MAGNETIC-FERROELECTRIC INTERACTIONS IN RMnO$_3$

A Dissertation
presented to
the Faculty of the Graduate School
at the University of Missouri-Columbia

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy

by

YUAN WANG

Dr. Owen Vajk, Dissertation Supervisor

December 2013
The undersigned, appointed by the dean of the Graduate School, have examined the dissertation entitled

MAGNETIC-FERROELECTRIC INTERACTIONS IN RMnO$_3$

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

______________________________
Prof. Owen Vajk

______________________________
Professor William Miller

______________________________
Professor Paul Miceli

______________________________
Professor Wouter Montfrooij
ACKNOWLEDGMENTS

The research experience for my dissertation is really impressive and benefits me a lot for my future work. The theories and concepts which I have been fortunately learned are so valuable that it extensively broaden the way of considering a problem. When I'm looking back all the cherished experience, I’m full of thanks to all the people who strongly supported me during those years. All the glittery memories will encourage and warm me all the life.

I would like to express my deepest gratitude and thanks to my advisor, Prof. Owen Vajk. Without his great guidance, encouragement and most of all, his patience, it’s impossible for me to complete my dissertation and related research. My advisor was there throughout all the processes from preparing the research, choosing the direction, instructing on writing, and to debate dissertation. His talent thought, mastered skill of programming and detailed instructions enabled me to complete the dissertation successfully.

The second people I would like to thank to is Dr. Carsten Ullrich. He provided me a secure atmosphere to pursue my research without concerning about the difficulties and troubles in my student life. I also would like to thank to Prof. William Miller, Prof. Paul Miceli and Prof. Wouter Montfrooij. As my dissertation committee members, they gave me many good suggestions and confirmations on my research. I would like to thank to Dr. Jagath Gunasekera, my lab partner and classmate. Without his help, I couldn’t operate all the labs myself. I also would like to thank to Dr. Thomas Heitmann. He offered all his help from neutron scattering on our samples from MURR and thanks for his being there for my comprehensive exam and
dissertation debate.

Finally, my husband, Dr. Li Ma, supported me all the time with no hesitance and doubt. He cheered me up and encouraged me no matter it was good or bad. My kids, Jason Ma and Nicholas Ma, kept me full of unending strength and energy to complete my dissertation. I thank my parents, Dejie Wang and Xueqing Zhou. They showed me good examples as how to be a scholar and always trust in my ability.
# TABLE OF CONTENTS

ACKNOWLEDGMENTS .................................................. ii

LIST OF FIGURES .................................................... vi

ABSTRACT .............................................................. viii

CHAPTER

1 Introduction ....................................................... 1

1.1 Multiferroic material ........................................... 1

1.1.1 Magnetism ................................................... 1

1.1.2 Ferroelectricity ............................................. 4

1.1.3 Ferroic Order ............................................... 6

1.1.4 Multiferroic Coupling ...................................... 7

1.2 Hexagonal manganite \( \text{RMnO}_3 \) ........................... 9

1.3 \( \text{HoMnO}_3 \) .................................................. 13

1.3.1 Phase transitions .......................................... 13

1.3.2 Magnetic-ferroelectric coupling .......................... 15

1.3.3 Field-dependent phase diagram .......................... 15

2 Experiment Setup and Process ................................. 18

2.1 Making the material into feed and seed rods ................ 18

2.2 Crystal Growth ................................................ 19

2.2.1 Structure of Traveling-Solvent Floating-Zone (TSFZ) .... 19
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.2.2</td>
<td>Growth Process</td>
<td>20</td>
</tr>
<tr>
<td>3</td>
<td>Magnetic structure transitions with Y doping in $R_{1-x}Y_xMnO_3$</td>
<td>22</td>
</tr>
<tr>
<td>3.1</td>
<td>$Ho_{1-x}Y_xMnO_3$</td>
<td>22</td>
</tr>
<tr>
<td>3.2</td>
<td>$Er_{1-x}Y_xMnO_3$ and $Dy_{1-x}Y_xMnO_3$</td>
<td>25</td>
</tr>
<tr>
<td>3.3</td>
<td>Inelastic Neutron Scattering</td>
<td>27</td>
</tr>
<tr>
<td>4</td>
<td>Crystal Field Levels in $HoMnO_3$</td>
<td>30</td>
</tr>
<tr>
<td>4.1</td>
<td>Introduction of spin waves and crystal-field excitations</td>
<td>30</td>
</tr>
<tr>
<td>4.2</td>
<td>Interactions between crystal-field levels and spin waves</td>
<td>37</td>
</tr>
<tr>
<td>4.2.1</td>
<td>Crossing near $(1,0,0)$</td>
<td>38</td>
</tr>
<tr>
<td>4.2.2</td>
<td>Crossing near $(1,0,1)$</td>
<td>39</td>
</tr>
<tr>
<td>5</td>
<td>Discussion and Conclusion</td>
<td>51</td>
</tr>
<tr>
<td>Bibliography</td>
<td></td>
<td>53</td>
</tr>
<tr>
<td>VITA</td>
<td></td>
<td>58</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>-----------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>1.1</td>
<td>Basic phenomenology of ferromagnets.</td>
<td>2</td>
</tr>
<tr>
<td>1.2</td>
<td>Orders in different magnetic phases.</td>
<td>3</td>
</tr>
<tr>
<td>1.3</td>
<td>Ferroelectrics</td>
<td>5</td>
</tr>
<tr>
<td>1.4</td>
<td>Double-well potential</td>
<td>6</td>
</tr>
<tr>
<td>1.5</td>
<td>Phase control in ferroics and multiferroics.</td>
<td>8</td>
</tr>
<tr>
<td>1.6</td>
<td>$RMnO_3$ crystal structure.</td>
<td>10</td>
</tr>
<tr>
<td>1.7</td>
<td>Ferroelectric polarization driven by MnO layer buckling.</td>
<td>11</td>
</tr>
<tr>
<td>1.8</td>
<td>Superexchange of electrons in Mn$^{3+}$ and O$^{2-}$.</td>
<td>11</td>
</tr>
<tr>
<td>1.9</td>
<td>Possible Mn$^{3+}$ magnetic symmetries for $RMnO_3$.</td>
<td>12</td>
</tr>
<tr>
<td>1.10</td>
<td>Magnetic phases for different $RMnO_3$</td>
<td>13</td>
</tr>
<tr>
<td>1.11</td>
<td>Neutron scattering order parameter measurements in HoMnO$_3$.</td>
<td>14</td>
</tr>
<tr>
<td>1.12</td>
<td>Field-dependent magnetic phase diagram for HoMnO$_3$.</td>
<td>16</td>
</tr>
<tr>
<td>2.1</td>
<td>TSFZ Front View</td>
<td>19</td>
</tr>
<tr>
<td>2.2</td>
<td>TSFZ Side and Top View</td>
<td>20</td>
</tr>
<tr>
<td>2.3</td>
<td>Process of Growth</td>
<td>20</td>
</tr>
<tr>
<td>2.4</td>
<td>Actual Growth Picture</td>
<td>21</td>
</tr>
</tbody>
</table>
3.1 Order parameter measurements of Ho$_{1-x}$Y$_x$MnO$_3$ ................................ 24
3.2 Order parameter measurements of Dy$_{1-x}$Y$_x$MnO$_3$ ................................ 25
3.3 Order parameter measurements of Er$_{1-x}$Y$_x$MnO$_3$ ................................. 26
3.4 Phase boundary transitions on the function of temperature. ........................... 27
3.5 Quasielastic scattering in YMnO$_3$ .......................................................... 28
3.6 Comparison of elastic and inelastic scattering for Ho$_{1-x}$Y$_x$MnO$_3$ ........ 29

