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The Effects of Synthesis, Sr-doping, and $Co_3O_4$ on the Perovskite $LaCoO_3$

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**THE EFFECTS OF SYNTHESIS, Sr-DOPING, AND $Co_3O_4$ ON THE PEROVSKITE $LaCoO_3$**

A dissertation submitted in partial satisfaction
of the requirements for the degree of

DOCTOR OF PHILOSOPHY

in

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by

**Alice Durand**

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# Contents

# List of Figures

ix

# List of Tables

# The Effects of Synthesis, Sr-doping, and $Co_3O_4$ on the Perovskite $LaCoO_3$

A.M. Durand

## Abstract

The effects of synthesis method, Sr-doping, and $Co_3O_4$ on the rare-earth perovskite $LaCoO_3$ were examined and quantified. Structural and magnetic measurements were taken using neutron diffraction, X-ray diffraction, transmission electron microscopy, X-ray fluorescence and SQUID magnetometry. An optimal method for synthesizing $LaCoO_3$ nanoparticles is described, and the solid-state synthesis method for nominal $LaCoO_3$ is found to result in the formation of an extra $Co_3O_4$ phase. Bulk $LaCoO_3$ materials containing systematically varying amounts of the $Co_3O_4$ phase (denoted as $La_wCoO_3$, where w is the molar ratio La:Co) were also synthesized. As the amount of $Co_3O_4$ was increased, the ferromagnetic transition at $T_c$ = 87 K was found to be sharper, the ferromagnetic moment larger, and the ferromagnetism more robust at high fields ($H$ > 100 Oe). This is a similar effect to that from increased tensile strain in $LaCoO_3$ thin films and from increased surface area in nanoparticles. We propose that tensile strain also exists in the LCO-$Co_3O_4$ interfaces, which enhances the ferromagnetism. The lattice parameters for $La_wCoO_3$ exhibited thermal expansion behavior that was best fit with a power law, indicating a second-order structural transition at $T_o$ = 37 K. A mathematical model for the magnetization, $M/H$, of $La_wCoO_3$ was developed which successfully described the behavior at both low and high external fields. The model consists of three contributions to the magnetization: one ferromagnetic contribution and two paramagnetic contributions with different antiferromagnetic exchange interactions. The ferromagnetic contribution is found to have a critical exponent of $\beta$ = 0.65, consistent with magnetic ordering of the

surface.

# Acknowledgements

To my family - Michele, Jacques, Bean, and Lucy

FIG. 1.1: Magnetic susceptibility of single crystal LaCoO$_3$ as a function of temperature. Two broad maxima can be seen near 90 K and 600 K. The low temperature fit shows the contribution of possible magnetic impurities. Image taken from Refs. [1, 2].

# 1 Introduction

LaCoO$_3$ (LCO), a rhombohedrally distorted perovskite, possesses several intriguing electrical and magnetic features that have been intently studied for decades [1, 3–6]. These include a magnetic susceptibility curve with two broad maxima near 90 and 600 K (see Fig. 1.1) which cannot easily be explained with a simple ferromagnetic/antiferromagnetic ordering model [1, 6], and an anomalous thermal expansion of the lattice parameters below 100 K [7, 8]. The magnetization maximum near 90 K and subsequent decrease in high fields is characteristic of an antiferromagnet, but at this temperature in low fields there is instead a phase transition to weak ferromagnetic order. However, no indication of long-range order at $T = 90$ K can be seen in neutron scattering measurements [9]. Sr-doped LCO, La$_{1-x}$Sr$_x$CoO$_3$, is no exception to interesting behavior, exhibiting a metal-to-insulator transition for x = 0.18 [10], roughly the same concentration for which ferromagnetic order appears at $T_c = 250$ K. However, the shape of the ferromagnetic magnetization curve below $T_c$ and the location of $T_c$ vary between

1

studies [11–13], particularly for low x. Podlesnyak *et al* found that Sr dopings as low as x $\approx$ 0.002 have a significant effect on the $LaCoO_3$ magnetic behavior, inducing low temperature magnetic polarons with enormous net moments of $13\mu_B$ (the usual net moment per $Co^{3+}$ ion in this system is around $3\mu_B$) [14].

In $LaCoO_3$, the magnetic susceptibility maximum arising near 90 K has been attributed to a thermal spin state transition associated with the octahedrally-coordinated Co ion [4, 15, 16]. However, the theory of thermally excited spins which are primarily localized on the Co ions has recently been disproved by the results of Medling *et al* [17], who showed that the oxygen atoms also contribute significantly to the magnetic moment in $La_{1-x}Sr_xCoO_3$. Other recent results [18, 19] indicate that it is incorrect to think of these moments as localized, and that a band theory picture is far more accurate. However, as many previous papers discuss results in the context of Co-related moments and localized spin states, an understanding of the theory behind their interpretation is useful. Conceptually, it is also helpful to consider localized behavior before making the leap to band theory.

## 1.1 $LaCoO_3$ Structure and Co Spin-States

To understand the motivation behind the local spin-state interpretation, the $LaCoO_3$ structure must first be considered. A perovskite is a material with the structure $AMO_3$, where A is a rare-earth or alkali-earth metal (usually with 2+ or 3+ valence) and M is a transition metal (usually 3+ or 4+ valence). An image of the $AMO_3$ structure is shown in Fig. 1.2. In the case of $LaCoO_3$, the structure is rhombohedrally distorted rather than cubic. Rhombohedral distortion can be thought of as taking the opposite corners along the cube diagonal and pulling outwards. As a result of this distortion, the $CoO_6$ octahedra twist, in such a way that the imaginary line connecting two nearest-neighbor Co atoms is no longer straight. The Co-O-Co bond angle bends from 180° down to around 165°. In the

FIG. 1.2: Generic perovskite structure with $AMO_3$. The large orange atom in the center represents the A atom, the smaller blue atoms on the corners are the M atoms, and the tiny red atoms arranged octahedrally around the M atoms are the O atoms.

case of $Sr^{2+}$ substitution for the $La^{3+}$ A ions, the lower valency of the $Sr^{2+}$ ion is thought to allow for the relaxation of the Co-O-Co bonds back towards $180°$. At sufficient Sr-doping (usually $La_{0.5}Sr_{0.5}CoO_3$), the material reverts to a cubic state.

The properties of the $MO_6$ octahedra are of particular interest in the rare-earth perovskites due to the energy splittings and bond length distortions which can occur. Co is a $3d$ transition metal with either 5 $d$ electrons (4+), 6 $d$ electrons (3+), or 7 $d$ electrons (2+). Nominally, the octahedra contain $Co^{3+}$ ions, although this may change depending on Sr-doping or defects. As shown in Fig. 1.3, there are five $d$ orbitals, two of which point along one or two axes ($d_{3z^2-r^2}$ and $d_{x^2-y^2}$), and three of which are off-axis ($d_{xz}$, $d_{yz}$, and $d_{xy}$). As a result of these different orientations, when the Co ion is octahedrally coordinated with the six $O^{2-}$ ions, the on-axis orbitals are higher in energy than the off-axis orbitals. The oxygen $2p$ valence orbitals are on-axis, and the electrostatic repulsion between the electrons in the Co $3d$ and the O $2p$ orbitals causes the $d_{3z^2-r^2}$ and $d_{x^2-y^2}$ orbitals to increase in energy. In the notation of crystal field theory, the lower energy $d_{xz}$, $d_{yz}$, and $d_{xy}$

FIG. 1.3: The five $d$ orbitals. When the $3d$ Co ion is octahedrally coordinated, the degeneracy of the $d$ orbitals is split, and the $e_g$ orbitals are higher in energy than the $t_{2g}$ orbitals (as explained in the text). Image taken from Ref. [20].

orbitals are called $t_{2g}$, while the higher energy $d_{3z^2-r^2}$ and $d_{x^2-y^2}$ orbitals are called $e_g$. The energy splitting is referred to as the crystal-field or ligand-field splitting, often denoted as $10\ Dq$, and was measured to be $0.9\pm0.3$ eV for $LaCoO_3$ by Abbate *et al* [21] - small compared to other $AMO_3$ perovskites with $3d$ transition metals [22].

The crystal-field splitting between the $t_{2g}$ and $e_g$ orbitals results in different spin states which depend on the strength of the electron exchange interaction relative to the energy splitting. For example, if the energy splitting is fairly large relative to the exchange energy, the 6 electrons in $Co^{3+}$ will fill the $t_{2g}$ states according to the low-spin (LS) configuration in Figs. 1.4 and 1.5 (the simplified energy configuration diagram is shown in Fig. 1.4, and a more detailed energy level diagram for the different states is shown in Fig. 1.5 [23, 24]). According to

FIG. 1.4: Energy configuration diagram of the $Co^{3+}$ $3d^6$ $t_{2g}$ and $e_g$ orbitals. The low-spin (LS), intermediate-spin (IS), and high-spin (HS) electron configurations depend on the relative strengths of the crystal-field splitting and the electron exchange interaction (Hund's coupling energy, which is not represented in the diagram). In the case of $LaCoO_3$, the difference between these two energies is very small, corresponding to approximately 80 K. Image taken from Ref. [23].

the Pauli principle, all of the electrons will be matched with an opposite spin pair and the total spin will be $S = 0$. However, if the exchange energy is larger than the 10 $Dq$ energy splitting, the electrons are able to fill the $t_{2g}$ and $e_g$ states with single electrons before doubly occupying the $t_{2g}$ state, corresponding to the high-spin (HS), $S = 2$ configuration in Figs. 1.4 and 1.5. For $LaCoO_3$, the difference between the crystal-field splitting and the electron exchange interaction is quite small, estimated to be $\Delta E \approx 0.007$ eV [23]. $\Delta E$ corresponds to the thermal energy given by approximately 85 K, using the equation $\Delta E = k_B T$ (where Boltzmann's constant is $k_B = 8.617 \times 10^{-5}$ eV $\cdot$ K$^{-1}$). A possible source of confusion is that other papers [16, 21] state the energy difference between the LS and HS states as 0.07 - 0.08 eV; note that this is not the same as $\Delta E$.

In order to lower the total energy of the system, the $MO_6$ octahedron can deform along the $z$ axis (corresponding to the two lobes in the $d_{3z^2-r^2}$ orbital). In what is called the Jahn-Teller effect, the elongated M-O bond lowers the energy

FIG. 1.5: Energy level diagram showing the LS, IS, and HS states in terms of the crystal field splitting ($\Delta_{CEF} = 10\ Dq$) and the exchange energy $J_{ex}$. A) shows the LS configuration, where $\Delta_{CEF} > J_{ex}$ and all of the electrons are paired in the $t_{2g}$ orbitals. B) shows the IS configuration, where the Jahn-Teller distortion ($\Delta_{J.T.}$) lowers the energy of one of the $e_g$ states down below the Fermi energy ($E_F$). C) shows the HS configuration, where $\Delta_{CEF} < J_{ex}$. Image taken from Ref. [24].

6

FIG. 1.6: Jahn-Teller effect for $Mn^{3+}$, which has a $3d^4$ electronic configuration. The leftmost portion shows the degenerate $3d$ orbitals, while the middle portion shows the crystal field splitting with the corresponding undistorted $MnO_6$ octahedron. The rightmost portion shows the effect of the Jahn-Teller distortion, lowering the $d_{3z^2-r^2}$ energy relative to that of $d_{x^2-y^2}$ by deforming the octahedron along the $z$ axis. Image taken from Ref. [25].

of the $d_{3z^2-r^2}$ orbital because the oxygen $2p$ electrons are now slightly farther away, reducing the electrostatic repulsion. The total energy for having a single electron in the $e_g$ state is therefore lowered by the distortion. Figure 1.6 shows a schematic for the strong Jahn-Teller distortion in $Mn^{3+}$, which has a $3d^4$ electronic configuration. Although the $t_{2g}$ state is also split, the degree of this distortion is smaller [26]. The $S = 1$ intermediate state (IS) in Figs. 1.4 and 1.5 is a theoretical Jahn-Teller distorted state proposed by Korotin *et al* for $LaCoO_3$. The HS state does not have a Jahn-Teller distortion, as the energy of two electrons in the split $e_g$ state averages out to the same value as for two in the unsplit state.

## 1.2   Spin-State Interpretations of Magnetism

With regards to the magnetic interactions taking place, several theories [4, 15, 27] relied on the Co ions having either a 3+ or a 4+ valence, each with either a LS or HS state. In his 1958 paper, Goodenough detailed extensively the relative energies of each of these states, and laid the groundwork for further interpretations in the context of spin-states [4]. Goodenough discussed the possibility of both antiferromagnetic and magnetic interactions based on the local configurations of different Co cations. He concluded that 1) "Any interaction between identical cations via an intervening, symmetrically bonded oxygen ion must, by symmetry, be antiferromagnetic" and 2) "If octahedral-site magnetic cations are located on opposite sides of a common anion, they interact ferromagnetically if one cation has completely empty $e_g$ orbitals and the other has half-filled $e_g$ orbitals" [4]. By "identical cations," Goodenough was referring to any matching pair of the four possible Co spin states: low spin $Co^{III}$ ($t_{2g}^6 e_g^0$) and $Co^{IV}$ ($t_{2g}^5 e_g^0$) and high spin $Co^{3+}$ ($t_{2g}^4 e_g^2$) and $Co^{4+}$ ($t_{2g}^3 e_g^2$). In this picture, a $Co^{IV}$-O-$Co^{IV}$ interaction is antiferromagnetic, while a $Co^{3+}$-O-$Co^{IV}$ is ferromagnetic. Goodenough noted that $Co^{III}$-O-$Co^{IV}$ and $Co^{III}$-O-$Co^{3+}$ interactions would be non-magnetic, as $Co^{III}$ has all paired electrons and is thus diamagnetic [4].

The presence of $Co^{IV}$ and $Co^{4+}$ was thought to be inherent to the $LaCoO_3$ lattice at the time of Goodenough; however, X-ray absorption spectra (XAS) studies [21, 28] indicated no change in Co valence from the nominal 3+. This does not preclude a very small concentration of $Co^{IV}$ cations due to defects in the lattice; indeed, Androulakis *et al* interpreted their results in the context of La-deficiencies in the lattice, which induced a small portion ($\approx 1\%$) of the Co atoms to appear as $Co^{IV}$ [29]. Earlier models proposed for the broad susceptibility maximum at 90 K focused primarily on the LS and HS states. Given that the energy splitting between the two states, was quite close to the temperature at which the susceptibility exhibited a maximum, one interpretation suggested that

LaCoO$_3$ began in the low spin, non-magnetic state at low temperatures ($T < 25$ K) and gained a net magnetization as the LS states were thermally excited to HS states with increasing $T$ [7, 27]. Another interpretation, based on experiments which detected no change in the Co spin state for $T < 500$ K, asserts that the LS-HS transition only takes place at high temperatures [21].

In 1996, Korotin *et al* calculated a possible intermediate spin state for the Co$^{3+}$ cation in LaCoO$_3$ [16]. The authors used an LDA $+ U$ method (a local-density-appoximation (LDA) functional with a potential $U$) in order to take into account the fact that LaCoO$_3$ demonstrates both localized and delocalized behavior. In LDA, the system is approximated as a homogeneous electron gas, and adding a $U$ term accounts for a constant potential between electrons. Korotin *et al* found that an IS state with spin configuration $t_{2g}^5 e_g^1$ was closer in energy to the low temperature LS state than was the HS state, and surmised that the transition near 90 K was due to the Co going from LS to IS rather than LS to HS. They specify that, rather than being localized in an $e_g$ orbital, the higher energy electron instead goes into a broad *band* of hybridized $e_g$ and O $2p$ orbitals (though it is unclear *how* broad the proposed $e_g$ band is). As a result of the single electron in the $e_g$ orbital/band, the authors noted that a strong Jahn-Teller distortion should take place in order to lower the energy of one $e_g$ orbital. Although the concept of a LS-IS and IS-HS transition proved popular with subsequent interpretations of the LCO properties, the presence of a Jahn-Teller distortion in LaCoO$_3$ remained ambiguous. Pair-distribution function (PDF) studies done via neutron scattering and Extended X-ray Absorption Fine Structure (EXAFS) which examined the range of bond lengths in LaCoO$_3$ (in particular to look at possible variations in the Co-O length, which would be expected for a Jahn-Teller distortion) showed no significant variation in the bond length, and most now agree that there is no Jahn-Teller distortion in LCO [28, 30].

Nonetheless, many variations on the three-state spin-state transition model have been proposed, and a continuing dispute still exists as to whether the elec-

FIG. 1.7: Plot showing the total energy of different magnetic states for a fixed spin moment calculation with LDA. $\delta x$ refers to the degree of rhombohedral distortion in LCO: a larger $\delta x$ indicates a larger distortion. Image taken from Ref. [18].

trons in the LS configuration excite into the IS configuration, the HS configuration, or a mixture of IS-HS [8, 31–35]. The interpretation of magnetism in the context of local spin state excitations has also been called into question, as the $e_g$ and $t_{2g}$ states have been found to extend over a rather large energy range (10 eV, where part of the band is 5 to 6 eV below the Fermi energy) [17, 18].

## 1.3    Band Theory Interpretation of Magnetism

Recent results from Lee and Harmon [18] reexamined the magnetic states of LaCoO$_3$ in the context of band theory. The authors performed band structure and density of state (DOS) calculations on LCO using LDA and GGA (generalized gradient approximation) methods. The GGA approximation is thought to be an improvement on the LDA method, as it takes into account the non-homogeneity of the electron charge density rather than assuming a uniform charge distribution.

FIG. 1.8: Density of states (DOS) of each of the Co $3d$ orbitals, shown for different amounts of rhombohedral distortion ($\delta x$). For large $\delta x$, a gap opens up, and for $\delta x = 0.072$, only the $d_{z^2}$ orbital is gapless. Image taken from Ref. [18].

Two important results from this study are as follows:

1) Both LDA and GGA approximations find that the lowest energy state is non-magnetic; however, the next-lowest energy state is magnetic, and only $\approx 3.2$ meV/Co ion away from the non-magnetic state. In fact, reducing the rhombohedral distortion ($\delta x$, the details of which are explained in the Neutron Scattering section of this work) of LCO induces the *magnetic* state to become the lowest energy state. Figure 1.7 shows the total energy for different values of the magnetic moment using a fixed spin moment (FSM) calculation with LDA. FSM entails choosing a fixed value for the moment per Co ion, then calculating the corresponding energy. The value of $\delta x = 0.052$ is very close to that found for our $La_wCoO_3$ bulk samples.

2) The DOS calculations for different rhombohedral distortions indicate that an energy gap opens up for large distortions ($\delta x = 0.092$). This corresponds

to a non-magnetic, insulating ground state, provided the magnetism is a result of itinerant electrons in a broad $e_g$ band. Notably, for a $\delta x = 0.072$, only the $d_{z^2}$ orbital (corresponding to $d_{3z^2-r^2}$) is gapless, indicating that electrons in this orbital may still be itinerant at relatively large distortions.

To summarize, Lee and Harmon show that the rhombohedral distortion/$\delta x$ parameter is an excellent marker for the presence of magnetism in $LaCoO_3$. It is also noted that even small changes in the temperature or lattice parameters could shift the lowest energy state from non-magnetic to magnetic, or vice versa. This is consistent with ours and other's findings that tensile strain on the lattice can induce a magnetic state.

## 1.4 Effect of Lattice Strain on LaCoO₃

In a theoretical study using the dynamical mean-field theory in the local density approximation, Krapek *et al* [36] found that a magnetic state is favored by lattice expansion, and that the latter acts as positive feedback for the appearance of local moments. These findings were echoed by an article theorizing that strained LCO heterostructures can induce thermal spin state transitions [37]. By depositing LCO thin films onto different substrates, Fuchs *et al* [38] were able to successfully tune the magnetic behavior of LCO. An increase in tensile epitaxial strain between the substrate and film was seen to correlate with an increase in the effective magnetic moment, $\mu_B/Co$. In a previous study, we suggested ferromagnetic effects induced by strain from Co-impurities in bulk powders of LCO [9]. In the latter two studies, the Co-O-Co bond angle has been scrutinized as a structural indicator of ferromagnetic interactions - however, other groups have also singled out the Co-O bond length [36, 39] and the unit cell volume [40] as linked to magnetic order. Lee and Harmon [18] interpreted their results in the context of $\delta x$; as such, we also incorporate $\delta x$ (here renamed $\delta y$ so as to avoid confusion with $x$ frequently

used to denote Sr concentration in $La_{1-x}Sr_xCoO_3$) when characterizing variations in the lattice structure of our samples.

Recently, a field-effect transistor geometry device was engineered that turns the ferromagnetism in an LCO thin film on or off as a function of epitaxial strain in a piezoelectrically stimulated $SrTiO_3$ substrate [41]. The resulting $LaCoO_3/SrTiO_3$ heterostructure contains alternating ferromagnetic and nonmagnetic regions, allowing for magnetoresistance which can be adjusted with applied voltage. Whereas many studies have been done on epitaxial strain in LCO thin films and on surface strain in the LCO bulk, to our knowledge no systematic studies have been done examining the effects of interface strain in LCO bulk. Notably, does the strain have to be along a well ordered, two-dimensional plane in order to affect magnetism, or could strain from grain boundaries or a different material ensconced within the bulk LCO similarly cause ferromagnetic order?

Given preliminary results indicating that a $Co_3O_4$ phase in the bulk may affect the ferromagnetism [9], we systematically varied the amount of $Co_3O_4$ in LCO bulk samples to observe whether ferromagnetism could be brought on by interface strain. The powder samples we investigate are as follows: $La_{0.7}CoO_3$, $La_{0.8}CoO_3$, $La_{0.9}CoO_3$, $LaCoO_3$, and $La_{1.1}CoO_3$, hereafter referred to as w = 0.7, 0.8, 0.9, 1.0, and 1.1, respectively (w is defined as the La:Co molar ratio, as in $La_wCoO_3$). In order to examine the combined effects of Sr-doping and $Co_3O_4$, we also synthesized samples of $La_{0.8}Sr_{0.1}CoO_3$ and $La_{0.65}Sr_{0.25}CoO_3$, along with stoichiometric $La_{0.9}Sr_{0.1}CoO_3$, $La_{0.75}Sr_{0.25}CoO_3$ and $La_{0.7}Sr_{0.3}CoO_3$ for comparison. X-ray diffraction, neutron diffraction, and magnetometry were used to determine the magnetic and structural properties of bulk powder samples synthesized with excess or deficient $Co_3O_4$. In brief, we found that the presence of $Co_3O_4$ has a significant effect on the magnetism in $LaCoO_3$, in that samples with more $Co_3O_4$ exhibited a sharper ferromagnetic phase transition. These samples had a large net ferromagnetic moment which persisted to higher external fields than that of stoichiometric $LaCoO_3$. Enhanced ferromagnetism at 87 K was also seen in the

neutron diffraction data for the $La_{0.8}Sr_{0.1}CoO_3$ sample, which showed a larger ferromagnetic Bragg peak than stoichiometric $La_{0.9}Sr_{0.1}CoO_3$.

## 1.5   Effects of Particle Size on LaCoO₃

Reducing the particle size of $LaCoO_3$ also produces unusual results. The weak ferromagnetic transition at 87 K in bulk $LaCoO_3$ becomes significantly sharper and stronger in nanoparticle $LaCoO_3$. However, this effect varies between studies, and depends on particle size and preparation method [33, 40, 42–44]. The increase in ferromagnetism has been attributed to ferromagnetic ordering of the surface, [42, 43] surface-induced lattice strain, [33] and unit-cell expansion [40, 44]. Yan *et al.* [42] found that the magnetic susceptibility of their samples increased as the surface-to-volume ratio increased and attributed this to localized spins on the surface of the material. Although they ruled out double exchange between $Co^{3+}$ and $Co^{IV}$ ions as the mechanism for the surface ferromagnetism, their study was inconclusive as to the *origin* of the ferromagnetic interaction. Harada *et al.* [43] found similar results; the magnetization increased with decreasing particle size and they suggested the source to be chemisorption of oxygen atoms at the surface. Again, the mechanism leading to ferromagnetism was not made explicit. Fita *et al.* [33] examined the lattice parameters of LCO nanoparticles and found that they increase with decreasing particle size but did not identify surfaces as the source of ferromagnetism. Instead, they pointed to the surface-induced lattice expansion which persists throughout the material as the cause.

In the above studies, LCO crystals and powders were synthesized using several different methods: floating-zone single-crystal synthesis, solid-state reaction, crushing the single-crystal into a powder, and a citric acid solution method. It is interesting to note that in all but one case, the sample magnetization increased monotonically with surface area and the transition temperature remained fairly constant at $T_c \approx 85$ K. Wei *et al.* [40] found that their nanoparticles showed a

decrease in magnetization and $T_c$ with particle size, despite also noting a similar increase in lattice parameters with the smaller sizes. It is possible that the citric acid sol-gel method employed in this case differed slightly from the one used by Harada *et al.* [43], although it is more likely that the difference in magnetic behavior can be attributed to a combination of surface effects and small particle sizes.

Over the course of this work, several studies have been carried out on the effects of synthesis and nanoparticle size on the magnetization of $LaCoO_3$, $La_wCoO_3$, and $La_{1-x}Sr_xCoO_3$. Here, we will focus on the results from three nanoparticle samples of $LaCoO_3$. Six different methods were used to synthesize LCO nanoparticles (all of which are discussed in the Synthesis section), and magnetization data from two different methods will be compared. The nanoparticle size can be controlled by the firing temperature, and the magnetization data from two different sizes (20 nm and $\geq$ 100 nm) will be examined. Different synthesis methods and firing temperatures were found to result in various amounts of the $Co_3O_4$ phase in the nanoparticle samples; this phase has a known effect on the magnetization of bulk LCO, and we will show that it has a similar effect on the nanoparticle material. Magnetization data from all three samples can be fit to the same model as that used for the bulk material, further evidence that our magnetization model is widely applicable to this system.

## 1.6   Mathematical Model for the Magnetization of LaCoO$_3$

The magnetization curve $M/H$ vs $T$ for $LaCoO_3$ can be roughly divided into three sections, as shown in Fig. 1.9. The sections correspond to the contributions from the ferromagnetic increase (blue), the decrease in the net magnetization (green), and the paramagnetic increase at low temperatures (red). Increases and decreases in the magnetization are relative to the value of $M/H$ above 90 K. Note

that the sections are rough delineations, and the descriptions only indicate which behavior is dominant/significant in each section. Although a region is marked corresponding to the decrease in the net magnetization in the 20 Oe data of Fig. 1.9, the contribution of this decrease is of low magnitude compared to that of the ferromagnetic increase; the net result is a slightly shallower ferromagnetic increase.

Although several studies have attempted to model the $M/H$ magnetization or susceptibility of $LaCoO_3$, these efforts were limited to either portions of the magnetization (e.g. the low temperature paramagnetic increase) [35] or measurements in one external field [6]. Androulakis *et al* proposed a general conceptual model for the different contributing effects to the susceptibility, but did not give a mathematical description of each contribution [29]. To the author's knowledge, no studies have been done attempting to mathematically model the small ferromagnetic portion of the susceptibility which can be seen only in low fields ($H \leq 100$ Oe).

Given the demonstrated lack of a significant Jahn-Teller distortion, it is difficult to put forth a plausible LS-IS spin state excitation model for the increase in the magnetic moment as $T$ increases from 25 K to 90 K. Furthermore, one of the most obvious failures of the models based on local spin states of the Co ion is the prediction of a non-magnetic LS state at low $T$, where all electrons are paired in the $t_{2g}$ state. Our data demonstrate that the low temperature state of bulk $LaCoO_3$ is actually magnetic rather than diamagnetic, and can be fit as such. Furthermore, no satisfactory explanation of observed cooperative behaviors, in particular the ferromagnetic phase transition, can come from the local spin state models.

By incorporating surface magnetism and two different types of antiferromagnetism in the interpretation of $M/H$ vs $T$, we will demonstrate that magnetic phase transitions play a central role in the observed behaviors of bulk and nanoparticle $LaCoO_3$. In low fields, we observe a transition to long-range ferromagnetism

FIG. 1.9: $M/H$ vs $T$ magnetization curves for $LaCoO_3$ in external fields of 5 kOe (top) and 20 Oe (bottom). The blue (1), green (2), and red (3) boxes roughly split the curves up into sections that can each be modeled. It is important to keep in mind that the boxes simply denote the *dominant* contribution(s) in each section, not that there is only one type of behavor in the section. The blue section corresponds to the contribution to $M/H$ from the ferromagnetic increase, the green section denotes the decrease in net magnetization (mostly seen at high fields), and the red section is the paramagnetic increase at low temperatures. The relative amounts of each contribution change with field, so although the decrease in net magnetization is indicated in the 20 Oe data, it is of low magnitude compared to the ferromagnetic increase.

near 87 K which is attributable to ordering near the surfaces and interfaces of LCO. The critical behavior is not that expected for a bulk material, but corresponds quite well to studies done on thin films and surface magnetism [45–47]. This transition temperature is intrinsic to LCO and is approximately the same as

17

that observed in thin films [38], and the strength of the ferromagnetic long-range order is dependent on the presence of surfaces and interfaces.

As the temperature decreases to roughly 35 K in the bulk material, the ferromagnetism long-range order *decreases*; this can be connected to the system gradually switching from one type of antiferromagnetic order to another with a smaller exchange interaction. The amount of distortion of the LCO lattice from a cubic structure as well as the anomalous thermal expansion near 35 K govern this antiferromagnetic behavior. The lattice parameter behavior near this temperature is more akin to a second-order structural phase transition than normal thermal expansion for a solid. As the antiferromagnetic order and ferromagnetic phase appear inextricably linked, we propose that the ferromagnetic phase is due to canting of the antiferomagnetic spins.

A crucial role in the model is played by the lattice distortion that accompanies the rotation of the $CoO_6$ octahedra. Successfully modeling the unusual magnetic behavior in $LaCoO_3$ should lend itself to understanding other oxides where the rotation of similar octahedra seems to be ubiquitous and largely underappreciated. For example, Mn [48], V [49, 50], Ru [51], Ti [52, 53], Zr [53], and Hf [53] all show octahedral twisting. It is becoming more recognized [54, 55] that twisting of these octahedra represents a degree of freedom crucial to the magnetic and electric properties.

In this work, we introduce a model of the system that accounts for the various magnetic behaviors in $LaCoO_3$. The model incorporates the dependence of the magnetization on the lattice distortion and the influence of surfaces and interfaces in producing a net ferromagnetic moment. The model also describes the magnetic behaviors of $LaCoO_3$ nanoparticles, which seemingly contrast that of the bulk particles in experimental data, but are actually consistent with the same model. In fact, studies of the nanoparticle systems were essential in motivating the development of the model. Also essential to the development of the comprehensive model were studies on nonstochiometric bulk samples; the $Co_3O_4$ phase

deliberately introduced into the $LaCoO_3$ system elucidated the role of impurity phases and interfaces.

A large part of the difficulty in modeling this material is that up to three (possibly more) different magnetic states are present in the material at any one temperature. Keeping this in mind, the following essential features of the model will be demonstrated:

**1)** For $100 < T < 300$ K, $LaCoO_3$ is well described as a paramagnet dominated by antiferromagnetic interactions. The average moment varies little with the details of the system, such as particle size and amount of $Co_3O_4$ phase.

**2)** For $35 < T < 90$ K, bulk LCO can still be described as a paramagnet dominated by antiferromagnetic interactions, but with an average moment and interaction that are distinctly smaller than that of the high $T$ paramagnetic region and which vary with the particular particle properties. We refer to the antiferromagnetic interactions here as AFM1.

**3)** For $T < 35K$, bulk LCO predominantly consists of a paramagnetic phase with antiferromagnetic interactions; however, the interaction strength is lower than that of the high $T$ paramagnetic phase as a consequence of lattice contraction. We refer to the antiferromagnetic interactions here as AFM2.

**4)** In bulk $LaCoO_3$ and $La_wCoO_3$, a crossover between the high and low $T$ paramagnetic phases (AFM1 and AFM2) occurs for $35 < T < 90$ K. This crossover is brought on by the anomalous thermal lattice expansion that occurs near 35 K, and contributes to the "dip" in $M/H$ seen in this temperature range (see Fig. 1.9, top plot).

**5)** A weak ferromagnetic moment is associated with surfaces and interfaces in the bulk and nanoparticle systems. In sufficiently large particles, and small external fields, ferromagnetic order is seen near 87 K. The power law exponent for the order parameter is characteristic of *surface* critical behavior ($\beta \approx 0.65$) rather than *bulk* critical behavior ($\beta \approx 0.33$). The ferromagnetic order is attributed to canting

of the AFM1 antiferromagnetic moments due to surface/interface-induced tensile strain, and is strengthened by the presence of short-range AFM1 antiferromagnetic order far from the surface [45, 46].

**6)** In very small ($\leq 20nm$) nanoparticles, the system neither orders ferromagnetically or exhibits AFM1, instead showing behavior characteristic of AFM2 for the entire temperature range. We believe this may be due to these nanoparticles being *entirely* surface and thus incapable of ordering with AFM1, which is strengthenened by an inner core of less-strained $LaCoO_3$ in larger nanoparticles and bulk. As such, no ferromagnetic canting can be seen in these nanoparticles as well.

