2 and the interlayer exchange J_z are illustrated in Fig. 5.1, Δ is the easy-plane anisotropy, and B is the magnetic field applied along $\mathbf{c}$. This system has a 120° spiral order with the axis of rotation normal to the triangular layers, and spins are aligned antiparallel in adjacent layers [see Figs. 5.1(b) and 5.1(c)]. In reciprocal lattice units of the hexagonal structural unit cell in Fig. 5.1(a), the corresponding magnetic ordering wave vector is $\mathbf{Q} = (\frac{1}{3}, \frac{1}{3}, 1)$. [Note that there are two possible chiralities of the 120° order, depicted in Fig. 5.1(c): domain 1, in which the spins rotate anticlockwise along $\mathbf{Q}$, and domain 2, in which the spins rotate clockwise. Neither is energetically favoured in the absence of D-M interactions, so domains of both chiralities are expected to be present in $\text{Ba}_3\text{CoSb}_2\text{O}_9$.] In a magnetic field applied normal to the spiral order, the spins retain their 120° order (below saturation) and also cant along the direction of the applied field; this is known as the “cone” phase and is the assumed ground state for the following LSWT calculation.

To describe the spin axes, a Cartesian coordinate system (x, y, z) is used with $\hat{\mathbf{x}} \parallel \mathbf{Q}$ and $\hat{\mathbf{z}} \parallel \mathbf{c}$ (normal to the triangular layers), as shown in Fig. 5.1(c). The analytic calculation is simplified by transforming to local spin coordinates (ζ, ξ, η) that rotate with the spins in the magnetic ground state, such that ζ is the ordered spin direction, ξ is perpendicular to the spin in the helical plane and η is normal to the plane. The transformation between this rotating frame of reference and the laboratory frame is illustrated in Fig. 5.6. It corresponds to performing a rotation of the local spin axes in the $\zeta\eta$ plane by the canting angle θ and then rotating in the xy plane by the helical ordering angle $\phi_i = \mathbf{Q} \cdot \mathbf{r}_i + \Phi$, where $\mathbf{r}_i$ is the position of the i th spin and Φ is the phase of the spin at the origin. [$\Phi = \frac{\pi}{2}$ in the case of the magnetic structure illustrated in Fig. 5.1.] The spins are therefore ferromagnetically aligned in the rotating frame and the calculation is reduced to one magnetic sublattice. The transformation of the

spin component operators is $(S_i^x, S_i^y, S_i^z)^\top = R_{\phi_i} \cdot R_\theta \cdot (S_i^\zeta, S_i^\xi, S_i^\eta)^\top$, which gives

$$S_i^x = S_i^\zeta \cos \theta \cos \phi_i - S_i^\xi \sin \phi_i - S_i^\eta \sin \theta \cos \phi_i, \quad (5.2)$$

$$S_i^y = S_i^\zeta \cos \theta \sin \phi_i + S_i^\xi \cos \phi_i - S_i^\eta \sin \theta \sin \phi_i, \quad (5.3)$$

$$S_i^z = S_i^\zeta \sin \theta + S_i^\eta \cos \theta. \quad (5.4)$$

The spin Hamiltonian for the NN intralayer interactions [first term of Eq. (5.1)] in the rotating coordinate system has the form

$$\begin{aligned} \mathcal{H}_{\text{NN}} = J_1 \sum_{\langle ij \rangle} [& (\cos^2 \theta \cos \phi_{ij} + \Delta \sin^2 \theta) S_i^\zeta S_j^\zeta + \cos \phi_{ij} S_i^\xi S_j^\xi \\ & + (\sin^2 \theta \cos \phi_{ij} + \Delta \cos^2 \theta) S_i^\eta S_j^\eta + \sin \theta \sin \phi_{ij} (S_i^\xi S_j^\eta - S_i^\eta S_j^\xi)], \end{aligned} \quad (5.5)$$

where $\phi_{ij} = \phi_i - \phi_j$. Similar expressions describe the NNN intralayer and interlayer interactions. The Zeeman term [the final term in Eq. (5.1)] is simply

$$\mathcal{H}_Z = -g\mu_B B \sum_i S_i^\zeta \sin \theta. \quad (5.6)$$

Terms that would be odd in the boson operators, defined by the Holstein-Primakoff transformation in Eqs. (2.27)–(2.29), have been neglected. These expressions therefore include the classical mean-field energy (zeroth order), the harmonic LSWT spectrum (second order) and the creation of magnon pairs (fourth order).

One can now follow the LSWT method outlined in Sec. 2.7.1 for a system with a single magnetic sublattice [substituting $(x, y, z) \rightarrow (\xi, \eta, \zeta)$]. Using the Holstein-Primakoff transformation, the Fourier transformation defined in Eqs. (2.32)–(2.33), and neglecting terms higher than second order in the boson operators, the spin Hamiltonian in the rotating frame is obtained as

$$\mathcal{H} = \frac{1}{2} \sum_{\mathbf{k}} \mathbf{X}^\dagger \mathbf{H} \mathbf{X} + E_{\text{MF}}, \quad (5.7)$$

where the sum is over all wave vectors $\mathbf{k}$ in the first Brillouin zone of the structural unit cell and the zeroth-order terms are equal to the classical mean-field energy E_{MF} . The

operator basis is chosen to be $\mathbf{X}^\dagger = (\alpha_{\mathbf{k}}^\dagger \quad \alpha_{-\mathbf{k}})$, where $\alpha_{\mathbf{k}}^\dagger$ ($\alpha_{\mathbf{k}}$) creates (annihilates) a spin flip.

Using the mean-field theory method described in Sec. 2.6.2 or (equivalently) by considering the zeroth-order terms in Eqs. (5.5) and (5.6), the mean-field energy is given by

$$E_{\text{MF}} = NS[J(\mathbf{Q})S \cos^2 \theta + \Delta J(\mathbf{0})S \sin^2 \theta - g\mu_{\text{B}}B \sin \theta], \quad (5.8)$$

where N is the total number of spin sites. The canting angle θ (the angle the spin makes with the xy plane) can be calculated by minimising the mean-field energy, which gives

$$\sin \theta = \frac{B}{B_{\text{s}}}, \quad g\mu_{\text{B}}B_{\text{s}} = 2S[\Delta J(\mathbf{0}) - J(\mathbf{Q})], \quad (5.9)$$

where B_{s} is the saturation field and the g factor is assumed equal to 4 (see Ref. [99]).

The Hamiltonian matrix in Eq. (5.7) can then be derived as

$$\mathbf{H} = \begin{pmatrix} A_{\mathbf{k}} + C_{\mathbf{k}} & B_{\mathbf{k}} \\ B_{\mathbf{k}} & A_{\mathbf{k}} - C_{\mathbf{k}} \end{pmatrix}, \quad (5.10)$$

where

$$A_{\mathbf{k}} = S(a_{\mathbf{k}} + b_{\mathbf{k}}), \quad (5.11)$$

$$B_{\mathbf{k}} = S(a_{\mathbf{k}} - b_{\mathbf{k}}), \quad (5.12)$$

$$C_{\mathbf{k}} = S \sin \theta [J(\mathbf{k} + \mathbf{Q}) - J(\mathbf{k} - \mathbf{Q})], \quad (5.13)$$

and

$$a_{\mathbf{k}} = [\Delta J(\mathbf{k}) - J(\mathbf{Q})] \cos^2 \theta + b_{\mathbf{k}} \sin^2 \theta, \quad (5.14)$$

$$b_{\mathbf{k}} = \frac{1}{2} [J(\mathbf{k} - \mathbf{Q}) + J(\mathbf{k} + \mathbf{Q})] - J(\mathbf{Q}). \quad (5.15)$$

$J(\mathbf{k})$ is the Fourier transform of the exchange interactions, given by

$$\begin{aligned} J(\mathbf{k}) = & J_1 [\cos 2\pi h + \cos 2\pi k + \cos 2\pi(h + k)] + J_z \cos \pi l \\ & + J_2 [\cos 2\pi(2h + k) + \cos 2\pi(h + 2k) + \cos 2\pi(h - k)], \end{aligned} \quad (5.16)$$

for a general wave vector $\mathbf{k} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*$ [expressed as (h, k, l) in reciprocal lattice units of the structural cell].

Using the Bogolyubov transformation in Eqs. (2.35)–(2.36) to diagonalise the bilinear boson Hamiltonian, the dispersion relation is given by

$$\hbar\omega(\mathbf{k}) = \sqrt{A_{\mathbf{k}}^2 - B_{\mathbf{k}}^2} + C_{\mathbf{k}}, \quad (5.17)$$

which by periodicity holds for a general wave vector in reciprocal space. Rotating back to the fixed laboratory frame, two in-plane modes $\omega(\mathbf{k} - \mathbf{Q})$ and $\omega(\mathbf{k} + \mathbf{Q})$ and one out-of-plane mode $\omega(\mathbf{k})$ are obtained; so there are three dispersion branches for a general wave vector $\mathbf{k}$. The results given are for domain 1 [left panel of Fig. 5.1(c)]; the results for domain 2 (right panel) are obtained by replacing $\mathbf{Q}$ with $-\mathbf{Q}$ throughout.

The dynamical structure factors defined by Eq. (3.37) can be derived by converting the spin component operators to the magnon operators using the Bogolyubov transformation and noting that the ground state is the magnon vacuum state. The one-magnon excitations are polarised transverse to the ordered spin direction ζ , and the dynamical structure factors (per spin in the rotating frame) are obtained as

$$\begin{aligned} S^{\xi\xi}(\mathbf{k}, \omega) &= \frac{Z_{\xi}S}{2}(u_{\mathbf{k}} + v_{\mathbf{k}})^2 \delta[\hbar\omega - \hbar\omega(\mathbf{k})] \\ &= \frac{Z_{\xi}S}{2} \frac{A_{\mathbf{k}} + B_{\mathbf{k}}}{\hbar\omega(\mathbf{k})} \delta[\hbar\omega - \hbar\omega(\mathbf{k})], \end{aligned} \quad (5.18)$$

$$\begin{aligned} S^{\eta\eta}(\mathbf{k}, \omega) &= \frac{Z_{\eta}S}{2}(u_{\mathbf{k}} - v_{\mathbf{k}})^2 \delta[\hbar\omega - \hbar\omega(\mathbf{k})] \\ &= \frac{Z_{\eta}S}{2} \frac{A_{\mathbf{k}} - B_{\mathbf{k}}}{\hbar\omega(\mathbf{k})} \delta[\hbar\omega - \hbar\omega(\mathbf{k})], \end{aligned} \quad (5.19)$$

$$S^{\xi\eta}(\mathbf{k}, \omega) = -S^{\eta\xi}(\mathbf{k}, \omega) = i\frac{S}{2}\delta[\hbar\omega - \hbar\omega(\mathbf{k})], \quad (5.20)$$

where Z_{ξ} and Z_{η} are amplitudes that were fitted to the experimental data (see Table 5.1), $u_{\mathbf{k}} = \cosh \Theta_{\mathbf{k}}$, $v_{\mathbf{k}} = \sinh \Theta_{\mathbf{k}}$ and $\tanh 2\Theta_{\mathbf{k}} = B_{\mathbf{k}}/A_{\mathbf{k}}$.

The leading terms in the longitudinal dynamical structure factor $S^{\zeta\zeta}(\mathbf{k}, \omega)$ are the elastic Bragg component $(S - \Delta S)^2$, where ΔS is the spin reduction given by

Eq. (2.39), and terms that create and destroy two magnons, which correspond to two-magnon ($2\mathcal{M}$) excitations. The corresponding dynamical structure factor (per spin in the rotating frame) is obtained as

$$S_{2\mathcal{M}}^{\zeta\zeta}(\mathbf{k}, \omega) = \frac{Z_\zeta}{2N} \sum_{\mathbf{k}_1, \mathbf{k}_2} (u_{-\mathbf{k}_1} v_{\mathbf{k}_2} + u_{\mathbf{k}_2} v_{-\mathbf{k}_1})^2 \delta[\hbar\omega - \hbar\omega(\mathbf{k}_1) - \hbar\omega(\mathbf{k}_2)] \delta(\mathbf{k} + \mathbf{k}_1 - \mathbf{k}_2 + \boldsymbol{\tau}), \quad (5.21)$$

where $\boldsymbol{\tau}$ is a reciprocal lattice vector of the structural unit cell and Z_ζ is a normalisation factor chosen to satisfy the neutron sum rules for a spin- $\frac{1}{2}$ system, given by Eq. (3.41).