4.1 Calculated in-plane spin-wave dispersion. .................................................. 31
4.2 Hydrogenic 4f shell electron states. .......................................................... 32
4.3 Crystal Field Excitations dependence on T. ............................................. 34
4.4 Crystal Field Excitations dependence on H. ............................................. 35
4.5 Low-Energy (1,0,0) spin gap at 50K and 20K. ......................................... 36
4.6 (1,0,0) Low-energy spin gap at 0.5K ....................................................... 37
4.7 Low-energy spin-wave dispersion measurements ........................................ 38
4.8 Avoided level crossing of spin waves and crystal-field level ...................... 40
4.9 (1,0,1) low-energy spin gap at 45K .......................................................... 41
4.10 (1,0,1) low-energy spin wave dispersion at 45K. ...................................... 42
4.11 Crystal field levels for HoMnO$_3$ .............................................................. 44
4.12 20K HoMnO$_3$ (H,0,1) inelastic scattering. ............................................. 45
4.13 20K HoMnO$_3$ (H,0,1) scattering with background subtracted. ............... 46
4.14 Spin wave scan at 1.7K in two different positions ...................................... 48
4.15 1.7K HoMnO$_3$ (1,0,L) Energy Scans ....................................................... 49
4.16 Constant-energy scans at 1.7K around (1,0,0) and (1,0,1) .................... 50
MAGNETIC-FERROELECTRIC INTERACTIONS IN RMnO$_3$

Yuan Wang

Dr. Owen Vajk, Dissertation Supervisor

ABSTRACT

Hexagonal $RMnO_3$ is multiferroic material as a combination of frustrated antiferromagnet ($T_N=72K$) and ferroelectric ($T_C=875K$) which consists of multiple temperature and field-dependent phases. Strong coupling between the ferroelectric and magnetic orders has been observed at a spin reorientation transition between a $P6'_3\overline{3}c'$ and a $P6'_3c'm$ magnetic phases in HoMnO$_3$, but the origin of this coupling is not well understood. Most $RMnO_3$ order in a single magnetic phase with no spin reorientation transition, and so do not show any such strong magnetic-ferroelectric coupling. This work focuses on investigating what distinguishes HoMnO$_3$ from other RMnO$_3$ in order to better understand the magnetic-ferroelectric coupling in RMnO$_3$.

In order to study the transition between $P6'_3c'm'$ and a $P6'_3c'm$ magnetic phases in RMnO$_3$, single-crystal samples of the hexagonal multiferroics Ho$_{1-x}Y_xMnO_3$, Er$_{1-x}Y_xMnO_3$ and Dy$_{1-x}Y_xMnO_3$ were grown at different compositions. YMnO$_3$ orders in a $P6'_3c'm'$, whereas ErMnO$_3$ and ErMnO$_3$ order in a $P6'_3c'm$ phase. HoMnO$_3$ is in the $P6'_3c'm$ phase at high temperatures and the $P6'_3c'm'$ phase at low temperature. Neutron diffraction measurements were used to establish the magnetic phase diagram as a function of temperature and composition. For Er$_{1-x}Y_xMnO_3$ the transition from $P6'_3c'm'$ to $P6'_3c'm$ happens over a very narrow composition range on the Y-rich side of the phase diagram. For Dy$_{1-x}Y_xMnO_3$ a spin reorientation transition
occurs for samples with up to 40% Dy, the highest concentration sample. Unlike Ho doping, both Er- and Dy- doping initially produces the P6'3c’m phase as a low-temperature phase as Y concentration decreases. Such differences suggest significant complexity in the magnetic phase competition in RMnO$_3$.

Our recent research is using inelastic neutron scattering to measure dynamics in HoMnO$_3$. Previous spin wave dispersion measurements have provided information about the Mn$^{3+}$ spin interactions, and results can be modeled with a Heisenberg antiferromagnet with anisotropy. In addition, there are several low-energy crystal-field excitations in HoMnO$_3$. These levels change whenever the system undergoes a magnetic phase transition. Furthermore, inelastic neutron scattering measurements suggest that there is a direct interaction between these crystal field levels and the Mn$^{3+}$ spin waves. Because ferroelectricity in RMnO$_3$ is due to displacement of the rare earth ions, we conclude that these interactions may be critical to the magnetic-ferroelectric coupling in HoMnO$_3$, and may help explain its unique properties.
Chapter 1

Introduction

1.1 Multiferroic material

For many years, physicists have been interested in multiferroic materials. The term “multiferroic” was introduced by Schmid in 1994 [23]. It means that this kind of material is simultaneously ferroelectric and ferromagnetic or antiferromagnetic. But what are ferromagnetic and ferroelectric materials? What is the relationship and difference between them? And why are people so interested in multiferroic material that combines both characters of these two materials? In following sections, the mechanism and structure of these materials will be introduced and explained in details.

1.1.1 Magnetism

The prefix “Ferro-” comes from “ferrum”, the Latin word for iron. Iron is the prototype, but ferromagnets do not need to contain iron to be ferromagnetic. In a
ferromagnet, the magnetic moments of unpaired electrons align parallel to each other at low temperature, creating a magnetic moment. A piece of iron may have many different regions of aligned moments, called domains, and each domain may be oriented in a different direction. If a large external magnetic field is applied to the iron, these domains will reorient along the field direction, creating a net magnetization for the entire piece of iron. There is some resistance to changing domain orientation, however, which leads to hysteresis, or history dependence: the magnetization \( M \) is determined not simply by the current magnetic field \( H \), but also what the prior magnetization and field were (Fig. 1.1 right).

Figure 1.1: Basic phenomenology of ferromagnets. Left: at zero temperature, magnetic moments align, creating a net magnetization \( M \). As temperature increases, thermal fluctuations disturb the alignment, decreasing the net magnetization. Above the Curie temperature \( T_C \), thermal fluctuations completely destroy the magnetic order. Right: in the ordered phase, microscopic domains can be magnetized in different directions, leading to zero net magnetization. Applying a magnetic field \( H \) can reorient domains, changing the macroscopic magnetization \( M \), but resistance to reorientation creates hysteresis, so that magnetization reversal will not occur until sufficiently large fields are applied.

All ferromagnets have a maximum temperature where the ferromagnetic property disappears as a result of thermal agitation (Fig. 1.1 left). This temperature is called the Curie temperature \( (T_C) \). Ferromagnetic materials undergo a 2nd-order phase
transition from a high-temperature phase that does not have a macroscopic magnetic moment to a low-temperature phase that has a spontaneous magnetization even in the absence of an applied magnetic field. The magnetic moments are aligned randomly in the high-temperature paramagnetic phase (Fig. 1.2(a)). The magnetic moments align in the same direction in the ferromagnetic phase (Fig. 1.2(b)).

Based on microscopic interactions, there are also many other possible forms of magnetic order, a few of which we will mention here. For antiferromagnets, the magnetic dipole moments in the atoms or ions are ordered antiparallel to each other (Fig. 1.2(c)). The ordering temperature of antiferromagnets is known as the Néel tempera-
ture, or $T_N$. Ferrimagnets are somewhat like antiferromagnets with the dipoles align antiparallel, however, some of the dipole moments are larger than others (Fig 1.2(d)). As a result, the material has a net overall magnetic moments as ferromagnetic material. So there is a spontaneous magnetic moment (uniform for ferromagnets, staggered for antiferromagnets) below the critical ordering temperature ($T_C$ for ferromagnets, $T_N$ for antiferromagnets).

