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Competing Magnetic Interactions in Complex Oxides

A Dissertation submitted in partial satisfaction of the requirements for the degree
Doctor of Philosophy
in
Materials
by
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for my family
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5. B. C. Melot, J. E. Drewes, R. Seshadri, and A. P. Ramirez, Magnetic phase evolution in the spinel compounds \(\text{Zn}_{1-x}\text{Co}_x\text{Cr}_2\text{O}_4\), \textit{J. Phys.: Condens. Mat-


**Publications from other collaborations**

6. Z. Hulvey, B. C. Melot, and A. K. Cheetham, Structure and magnetic field-induced transition in a one-dimensional hybrid inorganic-organic chain system, Co$_2$(4,4'-bpy)(tfhba)$_2$·4,4'-bpy (4,4'-bpy = 4,4'-bipyridine; tfhba = 2,3,5,6-tetrafluoro-4-hydroxybenzoate) (submitted for publication).


Abstract

Competing Magnetic Interactions in Complex Oxides

by

Brent C. Melot

Materials with strongly correlated electrons have been extensively studied because of the novel and often technologically useful properties that arise due to the interplay between spin, lattice, charge, and orbital degrees of freedom. [1] When one or more of these degrees of freedom is not allowed to attain a low-energy ground state, either due to competing interactions or the geometry of the lattice, a degree of local disorder arises and the material is said to be frustrated. [2–4]

The work presented here aims to develop an understanding of how this frustration in complex oxides affects the physical properties via careful study in a variety of structures. Through the use of detailed structural characterization; X-ray and neutron diffraction in conjunction with physical property measurements and in some cases Density Functional Theory (DFT) calculations, we explore the relationship between crystal structure and macroscopic properties.
Firstly we examine the solid solution $\text{Zn}_{1-x}\text{Co}_x\text{Cr}_2\text{O}_4$. By introducing magnetism onto an otherwise non-magnetic diamond lattice, we construct a phase diagram that shows the evolution of spiral magnetic order for concentrations of Co above $x = 0.5$. We then discuss the solid solution $\text{CoAl}_{2-x}\text{Ga}_x\text{O}_4$. We examine how site mixing between the tetrahedral and octahedral sites and lattice expansion affect frustration in $\text{CoAl}_2\text{O}_4$. We demonstrate that increasing the unit cell volume, and correspondingly increasing the length of superexchange pathways, reduces $\Theta_{CW}$ and that site mixing alters the shape of the inverse magnetic susceptibility curves.

We then present an investigation into several magnetic chain compounds which experience a competition between nearest and next-nearest neighbor interactions. We begin by examining $\text{CoSeO}_4$ and $\text{CoSe}_2\text{O}_5$. Both display complex magnetism including weak ferromagnetism and field-induced transitions. We also show that $\text{CoSeO}_4$ demonstrates magnetodielectric coupling. We conclude by presenting work on the polar ferrimagnet $\text{VOSe}_2\text{O}_5$. Using a combination of DFT calculations and powder neutron diffraction we suggest a complex ferrimagnetic spin structure sets in at low temperatures with interesting dielectric properties at higher temperature.
Contents

List of Figures xvi
List of Tables xix

1 Magnetism in Insulating Spinels 1
  1.1 Introduction ........................................... 2
  1.2 Crystal Structure ..................................... 3
  1.3 Magnetic Interactions ................................. 6
  1.4 B-site Only Magnetic Spinels ......................... 10
  1.5 A-site Only Magnetic Spinels ......................... 16
  1.6 Fully Magnetic Spinels ................................ 19

2 Magnetic phase evolution in (Zn,Co)Cr$_2$O$_4$ 26
  2.1 Experimental Details .................................. 30
  2.2 Computational Details .................................. 30
  2.3 Results and Discussion ............................... 32

3 Magnetic frustration on the diamond lattice of A-site magnetic spinels 50
3.1 Experimental Details .............................................. 52
3.2 Computational Details ........................................... 53
3.3 Results and Discussion ......................................... 56

4 Magnetic ordering and magnetodielectric coupling in CoSeO$_4$ 79
  4.1 Experimental Details ........................................... 81
  4.2 Computational Details ........................................ 84
  4.3 Results and Discussion ....................................... 86

5 Magnetic Structure and Susceptibility of CoSe$_2$O$_5$ 103
  5.1 Experimental Details .......................................... 104
  5.2 Results and Discussion ...................................... 106

6 An Experimental and Computational Investigation of the Polar Ferri-
magnet VOSe$_2$O$_5$ 121
  6.1 Experimental Details .......................................... 124
  6.2 Computational Details ....................................... 128
  6.3 Results and Discussion ...................................... 128

7 Summary and Future Directions 152

Bibliography 153
## List of Figures

1.1 Ideal spinel crystal structure ........................................ 6
1.2 Illustration of the magnetic exchange pathways in the $A$ and $B$ sublattices of spinel ........................................ 8
1.3 Magnetic and Dielectric properties of ZnCr$_2$O$_4$ .................. 11
1.4 Frustration in the Ge$M_2$O$_4$ compounds .......................... 14
1.5 Frustration on the diamond lattice and magnetic ordering phase diagram for diamond spinels ................................. 17
1.6 Magnetodielectric measurements on CoCr$_2$O$_4$ ................. 21
1.7 Magnetodielectric measurements on Mn$_3$O$_4$ .................... 24

2.1 Illustration of the spinel structure ................................. 27
2.2 Room temperature x-ray diffraction pattern for Zn$_{1-x}$Co$_x$Cr$_2$O$_4$ 33
2.3 Effective moment as a function of $x$ in Zn$_{1-x}$Co$_x$Cr$_2$O$_4$ ........ 38
2.4 DC magnetic susceptibility data for Zn$_{1-x}$Co$_x$Cr$_2$O$_4$ .......... 40
2.5 Scaled inverse susceptibility of Zn$_{1-x}$Co$_x$Cr$_2$O$_4$ ............ 41
2.6 Monte-Carlo simulations on Zn$_{1-x}$Co$_x$Cr$_2$O$_4$ .................. 44
2.7 More Monte-Carlo on Zn$_{1-x}$Co$_x$Cr$_2$O$_4$ ..................... 45
2.8 Proposed magnetic phase diagram for Zn$_{1-x}$Co$_x$Cr$_2$O$_4$ .......... 48

3.1 Room temperature time-of-flight neutron diffraction patterns of CoAl$_{2-x}$Ga$_x$O$_4$ ........................................ 55
3.2 Change in structural parameters with $x$ for CoAl$_{2-x}$Ga$_x$O$_4$  
3.3 Pair distribution function evolution of CoAl$_{2-x}$Ga$_x$O$_4$  
3.4 Normalized inverse susceptibility data for CoAl$_{2-x}$Ga$_x$O$_4$  
3.5 DC magnetic susceptibility of CoAl$_{2-x}$Ga$_x$O$_4$  
3.6 Isothermal magnetization curves obtained at 2 K for CoAl$_{2-x}$Ga$_x$O$_4$  
3.7 Effect of Ga substitution on the degree of magnetic frustration in CoAl$_{2-x}$Ga$_x$O$_4$  
3.8 Monte-Carlo simulations of the susceptibility as a function of site inversion in CoAl$_{2-x}$Ga$_x$O$_4$  
3.9 Monte-Carlo simulations of the susceptibility as a function of the ratio $J_2/J_1$ in CoAl$_{2-x}$Ga$_x$O$_4$  

4.1 Crystal structure of CoSeO$_4$  
4.2 Temperature-dependent magnetic susceptibility of CoSeO$_4$  
4.3 Isothermal magnetization curves for CoSeO$_4$  
4.4 Temperature dependent specific heat of CoSeO$_4$  
4.5 Calculated DOS for CoSeO$_4$  
4.6 Neutron diffraction patterns of CoSeO$_4$ at different temperatures  
4.7 5 K neutron diffraction pattern showing the the nuclear and magnetic contribution for CoSeO$_4$  
4.8 Illustration of the magnetic structure of CoSeO$_4$  
4.9 Temperature-dependent dielectric constant compared to the normalized inverse susceptibility for CoSeO$_4$  
4.10 Dielectric constant as a function of magnetic field for CoSeO$_4$  

5.1 Normalized inverse magnetic susceptibility of CoSe$_2$O$_5$  
5.2 DC Magnetic susceptibility of CoSe$_2$O$_5$  
5.3 Isothermal magnetization curve for CoSe$_2$O$_5$ emphasizing the weak ferromagnetic component  
5.4 Temperature dependence of the specific heat of CoSe$_2$O$_5$  

xvii
5.5 Variable temperature powder neutron-diffraction patterns of CoSe$_2$O$_5$ ......................................................... 116
5.6 Proposed magnetic structure of CoSe$_2$O$_5$ ......................... 117

6.1 Crystal structure of VOSe$_2$O$_5$ ........................................ 122
6.2 Illustration of the displacement of V(1), V(2), and V(3) from the center of their octahedra ................................................. 129
6.3 Temperature-dependent magnetization of VOSe$_2$O$_5$ ............ 131
6.4 Normalized inverse magnetic susceptibility of VOSe$_2$O$_5$ ........ 132
6.5 Isothermal magnetization curves for VOSe$_2$O$_5$ ................. 134
6.6 Real and Imaginary AC magnetic susceptibility of VOSe$_2$O$_5$ . 136
6.7 Low temperature specific heat of VOSe$_2$O$_5$ ..................... 137
6.8 Temperature dependence of the dielectric constant and high temperature specific heat of VOSe$_2$O$_5$ .............................. 139
6.9 Time-of-flight neutron diffraction patterns of VOSe$_2$O$_5$ ........ 140
6.10 Illustration of the ordered spin states considered for VOSe$_2$O$_5$ . 142
6.11 DOS calculated for VOSe$_2$O$_5$ ........................................ 144
6.12 Refinements on the constant-wavelength neutron diffraction data for VOSe$_2$O$_5$ .............................................................. 145
6.13 Illustration of the inter-chain and intra-chain magnetic exchange interactions in VOSe$_2$O$_5$ ................................. 149
List of Tables

1.1 Table of ions commonly found in the octahedral and tetrahedral sites of spinel ........................................ 5

2.1 Magnetic data extracted from Curie-Weiss fits to the high temperature susceptibility of Zn$_{1-x}$Co$_x$Cr$_2$O$_4$ ........................................ 35

2.2 Resulting magnetic exchange constants calculated from Monte-Carlo simulations on Zn$_{1-x}$Co$_x$Cr$_2$O$_4$ ........................................ 43

3.1 Magnetic data for CoAl$_{2-x}$Ga$_x$O$_4$ and other well-ordered A-site spinels ........................................ 63

4.1 Summary of results from the Rietveld refinement of the neutron diffraction data for CoSeO$_4$ ........................................ 95

4.2 Magnetic moment on each Co in CoSeO$_4$ ........................................ 99

5.1 Summary of the results of Rietveld structure refinements on CoSe$_2$O$_5$ ........................................ 119

5.2 Atomic positions from Rietveld refinements of CoSe$_2$O$_5$ ........ 119

6.1 Relative total energies of the spin configurations considered for VOSe$_2$O$_5$ ........................................ 143
Chapter 1

Magnetism in Insulating Spinels

The goal of the work here is to develop an understanding of competing magnetic interactions in complex oxides \textit{via} careful study of a variety of structures. We have used detailed structural characterization through X-ray and neutron diffraction in conjunction with physical property measurements and in some cases Density Functional Theory (DFT) calculations to elucidate the relationship between crystal structure and macroscopic properties. The purpose of this introductory chapter is to present a review of magnetic phenomena in the spinel family and use these compounds as a way of presenting concepts that will be considered in greater depth in the coming chapters.
1.1 Introduction

In the search for single phase inorganic materials incorporating technologically functional properties one of the most studied structural families is that of the spinels. In fact, the earliest discovery of magnetism itself can be attributed to the discovery of the mineral lodestone which contains naturally polarized magnetite: a spinel with the composition Fe$_3$O$_4$. Investigation into spinels, whose general formula is $AB_2X_4$, began in 1915 when Bragg and Nishikawa published the first descriptions of the structure via X-ray diffraction [5, 6]. Barth and Posnjak presented a more detailed description of the cation distribution between the sites and introduced the idea of the inverse spinel in 1932. [7] Early work on potential technological applications for spinels such as in ferrite cores was led by Lotgering, Jonker, and Blasse at the Philips Research Lab in Eindhoven throughout much of the 1950’s and 60’s. The list of physical phenomenon that have been discovered since that time has grown to include magnetoresistance (LiMn$_2$O$_4$ [8], FeCr$_2$S$_4$ [9, 10]), superconductivity (CuRh$_2$S$_4$ [11–13], LiTi$_2$O$_4$ [14]), heavy fermions (LiV$_2$O$_4$ [15, 16]), multiferroicity (CoCr$_2$O$_4$ [17, 18], Mn$_3$O$_4$ [19]), exchange bias (Zn$_x$Mn$_{3-x}$O$_4$ [20]) spin-driven Jahn-Teller distortions ($M$Cr$_2$O$_4$, $M = $ Zn[21, 22], Cd [22, 23]) and metal-insulator transitions (Fe$_3$O$_4$ [24–26], CuIr$_2$S$_4$ [27, 28]).
Rather than undertaking to comprehensively review all spinels, this chapter will present a review of the complex magnetic interactions found in well-ordered, insulating spinels. We begin with a detailed discussion of the structural considerations and the various magnetic exchange pathways between the A and B metal sites. We then consider the magnetism and related properties for spinels which have magnetic transition metal cations exclusively on the A- or B-sites. Finally, we discuss spinels with magnetic cations on both sites, and conclude with a discussion of magnetodielectric coupling in spinels.

1.2 Crystal Structure

Ideal cubic spinels crystallize in the high-symmetry space group $Fd\bar{3}m$ (#227) and are composed of a face-centered-cubic (fcc) arrangement of anions; where $X$ can be O, S, Se, or Te (See Figure 1.1). This fcc lattice has its origin at the anion position, $u_X$, and corresponds to a cubic-close-packing (ccp) of the anions along the unit-cell body diagonal. This ccp arrangement results in 32 octahedrally coordinated and 64 tetrahedrally coordinated interstitial sites, but only half of the octahedral sites and one eighth of the tetrahedral sites are actually occupied. In most compounds this $u_X$ parameter is generally larger than the ideal value of $u_X = 0.25$ (or 0.375 depending upon the choice of origin) cor-
responding to a shift along the [111] direction and resulting in a larger $A$-site and correspondingly smaller $B$-site.

Table 1.1 presents a list of transition metals which are commonly found on the octahedral and tetrahedral sites. It is important to note that, except for very specific cases, most transition metals do not have an overriding preference for either the octahedral or tetrahedral site. This gives rise to a significant degree of site-mixing which we will quantify as the inversion parameter, $\delta$. In the context of disorder between the sites it becomes more appropriate to write the spinel formula as $(A_{1-\delta}B_\delta)(A_\delta B_{2-\delta})X_4$ where $\delta$ can be any value $0 \leq \delta \leq 1$. Spinels which have $\delta$ closer to 0 are referred to as normal whereas those with $\delta$ closer to 1 as inverse.

Some notable exceptions to the problem of inversion include $d^{10}$ cations such as $\text{Zn}^{2+}$, $\text{Ga}^{3+}$, and $\text{Ge}^{4+}$ which have been shown to have a strong preference for the $A$-site due to the increased covalent character associated with the bonding in the tetrahedral sites. Similarly $\text{Cr}^{3+}$ ($d^3$), $\text{Rh}^{3+}$ ($d^6$), and $\text{Ni}^{2+}$ ($d^8$) prefer octahedral coordination due to strong crystal field stabilization.

While these two cases are always true for cubic spinels we should also consider the case of spinels which contain orbitally-degenerate cations which are Jahn-Teller (JT) active, see Table 1.1. These compounds, such as $\text{Mn}_3\text{O}_4$, which
Table 1.1. Table of metals commonly found in the octahedral and tetrahedral sites in the spinel structure with their respective number of $d$ electrons, electronic configuration, tendency for Jahn-Teller distortions, and if they exhibit single ion anisotropy.

<table>
<thead>
<tr>
<th>Cation</th>
<th>Valence</th>
<th>Electronic Config.</th>
<th>Jahn-Teller Active</th>
<th>Anisotropy</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>A-Site Tetrahedral Coordination</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ga$^{3+}$</td>
<td>$d^{10}$</td>
<td>$e^4 t_2^2$</td>
<td>no</td>
<td>no</td>
</tr>
<tr>
<td>Zn$^{2+}$</td>
<td>$d^{10}$</td>
<td>$e^4 t_2^6$</td>
<td>no</td>
<td>no</td>
</tr>
<tr>
<td>Cu$^{1+}$</td>
<td>$d^{10}$</td>
<td>$e^4 t_2^6$</td>
<td>no</td>
<td>no</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>$d^9$</td>
<td>$e^4 t_2^3$</td>
<td>yes</td>
<td>no</td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td>$d^8$</td>
<td>$e^4 t_2^4$</td>
<td>yes</td>
<td>no</td>
</tr>
<tr>
<td>Co$^{2+}$</td>
<td>$d^7$</td>
<td>$e^4 t_2^3$</td>
<td>no</td>
<td>no</td>
</tr>
<tr>
<td>Fe$^{2+}$</td>
<td>$d^6$</td>
<td>$e^3 t_2^3$</td>
<td>yes</td>
<td>no</td>
</tr>
<tr>
<td>Mn$^{2+}$</td>
<td>$d^5$</td>
<td>$e^2 t_2^3$</td>
<td>no</td>
<td>no</td>
</tr>
<tr>
<td><strong>B-Site Octahedral Coordination</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>$d^9$</td>
<td>$t_2^6 e_g^3$</td>
<td>yes</td>
<td>no</td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td>$d^8$</td>
<td>$t_2^6 e_g^3$</td>
<td>no</td>
<td>no</td>
</tr>
<tr>
<td>Co$^{2+}$</td>
<td>$d^7$</td>
<td>$t_2^6 e_g^2$</td>
<td>no</td>
<td>yes</td>
</tr>
<tr>
<td>Co$^{3+}$</td>
<td>$d^6$</td>
<td>$t_2^6 e_g^0$</td>
<td>no</td>
<td>no</td>
</tr>
<tr>
<td>Fe$^{2+}$</td>
<td>$d^6$</td>
<td>$t_2^4 e_g^2$</td>
<td>no</td>
<td>yes</td>
</tr>
<tr>
<td>Rh$^{3+}$</td>
<td>$d^6$</td>
<td>$t_2^6 e_g^0$</td>
<td>no</td>
<td>no</td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>$d^5$</td>
<td>$t_2^3 e_g^2$</td>
<td>no</td>
<td>no</td>
</tr>
<tr>
<td>Mn$^{3+}$</td>
<td>$d^4$</td>
<td>$t_2^3 e_g^1$</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>Cr$^{3+}$</td>
<td>$d^3$</td>
<td>$t_2^3 e_g^0$</td>
<td>no</td>
<td>no</td>
</tr>
<tr>
<td>V$^{3+}$</td>
<td>$d^2$</td>
<td>$t_2^2 e_g^0$</td>
<td>no</td>
<td>no</td>
</tr>
<tr>
<td>Ti$^{3+}$</td>
<td>$d^1$</td>
<td>$t_2^2 e_g^0$</td>
<td>yes</td>
<td>no</td>
</tr>
<tr>
<td>Al$^{3+}$</td>
<td>$d^0$</td>
<td>$t_2^0 e_g^0$</td>
<td>no</td>
<td>no</td>
</tr>
</tbody>
</table>
Figure 1.1. Illustration of the crystal structure of an ideal cubic spinel \(AB_2X_4\).

(a) Isolated segment of the tetrahedrally coordinated \(A\) sublattice. Note that there is no direct space connectivity between the neighboring tetrahedra. (b) Isolated segment of the octahedrally coordinated \(B\) sublattice. (c) Full unit cell showing both the \(A\) and \(B\) sublattices interpenetrated in relation to each other.

contains octahedral Mn\(^{3+}\), experience a symmetry-lowering structural distortion to tetragonal \(I\text{4}_1/\text{amd}\) (#141) which results in a cooperative elongation of the octahedral sublattice. The coherent and long-range nature of this distortion ensures a similarly well-ordered system since moving a JT ion out of a distorted octahedra and into a tetrahedral site would be very energetically disfavored.

