2011

A SYSTEMATIC STUDY OF THERMODYNAMIC AND TRANSPORT PROPERTIES OF LAYERED 4D AND 5D CORRELATED ELECTRON SYSTEMS

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A SYSTEMATIC STUDY OF THERMODYNAMIC AND TRANSPORT PROPERTIES OF LAYERED 4D AND 5D CORRELATED ELECTRON SYSTEMS

DISSERATION

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the University of Kentucky

By

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Lexington, Kentucky

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Lexington, Kentucky

2011

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ABSTRACT OF DISSERTATION

A SYSTEMATIC STUDY OF THERMODYNAMIC AND TRANSPORT PROPERTIES OF LAYERED 4D AND 5D CORRELATED ELECTRON SYSTEMS

Correlated electron materials have been at the forefront of condensed matter research in the past couple of decades. Correlation in materials, especially, with open d and f electronic shells often lead to very exciting and intriguing phenomenon like high temperature superconductivity, Mott metal-insulator transition, colossal magnetoresistance (CMR). This thesis focuses on triple-layered Sr$_4$Ru$_3$O$_{10}$, Sr substituted double layered (Ca$_{1-x}$A$_x$)$_3$Ru$_2$O$_7$ (A = Ba, Sr) and 5d system Sr$_2$IrO$_4$ and Sr$_3$Ir$_2$O$_7$. Triple-layered Sr$_4$Ru$_3$O$_{10}$ displays interesting phenomena ranging from quantum oscillations, tunneling magnetoresistance, unusual low temperature specific heat, strong spin-lattice coupling to switching behavior. The central feature, however, is the unique borderline magnetism: along the c-axis. Sr$_4$Ru$_3$O$_{10}$ shows spontaneous ferromagnetism, indicating a strong Coulomb exchange interaction, U and a large density of states at the Fermi surface, $g(E_F)$, hence $Ug(E_F) \geq 1$ (Stoner criterion). But within the ab-plane it features a pronounced peak in magnetization and a first-order metamagnetic transition. The coexistence of the interlayer ferromagnetism and the intralayer metamagnetism makes Sr$_4$Ru$_3$O$_{10}$ a really unique system. Also, in this thesis the spin-valve behavior exhibited by impurity doping at the Ca site by Ba and Sr in the double layered Ca$_3$Ru$_2$O$_7$ is reported. Spin valve effect is a phenomenon only realized in multilayer thin films. Here, spin valve is observed in bulk single crystals of impurity doped Ca$_3$Ru$_2$O$_7$, Ca$_3$(Ru$_{1-x}$Cr$_x$)$_2$O$_7$ and (Ca$_{1-x}$A$_x$)$_3$Ru$_2$O$_7$ (A = Ba, Sr). 5d Iridates are expected to be more metallic and less magnetic than their 3d and 4f counterparts because of the extended 5d orbitals. In marked contrast, many iridates are magnetic insulators with exotic properties. The focus in this thesis is on Sr$_2$IrO$_4$ which displays a novel $J_{\text{eff}} = 1/2$ Mott state. Magnetic, electrical, and thermal measurements on single-crystals of Sr$_2$IrO$_4$, reveal a novel giant magneto-electric effect (GME) arising from a frustrated magnetic/ferroelectric state. The GME and electric polarization hinge on a spin-orbit gapping of 5d-bands, rather than the magnitude and spatial dependence of magnetization, as traditionally accepted.
A SYSTEMATIC STUDY OF THERMODYNAMIC AND TRANSPORT PROPERTIES
OF LAYERED 4D AND 5D CORRELATED ELECTRON SYSTEMS

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October 28, 2011
(Date)
To my parents

Suresh Chikara and Inder Pal Singh
ACKNOWLEDGEMENTS

It gives me utmost pleasure and happiness to take this opportunity to express my gratitude to all the people without whom this accomplishment would not have been possible.

First of all, I wish to express my most sincere thanks and heartfelt gratitude to my advisor Prof. Gang Cao. Throughout the course of my Ph.D, he has made available his support in a number of ways. He has always been a source of inspiration, motivation and encouragement needed to complete this challenging journey. His enthusiasm towards research is amazing and definitely contagious. I can never forget the numerous discussions with Prof. Cao and our research group during the course of my Ph.D work. He gave me the guidance needed for the research work and the freedom to make mistakes as a part of the learning process. I am very appreciative for all the resources and equipments I had at my disposal and the opportunities to work at the National High Magnetic Field Lab and exposure to Oak Ridge National Lab. I gained invaluable experience and education not only in research but also interacting with world renowned scientists by being a part of the two workshops organized by Prof. Cao at University of Kentucky and all the March Meeting that he encouraged us to attend. To present your research is as important as doing the research and Prof. Cao’s encouragement and emphasis on presentations have been extremely helpful. His confidence and trust in my capabilities are extremely cherished.

I would also like to thank the DGS and my committee member Prof. Joseph Brill for helping me with the nuances of all the paperwork and deadlines for various stages towards my degree. I also wish to thank him for making suggestions to my dissertation.

I wish to thank Prof. Sean Parkin for the use of his lab and expertise to determine the crystal structures of many of the systems in my work. I would also like to thank Dr. Wen Hai Song for the opportunity to work with him on the development of the thermal power measurement set up and introducing me to Seebeck coefficient measurements.

I am also thankful to all the people in Physics office for handling all the paperwork. I especially thank Eva Ellis and Carol Cotrill for being extremely helpful in all matters administrative related to my work and for their friendship. I also wish to thank the machine shop and electronic shop personnel for their invaluable help with designing and troubleshooting of equipments throughout the course of my research.

It gives me great pleasure to thank Prof. William Crummett whose friendship and support I value a lot. His affable nature have always been welcome especially during tough
times and I greatly appreciate his help during measurements and for taking the time to
read my dissertation and make suggestions.

Any work becomes a lot more pleasant with nice colleagues to work with. I want to thank
my lab mates, Xiunu Lin, Esmat Elhami, Vinobalan Durairaj, Vijayalakshmi Varadarajan,
Angela Pooler, Alec Sim, Oleksandr Korneta, Tongfei Qi, Bishnu Thapa and Min Ge for
their help in the lab and their friendship outside the lab during this journey.

What we are comes from our background and our family. I am blessed with the most
loving family. I thank my family for their unfailing support and encouragement even when
I was not able to see them for years on end. My father for working really hard and never
compromising on the quality of our education. I can not thank my mother enough for
the boundless love she have given me and her confidence in me. Her energy and unyielding
optimism and seeing the bright side in things have always been a great motivator throughout
my life. I am thankful to have the most amazing sisters, Chhavi and Parul and brother
Gaurav. They have always stood by me and their love has made life away from home a
little bit easier. I am sincerely thankful to my parents-in-law for giving the encouragement
and help when needed most.

Lastly, I feel a sense of pride and happiness in thinking about my little family - my
loving husband, Ameya and my son, Iishir. I owe the deepest gratitude to my husband
for his love, patience and encouragement at each step. His help is irreplaceable both in my
personal and professional life. I deeply appreciate the fact that he introduced me to smarter
and efficient research practices, be it from using Linux to CSS to different softwares and
much more. His zeal for always finding a better, more efficient way of doing research has
made it easy for me to follow suit. He has been with me every step of the way and I cannot
imagine completing this work without his support. I am definitely lucky to have him. I
cannot think of words to thank my little one - Iishir. His smiling face and all his antics have
been a source of great motivation to move ahead and a huge stress buster in this especially
difficult year.
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CHAPTER 1: INTRODUCTION

In solid state physics, at one end of the spectrum, electrons are classified as non-interacting and treated with the free electron model. On the other end, they are completely bound to the atomic cores as localized electrons. Between these two extremes lies a class of electronic materials called *Strongly Correlated Electron Materials*, where electrons are no longer free or non-interacting and can no longer be considered as being in a “sea” of the averaged motion of the other electrons. The electron-electron interactions are comparable to or stronger than their kinetic energy leading to the emergence of a whole range of interesting physical and technologically applicable phenomena like high-$T_C$ superconductivity, colossal magnetoresistance (CMR), Mott insulators, Charge-Orbital order, Metal-Insulator transition, multiferroics and heavy fermions.

In recent years many important advances in the physics of strongly correlated electron systems and their potential for technological applications have been possible by the diligent development of new materials like high quality single crystals and thin films. This has not only led to superconducting and spintronic devices but has also motivated the research for the development of novel materials. One such class of materials is *Transition Metal Oxides* (TMO). The richness of the electronic phases and their sensitivity to external perturbations affords enhanced functionality to transition metal oxides. It is evident that “materials driven physics” such as the correlated electrons systems holds great promise for future physics and technology research.

1.0.1 Transition Metal Oxides

TMOs are materials with partially filled $d$– electron shells where the electrons occupy narrow orbitals and display properties that are hard to explain based on conventional theoretical models. The electron exhibits a dual character in solids depending upon its interaction with its nearest and sometimes next-to-nearest neighbors. An electron in a lattice can be treated like an extended Bloch wave. However, when the number of free electrons is comparable to the number of atoms in the solid, the electron-electron interaction becomes strong and electrons acquire the tendency to localize; in contrast the hybridization of $d$– orbitals with oxygen $p$– orbitals tend to make the electron itinerant or delocalized. This duality in electron property is most remarkably evident in correlated electron systems such as TMOs.
where the strong correlation determines the properties of the system \[91\].

An electron in a solid has charge, spin and orbital degrees of freedom. The orbital represents the electron’s probability distribution of spatial occupancy and takes different shapes when bound to the atomic nucleus. The interplay between these multiple degrees of freedom results in rich and complex phase diagrams. The energy scale of the dominant interaction is much larger compared to the subtle competition between different phases (for example, ferromagnetism and antiferromagnetism) such that even small perturbations lead to giant responses. Therefore, these systems are highly susceptible to perturbations such as partial or complete chemical substitution, application of magnetic fields and/or pressure, resulting in rich and complex phase diagrams. 3d transition metal oxides have been a subject of much research in the past with the discovery of high-$T_C$ superconductivity, CMR and many additional interesting phenomena. 4d and 5d systems, however, have received much less attention mainly because magnetism in these systems is expected to be much weaker or absent because of the larger spatial extent of the orbitals compared to the 3d orbitals. Contradicting this deduction, magnetism, when found in these 4d and 5d systems, leads to unanticipated and very interesting physical phenomenon: unconventional superconductivity in Sr$_2$RuO$_4$ a Mott insulating state in Ca$_2$RuO$_4$ CMR by avoiding the ferromagnetic state, quantum oscillations in an insulating state in Ca$_3$Ru$_2$O$_7$ a delicate competition between ferromagnetic and antiferromagnetic ground state in Sr$_4$Ru$_3$O$_{10}$ and spin-orbit coupling driven novel angular momentum state and a giant magnetoelectric effect in Sr$_2$IrO$_4$. In these materials the occurrence of such a wide range of ground states and phenomena arise from a delicate interplay between competing interactions.

Ruthenates and iridates, as stated above, seem an unlikely class of material to support strong correlations because of more extended and narrow orbitals which are expected to have a weaker tendency for electron localization. In ruthenates, for example, the electrons sometime appear to be localized and at other times itinerant depending on the chemical environment endowing this class of materials with interesting properties. In iridates, the relativistic corrections give rise to a strong spin-orbit coupling (SOC) which plays an important role, especially for $t_{2g}$ electrons. For example, the 5d electrons in layered iridium oxides lead to novel angular momentum states. The recent discovery of a novel spin valve effect in bulk single crystals, a giant magnetoelectric effect driven by strong spin-orbit coupling emphasizes the importance of this category of materials and provides an indication to a
possibility of undiscovered territories.

Figure 1.1: Crystal structure of the compounds in the Ruddlesden-Popper series \((Sr)_{n+1}Ru_nO_{3n+1}\). Here, \(n\) denotes the number of repeating RuO\(_2\) layers in a unit cell. RuO\(_6\) octahedra and Sr atoms (filled circles) are shown schematically [63].

1.0.2 Ruddlesden-Popper Series

A very interesting class of materials, and the focus of this thesis, is the Ruddlesden-Popper (RP) series of perovskite ruthenates \((Sr, Ca)_{n+1}Ru_nO_{3n+1}\) and iridates \((Sr, Ca)_{n+1}Ir_nO_{3n+1}\). These materials span almost every ordered state known in condensed matter physics, and exhibit a wide variety of unconventional phenomena characterized by the coexistence of different kinds of magnetic ordering and ground state instability such as spin-triplet superconductivity, orbital ordering and metamagnetic quantum criticality [11]. The Ruddlesden-Popper series may be represented by the general formula \((Sr, Ca)_{n+1}B_nO_{3n+1}\) with relevance to this thesis, where \(B\) stands for Ru or Ir. \(n (= 1, 2, 3, \infty)\) is the number of layers of corner sharing BO\(_6\) octahedra per formula unit separated by \((Ca, Sr)O\) rock salt layer. The progression of the number of layers \(n\) from 1 to infinity represents an increase in the structural dimensionality as the coordination number of B (=Ru, Ir) increase from four for \(n = 1\), to six for \(n = \infty\). The three-dimensional character increases with increasing \(n\) because of the increased number of \((Ca, Sr)BO_3\) layers. The Sr Ruddlesden-Popper series is shown in Figure 1.1.
Although Ru is octahedrally coordinated in all these oxides, in the ruthenate RP series they display a remarkable variety of magnetic and electronic phases - strong evidence of coupling to lattice and structural distortions. The extended orbitals lead to comparable and hence competing energies for crystalline fields, Hund’s rule interaction, spin-orbit coupling, $p-d$ hybridization and electron-lattice coupling. The deformation and relative orientation of the RuO$_6$ octahedra determine the crystal-field splitting, the band structure and hence, the ground state. As a result the physical properties are highly dimensionality-dependent and susceptible to external perturbation such as magnetic field, pressure and chemical doping. These characteristics are distinctly evident in the Ca- and Sr- ruthenate RP-series.

Ru sits in an octahedral environment surrounded by six oxygen ions O$^{2-}$, which lifts the degeneracy of the $d$ orbitals of the metal ion. The $e_g$ ($x^2 - y^2, 3z^2 - r^2$) orbitals pointing toward the O$^{2-}$ ion have higher energy, whereas the $t_{2g}$ orbitals pointing away have lower energy. The ground state is then determined by the Hund’s rule that each orbital in a subshell is singly occupied with an electron before any one orbital is doubly occupied. For Ru$^{4+}$, the energy to overcome the crystal field splitting is larger than the energy cost for a doubly occupied $t_{2g}$ orbital, resulting in a low spin state.

The dimensionality dependence is distinctly evident in the markedly different ground states of the end members of the Ca and Sr ruthenate series. The Ca ruthenate series shown in Figure 1.2 is flanked by a Mott insulator on one end and a “bad” metal on the other. The layered Ca RP-series are all on the verge of metal-nonmetal transition and tend to be antiferromagnetic. CaRuO$_3$ is a “bad” metal, Ca$_3$Ru$_2$O$_7$ is an antiferromagnetic Mott insulator at $T_N$=56 K in low fields, followed by a Mott-like metal-insulator transition at $T_{MI}$=48 K. The sensitivity of Fermi surface topography to the lattice or structural distortions is unusually strong in that the ground state can be drastically changed by the isostructural and isoelctronic cation substitution of Ca by Sr. The Sr series shown in Figure 1.3 is metallic and inclined to be ferromagnetic, except Sr$_2$RuO$_4$. Sr$_2$RuO$_4$ ($n = 1$) is a $p-$wave superconductor. Sr$_3$Ru$_2$O$_7$ is a strongly enhanced paramagnet ($n = 2$, $T_M$=18 K) and shows proximity to a metamagnetic quantum critical point. The $n = 3$ Sr$_4$Ru$_3$O$_{10}$ shows ferromagnetic behavior with $T_C$=105 K, followed by an additional magnetic transition at $T_M$=50 K, and the infinite layered itinerant ferromagnet SrRuO$_3$ ($n = \infty$, $T_C$=65 K) has a reduced magnetic moment of $1.1\mu_B$/Ru. The evolution of the ground state from paramagnetism to ferromagnetism follows the progression of Ru-O layers from $n = 1$ to
Figure 1.2: Magnetization $M$, as a function of temperature and resistivity, $\rho$ in the ab-plane for $Ca_{n+1}Ru_nO_{3n+1}$.
Figure 1.3: Magnetization $M$, as a function of temperature and resistivity, $\rho$ in the ab-plane for $\text{Sr}_{n+1}\text{Ru}_n\text{O}_{3n+1}$
\( n = \infty \), again indicates a strong dimensionality dependence. The 3d TMOs have been successfully explained by Mott physics. For 3d oxides, the ground state becomes a Mott insulator when the on-site Coulomb repulsion surpasses the bandwidth. But 5d oxides with spatially extended orbitals are expected to have weaker on-site Coulomb repulsion and a metallic ground state. The insulating behavior observed in \( \text{Cd}_2\text{Os}_2\text{O}_7 \) and \( \text{Ba}_2\text{NaOsO}_6 \) [68, 34] and other layered iridates \( \text{Sr}_2\text{IrO}_4 \) and \( \text{Sr}_3\text{Ir}_2\text{O}_7 \) [14, 25, 26], then, is remarkably puzzling. The question then is, how important is the role of correlations in 5d TMOs?

The spin-orbit coupling for 5d TMOs is about 0.3-0.4 eV which is much larger than that of 3d TMOs (20 meV). The SOC in 5d TMOs is comparable to their \( U \) values (about 0.5 eV) and leads to a cooperative interaction. Due to the large value of spin-orbit coupling, total angular momentum should be a good quantum number instead of the spin. For the layered iridates the SOC can induce a novel \( J_{\text{eff}} = 1/2 \) state which is different from the typical \( S = 1/2 \) Mott insulator stabilized by the cooperative interplay between SO coupling and Coulomb repulsion. Optical spectroscopy and first principle calculations reveal the electronic structural change for \( \text{Sr}_{n+1}\text{Ir}_n\text{O}_{(3n+1)} \) from insulator \((n = 1, 2)\) to metal \((n = \infty)\), an insulator-metal transition driven by the bandwidth change \( W \) and the associated correlated metallic state with a large effective mass [73].

The outline of the dissertation is as follows.

Chapter 2 presents the theoretical background and concepts relevant to issues discussed in this thesis such as magnetism, spin-orbit coupling, Mott transition, magnetoresistance, and quantum oscillations.

Chapter 3 details the experimental procedures and techniques used for single crystal synthesis using both flux and floating zone techniques. This is followed by sample characterization techniques such as X-ray diffraction, magnetic, thermal and transport properties measurements for data presented in this thesis.

Chapter 4 presents the result and discussion for the physical properties measurements for \( \text{Sr}_4\text{Ru}_3\text{O}_{10} \) and chemically substituted \( \text{Ca}_3\text{Ru}_2\text{O}_7 \) with the focus on bulk spin valve behavior evidenced in this system.

Chapter 5 presents the experimental results for the layered iridates \( \text{Sr}_2\text{IrO}_4 \) and \( \text{Sr}_3\text{Ir}_2\text{O}_7 \).

The focus is on the unexpected insulating state and a giant magnetoelectric effect in
weakly ferromagnetic Sr₂IrO₄. The results are compared with its sister compound Sr₃Ru₂O₇.

Chapter 6 presents the conclusions and summary of the physical phenomenon observed in chapter 4 and 5 with future research motivation.
CHAPTER 2: THEORETICAL BACKGROUND

2.1 Exchange Interaction

Exchange interactions are essential to the understanding of long range magnetic ordering. We express the dependence of the spin of a two-electron system on the singlet-triplet energy splitting which is of fundamental importance in analyzing the energies of the spin configurations of real insulating solids. When two protons are far apart, the ground state is fourfold degenerate on account of it describing two individual hydrogen atoms since each electron can have two spin orientations. When the distance between these atoms is reduced, there is a splitting of the degeneracy as the atoms interact with each other. This energy splitting \( E_s \neq E_t \), however, is small compared to all other excitation energies of the two-electron system. Under such conditions, these four states play a dominant role in the many important properties of the molecule. Henceforth, higher states are ignored and the molecule represented as a four-state system [5].