The density of states ($\text{meV}^{-1}\text{Co}^{-1}$) of the two-magnon excitations is given by

$$D(\mathbf{k}, \omega) = \frac{1}{N} \sum_{\mathbf{k}_1, \mathbf{k}_2} \delta[\hbar\omega - \hbar\omega(\mathbf{k}_1) - \hbar\omega(\mathbf{k}_2)] \delta(\mathbf{k} + \mathbf{k}_1 - \mathbf{k}_2 + \boldsymbol{\tau}), \quad (5.22)$$

cf. Eq. (5.21). The final intensities corresponding to the above dynamical structure factors and density of states also included an asymmetric lineshape of two Gaussian functions, which was fitted to scans through the incoherent scattering at the elastic line and parametrised the instrument resolution in energy.

Rotating back to the fixed laboratory frame using Eq. (5.4), the dynamical structure factors for the one-magnon ($1\mathcal{M}$) and two-magnon ($2\mathcal{M}$) excitations are as follows:

$$S_{1\mathcal{M}}^{zz}(\mathbf{k}, \omega) = S^{\eta\eta}(\mathbf{k}, \omega) \cos^2 \theta, \quad (5.23)$$

$$S_{2\mathcal{M}}^{zz}(\mathbf{k}, \omega) = S_{2\mathcal{M}}^{\zeta\zeta}(\mathbf{k}, \omega) \sin^2 \theta, \quad (5.24)$$

$$\begin{aligned} S_{1\mathcal{M}}^{xx}(\mathbf{k}, \omega) = & \frac{1}{4} [S^{\xi\xi}(\mathbf{k} - \mathbf{Q}, \omega) + S^{\xi\xi}(\mathbf{k} + \mathbf{Q}, \omega)] \\ & + \frac{1}{4} \sin^2 \theta [S^{\eta\eta}(\mathbf{k} - \mathbf{Q}, \omega) + S^{\eta\eta}(\mathbf{k} + \mathbf{Q}, \omega)] \\ & + \frac{i}{2} \sin \theta [S^{\xi\eta}(\mathbf{k} + \mathbf{Q}, \omega) - S^{\xi\eta}(\mathbf{k} - \mathbf{Q}, \omega)], \end{aligned} \quad (5.25)$$

$$S_{2\mathcal{M}}^{xx}(\mathbf{k}, \omega) = \frac{1}{4} \cos^2 \theta [S_{2\mathcal{M}}^{\zeta\zeta}(\mathbf{k} - \mathbf{Q}, \omega) + S_{2\mathcal{M}}^{\zeta\zeta}(\mathbf{k} + \mathbf{Q}, \omega)], \quad (5.26)$$

where the mixed contributions are neglected (as in Ref. [79]), and $S^{xx}(\mathbf{k}, \omega) = S^{yy}(\mathbf{k}, \omega)$ by symmetry. The above analytic expressions for the dispersion and dynamical structure factor were checked explicitly against the numerical predictions of SPINW [17].

The total scattering cross-section, including the neutron orientation factor, the (spherical) magnetic form factor for Co^{2+} ions, and the finite temperature Bose factor, becomes

$$I(\mathbf{k}, \omega) = Z[n(\hbar\omega) + 1]f^2(|\mathbf{k}|) \sum_{\alpha} \left(1 - \frac{k_{\alpha}^2}{|\mathbf{k}|^2}\right) S^{\alpha\alpha}(\mathbf{k}, \omega), \quad (5.27)$$

where $\alpha = x, y, z$, Z is an overall intensity scale factor (in addition to the relative scales $Z_{\xi, \eta, \zeta}$) that was fitted to the experimental data, $f(|\mathbf{k}|)$ is the spherical magnetic form factor for Co^{2+} ions, $n(\hbar\omega) = 1/(e^{\hbar\omega/k_{\text{B}}T} - 1)$, and k_{α} is the α component of the wave vector $\mathbf{k}$. This form, convolved with the estimated instrument resolution, was used throughout this chapter to calculate the intensity.

5.3.2.2 Comparison of spin wave calculation to data

The LSWT calculation provides only limited qualitative agreement with the measured spin dynamics. It correctly predicts the presence of three modes, two in-plane gapless modes and one out-of-plane gapped mode, and that only two carry significant weight at any given wave vector. Figure 5.7 presents a comparison of the experimental INS data with the calculated LSWT dispersion relations. The parameters used in the calculation ($J_1 = 1.67$ meV, $J_2 = 0$, $J_z = 0.08$ meV and $\Delta = 0.954$) have been extracted from previous magnetisation measurements of the saturation field [89], electron spin resonance measurements of the spin gap [91], and INS measurements of the interlayer dispersion [96]. The LSWT dispersion agrees with the low-energy spin dynamics, capturing the triangular spin wave cones emanating from the ordering wave vector, the spin gap opened by the easy-plane anisotropy and the interlayer

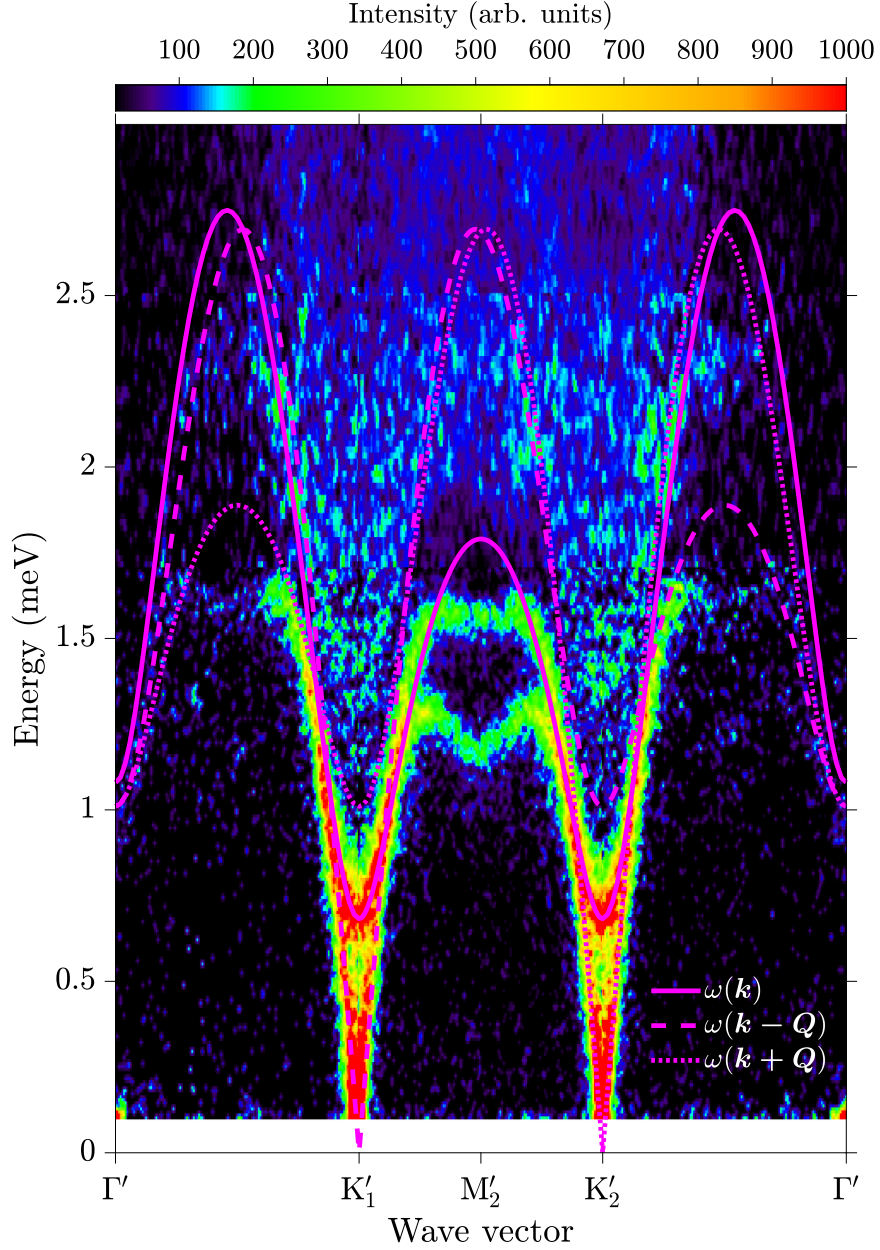


Figure 5.7: Comparison of the experimental INS data with the calculated LSWT dispersion relations, using parameters $J_1 = 1.67$ meV, $J_2 = 0$, $J_z = 0.08$ meV and $\Delta = 0.954$ extracted from previous measurements [89, 91, 96]. The plotted data and wave vector path are identical to those of Fig. 5.4, but over a smaller energy range. While the LSWT predictions match the data quite well at low energies, there are significant deviations at higher energies due to quantum fluctuations.

dispersion. However, at higher energies, the data demonstrate significant deviations from the spin wave predictions, including a downwards renormalisation of the magnon modes, mode softening at the M and K/2 points and strong continuum scattering up to at least $4\times$ the energy scale of the one-magnon excitations. These differences are evidence of strong quantum fluctuations beyond LSWT.

Previous studies of $\text{Ba}_3\text{CoSb}_2\text{O}_9$ have attempted to parametrise the magnetic excitations in the 120° ordered phase using spin wave theory. In Ref. [96], high-resolution INS measurements are compared to the LSWT calculation for NN intralayer XXZ exchanges and an interlayer Heisenberg exchange, *i.e.* Eq. (5.1) with $J_2 = 0$ and $\Delta = 1$ in the third term. This approach reproduced the magnon velocity at low energies, the spin gap and the interlayer dispersion, but overestimates considerably the maximum magnon energy. In Ref. [94], INS measurements are compared to the predictions of the LSWT+ $1/S$ calculation for NN interlayer and intralayer exchanges with an easy-plane anisotropy, *i.e.* Eq. (5.1) with $J_2 = 0$. Non-linear spin wave theory also captures well the features of the dispersion at low energies and includes some of the observed downwards renormalisation of the magnon energies, although it still overestimates the energy at the top of the dispersions. Furthermore, neither theory is able to account for the soft modes at both the M and K/2 points, which is evidence of significant magnon-magnon interactions beyond even the $1/S$ correction.

