NEUTRON SCATTERING STUDIES OF YTTRIUM DOPED RARE-EARTH HEXAGONAL MULTIFERROICS

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by
JAGATH C GUNASEKERA
Dr. Owen P. Vajk, Dissertation Supervisor
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The undersigned, appointed by the Dean of the Graduate School, have examined the dissertation entitled:

NEUTRON SCATTERING STUDIES OF YTTRIUM DOPED RARE-EARTH HEXAGONAL MULTIFERROICS

presented by Jagath C Gunasekera,
a candidate for the degree of Doctor of Philosophy and hereby certify that, in their opinion, it is worthy of acceptance.

________________________________________
Dr. Owen. P. Vajk

________________________________________
Dr. Wouter Montfrooij

________________________________________
Dr. Sashi Satpathy

________________________________________
Dr. Angela Speck

________________________________________
Dr. Steven Keller
To my parents
and to my loving wife
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ABSTRACT

According to the famous Maxwell’s equations that govern the dynamics of magnetic and electric fields, these two fields are intrinsically coupled to each other, rather than independent phenomena. An electric current, i.e. a charge in motion produces a magnetic field, whereas a varying magnetic field produces an electric field. In the solid states, electric charges of electrons and ions are responsible for the charge effect, whereas magnetism arises from the spin of the electron. Magnetic susceptibility in a material describes the magnetic response (M) of a substance to an applied magnetic field (H), electric susceptibility gives an idea about the displacement of charges which is the polarization (P) due to a electric field (E). The magnetoelectric effect describes the coupling between electric and magnetic properties in matter through the induction of magnetization (M) by an electric field (E) or polarization (P) generated by a magnetic field (H). In most materials this magnetoelectric coupling tends to be very weak. The first experimental report of such magnetoelectric coupling was published on Cr$_2$O$_3$. This sparked new avenues of research. Symmetry arguments led to the discovery of materials with multiple ferroic orders. These multiferroics are a subset of magnetoelectric materials which can exhibit a coupling between ferroic properties at different ranges of temperature, with magnetism that can be either ferromagnetic or antiferromagnetic. Our studies revolved around hexagonal $R$MnO$_3$ ($R = Ho, Y, Dy, Er$), where strong magnetic-ferroelectric coupling in hexagonal HoMnO$_3$ has been observed previously at the spin reorientation transition temperature between the P6$_3$cm and the P6$_3$c‘m magnetic phases. In contrast, YMnO$_3$ has only a single magnetic phase (P6$_3$cm‘) and no sign of strong magnetic-ferroelectric coupling, while ErMnO$_3$ and
DyMnO$_3$ order in the P6$_3$cm phase. Understanding the transition between these phases may shed light on magnetic-ferroelectric coupling observed in hexagonal multiferroics. In order to investigate the P6$_3$cm$'$ to P6$_3$cm$'$m spin reorientation transition, single crystals of Ho$_{1-x}$Y$_x$MnO$_3$, Er$_{1-x}$Y$_x$MnO$_3$ and Dy$_{1-x}$Y$_x$MnO$_3$ at varying compositions were grown. Neutron scattering measurements reveal quasielastic scattering in the Y-like phase (P6$_3$cm$'$) centered on the Bragg peak corresponding to the Er like phase (P6$_3$cm$'$m) and vice versa. This scattering may be due to short-lived fluctuations into the “wrong” magnetic phase at domain boundaries. These results suggest that there is strong phase competition between the P6$_3$cm$'$ and P6$_3$cm$'$m phases even in pure YMnO$_3$. Magnetic phase diagrams extracted from elastic scattering showed that the mechanism that drives the magnetic phase transition is complex. Doping different amounts of Y, Er and Dy yield different phase transition directions, which confirms the complexity of the driving force behind these magnetic phases.
Chapter 1

Introduction

1.1 Magnetolectric Effect

After the discovery of the relationship between electric and magnetic phenomena in the 19th century by Ampère, Faraday and others, James Maxwell formulated the unified theory of electromagnetism. In 1888, Röntgen observed the linear electric and magnetic susceptibilities in moving dielectrics [1].

\[ P_i = \epsilon_{ij} E_j \]  \hspace{1cm} (1.1)

and

\[ M_i = \mu_{ij} H_j \]  \hspace{1cm} (1.2)

where \( \epsilon, \mu \) are electric and magnetic susceptibilities, \( P, M \) are polarization and magnetization and \( E, H \) are electric and magnetic fields.
Later, the possibility of an linear magnetolectric effect in stationary materials was predicted by P. Curie from a symmetry arguments in 1894 [2]. In 1894, Debye named this kind of effect the “magnetolectric effect” [3]. This linear magnetolectric effect can be simply expressed as

\[ P_i = \alpha_{ij} H_j \]  \hspace{1cm} (1.3)

and

\[ M_i = \mu_0 \alpha_{ji} E_j \]  \hspace{1cm} (1.4)

where \( \alpha \) is the magnetolectric coupling tensor [4]. In 1959, this field really started with a short remark in a volume of “Course of Theoretical Physics” by Landau and Lifshitz [5]

“Let us point out two more phenomena, which, in principle, could exist. One is piezomagnetism, which consists of linear coupling between a magnetic field in a solid and a deformation (analogous to piezoelectricity). The other is a linear coupling between magnetic and electric fields in a media, which would cause, for example, a magnetization proportional to an electric field. Both these phenomena could exist for certain classes of magnetocrystalline symmetry. We will not however discuss these phenomena in more detail because it seems that till present, presumably, they have not been observed in any substance.”

This magnetolectric coupling tensor can be understood thermodynamically within the Landau theory of free energy, and some rigorous work will show that the magne-
toelectric response is limited by the condition [6]

$$
\alpha_{ij}^2 < \epsilon_{ii} \mu_{jj}
$$

(1.5)

where $\epsilon$ and $\mu$ are electric and magnetic susceptibilities.

Soon after, the realization of the linear magnetoelectric effect in the antiferromagnetic phase of Cr$_2$O$_3$ was predicted by Dzyaloshinskii based on symmetry arguments [7]. It was detected by Astrov, which led to the discovery of many other compounds with similar linear magnetoelectric effects [8].

According to the limitation (eq 1.5), the only way to achieve a considerable magnetoelectric response is to find materials with large dielectric and magnetic susceptibility. Ferromagnets display the largest magnetic permeability, while the largest dielectric coefficients are found in ferroelectric materials. Hence, ferroelectric ferromagnetic materials became a prime candidate for displaying a large magnetoelectric effect.

1.1.1 Magnetism

Magnetization in the macroscopic world is generated by the magnetic dipole moments of an atom. At high temperatures these magnetic dipoles tend to orient randomly (paramagnetic) as shown in figure 1.1a. Ferromagnetism occurs when there is a phase transition from a high-temperature paramagnetic phase to a low-temperature phase that has spontaneous magnetization where all the spins align into one direction (figure 1.1b) even in the absence of external applied field [9]. In our research, we focused on antiferromagnetic materials, where the magnetic dipole moments align antiparallel
Figure 1.1: a) Paramagnetic ordering of the dipoles, where all the dipoles order randomly at high temperatures. b) Ferromagnetic ordering, where all the spins align in one direction. c) Antiferromagnetic ordering of the magnetic dipoles, where there is no total magnetic moment. d) Ferrimagnetic, moments align antiparallel, but posses overall magnetization due to the unevenness of magnetic moments either individually or as layers.

to each other (figure 1.1c). Since they do not posses overall magnetization, antiferromagnets do not have as many applications. Another group of magnets that have similar alignments to antiferromagnets, but posses net magnetization, are ferrimagnets. Even though the magnetic moments are antiparallel, one sublattice of aligned spins has a larger moment, creating net magnetization (figure 1.1d).

Another important property of ferromagnets is that they have domains. There can be domains within the material wherein each domain’s spins are oriented in one direction in that domain but a different direction in another domain (figure 1.2). At the domain boundary, spins can align in different directions. Thermal fluctuations
For all these types of magnetic orderings, the basic microscopic origin of magnetism is same. The presence of localized electrons in partially filled $d$ or $f$ shells of rare-earth or transition-metal ions, which posses a magnetic moment or localized spins, gives rise to magnetism. Magnetic ordering is induced by exchange interactions between localized moments. Even though from the commercial perspective, ferromagnetic ferroelectric materials have the wider variety of applications, as physicists, we tend to study all these types of magnetism.

1.1.2 Ferroelectricity

The existence of ferroelectric materials came to light after finding a large piezoelectric constant in a material known as Rochelle salt over a century ago [10]. Further research led to the discovery and characterization of other ferroelectric materials. The
development of fundamental physics theories has led to specific device applications and optimization.

Ferroelectricity in the RMnO$_3$ family was first discovered early as 1963 by Bertaut et al.[11]. Many ferroelectric properties are similar to those of ferromagnets. Formally ferroelectric materials behave as normal dielectrics or paraelectrics at high temperatures (when an electric field is applied, it will induce an electric polarization, but that polarization will go to zero when the field is zero) and have a spontaneous polarization that can be switched by an applied field in lower temperatures.

Ferroelectrics are characterized as either “proper” or “improper.” Ferroelectrics with polarization originating from a structural instability towards the polar state associated with electronic paring or covalent bonding between $3d^0$ transition metals are called “proper” ferroelectrics. In “improper” ferroelectrics, the ferroelectricity is due either to charge ordering, or to the polarization which originates as a byproduct of a complex lattice distortion. In a unit cell below the Curie temperature, structural distortion to a lower symmetry phase gives rise to the ferroelectricity. Hexagonal manganites fall into the “improper” category, and the ferroelectricity is caused by structural distortion along the $c$ axis.

1.1.3 Multiferroics

The past few decades have also seen an increase of interest in the study of exotic magnetic materials. The fact that the electron has a spin as well as a charge has given an extra degree of freedom to the device design and something to think about for the physicist. What could fascinate the physicist even more would be the discovery of material with a combination of ferroelectric and magnetic properties through
the strong cross-coupling of responses in these properties. These responses are the appearance of electric polarization \( P \) generated by the application of a magnetic field \( H \), or the inverse effect of the appearance of magnetization \( M \) in an electric field \( E \). The first ferromagnetic and ferroelectric material to be discovered was nickel iodine boracite \( \text{Ni}_3\text{B}_7\text{O}_{13}\text{I} \) in 1966 [12]. Possible practical device applications for such magnetoelectric materials are multiple-state memory elements, electric-field-controlled ferromagnetic resonance devices, and transducers with magnetically modulated piezoelectricity [13].

The term multiferroic was first introduced first by Schmid in 1994 to describe materials in which either two or all three of the properties of ferroelectricity, ferromagnetism (could be ferro, ferri or antiferro) and ferroelasticity occur in the same phase in the absence of external field [9, 14]. The requirement that these properties coexist in a material made them very rare.

Other multiferroics include the 113 Perovskites (\( \text{BiMnO}_3, \text{BiFeO}_3 \) and \( \text{TbMnO}_3 \)), 125 manganites (\( \text{RMn}_2\text{O}_5 \) where \( R = \text{Ho-Lu} \)) and hexagonal manganites (\( \text{RMnO}_3 \) where \( R = \text{Ho-Lu, Y} \)). These multiferroics are divided into two types. In the first type (Type-I), the magnetism and ferroelectricity have independent origins. Because of these independent origins, magnetic and ferroelectric ordering temperatures have no relationship with each other. Generally, ferroelectric ordering temperatures for type-I multiferroics tend to be very high. In type-II multiferroics, magnetism causes ferroelectricity, so the ferroelectric ordering temperature is at or below the magnetic ordering temperature [15, 16]. In our work, we focus on type-I hexagonal manganite multiferroics. This family of hexagonal multiferroics are antiferromagnetic with a Néel temperature around 70K, but the exact antiferromagnetic structure varies as function
of composition, temperature, magnetic field and even pressure [17, 18]. Ferroelectric polarization occurs at high temperatures (\(\sim 900\text{K}\)).

1.2 Hexagonal \(RMnO_3\)

In hexagonal multiferroics, \(RMnO_3\), \(R\) is a rare earth element (Ho-Lu) or Y. Even though yttrium is not a rare earth element, it also forms a hexagonal multiferroic when combined with \(MnO_2\), since yttrium forms a stable trivalent cation with an ionic radius similar to rare earth materials. In this family of hexagonal structures, each \(Mn^{3+}\) ion with spin = 2 is surrounded by a total of 5 oxygen ions. Three of them are in-plane and two are apical (figure 1.4) forming a bipyramid structure that looks like two tetragonal pyramids joined at their base. The triangular lattices of \(Mn^{3+}\) ions are formed by these \(MnO_5\) bipyramids where they are “corner-linked” to each other along the in-plane oxygen ions [19]. \(R^{3+}\) ions are sandwiched between these 2D triangular lattices, which are stacked alternately in \(c\) (figure 1.5). The crystal structure of these hexagonal multiferroics was first reported in 1963 [20]. These \(MnO_5\) bipyramids undergo tilting to minimize their energy, which will induce ferroelectric polarization along \(c\) axis [21].

1.2.1 Magnetism in \(RMnO_3\)

Magnetism in materials can be categorized into two groups. In the first group, there is no interaction between the individual moments and each moment acts independently. Paramagnets are in this category. The second category consists of materials where the magnetism occurs because the magnetic moments couple to each other

8
Figure 1.3: Figure shows a schematic of the electrons involved in MnO superexchange. The 2p orbitals from oxygen and 3d orbitals from manganese can form a direct exchange. According to the Pauli exclusion principle, the singlet state is energetically favored, leading to antiferromagnetic alignment of neighboring Mn$^{3+}$ moments.

and form magnetically ordered states. This coupling is known as exchange interaction. There are three types which are currently believed to exist: direct, indirect and superexchange.

The magnetic structure of RMnO$_3$ was first reported by Koehler et al. and it is antiferromagnetic due to superexchange interactions [22]. Superexchange describes the coupling between moments through a non-magnetic material. In RMnO$_3$ family Mn$^{3+}$ spins are coupled to each other via a non-magnetic O$^{2-}$ anion. We know from the Heisenberg uncertainty principle that confining a particle to a smaller volume increases its kinetic energy. In order to minimize the kinetic energy of electrons, the wave function should expand its spatial extent, which means assigning a nonzero probability of electrons hopping between neighboring atoms. However, only hops which are consistent with the Pauli exclusion principle are permitted. Figure 1.3 shows a schematic of electrons involved in the Mn-O-Mn superexchange process. More electron hopping modes are permitted between the Mn$^{3+}$ 3d orbitals and the O$^{2-}$ orbital if the Mn$^{3+}$ moments are anti-aligned, leading to an antiferromagnetic interaction between Mn$^{3+}$ moments mediated by the O$^{2-}$ ion between them [23].

The antiferromagnetic structure of RMnO$_3$ is frustrated, this is due to the Mn$^{3+}$ triangular lattice structure [22]. Koehler et al. determined that Mn$^{3+}$ ions order in a
120° angle between the three moments in a triangle at low temperature (∼ 70K) to relieve frustration. Because adjacent layers are laterally offset from each other, the relative orientation of spins in adjacent layers affects the magnetic symmetry. The exact magnetic structure varies depending on factors such as which rare earth element occupies the space between MnO₅ layers, temperature and magnetic field. Multiferroism exists in RMnO₃ because of the coexistence of antiferromagnetically ordered Mn spins and the ferroelectric phase.