The Hamiltonian can be written as an “effective Hamiltonian” [8]

\[
H_{\text{spin}} = \frac{1}{4} (E_s + 3E_t) - (E_s - E_t) \mathbf{S}_1 \cdot \mathbf{S}_2
\] (2.1)

since \( S^2 = (S_1 + S_2)^2 = \frac{3}{2} + 2\mathbf{S}_1 \cdot \mathbf{S}_2 \) has eigenvalues \( S(S+1) \), which has the value \(-\frac{3}{4}\) in the singlet \( (S = 0) \) state and \(+\frac{1}{4}\) in the triplet \( (S = 1) \) state. Thus the eigenstates of the above Hamiltonian are \( E_s \) in the singlet state and \( E_t \) in the triplet state, as desired. The above Hamiltonian is the sum of a constant term and a term which depends on spin. The exchange (or exchange integral), \( J \) is defined by

\[
J = \frac{E_s - E_t}{2}
\] (2.2)

We can redefine the zero of the energy such that the constant term \( \frac{1}{4} (E_s + 3E_t) \) disappears for all four state, thus making the above expression

\[
H = -J \mathbf{S}_1 \cdot \mathbf{S}_2, \quad J = E_s - E_t.
\] (2.3)

Thus, if \( J \) is positive (negative), the spins will be parallel (anti-parallel). For many cases of interest, the form of the spin Hamiltonian is that of the two-spin case summed up over all pairs of ions

\[
H = - \sum J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j.
\] (2.4)
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Table 2.1: Various types of magnetic exchange interactions

2.1.1 Direct Exchange

If the electrons on neighboring magnetic atoms interact via an exchange interaction, this is known as *direct exchange*. It is named so because the exchange interaction proceeds directly without any intermediary. Direct exchange is usually not the prime mechanism for magnetic properties because there is insufficient overlap between neighboring magnetic orbitals. For example, in rare earths the $4f$ electrons are strongly localized and very close to the nucleus and hence not very conducive to direct exchange. Even in $d$ orbitals which extend further than the $f$ orbitals, direct exchange can not explain the magnetic properties. The metallic nature of these materials entails to take both the localized and band nature of the electrons.

2.1.2 Superexchange

Many ionic solids have magnetic ground state. For instance, MnO and MnF$_2$ have antiferromagnetic ground state which is rather surprising since there is no direct overlap between the Mn$^{2+}$ ions. Since direct exchange is very short ranged, the long range interaction operating in this case is termed "super". In case two magnetic ions are separated by a non-magnetic ion (one with all electron shells closed), it is possible for the magnetic ions to have a magnetic interaction mediated by the electrons in their common non-metallic neighbor which is more important than their direct exchange interaction. This type of magnetic interaction is called *Superexchange*. It arises because there is a kinetic energy advantage for antiferromagnetism.

Consider two transition metal ions with unpaired electrons separated by an oxygen ion. The antiferromagnetic coupling lowers the energy of the system by allowing these electrons
to become delocalized over the whole structure. The exchange integral $J$ is

$$J \sim -\frac{t^2}{U}$$

(2.5)

where $t$ is the hopping integral proportional to the bandwidth and $U$ is the Coulomb energy for making an excited state. The exchange integral consists of a potential energy term and a kinetic energy term. The potential energy is small since the ions are well separated. The kinetic energy term is dominant and depends strongly on the overlap of orbitals and therefore superexchange depends strongly on the metal-oxygen-metal bond.

2.1.3 Indirect Exchange

Yet another source of magnetic interaction can occur between electrons in the partially filled $f$-shells in the rare earth metals. In addition to their direct exchange coupling, the $f$-electrons are coupled through their interactions with the conduction electrons. This mechanism is known as indirect exchange. It can be stronger than the direct exchange coupling, since the $f$-shells generally overlap very little. A localized magnetic moment spin-polarizes the conduction electrons and this polarization in turn couples to a neighboring localized magnetic moment a distance $r$ away. It is known as the RKKY interaction (or itinerant exchange). The exchange integral $J_{RKKY}(r)$ is given by

$$J_{RKKY}(r) \propto \frac{\cos(2k_Fr)}{r^3}$$

(2.6)

The interaction is long range and has an oscillatory dependence on the distance between the magnetic moments and is ferromagnetic or antiferromagnetic depending upon the separation. In some oxides, it is possible to have ferromagnetic exchange interaction which occurs because the magnetic ion shows mixed valency. Such an interaction is called double exchange and is not discussed.

2.1.4 Anisotropic Exchange Interaction

There is a scenario where the spin-orbit coupling play a role similar to that of oxygen in superexchange. In this case the excited state is produced by the spin-orbit interaction in one of the magnetic ions \[8\]. There is then an exchange interaction between the excited state of one ion and the ground state of the other. This interaction is termed as anisotropic
exchange interaction or Dzyaloshinsky-Moriya interaction and leads to the following term in the Hamiltonian

$$H_{DM} = \vec{D} \cdot \vec{S}_1 \times \vec{S}_2$$

(2.7)

when acting between two spins \(\vec{S}_1\) and \(\vec{S}_2\). The Dzyaloshinsky-Moriya interaction usually lead to weak -ferromagnetism, slight canting (that is, rotation by a small angle) of the spins because it tries to force \(\vec{S}_1\) and \(\vec{S}_2\) to be at right angles in a plane perpendicular to the vector \(\vec{D}\) to ensure that the energy is negative. line connecting the two spins. \(\vec{D}\) lies parallel or perpendicular to the line connecting to the two spins, however, it vanishes when the crystal has an inversion symmetry with respect to the center between the two magnetic ions.

### 2.2 Giant Magnetoresistance

Giant Magnetoresistance (GMR) is a quantum mechanical magnetoresistance effect observed usually in thin film structures composed of alternating ferromagnetic an non-magnetic layers. GMR was first discovered in 1988 in Fe/Cr/Fe multilayers by Peter Grünberg and independently by Albert Fert. The GMR effect in magnetic multilayers is the dependence of the resistance on the angles between the magnetization directions of the successive magnetic layers. The effect originates from the spin-dependence of the electrical conduction in ferromagnetic materials. In this effect, the coupling between magnetic layers through a spacer layer oscillates in sign as the spacer thickness increases, i.e. the system alternates between being ferromagnetic and anti-ferromagnetic as the spacer thickness increases. The alternation occurs over spacer thickness of about 10 atomic spacings, or about 9-18 Å. Its value is mainly determined by the spacer material and not by the ferromagnetic metal.

The magnetoresistance ratio is defined as

$$\frac{\Delta \rho}{\rho} = \frac{R(H) - R(0)}{R(0)}$$

(2.8)

where \(R(H)\) and \(R(0)\) are the resistances in the magnetic field and zero field respectively. The term ‘giant’ MR effect was chosen because MR ratio can be much larger than observed at room temperature for the magnetoresistance effects known at the time of the discovery of GMR, ordinary magnetoresistance and the anisotropic (AMR) magnetoresistance. The ordinary MR occurs in non magnetic materials and is due to the Lorentz force on the trajectories of the conduction electrons ion the application of magnetic field. The AMR effect is of relativistic origin and is the dependence of the resistance of ferromagnetic
materials on the angle between the current and magnetization \[9\]. The origin of GMR

![Diagram](image-url)

Figure 2.1: Schematic diagram of electron transport in a multilayer for parallel (on left) and anti-parallel (on right) magnetization of the successive ferromagnetic layers. The magnetization direction are indicated by the arrows. The solid lines are individual electron trajectories within the two spin channels. Bottom panels shows the resistor network within the two current series resistor model (Figure taken from wikipedia).

can be qualitatively understood using the ‘two-current model’ by Mott \[75, 76\] to explain the sudden increase in resistivity of ferromagnetic materials as they are heated above their Curie temperature. There are two main points proposed by Mott. First, the electrical conductivity in metals can be described in terms of two largely independent conducting channels, corresponding to the up-spin and down-spin electrons which do not mix over long distances and, therefore, the electrical conduction occurs in parallel for the two spin channels. Second, irrespective of the scattering center, the scattering rates of the up-spin and down-spin electrons are quite different in ferromagnetic metals. The probability of scattering is proportional to the density of states for the up-spin and down-spin, which are different due to th exchange-split \(d\) bands. Thus, the scattering rates are spin dependent and different for the two conduction channels.
Using this argument GMR can be explained as follows. Assume that scattering is strong for electrons with spins antiparallel to the magnetization and, weak for electrons with spin parallel to the magnetization direction. For the parallel aligned layers, the up-spin electrons pass through the structure almost without scattering. On the contrary, the down-spin electrons are scattered strongly within one of the ferromagnetic layers. Therefore, in this case the total resistance is high. Each layer thus acts as a spin-selective valve: its magnetization direction determines whether it most easily transmits spin-up or spin-down conduction electrons. Therefore the GMR effect is, more appropriately, termed the spin-valve effect.

The antiferromagnetic interlayer coupling is not a necessary requirement for obtaining the GMR effect. GMR is observed in many other systems within which the relative alignment of the magnetization of nearly ferromagnetic regions can be changed the application of a magnetic field. Pseudo spin valves is one such option. Pseudo-spin valves are very similar to spin valve structures. The difference lies in the coercivities of the ferromagnetic layers. In pseudo-spin valve a soft magnet will be used for one layer, whereas, a hard ferromagnet is used for the other. This allows an applied field to flip the magnetization of the hard ferromagnet layer. for pseudo-spin valve, the non-magnetic layer thickness must be great enough so that exchange coupling is minimized. This reduces the chance that the alignment of magnetization of adjacent layers will spontaneously change at a later time.

2.2.1 Tunnel Magnetoresistance

Figure 2.2: Schematic diagram of tunnel current for TMR. Two-current model for parallel and anti-parallel alignment of the magnetizations

The Tunnel magnetoresistance (TMR) is a magnetoresistive effect that occurs in mag-
netic tunnel junctions (MTJs). This is a component consisting of two ferromagnets separated by a thin insulator. If the insulating layer is thin enough (typically a few nanometers), electrons can tunnel from one ferromagnet into the other. The direction of the two magnetizations of the ferromagnetic films can be switched individually by an external magnetic field. If the magnetizations are in a parallel orientation it is more likely that electrons will tunnel through the insulating film than if they are in the oppositional (antiparallel) orientation. Consequently, such a junction can be switched between two states of electrical resistance, one with low and one with very high resistance \[3\]. TMR is defined as

\[
TMR = \frac{R_{ap} - R_p}{R_p}
\]  

(2.9)

where \(R_{ap}\) is the electrical resistance in the anti-parallel state and \(R_p\) is the electrical resistance in the parallel state. The TMR effect was explained by Julli`ere with the spin polarization. The spin polarization \(P\) is calculated from the spin dependent density of states (DOS) at the Fermi energy

\[
P = \frac{D_\uparrow(E_F) - D_\downarrow(E_F)}{D_\uparrow(E_F) + D_\downarrow(E_F)}
\]  

(2.10)

The spin-up electrons have spin parallel to the external magnetic field and spin-down electrons are anti-parallel to the magnetic field. The relative resistance change is given by

\[
TMR = \frac{2P_1P_2}{1 - P_1P_2}
\]  

(2.11)

The electrons tunnel in both direction in the absence of an applied voltage, but with a bias voltage electrons tunnel preferentially to the positive electrode. The total current is described by the two-current model as explained in 2.2. TMR is theoretically predicted for ferromagnetic half-metals, where the conduction electrons are fully spin polarized, for instance, CrO\(_2\).

2.3 Curie-Weiss Law

A ferromagnet has a spontaneous magnetization even in the absence of an applied field due to exchange interactions. The Hamiltonian can be written as

\[
H = - \sum J_{ij} \vec{S}_i \cdot \vec{S}_j + g\mu_B \sum \vec{S}_j \cdot \vec{B}
\]  

(2.12)

with positive exchange constant for ferromagnetic alignment. The first term on the right hand side is the Heisenberg exchange energy and the second term is the Zeeman energy \[8\].
To solve the above equation, an effective molecular field is defined

$$\vec{B}_{mf} = -\frac{2}{g\mu_B} \vec{S}_j$$  \hspace{1cm} (2.13)

Equations 2.12 and 2.13 leads to the exchange interaction being replaced by an effective molecular field $\vec{B}_{mf}$ produced by the neighboring spins. The effective Hamiltonian then is

$$H = g\mu_B \sum \vec{S}_i \cdot (\vec{B} + \vec{B}_{mf})$$  \hspace{1cm} (2.14)

which looks like the Hamiltonian for a paramagnet in a magnetic field ($\vec{B} + \vec{B}_{mf}$). The underlying assumption is that all magnetic ions experience the same molecular field. For a ferromagnet the molecular field will act so as to align neighboring magnetic moments. Since molecular field measures the effect of the ordering of the system, the effective molecular field can be written as

$$\vec{B}_{mf} = \lambda \vec{M}$$  \hspace{1cm} (2.15)

where $\lambda$ is a constant which parametrizes the strength of the molecular field as a function of magnetization $M$. The problem can now be treated as a paramagnet placed in a magnetic field ($\vec{B} + \vec{B}_{mf}$). To solve the model, the following equations need to be solved simultaneously

$$\frac{M}{M_S} = B_J(y)$$  \hspace{1cm} (2.16)

and

$$y = \frac{g J \mu_B J (B + \lambda M)}{k_B T}$$  \hspace{1cm} (2.17)

Solution of these equations can be obtained graphically and using the approximation $y \ll 1$ gives

$$\frac{M}{M_S} \approx \frac{g J \mu_B (J + 1)}{3k_B} \left( \frac{B + \lambda M}{T} \right)$$  \hspace{1cm} (2.18)

so that

$$\frac{M}{M_S} \approx \frac{T_C}{\lambda M_S} \left( \frac{B + \lambda M}{T} \right)$$  \hspace{1cm} (2.19)

This gives

$$\frac{M}{M_S} (1 - \frac{T_c}{T}) \approx \frac{T_C}{B} \lambda M_S$$  \hspace{1cm} (2.20)

so that

$$\chi = \lim_{B \to 0} \frac{\mu_0 M}{B} \propto \frac{1}{T - T_C}$$  \hspace{1cm} (2.21)
which is known as the \textit{Curie Weiss law}. The Curie temperature is

\[ T_C = \frac{gJ\mu_B(J+1)\lambda M_S}{3k_B} = \frac{n\mu_{eff}^2}{3k_B} \quad (2.22) \]

With a similar treatment as in ferromagnet case, the magnetic susceptibility for antiferromagnet is

\[ \chi = \lim_{B \to 0} \frac{\mu_0 M}{B} \propto \frac{1}{T + T_N} \quad (2.23) \]

where \( T_N \) is the Neel temperature. This result gives a means of interpreting the susceptibility data in the paramagnetic state, that is, for temperatures above the transition to magnetic order). The magnetic susceptibility can be fitted to a Curie-Weiss dependence

\[ \chi \propto \frac{1}{T - \theta} \quad (2.24) \]

where \( \theta \) is the \textit{Weiss temperature}. If \( \theta = 0 \), the material is a paramagnet. If \( \theta > 0 \), the material is a ferromagnet and if \( \theta < 0 \), the material is an antiferromagnet.

\subsection*{2.4 Environments: Crystal Field Effect}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2_3.png}
\caption{The \( d_{x^2-y^2} \) and \( d_{z^2} \) orbitals are grouped together and called the \textit{e}_g levels. The \( d_{z^2} \) orbital is sometimes referred to as \( d_{3z^2-r^2} \).}
\end{figure}
The directionality in the bonding between a d-block metal ion and attached groups can be understood in terms of the directional quality of the d orbitals. The Crystal Field Theory is an electrostatic model which considers the effect of the electric field due to the chemical environment on the energies of the electrons in various d orbitals of the metal ion. The radial charge distribution of the d orbitals are represented schematically in Figure 2.3, 2.4. The $e_g$ ($d_{z^2}$ and $d_{x^2-y^2}$) orbitals are directed along the Cartesian axes, and the $t_{2g}$ ($d_{xy}$, and $d_{yz}$) orbitals are directed between the axes. If a metal ion is removed from vacuum into the electrostatic field created by a spherical shell of electron density equivalent to that of the six ligands (ions) in an octahedral complex, the d electrons will have higher energy because of the repulsive force produced by the surrounding shell of electronic charge. If the spherical charge is distributed to six equivalent points at the vertices of an octahedron, the degeneracy of the five d orbitals is partly lifted. This is because the electrons in the $d_{z^2}$ and $d_{x^2-y^2}$ orbitals will have larger overlap with the p orbitals on the ligand and will be raised in energy. The $d_{xy}$, and $d_{yz}$ orbitals has a lower overlap and hence, lower electrostatic energy. The difference in energies between the two sets of orbitals is known as the crystal field splitting and is represented by $\Delta$. For a partially filled d orbital, the precise order in which the orbitals are filled depends on the competition between the crystal field energy and the Coulomb energy cost of putting two electrons in the same orbital, known as the pairing energy and is usually positive. For a weak-field case, crystal field energy (CFE) is higher than the pairing energy. As the electrons are added to the system, they will first singly occupy each orbital before any orbital becomes doubly occupied. On the other hand,
for a strong-field case, that is, when CFE is higher than the pairing energy, the electrons doubly occupy the lower energy orbitals before occupying any higher energy orbitals.

2.4.1 The Jahn-Teller effect

The electronic structure and hence the magnetic properties depend upon the local environment. Sometimes, however, the magnetic properties themselves can influence the symmetry of the local environment. This is because it sometimes can be energetically favorable for a structure to distort because the energy cost of increased elastic energy is balanced by a resultant electronic energy saving due to distortion [8].

The Jahn-Teller theorem states that a non-linear molecule in an electronically degenerate state will change its geometry to lower its symmetry, removing the degeneracy and so attaining a lower energy [48]. Let us consider the energy cost of lowering the symmetry of the octahedral $d$ complex by moving two oxygen ions on the $z$-axis further from the metal. This results in a reduced electronic repulsion along the $z$ direction and lowers the energies for the orbitals with a $z$ component, with a corresponding increase in energy for those orbitals without a $z$ component, to maintain the barycenter of each set. Jahn-Teller effect is exhibited by an octahedral high-spin complex of a $d^4$ metal ion such as $Cr^{2+}$ or $Mn^{3+}$ with the electron configuration $t_{2g}^3e_g^1$. A metal ion with unoccupied $t_{2g}$ orbitals might also be expected to show Jahn-Teller effect, such as low spin $Ru^{4+}$. This is indeed the case in bilayer $Ca_3Ru_2O_7$. However, the $t_{2g}$ orbitals interact less strongly with the ligands than the $e_g$ orbitals, so the consequences are more difficult to observe.
2.5 Spin Orbit Coupling

Spin-orbit coupling is any interaction of a particle’s spin with its motion. The first and best known example of this is that spin-orbit interaction causes shifts in an electron’s atomic energy levels due to electromagnetic interaction between the electron’s spin and the nucleus’s electric field. In the field of spintronics, spin-orbit effects for electrons in semiconductors and other materials are explored and put to useful work. Consider an electron orbiting an atom. In the frame of the nucleus the electron orbits the nucleus which gives rise to a magnetic field. This magnetic field interacts with the spin of the electron to give a term in the Hamiltonian

$$H_{SO} = -\frac{1}{2} \mu_B \cdot B$$

where the orbital angular momentum is given by $\hbar \vec{L} = m_e \vec{r} \times \vec{v}$ and the magnetic moment $\vec{m} = (\frac{g_e \hbar}{2m_e}) \vec{S}$. This effect is known as the intrinsic spin-orbit interaction. The spin and orbit angular momenta are not always independent of one another but weakly couple, via the spin-orbit interaction, which acts as a perturbation on the states with well defined $\vec{L}$ and $\vec{S}$ and the total angular momentum $\vec{J} = \vec{L} + \vec{S}$ is conserved. Taking relativistic effects into consideration $\vec{L}^2 = L(L+1)$ and $\vec{S}^2 = S(S+1)$ as being conserved. From the definition of $\vec{J}$

$$\vec{J} = \vec{L} + \vec{S}$$

$$\vec{J}^2 = \vec{L}^2 + \vec{S}^2 + 2 \vec{S} \cdot \vec{L}$$

and since the spin-orbit interaction takes the form $\lambda \vec{S} \cdot \vec{L}$, where $\lambda$ is constant, the expected value of this energy is

$$\langle \lambda \vec{L} \cdot \vec{S} \rangle = \lambda \left[ \frac{1}{2} (J_9 J + 1) - L(L+1) - S(S+1) \right]$$

The multiplets split up into different fine structure levels labeled by $J$

2.6 Hund’s Rules

To determine the magnetic moment of an ion, we need to know the electronic configuration of the ion. For high $Z$ ions, it is helpful to use the Hund’s rules, which state that, within a given configuration of one-electron orbitals, the ground state of an isolated atom or ion
• Has the largest value of the total spin $S$ (Hund’s first rule)

• Has the largest value of the total orbital angular momentum $L$ which is permitted by the first rule (Hund’s second rule)

• The total angular momentum $J = |L - S|$ for less than half filled shells, and $J = |L + S|$ for more than half filled shells (Hund’s third rule)

For example, for free ion Mn$^{3+}$, we would predict $S = 2$, $L = 2$ and $J = 0$. However, in the real world, we are interested in ions as part of a system, e.g. LaMnO$_3$. Here we see that the prediction $S = 2$ is true and relevant, $L = 2$ is true but irrelevant, and Hund’s third rule no longer applies. On the other hand, the predictions $S = 2$, $L = 6$, and $J = 8$ remain valid for Ho$^{3+}$ in, say, HoF$_3$. The reason for these complications is that an ion embedded in a solid is subject to the crystal field of the surrounding atoms. The result is decided by the competition between crystal fields and the interactions responsible for Hund’s rules.