5.3.2.3 Empirical parametrisation of magnon dispersions

The inability of spin wave theory to parametrise the data motivated the development of an empirical model, based on the LSWT calculation, that captures all the features of the quantum-renormalised dynamics. This section details the proposed parametrisation of the observed one-magnon dispersion relations, which includes two major empirical modifications to the LSWT dispersion: (i) the energies are renormalised downwards by an energy-dependent scale factor, and (ii) an interaction is included

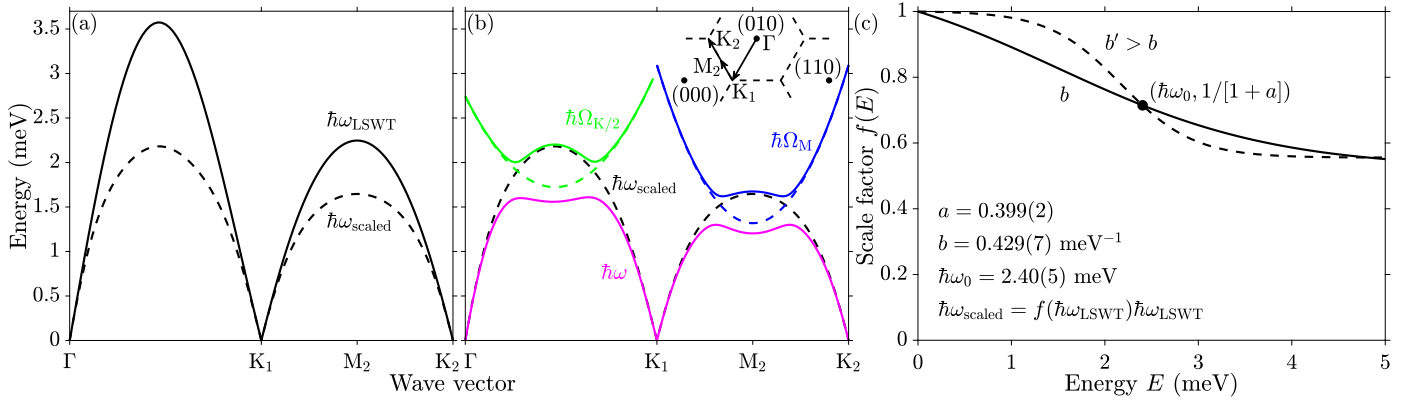


Figure 5.8: Empirical model to parametrise the observed dispersion renormalisations. (a) Downward renormalisation by an energy-dependent scale factor $f(E)$, given by Eq. (5.29). Solid line is the pure LSWT dispersion ($\hbar\omega_{\text{LSWT}}$) in Eq. (5.17), and the dashed line is the result of applying the scale factor ($\hbar\omega_{\text{scaled}}$). (b) Parametrisation of the soft modes at M and K/2 by adding an interaction with fictitious parabolic modes $\hbar\Omega_M$ (blue dashed line) and $\hbar\Omega_{K/2}$ (green dashed line). The resulting renormalised dispersion $\hbar\omega$ (solid magenta line) is the full calculation for the best-fit parameter values, with the NNN coupling, interlayer coupling and easy-plane anisotropy removed for simplicity. The top-right inset illustrates the plotted path in reciprocal space as arrows, with the Brillouin zone boundaries represented by dashed lines. (c) The functional form of the scale factor $f(E)$ applied to the LSWT dispersion, as shown in (a). The solid line is the scale factor for the best-fit parameter values given in the figure. The dashed line shows the scale factor for a larger b value, to illustrate the effect this has on its energy dependence.

with fictitious parabolic modes at the M and K/2 points to parametrise the mode softening at these positions.

Firstly, an energy-dependent scale factor $f(E)$ was applied to the LSWT dispersion $\hbar\omega_{\text{LSWT}}$ to parametrise the downwards renormalisation of the magnon energies, attributed to the effect of quantum fluctuations and interactions with the continuum states. The scaled dispersion $\hbar\omega_{\text{scaled}}$ is given by

$$\hbar\omega_{\text{scaled}} = f(\hbar\omega_{\text{LSWT}})\hbar\omega_{\text{LSWT}}, \quad (5.28)$$

where

$$f(E) = 1/\{1 + a[1 - \tanh b(\hbar\omega_0 - E)/\tanh b\hbar\omega_0]\}, \quad (5.29)$$

and a , b and ω_0 are parameters that allow the energy dependence of the renormalisation to be captured. The effect of this scaling is illustrated in Fig. 5.8(a), which plots $\hbar\omega_{\text{LSWT}}$ (black solid line) and $\hbar\omega_{\text{scaled}}$ (black dashed line) along high-symmetry directions, and the scale factor itself is plotted as a function of energy in Fig. 5.8(c). The form of $f(E)$ was chosen to leave the low-energy dispersion unchanged, as LSWT is expected to describe the data well in this region, and to have the greatest effect at the maximum of the modes, where the magnons are expected to interact most strongly with the continuum. Note that this renormalisation is consistent with the predictions of the LSWT+1/ S calculation [94]. The parameter a is a measure of the overall energy renormalisation, such that the dispersion is unchanged in the limit $a = 0$. $\hbar\omega_0$ is the energy scale at which the renormalisation becomes “significant”. In the limit $\hbar\omega_0 \gg \hbar\omega_{\text{LSWT}}$, the dispersion is therefore left unchanged. b parametrises the rate at which the scale factor drops off with energy. In the limit $b = 0$, the scale factor has no energy dependence and, as shown by the plotted curves in Fig. 5.8(c), a larger value of b results in a steeper drop-off (dashed line). The solid line is the scale factor used in Fig. 5.8(a) for the best-fit parameter values, listed in the following

section in Table 5.1.

In addition, to parametrise the mode softening at the M and K/2 points, an interaction was added between the magnon dispersion relation ω and fictitious parabolic modes Ω_i at higher energies. This interaction can be captured by a 2×2 Hamiltonian matrix

$$\mathbf{H} = \begin{pmatrix} \hbar\omega & c \\ c & \hbar\Omega_i \end{pmatrix}, \quad (5.30)$$

where the coupling is defined as $c \equiv \hbar\omega\delta_i$, so that the δ_i parameter is dimensionless.

The Hamiltonian can then be diagonalised to obtain the eigenenergies

$$\lambda_i^\pm = \frac{\hbar\omega + \hbar\Omega_i}{2} \pm \sqrt{\left(\frac{\hbar\omega - \hbar\Omega_i}{2}\right)^2 + c^2}, \quad (5.31)$$

where λ^+ is the final mixed fictitious mode and λ^- is the mixed magnon mode. Starting with the scaled dispersion $\hbar\omega = \hbar\omega_{\text{scaled}}$, this process was applied iteratively to include the effects of interactions with parabolic modes at symmetry-equivalent M and K/2 points, up to a radius of several Brillouin zones farther out, to ensure a smoothly-varying, three-fold periodic dispersion. The effect of adding an interaction with parabolic modes centred at the M and K/2 points is illustrated in Fig. 5.8(b): the scaled dispersion $\hbar\omega_{\text{scaled}}$ (black dashed line) interacts with the parabolic modes $\hbar\Omega_{\text{K/2}}$ (green dashed line) and $\hbar\Omega_{\text{M}}$ (blue dashed line), giving the mixed states represented as solid lines. The magnon modes are repelled by the parabolic modes, mimicking the physical interaction with the continuum states and softening the modes at the M and K/2 points, which allows the observed roton-like minima to be parametrised.

The fictitious modes were chosen to have the parabolic form

$$\hbar\Omega_i = \alpha_i + \beta_i \cos \pi l + \gamma_i [(q_x - q_{ix})^2 + \kappa_i (q_y - q_{iy})^2], \quad (5.32)$$

where $i = \text{M and K/2}$ indicate the location of the paraboloid in reciprocal space, (q_x, q_y) are the Cartesian coordinates of the in-plane wave vector in the first Brillouin

zone ($\text{\AA}^{-1}$) and (q_{ix}, q_{iy}) is the centre of the paraboloid in the same coordinates. α_i is the energy at the minimum of the paraboloids, which is approximately equal to the energy of the magnons in the corresponding soft mode. The β_i term allows the parabolic modes to disperse along $\mathbf{c}^*$, such that $\beta_i = 0$ corresponds to soft modes with no interlayer dispersion. The γ_i parameter allows control over the curvature of the paraboloids, corresponding physically to the dispersion of the magnons in the hk plane in the vicinity of the minima: the larger the value of γ_i , the more strongly the magnons disperse. In the case of $i = M$, the x component of the wave vector is along the Brillouin zone boundary and the y component is perpendicular to the boundary, *i.e.* along the lines connecting the Brillouin zone centres in the hk plane. By allowing κ_M to vary, it is possible to parametrise the anisotropic “rugby ball” shape of the minimum, visible around the M points in Fig. 5.5(g). For $i = K/2$, an isotropic description is sufficient and so $\kappa_{K/2} = 1$ was chosen. The M paraboloid is centred at the M point, but the K/2 paraboloid is centred at $(h, k) = (\epsilon, \epsilon)$, where $\epsilon = 0.15606 < h_K/2$. Choosing a paraboloid centred at the K/2 point produces a highly asymmetric minimum in the mixed state, as the one-magnon dispersion is not symmetric about K/2. The ϵ value chosen ensures the minimum in the calculated dispersion is symmetric along the $\Gamma \rightarrow K$ direction, as observed experimentally (see Fig. 5.4).

If the scale factor in Eq. (5.29) were large enough, the maxima in the dispersion could be reduced so much in energy that they become local minima. To ensure that the observed roton-like minima are parametrised solely by the fictitious parabolic modes, a was therefore constrained to always be below the maximum value that leaves the concavity of the LSWT dispersion unchanged, given by

$$a_{\max} = \tanh b\hbar\omega_0 / \{b\hbar\omega_{\max} \operatorname{sech}^2[b\hbar(\omega_0 - \omega_{\max})] - \tanh b\hbar\omega_0 + \tanh[b\hbar(\omega_0 - \omega_{\max})]\}, \quad (5.33)$$

Parameter	Best-fit value	
J_1	2.25(5)	meV
J_2	0.051(9)	meV
J_z	0.073(2)	meV
Δ	0.970(2)	
Z_ξ	1.68(3)	
Z_η	1	
Z_ζ	1.41	
ΔS	0.187	
$\hbar\omega_0$	2.40(5)	meV
a	0.399(2)	
b	0.429(7)	meV ⁻¹
α_M	1.301(3)	meV
β_M	0.017(2)	meV
γ_M	11.9(8)	Å ² meV
δ_M	0.1	
κ_M	1.4(2)	
$\alpha_{K/2}$	1.744(4)	meV
$\beta_{K/2}$	-0.021(4)	meV
$\gamma_{K/2}$	8.4(7)	Å ² meV
$\delta_{K/2}$	0.1	
$\kappa_{K/2}$	1	
ϵ	0.15606	

Table 5.1: Best-fit parameter values and errors (standard deviation σ) for the empirical parametrisation of the one-magnon dispersion. The parameters with errors listed were fitted to selected scans through the INS data using HORACE [35], and the ones without errors were fixed at the given value. The table omits the overall intensity scale, the parametrisation of the non-magnetic background and the instrument resolution, as these vary between the simulations and are discussed elsewhere.

where $\hbar\omega_{\max} \simeq 3.5$ meV is the maximum energy of the “bare” LSWT dispersion for the best-fit parameter values. As demonstrated in Fig. 5.8, the roton-like minima are parametrised purely by the parabolic modes when the fitting is performed with this constraint.

5.3.2.4 Best-fit empirical parametrisation of data

The best-fit parameters were found by fitting this empirical model of the dispersion to selected scans through the experimental data, using the dynamical structure factor