### 1.1.2 Ferroelectricity

Ferroelectric materials are materials that have a spontaneous electric polarization that can be reversed by the application of an external electric field. The first known ferroelectric material was Rochelle salt, NaKC$_4$H$_4$O$_6$·4H$_2$O. This material was first synthesized in 1655, but its ferroelectric properties were not discovered until the 1920’s [2]. Although there is no iron in many ferroelectric materials, the prefix “ferro” is still used because the electrical properties of ferroelectrics are analogous to the magnetic properties of ferromagnets. They also undergoes a phase transition from a high-temperature phase that behaves as an ordinary dielectric to a low-temperature phase that has a spontaneous polarization whose direction can be switched by an applied field, along with hysteresis in their polarization as a function of applied field (Fig. 1.3).

The complex crystal structure of Rochelle salt made study difficult. The discovery of ferroelectricity in perovskite BaTiO$_3$ in the 1940’s provided a much simpler system to work with [2]. Significant progress has been made since then, and now ferroelectric materials are widely applied in technological applications, including capacitors, memory for computers and cards, sensors, high quality infrared cameras and so on.
Figure 1.3: Basic phenomenology of ferroelectric materials. Left: at zero temperature, positive and negative sublattices are displaced from each other, creating a net polarization $P$. As temperature increases, thermal vibrations decrease this displacement, decreasing the net polarization. Above a critical temperature $T_C$, thermal vibrations completely destroy the ferroelectric order. Right: in the ordered phase, microscopic domains can be polarized in different directions, leading to zero net polarization. Applying a electric field $E$ can reorient domains, changing the macroscopic polarization $P$, but resistance to reorientation creates hysteresis, so that polarization reversal will not occur until sufficiently large fields are applied.

The existence or absence of the ferroelectric state is determined by the balance between short-range repulsions and stabilizing forces [9]. Short-range repulsions favor the non-ferroelectric symmetric state while stabilizing forces favor polarized asymmetric state as ferroelectric phase. At high temperature, short-range repulsions dominate the state, resulting in the symmetric, unpolarized state. But with the temperature decreasing, when polarized ions’ displacement increases, the stabilizing forces to make these displacements stable become stronger than the short-range repulsions. Then the polarized state becomes stable, even in the absence of an applied field. The state in low temperature now is in ferroelectric state.
Figure 1.4: (a) A double-well potential as a function of some order parameter leads to ferroic order. At zero temperature, the system will be in one of the two minima with non-zero order parameter (represented by the arrows), breaking a symmetry. At higher temperatures, thermal energy can overcome the potential barrier between the minima, and the average value for the order parameter will be zero. (b) By adding an external field, one nonzero value for the order parameter will be favored over the other, but the potential barrier can still lock the order parameter into a local energy minima different than the global energy minima if the field is not large enough.

1.1.3 Ferroic Order

Ferromagnetism and ferroelectricity are both examples of a more general phenomena known as a ferroic order. Ferroic order is a broken-symmetry state in a material characterized by some quantity (known as an order parameter) which can be switched by the application of some sort of field. Magnetically ordered states (both ferromagnetic and antiferromagnetic) break time-reversal symmetry, and ferroelectric states break spatial inversion symmetry [3]. The order parameter is uniform magnetization for ferromagnets and electric polarization for ferroelectrics, and the corresponding fields are the magnetic and electric fields. Ferroelasticity, a third form of ferroic order [25], involves lattice distortions which break a discrete rotational symmetry, and the corresponding field for switching the state is stress. We will not be concerned with ferroelasticity in this thesis.
The basic phenomenology of ferroic order can be understood in terms of a double-well potential as a function of an order parameter, as shown in Fig. 1.4(a). At high temperatures, when the thermal energy is larger than the barrier in the middle of the well, then the system is confined by the symmetric exterior well walls, and the expectation value of the order parameter for the system will be zero, and the symmetry of the system is not broken. When temperature decreases, the system will drop into one of the two minima, breaking the symmetry of the system. This explains the temperature dependence of the order parameter shown in Figs. 1.1 and 1.3 left.

When we apply the appropriate external field, we add a potential energy proportional to the order parameter. This is equivalent to adding a sloped background to our double-well potential, as shown in Fig.1.4(b). This breaks the degeneracy of the order parameter, but if the field is not large enough, the system can still be trapped by the potential energy barrier in the higher-energy state. This resistance to order parameter reversal leads to the hysteresis shown in Figs. 1.1 and 1.3 right.

1.1.4 Multiferroic Coupling

The term "multiferroic" is used to describe any material with two or more of the ferroic orders described in the previous section. In practice, however, it is the combination of magnetism (ferromagnetic or antiferromagnetic) and ferroelectricity that has attracted most of the attention because of potential cross-coupling. Electric fields always couple with polarization and magnetic fields always couple with magnetization, as shown by the vertical arrows in Fig. 1.5. In multiferroic materials, if the magnetic and ferroelectric orders are coupled to each other (horizontal arrow), then electric fields can hence couple with magnetism and magnetic fields can couple with
polarization, as shown by the diagonal arrows in Fig. 1.5 [25, 3]. A dramatic example of such coupling (but not the only one) was discovered in 2003, where Kimura et al. showed that the ferroelectric polarization of TbMnO$_3$ could be switched with an applied magnetic field [12]. The conditions required for ferroelectricity and magnetism were once argued to be rarely met since the d-electrons of transition metal favoring magnetism are incompatible with "proper" ferroelectricity found in materials such as BaTiO$_3$ [9]. However, there are other mechanisms which can produce ferroelectricity, which is why magnetic ferroelectrics can still exist.

\[ \text{Figure 1.5: Electric field can control polarization and Magnetic field can control magnetization. When polarization couples with magnetization, electric field hence could influence magnetization through polarization and magnetic field could influence polarization through magnetization.} \]

Multiferroic compounds can be classified into two types. For type one, the origin of the ferromagnetism and ferroelectricity is independent. Since the origin is independent, the ferromagnetic state happens at different temperature comparing with ferroelectric state. The advantage for this type is that the ordering temperatures could be high, which is a requirement for most commercial applications. But the coupling between ferromagnetism and ferroelectricity is usually weak, limiting potential
For type two, the origin of the ferroelectric state is induced by magnetic order. That is this type’s advantage as coupling is strong. Since the origin is induced from each other, the transitions of the magnetic and ferroelectric state happen at the same temperature [11]. But unfortunately the ordering temperature is low, which poses problems for any applications outside of a laboratory.

The ideal multiferroic would have both strong coupling between magnetism and ferroelectricity as well as high transition temperatures. At this point, it is unclear which path of research is better: studying type-one multiferroics in the hopes of finding materials with stronger multiferroic coupling, or studying type-two multiferroics in order to develop materials with higher transition temperatures. Both paths are being pursued, but this thesis takes the former approach. If we can understand the mechanism of multiferroic coupling, we may be able to find new multiferroic materials that can find applications in industry. In the following sections, our research focuses on the type-one multiferroic hexagonal $RMnO_3$.

1.2 Hexagonal manganite $RMnO_3$

The hexagonal manganites $RMnO_3$ ($R=Sc$, $Y$, $Er$, $Ho$, $Tm$, $Yb$, $Lu$ and $Dy$) are a family of type-one multiferroics with a common structure formed by triangular and layered $MnO_5$ polyhedra with $R$ layers between them, as shown in Fig. 1.6. All of these materials are ferroelectric at high temperatures ($\sim$900K) and antiferromagnetic at low temperatures ($\sim$70K) [20]. Among this family, HoMnO$_3$ in particular has attracted attention because of the coupling observed between its magnetic and
Van Aken et al. [29] studied the ferroelectric transition in YMnO₃ and found that buckling of the MnO layers displaces Y ions along the c axis (see Fig. 1.7). Both of these distortions move atoms both up and down from the planes perpendicular to the c axis where they are located in the paraelectric phase, breaking inversion symmetry. In that way it changes the original states from paraelectric P6₃/mmc, which is centro asymmetric, to ferroelectric P6₃cm. This also reduces the volume of the unit cell, lowering the electrostatic energy. RMnO₃ is called a geometric ferroelectric, since this size effect is not the standard cause of ferroelectricity. It is generally assumed that this same mechanism is responsible for ferroelectricity in the other RMnO₃ compounds.