To find the exact magnetic symmetries in this family, neutron powder diffraction experiments proved to be inadequate due to limited resolution in fitting different magnetic structure. Therefore, single crystal measurements with different techniques had to be employed. Fiebig et al. did extensive study of the magnetic symmetries on this RMnO₃ structures using the Second Harmonic Generation (SHG) method. SHG proved to provide a very sensitive and accurate method. Figure 1.6 shows the change
in magnetic phase symmetry groups in YMnO$_3$, HoMnO$_3$, ErMnO$_3$ and DyMnO$_3$ at
different temperatures. SHG is a nonlinear optical method which illuminates nonlinear
crystal surfaces with an optical wave and measures the second harmonic response
function [24].

HoMnO$_3$ and YMnO$_3$ are two of the widely researched multiferroics to date. In
HoMnO$_3$, s=2 Mn$^{3+}$ moments undergo a spin reorientation transition as a function of
temperature. HoMnO$_3$ orders in a non-collinear 120$^\circ$ spin structure below the mag-
netic ordering temperature ($T_N$). This magnetic space symmetry group is denoted
as P6′$_3$cm. A spin reorientation takes place at about 40K ($T_{SR}$) where the Mn spins
undergo an in-plane 90$^\circ$ rotation, changing the magnetic symmetry to P6′$_3$cm$'$. When
the temperature drops further ($T_{Ho} \sim$ 8K), a second spin reorientation transition
occurs and the Mn spins rotate into the P6$_3$cm space group, while half of the Ho mo-
ments order antiferromagnetically with moments aligned along the c axis [25]. Figure
Figure 1.6: Illustrations of the magnetic phase symmetry groups at different temperatures by SHG method. Dark gray (blue in color) corresponds to $P6'_3c'm$, medium gray (red) represents $P6_3cm$ and light gray (green) corresponds to $P6'_3$ magnetic phase symmetry group.

1.8 illustrates the corresponding spin alignment in two adjacent layers of Mn$^{3+}$ ions for each magnetic phase in $RMnO_3$ family.

The 3D spin Hamiltonian for $RMnO_3$ family can be written as,

$$H = \sum_{ij} J_{ij} S_i S_j + \sum_{ik} J_{ik} S_i S_k + D_\perp \sum_i S_i^z S_i^z + D_{||} \sum_i S_i^\alpha S_i^\alpha \quad (1.6)$$

where, $J_{ij}$ is the in-plane antiferromagnetic exchange interaction, $< i, j >$ indicates the sum is over nearest-neighbor in-plane pairs, $J_{ik}$ is the out-of-plane antiferromagnetic exchange interaction, sum $< i, k >$ is for nearest-neighbor out-of-plane pairs, $D_{||}$ is the easy-axis anisotropy and $D_\perp$ is the easy-plane anisotropy. Figure 1.7 shows the possible two different out-of-plane antiferromagnetic interactions. In an ideal
Mn$^{3+}$ ion triangular lattice $J_{k1} = J_{k2}$ and the position of each Mn$^{3+}$ ion within the triangular lattice would be $x = 1/3$ [26].

As of now, there are two models that describe what is driving this magnetic phase transition in $R$MnO$_3$. First, in 2009, Fabreges et al. claimed that this transition is driven by Mn$^{3+}$ relieving its frustration by shifting along the $a-b$ plane. The Mn-Mn interactions between adjacent Mn planes due to superexchange interactions via apical oxygen ions of MnO$_5$ will lead to a 3D magnetic ordering. The in-plane position of the Mn$^{3+}$ ion determines the relative strengths of the $J_{k1}$ and $J_{k2}$ exchanges, which in turn determines which 3D magnetic phase is stabilized. The spin reorientation in HoMnO$_3$ occurs when Mn$^{3+}$ moves from $x < 1/3$ above $T_{SR}$ to $x > 1/3$ below $T_{SR}$[26]. The second model was proposed by S.G. Condran et al. in 2010, where he claimed that this transition is driven by Ho-Mn coupling. At lower temperatures, Ho$^{3+}$ moments become more prominent. Since the Ho and Mn spins are coupled with each other, they hypothesized that increasing Ho$^{3+}$ moment causes the Mn$^{3+}$ spin reorientations with decreasing temperatures. The coupling between Mn$^{3+}$ and Ho$^{3+}$
below $T_{SR}$ was attributed to trigonal anisotropy based on theoretical calculations and symmetry arguments [27].

![Figure 1.8: Illustrations of the rotations of Mn spins located at Z=0 (dark circles) and Z=1/2 (light circles) layers in different magnetic phases.](image)

1.2.2 Ferroelectricity in $RMnO_3$

Ferroelectricity in $RMnO_3$ multiferroics is due to a geometric effect. A detailed analysis of the origin of ferroelectricity in $RMnO_3$ was done by Bas B. Van Aken et al.[19], who found that the ferroelectric phase is due to the tilting of the MnO$_5$ bipyramids by displacing oxygen from its centrosymmetric position with Mn remaining at the center. This tilting of the MnO$_5$ bipyramids satisfies the hexagonal close-packing requirement and minimize the total energy of the unit cell. Tilting is accompanied by large displacement of the R-O bonds along the $c$ axis due to a displacement of R atoms along the $c$ axis, which leads to local antiparallel electric dipoles with different magnitudes, resulting in net ferrielectric polarization. Careful structure analysis work and first principal calculation proves that Mn ions remain very close to the center of oxygen bipyramids and are not instrumental in generating ferroelectricity in this system. This is because off-center distortion of Mn$^{3+}$ is energetically unfavorable [19].
This structural distortion typically occurs at high temperatures for the $RMnO_3$ family. For example, the ferroelectric temperature $T_C$ of $YMnO_3$ was reported to be around 920K with space group $P6_3cm$ and the centrosymmetric high temperature phase was found to be above 1270K [28, 29].

1.2.3 Multiferroic coupling in $RMnO_3$

Hexagonal $RMnO_3$ gained attention because of the possibility of using $YMnO_3$ for nonvolatile ferroelectric memory devices [30]. Interest grew in hexagonal rare earth magnetites as a family of multiferroics for studying the coupling between magnetism and ferroelectricity after discovering the anomalies in the temperature dependence of the dielectric constant around $T_N$ for polycrystalline $YMnO_3$ [31]. One feature that makes hexagonal manganites appealing as multiferroics is that the ferroelectric transition occurs well above room temperature. However, single-crystal measurements revealed that this anomaly in the dielectric constant of $YMnO_3$ exists only in the $a-b$ plane, and not along the direction of the ferroelectric polarization, which is along the $c$ axis [32]. Similar results were found in $LuMnO_3$ [32]. These results suggest the anomaly is not a result of coupling between the ferroelectricity and magnetism. In contrast, dielectric measurements done on $HoMnO_3$ reveal strong magnetic-ferroelectric coupling [33, 34]. A very large and sharp spike in the $c$-axis dielectric constant at $T_{SR}$ (spin reorientation temperature) was reported, and a corresponding change in polarization at $T_{SR}$ was measured by N. Hur et al. [35]. It is important to mention that the dielectric anomaly was reportedly seen at $T_{SR}$ in $HoMnO_3$ but not in $LuMnO_3$. $YMnO_3$ does not have a temperature dependent spin reorientation, but both $HoMnO_3$ and $LuMnO_3$ do [36]. A more striking report on
this magnetoelectric coupling in HoMnO$_3$ was published by Thomas Lottermoser et al. in 2004 in “Letters to Nature,” where he showed that below $T_N$, an electric field changes the Mn$^{3+}$ spin order to $P6_3c'm'$ symmetry, and ferromagnetically polarize the Ho$^{3+}$ moments [37].
Chapter 2

Crystal growth

2.1 Floating-zone technique

For neutron scattering purposes, we require a large crystal, ideally a single grain. To achieve this task, we use a procedure called the “floating-zone” technique. This is a very powerful technique that uses the floating-zone furnace to fabricate high quality single-grain crystals under different environmental conditions.

The furnace we use has four ellipsoidal mirrors made out of Pyrex glass and coated with highly reflective aluminum, and four 1000W Halogen lamps mounted in a horizontally movable stage (Figure 2.1). This method uses a feed rod and a seed which rod are made out of the desired compound that will be turned into a crystal. The feed rod is hung by the upper shaft and the seed rod is attached to the lower shaft respectively. Both the feed and the seed rods are encapsulated in an air-tight quartz tube to satisfy the desired environmental conditions (figure 2.2). Only the upper
Figure 2.1: Both the seed and the feed rods will be encapsulated in a quartz tube in the middle of the mirror stage and will be surrounded by the mirrors. The vertical speed of the mirror stage can be adjusted.

The shaft can be moved vertically. Both upper and lower shafts can be rotated clockwise or counter-clockwise with speeds varying from 5-60 rpms. The vertical moving rate of the mirror stage and the upper shaft is 0.05-27 mm/hour. The optical floating-zone furnace can reach a maximum temperature of 2200°C in different atmospheres such as air, oxygen, nitrogen, and argon at a pressure range from 5x10^{-5} up to 10 bars.

The theory behind this technique is that the radiation generated from the lamps is reflected and focused by the mirrors onto the center of the furnace in order to form a molten zone at the tip of the feed rod. Once the molten zone formed, the attachment process begins. During this process, the feed rod will be lowered to the seed rod slowly until the molten zone on the tip of the feed rod touches the seed rod. Once the attachments succeed, the molten zone is held together between the seed and feed rods by surface tension. Both the feed rod and the seed rod are rotating in clockwise
Figure 2.2: The molten floating-zone is created by the focusing of the light from high-power halogen bulbs by four focusing mirrors. The molten zone is suspended by the surface tension between the polycrystalline feed and the grown crystal. The diameter of the crystal can be adjusted by the upper shaft’s upward or downward movement, which will change the rate at which material is added to the molten zone. As the mirror stage moves upward, the melt with freezes onto the growing crystal. To even out any asymmetries in heating and to mix the melt, upper and lower shafts are rotated in opposite directions. A video camera is used to monitor the growth process. Reproduced from [38].

and counter-clockwise directions, respectively, with pre-determined speeds. To grow the crystal, the molten zone is translated along the feed rod by moving the mirror stage upwards at a given rate. As the focal point of the mirrors (the ”hot zone”) moves upwards, material melts from the feed rod and solidifies onto the seed (figure 2.3). Crystals can be grown up to 150 mm in length and 10 mm in diameter.

This painstaking process of growing a crystal is based on experience and patience. At the beginning, the power, which is proportional to the amount of heat generated by the lamps, is gradually increased till the tip of the feed rod is fully melted. Once the tip of the feed rod is fully melted, it has to be lowered gradually using the controls onto the seed rod. This process generally takes up to one hour. After the rods are
attached, power should be modulated to keep the molten zone intact via surface tension. Too much heat will break the surface tension, resulting in detachment of the molten zone. Too little heat will result in an inadequate molten zone and will lead to the feed and seed rods grinding together, which will lead to the detachment of the molten zone. The growth rate that we used was 4 mm/hour to prevent nucleating new grains. The rotation of the rods ensures the proper mixing of the molten zone. A rotation rate of 34 rpm was utilized in our work for the seed rod and 29 rpm for the feed rod. In the beginning, the grown crystal is multi-grain, and each grain has a different orientation. Crystal growth is not and isotropic process, and layered materials typically grow faster in the in-plane direction. As the process continues, the grain with best alignment of fast-growth axis with the growth direction of the furnace will dominate, forcing out the other grains. The dominant grain will grow into a single crystal. In this crystal $c$ axis is always perpendicular to the growth direction. Due to different thermal expansion coefficients along different crystal axes [39], often most of the grains will cleave once the crystal is cooled down as the different grains try to contract in different directions relative to each other. This entire growth process takes up to four days.

2.1.1 Making of the seed and feed rods

Making the feed and seed rods is a vital part of the crystal growth process. Precise measurements of the powder, high quality chemical powders, proper mixing and heating vital for the growth of high quality crystal. First, calculated stoichiometric ratios of chemical compounds ($\text{Ho}_2\text{O}_3$, $\text{Y}_2\text{O}_3$, $\text{MnO}_2$, etc) are measured up to the $10^{-4}$ gram precision using a precision scale. Then, they are mixed and ground together
thoroughly using a mortar and pestle. The mixture is poured into a ceramic crucible and then calcinated at a temperature up to 1200°C for 8 hours. This process of grinding and heating is done two more times to ensure proper mixing and heating of the compound. Once this mixing and heating is done, the powder is packed into a cylindrical-shaped latex tube using a tamper. Powder is inserted into the tube using a funnel. Once the powder has started accumulating, a tamper is used to compress the powder. Fingers may also be used to pinch the tube from outside to ensure the uniform thickness of the rod. In practice, a great deal of manual dexterity and individual skill is necessary to produce a good feed rod. After enough powder has been fed into the tube to generate a compressed length of powder in excess of 10 cm, a cotton ball is shredded and fed into the tube. Then, the latex tube is removed from the glass funnel and most of the air trapped inside the powder is removed by attaching the latex head to a vacuum pump. The piece of cotton acts as a filter, preventing the powder from being sucked into the pump. While the pump is running, the head is sealed using a rubber band to make sure that no air gets in when the latex tube is removed from the vacuum pump. Then, the cylindrical latex tube with the powder is encapsulated inside a hollow aluminum rod and submerged in a hydraulic press. Encapsulation of the latex rod is essential to ensure both uniform thickness and the straightness of the rod during the compression. The press consists of a water-filled chamber with a piston at the opening. Once the tube is inserted into the chamber, it is capped off with the piston. Around 280 MPa of pressure is applied to the piston head. This makes the powder release the remaining air and compresses the powder into a rod which will be durable to handle. After several minutes, pressure is released slowly. Slow release of pressure will make the excess air leak from the solid rod and
form a bubble outside the rod, still inside the latex tube. Then the latex tube is taken out and sliced gently to separate the latex tube from the newly-formed rod. At this point, the rod is brittle, and extreme care must be exercised when handling it. Then a small hole (~1mm diameter) is carefully drilled on the top end of the rod using a small drill bit. The bit is twisted between the fingers to drill the hole. Once this has been accomplished, a platinum wire is inserted through the hole and tied off to form a closed loop. The rod is freely suspended from the platinum wire inside a large cylindrical shaped aluminum crucible. This will prevent any interaction between the rod and the crucible. The final step is to sinter the rod at 1400°C for 8 hour. Sintering ensures that the powders will diffuse into the desired compound and harden. During this step the density of the rod increases and it will be ready to be placed into the floating zone furnace.

Similar steps can be taken to make the seed rod as well. Since the growth is performed on top of the seed rod, it needs to be much shorter. Measured powder will be reduced to one third of the feed rod powder measurements.
Figure 2.3: (a) Mirrors melt the end of the feed rod (dark gray), which remains suspended from the feed rod by surface tension. Some melt penetrates into the feed rod on the surface (light gray). The dashed lines inside the molten zone indicate the interior solid-liquid boundary. (b) Initial attachment is accomplished by lowering the upper shaft until the molten zone contacts the seed crystal. (c) Growth proceeds by slowly raising the mirror stage (not shown) at 4 mm per hour. As the hot zone moves upward, material from the feed rod melts into the zone and solidifies onto the seed crystal. (d) Crystal growth rates are not isotropic, and grains with in-plane axes parallel to the growth direction grow faster than other grains. The grain with the best orientation for growth will expand faster than other grains, until it pushes other grains out completely. The remaining growth will then be single grain, with the c-axis approximately perpendicular to the crystal boule axis. Reproduced from [38].
Chapter 3

Neutron Scattering

3.1 Introduction to Neutron scattering

The basis of much research in physics, chemistry, material science and biology is a detailed understanding of the properties of the research material at the atomic scale. There are various experimental methods to achieve this. Among them, neutron scattering is especially powerful and flexible. In our research work, we utilized thermal neutrons available at University of Missouri Research Reactor (MURR).