It is our hope that with this strong mathematical model for $LaCoO_3$, further studies can elucidate the details of the magnetic behavior. The excellent fits for the magnetization data are a good indicator that LCO can be explained with the six features described above. As the model is able to account for the behavior of both LCO bulk and nanoparticles, at both high and low fields, we are confident that the insights gained more fully describe this system than any previous model.

The subsequent sections are organized in the following order: Synthesis and Characterization, Neutron Scattering results, Magnetometry results, Magnetization model, Nanoparticle results, and Conclusion. Each section also contains a discussion of the results, and the Conclusion will summarize the important points of these discussions.

# 2 Bulk Synthesis

## 2.1 Solid-State Synthesis Method

Bulk particles of LCO and LSCO were synthesized at the University of California, Santa Cruz, using a standard solid state reaction method similar to that used in earlier studies [56]. Desired amounts of $La_2O_3$, $SrCO_3$, and $Co_3O_4$ were ground thoroughly and fired five times at temperatures ranging from 850°C to 1050°C for 8 hours each. An extra firing for 24 hours at 1100°C was undertaken for some of the samples, but comparison of the X-ray diffraction spectra before and after this firing indicated that there were no significant structural or compositional differences.

The alumina boats used for firing were stained a deep blue color after the firing process was finished, indicating the formation of CoO. CoO can form when $Co_3O_4$ is fired to 900°C and above [57, 58]. Both the CoO and $Co_3O_4$ compounds are seen in the bulk materials because firing temperatures were likely not high enough to completely transform all of the $Co_3O_4$ into CoO. The nominally stoichiometric bulk materials showed trace amounts of both CoO and $Co_3O_4$, whereas the Co-excess materials showed significantly more of these compounds (as expected).

When determining the chemical reaction taking place for the parent compound LCO, we must note that the formation of $LaCoO_3$ from $La_2O_3$ and $Co_3O_4$ requires additional oxygen from the atmosphere (Eq. 2.1).

$$La_2O_3 + \frac{2}{3}Co_3O_4 + \frac{1}{6}O_2 \rightarrow 2LaCoO_3 \tag{2.1}$$

However, the presence of Co- and La-compound impurity phases in previous works on $LaCoO_3$ [9, 59] indicates that Eq. 2.1 may not fully describe the reaction taking place. Varying the stoichiometry of the starting materials allowed us to examine the amount of $Co_3O_4$ phase in the resulting samples.

One must first consider two possible final materials that could result from

FIG. 2.1: Neutron diffraction scans from the WAND instrument ($\lambda = 1.5$ Å) for bulk $\text{La}_w\text{CoO}_3$ at 10 K (w = 0.9) and 30 K (all other samples). The $\text{Co}_3\text{O}_4$ (1 1 1), (4 0 0), and (4 4 0) Bragg peaks are labeled with a box, and the CoO ($\frac{1}{2}\frac{1}{2}\frac{1}{2}$) antiferromagnetic Bragg peak is labeled with a filled circle. The Miller indices for the (2 0 2) and (0 0 6) $\text{LaCoO}_3$ peaks are given as well. Scans are offset for clarity.

reducing the ratio of La to Co in the starting materials (equivalent to increasing the amount of $\text{Co}_3\text{O}_4$). We denote the resulting material as $\text{La}_w\text{CoO}_3$, where w is the starting ratio of La:Co. The first possibility is a $\text{LaCoO}_3$ perovskite structure, but with La atoms missing from some of the sites, as in Eq. 2.2 (La:Co = 0.9 is used as an example). These vacant sites are distributed randomly throughout the lattice, a scenario discussed by Androulakis *et al.* [29]. The second possibility is the incomplete reaction of $\text{Co}_3\text{O}_4$ with $\text{La}_2\text{O}_3$: the $\text{LaCoO}_3$ phase forms, but there is still $\text{Co}_3\text{O}_4$ phase left in the sample, as in Eq. 2.3. Each scenario requires a different amount of oxygen from the atmosphere.

$$0.9\text{La}_2\text{O}_3 + \frac{2}{3}\text{Co}_3\text{O}_4 + \frac{19}{60}\text{O}_2 \rightarrow 2\text{La}_{0.9}\text{CoO}_3 \qquad (2.2)$$

$$0.9\text{La}_2\text{O}_3 + \frac{2}{3}\text{Co}_3\text{O}_4 + \frac{3}{20}\text{O}_2 \rightarrow 1.8\text{LaCoO}_3 + \frac{1}{15}\text{Co}_3\text{O}_4 \qquad (2.3)$$

There are small amounts of crystalline $\text{Co}_3\text{O}_4$ in our $\text{La}_{0.9}\text{CoO}_3$ sample, so we conclude that the scenario in Eq. 2.3 best describes our material. We believe this is a result of firing in air rather than in an oxygen-rich atmosphere, as Eq. 2.3 requires less $\text{O}_2$ from the atmosphere. Figure 2.1 shows the location of the neutron scattering Bragg peaks for the extra Co compounds in $\text{La}_\text{w}\text{CoO}_3$. Many researchers [12, 13, 29, 60–64] synthesize LCO and LSCO powder samples in an air atmosphere and describe their materials as not having impurity phases according to X-ray diffraction results. Because these X-ray diffraction results are frequently not shown, it is diffcult to assess whether they are actually single phase LCO or contain small peaks indicating low amounts of $\text{Co}_3\text{O}_4$ or other such phases. As an example, Ben Amor *et al.* [34] found that varying the La:Co ratio resulted in single phase LSCO. However, when closely examining their X-ray diffraction data, small Bragg peaks corresponding to $\text{Co}_3\text{O}_4$ are visible. It is surmisable that these peaks were passed over due to their small intensities. As will be shown here, however, even small peaks of $\text{Co}_3\text{O}_4$ can indicate an amount which will have significant effects on the magnetic properties of the sample.

The parent $\text{LaCoO}_3$ sample we synthesized contained a small (4.5%) amount of $\text{Co}_3\text{O}_4$ phase, which is consistent with synthesis in an air atmosphere. One possible reaction is

$$\text{La}_2\text{O}_3 + \frac{2}{3}\text{Co}_3\text{O}_4 + \frac{3}{20}\text{O}_2 \rightarrow 1.8\text{LaCoO}_3 + \frac{1}{15}\text{Co}_3\text{O}_4 + \frac{1}{10}\text{La}_2\text{O}_3, \qquad (2.4)$$

which indicates that a sample with 3.4% $\text{Co}_3\text{O}_4$ by weight must also contain $\text{La}_2\text{O}_3$. However, no $\text{La}_2\text{O}_3$ Bragg peaks are observed by X-ray or neutron diffraction. It is possible that very small ($\leq 10$ nm) nanoparticles of $\text{La}_2\text{O}_3$ form, which would

result in broad, low intensity peaks difficult to see in the diffraction spectra. The $La_2O_3$ phase could also be amorphous, but we do not understand yet why the phase would not crystallize. The presence of an amorphous La phase can be inferred more directly from micro X-ray fluorescence measurements of certain types of LCO nanoparticles, which will be discussed in a subsequent section. According to Imanaka *et al*, cubic $La_2O_3$ partially decomposes to LaO(OH) after being stored in a desiccator for a few days due to absorption of water from the atmosphere [65]. It is possible that both phases are present in the material, though in amounts not easily seen by X-ray or neutron diffraction. Micro X-ray fluorescence does not "see" light elements such as O and H as easily, which may be why we were not able to identify LaO(OH) in our material.

We also examined the effects of an excess $La_2O_3$ phase in the starting materials by synthesizing a sample with La:Co = 1.1. One possible reaction is

$$1.1La_2O_3 + \frac{2}{3}Co_3O_4 + \frac{1}{60}O_2 \rightarrow 2La_{1.1}CoO_3, \qquad (2.5)$$

where the extra La atoms may be located in interstitial sites. Contrary to expectations, a small amount of $Co_3O_4$ and the CoO magnetic Bragg peak were *still* seen in the La:Co = 1.1 sample. As in the previous samples, no $La_2O_3$ phase was observed.

In the $La_ySr_xCoO_3$ compounds, $Co_3O_4$ and CoO phases were also identified. The proposed chemical reaction for $La_{0.7}Sr_{0.3}CoO_3$ is

$$0.7La_2O_3 + \frac{2}{3}Co_3O_4 + \frac{3}{5}SrCO_3 + \frac{4}{25}O_2 \rightarrow 2La_{0.7}Sr_{0.3}CoO_3 + \frac{3}{5}CO_2. \qquad (2.6)$$

It is clear that some amount of atmospheric oxygen is still required for this reaction to take place, as $SrCO_3$ forms SrO and $CO_2$ after being heated above 1016°C [58]. As with the LCO compounds, CoO and $Co_3O_4$ will also form in order to reduce the amount of oxygen required from the atmosphere. We cannot speculate on the

FIG. 2.2: Neutron diffraction scans from the WAND instrument for bulk $La_ySr_xCoO_3$ at 5 K ($La_{0.9}Sr_{0.1}CoO_3$) and 10 K (all remaining samples). The $Co_3O_4$ Bragg peaks are labeled with a box, the CoO magnetic Bragg peak is labeled with a filled oval, and the LSCO magnetic Bragg peak is labeled with an x. Miller indices are given for these peaks, as well as for the (2 0 2) and (0 0 6) peaks of LSCO. Scans are offset for clarity.

relative amounts of the leftover La and Sr compounds here, as we do not see any crystalline La or Sr compounds in the neutron or the X-ray diffraction spectra. It suffices to say that the more atmospheric oxygen is required in the reaction, the more Co compounds will likely be in the resulting material.

As can be seen in Fig. 2.2, the $Co_3O_4$ peaks have higher intensities in the non-stoichiometric $La_{0.65}Sr_{0.25}CoO_3$ and $La_{0.8}Sr_{0.1}CoO_3$ samples than in the other, stoichiometric samples. The proposed chemical reaction for $La_{0.8}Sr_{0.1}CoO_3$ is

$$0.8La_2O_3 + \frac{2}{3}Co_3O_4 + \frac{1}{5}SrCO_3 + \frac{9}{25}O_2 \rightarrow 2La_{0.8}Sr_{0.1}CoO_3 + \frac{1}{5}CO_2. \qquad (2.7)$$

As expected, more atmospheric oxygen is required than by the reaction in Eq. 2.6.

TABLE 2.1: Amount of $O_2$ required to satisfy the chemical reactions shown in Eqs. 2.6 and 2.7 for the LSCO samples. The column titled "Peak ratio" is the ratio of the CoO $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ magnetic peak intensity to that of the tallest LSCO structural peaks (a composite of the (2 0 2) and (0 0 6) peaks in the neutron scattering).

| Sample | moles $O_2$ | Peak ratio |
|---|---|---|
| $La_{0.7}Sr_{0.3}CoO_3$ | 0.16 | 0.044 |
| $La_{0.75}Sr_{0.25}CoO_3$ | 0.29 | 0.045 |
| $La_{0.9}Sr_{0.1}CoO_3$ | 0.22 | 0.018 |
| $La_{0.8}Sr_{0.1}CoO_3$ | 0.36 | 0.138 |
| $La_{0.65}Sr_{0.25}CoO_3$ | 0.44 | 0.109 |

Despite the same synthesis process, the non-stoichiometric LSCO samples appear to have more CoO than the stoichiometric samples, as indicated by the higher intensity of the magnetic peak. When following the same chemical reactions for the other two LSCO samples, it can be seen in Table 2.1 that the samples with larger CoO peaks are those that require more atmospheric oxygen. This could be due to CoO forming more easily than $Co_3O_4$ in environments with less oxygen, as CoO requires less oxygen per formula unit.

We conclude that cobalt oxide phases in samples synthesized via the solid-state method are a consequence of firing in an air atmosphere and are difficult to precisely control for by varying the stoichiometry of the starting materials. Further experiments are needed to determine the effects of firing in an oxygen-rich atmosphere.

## 2.2   FullProf Extra Phase Characterization

FullProf fits of neutron data for all bulk samples included the LCO/LSCO phase and the $Co_3O_4$ phase. Other phases seen in the neutron and X-ray diffraction were either unidentifiable or difficult to include in the refinements. Diffraction spectra

TABLE 2.2: Calculated weight fraction of $Co_3O_4$ in bulk samples at room temperature, as found by FullProf using the neutron scattering data. Eqs. 2.8 and 2.9 are the equations used to find the weight percentage.

| Sample | $\%Co_3O_4$ |
|---|---|
| $La_{0.7}CoO_3$ | 17.1(0.5) |
| $La_{0.8}CoO_3$ | 11.7(0.4) |
| $La_{0.9}CoO_3$ | 9.3(0.3) |
| $LaCoO_3$ | 4.5(0.3) |
| $La_{1.1}CoO_3$ | $\leq 2.4$ |
| $La_{0.7}Sr_{0.3}CoO_3$ | 2.45 |
| $La_{0.75}Sr_{0.25}CoO_3$ | 0.60 |
| $La_{0.65}Sr_{0.25}CoO_3$ | 3.07 |
| $La_{0.8}Sr_{0.1}CoO_3$ | 4.38 |
| $La_{0.9}Sr_{0.1}CoO_3$ | 7.02 |

of bulk samples are shown in Figs. 2.1 and 2.2 with the extra phases identified. The relative weight fractions of LCO/LSCO and $Co_3O_4$ were determined from the neutron diffraction data using FullProf. These were found to match within a few percent to room temperature X-ray diffraction data refined using the PDXL software package [66]. Table 2.2 shows the percentage by weight of the $Co_3O_4$ phase for each sample at room temperature.

The weight fraction ($w_\phi$) calculation performed by FullProf is given by

$$w_\phi = \frac{m_\phi}{\sum_\phi m_\phi}, \tag{2.8}$$

where the mass of a phase $\phi$ in the sample, $m_\phi$, is given by

$$m_\phi = S_\phi M_\phi Z_\phi V_\phi. \tag{2.9}$$

FIG. 2.3: Weight fraction of $Co_3O_4$ as a function of temperature. The percent $Co_3O_4$ was determined by FullProf using neutron scattering data from WAND.

For each phase $\phi$, $S_\phi$ is the scale factor, $M_\phi$ is the molecular weight, $Z_\phi$ is the number of formula units per unit cell, and $V_\phi$ is the volume of the unit cell. In the version of FullProf used here, $Z_\phi$ and $M_\phi$ were incorporated into a value labeled $ATZ_\phi$. FullProf calculates $ATZ_\phi$ as

$$ATZ_\phi = \frac{Z_\phi M_\phi f^2}{t_\phi}. \tag{2.10}$$

The value $t_\phi$ is the Brindley microabsorption correction, which accounts for the different absorptions of each phase and can be set to 1 for neutron scattering [67]. $f$ is the site occupancy, which can be set to a value other than 1 if the phase is non-stoichiometric. As $Co_3O_4$ is a stoichiometric phase, we set $f = 1$ [68].

Given that the only refinable parameter in the weight fraction calculation is $S_\phi$, this is where most of the error will lie. Figure 2.3 shows the dependence of the weight fraction on temperature for the LCO samples. Although the weight fraction remains fairly constant down through 70 K, below this value it begins to

28

increase - particularly for the w = 0.7, 0.8, and 0.9 samples. This is likely a result of the antiferromagnetic ordering at 40 K in $Co_3O_4$ increasing the magnitude of the nuclear (1 1 1) and (1 1 3) peaks, as well as the appearance of the magnetic (2 0 0) peak [69]. The scale factor thus increases accordingly.

Refinements on data with a significant CoO antiferromagnetic $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ peak were attempted with the inclusion of the CoO cubic $Fm\bar{3}m$ phase; however, for most samples the CoO structural peaks were usually too small to refine. Other neutron diffraction studies [70, 71] confirm that the magnetic peak for CoO is significantly larger than the structural peaks. The Miller indices used in the literature for the antiferromagnetic peak at $2\theta = 17.3°$ were either absent or inconsistent. Therefore, the label used here is $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$, as the peak is located at half the $2\theta$ of the (1 1 1) $Fm\bar{3}m$ CoO structural peak.

It is interesting to note that for the $La_{0.8}Sr_{0.1}CoO_3$ and $La_{0.9}Sr_{0.1}CoO_3$ samples in Table 2.2, the calculated weight percentage of $Co_3O_4$ is larger for La = 0.9 than for La = 0.8, though the opposite effect is expected by stoichiometry. As can be seen in the neutron scattering data in Fig.2.2, however, the CoO $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ peak is significantly larger in the La = 0.8 sample. This likely indicates that the excess $Co_3O_4$ in $La_{0.8}Sr_{0.1}CoO_3$ formed CoO, although why this happened preferentially in the non-stoichiometric sample is not clear. Despite the intensity of the CoO $(\frac{1}{2}\frac{1}{2}\frac{1}{2})$ magnetic peak, the small intensities of the CoO structural peaks resulted in refinements which gave a CoO weight fraction of around 0.01 %. As detailed by Jauch *et al* [72], CoO undergoes a structural deformation to monoclinic $C2/m$ below its antiferromagnetic ordering temperature (260 K). To investigate the possibility that our samples contained such a phase, simulated spectra of $C2/m$ CoO using the lattice parameters from Ref. [72] were compared with the LCO/LSCO neutron scattering data. No evidence of $C2/m$ structural peaks was seen in the samples. The only other indication of CoO in our samples was a possible increase in the magnetization of LCO samples below 260 K, which will be discussed in the magnetometry section.

29

# 3 Nanoparticle synthesis

## 3.1 Overview of Sol-Gel Method

$La_ySr_xCoO_3$ nanoparticles were synthesized at the University of California, Santa Cruz, using a variation on the Pechini sol-gel method [73] which uses the amorphous heteronuclear complex DTPA as a precursor [28, 74]. There were five different synthesis methods employed for the nanoparticles, each using the same basic process, but with different amounts of NaOH and subsequent washing steps. The starting materials for all nanoparticles were lanthanum nitrate hexahydrate ($La(NO_3)_3 \cdot 6H_2O$), cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$), and when desired, strontium nitrate ($Sr(NO_3)_2$). Stoichiometric amounts of these metal nitrates were dissolved in de-ionized water to make a clear red solution. 1 M NaOH was then added dropwise to initiate the creation of metal hydroxides.

## 3.2 Method 1

In Method 1, the NaOH added was not enough to react with all of the metal ions. For example, in the synthesis of $La_{0.75}Sr_{0.25}CoO_3$ , the chemical reaction would be written as [75]

$$0.75La(NO_3)_3 \cdot 6H_2O + Co(NO_3)_2 \cdot 6H_2O + 0.25Sr(NO_3)_2 + mNaOH$$
$$\longrightarrow 0.75La(OH)_3 + Co(OH)_2 + 0.25Sr(OH)_2 + mNa(NO)_3 + 12H_2O. \tag{3.1}$$

In order to ensure that the NaOH provided all of the $OH^-$ ions required to react with the metals, $m = 4.75$ mols would be required. However, only a 12% stoichiometric amount of NaOH was added to the solution, with favorable results. In Refs. [28, 74], this substoichiometric addition of 1 M NaOH is referred to as a

30

FIG. 3.1: WAND neutron diffraction scans for Method 1 nanoparticles of
$La_{0.7}Sr_{0.3}CoO_3$ at $T$=10 K and 300 K. The LSCO characteristic peaks are labeled
with thick lines at the bottom and the $Co_3O_4$ peaks are labeled with boxes. The
LSCO ferromagnetic (0 1 2) peak is at $2\theta \approx 22.5^o$ and marked with an x.

"dropwise" addition, meaning only a few drops were used (around 5 mL for a 2
g. LCO sample). This was misleading, and the procedure should be clarified in
subsequent papers employing this method.

Lanthanum, cobalt, and strontium nitrates all dissolve readily in water, al-
though not all react readily with water to form metal hydroxides. Aqueous lan-
thanum reacts slowly in cold water to form $La(OH)_3$ and hydrogen gas, and the
speed of the reaction increases with temperature [76, 77]. Aqueous cobalt reacts
with NaOH to form $Co(OH)_2$ , and will bond with more hydroxides to form nega-
tive complexes when in solution with a strong base such as NaOH (e.g. $Co(OH)_4^{2-}$)
[58, 78]. This creates a blue color. Since strontium hydroxide is only slightly sol-
uble in water, adding a small amount of NaOH to aqueous strontium results in
the formation of $Sr(OH)_2$ [58]. Therefore, adding a substoichiometric amount of

FIG. 3.2: X-ray diffraction scans using the Cu $K_\alpha$ wavelength for Method 1 nanoparticles of $La_{0.7}Sr_{0.3}CoO_3$ nanoparticles taken at room temperature. The LSCO characteristic peaks are labeled with thick lines and the $SrCO_3$ peaks are labeled with dark ovals.

NaOH (on the order of 5 mL or less, stoichiometric would be 40 mL) and subsequently heating the sample is enough to form the metal hydroxides, because all other required $OH^-$ ions are provided by the water.

After the addition of 5 mL of NaOH to the metal nitrate solution, the solution remained clear red with some dark blue precipitates. The blue color is a result of $Co(OH)_2$ being formed [58]. Powdered diethylene triamine pentaacetic acid (also known as "pentetic acid" or DTPA) was then added to the solution. DTPA is a chelating agent with a charge of 5-, and thus binds strongly to metal cations [79]. As discussed by Hart *et al*, the stability of the chelate-metal complex depends on the metal ion [58]. This stability is quantified by log $K_{stab.}$, where $K_{stab.}$ is a constant depending on the equilibrium concentration of the individual metal ion and that of the chelate-metal complex. Notably, while the stabilities of $La^{3+}$

and Co$^{2+}$ complexes are about the same (19.48 and 19.15, respectively), that for Sr$^{2+}$ is much lower, at 9.68 [80]. This is likely a contributing factor for the Sr-deficiencies and SrCO$_3$ found in the LSCO nanoparticles, and indicates that in future studies on LSCO nanoparticles fired at low temperatures (620°C) it would be best to use a different precursor. SrCO$_3$ incorporates into the LSCO phase at higher firing temperatures, so the DTPA method is acceptable in this case.

A slight excess (1.005x stoichiometric) of DTPA was added to the solution in order to avoid the formation of an amorphous precipitate [79, 81]. Adding more than this amount resulted in not all of the DTPA dissolving due to the relatively small amount of liquid present. No precipitate was formed when using a 1.005x stoichiometric amount of DTPA. One possible chemical equation for the addition of DTPA to the metal hydroxides to form La$_{0.75}$Sr$_{0.25}$CoO$_3$ is [81]

$$
\begin{aligned}
0.75\text{La(OH)}_3 + \text{Co(OH)}_2 + 0.25\text{Sr(OH)}_2 + (0.95 + \alpha)\text{H}_5\text{DTPA} \\
\longrightarrow [\text{La}_{0.75}\text{Sr}_{0.25}\text{CoO}_3]\text{DTPA}_{0.95} + \alpha\text{DTPA} + 4.75\text{H}_2\text{O},
\end{aligned}
\tag{3.2}
$$

where $\alpha$ is the amount of excess DTPA added. Note that the oxygen in the final LSCO product can be drawn from the surrounding water molecules and precursor [82]. After the addition of the DTPA, the solution ("sol") was heated to 80°C on a hot plate while stirring with a magnetic stirring rod for 20 minutes. The DTPA gradually dissolved, and the solution turned a dark, clear purple. The solution was left on the hot plate to vaporize for 24 hours, or until it had dried and hardened to a resin-like consistency - the "gel." This gel consists of interconnected metal-DTPA complexes with the metals linked by oxygen atoms [83]. The gel was placed in a Thermolyne F1500 box furnace and heated to 300-350$^o$C at a rate of 5°/minute and left for 1 to 1.5 hours.

During this drying phase, all of the water molecules remaining in the resin-like gel boiled away over the temperature range 100 - 180°C [83]. The DTPA material is burned off in the temperature range 220 - 300°C. The gel became a

black, porous, ashy substance consisting of amorphous metal oxides. The advantage of this process over solid-state synthesis now becomes clear: the resulting metal oxides in the gel are intermixed on the atomic scale, whereas in the solid-state synthesis method the metal oxides remain as homogeneous crystals several hundred nanometers across prior to firing.

The ashy gel was then ground lightly and placed in an alumina boat for the final firing step. Due to the high degree of intermixing, the high temperatures usually required for diffusion of crystals were unnecessary, and lower temperatures were used in order to get small nanoparticles of $La_wSr_xCoO_3$. 620° had been previously found to be the lowest temperature at which the crystalline LSCO/LCO formed. However, we found that at temperatures this low, noticeable amounts of $Sr(CO)_3$, $Co_3O_4$, and other phases formed, which are seen as extra peaks in Figs. 3.1 and 3.2. This was a problem for the neutron scattering data, as the ferromagnetic Bragg peak for LSCO appeared to be obscured by a temperature-independent impurity phase in these data. The ferromagnetic (0 1 2) peak at $2\theta = 22.5°$ had the same intensity at 10 K and 300 K, which is not consistent with the ferromagnetic phase only appearing for T $\leq$ 250 K. Fortunately, this phase decreased as the firing temperature was increased to 850° C and higher, and the ferromagnetic portion of the peak can be easily distinguished in the 1000° C LSCO nanoparticles. The nanoparticles were all fired for four hours at temperatures between 620 and 1000° C, as suggested by previous researchers [28, 74, 84, 85].

Method 1 resulted in nanoparticles with the smallest amounts of extra phases out of all the nanoparticles, and is concluded to be the ideal method of synthesis for x-ray and neutron diffraction experiments.

## 3.3   Method 2

In Method 2, the metal nitrate solution is prepared identically to that in Method 1, but a *stoichiometric* amount of NaOH is added. That is, instead

of a few drops to start the reaction, 40.7 mL of 1 M NaOH is added to the metal nitrates and provides all of the $OH^-$ groups required to form the metal hydroxides. The reaction is

$$
\begin{aligned}
0.75La(NO_3)_3 \cdot 6H_2O &+ Co(NO_3)_2 \cdot 6H_2O + 0.25Sr(NO_3)_2 + 4.5NaOH \\
&\longrightarrow 0.75La(OH)_3 + Co(OH)_2 + 0.25Sr(OH)_2 + 4.5Na(NO)_3 + 12H_2O.
\end{aligned}
\tag{3.3}
$$

In strong bases, Co complexes with more $OH^-$ groups tend to form ($[Co(OH)_4]^{2-}$], $[Co(OH)_6]^{4-}$]) [58]; this effect may also occur with the La and Sr complexes, although no sources were found detailing the process. An excess of DTPA was then added and the entire mixture was heated while stirring, again identically to Method 1. When the resin-like gel was heated to 300 - 350$^o$ in the furnace, a reaction took place which resulted in much of the sample ($> 75\%$ by weight) being expelled from its container. An odorous brown gas was produced which likely consisted of small amounts of $NO_2$ The remaining material was black and ashy, but did not show the porous aerogel-like structure of the samples in Method 1. There were also very hard chunks about 2-5 mm in diameter present in the reacted sample. One possible cause of the explosive reaction is the presence of a significant amount of $Na(NO)_3$ in the material, which has a melting point of 308°C. No such reaction was observed in any of the other methods. After this firing step, the material was then placed in an alumina boat and fired for four hours at temperatures between 620 and 1090$^o$C.

Method 2 produced nanoparticles with significant amounts of the $Co_3O_4$ impurity phase. A $SrCO_3$ phase was also present in the 620$^o$C nanoparticles, as can be seen in Fig. 3.4; the amount decreased as firing temperature increased. No $SrCO_3$ was seen in the 1000°C and 1090°C nanoparticles, as in Fig. 3.5. However, many other impurities were found in the 1090°C sample. This is not due to decomposition of the LSCO into La- and Sr- oxide phases, as higher temperatures were used in the synthesis of the bulk material without such phases being observed. Rather,

FIG. 3.3: Neutron diffraction scans from the WAND instrument for nanoparticle $La_{0.75}Sr_{0.25}CoO_3$ at 10 K and 300 K. Data are shown for samples fired at 1000°C (lower two spectra) and 1090°C (upper two spectra) only. The LSCO characteristic peaks are labeled with thick lines, the $Co_3O_4$ magnetic peak locations are labeled with boxes, and the CoO antiferromagnetic peak is labeled with a triangle. The LSCO ferromagnetic (0 1 2) peak is at $2\theta \approx 22.5^o$ and is marked as an x.

these impurities consist of Na, La, Sr, and Co compounds formed as a result of the explosion during firing. We were not able to determine all of the compounds, but were able to eliminate simple La, Sr, and Na oxides as candidate phases. The $Co_3O_4$ phase persisted to higher firing temperatures and the structural peaks can be clearly seen in the neutron spectra (see Fig. 3.3). Data were taken on the WAND diffractometer for the 1000°C and 1090°C nanoparticles only. Notably, the amount of CoO increased dramatically for the 1090°C nanoparticles, as can be seen by the antiferromagnetic peak in the neutron data - this is likely a result of the higher firing temperature.

TEM images showed long fibers containing Na present in the material (Fig. 3.6).

FIG. 3.4: X-ray diffraction scans of $La_{0.75}Sr_{0.25}CoO_3$ nanoparticles (fired at 620, 775, and 850$^o$ C) taken at room temperature. The LSCO characteristic peaks are labeled with thick lines. The $Co_3O_4$ structural peak locations are labeled with empty boxes and the $SrCO_3$ peaks are labeled with dark ovals.

X-ray photoemission spectroscopy (XPS) measurements showed that the fibers had accumulated a disproportionally large amount of Sr on their surfaces, although we were not able to determine with this method if it was elemental Sr or a compound of Sr with other light elements (such as $SrCO_3$ or SrO). However, X-ray diffraction measurments clearly indicate $SrCO_3$ material in the sample. As can be seen in Fig. 3.7, La and Co were also found on the Na fiber, but the proportion of La:Sr:Co was approximately 1:1:1 rather than the expected 3:1:4 ratio for $La_{0.75}Sr_{0.25}CoO_3$. The decomposition point of $SrCO_3$ is significantly higher ($T_{decomp.} = 1494°C$) than the nanoparticle firing temperatures. It is possible that due to decreased stability of the Sr-DTPA metal complex, the Sr was not well intermixed within the gel during synthesis [80]. As a result, $SrCO_3$ was able to

FIG. 3.5: X-ray diffraction scans of $La_{0.75}Sr_{0.25}CoO_3$ nanoparticles fired at $1000°C$ and $1090°C$ taken at room temperature. The LSCO characteristic peaks are labeled with thick lines and the $Co_3O_4$ structural peak locations are labeled with empty boxes.



FIG. 3.6: TEM image of a fiber containing Na found in Method 2 nanoparticles fired at $620^oC$. Region 2 was found to contain a disproportionally large amount of Sr.

FIG. 3.7: X-ray photoemission spectroscopy results for Region 2 in Fig. 3.6. The relative percentages of Co, Sr, and La atoms were 35.1, 31.5, and 33.5 %, respectively.

form during the initial 350°C heating, and only at temperatures above 620°C was this phase successfully incorporated into LSCO. This is similar to the $SrCO_3$ in the bulk material being incorporated into the LSCO phase at temperatures of 850°C - 1100°C. The presence of Sr material on the Na fibers casts doubt on the Sr stoichiometry of the intended $La_{0.75}Sr_{0.25}CoO_3$ phase. However, the nanoparticles fired at 1000° showed ferromagnetic behavior consistent with that of other nanoparticles containing > 20% Sr in the magnetometry measurements.

Method 2 is not an ideal method for synthesizing pure LSCO and LCO nanoparticles due to large amount of $Co_3O_4$ phase, the presence of Na fibers possibly affecting Sr concentration within the LSCO, and the loss of over 50% of sample during the initial firing step.

FIG. 3.8: Neutron diffraction scans from the WAND instrument for nanoparticle La$_{0.7}$Sr$_{0.3}$CoO$_3$ at T=10 K and 300 K. The LSCO characteristic peaks are labeled with thick lines and the Co$_3$O$_4$ magnetic peak locations are labeled with boxes. The LSCO ferromagnetic (0 1 2) peak is at $2\theta \approx 22.5°$, and is absent in these data.

## 3.4  Method 3

In Method 3, a stoichiometric amount of NaOH was added in a way identical to Method 2, but the Na ions were then removed via dialysis. The aim of the dialysis step was to prevent the explosion during the initial firing step and to prevent the formation of the Na fibers in the final firing step. After the 1 M NaOH solution was added to the metal nitrate solution, the entire mixture was placed into a length of dialysis tubing (Fisher scientific, 32 mm wide, 28$\mu$m wall thickness, T2 membrane with 6000 to 8000 Dalton molecular weight cut-off) and sealed with clips. The tube was then placed into 1 L of deionized water, with the idea that the smaller Na$^+$ ions would exit the solution while the larger La$^{3+}$, Co$^{2+/3+}$, and

40

FIG. 3.9: X-ray diffraction scans of $La_{0.7}Sr_{0.3}CoO_3$ nanoparticles taken at room temperature. The LSCO characteristic peaks are labeled with thick lines, and the $Co_3O_4$ structural peak locations are labeled with empty boxes.