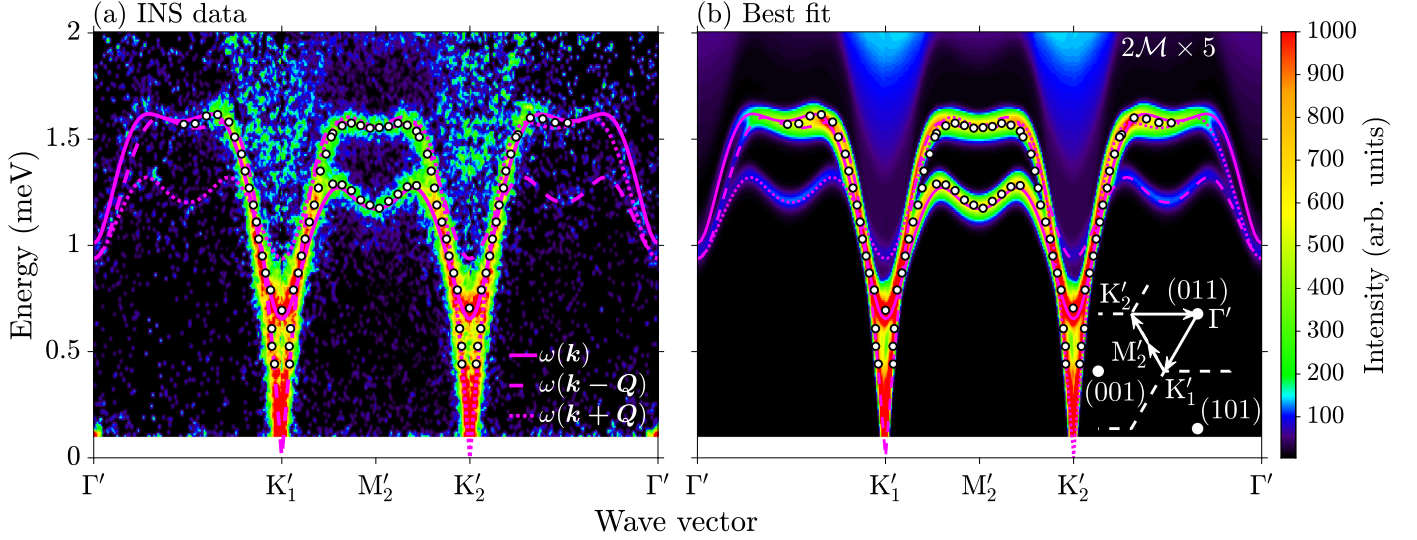


Figure 5.9: (a),(b) Comparison of the INS data along high-symmetry directions in reciprocal space and the corresponding one- and two-magnon calculation using the best-fit empirical parametrisation, respectively. The colour map shows the intensity in arbitrary units. The calculated two-magnon intensities have been scaled by a factor of 5 for clarity. The wave vector path is $\Gamma' (0, 1, 1) \rightarrow K'_1 (\frac{1}{3}, \frac{1}{3}, 1) \rightarrow M'_2 (0, \frac{1}{2}, 1) \rightarrow K'_2 (-\frac{1}{3}, \frac{2}{3}, 1) \rightarrow \Gamma'$, illustrated as arrows in the white bottom-right inset with the Brillouin zone boundaries represented by dashed lines. The integration width along both transverse directions is $\pm 0.05 \text{ \AA}^{-1}$. The data were collected at $T = 1.7 \text{ K}$ for incident energy $E_i = 3.53 \text{ meV}$. The quasielastic scattering below 0.1 meV has been omitted. The experimental dispersion points (filled white circles with error bars smaller than the symbols), found by fitting to constant energy and constant wave vector scans through the sharp modes, are overplotted to aid comparison. The calculated $\omega(\mathbf{k})$, $\omega(\mathbf{k} - \mathbf{Q})$ and $\omega(\mathbf{k} + \mathbf{Q})$ dispersions are plotted as solid, dashed and dotted magenta lines, respectively.

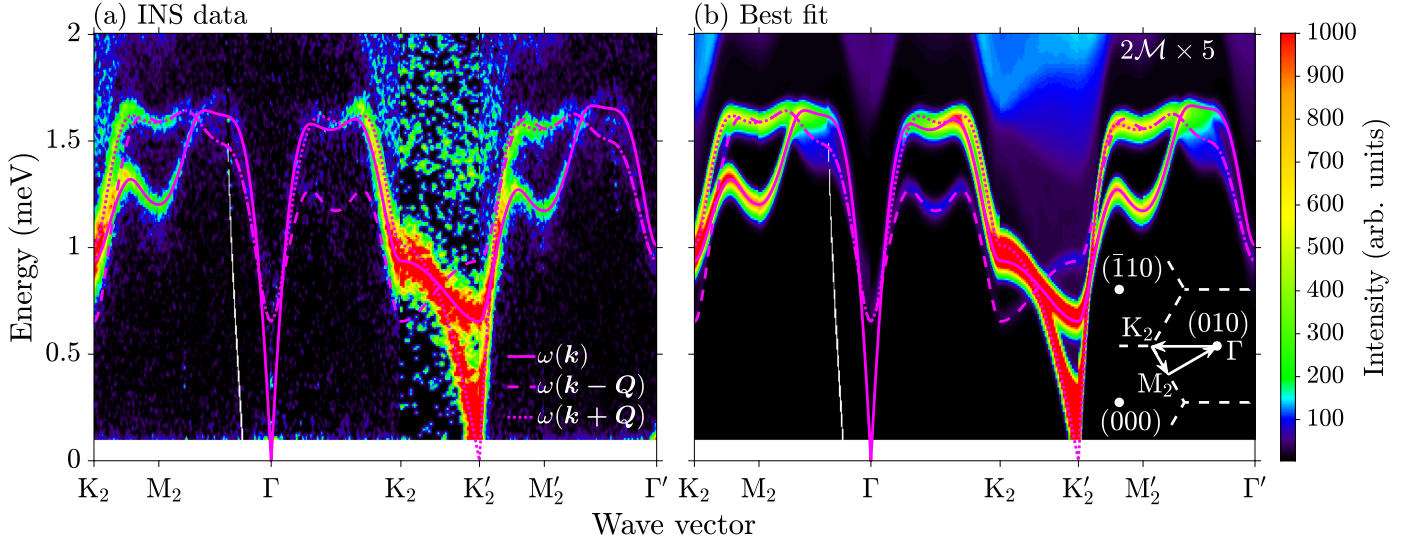


Figure 5.10: Same as Fig. 5.9 but for a different wave vector path that also illustrates the interlayer dispersion: $K_2 (-\frac{1}{3}, \frac{2}{3}, 0) \rightarrow M_2 (0, \frac{1}{2}, 0) \rightarrow \Gamma (0, 1, 0) \rightarrow K_2 \rightarrow K'_2 (-\frac{1}{3}, \frac{2}{3}, 1) \rightarrow M'_2 (0, \frac{1}{2}, 1) \rightarrow \Gamma' (0, 1, 1)$. The integration width in the hk plane is $\pm 0.05 \text{ \AA}^{-1}$ for panels 1–3 and 6, and is $\pm 0.02 \text{ \AA}^{-1}$ for panels 4 and 5. The integration width along l is $\pm 0.1 \text{ \AA}^{-1}$ for panels 1, 3 and 5, and is $\pm 0.3 \text{ \AA}^{-1}$ for panels 2 and 6.

derived from LSWT. As the scattering intensity is not expected to be captured exactly by LSWT, the relative intensity Z_ξ of the in-plane modes was allowed to vary in the fit to improve the agreement with the data. As mentioned previously, Z_ζ was fixed using the neutron sum rules and a spin reduction $\Delta S = 0.187$, which was determined using Eq. (2.39) and is comparable to previous calculations [78]. Throughout, the best-fit intensity calculation includes the magnetic form factor for Co^{2+} ions, the neutron orientation factor, the finite temperature Bose factor, and a constant broadening in energy, found by fitting to the instrument resolution at the elastic line. The parametrisation of the one-magnon dispersion also allowed the two-magnon scattering intensity to be numerically simulated, which will be discussed in Sec. 5.3.2.5.

The best-fit parameter values are listed in Table 5.1. The J_1 , J_2 , J_z and Δ values given here have no physical significance and deviate significantly from previous estimates [94, 96], due to the empirical renormalisations applied. The best-fit parameters should therefore be considered simply as an empirical parametrisation of the experi-

mental data. For these parameters, $f(E_{\text{max}}) \simeq 0.6$ and so the top of the dispersion is renormalised downwards by $\simeq 40\%$. The parameter α_i is the energy at the minimum of the fictitious modes; the fitted values $\alpha_{\text{M}} = 1.301(3)$ meV and $\alpha_{\text{K}/2} = 1.744(4)$ meV are therefore approximately equal to the energies of the magnons at the corresponding roton-like minima. As expected for this quasi-2D system, the interlayer dispersion of the soft modes is very small: $|\beta_i|/\alpha_i \simeq 0.01$ for both $i = \text{M}$ and $\text{K}/2$.

Figures 5.9 and 5.10 compare the INS data along high-symmetry directions with the best-fit intensity calculation. The data were collected at $T = 1.7$ K for incident energy $E_i = 3.53$ meV. The width of the observed sharp one-magnon modes is well accounted for by the fitted instrument resolution, suggesting that the magnons are long-lived with no evidence of lifetime broadening. The fitted dispersions (magenta lines) are in excellent agreement with the experimental data, passing through the measured one-magnon modes throughout the Brillouin zone. This agreement is best illustrated by the fitted dispersion points, plotted as filled white circles in Fig. 5.9. The empirical parametrisation is able to capture all the features of the one-magnon dispersions, including the gapless spin wave cone centred at the ordering wave vector K' , the small interlayer coupling (see the $\text{K}_2 \rightarrow \text{K}'_2$ panel in Fig. 5.10), the spin gap opened at K' by the easy-plane anisotropy, the strong downwards renormalisation of the magnon energies compared to LSWT, and the roton-like minima at the M and $\text{K}/2$ points.

However, the empirical parametrisation clearly overestimates the intensity at the top of the one-magnon modes [see Figs. 5.5(a)–(h), 5.9 and 5.10]. (Unless otherwise specified, the overall scale of the calculated intensities was chosen throughout to match the measured low-energy signal.) It is proposed that this discrepancy between the data and the LSWT structure factor is evidence of a transfer of spectral weight from the one-magnon modes to the multi-magnon continuum scattering. Magnon-magnon

interactions are neglected in the LSWT approach, but are expected to be significant in a spin- $\frac{1}{2}$ TLHAF, being largely responsible for the downwards renormalisation of the magnon energies and mode softening observed in the data. It is reasonable to expect that the interactions between the one-magnon modes and the continuum of states would be strongest where they meet, at the top of the dispersions. Any transfer of spectral weight between the two contributions would therefore be most noticeable in this region, which would explain why LSWT overestimates the intensity at high energies. More evidence will be provided to support this claim in the following section, where the numerical simulations of the two-magnon scattering intensity are discussed.

5.3.2.5 Simulated two-magnon continuum

This section presents numerical simulations of the two-magnon contribution to the scattering intensity. With a parametrisation of the one-magnon dispersion relations, kinematic constraints determine the possible energies of magnon pairs, thereby giving the energy range of the two-magnon continuum as a function of wave vector. The total scattering intensity for the two-magnon continuum has also been simulated, using the Monte Carlo method to perform the sum in Eq. (5.21).

First consider the energy range of the simulated two-magnon scattering in the rotating reference frame, in which the spins are ferromagnetically aligned. In this frame, only the main mode $\omega(\mathbf{k})$ is present and the energy of a magnon pair is

$$\hbar\omega_{2\mathcal{M}}(\mathbf{k}) = \hbar\omega(\mathbf{k}_1) + \hbar\omega(\mathbf{k}_2), \quad \mathbf{k} = \mathbf{k}_1 + \mathbf{k}_2. \quad (5.34)$$

In noncollinear magnets, one→two-magnon decay processes are expected when the kinematic conditions are satisfied, *i.e.* at wave vectors where $\omega_{2\mathcal{M}}(\mathbf{k}) \leq \omega(\mathbf{k})$ in the rotating frame. As the presence or absence of such decays cannot depend on the reference frame, calculations in the rotating frame provide a convenient way of determining the existence of one→two-magnon decay processes. Such decays would