2.7 Magnetism in Metals

2.7.1 Spontaneously spin-split bands - Stoner Criterion

Figure 2.6: Density of states showing spontaneous splitting of energy bands without an applied magnetic field

The localized picture can not account for the non-integer values of magnetic moment for
transition metals. Therefore, band ferromagnetism or itinerant ferromagnetism is proposed in which magnetization is due to spontaneously spin-split bands. The energy cost $\Delta E_{K.E.}$ of moving a small number of electrons from the spin-down bands and place them in the spin-up band is given as.

$$\Delta E_{K.E.} = \frac{1}{2} g(E_F)(\delta E)^2$$

(2.30)

The situation is illustrated in Figure 2.6. This is an energy cost and makes the process look unfavorable. However, the interaction of the magnetization with the molecular field gives an energy reduction which can outweigh this cost. The molecular field energy, $\Delta E_{P.E.}$, is

$$\Delta E_{P.E.} = -\frac{1}{2} U(g(E_F)(\delta E))^2$$

(2.31)

Hence, the total change of energy is

$$\Delta E = \Delta E_{K.E.} + \Delta E_{P.E.} = \frac{1}{2} g(E_F)(\delta E)^2(1 - U g(E_F))$$

(2.32)

Thus spontaneous ferromagnetism is possible if $\Delta E < 0$ which means that

$$U g(E_F) \geq 1$$

(2.33)

which is known as the Stoner criterion. This condition for the ferromagnetic instability requires that the Coulomb effects are strong and also the density of states at the Fermi energy is large. Spontaneous ferromagnetism splits the spin-up and spin-down bands with an exchange splitting $\Delta$ in the absence of magnetic field. However, even if spontaneous ferromagnetism does not occur, the susceptibility $\chi$ may be altered and is given by

$$\chi = \frac{M}{H} \sim \frac{\mu_0 M}{B} = \frac{\mu_0 \mu_B^2 g(E_F)}{1 - U g(E_F)} = \frac{\chi_P}{1 - U g(E_F)}$$

(2.34)

This is larger by a factor of $1 - U g(E_F)^{-1}$ than the susceptibility expected without the Coulomb interactions. This phenomenon is known as Stoner enhancement and is responsible for enhanced Pauli susceptibility in metals like Pt and Pd. The systems showing Stoner enhancement are said to be on the verge of ferromagnetism.

2.8 Fermi Liquid Theory

Landau postulated that electron-electron interactions may be adiabatically “switched-on” with respect to the ground state of a Fermi gas, so that there is a one-to-one correspondence between the eigenstates of the electron gas and those of the fluid of correlated
electrons, the Fermi liquid. A Fermi liquid, like a Fermi gas, has a Fermi surface separating empty and occupied states in \( k \)-space at the Fermi energy \( E_F \). The quantum numbers of the excitations of the Fermi liquid are not independent electrons but are Fermionic quasi-particles with well-defined charge and momentum. Unlike the eigenstates of a Fermi gas, Landau quasiparticles are not stationary. The rate of decay, \( -1 \), of a quasiparticle of energy \( E \) is proportional to \( (E - E_F)^2 \): although a quasiparticle is never an eigenstate of a Fermi liquid, those quasiparticles with \( E \sim E_F \) are long-lived and are an approximation to the true eigenstates of the electron liquid [35].

For a Fermi gas (in the first order of energy), the electronic component of the heat capacity is proportional to temperature and the paramagnetic spin susceptibility is independent of temperature [89]. These temperature dependences are also valid for an ideal Fermi liquid. The electronic component of the specific heat capacity, \( c_v \), and the paramagnetic susceptibility, \( \chi \), of a Fermi liquid (single band, with an isotropic Fermi surface) are predicted to be

\[
c_v = \frac{m^* k_F^2}{3\pi^2} k_B T, \tag{2.35}
\]

\[
\chi = \frac{m^* k_F}{\pi} \frac{1}{1 + F_0} \mu_B, \tag{2.36}
\]

where \( m^* \) is the thermodynamic quasiparticle mass, \( F_0^a (\sim 1 > F_0^a > 0) \) is one of the phenomenological Landau parameters in the theory, \( k_F \) is the Fermi wave vector and \( k_B \) and \( \mu_B \) are Boltzmann constant and the Bohr magneton, respectively. The electronic heat capacity and the magnetic susceptibility of a Fermi liquid are, therefore, renormalised by factors of \( m^* / m \) and \( (1 + F_0^a)^{-1} m^* / m \) with respect to \( c_v \) and \( \chi \) of a Fermi gas. The \( (1 + F_0^a)^{-1} \) factor is related to the Wilson ratio, \( R_W \), of a paramagnetic Fermi liquid,

\[
R_W = 7.3 \times 10^4 \frac{\chi_P}{\gamma} = (1 + F_0^a)^{-1}, \tag{2.37}
\]

where the Sommerfeld coefficient, \( \gamma \), is the value of \( c_v / T \) extrapolated to \( T = 0 \) (in units of mJ/mol K\(^2\)) and \( \chi_P \) is the Pauli susceptibility (in units of emu/mol) [19]. A Wilson ratio much greater than one may imply that a paramagnetic susceptibility is enhanced by magnetic exchange interactions above the enhancement associated with \( m^* \).

The electrical resistance of a Fermi liquid is concomitant with the aforementioned decay rate. Because \( (E - E_F) \sim k_B T \) [20] the electrical resistivity of a Fermi liquid is therefore proportional to \( T^2 \), such that

\[
\rho = AT^2, \tag{2.38}
\]

23
where $A = m^*k_B^2/\hbar c_F^2$. It is straightforward to show that $A$, generally known as the Fermi liquid $A$ coefficient, is proportional to $(m^*)^2$. In any real metal this $T^2$ resistivity term will act in addition to the residual resistivity, so that $\rho(T) = \rho_0 + AT^2$ at sufficiently low temperatures.

Fermi liquid theory is valid in a restricted region of phase space near a Fermi surface: if additional phase space can somehow be made available to a system (still in the context of a normal metallic state) it is possible that the Landau quasiparticle picture may breakdown altogether, in which case a non-Fermi liquid description of the system may be appropriate. Schofield provides a detailed discussion of non- Fermi liquids \cite{35}. 

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CHAPTER 3: EXPERIMENTAL TECHNIQUES

3.1 Materials Synthesis - Single Crystal Growth

The effort to develop new materials, driven largely by the potential for innovations and novel physics, is at the heart of present condensed matter and materials physics research. The motivation largely derives from the remarkable advances that were made possible by the development of new and high quality materials like high-temperature superconductors, giant magnetoresistive materials and materials exhibiting quantum oscillations, to name a few. Hence, the two activities in this field - discovering new crystalline materials and growing larger crystal of these materials - have long been intertwined. A single crystal is a material in which the crystal lattice of the entire sample is continuous and unbroken to the edges of the sample, with no grain boundaries. The absence of the defects associated with grain boundaries can give single-crystals unique properties particularly, electrical, mechanical, optical and anisotropy. Single crystal are crucial to the study of most of the correlated electron systems as they are highly anisotropic. Single crystals therefore, offer the advantage of uncovering the directionality-dependent properties and phenomena. A single crystal is called “bulk” when it can be physically separated from the growth medium and is large enough to be handled and measured independently from other crystals.

3.1.1 The phase diagram

Since most of the single crystals studied in our lab belong to the incongruently melting category, it is helpful to take a look at the phase diagram of such systems. The Gibbs’ phase rule can be written as the equality

\[ F = C - P + 2 \]  (3.1)

where P is the number of phases in thermodynamic equilibrium with each other and C is the number of chemically independent components of the system. F is the number of degrees of freedom, that is, the number of intensive properties such as temperature or pressure which are independent of other intensive variables. Figure 3.1 shows the phase diagram of a two component incongruently melting system [35].

\[ \text{Sr}_4\text{Ru}_3\text{O}_{10} \], for example, melts incongruently, which means it melts into its components but cannot itself form a liquid, therefore, P is equal to 1. The starting components for
Sr₄Ru₃O₁₀ are SrCO₃ and RuO₂ hence, C is equal to 2. The number of intensive variables is 3: pressure, temperature and the composition of the SrCO₃ and RuO₂ mixture. For my Floating zone crystal growth process, the pressure was kept constant. In Figure 3.1 C is the final desired product. A and B are the starting components. At peritectic point, the liquid L is in equilibrium with two solid phases, hence, melting a mixture of A and B and then cooling it will not produce C. C has to be directly extracted from the C+L region of the phase diagram. Extracting C from this region will change the composition of this region (C+L) and might cause a shift away from this area of the phase diagram. Also, the starting ratio of A and B should take into account any possible evaporation of A or B.

### 3.1.2 Floating Zone Technique of Crystal Growth

Oxide crystals are grown by a variety of crystal growth techniques like the Czochralski (CZ) or Bridgman methods, flux and others. All these methods need a crucible to hold the molten oxides. Ideally, the crucibles are quite inert and do not react with the molten material, but this is rarely true for high-temperature oxide melts as they are quite reactive. The most obvious advantages of using the Floating Zone (FZ) technique is that no crucible
is necessary. Both congruently and incongruently melting materials can be grown and the relatively high thermal gradient decreases the chance of supercooling, thus allowing for more rapid growth of incongruently melting materials \[9\]. FZ is a more preferred method when large, high-purity crystals of known composition are required.

The floating zone furnace in our lab is a two mirror water cooled NEC Apparatus shown in Figure 3.2. The mirrors are doubly elliptic with gold coating on the inside for increased reflectance. The heating source consists of two 1.5 kW halogen lamps located at the mirrors’ outer focus. These lamps are capable of creating temperatures of \(\sim 2000^\circ C\) at the focus which is referred to as the molten zone \[78\].

![Figure 3.2: The NEC Floating Zone furnace](image)

### 3.1.3 Preparation steps

There are a series of steps in the materials preparation for growing a single crystal before the actual growth process begins. These are described below.

**Preparation of the polycrystalline ceramic feed and seed rods**

Stoichiometric quantities of the starting chemical compounds are prepared by a solid state reaction. The starting compounds (SrCO\(_3\) and RuO\(_2\) for Sr\(_4\)Ru\(_3\)O\(_{10}\)) required for floating zone growth are usually 10-20 gm in weight. They are baked separately to get rid of any
moisture at 400° for about 5-6 hours. The starting materials are then mixed and ground uniformly with an agate mortar and cooked for 15 hours at 1100° (for Sr₄Ru₃O₁₀). For Ca and Sr ruthenates, the annealing temperature is between 900 - 1100°C. To ensure that the material are uniformly mixed and chemically reacted, the mixture is cooked for another 15-20 hours at 1000°C. The mixture after cooling is reground to a uniform powder and is ready to make the rod. We use commercially available latex balloons to form the rods. To avoid any contamination, the balloons are thoroughly cleaned with ethyl alcohol, dried and coated with the dried powder. The sintered powder is then filled in the balloon as uniformly as possible and tied at the end. The rod is then pressed in the hydraulic press to a pressure of about 45kN. The balloon is cut and the rod separated from it. The final rod is usually 5-6 mm in diameter and 6-8 cm in length. This rod is sintered again at 1100°C for 20 hours. To keep the same stoichiometric ratio and prevent any contamination or lattice mismatch, the seed is usually cut from the rod and is at least 2 cm in length. The “feed” rod and the “seed” are now ready for crystal growth.

Crystal growth process

The seed is attached to the ceramic holder using a Platinum wire to the lower shaft. The feed rod is hung using a Pt wire to top shaft in the chamber. The whole assembly is then enclosed in a clean quartz tube and then, depending upon the material grown, the gas-flow environment (consisting of oxygen, air, argon and nitrogen) is established and pressure is applied. (The maximum pressure in our furnace is 0.97 MPa.) The furnace is powered up to the melting temperature of the material and the tips of the feed rod and seed are slowly moved to the the central focus of the lamps which is referred to as the “molten zone”. The feed rod and seed are usually set to rotate in opposite directions to maintain the surface tension that holds the melt in place and also to ensure homogeneous melting of the materials. When the tips start to melt, they are joined together establishing a liquid floating zone between the feed (top) rod and the seed (bottom) and are slowly pulled out of the central focus such that the molten zone travels through the entire length of the feed rod. The pulling rate (or the shaft speed) again depends upon the type of material grown and can vary from 1 - 35 mm/h. The temperature is adjusted carefully to allow for establishment of steady state condition. As the molten zone is pulled down, establishing a temperature gradient, crystallization follows.
3.2 Influence of growth parameters

There are a number of variables that influence successful crystals growth with image furnace. I will discuss them based on our experience in crystal growth and the discussion in [57].

**Feed rod characteristics**: If the feed rod is very porous, it affects the stability of the molten zone due to bubble formation in the melt. The common method in our lab to make the feed rod was filling the balloon with powder and pressing by hand to remove any air. This leads to two problems - a non uniform thickness of the feed rod and broken or bent rod after pressing in the hydraulic press. I developed a slightly different version of making the feed rod. The powder is filled into the balloon and pressed very lightly. The balloon is then tied at the open end as before and pressed in the hydraulic press at higher pressure. The result was, a significant improvement in achieving denser, non-broken, and straight rods.

**Crystallization rate**: The growth speed or crystallization is one of the most critical parameter for crystal size and quality. Crystals grown at slower rates generally yield larger, more homogeneous crystals. However, the slowest possible growth rate is not the rule of thumb. RuO$_2$ has a very high vapor pressure and slow growth rates results in significant loss of RuO$_2$ and change in the stoichiometric ratio of the compounds and hence, the growth condition. Faster growth rates for materials like ruthenates is also necessary to exclude impurity phases which are very close in energy to the desired phase. Therefore, the growth rate is selected to optimize the RuO$_2$ loss and a stable crystallization rate. For Sr$_4$Ru$_3$O$_{10}$ the optimal growth rate turned out to be
20 mm/hour, whereas for CuO the best results were obtained with a growth rate of 2.5 mm/hour. Incongruently melting materials, where the composition of the molten zone differs from that of the original feed rod and that of the growing crystals usually requires slower growth rates.

**Growth atmosphere and gas pressure**: There are various options available for the gas environment during gas flow as mentioned earlier. We can also choose to have a static gas or constant gas flow in the sealed quartz tube containing the feed rod and seed. The choice of environment depends on the phase stability of the sample and thermodynamic data. Most of the oxides are usually grown in an oxygen atmosphere. Higher pressure is applied for more volatile components. However, higher pressure, in my experience, elevates the melting temperature. Therefore, for materials with very high melting points lower gas pressure is used.

**Molten zone temperature and temperature gradient**: Very large temperature gradients usually lead to cracks and defects in the crystal due to large thermal stresses. Very high temperature in the molten zone lead to a concave liquid/solid interface, whereas, lower temperature gives a convex interface.

**Rotation rate**: The rotation of feed and seed rod is essential to ensure uniform mixing and homogeneous heating in the molten zone. Higher rotation rates gives a more stale molten zone but at the same time lead to defects and bubble formation.

### 3.2.1 Flux Technique of Crystal Growth

In the Flux method of crystal growth, the starting constituents of the desired compound are dissolved in a solvent that lowers the melting point of the (flux). Key characteristics of a good flux are that it should have a low melting temperature, easily separate from products and not form a stable compound with the reactants. This mixture is placed in a non-reactive crucibles made of material like alumina, platinum, etc. The reaction takes place in high temperature furnaces with the temperature cycle selected based on the single crystal grown. A saturated solution is prepared by keeping the constituents of the desired crystal and the flux at temperatures slightly above the saturation temperature long enough to form a complete solution. Then the crucible is cooled in order to cause the desired crystal to precipitate. Nucleation happens in the cooler part of the crucible.
Single crystals of Sr$_4$Ru$_3$O$_{10}$ were grown using the flux method by heating SrCO$_3$ and RuO$_2$ with a SrCl$_2$ flux in a Pt crucible to 1500 °C, and then cooling the melt at 2 °C per hour to 1350 °C, followed by rapid cooling to room temperature. The flux method for Sr$_2$IrO$_4$ is described in §5.1.1. Flux methods are more efficient in exploring a complex compositional phase space and the probability of growing entirely new crystal is quite high. The advantage of flux growth is that the crystals grown display natural facets. Moreover, it doesn’t require any elaborate apparatus and is suitable for incongruently melting materials. The disadvantage is that flux method produces relatively smaller crystals.
3.3 Sample Characterization

3.3.1 Crystal Structure Characterization

X-Ray Diffraction

The physical and magnetic properties of strongly correlated electron systems are critically connected to their crystal structure. Therefore, knowledge of the crystal structure forms an integral part of the research in our lab. X-rays interact with a crystalline material results in a diffraction pattern. Since, the same crystal always gives the same pattern, the X-ray diffraction pattern is like a crystal’s fingerprint. The powder X-ray diffraction patterns are obtained from a Scintag powder X-ray diffractometer in our lab. An X-ray beam of known wavelength is focused on a powdered sample and X-ray diffraction peaks are measured using a germanium detector. The d-spacing of observed diffraction peaks follow Bragg’s Law,

\[ n\lambda = 2d\sin\theta \]  

(3.2)

The X-ray diffractometer uses a Cu (wavelength=1.54184 Å) X-ray tube and a liquid-nitrogen cooled germanium detector. X-ray diffraction patterns were obtained from a single piece of single crystal crushed in a small mortar and placed at the center of a quartz plate with ethanol. The scans were usually performed such that \(10^\circ < 2\theta < 70^\circ\), where \(2\theta\) is the detector angle, at a rate of 0.02° per step. The data from the diffraction spectrum are then compared to the powder diffraction data in the databases of known structure. The single crystal X-ray diffraction data were collected using a Nonius kappa CCD diffractometer with molybdenum X-ray source \[4\]. The low temperature machine delivers a constant, low-velocity flow of cold nitrogen gas over the crystal during data collection, which allows observation of diffraction patterns at 90 K.