Mn³⁺ have spin-2 magnetic moments which interact antiferromagnetically. From
the Heisenberg uncertainty principle, we know that in order to minimize kinetic energy, a particle has to increase the size of its spatial wave function. In a solid, this can occur through hybridization of electron orbitals on neighboring ions, which we can describe in terms of electron ”hopping” between ions. When an electron hops onto a magnetic ion, there is a spin-dependent interaction between the hopping electrons and the electrons already on that atom. The basics of this interaction are dictated by Hund’s Rule, which is a result of the exchange symmetry requirements of fermions [15]. Since electrons have lower kinetic energy if they can easily hop between ions, this creates a coupling between the spin states of electrons on neighboring atoms, or what is known as direct exchange [13].

\[
\begin{align*}
\text{Mn}^{3+} & \quad \text{O}^{2-} \quad \text{Mn}^{3+} \\
\text{S}=2 & \quad \text{S}=0 \quad \text{S}=2
\end{align*}
\]

Figure 1.8: Superexchange of electrons in Mn\(^{3+}\) and O\(^{2-}\).

In the case of \(\text{RMnO}_3\), however, the Mn\(^{3+}\) ions are separated by non-magnetic O\(^{2-}\) ions, and so direct exchange is not possible. The concept of direct exchange can be extended to the cases by taking into account hopping of electrons from the inter-
mediate $O^{2-}$ p-orbital, as shown in Fig. 1.8. This mechanism is called superexchange [13]. Electrons hopping onto an $\text{Mn}^{3+}$ ion will be lower-energy if they anti-align with the existing $S=2$ moment. If neighboring $\text{Mn}^{3+}$ moments are anti-aligned (as in Fig. 1.8), there will be more available ways for electrons to hop between $\text{Mn}^{3+}$ and $O^{2-}$ (and thus lower the total energy) than if neighboring $\text{Mn}^{3+}$ moments are aligned, so that the superexchange is antiferromagnetic. The triangular lattice frustrates these interactions, leading to a spin structure where neighboring spins are 120 degrees apart instead of 180 degrees. This configuration does not fully satisfy any one interaction, but minimizes the total magnetic energy. Different stacking arrangements of $\text{Mn}^{3+}$ satisfy this 120-degree in-plane spin structure as shown in figure 1.9.

![Diagram of possible $\text{Mn}^{3+}$ magnetic symmetries for $\text{RMnO}_3$](image)

Figure 1.9: Possible $\text{Mn}^{3+}$ magnetic symmetries for $\text{RMnO}_3$ [6]
When temperature and composition changes, the magnetic phase of hexagonal manganites will also change as well (Fig. 1.10). And these phase changes induced by temperature, magnetic field and composition of $R\text{MnO}_3$ are what we're interested in.

![Graph showing magnetic phases for different $R\text{MnO}_3$](image)

Figure 1.10: Magnetic phases for different $R\text{MnO}_3$, from [7]. Low-temperature phases involving rare-earth ordering are not shown here.

### 1.3 HoMnO$_3$

#### 1.3.1 Phase transitions

HoMnO$_3$ has three phases transition in zero-field with temperature $[22, 16, 28]$. Below $T_N \approx 72$K, Mn$^{3+}$ moment order antiferromagnetically and HoMnO$_3$ is in phase P6'$_3$c'm. At $T_{SR} \approx 40$K, the spin reorientation transition happens and the phase
changes from P6’_3c’m to P6’_3cm’. Below 8K, the third phase P6_3cm is observed along with ordering of the Ho^{3+} moments. The change in magnetic symmetry leads to changes in neutron scattering intensities for different Bragg reflections. Figure 1.11 shows neutron scattering measurements of the peak intensities of the (1,0,0) and (1,0,1) Bragg reflections [28]. This scattering intensity is proportional to the square of the magnetic order parameter, and reveals all three magnetic phase transitions by changes in the intensities of these two peaks.

![Figure 1.11: Neutron scattering measurements of the magnetic Bragg peak in HoMnO₃ show magnetic phase transitions.](image-url)
1.3.2 Magnetic-ferroelectric coupling

In 2004, Lorenz discovered a sharp peak in the temperature dependence of the $c$-axis dielectric constant $\xi(T)$ occurring at the spin reorientation temperature $T_{SR}=32.8$K [17]. This peak also shifted to lower temperature in the presence of a magnetic field applied along the $c$ axis, following the P6$_3$cm' to P6'$_3$cm' magnetic phase boundary established by previous work [5]. This anomaly in $\xi(T)$ at $T_{SR}$ suggested that the ferroelectric polarization (caused by displacement of Ho$^{3+}$ along $c$) was coupling to the Mn$^{3+}$ magnetic state. In 2009, Hur et al. showed that the magnitude of the ferroelectric polarization $P$ changes at the spin reorientation transition, proving that the $\xi(T)$ anomaly was an indicator of this change in $P$ [10].

Add Lottermoser 2004 Nature paper [21].

1.3.3 Field-dependent phase diagram

The magnetic phase diagram of HoMnO$_3$ has been studied by neutron scattering [14, 22, 16, 28], second-harmonic generation (SHG) [5], and susceptibility [17, 18, 30, 31]. Figure 1.12 shows the H vs. T phase diagram obtained from a combination of neutron scattering and SHG measurements [28].

When we compare to the result of dielectric and magnetic susceptibility measurement [19, 30, 31], we found that these phase diagrams agree well at higher temperature. At lower temperature, these susceptibility measurements only observed 1 intermediate phase. In their research, the hysteresis effects had been observed but they didn’t discuss or determine the region. Some of the phase boundaries are anomalies which they didn’t represent as another phase boundary, but indicates as a smooth change of the magnetic structure in that region of the phase diagram. For Hur’s result
Figure 1.12: Field-dependent magnetic phase diagram for HoMnO$_3$ [26]. Circles represent boundaries determined by neutron scattering measurements of the (1,0,0) and (2,1,0) Bragg reflections. Boundaries between regions 3 and 4 and between regions 1 and 8 are known from SHG measurements [5]. Near 5K, some of the boundaries become hard to distinguish.

[10], it proved that there’s at least one intermediate phase and hysteresis. The main reason for different phase boundary determination is that the dielectric susceptibility is not as critical as neutron scattering to determine the magnetic phase structure.

The physical nature and the magnetic structures of the different phases are still not completely resolved. For intermediate temperature phase, the symmetry of P6$_3$c’im and P6’$_3$cm’ is supposed to be determined by Mn spins in a axis. While for low temperature phase, P6$_3$cm is determined by Ho spin reorientation. Further
measurements of out-of-plane magnetic peaks will be necessary in order to determine the exact intermediate phases.
Chapter 2

Experiment Setup and Process

2.1 Making the material into feed and seed rods

To perform our experiments, we need large single-crystal samples. We prepare these samples using the optical floating-zone technique. The first step in this process is to create a powder of the material we want to grow.

