Singlet-Triplet Dispersion in the Geometrically Frustrated S = 1Antiferromagnetic Dimer Ba₃Mn₂O₈: An Experiment Using the SPINS Triple-Axis Spectrometer

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Abstract

We will study the singlet-triplet dispersion in the geometrically frustrated antiferromagnetic dimer $Ba_3Mn_2O_8$ using inelastic neutron scattering. In so doing, we will gain an understanding of the principles of Triple-Axis Spectroscopy (TAS) and learn how to analyze the TAS data obtained to extract physical information about the system being studied.

I. INTRODUCTION

One of the most useful properties of neutrons is that they have magnetic moments $(S = \frac{1}{2})$. As a result, neutrons interact with magnetic potentials in materials, which are ascribed to either unpaired electrons or nuclear moments. Contrary to the scattering strength from a nonmagnetic nucleus that is a scalar property, the scattering "strength" from a magnetic potential is in fact a vector property and is proportional to magnetic moment or *spin*. Therefore, orientational periodicity matters as much as positional periodicity for magnetic neutron scattering. If there are no spatial correlations, either orientational or positional, among magnetic moments to be studied, signals from magnetic neutron scattering will be incoherent. This is often the case for nuclear magnetic moments since their potential is strongly localized to each nucleus. On the other hand, electronic magnetic moments are often spatially correlated via long-range Coulomb exchange interactions, resulting in well-defined periodicity.

A. Magnetic structure

Once the positional periodicity of magnetic ions is given from crystal structure, one of the main features of interest in terms of magnetic correlations is the pattern of spin orientations, often called *magnetic structure*, and is one of the most often studied subjects of neutron diffractions. Figure 1 (a) shows disordered magnetic states at two extremes. *Paramagnet* is a state where each spin fluctuates rapidly and randomly without any correlations to its neighbor. Any magnetic material will become paramagnetic at high enough temperatures where the thermal energy is greater than the magnetic energy. The net magnetic moment for each spin will be zero for a time scale larger than the fluctuation. Such a state is similar to gases where the periodicity of atomic positions is lost due to thermal fluctuations. When the temperature is lowered, fluctuations will be suppressed and each magnetic ion will have a non-zero net moment. *Spin glass* is a state where there is no well-defined long-range periodicity even after thermal fluctuations are suppressed. Quite often, however, short-range correlations between nearby magnetic ions should exist, and the absence of long-range order is due mostly to extrinsic reasons. On the other hand, a majority of magnetic materials show long-range periodicity when the temperature is lowered enough. There are



FIG. 1: (a) Schematic illustrations of disordered spin states. (b) Examples of simple magnetic ordering patterns. (c) Classical representation of spin wave excitation in an one-dimensional ferromagnet.

a great diversity of known magnetic structures, yet most of them can be classified into the classes shown in Figure 1 (b). The simplest yet contrasting cases are a ferromagnet and an antiferromagnet, where the nearest neighbor spin correlations are opposite with respect to each other. Additional interactions, for instance, between the second nearest neighbors may induce non-collinear spin structures. The temperature of magnetic transition will depend on the strength of exchange interactions and the size of available spin moments. The strength of the major exchange interactions may be estimated from the temperature dependence of paramagnetic inverse susceptibility $(1/\chi)$. (See Figure 2) In antiferromagnets, $1/\chi - T$ curve makes an intercept at T < 0, which is referred to as *Curie-Weiss temperature*, Θ_{CW} .

B. Magnetic fluctuations

The magnetic ground state is where the magnetic energy of the system is minimized. Therefore, the ground state magnetic structure must be determined by the magnetic Hamil-

(a) ferromagnetism



FIG. 2: Typical temperature dependence of magnetic susceptibility $\chi = \partial M / \partial H$ and $1/\chi$ for (a) ferromagnets and (b) antiferromagnets. H and M are applied magnetic field and magnetization of the material, respectively.

tonian that describes the energy of the system. The simplest yet useful form of magnetic Hamiltonian may be written as below:

$$H = -\frac{1}{2} \sum_{i \neq j} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j, \tag{1}$$

where \mathbf{S}_i and \mathbf{S}_j are magnetic moments at *i*-th and *j*-th ions, respectively, and J_{ij} is an isotropic Heisenberg exchange strength constant between them. In the given form, the signs and strengths of J will determine the magnetic structure, that is, J > 0 for ferromagnets and J < 0 for antiferromagnets.

While the signs of major exchange interactions may be deduced from simply observing magnetic structures, their quantitative strengths can be obtained by measuring spin fluctuations or excitations. It is because such interaction strength will work as a restoring force when spins fluctuate and deviate from their ordered directions. In ordered magnets with isotropic spins, fluctuation of each spin will propagate through the lattice and produce wavelike excitations of finite energy depending on directions of propagation. Although spins and their fluctuations are *quantized* quantities, most of the time their fluctuations can be approximately yet fairly closely understood by mimicking behaviors of classical waves. A *classical* illustration of ferromagnetic *spin wave* propagation is shown in Figure 1 (c). Dynamics of magnetism is not limited to dispersive wave-like excitations, but also includes various localized excitations such as crystal field transitions, singlet-to-triplet excitations, etc. Neutron spectroscopy is, again, one of the most powerful technique to quantitatively investigate the diverse range of magnetic interactions in condensed matter.

The detailed understanding of spin wave excitations is beyond the scope of this experiment. Instead, we will study a different type of magnetic fluctuation arising from magnetic short-range correlations. If magnetic fluctuation of a magnetic ion is hampered from propagating through the lattice for any reason, the fluctuation may be localized and/or decay quickly. For the particular problem to be studied in this experiment, such a localized fluctuation is ascribed to topologically induced spin disorder.