3.3.2 Energy dispersive X-ray spectroscopy

Another experimental technique for chemical characterization of single crystals grown in our lab is Energy Dispersive X-ray Spectroscopy (EDX or EDS). For this purpose, we utilize the EDX system integrated into the S-3200 -N Hitachi scanning electron microscope in the Electron Microscopy Center. EDX is based on the fundamental principle that each element has a unique atomic structure allowing X-rays that are characteristic of an element’s atomic structure, to be identified uniquely. When a high energy electron beam interacts
Figure 3.5: An X-ray spectrum obtained from powder diffractometer for MnSbO$_3$

with matter X-rays are produced. An X-ray spectrometer detects and records the X-rays providing information on the elemental content of the substance at the point where the electron beam is focused. EDS can be used to find the chemical composition of materials down to a spot size of a few microns, and to create element composition maps over a much broader area. The spot analysis is used to determine the chemical composition of the crystal, especially for chemically substituted samples. It can also be used as a secondary tool for determining the phase composition of the samples. A typical EDS spectrum is shown in figure 3.6.

Figure 3.6: An EDX spectrum of Sr doped Ca$_3$Ru$_2$O$_7$
3.4 Magnetic properties characterization

The DC magnetization of samples is measured to determine the magnetic properties of the systems studied. The Quantum Design Magnetic Properties Measurement System (MPMS XL 7) uses a Superconducting Quantum Interference Device (SQUID) magnetometer to detect and measure the magnetic moment of the sample. The sample is magnetized by the magnetic field produced by a superconducting magnet. To measure the DC magnetization of the sample, the sample is first placed near the bottom of the pickup coil, which is a single superconducting coil wound by one clockwise turn at the top, and then by two counterclockwise turns at the middle, and finally by one clockwise turn at the bottom as shown in Figure 3.7. This type of coil is called a second-derivative gradiometer and the main purpose of winding in different directions is to cancel the uniform external magnetic field from the superconducting magnet of the MPMS and other stray fields in the lab. In principle, as a sample moves along the axis of the detection pickup coil to the top position, an electromotive force (EMF) is induced in the pickup coil. This induced EMF is proportional to the sample magnetization, and the MPMS electronics detect the amplified EMF signals using SQUID electronics as the sample moves along the pickup coil. Measurements can be made with the external magnetic field applied from 0 - 7 T and the temperature range of the system is 1.7 - 400 K. The sensitivity of the instrument is in the range of $10^{-8}$ emu \[^{83}\]. The single crystal is weighed accurately (to 0.01 mg) with an electronic balance and glued to a thin quartz tube with GE varnish and dried thoroughly to expel any air bubbles. The quartz rod is magnetically inert and care is taken to apply minimal amount of GE varnish on the sample. The sample is glued such that the desired crystallographic directions remain parallel to the applied magnetic field during measurements. The quartz rod is then fixed to the end of the sample rod and inserted into the sample chamber.

3.5 Transport property measurement

The resistance is measured using the four-point probe method. It is an electrical resistance measurement technique that uses separate pairs of current-carrying and voltage-carrying electrodes to make more accurate measurements than the two-point method which uses the same pair of leads for current and voltage. The key reason for using the four-point method is that the separation of current and voltage electrodes eliminates the resistance
Figure 3.7: The Squid response while the sample moves through the Squid pickup coils.

The current is supplied via a pair of current leads. This generates a voltage drop across the resistance to be measured according to Ohm’s law, \( V = RI \), with \( I \) being the current across the sample which has a resistance \( R \). This current also generates a voltage drop across the current leads themselves. To avoid including these lead resistances in the measurements, a pair of voltage leads are attached adjacent to the target resistance. The accuracy of the technique comes from the fact that almost no current flows through the voltage wires, so the voltage drop is extremely low. The resistivity measurements could be carried out in a temperature range \( 1.7 < T < 900 \) K. The added transport function to the MPMS XL is used for measuring the resistance in the temperature range \( 1.7 < T < 400 \) K and an external magnetic field 0 to 7 T. The high temperature measurements (\( 1.7 < T < 900 \) K) are done using the Displex closed cycle Helium cryostat (Advanced Research System). The Keithley Sourcemeter(2400) is used as the power supply and a Nanovoltmeter (2182) measures the resistance. The Linear Research 700 ac bridge is also sometimes used. The electrical contacts are made using 0.001 inch (1 mil) diameter gold wires attached to the sample using a two component epoxy (H20E) mixed in equal proportions and cured according to specifications. The sample is glued to the sample probe by GE varnish and the gold wires are attached to the probe wires using a silver paint. For the high temperature measurements, the gold leads are attached with epoxy E3084 and the sample is glued to the sample head with high temperature glue (AREMCO Ceramabond 865). It is important to place all four gold leads linearly in the direction...
measured. Since the samples are usually very small along c-axis, the contacts are made on the surface of the same side and the other two contacts are made on the corresponding positions of the other side. The resistivity of a bar shaped sample is

$$\rho = R \frac{A}{l}$$  \hspace{1cm} (3.3)

where R is the resistance of the sample, A is the area of cross-section and l is the length or the distance between two voltage leads.

3.6 Heat capacity measurements

The heat capacity of the single crystals are measured by the heat capacity function added to Quantum Design Physical Property Measurement System (PPMS) with a relaxation method \cite{82}. The measurement could be performed in the temperature range $1.8 < T < 400 \text{ K}$ and in an applied field as high as 9 T. The schematic diagram of heat capacity measurement using the relaxation method and the thermal connections to the sample and sample platform are shown in Figure 3.8. The sample surface is cleaned (and when possible polished) in order to get a flat surface to achieve good thermal contact. A very small amount of Apiezon H grease is applied to the sample platform and the sample is placed on the grease and pressed gently. The platform is also in contact to a thermal bath, the puck in which the setup is contained. Thermal contact between the platform and the puck is made with wires of a known conductance, $K_w$. A constant power $P_0$ is applied from the heater for a known amount of time which is followed by a cooling period of the same duration.

3.6.1 Simple model

The simple model, which is the most basic analysis of the raw measurement data, assumes that the sample and sample platform are in good thermal contact with each other and are at the same temperature during the measurement. In the simple model, the temperature $T$ of the platform as a function of time $t$ obeys the equation

$$C_{total} \frac{dT}{dt} = -K_w(T - T_b) + P(t),$$  \hspace{1cm} (3.4)

where $C_{total}$ is the total heat capacity of the sample and sample platform, $K_w$ is the thermal conductance of the supporting wires, $T_b$ is the temperature of the thermal bath (puck frame) and $P(t)$ is the power applied by the heater. The heater power $P(t)$ is equal to $P_0$ during
the heating portion of the measurement and equal to zero during the cooling portion. The solution of this equation is given by exponential functions with a characteristic time constant equal to $C_{total}/K$. The Heat Capacity software uses the simple model to measure the addenda and generally to measure most samples. However, when the thermal contact between the sample and sample platform is poor, the software uses the more sophisticated two-tau model to measure the heat capacity.

**Two-tau model**

The Heat Capacity software uses the two-tau model to measure the heat capacity of the sample when poor thermal attachment of the sample to the platform produces a temperature difference between the two. The two-tau model simulates the effect of heat flowing between the sample platform and sample, and the effect of heat flowing between the sample platform and puck. In the two-tau model, the first time constant ($\tau_1$) represents the relaxation time between the sample platform and the puck, and the second time constant ($\tau_2$) represents the relaxation time between the sample platform and the sample itself. The following equations express the two-tau model

$$C_{\text{platform}} \frac{dT_p}{dt} = P(t) - K_w(T_p(t) - T_b) + K_g(T_s(t) - T_p(t))$$

(3.5)

$$C_{\text{sample}} \frac{dT_s}{dt} = -K_g(T_s(t) - T_p(t)),$$

(3.6)
where \( C_{\text{platform}} \) is the heat capacity of the sample platform, \( C_{\text{sample}} \) is the heat capacity of the sample and \( K_g \) is the thermal conductance between the two due to the grease. The temperatures of the platform and sample are given by \( T_p(t) \) and \( T_s(t) \), respectively.

### 3.7 Dielectric Measurements

The dielectric measurements on the single crystals are performed using a QuadTech 7600 LCR meter with the *parallel plate capacitor method*. The parallel plate capacitor method involves sandwiching a thin sheet of material between two electrodes to form a capacitor. The data can be measured in the frequency range 10 Hz to 2 MHz and temperature ranging from liquid helium temperature (4.2 K) to room temperature. The sample surfaces are cleaned and polished thoroughly to ensure good contacts. The contacts are formed by smoothly depositing a very thin layer of conducting epoxy and curing it for half an hour. The sample is attached to the dielectric probe by placing it flat between two copper blocks that are tightened together with plastic screws attached to one of the copper blocks. Care is taken to make sure that the sample surface and copper block have very good contact with no air between them. However, at the same time the copper blocks aren't tightened so much as to develop cracks in the sample. The probe is then placed in the Oxford Helium Dewar for low temperature and in-field measurements. LABVIEW software program was developed in the lab that allows capacitance scans both as a function of frequency and temperature at various magnetic field strength (13/15 T).
CHAPTER 4: LAYERED RUTHENATES

4.1 Anomalous Itinerant Magnetism in Single-Crystal \( \text{Sr}_4\text{Ru}_3\text{O}_{10} \)

4.1.1 Introduction

\( \text{Sr}_4\text{Ru}_3\text{O}_{10} \) is the triple-layered \((n = 3)\) member of the Ruddlesden-Popper (RP) series \( \text{Sr}_{n+1}\text{Ru}_n\text{O}_{3n+1} \), where \( n \) is the number of Ru-O layers per unit cell. The Strontium RP series has been a very promising and active area of research as it displays a multitude of physical properties like unconventional superconductivity, Pauli paramagnetism, ferromagnetism and metamagnetism, antiferromagnetic insulating behavior and orbital ordering, resulting from the interplay between charge, spin, orbital and lattice degrees of freedom. \( \text{Sr}_{n+1}\text{Ru}_n\text{O}_{3n+1} \) exhibits a subtle interplay between the structural anisotropy and distortions and magnetic properties characterized by strong spin-phonon or spin-lattice coupling driven by dimensionality, that is, the number of RuO\(_6\) layers in the unit cell.

Ruthenium in \( \text{Sr}_{n+1}\text{Ru}_n\text{O}_{3n+1} \) has four valence electrons in 4\( d \) orbital and is in Ru\(^{+4}(4d^4)\), ionic state. The Ru\(^{+4} \) ion is at the center of the RuO\(_6\) octahedron with the oxygen atoms at the vertices. The crystal field results in lower lying threefold, \( t_{2g} \) and higher energy twofold \( e_g \) orbitals. Ru is in low spin state with all four electrons in the \( t_{2g} \) energy levels. All compounds in the series contain Ru\(^{+4} \), and have Fermi surfaces with strong character of 4\( d_{xy} \) and 4\( d_{xz,yz} \) orbitals of Ru, hybridized with O 2\( p \) states. The energy differences between the Ru\(^{+4} t_{2g} \) and \( e_g \) orbitals, and between the levels within the \( t_{2g} \) and \( e_g \) manifolds, is influenced by the individual Ru-O distances in each RuO\(_6\) octahedron, whereas the conduction bandwidth and thus the density of states at the Fermi level is sensitive to the RuO\(_6\) rotations. This latter factor plays an important role in determining the stability of a ferromagnetic ground state through the Stoner-Wohlfarth criterion \[45\] \[80\] \[37\] \[87\].

This evolution of Fermi surface topography with \( n \) is clearly illustrated in the evolution of physical and magnetic properties of \( \text{Sr}_{n+1}\text{Ru}_n\text{O}_{3n+1} \) series from \( n = 1 \) to \( n = \infty \). The \( n = 1 \) member of the series, \( \text{Sr}_2\text{RuO}_4 \), demonstrate an unconventional \( p \)-wave spin triplet superconductivity similar to the superfluidity in helium-3 \[66\]. The \( n = 2 \) member, \( \text{Sr}_3\text{Ru}_2\text{O}_7 \) is a strongly enhanced paramagnet with \( T_M = 18 \) K \[45\] and \( n = \infty \) \( \text{SrRuO}_3 \) is an itinerant ferromagnet. The triple-layered \( \text{Sr}_4\text{Ru}_3\text{O}_{10} \) lies intermediate between bilayered \( \text{Sr}_2\text{RuO}_4 \) which demonstrates proximity to itinerant metamagnetic state and the infinite
layered SrRuO$_3$ which is an itinerant ferromagnet with the Curie temperature, $T_C=165$ K and a reduced moment of $1.1\mu_B$/Ru [22].

Its position between Sr$_3$Ru$_2$O$_7$ with proximity to metamagnetic quantum critical point and the itinerant ferromagnet SrRuO$_3$ on other side endows it with borderline physical properties reflected in the complex behavior evidenced in magnetization, specific heat and resistivity. Sr$_4$Ru$_3$O$_{10}$ hosts very interesting physical phenomenon ranging from itinerant and anisotropic magnetism [11], tunneling magnetoresistance [11], switching behavior, strong spin-orbit coupling, anomalous low temperature specific heat, quantum oscillations.

Including the above mentioned phenomenon, the unique feature however, which is a constant source of motivation for this project is the *borderline magnetism*: Sr$_4$Ru$_3$O$_{10}$ displays spontaneous ferromagnetic ordering along $c$-axis, while the $ab$-plane features a pronounced peak in magnetization and a first-order metamagnetic transition. Placed delicately between the $n=2$ and $n=\infty$, the triple-layered Sr$_4$Ru$_3$O$_{10}$ is a ferromagnet with $T_C=105$ K followed by an additional magnetic transition at $T_M=60$ K along $c$-axis.

### 4.1.2 Structure

Sr$_4$Ru$_3$O$_{10}$ crystallizes in the $Pbam$ crystal structure shown in Figure 4.1. The orthorhombic unit cell is composed of triple-layers of corner-shared RuO$_6$ octahedra separated by double rock-salt layers of Sr-O. The structure is slightly orthorhombic with room-temperature (RT) lattice parameters $a=5.4982$ Å, $b=5.4995$ Å and $c=28.5956$ Å. The primary Bragg reflection could be indexed with a tetragonal unit cell (space group $I4/mmm$) with cell parameters, $a = b = 3.9001$ and $c = 28.573$ Å [29]. In this model the in-plane oxygen atoms were displaced from their ideal positions by rotations of RuO$_6$ octahedra around the $c$-axis. The synchrotron x-ray source however, yielded measurable intensities of superlattice reflections that could only be indexed by enlarging the crystallographic unit cell such that $a = b = \sqrt{2}a^*$, where $a^*$ is the $I4/mmm$ cell parameters, thus reducing the space-group symmetry from tetragonal to orthorhombic $Pbam$ [29].

Structurally two of the most important features are: (a) the RuO$_6$ octahedron in the outer layers of each triple layer are rotated by an average of $5.6^\circ$ around the $c$-axis, whereas the octahedron in the central layer are rotated by an average of $11.0^\circ$ in the opposite direction, and (b) RuO$_6$ octahedron in the outer layers are elongated at low temperatures. Single crystal diffraction shows that the $c$-axis is elongated by approximately $0.2\%$ from 300
K to 90 K. This lengthening of the $c$ axis lifts the degeneracy between the $t_{2g}$ orbitals and narrows $d_{zx}$ and $d_{yz}$ bands relative to the $d_{xy}$, thereby, weakening the inter plane hopping. These features might be responsible for driving the ferromagnetic coupling in this system.

4.1.3 Magnetic Properties

The anisotropic ground state of Sr$_4$Ru$_3$O$_{10}$ is reflected in the magnetization data presented in this section. Figure 4.2 shows the magnetization, $M$ as a function of temperature for both $c$-axis and $ab$-plane measured in a magnetic field, $B=0.01$ T. The $c$-axis shows a transition with $T_C = 105$ K, followed by an increased spin polarization below $T_M = 60$ K. Below this transition temperature, there is a huge irreversibility in $M$ between field cooled and zero
Figure 4.2: Magnetization as a function of temperature, $M(T)$, for the ab-plane and c-axis at $B = 0.01$ T for Sr$_4$Ru$_3$O$_{10}$. [11], [29]

field cooled behavior. This irreversibility indicated by the difference between the FC and ZFC magnetization is a signature of ferromagnetic behavior.

However, for the $ab$-plane, a weak cusp corresponding to the ferromagnetic transition along $c$-axis at $T_C$ is observed. Magnetization for the basal plane, $M_{ab}$ exhibits a pronounced peak at $T_M$, indicating antiferromagnetic like behavior as shown in Figure 4.3. Also, unlike the $c$-axis, the irreversibility for ab-plane between field cooled (FC) and zero field cooled (ZFC) is very small. This anisotropy between the $c$-axis and $ab$-plane is rather unexpected considering the evolution of magnetism in the Sr$_{n+1}$Ru$_n$O$_{3n+1}$ which would suggest an increasingly strong, but less anisotropic, coupling favorable for ferromagnetism as $n$ increases. The temperature variation of the susceptibility of a normal paramagnetic system should follow the Curie-Weiss law,

$$\chi = \chi_0 + \frac{C}{T - \theta}$$  \hspace{1cm} (4.1)

where $\chi_0$ is the temperature independent susceptibility. Curie-Weiss law holds even for paramagnetic metals in the vicinity of ferromagnetic instability [74]. The high temperature
data for magnetic susceptibility of $\text{Sr}_4\text{Ru}_3\text{O}_{10}$ when fitted to Curie-Weiss law yields, $\chi_0 = 4.1 \times 10^{-3}$ emu/mole for $c$-axis and $\chi_0 = 1.4 \times 10^{-4}$ emu/mole for $ab$-plane. The Stoner model of ferromagnetism establish the criterion for ferromagnetism as,

$$Ug(E_F) \geq 1 \quad (4.2)$$

where $U$ is an exchange interaction and $g(E_F)$ is the density of states at the Fermi surface.

The largely enhanced $\chi_0$ for $c$-axis suggests a large density of states near the Fermi surface, in accordance with the Stoner criterion that occurs along the $c$-axis. On the other hand, $\chi_0$ for the basal plane is more than an order of magnitude smaller compared to the $\chi_0$ for $c$-axis, implying a less energetically favorable condition for ferromagnetism evident in Figure 4.3. The surprisingly large anisotropy in $\chi_0(\chi_0^c/\chi_0^{ab} = 29)$ certainly points to a highly anisotropic density of states near the Fermi surface. Measurements of specific heat $C(T)$ yields the electronic specific heat $\gamma = 109 \text{ mJ/mol-K}^2$. The Wilson ratio $R_w(= 3\pi^2 k\chi_0/\mu^2 \gamma)$ is found to be 2.4 and 0.08 for the $c$-axis and basal plane, respectively, assuming $\gamma$ probes the average value of renormalization effect over the entire Fermi surface. This reflects a much higher density of states for $c$-axis which brings ferromagnetic instability. In contrast, the density of states for the basal plane is not large enough to cause a ferromagnetic instability.

Figure 4.5 shows magnetization as a function of magnetic field for $T = 1.7 \text{ K}$ for
Figure 4.4: $c$-axis resistivity $\rho_c$ as a function of temperature $T$ for a few representative magnetic fields $B$ parallel to the basal plane for Sr$_4$Ru$_3$O$_{10}$.

$ab$-plane and $c$-axis. The spins along the $c$-axis are easily polarized at a very modest field of $B = 0.2$ T, with a saturation moment $M_s = 1.13\mu_B$/Ru obtained by extrapolating to $B = 0$ for $T = 1.7$ K. The saturation moment expected for an $S = 1$ system is $2\mu_B$/Ru. The saturation moment for Sr$_3$Ru$_3$O$_{10}$ is comparable to that for SrRuO$_3$ whose easy axis lies within the basal plane [21] but the field dependence shown in Figure 4.5(a) and 4.5(b) is vastly different from its neighbors SrRuO$_3$ and Sr$_3$Ru$_2$O$_7$. While the huge irreversibility between FC and ZFC magnetization for $c$-axis is typical of a ferromagnet, magnetization, $M$ for the basal plane shows a sharp metamagnetic transition with a critical field, $B_c$, which decreases and broadens with increasing temperature and vanishes at $T_M = 50$ K, Figure 4.5(b). Itinerant metamagnets are characterized by a maximum in the temperature dependence of the paramagnetic susceptibility when the metamagnetic transition from the paramagnetic to ferromagnetic state is induced by external fields at low temperature [98].