### 1.3 Magnetic Interactions

Now that we have described the general characteristics of the structure we examine more closely the nature of the many magnetic exchange pathways
found in spinels. It is clear from simple inspection that the $B$ sites are much more densely packed than the $A$-sublattice. The octahedra of the $B$ sublattice share edges such that both direct exchange as well as a 90° superexchange contribute to the nearest neighbor $B–B$ coupling. In general, accounting for the nearest-neighbor interactions should be sufficient to explain the magnetism. However, Anderson pointed out that these interactions alone cannot explain the long-range antiferromagnetic order that has been observed in systems such as ZnCr$_2$O$_4$ and CdCr$_2$O$_4$. [29]

Figure 1.2 (a) illustrates the next-nearest-neighbor exchange pathways of the $B$ sublattice up to the fourth nearest neighbor. The mechanism through which the farther neighbor exchange occurs is not as obvious as that of the nearest neighbors, and several mechanisms have been proposed. Lotgering first suggested that these interactions were governed by a super-superexchange through four different types of $B–X–X–B$ paths. [31] Blasse and Fast, however, suggest that the superexchange occurs through, and is strongly influenced by, the intermediate $A$ site via $B–X–A–X–B$ [Illustrated in Figure 1.2 (b)]. [32] Bertaut has even suggested that the sixth neighbor exchange interaction through a 180° super-superexchange are important in determining the magnetic ground state. [33] While these longer-range interactions are significantly weaker than those with the nearest neighbor, the fact that there are 30 degenerate pathways
Figure 1.2. (a) Illustration of the magnetic interaction within the $B$ sublattice (some intermediate $X$ are omitted for clarity). $B_0$ denotes the reference atom with $B_i$ denoting the $i$th neighbor with respect to $B_0$. Note the extensive and often complicated superexchange pathways that exist. (Modified from Brasen et al. reference 30 ©1974 Elsevier B.V.) (b) Illustration of the superexchange pathway believed to govern the magnetic properties of the $A$ sublattice. (c) Illustration of the $B$–$B$ nearest neighbors as a pyrochlore lattice. In all cases the $A$ atoms are shown in red, the $B$ atoms are blue, and the $X$ atoms are shown in orange.
make their contribution to the magnetic order fairly significant.

Unlike the $B$ sublattice, the $A$ sites have no direct connectivity in space between neighboring tetrahedra [see Figure 1.1 (a)]. The direct space $A$–$A$ separation is given by $\sqrt{3}a/4$ where $a$ is the unit cell edge which generally ranges between 8.5 Å and 9 Å, resulting in a typical $A$–$A$ distance on the order of 3.75 Å. Such a large interatomic separation precludes the possibility for direct orbital overlap between neighboring $A$ atoms and therefore the interaction must occur through some superexchange [34], such as the $B$–$X$–$A$–$X$–$B$ pathway suggested by Blasse and Fast. [32] Due to this complicated exchange pathway and the large inter-atomic spacing it is not obvious that the $A$-sites should demonstrate any interesting magnetic order. However, given that the $A$-sites have 4 nearest neighbor (NN) $A$ interactions, 12 NN $B$, 12 next-nearest neighbor (NNN) $A$, and 16 NNN $B$ the large number of interactions that must be satisfied between the $A$ and the $B$-sites will be strongly frustrated and could be expected to give rise to complex magnetic ground states. [35]

Given the extensive number of competing interactions between the sites, it is often common for the parent lattice to be broken down into a more simple model of interpenetrating sublattices. One can then describe the atoms on the $B$-site as forming a pyrochlore lattice whereas the $A$-sites constitute a diamond lattice of corner-sharing $B_4$ tetrahedra.[29] Alternately, if one takes slices normal to the
(111) body diagonal of the unit cell the B sublattice can also be broken down into Kagomé planes which are stellated, and connected three dimensionally.

Both sublattices exhibit geometric frustration, but each in different ways. The frustration associated with the pyrochlore sublattice, which is composed of corner sharing tetrahedra of B-site metals, is essentially the same problem as trying to decorate the vertices of a triangle with spins which point antiparallel to all neighbors. The diamond sublattice, on the other hand, is not inherently frustrated if only nearest neighbor interactions are considered. It is only after one considers the next-nearest neighbor interactions that the frustration begins to arise as a competition between the two interpenetrating fcc sublattices. [36–38]

1.4 B-site Only Magnetic Spinels

As we mentioned in the previous section, when the magnetic interactions on the pyrochlore sublattice are antiferromagnetic, the system is strongly geometrically frustrated. The presence of geometric frustration is well-known to give rise to multiple, nearly degenerate and often non-collinear magnetic ground states. [4, 40, 41] The high multiplicity of the ground state makes it impossible for the system to find a unique lowest energy configuration. As a consequence
Figure 1.3. (a) Real and (b) imaginary part of the AC powder magnetic susceptibility of ZnCr$_2$O$_4$. Note that a transition to a long-range antiferromagnetic order occurs around 12.5 K as denoted by the vertical dashed line. (c) Temperature dependence of the real part of the dielectric constant. Figure reproduced with permission from Kagomiya et al. reference 39 © 2003 Elsevier B.V.
materials often remove the degeneracy of the ground state through some kind of structural distortion.

A prime example of how frustration on the pyrochlore lattice can be relieved is found in $\text{ZnCr}_2\text{O}_4$. At room temperature $\text{ZnCr}_2\text{O}_4$ is a fully site-ordered cubic spinel due to the strong driving force for $\text{Zn}^{2+}$ and $\text{Cr}^{3+}$ to stay on their respective sites. Despite having a $\Theta_{\text{CW}}$ of nearly $-400\,\text{K}$ the system does not establish long-range magnetic order until $12.5\,\text{K}$. Interestingly, this $12.5\,\text{K}$ transition is actually first-order due to the release of lattice-energy as the system undergoes a structural transition to a lower-symmetry crystal structure. [21]

The transition in $\text{ZnCr}_2\text{O}_4$ is usually referred to as a spin-driven Jahn-Teller (sometimes spin-Peierls), distortion. Despite the fact that a structural deformation has been known to occur at the magnetic ordering temperature for some time, the nature of the distortion is still not well understood. Lee et al. reported [21] that the structural distortion corresponds to a cubic to tetragonal elongation of the unit cell. However, recent magnetic resonance studies by Glazkov et al. point to the possibility that lattice distortion is more complex with signs of $\text{inter-plane}$ distortions which actually drive the system into an orthorhombic state. [42]

Another interesting aspect of $\text{ZnCr}_2\text{O}_4$ is the observation of short-range mag-
netic order beginning as high as 100 K. [21, 43] Kagomiya et al. have reported the temperature dependence of the dielectric constant collected in conjunction with magnetization measurements. [43] Their results, reproduced in Figure 1.3, indicate that starting near 70 K, short-range antiferromagnetic clusters begins to develop and are manifest in the inverse magnetic susceptibility data as deviations from the Curie-Weiss equation well above $T_N$. Simultaneously, a broad hump begins to develop in the real part of the dielectric constant, $\epsilon'$. The authors suggest that the large and strongly frequency-dependent bump points towards two distinct regions with different dielectric constants coexisting within this temperature regime. Indeed, Lee et al. more recently used inelastic neutron scattering to show that above the long-range ordering temperature nanometer-scale spin clusters begin to develop. They demonstrated that the individual spins self-organize into groups of antiferromagnetic hexagonal loops which then act as a collective unit and explains the origin of the two different dielectric constants.

A more exotic example of the magnetic frustration associated with the $B$ sublattice is found in GeCo$_2$O$_4$ and GeNi$_2$O$_4$. Both the Ni$^{2+}$ and Co$^{2+}$ are cubic spinels with the only significant structural difference being that they contain $d^6$ and $d^7$ cations on the $B$ sites respectively. This difference in $d$ occupancy results in no direct exchange in the Ni compound where as the Co compound experiences a ferromagnetic direct exchange. This is reflected in the Curie-Weiss
Figure 1.4. (a) Illustration of the geometric frustration in the triangular planes of the $B$ sublattice. Note the difficulty in making all vertices of corner-sharing tetrahedra antiferromagnetic. Solid lines represent satisfied interactions whereas the unsatisfied interactions are represented by dashed lines. (b) Illustration of the competition between $J_1$, $J_2$, $J'_2$, and $J_3$ where $J_2$, $J'_2$, and $J_3$ are AFM. (K) on the right side denotes the Kagomé planes and (T) denotes the triangular planes. Reproduced with permission from Diaz et al. reference 44 © 2006 American Physical Society.
fits with $\Theta_{CW} = +80.5$ K for Co and $\Theta_{CW} = -15$ K for the Ni compound. [44] With ordering temperatures of 23 K and 12 K neither compound exhibits a very strong degree of frustration. Despite the small frustration index, defined as $f = \Theta_{CW}/T_N$, the magnetic ordering transition observed in GeCo$_2$O$_4$ was reported to be first order and it was believed to correspond to a lowering of symmetry to a tetragonal unit cell similar to ZnCr$_2$O$_4$ which would seem to indicate the presence of frustration. [45, 46] 

Diaz et al. determined the magnetic structure of both GeCo$_2$O$_4$ and GeNi$_2$O$_4$ using powder neutron diffraction and found it to be incommensurate to the unit cell with a propagation vector of $(1/2, 1/2, 1/2)$. [44] The resulting order corresponds to antiferromagnetic stacking of ferromagnetic Kagomé planes which are intercalated by an antiferromagnetic stacking of the triangular lattice discussed earlier. Figure 1.4 (a) illustrates one aspect of the frustration where the triangular layers cannot satisfy the interlayer antiferromagnetic exchange. The second mechanism of frustration is related to the coupling between the Kagomé and triangular layers as illustrated in Figure 1.4 (b). This work underscored the importance of longer-range $B$–$B$ interactions in determining the magnetic ground state of the $B$ sublattice and demonstrated the presence of magnetic frustration despite an absence of the usual indicators.
1.5  *A*-site Only Magnetic Spinels

Unlike the geometric frustration on the *B* sublattice, the *A* sublattice experiences frustration through a competition between the nearest and next-nearest neighbor interaction as illustrated for the diamond lattice in Figure 1.5 (a). More importantly though, it is not clear that the *A* sublattice should experience long-range order at all, let alone frustration. Blasse originally proposed that *A–A* interactions occur through the same *A–X–B–X–A* linkages which is now generally accepted as the dominant superexchange pathway between all of the *A* sites, both nearest and next-nearest. [47] Such a long and complicated superexchange path should be expected to result in a very weak interaction between the sites, however several systems such as CoAl$_2$O$_4$ have been shown to exhibit large frustration indices ranging from 10 to 22 where $\Theta_{CW}$ has been shown to be as large as $-90$ K. [34, 48, 49] This large degree of frustration gives rise to spin liquid states which are characterized by short-range correlations which may or may not freeze in at low temperatures. [34, 36]

With a suggested $f \gtrsim 1000$, FeSc$_2$S$_4$ has far and away and the largest frustration parameter of any other *A*-site spinel. [36, 37, 50, 51] The case of Fe$^{2+}$ on the *A* sites is of particular interest because the $d^6$ spin configuration in a tetrahedral crystal field results in a hole in the $e$ orbitals and thus gives rise to
Figure 1.5. (a) Illustration of the frustration associated with an antiferromagnetic diamond lattice. Note that nearest neighbor interactions $J_1$ can be easily satisfied whereas considering next-nearest-neighbor $J_2$ interactions results in frustrated geometry. (b) Phase diagram resulting from Monte Carlo simulations on boxes containing $N = 8 \times L^3$ spins. 111, 111*, 110, and 100* indicate regions where spiral order develop on those planes. Note that the ordering temperature, $T_c$ is quickly suppressed upon introduction of a competing next-nearest-neighbor interaction $J_2$. Figure reproduced with permission from Bergman et al. reference 38 © 2007 Nature Publishing Group.
orbital degeneracy on top of magnetic anisotropy. Whereas orbitally degenerate systems are generally expected to result in a Jahn-Teller distortion to find the lowest energy ground state as we have discussed, no such structural change has been observed in FeSc$_2$S$_4$. [50] Recently it was proposed that the lack of long-range order is not necessarily attributable to geometric frustration, but rather to a competition between spin-orbit coupling and the magnetism. [52] Thus FeSc$_2$S$_4$ has been described as a spin-orbit liquid which experiences long-range entanglement of the spin and orbital degrees of freedom. [53]

Bergman and coworkers have conducted extensive Monte Carlo simulations on spinels with magnetism only on the diamond A sublattice. [38] From their simulations they constructed the phase diagram shown in Figure 1.5 which shows the change in the magnetic ordering temperature as the next-nearest neighbor interaction becomes stronger. Perhaps more importantly, they also demonstrated that spiral spin configurations begin to arise as the ratio of next-nearest ($J_2$) to nearest neighbor ($J_1$) exchange energy becomes larger than $1/8$ and the Néel, collinear antiferromagnet, state begins to destabilize. More recent work by Lee and Balents further demonstrated the validity of this theoretical framework by expanding their calculations to include effects from quantum fluctuations and magnetic anisotropy. [54]
1.6 Fully Magnetic Spinels

Now that we have considered the magnetism of the isolated sublattices we can begin to discuss the behavior that occurs when both sites contain magnetic cations. If both the $A$ and the $B$-sites contain magnetic cations, the $A$–$B$ interaction through the roughly $120^\circ$ $A$–$X$–$B$ superexchange path should be expected to dominate the magnetic behavior. This $A$–$X$–$B$ superexchange interaction is much stronger than any other exchange pathway due to the short path and higher degree of orbital overlap (particularly when the $t_{2g}$ are exactly half full as in Fe$^{3+}$ and Mn$^{2+}$ ions) and therefore will tend to completely dominate the weaker super-superexchange $B$–$X$–$X$–$B$ interactions using the same oxygen orbitals. \[55\]

If we only consider nearest-neighbor interactions, the simplest type of order observed in fully magnetic spinels corresponds to all of the spins $A$ on the sites aligning parallel to each other and then antiparallel to the $B$ sublattice. Such a ground state is commonly referred to as a Néel-type configuration \[56, 57\] and results in ferrimagnetism when the $A$ and the $B$ sites contain an unequal number of spins. A second possible ground state which is commonly found in distorted spinels corresponds to the spins on one site pointing at an angle to each other with their resultant pointing antiparallel to the magnetization of the
other sites. Such a ground state is referred to as a Yafet-Kittel state, but is only observed experimentally in tetragonally distorted systems such as Mn$_3$O$_4$. [58]

Lyons, Kaplan, Dwight, and Menyuk (LKDM) developed a model for predicting the ground state behavior of cubic spinels based around the competition between nearest neighbor $B$–$B$ and $A$–$B$ exchange interactions. [55, 59] They showed that the ground state can be fully described by the parameter $u = (4J_{BB}S_B)/(3J_{AB}S_A)$, where $J_{ij}$ represents the exchange constant for nearest neighbor $B$–$B$ and $A$–$B$ interactions. They find for $u \leq 8/9$ the Néel configuration is indeed the most stable whereas $8/9 < u \leq 1.3$ gives rise to a spiral magnetic configuration. More recent computational work by Ederer and Komelj [60] has shown that while the LKDM theory may describe the ground state of many spinels well, the strength of the $A$–$A$ interactions in systems such as CoCr$_2$O$_4$ and MnCr$_2$O$_4$ are not as small as previously believed and therefore may play a more important role in determining the ground state spin structure. Despite only taking into account $B$–$B$ and $A$–$B$ interactions, the LKDM model has still given a great deal of insight into understanding the origin of the spiral order found in ferrimagnetic spinels such as CoCr$_2$O$_4$ which we will consider presently. [17, 19, 61]

CoCr$_2$O$_4$ is a cubic spinel with tetrahedrally coordinated Co$^{2+}$ ($d^7$) and octahedrally coordinated Cr$^{3+}$ ($d^3$) and exhibits a transition to a long-range fer-
Figure 1.6. (a) and (b) Temperature dependent dielectric constant measured on two different sintered polycrystalline samples of CoCr$_2$O$_4$. The anomaly at 50 K was attributed to the development of short-range magnetic correlations while the 27 K peak corresponds to the onset of the spiral magnetic structure. Figures reproduced with permission from Lawes et al. reference 17 © 2006 American Physical Society. (c) Single crystal measurement of the polarization in CoCr$_2$O$_4$ (blue circles) as a function of changing external magnetic field (green triangles). Figure reproduced with permission from Yamasaki et al. reference 18 © 2006 American Physical Society.
rimagnetic state below 93 K. Further cooling reveals a transition to a conical spin arrangement with an incommensurate propagation vector of \([0.63, 0.63, 0]\) developing around 50 K and a lock-in transition at 15 K. [61, 62] Temperature-dependent dielectric measurements on sintered polycrystalline samples, shown in Figure 1.6 (a) and (b), showed the dielectric constant to be insensitive to the ferrimagnetic state which stabilizes at 95 K, but showed an increase as short-range correlations began to develop near 50 K. [17] These measurements also revealed a clear coupling of the dielectric constant to the long-range spiral magnetic order below \(T = 27\) K.

Mostovoy [63] and Katsura, Nagaosa, and Balatsky [64] developed theories explaining the magnetically-induced electric polarization in terms of broken inversion symmetry and spin currents. Measurements on single crystals by Yamasaki and coworkers [18], shown in Figure 1.6 (c), demonstrated a fully reversible electric polarization of \(1.5 \mu C m^{-2}\) which confirmed the magnetically-induced polarization \(P\) follows the relation:

\[
P = a e_{ij} \times (S_i \times S_j)
\] (1.1)

Where \(S_i\) and \(S_j\) are the canted spin vector, \(e_{ij}\) denotes the vector connecting the two sites, and \(a\) is a proportionality constant. This relation used in conjunc-
tion with the LKDM theory could be useful in locating new spinel compositions which display similar magnetoelectric effects.

Another system which has shown interesting magnetodielectric properties which are not believed to be caused by these spirals spiral magnetic structures is Mn\(_3\)O\(_4\). Mn\(_3\)O\(_4\) is a tetragonally distorted spinel below 1443 K [65] due to the presence of Jahn-Teller active Mn\(^{3+}\) (\(d^4\)) cations on the octahedral sites. On cooling below 42 K there is a transition from the high temperature paramagnetic regime to a Yafet-Kittel phase which is characterized by the A-site spins pointing ferromagnetically along the \(\langle 010 \rangle\) while the B spins point along the \(\langle 010 \rangle\). [19] Further cooling causes the spins on the B-site to reorient into an incommensurate spiral structure at 39 K and again at 34 K into a 16-ion magnetic unit cell with the moments pointing antiparallel to the spins on the A site.

Measurements on polycrystalline samples (see Figure 1.7 (a) and (b)) revealed magnetodielectric anomalies as well as magnetostriction associated with the transitions at 42 K and 34 K but not at the 39 K transition. [19, 66] Single crystal measurements by Suzuki and Katsufuji further explored this coupling in the context of the anisotropic coordination the Mn\(^{3+}\) octahedra. [67] They found that the magnetostriction, and thereby the source of the magnetodielectric anomalies, can be explained by the change in orbital state due to the single-ion anisotropy of the Mn. More specifically, they found that the application
Figure 1.7. (a) Temperature dependent dielectric constant of Mn$_3$O$_4$ in the absence and presence of 5 kOe field. Note there are magnetic transitions at each of the vertical dashed lines. (b) Dielectric constant as a function of external magnetic field at temperature above and below the magnetic transitions. Figure reproduced with permission from Tackett et al. reference 19 © 2007 American Physical Society.
of magnetic fields causes a reorientation of the lowest-lying orbital such that the elongated axis due to the JT distortion is always oriented parallel to the field. [67]

This chapter has given a brief review of the structural and magnetic exchange interactions present in the spinels. We have examined scenarios for magnetic cations isolated on the A and B sublattices as well as the fully magnetic spinels. We have focused on the magnetic interactions within and between the sites with a particular emphasis on the nature of the frustration. We have also presented a discussion of recent work showing the presence of spin-lattice coupling in several oxide spinels, and the possibility for multiferroic behavior.
Chapter 2

Magnetic phase evolution in (Zn,Co)Cr$_2$O$_4$

As we have mentioned in Chapter 1, the conventional wisdom when working with magnetic spinels is that the dominant magnetic interactions are between the $A$ and the $B$ sublattices provided magnetic ions occupies both sites. Adding to the complex nature of magnetic interactions in the structure is that superexchange interactions between $A$-sites are mediated by atoms on the $B$-site (even when the $B$-site is non-magnetic), and in the same vein, $B$–$B$ next-nearest-neighbor interactions are mediated by the $A$-site ion.[47] In the cubic

\footnote{Substantial portions of this chapter have been published in reference 35 © 2009 Institute of Physics}
Figure 2.1. Spinel $AB_2O_4$ structure showing edge-shared laths of $BO_6$ octahedra (blue-grey) with $B-B$ magnetic coupling across the edges. Tetrahedrally coordinated $A$ atoms (dark grey) connect the octahedral laths, and each $A$ atoms has four $B$ near-neighbors. Oxygen are orange. Reproduced with permission from reference 35 © 2009 Institute of Physics.
spinel, the number of near neighbors (NN) and next-near-neighbors (NNN) for $A$ are $4A$ (NN), $12B$ (NN), $12A$ (NNN), and $16B$ (NNN). For $B$, the distribution is $6A$ (NN), $6B$ (NN), $8A$ (NNN), and $12B$ (NNN). In addition, most of the coupling pathways are multiply degenerate. These result in next-near neighbors contributing in an important manner to the overall magnetic ordering behavior.[36, 37] The high connectivity of the spinel lattice has been shown to give rise to a vast array of interesting magnetic phenomenon. [17–19, 68–73]

Chromium spinels, where the $B$ sublattice is fully occupied by $Cr^{3+}$, present a unique opportunity to examine these complex magnetic interactions due to the fact that $Cr^{3+}$ will not invert to the tetrahedral $A$-sites unlike many other transition metals, as a result of the very strong crystal field stabilization of octahedral $d^3$ cation ($t_{2g}^3$ crystal field). Here we prepare and study clean samples of solid solutions of $ZnCr_2O_4$ and $CoCr_2O_4$, two well studied chromium spinels with very different magnetic ground states. $ZnCr_2O_4$, with a non-magnetic cation occupying the $A$-site, undergoes a spin-driven Jahn-Teller-like distortion at low temperatures which results in a Néel-type antiferromagnetic order.[21, 74] $CoCr_2O_4$, with magnetic cations on both sublattices, displays collinear ferrimagnetic as well as non-collinear spiral magnetic ordering.[61] By replacing the Zn with Co, our goal is to introduce magnetic interactions into an otherwise non-magnetic lattice and observe the effect this would have on the magnetic frustration of the
system. This series is particularly interesting because it provides the opportunity to study the effects of dilute magnetic interactions in the absence of changes to the superexchange angle (Co\textsuperscript{2+} and Zn\textsuperscript{2+} have very similar ionic radii) or site disorder (because of the strong octahedral site preference of Cr\textsuperscript{3+}). We find for low concentrations of Co, a seeming increase in frustration resulting from spin disorder which results in a glassy magnetic state. At higher Co concentrations there is evidence that the spins form non-collinear structures reminiscent of the CoCr\textsubscript{2}O\textsubscript{4} end member.