We measured the precise amount of $\text{R}_2\text{O}_3$ and $\text{MnO}_2$ powders to make the desired compound. These are mixed together in a mortar and grounded with a pestle. We calcined this mixture twice at $1200^\circ\text{C}$ up to 8 hours in a ceramic crucible by putting it in a furnace in order to make the powder react and form $\text{R MnO}_3$. After the mixture completely cooling down, we packed the powder into a cylindrical balloon and sucked the air out by a vacuum pump. But there’s still little air inside and the rod in the balloon is not compact enough. So we would use the hydraulic press to compressed the rod to make it tight without air. After waiting for 15~20 seconds for pressure...
time, we took the rod out of the hydraulic press and dry it out to peel the balloon off. We drilled a small hole on the rod and passed a platinum wire through the hole as a hanger. And last, the rod would be put in a ceramic cylindrical crucible and sintered at $1450^\circ$C for 8 hours.

2.2 Crystal Growth

2.2.1 Structure of Traveling-Solvent Floating-Zone (TSFZ)

Fig 2.1 shows the inside of our optical furnace. This technique is crucible free for growth of large, high-quality single crystals. There are 4 elliptical mirrors coated with highly reflective Aluminum and 4 high power 1000W Halogen bulbs in front of the mirrors mounted on a vertical movable stage. The growth is conducted inside an air tight quartz tube. Fig 2.2 shows a schematic of the furnace during operation.

Figure 2.1: TSFZ Front View
2.2.2 Growth Process

We hanged on the feed rod on the upper shaft and fixed the seed rod on the lower shaft. When the lamps are on and reach the required power, both ends of feed rod and seed rod were melted with the focused light from the lamps. Then we lower the upper shaft until molten zone makes contact with the lower seed rod. The surface tension suspends the melt without falling off. Lamp power is adjusted to stabilize the melt. We proceed with the growth by raising the mirror stage up which freezes material onto the seed and melts material from the feed. Fig 2.3 illustrates this growth process. Fig 2.4 is the actual growth picture from the camera view.

The grains on the rod with in-plane axis parallel to the growth direction would grow faster and push other grains out. Eventually the rod would grow into a single-grain crystal. Because $RMnO_3$ has very different thermal expansion coefficients for
different axes, misoriented grains would contract differently at their boundary as the rod cooled. This would often lead to the crystal cleaving itself along grain boundaries, leaving us with a single grain crystal.

When the TSFZ cooled down, we moved the crystal rod out from the quartz tube and bring it to MURR or NIST to perform neutron scattering measurements on it. We analyzed the raw data after neutron scattering to get all the information as we expected. The following chapters are the results from neutron scattering measurements at MURR and NIST.
Chapter 3

Magnetic structure transitions with Y doping in \( R_{1-x}Y_x\text{MnO}_3 \)

The magnetic structure and phase transitions of HoMnO\(_3\) has been discussed in Chapter 1. In order to investigate these magnetic transitions, which are known to show coupling between ferroelectricity and magnetism, we have expanded the phase diagram beyond HoMnO\(_3\) by including chemical doping. In this way we hope to discover more information about the physics of these phase transitions and the magnetic-ferroelectric coupling they reveal.

3.1 \( \text{Ho}_{1-x}Y_x\text{MnO}_3 \)

In section 1.3.1, Fig. 1.11 shows the magnetic phase transitions of HoMnO\(_3\). With temperature decreasing from \( T_N \) to below \( T_{SR} \), the magnetic phase of HoMnO\(_3\) changes correspondingly from P6\(_3\)c’m to P6\(_3\)cm’. Below \( T_{Ho}=8\text{K} \), the third phase P6\(_3\)cm
is observed along with ordering of the Ho\(^{3+}\) moments. This phase order character of HoMnO\(_3\) can also be seen from Fig. 1.10. For this chapter, we will focus on the P6\(^{3}c^{'m}\) and P6\(^{3}cm^{'}\) phases, but we will discuss the P6\(_3\)cm in chapter 4.

Also from Fig. 1.10, YMnO\(_3\) orders exclusively in the P6\(^{3}cm^{'}\) phase below T\(_N\) while ErMnO\(_3\) and DyMnO\(_3\) are totally in the P6\(^{3}c^{'m}\) phase (not counting low-temperature rare-earth ordering). If we want to find the relationship between the spin reorientation and coupling between ferroelectricity and antiferromagnetic order, one approach is to dope this kind of single phase rare earth element into other rare earth compounds as R\(_MnO_3\). We can expect that doping \(R_{1-x}Y_xMnO_3\) (here \(R=Ho, Er\) and \(Dy\)) will push the system towards the P6\(^{3}cm^{'}\) phase from whatever phase or phases the pure R\(_MnO_3\) would exhibit. If we want to find the relationship between the spin reorientation and coupling between ferroelectricity and antiferromagnetism order, Y doping provides a useful opportunity to see how the transition from P6\(^{3}c^{'m}\) to P6\(^{3}cm^{'}\) evolves without the additional complication of other rare earth elements.

We performed elastic neutron scattering at MURR on our single-crystals samples of Ho\(_{1-x}Y_xMnO_3\) using the triple-axis spectrometer TRIAX on (1,0,0) and (1,0,1) reciprocal lattice positions to obtain antiferromagnetic order parameters. For R\(_MnO_3\) below T\(_N\), the primary allowed magnetic Bragg reflections are (1,0,0) for P6\(^{3}cm^{'}\) and (1,0,1) for P6\(^{3}c^{'m}\). When we doped Yttrium with different composition into HoMnO\(_3\), we found that the magnetic phase changed as we expected from HoMnO\(_3\)-like phase below T\(_N\) to YMnO\(_3\)-like phase.

In Fig. 3.1, red squares represent intensity reflections from (1,0,0) and blue circles represent (1,0,1) reflection. We also measured the reflection on (1,0,2) which is represented by black triangles. The (1,0,2) reflection is both magnetic and structural,
and is present for both magnetic phase just in different intensities [22].

Figure 3.1: Order parameter measurements of Ho\(_{1-x}\)Y\(_x\)MnO\(_3\) at different compositions \(x\). Curves show order parameter fit results used to obtain \(T_N\).

If a spin reorientation transition happens, neutron scattering intensity will shift from (1,0,0) Bragg reflection to (1,0,1) reflection (or vice versa). That means that two curves for (1,0,0) and (1,0,1) will cross each other when there is a spin reorientation, and this point is the corresponded reorientation temperature \(T_{SR}\). From Fig. 3.1, the phase transition only happens at Yttrium composition \(x=0.825\), 0.75 and 0.625. The crossing point \(T_{SR}\) decreases a little with \(x\) dropping.
3.2 Er$_{1-x}$Y$_x$MnO$_3$ and Dy$_{1-x}$Y$_x$MnO$_3$

For pure ErMnO$_3$ and DyMnO$_3$, below $T_N$ the magnetic phase is P6’3c’. Now we doped Y ion into ErMnO$_3$ to form a single crystal hexagonal multiferroic Er$_{1-x}$Y$_x$MnO$_3$. We studied the transition completely from the P6’3c’ to P6’3cm’ in order to create this transition in a Ho-free system [27].

![Graphs showing order parameter measurements of Dy$_{1-x}$Y$_x$MnO$_3$ at different compositions $x$. Curves show order parameter fit results used to obtain $T_N$.](image)

Figure 3.2: Order parameter measurements of Dy$_{1-x}$Y$_x$MnO$_3$ at different compositions $x$. Curves show order parameter fit results used to obtain $T_N$.

Similar to Fig.3.1, in Fig. 3.2 and Fig. 3.3, the red squares are the scattering intensity of the (1,0,0) Bragg reflection, and the blue circles are the (1,0,1) Bragg reflection. The composition of Y ion is decreasing from $x=1$ to $x=0.6$ for DyMnO$_3$ and from $x=1$ to $x=0.94$ for Er$_{1-x}$Y$_x$MnO$_3$. From Fig3.3 we could see that a spin reorientation happens at $x = 0.95$ and $x = 0.94$. For $x = 0.94$ there are two broad transitions, and the phase seems to switch from P6’3c’m to P6’3cm’ and back to P6’3c’m. The
Figure 3.3: Order parameter measurements of Er$_{1-x}$Y$_x$MnO$_3$ at different compositions $x$. Curves show order parameter fit results used to obtain $T_N$.