II. BASICS OF NEUTRON SCATTERING

A. Neutron as a probe of matter

It is the ability of the neutron to exchange a *measurable* amount of energy with a liquid or solid sample that makes it useful as a probe of the various dynamical phenomena in condensed matter systems.¹ Typical neutron energies available at a reactor source can range from 100 – 500 meV (hot), to 5 – 100 meV (thermal), to 0.1 – 10 meV (cold), where 1 meV = 10^{-3} eV = 8.06 cm⁻¹. A number of different methods can be used to prepare a monochromatic (or monoenergetic) neutron beam having energies that are comparable in magnitude to, for example, those of the lattice vibrations in a solid (phonons), the spin excitations in a magnetic system (magnons), the torsional, bending, or stretching vibrations of a polymer chain, or the rotational motions in a molecular solid (librons). It is usually quite easy to detect the change in the neutron energy after scattering from a sample since the energy transferred to or from the sample $\Delta E = E_i - E_f$ generally represents a significant fraction of the initial and final neutron energies E_i and E_f .

The energy ΔE transferred during the interaction between neutron and sample can be used to create an excitation (such as a phonon or magnon) of the system, in which case the neutron loses an amount of energy ΔE equal to the energy of the excitation. Conversely, the same excitation can give up its energy to the neutron, in which case the excitation is said to be annihilated. In either case, the physics of the excitation as revealed by the absolute change in the neutron energy is the same. The energy transfer ΔE is often expressed as a frequency of vibration through the relation

$$\Delta E = \hbar \omega, \tag{2}$$

where $2\pi\hbar = h = 6.626 \times 10^{-34}$ Joules-seconds is Planck's constant, and ω is the frequency of vibration of the excitation. Since frequency and time are inversely related, the neutron energy transfer $\hbar\omega$ reflects the *time scale* of the dynamics.

Question: Estimate the value of $(\Delta E/E_i)$ required to observe an optic phonon with an energy of 10 meV using x-ray, light, and neutron scattering techniques assuming the values of $E_i = 7,000$ eV, 2 eV, and 30 meV (0.030 eV), respectively. Which technique is best suited for this measurement?

In addition to having energies that are well adapted to the study of a large variety of dynamical phenomena, neutrons also possess the ability to provide, simultaneously, unique information about the *geometry* of these dynamics through the exchange of momentum with the sample. This is done by measuring in what directions (i. e., through what angles) the neutrons scatter. The momentum of a neutron varies inversely with the neutron wavelength λ , and hence an accurate measure of the momentum transferred between sample and neutron during the scattering process will in turn provide information about the spatial scale of the dynamics being probed. Such an accurate measure is relatively easy to obtain as long as the neutron wavelength is comparable to the length scale of the motions of interest.

Question: The relationship between wavelength and energy for the neutron is given by:

$$E = \frac{h^2}{2m\lambda^2} = 81.81 (\text{meV} \cdot \text{\AA}^2) / \lambda^2, \qquad (3)$$

where $m = 1.675 \times 10^{-24}$ grams is the mass of the neutron. Using this equation, estimate the wavelengths corresponding to hot, thermal, and cold neutrons available at a reactor source. How do these wavelengths compare with the length scales associated with the dynamics or motions you are specifically interested in?

In the following sections we will discuss the partial differential scattering cross section, which is the actual physical quantity that is measured by neutron spectroscopy. We then outline the basic operating principles behind a triple-axis spectrometer (TAS), the concept for which Bertram Brockhouse earned the 1994 Nobel prize in physics shared jointly with Clifford Shull.

B. The Partial Differential Scattering Cross Section $\frac{d^2\sigma}{d\Omega dE_f}$

Most neutron spectroscopic techniques can be reduced to a measurement of what is called the *partial differential scattering cross section*, or $d^2\sigma/d\Omega dE_f$, as a function of the neutron energy transfer $\hbar\omega$ and the neutron momentum transfer \mathbf{Q} .¹ The quantity \mathbf{Q} is known as the scattering vector, and has units of inverse length. In the scattering process between the neutron and the sample, the total momentum and energy of the system are conserved, i.e.

$$\mathbf{Q} = \mathbf{k}_{\mathbf{i}} - \mathbf{k}_{\mathbf{f}},\tag{4}$$

$$\hbar\omega = E_i - E_f = \Delta E. \tag{5}$$

Hence the energy or momentum lost (or gained) by the neutron when it scatters from a sample is gained (or lost) by the sample. In the previous equation, the quantities $\mathbf{k_i}$ and $\mathbf{k_f}$ refer to the initial and final neutron wavevector, respectively, and point in the direction of the incident and final (scattered) neutron beam. The relationship between $\mathbf{k_i}$, $\mathbf{k_f}$, and \mathbf{Q} can be represented by the *scattering triangle* shown in Fig. 3. The magnitude of the neutron wavevector k is $2\pi/\lambda$, and is related to the neutron energy via



FIG. 3: Scattering triangle. The neutron is scattered through the angle 2θ and the scattering vector, \mathbf{Q} , is given by the vector relationship $\mathbf{Q} = \mathbf{k}_i - \mathbf{k}_f$.

$$E = \frac{(\hbar k)^2}{2m} = 2.072k^2 [\text{meV} \cdot \text{\AA}^2],$$
(6)

From this last equation, one can obtain the second equation in Fig. 3 which relates the energy transfer to the magnitude of the initial and final wavevectors. The angle between \mathbf{k}_i and \mathbf{k}_f is commonly denoted by 2θ , and represents the total angle through which a neutron is scattered by the sample. Note that the convention followed in this summer school is such that the energy transfer $\hbar\omega$ is positive when $E_i > E_f$, i. e. when the neutron loses energy to the sample during the scattering process. This convention of defining when $\hbar\omega$ is positive varies among neutron scattering facilities.