Metamagnetism is observed in Sr$_3$Ru$_2$O$_7$ in both the basal plane and the inter plane magnetization with a broader and higher critical field, $B_c$ which drives the ground state from a paramagnetic state at low fields to an induced ferromagnetic state at higher fields [80, 37]. In light of the itinerant and unusual magnetic character with ferromagnetism along
(a) Isothermal magnetization as a function of field $B$ at $T = 1.7$ K for the $ab$-plane and $c$-axis

(b) Isothermal magnetization as a function of field $B$ at $T = 1.7, 15, 30, 50, 90$ and $120$ K for the $ab$-plane

Figure 4.5: Isothermal Magnetization for (a) $c$ and $ab$-plane, (b) $ab$-plane at different temperatures for Sr$_4$Ru$_3$O$_{10}$. Notice that the metamagnetic transition decreases with increasing $T$ and vanishes at $T > 50$ K near [11]

c axis and antiferromagnetic like behavior within the basal plane shown in Figures 4.5, 4.2, 4.8(a) it is intriguing whether this metamagnetic transition represents a transition between a paramagnetic and ferromagnetic state similar to Sr$_3$Ru$_2$O$_7$, or a transition from AFM
state at low fields to FM state at higher fields, a process that manifests strong competing interactions between ferromagnetic and antiferromagnetic couplings, and is known to often occur in insulators \cite{90}. \textit{Sr}_4\textit{Ru}_3\textit{O}_10 ground state is not characteristic of either a robust ferromagnet or an antiferromagnet, implying the close energies of the states and an exotic ground state. The anomalous magnetic behavior is often driven by structural changes, and it is possible that the magnetic behavior observed in \textit{Sr}_4\textit{Ru}_3\textit{O}_10 is driven by structural changes below 60 K \cite{4.1.4}, which are yet to be observed and would indicate a strong spin-lattice coupling in the system.

Such a possibility is also supported by spectroscopic investigation where a magnetic-field induced frequency shift is observed below the curie temperature $T_C$ \cite{39}. The frequency of the $B_{1g}$ phonon, which is associated with the internal vibrations of the RuO$_6$ octahedra in \textit{Sr}_4\textit{Ru}_3\textit{O}_10 is highly sensitive to the onset of ferromagnetic order. This strong magnetoelastic coupling is manifest in the slope change in the temperature dependence of the $B_{1g}$ phonon frequency. The ferromagnetic ordering at $T = 105$ K exhibit a pronounced maxima in $B_{1g}$ line associated to O3 vibrations, which, corresponds to the vibrations in the $xy$ plane, which indicates that the electron-phonon coupling is related closely to the magnetic ordering. There is no discernible change in the vibrations in $z$ direction near $T_C$ \cite{46}. The structure and spin ordering correlation is further corroborated by the application of
Figure 4.7: Proposed phase diagram for Sr$_4$Ru$_3$O$_{10}$ for field parallel to $ab$-plane and $c$-axis. Reproduced from [39]. Red dots show the field dependence of $c$-axis magnetization magnetic field along $c$-axis, where $B_{1g}$ frequency increases indicating that the spin canting along $c$-axis is lifted due to an elongation of RuO$_6$ octahedra in the $c$ direction and at the same time causing a contraction of the octahedra in the $ab$ plane resulting in an increase in the in-plane frequency.

For a magnetic field applied in the plane, there is a decrease in the $B_{1g}$ frequency for temperatures below the magnetic anomaly temperature, $T_M$ and field less than 2 T, which is very close to the critical field $B_c = 2.2$ T as seen in Figure 4.5(a), which suggests an in-plane contraction of the RuO$_6$ octahedra. The phase diagram based on the Raman studies and isothermal magnetization measurements for $ab$-plane and $c$-axis are shown in Figure 4.7 [39]. The Ru moments transition from AFM or PM canted configuration to a FM canted configuration via a metamagnetic transition above 2 T at temperatures below $T_M$. Between $T_M$ and $T_C$, the $c$-axis is ferromagnetically ordered but the in-plane spins are not ordered at all. Above the Curie temperature, the system enters a paramagnetic state [39].
4.1.4 Transport Properties

(a) Inter plane resistivity $\rho_c$ and basal plane resistivity $\rho_{ab}$ as a function of temperature for Sr$_4$Ru$_3$O$_{10}$

(b) Inter plane resistivity $\rho_c$ and basal plane resistivity $\rho_{ab}$ at $B = 0$ and 9 T

Figure 4.8: Resistivity as a function of temperature for Sr$_4$Ru$_3$O$_{10}$ [11, 29].

Figure 4.8(a) shows the resistivity $\rho$ as a function of temperature for $c$-axis and $ab$-plane. Resistivity for $c$-axis exhibits anomalies corresponding to $T_C = 105$ K and $T_M = 60$ K. These anomalies (see Figure 4.8(b)) are also evident in basal plane resistivity but are much weaker than seen in $c$-axis. The most prominent features are the unexpectedly large anisotropy and unusual temperature dependence of $\rho_c$. The ratio $\rho_c/\rho_{ab}$ decreases from nearly 30 to 10 as the temperature is varied from 2 K to 350 K respectively, a nearly quasi-three dimensional characteristic despite the triple layer structure. $\rho_c$ drops by nearly an order of magnitude below 60 K corresponding to $T_M$. This drop in resistivity is similar to that seen in Sr$_2$RuO$_4$ and Sr$_3$Ru$_2$O$_7$ but more pronounced and less anticipated in Sr$_4$Ru$_3$O$_{10}$ because the triple layer structure should be more favorable for inter plane hopping. The system is possibly more spin polarized below $T_M$, as seen in Figure 4.2, thus reducing the inter plane resistivity. This is supported by Figure 4.8(b) where inter plane resistivity, $\rho_c$ is shown as a function of temperature at different magnetic fields.

With magnetic field, $B$ applied parallel to basal plane, the anomaly at $T_M$ rapidly decreases with increasing $B$ and eventually disappears at $B = 4$ T. There is a brief region between 50 K and 70 K with nonmetallic behavior (negative slope), possibly due to the elongation of RuO$_6$ octahedra in the outer layers at low temperatures which leads to a narrowing of $d_{yz}$ bands, leading to decreased conductivity along $c$-axis. If there is a structural transition below $T_M$ that leads to the rotation of RuO$_6$ octahedra, the domain
wall pinning at $T_M$ may become stronger, giving rise to stronger hysteresis, Figure 4.2. The reduced symmetry below $T_M$ breaks some symmetry restriction and increases the interlayer tunneling, thus reducing the $c$-axis resistivity. The transition and the rotation are strongly affected by the magnetic field $B$ because of strong spin orbit coupling, giving rise to the behavior seen in Figure 4.8(a). The low temperature resistivity follows Fermi liquid behavior $\rho = \rho_0 + A T^2$, for both $\rho_c$ and $\rho_{ab}$ from 2 $\leq T \leq$ 15 K, with $(\rho_0)_c = 1.30 \times 10^{-3}\Omega$ cm and $(\rho_0)_{ab} = 5.4 \times 10^{-5}\Omega$ cm and the coefficients $A$, $A_c = 1.04 \times 10^{-5}\Omega$ cm/K$^2$, $A_{ab} = 3.4 \times 10^{-7}\Omega$ cm/K$^2$. The $c$-axis values are close to those of Sr$_3$Ru$_2$O$_7$ [45], but the basal plane values are about an order larger, i.e., while triple layer Sr$_4$Ru$_3$O$_{10}$ has a more isotropic resistivity than double layer Sr$_3$Ru$_2$O$_7$, it is not because of better transport along $c$ but due to increased scattering in the $ab$ plane. It is also surprising that the anisotropies in $A(\sim 31)$ and $\rho_0(\sim 24)$ are similar, since the latter depends only on the band mass and elastic scattering rate, and unlike Sr$_3$Ru$_2$O$_7$, the susceptibility is anisotropic.

The parameters in Table 4.1 point towards a highly anisotropic surface. $A_c$ is much larger than that of ordinary Fermi liquids and, along with the $c$-axis Wilson ratio $R_w = 2.4$, suggests strong correlation effects along $c$-axis. The resistivity in either direction do not show a $T^{3/2}$ or $T^{5/3}$ dependence expected for a three-dimensional antiferromagnet and ferromagnet respectively [71], [47]. Beyond the transition regions, $\rho_{ab}$ shows essentially linear temperature dependence for temperature ranges, 18 $\leq T \leq$ 38 K, 50 $\leq T \leq$ 100 K and 8 $\leq T \leq$ 38 K, suggesting strong fluctuations.

Furthermore, $\rho_{ab}$ shows negative magnetoresistivity, defined as $[\rho_c(B) - \rho_c(0)]/\rho_c(0)$, that reaches as large as 28% in the vicinity of and below $T_M$ at $B = 5$ T applied parallel...
(a) $\rho_c$ as a function of $B$ at $\Theta = 28^\circ$ for a few representative temperatures.

(b) Shubnikov-de Hass effect as a function of $B^{-1}$ for various temperatures specified

Figure 4.9: Quantum Oscillations in Sr$_4$Ru$_3$O$_{10}$

...to the basal plane [see Figure 4.8(b)]. This is rather surprising because spin scattering is expected to be minimized at $B = 0$ in itinerant ferromagnets where electrons find the path of least resistance, and thus positive magnetoresistance (MR) is anticipated with $B$ which forces electrons to take a different path. The observed negative MR of $\rho_{ab}$ is a clear indication of large spin fluctuations existing in a non-ferromagnetic state. This point is consistent with the $T$ dependence of $\rho_{ab}$ at 5 T for 10-100 K shown in Figure 4.8(b)
The c-axis transport properties are dominated by the metamagnetic transition which reinforce the possibility of strong magnetoelastic coupling, that is, the magnetic ground state of Sr$_4$Ru$_3$O$_{10}$ depends on structural changes below 50 K. Figure 4.6 shows the magnetic field dependences of $A_c$ and $\rho_{0c}$, obtained by fitting the data below 15 K (Figure 4.8(b)) to $\rho_c = \rho_{0c} + A_c T^\alpha$, for $0 \leq B \leq 7$ T. For this field range, $\alpha = 2$ except between 2.7 and 2.9 T, for which $\alpha = 1.2$, as found in Ca$_3$Ru$_2$O$_7$ [69] and in heavy fermion compounds near quantum critical points [98], [59], [27]. The sharp peaks in $A_c$ and $\rho_{0c}$ suggests large changes in carrier density and is strikingly similar to that in Sr$_3$Ru$_2$O$_7$ near 7.85 T below 0.35 K, the key evidence for its magnetic field-tuned quantum criticality [37].

The transport properties driven by metamagnetism are also illustrated in Figure 4.9, where $\rho_c$ is plotted as a function of $B$, rotating from the c axis to the a axis (no difference is seen for $B$ parallel to the a- and b-axes). $\Theta$ is defined as the angle between c-axis and $B$. Resistivity initially increase with increasing $\Theta$ by nearly 40% from 1.58 mΩ cm at $\Theta = 0^\circ$ (B $\parallel$ c or the easy axis) to 2.47 mΩ cm at $\Theta = 42^\circ$ at 32 T. This behavior is consistent with decrease in spin scattering due to increased spin polarization. As $\Theta$ reaches 43.4°, $\rho_c$ starts to show negative magnetoresistivity characterized by a sudden drop at a critical field $B_c$. This $B_c$ systemically decreases with increasing $\Theta$, corresponding to the metamagnetic transition that leads to the rapid spin polarization evidenced in $M$ when $B \parallel ab$. The abrupt metamagnetic transition yields a negative magnetoresistivity ratio of more than 60%. Such a large inter plane magnetoresistivity is believed to be due to a tunneling effect facilitated by a field induced coherent motion of a spin-polarized electrons between Ru-O planes, which is also seen in bilayer systems such as Ca$_3$Ru$_2$O$_7$ [13, 12] and La$_{2-2x}$Sr$_{1+2x}$Mn$_2$O$_7$ [55]. Evidently the metamagnetic transition $B_c$ reconstructs the Fermi surface and sharply divides the large negative magnetoresistivity and quantum oscillations as can clearly be seen in Figure 4.9. The Shubnikov-de Hass (SdH) effect occurs at low $\Theta$ and becomes more pronounced at $\Theta = 28^\circ$ [?]. The SdH effect expectedly becomes stronger as temperature decreases. The SdH signal is defined as $(\sigma - \sigma_b)/\sigma_b$, where $\sigma$ is the conductivity and $\sigma_b$ is the background conductivity. Since the detected frequency is very low in the entire field range up to 32 T, the Fast Fourier analysis can not be used. The frequencies are then determined by directly measuring the period of oscillations. The data analysis reveals the frequency obtained corresponds to only 0.9% of the first Brillouin zone. The cyclotron effective mass, $\mu_c = 0.90 \pm 0.15$, which is smaller than expected and is attributed to the fact that it has

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been difficult to resolve the heavier effective masses in quantum oscillation experiments. This is also seen in Ca$_3$Ru$_2$O$_7$ and also seen in heavy fermion systems [40]. These results suggest a behavior that is characterized by an exotic ground state with proximity to the itinerant ferromagnetic instability and a possible quantum critical point. These properties combined with tunability of Sr$_4$Ru$_3$O$_{10}$ to external perturbations, it is further probed by impurity substitution presented in the next section.

4.2 Itinerant Ferromagnetism and metamagnetism Probed by Impurity Doping

4.2.1 Motivation

As seen so far, Sr$_4$Ru$_3$O$_{10}$ exhibits a novel and unusual borderline magnetism: It shows ferromagnetism, $[U_g(E_F) \geq 1]$ with a Curie temperature $T_c=105$ K followed by an increased spin polarization below $T_M=50$ K for $c$-axis and, a sharp peak in $M_{ab}(T)$ accompanied by a first order metamagnetic transition, a situation very similar to Stoner enhancement, $[U_g(E_F) < 1]$ responsible for the enhanced paramagnetism and itinerant metamagnetism in the $ab$ plane. The coexistence of the inter-layer ferromagnetism and the in-plane metamagnetism, which can not be explained by simple theoretical arguments, is one of the focal challenges in Sr$_4$Ru$_3$O$_{10}$. The detailed properties of the Stoner enhanced $\chi(T)$ are determined by the energy dependence of the density of states, $g(E)$ in the vicinity of the Fermi level. Peaks of $g(E)$ are often related to Van Hove singularities and intimately coupled to magnetism and phonons (lattice deformations). The anisotropy in the field response arise from a Von Hove singularity (logarithmic divergence) close to the Fermi level [7] in conjunction with the coupling of the spins to the crystalline field orbital states and the lattice. The field-induced itinerant metamagnetism [36, 97, 85, 98] observed in several materials such as Sr$_3$Ru$_2$O$_7$ [30, 37], Y(Co$_{1-x}$Al$_x$)$_2$ [85] and other Co compounds [98] is believed to be induced by a nearby Stoner instability. Studies on correlated metals such as MnSi$_9$ and Sr$_3$Ru$_2$O$_7$ [30, 37, 45] reveal phenomena consistent with quantum criticality due to the onset of itinerant ferromagnetism and the critical end point of a first order metamagnetic transition, respectively. The essence of this physics has been captured by a simple model [7] based on a minimum of the density of states, $g(E)$ (MnSi) and a two-dimensional Van Hove singularity for the ruthenates. Clearly, itinerant ferromagnetism and metamagnetism
sensitively depend on \( U \) and \( g(E_F) \), and are not expected to coexist. But \( \text{Sr}_4\text{Ru}_3\text{O}_{10} \) under doping defiantly shows the coexistence suggestive of a new physics.

Introducing small amounts of impurity provides an effective way of probing and understanding this borderline magnetism in \( \text{Sr}_4\text{Ru}_3\text{O}_{10} \). In the following section, the results of study of \( \text{Sr}_4\text{Ru}_3\text{O}_{10} \) are shown where \( \text{Sr}^{2+} \) ions have been replaced by \( \text{La}^{3+} \) and \( \text{Ca}^{2+} \). This offers an opportunity to probe the system with a two-fold approach:

- Electronic configuration of Lanthanum is \([Xe]5d^14s^2\). It loses 3 electrons to be \( \text{La}^{3+} \), hence it introduces an extra electron when it is replacing \( \text{Sr}^{2+} \) in \( \text{Sr}_4\text{Ru}_3\text{O}_{10} \), which have only lost two electrons. Hence, a concentration \( x \) of \( \text{La}^{3+} \) introduces \( x \) electrons on the Ru site in the system. This results in altering the density of states, \( g(E_F) \) and \( \Delta \), the exchange splitting.

- \( \text{La}^{3+} \) (\( r_{\text{La}}=1.03 \) Å) and \( \text{Ca}^{2+} \) (\( r_{\text{Ca}}=1.00 \) Å) are significantly smaller in ionic size than \( \text{Sr}^{2+} \) (\( r_{\text{Sr}}=1.18 \) Å). Hence, low concentration doping enhances the buckling of the \( \text{RuO}_6 \) octahedron, therefore, changing the extent of overlap in the \( d \) orbitals and hence varying the exchange interaction and/or the bandwidth but at the same time preserves the crystal structure.

The similarity in the ionic sizes of La and Ca ions is expected to produce similar impact on the structural distortions in \( \text{Sr}_4\text{Ru}_3\text{O}_{10} \). Therefore, studying and comparing the response of La and Ca doping enables the study of different phenomenon resulting from impurity introduction and, differentiate the effect of electron doping and structural distortions on \( \text{Sr}_4\text{Ru}_3\text{O}_{10} \) simultaneously.

### 4.2.2 Impact of La and Ca doping on the structure of \( \text{Sr}_4\text{Ru}_3\text{O}_{10} \)

The structure for pure \( \text{Sr}_4\text{Ru}_3\text{O}_{10} \) is slightly orthorhombic with a space group \( \text{Pbam} \). The room temperature (RT) lattice parameters are \( a=5.4982 \) Å, \( b=5.4995 \) Å and \( c=28.5956 \) Å. Figure 4.10 displays the change of lattice parameters \( a \)- and \( c \)-axis as a function of La and Ca doping concentration, \( x \). The values for \( b \)-axis are very close (slightly longer) to \( a \)-axis and behaves similarly and are not shown. Both La and Ca doping cause no changes in the structure and space group but variations in the lattice parameters are observed with both in a few interesting ways. As shown in Figure 4.10 the \( c \)-axis shortens with decreasing ionic size as expected with increasing \( x \), (with Ca doping having a stronger impact compared
to La). The $a$-axis on the other hand, increases with increasing $x$. This effect is stronger for La doping and leads to a slight increase in the overall unit cell volume. This increase might be partly attributed to the additional electron from $La^{3+}$. For pure $Sr_4Ru_3O_{10}$, the $c$-axis grows with decreasing temperature as mentioned in section 4.1.2 [29], [11]. With the increase in doping concentration, the change in $c$-axis gets smaller with temperature as shown in Figure 4.11 where $\Delta c$ (defined as $c(90K) - c(RT)$) vs $x$ is plotted. It is rather noticeable that the La doping rapidly reduces $\Delta c$ which becomes zero at $x = 0.13$. In contrast, Ca doping shows a smaller impact on $\Delta c$ which is still significant at $x = 0.13$. It is also interesting to note that the $c$-axis Curie temperature, $T_C$, appears to be somewhat
associated with the change in $\Delta c$, particularly for La doping where $T_C$ decreases with vanishing $\Delta c$, suggesting a significant magnetoelastic effect in the system.