$Sr^{2+}$ ions would remain. The water bath was replaced twice in one-hour intervals, then replaced a final time and left for 20 hours. Over the course of dialysis, the water bath was stirred constantly with a magnetic stir rod. The pH was measured prior to each water replacement, and for all samples we found the pH to go from very basic (14 for the LSCO samples, 12 for the LCO samples) down to neutral (7) with each progressive replacement. The solution inside the tube changed from blueish-purple to reddish-brown over the course of the dialysis. This color change can be attributed to the unstable blue $Co(OH)_2$ precipitate forming $Co(OH)_3$ and $Co_2O_3 \cdot H_2O$ (brown), as well as a more stable form of $Co(OH)_2$ (red) [58]. After dialysis, an excess amount of DTPA (1.3x stoichiometric) was added to the solution, along with approximately 50 mL of deionized water to ensure that the latter could dissolve (in Method 1, no extra water was added along with the

41

DTPA, so the amount of excess was limited). The mixture was then stirred while heating to 80°C on a hot plate. and the remainder of the procedure is identical to Methods 1 and 2.

Method 3 was successful in removing the Na fibers and preventing the explosion; however, the dialysis step also removed some of the strontium from the sample, resulting in material which was nominally $La_{0.7}Sr_{0.3}CoO_3$ having the magnetic properties of $LaCoO_3$. Some lanthanum was also missing from the sample after the dialysis step, which contributed to the large amounts of $Co_3O_4$ found in the end product. Sample composition is examined in more detail in the TEM results given in the next section. Neutron diffraction data (Fig. 3.8) show significant amounts of the $Co_3O_4$ phase but no other impurity phases. X-ray diffraction data (Fig. 3.9) do show other impurity phases, but these did not correspond to either CoO, $SrCO_3$, or $La_2O_3$.

While the explosion and Na remnants were avoided using Method 3, it is not an ideal method for synthesizing pure LSCO and LCO nanoparticles due to the loss of Sr and La ions during the dialysis step and the creation of difficult-to-determine impurity phases. This process is also time-intensive and generates liters of very basic liquid which must be disposed of properly. However, the presence of such large amounts of $Co_3O_4$ in the end product resulted in unusual magnetic properties, which will be discussed in the later section on magnetometry.

## 3.5   Methods 4 and 5

Methods 4 and 5 are identical to Method 3 up until the dialysis step. As in Method 2, a stoichiometric amount of NaOH was added to the metal nitrate solution. In order to remove the excess $Na^+$ ions, the resulting metal hydroxides were washed in distilled water (Method 4) or ethanol (Method 5). A cone of filter paper was placed in a large glass funnel over a beaker, and the metal hydroxides were poured into the paper. The metal hydroxide solution separated into a thick,

FIG. 3.10: Neutron diffraction scans from the WAND instrument for Method 4 and 5 nanoparticle $La_{0.7}Sr_{0.3}CoO_3$ at T=10 K and 300 K. Both samples were fired at 620°C. The LSCO characteristic peaks are labeled with thick lines and the $Co_3O_4$ magnetic peak locations are labeled with boxes. Two unidentified impurity peaks can be seen at $2\theta = 24.5°$ and $26.2°$.

dark blue precipitate (the metal hydroxides themselves) and a clear liquid (the excess NaOH). The clear liquid (pH = 13) was allowed to drain completely, then distilled water or ethanol was added to the remaining hydroxides. This process was repeated until the drained liquid had a pH of 7 (approximately 5 water/ethanol replacements over the course of 4 hours). The hydroxides remaining in the filter paper were then transferred to a beaker along with a 1.01x stoichiometric amount of DTPA and enough deionized water to dissolve the DTPA. The mixture was then heated while stirring and fired in a manner identical to all previous methods. No explosion occurred during the 350°C firing. Only 620°C nanoparticles were synthesized with these methods.

Neutron and X-ray diffraction data for these nanoparticles can be seen in

FIG. 3.11: X-ray diffraction scans of $La_{0.7}Sr_{0.3}CoO_3$ Method 4 and 5 nanoparticles taken at room temperature. The LSCO characteristic peaks are labeled with thick lines, and the $Co_3O_4$ structural peak locations are labeled with empty boxes.

Figs. 3.10 and 3.11. The neutron diffraction spectra indicate two unidentified impurity peaks at $2\theta = 24.5°$ and $26.2°$, whereas the X-ray diffraction spectra show $Co_3O_4$ as the only impurity phase in both methods, indicating that the $SrCO_3$ phase did not form. However, this may indicate that $Sr^{2+}$ ions were taken out along with the $Na^+$ ions during the washing phase, rather than improved crystallization of the LSCO phase. This conclusion is borne out by the magnetometry measurements, in which both Methods 4 and 5 show a magnetic transition at $T_C \approx 87$ K, which is characteristic of the parent $LaCoO_3$ compound. However, Method 5 also shows a magnetic transition at $\approx 250$ K, which indicates either the presence of $La_{1-x}Sr_xCoO_3$ or of CoO. We do not see the antiferromagnetic peak characteristic of CoO in the neutron scattering, indicating that this material may actually be showing *both* the LCO and the LSCO magnetic transitions. This will

44

be examined further in a later work.

We conclude that Methods 4 and 5 are not ideal methods for nanoparticle synthesis due to the unintentional removal of $Sr^{2+}$ ions during the washing process. This process is similarly time intensive to Method 3 and also produces a very basic liquid which must be disposed of (though in far smaller quantities). However, if the amount of $Sr^{2+}$ exiting the solution during Method 5 could be quantified and/or controlled, this could be a useful process for synthesizing nanoparticles which possess both LSCO and LCO phases.

# 4  Characterization

The sizes and compositions of Method 1-3 nanoparticles were examined via transmission electron microscopy (TEM), energy-dispersive X-ray fluorescence spectroscopy (EDS), micro X-ray fluorescence, small-angle X-ray diffraction (SAXS), and normal X-ray diffraction (XRD). Data were taken courtesy of Jane Howe, Feng Ye, and Andrew Payzant at ORNL (TEM and EDS, micro X-ray fluorescence, XRD), Yashar Abdollahian at UC Santa Cruz (SAXS and XRD), and Peter Klavins at UC Davis (XRD). TEM measurements were taken for a bulk $La_{0.75}Sr_{0.25}CoO_3$ sample and the Method 1-3 nanoparticles in order to determine particle size and distribution, and EDS measurements determined relative element concentration. Micro X-ray fluorescence experiments were performed on $LaCoO_3$ Method 3 nanoparticles, also to determine relative element concentrations. SAXS measurements were performed on Method 1-3 nanoparticles, and XRD was done for all samples.

## 4.1  Size Determination of Nanoparticles

A standard method for finding nanoparticle sizes is applying the Scherrer equation [86] to X-ray diffraction spectra. In the Scherrer equation, the full-width half-maximum (FWHM) of the Bragg peaks is inversely related to the crystallite size. In a perfect crystal, all of the lattice spacings for a particular set of lattice plane would be identical. The diffraction spectrum would have a delta function at the angle $2\theta$ corresponding to that set of planes (ignoring artificial widening due to instrument resolution). However, in actual materials, distortion of the lattice due to size effects or defects results in a distribution of lattice spacings for a particular set of planes, manifesting in a widening of the diffraction peak. For nanoparticles, this effect is signficant for crystallite sizes less than 100 nm, as surface distortion and other strain effects persist throughout a large portion of the crystal. [87]

The Scherrer equation is given by

$$D_{hkl} = \frac{K\lambda}{B_D \cos\theta}. \tag{4.1}$$

In Eq. 4.1, $D_{hkl}$ is the size of the crystal, $K$ is a constant which changes depending on the shape of the crystal (the equation was originally derived for cubic crystals), $\lambda$ is the wavelength of the incident X-rays, $B_D$ is the FWHM of the Bragg peak at (hkl) due to size, and $\theta$ is the Bragg angle for the given Miller indices. $K$ is usually approximated as 0.9 when the shape of the crystallites is unknown - this the case with our irregularly shaped nanoparticles.

Although it is possible to determine the size of individual crystals with X-ray diffraction using the Scherrer equation, this method has several disadvantages. First, this method only gives the size of single crystals in the sample, not the agglomerate particle size. As will be seen in the TEM measurements, nanoparticles tend to stick together and form agglomerations of several particles with different crystal orientations. Second, the Scherrer equation is only valid for nanoparticle sizes of 100 nm or less (70 nm or less for the Rigaku SmartLab at UC Santa Cruz) [87]. The widening effects for larger sizes are dwarfed by the limitations of the instrument resolution. Although this could theoretically be corrected for with characterization of the instrument resolution, this proved difficult to obtain for the instruments at ORNL and UC Davis.

In addition to peak broadening due to size effects, it is also possible to characterize the amount of broadening due to strain effects. The tensile strain, $\epsilon$, in a crystal is defined as the fraction of the crystal which falls outside the expected length. This can be written as $\epsilon = \frac{\Delta l}{l}$, where $l$ is the expected length and $\Delta l$ is the deviation. For example, if a nominally cubic crystal with side lengths 2 Å has a side length of 2.5 Å in one direction, $\epsilon = 0.5/2 = 0.25$. The formula developed by Stokes and Wilson in 1944 [88] estimates the broadening $B_S$ of the Bragg peak due to strain effects:

$$\epsilon = \frac{B_S}{4\,\tan\theta}. \tag{4.2}$$

In the Williamson-Hall method [89], the Scherrer equation is added to the Stokes-Wilson equation and gives an estimate of the total peak broadening $B_{tot}$ due to both size and strain (Eq. 4.3).

$$B_{tot} = B_D + B_S$$

$$\tag{4.3}$$

$$B_{tot}\cos\theta = 4\epsilon\,\sin\theta + \frac{K\lambda}{D_{hkl}}$$

Plotting $B_{tot}\cos\theta$ against $\sin\theta$ for each Bragg peak and fitting the points with a linear equation allows us to determine the strain from the slope ($4\epsilon$) and the crystallite size from the intercept ($K\lambda/D_{hkl}$). This method was used during the refinement processes for the Rigaku SmartLab diffractometer (UC Santa Cruz) and the PANalytical X'Pert Pro diffractometer (ORNL) and provided information on the crystallite sizes for nanoparticles of all synthesis methods. Particle size measurements for Method 1 - 3 nanoparticles were determined using either SAXS or TEM. All nanoparticle size information is summarized in Table 4.1.

## 4.2   Bulk: TEM and EDS

TEM and EDS measurements on bulk $La_{0.75}Sr_{0.25}CoO_3$ were taken along with the nanoparticle measurements in order to provide a reference point with regard to size and composition. Figure 4.1 shows a TEM image of the bulk material, and Fig. 4.2 shows EDS analysis of the element composition of the circled region in the TEM figure.

The average La:Sr:Co weight percentages found with EDS measurements of three different regions were 41:13:46 %, with errors $\leq 1.5$ % in each value. As the

TABLE 4.1: Calculated crystallite and particle sizes of Method 1 - 3 nanoparticles. Crystallite sizes are determined with the Williamson-Hall method on X-ray diffraction data, and agglomerated particle sizes are determined using SAXS. $T_{fire}$ is the firing temperature of the nanoparticles.

| Material | Method | $T_{fire}(°C)$ | Crystallite (nm) | SAXS (nm) |
|---|---|---|---|---|
| $LaCoO_3$ | 1 | 620 | 18 | 53 |
| $LaCoO_3$ | 1 | 1000 | $\geq 69$ | – |
| $La_{0.65}Sr_{0.35}CoO_3$ | 1 | 620 | 13.7 | – |
| $La_{0.7}Sr_{0.3}CoO_3$ | 1 | 620 | – | 60 |
| $La_{0.7}Sr_{0.3}CoO_3$ | 1 | 850 | – | 75 |
| $La_{0.7}Sr_{0.3}CoO_3$ | 1 | 1000 | – | 86 |
| $LaCoO_3$ | 2 | 620 | – | 65 |
| $La_{0.75}Sr_{0.25}CoO_3$ | 2 | 1000 | 37 | – |
| $La_{0.7}Sr_{0.3}CoO_3$ | 2 | 1000 | – | 90 |
| $LaCoO_3$ | 3 | 620 | 22 | 65 |
| $La_{0.7}Sr_{0.3}CoO_3$ | 3 | 620 | 23 | – |
| $La_{0.7}Sr_{0.3}CoO_3$ | 3 | 850 | 48 | – |
| $La_{0.7}Sr_{0.3}CoO_3$ | 3 | 1000 | $\geq 69$ | – |
| $La_{0.7}Sr_{0.3}CoO_3$ | 4 | 620 | 28 | – |
| $La_{0.7}Sr_{0.3}CoO_3$ | 5 | 620 | 24 | – |

expected La:Sr:Co ratio for $La_{0.75}Sr_{0.25}CoO_3$ is 37.5:12.5:50, these results indicate a substoichiometric amount of Co in the analyzed regions. We conclude that the Co is missing because the La:Sr ratio is nearly that which is expected. No $Co_3O_4$ phase was detected in this bulk sample.

The bulk material is composed of smaller crystals (500 nm and larger) that appear fused together. These crystals are of varying shapes and sizes. It is difficult to say much more about the crystal structure, because no measurements

FIG. 4.1: TEM image of $La_{0.75}Sr_{0.25}CoO_3$ bulk material. The scale at the bottom right of the image covers $5\mu$m. The elemental composition of the circled region was analyzed with EDS.



FIG. 4.2: EDS analysis of $La_{0.75}Sr_{0.25}CoO_3$ bulk material from the circled region in Fig. 4.1.

were taken over a smaller length scale.

## 4.3    Method 1 Nanoparticles: TEM and EDS

Figures 4.3 and 4.4 show $La_{0.65}Sr_{0.35}CoO_3$ nanoparticles fired at 620°C. A range of sizes is visible in Fig. 4.3, with nanoparticle diameters of 10 - 20 nm seen in the center of the image, and diameters of up to 100 nm seen on the outer edges of the agglomeration. The nanoparticle sizes seen in Fig. 4.4 are also in the 10 - 20 nm range. The crystallite sizes determined by X-ray diffraction were 13.7

FIG. 4.3: TEM image of $La_{0.65}Sr_{0.35}CoO_3$ Method 1 nanoparticles over a wide field. The scale on the bottom right of the image covers 200 nm in total.

nm (Table 4.1), consistent with the sizes seen in the center of the image. The larger particles are either agglomerations of smaller particles or unusually large crystallites which do not make up a significant portion of the sample (otherwise, the X-ray diffraction results would give a larger average crystallite size).

Figure 4.4 shows EDS determination of elements in a different portion of the same Method 1 sample. Whereas La and Co are both equivalently distributed throughout the large nanoparticle structure shown in the image, there are regions with less Sr (e.g. the left side of the image). This may indicate phase separation into Sr-rich and Sr-poor nanoparticles. The fact that there are *regions* with less Sr is surprising, as the synthesis process involved thorough mixing of the elements - one might instead expect Sr-poor nanoparticles and Sr-rich nanoparticles to be evenly intermixed.

$Co_3O_4$ and other unidentified phases were seen in the X-ray diffraction of these nanoparticles, but are not visible in the SEM element analysis. There are no regions in the image containing only Co, as well as no regions containing only La or Sr. Similar results were found when imaging a different part of the sample (not shown). As the proportion of $Co_3O_4$ to LSCO in the sample is low enough as to be unrefinable with FullProf, it is perhaps not surprising that the two sample regions imaged did not contain a Co phase. Another possibility is that the $Co_3O_4$

51

FIG. 4.4: TEM images and EDS analysis of elements for $La_{0.65}Sr_{0.35}CoO_3$ Method 1 nanoparticles fired at 620°C. Clockwise from top left: grayscale image of nanoparticles, La concentrations, Co concentrations, and Sr concentrations. The scale on the bottom right of each image is 100 nm.

material is well intermixed with the LSCO material in these images, making it difficult to distinguish between the two phases.

## 4.4  Method 2 Nanoparticles: TEM and EDS

TEM and EDS measurements were done on Method 2 $La_{0.75}Sr_{0.25}CoO_3$ nanoparticles fired at 620°C and 850°C. During the experiment, it was noted that the 620°C nanoparticles had Na fibers (discussed previously) with non-$La_{0.75}Sr_{0.25}CoO_3$ compounds on them. Consequently, the sample was sonicated in deionized water for approximately 45 minutes in order to "wash" off the Na fibers, then re-examined. Figure 4.5 shows TEM images from both before and after the washing step. No such Na fibers were observed in the 850°C sample, so

FIG. 4.5: TEM images for $La_{0.75}Sr_{0.25}CoO_3$ Method 2 nanoparticles fired at 620°C (before and after washing) and 850°C. (a) and (b) are 620°C nanoparticles which have not been washed shown at 150 nm and 0.2 $\mu$m scales, respectively. (c) shows 620°C nanoparticles after washing, and (d) and (e) show 850°C nanoparticles. The scale shown on the bottom right for (c) and (d) is 300 nm; the scale for (e) is 150 nm.

it was not washed.

Images obtained of the 620°C particles prior to washing show nanoparticles with diameters ranging from approximately 50 to 150 nm. As in the Method 1 nanoparticles, both large and small particles are observed - however, these nanoparticles are on average larger and the sizes are more intermixed. In comparing the images before and after washing, it is notable that the washed material shows particles which are much more cubic shaped than the unwashed material. This may be due to the washing removing amorphous material that had accumulated on the surface of the cubic nanoparticles. Cubic shapes are also seen in Fig. 4.5(b) in the lower left portion of the sample. When observed, the cubic structures are $\geq$ 100 nm in diameter - significantly larger than the Method 1 nanoparticles observed in TEM. EDS analysis of the cubic portions of the washed material indicated very low amounts of Sr (see the bottom three values for 620°C (w) in Table 4.2) as compared to La and Co, which eliminates the possibility of the cubic material being either $Co_3O_4$ or $SrCO_3$. Given that $SrCO_3$ was detected in the 620° material with X-ray diffraction, it is possible that the Sr was not fully integrated with the LCO lattice at this firing temperature, and that the cubic material remaining is $LaCoO_3$ with small amounts of $La_{1-x}Sr_xCoO_3$ phase.

Figure 4.5(d) shows the 850°C nanoparticles; the image shown and all other TEM images of these nanoparticles do not have the cubic shaped structures seen in the 620°C samples. Although it is difficult to distinguish individual nanoparticles, the size range is estimated to be 100 - 200 nm. Figure 4.5(e) shows a close-up of a small aggregate of nanoparticles with a similar size range. The particle surfaces seen in (e) are irregular, indicating surface reconstruction of the particle. At 850°, less $SrCO_3$ was seen in the X-ray diffraction, indicating that these nanoparticles have more Sr incorporated into the $La_{1-x}Sr_xCoO_3$. However, this is not reflected in the EDS measurements, which still show Sr-poor regions and Sr-rich regions.

TABLE 4.2: EDS measurements showing relative element concentrations for Method 2 $La_{0.75}Sr_{0.25}CoO_3$ nanoparticles fired at 620°C and 850°C. Also included are the concentrations of the 620°C nanoparticles after sonicating in deionized water (indicated with a "w" in the $T_{fire}$ column). The relative concentrations for ideal $La_{0.75}Sr_{0.25}CoO_3$ are La:Sr:Co = 37.5:12.5:50. Each row is a different region of the sample, and errors on the percentages are 1.2 % or less.

| $T_{fire}$ (°C) | % La | % Sr | % Co |
|---|---|---|---|
| 620 | 44.6 | 5.4 | 50.0 |
| 620 | 41.0 | 11.5 | 47.5 |
| 620 | 43.8 | 6.0 | 50.2 |
| 620 | 43.1 | 11.7 | 45.2 |
| 620 | 33.5 | 31.5 | 35.1 |
| 620 (w) | 35.0 | 14.5 | 50.5 |
| 620 (w) | 46.2 | 2.3 | 51.5 |
| 620 (w) | 47.2 | 2.9 | 49.9 |
| 620 (w) | 44.6 | 5.4 | 50.1 |
| 850 | 43.7 | 10.5 | 45.8 |
| 850 | 46.5 | 6.5 | 47.1 |
| 850 | 40.5 | 11.7 | 47.8 |
| 850 | 48.7 | 4.2 | 47.2 |

## 4.5 Method 3 Nanoparticles: TEM and micro X-ray fluorescence

Method 3 nanoparticles fired at 620 and 1000°C were examined using TEM, EDS, and micro X-ray fluorescence. TEM of the 620° nanoparticles showed sizes of 50 - 100 nm, consistent with Method 2 nanoparticles. The 1000° nanoparticles were 100 - 300 nm in diameter, with a few smaller ($\approx$ 50 nm) particles seen as well.

FIG. 4.6: TEM image and EDS analysis of Method 3 nanoparticles fired at 620°C. Clockwise from top left: grayscale image of nanoparticles, La concentrations, Co concentrations, and Sr concentrations. The outlined nanoparticles in the grayscale image are likely $Co_3O_4$. The scale on the bottom right of each image is 300 nm.

Although EDS measurements showing the element concentrations were done on the $La_{0.7}Sr_{0.3}CoO_3$ nanoparticles, no quantitative data were taken to determine the La:Sr:Co ratios. Instead, micro X-ray fluorescence data were taken for $LaCoO_3$ nanoparticles fired at 620°C to determine the La:Co ratio.

TEM and EDS measurements shown in Fig. 4.6 for samples fired at 620°C show two types of nanoparticles. The $La_{0.7}Sr_{0.3}CoO_3$ nanoparticles are rounded and consist of La, Sr, and Co (as expected). The nanoparticles with well-defined facets outlined in the grayscale image do not have any La and less Sr than in other regions, indicating $Co_3O_4$. This is consistent with X-ray diffraction results showing $Co_3O_4$ in Method 3 nanoparticles, although this contrasts the composition of the cubic Method 2 nanoparticles; these likely consisted of $LaCoO_3$. However, as $Co_3O_4$ has a cubic crystal structure and $LaCoO_3$ has a rhombohedrally distorted cubic crystal structure, it is reasonable that they look similar in TEM.

Figure 4.7 shows TEM and EDS measurements for nanoparticles fired at 1000°C. Notably, many of the small particles on the outer edges of the large

56

FIG. 4.7: TEM image and EDS analysis of Method 3 nanoparticles fired at 1000°C. Clockwise from top left: grayscale image of nanoparticles, La concentrations, Co concentrations, and Sr concentrations. Two of the Co-deficient regions are circled in the grayscale image. The scale on the bottom right of each image is 400 nm.

ones (see circled regions in Fig. 4.7) appear to be deficient in Co. Unlike in the 620°C nanoparticles above, no $Co_3O_4$ material is detected.

When comparing the relative amounts of the Co and La atoms in the Method 3 $LaCoO_3$ 620° material using micro X-ray fluorescence measurements, we find a Co:La ratio of 35:65 by weight percentage. The nominal Co:La weight ratio for pure $LaCoO_3$ is 30:70, indicating that some of the La must have left the sample during the dialysis phase. An amorphous phase can be ruled out as the *cause* of this discrepancy, as X-ray fluorescence simply detects the amount of a particular element regardless of whether or not it is in a compound. If we assume all of the

FIG. 4.8: TEM image of a $La_{0.7}Sr_{0.3}CoO_3$ Method 3 nanoparticle fired at 1000°C. (b) shows a close-up of the bottom left hand section of (a). Periodic lattice planes are seen as alternating bright and dark stripes. The circled region at the top right of (a) shows lattice planes with a different spacing and orientation than the rest of the nanoparticle. There is a bright region approximately 20 Å thick on the underside of the particle in (b). The scale on each image covers 5 nm.

La in this sample reacts to form $LaCoO_3$ and the remainder forms $Co_3O_4$, the calculated weight fraction of $Co_3O_4$ in the sample is 10.6 %. However, Rietveld refinements give a weight fraction of 29 % in the 620°C nanoparticle LCO sample, which indicates that 39 % of the La in the sample is not contained within the LCO compound. Given that no other La - related phases were identified in the neutron or X-ray diffraction, we conclude that this La is in an amorphous phase.

In summary, micro X-ray fluorescence data and EDS are consistent with the presence of both $Co_3O_4$ and an amorphous La compound (which is likely also Co-deficient) in nanoparticles synthesized with Method 3. Although no $Co_3O_4$ was detected by EDS in the 1000°C nanoparticles, this may simply be a result of the analysis only being performed on two different nanoparticle agglomerations.

Certain TEM images were of high enough resolution to determine the spacing between lattice planes. Figure 4.8(a) shows a 1000°C nanoparticle with lattice planes in three different orientations. As can be seen in Fig. 4.8(b), the main body of the nanoparticle is made up of planes approximately 5.8 Å apart, as determined by measuring the total length in pixels of alternating bright-dark

stripes, then converting to Angstroms and dividing by the number of stripes. The underside of the nanoparticle consists of a layer approximately 20 Å thick of planes 3.0 Å apart (seen in Fig. 4.8(b)), although the angle of the viewer here may be artificially shortening the plane spacing. In the upper right corner of (a), the circled region consists of bright-dark regions which are significantly further apart than in the rest of the nanoparticle, with a separation of approximately 9.5 Å. This region is 10 nm in vertical diameter.

LSCO nanoparticles have a lattice constant $a \approx 5.4$ Å, indicating that the lattice planes making up the majority of the nanoparticle are along the (100) direction. The (110) lattice planes have a separation of 2.8 Å, which may correspond to the planes on the underside of the particle. Given that the values obtained via this image are approximately 7 % larger than the expected lattice spacings from X-ray diffraction, we suspect there may be a systematic error due to the 10 nm scale given in the image. It is unknown how the scale was obtained, or the error on the scale. We can rule out error from obliquely viewing a facet, as this would shorten the apparent spacings instead of lengthening them. As such, we are unable to determine whether or not there is surface lattice expansion for the nanoparticles using this image. The larger, 9.5 Å stripes in the circled region do not correspond to any known spacing in LSCO even correcting for the +7% error (the closest would be the lattice constant $c \approx 13$Å). The corrected spacing of $\approx 8.8$Å is instead closer to the lattice constant of $Co_3O_4$, $a \approx 8.1$ Å, although this would represent an additional expansion of about 8 %.

Figure 4.9 shows a $La_{0.7}Sr_{0.3}CoO_3$ Method 3 nanoparticle fired at 620°C, approximately 50 nm in diameter. The rounded facets of the nanoparticle are clearly visible in Fig. 4.9(a), and the close-up in Fig. 4.9(b) shows the periodic lattice planes as in the 1000°C nanoparticles. The lattice planes are 3.2 Å apart, which does not match any of the d-spacings for LSCO or $Co_3O_4$. However, small particles ($\approx 100$ nm) attached to the outer surfaces of 1000°C nanoparticles (see Fig. 4.7) were found to be Co-deficient - this particle may be of the same genre.

FIG. 4.9: TEM image of a $La_{0.7}Sr_{0.3}CoO_3$ Method 3 nanoparticle fired at 620°C. The boxed region in (a) is shown in (b). Periodic lattice planes are seen as alternating bright and dark stripes in (b). The scale on the bottom left of the image covers 10 nm in total.

One of the Method 3 620°C nanoparticles showed at least three different sets of lattice planes in different regions on the surface, with indistinguishable structure between the regions. Regions 1 and 3 in Fig. 4.10 were each found to have two cross-hatched sets of lattice planes with spacings of approximately 2.9 Å and 3.6 Å. Both regions were ≥ 15 nm in diamater and extended in two dimensions. Region 2 was only around 10 nm in diameter, with a spacing of approximately 10.3 Å. As with the previously examined nanoparticles, none of these spacings correspond exactly with d-spacings of $Co_3O_4$ or LSCO. The closest theoretical spacings are 2.81 Å and 3.8 Å, which are d-spacings for the (110) LSCO peak and the hexagonal $a_h$ lattice parameter for LSCO, respectively. Again, this systematic lengthening of the measured spacings may be due to an error of approximately 3 % in the scale of this image as well. Region 2 is similar in size and spacing to the circled region in Fig. 4.8(a), and would be a candidate for $Co_3O_4$ embedded in the LSCO lattice; however, even the corrected measured spacing is too large for any known $Co_3O_4$ spacing.

The TEM results show that although there are some single domain nanoparticles (Fig. 4.9), other nanoparticles have one smaller domain embedded in a mostly

FIG. 4.10: TEM image of a $La_{0.7}Sr_{0.3}CoO_3$ Method 3 nanoparticle fired at 620°C. The d-spacings for visible lattice planes were measured for regions 1, 2, and 3. The scale on the top left of the image covers 5 nm in total.

pure sample (Fig. 4.8). Even others (Fig. 4.10) have many different domains comprising one nanoparticle. Several factors must therefore be considered when accounting for nanoparticle structural effects. In addition to taking into account surface distortions, we must also consider the effects of interfaces between different crystal orientations of LCO/LSCO crystals as well as between LCO/LSCO and other phases.

In particular, $Co_3O_4$ is present in nearly all of the nanoparticle neutron and X-ray diffraction data, and in some cases (Method 3) comprises a significant portion of the sample by weight. During the formation of bulk LCO and LSCO, $Co_3O_4$, $La_2O_3$ and $SrCO_3$ bulk material is ground together and heated; during this process, crystals of all three component materials combine and interdiffuse in order to create the final product [90]. This process takes place on a much smaller scale during the nanoparticle formation - although the sol-gel process theoretically results in well inter-mixed metal ions, very small crystals of $La_2O_3$, $SrCO_3$, and $Co_3O_4$ could also form during firing. These crystals would then combine into

LCO/LSCO during the four hours of extended firing time. In both nanoparticle and bulk, interfaces between all four materials exist in the intermediate phase, and the rates of interdiffusion may differ between the compounds. Therefore, if $Co_3O_4$ is particularly slow or difficult to combine with $La_2O_3$ and $SrCO_3$, two indicators would be as follows. First, that more $Co_3O_4$ be left over after the firing stage than either of the other two compounds. This is certainly seen in all of our LCO/LSCO material, in particular those made at lower firing temperatures and with excess $Co_3O_4$ added in the beginning. Second, there would exist some particles made of a compound from $La_2O_3$ and $SrCO_3$, with very little Co. Such particles are seen in both 620°C and 1000°C Method 3 nanoparticles.

An apparent inconsistency with this theory is with regards to the Method 2 nanoparticles. Here, the LSCO material is to be Sr-deficient rather than Co-deficient as measured with X-ray fluorescence. However, this method of element detection simply gives the average amount of each element over the entire region studied - it does *not* indicate whether there are Co-rich or Co-deficient areas within this region. Fortunately, a couple of region-scanning measurements were done with X-ray fluorescence on the washed Method 2 nanoparticles, as shown in Fig. 4.11. Figure 4.11(b) shows a region between approximately 726 and 1090 nm in which the ratio of Co to the La and Sr increases significantly. This may be a result of $Co_3O_4$ nanoparticles in the analysis region. The Sr-deficiency can also be explained with regards to Sr accumulating on the Na fibers in this sample, and subsequently being washed away. Any Sr on the unwashed material would still have contributed to the amount of Sr seen in the EDS analysis, accounting for the discrepancy seen in the EDS analysis between the washed and unwashed sample.

FIG. 4.11: X-ray fluorescence analysis for $La_{0.75}Sr_{0.25}CoO_3$ Method 2 nanoparticles fired at 620°C after washing (same region as shown in Fig. 4.5(c)). The yellow line across (a) shows the path over which the elemental analysis was taken, and the green, blue and yellow lines are rough values for the Sr, La, and Co concentrations. (b) shows a more detailed analysis of the element concentrations across the sample. Sr, La, Co, and O are shown by blue, purple, green, and red lines, respectively.

# 5 Neutron Scattering

## 5.1 WAND Neutron Diffractometer

Bulk and nanoparticle $La_wCoO_3$ and $La_wSr_xCoO_3$ samples were all examined using the Wide-Angle Neutron Diffractometer (WAND) at Oak Ridge National Labs (ORNL). The WAND is housed at the high-flux isotope reactor (HFIR). WAND is capable of fast measurements of powder diffraction spectra, with a resolution quite adequate for our purposes. A large advantage of the WAND is the area detector arranged in an arc around the sample, which can simultaneously detect scattering over a range $2\theta = 125°$. A schematic of the WAND can be seen in Fig. 5.1. Samples were all placed in vanadium cans for the measurement, because vanadium exhibits a broad diffuse background without any strong, sharp neutron diffraction peaks that might interfere with the sample spectra. There was some concern as to whether or not this broad background was preventing us from seeing low-intensity peaks from the sample; however, further tests on a higher resolution

FIG. 5.1: Schematic of the WAND neutron diffractometer (a.k.a HB-2C) at ORNL. Neutrons created by the high-flux isotope reactor enter through the monochromator, pass through the flight tube, then hit the sample. The diffracted neutrons are detected with an area detector covering $125°$ of the scattering angle.

diffractometer (HB-1) using an aluminum can with a very low background and sharp diffraction peaks did not reveal any such small sample peaks.

Neutron scattering was the method of choice for our structural and magnetic measurements for several reasons. First, the neutrally charged neutrons are able to penetrate deeply into a sample. This was particularly important for the nanoparticle measurements, as we wanted to get data for the core and the surface of the nanoparticles. Second, as the $S = \frac{1}{2}$ neutrons interact with both the atomic nuclei and the magnetic moment from the atomic electrons, they can "see" the lattice structure as well as the magnetic structure of a material. This sensitivity to magnetism is absent in X-ray diffraction, as X-rays are $S = 0$. Finally, while X-rays are electrically neutral, they interact primarily with the outer electrons of atoms. As such, they do not penetrate very far into a sample before scattering, and they are not very sensitive to light elements with fewer electrons (e.g. oxygen). On the other hand, the neutron scattering cross-section for lighter elements is actually

64

FIG. 5.2: Neutron diffraction scans showing the spectra of LaCoO$_3$ Method 1 nanoparticles (1000°C firing) before (black) and after (red) the collimators were repaired. The broad hump near $2\theta = 20°$ and the extra peaks at $2\theta = 31, 43, 59,$ and $75°$ are all due to improper absoprtion from the collimator. The inset is an expansion of the boxed region and shows the electrical problem which causes intensity repetition.

quite large. Therefore, neutrons were ideal for quantifying the oxygen positions in our samples.