Neutron scattering is a technique involving shooting neutrons with a defined energy and momentum at a sample and analyzing neutrons scattered from the sample. Neutrons interact with the atomic nucleus, so neutrons can distinguish atoms of comparable atomic numbers and even isotopes of the same element. This allows us to focus on one specific feature of that material. The wavelength of thermal neutrons are comparable to inter-atomic distance, so interference effects can be used to mea-
sure structure. The energy of a thermal neutron is on the order of an elementary excitation in matter, so neutrons are well-suited for inelastic scattering. Therefore, neutrons allow us to investigate the dynamic properties of atomic arrangements as well as static atomic structures which are directly related to the physical properties of the material. Since neutrons do not have a charge, they interact only weakly with the matter. Because of this, linear-response theory is a good approximation to analyze the experimental data. This also means that the neutrons have a large penetration depth that will assist in exploring the bulk properties of matter. Having such large penetration depth helps immensely with studying the sample under different environments, such as high and extremely low temperatures, high pressure, and different magnetic and electric fields. One disadvantage of this is that we need a big sample to produce enough signal to measure. Most of the sample holders are made using aluminum, which is practically invisible to neutrons. Even though neutrons do not have an electric charge, they do possess a magnetic moment and can scatter from magnetic moments in a sample. This makes them an excellent candidate for probing static and dynamic magnetic properties such as spin waves and magnetic ordering.

All the neutron scattering measurement were carried out at Missouri University Research Reactor (MURR) using the Triple-Axis Spectrometer (TRIAX). MURR is a 10MW reactor. Three instruments, a reflectometer, powder diffractometer and the triple-axis spectrometer, are distributed equally around the biological shielding. Because the instruments are spaced at maximum distance from each other, there is a lower probability that neutrons scattered by one instrument will influence the measurements taken by another (referred to as background scattering). The lower power of the MURR reactor also helps to reduce background scattering compared to
Figure 3.1: a) Basic configuration of an triple axis spectrometer. b) Scattering triangle for tetragonal lattice in reciprocal-space. Reproduced from [38]

other reactors such as at Oak Ridge, which has a 85MW reactor, and consequently, higher background scattering.

### 3.2 Triple-axis spectrometer

The triple-axis spectrometer was developed by Bertram Brockhouse in the 1950’s [40]. Triple-axis spectrometers are the most versatile instruments for inelastic neutron scattering experiments, because they allow controlled access to the momentum ($Q$) and energy ($\omega$) variables of the scattering function $S(Q, \omega)$. A schematic is given in figure 3.1a. Neutrons produced from a nuclear fission process in a reactor become thermalized by the moderator due to scattering inelastically off of hydrogen or deuterium nuclei. Emitted neutrons possess a Maxwellian distribution, with the characteristic temperature determined by the moderator temperature. An incident beam of collimated neutrons with well-defined momentum $k_i$ (and corresponding wavelength and energy) is selected from the white spectrum of the neutrons’ source by the monochromator crystal (first axis). The monochromatic beam is scattered from the sample (second axis). The intensity of the scattered beam with momentum $k_f$ is reflected
by the analyzer crystal (third axis) onto the neutron detector, thereby defining the energy transfer $h\omega$ as well. Both the monochromator and the analyzer are used to select neutrons with specific wavelength and energy. They consist of crystals oriented to produce Bragg scattering according to Bragg’s law

$$n\lambda = 2d \sin(\theta), \quad (3.1)$$

where $n$ is an integer, $\lambda$ is the wavelength of the neutrons scattered by the monochromator, $d$ is the lattice spacing of the reflection, and $\theta$ is the angle between incident neutron and the crystal. Neutrons with different incident and final energies can be selected by varying the $\theta$ angle on the monochromator or analyzer. That will allow one to measure inelastic processes in matter.

One common problem when using Eq.(3.1) is higher-order wavelengths caused by $n \geq 1$ terms. These are diffracted from the monochromator with the same angle. To negate this problem of higher order neutrons, we use a Pyrolitic graphite filter. This filter passes primary neutrons with $n=1$ and blocks most of the higher order ($n \geq 1$) neutrons for certain incident neutron energies. At MURR, there are three options for monochromators. Pyrolittic graphite (PG002) would have high reflectivity, yielding a higher number of neutrons. A copper (Cu(220)) monochromator can be used to access higher energies, while silicon (Si(110)) can be used to completely eliminate second order ($n=2$) neutrons. For our research work, we employed a PG monochromator to obtain higher flux at the sample.

Apart from taking general scans in $Q$ and $\omega$, a major advantage of the triple-axis spectrometer is that the data can be taken at any pre-determined point in reciprocal space (constant $Q$ scans) or fixed energy transfers $h\omega$ (constant $E$ scans) along a par-
ticular direction in reciprocal space. In a neutron scattering spectrometer, momentum and energy transfers are defined as

\[ Q = k_i - k_f \] (3.2)

\[ \hbar \omega = E_i - E_f = \frac{\hbar^2}{2m}(k_i^2 - k_f^2) \] (3.3)

The derivation of many of the formulas in this section follows Shirane et al.\[41\]. In an attempt to keep this simple, a minimum of equations was used.

Reciprocal-space momentum transfer of Eq.(3.2) is illustrated in figure 3.1b. If \( \phi \) is the neutron flux on the sample and the \( \sigma \) is the total scattering cross section, then the total number of neutrons that will scatter from the sample is given by \( \phi \sigma \). We are interested in the partial differential cross section \( \frac{d^2 \sigma}{d\Omega dE_f} \), not the total cross section. The partial differential cross section is defined as the fraction of neutrons that scattered in the a solid angle \( d\omega \) in the direction of \( k_f \) with final energy between \( E_f \) and \( E_f + dE_f \).

The partial differential cross-section can be elegantly written according to the informative formalism due to Van Hove, who expressed it in terms of the dynamic structure factor \( S(Q, \omega) \) as \[42\]

\[ \frac{d^2 \sigma}{d\Omega dE_f} = N \frac{\sigma}{4\pi k_i} S(Q, \omega) \] (3.4)

The dynamic structure factor is the space and time Fourier transformation of the unequal-time pair correlation function. In general, it is a tensor quantity that relates two vector quantities, such as the spin moments, but for the moment we will consider
the scalar case of the neutron scattering. For such structural scattering $S(Q, \omega)$ is given by [43]

$$S(Q, \omega) = \frac{1}{2\pi\hbar N} \sum_{ij} \int_{-\infty}^{\infty} dt e^{-i\omega t} \langle e^{iQ[r_i(0) - r_j(t)]} \rangle$$  \hspace{1cm} (3.5)

where the average $\langle ... \rangle$ is over initial states of the system.

### 3.3 Alignments

#### 3.3.1 Spectrometer alignment

The triple-axis spectrometer must be aligned before running an experiment in order to take reliable data. Since at MURR, TRIAX is retracted for refueling purposes and the spectrometer axes shift due to mechanical and electrical reasons, it must be aligned before starting a new experiment after a layoff. TRIAX is controlled by the “SPICE” software developed at Oak Ridge National Laboratory. Following are the basic important steps for aligning any triple-axis spectrometer. The first step in aligning the spectrometer is to align the monochromator crystal. To achieve this, we use the neutron monitor counter with a mask as the detector and perform a rocking scan and drive the monochromator to the peak position. This will ensure a maximum number of neutrons for the experiment. The next step is to calibrate the energy of the incident neutron beam on the sample. For this, the analyzer has to be taken off and the detector set to looking at the straight beam. We then used a silicon powder sample to measure calculated peak positions. Next, we calculated $\theta$ values for at least 3 powder peaks at the incident energy of the neutrons, then drove the second
axis for each calculated $\theta$ value, performed scans over those peaks and noted the peak positions. Using the least squares method and the measured silicon peak positions, we determined the offsets in both the scattering angle $\theta$ and the monochromator angle for the TRIAX. We then encoded those offsets in the SPICE software. The next step was to find out the offset in the analyzer angle $\theta_a$. For this, we used vanadium. Any strong incoherent scattering sample would work. We then replaced the analyzer crystal. Next, we moved the spectrometer third axis to the correct energy and rocked $\theta_a$ to find the center of mass of the scan. We encoded the offset in $\theta_a$ in SPICE. The above steps are very basic steps for aligning a triple-axis spectrometer. For the complete alignment process please refer to “Practical Neutron Scattering at a Steady State Source” by Wouter Montfrooij and Tom Heitmann [44].

### 3.3.2 Sample alignment

When using a single grain crystal in neutron scattering experiments, a crucial part is aligning the crystal. For this procedure, we used the graphical user interface provided in “SPICE” software. Crystal alignment requires identifying two non-colinear reflections and creating a UB matrix to determine the orientation of the crystallographic axes. The UB Matrix relates the Miller indices of reciprocal vector (hkl) with its Cartesian coordinates in the lab reference system (XYZ) at zero goniometer position. UB matrix is composed of two sub-matrices, U and B. U describes the orientation of the crystal axes with respect to the XYZ reference system, while B stores information about the unit cell parameters. The UB matrix requires motor positions of the TRIAX corresponding to two peaks in those non-colinear planes and lattice constants with respective unit cell angles. In the $RMnO_3$ family, we used (H,K,0) and
(H,0,L) planes. The nuclear Bragg reflections used for alignment are at the (3,0,0) and (0,0,2) positions. We aligned one of these reflection planes along one of the Goniometer’s tilt axes to de-couple these crystal planes. Generally, crystal alignment is a time consuming process which tests your inner strength. Luckily, in floating-zone grown $\text{RMnO}_3$, we could identify the out-of-plane facet just by careful observations. Figure 3.2 shows the growth directions. The $c$ axis of $\text{RMnO}_3$ is perpendicular to this facet. The crystal grows more slowly along the $c$ axis. Because of this the crystal would not have a perfect cylindrical shape. The two facets at the end of the growth, perpendicular to $c$ axis will be flat (figure 3.2 top and bottom surfaces). This helped us identify the crystal’s (H,0,L) plane. Once we identified those peak positions, all the motor positions were entered into SPICE to calculate the UB matrix.

Once the sample was properly aligned, we put it inside the closed cycle helium cryostat. This enabled us to lower the temperature of the sample. The closed cycle helium cryostat can reach temperatures down to 4K. Once the sample cooled down below 70K, we again re-aligned the sample by creating a new UB matrix. This was carried out to compensate for any thermal contractions of the crystal due to cooling.

3.4 Elastic Magnetic Scattering

3.4.1 Antiferromagnetic Order Parameter

In a scattering process, the interaction operator ($\hat{U}$) of the neutron with the sample is given as

$$\hat{U} = -\gamma \mu_N \hat{\sigma}$$  \hspace{1cm} (3.6)
Figure 3.2: Illustrates the growth directions in \( RMnO_3 \) family. The crystal grows faster along the \( a-b \) plane. The top and bottom facets perpendicular to the \( c \) axis are flat.

where \( \gamma = -1.91 \) is the neutron gyromagnetic ratio, \( \mu_N = 5.05079 \times 10^{-27} \) J/T is the nuclear magneton, and \( \hat{\sigma} \) is the Pauli spin operator. This operator will act on a magnetic moment generated by unpaired electrons in a sample, and this interaction between the neutron’s magnetic dipole and the electron magnetic dipole will give rise to a scattering pattern. For unpolarized neutrons and identical magnetic ions with localized electrons, the spin-only differential magnetic cross section can be written as

\[
\frac{d^2\sigma}{dOmega dE_f} = (\gamma r_0)^2 \frac{k_f}{k_i} F^2(Q) e^{-2W(Q)} \sum_{\alpha, \beta} \left( \delta_{\alpha\beta} - \frac{\hat{Q}_{\alpha} \hat{Q}_{\beta}}{Q^2} \right) S^{\alpha\beta}(Q, \omega)
\]  

(3.7)

where \( r_0 \) is the classical electron radius, the sum is over all axes \( \alpha \) and \( \beta \), \( F(Q) \) is the dimensionless magnetic form factor defined as the Fourier transformation of the normalized spin density associated with the magnetic ions, and \( e^{-2W(Q)} \) is the Debye-Waller factor. The polarization factor \( \left( \delta_{\alpha\beta} - \frac{\hat{Q}_{\alpha} \hat{Q}_{\beta}}{Q^2} \right) \) tells us that only magnetic moments or spin fluctuations perpendicular to \( Q \) contribute to magnetic scattering. \( S^{\alpha\beta}(Q, \omega) \) is the magnetic dynamic structure factor, and is the Fourier transformation.
of the pair correlation function in space and time between spins. This can be written as

$$S^{\alpha\beta}(Q, \omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} \sum_l e^{iQ \cdot l} \left< S^{\alpha}_0(0) S^{\beta}_l(t) \right> e^{-i\omega t} dt$$  (3.8)

Elastic scattering ($\omega = 0$) measures the time-averaged magnetic structure. For antiferromagnets, spins orient anti parallel to each other. Thus, $<\hat{S}^z>$=0 and $S^z$ is defined as “staggered spin” which corresponds to zero field magnetization. For a magnetically ordered crystal, the elastic differential cross section is given as,

$$\frac{d\sigma_{coh}}{d\Omega_f} = N_M \frac{(2\pi)^3}{V_M} \sum_{G_M} \delta(Q - G_M) \left| F_M(Q) \right|^2$$  (3.9)

where $N_M (=N/2)$ is the number of magnetic unit cells in the crystal, and $V_M$ is the volume of the unit cell. The elastic magnetic form factor $F_M(Q)$, is given by

$$F_M(Q) = \frac{\gamma R_0}{2} \sum_j g_{fj}(Q) S^z_j e^{iQ \cdot d_j} e^{-w_j}$$  (3.10)

where $S^z_j$ is the spin component of site $j$ perpendicular to $Q$. This magnetic scattering will produce Bragg reflections according to 3.1, but due to the dependence of the scattering spin direction, determining which reflections are observable is more complicated.

Above the Néel temperature, where there are no long-range magnetic orders, the time-averaged moments are zero, so there is no magnetic Bragg scattering. For antiferromagnets below the Néel temperature, from Eq.(3.9), Eq.(3.10), the scattering intensity is proportional to the square of the staggered magnetization $M_{st}$, hence the
Figure 3.3: Figure illustrates the magnetic phase change in pure HoMnO$_3$. Circles correspond to the (1,0,0) reflection and the solid squares represent the (1,0,1) reflection. Black triangles correspond to (1,0,2) reflection.

The order parameter is given by:

$$I_m \sim |F_m(Q)|^2 \sim M_{st}^2 \sim (T_N - T)^{2\beta},$$

where $\beta$ is the critical exponent.