Monte Carlo simulations of Heisenberg spin systems have been performed by Miles Stoudenmire which allow comparisons with the experimental magnetic susceptibility, and yield the appropriate range of $J$ couplings between the different sites to be estimated. They also suggest the minimal models required to describe the gross aspects of the magnetic susceptibility in these systems. We also demonstrate here that appropriate scaling of Curie-Weiss plots of the inverse magnetic susceptibility as a function of temperature allows for systems with purely antiferromagnetic interactions to be distinguished from systems with more complex interactions.
2.1 Experimental Details

Polycrystalline samples in the series were prepared by solid state routes. Appropriate stoichiometric amounts of cobalt oxalate (CoC$_2$O$_4$·2H$_2$O), ZnO, and Cr$_2$O$_3$ were mixed and ground with ethanol in an agate mortar. The powders were then pressed into 13 mm pellets and calcined in alumina crucibles at 800°C for 12 h. These pellets were then reground, pressed back into pellets, and fired at 1150°C for 12 h. The pellets were then briefly annealed at 800°C for 24 h. During all heatings, the pellets were placed on a bed of powder with the same stoichiometry to minimize reaction with the crucible. X-ray diffraction patterns were obtained using Cu-Kα radiation on a Philips X'Pert MPD diffractometer operated at 45 kV and 40 mA. Phase purity was subsequently determined by refining the structure against the data using the Rietveld method as implemented in the XND Rietveld code.[75] DC magnetization measurements were carried out using a Quantum Design SQUID magnetometer.

2.2 Computational Details

Classical Monte Carlo simulations of the magnetic behavior of the system were performed using the ALPS project’s SPINMC application [76]. We generated
a lattice with the appropriate fraction of $A$-sites occupied for each simulation run in order to perform disorder averaging. The magnetic interactions were modeled by a nearest-neighbor Heisenberg Hamiltonian with antiferromagnetic couplings $J_{BB}$, $J_{AB}$ and $J_{AA}$ where the subscripts specify the sublattice types of the two spins connected by a given interaction. Since the number of $J_{BB}$ interactions in the system does not vary with $x$, the other two couplings are varied relative to $J_{BB}$, which is set to unity (in Monte-Carlo units) throughout.

The inverse magnetic susceptibility of each simulated system was fit to the experimental data by scaling both sets of data such that they satisfy the Curie-Weiss relationship at high temperature. This is the same method used to plot the experimental data described below – see Equation 2.3. It should be noted, however, that in these simulations, “high temperature” means high relative to the temperature at which the inverse susceptibility strongly deviates from linear behavior. As discussed in what follows, the experiments could not actually be performed above $T = |\Theta_{cw}|$ where the Curie-Weiss law is strictly applicable. Numerical simulations could indeed verify the following analytic expression for the Curie-Weiss temperature of the nearest-neighbor model

$$\Theta_{cw} = \frac{-2S(S + 1)}{3(1 + \frac{x}{2})}(3J_{BB} + 6xJ_{AB} + x^2J_{AA})$$  (2.1)
After a reasonable fit to the susceptibility was found for each experimental dataset, corresponding to the different $x$ values, the simulations were run again using a newly generated random lattice as many as 3 times to determine the effect of disorder. A disorder average was then performed by averaging the resulting inverse susceptibilities and the disorder error bars were taken to be the standard deviation of this average. Finally, it should be noted that since the simulations were run until the Monte Carlo error was negligible (relative errors of about $10^{-4}$), all numerical error bars shown below represent only the disorder error bars with the exception of the disorder-free $x = 1.0$ end member.

2.3 Results and Discussion

A portion of the X-ray diffraction patterns of the solid solution series are presented in Figure 2.2. All samples were found to be single phase with no extraneous peaks. The patterns were fit using the Rietveld method to the normal cubic spinel crystal structure with appropriate mixed occupancies on the $A$-site. The cubic cell parameter and the position of the oxygen atom $(u, u, u)$ in the unit cell were obtained from the refinement. Because Co and Zn are relatively similar in terms of their x-ray scattering powers, no attempt was made to extract the relative concentrations of these ions in the lattice.
Figure 2.2. A portion of the room temperature x-ray diffraction patterns of Zn$_{1-x}$Co$_x$Cr$_2$O$_4$. (a) Points are data and solid grey lines represent the Rietveld least-squares analysis. (b) Evolution of the cubic cell parameter with Co content $x$. The line connecting end members is drawn as a guide to illustrate the Végard law. (c) Shows the steady decrease with $x$ of the internal positional parameter $u$ of oxygen. Reproduced with permission from reference 35 © 2009 Institute of Physics.
The cell parameter $a$ and oxygen position $u$ extracted from the Rietveld refinements are presented in Figure 2.2(b) and (c). $\text{Co}^{2+}$ and $\text{Zn}^{2+}$ in tetrahedral coordination have very similar ionic radii, 0.58 Å and 0.60 Å respectively,[77] with $\text{Co}^{2+}$ the slightly smaller ion. Increasing Co in the compounds should therefore lead to a contraction of the cell parameter. We find, however, a small expansion of the unit cell volume. This is consistent with previously reported structures of the end members.[78] A possible reason for the expansion is that tetrahedral $\text{Co}^{2+}$ is more ionic than $\text{Zn}^{2+}$ and the substitution of Zn by Co introduces $A-B$ cation-cation repulsions which expand the lattice. Expansion in the cell parameters in order to minimize repulsion between neighboring cations has been suggested in other spinel systems.[79]

Changes in the $u$ parameter associated with O atoms in the unit cell occur as the structure tries to accommodate cations of different sizes. When $u = 0.25$, the anions are in an ideal cubic-close-packed arrangement, with perfect $\text{CrO}_6$ octahedra, while values of $u > 0.25$ indicate an increase in size of the tetrahedron with a corresponding shrinkage and trigonal compression of the octahedron.[78] As seen from Figure 2.2 (c), there is a systematic decrease in $u$ with $x$ which brings it closer to the ideal value. This decrease implies that the tetrahedral sites shrink across the series, in keeping with the smaller size of $\text{Co}^{2+}$, but in contradiction with the unit cell expansion.
Table 2.1. Results from fitting the inverse magnetic susceptibility data to the Curie-Weiss equation. $\Theta_{CW}$ is taken as the $x$-intercept of the inverse susceptibility curve while $T_c$ is chosen as the first point of inflection in the first derivative of the susceptibility with respect to temperature. $f$ is defined as the absolute ratio of $\Theta_{CW}$ to $T_c$. The experimental effective moment is calculated using the relation $\mu_{\text{eff}}^2 = 3Ck_B/N$ where $C$ is the slope of the inverse susceptibility versus temperature. The estimated moments (spin-only, and unquenched) are obtained using $\mu_{\text{eff}} = \sqrt{\mu_{\text{Co}}^2 + 2\mu_{\text{Cr}}^2}$. Reproduced with permission from reference 35 © 2009 Institute of Physics.

<table>
<thead>
<tr>
<th></th>
<th>$\Theta_{CW}$ (K)</th>
<th>$T_c$ (K)</th>
<th>$f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnCr$_2$O$_4$</td>
<td>5.2</td>
<td>5.5</td>
<td>5.5</td>
</tr>
<tr>
<td>$x = 0.2$</td>
<td>$-298$</td>
<td>19</td>
<td>16</td>
</tr>
<tr>
<td>$x = 0.4$</td>
<td>$-380$</td>
<td>8</td>
<td>51</td>
</tr>
<tr>
<td>$x = 0.6$</td>
<td>$-424$</td>
<td>15</td>
<td>28</td>
</tr>
<tr>
<td>$x = 0.8$</td>
<td>$-592$</td>
<td>20</td>
<td>30</td>
</tr>
<tr>
<td>CoCr$_2$O$_4$</td>
<td>7.5</td>
<td>6.7</td>
<td>7.2</td>
</tr>
<tr>
<td>$-568$</td>
<td>75</td>
<td>8</td>
<td></td>
</tr>
</tbody>
</table>
The high temperature (200 K to 300 K) susceptibility of the samples was fit to the Curie-Weiss equation, $\chi = C/(\chi - \Theta_{CW})$, to obtain the effective paramagnetic moment $\mu_{\text{eff}}$ from the Curie constant $C$, and the Curie-Weiss intercept $\Theta_{CW}$. These values are presented in Table 2.1. The orbital-quenched, spin-only effective moment ($\mu_S = 2\sqrt{S(S+1)}$) for free ions of both Co$^{2+}$ and Cr$^{3+}$ is 3.88 $\mu_B$. Figure 2.3 shows an increase in the experimental $\mu_{\text{eff}}$ with increasing values of $x$. It is noted that samples with $x \leq 0.4$ agree well with the spin-only moment. $x \geq 0.6$ is anomalous in terms of the trend with $x$. The $x = 0.8$ and $x = 1.0$ samples tend increasingly to an effective moment value that is closer to the value expected for the unquenched orbital contribution from Co$^{2+}$, $\mu_S = \sqrt{4S(S+1) + L(L+1)}$. While this may be unexpected for Co$^{2+}$ in a tetrahedral coordination environment which has no orbital degeneracy, the presence of the low lying ($e^{3t^4}_{2}$) excited state could be a source for this increased moment.[80] Cr$^{3+}$ is expected to remain strongly orbital quenched. The change from orbital quenched (spin-only) to unquenched behavior for Co$^{2+}$ in this system may have to do with the small changes in structure as $x$ is increased.

It was recently suggested that the introduction of magnetic cations into ZnCr$_2$O$_4$ has the effect of introducing short range order in the high temperature paramagnetic regime,[81] and this can be a source of the small underestimation observed here. In addition, even in dilute spinel systems with Cr$^{3+}$,
near-neighbor coupling effects are known,[82] and such coupling can invalidate the assumption made here of independent spins. We note, however, that the effective moment we have determined for ZnCr$_2$O$_4$ falls within the range of previously reported values [83, 84] which vary from 5.1–5.6 $\mu_B$ f.u.$^{-1}$. We were unable to find any previous reports for the effective moment of CoCr$_2$O$_4$.

As $x$ increases, so do the magnitudes of the Curie-Weiss $\Theta_{CW}$, reflecting the increasing numbers of the dominant antiferromagnetic $A$–$B$ interactions. The increase is monotonic with the exception of $x = 0.6$, which seem anomalous in this series.

Figure 2.4 illustrates the temperature dependence of the DC magnetization with the response of the end members in good agreement with previously reported data.[61, 74] The sharp drop in the susceptibility of ZnCr$_2$O$_4$ is characteristic of the spin-driven Jahn-Teller distortion that allows the system to order in a Néel-type antiferromagnetic ground state.[74] Dilute concentrations of Co result in this sharp drop being lost, which indicates the structural distortion is likely suppressed and instead the characteristic behavior is of spins freezing into a glassy state. For concentrations of Co above 60%, Néel-type ferrimagnetism is stabilized. The highest ordering temperatures $T_c$ for the different compounds are also listed in Table 2.1, obtained by taking the first derivative of the susceptibility with respect to temperature. The frustration index $f = \Theta_{CW}/T_c$ is listed
Figure 2.3. Effective magnetic moment obtained from the Curie-Weiss fit to the high temperature inverse susceptibility data for Zn$_{1-x}$Co$_x$Cr$_2$O$_4$. The two lines represent the expected values calculated for a fully quenched ($\mu_S$) Co$^{2+}$ and Cr$^{3+}$, and a fully unquenched ($\mu_{L+S}$) Co$^{2+}$ orbital contribution to the magnetic moment. Reproduced with permission from reference 35 © 2009 Institute of Physics.
in the last column of the table. It is seen that all the compounds order at temperatures much lower than would be otherwise expected, i.e. all the compounds in the series are frustrated. The initial increase in the frustration index with $x$ arises because of quenched disorder introduced by some of the $A$-sites having magnetic moments, and is not a true measure of geometric frustration.

We can rearrange the Curie-Weiss equation:

$$\chi = \frac{C}{T - \Theta_{CW}}$$ \hspace{1cm} (2.2)

in the following manner:

$$\frac{C}{\chi \Theta_{CW}} = \frac{T}{\Theta_{CW}} - 1$$ \hspace{1cm} (2.3)

A plot of $C/(\chi|\Theta_{CW}|) - 1$ as a function of $T/|\Theta_{CW}|$ collapses all the high temperature susceptibility data in the manner displayed in Figure 2.5. The straight line through the origin corresponds to ideal Curie-Weiss behavior and can be used as a measure of the quality of the fits in the high temperature regime. It is evident once again that all magnetic ordering takes place at temperatures much smaller than $T = \Theta_{CW}$ suggesting frustration. (Note the horizontal axis in this plot is an inverse of the frustration index $f$.) The modified Curie-Weiss plot displayed in Figure 2.5 also quickly allows one to distinguish the nature
Figure 2.4. Field cooling curves were collected under a static DC field of 1000 Oe. Pure ZnCr$_2$O$_4$ sample orders antiferromagnetically below its Néel temperature while samples with $0 < x \leq 0.6$ exhibit glassy behavior resulting from the dilute uncompensated antiferromagnetic interactions because of $A$–$B$ interactions between Co$^{2+}$ and Cr$^{3+}$. Samples with $x = 0.8$ and $x = 1.0$ order ferrimagnetically below their highest transition temperature, and then transform to more complex orderings. Reproduced with permission from reference 35 © 2009 Institute of Physics.
Figure 2.5. Scaled inverse susceptibility as a function of scaled temperature, as described by the formula in 2.3. The dashed line represents ideal Curie-Weiss paramagnetism. Positive deviations from this line reflect the presence of compensated antiferromagnetic interactions, while negative deviations reflect uncompensated interactions and a tendency to ferrimagnetic ground states. Reproduced with permission from reference 35 © 2009 Institute of Physics.
of the dominant magnetic exchange interactions. Positive deviations from the ideal Curie-Weiss line (dashed) correspond to samples with purely compensated antiferromagnetic interactions. Even small amounts of Co\(^{2+}\) on the A-site result in uncompensated antiferromagnetism (ferrimagnetism) and this manifests as negative deviations from the ideal line. As larger amounts of Co\(^{3+}\) are substituted, this residual paramagnetism is lost and the ground states resemble partially saturated ferrimagnets.

The modified Curie-Weiss plot depicted in Figure 2.5 superficially resembles a semilog plot of resistivity versus temperature for a series of samples undergoing (typically) a composition driven metal-insulator transition. The line or curve separating insulators from metals is almost horizontal and frequently extrapolates, at 0 K, to the inverse of the Mott minimum metallic conductivity.[85, 86] Insulators (localized systems) lie above this line, and metals (extended systems) lie below. In the same vein, samples in the series considered here show (appropriately scaled) inverse susceptibilities which lie above the Curie-Weiss line provided all interactions are antiferromagnetic and fully compensated, and these are distinct from samples with uncompensated interactions or with ferromagnetic interactions which are analogues of extended states. Analogies with thermal expansion can be drawn as well. Localized (Einstein) modes can decrease thermal expansion coefficients in crystals, and even make it negative. Extended
Table 2.2. Estimates of the Heisenberg coupling constants that best describe the experimental data. The $J_{BB}$ estimates were obtained by solving equation 2.1 for $J_{BB}$ using the $\Theta_{CW}$ estimates in Table 2.1. The range of $J_{BB}$ values for $x = 0.2$ corresponds to a $J_{AA}/J_{BB}$ between 0.0 and 0.5.

<table>
<thead>
<tr>
<th></th>
<th>$J_{AA}/J_{BB}$ estimate</th>
<th>$J_{AA}/J_{BB}$ error</th>
<th>$J_{AB}/J_{BB}$ estimate</th>
<th>$J_{AB}/J_{BB}$ error</th>
<th>$J_{BB}(K)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnCr$_2$O$_4$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$x = 0.2$</td>
<td></td>
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<td>42.0-42.3</td>
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<tr>
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<td>$x = 0.6$</td>
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<td>0.2</td>
<td>0.377</td>
<td>0.003</td>
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</tr>
<tr>
<td>$x = 0.8$</td>
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<td>0.930</td>
<td>0.02</td>
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<tr>
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<td>0.55</td>
<td>0.05</td>
<td>1.02</td>
<td>0.01</td>
<td>35.2</td>
</tr>
</tbody>
</table>

modes (Debye) usually give rise to the more common positive coefficients of thermal expansion.[87]

It turns out that a simple quantitative understanding of the susceptibility data in Figure 2.5 is possible as well. We performed classical Monte Carlo simulations of the nearest-neighbor Heisenberg model on a $B$-site spinel with $A$-site doping and found a series of Heisenberg coupling parameters $J_{AA}/J_{BB}$ and $J_{AB}/J_{BB}$ that bring the simulations into rather close agreement with the experimental susceptibility measurements.

The best fits obtained are shown in Figure 2.6 and the resulting coupling constant estimates are summarized in Table 2.2. The fits were first found using
Figure 2.6. Comparison of the experimental magnetic susceptibilities with Monte Carlo simulations performed for the corresponding $x$ values using the $J$ couplings listed in Table 2.2. $L$ corresponds to the system size used in the simulation. Reproduced with permission from reference 35 © 2009 Institute of Physics.
Figure 2.7. Results of Monte Carlo simulations on Heisenberg spin systems with a system size of \( L = 4 \) and the following coupling parameters: \( J_{AA}/J_{BB} = 0.45 \) and \( J_{AB}/J_{BB} = 0.90 \). Reproduced with permission from reference 35 © 2009 Institute of Physics.

systems consisting of \( 4^3 \) conventional cubic unit cells (1024 \( B \)-sites) with periodic boundary conditions. Finite-size scaling on systems of \( 5^3 \) unit cells (2000 \( B \)-sites) were checked as well. It should also be noted that these best fits were determined by searching the parameter space, not by an optimization algorithm, so that quite likely even better agreement is possible using the same model.