P6’3c’m to P6’3cm’ phase transition in Er$_{1-x}$Y$_x$MnO$_3$ is thus very different than in HoMnO$_3$, where the P6’3c’m is exclusively the high-temperature phase.

We extracted $T_{SR}$ and $T_N$ values on the function of yttrium composition $x$ value and temperature to draw the phase boundary transitions for all three doping materials as Ho$_{1-x}$Y$_x$MnO$_3$, Dy$_{1-x}$Y$_x$MnO$_3$ and Er$_{1-x}$Y$_x$MnO$_3$, see Fig. 3.4. The boundaries are seperated from $T_N$ and $T_{SR}$ changing with temperature. For Ho$_{1-x}$Y$_x$MnO$_3$ and Dy$_{1-x}$Y$_x$MnO$_3$, the phase transition window is broad and they are in opposite phase transitions. But for Er$_{1-x}$Y$_x$MnO$_3$ the window for same phase transition as Dy$_{0.5}$Y$_{0.5}$MnO$_3$ is so shallow.
3.3 Inelastic Neutron Scattering

We performed inelastic neutron scattering measurements on $\mathrm{Ho_{1-x}Y_xMnO_3}$, $\mathrm{Er_{1-x}Y_xMnO_3}$ and $\mathrm{Dy_{1-x}Y_xMnO_3}$. The scanning energy is $\hbar\omega = 0.7$ meV. With temperature decreasing from $T_N$, we find a broad quasi-elastic scattering peak around $(1,0,1)$. All the results of these three doping materials are similar to our YMnO$_3$ results. Since YMnO$_3$ has common characters with inelastic neutron scattering, here we only discuss the result from it.

Figure 3.5 shows scanned along direction $(1,0,Q_l)$ at a temperature of 30K with energy transfer of 0.7 meV. We find large $Q_l$ dependence to the quasielastic scattering, with peaks around both the $(1,0,1)$ and $(1,0,2)$ positions. It is important to note that for elastic neutron scattering, YMnO$_3$’s magnetic Bragg reflection is at the $(1,0,0)$
Figure 3.5: Quasielastic scattering in YMnO$_3$, from [7]. (a) Energy scans reveal a peak which is broader in energy than the resolution. (b) In-plane momentum scans are relatively sharp. (c) Out-of-plane momentum scans are much broader (note the difference in scale). The red line shows a fit using a Lorentzian line shape for the out-of-plane dependence, the black shows a fit using a Gaussian line shape.

This quasi-elastic scattering appears in all Y-heavy compounds, but is not present in pure HoMnO$_3$. Although both magnetic phases exist in HoMnO$_3$, the phase competition between these two phases appears to be suppressed, and the phase changes for Ho$_{1-x}$Y$_x$MnO$_3$ in elastic and quasi-elastic scattering are reversed.

When we looked at bottom panel of Fig. 3.6, the Bragg peak for elastic neutron scattering happens at (1,0,1) between temperature $T_{SR}$ to $T_N$. While quasi-elastic peak for inelastic neutron scattering is at (1,0,0) on top panel in the same temperature
Figure 3.6: Comparison of elastic and inelastic scattering for Ho$_{1-x}$Y$_x$MnO$_3$. Top panels: inelastic measurements showing the shift in the quasielastic peak from the (1,0,0) position above $T_{SR}$ to (1,0,1) below $T_{SR}$. Bottom panels: elastic scattering measurements showing the shift in the primary Bragg reflection from (1,0,1) above $T_{SR}$ to (1,0,0) below $T_{SR}$ for the same samples.

range. And blow $T_{SR}$, the Bragg peak is at (1,0,0) in bottom panel while quasielastic peak is at (1,0,1) on top panel. This discrepancy shows the complex magnetic structure for HoMnO$_3$. And the reason is still unknown.
Chapter 4

Crystal Field Levels in HoMnO$_3$

4.1 Introduction of spin waves and crystal-field excitations

The spin waves dispersion spectrum of HoMnO$_3$ can be measured by inelastic neutron scattering. The Hamiltonian $H$ for the Heisenberg antiferromagnet with anisotropy

$$H = \sum_{(i,j)} J_{\parallel} S_i \cdot S_j + \sum_{(i,k)} J_{\perp} S_i \cdot S_k + \sum_i D_{\perp} S_i^z S_i^z + \sum_i D_{\parallel} S_i^\alpha S_i^\alpha$$

(4.1)

explains the spin-wave spectrum well. $J_{\parallel}$ is in-plane exchange and $D_{\perp}$ is easy plane anisotropy. Both of them are higher energy than $J_{\perp}$, the out-of-plane exchange, and $D_{\parallel}$, the easy-axis anisotropy. $J_{\parallel}$ determines the overall scale of the spin-wave dispersion and $J_{\perp}$ determines the energy dispersion along the out-of-plane momentum $L$, while $D_{\perp}$ and $D_{\parallel}$ determine the two spin gaps. Although $J_{\perp}$ and $D_{\parallel}$ are weak, they are not zero.
Figure 4.1 is in-plane Mn spin wave dispersion calculated from equation 4.1 [1]. The energy $\omega$ was strongly dependent on $H$ and $K$ (the in-plane momentum) but only weakly dependent on $L$ (the out-of-plane momentum).

Vajk et al. measured the spin-wave dispersion in HoMnO$_3$ and fit their data to a simpler two-parameter spin-wave model, and found $J_{||} = 2.447$ meV and $D_{||} = 0.387$ meV [28, 26]. They also reported the existence of two crystal-field excitations of Ho at 1.5 and 3.1 meV. These excitations made determination of $J_{\perp}$ and $D_{\perp}$ difficult, since the low-energy portion of the spin waves was the most sensitive to these weaker terms in our Hamiltonian and distinguished spin-waves from crystal-field excitations in the same range requiring high energy resolution.

More recent measurements of the out-of-plane dependence of the low-energy spin-wave dispersion were able to provide information about $J_{\perp}$ and $D_{\perp}$ [4] for HoMnO$_3$ as well as for YMnO$_3$ and YbMnO$_3$. The energy difference between the low-energy mode at (1,0,0) and (1,0,1) was due to $J_{\perp}$, while the gap to the bottom of this mode was due to $D_{\perp}$. Fabreges et al.’s measurements also revealed that in the low-energy side
of this dispersion switched from (1,0,0) in the P6'_3c'm phase to (1,0,1) in the P6'_3cm' phase.

![Hydrogenic 4f shell electron states](image)

**Figure 4.2:** Hydrogenic 4f shell electron states [8].

The crystal-field excitations reported by Vajk et al. [28, 26] were due to electrons in the 4f shell of Ho. Figure 4.2 shows the Hydrogen-like 4f orbital states. These states are degenerate for a free atom, but the anisotropy of the crystal environment breaks this degeneracy. Since this shell is partially occupied, electrons can be excited from lower energy orbitals to higher energy orbitals within the f shell. Because these excitations are localized to individual Ho^{3+} ions, inelastic scattering from these excitations is dispersionless (the energy does not change with momentum).