To date, HoMnO$_3$ has been a focal point when talking about hexagonal multiferroics due to its strong magnetic-ferroelectric coupling observed at the spin re-orientation temperature [35]. Magnetic structure in this compound exhibits multiple complex spin structures due to stacked triangular antiferromagnetic Mn ions. Key features of these magnetic phases include spin reorientation transitions around 40K and 5K involving triangular layers of Mn spins which form a 120° spin structure in-plane below the Néel temperature. Magnetic symmetry groups in HoMnO$_3$ are P6$_3$cm' and P6$_3$c'm[18]. Another interesting hexagonal multiferroic compound, YMnO$_3$, orders
only in the P6′3c′m phase, whereas both ErMnO3 and DyMnO3 were found to order only in the P6′3c′m magnetic phase group [36, 45].

Our primary objective was to study this spin reorientation from the P6′3c′m to the P6′3cm′ magnetic phase observed in pure HoMnO3 around 40K. YMnO3 orders in P6′3cm′, both ErMnO3 and DyMnO3 order in P6′3c′m and HoMnO3 exhibits both these phases. It would be logical to assume that HoMnO3 acts as a midway point between these phases. Doping yttrium into HoMnO3 should vary this spin reorientation temperature (T_{SR}). Mixing yttrium with either erbium or dysprosium should induce a similar spin reorientation, from P6′3c′m to P6′3cm′ in both Er_{1-x}Y_xMnO3 and Dy_{1-x}Y_xMnO3 for a given concentration (x) of yttrium.

In order to study this magnetic phase transition in Ho_{1-x}Y_xMnO3, Er_{1-x}Y_xMnO3 and Dy_{1-x}Y_xMnO3, we grew single grain crystal with different x compositions. We performed elastic neutron scattering on these crystals at varying temperatures in order to observe this spin reorientation. The crystals were each encapsulated inside a closed-cycle helium cryostat which has the capability of changing the temperature from room temperature down to 4K.

3.4.2 Ho_{1-x}Y_xMnO3

For hexagonal antiferromagnetic R锰O3, below T_N, the primary allowed magnetic Bragg reflections are (1,0,0) or (1,0,1). The (1,0,0) reflection corresponds to the P6′3cm′ magnetic phase and (1,0,1) corresponds to the P6′3c′m magnetic phase. The (1,0,2) reflection is both magnetic and structural, and is present in both magnetic phases but at different intensities [25]. Figure 3.3 shows the order parameter for pure HoMnO3 single crystal. When the spins undergo a 90° reorientation from P6′3c′m to
P6′_3cm′, there is a change in intensity of the magnetic Bragg reflections. In the P6′_3cm phase between T_N and above T_{SR} the (1,0,1) Bragg reflection dominates, while in the P6′_3cm phase below T_{SR} the (1,0,0) Bragg reflection dominates.

Figure 3.4: Figure illustrates the magnetic phase transitions in Ho_{1-x}Y_xMnO_3 for different yttrium concentrations. Squares represents the (1,0,0) reflection, whereas the solid circles represents the (1,0,1) reflection and (1,0,2) reflection is shown by solid triangles. The line is associated with the fit to the data near T_N.

Figure 3.4 shows the changes in spin reorientation temperature for different yttrium-doped HoMnO_3 single crystals. Here x is the yttrium concentration. The Néel temperature, T_N was obtained by fitting the peak intensity I of the dominant reflection above 60K to the form of a second-order phase transition Eq.(3.11). The values of
the critical exponent, $\beta$, vary from 0.187 to 0.244 and are very sensitive to the fitting range of data. These critical exponent values should not be considered as the true critical exponents of the Néel transition, but $T_N$ obtained from fitting can be considered reliable since they are not very sensitive to the fitting range. The fits include a small Gaussian spread in the transition temperature (shown by the error bars for $T_N$).

The magnetic phase boundary diagram for $\text{Ho}_{1-x}\text{Y}_x\text{MnO}_3$ with different yttrium concentrations using the results for $T_N$ and $T_{SR}$ is shown in Figure 3.5. The shift in scattering intensity from the (1,0,1) to the (1,0,0) with decreasing temperature indicates $T_{SR}$, and error bars indicate the width of this first-order transition. With increasing yttrium concentration, $T_{SR}$ increases towards $T_N$ and eventually at $x = 0.88$, $T_{SR}$ completely vanishes. The magnetic phase diagram for $\text{Ho}_{1-x}\text{Y}_x\text{MnO}_3$ we obtain is consistent with previous work done by Zhou et al. [46].

3.4.3 Dy$_{1-x}$Y$_x$MnO$_3$

DyMnO$_3$ orders in $P6'_3cm'$, and YMnO$_3$ orders in the $P6'_3c'm$ magnetic phase. In HoMnO$_3$, the magnetic phase shifts from $P6'_3c'm$ to $P6'_3cm'$ with decreasing temperature. In order to study this phase boundary without holmium, we mixed different compositions of Dy$_{1-x}$Y$_x$MnO$_3$. According to our previous assumption, the Néel temperature for these compositions should be similar to the $T_N$ observed in $\text{Ho}_{1-x}\text{Y}_x\text{MnO}_3$. The magnetic phase transition should occur at a temperature below Néel temperature.

Figure 3.6 shows the magnetic phase changes for different $x$ values of Dy$_{1-x}$Y$_x$MnO$_3$. Results were obtained by elastic neutron scattering measurements. A major draw-
Figure 3.5: Figure shows the phase diagram of Ho$_{1-x}$Y$_x$MnO$_3$ extracted from the order parameter measurements with different yttrium concentrations. White circles indicate $T_N$, black triangles indicate onset of $T_{SR}$. Dashed line is a guide to the eye. Solid line is a linear least-squares fit for $T_N$ data.

back we encountered while taking these data was the higher absorption of neutrons by dysprosium. The Néel temperature, $T_N$, was obtained by fitting (1,0,0) peak intensity data above 60 K to the form of a second-order phase transition. The obtained values of the critical exponent $\beta$ varied from 0.187 to 0.333. At Y concentrations $x$ of 0.8 and below (Dy concentrations of 0.2 and above), a decrease in the scattering intensity at the (1,0,0) position is observed at low temperatures, along with a clear increase in scattering intensity at the (1,0,1) position for $x = 0.7$ and 0.6. These shifts in scattering intensity indicate the onset of a spin reorientation, which appears to be spread out in temperature. Sample environment limitations prevented measurements at low enough temperatures to determine the lower limit of the transition region, but the upper onset temperature of the transition has been plotted in the lower right panel.
Figure 3.6: Order parameters for Dy$_{1-x}$Y$_x$MnO$_3$ at different concentrations $x$. Squares show the (1,0,0) peak intensity, circles show the (1,0,1) peak intensity. The (1,0,0) reflection is associated with the $P6'_3cm'$ phase, while the (1,0,1) reflection is associated with the $P6'_3c'm'$ phase. Lines show fits to the (1,0,0) order parameter data near $T_N$. Lower right panel shows the phase diagram extracted from order parameter measurements. White squares indicate $T_N$ and black circles indicate the onset of $T_{SR}$, and lines are linear least squares fits.

of figure 3.6. Interestingly, (1,0,0) has dominant scattering above $T_{SR}$, in contrast to pure HoMnO$_3$ or yttrium doped Ho$_{1-x}$Y$_x$MnO$_3$, while $T_{SR}$ decreases with decreasing yttrium concentration. This trend in $T_{SR}$ reverses when holmium is present.

3.4.4 Er$_{1-x}$Y$_x$MnO$_3$

Similarly to dysprosium, erbium orders in $P6'_3c'm'$. When we doped dysprosium to yttrium, the phase transition occurred from $P6'_3cm'$ to $P6'_3c'm'$, which was the reverse
of what was observed when holmium was present, and the spin reorientation temperature decreased with decreasing yttrium. We decided to dope yttrium into erbium to study this reversal of magnetic phases in the absence of holmium. Figure 3.7 illustrates our data. When $\text{Er}_{1-x}\text{Y}_x\text{MnO}_3$ undergoes a spin reorientation transition, the neutron scattering intensity shifts from the (1,0,0) Bragg reflection to the (1,0,1) reflection (or vice versa). As with $\text{Dy}_{1-x}\text{Y}_x\text{MnO}_3$, for $x \geq 0.95$, $P6'_3c'm'$ is the higher temperature phase. We can estimate the spin reorientation temperature $T_{\text{SR}}$ from our order parameter data for $x=0.94$ and 0.95 samples as well, though for our $x=0.94$ the upper transition is not very well defined (figure 3.7 top right). By measuring the full temperature dependence of the order parameters at (1,0,0) and (1,0,1) we are able to form a picture of the phase boundary between the $\text{ErMnO}_3$ and the $\text{YMnO}_3$ sides.

Figure 3.7: Order parameters for $\text{Er}_{1-x}\text{Y}_x\text{MnO}_3$ at different concentrations $x$. Squares show the (1,0,0) peak intensity, triangles show the (1,0,1) peak intensity. The (1,0,0) reflection is associated with the $P6'_3c'm'$ phase, while the (1,0,1) reflection is associated with the $P6'_3cm'$ phase. Lines show order parameter fits to data near $T_N$. 
of the Er$_{1-x}$Y$_x$MnO$_3$ phase diagram (figure 3.8). The phase boundary appears to be confined to a very narrow compositional range close to the YMnO$_3$ side of the phase diagram, and the P6$'_3$c$'$m phase is actually a low-temperature reentrant phase for $x = 0.94$. These results compare well to previous reports for $T_N$ from powder diffraction by Chandra Sekhar et al. [47]. Although they did not report a spin reorientation temperature, they did report a dramatic change in the 10K magnetic ordering between $x=1$ and $x=0.93$, in agreement with our single-crystal results.

Figure 3.8: Magnetic phase diagram for Er$_{1-x}$Y$_x$MnO$_3$. White squares are $T_N$ and black triangles are $T_{SR}$, obtained from the order parameter measurements shown in Figure 3.7. White circles are low-concentration results from Chandra Sekhar et al. [47], and our results are in good agreement with their higher concentrations as well. Lines are guides to the eye. The grey area shows the approximate extent of the P6$'_3$c$'$m phase. (b) Shows an expanded view of the phase boundary. Note that at $x = 0.06$, the P6$'_3$c$'$m phase exhibits reentrant behavior, and that at $x \geq 0.05$, the P6$'_3$cm$'$ phase is the high-temperature phase, in contrast to Ho$_{1-x}$Y$_x$MnO$_3$[46].

3.5 Quasielastic Magnetic Scattering in RMnO$_3$

Inelastic neutron scattering experiments where a finite energy is exchanged between neutrons and the sample are used to study either periodic motions like atomic vibra-
Figure 3.9: Figure illustrates the distinction between elastic scattering and quasielastic scattering. Both scattering types centered at the 0 meV energy transfer. The dashed line corresponds to the elastic scattering while the solid line shows the quasielastic scattering. The elastic scattering is in the form of a sharp peak, while the quasielastic scattering is much broader.

...tions, spin waves or the thermally activated stochastic molecular motions which show up as a broadened elastic line known as quasielastic line. Quasielastic neutron scattering contains both coherent and incoherent scattering components. Measurements of quasieelastic scattering usually involves small energy transfer, typically less than 1 meV, centered at zero energy transfer (figure 3.9).

Below the Néel temperature, inelastic measurements of YMnO$_3$ revealed quasielastic scattering mainly around (1,0,1) and secondary scattering around the (1,0,2) Bragg positions. Example data taken at 30K are shown in figure 3.10, which reveal a peak centered at zero energy transfer but with an energy width much larger than instrumental resolution. Scans along the $H$ and $L$ directions (in-plane and out-of-plane, respectively) were performed at a constant energy transfer of 0.7 meV in order to
Figure 3.10: Measurements of the quasielastic scattering in YMnO$_3$ at 30K. Scattering is centered at the $Q=(1,0,1)$ position, and scans were taken with varying energy (a), in-plane momentum (b), and out-of-plane momentum (c). Momentum scans were taken with fixed energy transfer of 0.7 meV to reduce elastic scattering background. Note that quasielastic scattering is also present around the $(1,0,2)$ position.

reduce elastic Bragg scattering. Previous work done by Sato et al. [48] reported quasi-elastic scattering with similar in-plane $H$ momentum transfers, but with no observed out-of-plane momentum dependence.

We carried out quasielastic measurements for other compositions of Ho$_{1-x}$Y$_x$MnO$_3$. Similar quasielastic scattering was also observed in Ho$_{1-x}$Y$_x$MnO$_3$ samples for $0 < x \leq 1$. No quasielastic scattering was observed for pure HoMnO$_3$. Figure 3.11 shows scattering intensity maps as a function of $H$ and $L$ at three different temperatures for Ho$_{0.25}$Y$_{0.75}$MnO$_3$. Measurements were taken at a constant energy transfer of 0.5 meV to reduce elastic background scattering. Above $T_N$, the scattering is broad in the H direction and shows no L dependence, as shown in figure 3.11(a), indicating short-range in-plane correlations with no out-of-plane correlations. Near $T_N$ the
quasielastic scattering shows two quasielastic peaks (figure 3.11 (b)) centered at the (1,0,0) and (1,0,1) positions. Below T_N, scattering becomes sharper in both in plane and out of plane directions, and is only centered around the (1,0,0) position at 60K (figure 3.11(C)). A striking result is the position of this quasielastic scattering below T_N. For the 25% holmium sample, below T_N and above T_{SR}, the system is in the P6\text{3}c\text{'}m magnetic phase. The corresponding Bragg reflection is (1,0,1). The observed quasielastic peak is in the “wrong phase”. Further analysis of our results revealed a similar shift in the quasielastic scattering for other samples and temperatures. Figure 3.12 illustrates the shifting of the quasielastic peak position from (1,0,0) to (1,0,1) around T_{SR} for two different concentrations of Ho_{1-x}Y_xMnO_3. When the system is in the P6\text{3}cm\text{'} phase below T_{SR}, the magnetic Bragg reflection is located at (1,0,0)
(lower panel) and the quasielastic scattering is located at (1,0,1)(upper panel). Above $T_{SR}$, the magnetic Bragg reflection is located at (1,0,1) and the quasielastic scattering shifts to (1,0,0) positions. Figure 3.12 illustrates that with decreasing temperature, the intensity of the scattering from corresponding magnetic phase decreases as well.

Figure 3.12: Top panels: measurements of the out-of-plane dependence of quasielastic scattering versus temperature for two compositions of Ho$_{1-x}$Y$_x$MnO$_3$. Bottom panels: order parameter measurements of the same samples over the same temperature range. At the spin reorientation temperature, elastic Bragg scattering shifts from the (1,0,1) position to the (1,0,0) position upon cooling, while quasielastic scattering shifts from the (1,0,0) position to the (1,0,1) position at the same temperature. Scattering with a very narrow L width is also visible in the top panel, and is due to the tail end of the resolution ellipsoid clipping the Bragg reflection.

Inelastic neutron scattering measurements of Er$_{1-x}$Y$_x$MnO$_3$ have revealed similar quasielastic magnetic scattering centered around zero energy transfer but much broader than energy resolution. Example constant-Q energy scans are shown in figure 3.13 for various temperatures in Er$_{0.2}$Y$_{0.8}$MnO$_3$. The sharp central peak is incoherent.
Figure 3.13: Figure shows the inelastic scan for $\text{Er}_0.2\text{Y}_0.8\text{MnO}_3$ at different temperatures. The central sharp peak at $E=0$ is from the elastic scattering. As the temperature approaches the Néel temperature, a broad peak emerges due to the quasielastic scattering. Intensity is plotted in log scale, and scans are offset vertically for clarity.