We were encouraged to see that all of the best \( J_{AA}/J_{BB} \) and \( J_{AB}/J_{BB} \) pa-
rameters do not differ much from each other (the \( x = 0.2 \) data had too weak a dependence on \( J_{AA} \) for us to determine it effectively). Evidently, the bulk magnetic behavior of the entire series of materials is well described by taking \( J_{AB} \) to be comparable to \( J_{BB} \) and taking \( J_{AA} \) to be about half of \( J_{BB} \). Accordingly, it was considered useful to actually fix all the couplings to such values and only vary \( x \) – the resulting scan (see Figure 2.7) shows that it is indeed the value of \( x \) that most strongly determines the bulk magnetic properties of the system. The surprise is that for the range of parameters studied by which seem to be close to the experimentally measured susceptibility, \( J_{AB} \) and \( J_{BB} \) are effectively equal, rather than \( J_{AB} \) being significantly larger than \( J_{BB} \); the frequent expectation. Lyons, Kaplan, Dwight, and Menyuk (LKDM) [59] have proposed the following inequality: \( \frac{4J_{BB}S_B}{3J_{AB}S_A} \leq 8/9 \) implies collinear Néel ordering of moments in spinels such as CoCr\(_2\)O\(_4\). For \( \frac{4J_{BB}S_B}{3J_{AB}S_A} > 8/9 \) non-collinear ordering is suggested. Since in CoCr\(_2\)O\(_4\), \( S_A = S_B \), we expect that if \( J_{BB} \approx J_{AB} \), the ground state will be non-collinear, which is certainly true for CoCr\(_2\)O\(_4\). So the Monte Carlo estimates of \( J_{BB} \) and \( J_{AB} \) are consistent with the experimental realization of non-collinear ground states.[61] Recently Ederer and Komeilj[60] have performed detailed density functional calculations on the \( x = 1 \) end-member, CoCr\(_2\)O\(_4\). They suggest that \( J_{AA} \) is important (ignored by LKDM) as determined here as well. While \( J_{AA} \) in their calculations is
determined to be typically less than $J_{BB}$, they estimate that $J_{AB}$ can be even twice as large as $J_{BB}$ which is not the result obtained in the preliminary analysis presented here.

The results of the field-cooled susceptibility traces was used to construct a tentative magnetic phase diagram for the solid solutions as depicted in Figure 2.8. We use changes in the slope of the field-cooled susceptibility as a function of temperature to obtain the boundaries between different magnetic phases. Regardless of composition, all samples demonstrate paramagnetic behavior at high temperatures and begin to show transitions to long range order starting near 100 K. The end member ZnCr$_2$O$_4$ is the only compound which exhibits long range antiferromagnetic order because of its structural distortion. We make the reasonable assumption that even small amounts of Co result in glassy behavior as indicated by the line separating frustrated antiferromagnetism from glassy states. For concentrations of $x \geq 0.6$ the magnetic behavior begins to look more like that of CoCr$_2$O$_4$ with a collinear ferrimagnetic transition between 50 K and 100 K followed by a transition into a non-collinear spiral at lower temperatures. The behavior near $x = 0.6$ is rather complex and more experiments will be particularly important for this region of the phase diagram. The transition temperatures for the spiral appear to be slightly suppressed by Zn substitution with respect to the end member as illustrated by the positive slope of the phase
Figure 2.8. Tentative magnetic phase diagram as a function of Co content and temperature. Low concentrations of Co results in a glassy freezing of the spins at low temperature while higher concentrations drive the system to order in a non-collinear spiral structure. The points in the diagram correspond to changes of slope in the susceptibility as a function of temperature. (SG = spin glass, AF = antiferromagnetism, FiM = ferrimagnetism, SRO = short-range ordering).

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boundary as the CoCr$_2$O$_4$ end member is approached. For the Co-rich compounds at the lowest temperatures, the structures begin to develop some spiral short-range order (SRO).[61]

In summary, we have prepared and studied the magnetic properties of a solid solution of ZnCr$_2$O$_4$ and CoCr$_2$O$_4$. We have found that replacing non-magnetic cations with magnetic cations in the tetrahedral sites of a well ordered spinel results in a transition from glassy behavior at low concentrations of magnetic cations into a Néel-like ferrimagnetic order as well as commensurate and incommensurate magnetic spirals. These results are significant because they demonstrate that the presence of magnetic cations on the $A$-site can have the effect of relieving magnetic frustration on the $B$-site by allowing the system to find a lower energy state in the form of non-collinear magnetic spirals. Monte Carlo simulations suggest the minimum physics required to describe trends in the magnetic behavior, and suggest the range of strengths of the different magnetic couplings. We also present a useful form for plotting susceptibility data as a function of temperature which allows us to easily recognize the existence of uncompensated magnetic interactions in otherwise antiferromagnetic systems.
Chapter 3

Magnetic frustration on the diamond lattice of $A$-site magnetic spinels

In a recent work Tristan et al. demonstrated that normal spinels, $\delta \ll 1$, with magnetic cations on the $A$-site and non-magnetic cations on the $B$ site can exhibit strong magnetic frustration. [34] These $A$-site magnetic spinels have been studied in the past by Roth[88] and Blasse. [47] Recent modelling studies by Bergman et al. suggested that the magnitude of the ratio $J_2/J_1$ can strongly

\[\text{Subtential portions of this chapter have been published in reference 49 ©2009 American Physical Society}\]
influence the dominant magnetic ground state in these systems. [38] In the limit that $J_2/J_1 \approx 0$, the magnetic ordering is a simple Néel state (magnetically speaking, a diamond to zinc blende transition). As the ratio becomes larger, the nature of the magnetic ground state can change from Néel to a complex spiral pattern with the spirals oriented parallel to (111) planes. Tristan et al. [89] have also recently examined solid solutions between CoAl$_2$O$_4$ and Co$_3$O$_4$ to investigate the effect of the $B$-site cation in the superexchange pathways that connects neighboring $A$-sites.

These recent studies encouraged us to attempt to alter this ratio of $J_2/J_1$ in these $A$-site magnetic spinels by controlling interatomic spacings through appropriate substitution on the $B$-site of the spinel structure. We use Ga substitution ostensibly on the $B$-site of spinels CoAl$_{2-x}$Ga$_x$O$_4$ as a means of separating the Co from one another, given that Ga$^{3+}$ is significantly larger than Al$^{3+}$ (the respective 6-coordinate radii are 0.62 Å and 0.535 Å). [77] We find that while the effect of such substitution is indeed to steadily increase the distance between neighboring Co atoms, there is the additional effect that site inversion in the structure steadily increases simultaneously. While separating the effects of these simultaneous changes in the structure is difficult, we discuss the role each change plays in the context of the altered frustration parameter.
3.1 Experimental Details

Polycrystalline samples of the compounds were prepared using ceramic routes. Cobalt oxalate (CoC$_2$O$_4$·2H$_2$O) was mixed with stoichiometric amounts of Ga$_2$O$_3$ and Al$_2$O$_3$ and intimately ground with ethanol in an agate mortar. The powders were then pressed into 13 mm pellets and fired in air in alumina crucibles at 800°C for 24 h. The pellets were then reground, pressed again into pellets, and fired at 1200°C (1000°C for $x = 0.0$) for 12 h. In order to obtain equilibrated samples, all pellets were annealed by heating to 700°C for 12 h, cooling to 400°C at a rate of 3°C min$^{-1}$, soaking at 400°C for 120 h [90] followed by cooling in the furnace to the room temperature. For all heat treatments, pellets were placed on a bed of powder with the same stoichiometry to minimize reaction with the crucible.

X-ray diffraction patterns were obtained using CuK$_\alpha$ radiation on a Philips X’Pert MPD diffractometer operated at 45 kV and 40 mA. Phase purity was determined by refining the structure against the data using the Rietveld method as implemented in the XND Rietveld code. [75] Neutron diffraction data were collected on the neutron powder diffractometer (NPDF) at the Lujan Center at Los Alamos National Laboratory at room temperature, on samples sealed in vanadium cans. [91] The structures were refined against the neutron diffraction
data using the Rietveld method as implemented in the EXPGUI-GSAS software suite. [92, 93]. Local structures as obtained from pair distribution function (PDF) analysis of the total neutron scattering were extracted from the total scattering data using the program PDFgetN [94] and with a maximum momentum transfer \( Q_{\text{max}} = 40 \text{ Å}^{-1} \). The obtained PDFs were analyzed using the PDFGUI software package. [95] DC magnetization was measured using a Quantum Design MPMS 5XL SQUID magnetometer.

### 3.2 Computational Details

Classical Monte Carlo simulations of the magnetic behavior of the system were performed using the ALPS project’s spinmc application in collaboration with Miles Stoudenmire and Leon Balents. [76] A custom lattice with periodic boundary conditions was generated for each simulation run in order to allow disorder averaging. The lattice generation code first randomly selected an \( A \) site and then moved its spin to a \( B \)-site, also chosen at random and independent of the position of the \( A \) site. The simulation was then run using a Heisenberg Hamiltonian with \( J_1 \) and \( J_2 \) bonds as described above, and with \( J_i \) impurity bonds connecting spins on \( B \) sites with their nearest-neighbor occupied \( A \) sites. Finally, because the typical error bars obtained from each Monte Carlo suscep-
tibility simulation were negligible (about \(1 \times 10^{-4}\) relative error), the error bars plotted represent only variation due to the presence of disorder as obtained by averaging over several runs.

A numerically calculated inverse susceptibility curve was fit to the experimental curves as follows: first, using the fact that the Curie-Weiss temperature for the \(J_1-J_2-J_i\) model with an inversion parameter, \(\delta\), is given by

\[
\Theta_{CW}/J_1 = \frac{-4S(S + 1)}{3} \left[ (1 + 3J_2/J_1)(1 - \delta)^2 + 3J_i/J_1(\delta - \delta^2) \right], \tag{3.1}
\]

one can calculate the value of \(J_1\) necessary to match the experimentally measured Curie-Weiss temperature. This value of \(J_1\) is then used to scale the temperature by a factor of \(J_1 S(S + 1)\) and the inverse susceptibility by a factor of \((k_B J_1 S(S + 1))/(\mu_{\text{eff}}^2 \mu_B^2 N_A)\). Such a fitting procedure always guarantees that the high temperature behavior of the simulation data is in exact agreement with that of the experimental data.
Figure 3.1. Highest $d$-spacing bank of powder neutron diffraction data from the different samples of $\text{CoAl}_{2-x}\text{Ga}_x\text{O}_4$ collected at room temperature. Circles are data and solid lines are Rietveld fits to the spinel phase [space group $Fd\bar{3}m$, A $(\frac{1}{8}, \frac{1}{8}, \frac{1}{8})$, B $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, O $(u, u, u)$]. Asterisks denote locations where contributions to the scattering from the $\text{Al}_2\text{O}_3$ impurity arise. Reproduced with permission from reference 49 © 2009 American Physical Society.
3.3 Results and Discussion

3.3.1 Structure

Rietveld analysis of the highest \( d \)-spacing bank (from four banks of data for each sample) of time-of-flight neutron diffraction data are displayed in Figure 3.1 for the different spinel samples. There were no peaks in the diffraction data that could not be assigned to either the spinel phase or a small \( \text{Al}_2\text{O}_3 \) impurity in the \( x = 0.0 \) sample, indicating no magnetic impurities and that a complete solid solution is achieved for all values of \( x \). The oxygen stoichiometry refined within error to the correct stoichiometric value excluding the possibility that any of the \( \text{Co}^{2+} \) was oxidized to \( \text{Co}^{3+} \). Given the close-packed nature of the oxygen lattice this was not surprising. From the Rietveld analysis, evolution of the lattice parameter, site occupancy of the cations on the \( A \) site, and the internal structural parameter (the \( u \) of oxygen) are presented in the different panels of Figure 3.2. It is seen that substitution of the larger \( \text{Ga}^{3+} \) for \( \text{Al}^{3+} \) results in the spinel unit cell edge increasing from 8.1 Å to 8.3 Å. The Végard law is not strictly followed, and for all intermediate \( x \) values, the cell parameter is slightly reduced from the values suggested by a weighted average of the end-members.

Panel (b) of Figure 3.2 shows the results of allowing all ions, \( \text{Al}, \text{Ga}, \) and
Figure 3.2. Evolution of different refined structural parameters with $x$ for the different CoAl$_{2-x}$Ga$_x$O$_4$ samples obtained from time-of-flight neutron diffraction. (a) The cell parameter, showing a nearly increase in size. The line connects end members to illustrate the Végard law. (b) Occupancies of the different cations on the $A$ site. (c) Internal parameter $u$ indicative of the oxygen position. $u = \frac{1}{4}$ means the $BO_6$ octahedra are perfectly regular. Reproduced with permission from reference 49 © 2009 American Physical Society.
Co to distribute themselves between the \( A \) and \( B \) sites in the refinements, with the constraint that the total amounts of the different atoms were as dictated by the starting stoichiometry. The process of achieving this refinement involved declaring on each of the \( A \) and \( B \) sites, two separate Co atoms, one of which exchanged with Al and the other with Ga. A related procedure has been described by Joubert et al. [96] Due to the nature of multiple constraints in the refinements, errors on the occupancies are likely to be underestimated. It is noted from Figure 3.2(b) that as larger amounts of Ga are substituted into the system an increasing displacement of Co from the tetrahedral site to the octahedral site occurs. While it might be expected that the Ga\(^{3+}\) ions would prefer the octahedral site based upon its large size, the amount of Ga\(^{3+}\) found on the smaller tetrahedral site steadily increases across the substitution series. In contrast Al\(^{3+}\) ions are found to remain mostly normal with a tetrahedral site occupancy never exceeding 20\%. The site preference of Ga\(^{3+}\) for the tetrahedral site is in agreement with the tendency of \( d^{10} \) Ga\(^{3+}\) to adopt \( sp^3 \) hybridization. In fact, from electrostatic arguments Miller [97] has determined that the relative octahedral site preference of Al\(^{3+}\) and Ga\(^{3+}\) are respectively \(-2.5 \text{ kcal mol}^{-1}\) and \(-15.4 \text{ kcal mol}^{-1}\) with the larger number indicative of the greater octahedral preference. In contrast, Co\(^{2+}\) has a site preference energy of \(-110.5 \text{ kcal mol}^{-1}\). Nakatsuka et al. [98] have conducted a recent study on the energetics of differ-
ent local bonding configurations and found that replacing the relatively large
Co$^{2+}$ ($r_{tet} = 0.58 \text{ Å}$) on the tetrahedral site with Al$^{3+}$ ($r_{tet} = 0.39 \text{ Å}$) results
in abnormally long bond lengths which is not favored. This effect is not as
pronounced when Ga$^{3+}$ moves to the tetrahedral site given the larger radius
($r_{tet} = 0.47 \text{ Å}$) and that the end member CoGa$_2$O$_4$ is commonly found to be al-
most completely inverted. [79] Site mixing also serves to explain the deviation
from the Végard law that is observed in Figure 3.2(a).

In Figure 3.2(c), the internal parameter $u$ reflecting the position of oxygen is
displayed for the different compounds in the series. It is seen that with increas-
ing $x$, this value progressively decreases. Hill et al. [78] have pointed out that
in normal spinels (without any inversion) this parameter $u$ depends on the ratio
$R$ of the octahedral to tetrahedral bond lengths according to:

$$u = \frac{R^2/4 - 2/3 + (11R^2/48 - 1/18)^{1/2}}{2R^2 - 2}$$  (3.2)

The expected values for ordered CoAl$_2$O$_4$ and CoGa$_2$O$_4$ using the appropriate
ionic radii [77] would be respectively 0.265 and 0.261. The observed trend
of a decreasing $u$ agrees with this expectation for the normal end-members.
However, we see from Figure 3.2(c) that while CoAl$_2$O$_4$, with very small inver-
sion has an experimentally determined $u$ value very close to what is calculated
from Equation 3.2, the value determined for CoGa$_2$O$_4$ ($u = 0.258$) is significantly smaller than suggested by Equation 3.2. Again, we believe this discrepancy arises because of the growing inversion in the compounds as $x$ increases.

The pair distribution functions extracted from total scattering neutron diffraction are shown for each composition in Figure 3.3(a) along with fits (shown as lines) obtained by refining the average spinel unit cells with the appropriate site inversion. Several characteristics can be observed directly. The unit cell expansion is apparent in the movement of atom-atom peaks to longer $r$ with increasing $x$. The first atom-atom peak become increasingly broad as $x$ increases, perhaps as a result of increased site mixing, in turn resulting in a distribution of cation-oxygen distances. Furthermore, features in the intermediate compositions can be linked to the CoAl$_2$O$_4$ and CoGa$_2$O$_4$ end-member PDFs, with an increasing resemblance to the CoGa$_2$O$_4$ PDF as $x$ increases.

Refinements in real space were carried out starting with the average structure results. A stable refinement of the site occupancies could not be achieved and values were therefore fixed to the results obtained from the Rietveld analysis of the neutron scattering data. The parameters refined in the PDF analysis include lattice parameters, isotropic atomic displacement parameters for each atomic species, a scale factor, and quadratic peak sharpening. The refinements yielded $\chi^2 < 1$ and $R_{wp}$ less than 15\% for $r$-ranges from 1 to 20\AA. From the fits
Figure 3.3. (a) Neutron pair distribution functions (PDF) collected at room temperature for the different CoAl$_{2-x}$Ga$_x$O$_4$ samples with $x = 0.0$ at the top of the panel and $x = 2.0$ at the bottom. Experimental data are filled grey circles and the lines are fits obtained by refining data against the average spinel structure. (b) Experimental PDFs of the $x = 0.4$ sample (filled grey circles) compared with the refinement using the average structure (labeled “fit”) and compared with a simulation (labeled “simulation”) prepared by taking the weighted average of experimental PDFs of the $x = 0.0$ sample (80% weighting) and $x = 2.0$ (20% weighting). Reproduced with permission from reference 49 © 2009 American Physical Society.
of the PDF displayed in Figure 3.3(a), it is seen that of all the samples, only in the data corresponding to the $x = 0.0$ sample are all the peaks well described by the model. This is keeping with the fact that only in the $x = 0.0$ sample does the average spinel structure accurately describe all the local distances, since this structure has the lowest inversion and no substitution.

In Figure 3.3(a), this is shown for a particular sample with $x = 0.4$. The experimental PDF is only very poorly fit in the short $r$ region by the average structure model (labeled “fit”). Upon close inspection of the $x = 0.4$ refinement around 3 Å and 5 Å, which correspond respectively to the first and second nearest Co neighbors, there is significant splitting of the experimental peaks which is not well represented by the average structure. However, a much better description of the $x = 0.4$ sample is a stoichiometrically weighted (80:20) average of the experimental PDFs of the end members ($x = 0.0$ and $x = 2.0$) rather than as a single phase as illustrated in Figure 3.3(b). In this, a resemblance to systems such as $\text{In}_{1-x}\text{Ga}_x\text{As}$ [99] is noted wherein the alloy compositions locally follow the bonding rules of the end-member structures, and alloy PDFs can be described using weighted averages of the end members. This result of averaging end-members only holds true for distances within a unit cell (approximately 8 Å). Outside of this range the superposition model begins to fail and the average structure proves to be a good model of the data. Thus from the local
Table 3.1. Magnetic data of different spinel compounds. $\Theta_{CW}$ is obtained from the fit to the high temperature inverse susceptibility data as described in the text. $T_N$ is taken as the point where the ZFC and FC magnetization curves diverge with respect to temperature. $f$ is obtained from $\Theta_{CW}/T_N$. The inversion parameter $\delta$ is also indicated for all samples.

<table>
<thead>
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<th>Compound</th>
<th>$\delta$</th>
<th>$\mu_{\text{eff}}$ ($\mu_B$)</th>
<th>$\Theta_{CW}$ (K)</th>
<th>$T_N$ (K)</th>
<th>$f$</th>
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<td>-42</td>
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<td></td>
<td>25</td>
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</tbody>
</table>

structure analysis we can see that our samples have a homogeneous distribution of substituted cations and there does not seem to be any evidence for local clustering of cations.

3.3.2 Magnetism

Figure 3.4 displays the temperature dependence of the DC magnetic susceptibility $\chi$ of the different spinel samples on a single scaled plot. For all samples, data between 350 K and 400 K were fit with high reliability by the Curie-Weiss
Figure 3.4. Temperature dependence of the scaled zero-field cooled magnetic susceptibility of the different spinel samples. Data were acquired under a 100 Oe field. The nature of the scaling is described in the text. Reproduced with permission from reference 49 © 2009 American Physical Society.
formula: $\chi = C/(T - \Theta_{CW})$, where $C$ is the Curie constant, and $\Theta_{CW}$ is the Curie-Weiss ordering temperature. As we mentioned in the previous chapter, we can recast this formula as:

$$\frac{C}{\chi|\Theta_{CW}|} = \frac{T}{|\Theta_{CW}|} - 1$$  \hspace{1cm} (3.3)

Evidence of Curie-Weiss behavior at high temperatures is seen from the right, higher temperature, panel of Figure 3.4. For each sample, and at all temperatures above the individual $\Theta_{CW}$ (indicated in Table 3.1, and approximately ranging between $-100$ K and $-40$ K) the scaled inverse susceptibility (left-hand side of Equation 3.3) is precisely equal to $T/|\Theta_{CW}|$. All the samples order at temperatures well below $|\Theta_{CW}|$ as seen in the left-hand low-temperature panel of Figure 3.4. A curious point to note is that while all the samples display a downturn in plots of $\chi$ vs. $T$, it is only the $x = 0.0$ sample, CoAl$_2$O$_4$, that stays largely superior to the dotted Curie-Weiss line. The behavior of $x = 0.0$ is distinctly different from all other samples which progressively deviate from the dotted Curie-Weiss line at higher temperatures as $x$ increases. The utility of plotting the inverse susceptibility of a solid solution in the manner shown in Figure 3.4 becomes evident in the way compounds with uncompensated spins due to inversion ($x \geq 0.4$) are separated from the antiferromagnetic $x = 0.0$ end mem-
A plot of $1/\chi$ vs. $T$ does not reveal this since the magnitude of the susceptibilities varies through the series.