A few instrumental difficulties were encountered while working with the WAND, and these will be reflected in the data shown here (see Fig. 5.2). In a series of runs in May 2013, it was found that the collimator plates did not have enough cadmium coating to sufficiently absorb extra scattering from the Al heat shields. As a result, there was extra background scattering in the runs taken during this period; although the bulk samples were crystalline enough that this did not significantly affect the refinements, the nanoparticle results were observed to have a background that was difficult to account for during refinement. This, coupled with the lower intensities, wider peaks, and increased number of impurities,

65

TABLE 5.1: Summary of all bulk samples examined using the WAND neutron diffractometer.

| $La_wCoO_3$ | $La_wSr_xCoO_3$ |
|---|---|
| $LaCoO_3$ | $La_{0.7}Sr_{0.3}CoO_3$ |
| $La_{0.7}CoO_3$ | $La_{0.75}Sr_{0.25}CoO_3$ |
| $La_{0.8}CoO_3$ | $La_{0.9}Sr_{0.1}CoO_3$ |
| $La_{0.9}CoO_3$ | $La_{0.65}Sr_{0.25}CoO_3$ |
| $La_{1.1}CoO_3$ | $La_{0.8}Sr_{0.1}CoO_3$ |

made it difficult to obtain the highest quality refinements for the nanoparticles. The issue was corrected, and the nanoparticle data taken afterward do not have this problem. Second, an electrical problem causing "repetition" of the intensities in the detector range $2\theta = 67 - 70°$ was detected around this time as well. It was noted that every two intensity readings were repeated once over this region, as can be seen in the inset of Fig. 5.2. This issue has proved extremely difficult to solve, so all data taken after May 2013 have this region of incorrect intensities. The corresponding $2\theta$ range was removed from the refinements (though is shown in the figures for this section), but still had the effect of decreasing the goodness-of-fit reported by FullProf.

## 5.2  Neutron Scattering: Bulk

All bulk samples that were examined using WAND are listed in Table 5.1. Data were taken on every sample over a temperature range of 10 K - 300 K in order to quantify the effect of temperature on the lattice parameters, as well as to track the appearance of magnetic peaks. Rietveld refinements were performed using the FullProf refinement suite [91], and the refinement results are shown here for four of the samples (Figs. 5.3 - 5.6).

FIG. 5.3: Rietveld refinements for bulk $LaCoO_3$ at 10 K. Data are shown by black squares, the theoretical fit is a red line, and the difference is a blue line. The upper row of triangles corresponds to the $LaCoO_3$ $R\bar{3}C$ phase, and the lower row corresponds to the $Co_3O_4$ $F\bar{4}3m$ phase.



FIG. 5.4: Rietveld refinements for bulk $La_{0.7}CoO_3$ at 7.5 K. Data are shown by black squares, the theoretical fit is a red line, and the difference is a blue line. The upper row of triangles corresponds to the $LaCoO_3$ $R\bar{3}C$ phase, and the lower row corresponds to the $Co_3O_4$ $F\bar{4}3m$ phase. Note that the region $2\theta = 67$ - $70°$ is poorly fit due to an instrument error. This region was not included in the actual refinement.

FIG. 5.5: Rietveld refinements for bulk $La_{0.8}Sr_{0.1}CoO_3$ at 10 K. Data are shown by black squares, the theoretical fit is a red line, and the difference is a blue line. The upper row of triangles corresponds to the $LaCoO_3$ $R\bar{3}C$ phase, the middle row corresponds to the $Co_3O_4$ $F\bar{4}3m$ phase, and the bottom row corresponds to the CoO $Fm\bar{3}m$ phase.



FIG. 5.6: Rietveld refinements for bulk $La_{0.7}Sr_{0.3}CoO_3$ at 10 K. Data are shown by black squares, the theoretical fit is a red line, and the difference is a blue line. The upper row of triangles corresponds to the $LaCoO_3$ $R\bar{3}C$ phase, and the lower row corresponds to the $Co_3O_4$ $F\bar{4}3m$ phase.

68

FIG. 5.7: Visual of the LSCO unit cell and the corresponding hexagonal and rhombohedral axes. $a_r$ and $\alpha_r$ are the rhombohedral lattice parameter and angle, while $a_h$ and $c_h$ are the hexagonal lattice parameters. The latter will be used to describe our system. Image taken from Ref. [92].

The structures of $La_wSr_xCoO_3(x \leq 0.5)$ and $LaCoO_3$ are well described by the space group $R\bar{3}C$ [3, 92]. This rhombohedral structure can be interpreted using either hexagonal axes ($\alpha = \beta = 90°, \gamma = 120°$; $a = b \neq c$) or rhombohedral axes ($\alpha = \beta = \gamma \neq 90°$; $a = b = c$), which are equivalent. We will be using the hexagonal axes to describe this system. Figure 5.7 depicts the difference between the hexagonal and rhombohedral descriptions.

About half of the samples contained $Co_3O_4$ as a secondary phase. This phase was included in the refinements using the $F\bar{4}3m$ space group rather than the more commonly accepted $Fd\bar{3}m$ space group because the relative intensities of the neutron scattering peaks were a better match to the data, and only $F\bar{4}3m$ accounted for the antiferromagnetic (2 0 0) Bragg peak [93]. We find that in general, the $F\bar{4}3m$ space group better fits the $Co_3O_4$ diffraction spectrum, including X-ray diffraction data taken on this $Co_3O_4$ alone. A visual comparison of the two space groups can be seen in Fig. 5.8.

FIG. 5.8: Neutron diffraction simulations of the Fd$\overline{3}$m and F$\overline{4}$3m space groups for Co$_3$O$_4$. The green triangles indicate the expected peak positions. Note the difference in peak intensities and the expected presence of the (2 0 0) ($2\theta = 21°$) antiferromagnetic peak in the F$\overline{4}$3m plot (simulations were done for room temperature, so the magnetic peak is not actually visible). F$\overline{4}$3m was found to be the better fit for the Co$_3$O$_4$ phase in LCO and LSCO.

The presence of Co$_3$O$_4$ peaks in the diffraction spectra indicates that this phase is crystalline, rather than amorphous. It is unlikely that any amorphous Co$_3$O$_4$ exists in our samples, as the weight fractions of Co$_3$O$_4$ in the La$_w$CoO$_3$ samples (noted in the Characterization section) show that there is a larger amount of Co$_3$O$_4$ than would be expected from stoichiometry calculations. X-ray diffraction of bulk La$_w$CoO$_3$ and refinement with the Rigaku PDXL software [66] calculated the size of the Co$_3$O$_4$ crystals to be approximately 10 - 20 nm in diameter.

Nearly all of the data also show the CoO antiferromagnetic peak at $2\theta = 17.2°$, though the phase (space group Fm$\overline{3}$m) was only successfully included in a few of the refinements. The samples with extra Co$_3$O$_4$ *and* Sr had structural CoO peaks large enough to be refined. Notably, the presence of Co$_3$O$_4$ is always accompanied by the magnetic phase of CoO, but CoO can appear without Co$_3$O$_4$. This is likely due to the firing temperatures for all the bulk samples exceeding that for the formation of CoO from Co$_3$O$_4$ - it would be unusual for a Co$_3$O$_4$ phase to be present without some having been converted into CoO.

70

FIG. 5.9: Magnetic Bragg peaks seen at low angles in the $La_wCoO_3$ bulk samples. The CoO AFM peak is indicated with a black circle, the $Co_3O_4$ AFM peak with a box, and the location of the LSCO FM peak with an "x". All data were taken at 10 K and below.



FIG. 5.10: Magnetic Bragg peaks seen at low angles in the $La_wSr_xCoO_3$ bulk samples. $LaCoO_3$ is also included for reference. The CoO AFM peak is indicated with a black circle, the $Co_3O_4$ AFM peak with a box, and the LSCO FM peak with an "x". All data were taken at 10 K and below.

Figures 5.9 and 5.10 show the low-angle magnetic peaks in the neutron scattering data for $La_wCoO_3$ and $La_wSr_xCoO_3$, respectively. The data have been normalized to the large (2 0 2) $LaCoO_3$ peak for clarity and ease of comparison. Although the magnetometry measurements indicate that there is ferromagnetic order in the $La_wCoO_3$ materials at $T_c = 87$ K, no magnetic diffraction peak has been observed. High resolution neutron diffraction experiments focusing on the low-angle region where magnetic Bragg peaks are expected showed no peak corresponding with this transition temperature. The CoO antiferromagnetic ordering peak ($T_{c,CoO} \approx 290K$) is seen in all but the $La_{1.1}CoO_3$ sample [71]. A small structural CoO peak at $2\theta = 58.8°$ is also visible in all but this sample. The $Co_3O_4$ structural/AFM (1 1 1) peak at $2\theta = 18°$ and AFM (2 0 0) peak at $21°$ are present in all of the samples with w + x < 1 apart from $La_{0.65}Sr_{0.25}CoO_3$. The LSCO ferromagnetic ordering peak at $2\theta \approx 22.2°$ (0 1 2) is apparent in all samples doped with Sr, apart from $La_{0.9}Sr_{0.1}CoO_3$ [94]. This is consistent with the estimated critical Sr concentration of $x \approx 0.18$ for the appearance of ferromagnetism in $La_{1-x}Sr_xCoO_3$ [35].

It is interesting to note that the FM ordering peak appears for the non-stoichiometric $La_{0.8}Sr_{0.1}CoO_3$ sample, at a Sr concentration *below* the supposed cut-off point of x = 0.18. The fact that this peak does not appear for the stoichiometric sample with the same Sr concentration, $La_{0.9}Sr_{0.1}CoO_3$, strongly indicates that a sub-stoichiometric La concentration enhances the ferromagnetic order associated with $T_c = 250$ K. Caciuffo *et al* found a small ferromagnetic peak for $La_{0.9}Sr_{0.1}CoO_3$ as well [8], indicating that the amount of ferromagnetic correlations varies within the same Sr concentration, likely as a function of synthesis or of phase separation into Sr-rich and La-rich regions.

Another correlation which can be seen in these fits is that the FM peak at $22.2°$ is always accompanied by the strong CoO AFM peak. This does not imply that they are of the same origin, however, as the CoO peak appears around 290 K, while the LSCO FM peak appears around 250 K (as seen with neutron scattering).

Nonetheless, this may indicate the presence of CoO on the surface of the LSCO, possibly as a consequence of the reduced coordination. Clearly, although there is not enough CoO to produce significant structural peaks, there is enough to order magnetically. It is easy enough to extend the possibility of surface reconstruction forming CoO on the surface of the LCO samples, where the magnetic ordering may have an effect on the magnetization of the LCO lattice. As a side note, it is difficult to disentangle the effects of CoO and $Co_3O_4$ on the $La_wCoO_3$ samples, as both Co phases are frequently seen together. CoO exhibits a stronger magnetic peak, but the structure and weight percentage of the $Co_3O_4$ phase are more easily refinable. In addition to this, CoO can revert back to $Co_3O_4$ at room temperature [71]. Indeed, the surface reconstruction into CoO could also be into $Co_3O_4$.

## 5.3   Bulk Lattice Parameters

Figure 5.11 shows the $La_wCoO_3$ lattice parameters and related values over a temperature range of approximately $5 < T < 300$ K. $a$ and $c$ are the hexagonal lattice parameters, the Co-O bond length corresponds to that in the $CoO_6$ octahedra, and the Co-O-Co bond angle can be thought of as the angle between adjacent octahedra. Due to a "buckling" effect of the octahedra, the Co-O-Co angle is around 163° instead of the expected 180° for perfectly aligned octahedra. In the $La_{1-x}Sr_xCoO_3$ samples, Sr doping past x = 0.5 results in the formation of a cubic Brownmillerite phase of $Sr_2Co_2O_5$, in which the Co-O-Co angles revert to 180° [94]. The oxygen position is also a measure of the octahedral buckling - in a cubic cell, the position would be 0.5. Figure 5.12 illustrates this distortion of the unit cell. Note that it is not the octahedra themselves which are distorting, but rather their relative alignments.

The parameter $\delta y$ is defined as $\delta y = \frac{d}{a}\cos(\gamma/2)$, where $d$ is the Co-O bond length and $\gamma$ is the Co-O-Co bond angle. $\delta y$ is another quantity relating to the deviation of the oxygen position from the straight line connecting Co ions. It is

FIG. 5.11: Lattice parameters and related values for $La_w CoO_3$ calculated using the FullProf refinement suite with neutron diffraction data over the temperature range $5 < T < 300$ K. From left to right, the top row shows the hexagonal lattice parameters $a$ and $c$, the middle row shows the Co-O bond length and the Co-O-Co bond angle, and the bottom row shows the oxygen position in the unit cell and the rhombohedral distortion parameter $\delta y$.

FIG. 5.12: Example LSCO unit cell showing the buckling of the $CoO_6$ octahedra (only one full octahedron is shown). The numbers 1, 2, and 3 indicate different possible positions of the oxygen atoms. Image is from Ref. [92]

thus an excellent measure of the rhombohedral distortion [17, 19, 95]. Because $d$ varies by less than 0.5% for $5 < T < 300$ K, $\delta y$ closely correlates with $\gamma$. A smaller $\delta y$ correlates with enhanced FM interactions due to the straightening of the Co-O-Co bonds that allow increased overlap of the O $2p$ and the Co $3d$ and $4p$ orbitals [18, 19, 96, 97]. Although $\delta y$ and the Co-O-Co angle are each measures of the lattice distortion, it is instructive to include both because both are used as a structural indicator of ferromagnetic order in various works.

As can be seen in Fig. 5.11 for all samples, the $a$ and $c$ lattice parameters both increase significantly for T $> 40$ K while remaining nearly constant for T $\leq 40$ K. The sample and data for w $= 1.0$ were done over a finer range of temperature as well as averaged over multiple measurements. The w $= 1.0$ sample has the smallest unit cell as defined by the lattice parameters, while the w $= 0.8$ sample has the largest unit cell. The values of the lattice parameters are close to those found for $LaCoO_3$ by other authors [12, 98].

Considering trends across all of the parameters, it can be seen that in addition to having the smallest unit cell, the w $= 1.0$ sample also has the smallest $CoO_6$ octahedra and the largest rhombohedral distortion (keeping in mind that the paramaters measured are *averages* over the entire structure). As previously noted, an increase in the rhombohedral distortion corresponds to a decrease in the

ferromagnetic order - however, the w = 1.1 has less magnetization than the w = 1.0, as will be seen in the magnetometry measurements. In addition to this, one would also expect the w = 0.7 sample to have the least rhombohedral distortion because it has the largest ferromagnetic moment out of all the $La_wCoO_3$ samples. Instead, its parameters more closely align with those of the w = 1.1, and the w = 0.8 is the one with the least distortion. The w = 0.9 is in the position one might expect, that is, a slightly larger unit cell and a slightly smaller rhombohedral distortion than the w = 1.0 sample.

It is also notable that when looking at each parameter, the samples stay in more or less the same order (e.g. the w = 0.9 sample is always between the w = 1.0 and w = 0.8 sample). However, there are slight shifts within this order: with regards to $a$ and $c$, the w = 0.7 sample matches closely with the w = 0.9; with regards to the oxygen position, Co-O-Co bond angle, and $\delta y$ (keep in mind these are all correlated, so this grouping is not surprising), w = 0.7 matches more with w = 1.1. As to the Co-O bond length, w = 0.7, 1.1, and 0.9 are all very close together.

In short, the lattice parameters do not vary monotonically with $Co_3O_4$ amount. One might expect that more $Co_3O_4$ - LCO interfaces would lead to larger regions of strained LCO, hence causing the $a$ and $c$ parameters to either expand or contract accordingly. It is a possibility that adding excess $Co_3O_4$ to a sample results in a variation of lattice parameters that depends on the amount of $Co_3O_4$-LCO interfaces and $Co_3O_4$ crystal sizes in a particular sample. In further experiments, variations within samples with the same initial stoichiometry could be quantified in order to determine whether the lattice parameters shown here depend strictly on the $Co_3O_4$ amount.

Another more insidious possibility for the lack of w-related trend in the lattice parameters is that the refinement conditions in FullProf are themselves affecting the calculated parameters. It was noticed that including the CoO phase in the refinement affected the weight fraction of the $Co_3O_4$ phase more than would be

expected by simple proportionality (as a result, the CoO phase was only included when there were significant CoO structural peaks, as in the case of $La_{0.8}Sr_{0.1}CoO_3$ and $La_{0.65}Sr_{0.25}CoO_3$). In order to determine whether or not the presence of the $Co_3O_4$ phase in the w = 0.7 through 1.0 samples was affecting the lattice parameters, refinements were done both with and without the phase. A maximum difference of 0.04% was found between the two types of refinements, and the refinements without $Co_3O_4$ were consistently found to have slightly smaller lattice parameters than those with the phase. However, these differences did not affect the sample parameters relative to other paramaters (e.g. if sample A had a larger $a$ than sample B, this did not change whether the CoO phase was included or not).

As mentioned, the order of the samples stays nearly static for each parameter - this also begs the question as to whether $a$, $c$, and the oxygen position are correlated, either in the calculation by FullProf or in the lattice itself. These results seem to indicate that the LCO lattice expands along both $a$ *and* $c$ as the temperature increases, and that the octahedra begin to straighten out (as indicated by the oxygen position nearing 0.5). As will be seen, this ordering does not hold nearly as well for the LSCO samples, leading to the conclusion that the Sr-doped lattice expands in a different manner than the LCO lattice.

Figure 5.13 shows the lattice parameters of $La_wSr_xCoO_3$ as a function of temperature, as determined by Rietveld refinements of the neutron scattering data. The $LaCoO_3$ data are also shown for comparison. All of the samples exhibit an expansion of the lattice and related paramaters with temperature, although only the $La_{0.9}Sr_{0.1}CoO_3$ sample has the sharp increase near $T \approx 40$ K. The other Sr-doped samples have much smoother thermal expansion behavior. This was also noted by Asai *et al* [7], and fits to this behavior will be discussed in a subsequent section, though we do note here that the anomalous thermal behavior only appears in the samples without the ferromagnetic ordering Bragg peak at $T_c = 250$ K.

The $a$ and $c$ lattice parameters, unlike the $La_wCoO_3$ parameters, do not show

FIG. 5.13: Lattice parameters and related values calculated using the FullProf refinement suite on neutron diffraction data for $La_wSr_xCoO_3$ over the temperature range $5 < T < 300$ K. From left to right, the top row shows the hexagonal lattice parameters $a$ and $c$, the middle row shows the Co-O bond length and the Co-O-Co bond angle, and the bottom row shows the oxygen position in the unit cell and the rhombohedral distortion parameter $\delta y$.

a consistent ordering of the samples. For example, although $La_{0.65}Sr_{0.25}CoO_3$ has the lowest $a$ parameter, it has a middling $c$ parameter compared to the other samples. The $c$, Co-O-Co angle, oxygen position, and $\delta y$ parameters all have roughly the same sample ordering. The $La_{0.65}Sr_{0.25}CoO_3$, $La_{0.75}Sr_{0.25}CoO_3$, and $La_{0.7}Sr_{0.3}CoO_3$ all have the least octahedral twisting as indicated by the oxygen position and the larger Co-O-Co bond angle, whereas the $La_{0.9}Sr_{0.1}CoO_3$ sample has a rhombohedral distortion much closer to that of the $LaCoO_3$. The $La_{0.8}Sr_{0.1}CoO_3$ is intermediate between the two groups. These sample groupings correspond closely with the amount of ferromagnetic ordering in each group: both the $LaCoO_3$ and $La_{0.9}Sr_{0.1}CoO_3$ samples lack an FM ordering peak, while the $La_{0.65}Sr_{0.25}CoO_3$, $La_{0.75}Sr_{0.25}CoO_3$, and $La_{0.7}Sr_{0.3}CoO_3$ group exhibit relatively large FM Bragg peaks. The $La_{0.8}Sr_{0.1}CoO_3$ sample has a middling angle and distortion compared to the other two groups, and a small FM ordering peak. It is hence inferrable that the Co-O-Co angle and rhombohedral distortion are excellent indicators of whether or not the $T_c \approx 250$ K ferromagnetic transition takes place in an LSCO sample. Here, we can use the parameter $\delta y$ as the critical parameter for this transition, as it includes both the Co-O-Co angle and oxygen position. We note that although the $a$ parameter and the Co-O bond length correlate fairly well with each other, they are not good indicators of the 250 K FM ordering.

As $Sr^{2+}$ replaces $La^{3+}$ in the $LaCoO_3$ lattice, the lattice expands, which has been attributed to the lower ionic charge of the $Sr^{2+}$ [94]. When comparing the $La_w CoO_3$ lattice parameters to those of $La_w Sr_x CoO_3$, the lattice expansion is only seen in the $c$ parameter, where the length of $c$ increases with x (though the $La_{0.75}Sr_{0.25}CoO_3$ sample has a larger than expected $c$ compared to the other samples). The $a$ parameter does not show a monotonic trend for x $\geq$ 0.1, which is in contrast to the systematic structural measurements done by Mineshige $et$ $al$ [92]. Their study found that $a$ at room temperature had a slight initial increase from x = 0 to 0.05, then decreased from 5.453 Å to 5.433 Å as x increased from 0.05 to 0.3, with a sharp drop between 0.2 and 0.3. However, when looking at

the behavior of $a$ and the Co-O bond length for $0 \leq x \leq 0.3$, a qualitative similarity is seen between our data and that of Mineshige. Both parameters show an increase from x = 0 to x = 0.1 or 0.25, then a decrease for x = 0.3. It appears that, unlike the monotonic increase in $c$ with x, the $a$ and Co-O bond length go through a maximum. One might speculate that this maximum corresponds with the suggested point of ferromagnetic ordering, but more data are needed near this concentration for a viable hypothesis.

Also interesting is that the two sub-stoichiometric samples ($La_{0.8}Sr_{0.1}CoO_3$ and $La_{0.65}Sr_{0.25}CoO_3$) exhibit structural behavior consistent with that of a higher x. That is, $La_{0.8}Sr_{0.1}CoO_3$ has a larger $c$ and Co-O-Co angle than $La_{0.9}Sr_{0.1}CoO_3$; likewise for $La_{0.65}Sr_{0.25}CoO_3$ and $La_{0.75}Sr_{0.25}CoO_3$. This is consistent with the FM peak appearing in $La_{0.8}Sr_{0.1}CoO_3$ and not $La_{0.9}Sr_{0.1}CoO_3$, and leads us to conclude that a sub-stoichiometric Sr-doped material with extra $Co_3O_4$ has a structure more conducive for ferromagnetic ordering. Despite the fact that the LCO and LSCO samples have ferromagnetic order at different $T_c$ and exhibit different values for $\delta y$, in *both cases* the presence of $Co_3O_4$ and/or CoO appears to enhance ferromagnetic order.

Recalling the interpretation by Androulakis *et al* [29], this is also consistent with the presence of La-vacancies caused by a sub-stoichiometric amount of $La^{3+}$ in the starting materials. These vacancies could introduce holes into the LCO system in the same manner as $Sr^{2+}$ doping, as a result of the new charge imbalance in LCO or LSCO. These mobile holes could then act as carriers, providing an enhanced mechanism for itinerant magnetism in the system, thus increasing the amount of ferromagnetism. The presence of La-vacancies is not likely, however, given the large amount of crystalline $Co_3O_4$ seen in the system. If La-vacancies were spread throughout the LCO/LSCO lattice, the system would likely remain single phase LCO/LSCO without the formation of a $Co_3O_4$ phase; nonetheless, we cannot rule out the presence of some La-vacancies in our material.

FIG. 5.14: Fit to the rhombohedral lattice parameter of $La_{0.92}Sr_{0.8}CoO_3$ using Eq. 5.1, as compared to data from $LaCoO_3$. Image and data are from Ref. [7].



FIG. 5.15: Fit to the rhombohedral lattice parameter $a_r$ of $La_{1-x}Sr_xCoO_3$ using Eq. 5.1, for x = 0.10, 0.15, 0.20, and 0.25. Image and data are from Ref. [8].

## 5.4   Fits to the Lattice Parameters

As previously mentioned, the temperature dependence of the $a$ and $c$ parameters is unusual in $La_wCoO_3$, and does not correspond to the expected thermal expansion for an insulating solid. To our knowledge, this was first noted by Asai *et al*, who were able to successfully fit the thermal expansion of the $La_{0.92}Sr_{0.08}CoO_3$

rhombohedral lattice parameter, $a_r$ (Fig. 5.14). They employed the Grüneisen formulation using the Einstein model for specific heat,

$$y(T) = y_0 \left[ 1 + \alpha T_E \left( \coth \left( \frac{T_E}{2T} \right) - 1 \right) \right] \quad , \tag{5.1}$$

where $y(T)$ is the lattice parameter, $y_0$ is the parameter at $T = 0$, $T_E$ is the Einstein temperature, and $\alpha$ is the thermal expansion coefficient for $T >> T_E$ [7]. Asai *et al* found a $T_E = 246$ K and $\alpha = 1.75 \times 10^{-5}$, which are consistent with $T_E$ for other perovskites [99] and $\alpha$ for other solids [100]. However, they were not able to fit the data for $LaCoO_3$ due to the anomalous expansion near 50 K. Caciuffo *et al* fit their data for the $a_r$ of $La_{1-x}Sr_xCoO_3$ (x = 0.10, 0.15. 0.20, 0.25) using this model, and found good agreement up through $T_c = 250$ K (Fig. 5.15) [8]. Above 250 K, the lattice parameters grew faster than predicted by Eq. 5.1. The $T_E$ and $\alpha$ found by Caciuffo *et al* range from $140 \leq T_E \leq 160$ K and $5 \times 10^{-6} \leq \alpha \leq 17 \times 10^{-6}$, where both parameters decrease as x is increased. In both studies, it can clearly be seen that as x decreases, $a_r$ near 50 K exhibits sharper and sharper increases. This sharp rise in lattice parameter can be seen in all of our $La_wCoO_3$ samples, as well as in our $La_{0.9}Sr_{0.1}CoO_3$. We attempted to model our data for $LaCoO_3$, first with the Grüneisen fit and then with a power-law fit. The latter appears to better account for the rapid expansion near 40 K.

The derivation for Eq. 5.1 was not made clear in either of the works by Asai or Caciuffo, and so will be laid out here prior to the discussion of the fit results. We first begin with the equation for the thermal expansion coefficient $\alpha_y$ for a one-dimensional lattice parameter $y$,

$$\alpha_y = \frac{1}{y_0} \left( \frac{dy}{dT} \right). \tag{5.2}$$

Separating the variables, we obtain

$$\alpha_y dT = \frac{dy}{y_0}. \tag{5.3}$$

Here it is important to note that $\alpha_y$ will not be constant over the entire temperature range. Rather, at low temperatures it will have a $T^3$ dependence, and at high temperatures it will reach a constant value proportional to the high-temperature specific heat. This can be seen when we write $\alpha_y$ in the form given by Ashcroft and Mermin [100],

$$\alpha_y = \frac{\gamma c_v}{3B},$$

(5.4)

where $\gamma$ is the Grüneisen parameter (hence this expression for $\alpha_y$ is referred to as the Grüneisen formulation), $B$ is the temperature-independent bulk modulus, and $c_v$ is the Einstein model for the specific heat at constant volume. For perovskites, $\gamma \approx 2$ [98], a value which was glossed over in the studies by Asai and Caciuffo. It is possible that both groups assumed the typical value of $\gamma = 1$, which may partially account for the discrepancies between our fits and theirs [100].

We can write $c_v$ as the derivative of the temperature-dependent portion of the internal energy $U$,

$$
\begin{aligned}
c_v &= \left(\frac{\partial U}{\partial T}\right)_V \\
&= 3Nk_B\left(\frac{T_E}{T}\right)^2 \frac{e^{T_E/T}}{(e^{T_E/T}-1)^2},
\end{aligned}
$$

(5.5)

where N is the number of atoms and $k_B$ is the Boltzmann constant. The Einstein temperature is defined as $T_E = \hbar\omega/k_B$, where $\omega$ is the oscillation frequency of the atoms. Returning to Eq. 5.3, we integrate both sides to obtain

$$\int \alpha_y(T)dT = \int_{y_0}^{y} \frac{dy}{y_0},$$

(5.6)

from which a standard equation for the change in $y$ with temperature follows,

$$y = y_0\left(1 + \int \alpha_y(T)dT\right).$$

(5.7)

Plugging in Eq. 5.4 with $\gamma = 2$, we obtain

$$
\begin{aligned}
y &= y_0 \left( 1 + \frac{2}{3B} \int c_v dT \right) \\
&= y_0 \left( 1 + \frac{2}{3B} \int \frac{\partial U}{\partial T} dT \right) \\
&= y_0 \left( 1 + \frac{6Nk_B T_E}{3B} \frac{1}{e^{T_E/T} - 1} \right).
\end{aligned}
\tag{5.8}
$$

After some manipulation of the exponentials, the form of Eq. 5.1 can be seen,

$$
y = y_0 \left[ 1 + \frac{Nk_B T_E}{B} \left( \coth\left( \frac{T_E}{2T} \right) - 1 \right) \right].
\tag{5.9}
$$

Using the fact that the high temperature limit of $c_v$ is $3Nk_B$ and that at high temperatures $(T \gg T_E)$, $\alpha_y$ is a constant, we have

$$
\alpha_y = \frac{c_v}{3B} = \frac{Nk_B}{B}.
\tag{5.10}
$$

The original equation,

$$
y(T) = y_0 \left[ 1 + \alpha_y T_E \left( \coth\left( \frac{T_E}{2T} \right) - 1 \right) \right],
\tag{5.11}
$$

is then recovered.

Equation 5.11 proves inadequate for describing the behavior of any of our LCO lattice parameters; the abrupt change in slope near 40 K was particularly problematic because the Grüneisen-Einstein model smoothly increases with temperature. This discrepancy of LCO with the expected thermal expansion model might be explained in two ways. The first is to assume that the Grüneisen model has the correct idea, but needs additional modifications to account for other effects on the lattice parameters. The second is to interpret the sharp rise as a second-order phase transition in the structure, which would be fit more adequately by a power law.

FIG. 5.16: Plot by Radaelli and Cheong showing the contributions of phonons (Grüneisen model), a thermal spin-state transition, and oxygen vacancies to the linear lattice expansion $\alpha$. Image and data are from Ref. [98].

Radaelli and Cheong [98] chose to expand on the Grüneisen model in their examination of the lattice expansion $\alpha$ of LaCoO$_3$, incorporating the effects of oxygen vacancies and a thermal spin-state transition in addition to the Grüneisen model's phonon contribution. Their plot showing each contribution is reproduced in Fig. 5.16; notably, the data examined by these authors cover a much larger range of temperatures and broader sampling of $T$. In their paper, the Debye-Grüneisen model for thermal expansion is used rather than the Einstein-Grüneisen model. The Debye model for the specific heat allows for a continuous spectrum of the vibrational frequencies $\omega$ of the atoms in the solid, rather than assuming all of the frequencies are identical (as in the Einstein model). As such, the Debye specific heat has a gentler increase at low temperatures, and better fits experimental data in general [101]. However, over the ranges examined by Asai and Caciuffo, the Debye model would likely make little difference given that the Einstein model already fits well for x $\geq$ 0.08. When considering the x = 0 case, the Debye model would not account for the sharp rise at 40 K, as it is qualitatively similar in shape to the Einstein model.

Oxygen vacancies were noticeable in samples used in the Radaelli study, ranging from 98% to 95% stoichiometric as the measurement temperature was in-

creased. The stoichiometry at low temperatures is comparable to that found by Mineshige *et al* for similar Sr doping amounts [92]. With respect to the lattice expansion coefficient, the contribution of oxygen vacancies in their model only becomes meaningful above 800 K and thus the effect is expected to be minimal for the $10 \leq T \leq 300$ K range we examined.

Essentially, only the thermal spin-state transition portion of the expansion coefficient is relevant to our analysis. The interpretation by Radaelli and Cheong is based on a transition from the low spin $Co^{3+}$ state ($S = 0$) to the intermediate spin ($S = 1$) and subsequently high spin ($S = 2$) states. The ionic radius increases with $S$, and the lattice expansion is believed to correspond to this increase. As indicated by their fits, this model works well over their temperature range and effectively accounts for the anomalous portion of $\alpha$ up until 800 K. However, it is difficult to determine the accuracy of this fit in the 40 K range due to the broad temperature sampling. A larger issue is that the fits assume a large Jahn-Teller energy associated with the intermediate spin state - that is, no orbital degeneracy. However, no evidence of a significant Jahn-Teller distortion has been found in zero field measurements, and EXAFS experiments by Jiang *et al* demonstrate a lack of variation in the Co-O bond length [28]. Note that this does not preclude the existence of such a distortion, just that any distortion will either be small or confined to a few sites.