The crystal field excitation levels changed with temperature and applied magnetic field, as shown in Figs. 4.3 and 4.4. These changes coincided with magnetic phase transitions of the Mn^{3+} lattice, indicating that the Ho^{3+} crystal field levels were coupled to the Mn^{3+} spins. This was true even for the low-temperature hysteretic
phase change, where the results at 1.1 Tesla depended upon whether the field was ramping up or down.
Figure 4.3: Crystal Field Excitations dependence on T in zero field. Symbol colors corresponded to the phases shown in figure 1.12. Note that 75K was above $T_N$. Blue and green curves showed fits to the data, and red curves showed individual peaks from the fits.
Figure 4.4: Crystal Field Excitations dependence on H at T=0.5K. Symbol colors corresponded to the phases show in figure 1.12. Arrows by the 1.1T labels indicated whether the field was increasing or decreasing. Blue curves showed fits to the data, and red curves showed individual peaks from the fits.

We also measured the low-energy spin-wave mode at the (1,0,0) position for dif-
ferent temperatures, shown in Fig. 4.5, and our results agreed with the Fabreges et al. data for the high and intermediate temperature phases. However, Fig. 4.3 and 4.5 revealed that Fabreges et al. made an error in their analysis of their intermediate-temperature HoMnO$_3$ data. They mistook the 1.5 meV crystal field level as the top of the low-energy spin dispersion at (1,0,0), when the spin gap in the intermediate temperature phase was at 2.4 meV. As a result, the $J_{\perp}$ they calculated for the intermediate-temperature phase was too small. The correct 2.4 meV excitation was visible within their data, but because the out-of-plane dispersion was shallow, it was easy to mistake for a crystal field excitation without comparing to data taken at $H \neq 1$, as in Fig. 4.3.

![Figure 4.5: Low-Energy (1,0,0) spin gap at 50K and 20K.](image)

Data taken at (1,0,0) and (1.2,0,0) at 0.5K in the low-temperature phase showed which excitations were crystal fields (no Q dependence) and which was the spin-wave mode (Fig. 4.6). The spin gap at (1,0,0) was at around 2.4 meV, as in the intermediate-temperature phase. The meaning of the vertical arrows will be discussed.
in the next section.

![Graph showing intensity vs. angular frequency](image)

**Figure 4.6**: Low-energy spin gap at 0.5K. Data taken at the (1,0,0) included both the spin wave and the crystal field excitations. Data taken at (1.2,0,0) showed only the crystal field levels. Vertical arrows indicated energies used for constant-Q scans in Fig. 4.7.

### 4.2 Interactions between crystal-field levels and spin waves

As we discussed above, when the magnetic phase changed with temperature and applied magnetic field, the crystal field excitation levels also changed. This suggested that the Ho$^{3+}$ 4f electrons interacted with the Mn$^{3+}$ spins, and this interaction should affect the dynamics of both, the crystal field levels for Ho$^{3+}$ and the spin waves for Mn$^{3+}$. Furthermore, because ferroelectricity in HoMnO$_3$ was caused by displacement of Ho$^{3+}$, any interaction between Ho$^{3+}$ and Mn$^{3+}$ spins was potentially significant for multiferroic coupling in HoMnO$_3$. We had performed measurements of the spin waves near the crystal field excitations in order to find signs of such potential interactions.
in the dynamics of HoMnO$_3$.

Figure 4.7: Constant-energy scans through the low-energy spin wave dispersion at 0.5 K. Solid lines were fits to either one Gaussian (2.4 and 3.3 meV) or two Gaussians (all other energies). Energies correspond to arrows were shown in Fig. 4.6.

4.2.1 Crossing near (1,0,0)

The low-energy measurements of the spin wave dispersion revealed interesting behavior around the crystal field levels. Constant-energy scans taken at six different energies (corresponding to the arrows in the right panel of Fig. 4.6) around the (1,0,0)
were shown in Fig. 4.7 for 0.5 K. These measurements were taken with the crystal oriented in the (H,K,0) scattering plane, so that the broad vertical resolution of the spectrometer aligned with the shallow direction of the spin-wave dispersion, which helped to increase the signal from spin-wave scattering.

The bottom of the spin wave was around 2.4 meV, and constant-E scans here showed a single narrow peak. Upon increasing the energy, the peak splitted in two, and the two peaks moved outward as the energy increasing, as expected for the spin-wave dispersion. Upon reaching 3.1 meV, which corresponded to the top of the crystal field excitation, the spin wave appeared damped and spreaded out. Above the crystal field excitation the spin wave re-emerged as a single peak which began to spread out again. Scans at 50 K in the high-temperature phase (not shown) revealed no such anomalies at the crystal field level, while scans at 20 K in the intermediate phase also showed signs of an anomaly. There should be an avoided level crossing of the spin wave dispersion and the crystal field level, due to an interaction between the two excitations. The energy comparison on (1,0,0) between 50K and 0.5K scan could be seen at Fig. 4.8. 50K spin wave crossed the two dashed green lines as crystal field levels. There’s no coupling between spin wave and crystal excitation field. But 0.5K spin wave interacted with top crystal excitation field and the spin wave’s curve changed its shape. As dashed red line showed, the avoid level crossing appeared here.

4.2.2 Crossing near (1,0,1)

We have seen previously that Bragg scattering, quasi-elastic scattering, and the out-of-plane dispersion at the (1,0,0) and (1,0,1) positions switched places at $T_{SR}$, so it is important to determine what happens to the spin wave-crystal field crossing near
Figure 4.8: Comparison of the 0.5 K spin wave fits to 50 K fit results (not shown), along with the major crystal field excitation levels. Dashed lines are guides to the eye.

the (1,0,1) position as well. For the following measurements, a HoMnO$_3$ crystal was aligned in the (H,0,L) scattering plane, which meant that the broad vertical resolution now lay along the K direction. The steep dispersion along K meant that this broad vertical resolution did not increase the spin-wave scattering signal.

Fig. 4.9 showed the spin gap for (1,0,1). The top panel was for 45K energy scans at Q=(1,0,1) and Q=(0.8,0,1). The scan on (0.8,0,1) was the background which was subtracted from the bottom panel. The peak in the bottom panel was spin gap and its center was around 2.35 meV which was consistent with Fabreges’ result at (1,0,1) in the high-temperature phase.
Figure 4.9: (1,0,1) low-energy spin gap at 45K. Top panel: Energy scans at two different momentum transfers. Bottom panel: the (1,0,1) data with crystal field levels from (0.8,0,1) subtracted.

Fig. 4.10 showed constant-energy scans around (1,0,0) position. The 2.0 meV scan picked up a single peak from the bottom of the spin-wave dispersion. With energy increasing, the single peak slitted into two peaks and those two peaks kept moving outward because of spin-wave dispersion, as for 0.5K (Fig. 4.7). But when the energy reached 3.1 meV, there was no indication of damping. The two peaks still
kept moving outward at 3.6 meV. No avoid level crossing was found at the (1,0,1) position for 45K, indicating that this interaction did not simply move from (1,0,0) to (1,0,1) at $T_{SR}$.

Figure 4.10: Constant-energy scans through the low-energy spin wave dispersion around (1,0,1) at 45K. Solid red lines are Gaussian fits.

Figure 4.11 showed 20 K energy scans at $Q=(1,0,0)$ and $Q=(1,0,1)$, as well as $Q=(1.2,0,0)$ which measured only the crystal-field excitations without any spin waves. The bottom two panels showed the (1,0,0) and (1,0,1) data with the crystal field excitations subtracted. The dispersion of the low-energy mode from about 1.2 meV at (1,0,1) to 2.4 meV at (1,0,0) was clearly visible, and agrees with the Fabreges et
al. data (though not their analysis) [4]. The 1.2 meV gap at (1,0,1) was due to the uniaxial anisotropy $D_\parallel$ and the increase to 2.4 meV at (1,0,0) was due to $J_\perp$. 
Figure 4.11: Top panel: 20K HoMnO$_3$ energy scans at three different momentum transfers. Middle panel: the (1,0,0) data with crystal field levels from (1.2,0,0) subtracted. Bottom panel: the (1,0,1) data with crystal field levels from (1.2,0,0) subtracted.
Figure 4.12 showed extensive data for the crossing of the spin-wave dispersion and the crystal field excitations around the (-1,0,1) position at 20 K.