### 4.2.3 Magnetization for $(Sr_{1-x}La_x)_4Ru_3O_{10}$ and $(Sr_{1-x}Ca_x)_4Ru_3O_{10}$

![Diagram](image)

(a) The magnetization for $c$-axis, $M_c$ as a function of temperature at $B = 0.01$ T for field along $c$-axis

![Diagram](image)

(b) The magnetization for the basal plane, $M_{ab}$ as a function of temperature at $B = 0.01$ T for field along $ab$-plane

Figure 4.12: $M(T)$ as a function of temperature at $B = 0.01$ T for $(Sr_{1-x}La_x)_4Ru_3O_{10}$ for different La concentration of $x = 0, 0.05, 0.08, 0.11, 0.13$ [26]

Figure 4.12(b) 4.12(a), 4.13(b) 4.13(a) and displays the magnetization, $M$ as a function of temperature for $(Sr_{1-x}La_x)_4Ru_3O_{10}$ and $(Sr_{1-x}Ca_x)_4Ru_3O_{10}$ for different dopant con-
(a) The magnetization $M_c$ as a function of temperature at $B = 0.01 \, \text{T}$ for field along $c$-axis

(b) The magnetization $M_{ab}$ as a function of temperature at $B = 0.01 \, \text{T}$ for field along $ab$-plane.

Figure 4.13: $M(T)$ as a function of temperature at $B = 0.01 \, \text{T}$ for $(\text{Sr}_{1-x}\text{Ca}_x)\text{Ru}_3\text{O}_{10}$ for different Ca concentration of $x = 0, 0.02, 0.13$ [26]

centrations for both $c$-axis and $ab$-plane. La doping introduces a stronger anisotropy in the system as depicted in Figure 4.23. $M_c$ (the magnetization along $c$ axis), evolves gradually from a ferromagnetic to paramagnetic state with increasing La doping as is seen in the rapid suppression of $T_c$ from 105 K for $x = 0$ to about 15 K for $x = 0.13$. On the other hand, $T_M$, which represents the magnetic anomaly temperature at 50 K in the pure Sr$_4$Ru$_3$O$_{10}$ and corresponds to the increase in $T_c$, develops into a sharp downturn for La concentrations, $x$.
0.05, 0.08 and 0.11. It eventually evolves into an enhanced peak for $x = 0.13$ suggesting the system is now paramagnetic.

For $ab$-plane on the other hand, $M_{ab}$ emerges into a fully developed ferromagnetic state as indicated by the arrows in Figure 4.12(b). Another interesting feature is that $M_{ab}$ shows only a weak anomaly at $T_C$ which is much weaker compared to the anomaly in $c$-axis magnetization, $M_c$. In essence, La doping causes a strong anisotropy in magnetization favoring ferromagnetism along $c$ axis for $T_M < T < T_C$. If we now look at the $M(T)$ for $(\text{Sr}_{1-x}\text{Ca}_x)_4\text{Ru}_3\text{O}_{10}$, we see that Ca doping preserves the temperature dependence of magnetization along $c$ axis while increasing both $T_C$ and $T_M$. The magnetization for low Ca doping in the $ab$-plane is very similar to the pure sample, whereas for $x = 0.13$, the anomaly at $T_C$ is considerably weaker and, $T_M$ is completely washed out. The arrows and arrowheads in Figures 4.23 and 4.13 highlight the key features of the temperature dependence of magnetization, $M$.

It has been proposed [7] that the low-temperature behavior of the $n$-layer ruthenates can be understood as a result of proximity to a Van Hove singularity (VHS). A Van Hove Singularity occurs at the points where $|\nabla_k (E)|$ vanishes. There is a discontinuity in the Density of States (DOS) of a solid and as a result even weak interactions can produce large effects. When the Fermi level reaches these points, many response functions diverge.

A system very close to the VHS depicts a Stoner instability. For the Strontium - ruthenates, it is believed that the trend of one of the bands originating from $4d_{xy}$ orbitals of Ru approaching the VHS increases with increasing $n$, that is, increase in the number of Ru-O layers. Quantum critical end-point (QCEP) occurs when one band is at the Von Hove filling. This circumstance may influence unconventional transport properties in the vicinity of QCEP, for example non Fermi liquid behavior is suggested as one consequence of an itinerant electron band being at the Van Hove filling. When pushed further away from the VHS, there is a weak re-entrant behavior, i.e. the system is ferromagnetic for intermediate temperatures. The strong magnetic anisotropy in the La and Ca doped Sr$_4$Ru$_3$O$_{10}$ and the spectacular difference in the temperature dependence is indicative of a two-dimensional Van Hove singularity in conjunction with the coupling of the spins to crystalline field orbital states and the lattice.

Figure 4.14(a) and Figure 4.14(b) shows the isothermal magnetization, $M(B)$ for the $ab$-plane and $c$-axis respectively at $T = 2$ K for $(\text{Sr}_{1-x}\text{La}_x)_4\text{Ru}_3\text{O}_{10}$ for different doping.
(a) The $c$-axis magnetization, $M_c$ as a function of $B$ for field along $c$-axis for different La concentrations

(b) The $ab$-plane magnetization $M_{ab}$ as a function of $B$ for field along $ab$-plane for different La concentration

Figure 4.14: $M(B)$ as a function of magnetic field, $B$ at $T = 2$ K for $(\text{Sr}_{1-x}\text{La}_x)_4\text{Ru}_3\text{O}_{10}$ for different La concentration of $x = 0, 0.05, 0.08, 0.11, 0.13$ [26]

concentrations. For the pure sample ($x=0$), $M(B)$ for $c$-axis saturates at a very small magnetic field of 0.2 T, yielding a saturation moment, $M_S$ of 1.13 $\mu_B$/Ru, which is more than half of the 2 $\mu_B$/Ru expected for an $S=1$ system and comparable to that of SrRuO$_3$[23]. Metamagnetic behavior develops with increasing La concentration which becomes clearly evident and defined for 8% La concentration as seen in figure 4.14(a). This supports the temperature dependent magnetization behavior showing an enhanced paramagnetism for
(a) The c-axis magnetization, $M_c$ as a function of $B$ for field along c-axis for different Ca concentrations

(b) The ab-plane magnetization, $M_{ab}$ as a function of $B$ for field in basal plane for different Ca concentrations

Figure 4.15: $M(B)$ as a function of magnetic field, $B$ at $T = 2$ K for $(Sr_{1-x}Ca_x)Ru_3O_{10}$ for different Ca concentration of $x = 0, 0.02, 0.13$ [26]

$T_C < T < T_M$. On the other hand, $M(B)$ for $ab$ plane in the pure sample shows a first-order metamagnetic transition at a critical field, $B_c=2.5$ T at 2 K. This metamagnetic transition essentially disappears for La doping greater than 5% where the $ab$ plane shows ferromagnetic behavior, Figure 4.14(a) In contrast, introducing Ca produces quite a different effect. Figure 4.15(a) and Figure 4.15(b) shows the isothermal magnetization,$M(B)$ for the c-axis
and ab-plane respectively at $T = 2$ K for $(\text{Sr}_{1-x}\text{Ca}_x)\text{Ru}_3\text{O}_{10}$ for different Ca concentrations. The ferromagnetism observed along c-axis in pure sample is strengthened by Ca doping but the ab plane critical field is now enhanced to 3.5 T at 2 K for $x = 0.02$. The metamagnetic transition in the ab completely disappears for $x = 0.13$ and is replaced by a nearly linear field dependence as shown in Figure 4.15(b) indicating a vanishing ferromagnetism in the basal plane.

4.2.4 Qualitative summary of the impact of La and Ca doping

![Graph](image1)

(a) The dependence of $T_C$, $T_M$ (dashed lines) and $M_S$ (solid lines) on doping concentration, $x$ for La doping

![Graph](image2)

(b) The dependence of $T_C$, $T_M$ (dashed lines) and $M_S$ (solid lines) on doping concentration, $x$ for Ca doping

Figure 4.16: The arrows indicate spins in the triple layers and schematically describe the effects of La and Ca doping on the spin configuration. [26]
Figure 4.16(a) and Figure 4.16(b) summarizes and compares the major impact and the differences thereof, for La and Ca doping. La doping effectively reduces the Curie temperature, $T_C$, magnetic anomaly temperature, $T_M$ (dashed lines), and the saturation moment, $M_S$ (solid lines). However, Ca doping enhances ferromagnetism along the $c$ axis but weakens in the basal plane, $M_{ab}$. The effect of the different kind of doping on the spin configuration of the system are depicted by the arrows. The magnetic field corresponding to the metamagnetic transition decreases with increasing temperature both for pure [11] and impurity doped samples. This behavior is in good agreement with that seen in the metamagnet Sr$_3$Ru$_2$O$_7$ and the theoretical model based on the mean field theory that concludes metamagnetism in the layered ruthenates is a result of a Van Hove singularity [7].

The temperature dependence of metamagnetic transition in bilayer ruthenates, for example, Sr$_3$Ru$_2$O$_7$ [80] and Ca$_3$Ru$_2$O$_7$ [62], [11] is opposite to that observed in many other systems such as Co based compounds [85] and the theoretical predictions using the Landau-Ginzburg theory that suggests the temperature dependence of the critical field follow a term proportional to $T^2$ [98]. On the other hand the transition could be associated with a first-order magnetization process for a hard direction of a uniaxial system. La doping in particular, shows ferromagnetic like behavior in the magnetization $M_{ab}$ for basal plane but develops a metamagnetic like transition at higher La concentrations. This might be either uncompensated low-temperature antiferromagnetism or even a canted ferromagnetic ordering. In this sense the anomaly at $T_M$ may be attributed to a spin-reorientation transition and such a transition may stimulate a first order magnetization process. All these observations point towards the complexity of the itinerant metamagnetism in Sr$_4$Ru$_3$O$_{10}$ and layered ruthenates in general.

### 4.2.5 Resistivity for $(Sr_{1-x}La_x)_4Ru_3O_{10}$ and $(Sr_{1-x}Ca_x)_4Ru_3O_{10}$

Figure 4.17 and Figure 4.18 shows the temperature dependence of resistivity as a function of temperature at zero magnetic field $(B = 0)$ for $(Sr_{1-x}La_x)_4Ru_3O_{10}$ for the $c$ axis (Figure 4.17(a)) and $ab$ plane (4.17(b)), and for $(Sr_{1-x}Ca_x)_4Ru_3O_{10}$ for the $c$ axis (Figure 4.18(a)) and $ab$ plane (Figure 4.18(b)). For the pure sample ($x = 0$), the $c$ axis resistivity, $\rho_c$ exhibit anomalies corresponding to $T_C$ and $T_M$ in the magnetization. Also, $\rho_c$ drops precipitously by an order of magnitude from $T_M(=50 \text{ K})$ to 2 K due to the reduction of spin scattering as
(a) The \( \rho_c \)-axis resistivity, \( \rho_c \) as a function of temperature for La doping.

(b) The \( \rho_{ab} \)-plane resistivity, \( \rho_{ab} \) as a function of temperature for La doping.

Figure 4.17: Resistivity as a function of temperature for \((\text{Sr}_{1-x}\text{La}_x)_4\text{Ru}_3\text{O}_{10}\) for different La concentration of \(x = 0, 0.05, 0.08, 0.11, 0.13\).\[26\]

The spins become strongly polarized below \(T_M\) \[11\]. This drop in \(\rho_c\) at low \(T\) disappears upon La doping as a result of the strong reduction of spin polarization below \(T_M\) as seen in Figure 4.14(a). The residual resistivity \(\rho_0\) increases for La doped system and may be attributed to an enhancement of elastic scattering rate \(\tau^{-1}\) either due to increased spin-flip scattering or due to disorder induced by impurity doping. In either case the contribution to \(\tau^{-1}\) are essentially temperature-independent. Another interesting effect of La doping is that \(\rho_c\) decreases by as much as a factor of 2 with \(x\), but at the same time \(\rho_{ab}\) increases significantly.
The $c$-axis resistivity, $\rho_c$ as a function of temperature for Ca doping.

(b) The $ab$-plane resistivity, $\rho_{ab}$ as a function of temperature for Ca doping.

Figure 4.18: Resistivity as a function of temperature for $(\text{Sr}_{1-x}\text{Ca}_x)_4\text{Ru}_3\text{O}_{10}$ for different Ca concentration of $x = 0, 0.02, 0.13$ [20]

for temperatures above $T_M=50$ K. This suggests an enhanced inter plane hopping but weakened intra layer transport. It is likely that La and Ca impurities break the symmetry and degeneracy of $t_{2g}$ orbitals and give rise to a stronger overlap of the $t_{2g}$ and $d_{yz}$ orbitals and hence to larger conductivity along the $c$-axis but reduced conductivity in the basal plane due to scattering. In addition, introducing a smaller ion in the system shortens the separation between the layers and hence, making the system more three-dimensional, enhancing a dimensional crossover. This is similar to the temperature-driven crossover in the interlayer
transport in layered materials such as NaCo$_2$O$_4$ and Sr$_2$RuO$_4$.

Figure 4.19: Magnetoresistivity ratio $\Delta \rho / \rho(0)$ for Ca doping for $x = 0.02$ as a function of $B$ applied within the basal plane. Also shown is the magnetoresistivity ratio for 5% La doping (dashed line).

The temperature dependence of $\rho_c$ can be associated with changes in the quasiparticle effective mass, $m_{eff}$. With the exception of $x = 0.05$, the Fermi liquid behavior survives up to $T < 17$ K for the La doped samples as both $\rho_c$ and $\rho_{ab}$ follow the dependence $\rho = \rho_0 + AT^2$, where $A \sim m_{eff}^2$. For $x = 0$, $A_c / A_{ab} = 31$ as mentioned in section 4.1.4 is unusually large, suggesting a strongly anisotropic Fermi surface or $m_{eff}$. This ratio is drastically reduced to 3.9 for $x = 0.08$ and 1.4 for $x = 0.11$ for La doping. This drop happens primarily due to the decrease in $A_c (= 2.5 \times 10^{-7}$ cm/K$^2$) for $x = 0.11$ because $A_{ab} = 1.8 \times 10^{-7}$ cm/K$^2$ is only slightly smaller. The smaller $A_c$ implies a smaller $m_{eff}$, therefore larger electron mobility for interlayer transport.

Fermi liquid behavior is violated for $x = 0.05$ for La doping and $x = 0.13$ for Ca doping. First, $\rho_{ab}$ for 5% of La doping is exceptionally larger than that of other $x$. Second, both $\rho_{ab}$ and $\rho_c$ below 17 K obey a $T^{5/3}$-power law as shown (for $\rho_{ab}$) in Figure 4.20. Marginal Fermi-liquid models predict power laws of the resistivity as a function of $T$ with non-integer and even non-universal exponent at low $T$. The $T^{5/3}$ power law is anticipated when small angle electron scattering dominates the electronic transport, but is rarely observed in a
ferromagnetic state far below $T_C$. This behavior is intrinsic and unlikely to be due to disorder because the Fermi-liquid behavior is recovered when doping concentration $x$ is increased. For Ca doping, both $\rho_{ab}$ and $\rho_c$ for 13\% Ca doping show a $T^{3/2}$ dependence for $3 < T < 46$ K. The $T^{3/2}$ dependence which remains when magnetic field is applied, marks the break own of Fermi-liquid properties. Such a behavior is also observed in itinerant ferromagnets like MnSi at high pressure and is believed to be associated with the effects of diffusive motion of the electrons caused by the interaction between the itinerant electrons and critically damped magnons \[81\].

Figure 4.19 shows the magnetoresistivity ratio defined as $(\rho_c(B) - \rho_c(0))/\rho_c(0)$ for Ca doping at $x = 0.02$ as a function of applied magnetic field, $B$ within the basal plane. The magnetoresistivity ratio features a sharp drop at the critical field, $B_c$ and reaches a value as large as 40\% in the vicinity of and below $T_M$. The large reduction in $c$-axis resistivity for $B_{ab} > B_c$ implies large ferromagnetic fluctuations in a state without ferromagnetic ordering immediately above the transition. In contrast, $\rho_c$ for $x = 0.05$ La doping shows much smaller magnetoresistance, suggesting that scattering is much less spin-dependent as a result of the electron doping.

The rare borderline magnetism in Sr$_4$Ru$_3$O$_{10}$ is highly sensitive to the tuning of the density of states which is critically linked to band filling and structural distortions. Magnetism in Sr$_4$Ru$_3$O$_{10}$ seems to be more susceptible to band filling than to structural distortions. The different $T_C$ for the $c$-axis and basal plane, large magnetic anisotropy and breakdown of Fermi-liquid behavior, all points towards an unusual magnetism in Sr$_4$Ru$_3$O$_{10}$ and is further
studied by low temperature specific heat measurements. The results are presented in the next section.

4.3 Anomalous Itinerant Electron Magnetism at low temperatures

The salient features of Sr$_4$Ru$_3$O$_{10}$ which have been discussed so far can be summarized as follows,

- The $c$-axis magnetization, $M_c$ exhibits ferromagnetically ordered moments with a Curie temperature of $T_c=105$ K followed by an increased spin polarization below $T_M=60$ K with large irreversibility upon in-field and zero-field cooling [29], [11]. On the other hand, $ab$-plane magnetization, $M_{ab}$ is much smaller and exhibits a weak cusp at $T_c$ and a broad peak at about 60 K close to $T_M$ in $c$-axis.

- The isothermal magnetization shows that the spins are readily polarized and saturated along the $c$-axis at $B = 0.2$ T, yielding a saturation moment of 1.2 $\mu_B$/Ru. The basal plane magnetization on the other hand, undergoes a first-order metamagnetic transition at $B_c$.

- The transport study shows a sign of divergent coefficient $A$ of $\rho \sim aT^2$, where $\rho$ is the resistivity near the metamagnetic transition at critical magnetic filed, $B_c$.

The zero field specific heat measurements were done with ac calorimetry [61]. A small mean-field like anomaly with $\Delta C \sim 0.4R$, (where $R=8.314$ J mol$^{-1}$K$^{-1}$ is the gas constant) is seen at the Curie temperature $T_C$. No anomalies are observed corresponding to $T_M$. The expected entropy change is, $\Delta S = k_Bln(3)$ for each ordering spin, where $k_B$ is the Boltzman’s constant. Therefore, the expected entropy change if all three spins order is, $\Delta S = 3.3R$. The entropy change is obtained by fitting the data away from the transition which gives the lower limit $\Delta S > 0.02R$. The upper limit is estimated from $\Delta S \sim \Delta C(\sim 0.4R)$, as expected from a mean field anomaly. The specific heat anomaly is much smaller than expected. For example, per ruthenium ion, the anomaly is an order of magnitude smaller than expected for complete spin ordering and that observed in SrRuO$_3$, suggesting that either the spin ordering is not spatially uniform or that only a small component of the spins order. It is noted that the magnetic entropy removal at $T_C$ is generally small for weakly ferromagnetic metals, chiefly due to spin fluctuations.
There is no structure corresponding to the magnetic and resistivity peak at $T_M$ suggesting that the structure observed in magnetic and transport properties reflect gradual crossover behavior as the spin order changes, rather than a thermodynamic phase transition, at least in zero field. The specific heat data at low temperature, $C/T$ vs. $T^2$ has a negative curvature for $T < 9$ K. Such a curvature implies that, in addition to the usual phonon ($C_{ph} = \beta T^3$) and electronic ($C_e = \gamma T$) contributions to the specific heat, there must be a term $C_S \sim \eta T^p$ with $1 < p < 3$, presumably due to spin excitations.

For the fits to give (per atom) Debye temperatures below $\sim 500$ K, we must have $p < 2$. Estimating $\beta$ from the linear portions of the curves only, that is, from the data for $T > 9$ K, average Debye temperature for the two samples of $\Theta = (367 \pm 15)$ K is obtained, close to the values for cubic SrRuO$_3$ and double layer Sr$_3$Ru$_2$O$_7$. Therefore, including a term with $p < 3$ decreases the value of $\beta$ and increases $\Theta$. These constraints on $p$ suggest magnetic order in apparent contradiction to the measured magnetic properties, again indicating the complexity of the magnetic order found in Sr$_4$Ru$_3$O$_{10}$. Also, the low temperature specific heat can be fit with a spin term $C_S = \eta T \ln(T/T_0)$, as is the case for ferromagnetic fluctuations near a quantum critical point.