The partial differential scattering cross section is defined as the total number of neutrons scattered per second by the sample into a unit of solid angle $d\Omega$ in a given direction, having final energies E that lie between E_f and $E_f + dE_f$. It is normalized by the neutron flux incident on the sample Φ_0 (measured in neutrons/sec/cm²) so that it has units of area/(solid angle)/energy. If one integrates the partial differential scattering cross section over the entire solid angle (= 4π steradians), and all final energies ($0 \le E_f \le \infty$), one obtains the total number of neutrons scattered out of the beam per second by the sample. (This assumes that the absorption of neutrons by the sample, which can often occur, is negligible.) This is known as the total scattering cross section σ , which has units of area. Thus σ represents the scattering strength of the sample, and can be viewed as an unnormalized probability that an incident neutron will be scattered. If one compares the value of σ for hydrogen with that of aluminum, it will be clear that different elements can have enormously different scattering strengths.

Question: The scattering cross section for x-rays is a strong and monotonically increasing function of atomic number Z. This is because x-rays scatter from the electrons of an atom, which increases with increasing Z. Neutrons, by contrast, scatter from the atomic nucleus via short-range nuclear forces. If you plot σ for neutrons versus Z, do you see any trend? In what ways might this be advantageous? (Values for σ can be obtained from the NCNR Summer School web page under "Course Materials," or at http://www.ncnr.nist.gov/resources/n-lengths/.)

It is instructive to consider the relative sizes of σ and $d^2\sigma/d\Omega dE_f$. Clearly σ , which represents the total number of neutrons scattered per second by the sample, is many orders of magnitude larger than $d^2\sigma/d\Omega dE_f$, which is an analyzed quantity both in energy and direction. On the other hand, the partial differential scattering cross section provides a correspondingly greater amount of information because it contains all of the details of the individual and collective motions of the atoms, molecules, and/or any atomic magnetic moments that comprise the sample. The *differential cross section* $d\sigma/d\Omega$, which is what is measured in a diffraction experiment, lies between σ and $d^2\sigma/d\Omega dE_f$ in size. As the elastic component dominates in $d\sigma/d\Omega$, it gives the time-averaged (equilibrium) positions of all of the nuclei in the sample, and is used to determine the crystal structure.

The partial differential scattering cross section can be cast into a useful mathematical form via the formalism outlined at the end of the neutron scattering primer written by Roger Pynn² (which the summer student is presumed to have read). With a small deviation from the notation used by Pynn we can write the partial differential cross section for a system composed of a single atomic element as

$$\frac{\mathrm{d}^2 \sigma}{\mathrm{d}\Omega \mathrm{d}E_f} = \frac{1}{4\pi} \left(\frac{k_f}{k_i} \right) \left[\sigma_{coh} S_{coh}(\mathbf{Q}, \omega) + \sigma_{inc} S_{inc}(\mathbf{Q}, \omega) \right],\tag{7}$$

where $S(\mathbf{Q}, \omega)$ is exactly same quantity as $I(\mathbf{Q}, \epsilon)$ used by Pynn to express Van Hove's scattering law. The subscripts *coh* and *inc* refer to the coherent and incoherent parts of the scattering, and pertain to the collective or individual motions of the atoms, respectively, as described on page 9 of Pynn's primer. Whenever spatial correlation of scatterers is of interest, however, the coherent term only needs to be considered.

The scattering function $S_{coh}(\mathbf{Q}, \omega)$ contains a double sum over pairs of nuclei as shown in Eq. 3 on page 28 of Pynn's primer.² Each term in this sum represents the *correlation* between the position of one nucleus at a time t = 0 with that of another nucleus at an arbitrary time t later. These correlations are important for systems in which the nuclei are strongly coupled via some type of interaction, and less so when this coupling is weak. In either case $S_{coh}(\mathbf{Q}, \omega)$ provides a measure of the strength of this coupling, and hence the resulting *collective* motions. It is therefore extremely useful, for example, in mapping out the dispersion relations of lattice vibrations, that is how the energy $\hbar\omega$ of the lattice vibrations changes at different \mathbf{Q} positions, in solids. For the remainder of this discussion, we will drop the subscript *coh* with the understanding that we are referring to the coherent part of the scattering function.

The scattering function $S(\mathbf{Q}, \omega)$ can be simply related to the imaginary part of the dynamical susceptibility according to

$$S(\mathbf{Q},\omega) = \frac{\hbar}{\pi} \left(\frac{1}{e^{\hbar\omega/k_B T} - 1} + 1 \right) \chi''(\mathbf{Q},\omega), \tag{8}$$

where $k_B = 1.381 \times 10^{-23}$ Joules/K is Boltzmann's constant (note: $\hbar/k_B = 11.60$ K/meV is a handy conversion factor). This is a very important equation since it shows that $S(\mathbf{Q}, \omega)$, which is readily obtained from the experimentally measured partial differential scattering cross section via Eq. (7), is also related to a quantity that is easily calculated by theorists, $\chi''(\mathbf{Q}, \omega)$. The dynamical susceptibility is a measure of how the system responds when it is "wiggled". $\chi''(\mathbf{Q}, \omega)$ refers to the imaginary part of this quantity, which is related to how energy is dissipated by the system. Therefore a measurement of the partial differential scattering cross section via neutron spectroscopy allows for a direct test of theoretical mod-



FIG. 4: The relationship between the neutron scattering cross section and the spin-spin correlation function. The relaxation rate Γ is HWHM in energy of $S(Q, \omega)$, and is inversely proportional to the lifetime of the excitation τ . The line-width κ is the HWHM in momentum transfer of $S(Q, \omega)$, and is inversely proportional to the correlation length ξ .

els. By recording the scattered neutron intensity as a function of energy transfer $\hbar\omega$ and momentum transfer \mathbf{Q} , and removing the instrumental effects, one obtains $S(\mathbf{Q}, \omega)$, which contains all of the dynamical information about the system.