Elastic scattering. The broad quasielastic scattering is strongest near $T_N$, and drops off at lower temperatures, almost vanishing at the lowest temperatures. The figures 3.14 and 3.16 show inelastic scattering measurements at constant energy transfer of 0.7 meV for two compositions. Above $T_N$, the quasielastic scattering is essentially independent of $L$, but becomes $L$-dependent below $T_N$. In $\text{Er}_{0.05}\text{Y}_{0.75}\text{MnO}_3$ (figure 3.14) the quasielastic peak is centered around the $Q=(1,0,1)$ position in the magnetic phase. The sharp peak near the $(1,0,0)$ position is due to the scattering resolution ellipsoid clipping the magnetic Bragg peak. In contrast, the quasielastic peak in $\text{Er}_{0.2}\text{Y}_{0.8}\text{MnO}_3$ (figure 3.16) is centered around the $Q=(1,0,0)$ position in the magnetic phase, as shown below right. These measurements reveal similar results to the $\text{Ho}_{1-x}\text{Y}_x\text{MnO}_3$ system. When the system is in the $P6'\text{cm}'$ phase and the Bragg peak is located at $Q=(1,0,0)$, then the quasielastic peak is located at $Q=(1,0,1)$, and when the system is in the $P6_3\text{cm}'$ phase and the Bragg peak is located at $Q=(1,0,1)$, then
the quasielastic peak is located at $Q=(1,0,0)$. Figure 3.14 and 3.15 clearly shows the dropping of the intensity of the quasielastic peak with decreasing temperatures down to 5K. Above $T_N$ the temperature smeared out faster. Other systems also exhibit this correlation between intensity and temperature. It is noteworthy to mention that as with pure HoMnO$_3$, no quasielastic scattering is observed in pure ErMnO$_3$ [47].

![Contour map of inelastic scattering intensity for Er$_{0.05}$Y$_{0.95}$MnO$_3$ at constant energy transfer of $\omega=0.7$ meV as a function of out-of-plane momentum transfer $Q_L$ and temperature $T$. Above $T_N$, the quasielastic scattering shows no significant $Q_L$ dependence. Below $T_N$, the quasielastic scattering shows a broad peak centered around $Q=(1,0,1)$. The intensity of this quasielastic scattering is suppressed at lower temperatures. The narrow peak observed near $Q=(1,0,0)$ below $T_N$ is due to the resolution ellipsoid clipping the magnetic Bragg peak, and is offset from (1,0,0) due to the tilting of the resolution ellipsoid in the $Q_L$-$\omega$ plane. The data extends down to 5 K, so the region of the graph below that is left blank.](image-url)
Figure 3.15: Figure illustrates the temperature dependence of the out-of-plane quasielastic scattering. Line is a guide to the eye. Shows the highest scattering at $T_N$ and the intensity drops with temperature.

Figure 3.16: Figure shows the inelastic contour map for $\text{Er}_{0.2}\text{Y}_{0.8}\text{MnO}_3$. Quasielastic scattering is located at (1,0,0).

We found similar quasielastic scattering for $\text{Dy}_{1-x}\text{Y}_x\text{MnO}_3$ as well. But due to the higher neutron absorption in Dy, scattering intensity drops considerably for higher concentrations of Dy single crystals. Figure 3.17 shows the comparison between elastic scattering and quasielastic scattering at 50K for $\text{Dy}_{0.2}\text{Y}_{0.8}\text{MnO}_3$. Width of
energy scan is much broader than the resolution width, indicating that (1,0,1) corre-
sponds to quasielastic scattering. From figure 3.6, it is evident that system is in the
P6′3′cm′ magnetic phase, but figure 3.17 indicates quasielastic scattering originating
from the P6′3′c′m magnetic phase.

Figure 3.17: Measurements of the quasielastic scattering in Dy_{0.2}Y_{0.8}MnO_3 at 50K.
Scattering is centered at the Q=(1,0,1) position, and scans were taken with varying
energy (a), in-plane momentum (b), and out-of-plane momentum (c). Momentum
scans were taken with fixed energy transfer of 0.7 meV to reduce the elastic scattering
background. A sharp peak near the (1,0,0) position is due to the tail of the resolution
ellipsoid clipping the magnetic Bragg peak.

Figure 3.18 illustrates inelastic scans performed along the out-of-plane direction
(1,0,L). For the Dy_{0.3}Y_{0.7}MnO_3 composition, T_{SR} is around 17K and P6′3′c′m is the
low temperature magnetic phase (figure 3.6). Scans were done at 5K and 66K and
show the shifting of this quasielastic peak from (1,0,0) to (1,0,1) with increasing
temperature.
Figure 3.18: Inelastic scans performed along (1,0,L) for Dy$_{0.3}$Y$_{0.7}$MnO$_3$ show the shifting of this quasielastic peak from (1,0,1) Bragg position to (1,0,0) Bragg with decreasing temperature. Solid line and square data points correspond to data taken at 5K. Dashed line and circular data points are from 66K measurements. For this composition, T$_{SR}$ is around 17K.

3.6 Quasielastic scattering using triple-axis spectrometer RMnO$_3$

A triple-axis spectrometer does not simply measure the partial differential cross section directly, but a convolution of the differential cross section with the instrumental resolution. This is due to the fact that the neutron beam has a nonzero divergence which depends on the width of the blades in collimator, and due to mosaic spread in the monochromator and analyzer (see figure 3.1). Due to these multiple variables, the resolution function is a complex function [50].

The measured intensity $I$ can be expressed as

$$I(Q,\omega) = \phi \int R(\Delta Q, \Delta \omega) \left[ \frac{d^2\sigma}{d\Omega dE_r}(Q - \Delta Q, \omega - \Delta \omega) \right] d\Delta Q d\Delta \omega \quad (3.12)$$

The resolution function $R(\Delta Q, \Delta \omega)$ is determined by the instrument parameters, which are collimations, the mosaic spread of both monochromator and the analyzer,
Figure 3.19: Plot of a 3-D representation of the spin wave dispersion in a one-dimensional s=1 antiferromagnet near the 1D zone-center. On top of that, it shows resolution ellipsoids for each point of a pre-defined constant-Q scan, as well as projections of these ellipsoids on the coordinate planes. The dispersion surface is cut open for better visibility of the resolution ellipsoid. Image from [49].

the scattering wave vector $\mathbf{Q}$, and the energies $E_i$ and $E_f$ [51, 52, 53]. This resolution function can be visualized as an ellipsoid in $(\omega, \mathbf{Q})$ space. During our data analysis, the fitting functions were convoluted with the instrumental resolution function to get a better fit.

The most significant part of analyzing data measured by the Triple-Axis Spectrometer (TRIAX) is the proper evaluation of the experimental resolution function. In general, one needs to 1) calculate the resolution function at each data point, using
sample parameters and TRIAX configurations, 2) convolute the resolution function with the theoretical cross section and 3) fit the numerically convoluted cross section to the data in order to extract the information from the raw scattering data.

Due to the complexity of the resolution function, a numerical fitting function is necessary to simulate its effect. One package that includes such capability is ResLib, written by A.Zheludev at ORNL [49]. This package needs to be used in conjunction with MATLAB software. An example of the resolution function as calculated by the ResLib package is shown in figure. 3.19. The central ellipsoids in the figure represent the movement of the resolution function along the energy axis, corresponding to a constant-$Q$ scan through the dispersion surface, along with various projections of the resolution ellipsoids. We used ResLib library with MATLAB to analyzer our quasielastic data. ResLib utilizes Cooper-Nathans and Popovici approximations to calculate the resolution function. Sample parameters include lattice constants, unit cell angles and rough sample mosaic. Instrument parameters include monochromator and analyzer crystal d-spacings, rough mosaic, scattering directions and collimation, as well as fixed neutron energy, including fixed axis.

### 3.7 Mathematical model fits for quasielastic scattering data

When correlations are exponentially damped in time, the form factor takes the form of a Lorentzian distribution in energy. To understand the quasielastic scattering function, one would typically use dynamic susceptibility. The generalized susceptibility $\chi$ is a complex function with both imaginary and real parts. The imaginary and the
Figure 3.20: Measurements of the quasielastic scattering in YMnO$_3$ at 30K. Scattering is centered at the $Q=(1,0,1)$ position, and scans were taken with varying energy (a), in-plane momentum (b), and out-of-plane momentum (c). Momentum scans were taken with fixed energy transfer of 0.7 meV to reduce the elastic scattering background. Note that quasielastic scattering is also present around the (1,0,2) position. Lines are fits to the data described in the text. The solid line in (c) shows the fit result using a Gaussian for the out-of-plane dependence, while the dashed line shows the fit result using a Lorentzian.

Real parts are connected through a correlation function $\chi''$

$$\chi''(Q, \omega) = \chi'(Q, 0)\omega F(Q, \omega)$$  \hspace{1cm} (3.13)

where spectral weight function $F(Q, \omega)$ satisfying the normalization condition

$$\int_{-\infty}^{\infty} F(Q, \omega) d\omega = 1$$  \hspace{1cm} (3.14)
Since, the spin excitations are damped exponentially in time, the appropriate form of the weight function is a Lorentzian in the form,

\[ F(Q, \omega) = \frac{1}{\pi} \frac{\Gamma}{\omega^2 + \Gamma^2} \]  

so that modified

\[ \chi''(Q, \omega) = \frac{\chi'(Q, 0)}{\pi} \frac{\omega \Gamma}{\omega^2 + \Gamma^2} \]  

where \( \Gamma \) is the width of the energy and has to be comparable to the energy resolution. The data were fitted to a structure factor \( S(Q, \omega) \) convoluted with the spectrometer resolution, where the structure factor model was given by the following equation:

\[ S(Q, \omega) = \frac{\chi''(Q, \omega)}{1 - e^{-h\omega/k_BT}} \]  

4-dimensional structure factor involving energy, two in-plane and out-of-plane momentum transfers, can be written as

\[ S(Q, \omega) \propto \frac{1}{1 - e^{-h\omega/k_BT}} \frac{\Gamma \omega}{\Gamma^2 + \omega^2} \frac{W^2_\parallel}{\Delta H^2 + W^2_\parallel} \frac{W^2_\parallel}{\Delta K^2 + W^2_\parallel} e^{-\frac{\Delta L^2}{W^2_\perp}} \]

where, \( \omega \leq E_i \)

\( W_\parallel \) is the in-plane width of the scattering, \( W_\perp \) is the out-of-plane width, and \( \Gamma \) is the energy width. \( \Delta H, \Delta K, \) and \( \Delta L \) are the difference in H, K, and L respectively from the center of the quasielastic scattering. The first fraction is the Boltzmann term, followed by Lorentzian in energy and in-plane momenta \( H \) and \( K \). The last term is a Gaussian in out-of-plane momentum \( L \). Figure 3.20(c) shows fits using both the above static structure factor (solid line) and a similar form using a Lorentzian instead of
a Gaussian for the out-of-plane dependence, and the Gaussian fits produced visibly better results. Fits were performed for various temperatures as well as different Ho\(_{1-x}Y_x\)MnO\(_3\) compositions. The Gaussian function for out-of-plane momentum transfer consistently gave better results. \(\omega\), the energy is always less than or equal to the energy of the incoming neutrons. Otherwise, this function will diverge.

![Figure 3.21: Out-of-plane correlation length for quasielastic scattering in YMnO\(_3\) versus temperature. The line is a fit to the heuristic form described in the text. Correlation length is given in lattice constant units (l.c.u)](image)

The out-of-plane correlation length in lattice units is \(\propto 1/W_\perp\), and results are plotted in Figure 3.21. The data were fit to the heuristic form. Out-of-plane lattice constant \(c\) is generally around 11.4 Å.

\[
I \propto (T_N - T)^{2\lambda}.
\]  

(3.19)

where \(\lambda \approx 0.26\) for the above fit. With increasing temperature, the out-of-plane correlation length decreases, and above \(T_N\) no apparent out-of-plane correlations persist. Similar results were observed for other compositions of Ho\(_{1-x}Y_x\)MnO\(_3\).

When performing inelastic scans, especially at low energy transfer, the resolution ellipsoid tail clipping the Bragg peak can be a problem. When performing mathe-
Figure 3.22: Measurements of the quasielastic scattering in Ho$_{0.25}$Y$_{0.75}$MnO$_3$ at 70K. Scattering is centered at the Q=(1,0,0) position, and scans were taken with varying energy (a), in-plane momentum (b), and out-of-plane momentum (c). Momentum scans were taken with fixed energy transfer of 0.5 meV to reduce elastic scattering background. Lines are the fitted model explained in the text. Circular data points were considered for the fitting, while triangular data points were omitted.

Mathematical fits for data, accounting for this clipping is essential for obtaining a better fit. Consequently, this will improve the accuracy of the extracted data from the fits. Figure 3.22(C) illustrates such a situation. For the out-of-plane scan, $L=0.05$ and 0.1 show an unusually high scattering intensity. The best way to resolve this situation and get a better understanding of this high scattering is to plot the resolution ellipsoid for these points. This will show if the ellipsoid is clipping the Bragg peak or not. Figure 3.23 illustrates the calculated resolution ellipsoid projections at Q = (1,0,0.05), (1,0,0.1) on various axes at (1,0,0) momentum transfer with 0.5 meV energy transfer. On the upper left is the projection onto the scattering plane (H,L).
Figure 3.23: Calculated resolution function for a the data point at (1,0,0.05) and (1,0,0.1) using sample parameters and instrument configurations.

On the upper right is the H (Q_Y) - E projection, while on the lower left is the L(Q_X) - E projection. A careful look at the L - E projection shows the the scan performed at Q=(1,0,0.1) clipping of the Bragg peak and scan Q=(1,0,0.05) very close to the Bragg peak. The Bragg peak is located at 0 meV. Since ResLib gives an approximation of the resolution ellipsoid, it is safe to assume based on the data, that the Q = (1,0,0.05) scan clips the resolution ellipsoid as well. Allowing these data points in the fitting would skew our fitting. In our analysis work, we omit these clipping points to gain better fits.
Chapter 4

Discussion

Our neutron scattering studies provided new insights into this family of $RMnO_3$. Elastic neutron scattering showed that the phase transition from one magnetic phase to other is much more complicated than we had assumed previously. Quasielastic neutron scattering established that the presence of yttrium induces strong magnetic phase coupling. Following is a detailed discussion of conclusions drawn regarding the $RMnO_3$ family, from our data.

4.1 Magnetic order parameter analysis

Elastic neutron scattering revealed the magnetic structure in the $RMnO_3$ family. Our studies were concentrated between the 80K - 5K temperature region. At this range, the magnetism is due to the magnetic spin ordering of $Mn^{3+}$ ions.

The $Mn^{3+}$ spins in all hexagonal manganites order antiferromagnetically below their respective Néel temperatures, $T_N$. The $Mn^{3+}$ sublattice structure stacked along
the $c$ axis is the key to the magnetic order in hexagonal symmetry. The four key in-plane magnetic space groups associated with Mn$^{3+}$ spin orientations are, $P6_3cm$, $P6_3c'm'$, $P6'_3cm'$ and $P6'_3c'm$. Corresponding irreducible representations are $\Gamma_1$, $\Gamma_2$, $\Gamma_3$ and $\Gamma_4$. Apart from the above in-plane space groups, there exist two more two-dimensional irreducible representations [54]. Analysis of the magnetic phase diagram of $R\text{MnO}_3$ compounds via neutron scattering is complicated by the fact that different phases can produce almost identical unpolarized neutron scattering signatures. For the Mn$^{3+}$ order, the $P6_3c'm'$ and $P6'_3c'm$ phases both have strong Bragg scattering at the $(1,0,1)$ position and weak Bragg scattering at $(1,0,0)$, while the $P6_3cm$ and $P6'_3cm'$ phases have strong scattering at $(1,0,0)$ and zero scattering at $(1,0,1)$ [55].