![Figure 4.12: 20K HoMnO$_3$ (H,0,1) inelastic scattering intensity map showing both crystal field excitations and a spin wave centered at (-1,0,1).](image)

Using the (1.2,0,0) scan shown in Fig. 4.11, we subtracted the crystal field excitations from these measurements to obtain the spin-wave component, shown in Fig. 4.13. Unlike at the (1,0,0) position, there was no apparent avoided level crossing at the (1,0,1).

In order to search for any possible avoided levels crossing around the (1,0,1) in the low-temperature phase, we needed to determine the spin gap at (1,0,1). Figure 4.14 showed constant-Q scans at the (1,0,1), (1,0,0), and (0.8,0,1) positions. Subtraction
Figure 4.13: 20K HoMnO$_3$ (H,0,1) inelastic scattering intensity map with crystal field excitations subtracted.

of the (0.8,0,1) background did not produce very reliable data for the spin gap at either (1,0,1) or (1,0,0) positions. Note the difference between the (1,0,0) results from Fig. 4.14, where the crystal was oriented in the (H,0,L) scattering plane, and Fig. 4.6, where the crystal was oriented in the (H,K,0) scattering plane. The loss of spin-wave scattering intensity because of the vertical resolution misorientation made it very hard to pick out the spin wave from the crystal-field excitations.

We had tried to measure the low-energy spin-wave dispersion along L in the low-temperature phase, to complement the measurements done in the intermediate and high-temperature phases [4]. The results were shown in Fig. 4.15. Unfortunately
there was insufficient intensity to clearly distinguish the spin-wave dispersion from the crystal-field excitations. It may also be that in this low-temperature phase, $J_\perp$ may be very small, so that the dispersion along $L$ was small as well, making it even harder to pick out the spin waves from the crystal field levels.

Figure 4.16 showed constant-energy scans at 1.7K around the $(1,0,0)$ and $(1,0,1)$ positions. The $(1,0,0)$ data revealed an avoided level crossing, in agreement with Fig. 4.8. However, there was too little signal to determine whether any avoided levels crossing happens around the $(1,0,1)$ position.

We have identified signals of coupling between the Ho$^{3+}$ crystal-field levels and the Mn$^{3+}$ spin waves which could be a critical part of the magnetic-ferroelectric coupling in HoMnO$_3$. In order to fully understand the significance of this data, however, we need to be able to assign these excitations to specific f-shell orbitals. There are various tools available to help assist in such analysis, and the results should help us better understand what makes HoMnO$_3$ unique among the RMnO$_3$ compounds.
Figure 4.14: Top panel: 1.7K HoMnO$_3$ energy scans at three different momentum transfers. Middle panel: the (1,0,0) data with (0.8,0,1) crystal field levels subtracted. Bottom panels: the (1,0,1) data with (0.8,0,1) crystal field levels subtracted.
Figure 4.15: 1.7K HoMnO$_3$ (1,0,L) Energy Scans
Figure 4.16: Constant-energy scans at 1.7K around (1,0,0) (left) and (1,0,1) (right).
Chapter 5

Discussion and Conclusion

HoMnO$_3$ stands out as unique among the RMnO$_3$ family due to the strong observed magnetic-ferroelectric coupling at its spin reorientation. We have sought information about what makes HoMnO$_3$ complexity and how the magnetism and ferroelectricity couple together. Our results give some clues about both questions, and provide avenues for further research.

HoMnO$_3$’s magnetic phase diagram is more complicated than YMnO$_3$, ErMnO$_3$, or DyMnO$_3$. HoMnO$_3$ undergoes a spin reorientation transition between P6’$_3$c’m and P6’$_3$cm’ magnetic phases, and exhibits large magnetic-ferroelectric coupling at this transition. Mixed composition samples of Er$_{1-x}$Y$_x$MnO$_3$ and Dy$_{1-x}$Y$_x$MnO$_3$ also exhibit a phase transition between P6’$_3$c’m and P6’$_3$cm’ magnetic phases, but with the temperature sequence inverted compared to HoMnO$_3$ or even Ho$_{1-x}$Y$_x$MnO$_3$. Quasielastic scattering in Y-rich compounds indicates strong magnetic phase competition between the P6’$_3$c’m and P6’$_3$cm’ phases. For HoMnO$_3$, ErMnO$_3$, and DyMnO$_3$ there are also additional very low temperature phases associated with ordering of the
rare earth magnetic moments.

There are multiple differences between the different R-site atoms which could in principle lead to different behavior. One obvious difference is simply the size of the R-site ion. Since ferroelectricity in this system is driven by a structural distortion and since the frustration of the out-of-plane magnetic interactions are relieved because of such distortions, it's reasonable to expect ion size to play a role. However, this cannot provide a full explanation of the phase diagrams of $R_{1-x}Y_xMnO_3$. Ho$^{3+}$ has an ionic radius between Dy$^{3+}$ and Er$^{3+}$, but the phase diagram of Ho$_{1-x}Y_xMnO_3$ is not somewhere between Dy$_{1-x}Y_xMnO_3$ and Er$_{1-x}Y_xMnO_3$.

The magnetism of the rare earth itself may also play an important role. Y$^{3+}$ has a completely filled electron shell, while Dy$^{3+}$, Ho$^{3+}$, and Er$^{3+}$ all have partially filled f electron orbitals. The size of the magnetic moments for Dy$^{3+}$, Ho$^{3+}$, and Er$^{3+}$ are all similarly large, but differences in the exact structure of the f shell may be important. We have found clues in our inelastic scattering measurements that the f-shell Ho$^{3+}$ electrons couple to the d-shell Mn$^{3+}$ electrons. Crystal field excitations in HoMnO$_3$ show that the energy levels depend upon the magnetic phase of the Mn$^{3+}$ ions. Furthermore, the spin-wave dispersion of Mn$^{3+}$ appears to show an avoided level crossing where it should cross the crystal field excitations near the (1,0,0) position in the intermediate and low temperature phase, indicating an interaction between these Ho$^{3+}$ crystal field excitations and the Mn$^{3+}$ spin waves. No such avoided level crossing was observed near the (1,0,1) position or in the high temperature phase. Further work needs to be done in order to identify the f-shell states corresponding to these excitations. This may help us understand the interaction between magnetism and ferroelectricity in HoMnO$_3$. 

52
Bibliography


VITA

Yuan Wang was born in Lanzhou, Gansu, China on Nov 12, 1978. After completing her study at Lanzhou No. One high school in 1997, she entered the department of physics in Lanzhou university with major in nuclear physics. She received science bachelor degree in 2001. From 2007 to 2013, she pursued her Ph.D. study in department of Physics and Astronoty in University of Misouri-Columbia, Columbia, MO, USA. Her research was in experimental condensed matter physics, especially in magnetic phase structure of rare earth element, under the supervision of Prof. Owen Vajk. She achieved Ph.D. degree in physics in December 2013.

Yuan Wang married to Li Ma in January 2006. After marriage, both of them were in University of Missouri-Columbia to work on their Ph.D. research in different departments. In November 2007, their new family members, Jason Ma and Nicholas Ma, were born. After graduation, the family moved to China and Yuan Wang found a faculty position in Sun Yat-Sen University in south of China. Her future research will be in experimental condensed matter physics and health physics.