Table 3.1 also shows values of $\mu_{eff}$ obtained from the Curie constant $C$ for the different spinel samples. The expected spin-only value of the magnetic moment for tetrahedral Co$^{2+}$ is 3.87 $\mu_B$ whereas a value of 5.20 $\mu_B$ [101] is expected for systems with completely unquenched orbital contribution. The values obtained here run between 4.59 $\mu_B$ and 4.85 $\mu_B$, and are therefore sandwiched by the limits of the completely quenched and unquenched orbital contributions. Measured values from the literature are in the range of 4.4 $\mu_B$ to 4.8 $\mu_B$. [101] Cossee and van Arkel [80] have argued that for tetrahedral Co$^{2+}$, the proximity of a low-lying excited spin state adds a temperature-independent term to the Curie-Weiss law and that after making such a correction, magnetic moment is close to 4.4 $\mu_B$. We expect CoAl$_2$O$_4$, with a very small degree of inversion, to display a $\mu_{eff}$ value which is close to 4.4 $\mu_B$. We find that for $x \neq 0$ in the substitution series, the value of $\mu_{eff}$ is always larger than for $x = 0.0$, which we attribute to the increasing amount of octahedral Co$^{2+}$ which has a larger orbital contribution to the effective moment and correspondingly has an experimental range of $\mu_{eff}$ from 4.7 $\mu_B$ to 5.2 $\mu_B$. [101]

Figure 3.5 shows in closer detail, the temperature dependence of the magnetic susceptibilities of the title spinel compounds at low temperatures. All
the compounds display splitting of the FC and ZFC data between 4 K and 12 K. 

CoAl$_{2}$O$_{4}$ ($x = 0.0$) shows very little irreversibility and only a gentle downturn near 12 K. Below 4 K, there is a small upturn in the susceptibility which could arise from uncompensated spins. All other compounds with $x \geq 0.4$ show the characteristic cusps of glassy systems associated with freezing of spins and no long range order as may be expected for cryptographically disordered antiferromagnets. For all samples $T_{N}$ was taken as the point of splitting between the ZFC and FC curves.

A gradual opening of the $M$–$H$ traces as $x$ is increased is seen in Figure 3.6 which accompanies the increasing concentration of Co atoms on the octahedral site. As the magnetic ions enter the $B$-site the $A$–$B$ interaction begins to dominate [47, 60], and even though both sites have the same number of spins, this interaction can give rise to uncompensated spins which could open the $M$–$H$ loops due to the unequal number of $A$ and $B$ sites. The near neighbor antiferromagnetic interaction between Co on the $A$ and $B$ sites, which are only separated by a single O atom will compete strongly with the pure $A$–$A$ interactions where the magnetic ions are separated by $–O–B–O–$ linkages. This interaction thereby adds another competing exchange pathways which may prevent long range antiferromagnetic order between Co atoms on the tetrahedral sites from being achieved and give rise to glassy behavior instead. [102] It should also be noted
Figure 3.5. Field-cooled (FC, solid) and zero-field cooled (ZFC, dashed) molar DC susceptibility of the spinel compounds at low temperatures. Data were acquired under a magnetic field of 1000 Oe. Reproduced with permission from reference 49 © 2009 American Physical Society.
Figure 3.6. Magnetization as a function of magnetic field for all samples obtained at 2 K in fields up to 5 T. Note that each curve has been shifted in 3 T increments to show more clearly the opening of the loops with increasing \( x \). Reproduced with permission from reference 49 © 2009 American Physical Society.

For high enough concentrations of Co\(^{2+}\) on the \( B \)-site that a ferromagnetic direct exchange between neighboring \( B-B \) atoms will begin to arise which could also give rise to the open \( M-H \) loops. [44]

For higher concentrations of Ga, it can be seen in Table 3.1 and Figure 3.7 (a) that \( \Theta_{CW} \) gradually decreases. Comparing the title compounds with systems
that have a well ordered magnetic $A$ lattice such as $\text{Co}_3\text{O}_4$ and $\text{CoRh}_2\text{O}_4$ shows an almost linear dependence of $\Theta_{CW}$ with respect to nearest neighbor separation $d_{AA}$ (and correspondingly next-nearest neighbor $A$–$A$ separation). We note that the deviation from the linear trend for samples with $x \geq 0.8$ can be understood by the site mixing in the samples reducing the number of magnetic cations on the $A$ site. Further evidence that this the deviation from linearity is a result of site disorder is the fact that a separate report on a sample $\text{CoGa}_2\text{O}_4$ with half of the site mixing present in our samples lays on the line.

The structural changes also affect the temperature where the system transitions from the paramagnetic to glassy state which we take to occur where the zero field cooling and field cooling data deviate as discussed earlier (Figure 3.7 (a)). For small concentrations of Ga with $x = 0.4$, a sharp drop of the transition temperature to 5 K from 10 K for the pure $\text{CoAl}_2\text{O}_4$ which we attribute to the sudden increase in atomic disorder and dilution of the magnetic $A$-site lattice [103]. This decrease is then followed by a gradual increase as more Al is replaced by Ga. Tristan et al. have studied the effect of replacing the $\text{Al}^{3+}$ with non-magnetic octahedral $\text{Co}^{3+}$. [89] It is interesting to note that changes in the non-magnetic $B$-site cation result in little to no change in $\Theta_{CW}$, however a clear increase in the ordering temperature is observed.

Figure 3.7 (b) plots the measured frustration parameter, $f = \Theta_{CW}/T_N$, as
Figure 3.7. (a) Curie-Weiss theta ($\Theta_{CW}$) and ordering temperature ($T_N$) as a function of near-neighbor spacing between the $A$-site atoms. The ordering temperature is taken as the point of deviation between the field cooling and zero field cooling data shown in Figure 3.5. (b) Frustration index $f = \Theta_{CW}/T_N$ for the title compounds as a function of near-neighbor spacing between the $A$-site atoms ($d_{AA}$ increases with increasing Ga content, $x$). Also displayed is published data for CoAl$_2$O$_4$ with different degrees of inversion: $\delta = 0.04$. By comparison, the degree of inversion of the CoAl$_2$O$_4$ sample measured in this work is close to 0.09. Values for Co$_3$O$_4$ and CoRh$_2$O$_4$ were also obtained from reference 48 while values for CoGa$_2$O$_4$ were taken from 100. Note that the values from reference 48 were not reported with lattice constants so the near-neighbor separation was taken from separate structure reports. Reproduced with permission from reference 49 © 2009 American Physical Society.
a function of \( d_{AA} \), the separation between \( A \) ions in the different structures, including values for \( \text{Co}_3\text{O}_4 \) and \( \text{CoRh}_2\text{O}_4 \) taken from the literature. Considering the changes in \( \Theta_{CW} \) and \( T_N \) we find with the exception of \( x = 0.4 \) the frustration index decreases systematically with increasing \( d_{AA} \) separation.

In order to better understand the behavior of the samples, classical Monte Carlo simulations were preformed for the \( J_1-J_2 \) model on the \( A \)-site spinel lattice. A certain amount of inversion was randomly introduced each time a simulation run was performed. We also assumed that impurity spins occupying \( B \)-sites interact with their nearest neighbors on occupied \( A \)-sites via a Heisenberg exchange coupling \( J_i \).

In Figure 3.8, we show the results of a scan of various parameters. \( J_2/J_1 \) was set to 0.1, 0.2, and 0.3 while the inversion \( \delta \) set to 0.0, 0.05, 0.10 and 0.20. The ratio \( J_i/J_1 \) was fixed to 1.7 throughout the scan. After plotting the resulting inverse susceptibilities in the manner described in eqn. 3.3, we can make a few qualitative observations. As expected, increasing \( J_2/J_1 \) increases the frustration of the system in the sense that it lowers the temperature at which evidence of ordering appears. Additionally upon introducing even a small amount of inversion, the behavior of the susceptibility below the Curie-Weiss temperature rapidly changes from antiferromagnetic (sharp upward kink) to ferrimagnetic (smooth downturn) in rough qualitative agreement with the experimental re-
Figure 3.8. Magnetic susceptibility results from Monte Carlo simulations plotted in the form of Equation 3.3 compared to experimental data. From top to bottom one can see the change in the shape of the low temperature susceptibility curves for increasing competition between \( J_2 \) and \( J_1 \). Within each panel the effect of atomic disorder is shown. Note that \( J_i / J_1 \) is held constant at 1.7 for all of these simulations. The dotted line represents the expected result for a perfect Curie-Weiss system. Reproduced with permission from reference 49 © 2009 American Physical Society.
We also attempted to use the model to fit the individual susceptibility curves of the various experimental samples with mixed success. We first conducted simulations of the model with no inversion, in which case the fit was controlled by only one parameter, namely $J_2/J_1$. These simulations were all performed on a system consisting of a cube of 64 conventional unit cells (512 spins), though for certain values of $J_2/J_1$, simulations were also done using a system of 125 unit cells (1000 spins) to check for finite size effects, which were found to be negligible for the susceptibility data.

Although all of the inverse susceptibility curves produced from the numerics for the $\delta = 0.0$ case were systematically above the experimental data, they showed the correct qualitative behavior in that they exhibited an upward turning kink, presumably at the ordering temperature $T_N$. By increasing the value of $J_2$ until $J_2/J_1$ is around 0.15 to 0.18 (and correspondingly a $J_1$ between 12.1 and 12.8 K), the transition temperature $T_N$ was brought into approximate agreement with the experimentally observed value as shown in Figure 3.9. We also considered simulations with small amounts of inversion between 1 and 2% given that even pure CoAl$_2$O$_4$ exhibits a small amount of disorder. However, unless we ran our simulations with a value of $J_i/J_1$ far from the range that gave a good fit to the doped sample with $x = 0.4$ (discussed next), such a small amount
Figure 3.9. (a) Susceptibility curves obtained from Monte Carlo simulations where the effect of varying the ratio $J_2/J_1$ is tested in a system with no atomic disorder. (b) Susceptibility curves where the effect of varying the ratio $J_2/J_1$ is tested on a system with a fixed amount of atomic disorder around $\delta = 0.36$. Reproduced with permission from reference 49 © 2009 American Physical Society.
of disorder changed the resulting susceptibilities very little.

We have also fit the \( x = 0.4 \) data by running simulations with an inversion of \( \delta = 0.36 \). To improve the disorder averaging, the simulations were done using a 5×5×5 supercell (1000 spin) with the data presented here being the average of three independent runs. As in the case above, all of the inverse susceptibility data produced by the Monte Carlo simulations was systematically larger than the experimental curve excluding the region below the downturn. Interestingly the data could be fit equally well by a range of \( J_2/J_1 \) and \( J_i/J_1 \) values, as long as both parameters were increased together, as can be seen from Figure 3.9. Since it is probably reasonable to assume that \( J_2/J_1 \) decreases slightly from the value obtained for the \( x = 0.0 \) sample, we can take \( J_2/J_1 \) between 0.10 and 0.15 and find that the ratio \( J_i/J_1 \) should lay between 2.0 and 2.3 whereas \( J_1 \) is found to be between 8.5 and 9.7 K.

It is worth noting at this point that if we judge the quality of the fit in a least-squares sense, the Curie-Weiss law describes the data better than the numerical susceptibility data given that the numerical data lies above the experimental data through a wide temperature range for which a straight line fits the experimental data almost perfectly. Despite this fact, it is valuable to see that the simulation data exhibits the same qualitative low temperature behavior as the experiments. One possible explanation for the deviation between the theory and
experimental data, aside from the assumption that only nearest and next nearest neighbor exchange play a role, is the possible over simplification of the $g$ factor. One way to improve our simulations would be to allow for a temperature dependent $g$ or also assigning a different value of $g$ to each site.

Finally, we attempted to fit the experimental susceptibilities for the samples with $x \geq 0.8$ and were unable to obtain a good fit without changing the $J_2/J_1$ and $J_i/J_1$ by an unreasonable amount. For every set of parameters considered, the numerically calculated inverse susceptibilities exhibited strong downturns and dropped far below the experimental curve after initially matching at high temperature. Though the reasons for this negative result are somewhat unclear, it seems that either the appropriate $J_2/J_1$ and $J_i/J_1$ ratios are very far from those found above or more likely the use of only two parameters is an over simplification considering that atomic disorder will locally modify exchange pathways and make the true exchange couplings site dependent. This possibility is supported by the PDFs presented which show the local bond lengths of the end members is retained upon substitution. Such behavior may indicate that substitution actually generates new competing $J$ values which are not accounted for in our Monte-Carlo simulations rather than a simple modification to the existing pathways as may have been expected.

We have attempted to understand the nature of the magnetic frustration in
the $A$-site magnetic spinels $\text{CoAl}_{2-x}\text{Ga}_x\text{O}_4$ by substituting Ga for Al, in the hope of decreasing the relative magnetic coupling between near and next-near $A$ atom neighbors. We have found, however, that in the compounds presented there is a significant mixing of the $A$ and $B$ sites in the Ga-rich samples, and this inversion has a significant influence on the magnetic coupling. The complexity of the structural changes which occur with substitution of Ga make isolating the influence of lattice expansion and site mixing a significant challenge. We have used Monte Carlo calculations to demonstrate the importance of site mixing through a change of shape in the simulated susceptibility curves which agrees closely with our experimental findings. By comparing with samples that are perfectly ordered such as $\text{Co}_3\text{O}_4$ and $\text{CoRh}_2\text{O}_4$, we have demonstrated that there appears to be a trend in which the frustration index $f$ depends weakly upon the separation between magnetic ions. We have also used a variety of structural characterizations and magnetic measurements to demonstrate how both lattice expansion and site mixing can simultaneously influence the frustration parameter.
Chapter 4

Magnetic ordering and magnetodielectric coupling in $\text{CoSeO}_4$.

In the previous chapters we have primarily focused on compounds with the spinel structure. This approach afforded us a way to investigate chemical substitution as a way to modify the nature of the frustration in some well-studied compounds. The following chapters now shift our focus towards investigating single-phase materials which contain chains of transition metals coordinated by oxygen.
This is motivated by the fact that materials with reduced crystallographic dimensionality are of great interest because their physics is dominated by strong interplay between charge, lattice, and magnetic degrees of freedom. \[104, 105\]

From the perspective of magnetism and frustrated interactions, one-dimensional chains of spins are especially interesting because of the possibility of competing nearest and next-nearest neighbor exchange interactions. \[106\] Examples of recently studied compounds with magnetic chains include those showing geometric frustration, magnetoelectric coupling, and possible quantum tunneling of the magnetization, as exemplified by Ca$_3$Co$_2$O$_6$, \[107–109\] MnWO$_4$, \[110\] and LiCu$_2$O$_2$. \[106, 111\]

In this chapter we begin by discussing the preparation and detailed magnetic and dielectric characterization of CoSeO$_4$: a magnetic chain compound which adopts a crystal structure analogous to $\beta$-CoSO$_4$ (Figure 4.1). The orthorhombic unit cell contains chains of octahedrally coordinated Co$^{2+}$ which are bound together by SeO$_4^{2-}$ tetrahedra via shared oxygen atoms at the edges of the octahedra. The chains of octahedra are tilted with respect to neighboring chains where the axis of the octahedra tilted $-35^\circ$ and $+35^\circ$ off the $a$-axis for the chains on the edge and in the center of the cell respectively. Previous reports have characterized the nuclear and magnetic structure using neutron diffraction,\[112, 113\] but no reports on the magnetic susceptibility or dielectric properties have been
made to date, and the effects of magnetic fields have not been fully investigated. Using detailed magnetization, heat capacity, powder neutron diffraction, and dielectric measurements, we show that the transition to long-range antiferromagnetic behavior below 30 K is accompanied by a significant change in the slope of the temperature dependence of the dielectric constant. We also find a field-induced change in the magnetic structure. The dependence of the dielectric constant on the external field, which is quadratic in nature, changes dramatically above the field-induced magnetic transition.

4.1 Experimental Details

The title compound was prepared following a previously reported procedure[114] by neutralizing a solution of selenic acid [(2.559 g, 23.06 mmol) of SeO\textsubscript{2} dissolved in 50 mL of water] with Co\textsubscript{2}CO\textsubscript{3}(OH)\textsubscript{2} (1.629 g, 7.69 mmol) at 70°C and recrystallizing from water. The final crystallization step was performed by allowing the remaining water to evaporate slowly at room temperature over several days. Faceted crystals of dark red CoSeO\textsubscript{4}·6H\textsubscript{2}O with dimensions of up to 2 cm on a side were obtained by this procedure. These crystals were finely ground and dehydrated at 125°C overnight to yield a bright pink powder of CoSeO\textsubscript{4}·H\textsubscript{2}O which was subsequently heated at 315°C for sev-
Figure 4.1. Illustration of the crystal structure of CoSeO$_4$. Chains of octahedrally coordinated Co$^{2+}$ (purple) are bound together by SeO$_4$ tetrahedra via shared oxygen atoms at the edges of the octahedra. Note that the chains are alternately tilt $+35^\circ$ and $-35^\circ$ off the $a$-axis. (a) View down the $c$-axis of the unit cell. (b) View off the $c$-axis to illustrate the chains of edge sharing CoO$_6$
eral days to produce a light violet powder of anhydrous CoSeO$_4$. Co$_2$CO$_3$(OH)$_2$ was prepared following a separate previously reported procedure. [115] Stoichiometric amounts of CoNO$_3$·5H$_2$O and Na$_2$CO$_3$ were separately dissolved in H$_2$O with a 2:1 (NaCO$_3$:CoNO$_3$) volume excess. The solution of CoNO$_3$ was added to the solution of Na$_2$CO$_3$, which had been preheated to 90°C. After stirring for 2 hours the resulting dark purple precipitate was collected by vacuum filtration and subsequently washed with H$_2$O and ethanol. Purity of the precursors and final product was confirmed by powder X-ray diffraction on a Philips X'Pert MPD diffractometer operated at 45 kV and 40 mA.

Temperature dependence of the DC magnetization was measured on well-ground powder samples using a Quantum Design MPMS 5XL SQUID magnetometer. Specific heat data were collected using the semiadiabatic technique as implemented in a Quantum Design Physical Property Measurement System (PPMS), under zero as well as under a 50 kOe applied field. Heat capacity samples were prepared by mixing the compound with equal parts by mass Ag powder and pressing into a pellet in order to improve thermal coupling to the stage. The contribution from Ag was measured separately and subtracted. Variable temperature neutron diffraction data under a magnetic field were collected on the BT-1 powder diffractometer at the National Institute of Standards and Technology, Gaithersburg, MD, using a wavelength of 2.0797 Å. Dielectric properties
were measured by attaching polished copper electrodes to opposite faces of a cold-pressed pellet of CoSeO$_4$, using a Quantum Design PPMS for temperature and field control, and an Agilent 4980A LCR meter to measure the capacitance.

4.2 Computational Details

Density functional theory (DFT) calculations were performed using the Vienna Ab-initio Simulation Package (VASP) [116, 117] at the experimental lattice parameters. The projector augmented-wave (PAW) method [118] was used together with the local density approximation (LDA) Ceperley-Alder exchange correlation functional. [119] A plane-wave energy cutoff of 500 eV and a $6 \times 3 \times 9$ $\Gamma$-centered Monkhorst-Pack[120] $k$-point mesh corresponding to 162 irreducible $k$-points was used to sample the Brillouin zone. The tetrahedron method with the Blöchl correction [118] was used for Brillouin zone integrations. Correlation was treated using the LDA+$U$ formalism within the rotationally invariant approach of Liechtenstein et al. [121] The applicability of the LDA+$U$ formalism is validated in the example of $d^7$ Co$^{2+}$ where crystal symmetry results in a complete absence of orbital degeneracy. Several values of $U$ were tested with only qualitative changes to the band structure being found. Therefore, a $U$ of 5 eV and a $J$ of 1 eV was chosen to agree with previously published DFT results
Figure 4.2. Field-cooled (FC, circles) and zero-field cooled (ZFC, squares) magnetic susceptibility of a powder sample of CoSeO$_4$ acquired under increasing strengths of the external magnetic field. At 30 K, the system orders to an antiferromagnetic state. A weak ferromagnetic component is found in the 100 Oe data, suggested by the separation in ZFC and FC traces. Note also that the cusp indicating the magnetic ordering is smeared out with increasing field strength.
calculated on octahedrally coordinated \( \text{Co}^{2+} \). \[122\]

### 4.3 Results and Discussion

The high temperature region (200 K to 300 K) of the inverse susceptibility was fit to the Curie-Weiss equation, \( C/(T - \Theta_{CW}) \). A Curie-Weiss temperature of \(-36 \text{ K}\) and an effective moment \( \mu_{\text{eff}} \) of 4.38 \( \mu_B \) was determined for the data collected under a 10 kOe field. The effective moment lies between the spin-only value of 3.87 \( \mu_B \) and the value of 5.2 \( \mu_B \) expected for octahedrally coordinated \( \text{Co}^{2+} \) \((d^7, t_{2g}^5 e_g^2, S=3/2, L=3)\) with a fully unquenched orbital contribution as obtained using the relationship \( \mu_{L+S} = \sqrt{4S(S+1) + L(L+1)} \).[123] The existence of an orbital contribution is common for high-spin \( d^7 \) systems in an octahedral \( d^7 \) crystal field due to the orbital degeneracy in the \( t_{2g} \) levels. The small reduction of the orbital contribution likely arises from the irregular octahedral environment of the magnetic sites reducing some hybridization with the surrounding oxygen anions.