In summary, the Radaelli model for the thermal lattice expansion parameter yields good fits over a wide temperature range, but needs to incorporate more recent results indicating the absence of a large/widespread Jahn-Teller distortion. A further study examining the accuracy of this model at low temperatures ($10 \leq T \leq 300$ K) and at finer sampling would be an interesting future project.

In contrast to the fits done using the Grüneisen-Einstein model (Fig. 5.17), at temperatures above 40 K, the $a$, $c$, Co-O-Co angle, and $\delta y$ parameters are well described by a simple $(T - T_o)^\sigma$ power-law, as seen in Table 5.2 and Fig. 5.18. This implies that the sudden increase in lattice parameters for $LaCoO_3$ may correspond

FIG. 5.17: Lattice parameters $a$, $c$, $\delta y$, and the Co-O-Co angle for LCO. Solid curves represent fits corresponding to the Gruneisen-Einstein model (Eq. 5.1). Error estimates are shown and are significantly smaller than the systematic deviations of the data from the fits for the $a$ and $c$ parameters. The inset in panel (d) expands the region near $T_o$ for $c$ vs $T$.



FIG. 5.18: Lattice parameters $a$, $c$, $\delta y$, and the Co-O-Co angle for LCO. Solid curves represent power-law behavior $(T - T_o)^{\sigma}$ for $T > T_o$, and the dashed lines represent linear behavior for $T < T_o$. The inset in panel (d) expands the region near $T_o$ for $c$ vs $T$.

TABLE 5.2: The fits to the lattice parameters using the equation $y = A(T - T_o)^\sigma + B$, where $T_o = 37$ K (K) is the transition temperature determined by the best overall fits and $y$ corresponds to the lattice parameter being fit. These fits correspond to those shown in Fig. 5.18. $A$, $B$, and $y$ have units appropriate to the parameters being fit, The errors on all the $A$ and $\sigma$ are at most 2% of the values given for the parameters. Errors on $B$ are given in the table.

| Parameter | $A$ | $\sigma$ | $B$ |
|---|---|---|---|
| a | $2.08 \times 10^{-4}$ | 0.83 | 5.396(1) |
| c | $6.95 \times 10^{-4}$ | 0.91 | 12.92(1) |
| $\delta y$ | $-1.73 \times 10^{-5}$ | 0.86 | 0.0529(1) |
| Co-O-Co | $6.07 \times 10^{-3}$ | 0.85 | 162.84(1) |

to a second-order structural phase transition with a critical temperature $T_o \approx$ 40 K. The full form of the fitting equation used is

$$y = A(T - T_o)^\sigma + B, \qquad (5.12)$$

where A and B are constants, and $\sigma$ is the structural transition critical exponent. $T_o = 37(2)$ K is the best overall fit to the transition temperature. The behavior below $T_o$ is well described by a linear fit in each case. To the author's knowledge, a phase transition of this type has not yet been proposed in the literature. It is an unusual transition, in that the lattice appears to be nearly "frozen" - the lattice parameters change very little - *below $T_o$ = 37 K*. Above this temperature, the parameters increase quickly, exhibiting the power law behavior fit. Remarkably, this abrupt increase occurs for *all* of the $La_wCoO_3$ samples.

Figure 5.19 shows the power-law fit and the Grüneisen-Einstein (GE) fit for the change in the $a$ lattice parameter with $T$ for each w sample and $La_{0.9}Sr_{0.1}CoO_3$. The parameters found by Asai *et al* for $La_{0.92}Sr_{0.08}CoO_3$ were used as a starting point, with poor results. Fits using $T_E \approx 240$ K drastically underestimate the curvature at 37 K, while fits using $\alpha \approx 1.7 \times 10^{-5}$ significantly overestimate the

FIG. 5.19: Fits to the $a$ lattice parameter for all $La_wCoO_3$ and the $La_{0.9}Sr_{0.1}CoO_3$ samples. "Power fit" refers to fits done using a power law (Eq. 5.12), and "Grun fit" is an abbreviation referring to fits done using the Grüneisen-Einstein model (Eq. 5.11). Efforts were made to best fit the lowest $T$ data with the Grüneisen-Einstein model, as these gave the values of $T_E$ closest to those expected in the literature (nonetheless, they were still too low to match completely).

89

TABLE 5.3: Fits to the $a$ lattice parameter for all $La_wCoO_3$ and $La_{0.9}Sr_{0.1}CoO_3$ using the equation $y = A(T - T_o)^\sigma + B$. These fits correspond to those shown in Fig. 5.19. Errors for $A$ and $B$ are approximately $\pm 1$ of the smallest significant digit, while the error for $\sigma$ is $\pm 2$ of the smallest significant digit, and that for $T_o$ is given in the table.

| w | $A$ $(10^{-4}\ \frac{\text{Å}}{K})$ | $T_o$ | $\sigma$ | $B(\text{Å})$ |
|---|---|---|---|---|
| 1.1 | 2.30 | 34(3) | 0.85 | 5.4135 |
| 1.0 | 2.08 | 37(2) | 0.83 | 5.3960 |
| 0.9 | 2.15 | 35(3) | 0.83 | 5.4047 |
| 0.8 | 2.80 | 34(3) | 0.80 | 5.4185 |
| 0.7 | 2.37 | 32(3) | 0.84 | 5.4050 |
| 0.9, x=0.1 | 2.14 | 38(3) | 0.81 | 5.4215 |

slope of the data above 150 K. The best fits for the $La_wCoO_3$ were obtained with $60 \leq T_E \leq 110$ K and $8.0 \times 10^{-6} \leq \alpha_y \leq 9.4 \times 10^{-6}$, while that for $La_{0.9}Sr_{0.1}CoO_3$ had $T_E = 120$ K and $\alpha_y = 7.3 \times 10^{-6}$. In all cases, the curvature of the GE fit could not be made to match that of the data both above and below 37 K. To compare, Fig. 5.17 shows GE fits which match the high $T$ data, while the GE fits in Fig. 5.19 better match the data below $T_o$. The latter fits gave higher values of $T_E$, which are more consistent with the theory. Nevertheless, all of our values for $T_E$ were too low to be plausible and did not agree with the values found in Ref. [99]. Although the small $\alpha_y$ is within the realm of Caciuffo's results, it is two to three times lower than the $\alpha_y$ they reported for $LaCoO_3$. Comparing the $\alpha_y$ found here for $La_{0.9}Sr_{0.1}CoO_3$ and $La_wCoO_3$, we see that the trend seen by Caciuffo of $\alpha_y$ decreasing as Sr concentration increases still holds.

Table 5.3 shows the power law fit parameters for the $a$ vs. $T$ data for all $La_wCoO_3$. Although the fitting was done as consistently as possible, the lack of data near the 37 K transition made it difficult to precisely fit $T_o$. Regrettably, time constraints limited our ability to take extensive data nearer to this transition. The data for $LaCoO_3$, however, were able to be taken multiple times at smaller $T$

FIG. 5.20: Model of the SrTiO$_3$ (001) plane in the cubic phase above $T_c = 105$ K (a) and in the tetragonal, "buckled" phase below $T_c = 105$ K (b). Image taken from Ref. [102].

intervals, lending greater confidence to the $T_o = 37$ K result. The linear fits below $T_o$ were not done for any of the samples aside from w $= 1.0$, as there were only a couple of data points in this temperature range. Overall, the power-law fits are in good agreement with the data, although there are still some small discrepancies with the curvature at low $T$ and high $T$. The fit for $50 \leq T \leq 150$ K tends to undershoot the data while overshooting the higher temperature points. This is not strictly a consistent issue across all data sets, and again the broad $T$ sampling makes it difficult to assess the quality more quantitatively.

## 5.5   Physical Implications of Power-Law Behavior

While the power-law fit works quite well for modeling the parameters, the implications for the physics of the system are not so clean-cut. As was noted, the $a$, $c$, Co-O-Co angle *and* the Co-O bond length all exhibit this power-law behavior. Although we do not see a change in symmetry accompanying the transition at 40 K in LCO, and there are no sharp discontinuities in the parameters, the power-law behavior brings to mind a first order structural transition of the type seen in the perovskite SrTiO$_3$. The structure in this material abruptly changes from cubic to tetragonal as the temperature is lowered through 105 K [102, 103]. In other words, the straight line between the TiO$_6$ octahedra undergoes buckling as the transition temperature is neared, as can be seen in Fig. 5.20. In addition to the octahedra

91

buckling dynamically ("librating"), the Ti atom also oscillates around its position in the $TiO_6$ octahedra, resulting in a dynamic Jahn-Teller distortion [104]. Below the structural transition temperature, these positional and rotational distortions are frozen in. This is indicated by the lowering of the anharmonic frequency of one of the phonon modes as the temperature decreases towards the transition point; at the transition temperature, the frequency goes to zero and the mode "freezes out" [104, 105].

Any Jahn-Teller distortion in the $LaCoO_3$ would have to be very small (e.g. a change in the Co-O bond length of 0.03 Å or less) or, in the case of a dynamical distortion, very high frequency. The latter possibility is ruled out by EXAFS measurements, which can detect frequencies even higher than what would be expected from a dynamical distortion [28]. However, as mentioned in the paper by Abramov *et al*, there can be more than one type of distortion in perovskites; these include a Jahn-Teller distortion resulting from the displacement of the octahedral cation (Ti or Co), and a rotation of the octahedra caused by lattice instability from the modified Ti-O (or Co-O) bond [104]. A small Co-O Jahn-Teller distortion, accompanied by octahedral tilting in $LaCoO_3$ and its related compounds could be the cause of the structural phase transition. As was noted, this type of transition in $SrTiO_3$ was accompanied by phonon mode softening. Yamaguchi *et al* did find anomalous phonon modes in $LaCoO_3$; between 30 and 50 K, three extra phonon modes at 0.035, 0.05, and 0.073 eV appear in the optical spectrum (Fig. 5.21) [106]. The anomalous behavior of these modes was said to result from local lattice distortions, although a detailed analysis is only done for the highest energy mode corresponding to the stretching of the Co-O bonds The modes studied by Yamaguchi do not show the frequency decrease and subsequent freezing as in the studies on $SrTiO_3$, however, this does not preclude a more detailed, higher resolution study from finding this effect (to the knowledge of the author, none have been done at the time of writing).

Clues to the origin of the structural phase transition and its relation to the

FIG. 5.21: Optical phonon spectra for a single crystal of $LaCoO_3$ at different temperatures (offset for clarity). $\epsilon_2$ represents the intensity of the phonon mode. The three arrows indicate the anomalous phonon modes at 0.035 eV, 0.05 eV, and 0.073 eV which appear between 30 and 50 K. Image taken from Ref. [106].

surfaces and interfaces can also be found via comparison between the $La_wCoO_3$ and the $La_wSr_xCoO_3$ lattice parameters. The fact that the thermal expansion of $La_{0.9}Sr_{0.1}CoO_3$ better fits to a power law, while that of $La_{0.8}Sr_{0.1}CoO_3$ is more consistent with the GE model indicates that La stoichiometry plays a role in the structural behavior of the system. On the whole, material with Sr homogeneously distributed throughout (at least, homogeneously enough to result in ferromagnetic ordering at 250 K throughout the material) follows the expected GE thermal expansion. This is likely due to the Sr ions contributing strain throughout the lattice. As such, octahedra which can ordinarily tilt in a $LaCoO_3$ lattice may now tilt less due to the $Sr^{2+}$ ion slightly expanding the unit cell [94]. This expansion appears to occur mainly along the $c$ axis, as $a$ and the Co-O bond length are similar between the LCO and LSCO compounds, whereas $c$ is consistently larger for $La_wSr_xCoO_3$. Comparison of the Co-O-Co bond angle between the two types of compounds confirms that material with more Sr exhibits a larger angle.

On the contrary, material with an La-deficiency - that is, extra $Co_3O_4$ crystals

in the sample - has strain which is definitely not homogeneous. As found by multiple thin film studies [38, 47, 107], the LCO lattice is strained when it is deposited on a substrate with a different lattice parameter. In the case of films deposited on $(LaAlO_3)_{0.3}(SrAl_{0.5}Ta_{0.5}O_3)_{0.7}$, the effects of tensile strain persist over 100 nm away from the substrate [47]. It is thus conceivable that the $Co_3O_4$ crystals are straining the surrounding LCO lattice in a manner similar to that of a substrate. Clearly, there are significant differences between the two types of strain: $Co_3O_4$ does not have a lattice parameter comparable to that of $LaCoO_3$, their space groups are different, and the $Co_3O_4$ is in the form of a crystal rather than a flat substrate. However, given the susceptibility of the behavior of $LaCoO_3$ to even tiny defects in the crystal structure (e.g. La vacancies [29] or Sr dopings with $x = 0.002$ [14]), it is quite reasonable to assume that the presence of a relatively large $Co_3O_4$ crystal would have notable effects on the lattice. Also of note is the similarity of the $CoO_6$ octahedra in $Co_3O_4$ and LCO (though $Co_3O_4$ has $CoO_4$ tetrahedra as well); the Co-O bond length in the former is 1.91 Å as compared to 1.92 Å in the latter. We may then speculate that the two materials could share octahedra, although it is difficult to demonstrate this with any certainty.

At any rate, the strain induced by $Co_3O_4$ crystals embedded in the lattice could potentially penetrate up to 100 nm (though given the irregular shape of the crystal, may have effects somewhat less far-reaching), which is a significant portion of a bulk particle approximately 5000 nm in diameter. As such, samples with an extra $Co_3O_4$ phase would have two types of lattice strain: one in the region far from the interfaces, where the octahedra are free to tilt, and the other nearer to the interfaces, where strain may be increasing the angle between the octahedra, reducing their freedom of motion. One may of course ask why the strain is necessarily increasing the Co-O-Co bond angle rather than decreasing it. After all, the Co-O-Co angle does not follow any monotonic increase with w, as can be seen in the $La_wCoO_3$ lattice parameter measurements (Fig. 5.11). The answer lies in the magnetism data for $La_wCoO_3$; as w decreases, the ferromagnetic

moment becomes larger and more robust with field (this is discussed in more detail in the section on magnetometry). The w = 1.1 sample, however, has very little $Co_3O_4$ and correspondingly a small ferromagnetic moment. Strong evidence has been found correlating an increase in the Co-O-Co bond angle with the appearance of ferromagnetic order [9]. Given that the only likely source of a Co-O-Co angle increase in the $La_wCoO_3$ materials is the presence of an extra phase - almost certainly $Co_3O_4$ - it is not unreasonable to conclude that the interface between the LCO and $Co_3O_4$ is the culprit.

It is unlikely that the strain induced by $Co_3O_4$ is of the same type as that induced by Sr. Although both will act to increase the Co-O-Co bond angle, the degree to which this parameter is affected is different. This is clearly seen when comparing the values for Co-O-Co angle between the $La_wCoO_3$ and $La_wSr_xCoO_3$ samples. The samples with the power-law lattice parameter behavior have bond angles with a maximum of $163.6°$ at room temperature, while those with GE behavior have bond angles with a minimum of $164.6°$ at 10 K, with the $x \geq 0.25$ samples clustering around $167°$. The ferromagnetic transition temperatures for the samples is also quite different, with $T_c = 87$ K for $La_wCoO_3$ and $T_c = 250$ K for $La_wSr_xCoO_3$ (where $T_c$ changes somewhat with x [13]). The higher $T_c$ for the latter indicates that the greater Co-O-Co angle and a strain that is more widespread throughout the lattice makes it easier for the system to order.

The $La_{0.9}Sr_{0.1}CoO_3$ is unusual in this regard, as the sample is nominally stoichiometric but the lattice parameters are best fit with the power law. In addition, the $La_{0.8}Sr_{0.1}CoO_3$, which *is* non-stoichiometric, does not exhibit the power-law behavior expected in the La-deficient samples. This issue is resolved however, when comparing the neutron scattering data for the two samples (Figs. 5.9 and 5.10). The $Co_3O_4$ peak is visible for $La_{0.9}Sr_{0.1}CoO_3$ but not for $La_{0.8}Sr_{0.1}CoO_3$, reinforcing the idea that the lattice strain associated with the structural phase transition is connected to the presence of $Co_3O_4$ crystals in the sample. It is unexpected that the $La_{0.9}Sr_{0.1}CoO_3$ has more $Co_3O_4$ than $La_{0.8}Sr_{0.1}CoO_3$. How-

ever, we also note that the latter sample has significantly more CoO, indicating that any $Co_3O_4$ was converted to CoO during the firing. It is not clear why this happened in one sample but not the other, as the firing processes were the same.

In summary, the neutron scattering data for the $La_wCoO_3$ and $La_wSr_xCoO_3$ phases are fit to the space group $R\bar{3}C$, and the accompanying $Co_3O_4$ phase is fit to $F\bar{4}3m$. The antiferromagnetic Bragg peak of CoO is prominent, but only in a few cases can the CoO phase be fit due to the low intensities of the structural peaks. Ferromagnetic ($T_c = 250$ K) and antiferromagnetic ($T_N = 40$ K) ordering peaks are seen for $La_wSr_xCoO_3$ and $Co_3O_4$, respectively. Rietveld refinements were done on all samples, and the temperature-dependent lattice parameters $a$ and $c$ were extracted, along with the Co-O bond length, the Co-O-Co bond angle, the oxygen position, and $\delta y$.

The lattice parameters exhibited different behavior depending on the Sr concentration and amount of $Co_3O_4$ in the sample. The first group, $La_wSr_xCoO_3$ showed the expected thermal expansion of a solid, in the manner of the Grüneisen formulation using the Einstein model of specific heat. The second group, $La_wCoO_3$ and $La_{0.9}Sr_{0.1}CoO_3$, showed unusual behavior which was better fit with a power law, indicating the presence of a structural phase transition at $T_o = 37(2)$ K. This phase transition was linked to the tilting of the $CoO_6$ octahedra, similar to the case for $SrTiO_3$. The different straining effects of $Co_3O_4$ crystals and Sr-doping on the LCO lattice were discussed, and we concluded that the Sr-doped samples have a larger strain (indicated by a larger Co-O-Co angle) which is more evenly spread throughout the lattice. The $Co_3O_4$-related strain, however, is more localized near the surfaces, allowing for two different regions within the LCO lattie. In the first, the lattice is far from the $Co_3O_4$ surface and is thus free to exhibit octahedral tilting and "freezing" below $T_o$. In the second, the strain from $Co_3O_4$ increases the Co-O-Co angle, allowing the system to exhibit weak ferromagnetic order at $T_c = 87$ K.

# 6 Magnetometry

The magnetic behavior of bulk and nanoparticle $La_wCoO_3$ and $La_wSr_xCoO_3$ samples was examined with SQUID magnetometry. Field cooled and zero field cooled measurements of the magnetization $M$ were taken for $10 \leq T \leq 300$ K at external fields 20 Oe $\leq H \leq$ 60 kOe. Zero field cooled hysteresis measurements tracked the dependence of $M$ on $H$ over ranges of $\pm 5$ kOe and $\pm 60$ kOe.

## 6.1 SQUID Magnetometer

An MPMS SQUID (Magnetic Property Measurement System using a Superconducting Quantum Interference Device) magnetometer was used for all magnetization measurements. The instruments at two locations were used, the first at Lawrence Berkeley National Labs with the aid of Corwin Booth, and the second at the Ramirez Lab at UC Santa Cruz, with the aid of Art Ramirez. A *dc* SQUID measures the magnetization of a sample via two Josephson junctions, which can detect very small changes in the magnetic flux. A SQUID consists of a loop of superconducting wire which is "broken" in two places by narrow strips of insulating material (the actual Josephson junctions). A schematic can be seen in Fig. 6.1. A current is still able to flow through the device, because superconducting electron pairs can tunnel across the junctions [108]. In order to measure the magnetization, a current is induced in the SQUID; in the absence of any changing external field or stray induced current, there will be no voltage drop across the device (as the resistance is zero). The current will split in two directions from the source $A$ (see red arrows in Fig. 6.1), travel through the junctions, and rejoin at $B$. Once the magnetic flux changes, an additional current (see green arrow in Fig. 6.1) will be induced in the SQUID in accordance with Faraday's Law. The induced current will travel either clockwise or counterclockwise around the superconducting loop - however, on one side of the loop it will *add* to the original current while on the

FIG. 6.1: A schematic of a Josephson junction device. The actual junctions, or insulating material, are indicated by thick black lines. The remainder of the device is made of superconducting material. A current $A$ splits (red arrows), flows through both sides of the junction, then recombines to make current $B$. Small changes in magnetic flux through the loop result in an induced current around the loop (green arrow), creating current variations in $A$ which can then be measured as changes in the voltage. Image from on Ref. [108].

other side it will *subtract* from the original current [108]. As such, there will be a phase difference between the currents on either side of the loop. When the currents recombine, the voltage detected will vary as a result of this phase difference, and the change in voltage will be proportional to the change in the magnetic flux.

The Josephson junction is sensitive enough to measure individual flux quanta, $\Phi_0$,

$$\Phi_0 = \frac{h}{2e} = 2.0678 \times 10^{-17} \ \ T \cdot m^2. \tag{6.1}$$

It is rarely required to measure magnetization this tiny, however. In the case

FIG. 6.2: The MPMS superconducting coils ("gradiometer") through which the sample is moved. The top and bottom loops are wound counterclockwise, while the two middle loops are wound clockwise. Image taken from Ref. [109].

of the SQUID magnetometer, the device is coupled via superconducting wires to a series of superconducting coils ("gradiometer") which the sample is passed through (Fig. 6.2). These coils are placed within the magnet, a superconducting solenoid, and wrapped around the sample chamber. As such, they can be cooled with liquid helium while the temperature in the sample chamber can be warmed or cooled separately. The primary reason for multiple, oppositely wound coils is to cancel out any magnetic noise that might occur. The detection coils will unfortunately pick up any drifting flux from the external magnet; however, the current induced in the top and bottom coils will cancel out that from the two middle coils. The sample's magnetic field is not cancelled, though, as the sample is moved through the coils one (or two) at a time [109].

Over time and multiple field changes, stray currents can build up in the detection coil, leading to noise in the magnetic measurements. In order to solve this, a small section of the coil can be heated during field changes to halt the superconductivity and remove the extra currents. A small remanent field was noticed in some of our data, which corresponds to a small magnetic field being trapped in the magnet after the magnet has been zeroed. Although this can be removed

99

by oscillating the field as it is reduced to zero, this method is only good to a few Gauss [109]. We took measurements down to 10 G, so the background field seen in these measurements may be due to this effect. This will not affect any of the $M(T)$ data analysis, as we primarily examine the changes in the sample's magnetization with $T$ at a constant $H$, where $H$ is simply adjusted by a few Gauss if an offset is noticed. Such an offset becomes apparent in the high-field data above the transition temperature, where the sample is paramagnetic and $M/H$ should be identical for all values of $H$. A small, non-zero $H$ may instead affect the $M$ vs $H$ measurements by shifting the hysteresis curve up or down slightly. Such an asymmetry is seen in our data, but it is on the order of $\leq 1$ G. This is not to be confused with the remanent field of the *sample*, as this depends on the material being examined and not on trapped fields in the magnet.

## 6.2   Magnetization M(H)/T of La$_w$CoO$_3$

Field cooled (FC) and zero field cooled (ZFC) magnetization data were taken at applied fields of 20, 200, 500, 2000, and 5000 Oe. In the Ramirez lab, $M(T)$ data were examined in the range $10 \leq T \leq 110$ K for La$_w$CoO$_3$ (w = 0.7, 0.8, 1.0, 1.1), and in the Booth lab in the range $10 \leq T \leq 300$ K for w = 1.0 and 0.9. Data collection varied with respect to the fields and temperatures examined for different samples, as data were taken over several years and each magnetometer had slightly different capabilities (e.g. the Ramirez magnetometer had difficulties warming up to 300 K and cooling back down again).

La$_w$CoO$_3$ $M/H$ data taken with FC are presented for 20 Oe in Fig. 6.3 and for 2 kOe in Fig. 6.4. In $H = 20$ Oe, the magnetic transition at $T = 87$ K becomes sharper as the amount of Co$_3$O$_4$ increases. The magnitude of the magnetization $M/H$ in general becomes larger as w decreases, although it does not saturate for any of the samples. At T = 10 K, the w = 0.7 sample exhibits the largest $M/H$ value, 0.42 emu·(mol·Oe)$^{-1}$, whereas the w = 1.1 has a value nearly ten

FIG. 6.3: $M/H$ vs $T$ FC data with H = 20 Oe for bulk $La_wCoO_3$ (w = 1.1, 1.0, 0.9, 0.8, and 0.7), while the inset shows the region near $T_C = 87$ K.

times smaller, 0.053 emu·(mol·Oe)$^{-1}$. As can be seen in the inset of Fig. 6.3, the increase in $M/H$ for all samples begins at T $\approx$ 92 K; in the plots containing FC and ZFC data (Fig. 6.7) the hysteresis between FC and ZFC also begins at this temperature. The cause of the rounding above $T_c$ depends on the type of magnetic order taking place. A truly ferromagnetic transition will be rounded in any field, as the critical point is at $H = 0$. The material will exhibit short-range order with an increasing correlation length above $T_c$, causing a slight increase in magnetization, but the correlation length will not go to infinity at $T_c$ in an external field. However, if the transition is antiferromagnetic, a slight increase in the magnetization will be seen above $T_c$ regardless of $H$, as the field-induced moment builds with decreasing temperature. Once the antiferromagnetic correlations start to form, the magnetization drops, with a maximum rate of decrease at $T_c$ when the correlation length diverges. Indeed, the apparent ferromagnetic transition seen in these materials may be due to canted ferromagnetic moments superimposed on an

101

antiferromagnetically ordering lattice (this possibility will be examined in more detail in the discussion). In this case the data can still be interpreted reasonably well in terms of a ferromagnetic transition, so the transition at $T_c = 87$ K is simply referred to as ferromagnetic. At any rate, since the transition in even the lowest fields is rounded, we chose to use the inflection point of the $M/H$ curve as $T_c$. This was found to be $87 \pm 1$ K in all of the 20 Oe data.

In all samples, a "kink" is visible at 35 K. This slight reduction of slope at 35 K is most noticeable for $H \leq 20$ Oe. $Co_3O_4$ is known to achieve antiferromagnetic (AFM) ordering between $25K \leq T \leq 40K$ for bulk powders [110], and this may be connected to the kink behavior. As the $Co_3O_4$ is paramagnetic above $T_N$, it may be aligning along with the external field or with the field produced by the ferromagnetically ordered LCO moments. When $T$ drops below $T_N$, the $Co_3O_4$ moments that had been contributing to the net magnetization order antiferromagnetically, and the total moment drops as a result. The new AFM-FM interface could also result in frustration of magnetic moments. As such, we would see a reduction in the slope of the magnetization near 40 K. In higher fields and for samples with little $Co_3O_4$, however, this temperature range *also* corresponds to a global minimum in the net magnetization which may actually be due to an intrinsic property of LCO. Hence it is difficult to pinpoint the mechanism for this kink in the low w samples, and both the $Co_3O_4$ and LCO could be contributing. Unusual structural behavior is found near this temperature range for all $La_wCoO_3$ samples which may be connected with the magnetization.

As can be seen in Fig. 6.4, the FC data for $H = 2$ kOe still show a ferromagnetic transition around 87 K for w = 0.7 and 0.8. This transition is more rounded than in lower fields, as is expected from the high fields precluding long-range order at $T_C$. There is still a feature near 35 K, although, as noted previously, for $H = 2$ kOe the slope *increases* below this temperature. It is possible that the ferromagnetic portion of these samples is saturating at high fields and the Curie-Weiss paramagnetic portion begins to dominate at low $T$. In contrast, for w

FIG. 6.4: $M/H$ vs $T$ FC data with H = 2 kOe for bulk $La_w CoO_3$.

= 1.0 and 0.9 the ferromagnetic "transition" is very broad; the magnetization barely increases and there is little sign of ordering. For these two samples, $M/H$ reaches a maximum at T $\approx$ 70 K before beginning to drop again. $M/H$ for the w = 1.1 sample is nearly flat in the vicinity of the transition, and drops almost immediately. Each of the 0.9, 1.0, and 1.1 samples have a minimum in $M/H$ whose location increases in temperature as the amount of $Co_3O_4$ decreases ($T_{min}$ = 40, 35, and 30 K, respectively). Below $T_{min}$, $M/H$ increases monotonically for all samples down to 10 K.

It is interesting to note that magnetization results differ between two $LaCoO_3$ samples made in nearly the same manner approximately one year apart. For comparison, Fig. 6.5 shows the magnetization data for the two $LaCoO_3$ samples taken on two different magnetometers, along with $La_{0.9}CoO_3$ data. $LaCoO_3$ #44 and $La_{0.9}CoO_3$ were examined with the Booth magnetometer, whereas $LaCoO_3$ #90 was examined with the Ramirez magnetometer. The $La_{0.9}CoO_3$ sample and #44 were made prior to sample #90, and apart from the date of synthesis, the

FIG. 6.5: $M/H$ vs $T$ FC data with H = 20 Oe for two samples of bulk LaCoO$_3$ (#44 and #90), and one sample of bulk La$_{0.9}$CoO$_3$. #44 and the w = 0.9 sample (Booth magnetometer) were synthesized approximately one year before #90 (Ramirez magnetometer).

only difference between #44 and #90 is that #90 was fired one extra time at 1100° C during the synthesis process. X-ray scans taken of these two samples show no difference that cannot be attributed to noise (see Fig. 6.6), and any Co$_3$O$_4$ present cannot be discerned accurately. Neutron scattering data were only taken on #44. Remanent fields in the different magnetometers are questionable as the cause of the discrepancy between #44 and #90 because the $M/H$ are nearly identical above the transition temperature. A remanent field would have shifted the entire curve upwards, not simply the portion below $T_c$. The 20 Oe $M/H$ curves also differ in shape, with #44 exhibiting nearly linear behavior below the transition, while #90 rises more sharply just below $T_c$. Compared to the La$_{0.9}$CoO$_3$ sample, #44 has a lower magnetization, whereas #90 has a higher magnetization. All of these factors indicate that #44 has less Co$_3$O$_4$-induced surface magnetism than #90, although it is unclear exactly why this is the case. An extra firing might be expected to

FIG. 6.6: X-ray diffraction scans of two samples of $LaCoO_3$ taken with a Rigaku Miniflex Plus (#44) and a Rigaku Smartlab (#90). Both samples have the same structure, and no differences in the amount of $Co_3O_4$ can be distinguished, particularly given the noisiness of the #44 data. The large background for the data taken with the Miniflex is because a monochromator was not used to eliminate the X-ray fluorescence caused by the Co in the sample.

convert more of the $Co_3O_4$ into CoO, but this would result in the opposite effect from that observed. As mentioned in the neutron scattering section, this may also simply be due to random processes resulting in larger or smaller $Co_3O_4$ crystals embedded in the LCO. Unless otherwise specified, the magnetometry data in this section are from sample #90 because #44 was no longer accessible during the time of the most recent measurements.

In the 20 Oe discussed above (Fig. 6.3), it is apparent that the w = 1.0 exhibits a slightly larger magnetization than the w = 0.9 sample. This is contrary to the trend of increased magnetization with $Co_3O_4$ content, and is not the case for the 2 kOe data (Fig. 6.4). As such, the cause of this discrepancy could in this case be a slightly higher remanent field in the Ramirez magnetometer (on the order of

a few Oe). Notably, the #90 data at 2 kOe have a smaller magnetization than the w = 0.9 data; this is as expected, because a remanent field of a few Oe would be insignificant at 2 kOe. The lack of remanent field observed in Fig. 6.5 remains problematic, however.

ZFC data were taken in conjunction with FC data for all samples. Figure 6.7 shows data for w = 1.1, 1.0, and 0.7 at $H = 200$ Oe. The data not shown (w = 0.8 and 0.9) exhibit intermediate behavior between 0.7 and 1.0. The ZFC drops below 0 for the w = 0.7 sample, which is attributable to a negative remanent field in the magnetometer. Field-cycling (alternating back and forth between negative and positive fields) from high to low fields corrected this problem and gave a positive ZFC for all samples done afterward. All of the ZFC curves have a minimum at 25 K, and the $M/H$ ZFC values remain small in comparison to the FC values. This large hysteresis indicates that the net magnetization is limited by domain structure for $H \leq 200$ Oe, characteristic of an isotropic ferromagnet [9]. Notably, the ZFC curve for each sample shows a marked increase in the magnetization as $T$ increases up to 80 K. This could be due to a number of causes, such as ferromagnetic domains which were previously frozen in at low temperatures gradually aligning with one another (most likely in this case), antiferromagnetically interacting moments reducing their total free energy by aligning with the field rather than each other, or an increase in the number of moments (the latter in accordance with the frequently evoked thermal spin state excitation model). Each possibility will be discussed along with the model presented for the magnetization. Note the vertical scale of the plots when considering the magnitude of the ZFC increase in Fig. 6.7 from 25 to 50 K; the largest change occurs in the w = 0.7 sample, approximately 0.015 emu·(Oe·mol)$^{-1}$ whereas that for w = 1.0 and 1.1 is approximately 0.004 emu·(Oe·mol)$^{-1}$.