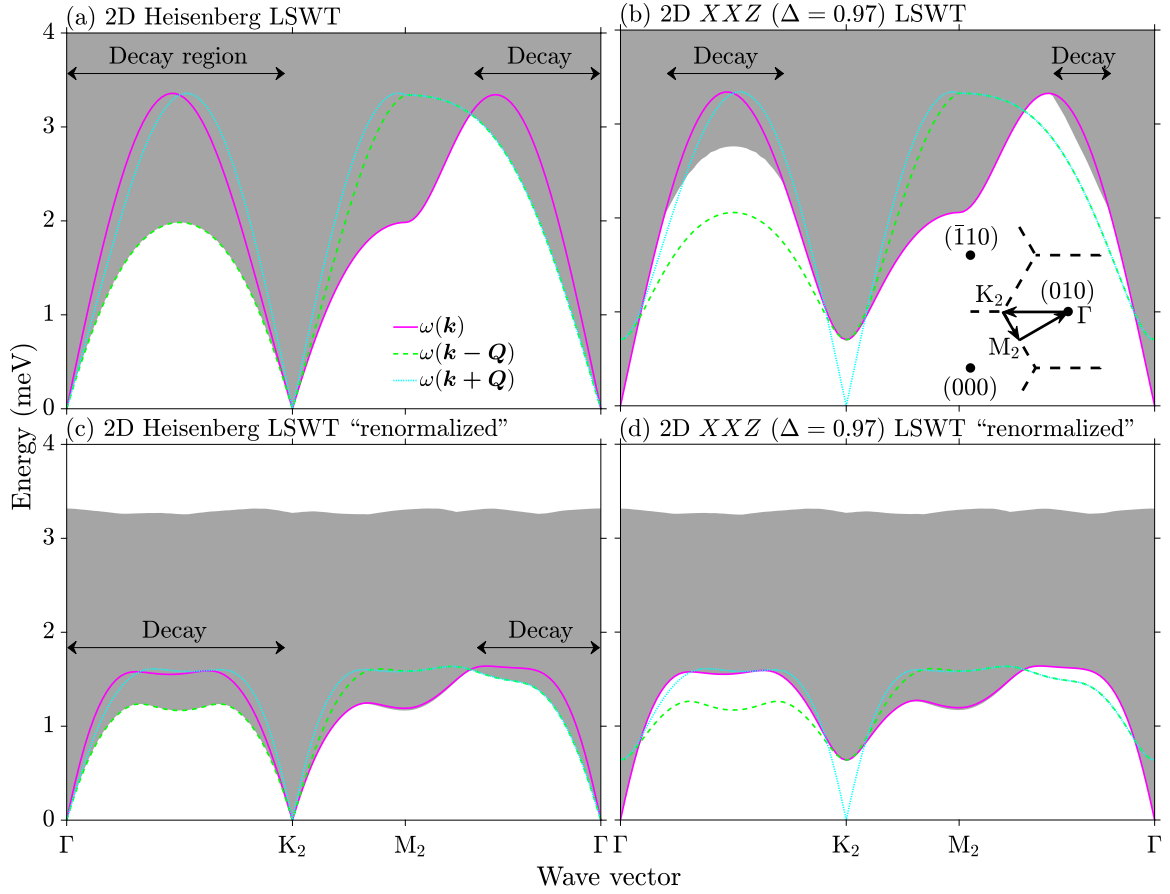


Figure 5.11: Comparison of the calculated two-magnon phase space (shaded area), and the resulting one→two-magnon decay regions, along high-symmetry directions for different models of the one-magnon dispersion. The reciprocal space path is $\Gamma(0, 1, 0) \rightarrow K_2(-\frac{1}{3}, \frac{2}{3}, 0) \rightarrow M_2(0, \frac{1}{2}, 0) \rightarrow \Gamma$, illustrated as arrows in the bottom-right inset in (b) with the Brillouin zone boundaries represented by dashed lines. These calculations were performed in the rotating frame of reference, in which the spins are ferromagnetically aligned, for simplicity. Note that decay is therefore kinematically allowed when the $\omega(\mathbf{k})$ dispersion (solid magenta line) enters the two-magnon continuum. The $\omega(\mathbf{k} - \mathbf{Q})$ and $\omega(\mathbf{k} + \mathbf{Q})$ modes (dashed green and dotted cyan lines, respectively), which are present in the laboratory frame, are included purely for reference. Unless specified otherwise, the parameters used are the best-fit values found by comparison with the experimental data. (a) LSWT calculation for 2D NN and NNN Heisenberg interactions [$\Delta = 1$ and $J_z = 0$ in Eq. (5.1)], showing extended regions of magnon decay. (b) LSWT calculation for 2D NN and NNN XXZ interactions ($\Delta = 0.97$ and $J_z = 0$), showing significantly reduced decay regions due to the gap opening at the K points. (c) Empirical parametrisation for 2D NN and NNN Heisenberg interactions ($\Delta = 1$ and $J_z = 0$), with similar decay regions to the LSWT case in (a). (d) Empirical parametrisation for 2D NN and NNN XXZ interactions ($\Delta = 0.97$ and $J_z = 0$), with no regions where one→two-magnon decay is kinematically allowed. As the addition of interlayer coupling has very little effect, the best-fit empirical parametrisation therefore predicts sharp magnon modes everywhere, as observed experimentally.

result in a broadening in energy of the one-magnon modes, due to the finite lifetime of the magnons, as discussed earlier in Sec. 3.2.2.

Figure 5.11 shows the extent of the two-magnon continuum (grey shaded areas) along high-symmetry directions in the rotating frame for different models of the dispersion $\omega(\mathbf{k})$ (solid magenta lines). The $\omega(\mathbf{k} - \mathbf{Q})$ and $\omega(\mathbf{k} + \mathbf{Q})$ modes are also plotted for reference (dashed green and dotted cyan lines, respectively), although they are not present in the rotating frame. All four panels show calculations for triangular-lattice antiferromagnets with NN and NNN intralayer exchange couplings and no interlayer coupling, *i.e.* the 2D case. In the LSWT calculation for Heisenberg exchanges in Fig. 5.11(a), there are extended regions where the two-magnon continuum drops below $\hbar\omega(\mathbf{k})$ and so one→two-magnon decay is possible (as annotated in the figure). The minimum-energy magnon pair at any given wave vector $\mathbf{k}$ corresponds to one of the two magnons being created at either the Brillouin zone centre Γ ($\mathbf{k}_1 = \mathbf{0}$) or the ordering wave vector $\mathbf{K}'$ ($\mathbf{k}_1 = \pm\mathbf{Q}$), where the dispersion is gapless for Heisenberg exchanges. By momentum conservation, the other magnon in the pair must then have wave vector $\mathbf{k}_2 = \mathbf{k}$ or $\mathbf{k} \mp \mathbf{Q}$, respectively. The threshold energy of the two-magnon continuum is therefore either $\hbar\omega(\mathbf{k})$, $\hbar\omega(\mathbf{k} - \mathbf{Q})$ or $\hbar\omega(\mathbf{k} + \mathbf{Q})$, whichever is smaller. If an easy-plane anisotropy is added, as in Fig. 5.11(b), the dispersion becomes gapped at the ordering wave vector, increasing the minimum energy cost of creating two magnons and significantly reducing the regions of one→two-magnon decay. A comprehensive discussion of the decay regions predicted by LSWT calculations in the rotating frame is given in Ref. [78].

Figures 5.11(c) and (d) show the simulated extent of the two-magnon continuum for the empirical parametrisation of the dispersion, using the best-fit parameter values in the absence of interlayer coupling. For Heisenberg exchanges in Fig. 5.11(c), the decay regions have a similar extent to those in the LSWT calculation in Fig. 5.11(a), de-

spite a significant reduction in the overall energy scales of the one-magnon mode $\omega(\mathbf{k})$ and the resulting two-magnon continuum. However, when an easy-plane anisotropy is added in Fig. 5.11(d), the two-magnon threshold coincides with $\omega(\mathbf{k})$ and so there are no regions of one→two-magnon decay. This contrasts with the LSWT calculation in Fig. 5.11(b), where parts of the dispersion still enter the continuum and decay is possible. One→two-magnon decay processes are therefore kinematically forbidden by the combined effects of the empirical dispersion renormalisation and the easy-plane anisotropy, which push the simulated two-magnon continuum completely above $\omega(\mathbf{k})$. This prediction is unaffected by the interlayer coupling, which is very small in the present system, and is consistent with the previously-discussed observation of sharp magnons throughout the Brillouin zone. This observation seems to support previous DMRG calculations for a spin- $\frac{1}{2}$ TLHAF, which suggest that quasiparticle decay is prevented by strong interactions with the continuum of states [98].

The full one- and two-magnon dynamical structure factor for the best-fit parameter values is compared to the experimental data in Figs. 5.12, 5.13 and 5.14. The data were collected at $T = 1.7$ K, with incident energy $E_i = 7.01$ meV in Figs. 5.12 and 5.13, and a combination of $E_i = 3.53$ meV (circles and squares) and 7.01 meV (diamonds) in Fig. 5.14. The overall scale of the simulated intensity was chosen to match the measured intensity of the main mode $\omega(\mathbf{k})$ at M $(\frac{3}{2}, -\frac{1}{2}, 0)$ in Figs. 5.12 and 5.13, and at K₂' in Fig. 5.14. The simulated two-magnon contribution was scaled to have the correct total intensity relative to the in-plane modes, as specified by the sum rules in Eq. (3.41). In the colour plots in Figs. 5.9(b), 5.10(b) and 5.12(b), the two-magnon contribution is additionally scaled by a factor of 5 for clarity. The structure of the simulated two-magnon scattering in Fig. 5.12(b) agrees qualitatively with the experimental data in Fig. 5.12(a) at low energies: most of the intensity is in cones centred at the K points, with the continuum apparently well-separated from

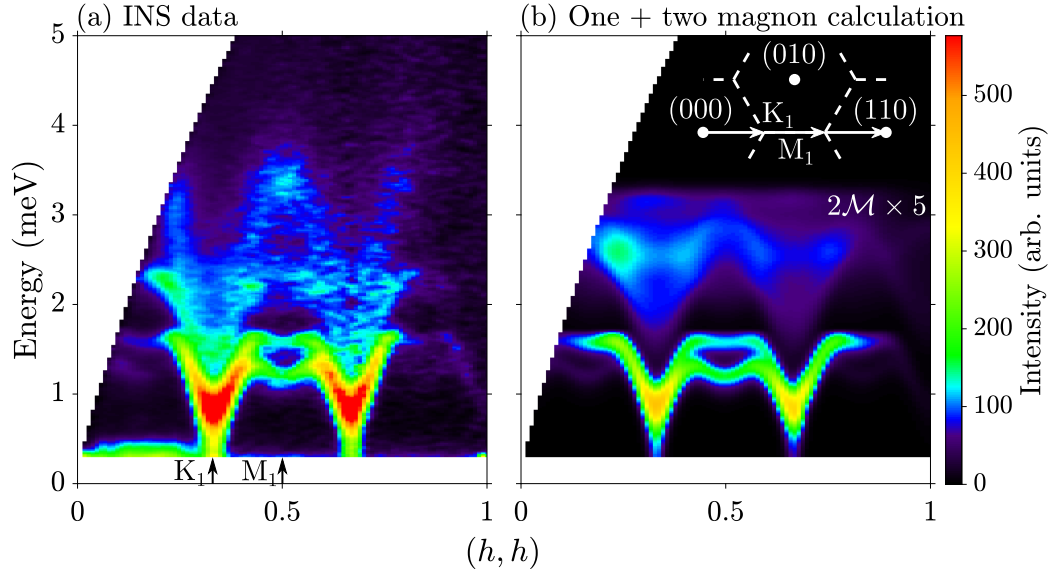


Figure 5.12: High-energy INS data and one- and two-magnon simulations, showing the full range of measured continuum scattering. (a),(b) Colour maps showing the measured intensity and best-fit calculation in arbitrary units as a function of energy and wave vector along $(h \mp 0.05, h \pm 0.05, \pm 2.39)$, where the $\pm$ sign indicates the integration width. The wave vector path is illustrated by the arrows in the white top-right inset in (b), with the Brillouin zone boundaries represented by dashed lines. The data were collected at $T = 1.7$ K with incident energy $E_i = 7.01$ meV. The simulated intensity in (b) was scaled to match the experimental data at $\simeq 1.2$ meV and the simulated two-magnon intensity has been further scaled by a factor of 5 for clarity. The K_1 $(\frac{1}{3}, \frac{1}{3}, 0)$ and M_1 $(\frac{1}{2}, \frac{1}{2}, 0)$ points are labelled in (a) for reference.