Figure 4.2 shows the temperature dependence of the magnetic susceptibility of CoSeO\(_4\) under a variety of magnetic field strengths. The spins begin to order below 30 K which is very near the expected Curie-Weiss temperature indicating that there is very little frustration from competing exchange interactions.
Figure 4.3. (a) Isothermal magnetization loops at various temperatures below the Néel temperature. Note the field induced transition which pushes to higher fields at low temperatures.
When measured in a 100 Oe field, a sudden jump in the susceptibility occurs at 30 K which can be attributed to some weak ferromagnetism which results from a canted antiferromagnetic arrangement of the spins. Measuring the sample in larger fields minimizes the contribution from the weak-ferromagnetic component and gives rise to the cusp-like behavior expected from a well-compensated antiferromagnet. This cusp is found to broaden with increasing field strength indicating that the magnetic order may be driven to a different ground state in the presence of sufficiently large external fields. To further examine the nature of the field-dependence of the magnetic order, isothermal magnetization loops were collected at a variety of temperatures (Figure 4.3). An upturn from the linear field-dependence expected for a well-behaved antiferromagnet is found beginning in a field of approximately 20 kOe at 28 K. The upturn shows a strong temperature dependence, with the field required to induce it increasing to 45 kOe by 18 K and subsequently out of the 50 kOe range of the magnetometer used here by 10 K. Such a field-induced magnetic transition may be attributed to overcoming of the magnetocrystalline anisotropy of the octahedral Co$^{2+}$ cations which would manifest as a spin-flop transition where the spins realign from one preferred axis to another.

Figure 4.4 (a) shows the specific heat of CoSeO$_4$ measured in zero field, and under an external magnetic field of 50 kOe. The specific heat shows a sharp
Figure 4.4. (a) Temperature dependence of the specific heat of CoSeO$_4$ measured on a powdered sample in $H = 0$ kOe and 50 kOe field. (b) Entropy released due to the magnetic ordering, obtained by integration of the magnetic heat capacity.
anomaly at the magnetic ordering temperature of 30 K in the absence of an external magnetic field. Application of a 50 kOe field results in a smearing out of the transition in a manner similar to the behavior observed in the susceptibility data shown in Figure 4.2. The lattice contribution to the specific heat was approximated by fitting the data above the magnetic transition to a polynomial expansion \((\beta T^3 + \gamma T^5 + \delta T^7)\). Subtracting the lattice contribution and integrating \(C_p/T\) yields a change in entropy due to magnetic ordering of 2.1 J mol\(^{-1}\) K\(^{-1}\) and 2.5 J mol\(^{-1}\) K\(^{-1}\) in zero field and a 50 kOe field respectively. This value is significantly smaller than the value of 11.5 J mol\(^{-1}\) K\(^{-1}\) predicted by the Boltzmann equation \((\Delta S = R \ln(2S + 1), S = 3/2)\). This considerable diminution of the spin entropy from what is expected may indicate that the reduced dimensionality of the system prevents complete ordering of the spins, or that possibly the order within chains is not well correlated with that in neighboring chains.

To better understand the electronic structure and chemical bonding in the title compound, density functional theory calculations were performed using the LDA+U formalism. Figure 4.5 illustrates the density of states (DOS) calculated for the experimental room temperature structure of CoSeO\(_4\). The DOS show a significant degree of overlap between the Se-\(p\) and O-\(p\) states and between Co-\(d\) and O-\(p\) states below the Fermi energy. However, there is a gap of approximately 250 meV between the Co and Se states. It can be seen that a majority of the Se
Figure 4.5. Densities of state of CoSeO$_4$ from a collinear spin structure calculation. The magnetic structure used in the calculation was that of antiferromagnetic chains aligned antiparallel to neighboring chains.
and O overlap is related to bonding between Se and O. The O3 position forms two bonds within the Se tetrahedron which are 1.56 Å; short in comparison with the Se–O1 and Se–O2 bond lengths which are 1.74 Å and 1.78 Å respectively. Such bonding is consistent with the idea that the SeO₄ tetrahedra contains two double and two single bonds with surrounding oxygens to satisfy its octet. It is interesting to note that the Se-O3 bonds correspond to the shared oxygens at the corners of the CoO₆ octahedra within a single chain. This arrangement of double bonds can be expected to significantly influence magnetic superexchange between the CoO₆ chains.

The DOS calculated using the LDA formalism results in metallic densities of state, but by accounting for correlations within LDA+U, with \( U = 5 \text{ eV} \) and \( J = 1 \text{ eV} \), a gap of approximately 3 eV opens between the occupied and unoccupied minority spins. We also note that the band gap which is approximately 2 eV corresponds to the gap between the highest filled states and unoccupied O-\( p \) orbitals. The distorted octahedral environment of the Co²⁺ breaks the degeneracy of the unoccupied \( e_g \) orbitals corresponding to \( d_{x^2} \) and \( d_{x^2-y^2} \) with unoccupied \( d_{xz} \) above the Fermi energy.

The antiferromagnetic state is stabilized by more than 0.5 eV compared to a ferromagnetic alignment of spins. The calculated spin magnetic moment on each Co is 2.72 \( \mu_B \), which is slightly reduced from the full value of 3 \( \mu_B \) expected
Figure 4.6. Low angle region of the powder neutron-diffraction patterns of CoSeO$_4$ (BT-1,NIST) obtained at different temperatures.
Figure 4.7. Low angle region of the powder neutron-diffraction pattern of CoSeO$_4$ obtained at 5 K and broken down in to the contributions from the nuclear, magnetic, and a small non-magnetic impurity phase of Se$_2$O$_5$. 
Table 4.1. Summary of the results of Rietveld structure refinement of variable temperature neutron diffraction data obtained in zero magnetic field.

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<td>$R_{\text{mag.}}$ (%)</td>
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<td>14.1</td>
</tr>
</tbody>
</table>

for a $d^3$ cation in an octahedral coordination environment. Such a reduction may be associated with the covalent bonding to the surrounding oxygens or may be related to the fact that the calculation is restricted to a collinear spin configuration which is not the true ground state observed via neutron diffraction.

The thermal evolution of the neutron-diffraction patterns collected from 300 K to 5 K are shown in Figure 4.6 with Table 4.1 showing a summary of refined parameters. Three magnetic reflections appear below 30 K at $12^\circ$, $18^\circ$, and $23^\circ$, all of which are consistent with a propagation vector $k = 0$. It was only possible to simultaneously fit all three magnetic peaks by using the basis vectors of the irreducible representation $\Gamma_1$. The resulting magnetic structure is illustrated in Figure 4.8. The spins on each Co align antiferromagnetically down the length of the chain and with respect to the neighboring chains. The moment of each spin has components along all three axes of the unit cell as
Figure 4.8. Proposed magnetic structure of CoSeO₄ as determined from Rietveld refinements of the neutron diffraction pattern obtained using a $\lambda = 2.08 \, \text{Å}$ at 2 K. (a) View down the $b$-axis of the $Pnma$ structure. (b) View down the $c$-axis. The small light grey atoms are oxygen while the larger and darker grey atoms are selenium.
listed in Table 4.2 with a total magnetic moment of 3.59 $\mu_B$ at 5 K. The magnetic structure in the absence of a magnetic field shown in Figure 4.8 agrees well with the previously reported structure of Fuess. [113] We note that while Fuess reported the structure in $Pbnm$ we have chosen the standard setting of $Pnma$. The resulting spin configuration (compared to that reported by Fuess) has spins oriented largely in the $ac$ plane with the moments tilting $60^\circ$ ($60^\circ$) off the $a$-axis, $70^\circ$ ($69^\circ$) off the $b$-axis, and $44^\circ$ ($41^\circ$) off the $c$-axis again at 5 K. The moment within individual chains does not cancel completely with a resulting uncompensated moment along the $a$-axis which is canceled by the neighboring chains. This uncompensated moment within the individual chains may be a source of the weak ferromagnetism observed in small external magnetic fields.

The effect of applying a magnetic field of 70 kOe is to first reduce the total magnetic moment to 2.60 $\mu_B$ at 5 K. The field also causes the spins to reorient with respect to the unit cell. At 20 K the moments form angles of $66^\circ$ off the $a$-axis, $64^\circ$ off the $b$-axis, and $37^\circ$ off the $c$-axis. From examination of the isothermal magnetization measurements in conjunction with the reorientated moments the field-induced magnetic transition appears to corresponds to a spin-flop transition on to the $c$-axis.

Figure 4.9 (a) shows the inverse magnetic susceptibility normalized by the fits of the high temperature region (between 200 K and 300 K) to the Curie-Weiss
Figure 4.9. (a) Inverse magnetic susceptibility normalized by the values extracted from fits to the Curie-Weiss formula in the high temperature region. Note that this manner of plotting emphasizes short-range correlations which cause deviations from ideal Curie-Weiss behavior which is illustrated as the dashed line. (b) Temperature dependence of the dielectric constant of CoSeO$_4$ measured on a pressed pellet of a polycrystalline sample at a frequency of 1 MHz. The dashed line is a guide to emphasize the transition at the magnetic ordering temperature.
Table 4.2. Components of the magnetic moment on each Co in the magnetic structure described by $\Gamma_1$. Note that Co at the origin occupies a $4a$ Wyckoff site. The Co within the unit cell are: Co1 (0, 0, 0), Co2 ($\frac{1}{2}$, 0, $\frac{1}{2}$), Co3 (0, $\frac{1}{2}$, 0), Co4 ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$).

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<tr>
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<td>−2.51</td>
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<tr>
<td>Co4</td>
<td>1.51</td>
<td>−1.05</td>
<td>−2.51</td>
</tr>
</tbody>
</table>

formula. Normalizing in this manner emphasizes deviations from the Curie-Weiss equation in the form of short-range correlations between the spins which develop above the ordering temperature.[35] Figure 4.9 (b) shows the temperature dependence of the dielectric constant with a very clear change in slope in the dielectric constant at the magnetic ordering temperature.

To further characterize the coupling between the magnetism and dielectric properties, the dielectric constant was measured as a function of external magnetic field. A quadratic dependence of the dielectric constant with field was found and is shown in Figure 4.10. Above the field-induced magnetic transition, the dielectric constant no longer exhibits a quadratic increase but rather
Figure 4.10. Change in the dielectric constant measured at 1 MHz plotted as a function of the strength of the external magnetic field. Note there is a roughly quadratic response for low field both above and below the magnetic transition. There is also a sharp decrease for magnetic fields above the field-induced transition.
changes abruptly to what appears to be a linear decrease. A similar temperature-and field-dependent behavior has been reported by Nénert and coworkers [124] for a hybrid Cr(II) inorganic-organic material. They attribute the behavior they find to the always allowed $P^2H^2$ order parameter. However, in their particular system they find a quadratic response to field above the magnetic ordering temperature as well as below. In that aspect, our results differ in that we see no response in the dielectric constant in that paramagnetic regime. This likely reflects the possibility that the low-field magnetic structure allows for a magnetodielectric response whereas the high-field magnetic structure does not.

**Summary**

We have discussed the preparation and detailed magnetic and dielectric characterization of a magnetic chain compound, CoSeO$_4$. Magnetization and specific heat measurements show the transition to a long-range canted antiferromagnetic state below 30 K and a temperature-dependent, field-induced magnetic transition. Powder neutron diffraction shows the spins lay predominantly in the $ac$-plane with the moments tilting $60^\circ$ off the $a$-axis, $70^\circ$ off the $b$-axis, and $44^\circ$ off the $c$-axis again at 5 K. Temperature and field dependent measurements of the dielectric constant show an anomaly at the magnetic ordering temperature
which, at fixed temperature, is quadratic in the external magnetic field. We also find that the field-induced magnetic transition causes an abrupt change in the field dependence of the dielectric constant. Such behavior likely indicates the changes in the dielectric constant are indicative of a linear magnetoelectric coupling which is not compatible with the high-field magnetic structure.
Chapter 5

Magnetic Structure and Susceptibility of CoSe$_2$O$_{5}$

In this chapter we report a detailed magnetic study of polycrystalline CoSe$_2$O$_5$, an orthorhombic compound crystallizing in the $Pbcn$ space group, comprising chains of edge sharing CoO$_6$ octahedra that zig-zag along the $c$-axis. Each chain is bound together by Se$_2$O$_5^{2-}$ units via shared oxygen atoms at the corners of the octahedra. The diselenite units can be visualized as two trigonal pyramids of SeO$_3$ which share a corner and contain two lone-pairs of electrons which point in antiparallel directions. This compound and its structure was reported by Harrison, McManus, and Cheetham [125] but no reports
on the properties have been made so far. We were particularly interested in this
compound because of its chain structure, the presence of orbitally degenerate
octahedral Co$^{2+}$, and the presence of symmetry reducing lone pairs.

We have used a combination of magnetic susceptibility and magnetization
measurements, specific heat measurements, and low-temperature powder neu-
tron diffraction to characterize the nature of the magnetic ground state below
$T_N = 8.5 \text{ K}$ and at low magnetic fields. We suggest the presence of more complex
magnetic structures in the presence of large fields, and point to the presence of
a 6.5 K gap in the magnon dispersion from heat capacity measurements.

5.1 Experimental Details

CoSe$_2$O$_5$ was prepared following the reported hydrothermal
procedure.[125] SeO$_2$ (5.0 g, Cerac, 99.99%) was dissolved in 15 cm$^3$ of
water and combined with CoSO$_4 \cdot x$H$_2$O (2.0 g, Sigma-Aldrich, 98%). The
mixture was sealed in a 23-mL poly(tetrafluoroethylene)-lined pressure vessel
(Parr Instruments) and heated to 200$^\circ$C for 48 hours. The resulting product
consisted of dark purple single crystals averaging 1.5 mm $\times$ 1.5 mm $\times$ 0.5 mm.

ZnSe$_2$O$_5$, a non-magnetic analogue to the title compound, was also prepared
in order to estimate the lattice contribution to the specific heat. SeO$_2$ (0.7317 g,
Cerac, 99.99%) was ground in an agate mortar with ZnO (0.2683 g, Sigma-Aldrich, 98%), sealed in a quartz tube, and heated at 350°C for 48 hrs.[126] The resulting product consisted of an off-white polycrystalline powder.

Temperature dependence of the DC magnetization was measured on well-ground powder samples using a Quantum Design MPMS 5XL SQUID magnetometer. Powders were preferred for magnetization measurements since the shape and dimensions of the available single crystals made them difficult to align with respect to the field direction. The specific heat data were collected on a 9.5 mg single crystal using the semiadiabatic technique as implemented in a Quantum Design Physical Property Measurement System (PPMS), under zero applied field, as well as under a 10 kOe field. The measurement on non-magnetic ZnSe₂O₅ was made by mixing the compound with equal parts by mass of Ag powder and pressing into a pellet in order to improve thermal coupling. The contribution from Ag was measured separately and subtracted.

Neutron diffraction data were collected in collaboration with Emmanuelle Suard on a sample of well-ground single crystals at the D2B powder diffractometer at the Institut Laue-Langevin (ILL), France[127] using a wavelength of 1.5949 Å. The precise wavelength of the incident neutrons was refined from the data obtained at 300 K by fixing the cell parameters to the values determined from a room temperature x-ray diffraction pattern collected on a Philips X'Pert
MPD diffractometer operated at 45 kV and 40 mA. In order to achieve a better fit to the lowest lying magnetic reflections, a diffraction pattern was also collected at 2 K using a wavelength of 2.399 Å.

5.2 Results and Discussion

The high temperature region (350 K to 400 K) of the inverse susceptibility was fit to the Curie-Weiss equation, \( C/(T - \Theta_{CW}) \), to obtain the effective moment \( \mu_{eff} \) from the Curie constant, and the Curie-Weiss intercept \( \Theta_{CW} \). A Curie-Weiss temperature of \(-34\) K and an effective moment of \( 5.19 \mu_B \) were extracted from the fits to the data collected under a 100 Oe field. This effective moment can be compared to the value of \( 5.2 \mu_B \) expected for octahedrally coordinated \( \text{Co}^{2+} \) (\( d^7, t^2_{2g} e^2_g, S = 3/2, L = 3 \)) where the spin and orbital contributions to the effective moment are completely decoupled from one another as obtained using the relationship \([123]\) \( \mu_{L+S} = \sqrt{4S(S+1) + L(L+1)} \).

Using the values of \( C \) and \( \Theta_{CW} \) from the fit to the high temperature susceptibility, we display in Figure 5.1 a plot of the scaled field cooled (FC) susceptibility of \( \text{CoSe}_2\text{O}_5 \) in a manner that emphasizes deviations from Curie-Weiss behavior. The scaling is performed by plotting \( C/|\chi|\Theta_{CW}| - 1 \) as a function of \( T/|\Theta_{CW}| \), for which Curie-Weiss behavior should yield a straight line through the origin.
Figure 5.1. Field-cooled (FC) DC magnetic susceptibility of polycrystalline CoSe$_2$O$_5$ acquired under magnetic fields of 100 Oe and 10000 Oe. The data have been scaled as indicated in the text, to emphasize deviations from Curie-Weiss behavior.
The purpose of such scaling has been discussed in prior work.\[35\] Deviations from Curie-Weiss behavior start at temperatures near 34 K (note that the frustration index \[f = |\Theta_{CW}|/T\] can be read from the inverse of the \(x\)-axis). At \(T_N\) near 8.5 K, there is a sharp transition to an ordered ground state.

The ordering temperature of 8.5 K is significantly smaller than \(\Theta_{CW}\) as is commonly found in systems with reduced crystallographic dimensionality. One of the advantages of the scaling used in Figure 5.1 is that systems with purely antiferromagnetic ordering display positive deviations from the Curie-Weiss line. In contrast, systems with ferromagnetic interactions, or more generally, uncompensated magnetic ordering, display negative deviations, reaching a limiting value of \(-1\) for the case \(\chi \rightarrow \infty\).\[35\] While the FC susceptibility under a 10000 Oe field clearly attains a ground state that is completely compensated and antiferromagnetic, the lower field measurement obtained at 100 Oe, while also resulting in a transition near 8.5 K, results in a ground state that retains some uncompensated moment rather than being purely antiferromagnetic.

To better understand the nature of the 8.5 K transition, we show in Figure 5.2 the temperature dependence of the magnetic susceptibility for a powder sample of CoSe\(_2\)O\(_5\) collected under different magnetic fields. When measured in fields smaller than 1000 Oe, a sharp jump in the susceptibility is observed below 8.5 K.
Figure 5.2. (a) Field-cooled (FC, open symbols) and zero-field cooled (ZFC, closed symbols) magnetic susceptibility of a powder sample of CoSe$_2$O$_5$ acquired under increasing strengths of the external magnetic field. At 8.5 K, the system orders to an antiferromagnetic state. A weak ferromagnetic component is found in low-field data, suggested from the separating ZFC and FC traces. This component is suppressed under increasing external magnetic fields. Note also the field-independence of the magnetic ordering temperature.
Such a jump would not be expected for an antiferromagnet with complete cancellation of the magnetic moment within the unit cell. Instead, we attribute the jump to the presence of weak ferromagnetism that can be found in systems with a canted antiferromagnetic spin structure [128]. The weak ferromagnetism is an intrinsic property of the material since there is no change in the ordering temperature as a function of field and no magnetic impurities were detected in the powder neutron diffraction data as will be discussed in the following. Additionally, we find that the contribution from the weak ferromagnetism can be minimized by application of sufficiently large fields. Indeed, magnetic measurements under fields from 1000 Oe to 10000 Oe display the characteristic, somewhat rounded downturn expected for a well-compensated antiferromagnet.