Pure YMnO$_3$ orders antiferromagnetically only in the $P6'_3cm'$ symmetry group, and experiences no spin reorientation at zero field [17]. Both ErMnO$_3$ and hexagonal DyMnO$_3$ initially order in the $P6'_3c'm$ phase, and transition to $P6'_3c'm'$ phase at very low temperature, and even have very similar magnetic-field-dependent phase diagrams [17, 45]. yttrium does not posses magnetic moment, but both erbium and dysprosium do. The Mn$^{3+}$ moments in HoMnO$_3$ initially order in the $P6'_3c'm$ phase before undergoing a spin reorientation into the $P6'_3cm'$ phase at around 40K, and finally a second spin reorientation (and ordering of Ho$^{3+}$ moments) into a $P6_3cm$ phase around 7K [56]. Our studies found that YMnO$_3$, HoMnO$_3$, and ErMnO$_3$ all have similar Neel temperatures and confirmed that ErMnO$_3$ orders exclusively in the $P6'_3c'm$ phase, YMnO$_3$ orders exclusively in the $P6'_3cm'$ phase, and HoMnO$_3$ experiences a spin reorientation between the two phases at roughly half its $T_N$. These observations are true for temperatures above 5K.

The $T_N$ values obtained from the heuristic fits for the second order phase transi-
tions for all the hexagonal compounds were not very sensitive to the data range, but the critical exponent, $\beta$, was very sensitive. This could be attributed to the extinction effect which occurs in neutron scattering when using single grain crystals with considerably larger diameters. The back of the crystal gets exposed to a lower number of neutrons than the front side. The fits also include a convoluted small Gaussian spread at the transition temperature (shown by the error bars for $T_N$) to account for Mn$^{3+}$ in transition.

4.1.1 Ho$_{1-x}$Y$_x$MnO$_3$

Our order parameter studies using neutron scattering for yttrium doped HoMnO$_3$ (figure 3.4 and 3.5) confirmed the previous work by Zhou et al. [46]. They used magnetic susceptibility measurements to map out the translation of the $T_{SR}$. With increasing yttrium concentrations, the $T_{SR}$ increases as well. In pure HoMnO$_3$, the sample preparation method has an impact on $T_{SR}$. Samples prepared by different groups, using floating zone or flux grown techniques, have reported slightly different transition temperatures and in some occasions even different phases [33, 35, 57]. Our measurements yield a $T_{SR}$ around 38K for pure HoMnO$_3$, which agrees with Zhou’s measurements. Zhou also used floating zone grown crystals [46]. In our studies, the magnetic phase transition in Ho$_{1-x}$Y$_x$MnO$_3$ was pushed to 58K by the 82.5% yttrium.

4.1.2 Dy$_{1-x}$Y$_x$MnO$_3$

Elastic scattering measurements of Dy$_{1-x}$Y$_x$MnO$_3$ revealed some interesting results which are the opposite of those observed for Ho$_{1-x}$Y$_x$MnO$_3$. Recent results ob-
tained by Helton et al. indicate that the high-temperature magnetic phase for Dy<sub>0.5</sub>Y<sub>0.5</sub>MnO<sub>3</sub> is either P6<sub>3</sub>cm or P6<sub>3</sub>'cm<sup>'</sup>[55]. Our current work does not conclusively prove which of the two phases Dy<sub>1-x</sub>Y<sub>x</sub>MnO<sub>3</sub> exhibits, since both magnetic phases P6<sub>3</sub>cm and P6<sub>3</sub>'cm<sup>'</sup> produce similar scattering for unpolarized neutrons. Due to the identical scattering patterns, it is not possible to differentiate the phases when using unpolarized neutrons. However, since Dy<sub>1-x</sub>Y<sub>x</sub>MnO<sub>3</sub> contains yttrium and we know that it is in the P6<sub>3</sub>'cm<sup>'</sup> phase, this suggests that it is unlikely that the P6<sub>3</sub>cm phase exists in Dy<sub>1-x</sub>Y<sub>x</sub>MnO<sub>3</sub>. Further evidence is the fact that the order parameter transitions smoothly from x = 1 (pure YMnO<sub>3</sub>) to x = 0.6.

In our work, we found that the onset of the phase transition occurs around 14K for 2% dysprosium doped Dy<sub>1-x</sub>Y<sub>x</sub>MnO<sub>3</sub> and that the onset temperature increases with increasing Dy concentration. For 4% dysprosium, the upper bound of T<sub>SR</sub> was found to be around 25K. However, our results appear to be inconsistent with the results found by Helton et al. and Nair et al., who found T<sub>SR</sub> for their Dy<sub>0.5</sub>Y<sub>0.5</sub>MnO<sub>3</sub> sample to be around 10K using neutron scattering measurements [55, 58]. Our measured T<sub>SR</sub> data for different Dy<sub>1-x</sub>Y<sub>x</sub>MnO<sub>3</sub> compositions changes linearly with dysprosium concentration (figure 3.6 bottom right). It is unlikely that T<sub>SR</sub> would go to 10K for Dy<sub>0.5</sub>Y<sub>0.5</sub>MnO<sub>3</sub> according to our data. Because this discrepancy appears in similar types of neutron scattering measurement, the most likely source is some difference in the samples themselves beyond simply concentration.

All our samples (Dy<sub>1-x</sub>Y<sub>x</sub>MnO<sub>3</sub>, x=1, 0.9, 0.8, 0.7, 0.6), and the previously mentioned Dy<sub>0.5</sub>Y<sub>0.5</sub>MnO<sub>3</sub>, were grown using an optical floating zone furnace, but the atmospheric conditions where the Dy<sub>0.5</sub>Y<sub>0.5</sub>MnO<sub>3</sub> was grown were not specified. It is known that hexagonal DyMnO<sub>3</sub> must be grown in an argon atmosphere, while
Figure 4.1: Proposed magnetic phase diagrams for Dy\(_{1-x}\)Y\(_x\)MnO\(_3\) with different growth conditions. Light gray (red in color) represents the P6\(_3\)cm\(^{'}\) phase corresponds to (1,0,0) magnetic Bragg peak, while dark gray (blue) corresponds to (1,0,1) Bragg peak, which is prominent for P6\(_3\)cm phase. White colored phase corresponds to Dy\(^{3+}\) ordering in P6\(_3\)cm phase. Our samples would correspond to the left graph, Helton et al. would corresponds to the right.

Pure DyMnO\(_3\) grown in an air turns out to be in an orthorhombic structure [59]. We were successful in growing single grain hexagonal crystals of Dy\(_{1-x}\)Y\(_x\)MnO\(_3\) for \(x \geq 0.6\) in air. Attempts to grow hexagonal Dy\(_{1-x}\)Y\(_x\)MnO\(_3\) crystals with higher dysprosium concentration failed. This was confirmed by X-Ray analysis work we did with a high concentration of Dy in Dy\(_{1-x}\)Y\(_x\)MnO\(_3\) powders, where both hexagonal and orthorhombic phases showed up. It is not clear from previous reports whether the Dy\(_{0.5}\)Y\(_{0.5}\)MnO\(_3\) samples were grown under air or argon. The fact that DyMnO\(_3\) is orthorhombic when grown under air means that it is sensitive to oxygen. Having extra oxygen concentration in Dy\(_{1-x}\)Y\(_x\)MnO\(_3\) could create lattice stress, which may favor one structural phase over the other. Generally, RMnO\(_3\) is orthorhombic if the rare earth ionic radius is large enough, i.e. \(r_R \geq r_{Dy}\) [60]. The source of sample differences remains an open question, but there is little doubt that some difference exists. Figure 4.1 illustrates a possible phase boundary diagram for Dy\(_{1-x}\)Y\(_x\)MnO\(_3\) grown under different conditions. The diagram was drawn based on data from our work and Helton et al.
Despite these differences, we can still draw some conclusions about the general low-temperature phase diagram of Dy$_{1-x}$Y$_x$MnO$_3$. It is well established that Ho$^{3+}$ ordering occurs below 5K [59, 61]. Due to this, our observed transition, which begins at 25K in Dy$_{0.4}$Y$_{0.6}$MnO$_3$, is unlikely to be due to Dy$^{3+}$ ordering, so it must be a spin reorientation of the Mn$^{3+}$ ordering into either a P6$_3$cm' or P6$_3$c'm phase. Polarized neutrons are required to exactly distinguish these orderings, but pure DyMnO$_3$ exhibits the P6$_3$c'm phase, so it seems most probable that this low temperature transition is into the P6$_3$c'm phase. This would produce an inverted phase boundary transition compared to Ho$_{1-x}$Y$_x$MnO$_3$ (figure 3.4). At temperatures below what we could access, we expect that the Dy$^{3+}$ moments should order, and Dy$_{1-x}$Y$_x$MnO$_3$ will likely enter into a P6$_3$c'm phase.

Previous work done on Dy$_{0.5}$Y$_{0.5}$MnO$_3$ by Helton et al. did not observe the P6$_3$c'm phase and concluded that the phase transition was either P6$_3$cm' or a P6$_3$cm directly to P6$_3$c'm'. It may be that at low temperatures, the P6$_3$c'm', P6$_3$cm' and P6$_3$c'm phases are all in competition with each other, and that differences in sample preparation have favored one phase over the other. Our quasielastic studies (described later) further prove this competition between phases. Since even in pure DyMnO$_3$, the P6$_3$c'm' phase is confined to low temperatures, where Dy$^{3+}$ moments play a large role, we expect that, regardless of the method of sample preparation, the P6$_3$c'm phase will emerge at increasing temperatures as Dy concentration is increased.

4.1.3 ErMnO$_3$

Our results indicate that the phase transition that occurs in ErMnO$_3$ (figure 3.7) is similar to the phase transition in Dy$_{1-x}$Y$_x$MnO$_3$ (figure 3.6), but occurs at a differ-
ent spin reorientation temperature and compositional range. ErMnO₃’s phase transition occurs from P6’₃cm’ to P6’₃c’m up to x=0.95, which is inverted, compared to Ho₁₋ₓYₓMnO₃, and at very narrow compositional range compared to Dy₁₋ₓYₓMnO₃. Just 7% of erbium was enough to completely push the boundary to the P6’₃c’m phase. At 6% Er, two spin reorientations occur around 50K and 17K, where the Mn³⁺ ions rotate from P6’₃c’m to P6’₃cm’ and back to P6’₃c’m. This indicates strong competition between both phases.

4.1.4 Phase transition in RMnO₃ family

Figure 4.3: Magnetic phase diagrams drawn according to our elastic neutron scattering data. a) Phase diagram for Ho₁₋ₓYₓMnO₃. b) Diagram for Dy₁₋ₓYₓMnO₃. c) Phase diagram for Er₁₋ₓYₓMnO₃. Squares represent Tₙ, while circular data points represent Tₜₙ. 64
Our initial assumption was that HoMnO$_3$ acts like half-way point between ErMnO$_3$ and YMnO$_3$ (figure 4.2). This is because ErMnO$_3$ orders exclusively in P6$_3$cm$'$, YMnO$_3$ orders exclusively in P6$_3'm'$, and HoMnO$_3$ experiences a phase transition between P6$_3$cm$'$ and P6$_3'c'm'$ around 40K. But the phase diagrams (figure 4.3) tell a very different story. Only 7% Er is sufficient to push Er$_{1-x}$Y$_x$MnO$_3$ onto the Er side (figure 4.3c), but even at 40% Er, $T_{SR}$ only drops from about 40 K to about 25 K in Ho$_{1-x}$Er$_x$MnO$_3$ [62]. The effect of Er on the magnetic phase is therefore much weaker in Ho$_{1-x}$Er$_x$MnO$_3$ than in Er$_{1-x}$Y$_x$MnO$_3$. In Ho$_{1-x}$Y$_x$MnO$_3$, $T_{SR}$ increases from 38K to 58K with 0 to 80% yttrium (figure 4.3a). Our explanation is that Ho somehow serves to stabilize both the magnetic phases. Further support for this possibility comes from our inelastic neutron scattering measurements, which will be discussed in next section.

In Ho$_{1-x}$Y$_x$MnO$_3$, the transition occurs from P6$_3$c$'$m to P6$_3'c'm'$, while in both Er$_{1-x}$Y$_x$MnO$_3$ and Dy$_{1-x}$Y$_x$MnO$_3$ the transition is reversed (P6$_3'c'm'$ to P6$_3''c'm'$). From the above, we can conclude that this phase transition is complex and not straightforward. HoMnO$_3$ does not lie between YMnO$_3$ and ErMnO$_3$ in a 1D parameter space (figure 4.2a), but must be displaced from both along some other direction in a higher-dimension parameter space (figure 4.2b).

### 4.2 Quasielastic scattering analysis

In order to further cement the possibility of holmium acting as a stabilizer between magnetic phases we had to look into other avenues. One path was the random claims of the existence of quasielastic scattering just above and below $T_N$. We per-
formed a complete range of inelastic neutron scattering measurements on various Ho$_{1-x}$Y$_x$MnO$_3$, Er$_{1-x}$Y$_x$MnO$_3$ and Dy$_{1-x}$Y$_x$MnO$_3$ crystals at different temperatures and at both magnetic and non-magnetic locations. These quasielastic measurements were instrumental in our model for $R$MnO$_3$ family.

### 4.2.1 Previously observed quasielastic scattering

Quasielastic neutron scattering in $R$MnO$_3$ for both powder and single crystal samples has been previously reported in several papers [48, 63, 64, 47, 65]. Sato et al. reported quasielastic scattering above and below $T_N$ in pure YMnO$_3$, with an in-plane width that became resolution limited below $T_N$, and an energy width that remained wider than resolution down to the lowest temperatures, but with no reported out-of-plane correlation [48]. Park et al. also reported quasielastic scattering above and below $T_N$ in YMnO$_3$, but their samples were powder and so the data does not provide directional information[63]. Roessli et al. measured quasielastic scattering in pure YMnO$_3$ around the (1,0,0) position above $T_N$ but not below. Far above $T_N$, the scattering had no out-of-plane correlations, but near $T_N$ the scattering developed $L$ dependence with a peak centered around (1,0,0), and a peak shape well-described by a Lorentzian in both the in-plane and out-of-plane direction. Polarized neutron measurements indicated that the quasielastic scattering was due to in-plane fluctuations [64]. Lewtas et al. reported diffuse elastic scattering in LuMnO$_3$ around the (1,0,0) position above $T_N$, while the primary magnetic Bragg reflection below $T_N$ was at the (1,0,1) position [65]. This scattering may have been quasielastic, but no energy-dependent measurements on the diffuse scattering were reported. Sekhar et al. reported diffuse scattering below $T_N$ in powder neutron mea-
measurements of Er$_{1-x}$Y$_x$MnO$_3$, but only in samples with high yttrium concentrations. This scattering occurs at 2$\theta$ angles similar to the (1,0,0) and (1,0,1) peaks, but they did not identify which of those two positions this scattering was associated with [47].