With the exception of the neutron spin-echo (NSE) technique, all other neutron spectroscopic methods measure $d^2\sigma/d\Omega dE_f$ using a neutron detector to count the number of neutrons scattered per unit time from a sample as a function of the energy transfer $\Delta E = \hbar \omega$ and the momentum transfer **Q**. To do this requires that one knows the energy and wavevector of the neutron before $(E_i, \mathbf{k_i})$ and after $(E_f, \mathbf{k_f})$ it scatters from the sample. There are many ways of doing this, and most will be illustrated by the different experiments in this summer school. As will be seen, each method has its own particular advantages and limitations, depending on the range of energy transfers (time scales) and momentum transfers (length scales) one wishes to study.

C. Understanding The Spin-Spin Correlation Function $\langle S_R(t) \cdot S_{R'}(0) \rangle$

The intensity of neutrons scattered from the magnetic moments in a solid is proportional to the spin-spin correlation function:¹

$$\frac{\mathrm{d}^2 \sigma}{\mathrm{d}\Omega \mathrm{d}E_f} = r_0^2 \frac{k_f}{k_i} |\frac{g}{2} F(Q)|^2 \sum_{\alpha\beta} (\delta_{\alpha\beta} - \hat{Q}_{\alpha} \hat{Q}_{\beta}) \\ \times \frac{1}{2\pi\hbar} \int dt \ e^{i\omega t} \frac{1}{N} \sum_{\mathbf{RR'}} \left\langle S^{\alpha}_{\mathbf{R}}(t) S^{\beta}_{\mathbf{R'}}(0) \right\rangle e^{-i\mathbf{Q}\cdot(\mathbf{R}-\mathbf{R'})}$$
(9)

where $r_0 = -0.54 \cdot 10^{-12}$ cm, g is the gyromagnetic ratio, F(Q) is the magnetic form-factor and N is the number of unit cells in the solid. Basically the partial differential scattering cross section $d^2\sigma/d\Omega dE_f$ is the Fourier transform in space and time of the spin-spin correlation function $\langle S_R(t) \cdot S_{R'}(0) \rangle$. Thus, neutron elastic scattering probes static ordered moments, whereas neutron inelastic scattering probes fluctuating (dynamic) moments.

While this equation appears formidable, Fig. 4 can help shed substantial light on the relationship between the measured magnetic neutron scattering cross section and the timedependent spin-spin correlation function. The spatial dependence of the spin correlations can be determined from the Q-dependence of $S(\mathbf{Q}, \omega)$. For example, if $S(\mathbf{Q}, \omega)$ is Q-resolution limited, then this would indicate that the spatial correlations are of long-range. However, if $S(\mathbf{Q}, \omega)$ is broader than the instrumental Q-resolution, then the correlations are shortranged. A similar argument can be made for linewidths, which is the peak widths observed in energy scans. If $S(\mathbf{Q}, \omega)$ is $\hbar \omega$ -resolution limited, then this would indicate that the temporal correlations are of long-range. However, if $S(\mathbf{Q}, \omega)$ is broader than the instrumental $\hbar \omega$ resolution, then the excitations are only short-lived in time.

III. TRIPLE-AXIS SPECTROSCOPY

A. Introduction to The Triple-Axis Spectrometer

The triple-axis spectrometer (TAS) is an extremely versatile instrument that is primarily intended for the study of the collective motions of the atoms and their magnetic moments in single crystal samples. The first TAS system was used to obtain the first experimental demonstration of phonon and magnon dispersion curves (in aluminum and magnetite) in the mid 1950's.³ The instrument derives its name from the fact that the neutrons interact with three crystals on their way from reactor to detector, each crystal being able to rotate independently about a vertical axis passing through its center. This is shown schematically in Fig. 5. The first crystal is called the monochromator, as it selects a single monochromatic component from the white neutron beam emanating from the reactor or neutron guide. The second crystal is the sample itself (although it may be either a single crystal or a powder). The third crystal is called the analyzer, as it is used to analyze the energy spectrum of the neutron beam that scatters from the sample. The last primary element of the instrument is, of course, the neutron detector.

In a triple-axis spectrometer, the initial and final neutron energies are determined by exploiting the process of Bragg diffraction from the monochromator and analyzer single crystals. This is done by rotating the crystals about their respective vertical axes such that a specific set of atomic Bragg planes, having a well-defined interplanar spacing d, makes an angle θ , known as the Bragg angle, with respect to the initial (or scattered) beam direction. When this is done, only neutrons with wavelengths that satisfy the Bragg condition (see pages 9-11 of Pynn's primer)

$$n\lambda = 2d\sin\theta,\tag{10}$$

where n is an integer greater than zero, will Bragg scatter from each crystal and proceed successfully to the next element of the spectrometer.

Question: Because the variable n in Bragg's law can be any integer greater than zero, more than one monochromatic component can be present in the neutron beam diffracted by either monochromator or analyzer. List the possible wavelengths of these other components. How might their presence affect the experimental data?

To remove the extra and unwanted monochromatic components from a Bragg diffracted beam, while preserving the neutron flux at the desired fundamental (n=1) wavelength λ , it is common practice to place a filter composed of some solid material in the path of the beam. The choice of material depends on the primary wavelength λ . For thermal neutrons, a special form of graphite (pure carbon) known as highly-oriented pyrolytic graphite (HOPG or just PG) is often used. Graphite has a layered structure in which the crystalline [001]



FIG. 5: Schematic scattering configuration for a conventional triple-axis spectrometer. It measures a scattering event at a single value of $(\mathbf{Q}, \hbar \omega)$ at a time.

or *c*-axis is normal to the layers. HOPG behaves like a crystal of graphite in which the various graphite layers have all been randomly spun about the *c*-axis. Therefore HOPG can be viewed as a single-crystal along [001], and a powder along the two orthogonal directions. It exhibits very good transmission at certain neutron energies including 13.7, 14.7, 30.5, and 41 meV. Neutrons of other energies are preferentially (though not completely) scattered out of the beam, thereby minimizing the chance they will enter the detector and contribute to the background.