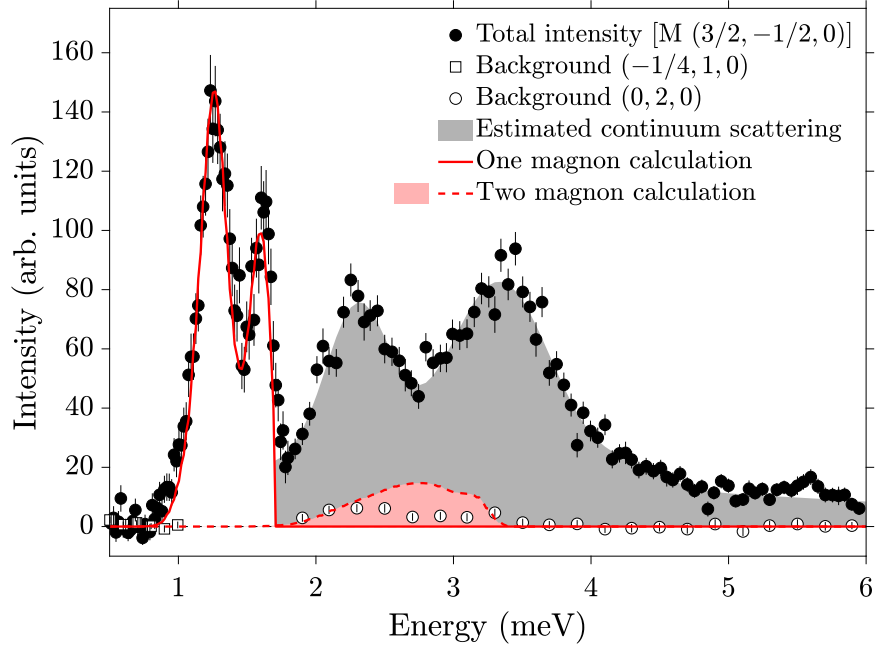


Figure 5.13: Scan along energy through the INS data (solid black circles) and best-fit empirical parametrization (red solid line) at $M (\frac{3}{2}, -\frac{1}{2}, 0)$, including the numerical simulation of the two-magnon scattering intensity (red dashed line and shading). The integration widths are $\zeta = [0.15, 0.35]$ along $(\zeta, 0, 0)$, $\xi = [1.4, 1.6]$ along $(-\xi/2, \xi, 0)$, and $\eta = [-0.5, 0.5]$ along $(0, 0, \eta)$. The simulated intensities were scaled to match the experimental data at $\simeq 1.2$ meV. The estimated continuum contribution to the data is also shown (grey shading). The scans at $(-\frac{1}{4}, 1, 0)$ and $(0, 2, 0)$ (open symbols) demonstrate the quality of the non-magnetic background subtraction applied to all the plotted scans.

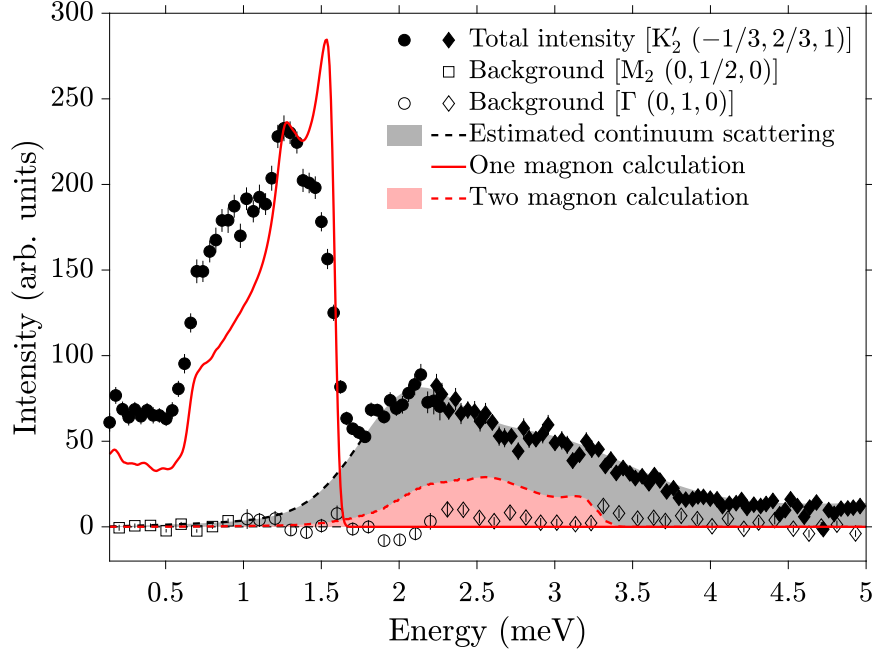


Figure 5.14: Scan along energy through the INS data (solid black points) and best-fit empirical parametrisation (red solid line) at $K'_2 (-\frac{1}{3}, \frac{2}{3}, 1)$, including the numerical simulation of the two-magnon scattering intensity (red dashed line and shading). The scan was performed by integrating over a cylindrical region in reciprocal space, which extends over the full range of l with a circular cross-section in the hk plane, illustrated by the grey circle in the bottom-left inset of Fig. 5.4. The simulated intensity was chosen here to match the experimental data at $\simeq 1.2$ meV. The estimated continuum contribution to the data is also plotted (black dashed line and grey shading), where the contribution has been extrapolated below 1.7 meV by scaling the simulated two-magnon intensity. The non-magnetic background has been subtracted from all the plotted data, and scans through the $M_2 (0, \frac{1}{2}, 0)$ and $\Gamma (0, 1, 0)$ points (open symbols) demonstrate the quality of this background subtraction. The data were collected at $T = 1.7$ K, and the circles and squares (diamonds) correspond to an incident energy $E_i = 3.53$ meV (7.01 meV).

the one-magnon signal elsewhere, and there are bridges of intensity between these cones at higher energies. However, the simulation seems to overestimate the energy scale of the low-energy continuum scattering and there is structure in the measured signal up to at least $4\times$ the maximum one-magnon energy [see Fig. 5.13], including a second set of cones centred at the K points that become apparent above $\simeq 2.4$ meV. This indicates the presence of significant higher-order scattering processes that are not captured by the two-magnon simulation. By inspecting Figs. 5.13 and 5.14, it is clear that the continuum contributions observed in the data (black dashed line and grey shaded areas) are much greater than the simulated intensity of the two-magnon scattering (red dashed lines and red shaded areas). It is proposed here that this discrepancy is evidence of a transfer of spectral weight from the one-magnon modes to the continuum scattering in the data, which would also account for the lower-than-expected intensity observed at the top of the dispersion, as discussed previously in Sec. 5.3.2.2.

The apparent separation of the one-magnon modes and the continuum scattering is observed in both the experimental data (see Fig. 5.4) and the simulation (see Fig. 5.12). It is attributed to a sharp increase in the two-magnon density of states $D(\mathbf{k}, \omega)$, given by Eq. (5.22) and shown as a contour plot along high-symmetry directions in Fig. 5.15. The red dots plotted represent 10^4 simulated “ Γ -type” two-magnon scattering events, where one of the magnons is created close to the Brillouin zone centre Γ , and the blue dots represent 10^4 “ K' -type” events, where one magnon is created close to the ordering wave vector K' , as illustrated by the red and blue dots in the bottom-right inset. Due to the easy-plane anisotropy and the resulting gap at the K' point, there is a difference in the energy of these two families of events. So while it is possible to create a Γ -type magnon pair close to the one-magnon modes, significantly more energy must be supplied to create a K' -type magnon pair. The sharp increase

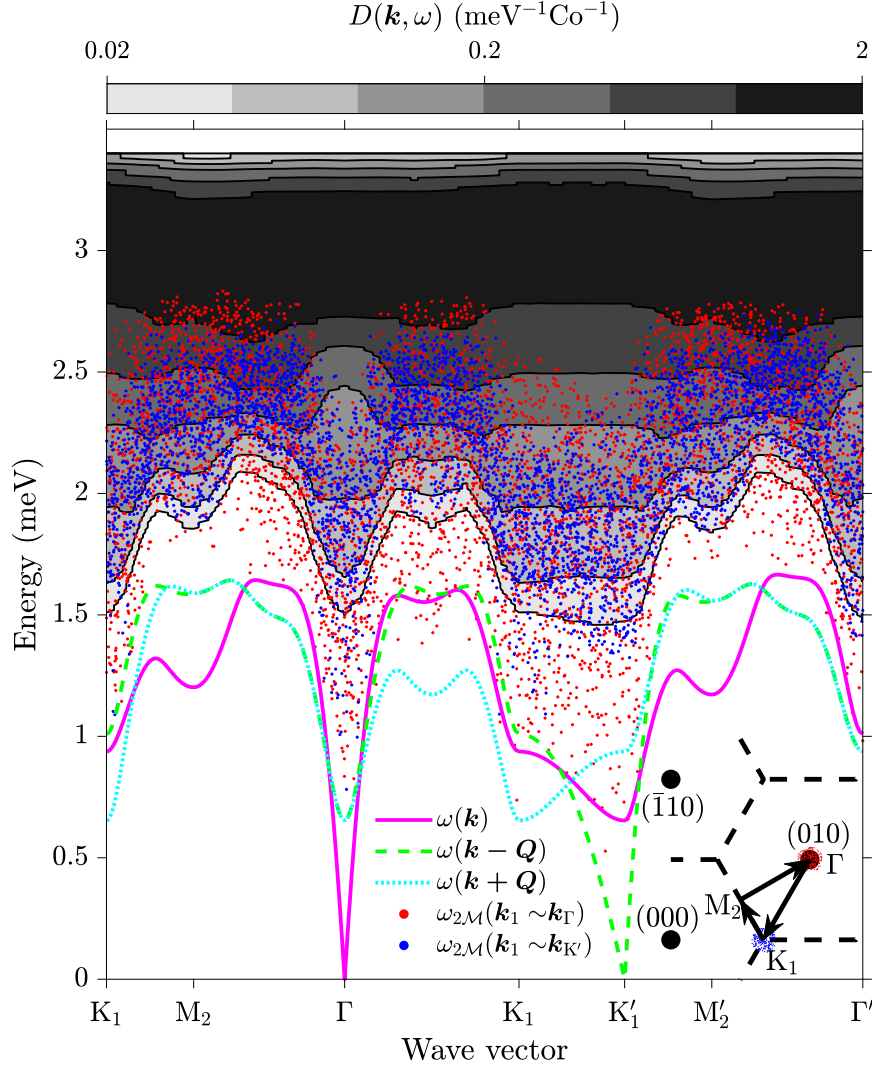


Figure 5.15: Simulated contributions to the two-magnon density of states as a function of energy and wave vector along high-symmetry directions in reciprocal space. The wave vector path is $K_1 (\frac{1}{3}, \frac{1}{3}, 0) \rightarrow M_2 (0, \frac{1}{2}, 0) \rightarrow \Gamma (0, 1, 0) \rightarrow K_1 \rightarrow K'_1 (\frac{1}{3}, \frac{1}{3}, 1) \rightarrow M'_2 (0, \frac{1}{2}, 1) \rightarrow \Gamma' (0, 1, 1)$, illustrated as arrows in the bottom-right inset with Brillouin zone boundaries represented by dashed lines. The contour plot gives the total density of states on a logarithmic scale, calculated using the best-fit empirical parametrisation of the dispersion. The red dots represent two-magnon scattering events where one of the magnons is close to the Γ point and the blue dots represent two-magnon events where one is close to the K'_1 point, as shown by the coloured dots in the inset. The calculated $\omega(\mathbf{k})$, $\omega(\mathbf{k} - \mathbf{Q})$ and $\omega(\mathbf{k} + \mathbf{Q})$ dispersions are plotted as solid magenta, dashed green and dotted cyan lines, respectively. Although there are some two-magnon events below the one-magnon modes, decay to these magnon pairs is not possible as the modes above them have a different polarisation. An increase in the two-magnon density of states is associated with the energy threshold of two-magnon events where one of the magnons is created close to K'_1 .