4.2.2 \textit{RMnO}_3, Out-of-plane correlations exist or not?

There is agreement among all the single-crystal measurements that well above T$_N$, the diffuse/quasielastic scattering has no out-of-plane correlations and very short in-plane correlations. Figure 3.11a shows our work performed for Ho$_{0.25}$Y$_{0.75}$MnO$_3$, similar results were seen for all other \textit{RMnO}_3 compounds. Both Lewtas \textit{et al.} and Roessli \textit{et al.} report that the scattering develops \textit{L} dependence centered around the (1,0,0) position in LuMnO$_3$ and YMnO$_3$, respectively, but neither report measuring around the (1,0,1)[65, 64]. This omission is significant because the (1,0,1) position is the magnetic Bragg position for LuMnO$_3$, but the (1,0,0) is the magnetic Bragg position for YMnO$_3$.

Below the Néel temperature, there is significant discrepancy between our work and the work of Sato \textit{et al.}[48], since the latter report that the quasielastic scattering has no out-of-plane dependence, while we observe very strong out-of-plane dependence below T$_N$ (figures 3.10c). We speculate that the Sato \textit{et al.} measurements may simply not have extended far enough. Only one \textit{L} scan was shown, and the range covered, from \textit{L} = −0.2 to \textit{L} = 0.5, corresponds to an essentially flat region of our scans, as seen in Figure 3.10. Our own work on Ho$_{1-x}$Y$_x$MnO$_3$, Er$_{1-x}$Y$_x$MnO$_3$ and Dy$_{1-x}$Y$_x$MnO$_3$, has shown that there are significant out-of-plane correlations in the quasielastic scattering of \textit{RMnO}_3 below T$_N$ (figures 3.14, 3.18).
4.3 A model for RMnO$_3$ family

However, while these quasielastic excitations have now been observed in YMnO$_3$, LuMnO$_3$ [65], as well as Ho$_{1-x}$Y$_x$MnO$_3$, Er$_{1-x}$Y$_x$MnO$_3$ and Dy$_{1-x}$Y$_x$MnO$_3$ at high yttrium concentrations, they were not observed in inelastic neutron scattering measurements of pure HoMnO$_3$ [57] or in pure ErMnO$_3$ diffraction measurements [47].

Well above $T_N$, the quasielastic scattering in these materials shows no sign of $L$ dependence (figure 3.11a). Correlations are in-plane only, and so no distinction can be made between phases that differ in their out-of-plane stacking arrangement. Near $T_N$, however, $L$ dependence begins to emerge as correlations begin to develop between MnO planes. The presence of quasielastic scattering at both the (1,0,0) and (1,0,1) positions near the $T_N$ indicates that correlated regions of both phases exist above $T_N$ (figure 3.11b). Neither phase is strongly preferred, but instead they appear to compete with each other. According to our interpretation there should be a peak in the quasielastic scattering just above $T_N$ at the (1,0,1) position in LuMnO$_3$ in addition to the observed peak around (1,0,0) [65], but it may simply not have been measured.

Below $T_N$, YMnO$_3$ orders in only one phase, and quasielastic scattering for the ordered phase disappears as the correlations become static (figure 3.11c). But quasielastic scattering for the “wrong” phase persist below $T_N$. These patches are broad in-plane and narrow out-of-plane. This would suggest that there is a phase competition between the P6$_3$c’m and P6$_3$cm’ phases, with the “wrong” phase being only slightly disfavored (figure 4.5). In such a scenario, those quasielastic excitations should be damped at low temperature, as observed. We hypothesize that the quasielastic scattering originates from domain boundaries within our crystal. Mn$^{3+}$ moments located
Figure 4.4: Figure shows a comparison between Lorentzian function and a Gaussian function fitted to out-of-plane quasielastic scattering data for YMnO$_3$ at 30K. Solid line is the Gaussian fit while, dashed line is the Lorentzian fit between different domains will be frustrated. At $c$-axis domain boundaries, the weak, frustrated out-of-plane interactions may prevent long-range static order, but in-plane correlations within those boundaries could still lead to short-range correlated fluctuations. Thermal fluctuations may excite spins at the boundary into the wrong magnetic phase, which still satisfies the in-plane interactions. If the correlations which form are short-lived, they will lead to quasielastic scattering. Because the in-plane coupling is so much stronger than the out-of-plane coupling, fluctuations at in-plane domain boundaries may not be able to form correlated patches of any significant size, and so would not contribute to the observed quasielastic scattering. This would also explain the line shape of the quasielastic scattering: the shape of the domain walls would constrain correlations along the $c$ axis, but correlations could grow to much larger size along the in-plane direction. The neighboring ordered domains will not only act to limit the size of the out-of-plane correlation length, they may also cause those correlations to decay faster than an exponential. A Lorentzian line shape
indicates correlations which decay exponentially with distance, while a Gaussian indicates correlations which decay much faster than exponential. This is due to that fact that in reciprocal space, Fourier transformation of a Lorentzian function will give an exponential function, while Gaussian would give a Gaussian. Gaussian fitting gave much better fits compared to Lorentzian fits for the out-of-plane correlations (figure 4.4). This contrasts with the analysis of Roessli et al., who used a Lorentzian to analyze the $L$ dependence of the quasielastic scattering above $T_N$ [64]. Without an ordered phase to constrain the fluctuations, correlations could extend as a decaying exponential along the $c$ axis, so their model is still consistent with our hypothesis.
We also hypothesize that the existence of quasielastic scattering in yttrium-rich $RMnO_3$ but not pure $HoMnO_3$ is due to the larger in-plane easy-axis anisotropy in $HoMnO_3$. This in-plane anisotropy for $Mn^{3+}$ moments gives rise to a spin gap which was measured by Fabreges et al. for both yttrium and holmium, who found a significantly larger gap for $HoMnO_3$ than for $YMnO_3$ [26]. This anisotropy acts as an energy barrier to in-plane rotation, and so a large anisotropy may prevent the quasielastic fluctuations at the domain boundaries (figure 4.6). Further evidence for this interpretation comes from the polarized scattering measurements of Roessli et al., who found that the quasielastic scattering is due to spins fluctuating within the plane [64]. Out-of-plane fluctuations gave rise to inelastic scattering due to the easy-plane anisotropy, which is much larger than the in-plane anisotropy for all $RMnO_3$. The observation of quasielastic scattering in $LuMnO_3$ is consistent with this interpretation, since the spin-wave dispersion measured by Lewtas et al. had a vanishingly small gap indicating very little in-plane anisotropy [65].

One might argue that having domains is energetically unfavorable. In general this is true, but in $RMnO_3$, the interaction between antiferromagnetic domain walls with lattice strains, known as piezomagnetism, lowers the total free energy of the system by creating antiferromagnetic domain walls pinned to the ferroelectric domain walls [37]. Free antiferromagnetic domain walls can also exist within ferroelectric domains. Cycling a sample through the Néel transition can change the free walls, but the pinned walls always remain unless the ferroelectric domains are disrupted. This has been observed experimentally for $YMnO_3$ at 10K and for $HoMnO_3$ [37, 66].

Recent piezoresponse force microscopy on $YMnO_3$ by S.M. Griffin et al. revealed that this ferroelectric domain structure appears isotropic and the domain walls are
very narrow. Nevertheless, free domain walls do not have to be narrow. Griffin also
claims that these free domain walls could be non-isotropic and primarily exist along
the c-axis [67], which could agree with our predicted out-of-plane correlation length
(figure 3.21) of around 70K.

One possible objection to our interpretation is that the observed quasielastic scat-
tering may simply be the spin-wave dispersion approaching zero energy. The spin-
wave measurements by Fabreges et al. [26] do indicate that the dispersion is close to
gapless for YMnO$_3$ at the (1,0,1) position, and in HoMnO$_3$ it has a minimum at either
the (1,0,1) or the (1,0,0), depending on the temperature, in the same place as the
observed quasielastic scattering for YMnO$_3$ and Ho$_{1-x}$Y$_x$MnO$_3$. However, the obser-
vation of quasielastic scattering at the (1,0,2), where the dispersion should move to
higher energy in YMnO$_3$ due to out-of-plane coupling, indicates that the quasielastic
scattering is not simply a measurement artifact of a gapless dispersion, but is instead
related to correlations matching an ordered magnetic phase, albeit the wrong phase.

Our model of quasielastic scattering in $\text{RMnO}_3$ explains both our own obser-
vations as well as a number of disparate previous results. It also explains the absence
of quasielastic scattering for HoMnO$_3$. If our model is correct, then other
$\text{RMnO}_3$ compounds with large in-plane anisotropy, such as YbMnO$_3$ [26], should not
exhibit quasielastic scattering either. This scattering indicates strong competition
between competing 3D-ordered phases. It is particularly interesting that even though
HoMnO$_3$ exhibits both P6$_3$cm$'$ and P6$_3$c$'$m phases, quasielastic scattering is absent.
The in-plane anisotropy appears to stabilize both magnetic phases in HoMnO$_3$. This
suggests that the spin reorientation transition in HoMnO$_3$ is driven by something
besides purely magnetic interactions.
We know that the magnetism and the ferroelectricity are clamped together below $T_N$. Recent work done by B.G. Ueland et al. using polarized small angle neutrons with an applied electric field at a non-magnetic location showed the suppression of the magnetic scattering below $T=50K$ [68]. This indicates that the magnetism is affected by an electric field via antiferromagnetic domain walls rather than changes to long-range bulk magnetic order. An applied electric field would alter the ferroelectric domains. As a result, this would alter the pinned antiferromagnetic domain walls. In spite these $RMnO_3$ crystals have layered crystal structure, these domain structures are isotropic [67]. A better understanding of the dynamics involved at the out-of-plane domains may help illuminate the nature of this magnetic-ferroelectric interaction.

4.4 Testable predictions

Following are few predictions based on our model, which will enable us to verify the validity of our model.

Fabreges et al. found that YbMnO$_3$ posses large in-plane anisotropy [26]. According to our model, any $RMnO_3$ with large in-plane anisotropy should not show quasielastic scattering. This implies that no quasielastic scattering will be visible in YbMnO$_3$.

Similar to HoMnO$_3$, ErMnO$_3$ does not have any quasielastic scattering. Hence, according to our model, ErMnO$_3$ should posses large in-plane anisotropy.

If the above predictions hold true, then this will be further evidence of the accuracy of our model.
Appendix A

Fourier Transformations

A.1 Fourier transformation of a Gaussian function

Assume the Gaussian function is in the form of

\[ f(x) \equiv e^{-ax^2} \]  \hspace{1cm} (A.1)

If the Fourier transformation of the Gaussian function is \( f(k) \), then

\[
\begin{align*}
    f(k) &= \int_{-\infty}^{\infty} e^{-ax^2} e^{-2\pi ikx} \, dx \\
        &= \int_{-\infty}^{\infty} e^{-ax^2} [\cos(2\pi kx) - i\sin(2\pi kx)] \, dx \\
        &= \int_{-\infty}^{\infty} e^{-ax^2} \cos(2\pi kx) \, dx - i \int_{-\infty}^{\infty} e^{-ax^2} \sin(2\pi kx) \, dx
\end{align*}
\]  \hspace{1cm} (A.2, A.3, A.4)
but,
\[ \int_{-\infty}^{\infty} e^{-ax^2} \sin(2\pi kx) dx = 0 \quad (\because \text{odd function}) \quad (A.5) \]

and, according to “Abramowitz and Stegun” (1972, p. 302, equation 7.4.6)

\[ \int_{-\infty}^{\infty} e^{-ax^2} \cos(2\pi kx) dx = a' \exp \frac{-2k^2}{a} \quad (A.6) \]

\[ f(k) = a' \exp \frac{-2k^2}{a} \quad (A.7) \]

So, a Fourier transformation of a Gaussian is an another Gaussian.

### A.2 Fourier transformation of a exponential function

Assume the exponential function is in the form of

\[ f(x) \equiv e^{-bx} \quad (A.8) \]

If the Fourier transformation of the exponential function is \( f(k) \), then

\[ f(k) = \int_{-\infty}^{\infty} e^{-bx} e^{-2\pi ikx} dx \quad (A.9) \]

\[ = \int_{-\infty}^{0} e^{2\pi bx} e^{-2\pi ikx} dx + \int_{0}^{\infty} e^{-2\pi bx} e^{-2\pi ikx} dx \quad (A.10) \]

\[ = \int_{-\infty}^{0} e^{2\pi bx} [\cos(2\pi kx) - isin(2\pi kx)] dx \quad (A.11) \]

\[ + \int_{0}^{\infty} e^{-2\pi bx} [\cos(2\pi kx) - isin(2\pi kx)] dx \quad (A.12) \]

Now let \( u \equiv -x \), so that \( du = -dx \), then
\[= \int_0^\infty e^{-2\pi bu} [\cos(2\pi ku) + \sin(2\pi ku)] du \quad (A.13)\]

\[+ \int_0^\infty e^{-2\pi bu} [\cos(2\pi ku) - \sin(2\pi ku)] du \quad (A.14)\]

\[= 2 \int_0^\infty \cos(2\pi ku)e^{-2\pi bu} du \quad (A.15)\]

Which is of the form of damped exponential cosine integral, gives

\[f(k) = \frac{1}{\pi} \frac{b}{k^2 + b^2} \quad (A.16)\]

Fourier transformation of a exponential function is a Lorentzian function.
Appendix B

MATLAB code for order parameter data fittings

Following code requires “loadmurrdata.m”, which will extract data from the TRIAX data file, and it is specific to TRIAX at MURR. It also requires “nlfit.m” and “orderparameter.m” MATLAB files.

```matlab
set(gcf, 'PaperPositionMode', 'manual');
set(gcf, 'PaperPosition', [0 0 8 4]); %[0 0 5 2])

% YMnO3 Order Parameter Fit

% Loading data
[op100, header, column_labels]=loadmurrdata('TRIAX_exp0023_scan1608.dat');
[op101, header, column_labels]=loadmurrdata('TRIAX_exp0023_scan1609.dat');

% Initial guessed parameters P=[Amplitude Tc deltaTc Beta Background]
p100 = [65765 71.6697 1.2774 .1870 231.734];
isfit = [1 1 1 1];

% 'nlfit' will perform nonlinear least-squares data fitting using Levenberg-Marquardt method
[BETA100,CHISQUARE100,ERR100,FIT] = nlfit(op100(113:153,29),op100(113:153,34),'orderparameter',
```

\texttt{p100, isfit, sqrt(op100(113:153,34))};
\texttt{21 \% convolve signal with gaussian of width p}
\texttt{22 fit100 = orderparameter(BETA100,[0:0.2:90]')};
\texttt{23 plot([0:0.2:90],fit100/10000,'-k')};
\texttt{24}
\texttt{25 axis([0 80 0 5]);}
\texttt{26 xlabel('Temperature (K)');}
\texttt{27 ylabel('Intensity (counts/30 sec)');}
\texttt{28 text(60, 4.375, 'x = 1');}
\texttt{29}
\texttt{30 \% Manually constructed legend}
\texttt{31 plot(10, 2.5, 'sr');}
\texttt{32 text(20, 2.5, '(1,0,0)');}
\texttt{33 plot(10, 1.8, 'ob');}
\texttt{34 text(20, 1.8, '(1,0,1)');}
\texttt{35 plot(10, 1.1, '^k');}
\texttt{36 text(20, 1.1, '(1,0,2)');}
\texttt{37}
\texttt{38 hold off;}
\texttt{78}
Appendix C