For cold neutrons, such as those used on the SPINS spectrometer, a polycrystalline block of beryllium (Be) or beryllium oxide (BeO) is used as a wavelength filter. The requirement for this filter to work is that there be enough tiny crystallites to span all angular orientations, *i.e.* all values of the Bragg angle θ , so that all unwanted neutrons are Bragg scattered out of the neutron beam. Question: (1) Consider a white (polychromatic) beam incident on a polycrystalline Be filter. What happens to those neutrons with wavelengths $\lambda > 2d_{max}$, where $d_{max} = 1.98$ Å is the largest interplanar d spacing available in beryllium? What happens to those neutrons with $\lambda \leq 2d_{max}$? Make a simple sketch of transmission versus energy for this filter.

(2) What are the criteria for ideal materials for designing neutron low-pass filters?

As can be seen from Fig. 5, when the incident neutron beam from the reactor strikes the monochromator, it is scattered through an angle $2\theta_m$ from its initial direction. This is commonly referred to as the monochromator *scattering angle*. In order for the resulting monochromatic beam to hit the sample, it is necessary to rotate the subsequent elements (sample, analyzer, and detector) of the spectrometer about the monochromator axis through an angle of $2\theta_m$. The same situation applies for the sample, and the analyzer, i. e. associated with each crystal is a Bragg angle θ , and a scattering angle 2θ . Hence each axis of the tripleaxis spectrometer is actually composed of two motors, one to control the crystal Bragg angle θ , and the other to rotate the subsequent (downstream) elements of the instrument by the appropriate scattering angle 2θ . While there are many different motors involved in the operation of a triple-axis spectrometer, such as those that control mechanical slits that limit the horizontal and vertical extent of the neutron beam, the primary instrument motors are those that control the values of θ and 2θ for the monochromator, sample, and analyzer. (NOTE: The convention of naming θ and 2θ comes from the fact that $2\theta = 2 \times \theta$ for elastic Bragg scattering. Even though this relation no longer holds for inelastic scattering, they are still called the same way.)

The material most commonly used as monochromator and analyzer in a TAS system is also HOPG. Its utility lies in its very high reflectivity for neutrons over a wide range of energy, along with its negligible incoherent scattering and adsorption cross sections, and its low atomic number so that scattering by gamma rays is small. The (002) Bragg planes of HOPG have an interplanar d spacing of 3.354 Å. Other materials that also find use in triple-axis spectroscopy are silicon, germanium, and copper. Question: Calculate the monochromator Bragg and scattering angles required to obtain a neutron beam having initial energies $E_i = 14.7$ meV, and 100 meV using the (002) reflection of HOPG. The (220) reflection of copper has a d spacing of 1.278 Å. Would this be a better choice of monochromator in either case?

During the interaction with the sample, neutrons can lose or gain energy, and thus can emerge with an energy $E_f \neq E_i$. The resulting energy transfer can be computed according to

$$\hbar\omega = E_i - E_f = \frac{h^2}{8m} \left(\frac{1}{d_m^2 \sin^2 \theta_m} - \frac{1}{d_a^2 \sin^2 \theta_a} \right),\tag{11}$$

where d_m and d_a are the *d*-spacings of the monochromating and analyzing crystals, respectively. If the analyzer is set to select the same energy as that of the incident beam $(E_i = E_f)$, then $\hbar \omega = 0$, and the scattering is said to be *elastic*. If not, one detects *inelastic* scattering events.

Measuring the momentum transfer \mathbf{Q} between neutron and sample is achieved by orienting the incident and final neutron wavevectors with respect to each other to obtain the desired vector difference $(\mathbf{k_i} - \mathbf{k_f})$. Unlike the case of the monochromator and analyzer crystals, the Bragg and scattering angles for the sample needn't be related by a simple factor of 2. Indeed, when measuring inelastic scattering they usually are not. Hence the notation 2θ (which is quite common) can be misleading for the novice scatterer. With this warning in mind, we can calculate the magnitude of the momentum transfer from the scattering triangle diagram in Figure 3 as below.

$$Q = \sqrt{k_i^2 + k_f^2 - 2k_i k_f \cos 2\theta}.$$
 (12)

Note that the momentum transfer does not depend on the sample Bragg angle θ , but only on the sample scattering angle. The purpose of the Bragg angle is to allow the crystalline axes of the sample (if it happens to be a single crystal) to be aligned in specific ways with respect to the scattering vector **Q**. This allows one to probe the geometry of the dynamics in question along different symmetry directions. The utility of the sample Bragg angle becomes moot, however, in the case of a powder sample (composed of many tiny and randomly-oriented single crystals). **Question:** What is the maximum momentum transfer one can obtain in the case of elastic scattering, i.e. $|\mathbf{k}_i| = |\mathbf{k}_f|$? What is the minimum? Why might these two configurations be problematic from an experimental point of view?

By stepping the analyzer Bragg angle θ_a , or the monochromator Bragg angle θ_m , by computer in small angular increments, one can effectively scan the energy transfer $\hbar\omega$. Generally this is done while keeping the momentum transfer \mathbf{Q} constant, and is known as a constant- \mathbf{Q} scan. The complement to the constant- \mathbf{Q} scan is the constant-E scan in which the energy transfer is held constant while one varies the momentum transfer. These two scans are fundamental to the triple-axis method, and are used commonly to map out the dispersion relations for both phonons and magnons in condensed matter systems.

In the case of a constant- \mathbf{Q} scan, one has the choice of fixing either the incident or final energy, through fixing the Bragg angles of either the monochromator or the analyzer. As a rule, it is best not to vary both as one needs to place a wavelength filter in the path of either the incident beam (before the sample) or the scattered beam (after the sample) in order to remove the higher order harmonic content of the Bragg diffracted neutron beam (remember the effect of the integer n in Bragg's law). If the analyzer angle θ_a is fixed and one varies θ_m , the result is an E_f -fixed configuration. Doing the opposite results in an E_i -fixed configuration. Both methods yield data that contain the same physics. Deciding which to choose depends largely on the specific problem being studied.