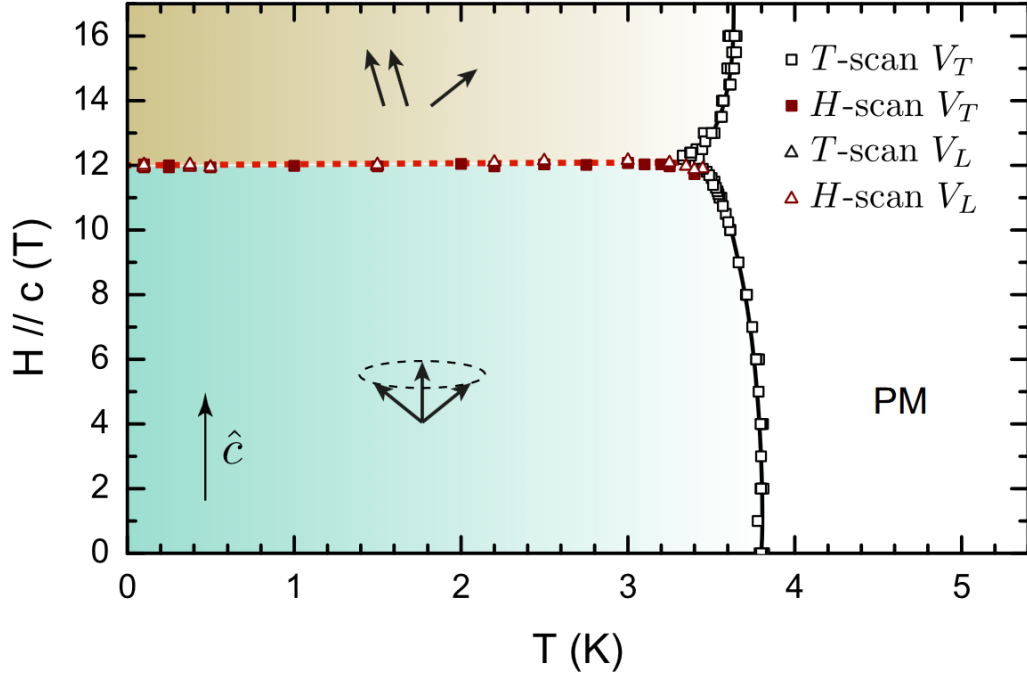


Figure 5.16: Magnetic phase diagram of $\text{Ba}_3\text{CoSb}_2\text{O}_9$ for $\mathbf{H} \parallel \mathbf{c}$. The plotted points represent previous ultrasound velocity measurements with varying temperature (black points) and field (red points). The cone phase and V-type phase are separated at 12 T at low temperatures by a first-order phase transition (red dashed line). At ~ 3.8 K, these phases undergo a second-order phase transition (black solid line) to the paramagnetic phase. Reproduced with permission from Ref. [93].

in the density of states coincides with the energy threshold for the creation of K' -type magnon pairs, suggesting that this increase at higher energies is driven by the greater availability of channels for magnon pair creation. This would explain why the observed continuum is well separated from the sharp modes over extended regions of reciprocal space, despite the theoretical prediction in Fig. 5.11(d) that the onset of the two-magnon continuum is directly above the dispersions.

5.4 Spin dynamics in cone phase in transverse applied magnetic field

Here INS measurements are presented of $\text{Ba}_3\text{CoSb}_2\text{O}_9$ in a finite magnetic field up to 9 T applied along $\mathbf{c}$, normal to the triangular layers. This experiment therefore

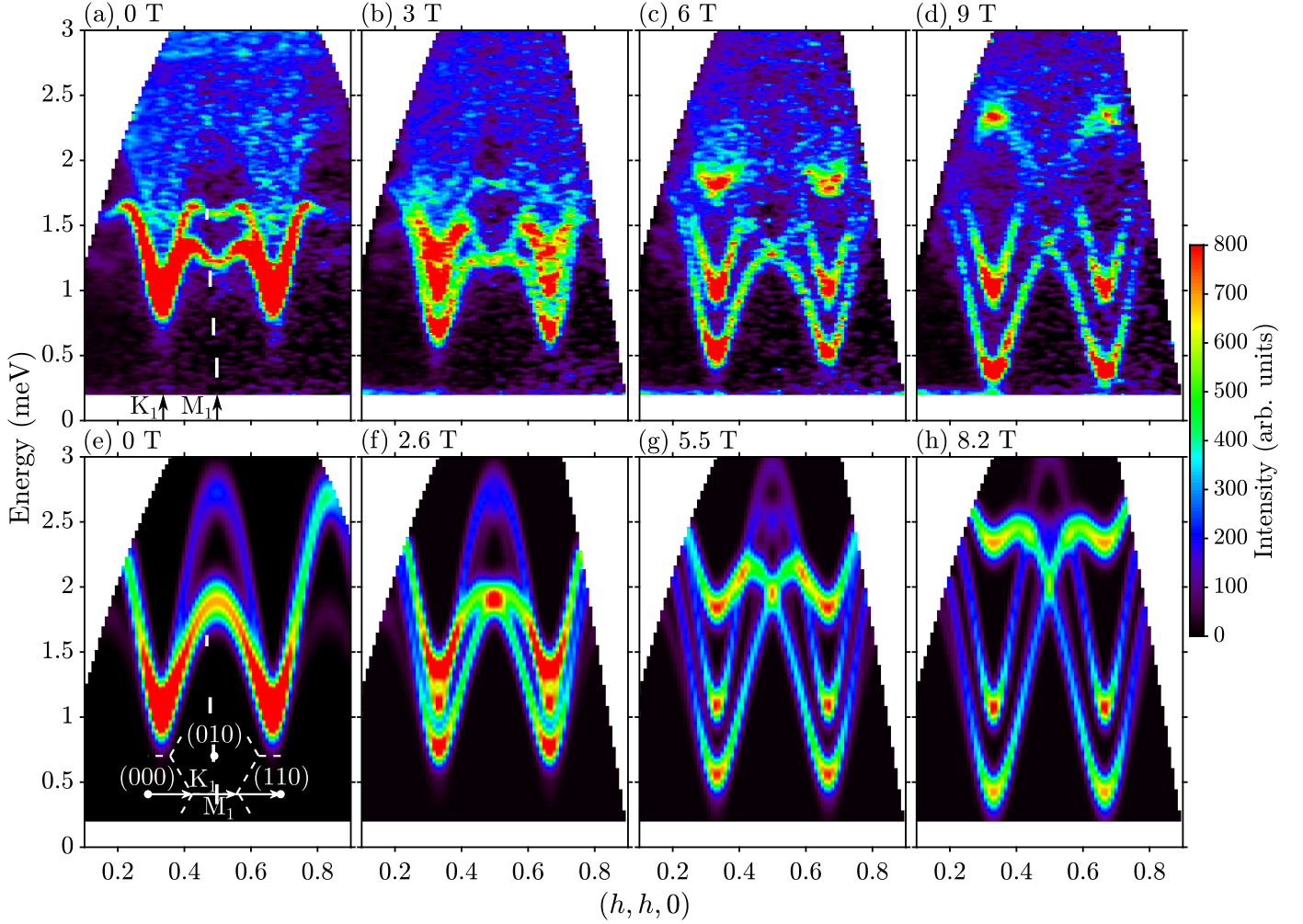


Figure 5.17: Comparison of the INS data collected in zero applied magnetic field and finite field, and the corresponding LSWT calculations. The colour map gives the intensity in arbitrary units as a function of energy and wave vector along the $(h \mp 0.05, h \pm 0.05, \pm 0.3)$ direction, where the $\pm$ values indicate the integration ranges. The wave vector path is shown as arrows in the white bottom-center inset in (e), with the Brillouin zone boundaries represented by dashed lines. The K_1 and M_1 points are also labelled in (a) for reference. (a) Data collected in zero applied magnetic field with incident energy $E_i = 3.53$ meV and $T = 1.7$ K. (b)–(d) Data collected in applied magnetic fields $B = 3, 6$ and 9 T, respectively, with $E_i = 3.81$ meV and $T = 0.1$ K. (e)–(h) LSWT calculations of the data in (a)–(d), respectively, using parameters extracted from previous measurements [89, 91, 96] and fitting the intensity scale and magnetic field to energy scans through the K_1 point. The calculations assume equal intensity contributions from domains 1 and 2, as expected in the absence of D-M interactions.

probed the “cone” phase, in which the spins retain their spiral order in the ab plane and become canted along the field direction. Previous magnetisation [91], nuclear magnetic resonance [92] and ultrasound velocity [93] measurements in this configuration have indicated that this phase persists up to 12 T. Figure 5.16 shows the magnetic phase diagram for $\text{Ba}_3\text{CoSb}_2\text{O}_9$ in an applied field $\mathbf{H} \parallel \mathbf{c}$, obtained from ultrasound velocity measurements [93]. The measurements presented here were performed in the cone phase (bottom left). Note that there is a first-order phase transition (red dashed line) to the V-type phase at 12 T and a second-order phase transition (black solid line) to the paramagnetic phase at ~ 3.8 K. While the magnon dispersion relations for the opposite chirality domains are degenerate in zero applied magnetic field, they are expected to split in the cone phase. These measurements therefore provided information on the domains present in $\text{Ba}_3\text{CoSb}_2\text{O}_9$.

Figure 5.17(a) shows the INS data collected in zero applied magnetic field at base temperature $T = 1.7$ K and with incident neutron energy $E_i = 3.53$ meV, and Figs. 5.17(b)–(d) show the data collected in magnetic fields $B = 3, 6$ and 9 T, respectively, at temperature $T = 0.1$ K and with incident energy $E_i = 3.81$ meV. Upon applying a magnetic field, the two intense sharp modes appear to split into three: one that increases in energy with field, one that decreases in energy and one that is unaffected. At $B = 9$ T in Fig. 5.17(d), the lowest energy mode is almost touching the quasielastic line and the highest appears to have changed concavity.

The experimental data were compared to the LSWT calculation of the dispersion and dynamical structure factor in the cone phase, detailed in Sec. 5.3.2.1. The two possible chiralities of the magnetic ground state, depicted in Fig. 5.1(c), can be represented in the calculation by a change in sign of the ordering wave vector: replacing $\mathbf{Q}$ with $-\mathbf{Q}$ in the derived expressions is equivalent to changing the domain from spins rotating anticlockwise along $\mathbf{Q}$ (domain 1) to spins rotating clockwise (domain 2).

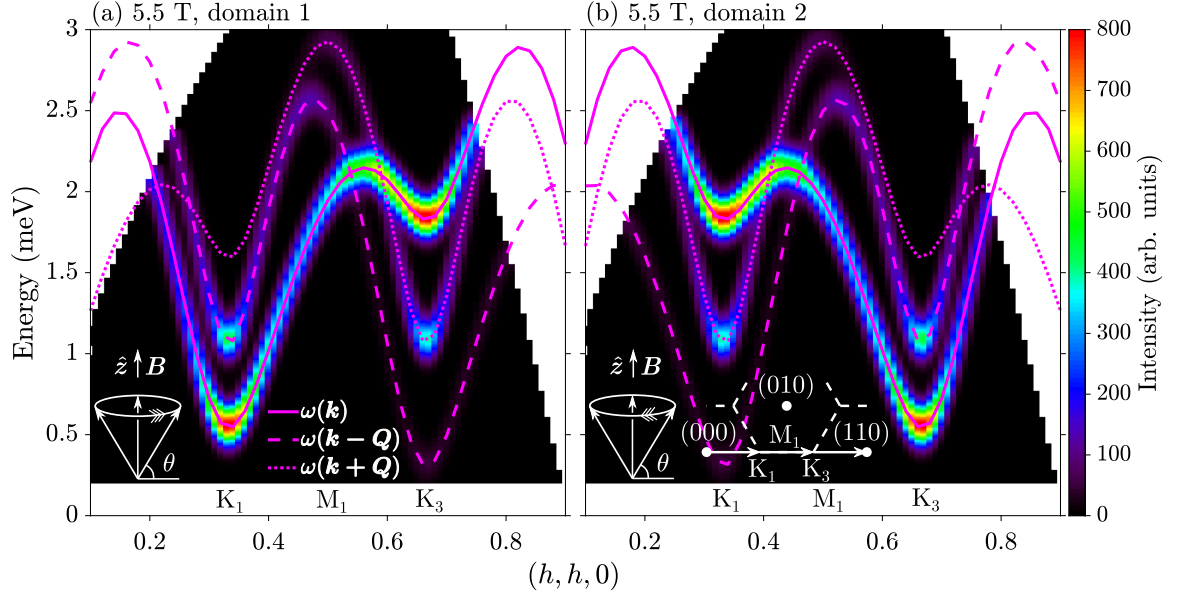


Figure 5.18: (a),(b) LSWT calculations of the structure factor in the cone phase for magnetic ground states of domains 1 and 2, respectively. The parameters used are the best-fit values for the $B = 6$ T data, the same as in Fig. 5.17(g). The colour map gives the intensity in arbitrary units as a function of energy and wave vector along the $(h \mp 0.05, h \pm 0.05, \pm 0.3)$ direction, where the $\pm$ values indicate the integration ranges. The wave vector path is shown as arrows in the white bottom-centre inset in (b), with the Brillouin zone boundaries represented by dashed lines. The K_1 and M_1 points are also labelled in (a) for reference. The $\omega(\mathbf{k})$, $\omega(\mathbf{k} - \mathbf{Q})$ and $\omega(\mathbf{k} + \mathbf{Q})$ dispersions are plotted as solid, dashed and dotted magenta lines, respectively. The white bottom-left insets in the two panels illustrate the senses of rotation for the different chiralities relative to the direction of the applied magnetic field $\mathbf{B}$ [see also Fig. 5.1(c)]. Note that the three sharp modes observed in the data in Fig. 5.17(c) cannot be explained unless domains with both chiralities are present, as in the calculation plotted in Fig. 5.17(g).