The application of magnetic field tends to align the spins in the field direction and usually suppresses spin fluctuations and hence the specific heat. It is quite unusual and interesting to see that the specific heat of Sr$_4$Ru$_3$O$_{10}$ responds to the magnetic field oppositely. Figure 4.21(a) and Figure 4.21(b) shows the specific heat divided by $T$ as a function of $T$ for $1.8 \leq T \leq 12$ K with $B \parallel ab$ plane and $c$-axis respectively. There are a few crucial features to be noted:

- $C/T$ at low $T$ increases radically for plane, particularly in the vicinity of the metamagnetic transition (Figure 4.21) in contradiction to the anticipated behavior implying a considerable enhancement of the quasiparticle mass $m^*$ in density of states, $g(E_F)$.

- Second, $C/T$ for $B \parallel c$ axis shows very different temperature dependence as seen in figure 4.21(b) decreasing with increasing $B$ for $T > 6$ K, consistent with a suppression of spin fluctuations as anticipated for a regular magnetic state. But it increases, though less drastically, for $T < 6$ K by showing a broad peak near 8 T, suggesting that unexpected low-energy excitations develop in the spontaneous ferromagnetic state.

- For both $B \parallel ab$ and $B \parallel c$-axis, $C/T$ for $B \leq 2.7$ T and $T < 10$ K nearly follows a
Figure 4.21: Specific heat divided by temperature, $C/T$ as a function of temperature for $\text{Sr}_4\text{Ru}_3\text{O}_{10}$.

linear $T$ dependence, $C/T + bT$. The rapid increase of $a$ with $B$ could be indicative of a Fermi liquid with a nearby two-dimensional (2D) critical point \cite{70}. 

(a) $C/T$ vs $T$ for $B \parallel ab$-plane for $\text{Sr}_4\text{Ru}_3\text{O}_{10}$; inset: $C/T$ for $B \parallel ab$ vs $T$ as a function of $T$ for a few representative fields.

(b) $C/T$ vs $T$ for $c$-axis
This interpretation requires a very small phonon contribution, $\beta T^3$ (as is apparent in the positive curvature in $C/T$ vs $T^2$ for $T > 10$ K) and therefore an unphysically large value of the Debye temperature. Alternatively, the specific heat can be fit to $C/T = \gamma + \beta T^2 + \delta T^{1/2}$ with a typical value of $\beta \sim 0.04$ mJ mol$^{-1}$K$^{-4}$, where the $T^{1/2}$ term is associated with an unexpectedly large contribution from ferromagnetic spin waves [61]. As $B$ increases further the temperature dependence of $C/T$ weakens from almost $T$-linear at $B < B_c$ to a shoulder with a small peak at $B = 5$ T and a plateau for $B \geq 6$ T, Figure 4.21(a), 4.21(b).

Figure 4.22 shows the plot of $C/T$ as a function of $T^2$ for $ab$-plane. The unusual temperature dependence is further emphasized in the negative curvature associated with the $T^{1/2}$ term for $T < 8$ K [61]. The inset clearly shows the sharp peak at 2.5 K for $B = 5$ T that diminishes at higher fields and eventually evolves into a rapid downturn at 9 T. It is clear that the amplitude of the fluctuations grows rapidly as $B$ increases. It will be helpful to look at the magnetic field contribution to the specific heat. To do so, the zero field contribution to specific heat $C(0)$ is subtracted from $C(B)$, $\Delta C = C(B) - C(0)$ to give the field induced contribution, $\Delta C$. Figure 4.23(a) and Figure 4.23(b) shows $\Delta C/T$ plotted as a function of $T$ for $B \parallel ab$-plane and $B \parallel c$ axis, respectively.

A dominant feature is that $\Delta C/T$ increases logarithmically with decreasing $T$ as $B$ rises. The slope of the log-dependence gets stronger when magnetic field approaches 5 T and 7
(a) Logarithmic temperature dependence of $\Delta C/T$ for $B \parallel ab$-plane; inset: for $5 \leq B \leq 9$ T

(b) Logarithmic temperature dependence of $\Delta C/T$ for $c$-axis

Figure 4.23: Logarithmic temperature dependence of $[C(B) - C(0)]/T$ for Sr$_4$Ru$_3$O$_{10}$. The arrows track the shift of the peaks.

$T$ for $B \parallel ab$-plane and , respectively. (While there is a gradual change in slope (at $\sim 4$ K) in the log plot (see inset), the variation of $\Delta C/T$ is approximately logarithmic for a range of over 10 K. Furthermore, for $T < 4$ K, the slopes are constant where $\Delta C/T$ changes by a
factor of 2. At 1.8 K, $\Delta C/T$ for $B \parallel ab$ plane increases by a factor of three from less than 0.04 J/mol K$^2$ at 1 T to nearly 0.12 J/mol K$^2$ at 5 T. At higher $T$, there exists a broad peak marked by an arrow. It moves to lower $T$ and eventually vanishes as $B$ increases so that the entropy is shifted into the logarithmic upturn. Remarkably, for $B \parallel ab$ plane, as $B$ approaches $B_c$, $C/T$ shows a jump at $B = 2.8$ T near 10 K. This jump develops into a pronounced peak at $B_c = 2.9$ T near 7 K and then broadens for $B > B_c$. For $B \parallel c$-axis, no such abrupt jump in $C/T$ is seen near $B_c$. The broad peak similar to that for $B$ parallel to $ab$-plane is progressively suppressed by the magnetic field and vanishes at $B > 6$ T.

The emergence of the peak is a signature of the large amplitude of the spin fluctuations in the vicinity of a quantum phase transition, and the divergent $\Delta C/T$ at lower temperatures indicates a divergence in the density of states and long range correlations as the magnetic field effectively pushes the system towards a quantum critical point. A similar peak although weaker is also seen in Sr$_3$Ru$_2$O$_7$[100]. The $c$-axis spontaneous ferromagnetic state is well established, and thus the spontaneously spin-split bands are robust. Therefore, the divergence of $\Delta C/T$ for $B \parallel c$-axis, however weak, is quite unexpected. The spin-wave excitations and Stoner excitations, which may exist in any itinerant ferromagnet, generate no such divergence as seen in $\Delta C/T$ for Sr$_4$Ru$_3$O$_{10}$.

The abrupt jump in $C/T$ and the metamagnetic transition for $B \parallel ab$-plane are once more emphasized in Figure 4.24, in which the magnetic field dependence of $C/T$ is compared to the magnetic field dependence of resistivity and magnetization for Sr$_4$Ru$_3$O$_{10}$. The jump in $C/T$ is drastic and persists up to about 12 K, suggesting a critical end point of the metamagnetic transition (Figure 4.24(b)). This behavior is reflected in La doping where La pushes the anomalies to lower $T$ and $B$, indicating that a QCP is reached near 13% of La-doping as seen in Figure 4.23 and 4.14[26]. The magnetoresistance ratio, defined as $[\rho_c(B) - \rho_c(0)]/\rho_c(0)$, is influenced by the metamagnetic transition and changes by more than 40% near $B_c$, confirming large spin fluctuations in a state without long-range order immediately above the transition as shown in Figure 4.25 (left scale).

The presence of quantum fluctuations is also evident in the behavior of the resistivity coefficient $A_{ab}$ obtained from the fit $\rho_{ab} = \rho_0 + A_{ab}T^2$ as $B$ approaches the metamagnetic transition. Figure 4.26 shows the $ab$-plane resistivity $\rho_{ab}$ at a few representative fields as a function of $T^2$ or $T^{5/3}$ (upper axis) for $1.7 < T < 17$ K. There are a few key features to be deduced from the temperature dependence of resistivity discussed below,
• The linear dependence of $\rho_{ab}$ in the plot suggests a well-defined power law followed at various magnetic fields, $B$.

• Figure 4.27 maps the details of the coefficients of the $T^2$ and $T^{5/3}$-dependence of $\rho_{ab}$
as a function of $B$. $\rho_{ab}$ fits well to the Fermi liquid behavior, $\rho_{ab} = \rho_0 + A_{ab}T^2$, for $B < 2T$ where $\rho_0$, the residual resistivity, is $6\,\mu\Omega\,\text{cm}$ at $B = 0$, indicative of the high purity of the sample. The coefficient $A_{ab}$, which depends on the effective mass $m^*$, rapidly increases with $B$, indicating a divergent $m^*$

- $\rho_{ab}$ starts to deviate from the $T^2$-dependence at $B = 2.2$ T, signaling the breakdown of Fermi liquid properties. For $2.2 \leq B \leq 5.5$ T, $\rho_{ab}$ is proportional to $A_{ab}$, where $\alpha$ is smaller than 2. $\alpha$ briefly varies between 1.5 and 1.6 for $2.0 < B < 2.4$ T and then settles at $5/3$ for $2.4 \leq B \leq 5.5$ T.

- The coefficient $A_{ab}^*$ for $\alpha = 5/3$ rises steeply with $B$, peaks at magnetic field value of 2.9 T and then decreases for larger fields. The Fermi liquid behavior is recovered for $B > 5.5$ T. This is consistent with the behavior of specific heat $C$ which at low temperatures starts to decrease when $B > 5$ T. The residual resistivity $\rho_0$ consistently...
Figure 4.26: The ab-plane resistivity $\rho_{ab}$ at a few representative fields as a function of $T^2$ (lower axis) or $T^{5/3}$ (upper axis) for a range of $1.7 < T < 17$ K shows a similar field dependence and diverges near $B_c$ [11].

A singular $T$-dependence of the resistivity with $\alpha < 2$, specifically, $\alpha = 3/2$ and $5/3$ is seen in systems with quantum criticality such as MnSi [81], Sr$_3$Ru$_2$O$_7$ [80], [37], [100], heavy fermion systems [28] as well as impurity doped Sr$_4$Ru$_3$O$_{10}$ [26]. The $T^{5/3}$-dependence of resistivity is often attributed to either dominating low-angle electron scattering (low-$q$ fluctuations) or high-$q$ fluctuations scattering electrons in the vicinity of a QCP [74], [71], [81], hence weakening the temperature dependence from $T^2$. The power-law $T^{3/2}$ is thought to be associated with the effects of the diffusive motion of the electrons caused by the interactions between the itinerant electrons and critically damped magnons [83]. The change of $A_{ab}$ and $A_{ab}^*$ with $B$ entirely tracks $C/T$ and $M_{ab}$, suggesting a possible proximity of a QCP and an intimate connection between the critical fluctuations and metamagnetism.
What is equally intriguing is that $C/T$ for $B \parallel c$-axis, shows a weaker yet well defined peak at 7 T followed by a minimum at 8 T [Figure 4.24(a)]. This peak changes with $T$, and nearly vanishes for $T > 6.8$ K, where $C/T$ no longer increases with $B$, this behavior is expected for regular metals. It is intriguing that field-driven quantum critical fluctuations and nesting properties should not be expected given the fact that Sr$_4$Ru$_3$O$_{10}$ shows ferromagnetic behavior in the $c$-axis suggesting the spin-split bands are stable and well defined. These results provides strong evidence for the existence of quantum critical fluctuations in a system where spontaneous ferromagnetism and field-induced metamagnetism coexist. These results, which cannot be explained using existing models, strongly suggest an exotic ground state.

Figure 4.27: The field dependence of the coefficient $A_{ab}(\alpha = 2)$ (left scale) and $A_{ab}^{*}(\alpha = 5/3)$ (right scale) for Sr$_4$Ru$_3$O$_{10}$ for $B \parallel$ab-plane [15]
4.4 Bulk spin valve behavior in impurity substituted $\text{Ca}_3\text{Ru}_2\text{O}_7$

4.4.1 Magnetoresistance

The physical limitation of accommodating more and more devices into smaller and smaller chips have led to the quest for developing newer, more sophisticated technologies for data storage and computations. This motivation have lead to the burgeoning field of spin based electronics or *spintronics*. Spintronics exploits the spin degrees of freedom of the electron in addition to the charge degree of freedom. Magnetism (or electron spin) has always been important for information storage because even the earliest computers used magnetoresistance to read data stored in magnetic domains. The large application potential of magnetoresistive devices has motivated the research for materials with large resistivity changes on the application of external magnetic field.

The most widely acknowledged breakthrough in the field of spintronics was the discovery of Giant Magnetoresistance (GMR). The 2007 Nobel Prize was awarded to Albert Fert and Peter Grunberg for the discovery of GMR. GMR is extensively used in read heads of modern hard drives and non-volatile, magnetic random access memory. In order to observe GMR, one has to provide an opportunity to reorient the magnetic moments of the ferromagnetic layers relative to one another. In magnetic multilayers this can be achieved due to the effect of antiferromagnetic interlayer exchange coupling, which is basically interlayer exchange coupling [92].

The presence of an antiferromagnetic interlayer coupling is not, however, a necessary condition for GMR to occur. Antiparallel alignment can also be obtained by introducing different coercivities of the successive ferromagnetic layers. In this case the magnetic moments of the soft and hard magnetic layers switch at different values of the applied magnetic field, providing a field range in which they are antiparallel and the resistance is higher. Another way to change the alignment of the magnetization is to use a spin valve or a pseudo spin valve. In the spin valve the magnetization of one ferromagnetic layer is pinned by the exchange coupling with an adjacent antiferromagnetic layer, whereas the magnetization of the other ferromagnetic layer is free to rotate with applied magnetic field. In pseudo spin valve the antiparallel alignment can be obtained due to different coercivities of the two ferromagnetic layers. The magnetic moments of these layers switch at different magnetic fields. Thus, there is a field range in which they are antiparallel and the resistance is higher.
Spin valves offer an edge over multilayers where application potential is concerned, because only small magnetic fields can drive large changes in resistance. The spin valve effect is thought to be a delicate quantum phenomenon that depends upon precision deposition and nanoscale patterning of artificial thin-film heterostructures whose quality, consistency and performance are difficult to control\cite{92}, \cite{18}. Results of our measurements on Ca$_3$(Ru$_{1-x}$Cr$_x$)$_2$O$_7$, (Ca$_{1-x}$Ba$_x$)$_3$Ru$_2$O$_7$ and (Ca$_{1-x}$Sr$_x$)$_3$Ru$_2$O$_7$ reveal a novel, strong spin valve effect that exists in bulk single crystals. This is a new window into spin valve devices utilizing single crystals that are naturally endowed with the layered structure which are otherwise so difficult to engineer.

4.5 \textit{Ca}_3\textit{Ru}_2\textit{O}_7

Figure 4.28: (a) The bilayer structure of Ca$_3$Ru$_2$O$_7$ in the $bc$–plane, and (b) the corresponding TEM image. The dark stripes are magnetic Ru-O layers and light gray stripes are insulating Ca-O layers.
$\text{Ca}_3\text{Ru}_2\text{O}_7$ is a bilayer ($n = 2$) system belonging to the Ca Ruddlesden-Popper series. The bilayer compounds are especially interesting because they usually exhibit unique borderline properties. For instance, $\text{Sr}_3\text{Ru}_2\text{O}_7$ [37] lies between $n = \infty$ compound $\text{SrRuO}_3$ [49] which is a metallic ferromagnet (FM) and $\text{Sr}_2\text{RuO}_4$ [65], a paramagnetic Fermi liquid. The $n = 2$ system, $\text{Sr}_3\text{Ru}_2\text{O}_7$ [65] exhibits a metamagnetic quantum critical point, an evidence to its borderline physics [37]. $\text{Ca}_3\text{Ru}_2\text{O}_7$ lies between the bad metal $\text{CaRuO}_3$ [22] and the Mott insulator $\text{Ca}_2\text{RuO}_4$ [77], and presents an opportunity into the physics of pure undoped system near the metal-insulator transition [88]. Evidence of borderline physics in $\text{Ca}_3\text{Ru}_2\text{O}_7$ includes [21],

- strong sensitivity of major properties to minor sample variations,
- observation of metallic like properties such as quantum oscillations and finite linear specific heat coefficients in non conducting material,
- a large lattice anomaly at the magnetic ordering temperature, and
- low field metamagnetic transitions with strong transport signatures.

$\text{Ca}_3\text{Ru}_2\text{O}_7$ is composed of magnetic $\text{RuO}_2$ bilayers with intermediate nonmagnetic CaO rocksalt layers which functions as insulating spacer layers. The crystal structure of $\text{Ca}_3\text{Ru}_2\text{O}_7$ shown in Figure 4.28 is orthorhombic (space group $\text{Cmc}_2_1$). The crystal structure is severely distorted by a tilt of the $\text{RuO}_6$ octahedra. this tilt is mainly projected in the $ac$ plane with Ru-O-Ru bond angle of 153.22° for Ru ions in adjacent layer. The Ru–O–Ru bond angle in the $ab$ plane is only slightly affected and is 172.0°. This tilting and rotation of the $\text{RuO}_6$ octahedral affects the band structure and hence the properties of the system. the change in the band structure manifests in the highly anisotropic nature of $\text{Ca}_3\text{Ru}_2\text{O}_7$ and the rich borderline physics. In the ruthenium $\text{Ru}^{4+}$ ($4d^4$) ions, the octahedral crystalline field splitting gives two-fold $e_g$ and three-fold degenerate $t_{2g}$ energy levels. The octahedral rotations and tilt in $\text{Ca}_3\text{Ru}_2\text{O}_7$ leads to band narrowing which in turn separates the $t_{2g}$ manifold from the higher lying $e_g$ manifold by an energy gap. $\text{Ca}_3\text{Ru}_2\text{O}_7$ features Mott-like transition, a metamagnetic transition, unusual colossal magnetoresistance (CMR) [12], [62] which is achieved when the magnetic field, $B$ is parallel to the easy axis of magnetization, that is, when spin polarized state is avoided. $\text{Ca}_3\text{Ru}_2\text{O}_7$ also features tunneling magnetoresistance and quantum oscillations periodic in $1/B$ and $B$ [13] and [12].
Density functional calculations show that the ferromagnetic bilayers stacked antiferromagnetically along the \( c \)-axis is the most energetically favorable ground state configuration. This is in agreement with the experimental observations [21, 69, 62]. \( \text{Ca}_3\text{Ru}_2\text{O}_7 \) undergoes an antiferromagnetic (AFM) phase transition at \( T_N=56 \) K in low magnetic fields, followed by a Mott-like metal-insulator transition \( T_{MI}=48 \) K which is accompanied by an abrupt shortening of \( c \)-axis, Figure 4.30. The magnetoelastic coupling results in Jahn-Teller distortions of the \( \text{RuO}_6 \) octahedra, thus lowering \( d_{xy} \) orbitals relative to \( d_{zx} \) and \( d_{yz} \). In contrast, \( M(T) \) for \( a \)-axis exhibits no anomaly at \( T_{MI} \) but a sharp peak at \( T_N \). As a consequence of a strong spin-orbit coupling, this system shows really interesting properties in the presence of external magnetic field, \( B \), like colossal magnetoresistance (CMR). CMR usually is driven by the FM state but for \( \text{Ca}_3\text{Ru}_2\text{O}_7 \), it is achieved by avoiding the ferromagnetic state. This suggests the existence of a novel mechanism based upon orbital ordering and a highly anisotropic antiferromagnetic metallic state (AFM-M). The first order metamagnetic transition leads to a spin-polarized or ferromagnetic state with a saturation moment \( M_S = 1.73\mu_B/\text{Ru} \) along \( b \)-axis, Figure 4.31. Expected saturation moment for an \( S=1 \) system gives a total saturation moment of \( 2\mu_B/\text{Ru} \). Hence 85% of saturation moment is achieved.
Figure 4.30: The magnetization, $M$ of $\text{Ca}_3\text{Ru}_2\text{O}_7$ as a function of temperature $T$ at $B = 0.5\, \text{T}$ for $a$-, $b$- and $c$-axis. The gray shaded area depicts the Antiferromagnetic-Metallic region between $T_{MI}$ and $T_N$.\cite{10,20}

Figure 4.32 shows the $a$- and inter plane, $c$-axis resistivity for $2 \leq T \leq 80\, \text{K}$. Also shown is the change in the $c$-axis lattice parameter as a function of temperature. The much larger value of $\rho_c$ compared to $\rho_a$, especially below $T_{MI}$ reflects the anisotropy observed in the magnetization. $\text{Ca}_3\text{Ru}_2\text{O}_7$ exhibits metallic behavior for $T \geq 56\, \text{K}$, followed by a very abrupt first-order nonmetal-metal transition at $48\, \text{K}$. For $48 \leq T \leq 56\, \text{K}$ there is a relatively weak but well defined decrease in $\rho(T)$ and it follows Fisher-Langer behavior. The metallic conductivity in the AFM phase persists for up to a magnetic field of $4\, \text{T}$, though the rather abrupt decrease in resistivity at $56\, \text{K}$ shifts to lower $T$ (terminating at $48\, \text{K}$), and becomes less defined\cite{21}. This Mott-like transition is accompanied by a collapse in the $c$-axis parameter. The AFM-M region is highlighted in Figure 4.32. A decrease in the $c$-axis is akin to applying pressure and is expected to increase the orbital overlap and hence the conductivity. But instead there is a metal-nonmetal transition. This unexpected behavior is attributed to the Jahn-Teller distortion as explained earlier.
and emphasizes the orbital ordering in this system. Furthermore, the field dependence of $c$-axis resistivity, for field applied parallel to the easy axis of magnetization, there is an abrupt decrease in $\rho_c$ corresponding to the first order metamagnetic transition [10]. The reduction of $\rho_c$ is attributed to a tunneling effect facilitated by a field-induced coherent motion of spin-polarized electrons between Ru-O planes separated by insulating (I) Ca-O spacer layers. This situation is similar to an array of FM/I/FM junctions where the probability of tunneling and thus electronic conductivity depend on the angle between the spins of adjacent ferromagnets.