From Figure 5.2 we see that the separation between the ZFC and FC susceptibility corresponding to the weak ferromagnetic component is gradually reduced with increasing field strength as the weak ferromagnetism saturates and the antiferromagnetism begins to dominate the susceptibility. By fitting a straight line to measurements of $M$ vs. $H$ at $T = 2$ K, and subtracting this straight line from the 2 K magnetization, we obtain plots of $\Delta M$ as a function of the ascending and descending magnetic fields at $T = 2$ K displayed in Figure 5.3. The resulting trace shows a small maximum near $H = 0$, which indicates the ferromagnetic component has a saturation value around $2 \times 10^{-4} \mu_B$ per Co.
Figure 5.3. $\Delta M$, obtained by subtracting as explained in the text, at $T = 2\,\text{K}$.

At low fields, the weak ferromagnetic component displays a somewhat S-shaped trace which saturates quickly in fields near $H = 100\,\text{Oe}$.
The temperature dependence of the specific heat $C_p$ of CoSe$_2$O$_5$ shown in Figure 5.4 (a) exhibits a $\lambda$-type anomaly around 8.5 K corresponding to the transition to long-range magnetic order observed in the susceptibility and in the neutron diffraction data. Measurements on non-magnetic ZnSe$_2$O$_5$ give an estimate of the lattice contribution using a three term expansion with the best fit yielding a Debye temperature, $\Theta_D$, of 222 K. An estimate of the change in entropy associated with the magnetic transition can be obtained by integrating $C_{p,mag}/T$ defined between the specific heat data of CoSe$_2$O$_5$ and ZnSe$_2$O$_5$ [Figure 5.4 (b)]. The change in entropy due to the magnetic transition, thus determined, was 5.3 J mol$^{-1}$ K$^{-1}$ which is smaller than the value of 11.5 J mol$^{-1}$ K$^{-1}$ predicted by the Boltzmann equation ($\Delta S = R \ln(2S + 1)$, $S = 3/2$).

The relatively large temperature range (nearly 15 K) over which the 8.5 K ordering takes place is consistent with the large range of temperature over which the deviation from Curie-Weiss behavior commences in the magnetic susceptibility. This is also a characteristic of the reduced dimensionality of the system. In contrast, in three-dimensional antiferromagnets such as the rutile difluorides of Fe, Co, and Ni, the $\lambda$ anomaly has a width of only a few Kelvin.[129]

The specific heat was also measured with a field of 10000 Oe applied along $b$-axis. As seen in Figure 5.4 (a) there is very little change in the character of the transition as might be expected for a small reorientation of the spin
Figure 5.4. (a) Temperature dependence of the specific heat of CoSe$_2$O$_5$ measured on a 9.5 mg single crystal under zero field, and with a $H = 10$ kOe field applied along the $b$-axis of the crystal. A nonmagnetic analogue, ZnSe$_2$O$_5$, was also measured in order to obtain the lattice contribution to the specific heat. Note the large width of the ordering peak and the release of entropy well above the transition temperature of 8.5 K. (b) Entropy released due to the magnetic ordering, obtained by integration of the magnetic heat capacity.
axis. It should also be noted that the entropy is slightly increased to a value of 6.3 J mol$^{-1}$ K$^{-1}$, closer to the predicted value of 11.5 J mol$^{-1}$ K$^{-1}$.

A proper fit to the specific heat below the transition temperature could not be obtained using only the $T^3$ term as expected for a typical insulating antiferromagnet. Instead, the best fit to the data was found when an exponential term was included, using $C_{\mu,\text{mag}} \propto T^3 \exp(-\Delta/k_B T)$.[130] This result reflects the presence of low-energy magnetic excitations in the magnon dispersion with a gap, $\Delta$, determined here to be 6.5 K in zero field and 5.8 K under 10 kOe. The size of the gap in this system is on the order of the energies associated with the spin-orbit splitting of the lowest-lying electronic states of octahedral Co$^{2+}$ as determined by ab-initio calculations,[131] although other microscopic origins for the gap are also possible.

The nuclear and magnetic structure of CoSe$_2$O$_5$ were refined using the Rietveld method as implemented in the FULLPROF software suite.[132] The peak shape was described using the Thompson-Cox-Hastings pseudo-Voigt function, and the background was fit by interpolation between regions showing no Bragg reflections. The crystal structures were analyzed based on the model proposed by Harrison et al.[125], although it should be noted that we use the standard setting of space group number 60 (Pbcn) instead of the alternate Pnab description used in the original work. A summary of key refinement results is shown in
Table 5.1 and in Table 5.2. For the magnetic structure, group theoretical analysis was performed using representational analysis as implemented in the program SARA \cite{133} to determine all of the possible spin configurations which were compatible with the crystal symmetry.

The thermal evolution of the neutron-diffraction patterns collected from 300 K to 2 K are shown in Figure 5.5. Three magnetic reflections appear below 10 K at 8°, 17°, and 20° in the 1.5943 Å pattern. These three peaks could only be fit simultaneously by using the basis vectors of the irreducible representation $\Gamma_4$. The resulting magnetic structure associated with $\Gamma_4$ refined from the 2.4 Å data is illustrated in Figure 5.6. The propagation vector consistent with the neutron diffraction data is $k = 0$. Each chain of Co moments align antiferromagnetically down the length of the chain and with respect to the neighboring chains. The moments tilt in the $ac$ plane, forming, alternately, angles of $+14^\circ$ and $-14^\circ$ with respect to the $a$-axis. The moments have no component along $b$. The magnetic moment on every Co atoms refined to a value of 3.2 $\mu_B$ at 2 K using the $\lambda = 2.399$ Å neutron diffraction data. This value corresponds to the three unpaired spins per Co atom in the ordered antiferromagnetic structure with a small contribution from the orbital moment. Clarke and coworkers at the University of Oxford have described the moment on other octahedral Co$^{2+}$-containing compounds as being composed of a spin moment which has been re-
Figure 5.5. Low angle region of the powder neutron-diffraction patterns of \( \text{CoSe}_2\text{O}_5 \) (D2B, ILL). Note the development of magnetic Bragg peaks in the 5 K and 2 K patterns.
Figure 5.6. Magnetic structure of CoSe$_2$O$_5$ as determined from Rietveld refinements of the neutron diffraction pattern obtained using a $\lambda = 2.4$ Å at 2 K. (a) View down the $c$-axis of the $Pbcn$ structure. (b) View down the $b$-axis. The small light grey atoms are oxygen while the larger and darker grey atoms are selenium.
duced by covalency and some orbital contribution obtained by mixing of excited states of $E_g$ symmetry. While the refined moment is smaller than that observed for other Co$^{2+}$ containing complexes, this may be explained by considering that the irregular octahedral environment reduces the symmetry of the octahedral environment from the $T_{1g}$ ground state and thereby decreases the contribution from the orbital moment. [134, 135]

To summarize our understanding of CoSe$_2$O$_5$, we note that magnetic susceptibility measurements under small fields (less than 5000 Oe) reveal a ZFC-FC separation that suggests weak ferromagnetism overlaid on the antiferromagnetic crystal structure. The weak ferromagnetism is not expected from the completely compensated antiferromagnetic structure that we determine to be most consistent with the low temperature powder neutron diffraction data. However, we note that the estimated saturation magnetization of the weak antiferromagnetic component $\mathcal{O}(10^{-4} \mu_B)$ per Co atom, is significantly smaller than what can be resolved with powder neutron diffraction. ZFC-FC separation of the kind observed at low fields in Figure 5.2 has been attributed to intrinsic weak ferromagnetism in a number systems as a consequence of the Dzyaloshinskii-Moriya interaction (DM).[136–140] Spin canting leading to weak ferromagnetism in the absence of the DM interaction has also been observed previously in Ba$_2$Cu$_3$O$_4$Cl$_2$. [141] The weak ferromagnetism could also arise from local dis-
Table 5.1. Summary of the results of Rietveld structure refinement of variable
temperature neutron diffraction data. The employed neutron wavelength $\lambda$ is
indicated. *Fixed from the room-temperature Rietveld refinement of laboratory
XRD data. (See text)

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Table 5.2. Atomic positions from Rietveld refinements carried out on data ac-
quired at 300 K and at 2 K using 1.6 Å neutrons. All error bars on the atomic
positions were less than $4 \times 10^{-4}$.

<table>
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ordering of the spin structure as a result of a combination of competing interactions, and the reduced dimensionality. Such disorder would not necessarily generate extra Bragg reflections in the neutron diffraction data due to the lack of long range coherency.

5.2.1 Conclusions

We have examined the magnetic properties of CoSe$_2$O$_5$ using neutron diffraction, magnetization and magnetic susceptibility, and specific heat measurements. We show that below the magnetic ordering temperature, the magnetic chains arrange their moments antiferromagnetically down the length of the chain and with respect to neighboring chains. The magnetic order in small fields is found to additionally exhibit signatures of weak ferromagnetism. We also find evidence in the heat capacity of a gap in the magnon dispersion of 6.5 K, that is unrelated, based on the energy scale, to the weak ferromagnetism but may still be relevant for understanding the magnetic ground state of CoSe$_2$O$_5$. All evidence points to a rich $H-T$ phase diagram.
Chapter 6

An Experimental and Computational Investigation of the Polar Ferrimagnet VOSe$_2$O$_5$

Magnetoelectric multiferroics – materials in which an electric polarization coexists with a magnetically ordered phase – are attractive because of their potential application in next generation sensors and data storage. In general these materials are rare since magnetism and ferroelectricity generally require opposing valence-shell configurations – magnetism requires the presence of unpaired electrons in the valence shell whereas ferroelectrics materials generally have
Figure 6.1. (a) Crystal structure of VOSe$_2$O$_5$ viewed down the $c$-axis. Note that V(1) and V(2) sit on the 2$a$ and 2$b$ Wyckoff sites whereas V(3) sits on 4$c$. Such occupancies indicate that the chain composed of V(3) atoms will contain twice as many magnetic sites as the other two chains. (b) View down the $a$-axis so as to emphasize the Se$_2$O$_5$ units which join the chains, and which alternate between running along the $a$- and $b$-axis.

empty valence shells which can then hybridize with surrounding anions. [142] Additionally, the presence of an electric polarization within a crystal requires that the inversion center of the unit cell be broken – either through magnetic ordering or through a structural distortion. Given the contraindicated nature of multiferroics, a useful starting point to discovering new multiferroics would be to examine polar non-centrosymmetric materials that contain magnetic cations. Materials of this type include BiFeO$_3$ [143] and MnWO$_4$ [110, 144] as well as BaNiF$_4$. [122]
With respect to polar non-centrosymmetric \( V^{4+} \) oxides, \( \text{PbVO}_3 \) has been reported and recently grown as thin films. \([145, 146]\) This material contains a cation with a lone-pair, \( \text{Pb}^{2+} \), and was recently shown to be antiferromagnetic with an ordering temperature between 43 K and 50 K. \([146]\) In this chapter, we investigate \( \text{VOSe}_2\text{O}_5 \), a magnetically ordered material that crystallizes in the polar non-centrosymmetric space group \( P4_{cc} \). \([147, 148]\) The structure consists of three independent chains of corner-shared \( \text{VO}_6 \) octahedra that run parallel to the \( c \)-axis. These octahedral chains are connected via \( \text{Se}_2\text{O}_5 \) groups which run parallel to the \( a \)- and \( b \)-axes. The \( \text{Se}_2\text{O}_5 \) group can be visualized as two corner sharing \( \text{SeO}_3 \) trigonal pyramids that each contain stereochemically active lone-pairs at the apex of the pyramids which are directed in an anti-parallel manner.

Previous work reported complicated magnetic behavior below 10 K, and ferromagnetic ordering near 4 K. \([147]\) This was, however, based solely upon temperature-dependent susceptibility data. No additional investigation has been reported to further characterize the magnetic, dielectric, and functional properties of this potentially very interesting material. In this chapter we present magnetic susceptibility, heat capacity, dielectric, second-harmonic generation, and powder neutron diffraction measurements, as well as density functional theory (DFT) calculations to elucidate the functional properties of \( \text{VOSe}_2\text{O}_5 \). The dielectric properties show no evidence of an anomaly associated with the mag-
nectic ordering, however, a peak in the dielectric constant which is unaffected by the application of a magnetic field is observed near 240 K. Using neutron diffraction data in combination with DFT calculations, we propose a ferrimagnetic structure that is consistent with our theoretical and experimental results. Much of this chapter, including the DFT calculations and non-centrosymmetric property measurements was done in close collaboration with Sang-Hwan Kim and Professor P. Shiv Halasyamani at the University of Houston.

6.1 Experimental Details

VOSe$_2$O$_5$ was prepared via conventional solid state synthesis. Stoichiometric amounts of VO$_2$ and SeO$_2$ (99.8%, Alfa Aesar) were thoroughly ground, mixed, and pressed in a pellet. The pellet was placed in a pyrex tube that was flame-sealed under vacuum. The sealed ampoule was heated at 400°C for four days with several intermediate grindings giving a product consisting of pale green crystals. VO$_2$ was prepared from a stoichiometric mixture of V$_2$O$_5$ (99.9%, Alfa Aesar) and V$_2$O$_3$. The V$_2$O$_3$ was prepared by reduction of V$_2$O$_5$ under flowing 5%-H$_2$ in N$_2$ gas at 900°C. Phase purity was confirmed using powder X-ray diffraction collected on a PANalytical X’Pert PRO diffractometer using Cu-Kα radiation.
Powder X-ray diffraction (PXRD) data were collected using a PANalytical X'Pert PRO diffractometer using Cu-K$_\alpha$ radiation. The $2\theta$ range was $5^\circ$–$100^\circ$ with a step size of $0.0167^\circ$ and a fixed time of 0.2 s. The PXRD pattern is in good agreement with the calculated PXRD from the single crystal model.

Constant wavelength neutron diffraction data were obtained at temperatures of 10 K, 8 K, 6 K, and 4 K. The data were collected using the BT-1 diffractometer at the NIST Center for Neutron Research (NCNR), over the range of $1.3^\circ$–$166.3^\circ$ $2\theta$ with a step size of 0.05°. A Ge (311) monochromator at a 75° take-off angle and 15° in-pile collimator were used, resulting in $\lambda = 2.0787(2)$ Å. The instrument is described at the NCNR web-site (http://www.ncnr.nist.gov/). Rietveld refinements of the structure against the diffraction data were performed using FULLPROF software package. [132] A group theoretical analysis was performed using representational analysis as implemented in the program SARAh [133] was used to determine all of the possible spin configurations which were compatible with the crystal symmetry. Time-of-flight (TOF) neutron powder diffraction data on samples held in vanadium cans were also collected at the NPDF instrument at Los Alamos National Laboratory at several temperatures from room temperature to 6 K. Rietveld refinement of the TOF data were performed using GSAS suite of programs. [92, 93]

Powder SHG measurements were performed on a modified Kurtz-NLO34 sys-
tem using a pulsed Nd:YAG laser with a wavelength of 1064 nm. A detailed description of the equipment and methodology has been published. [149] The SHG efficiency has been shown to depend strongly upon particle size, thus polycrystalline samples were ground and sieved into distinct particle size ranges (20-45, 45-63, 63-75, 75-90, >90 µm). [150] In order to make relevant comparisons with known SHG materials, crystalline α-SiO$_2$ and LiNbO$_3$ were also ground and sieved into the same particle size ranges (see Noncentrosymmetric Functional Properties section). No index matching fluid was used in any of the experiments.

The polarization was measured on a Radiant Technologies RT66A Ferroelectric Test System with a TREK high voltage amplifier between room temperature and 165 °C in Delta 9023 environmental test chamber. VOSe$_2$O$_5$ was pressed into 12-mm diameter, approximately 1-mm-thick pellets using a cold isostatic press at 3500 psi at room temperature, after which the material was heated to 300 °C for three days under dynamic vacuum. Gold was deposited on both sides of the pellet. The unclamped pyroelectric coefficient, defined as the change in the polarization with respect to the change in temperature, was determined by measuring the polarization as a function of temperature. A detailed description of the methodology used has been published elsewhere. [149] Isothermal polarization loops were measured at room temperature under a static electric
field of 70 kV cm\(^{-1}\) at frequencies of 12.5 Hz, 16.7 Hz and 20 Hz. Temperature dependent polarization traces were measured statically from room temperature to 165 °C settling in 10 °C increments, with an electric field of 60 kV cm\(^{-1}\) at 100 Hz, 200 Hz, 333 Hz, 500 Hz and 1000 Hz.

A Quantum Design Magnetic Property Measurement System (MPMS) SQUID magnetometer was used to collect the AC and DC magnetic susceptibility on well-ground powder samples since a single crystal of sufficient size and quality could not be obtained. The powders were embedded in paraffin wax within a gelatin capsule to prevent particle motion with the application of large fields. Specific heat data were collected using the semi-adiabatic technique as implemented in a Quantum Design Physical Property Measurement System (PPMS). A well ground powder of the title compound was mixed with equal parts by mass of Ag powder and pressed into a pellet in order to improve thermal coupling. The contribution from Ag was measured separately and subtracted.

The dielectric properties were measured by attaching polished copper electrodes to opposite faces of a pellet of cold-pressed powder using a fixture built in-house. This fixture was inserted into a Quantum Design PPMS which was used for temperature and field control. An Agilent 4980A LCR meter was used to measure the capacitance which was then converted into the dielectric constant by correcting for the geometry of the sample.
6.2 Computational Details

First principles electronic structure calculations were performed using a plane-wave pseudopotential method [151] of density functional theory (DFT) [152, 153] as implemented in the Quantum ESPRESSO (4.0.1 version) package. [154] Ultrasoft pseudopotentials (USPP) [155] were utilized with a generalized gradient approximation (GGA) [156] for the exchange-correlation corrections. To properly take into consideration the electron correlation in the vanadium $3d$ states, the GGA plus on-site repulsion $U$ (GGA+$U$) method [157] was utilized with different values of effective ($U_{\text{eff}}$) on the vanadium atoms. In order to examine the effect of $U_{\text{eff}}$ on the relative energies of differently ordered magnetic states, the values of $U_{\text{eff}}$ of 1 eV, 2 eV and 3 eV were employed. A plane wave energy cutoff was set to 37 Ry. A $k$-point grid of $5 \times 5 \times 9$ was used for Brillouin zone integrations. Self-consistency was achieved within the total energy change smaller than $10^{-7}$ Ry.

6.3 Results and Discussion

Figure 6.1 shows the crystal structure of VOSe$_2$O$_5$ viewed down the $c$- and $a$-axes (space group: $P4_{2}2_{1}2$, $a = 11.2338(8)$ Å, $c = 7.8711(11)$ Å, $Z = 8$). Three
Figure 6.2. The individual V(1), V(2), and V(3) chains. The black solid line represents the equatorial planes is drawn to guide the eye. The $\Delta d_z$ indicates the displacements of $V^{4+}$ ions from the octahedral centers along the $c$-direction. Linear chains of corner-shared VO$_6$ octahedra run parallel to the $c$-direction. Each chain contains a crystallographically unique vanadium which we will refer to as V(1), V(2), and V(3) where they sit on the corners, the body-center, and the edges of the unit cell, respectively. The V(1)- and V(3)-chains are gauche-type with alternating rotations of $\pm 16.4(1)^\circ$ and $\pm 24.3(1)^\circ$ of the adjacent octahedra, respectively, down the length of the chains, whereas the V(2)-chain is eclipse-type, i.e., the octahedra do not rotate down the length of the chain. Figure 6.2 shows each unique chains so as to emphasize how the $V^{4+}$ cations are shifted along the $c$-direction by $\Delta d_z$ from the center of the octahedra. The values of $\Delta d_z$ are +0.322, +0.391, and −0.328 Å for the V(1), V(2), and V(3) cations, respectively. Such displacements mean there is one short
and one long axial bond in addition to four equivalent V–O equatorial bonds. These short and long bonds are in the range of 1.593(3) Å to 1.630(6) Å and 2.305(6) Å to 2.341(3) Å, respectively while the equatorial V–O bonds range between 1.973(2) Å to 2.002(2) Å. The Se–O bonds within the Se₂O₅ groups range between 1.647(3) Å to 1.823(2) Å. Bond valence sum calculations \cite{158, 159} give values near 3.9 for the Se⁴⁺ cations and between 4.1 and 4.2 for the V⁴⁺ cations.

### 6.3.1 DC and AC Magnetization and Heat Capacity Measurements

Figure 6.3 shows the temperature dependence of the DC magnetic susceptibility measured under field cooled (FC) and zero field cooled (ZFC) conditions at both 50 Oe and 500 Oe. A transition to a magnetically ordered phase is found near 8 K. Interestingly, there is a change in the slope at 4 K and 6 K in the susceptibility measured at 50 Oe that is not observed for data measured at 500 Oe. Additionally, the change near 4 K is not observed when measured in the presence of the larger magnetic fields.