In contrast to the lower fields, the FC-ZFC hysteresis for $H = 5$ kOe is significantly reduced for all samples (Fig. 6.8). The ZFC and FC curves separate for w = 1.1, 1.0, and 0.7 at 50 K, 70 K, and 77 K, respectively. Less hysteresis in

106

FIG. 6.7: FC (filled triangles) and ZFC (open triangles) plots of $M/H$ vs $T$ for $H = 200$ Oe. Samples shown are $La_{1.1}CoO_3$, $LaCoO_3$, and $La_{0.7}CoO_3$.

107

FIG. 6.8: FC (filled triangles) and ZFC (open triangles) plots of $M/H$ vs $T$ for $H = 5$ kOe. Samples shown are $La_{1.1}CoO_3$, $LaCoO_3$, and $La_{0.7}CoO_3$.

FIG. 6.9: Susceptibility data taken by Yan *et al* on three different sizes of LaCoO$_3$ single crystals at 500 Oe. Data with a solid line are ZFC and those with a dashed line are FC. Image taken from Ref. [42]

the 5 kOe data is expected as the paramagnetic behavior begins to dominate in higher fields because the external field strength overcomes the interaction of the moments with each other. The curves for both the w = 1.1 and 1.0 samples are similar in shape, with the magnetization decreasing significantly (approximately 0.0025 emu·(Oe·mol)$^{-1}$) as $T$ goes from 90 K to 35 K. This behavior is more similar to that seen in the LaCoO$_3$ single crystals at low and high fields [42, 43]; data from Yan *et al*'s single crystals at $H = 500$ Oe is shown in Fig. 6.9 for comparison. The magnetization "dip" is more dominant in samples with little Co$_3$O$_4$. We note this in contrast to the behavior in the w = 0.7 sample, which only begins to dip below 60 K, after an initial rise in $M/H$ more indicative of ferromagnetic ordering at $T_c$. Indeed, a close look at the w = 1.0 data reveals a very small initial rise at $T_c$ as well, whereas the w = 1.1 data exhibit a consistent decrease. The ferromagnetic ordering at $T_c$ is thus seen to be more robust in the samples with more Co$_3$O$_4$.

FIG. 6.10: Magnetization above $T_c$ for $La_wCoO_3$ bulk samples at 20 Oe (left) and 2 kOe (right).

As in the 200 Oe data, the ZFC minima for w = 1.0 and 1.1 are at 25 K, but the FC minima are at 30 K, indicating that the transition to the paramagnetic "tail" (i.e. the low temperature increase in $M/H$) occurs more easily in FC. We are able to model this tail with slightly modified Curie-Weiss behavior, although the parameters for the Curie-Weiss fit are different from those for the behavior at $T \geq 100$ K, i.e. the low temperature AFM interactions are different from those at high temperature. Podlesnyak *et al* [14, 111] have named polarons as the root cause of the tail, whereas other groups have simply attributed it to magnetic impurities [1, 35, 112]. Curiously, whereas the FC minima remain constant across w, the ZFC for w = 0.7 has a minimum at 15 K. Any impurities or polarons contributing to the paramagnetic tail become noticeable at a significantly lower temperature for this sample. This is likely a result of the larger net magnetization due to the ferromagnetic ordering; if the low temperature tail has a more or less constant magnitude and behavior across the samples, the net moment of more ferromagnetic samples will dominate the magnetization curve, whereas the tail will be more visible in samples with a lower net moment.

As previously mentioned, the CoO antiferromagnetic Bragg peak is seen in the neutron scattering data below room temperature. A previous work [33] with significant amounts of CoO phase in their nanoparticle samples saw an increase

in the net magnetization below 290 K due to ferromagnetic ordering on the CoO surfaces. As can be seen in Fig. 6.10, $M/H$ data starting at T = 110 K do not show large differences in magnitude above $T_c$ ($T > 90$ K). In general, the samples with lower w have a slightly higher ($\leq 0.001$ emu·(Oe·mol)$^{-1}$) magnetization for $H = 2$ kOe. The differences seen in $M/H$ within the same sample (e.g. $M/H$ at 110 K for w = 1.1 is 0.0039 emu·(Oe·mol)$^{-1}$ at 20 Oe, and 0.0048 emu·(Oe·mol)$^{-1}$ at 2 kOe) likely indicate a small remanent field in the magnet on the order of a few Gauss, only noticeable in low fields. Indeed, the 110 K $M/H$ at 5 kOe is virtually identical to that at 2 kOe for w = 1.1. We conclude that any amount of CoO phase decreases slightly as w increases, in accordance with the intensity of the CoO AFM peak seen in the neutron scattering, and that the contribution of a CoO phase is overshadowed by the phenomena occuring below 87 K in the LaCoO$_3$ phase. We thus treat the effect of CoO in our samples as effectively negligible, as our net magnetization values are only very slightly increased from their true values.

## 6.3   Inverse Magnetization of LaCoO$_3$

The inverse magnetization, $H/M$, was determined from the magnetization data for LaCoO$_3$, sample #44, for $10 \leq T \leq 300$ K. $H/M$ was examined for fields $H$ = 10, 50, 100, 1000, 2000, and 60,000 Oe, and the results are shown in Fig. 6.11. As can be seen from the figure, $H/M$ for all fields is approximately independent of $H$ for $T > 87$ K. Hence, we may approximate these data as the inverse of the susceptibility $\chi$. Note that when long-range order is present, this approximation is no longer valid. The linear behavior for $170 \leq T \leq 300$ K is fit using the Curie-Weiss (CW) approximation,

$$\frac{H}{M} \approx \frac{1}{\chi} = \frac{T - \theta_{CW}}{C} \quad . \tag{6.2}$$

Averaging the fits for all fields yields a CW temperature $\theta_C = -182(3)$ K and

FIG. 6.11: $H/M$ vs $T$ for LCO for several values of $H \leq 60$ kOe, all of which show paramagnetic behavior with AFM interactions for $T > 100$ K. For $H \leq 100$ Oe, linear behavior for $T \leq 30$ K also suggests AFM paramagnetic behavior for $H \leq 100$ Oe, but with a moment that increases with $H$. The inset shows the linear behavior for $H = 20$ Oe for $10 < T < 30$ K. The downturn for all $H$ below 10 K is consistent with the alignment of nearly independent moments.

a Curie constant $C = 1.5(3)$ emu·K·mol$^{-1}$. The average effective moment is $\mu_{eff} = 3.5(2)$ $\mu_B$ per Co ion, using

$$\frac{\mu_{eff}^2}{\mu_B^2} = \frac{3k_B C}{N_A}, \tag{6.3}$$

where $\mu_B$ is the Bohr magneton, $N_A$ is Avogadro's number, and $k_B$ is the Boltzmann constant. This matches well with a previous value $\mu_{eff} = 3.07\mu_B$ below 400 K [113] and reasonably well with a high field, low $T$ result [114]. The negative value obtained for $\theta_{CW}$ indicates that AFM interactions dominate the paramagnetic behavior. As can be seen in Table 6.1, there is a variation of the strength of the AFM interactions with field; that is, $\theta_C$, C, and $\mu_{eff}$ initially increase slightly,

112

TABLE 6.1: Fits to the CW behavior of the LaCoO$_3$ #44 inverse magnetization for all fields in the $170 \leq T \leq 300$ K range. The error on all $\theta_C$ is $\pm$ 3 K, the error on all C is $\pm$ 0.3 emu·K·mol$^{-1}$, and the error on all $\mu_{eff}$ is $\pm$ 0.2$\mu_B$.

| H(Oe) | $\theta_C$(K) | C(emu·K·mol$^{-1}$) | $\mu_{eff}(\mu_B)$ |
|---|---|---|---|
| 10 | -184 | 1.5 | 3.5 |
| 20 | -189 | 1.5 | 3.5 |
| 50 | -198 | 1.6 | 3.6 |
| 100 | -202 | 1.6 | 3.6 |
| 1000 | -164 | 1.4 | 3.3 |
| 2000 | -166 | 1.4 | 3.3 |
| 60000 | -173 | 1.4 | 3.4 |

TABLE 6.2: Fits to the CW behavior of the LaCoO$_3$ #44 inverse magnetization for fields $H \leq 100$ Oe in the $10 \leq T \leq 30$ K range. The error on all $\theta_C$ is $\pm$ 3 K, the error on all C is $\pm$ 0.3 emu·K·mol$^{-1}$, and the error on all $\mu_{eff}$ is $\pm$ 0.2$\mu_B$.

| H(Oe) | $\theta_C$(K) | C(emu·K·mol$^{-1}$) | $\mu_{eff}(\mu_B)$ |
|---|---|---|---|
| 10 | -48 | 3.8 | 5.5 |
| 20 | -57 | 3.3 | 5.1 |
| 50 | -41 | 1.7 | 3.7 |
| 100 | -37 | 1.1 | 3.0 |

then decrease as the field goes up. It is not clear why this happens *above* $T_c$, where the sample is in theory paramagnetic and the C-W behavior should not vary. A small remanent field in the magnetometer could potentially shift $H/M$ up or down, but would not affect the data for $H \geq 100$ Oe.

The sudden decrease of the inverse magnetization near $T_c = 87$ K is consistent with a transition to FM long-range order for $H \leq 100$ Oe. At lower temperatures,

though, the increase of the inverse magnetization is not the typical behavior of a FM phase. Instead, a sharp increase in $H/M$ is more characteristic of AFM order. Other data do not provide a compelling argument for long-range AFM order; however, these inverse magnetization data are consistent with the presence of two paramagnetic phases with different antiferromagnetic coupling constants. This interpretation can also be modeled quite well, as will be seen in a subsequent section.

The inverse magnetization upon FC appears to follow the linear behavior suggestive of CW behavior (Eq. 6.2) for the approximate range $10 \leq T \leq 30$ K. However, the parameter $C$ varies with $H$, which should not be the case if the sample were completely paramagnetic. This may be due to interference from a ferromagnetic phase which is only apparent in the low field magnetization below $T_c$. Interpreting the linear behavior for $H \leq 100$ Oe as CW behavior suggests a predominantly paramagnetic system with AFM interactions, rather than long-range AFM or FM magnetic order for $10 \leq T \leq 30$ K. Note that this does not preclude a system with short-range magnetic order, as the low temperature rise characteristic of all paramagnets could simply be dominating the magnetization in this temperature range. A CW fit of the $H = 20$ Oe data in this region is shown in the inset of Fig. 6.11 and the fitted values for this and other low fields are given in Table 6.2. The temperature range over which linear behavior is observed decreases with increasing $H$. For $H \geq 1$ kOe, neither linear behavior below 30 K nor long range ferromagnetic order below $T_c$ is observed. This is consistent with the paramagnetic phase beginning to overwhelm the magnetization in higher fields. Notably, the $10 \leq T \leq 30$ K $\mu_{eff}$ for $H \leq 100$ Oe increases with decreasing $H$, again indicating that the system is not purely paramagnetic at low fields, instead possessing some degree of ferromagnetic order. Upon ZFC, the net FM moment is very small and the CW behavior is not observed in the inverse magnetization for $H \leq 100$ Oe.

FIG. 6.12: $M$ vs $H$ data for all samples at 90 K, from an applied field of -5 kOe to 5 kOe. Inset shows the small hysteresis for w = 0.7 and 0.8 near $H = 0$.



FIG. 6.13: $M$ vs $H$ data for all samples at 70 K, from an applied field of -5 kOe to 5 kOe.

## 6.4  M(H) for $La_wCoO_3$

ZFC measurements of the magnetization, $M$, as a function of the applied field $H$ were taken at T = 40, 70, and 90 K for the w = 0.7, 0.8, 1.0, and 1.1 samples.

FIG. 6.14: $M$ vs $H$ data for all samples at 40 K, from an applied field of -5 kOe to 5 kOe.



FIG. 6.15: $M$ vs $H$ data for w = 0.7 and 1.1 from an applied field of -5 kOe to 5 kOe at T = 10 K.

Data were also taken at T = 10 K for the w = 1.1 and w = 0.7 samples, and at T = 5 K for the w = 1.0 (#44) and w = 0.9 samples. Figures 6.12 through 6.15 show the hysteresis curves at different temperatures for all the samples from external fields of -5 kOe to 5 kOe. Figure 6.16 shows the hysteresis at 5 K in

116

external fields of -60 kOe to 60 kOe for w = 1.0 and 0.9.

All samples show a nearly linear response with no hysteresis at T = 90 K. This is to be expected, as the transition temperature $T_C$ measured in the $M/H$ vs T is $\approx$ 87 K for all samples. A small kink can be seen in the w = 0.7 and 0.8 samples at $H = 0$, consistent with the magnetization curves showing a small rise in $M/H$ beginning at 92 K. This is likely due to small ferromagnetic domains forming even in very low fields. The magnetization at 5 kOe increases by about 4.5 emu/mol as w decreases from 1.1 to 0.7, indicating either more ferromagnetic correlation or a larger number of unpaired spins free to align with the field in the lower w samples.

At 70 K, all of the samples begin to show hysteresis, indicating the onset of ferromagnetic order, in accordance with the behavior seen below 87 K in the $M/H$ vs T curves. Both the coercive field $H(M = 0)$ and the remanent magnetization $M(H = 0)$ increase as w decreases. At this temperature, it is notable that the samples with w = 1.0 and 1.1 show a 5 kOe magnetization *smaller* than that in the 90 K data, but the samples with w = 0.8 and 0.7 show one *larger* than in the 90 K data. It is thus surmisable that there is a larger net moment at 90 K than at 70 K in the w = 1.0 and 1.1 samples, possibly as a result of an increase in the antiferromagnetic short-range order as the temperature decreases. In the w = 0.7 and 0.8 samples, the larger net magnetization is likely due to ferromagnetic ordering of the moments. Note that both antiferromagnetic and ferromagnetic interactions are present in all samples - these data simply indicate which interaction is dominant. For example, the w = 1.0 sample likely has more ferromagnetic regions in the lattice as compared to the w = 1.1 sample due to a larger amount of $Co_3O_4$ in the former. As such, the 5 kOe w = 1.0 magnetization is larger than that of w = 1.1.

For T = 40 K, all of the samples exhibit hysteresis up through $H = 5$ kOe. The magnetization at 5 kOe increases by about 20 emu/mol as w decreases from 1.1 to 0.7. When comparing $M(H = 5$ kOe) at 70 K with that at 40 K, we

117

note that in the w = 0.8 and 0.7 samples the magnetization drops by 4 and 1 Oe (respectively) as the temperature drops. However, in the w = 1.1 and 1.0 samples, the magnetization drops by 10 and 8.5 Oe (respectively) with temperature. This is consistent with temperature-dependent ferromagnetic moments in all samples. Compared with the other samples, the net magnetization in the w = 0.7 and 0.8 samples does not increase as much with respect to temperature, indicating that a larger portion of the moments are frozen-in. In other words, the structure is strained enough that changes in temperature will not significantly reduce the Co-O-Co bond angle and thus the ferromagnetism (this will be examined in more detail in Discussion section).

Data were taken at 10 K for only the w =0.7 and 1.1 samples. In both samples, the hysteresis persists through $H = 5$ kOe. However, the remanent magnetization in both cases decreases: $M(H = 0)$ of w = 1.1 is half of its value at 40 K, and that of w = 0.7 is one third of its value at 40 K. This echoes the results seen in the $M/H$ ZFC and may be a result of frozen-in domain structure at low temperatures, in that the frozen ferromagnetic moments cannot all align coherently and cannot give a large net magnetization in one direction. As neither sample shows saturation, there must still be a paramagnetic contribution to $M$, also consistent with the paramagnetic tail seen in the $M/H$ plots for $T \leq 25$ K.

The hysteresis at 5 K was examined for the w = 1.0 (#44) and 0.9 samples in high fields ($H = 60$ kOe). The w = 1.0 sample appears to be approaching saturation at high fields, and $M(H = 60$ kOe) is 89.3 emu/mol. The hysteresis becomes negligible above 40 kOe and the remanent magnetization is only about 0.2 emu/mol larger than that in the sample at 40 K. The w = 0.9 sample does not appear to be saturating at 60 kOe, and $M(H = 60$ kOe) is 133 emu/mol. Although the remanent field is larger in this sample than in the w = 1.0 sample (8.1 emu/mol as compared to 3.3 emu/mol), the hysteresis is also nearly gone above 40 kOe. These data suggest that there may be more frozen-in ferromagnetic domains for the w = 0.9 sample, and that this sample also has a larger strained region available

FIG. 6.16: $M$ vs $H$ data for w = 1.0 and 0.9 at 5 K, from an applied field of -60 kOe to 60 kOe. The LaCoO$_3$ used was from sample #44.

to be magnetized at lower temperatures.

## 6.5  Discussion Preamble

All of the $M(T)/H$ and $M(H)$ data are consistent with Co$_3$O$_4$ strengthening the ferromagnetism in La$_w$CoO$_3$. As w decreases, the transition at $T_c = 87$ K becomes increasingly sharp, retaining its ferromagnetic nature (that is to say, $M(T)$ increasing below $T_c$) to larger and larger fields. The magnitude of the net moment below $T_c$ increases correspondingly. This is in contrast to the w = 1.0, 1.1, and single crystal samples exhibiting what appears to be predominantly antiferromagnetic behavior below $T_c$, especially for higher external fields. Although a small increase in the net moment is seen below $T_c$ in these samples for low fields, this increase becomes a drop at $H = 5$ kOe (w = 1.0), $H = 2$ kOe (w = 1.1), and $H = 500$ Oe (single crystal [42]). As was proposed in the neutron scattering section, the ferromagnetism is induced by strain on the lattice from the Co$_3$O$_4$ - LCO interfaces.

119

FIG. 6.17: Data by Yan *et al* showing the effect of surface area on the susceptibility, $\chi$, of $LaCoO_3$ at $H = 500$ Oe. All samples were taken from the same single crystal ("bulk crystal"). Samples were then ground ("Powder"), cold-pressed into a pellet ("CP"), cold-pressed and subsequently annealed at $400°C$ ("CP 400 Ann") or at $1000°C$ ("CP 1000 Ann"). Open symbols represent FC, while closed symbols represent ZFC. Note the logarithmic scale for $\chi$. Image taken from Ref. [42].



FIG. 6.18: Data by Harada *et al* showing the effect of surface area of various samples of $LaCoO_3$ on the susceptibility, $\chi$, at 100 Oe. The numbers for each data set indicate the particle radii for each sample, while "s.c." indicates the single crystal data. Image taken from Ref. [43].

120

## 6.6 Surface Effects vs. Interface Effects

Experiments by Harada *et al* and Yan *et al* examining the effects of size on LaCoO$_3$ indicate that increasing the surface area of the material also increases the magnetization, in a similar way to Co$_3$O$_4$ [42, 43]. Data from each study are shown in Fig. 6.17 (Yan) and Fig. 6.18 (Harada). The vertical axes in both are labeled as the suscepbility, $\chi$, which corresponds to the definition of susceptibility as $\chi = M/H$ rather than the more general definition $\chi = \partial M/\partial H$. Neither author divides $M$ by $H$, so the label of $\chi$ is misleading; however, the data were taken with the same method as our $M/H$ data and are thus able to be compared. In particular the effects seen by Yan *et al* cannot be attributed to different amounts of Co$_3$O$_4$ as a result of differences in synthesis, as all of the samples were taken from the same single crystal. These were either ground, or ground and cold pressed into pellets, some of which were then annealed at 400°C or 1000°C. Microcracks were seen in the pellets, which contributed to the total surface area, accounting for the increased magnetization in these samples. It is curious that the pellets showed a larger susceptibility than the bulk powder, as the particle size was likely not any different. However, pressing the sample into pellets introduces large amounts of strain due to the high pressures encountered, which may have introduced more regions conducive to ferromagnetic ordering. Data on the Co-O-Co angles for the Yan samples would help to clarify the effects of cold-pressing on the material. The experiments done by Harada *et al* using a scanning SQUID microscope (SSM) indicate clearly that a ferromagnetic phase with a $T_c = 85$ K exists on the surface of single crystal LaCoO$_3$, in agreement with our findings for bulk and Co$_3$O$_4$-rich LaCoO$_3$. By undertaking similar experiments to Yan *et al*, albeit with different-sized samples synthesized separately, they estimated the thickness of the surface ferromagnetism region to be a few unit cells. This is in contrast to the thickness calculated by Fuchs *et al* of roughly 100 nm for their thin film studies [47]. However, thin films are grown on a flat, even substrate,

whereas particle surfaces are much rougher and likely do not strain the lattice as evenly as in the films.

The most significant element in the studies by Harada and Yan is the critical temperature for the ferromagnetic phase transition. According to Harada *et al*, the susceptibility curves in Figure 6.18 exhibit a transition temperature between 70 and 85 K, which is consistent with the transition temperature found in their SSM experiment. Although the ferromagnetism in these studies is attributed solely to surface effects, $T_c$ is essentially the same as the ferromagnetism from $Co_3O_4$-LCO interfaces. Note that we may eliminate surface effects as the sole cause of the ferromagnetism in $La_wCoO_3$, as all samples underwent the same synthesis process with firing temperatures which were nearly identical; thus the surface area should not vary systematically between samples. In addition, the intensity of the $Co_3O_4$ AFM Bragg peak correlates well with the degree of ferromagnetism seen in our samples. However, this alone does not remove the possibility that the effects of the $Co_3O_4$ interfaces and the LCO surfaces have a common origin. As was previously mentioned, the surface of LCO may undergo some reconstruction to CoO or $Co_3O_4$. The problem with this interpretation is that (to the author's knowledge) no evidence has been found indicating a widespread $Co_3O_4$ surface on LCO. However, Senaris-Rodriguez *et al* discuss the possibility of a Co-rich surface region which contributes to the magnetic susceptibility [15]. Our conclusion is thus that the surfaces and $Co_3O_4$ interfaces affect the LCO lattice in a very similar way: both introduce strain in the form of an expanded Co-O-Co bond angle, which is conducive to increased ferromagnetism. Studies are currently underway to examine the effects of size on $La_wCoO_3$ via synthesis of nanoparticles, and in the future we hope to be able to determine the exact differences between the surface and interface contributions.

Although we have now established that LCO surfaces and the $Co_3O_4$ - LCO interfaces both enhance ferromagnetic order, a few important questions remain. First, how does the lattice behave structurally and magnetically as the distance

from the interface increases, and how deep does the effect of $Co_3O_4$ extend? Second, what exactly is the nature of the ferromagnetic ordering? Given the antiferromagnetic interactions in the LCO lattice, is it canting of the AFM moments, or is it actually a separate ferromagnetic phase? Third, can we model the data while incorporating contributions from the antiferromagnetic and ferromagnetic interactions, and is this model consistent with the ferromagnetism residing primarily near the surface, while the antiferromagnetism dominates the bulk material?

## 6.7  Regions of Lattice Strain

To explain the results of these experiments, we introduce a simple conceptual model with three different regions contributing to the net magnetization. Region 1 is near the surfaces and interfaces with $Co_3O_4$, where strain-induced magnetic moments order ferromagnetically at $T_c = 87$ K. Region 3 is antiferromagnetically interacting, unstrained bulk material far from the surfaces and interfaces. Region 2 is between Regions 1 and 3, where the lattice is strained enough to stabilize magnetic moments at temperatures $T \geq 87$ K, and is barely able to order ferromagnetically. As the temperature decreases from 87 K to 35 K the lattice contracts, the Co-O-Co angle contracts, and Region 2 is no longer able to order. In contrast, Region 1 is sufficiently strained by the surface/interfaces that lattice contraction will not remove the ferromagnetic order. Yan *et al* proposed a very similar decomposition of the susceptibility curve which also included the paramagnetic tail below 35 K [42]. Modifying their notation for this discussion, the magnetization $M(T)$ in a field $H$ can be written as:

$$M(T) = M_{tail} + M_{R1} + M_{R2}, \qquad (6.4)$$

where $M_{tail}$ is the contribution from the low-temperature paramagnetic tail, $M_{R2}$ is from the temperature-dependent structure-induced ferromagnetism in Region 2, and $M_{R1}$ is from the ferromagnetic moments near the surfaces and interfaces of

Region 1. Keep in mind that this is only a conceptual model of the magnetization - a more involved, mathematically-based model will be discussed shortly.

## 6.8    Parameters Related to Lattice Strain

Thin film studies [39, 47] have shown that LCO on a substrate is strained in such a way as to induce ferromagnetic ordering, although they focus more heavily on the Co-O bond length rather than the angle. We do not find this parameter to be exceptionally well correlated to the ferromagnetism in our $La_wCoO_3$ samples, but it is still of use to examine these results, as strain along the Co-O length can also affect the Co-O-Co bond angle (a better indicator of ferromagnetism). Sterbinsky *et al* saw that a 20 nm film of LCO deposited on a $SrTiO_3$ (STO) substrate had a significantly elongated in-plane Co-O bond length and a shortened out-of-plane bond length as compared to the bulk value of 1.934 Å [39]. The average bond length for our samples ranges between 1.923 Å and 1.932 Å at room temperature, smaller than Sterbinsky's average of 1.950 Å (it is unclear at which temperature the latter value was obtained). Fuchs *et al* obtained an average value of 1.92 $\pm$ 2 %Å for their ferromagnetically ordered thin films at 15 K [47]. This indicates that our samples are not strained to the extremes of Sterbinsky's films, which is consistent with a significant amount of non-ferromagnetic, unstrained material (Region 3). Indeed, our values at room temperature are between 0.1 and 0.6 % lower than the expected bulk LCO value, although this could be accounted for in part by variations in experimental technique.

Sterbinsky *et al* calculated Co-O-Co angles of 168° and 159° for the in- and out-of- plane bond lengths, respectively, and experiments by Fuchs *et al* indicated that the Co-O-Co angle above which there can be ferromagnetism is $\approx$ 160° [39, 47]. Our average values are well within this range of ferromagnetism for all temperatures, the lowest bond angle value being 162.8°. It is important to stress that these are *average* values between Regions 1, 2, and 3, and that it is likely that

Region 1 has a larger angle than Regions 2 and 3. Knizek *et al* discussed the strong hybridization between the Co $e_g$ states and the O $p$ states leading to the presence of spins in the nominally higher energy magnetic state. This hybridization corresponds to a larger Co-O-Co angle, a longer Co-O bond length, and a lower amount of rhombohedral distortion (smaller $\delta y$) [115]. A theoretical paper by Lee and Harmon found that the magnetic state was only 3.2 meV/Co higher in energy for a $\delta y = 0.052$, and suggested that even small distortions in the lattice or thermal energy could be enough to shift the minimum energy to that corresponding to a magnetic state. As $\delta y$ decreases, the energy minimum shifts to a magnetic state according to their GGA calculation [18].

## 6.9  Penetration Depth of Lattice Strain

Although the magnetic moments in Region 1 can be explained in terms of surface/interface - induced strain by generalizing the bulk interface behavior to that of thin films, the extent to which this strain propagates into the bulk material is less clear. Fuchs *et al* found that films up through 100 nm thick exhibited a ferromagnetic transition, though according to their interpretation the fraction of non-magnetic regions increased as the film thickness increased. Other experiments on films have found that ferromagnetism exists for film thicknesses of 20 and 30 nm [39, 41]. However, given that the $Co_3O_4$ crystals are likely contained within bulk LCO for our samples as opposed to being on a well-ordered, flat surface, and that we were not able to take measurements determining the geometry of these crystals, it is difficult to gauge the depth of the strain in the LCO lattice. We are simply able to place a rough upper estimate of 100 nm on the depth of the interface-induced ferromagnetism; that is, the combined thicknesses of Regions 1 and 2 will likely not extend much further.

FIG. 6.19: Molar heat capacity data taken for bulk powder $LaCoO_3$ at constant pressure by Stolen *et al*, over the range of temperatures where long range magnetic order would be expected. The circles represent $LaCoO_3$, while the crosses represent $LaFeO_3$ (another perovskite studied in their work). Image taken from Ref. [116].

## 6.10    Antiferromagnetic Interactions in $La_wCoO_3$

Many papers examining $LaCoO_3$ invoke the low-spin to high-spin thermal transition in order to explain the magnetization behavior below $T_c$. It is understandable why this picture is often evoked, as the dip in the susceptibility (Fig. 6.9) for higher fields ($H \geq 500$ Oe) and pure LCO (little to no $Co_3O_4$ phase) does not appear to correspond to long-range antiferromagnetic ordering. In particular, our studies on the LCO bulk powder sample show no evidence of a transition to long-range AFM order in either the neutron scattering (as would be indicated by a magnetic Bragg peak appearing near the ordering temperature) or the inverse magnetization data. The susceptibility for a material undergoing antiferromag-

126

netic ordering has a rounded cusp above the Neel temperature ($T_N$), which is defined as the temperature of the steepest decrease in the susceptibility. The inverse susceptibility shows a corresponding peak at $T_N$. Historically, no significant upturn has been seen in the LCO $M/H$ data - instead, there is a broad peak near 87 K, while the inverse susceptibility shows a peak centered at around 35 K for high fields. The specific heat, which normally shows a peak at the critical temperature if there is long range order, appears smooth near 35 K and 87 K [116]. Figure 6.19 shows a plot of molar heat capacity data taken by Stolen *et al* of bulk powder $LaCoO_3$ in the temperature range where long-range order (ferromagnetic or antiferromagnetic) would be expected; no peaks can be seen. However, this does not preclude a small number of spins ordering, or weak ordering as heat capacity measurements are not very sensitive to this type of behavior. Despite a lack of long-range order, $\theta_C$ is large and negative for LCO, indicating strong antiferomagnetic interactions.

One explanation for this lack of long-range order is that any antiferromagnetic interactions must be frustrated, and the ferromagnetic order seen in low fields takes place within this frustrated AFM environment. However, a simple geometric reason for frustration is not obvious, as the LCO lattice is essentially cubic (one can more easily imagine frustration in systems with triangular geometry). Another possibility is that of a *second* type of AFM order (AFM2), e.g. one with a weaker coupling constant as a result of lattice contraction, which is parasitic on the first type of AFM (AFM1) beginning at temperatures below $T_c$. The presence of two types of AFM would make it nearly impossible for long-range order involving either one to take place. As it turns out, the idea of multiple possible AFM states with slightly different interaction strengths has already been suggested by Seo *et al* [37], and that of a low temperature ($T \leq 28$ K) AFM state by Androulakis *et al* [29]. The second hypothesis is the one most strongly borne out by our data, in particular by the presence of the two paramagnetic (with AFM interactions) regions for $10 \leq T \leq 30$ K and $T \geq 100$ K (see Fig. 6.11). The presence of

ferromagnetic order is undeniable in our magnetization data and thus it is quite likely that there are both FM and AFM interactions; however, these interactions do not necessarily compete.

## 6.11 Coexistence of Antiferromagnetic and Ferromagnetic States

The possibility of coexisting FM and AFM coupling in LCO was also proposed by Seo *et al* with a focus on the case of tensile strain [37]. Although their calculations were done in the context of a local LS/HS mixed-spin state configuration assuming two different types of $Co^{3+}$ ion, our data are consistent in some ways with their findings. Using a model in which Co ions alternate between LS or HS (that is, nonmagnetic or magnetic), Seo *et al* found that there are both ferromagnetic nearest-neighbor couplings and antiferromagnetic next-nearest-neighbor couplings between HS Co ions, and that these couplings are only separated by approximately 2 to 3 meV/$Co^{3+}$ ion. As the tensile strain of the lattice increases (in our case, this is particularly applicable to the surface/interface regions), the magnetic configurations with mixed LS/HS states become stabler than the nonmagnetic solutions. In addition to this, they calculate that several simple collinear AFM ground state configurations are degenerate with a non-collinear (canted) configuration. A simplified visualization of spin canting is shown in Fig. 6.20. The canted configuration may lead to a stable solution with FM ordering, which is further stabilized by the application of an external magnetic field.

## 6.12 Canting and Saturation of the Ferromagnetic Moments in $La_wCoO_3$

Ferromagnetic canting of antiferromagnetic moments can account for another curious aspect of the magnetization data. The ferromagnetic ordering tempera-

FIG. 6.20: Spin configurations demonstrating ferromagnetic, antiferromagnetic, and canted antiferromagnetic order. The red arrows indicate the net magnetization.

ture at low fields, 87 K, is the same temperature below which the magnetization dips in high fields. The decrease in magnetization can be interpreted as short-range antiferromagnetic ordering of the AFM1 type. If the ferromagnetic order is dependent on the antiferromagnetic ordering of the sample, it stands to reason that the ferromagnetic spin canting would only appear once the system began to exhibit AFM order. Thus, both behaviors would appear at the same $T_c$.

One potential issue with the canting intepretation of the FM order is why the FM order doesn't appear to get stronger in higher fields. As the external field increases, one would expect more of the moments to cant, and thus an increase in the ferromagnetic moment. Instead, the magnetization begins to dip more and more strongly at $T_c$ as $H$ goes up. As it turns out, this can partly be accounted for with a low saturation moment for the canted ferromagnetism, and partly with the rounding of the transition for larger fields. Recall that if only the moments near the surfaces and interfaces are strained in such a way as to allow ferromagnetic canting, the net moment will saturate as a function of this. Once the FM moment is saturated, non-ordering AFM interactions then dominate the magnetization curve. As the external field increases, the rounding of the magnetic transition near $T_c$ increases; only for $H = 0$ will the transition be truly sharp. We see that the magnetization data for $La_wCoO_3$ samples (Figs. 6.3 and 6.4) are consistent with this: the saturation moment in low fields increases significantly as w decreases, and the ferromagnetic rise is more visible at higher fields in the low w than in the

high w samples.