MATLAB code for quasielastic data fittings

C.1 Experimental Parameters

“setup_exp.m” includes all the experimental parameters that are needed for calculating the resolution ellipsoid. When called, this will create a data buffer named “EXP”. The parameters in this file must be changed manually according to the spectrometer and for each crystal.

```matlab
% Experimental parameters:
EXPMono.tau='pg(002)'; % PG(002), PG(004), GE(111), GE(220), GE(311), BE(002) or PG(110)...
EXPMono.tau=1.807; % ... or any manual input, in reciprocal angstroms
EXPMono.mosaic=95; % Minutes of arc
EXPMono.vmosaic=45; % For anisotropic mosaic: vertical mosaic, minutes of arc
EXPAna.tau='pg(002)'; % PG(002)
EXPAna.mosaic=95; % Minutes of arc
EXPAna.thickness = 30;
EXPAna.vmosaic=75; % For anisotropic mosaic: vertical mosaic, minutes of arc
EXPAna.Q = .01287;
% Sample
EXP.Sample.a=6.09; % Angstroms
```
C.2 \( S(q, \omega) \) model fit

The following “sqw_QE_3D.m” function contains the fitting model for structure factor \( (S(q, \omega)) \) for the data.

```matlab
function sqw = sqw_QE_3D(H,K,L,W,p)

% sqw = sqw_QE_3D(H,K,L,W,p)
% S(q,w) intensity for a quasielastic peak with finite H, K, L, and W widths
% Models a Gaussian in H, K, and L, and a Lorentzian in W.
% %
% X = nx4 matrix containing H, K, L, and W as columns
% %
% parameters p = [p1 p2 p3]
% %
% p1 = sqw_QE_3D parameters (8)
% p2 = sqw_bragg (8)
% p3 = pref_bg (4)
```
% Amplitude
% gamma (energy width)
% H FWHM
% L FWHM
% E center
% H center
% L center
% Temperature
%

p1 = p1(1:8);
A = p1(1); % Amplitude
gamma = p1(2); % gamma (energy width)
wH = p1(3)/(4*log(2)); % Convert from FWHM to gaussian width — also used for width in K
wL = p1(4)/(4*log(2)); % Convert from FWHM to gaussian width
cE = p1(5); % E center
cH = p1(6); % H center
cL = p1(7); % L center
T = p1(8); % Temperature in Kelvin — generally not fit

kb = 8.6173*(10^(-2)); % meV/K

% Offset energy by cE
W = W - cE;

chi = (gamma*W)./(W.^2+gamma.^2); % imaginary component of dynamic susceptibility
boltzmann = 1./(1-exp(-W/(kb*T))); % thermal factor — won’t work correctly if W = 0

% check for any W = 0 cases and correct them manually
for i = 1:length(W)
    if W(1,i) == 0
        chi(1,i)=kb*T/gamma;
        boltzmann(1,i)=1;
    end
end

sE = chi .* boltzmann;

In plane lorentzian fit function and ou-of-plane Gaussian
sqw = sE .* s_q;

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C.3  Fitting for quasielastic data

Function “qe_fit_30K.m” is the actual fitting function, which will call above “sqw_QE_3D.m” function to fit the structure factor and will do the convolution with the resolution ellipsoid. Before running this function, the user must run the “setup_exp.m”. This function will allow user to fit either just the quasielastic data or quasielastic data with the Bragg peak. This function requires “ConvRes.m”, “ConvResSMA.m” and “FitConv.m” built-in RESLIB functions. While fitting, it is advised to fit energy first, then do the out-of-plane data fit. Then the in-plane and out-of-plane data must be fitted individually. Finally, all three, energy and both in-plane and out-of-plane parameters should be fitted simultaneously.

1 % Quasielastic fits
2 % required functions:
3 % sqw_QE_3D
4 % sqw_bragg
5 % pref_bg
6 %
7 % Note: make sure to run setup_exp before doing fits
8 %
9 % Load data
10 [hdata, h_header, labels]=loadmurrdata('TRIAX_exp0023_scan2271.dat');
11 [ldata, l_header, labels]=loadmurrdata('TRIAX_exp0023_scan1615.dat');
12 [edata, e_header, labels]=loadmurrdata('TRIAX_exp0023_scan2272.dat');
13 14 % Columns & labels for data
15 h_column = 2;
16 k_column = 3;
17 l_column = 4;
18 e_column = 5;
19 i_column = 8; % intensity
20 h_label = 'H (rlu)';
21 l_label = 'L (rlu)';
22 e_label = 'Energy (meV)';
23 i_label = 'Counts';
24 25 % Plot raw data
26 subplot(1,3,3);
27 plot(hdata(:,h_column),hdata(:,i_column),'ob');
28 xlabel(h_label);
29 ylabel(i_label);
30 subplot(1,3,2);
31 plot(ldata(:,1_column),ldata(:,1_column),'ob');
32 xlabel(1_label);
33 ylabel(1_label);
34 subplot(1,3,1);
35 semilogy(edata(:,e_column),edata(:,e_column),'ob');
36 xlabel(e_label);
37 ylabel(e_label);
38

% Set up fitting parameters
% splitting into parts done to simplify management
% Some parameters (in particular, background and amplitude)
% should be changed for each fit.

% quasielastic scattering parameters

A_qe = 1.767; % quasielastic amplitude
gamma = 0.3084; % width in energy
wH = 0.0045; % FWHM in H and K
wL = 0.4744; % FWHM in L
x_E = -0.195; % center in E -- nominally 0 but may be off
x_H = 1.00771; % center in H
x_L = 0.918703; % center in L
T = 30; % temperature

% bragg scattering parameters

A_bragg = 0.003; % Bragg peak amplitude
cEB = 0; % center in E -- nominally zero but may be off
cHB = 1; % center in H
cLB = 1; % center in L
wE = 0; % energy HWHM -- can be set to zero
wHB = 0.001; % width in H -- should be small
wKB = 0.001; % width in K
wLB = 0.002; % width in L

% pre_bg parameters

bg_constant = 21.07256;
b_avg = 83.659;
b_avg = 10.34;
bg_slope = 3.48933;
% Fit energy scan

% Select which parameters to fit
isfit1 = [1 1 0 0 1 0 0 0];
isfit2 = [0 0 0 0 0 0 0 0];
isfit3 = [1 0 0 1];

% Assemble fitting parameters
p1 = [A qe gamma wH wL cE cH cL T];
p2 = [A bragg cEB cHB cLB wE wHB wKB wLB];
p3 = [bg constant bg Hslope bg Lslope bg Eslope];
p = [p1 p2 p3];
isfit = [isfit1 isfit2 isfit3];

% Select data to fit
datarange = [1:29 34:61]; % exclude Bragg peak
datarange = [1:61]; % include Bragg peak
H = edata(datarange, h_column);
K = edata(datarange, k_column);
L = edata(datarange, l_column);
W = edata(datarange, e_column);
Iobs = edata(datarange, i_column);
dIobs = sqrt(Iobs);

% Points for fit curve
Hfit = 1;
Kfit = 0;
Lfit = 1;
Efit = [-3:0.05:3];

subplot(1,3,1);
hold on;

% Overplot which points are being fit
plot(W, Iobs, 'ob', 'MarkerFaceColor', 'b');

% Plot original parameters
QEinital = ConvRes('sqw_QE3D', 'pref_blank', Hfit, Kfit, Lfit, Efit, EXP, 'fix',[8 8],p);
Binital = ConvResSMA('sma_bragg', 'pref_bg', Hfit, Kfit, Lfit, Efit, EXP, 'fix',[8 8],p);
initialcurve = QEinitial + Binital;
semilogy(Efit, initialcurve, '-b');

% Perform fit

% QE + Bragg scattering
[p, dpe, chisqN, sim, CN, PQ, nit, kvg, details] = ...
FitConvBoth(H, K, L, W, EXP, Iobs, dIobs, 'sqw_QE3D', 'pref_blank', ...
% 'sma_bragg', 'pref_bg', p, isfit, 'fix', [8 8], [8 8]);
% % % QE only scattering
%
[p, dpe, chisqN, sim, CN, PQ, nit, kvg, details] = ... 
FitConv(H, K, L, EXP, Iobs, dIobs, 'sqw_QE3D', ... 
'pref_bg', p, isfit, 'fix', [8 8], [8 8]);
%
% Plot fitted parameters
QEfit = ConvRes('sqw_QE3D', 'pref_blank', Hfit, Kfit, Lfit, Efit, EXP, 'fix', [8 8], p);
Bfit = ConvResSMA('sma_bragg', 'pref_bg', Hfit, Kfit, Lfit, Efit, EXP, 'fix', [8 8], p);
fitcurve = QEfit + Bfit;
semilogy(Efit, fitcurve, 'r');
%
hold off;
%
% % % L scan
%
% parameter changes specific to L scan
A_qe = 13.72; % quasielastic amplitude
bg_constant = 22.12;
%
% Select which parameters to fit
isfit1 = [1 0 0 1 0 0 1 0];
isfit2 = [0 0 0 0 0 0 0 0];
isfit3 = [1 0 1 0];
%
% Assemble fitting parameters
p1 = [A_qe gamma wH wL cE cH cL T];
p2 = [A_bragg cEB cHB cLB wE wHB wLB];
p3 = [bg_constant bg_Hslope bg_Lslope bg_Eslope];
p = [p1 p2 p3];
isfit = [isfit1 isfit2 isfit3];
%
% Note: we’re cutting out some data points here
datarange = [1:12 14:30 32:44 56:61];
H =idata(datarange, h_column);
K =idata(datarange, k_column);
L =idata(datarange, l_column);
W =idata(datarange, e_column);
Iobs = idata(datarange, i_column);
dIobs = sqrt(Iobs);
%
% Points for fit curve
Hfit = 1;
Kfit = 0;
Lfit = [−0.5:0.02:2.5];
Efit = 0.7;

subplot(1,3,2);
hold on;

% Overplot which points are being fit
plot(L, Iobs, 'ob', 'MarkerFaceColor', 'b');

% Plot original parameters
QEinitial = ConvRes('sqw_QE_3D', 'pref_blank', Hfit, Kfit, Lfit, Efit, EXP, 'fix', [10 10], p);
Binitial = ConvResSMA('sma_bragg', 'pref_bg', Hfit, Kfit, Lfit, Efit, EXP, 'fix', [10 10], p);
initialcurve = QEinitial + Binitial;
plot(Lfit, initialcurve, '-b');

% % % --
% % Perform fit
% % % --
% % QE + Bragg scattering
% [pl, dpl, chisqN, sim, CN, PQ, nit, kvg, details] = ...% FitConvBoth(H,K,L,W,EXP, Iobs, dIobs, 'sqw_QE_3D', 'pref_blank', ...% 'sma_bragg', 'pref_bg', p, isfit, 'fix', [8 8], [8 8]);% QE only scattering
% [pl, dpl, chisqN, sim, CN, PQ, nit, kvg, details] = ...% FitConv(H,K,L,W,EXP, Iobs, dIobs, 'sqw_QE_3D', ...% 'pref_bg', p, isfit, 'fix', [8 8], [8 8]);% Plot fitted parameters
QEfit = ConvRes('sqw_QE_3D', 'pref_blank', Hfit, Kfit, Lfit, Efit, EXP, 'fix', [8 8], p);
Bfit = ConvResSMA('sma_bragg', 'pref_bg', Hfit, Kfit, Lfit, Efit, EXP, 'fix', [8 8], p);
fitcurve = QEfit + Bfit;
plot(Lfit, fitcurve, '-r');
hold off;

% % % --
% % Fit H scan
% % % --
% % parameter changes specific to H scan
% A_qe = 2.64; % quasieystalic amplitude
% bg_constant = 19.7257;
% Select which parameters to fit
% isfit1 = [1 0 1 0 0 1 0 0];
% isfit2 = [0 0 0 0 0 0 0 0];
% isfit3 = [1 1 0 0];
% Arrange fitting parameters
% p1 = [ A_qe gamma wH wL cR cH cL T ];
% p2 = [ A_bragg cEB cHB cLB wE wHB wKB wLB ];
p3 = [ bg_constant bg_Hslope bg_Lslope bg_Eslope ];
p = [p1 p2 p3];
isfit = [isfit1 isfit2 isfit3];

% Select data to fit
H = hdata(:,h_column);
K = hdata(:,k_column);
L = hdata(:,l_column);
W = hdata(:,e_column);
Iobs = hdata(:,i_column);
dIobs = sqrt(Iobs);

% Points for fit curve
Hfit = [0.9:0.002:1.1];
Kfit = 0;
Lfit = 1;
Efit = 0.7;

subplot(1,3,3);
hold on;

% Plot original parameters
QEinital = ConvRes('sqw_QE_3D','pref_blank',Hfit,Kfit,Lfit,Efit,EXP,'fix',[8 8],p);
Binital = ConvResSMA('sma_bragg','pref_bg',Hfit,Kfit,Lfit,Efit,EXP,'fix',[8 8],p);
initialcurve = QEinitial + Binitial;
plot(Hfit,initialcurve,'-b');

% Perform fit
% -- -- -- -- -- -- -- --
% QE + Bragg scattering
% -- -- -- -- -- -- -- --
[ph, dph, chiqN, sim, CN, PQ, nit, kvg, details] = ...
FitConvBoth(H,K,L,EXP, Iobs ,dIobs , 'sqw_QE_3D' , 'pref_blank' , ...% 'sma_bragg', 'pref_bg', p, isfit , 'fix', [8 8], [8 8]);
% QE only scattering
[ph, dph, chiqN, sim, CN, PQ, nit, kvg, details] = ...
FitConv(H,K,L,EXP, Iobs ,dIobs , 'sqw_QE_3D' , ...% 'pref_bg', p, isfit , 'fix', [10 10], [10 10]);

% Plot fitted parameters
QEfit = ConvRes('sqw_QE_3D','pref_blank',Hfit,Kfit,Lfit,Efit,EXP,'fix',[10 10],ph);
Bfit = ConvResSMA('sma_bragg','pref_bg',Hfit,Kfit,Lfit,Efit,EXP,'fix',[10 10],ph);
fitcurve = QEfit + Bfit;
plot(Hfit,fitcurve,'-r');

hold off;
Bibliography


VITA

Jagath C. Gunasekera was born in Panadura, Sri Lanka. He received his B.S. in Computational Physics from the University of Colombo, Sri Lanka. After completion of his B.S. degree in 2007, he worked as a lab instructor and a network administrator at the Department of Physics, University of Colombo. In fall of 2008, he joined the Department of Physics and Astronomy, University of Missouri - Columbia to pursue his graduate studies and started working as a research assistant with Prof. Owen Vajk on neutron scattering studies of strongly correlated systems. He received his M.S. in Physics in 2011 and received his Ph.D. in Experimental Condensed Matter Physics in July of 2013. His research work during graduate studies focused on growing single-grain multiferroic crystals and studying them using neutron scattering. He was also the teaching laboratory in-charge for the department of Physics and Astronomy from 2010 until 2013, and also was a teaching assistant during that time period. He won the best teaching assistant award in 2013 and received the fellowship in physics for research achievements in 2013.

He married Crystal Rose Allen in October, 2012. He also was the national powerlifting champion in 2010, 2011 and 2012, and represented team USA in 2011 at the world championships.