As seen in Figure 6.4, the inverse magnetic susceptibility data from 25 K to 300 K fits well to a modified Curie-Weiss equation given as \( C/(T-\Theta_{CW}) + \chi_0 \)
Figure 6.3. The temperature-dependent magnetization of VOSe$_2$O$_5$ collected under magnetic fields of 50 and 500 Oe. Empty and filled circles present zero-field cooled (ZFC) and field cooled (FC) dc magnetic susceptibilities, respectively. Note that there is no deviation between the ZFC and FC data. The magnetic ordering temperature is found to be 8 K with subsequent changes to the slope of the curves around 7 K and 4 K.
Figure 6.4. Inverse magnetic susceptibility of VOSe$_2$O$_5$ collected under a 1000 Oe field and normalized by the parameters extracted from the fit of the susceptibility data (25–300 K) to the Curie-Weiss equation. Note that the negative deviations from linearity correspond to ferromagnetic correlations above the actual ordering temperature.
where $C$, $\Theta_{CW}$, and $\chi_0$ represent the Curie constant, the Weiss temperature, and a temperature independent term, respectively. From the Curie constant an effective moment, $\mu_{\text{eff}}$, of 1.69 $\mu_B$ was obtained which agrees well with the theoretical spin-only value of 1.73 $\mu_B$ for $V^{4+}$. A Weiss temperature, $\Theta_{CW}$, of -8.9 K was determined, that indicates the dominant interaction is an antiferromagnetic coupling between the moments. The temperature independent term was estimated to be $-3.2 \times 10^{-4}$ emu mol$^{-1}$ Oe$^{-1}$ and likely reflects the diamagnetic contribution from the straw, gel cap, and wax that held the sample during the measurement.

Figure 6.5 (a) shows isothermal magnetization traces at different temperatures above and below the ordering temperature of 8 K. Below 8 K the magnetization rapidly increases and exhibits the hysteretic behavior of a soft ferromagnet with a coercive field on the order of tens of Oe as emphasized in Figure 6.5 (b). However, the trace taken at 2 K saturates to a value of 4 $\mu_B$ per unit cell which corresponds to a value of 0.5 $\mu_B$ per formula unit (f.u.$^{-1}$) with the application of a few hundred Oe.

Unexpectedly, this saturated magnetic moment of 0.5 $\mu_B$ f.u.$^{-1}$ is one half the value for a fully saturated ferromagnetic alignment of $V^{4+}$ ($d^1$, $S=1/2$, $L=2$). In order to accurately obtain the Curie temperature, the magnetization curves were plotted in the style of Arrott [160] ($M^3$ vs. $H$) as shown in Figure 6.5 (c) where
Figure 6.5. (a) Isothermal magnetization curves of VOSe$_2$O$_5$ measured at different temperatures above and below the magnetic ordering transition. (b) Magnetization curves expanded around the origin to show the small coercive field. (c) Magnetization curves plotted in the style of Arrott to emphasize the true Curie temperature as indicated by the approximately straight line at 8 K.
the linear behavior of the 8 K data reflects that this is very near the long-range ordering temperature.

The real part of the AC magnetic susceptibility, collected in the absence of an external DC field, indicates the behavior of the low-field DC susceptibility curves with no frequency dependence observed for frequencies of 1 Hz, 10 Hz, 100 Hz or 1000 Hz [see Figure 6.6 (a)]. The imaginary part of the susceptibility, shown in Figure 6.6 (b), however, does exhibit anomalies which correlate to the changes in the slope of the low field susceptibility data. Three peaks are observed in the imaginary part of the AC susceptibility which could reflect the possibility of three different magnetic transitions. Additionally, the 5.5 K peak shows a frequency dependence that may indicate some short-range fluctuations which could be associated with relatively delocalized magnetic interaction pathways through the nearest neighbor (NN) inter-chain magnetic interactions in the \( ab \)-plane.

In addition to the magnetic measurements, the specific heat of VOSe\(_2\)O\(_5\) was also investigated. The specific heat of VOSe\(_2\)O\(_5\) was measured between 2.5 K and 300 K. Figure 6.7 shows that a single \( \lambda \)-type anomaly is observed in the specific heat near 7 K that indicates the rise of three dimensional long-range magnetic ordering near the magnetic transition temperature.
Figure 6.6. (a) Real and (b) imaginary part of the AC magnetic susceptibility collected at frequencies of 1, 10, 100, and 1000 Hz. Note that the peak at 5.5 K has strong frequency dependence and is suppressed in the presence of very high frequency fields in the imaginary component.
Figure 6.7. Specific heat of VOSe$_2$O$_3$ as a function of temperature measured upon cooling. Note the $\lambda$-anomaly that has a peak occurring at 7 K signaling the onset of long-range magnetic ordering.
The temperature dependence of the dielectric constant is shown in Figure 6.8 (a). At low temperatures, no evidence of an anomaly near the magnetic ordering temperature was observed. However, a broad peak corresponding to a 30% increase in the dielectric constant was found to occur around 240 K. Similarly, the high temperature region of the heat capacity also reflects some additional features which occur near this temperature [see Figure 6.8 (b)]. Interestingly, no change in the feature was found with the application of a magnetic field and no changes to the crystal structure were observed in the neutron diffraction data. An electronic effect is also negligible from our preliminary electrical resistivity measurement. At present the origin of the dielectric anomaly is unclear.

### 6.3.2 Magnetic Structure Determination

Figure 6.9 shows the neutron powder diffraction (NPD) patterns of VOSe$_2$O$_5$ collected at 6 K, 7 K, 8 K, 10 K, 15 K, 150 K, and 300 K in time-of-flight mode at Los Alamos National Laboratory. There is no indication of a structural phase transition at any of the measured temperatures. Nor is there any evidence of new magnetic reflections below the ordering temperature of 8 K. This means that the spin structure which develops below the ordering temperature has the same unit cell as the nuclear structure.
Figure 6.8. (a) Temperature dependence of the dielectric constant for VOSe$_2$O$_5$ for different frequencies normalized to the room temperature value. Note the anomaly observed near 240 K. (b) High temperature region of the specific heat. The broad hump observed from 220 K to 260 K corresponds well to the anomaly in the dielectric data.
Figure 6.9. Refinement of the TOF neutron diffraction data at different temperatures. No extra peaks are observed below the magnetic ordering temperature indicating that the magnetic structure must be fully contained within the room temperature description of the structure.
It is important to recall at this point that the unit cell contains three unique V atoms and that the multiplicity is not equivalent. V(1) and V(2) occupy the $2a$ and $2b$ Wyckoff positions whereas V(3) occupies a $4c$ position. Thus several plausible spin alignments can be envisioned which would satisfy the obtained neutron diffraction data. For example, each chain could have its spins ferromagnetically aligned, while the chains are antiferromagnetically arranged between the V(1)- and V(2)-chains and between the V(2)- and V(3)-chains. However, the additional intensities attributable to magnetic contributions in the data taken below 8 K were too weak to obtain reliable refinements of the magnetic structure.

Therefore DFT calculations were performed on a variety of ordered magnetic states in order to ascertain the lowest energy magnetic ground state. We considered a total of eight different magnetic states, illustrated in Figure 6.10, and calculated their total energies using the GGA+$U$ formalism for several values of $U_{\text{eff}}$ (1 eV, 2 eV, and 3 eV). We note that the GGA+$U$ method would not be appropriate if VOSe$_2$O$_5$ exhibited any orbital degeneracy, however, the highly distorted VO$_6$ octahedra in the structure ensure that this is not the case. Spin polarized state calculations with GGA alone result in metallic states for VOSe$_2$O$_5$. One ferromagnetic (FM) and seven antiferromagnetic orderings (AF1-AF7) of the spin of V$^{4+}$ cations are shown in Figure 6.10 where the unit cell of their magnetic structures is equivalent to that of the crystal structure. Their rela-
Figure 6.10. Schematic representations of the eight different spin states employed in order to evaluate magnetic exchange parameters, $J$. For clarity, only the V sites are present with blue-filled circle denoting up-spin and red-filled circles down-spin.

The lowest energy spin configuration corresponds to the AF1 state in which the spins in each intra-chain are ferromagnetically aligned whereas the spins between the V(1)–V(2) and V(2)–V(3) inter-chains are antiferromagnetically arranged. The order of the magnetic states in energy is retained with respect to the $U_{eff}$ values except for the AF4 state that is almost degenerate with the FM
Table 6.1. Relative energies $\Delta E$ (meV per unit cell) calculated for different magnetic states of VOSe$_2$O$_5$ for different values of $U_{\text{eff}}$. All energies are shown relative to the least-favored FM configuration. *The calculated ground state.

<table>
<thead>
<tr>
<th>Magnetic state</th>
<th>$U_{\text{eff}} = 1$ eV</th>
<th>$U_{\text{eff}} = 2$ eV</th>
<th>$U_{\text{eff}} = 3$ eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>AF2 ($4\mu_B$)</td>
<td>4.4</td>
<td>4.1</td>
<td>3.8</td>
</tr>
<tr>
<td>AF6 ($6\mu_B$)</td>
<td>1.2</td>
<td>1.5</td>
<td>1.7</td>
</tr>
<tr>
<td>AF4 ($0\mu_B$)</td>
<td>$-0.6$</td>
<td>0</td>
<td>0.7</td>
</tr>
<tr>
<td>FM ($8\mu_B$)</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>AF7 ($4\mu_B$)</td>
<td>$-14$</td>
<td>$-11$</td>
<td>$-6.6$</td>
</tr>
<tr>
<td>AF5 ($6\mu_B$)</td>
<td>$-16$</td>
<td>$-12$</td>
<td>$-8.8$</td>
</tr>
<tr>
<td>AF3 ($0\mu_B$)</td>
<td>$-28$</td>
<td>$-20$</td>
<td>$-15$</td>
</tr>
<tr>
<td>*AF1 ($4\mu_B$)</td>
<td>$-33$</td>
<td>$-24$</td>
<td>$-18$</td>
</tr>
</tbody>
</table>

It is important to also note that the AF1 state has $4\mu_B$ per unit cell which is consistent with the isothermal magnetization data.

As shown in Figure 6.11, the total and projected densities of states (DOS) for the AF1 state with $U_{\text{eff}} = 2$ eV show a energy band gap at the Fermi level that is also in agreement with the insulating nature of the title compound. The V-3$d$ orbitals exhibit oppositely spin polarized 3$d$ states, i.e. the V(1) and V(3) are positively spin polarized whereas the V(2) is negatively spin polarized. Based on the DFT calculations, the proposed AF1 magnetic structure was refined against the low temperature neutron data (see Figure 6.12). The possibility for the spins to point along the $a$-, $b$-, or $c$-axis were all considered with the lowest $R_{\text{mag}}$ (15%) corresponding to the spins forming a tilted antiferromagnetic structure.
Figure 6.11. (a) Total and projected DOS of V-3d, Se-4sp, and O-2sp of the AF1 state calculated for $U_{\text{eff}} = 2$ eV. (b) Projected DOS plots for the 3d orbitals of V(1), V(2) and V(3).
Figure 6.12. Low angle region of the constant wavelength neutron data collected at BT-1. Note that while the ferromagnetic fit shown on the left corresponds to the best model refined, however, in reality the contribution from magnetic reflections is so small that obtaining a good fit is very difficult. Particularly notice that the magnetic intensity on the peak at 15° and 35° is completely missed by the ferromagnetic model whereas the model corresponding to AF1 does capture these features.
similar to AF1 with the spins laying in the $ab$-plane. The best refinements were obtained from ferromagnetic (FM) or antiferromagnetic (AF4) alignments, as well as a commensurate spin density wave (SDW) that were identified based upon symmetry analysis. With the FM and AF4 alignments, the spins are parallel to the $c$-axis. For the three magnetic states, FM, AF4, and SDW, the reliability factors from the refinements were nearly equal, $R_{\text{mag}} \sim 5.6\%$. However, these three magnetic states contradict the magnetic susceptibility and magnetization data. The actual magnetic information from the neutron diffraction data is very limited attributable to the small effective ordered moment on vanadium. Therefore the calculated AF1 state appears to be the most reasonable state, consistent with the magnetic and specific heat data.

To further evaluate the magnetic interactions, we extracted magnetic exchange parameters ($J$) by assuming pair-wise magnetic interactions with the calculated energy of the eight magnetic states. Three different $V^{4+}$ intra-chain interactions and four different $V^{4+}$ inter-chain interactions were considered. To evaluate the magnetic exchange parameters, we performed mapping analysis based on our DFT calculations.

Since we have the relative energies of the eight ordered magnetic states (see Table 6.1), we can express a magnetic exchange parameter with differently combined magnetic states. Our calculations revealed that the $J$ values were,
unexpectedly, inconsistent, *i.e.*, different expressions for the same parameter gave different values. This inconsistency may be indicative that the magnetic exchange interactions are not well localized despite the insulating nature of VOSe$_2$O$_5$. As seen in Figure 6.13, there are four different *inter-chain* magnetic interaction pathways. Two may be considered nearest neighbor (NN) interactions, *i.e.*, between the V(1) and V(3) cations and between the V(2) and V(3) cations, $J_{13}$ and $J_{23}$ respectively, and two are next nearest neighbor (NNN) interactions, *i.e.*, between the V(1) and V(2) cations and two symmetry equivalent V(3) cations, $J_{12}$ and $J_{33}$ respectively. With the NN interactions, two pathways are possible – a ‘short’ pathway, *e.g.*, V(1)–O–Se–O–V(3), and a ‘long’ pathway, *e.g.*, V(1)–O–Se–O–Se–O–V(3).

For the NNN interactions, only a ‘long’ pathway is possible, *e.g.*, V(1)–O–Se–O–Se–O–V(2), that is nearly equivalent to the long NN pathway (see Figure 6.13). Clearly the strongest magnetic interactions should be expected to occur through the short NN pathway. We suggest, however, that the long NN and NNN magnetic interactions are not negligible, and manifest themselves through the observed frequency dependence in the AC magnetic susceptibility. There is support for our interpretation if we examine the magnetic behavior of other $V^{4+}$ oxides, specifically Li$_2$VOTO$_4$ ($T = Si^{4+}$ or Ge$^{4+}$) [161] and VOMoO$_4$ [162]. These oxides were shown to be two-dimensional spin-half antiferromagnets,
where the NN and NNN interactions are mediated by non-magnetic polyhedra, 
i.e., $TO_4$ or $MoO_4$ tetrahedra. In fact, it is theoretically predicted that the relative strength of the NNN/NN ratio could give rise to spin fluctuations in the spin-half frustrated square lattice. [163, 164] Thus, the observed frequency dependence in the AC magnetic susceptibility may reflect this feature of the spin frustration.

6.3.3 Noncentrosymmetric Functional Properties

Powder SHG measurements [149, 150] using 1064 nm radiation indicated VOSe$_2$O$_5$ has a SHG efficiency comparable to $\alpha$-SiO$_2$. The relatively weak SHG efficiency may be understood by closely examining the structure. There are two acentric polyhedra that can contribute to the SHG – the SeO$_3$ pyramids and the VO$_6$ octahedra. Although the Se$^{4+}$ cation is in a highly asymmetric coordination environment, the net polarization attributable to the SeO$_3$ groups is minimal. The polarization associated with the SeO$_3$ pyramids are directed in an anti-parallel manner with respect to neighboring units, cancelling any contribution to the SHG efficiency. With the V$^{4+}$ cations, there is a net polarization along the $c$-axis, as a result of unequal cancelation of the V$^{4+}$ moments. Thus the SHG contribution from the VO$_6$ octahedra is reduced. All of these factors result in a
Figure 6.13. Four *inter-chain* magnetic interactions given as $J_{13}$, $J_{23}$, $J_{12}$, and $J_{33}$ are shown. $J_{13}$ and $J_{23}$ represent nearest neighbor (NN) interactions, whereas $J_{12}$ and $J_{33}$ represent next nearest neighbor (NNN) interactions. Note that with the NN interactions, ‘short’ and ‘long’ pathways are possible, e.g., V(1)–O–Se–O–V(3) and V(1)–O–Se–O–Se–O–V(2) respectively. Two possible magnetic exchange pathways of the magnetic interactions are enclosed in the black solid and dashed ellipses respectively.
weak SHG efficiency and negligible size dependence.

The polarization of VOSe$_2$O$_5$ was measured from room temperature to $210^\circ$C. It was found that the polarization could not reversed with the application of an external electric field and that even though VOSe$_2$O$_5$ is polar, the material is not ferroelectric. While the polarization loops were found to be open and hysteretic, the shape is attributable to dielectric loss and not polarization reversal. [165] The experimental results are consistent with our frozen phonon DFT calculation results with the AF1 state at $U_{eff} = 2$ eV. It is reasonable to assume that the electric polarization in VOSe$_2$O$_5$ is mainly attributable to the off-centered $V^{4+}$ cations, since the polarization associated with the SeO$_3$ groups are pointed in anti-parallel directions. It is also known that an umbrella-type inversion of SeO$_3$ is energetically unfavorable and therefore not likely to occur. [166] Subsequently, the only manner in which electrical polarization reversal may occur is via the displacement of $V^{4+}$ cation parallel to the $c$-axis in each VO$_6$ chain. Our calculations in the AF1 with $U_{eff} = 2$ eV indicate that for the inversion process, $\sim 6.0 \times 10^{-1}$ eV per VO$_6$ is required on average. This energy is higher than those calculated in well-known ferroelectrics such as BaTiO$_3$ ($\sim 1.8 \times 10^{-1}$ eV) and PbTiO$_3$ ($\sim 2.0 \times 10^{-1}$ eV). [167] The macroscopic polarization of VOSe$_2$O$_5$ does, however, change as a function of temperature and can therefore be considered pyroelectric. The pyroelectric constant of VOSe$_2$O$_5$
given as the first derivative of spontaneous polarization with respect to temperature is $\sim -20 \mu \text{C m}^{-2} \text{K}^{-1}$ at 75°C.

### 6.3.4 Conclusion

Through our investigation of the magnetic, dielectric, and functional properties of VOSe$_2$O$_5$, we demonstrated that the material undergoes a ferrimagnetic transition beginning at $\sim 8$ K. This transition is consistent with our neutron diffraction data combined with our DFT calculations. The frequency dependence of the AC magnetic susceptibility observed near 5.5 K may be associated with NN and NNN inter-chain magnetic interactions. This is also compatible with the inconsistent magnetic exchange parameters extracted from our DFT calculations, attributable to the magnetic interaction pathways being not well localized. Finally, although VOSe$_2$O$_5$ is polar, the material is not ferroelectric, *i.e.*, the macroscopic polarization is not reversible, attributable to the energetically unfavorable VO$_6$ polarization inversion. The concurrent observation of SHG intensity in a magnetically ordered material suggests possible exotic nonlinear magneto-optical behavior in this material. The dielectric anomaly near 240 K also bears further investigation.
Chapter 7

Summary and Future Directions

The purpose of this dissertation has been to present a comprehensive study of complex oxides with competing magnetic interactions. We have presented work demonstrating the effect of chemical substitution in well-studied spinels as well as several detailed investigations on compounds containing magnetic chains. By using a combination of structural characterization in the form of X-ray and neutron diffraction along with physical property measurements and computational tools, we have explored the relationship between crystal structure and macroscopic properties.

Through our studies on the spinels we have endeavored to increase our understanding of the highly studied materials: CoAl$_2$O$_4$, ZnCr$_2$O$_4$, and CoCr$_2$O$_4$. 
We have shown the evolution of a complex magnetic phase diagram with the substitution of magnetic cations onto the $A$-site in $\text{Zn}_{1-x}\text{Co}_x\text{Cr}_2\text{O}_4$. While distinguishing between the effect of site disorder and lattice expansion on the frustration in $\text{CoAl}_{2-x}\text{Ga}_x\text{O}_4$ proved to be a significant challenge, we were able to demonstrate that there is clearly a weak dependence of the frustration on the separation between the magnetic ions and that site mixing changes the shape of the inverse susceptibility curves.

In the magnetic chains compounds we encountered rich $T$–$H$ phase diagrams for all of the systems investigated. $\text{CoSeO}_4$ demonstrates magnetodielectric coupling in conjunction with weak ferromagnetism and field-induced magnetic transitions. $\text{CoSe}_2\text{O}_5$ also demonstrates weak ferromagnetism as well as evidence for low-lying magnetic excitations seen in the specific heat data. $\text{VOSe}_2\text{O}_5$ was found to be a polar ferrimagnet with a complex temperature-dependent ordering of three separate magnetic chains.

Work still remains to be done regarding the high field state of the Co-based compounds. More specifically, $\text{CoSe}_2\text{O}_5$ as well as $\text{CoSeO}_4$ warrant further investigation of the high-field magnetic structures as well as the field-dependent dielectric constants. The dielectric anomaly found in $\text{VOSe}_2\text{O}_5$ also warrants a more detailed study to determine the source of the anomaly.
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