Plotting the maximum ferromagnetic moment versus $H$ for the w $= 0.7$, $1.0$ and $1.1$ samples, as can be seen in Fig. 6.21, effectively demonstrates the saturation effect. Note we take the maximum *ferromagnetic* magnetization; for the high field and high w data, this was taken as the maximum value of the rise near $T_c$, while for the low field and low w data, this was taken as the extrapolation of the ferromagnetic rise down to 10 K. In this way, the rise from the low temperature paramagnetic tail in high fields and w $= 1.0$ and $1.1$ was excluded from the data, and only the ferromagnetic portion of the magnetization was examined. The sharp initial rise and flattening out of $M$ indicates the ferromagnetic moment increasing and subsequently saturating at $H_{sat}$. $M$ above $H_{sat}$ again starts to rise, and the slope for $M$ vs $H$ is qualitatively similar for all three samples (though the dearth of high field data prevents much further interpretation here). The second, shallower rise after $H_{sat}$ appears to occur at lower fields as w increases, consistent with a larger Region 1 and hence more FM moments in the low w samples. In comparing this plot with the $M(H)$ hysteresis plot, we must keep in mind that the lack of saturation seen in the latter is showing the contributions from both the ferromagnetically ordering region (Region 1) and the largely paramagnetic bulk AFM region (Region 3).

## 6.13    Effects of Strain on the Ferromagnetic Moments

In light of the discussion by Seo *et al*, we conclude that strain near the surfaces and interfaces allows for a stable non-collinear configuration where the AFM ordering at $T_c$ allows for the canted spins to order ferromagnetically. The strain is mainly quantified by the Co-O-Co bond angle, which increases in regions of tensile strain, while small increases in the Co-O bond lengths also accomodate strain [37]. As the temperature decreases, however, both of these parameters decrease as the lattice contracts, thus introducing a competing temperature-dependent decrease

FIG. 6.21: $M$, the maximum magnetization (excluding that from the low-$T$ paramagnetic tail) versus $H$, the external field, for w = 0.7, 1.0 and 1.1 bulk $La_w CoO_3$ samples. A sharp initial increase in $M$ is seen up through $H_{sat}$, with a shallower increase above this field. Solid lines are guides to the eye.

in the tensile strain, at least in Region 2. Since the ferromagnetic ordering depends on the presence of tensile strain, a slight weakening of this net moment will occur as the temperature decreases and compels the Co-O-Co bond angle to decrease (this will be effectively modeled in the subsequent section). Region 2 will then shrink, and the number of ferromagnetic moments will go down. To reiterate, as $T$ decreases, two things are happening to the ferromagnetism: 1) The moments are saturating, and 2) The net moment decreases.

The relative amounts of Regions 1, 2, and 3 in the different w samples are important considerations when modeling the magnetic behavior. As w decreases, there should be more and more of Region 1 in the sample; there are more surfaces and interfaces, thus more of the LCO lattice is strained near these. Consequently, there should be more and more of Region 2, where the material is not *as* strained by the surfaces/interfaces, and as a result is more susceptible to lattice contraction

effects. Finally, as w decreases, the relative proportion of Region 3 should decrease. So, in a low w sample, one would expect 1) a larger FM moment which is 2) more susceptible to lattice contraction, but with 3) a lower amount of bulk AFM order. Although it is difficult to disentangle exactly the contribution of each effect, the magnetization model we propose is able to account for the total effect of these phenomena.

# 7 Fits to the Magnetization of Bulk $La_w CoO_3$

The $M/H$ magnetization of $LaCoO_3$ has not, to our knowledge, been fit with a theoretical curve down to low temperatures by previous investigators. Whereas Bhide *et al* [6] show a fit to the susceptibility for $T > 78$ K, they do not put forth a comprehensive model for the magnetic behavior in a range of external fields. Several authors do discuss the possibility of a composite susceptibility including AFM, FM, and paramagnetic contributions. For example, Yan *et al* [42] put forth a three-part expression for the susceptibility which consists of Curie-Weiss paramagnetism, the Co(III) LS-IS transition, and a field-dependent $M/H$ ferromagnetic contribution which saturates at high fields. Androulakis *et al* [29] discuss the possibility of different ferromagnetic regions ($T < 10$ K and $20 \leq T \leq 100$ K) and an antiferromagnetic region for $T < 30$ K.

## 7.1 Introduction to the Magnetization Model

We propose a magnetic susceptibility model similar in concept to that by Androulakis. Our model consists of two antiferromagnetically-correlated Curie-Weiss contributions and two ferromagnetic contributions, each entering at a different temperature. In this model, the magnetization $M(T)$ at a temperature $T$ and external field $H$ is given by

$$M(T)/H = C_{tail} + C_{high} + F_{12}, \tag{7.1}$$

where $M(T)$ depends on $C_{tail}$, the Curie-Weiss contribution of the low-temperature tail, $C_{high}$, the Curie-Weiss contribution for $T \leq 120$ K, and $F_{12}$, a combination of two ferromagnetic contributions for different temperature ranges below $T_c$. It is important to keep in mind that this model is predominantly a mathematical description and is meant to serve as a guide for further investigations and the development of more rigorous theoretical models of the data.

133

FIG. 7.1: Plot of three different sigmoids showing the effects of the different parameters $W$ and $C$ (Eq. 7.2). The red line shows a sigmoid with $W = 0.1$ and $C = 35$, the blue line for $W = 0.2$ and $C = 35$, and the green line for $W = 0.1$ and $C = 50$.

In order to successfully fit the data, each of the contributions was convoluted with sigmoid functions; that is, the contributions increase or decrease with temperature as dictated by the sigmoid function $s(T)$, where

$$s(T) = \frac{1}{1 + \exp(-W(T - C))}. \tag{7.2}$$

The constant $W$ can be thought of as the "inverse width" of the sigmoid - as it gets smaller, the region over which the sigmoid varies strongly with $T$ gets larger. The constant $C$ is the location of the inflection point of the sigmoid. Figure 7.1 shows the effects of varying $W$ and $C$.

Equations 7.3, 7.4, and 7.5 show each portion of the magnetization. A description of all parameters is given in Table 7.1, and example plots of $C_{tail}$, $C_{high}$, $F_{12}$, and $M(T)$ are shown in Fig. 7.2.

$$C_{high} = \left(d + \frac{E_1}{T + t_1}\right)s(T), \tag{7.3}$$

134

TABLE 7.1: List of parameters used when fitting $M(T)$ of $La_wCoO_3$. Refer to Eqs. 7.3, 7.4, and 7.5 for the complete model. Constant values are indicated in the Value column, all other parameters indicated with a "–" vary between fits.

| Parameter | Description | Value |
|---|---|---|
| $d$ | Remnant field constant | – |
| $t_1$ | Temperature for the onset of $C_{high}$ | 120 K |
| $t_2$ | Temperature for the onset of $C_{tail}$ | – |
| $E_1$ | Multiplicative constant for $C_{high}$ | – |
| $E_2$ | Multiplicative constant for $C_{tail}$ | – |
| $W$ | Inverse width of the sigmoid | 0.09 K$^{-1}$ |
| $C$ | Location of the sigmoid inflection point | – |
| $T_c$ | Ferromagnetic transition temperature | – |
| $\beta$ | Critical exponent for $F_{12}$ | 0.65 |
| $M_{12}$ | Field-dependent constant for $F_{12}$ | – |
| $L$ | Multiplicative constant for the low-temperature reverse sigmoid in $F_{12}$ | – |

$$C_{tail} = \left(\frac{E_2}{T + t_2}\right)(1 - s(T)), \tag{7.4}$$

$$F_{12} = M_{12}\left(\frac{T_c - T}{T_c}\right)^{\beta}[s(T) + L(1 - s(T))] \tag{7.5}$$

The primary difficulty in modeling $M(T)$ for this system is the disparity between the low and high field behaviors. In *high* fields the data are characteristic of a predominantly paramagnetic system with AFM correlations; however, as the temperature decreases below $T \approx 120K$, the average magnetic moment drops smoothly. This has previously been attributed to the spins becoming thermally

FIG. 7.2: The $C_{tail}$, $C_{high}$, and $F_{12}$ portions of the total magnetization $M(T)$. The figure for $M(T)$ shows the total plotted along with each individual component for a sample at an external field of 2 kOe.

deactivated as electrons are paired in the lowest energy $Co^{3+}$ orbitals, as in an IS/HS to LS thermal transition. However, in *low* fields the data are more akin to a system with weak ferromagnetic order, exhibiting a steady increase in the average magnetic moment as the temperature decreases to 25 K. This contradicts the thermal deactivation hypothesis, as it is not expected to be field-dependent. In nearly all fields, a marked rise in the magnetization occurs at low temperatures (10 - 30 K). As such, the function used to model the magnetic behavior must account for field-dependent effects, as well as allowing for different behaviors to dominate in different temperature regions.

$C_{high}$ is the Curie-Weiss paramagnetism with antiferromagnetic correlations which begins at "high" temperature ($T > 120$ K) and continues down to low

136

FIG. 7.3: Plots showing the effects of changing the $E_1$ and $d$ parameters in $C_{high}$ (see Eq. 7.3).

temperatures. If the system in question were a simple paramagnet with AFM correlations, $C_{high}$ would be the only contribution to the magnetization. However, this contribution to $M(T)$ decreases with temperature, which can be modeled by convoluting the Curie-Weiss paramagnetic behavior,

$$M/H \propto \frac{E_1}{t_1 + T},\qquad(7.6)$$

with a sigmoid function (Eq. 7.2). $C_{high}$ alone already looks similar to high field ($\geq 2$ kOe) magnetometry data seen for the bulk $LaCoO_3$ and $La_{1.1}CoO_3$ samples. The constant $d$ term accounts for a remnant field, and primarily affects the size of the magnetization above $T_c$. $d$ also has a small effect on the slope of the magnetization above $T_c$, and attempts to fit the data *without* convoluting $d$ and $s(T)$ resulted in a poor fit to this region. The parameter $E_1$ has a much larger effect on the slope of $C_{high}$ above $T_c$. It is possible that the $d$ parameter could be added in as a simple constant rather than as $d \cdot s(T)$ if $E_1$ were modified in a particular manner, however, attempts to do this have so far been unsuccessful. The effects of both parameters on $C_{high}$ are illustrated in Fig. 7.3. Although $C_{high}$ increasingly dominates the high field data as the amount of $Co_3O_4$ in a sample decreases (i.e. the w in $La_wCoO_3$ increases), for low field data it is inadequate.

137

FIG. 7.4: Plot of $C_{tail}$ as given in Eq. 7.4 (red line) and of the paramagnetic portion of $C_{tail}$, $\frac{E_2}{T+t_2}$ (green line).

$C_{tail}$ is the Curie-Weiss paramagnetism entering at low temperatures (between 15 and 35 K). Although the paramagnetic portion of the expression is essentially the same as in Eq. 7.6, it is modulated by $(1 - s(T))$. At first glance this seems unnecessary, as the paramagnetic portion independently gives a sharp rise with decreasing $T$ in the low temperature region. However, the sigmoid portion forces $C_{tail}$ into a gentler, more linear rise which better fits the data at these temperatures. For higher temperatures, the sigmoid brings $C_{tail}$ down to nearly zero, ensuring that it only contributes significantly to the magnetization for $T \leq 35$ K. Figure 7.4 shows the effect of the $(1 - s(T))$ modulation on the Curie-Weiss paramagnetism. Without the $(1 - s(T))$ modulation, the data near 10 K and 40 K cannot be simultaneously fit.

$F_{12}$ is the ferromagnetic contribution to the susceptibility, and is only clearly visible in low fields ($H < 100$ Oe) for the LaCoO$_3$ and La$_{1.1}$CoO$_3$ samples. Samples with larger amounts of Co$_3$O$_4$ (w = 0.7, 0.8, 0.9) have a ferromagnetic contribution which persists to higher fields, as do La$_w$CoO$_3$ nanoparticles (to be discussed in a separate work). This strongly suggests that the ferromagnetism is linked to the

138

amount of surface and interface area in this system. Our model allows for the ferromagnetism to be adjusted independently of the paramagnetic portions, and thus we are able to fit the full range of $La_wCoO_3$ synthesized.

The equation for the magnetization of a ferromagnet in $F_{12}$ corresponds to

$$M/H \propto \left(\frac{T_c - T}{T_c}\right)^\beta,$$
(7.7)

where $T_c$ is the critical temperature and $\beta$ is the critical exponent valid for $T$ within a few degrees of $T_c$. We convolute this form with two sigmoid functions, shown in Eq. 7.5. The sigmoid functions modify the behavior below $T \approx 40K$ in an attempt to account for the deviations from the expected power law behavior of $M/H$ in this temperature range.

In this system, $T_c$ is generally accepted to be approximately 87 K, as the interpretation of the onset of order varies. We define $T_c$ as the inflection point of the magnetization curve and do not include the rounding above this temperature. As such, the fits near $T_c$ appear truncated. The values of $T_c$ found via fitting range between 88 K and 90 K, with a trend towards a slightly higher $T_c$ as w decreases.

The exponent $\beta$ was consistently found to be approximately 0.65. This is nearly twice as large as the empirical value of $\beta_b = 0.30$ - 0.36 [117] for bulk ferromagnets. However, it is smaller than the predicted $\beta_s = 1$ for surface magnetization [118, 119]. This is not wholly unexpected, however, as Kaneyoshi [119] predicted the value for $\beta_s$ using a modification to the (incorrect) mean field theory prediction of $\beta_b = 1/2$. As it is relevant to the discussion of possible surface/interface magnetism in this system, a brief summary of the mean field derivations for both $\beta_b$ and $\beta_s$ will be given for an Ising ferromagnet in a subsequent section.

## 7.2   Fitting Results

The $M/H$ curves for the $La_wCoO_3$ (w = 0.7, 0.8, 1.0, 1.1) bulk samples were all fit using the model discussed above. The parameters for each sample remained

FIG. 7.5: Fits to the magnetization $M/H$ and the inverse magnetization $H/M$ for La$_{0.7}$CoO$_3$. Parameters are listed in Table 7.2.

constant while the field $H$ was varied from 20 Oe to 5 kOe, apart from the magnetization constant $M_{12}$ in the $F_{12}(T)$ contribution. $M_{12}$ was found to decrease with field, which is notable because the fits are to $M/H$; behavior that is strictly field-dependent would have been accounted for by dividing by $H$. In order to demonstrate that this model accounts for the features seen in high and low fields, fits for the inverse magnetization $(H/M)$ are also shown for each sample. Each $M/H$ and $H/M$ curve was fit individually, and once good fit parameters were determined for several of the plots, these were used to fit the rest of the data. Adjustments were then made in order to best fit all of the different fields with the same parameters. Table 7.2 summarizes the results for all of the parameters, and Figs. 7.5 - 7.8 show the $M/H$ and $H/M$ fits for all samples. Each of the fitting parameters gives insight into the physics of this system, although we must be careful not to overinterpret, as the fits are not perfect in all temperature/field ranges.

| Sample | Tc (K) | C (K) | W (1/K) | t2 (K) | L | E1 | E2 |
|---|---|---|---|---|---|---|---|
| w = 1.1 | 88 | 45 | 0.115 | 5 | 1.27 | -0.85 | 0.048 |
| w = 1.0 | 88 | 43 | 0.09 | 11 | 1.28 | 0.5 | 0.09 |
| w = 0.8 | 89 | 39 | 0.09 | 40 | 1 | 1 | 0.232 |
| w = 0.7 | 90 | 34 | 0.09 | 35 | 1 | 1.41 | 0.26 |

| Sample | d (emu/mol) | H = 20 Oe M (emu/mol) | H = 100 Oe M (emu/mol) | H = 200 Oe M (emu/mol) | H = 500 Oe M (emu/mol) | H = 2 kOe M (emu/mol) | H = 5 kOe M (emu/mol) |
|---|---|---|---|---|---|---|---|
| w = 1.1 | 0.0077 | 0.045 | 0.018 | 0.0105 | 0.0046 | 0.00105 | 0.0002 |
| w = 1.0 | 0.0031 | 0.0935 | -- | 0.02 | 0.009 | 0.0018 | 0.0002 |
| w = 0.8 | 0.00146 | 0.34 | -- | 0.07 | 0.03 | 0.0068 | 0.0017 |
| w = 0.7 | 0 | 0.51 | -- | 0.097 | 0.043 | 0.0097 | 0.0026 |

TABLE 7.2: Table showing the fit parameters for the magnetization of $La_wCoO_3$, w = 0.7, 0.8, 1.0, and 1.1. Apart from the parameter $M_{12}$ (here denoted as $M$), parameters for each w remain constant as $H$ varies. The constant parameters $t_1$, $W$, and $\beta$ can be seen in Table 7.1.

141

FIG. 7.6: Fits to the magnetization $M/H$ and the inverse magnetization $H/M$ for La$_{0.8}$CoO$_3$. Parameters are listed in Table 7.2.



FIG. 7.7: Fits to the magnetization $M/H$ and the inverse magnetization $H/M$ for LaCoO$_3$. Parameters are listed in Table 7.2.

## 7.3  Discussion of Fits to the Bulk Magnetization

As previously mentioned, the transition temperature $T_c$ corresponding to the weak ferromagnetic order seen in low fields increases by about 2 K as w goes from 1.1 to 0.7. This is consistent with the ferromagnetism resulting primarily from the interfaces between adjoining Co$_3$O$_4$ and LaCoO$_3$ phases. If the interface effect extends several lattice spacings deep into the LaCoO$_3$ phase, a higher concentra-

FIG. 7.8: Fits to the magnetization $M/H$ and the inverse magnetization $H/M$ for $La_{1.1}CoO_3$. Parameters are listed in Table 7.2.

tion of small (10 - 20 nm in diameter) embedded $Co_3O_4$ crystals could lead to interacting interfaces, thus allowing for a stronger collective phase transition and resulting in a slightly higher $T_c$.

The parameter $L$ differs markedly between the w $= 1.0$, 1.1 and the w $= 0.7$, 0.8 samples. Note that an $L = 1$ corresponds to the ferromagnetic portion of the magnetization, $F_{12}$, no longer being convoluted by the sigmoid function. Instead, the ferromagnetic term matches what would be expected using $\beta = 0.65$ over the entire temperature range $T < T_c$,

$$F_{12} = M_{12}\left(\frac{T_c - T}{T_c}\right)^{\beta}. \tag{7.8}$$

According to this function, the net moment in all of the samples continues to increase at low temperatures, but more so for w $= 1.0$ and 1.1 . In low fields ($H = 20$ Oe), the ferromagnetic behavior is the most obvious for all samples - however, for $T < C$, the model significantly overestimates the magnetization. Although this may appear to be a shortcoming of the ferromagnetic portion of the model, it is also important to keep in mind that $C_{tail}$ is increasing significantly in this region. In fact, the w $= 1.0$ and 1.1 samples have less $Co_3O_4$, and therefore

FIG. 7.9: Plot of the w = 1.0 data at $H = 20$ Oe as compared to the sigmoid-convoluted ferromagnetic portion, $F_{12}(T)$ (green line), the unconvoluted $M(T)$ portion of $F_{12}(T)$ (blue line, see Eq. 7.8), and the component parts of $F_{12}(T)$ (red and purple lines). Note that these fits do not include either the $C_{high}$ or $C_{tail}$ contributions.

a lower ferromagnetic moment; however, there is a significant contribution from the $C_{tail}$ paramagnetic moment. This highlights the difficulty of separating out the types of magnetic behavior in the same temperature range with this model: the low temperature increase is due to both the ferromagnetic and paramagnetic contributions. Nonetheless, it is notable that the data are well fit by the model in all of the higher fields.

Figure 7.9 shows an example fit to data of just $F_{12}(T)$ and its component parts, $M(T)s(T)$ and $M(T)[1 - s(T)]$. Note that the fits do not include either $C_{high}$ or $C_{tail}$ contributions to the magnetization. As can be seen, the total $F_{12}(T)$ portion fits the data quite well by itself for $T \leq 20$ K, but falls short of the data for all higher temperatures. The component portions of $F_{12}(T)$ convoluted by $1 - s(T)$ and $s(T)$ are also shown. Although fits were attempted with $L = 1$ for the w = 1.1 and 1.0 samples, the curvature of the data were more indicative of a two-part ferromagnetic ordering. This may be a result of the ordering of the LCO surface

144

at $T_c \approx 88$ K, and of the $Co_3O_4$ ordering at $T_{c1} \approx 40$ K. However, the cause of the apparent two-part ferromagnetism remains unclear, as the ferromagnetism is very weak, and small effects from unpaired $Co_3O_4$ spins, the contribution from $C_{tail}$, and the lattice contraction and subsequent "freezing in" of the parameters may all be contributing.

The $C_{tail}$ portions of the magnetization account for the low-temperature rise in the $M/H$ plots and the sharp rise in $H/M$ slightly below $T_c$. The multiplicative constant $E_2$ increases as w decreases, mainly to account for the latter effect. The larger magnetization at low $T$ for the w $= 0.7$ and 0.8 samples also requires a larger $E_2$. Balancing both of the effects contributes to the model overshooting $M/H$ at low temperatures for $H = 20$ Oe, but which matches well for the higher fields. As was alluded to in the previous discussion of $F_{12}(T)$, at low temperatures $C_{tail}$ and $F_{12}$ both contribute significantly to the rise in magnetization, and separating out the two contributions unambiguously for all samples was quite difficult. Data below 10 K at higher fields would also help to assess the validity of this portion of the model. The parameter $t_2$ allows for the onset temperature of $C_{tail}$ to be varied. As w is decreased, $t_2$ increases, which indicates that onset of the $C_{tail}$ paramagnetism is favored when there are more $Co_3O_4$ interfaces.

The $C_{high}$ portion describes the behavior above $T_c$ and accounts for the drop in magnetization below $T_c$ for the high field and high w samples. $t_1$ is the onset temperature for $C_{high}$, and was consistently found to be 120 K. Note that the sigmoid-convoluted $C_{high}$ does not model the behavior from 300 K down to 120 K, as this can be done with a simple Curie-Weiss law as was discussed in the previous section on magnetometry. $t_1$ is the temperature at which the inverse magnetization begins to flatten out as it nears $T_c$. $d$ is a small remnant field added to better match the data (also previously discussed). Finally, $E_1$ describes either the rise or fall of the inverse magnetization data beginning a few degrees above $T_c$. As can be noted in the $M/H$ plots for w $= 1.1$ in the magnetometry section, the net moment begins falling at $T_c$ for high fields. All other samples

exhibit an increase in the moment at $T_c$ (with the magnitude directly related to the amount of $Co_3O_4$ in the sample). Correspondingly, the $E_1$ for w = 1.1 is negative, whereas for all other samples it is positive, increasing in magnitude as w decreases. This is likely due to the w = 1.1 sample having too few $Co_3O_4$ interfaces to have a noticeable net ferromagnetic moment in high fields.

## 7.4   Discussion of the Surface Critical Exponent $\beta_s$

We begin with the magnetization per spin for a system of $N$ spins, $m$, defined as a function of the total magnetization $M$ (units of $\mu_B$). $m_b$ refers to the magnetization for the bulk; that is, far from the surface.

$$m_b = \frac{M}{N\mu_B}. \tag{7.9}$$

We may then use the transcendental equation for $m_b$ [117],

$$m_b = \tanh\left(\frac{1}{k_B T}(Jzm_b + \mu_B H)\right), \tag{7.10}$$

where $J$ is defined as the exchange interaction, and $z$ is the coordination number for the system (e.g. $z = 6$ for a three dimensional cubic system). Setting the external field $H = 0$, Eq. 7.10 becomes

$$m_b = \tanh\left(\frac{1}{k_B T}(zJm_b)\right). \tag{7.11}$$

As T approaches the critical temperature $T_c$ from below, the magnetization $M$ decreases, to the point where we can use the expansion for $\tanh(x)$ as $x \ll 1$, $\tanh(x) \approx x - \frac{x^3}{3}$. At $T_c$ we obtain the following:

$$m_b = \frac{zJm_b}{k_B T_c}$$
$$T_c = \frac{zJ}{k_B}. \tag{7.12}$$

Using the expansion for tanh and the result of Eq. 7.12, we can derive the expression for $m_b$ near $T_c$,

$$m_b = \left[ 3\frac{T^2}{T_c^2} \left( \frac{T_c - T}{T_c} \right) \right]^{1/2} \tag{7.13}$$

$$m_b \approx \left[ 3\left( \frac{T_c - T}{T_c} \right) \right]^{1/2} \tag{7.14}$$

For $T \approx T_c$, the $T^2/T_c^2$ factor can be approximated as 1, and we are left with the expected mean field relation,

$$m_b \propto \left( \frac{T_c - T}{T_c} \right)^{\beta} \quad (\beta_b = 1/2) \tag{7.15}$$

$m_b$ is calculated assuming an identical spin environment in all directions, as would be expected deep within the bulk material. However, near the surface it has been shown [118, 119] that the spin environment varies depending on the proximity to the surface. This can be caused by surface strain and reduced coordination at the surface, among other effects. As such, the mean field approximation must be modified to account for these different magnetization "layers." In accordance with the derivation by Kaneyoshi [119], two magnetizations $m_s$ and $m_n$ are defined separately from the bulk. The magnetization $m_s$ *at* the surface is

$$m_s = \tanh \left( \frac{4J_s}{k_B T} m_s + \frac{J}{k_B T} m_1 \right). \tag{7.16}$$

$J_s$ is the exchange interaction at the surface (as opposed to the bulk interaction $J$), and $m_1$ is the magnetization one layer below the surface layer. In this description of $m_s$, octahedral ($z = 6$) coordination is assumed throughout the lattice, with no

significant surface reconstruction. Consequently, $m_s$ contains contributions from the 4 spins in the surface plane and one spin in the layer below. Using $n$ to denote the number of layers away from the surface, $m_n$ can be written as

$$m_n = \tanh\left(\frac{4J}{k_BT}m_n + \frac{J}{k_BT}m_{n-1} + \frac{J}{k_BT}m_{n+1}\right). \tag{7.17}$$

For simplicity, $J$ has been assumed to only change *at* the surface; however, this does not account for the possibility of the surface effects extending several layers deep. One way to accomodate this issue is to calculate the total magnetization assuming all of the layers are identical to bulk, then to recalculate assuming all but the surface layer are identical to bulk, then that all but the first two layers are identical to bulk, etc. Although this does not allow for more than two different $J$s, we can define a quantity $j = J_s/J$ and incorporate it into the solution for $m_n$. Wolfram *et al* then vary $j$ to examine the effects on $m_n$ [118]. Equations 7.16 and 7.17 can be solved approximately by taking the expansion for $\tanh(x)$ at small $x$. This gives a form for $m_n$ of

$$m_n \approx m_b \tanh\left(m_b\left[n - \frac{4(1-j)}{1+4(1-j)}\right]\right), \tag{7.18}$$

where $m_b$ is that given by Eq. 7.14. In contrast to the derivation by Wolfram, note that here we neglect the spin-dependent constant $C_S$ in the expression for $m_n$ - this is purely for simplicity, as the goal here is to determine the critical exponent for the temperature dependence. Indeed, to extract $\beta_s$ from Eq. 7.18, we may take $j = 1$ and $m_b n$ as small, and again apply the $\tanh(x)$ expansion for $T \to T_c$,

$$m_n \approx nm_b^2$$
$$m_n \propto m_b^2 \propto \left(\frac{T_c - T}{T_c}\right), \quad (\beta_s = 1) \tag{7.19}$$

$\beta_s = 1$ has been found experimentally by Fuchs *et al* in their study on the magnetization of LCO thin films [47]. The apparent agreement with mean field theory

148

is surprising, given how notoriously inaccurate it is for bulk three-dimensional systems.

Notably, the $\beta_s$ derived here applies to any layer $n$ near the surface, up until the point where the system may be approximated as bulk and we must use $\beta_b$. Using this model, it is thus quite difficult to predict the effective $\beta$ of a system with surface layers extending past a few lattice spacings into the sample. In addition to this, the idea that the system will "switch" from $\beta_s$ to $\beta_b$ appears unphysical - if the surface layer is "thick" (e.g. $\geq 100$ nm), is it correct to assume that it will behave the same way as a "thin" surface, despite the increased correlation length? Wolfram [118] notes that the magnetization near the surface is inversely proportional to the correlation length $\xi(T)$, and can be expressed as

$$m_n(T) \propto \frac{m_b(T)}{\xi(T)} \propto \left(\frac{T_c - T}{T_c}\right)^{\beta + \nu}, \tag{7.20}$$

where $\xi(T)$ is

$$\xi(T) = a\left(\frac{T_c - T}{T_c}\right)^{-\nu}. \tag{7.21}$$

The constant $a$ is the spacing between the layers, and $\nu$ is the critical exponent associated with the correlation length. The predicted mean field value of $\nu$ is 0.5, while the empirically determined value for a three dimensional magnetic system is 0.62 - 0.68 [117]. As is the case for $\beta$, $\nu$ will also change depending on the dimensionality of the system, going to 1 for a two-dimensional system. Again, a "thick" surface provides complications, as the correlation length will be able to diverge at $T_c$ along the surface, but will be limited in the direction of the surface thickness. In following Eq. 7.20, however, we note that if the $\nu$ and $\beta$ for our system are approximated as the two-dimensional case, the effective exponent of $m_n(T)$ moves even *farther* from our experimental value of 0.65. Clearly, attempting to condense the behavior of this system into one $m_n$ or one $\xi$ by extensions of the mean field theory is inadequate.

Binder and Hohenberg [45, 46] realized that the traditional mean field exponents would not suffice to describe the effects of surfaces on magnetic phenomena, and developed new critical exponents for the semi-infinite Ising and Heisenberg models. In essence, Binder and Hohenberg modify the free energy by introducing boundary conditions and a surface contribution, thus separating the latter from the bulk term. At the surface, translational invariance no longer holds in all directions, and geometrical anisotropy becomes a factor (here we specify that this is near $T_c$, and that we would not expect anisotropy in the bulk in this temperature range as the correlation length becomes infinite in all directions). The surface contribution to the magnetization is treated mathematically as a boundary condition on the magnetization, and the term is included in derivations of the surface magnetization and the surface specific heat. The new critical exponents derived are termed "local" exponents which apply at (and one would presume *near*) the surface, denoted by a *. Here we will simply give the result for the exponents $\nu$ and $\beta^*$ in the three dimensional case [45]:

$$\nu = 0.64 \pm 0.05 \tag{7.22}$$

$$\beta^* = 0.64 \pm 0.08 \tag{7.23}$$

Notably, the result for $\beta^*$ does not match with the expected surface magnetization exponent $\beta_s = 1$. As previously indicated, $\beta$ found for thin films (which would be expected to be nearly entirely surface) [47] and for materials in which only the surface magnetization was probed [118] is closer to the mean field value of 1. However, this exponent matches almost exactly with that found for the $La_wCoO_3$ system examined here.

A result $\beta \approx 0.65$ for this system can actually be reproduced in two ways, each of which implies different things about the magnetic ordering of the material. First, we can simply add the expected magnetic behavior of the surface to that of

FIG. 7.10: Simulation of the effective magnetization behavior of a system with bulk and surface contributions. Proportions shown here are 60 % surface ($m_s(T)$, blue line) and 40 % bulk ($m_b(T)$, green line). Each contribution is shown separately, as well as the sum, $0.6m_s(T) + 0.4m_b(T)$ (black line). For reference, the magnetization $m(T)$ (red line) with $\beta = 0.65$ is also shown.

the bulk, using the empirical exponents $\beta_b = 0.33$ and $\beta_s = 1.0$ and adjusting the proportion of each. The effective magnetization is then

$$m_{eff}(T) \approx A_s \left( \frac{T_c - T}{T_c} \right) + A_b \left( \frac{T_c - T}{T_c} \right)^{0.33}, \tag{7.24}$$

where $A_s$ and $A_b$ are the surface and bulk proportionality constants, respectively. The values $A_s \approx 0.6$ and $A_b \approx 0.4$ give the best approximation of an effective magnetization with $\beta = 0.65$, as can be seen in Fig. 7.10.

The first method inherently assumes that the magnetization is a result of both the bulk and the surface ordering ferromagnetically with the same $T_c$. However, if all of the bulk and all of the surface order, and if we are to believe the proportionality constants, a 500 nm - diameter bulk particle would have a "surface" extending 65 nm into the particle! Although 100 nm - thick thin films have been synthesized [47], it is unlikely that the rounded and irregular (compared to a film) surface of a bulk particle would sustain surface-type order that deeply into the

151

particle. A more plausible explanation for the combination bulk-surface effective magnetization is that only part of the bulk orders at $T_c$, while the other part remains non-magnetic, does not order, or orders at a lower temperature. As was noted when discussing the portions of the magnetization, the amount of ferromagnetism in $La_wCoO_3$ correlates well with the amount of surfaces and interfaces, and becomes much less robust in materials with higher w and larger crystals [42]. As such, the effective magnetization with $\beta = 0.65$ can be reproduced in a much simpler way: assuming that *all* of the ferromagnetism comes from surfaces and interfaces. This is reasonable for our system because it does not strongly order ferromagnetically away from the surfaces. The LCO system is rather unique in that we can observe the surface effects because they are not overwhelmed by the bulk behavior.