These chiralities have the same ground state energy in the absence of D-M interactions, which are almost completely forbidden by the symmetry in $\text{Ba}_3\text{CoSb}_2\text{O}_9$ [89]. An inspection of the dispersion given by Eq. (5.17) reveals that the $C_{\mathbf{k}}$ term changes sign between the two chiralities and the difference in energy increases with increasing field. Measurements of the spin dynamics in the cone phase should therefore be sensitive to the chirality of the 120° spiral order.

Figures 5.17(e)–(h) show the LSWT calculations including equal-weight domains for both chiralities, where the overall intensity scale and the magnetic field have been fitted to energy scans through the data at the K_1 point. The other parameters are the same as those used in Sec. 5.3.2.2 when comparing the experimental data to the LSWT calculation. Although the observed high-energy modes again exhibit significant downwards renormalisation, the LSWT calculation is able to qualitatively capture the key features of the evolution of the modes in applied field: there are two intense modes in zero field, one of which seems unaffected by an applied field and the other splits into two modes that separate with increasing field. The fitted values for the applied magnetic field only deviate by $\simeq 10\%$ from the actual values, suggesting that this simple model provides an almost quantitative description of the evolution of the modes in an applied field.

Figure 5.18 compares the calculated contributions from the different chiral domains at $B = 5.5$ T. Each chiral domain has three associated magnon modes: one out-of-plane mode $\omega(\mathbf{k})$, and two in-plane modes $\omega(\mathbf{k} - \mathbf{Q})$ and $\omega(\mathbf{k} + \mathbf{Q})$. At any given wave vector, one of the in-plane modes is intense and the other is weak: in domain 1, the $\omega(\mathbf{k} - \mathbf{Q})$ mode is intense at $(\frac{1}{3}, \frac{1}{3}, 0)$ and the $\omega(\mathbf{k} + \mathbf{Q})$ mode is intense at $(\frac{2}{3}, \frac{2}{3}, 0)$, and these modes interchange for domain 2. The energy of the intense in-plane mode at the K point is only weakly dependent on the applied field and this accounts for the middle intense mode that appears unaffected by the changing field in

Fig. 5.17. The out-of-plane mode, on the other hand, is intense throughout most of the Brillouin zone and is strongly dependent on the applied field at the K point. This accounts for the two intense modes that appear to separate as the field is increased: in domain 1, the $\omega(\mathbf{k})$ mode lowers in energy with increasing field at $(\frac{1}{3}, \frac{1}{3}, 0)$ and rises in energy at $(\frac{2}{3}, \frac{2}{3}, 0)$, and the opposite is true for domain 2. So although there are only three modes that carry significant spectral weight at any given wave vector, a total of six modes are present, as expected for two chiral domains with three magnetic sublattices each.

Comparing Figs. 5.17 and 5.18, it is clear that the three intense sharp modes observed in the data can only be explained if both chiral domains are present in $\text{Ba}_3\text{CoSb}_2\text{O}_9$, as each domain individually would be expected to exhibit only two intense modes. This is consistent with the earlier observation that neither chirality is energetically favoured over the other in the absence of D-M interactions, providing further evidence of the high symmetry of this system.

5.5 Conclusion

To summarise, single-crystal high-resolution inelastic neutron scattering (INS) measurements have been reported, probing the spin dynamics in the 120° ordered phase of the spin- $\frac{1}{2}$ triangular antiferromagnet $\text{Ba}_3\text{CoSb}_2\text{O}_9$. The key features include roton-like minima at the zone boundary and half the ordering wave vector, a substantial downwards renormalisation of the magnon energies, and strong continuum scattering up to at least $4\times$ the maximum one-magnon energy, which suggest significant quantum fluctuations and are beyond the predictions of existing theoretical models. An empirical parametrisation has therefore been proposed, based on a modified form of the linear spin wave theory (LSWT) dispersions, which captures quantitatively all the features of the one-magnon dispersion relations. The LSWT calculation of the

dynamical structure factor is found to overestimate the intensity at the top of the one-magnon modes, suggesting a transfer of spectral weight to the continuum scattering. Using the empirical parametrisation of the dispersion, a numerical simulation of the two-magnon continuum scattering has also been performed. Although the simulation reproduces the cone of continuum scattering emanating from the ordering wave vector at low energies, it is unable to account for the full structure of the continuum up to much higher energies, due to the presence of strong quantum fluctuations. It has further been established that one $\rightarrow$ two-magnon decay is kinematically forbidden in $\text{Ba}_3\text{CoSb}_2\text{O}_9$, which is consistent with the observation of sharp, resolution-limited magnons throughout the Brillouin zone. Finally, INS measurements have been presented of the spin dynamics in the cone phase in a magnetic field up to 9 T applied normal to the triangular layers. The observed evolution of the magnon dispersions with applied field is consistent with the presence of two equal-weight domains of opposite chirality, as expected in the absence of D-M interactions.

5.6 Acknowledgements

D. Prabhakaran (Oxford) grew and characterised the $\text{Ba}_3\text{CoSb}_2\text{O}_9$ single crystals. S. Williams (Oxford) designed the sample mount and aligned the crystals for the experiments. I am grateful to the Science and Technology Facilities Council for the beamtime allocations that enabled our measurements at the ISIS Neutron and Muon Source. I helped to perform these measurements, together with S. Williams, R. Coldea, R. I. Bewley (ISIS) and D. Voneshen (ISIS). I performed the data processing and analysis, including the MFT and LSWT calculations, the two-magnon numerical simulations and the data fitting, with the assistance of R. Coldea.

Chapter 6

Conclusions

Firstly, inelastic neutron scattering (INS) measurements have been presented for the spin dynamics in $\text{Ba}_2\text{CuTeO}_6$, proposed by *ab initio* calculations to magnetically realise weakly-coupled spin- $\frac{1}{2}$ ladders. The observed spectrum is consistent with that expected for two-leg antiferromagnetic ladders with finite interladder couplings in the ladder plane and almost negligible couplings between planes. Through quantitative comparison with linear spin wave theory (LSWT) and quantum Monte Carlo (QMC) calculations, values have been proposed for all relevant exchange parameters, both intraladder as well as interladder. The deduced values put the system on the ordered side of the phase diagram for coupled two-leg ladders, in proximity to the critical point separating the singlet phase and Néel order. High-field magnetisation data were also compared with the QMC predictions for the proposed model of coupled ladders, providing a consistency check of the sum of the exchanges deduced by comparing the observed spin dynamics with the QMC calculations.

The inelastic data presented are unable to unambiguously determine the magnetic ordering wave vector, as they are not sensitive enough to observe weak magnetic Bragg peaks and only structural Bragg peaks are detected on the elastic line. However, separate high-sensitivity neutron diffraction experiments conducted by A. S. Gibbs have observed magnetic Bragg peaks with a primary ordering wave vector consistent with

the proposed minimal model. The detailed determination of the magnetic structure will therefore be the subject of a future publication, although it is beyond the scope of this thesis.

As discussed previously, single-crystal measurements yield more information about the magnetic structure and excitations than powder measurements, but are often not experimentally accessible. In fact, single crystals have been grown for $\text{Ba}_2\text{CuTeO}_6$ [60, 61], so studying the spin dynamics in such samples could be an avenue for future research. One possible application is to study the longitudinal fluctuations in the amplitude of the sublattice magnetisation, which are expected to be significant close to the quantum critical point. This amplitude mode has recently been directly observed in the two-dimensional spin- $\frac{1}{2}$ quantum antiferromagnet $\text{C}_9\text{H}_{18}\text{N}_2\text{CuBr}_4$, where it is stabilised by an anisotropic energy gap [100]. A polarised single-crystal INS experiment would be particularly well suited to any future search for an amplitude mode in $\text{Ba}_2\text{CuTeO}_6$, as it would allow the longitudinal scattering cross-section to be examined in detail.

A natural question to ask is whether chemical substitution could produce a system of coupled spin ladders that is closer to the quantum critical point than $\text{Ba}_2\text{CuTeO}_6$. Based on the observation of a spin-liquid-like state in $\text{Sr}_2\text{Cu}(\text{Te}_{1-x}\text{W}_x)\text{O}_6$, it has recently been suggested that mixing $\text{Ba}_2\text{CuTeO}_6$ with Ba_2CuWO_6 in a solid solution could drive the system towards the critical point and destabilise the Néel state [101]. It may therefore be insightful to conduct further INS experiments on $\text{Ba}_2\text{Cu}(\text{Te}_{1-x}\text{W}_x)\text{O}_6$ samples to determine their suitability for studies of quantum criticality in coupled ladder systems.

In addition, this thesis has presented measurements of the spin dynamics in the spin- $\frac{1}{2}$ triangular antiferromagnet $\text{Ba}_3\text{CoSb}_2\text{O}_9$ from single-crystal high-resolution INS experiments. The first experiment probed the 120° ordered phase in zero ap-

plied magnetic field, revealing roton-like minima at the zone boundary and half the ordering wave vector, a substantial downwards renormalisation of the magnon dispersion relations, and strong continuum scattering up to high energies, which suggest significant quantum fluctuations beyond the predictions of existing theoretical models. The one-magnon scattering intensity is also found to decrease much faster with increasing energy than predicted by LSWT, which suggests a transfer of spectral weight to the continuum states. Major empirical renormalisations to the LSWT dispersions have been proposed, which are able to quantitatively capture all the features of the measured one-magnon dispersion relations.

Furthermore, numerical simulations of the two-magnon continuum scattering have been performed, using the empirical parametrisation of the one-magnon dispersions. Although the simulations reproduce some of the low-energy features in the observed continuum scattering, they are unable to account for the full structure of the continuum up to much higher energies, which is further evidence of strong quantum fluctuations. It has also been explicitly verified that one $\rightarrow$ two-magnon decay is kinematically forbidden for the renormalised dispersions in $\text{Ba}_3\text{CoSb}_2\text{O}_9$, which is consistent with the observation of sharp, resolution-limited magnons throughout the Brillouin zone.

Finally, single-crystal INS measurements have also been presented of the spin dynamics in the “cone” phase in a magnetic field up to 9 T applied normal to the triangular layers. The observed splitting of the magnon dispersions and their evolution with applied field are consistent with the presence of two equal-weight domains of opposite chirality, as expected in the absence of Dzyaloshinskii-Moriya interactions, which are almost completely forbidden by the high symmetry of this system.

There is clearly a need for a new theoretical framework to describe the observed spin dynamics in $\text{Ba}_3\text{CoSb}_2\text{O}_9$, as the significant renormalisation of the dispersions and the strong, highly-structured scattering continuum up to high energies cannot

be fully explained by magnons using a series expansion method [94] nor by a spinon picture using a mean-field Schwinger boson approach [84]. The empirical parametrisation presented in this thesis should make it easier for any future theoretical model to be compared to the experimental data.

It could also be interesting to study the in-field spin dynamics in more detail. As discussed previously, magnon decays are disallowed in a LSWT model with a sufficiently strong easy-plane anisotropy. However, recent spin wave calculations by P. A. Maksimov *et al.* [102] predict that, even with an easy-plane anisotropy, decays may be possible in the presence of an out-of-plane applied magnetic field, which causes one of the magnon modes to rise in energy and intersect the two-magnon phase space. The same authors predict substantial one-magnon lineshape broadening for parameters that approximate $\text{Ba}_3\text{CoSb}_2\text{O}_9$ in a field of 6 T [102], which coincidentally matches one of the experiments presented in this thesis. Despite this, no evidence has been found of the dramatic finite-lifetime effects predicted in Ref. [102], such as sharp cut-off points where the one-magnon modes enter the continuum. These predictions could be further tested by fitting the empirical model to the in-field INS data and then simulating the two-magnon phase space to look for possible decay regions.

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