B. The NCNR Spin Polarized Inelastic Neutron Scattering (SPINS) Spectrometer

SPINS is a cold-neutron triple-axis spectrometer. Fig. 6 show an overview of the SPINS spectrometer and the schematics of the neutron path. Its incident energy range can be changed between 2.4 and 14 meV. The monochromator of SPINS consists of 5 blades of PG crystals can vertically focus incoming neutron flux to a sample with a size smaller than the height of the beam. On the other hand, the analyzer consists of 11 blades also of PG crystals that are standing vertically in a row and can individually be rotated. Taking advantage of this multi-crystal analyzer, SPINS is designed to operate in various configurations including (1) conventional triple-axis mode, (2) horizontally focusing analyzer mode, and (3) multiplexing mode. Since many components of the SPINS instrument can be changed as



FIG. 6: Overview of the SPINS spectrometer. The arrows show the path of the neutron beam during a scattering experiment. M, S, A, and D stand for monochromator, sample, analyzer, and detector.

necessary, other modes not described here are also possible. For instance, polarized-neutron scattering mode is also optionally available.

(1) Conventional triple-axis mode has been discussed previously, and shown in Fig. 5. At SPINS, it can be achieved by using just a few analyzer blades in the middle, typically three, which are aligned flatly with respect to each other. A single tube detector is used with necessary collimators through the beam path.

(2) Horizontally focusing analyzer mode is schematically shown in Figure 7. The basic idea of this mode is to focus scattered neutrons over a wide solid angle into a single tube detector. It has an effect of relaxing momentum resolution while maintaining energy resolution. As a result, detected neutron intensity will increase roughly proportionally to the number of the focusing blades. It is very efficient in data collection rate when the features to be measured are broad in momentum space. Ideally the blades need to be positioned on an arc of a circle encompassing the positions of the sample and the detector, so that Bragg angles for all the blades are equal. In practice, one can achieve an approximate focusing



FIG. 7: Schematic scattering configuration of a horizontally focusing analyzer mode utilizing a multi-blade analyzer for a triple-axis spectrometer. It collects intensity from a broad range of momentum transfer simultaneously while maintaining a good energy resolution.



FIG. 8: Schematic scattering configuration of a multiplexing detection system utilizing a Position-Sensitive-Det spectrometer. It simultaneously measures scattering events at different values of $(\mathbf{Q}, \hbar \omega)$.

TABLE I: Comparison chart of neutron scattering spectrometers at NCNR in terms of the needs for this particular experiment.

Issues	SPINS	BT7/9	DCS	HFBS	NSE	FANS
$ \Theta_{CW} \approx 88~{\rm K}$ corresponds to $J\approx 1~{\rm meV}$	0	×	0	×	×	×
$S(\mathbf{Q}, \omega)$ at well-defined $\mathbf{Q}(hkl)$ space	0	0	\triangle	×	×	×
diffraction can also be done with good resolution	0	\triangle	×	×	×	×

condition by placing the row of the blades tangential to the relevant arc, and maintain a constant incident angle of neutrons for each blade. The momentum resolution can be adjusted by appropriately selecting the number of focusing blades.

(3) In multiplexing modes, a wide area of the position sensitive detector (PSD) is used together with the multi-crystal analyzer. In the most typical setup, schematically shown in Figure 8, the 11 analyzer blades are aligned in such a way to scatter neutrons into equallyspaced columns on the PSD. If the blade arrangement is nearly flat as in Figure 8, each blade will have a different Bragg angle and subsequently a different energy. Therefore, signal from each blade will correspond to both different momentum and different energy transfers. The positional sensitivity of the PSD can efficiently discriminate this information. This mode is very efficient in data collection when momentum dependence of excitation is two-dimensional or less. Typically a calibration run should be performed for a given setup using an incoherent scatterer, and used as a reference for energy and intensity calibrations. Various creative combinations of the analyzer-PSD setups are possible depending on the necessity of the experiment.

At NCNR there are several neutron scattering spectrometers with diverse experimental capabilities that are available to internal and external users. Whenever neutron scattering experiment is planned, it is very important to consider various aspects of experimental needs and select the best suited instrument. Table I summarizes the most important reasons why SPINS, the cold neutron triple-axis spectrometer, is the best instrument for this particular study in comparison with other instruments. An additional advantage of using SPINS is that various experiments requiring different experimental configurations, such as elastic versus inelastic, high versus low Q resolution, and high versus low energy resolution, can be performed in series on the same instrument.

IV. DISPERSIVE MAGNETIC EXCITATIONS IN ADDITIONALLY FRUS-TRATED TRIANGULAR LATTICE DIMER COMPOUND BA₃MN₂O₈

A. Geometrically frustrated magnets and quantum critical phenomena

In certain magnetic materials, magnetic order would not appear even when the system is cooled down much below the temperature comparable to the major exchange strength. In some cases crystal structure is responsible for the suppression of magnetic order, which is often called *geometrical frustration*. As the simplest example, consider a case where antiferromagnetic spins are placed on an equilateral triangle as in Figure 9, and assume only two spin orientations are allowed, either up or down. After placing the first two spins antiparallel to each other, the third spin cannot simultaneously satisfy antiferromagnetic correlations with the two other spins. It is often said that the third spin is *frustrated*. In fact, it is not just the third spin but the three-spin system that is frustrated, and there are more than one lowest energy state possible for the given system. Such topologically induced multiply degenerate ground states that prevent the system from ordering is a characteristic of geometrically frustrated magnets. Most geometrically frustrated magnets will eventually order when the temperature is lowered enough. Another approach to induce the long range magnetic order in frustrated systems is via the use of an external agent such as magnetic field.⁴ If the system has singlet ground state, as in s=1/2 spin system, then it also provides good opportunity to explore the novel quantum behavior in applied magnetic field. Low temperature quantum behavior usually lead to quantum critical point (QCP) which separates the parametric state from the magnetically ordered state. New electronic phases of matter have been predicted to occur in the vicinity of a QCP by two-dimensional theories, and explanations based on these ideas have been proposed for significant unsolved problems in condensed matter physics, such as non-Fermi-liquid behavior and high temperature superconductivity. But the real materials to which these ideas have been applied are usually the three-dimensional systems with finite electronic coupling between their component layers. The observation of two-dimensional QCP in three-dimensional bulk materials has been very limited. In addition to that, the driving mechanism behind the dimensionality reduction has been a subject of debate in these systems. In order to understand the mechanism behind QCP in geometrically frustrated systems, one needs to identify the exchange paths and