TABLE 8.1: Summary of the LaCoO$_3$ nanoparticle samples. Listed are the sample name, the synthesis method used, firing temperature, crystallite size as determined with X-ray diffraction, and weight fraction of Co$_3$O$_4$ as determined by Rietveld refinements on the neutron diffraction data.

| Name | Method | T$_{fire}$(°C) | Crystallite size (nm) | %Co$_3$O$_4$ |
|------|--------|----------------|-----------------------|--------------|
| N52 | 3 | 620 | 22 | 28 |
| N82 | 1 | 620 | 18 | 11 |
| N94 | 1 | 1000 | $\geq 69$ | 0 |

# 8 Magnetism in Nanoparticle LaCoO$_3$

The nanoparticles of LaCoO$_3$ pose a different set of challenges from the bulk for data collection and analysis. The various synthesis methods described here affect the behavior of the nanoparticles greatly due to variations in size, firing temperature and amount of impurity phases. As such, we have here limited our analysis to three nanoparticle samples, N52, N82, and N94. The synthesis method and characteristics of each sample are summarized in Table 8.1.

## 8.1 Neutron Scattering: Nanoparticles

Neutron diffraction data were taken on the WAND diffractometer for all three samples. The temperature range $6 \leq T \leq 300$ K was examined, and scans at each temperature were fit using the FullProf Rietveld refinement package [91]. Refinements were more difficult for the nanoparticles than for the bulk, likely due to a distribution of small, non-spherical particles which results in wider peaks that are difficult to model precisely. The width of the peaks decreases noticeably as the firing temperature increases and larger particles are formed, contributing to better quality refinements for the 1000°C nanoparticles. Noticeable Bragg peaks in the diffraction patterns correspond to impurity phases resulting from the low

FIG. 8.1: FullProf refinement of WAND neutron scattering data for N52 at $T = 10$ K. Data are shown as black circles, the theoretical fit is a red line, and the difference is a blue line. The upper row of triangles corresponds to the LaCoO$_3$ R$\bar{3}$C phase and the lower row corresponds to the Co$_3$O$_4$ F$\bar{4}$3m phase. The uneven background and large impurity peaks (indicated by purple ellipses) resulted in a poor fit.

firing temperature used to create small LCO particles.

As with the diffraction patterns for bulk particles, there are peaks in the nanoparticle spectra corresponding to a Co$_3$O$_4$ phase. The CoO phase observed in some bulk samples was not evident in the nanoparticles. Refinements indicate weight fractions of 28% and 11% Co$_3$O$_4$ in the N52 and N82 nanoparticles, respectively, whereas the N94 nanoparticles do not have a significant Co$_3$O$_4$ phase. In addition to the Co$_3$O$_4$ phase, there are also some Bragg peaks that were not identified as expected oxides of La or Co. When comparing the bulk to the nanoparticle patterns, the lattice structures of these phases appear distinct from that of the LCO bulk. Unless there were a significant amount of impurity peaks directly overlapping the LCO peaks, we would not expect them to significantly affect the quality of the LCO lattice parameters determined from the refinements.

FIG. 8.2: FullProf refinement of WAND neutron scattering data for N82 at $T = 6$ K. Data are shown as black circles, the theoretical fit is a red line, and the difference is a blue line. The upper row of triangles corresponds to the $LaCoO_3$ $R\bar{3}C$ phase and the lower row corresponds to the $Co_3O_4$ $F\bar{4}3m$ phase. Purple ellipses indicate an unidentified impurity phase.

The first sample, referred to in the text as N52, was synthesized using Method 3 (the dialysis method discussed in a previous section) and fired at 620°C. The average diameter of the individual crystallites as given by X-ray diffraction was 22 nm, and SAXS analysis of an LCO sample made in a similar way gave an agglomerate particle size of 65 nm. As can be noted in the TEM results, however, the size of the Method 3 nanoparticles varied significantly within a sample. Individual particles 50 nm and larger were frequently seen in the TEM images. This sample had a large amount of $Co_3O_4$ and unidentified impurities, likely as a combined result of the dialysis step in Method 3 and the low firing temperature. Rietveld refinements using FullProf were done on the neutron scattering data, although the variable background (possibly as a result of the collimator plate issue discussed in the neutron scattering section) and impurity peaks made it difficult to obtain

FIG. 8.3: FullProf refinement of WAND neutron scattering data for N94 at $T = 15$ K. Data are shown as black circles, the theoretical fit is a red line, and the difference is a blue line. The triangles correspond to the $LaCoO_3$ $R\overline{3}C$ phase. No significant $Co_3O_4$ phase was detected for this sample. Purple ellipses indicate an unidentified impurity phase.

high quality refinements. Figure 8.1 shows an example fit done for $T = 10$ K.

The second sample, referred to as N82, was synthesized using Method 1 and fired at 620°C. The average crystallite size determined with X-ray diffraction was 18 nm, while the agglomerate particle size from SAXS was 53 nm. TEM results of these nanoparticles show small, well-separated nanoparticles with little variation in size. The N82 neutron diffraction data were much cleaner than those for N52, although an uneven background and some unidentified impurity peaks are still in evidence. FullProf refinements were of better quality, and the fit at $T = 6$ K can be seen in Fig. 8.2. As was previously noted, firing at 620°C results in small nanoparticles (ideal for studying surface effects), but this temperature is not high enough for the extra phases to fully incorporate into the LCO lattice.

The final sample, referred to as N94, was synthesized using Method 1 and fired

at 1000°C. This resulted in very large nanoparticle sizes, too large to calculate using the Scherrer method for X-ray diffraction data. The PDXL software package [66] used to analyze the X-ray data was only able to place a lower bound of 69 nm on the crystallite size. Based on the size of the Method 3 nanoparticles fired at 1000°C as determined with TEM ($\leq$ 400 nm), we estimate an upper bound of 400 nm for N94. Unlike the samples fired at 620°C, N94 did not contain a significant $Co_3O_4$ phase. As can be seen in Fig. 8.3, the FullProf refinement gave a much better fit than the other two samples, although there are still a few unidentified impurity peaks.

The $a$ and $c$ hexagonal lattice parameters, the oxygen position, the Co-O bond length, the Co-O-Co bond angle, and the $\delta y$ parameter for the rhombohedral distortion are all presented in Figs. 8.4 and 8.5 for LCO bulk and nanoparticles. Note that the values of these parameters from the FullProf fits are average ones, and that the nanoparticle interiors and surfaces surely have different values and behaviors. Contrasting the sharp changes observed near 37 K in bulk LCO and N94, the $a$ and $c$ parameters, as well as the Co-O bond length for N52 and N82 exhibit no abrupt change in slope. For these three parameters, the values for the N94 sample are the same as or larger than the other nanoparticles; it can be seen that all of the nanoparticles have a larger unit cell than bulk LCO. This is consistent with the findings of other researchers [33, 40].

However, when looking at the degree of octahedral twisting as indicated by the oxygen position, Co-O-Co bond length, and $\delta y$, N94 matches more closely to the bulk values than to the other nanoparticles. N82 exhibits the largest Co-O-Co bond angle, and the lowest $\delta y$, while N52 is middling between N82 and N94. One might then conclude that because N82 is the most strained, it will exhibit the largest amount of ferromagnetic order. As will be seen in the $M/H$ measurements, however, N52 actually has the largest ferromagnetic moment. This will be discussed in the nanoparticle magnetometry section.

FIG. 8.4: Lattice parameters and related values for nanoparticles and bulk LaCoO$_3$. From top to bottom: the hexagonal lattice parameters $a$ and $c$, and the Co-O bond length.

FIG. 8.5: Lattice parameters and related values for nanoparticles and bulk LaCoO$_3$. From top to bottom: the Co-O-Co bond angle, the oxygen position in the unit cell and the rhombohedral distortion parameter $\delta y$.

FIG. 8.6: Fits to the $a$ lattice parameter for LCO bulk (for reference) and nano samples. "Power fit" refers to fits done using a power law, and "Grun fit" refers to fits done using the Grüneisen-Einstein model. As with the bulk $La_wCoO_3$ samples, the latter fits were made to best fit the lowest $T$ data.

## 8.2 Fits to the Nanoparticle Lattice Parameters

The temperature dependence of the nanoparticle $a$ lattice parameters are shown in Fig. 8.6, along with a qualitative fit using the Grüneisen-Einstein model for thermal lattice expansion,

$$y(T) = y(0)[1 + \alpha(\coth(\frac{T_E}{2T}) - 1)] \quad , \tag{8.1}$$

where the lattice parameter being fit is $y(T)$, $y(0)$ is its value at $T = 0$, $T_E$ is the Einstein temperature, and $\alpha$ is the thermal expansion coefficient for $T >> T_E$ [8].

TABLE 8.2: Fits to the $a$ lattice parameter for LCO bulk and N52, N82, and N94 nanoparticle samples using the Grüneisen-Einstein equation $y(T) = y(0)[1 + \alpha(\coth(\frac{T_E}{2T}) - 1)]$. These fits correspond to those shown in Fig. 8.6. The qualitative nature of these fits prevents the assigning of any meaningful error to the parameters.

| Sample | $\alpha$ ($10^{-5}$) | $T_E$ (K) | $y_0$(Å) |
|--------|------|------|--------|
| Bulk | 0.82 | 110 | 5.3957 |
| N52 | 0.57 | 100 | 5.4059 |
| N82 | 0.57 | 100 | 5.4075 |
| N94 | 0.97 | 90 | 5.4085 |

TABLE 8.3: Fits to the $a$ lattice parameter for LCO bulk and N52, N82, and N94 nanoparticle samples using the power law equation $y = A(T - T_o)^\sigma + B$. These fits correspond to those shown in Fig. 8.6. Errors for $A$ and $B$ are approximately $\pm 1$ of the smallest significant digit, while the error for $\sigma$ is $\pm 2$ of the smallest significant digit, and that for $T_o$ is given in the table.

| Sample | $A$ ($10^{-4}$ $\frac{Å}{K}$) | $T_o$ (K) | $\sigma$ | $B$(Å) |
|--------|------|--------|------|--------|
| Bulk | 2.08 | 37(2) | 0.83 | 5.3960 |
| N52 | 1.42 | 30(3) | 0.83 | 5.4060 |
| N82 | 2.10 | 30(3) | 0.76 | 5.4078 |
| N94 | 4.05 | 37(3) | 0.75 | 5.4090 |

Much like in bulk $La_wCoO_3$, the lattice parameters are not well fit at low temperatures by the thermal expansion model. $T_E$ also remains unrealistically low. Although the N52 and N82 samples exhibit a smooth, nearly linear increase in $a$ with temperature, the slight curvature remains negative, and thus the Grüneisen-Einstein model, which has positive curvature, is not a good fit. Table 8.2 shows a summary of the Grüneisen-Einstein fitting parameters for the bulk and nanoparticles.

The fits using the power law behavior (first introduced for the bulk material)

are somewhat better than the Grüneisen-Einstein fits, although it is difficult to quantify the improvement for N52 and N82 without more data. The power law fit equation is

$$y(T) = A(T - T_o)^\sigma + B, \qquad (8.2)$$

where A and B are constants, and $\sigma$ is the structural transition critical exponent. As can be seen in Fig. 8.6, N94 is clearly best fit by the power law above for $T \geq 37$ K. The data for N52 are too linear for either the power law fit or the Grüneisen-Einstein fit, whereas the negative curvature in the N82 data is better fit with a power law. Table 8.3 summarizes the power law fitting parameters for the bulk and nanoparticles. Notably, $T_o$ is around 30 K for the smallest nanoparticles, whereas N94 and bulk LCO both have a $T_o$ of 37 K. Given that N52 and N82 have a relatively large proportion of surface area as compared to N94 and the bulk, it is unsurprising that their structural parameters show no sharp features. A similar lack of such features can also be noted in the $La_ySr_xCoO_3$ bulk samples. In both cases, this is likely due to large amounts of strain spread throughout the lattice: as a result of surfaces in the nanoparticles, and of Sr in the LSCO. In summary, although N94 exhibits a structural phase transition at 37 K similar to that seen in bulk LCO, no such transition is detected in the N52 and N82 nanoparticle samples.

## 8.3   Nanoparticle Magnetometry

$M/H$ vs $T$ for the N94 and N52 LaCoO$_3$ nanoparticles is shown for FC in Figs. 8.7 and 8.8. The nanoparticle ferromagnetic phase transition for N94 and N52 occurs near the transition temperature of the bulk, indicating that the magnetism in both materials is of the same origin. N52 has a $T_c \approx 82$ K and N94 has a $T_c \approx 87$ K; the lower transition temperature of N52 is likely due to more disorder in the lattice as a result of increased surface area, and a distribution

FIG. 8.7: Fits to the magnetization $M/H$ and the inverse magnetization $H/M$ for N94. Parameters are listed in Table 8.4.

of $T_c$'s due to the large variance in particle sizes. Rounding of the magnetization near the transition is partly due to the increased surface area of the nanoparticles; the transition for the larger N94 particles is sharper than that for the smaller N52 particles.

The low temperature magnetization in $H = 20$ Oe for N94 ($M/H \approx 0.12 \frac{\text{emu}}{\text{mol·Oe}}$) is very similar to that for bulk LCO ($M/H \approx 0.11 \frac{\text{emu}}{\text{mol·Oe}}$). Previous results indicate that LCO nanoparticles have a larger ferromagnetic moment due to their increased surface area [42, 43]. N94 ($\leq 400$ nm) has a notably lower particle size than bulk LCO ($\geq 500$ nm); therefore, the similarity in the magnetization data indicate that another factor is contributing. In this case, it is likely the fact that the LCO bulk has approximately 4.5 % $Co_3O_4$ and that N94 has no detectable $Co_3O_4$ phase. Possibly as a result of the $Co_3O_4$ interfaces, the magnetization of LCO bulk nearly matches that of the N94 nanoparticles, which have a larger proportion of surface area.

The N52 nanoparticles, however, show a much larger FC ferromagnetic moment than either the bulk LCO or the N94 sample. Despite their small size, the low temperature magnetization in $H = 20$ Oe is approximately 2.2 $\frac{\text{emu}}{\text{mol·Oe}}$, nearly 20 times larger than for bulk LCO. This is likely a result of the combined effects of smaller size (thus a larger proportion of tensile-strained surface area conducive to

163

FIG. 8.8: Fits to the magnetization $M/H$ and the inverse magnetization $H/M$ for N52. Parameters are listed in Table 8.4.



FIG. 8.9: FC and ZFC $M/H$ vs $T$ data for N52 at $H = 20$ Oe and 60 kOe. Open symbols are ZFC, and closed symbols are FC. The data at 60 kOe have been multiplied by a factor of 100 to facilitate comparison with the 20 Oe data.

ferromagnetism), and a large weight percentage of $Co_3O_4$.

As can be seen in Fig. 8.9, even at $H = 60$ kOe the magnetization does not show the antiferromagnetic decrease seen in the bulk and N94 samples. Instead, the N52 moment increases monotonically as $T$ decreases over the entire temperature range. In the $H/M$ vs $T$ data for 60 kOe (Fig. 8.8), no large peak can be seen

FIG. 8.10: Fits to the magnetization $M/H$ and the inverse magnetization $H/M$ for N82. Parameters are listed in Table 8.4.

near 35 K, indicating an absence of the antiferromagnetic short range order seen in the N94 and bulk $La_wCoO_3$ samples. This indicates a strong influence of the ferromagnetic interactions in high field. The bulk LCO and N94 data indicate no such signifcant ferromagnetic interaction at high fields, consistent with the small net ferromagnetic moment observed in the bulk.

Figure 8.10 shows the $M/H$ vs $T$ magnetization for the N82 nanoparticles, which differs from N52 and N94 in several ways. The ferromagnetic transition temperature is lower, with a significant rise in the net moment appearing near 60 - 70 K in the FC data, and the transition itself is much more rounded. The inverse magnetization plots clarify the location of the transition for low fields: the decrease in $H/M$ happens at 75 K. The net moment at low $T$ is approximately $0.25 \frac{emu}{mol \cdot Oe}$, twice as large as that for LCO bulk and N94, but still 10 times smaller than that for N52. The magnetization above $T_c$ is not field-independent, indicating that there is some short-range order in this temperature range. A remnant field from the magnetometer can be eliminated as the cause, as the contribution from a remnant field would not vary with $H$. The magnetization data from these nanoparticles is most similar to that found by Fita $et$ $al$, with a rounded transition and a nearly linear magnetization increase as $T$ decreases [33]. As with Fita $et$ $al$, it is possible that there is a small amount of CoO phase in

165

the N82 sample. They were not able to detect the amount with X-ray diffraction (and indeed, we do not see any indicators of CoO in our neutron scattering data) - however, they did see a net moment below 250 K attributable to AFM ordering of CoO. Note that although CoO orders antiferromagnetically, uncompensated spins at the surface contribute a net ferromagnetic moment which can be seen in magnetization measurements [70].

## 8.4    Fits to Nanoparticle Magnetization

The magnetization model developed for bulk particles can be applied to nanoparticles and gives insights into behaviors observed previously, but never adequately explained. We compare the results already described for the bulk $w = 1.0$ LCO sample to the three LCO nanoparticle samples, each showing strikingly different behavior that appears to be governed by the amount of $Co_3O_4$ interfaces and the relative amount surface area in the sample (determined primarily by the average crystallite size). Fits to the nanoparticle data were done in a similar way as those for the bulk data, and are represented in Figs. 8.7, 8.8, and 8.10. The fitting parameters are shown in Table 8.4. Fits correspond to the same fitting equations and parameters used for the bulk,

$$C_{high} = \left(d + \frac{E_1}{T + t_1}\right)s(T), \tag{8.3}$$

$$C_{tail} = \left(\frac{E_2}{T + t_2}\right)(1 - s(T)), \tag{8.4}$$

$$F_{12} = M_{12}\left(\frac{T_c - T}{T_c}\right)^\beta [s(T) + L(1 - s(T))]. \tag{8.5}$$

The magnetization for $H = 20$ Oe below the ferromagnetic phase transition in N52 and N94 exhibits the usual power law behavior $(\frac{T_c - T}{T_c})^\beta$ as the moments spontaneously align with each other. Fits yielded $\beta = 0.63$ in these nanoparticles,

166

| Sample | Tc (K) | C (K) | W (1/K) | t1 (K) | t2 (K) | L | β | E1 | E2 |
|---|---|---|---|---|---|---|---|---|---|
| N94 | 87.5 | 47 | 0.09 | 70 | 5 | 1.15 | 0.63 | 0.15 | 0.077 |
| N82 | 75 | 50 | 0.09 | 40 | 40 | 1 | 1.5 | 0.73 | -- |
| N52 | 82 | 80 | 0.05 | 80 | 80 | 1.4 | 0.63 | 0.88 | 1.5 |

| Sample | H = 20 Oe M (emu/mol) | H = 50 Oe M (emu/mol) | H = 100 Oe M (emu/mol) | H = 200 Oe M (emu/mol) | H = 500 Oe M (emu/mol) | H = 1 kOe M (emu/mol) | H = 2 kOe M (emu/mol) | H = 5 kOe M (emu/mol) | H = 60 kOe M (emu/mol) |
|---|---|---|---|---|---|---|---|---|---|
| N94 | 0.11 | 0.063 | 0.039 | 0.022 | 0.0092 | 0.0043 | 0.0017 | 0.00006 | -- |
| N82 | 0.31 | -- | 0.29 | 0.23 | -- | -- | 0.052 | 0.023 | -- |
| N52 | 1.61 | -- | -- | -- | -- | -- | -- | -- | 0 |

| Sample | All fields d (emu/mol) | H = 20 Oe d (emu/mol) | H = 100 Oe d (emu/mol) | H = 200 Oe d (emu/mol) | H = 2 kOe d (emu/mol) | H = 5 kOe d (emu/mol) |
|---|---|---|---|---|---|---|
| N94 | 0.0036 | -- | -- | -- | -- | -- |
| N82 | -- | 0.0115 | 0.0046 | 0.0033 | 0.0007 | 0.00036 |
| N52 | 0.0004 | -- | -- | -- | -- | -- |

TABLE 8.4: Fit parameters for the magnetization of $La_wCoO_3$ nanoparticles. Apart from the parameter d for N82 and the parameter $M_{12}$ (here denoted as $\mathbf{M}$) for all samples, the parameters for all nanoparticles remain constant as $H$ varies.

very close to $\beta = 0.65$ found in bulk $La_wCoO_3$. As discussed in the context of the bulk powders, this exponent is consistent with surface ordering as described by the Binder-Hohenberg model [45, 46].

Using the conceptual model developed for the bulk particles, we can make the following observations regarding the behavior of our nanoparticle systems. The largest of the nanoparticle samples (N94) behaves similarly to the LCO bulk particles, except that $T_c$ is lower and the deviation of $M/H$ vs $T$ below 40 K from the power law behavior (Eq. 8.5) for $H = 20$ Oe is weaker. In essence, the physics of the largest nanoparticles is not significantly different from that of the bulk. In contrast, the N52 nanoparticles do not show signs of the crossover from $C_{high}$ to $C_{tail}$ in $M/H$ vs $T$ at 60 kOe; fits to these Curie-Weiss behaviors at high and low $T$ have the same Curie temperature ($t_1 = t_2$). The most obvious difference between the N52 and LCO bulk is the strength of the $F_{12}$ portion of $M/H$ vs $T$ for $H = 20$ Oe, with $M_{12} = 1.61$ for N52 as compared to $M_{12} = 0.0935$ for the bulk. The N52 data follow the $F_{12}$ power law behavior closely down to low $T$.

The stronger net ferromagnetic moment in N52 is consistent with the greatly increased surface area compared to the bulk and N94, as well as the large amount of $Co_3O_4$ and resulting interfaces. The surfaces and interfaces order in accordance with the Binder-Hohenberg surface ordering mechanism, aided by the antiferromagnetic ordering of the relatively unstrained "core" of the nanoparticles (corresponding to Region 3 in the bulk $La_wCoO_3$ model). The lack of a visible crossover (the large bump around 35 K in the bulk and N94 samples) may be due to the sheer size of the ferromagnetic contribution relative to the antiferromagnetic contributions to the magnetization, making it difficult to determine the parameters for $C_{high}$ and $C_{tail}$.

The smallest nanoparticle system (N82) showed behaviors not observed in the other samples. The large $H$ behavior showed no clear crossover effects, and in fact the $C_{high}$ contribution appeared entirely absent from the magnetization in preliminary fits. The constant FM moment seen above $T_c$, possibly attributable

168

to CoO, was simply fit with a constant d. Unlike in the bulk and other nanoparticle samples, d was not convoluted with a sigmoid. There is little evidence of a FM phase transition near 80 K apart from the somewhat sharp decrease seen in the $H/M$ vs T data at low fields. In order to fit the $M/H$ data, the $F_{12}$ portion of the magnetization was modified to

$$F_{12}^{new} = M_{12}\left(\frac{T_c - T}{T_c}\right)^{\beta}. \tag{8.6}$$

With this modification, the ferromagnetic rise begins to contribute significantly at 50 K rather than at 87 K. As there did not appear to be a crossover, the paramagnetic behavior was better fit with a simple Curie-Weiss law and the contribution can be written as $C_{new}$,

$$C_{new} = \frac{E_1}{T_c + t_1}, \tag{8.7}$$

where the parameters $E_1$ and $t_1$ are used for simplicity. Including the constant d, the total magnetization $M(T)/H$ of N82 was fit with

$$M(T)/H = d + C_{new} + F_{12}^{new}. \tag{8.8}$$

It is unclear why the N82 nanoparticles are so different from the other nanoparticles and bulk. In particular, it is curious why, despite the large Co-O-Co angle and low $\delta y$, N82 does not show robust ferromagnetic order. Instead the value for $\beta$ is 1.5, which does not correspond to ordering. This value for $\beta$ may also be a consequence of $F_{12}^{new}$ and a paramagnetic portion overlapping, making it difficult to extract the parameters for each contribution. We propose that the lack of order is due to a combination of size effects and a small amount of $Co_3O_4$ as compared to N52. It is possible that the small *size* of N82 prevents any significant ferromagnetic ordering, due to the nanoparticles being strained nearly throughout by surface effects. Although the average size of N52 was only 4 nm larger than that for N82, the TEM results indicated a large spread in the N52

sizes, with some nanoparticles reaching up to 100 nm. The N82 nanoparticles were consistently small and showed little size variation. Wei *et al* also found a reduction in the ferromagnetic moment as their nanoparticle sizes decreased [40], in contrast to other studies [33, 42, 43]. If the ferromagnetism at the strained surface of the nanoparticles is stabilized by an antiferromagnetic core (as in the Binder-Hohenberg model [45, 46]) the lack of a significant AFM core in these small nanoparticles may prevent the surface from ordering via ferromagnetic canting. For particles this small, it is likely that all of the system is essentially surface region (Regions 1 and 2), and no region can be considered to belong to the interior region (Region 3). If the N82 nanoparticles are entirely surface, tensile strain along a particular direction is essentially nonexistent (as they are strained throughout), so the ferromagnetic order may vanish as a result. As this effect may also be a factor for the N52 sample, we turn to $Co_3O_4$ as a possible reason for the large ferromagnetic moment in N52. Tensile strain from the $Co_3O_4$ interfaces may contribute significantly to the net ferromagnetism. Given that these nanoparticles are also small on average, the lack of antiferromagnetic behavior may be due to a small core in N52 - the core is present, providing tensile strain, but is too small to contribute significantly to the antiferromagnetic portion of the magnetization curve. The findings for N82 and N52 indicate there may be an ideal size and $Co_3O_4$ content for maximum ferromagnetic ordering in nanoparticles.

The fit results for the smallest nanoparticles indicate that there is still room for improvement and additional physical interpretation with regards to the magnetization model. In general, however, the behavior of nanoparticle LCO can be explained using the basic ideas behind the model developed for the LCO bulk particle system. For that reason, the nanoparticle results lend credence to the model and demonstrate the utility of this model to understand systems that exhibit diverse magnetization behaviors.

# 9 Conclusion

In summary, we examined different methods of synthesis for LCO and LSCO nanoparticles, and further investigated the commonly-used solid-state synthesis method for LCO and LSCO. Samples were characterized using X-ray diffraction, TEM, and X-ray fluorescence methods. Neutron scattering data were taken on bulk and nanoparticle samples and fit using the FullProf refinement suite, and the temperature dependence of the lattice parameters extracted from the refinements were also fit. Neutron and X-ray diffraction results were used to estimate the amount of $Co_3O_4$ in the LCO and LSCO samples. Magnetometry data were taken using an MPMS SQUID magnetometer, and the ferromagnetic transition at 87 K was examined as a function of field, $Co_3O_4$ amount, and surface area. A mathematical model for the magnetization $M/H$ was proposed, and fits are done for all $La_wCoO_3$ bulk and three nanoparticle samples. The fits show that there are two regions of paramagnetism with antiferromagnetic interactions and one region of weak ferromagnetic order. The ferromagnetic contribution to the fit uses a critical exponent consistent with ordering of the surfaces and interfaces.

Over the course of the nanoparticle synthesis, we found that firing temperatures higher than 620°C are best for synthesizing nanoparticles without unidentifiable impurity phases, although firing at 1000°C results in particles that are nearly the same size as bulk. The optimal synthesis method for LCO and LSOC nanoparticles was determined to be Method 1, in which a sub-stoichiometric amount of NaOH is added to the starting materials. This method resulted in nearly phase-pure nanoparticles with a small spread in size, which were the easiest to characterize. However, the Method 3 nanoparticles, which underwent a dialysis treatment, had by far the largest ferromagnetic moment compared to other LCO nanoparticles and bulk. This is likely a result of the sample having nearly 30 % $Co_3O_4$ by weight, which introduces many LCO-$Co_3O_4$ interfaces. Overall, all of the LCO nanoparticle samples examined (N52, N82, and N94) had larger ferromagnetic

moments than the bulk, and this effect increased with surface area and $Co_3O_4$ amount.

Bulk $La_wCoO_3$ created using the solid-state synthesis method tended to have an extra $Co_3O_4$ phase even when adding excess $La_2O_3$ to the starting materials. Extra phases containing La were not seen, indicating that any excess La compounds are either amorphous, or form nanoparticles too small to be seen with diffraction methods. When excess $Co_3O_4$ was added to form the $La_wCoO_3$ (w = 0.7, 0.8 and 0.9) samples, the resulting percentage of $Co_3O_4$ phase was larger than would be expected with stoichiometry calculations. We conclude that it is difficult to completely eliminate the $Co_3O_4$ phase from LCO and LSCO samples, and that further studies should take this phase into account because $Co_3O_4$ has significant effects on the amount of ferromagnetic order in these materials.

Neutron scattering results indicated no ferromagnetic Bragg peak for LCO at 87 K, indicating weak magnetic order. The ferromagnetic ordering peak for LSCO was seen at 250 K; notably, this peak was seen for $La_{0.8}Sr_{0.1}CoO_3$ and not for $La_{0.9}Sr_{0.1}CoO_3$, indicating that non-stoichiometry also enhances the Sr-induced ferromagnetism. $Co_3O_4$ and CoO antiferromagnetic Bragg peaks were seen in nearly all samples, indicating that these materials were crystalline and able to order magnetically. The lattice and other parameters extracted from the refinements of neutron scattering data did not show consistent changes depending on $Co_3O_4$ content, and indicated that lattice strain from the $Co_3O_4$ was relatively small. Both nanoparticle and bulk lattice parameters could not be adequately fit with the Gruneisen-Einstein model for thermal expansion, and were instead much better fit with a power-law behavior. This indicates a possible second-order structural transition into a "frozen in" structural state below 37 K; no symmetry change is seen at 37 K, so the system does not have a first order transition (as in $SrTiO_3$). The N52 and N82 nanoparticle parameters were more difficult to fit with a power-law, likely as a result of their small particle size and larger amount of surface disorder.

Despite the lack of a magnetic ordering Bragg peak at 87 K, $M/H$ data show a transition to ferromagnetic order at 87 K in the $La_wCoO_3$ samples as well as the N52 and N94 nanoparticles. This transition is seen mostly in low fields ($H \leq 100$ Oe). At high fields, a decrease in $M/H$ is seen which is attributable to short-range antiferromagnetic order or the transition from one type of paramagnetism with an antiferromagnetic exchange interaction to another with a smaller exchange interaction. The latter explanation is consistent with two regions of Curie-Weiss paramagnetism for different temperature ranges which were seen in plots of $H/M$ for $LaCoO_3$. The strength of the ferromagnetism, sharpness of the ferromagnetic transition at 87 K, and robustness of the ferromagnetic transition at high fields increases significantly with $Co_3O_4$ amount for the bulk and nanoparticle samples. This effect of $Co_3O_4$ is the same as that seen by other researchers when increasing the surface area of LCO and when depositing thin films of LCO on a substrate, which resulted in tensile strain on the lattice [38, 42]. We thus concluded that adding $Co_3O_4$ resulted in an increase in the amount of LCO-$Co_3O_4$ interfaces, which behaved much in the same way as surfaces by increasing the amount of ferromagnetism. We proposed three regions of lattice strain as a result of surfaces and interfaces, with the region closest to the surface/interface undergoing the largest amount of tensile strain, while the inner regions were less strained. These findings are consistent with calculations showing that lattice strain could result in a magnetic ground state for LCO [18]. Although the nature of the ferromagnetism remains unclear, we suggest it may be due to canting of the antiferromagnetically short-range ordered spins near the surfaces/interfaces of the material.

The model proposed for the magnetization of $La_wCoO_3$ bulk and LCO nanoparticles represents the first attempt to mathematically model $M/H$ for all fields. Conceptually, the model consists of three contributions to the magnetization. One contribution is from ferromagnetic order beginning at 87 K, and two are paramagnetic with different antiferromagnetic exchange interactions. A sigmoid function convoluted with each contribution allows for the proportion of each con-

173

tribution to change with temperature. Contrary to previous theories predicting a non-magnetic state for $T \leq 30$ K, we find that this temperature range exhibits paramagnetic behavior. Notably, in each sample the magnetization and inverse magnetization data can be fit using the same parameters for the paramagnetic contributions across all fields. This also holds for the ferromagnetic contribution, with the exception of the magnitude M of the contribution, which decreases as the external field increases. The critical exponent $\beta$ for the ferromagnetic portion of the fit was found to be 0.65, consistent with the findings by Binder and Hohenberg for the magnetic ordering of a surface [45, 46]. The consistency of all the fit parameters indicates that the model successfully describes the underlying magnetic behavior of the bulk material. The parameters varied more with the nanoparticle fits, though this may be due to surface effects and increased disorder. The description of these magnetic phenomena in the context of phase transitions and collective behavior indicates that the localized spin-state models are inadequate for modeling the system, and that a band theory approach is far more constructive and realistic.

It is our hope that the model for the magnetization will be improved by subsequent studies, and that the theoretical basis for the changes in magnetization will be clarified, particularly for the nanoparticles. The precise mechanism by which ferromagnetism appears on the surfaces/interfaces is still uncertain, and more detailed studies on thin films and tensile strain in the context of the Binder-Hohenberg model for surface magnetism would likely elucidate this phenomenon. The ferromagnetic-enhancing effects of $Co_3O_4$ are extremely significant for the community studying LCO and related materials, and must be taken into account for subsequent magnetization studies. A detailed structural model for *why* $Co_3O_4$

affects the magnetism would be an invaluable contribution to this field of study.

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