FIG. 9: (a) Three spins on a triangle cannot simultaneously satisfy antiferromagnetic correlations with all of their neighbors. (b) Spinel B sites form a corner-shared network of tetrahedra, which consists of many edge-shared triangles. It is often called a pyrochlore lattice.

their strength between neighboring magnetic ions. Numerical modeling, using the appropriate Hamiltonian, of the resulting spin dispersion curve leads to the identification of the strength of the tuning parameter, thus provide important imformation about the underlying mechanism.⁶

B. Singlet-triplet dispersion in triangular lattice dimer compounds

Dimer compounds, for example $Ba_3Mn_2O_8$, provide an ideal platform to study the physics of quantum phase transition in geometrically frustrated systems, using external magentic field as the tuning parameter.⁵ In dimer compounds, the application of external magnetic field closes the energy gap between singlet ground state and the lowest excited level of triplet state via Zeeman splitting of triplet. Such systems thus provide an elegant realization of a lattice of bosons in which the external magnetic field plays the role of the chemical potential and the inter-dimer coupling determines the energy of the delocalized triplets. Under the right set of conditions, these delocalized triplets crystallize or condense at low temperatures; thus paves the way for long range magnetic order via second order phase transition. Since the magnetic field acts as the tuning parameter which separates the paramagnetic state from the ordered state at high magnetic field(s), QCP(s) can be identified in temparaturefield phase diagram. In $Ba_3Mn_2O_8$, two sequential magnetically ordered phases, i.e. four QCPs are observed as a function of applied magnetic field at 9 T, 26 T, 32.3 T and 48 T.⁷ Most importantly, the nature of the high field phases depends upon the exchange constants between neighboring ions at zero field. Therefore, strong understanding of the exchange paths and their strengths at zero magnetic field is necessary to understand the underlying mechanism behind the QCP as well as the role of geometrical frustration.

 $Ba_3Mn_2O_8$ is a particularly promising candidate for the detailed study of the magnetic field dependent QCP.⁷ Ba₃Mn₂O₈ is a S = 1 coupled spin dimer antiferromagnetic system which consists of Ba^{2+} cations and MnO_4^{3-} anions. It crystallizes in a trigonal structure with the space group R3m. The lattice constants are a = 5.711 AA and c = 21.444 AA at room temperature. Since the Mn^{5+} ion, in this compound, is tetrahedrally surrounded by four O^{2-} ions, the orbital ground state is nondegenerate. Therefore the magnetic moment is approximately given by spin only. Figure 10 shows the arrangement of Mn^{5+} ions and possible dimer, J_0 , and inter-dimer, J_i , exchange paths. Inelastic neutron scattering measurements on powder sample yielded three independent exchange constants through comparison to a spherically averaged scattering intensity. Recent neutron scattering measurements on single crystal sample revealed that the next-nearest-neighbor (NNN) interaction, J_4 , plays a significant role in the propagation of triplet excitations. As mentioned earlier, since the critical field(s) depends on the exchange path and the strength of the interactions, the exchange constants can be determined by fitting the dispersion bandwidths at the measured critical fields. While the complete understanding requires the detailed measurements and analysis at different fields, in this experiment we will primarily focus on measuring and analyzing the exchange interactions of Mn-ions of $Ba_3Mn_2O_8$ in zero field. In doing so, we will learn (1) how cold triple-axis spectrometers can be the most effective tool to study the low energy magnetic excitations, (2) how the magnetic excitation evolve as a function of wave-vector i.e. the dispersive bahavior of low energy spin waves, and (3) how to correlate the extracted information, using the numerical modeling of the experimental data, to the underlying physics of the system.



FIG. 10: Crystal structure of $Ba_3Mn_2O_8$. Oxygen atoms are not shown for clarity. Grey dashed lines indicate chemical unit cell. (a) Polyhedra presentation of structure. Light green and dark green polyhedra around Ba sites represent the two types of Ba coordination that alternate along the *c* axis. Red tetrahedra illustrates the Mn^{5+} coordination. (b) Crystal structure of $Ba_3Mn_2O_8(caxisvertical)showingMn^{5+}$ dimers (red dimer bonds along c-axis). Oxygen sites (small blue sphere) involved in coordination of two dimers are shown to illustrate interdimer connectivity and tetrahedral coordination of the Mn^{5+} .

Question: Consider the case of a triangular lattice with isotropic Heisenberg spins. If nearest neighbor exchange is antiferromagnetic, is geometrical frustration expected or not?

V. EXPERIMENT AND ANALYSIS

A. Experimental Planning and Setup

In order to determine the exchange constants, we perform inelastic neutron scattering measurements at different wave vectors in the Brillouin zone. Neutron scattering data are then fitted with a statistical function, such as a Gaussian lineshape, to determine the magnetic excitation energy, E, at a particular wave vector, \mathbf{Q} . The plot of E vs. \mathbf{Q} provides us information about the dispersive nature of magnetic excitations. The magnetic dispersion curve is numerically fitted with the appropriate Hamiltonian to obtain the exchange constants of the system.

While the energy of the analyzer may be arbitrarily chosen for triple-axis spectrometers, the typical energy of the analyzer at SPINS is either 5.0 meV or 3.7 meV. This is mostly because these numbers are just below the cut-off energies of low-pass Be and BeO filters, respectively. One may access wider momentum space with reasonable intensity with $E_f =$ 5.0 meV, while better energy resolution is obtained with $E_f = 3.7$ meV. The low-pass filters are inserted between the sample and the analyzer, and will prevent scattered highenergy neutrons from entering analyzer-detector assembly and leaving spurious experimental artifacts. For elastic scattering an additional low-pass filter is usually inserted between the monochromator and the sample.

Single crystal samples of $Ba_3Mn_2O_8$ were oriented in the hk0 scattering plane, where the *a* and *b* axes are located in the horizontal scattering plane. An alternative orientation is the *hhl* scattering geometry, where one of the two axes are rotated out of the horizontal plane by 60° while the other remains. In the case of inelastic scattering, five pieces of crystals were co-aligned and mounted together to enhance scattering intensity. The samples are then sealed in a He-filled aluminum can and cooled down by a liquid-He filled cryostat. The instrument will be operated in fixed- E_f mode with $E_f = 5.0$ meV. The instrumental configuration for inelastic measurements following the neutron path downstream is: neutron guide-monochromator-80' collimator-sample-Be filter-radial collimator-11 blade horizontally focusing analyzer-detector (G-80'-Be-RC-11HFA-D in short). The energy resolution for the above configuration is about 0.3 meV.

B. Data and analysis

Figure 11 shows the energy dependence of magnetic inelastic neutron scattering intensity measured at various \mathbf{Q} at T = 1.7 K. The experimental data show a single resolution limited spin wave mode propagating along the (hh3/2) direction between energy transfer E of 1 to 3 meV. Similar bahvior of spin wave propagation is observed in the measurements at several



FIG. 11: Constant \mathbf{Q} scans in the (hhl) and (hk0) planes. Solid lines are the Gaussian fits. Data are offset vertically for presentation.

high symmetry locations in (hk0) scattering plane also, perhaps with weaker intensity. In order to understand the spin wave dispersion and quantitatively determine the wave-vector dependent scattering intensity, individual constant Q scans are fitted to an inelastic Gaussian lineshape. The peak positions along several high-symmetry directions are plotted in Figure 12 and 13. We see that the singlet-triplet excitation is fairly dispersive along the (00l)direction but almost no dispersion along l for $0.3 \le h \le 0.7$ is observed.

Previously, three nearest neighbor exchange constants J_i , i=0,1,2, were determined from the powder measurements of Ba₃Mn₂O₈. However, the lack of dispersion along the *l* direction near the zone center cannot be explained by nearest neighbor exchange constants only. That means, an additional interlayer NNN exchange constant must be competing against the nearest neighbor interactions. Therefore, we must include the NNN interbilayer interaction, J_4 , in the Heisenberg Hamiltonian. Please refer to the reference by M. Stone et.al. for the Heisenberg Hamiltonian equations. A simultaneous fit of the peak positions of the constant **Q** scans in the (*hhl*) scattering plane yields $J_0 = 1.642$, $J_1 = -0.118$, ($J_2 - J_3$) = 0.1136 and $J_4 = -0.037$ meV. J_2 and J_3 represent interdimer exchange between the same spin dimers.



FIG. 12: (a)-(d) T = 1.7 K scattering intensity of Ba₃Mn₂O₈ vs E and **Q**. Figure is interpolated from constant **Q** scans in the (*hhl*) plane. White circles are peak positions from Gaussian fits. Solid line is the fitted dispersion. (e)-(h) Integrated scattering intensity from Gaussian fits to constant **Q** scans. Solid line is the fitted scattering intensity. (1) Path through the (*hhl*) plane shown in (a)-(h). Contour lines are the fitted dispersion with dark (light) lines representing smaller (larger) energy transfers shown at 0.2 meV intervals.

The phase shift for triplets propagating between dimers via J_2 or J_3 is due to the opposite symmetries of the singlet and triplet state under a permutation of the two sites that form the dimer. The corresponding dispersion curves shown in Fig. 12 and 13 agree very well with the measurements. The dispersion along $(1/2 \ 1/2 \ l)$ is also fitted in Fig. 13 for $J_4 = 0$ (dashed line). We clearly see that the calculated curve does not fit the experimental data. Hence, additional NNN exchange (J_4) is required to describe the measured dispersion. The additional interlayer exchange interaction also indicates that the Mn⁵⁺ sites are additionally frustrated.

During the Summer School experiments, students will be provided the inelastic neutron scattering data of $Ba_3Mn_2O_8$ in (hhl) and (hk0) scattering planes. We will analyze the experimental data using DAVE software and estimate the various exchange constants. In



FIG. 13: (a) Dispersion and (b) integrated intensity of $Ba_3Mn_2O_8$ determined from Gaussian fits to energy scans. Solid lines in (a) are fits to the dispersion as discussed in the text. Dashed lines in (a) is the fitted dispersion for $(1/2 \ 1/2 \ l)$. Solid lines in (b) are fits to the scattering intensity.

this process, we will learn not only the magnetic properties of geometrically frustrated quantum magnets but also gain experinece in plotting and modeling the spin dispersion behavior of the system.

VI. SUMMARY

Triple-axis spectroscopy is one of the most widely used neutron scattering techniques for studying lattice and magnetic dynamics in condensed matter. Its strength is in its capability to measure $S(\mathbf{Q}, \omega)$ at desired momentum and energy transfers with great flexibility. In this experiment, we have studied the geometrically frustrated antiferromagnetic dimer Ba₃Mn₂O₈. Through single crystal inelastic neutron scattering measurements of Ba₃Mn₂O₈, it was shown that the NNN exchange interactions are significant in describing the system. The antiferromagnetic interactions within the bilayer lead to a geometrically frustrated system. The refined exchange constants provide a zero-field confirmation of the high magnetic field QCPs. We also learned that the use of cold triple axis spectrometr, SPINS, is vital in understanding the low energy magnetic excitations in a range of magnetic systems, such as geometrically frustrated magnets or low dimensional quantum systems.

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