The property that is most relevant in the results presented pertains to the density functional calculations which suggests that Ca$_3$Ru$_2$O$_7$ is a nearly half-metallic system [88]. A half-metal is a system that acts as a conductor to electrons of one spin orientation, but as an insulator to those of the opposite orientation. In half-metals, the valence band related to one spin type are fully filled and for the other spin type, partially empty. Hence,
Figure 4.32: Left scale, Resistivity $\rho_a$ and $\rho_c$ as a function of temperature for $a$- and $c$-axis respectively for Ca$_3$Ru$_2$O$_7$. Right scale show the $c$-axis lattice parameter as a function of temperature. The gray shaded area between 48 K and 56 K is the AFM-M region [10].

only electrons in partially filled band can pass through. As such, half-metals have the potential to exhibit spin-valve behavior. The ferromagnetic Density of States (DOS) shows that the bilayers are almost but not exactly half-metallic[88]. This is similar to the colossal magnetostrictive (CMR) manganites such as ($La, Ca$)$_3$MnO$_3$. However in manganites, there is a finite density of states in both spin channels but $E_F$ falls near the minority spin band edge and those states are Anderson localized. In Ca$_3$Ru$_2$O$_7$, $E_F$ falls very near the majority spin band edge. But this is a clean material and hence there is no mechanism for Anderson localization. Therefore, unlike the manganites, in Ca$_3$Ru$_2$O$_7$ the majority spin channels will cross over from localized to metallic, yielding an anisotropic partially spin polarized metal.

The spin valve behavior, however, is not observed in the pure compound because the uniform exchange coupling in the $RuO_2$ layers is unable to give the hard and soft layers essential to spin-valve behavior. Also, the AFM-M region spans only 8 K, which is too narrow to investigate the underlying physics completely. One possibility is to alter the exchange coupling of the system by tuning some external parameter, for instance, impurity doping.
And indeed, with the half-metal characteristic coupled with tunneling magnetoresistance, spin-valve like behavior have been observed in doped Ca$_3$Ru$_2$O$_7$. A strong spin valve effect in bulk single crystals of Ca$_3$(Ru$_{1-x}$Cr$_x$)$_2$O$_7$ was first observed by substituting Cr on Ru site \[18\]. The next three sections present the experimental results for Ca$_3$(Ru$_{1-x}$Cr$_x$)$_2$O$_7$, (Ca$_{1-x}$Sr$_x$)$_3$Ru$_2$O$_7$ and (Ca$_{1-x}$Ba$_x$)$_3$Ru$_2$O$_7$. The motivation for this project is to gain understanding of this bulk spin valve behavior in Ca$_3$Ru$_2$O$_7$ by introducing chemical pressure by doping the pure system with Cr, Ba and Sr. The impact of these ions are compared and contrasted to shed some light on the nature of AFM-M state which is critically connected to the spin valve behavior.

4.6 Ca$_3$(Ru$_{1-x}$Cr$_x$)$_2$O$_7$

Introducing different dopants in the pure Ca$_3$Ru$_2$O$_7$ system effectively broadens the AFM-M state to various degrees while preserving the borderline physics, in fact, enhancing the predicted spin valve behavior for the pure system. Pertinent to this chapter is the introduction or evidence of bulk spin valve behavior. Depending on the dopant and the site (Ca or Ru) at which it is introduced, the doped Ca$_3$Ru$_2$O$_7$ exhibits bulk spin valve behavior of different strength. The spin valve behavior was first seen in the Cr doped Ca$_3$Ru$_2$O$_7$ \[18\]. The transport and thermodynamic studies were done on Ca$_3$(Ru$_{1-x}$Cr$_x$)$_2$O$_7$ for different Cr concentrations, 0 < x < 0.20.

The magnetization data for x=0.20 for $B \parallel a$-axis ($M_a$) shows that Cr substitution lowers $T_{MI}$ and rapidly increases the Néel temperature $T_N$, greatly extending the AFM-M state from 8 K to 70 K (Figure 4.34). The magnetization for $B \parallel b$-axis, $M_b$ also shows a similar trend. Also, for $B \parallel b$-axis $M_a$ has an upturn below $T_{MI}$ for $x > 0$, may be due to spin canting in AFM-M state. The decrease in $T_{MI}$ indicates delocalization of the d-electrons and an increase in $T_N$ suggests enhanced exchange coupling between nearest neighbor moments. Presented ahead are the results for a representative composition x=0.17 as a function of temperature, magnetic field strength and orientation. Figure 4.34 shows the magnetization $M_a$ and $M_b$. $T_{MI}$=42 K and $T_N$=86 K for a field strength of B=0.5 T and the specific heat data as a function of temperature.

The specific heat data exhibits anomalies corresponding to both $T_{MI}$ and $T_N$ although they are a little smeared due to (possible) inhomogeneous Cr distribution. The anomaly near $T_N$ occurs at a slightly lower temperature of 83 K. $\Delta C \sim 0.28R$ for this anomaly which
Figure 4.33: The magnetization, $M$ of $\text{Ca}_{3}(\text{Ru}_{1-x}\text{Cr}_x)_2\text{O}_7$ as a function of Temperature $T$ for $a$-axis at $B = 0.5$ T for different Cr concentrations, $x$ \[18\]

is slightly broader than $\Delta C \sim 0.31R$ for $T_{MI}$. Low temperature data, $1.7K < T < 30K$ is fitted to $C = \gamma T + \beta T^3$ gives the coefficient of electronic contribution to specific heat, $\gamma \sim 31$ mJ/mol-K$^2$ and the coefficient of phonon contribution, $\beta \sim 3.0 \times 10^{-4}$mJ/molK$^3$ which are comparable to the values in the pure system [69, 94]. The fit above $T_N$ in the paramagnetic state gives $\gamma \sim 680$mJ/molK$^2$ and 79mJ/mol K$^2$ below $T_N$ in the AFM-M state. This large difference in $\gamma$ implies that the paramagnetic to AFM state is accompanied by a large reduction in Fermi surface. Further, transition entropy, $\Delta S \sim 0.037R$ which is much smaller than $2R\ln3$ expected for a localized $S = 1$ system. For an AFM ordered itinerant system $\Delta S \sim \Delta \gamma T_N$ and a mean field like step $\Delta C \sim (1.43)\Delta \gamma T_N$, which is qualitatively consistent with our data, but implies $\Delta \gamma / R \sim 0.0024K^{-1}$. But if there is a charge density wave accompanying the transition, $\Delta S \sim \Delta \gamma T_{MI}$ yields $\Delta \gamma / R \sim 8.8 \times 10^{-4}K^{-1}$, which is in disagreement with our data.

The anomaly at $T_N$ is inconsistent with both conventional itinerant and localized pictures of AFM. Indeed this is reflected in the suppression of $T_N$ for $(\text{Ca}_{0.83}\text{Cr}_{0.17})_3\text{Ru}_2\text{O}_7$ at an astonishing rate of $-7.5 \text{ K/T}$ for $B \parallel a$-axis. However, the system is driven to a FM state at $B > 5$T for $B \parallel b$-axis, as $T_N$ decreases, suggesting that the magnetic lattice softens. This strong anisotropy is reflected in the resistivity measurements also shown in Figure 4.35. The $c$-axis resistivity $\rho_c$ at zero magnetic field sharply drops below $T_N$, despite
the Fermi surface reduction. This behavior is different from the Cr and Mn doped systems where the onset of AFM order at $T_N$ is accompanied by an increase in resistivity.

The conductivity in the AFM-M region is strongly spin dependent and anisotropic. For $B \parallel a$-axis, $\rho_c$ decreases with applied field whereas for $B \parallel b$-axis, the AFM state becomes semiconducting despite the emerging field-induced FM state for magnetic fields greater than 5 T. In the range $T_{MI} < T < T_N$ the system remains an AFM-M for $B \parallel a$-axis, but becomes FM and semiconducting for $B \parallel b$-axis. This behavior is similar to what is predicted for half-metallic systems. The majority-spin electrons are metallic, whereas the minority-spin electrons are semiconducting [31].

Spin Valve Behavior

The magnetoresistance (MR) ratio is defined as $[\rho_c(B) - \rho_c(0)]/\rho_c(0)$. The field dependence of the MR ratio and magnetization $M(B,T)$ show two interesting trends:

1. The rotation of easy axis from $b$-axis to $a$-axis for $T > 30$ K as indicated by the reversed anisotropy compared to parent system, Ca$_3$Ru$_2$O$_7$. Figure 4.37(a) shows a metamagnetic transition for $T < 30$ K for $M_a$ but for $T > 30$ K for $M_b$.

2. Although $M_a$ is notably smaller than $M_b$ at $T \geq 30$ K, $[\rho_c(B) - \rho_c(0)]/\rho_c(0)$ for $a$-axis is greater than for $b$-axis Figure 4.38. This trend implies an inverse relation
exists between the magnetization and the magnetoresistance. This is a really a novel magnetotransport mechanism based on orbital ordering rather than a spin-polarized state. \[62, 50\].

The phenomenon that is centrally important to our study is the spin valve behavior in bulk single crystals. Figure 4.39 shows that $\rho_c(B)$ for $B \parallel a$–axis peaks at a critical field designated $B_{c2}$ that marks a sharp change in slope of $M_a(B)$. $a$-axis magnetization maximizes between 35 K and 45 K via two distinct transition, $B_{c1} > B_{c2}$ with a saturation magnetization $M_s \sim 3 \mu_B / f \cdot u$ at 7 T. An increase in magnetization, that is an increase in the spin ordering normally leads to a monotonic reduction of spin scattering with increasing magnetic field as seen in $x = 0$, Figure 4.52 and in $x = 0.17$ Figure 4.37(a), 4.38(a) for $M_b$. But the results in Figure 4.38(b), 4.39 and 4.40 are in obvious contradiction to the above statement. There is a peak in $\rho_B$ which is observed for $B \parallel a$–axis over an extended range of $35 \leq T \leq 65$ K.

This interesting trend can be explained with a spin valve scenario as shown in Figure 4.39. The AFM inter-bilayer coupling is far weaker than the FM interactions within the bilayer for Ca$_3$Ru$_2$O$_7$. For a spin valve behavior the Cr substitution should replace Ru rich Ru-O layer with Cr. The x-ray diffraction does not have any superlattice peaks
Figure 4.36: The magnetization, $M_a$ and $M_b$ for $\text{Ca}_3(\text{Ru}_{1-x}\text{Cr}_x)_2\text{O}_7$, $x = 0.17$ as a function of temperature $T$ at $B = 0.5$ T. Right scale: $C/T$ as a function of $T$ for $x = 0.17$ [18].

corresponding to the ordered stacking of Cr-O layer. But as shown in our measurements, ordered distribution of Cr is not a precursor for spin valve behavior in the Cr doped system.

The presence of Cr-O layer causes a spin canting at low fields and temperatures, which gives rise to the upturn in $M_a$ at $T_{MI}$ (Figure 4.37(a)). The magnetization of each unsubstituted Ru-O bilayer, or hard magnetic layer is pinned due to the strong exchange coupling within the bilayer, whereas the magnetization of a substituted Cr-rich layer, which constitutes a a soft magnetic layer, more freely rotates towards the applied field because of the weakened exchange coupling due to Cr replacing Ru. Antiparallel alignment in the soft bilayer is achieved when the spin in the Cr-rich layer fully switches at $B = B_{C2}$ shown in Figure 4.39.

This spin switching enhances $M_a$ at $B_{C2}$ but at the same time, changes the density of states for the up- and down-spin electrons at the Fermi surface. the probabilities of scattering for both up- and down-spin electrons are enhanced within the soft bilayers having an antiparallel alignment, which requires transport electrons to flip spin to find an empty energy state, which explains the pronounced peak in (Figure 4.39, 4.40. The remaining antiparallel spins of Ru-O layers in both the soft and hard bilayers also switch with further increase in $B$, finally completing the spin alignment at $B = B_{(C1)}$. Scattering is now zero for the up-spin electrons and still finite for down spin electrons. Since conduction
Figure 4.37: In plane Magnetization, \( \mathbf{M} \) as a function of magnetic field, \( \mathbf{B} \) for \( \text{Ca}_3(\text{Ru}_{1-x}\text{Cr}_x)_2\text{O}_7 \) for \( x = 0.17 \) at various temperatures \[18\]

Figure 4.38: Magnetic field dependence of magnetoresistance ratio of \( \frac{[\rho_c(B) - \rho_c(0)]}{\rho_c(0)} \) for \( \mathbf{B} \parallel \mathbf{a} \) and \( \mathbf{B} \parallel \mathbf{b} \) axis for \( 2 \leq T \leq 50 \text{ K} \)

occurs in parallel for the two spin channels, the total resistivity is chiefly determined by highly conductive up-spin electrons and, consequently, \( \rho_c \), drops dramatically by as much as 40%. This magnetoresistive effect is much larger than that seen in thin-film layers \[92\], and could have important technological applications. While \( B = B_{C1} \) decreases with temperature, there is a slight increase in \( B = B_{C2} \) and disappears at \( T > 45 \text{ K} \). This may be due to reduction in the difference in soft and hard layer coercivities that becomes
Figure 4.39: Field dependence of \(\frac{\rho_c(B) - \rho_c(0)}{\rho_c(0)}\) and \(M\) (right scale) for \((\text{Ca}_{0.83}\text{Cr}_{0.17})_3\text{Ru}_2\text{O}_7\) for axis at \(T = 40\) K. The thin (thick)-line arrow indicates the spin direction in the Cr-O rich (Ru-O) layer.

Figure 4.40: Field dependence of Magnetoresistance ratio, \(\frac{\rho_c(B) - \rho_c(0)}{\rho_c(0)}\) and magnetization, \(M\) (right scale) for \((\text{Ca}_{0.83}\text{Cr}_{0.17})_3\text{Ru}_2\text{O}_7\) as a function of magnetic field, \(B\) for \(B \parallel a\) and \(B \parallel b\) axis for \(x = 0.17\) for .
insignificant in applied fields at higher temperatures. Consequently, switching may almost occur simultaneously for both Cr-rich and Ru-O bilayers, resulting in one sharp transition at $B = B_{C1}$ seen in both $M_a$ and $\rho_c$ (Figure 4.40), which persists up to 70 K. Figure 4.41 is the phase diagram and shows all the transitions, $T_N$, $T_{MI}$, $B_{C1}$, $B = B_{C2}$ meet at a tetra-critical point at $B = 3.8$ T and $T = 45$ K. It is in the vicinity of this point that spin-valve behavior exists.

4.6.1 (Ca$_{1-x}$Sr$_x$)$_3$Ru$_2$O$_7$

Sr substitution decreases $T_N$ and increases $T_{MI}$ similar to what is observed for Cr substitution. One noticeable difference between the two systems is the site on which the foreign dopant is introduced. Cr is substituted at the Ru site in Ca$_3$Ru$_2$O$_7$ whereas Sr (and Ba) goes to the Ca site in the pure system.

In this section I will discuss the results for 15% Strontium doping on Ca$_3$Ru$_2$O$_7$ as the representative concentration because it encompasses the essence of Sr doping of different

Figure 4.41: $T - B$ diagram for Ca$_3$(Ru$_{1-x}$Cr$_x$)$_2$O$_7$, $x = 0.17$ based on the data for $B \parallel b$–axis. The thin (thick) line arrow indicates the spin direction in the Cr-O rich (Ru-O) layer. [18].
concentrations and also because the spin-valve effect which is the main motivation for this study is most prominent for $x = 0.15$. 15% Sr doping widens the AFM-M region by about 15 K (almost doubles the temperature range compared to the pure system) by pushing the $T_N$ to 64 K and $T_{MI}$ to about 45 K for magnetic field parallel to $b$-axis. For field direction in $a$-axis $T_N$ is at 64 K similar to $b$-axis and an additional anomaly appears at 45 K corresponding to the $T_{MI}$ which is absent along $M_a$ for the pure system.

The inter plane resistivity, $\rho_c$, as a function of temperature is shown in Figures 4.43(a) and 4.43(b). Figure 4.43(a) shows the $c$-axis resistivity for $x = 0.15$ and $x = 0$ for the entire temperature range to 200 K, whereas, Figure 4.43(b) shows the details of resistivity behavior in the Antiferromagnetic-Metallic region for the pure ($x = 0$) and Sr substituted ($x = 0.15$) system. Sr substitution shows a rather interesting behavior because it qualitatively preserves the characteristics of the antiferromagnetic-metallic region including a sharp decrease in resistivity corresponding to $T_N$ and the Mott like transition. Additionally, on the one hand it tends to make the system slightly conducting compared to pure Ca$_3$Ru$_2$O$_7$ in the temperature region away from the AFM-M region (both above and below), on the other hand it widens the AFM-M region with $T_N$ and $T_{MI}$ corresponding to the magnetization
Figure 4.43: The c-axis resistivity for (Ca$_{1-x}$Sr$_x$)$_3$Ru$_2$O$_7$ for $x = 0$ and $x = 0.15$ as a function of temperature over the entire range of $1.7 \leq T \leq 200$ K.

Figure 4.44: Magnetization, M as a function of magnetic field of (Ca$_{1-x}$Sr$_x$)$_3$Ru$_2$O$_7$ for $x = 0.15$ for different temperatures.

The specific heat measurements for $x = 0.15$ reveal two specific heat anomalies observed at 45 K and 60 K, consistent with the anomalies observed in the magnetization data (Figure 4.42). The $T_{MI}$ anomaly is approximately symmetric, suggestive of a broadened first order transition. The entropy change, $\Delta S \sim 0.08$ is much smaller compared to the pure sample suggesting either a smaller structural change or a smaller change in the $\gamma$ and hence, density of states. In contrast, the specific heat above $T_N$ extrapolates to a lower value than that measured below $T_N$, so the anomaly appears to be “broadened mean-field”. 


(a) The field dependence of \( \frac{\rho_c(B) - \rho_c(0)}{\rho_c(0)} \) for \( a \)-axis.

(b) The field dependence of \( \frac{\rho_c(B) - \rho_c(0)}{\rho_c(0)} \) for \( b \)-axis.

Figure 4.45: The field dependence of MR, \( \frac{\rho_c(B) - \rho_c(0)}{\rho_c(0)} \) for \((\text{Ca}_{1-x}\text{Sr}_x)_3\text{Ru}_2\text{O}_7\) for \( x = 0.15 \) for \( 30 \leq T \leq 50 \) K \[18\] with \( \Delta C_p \sim 0.7R \), slightly smaller compared to the pure system. In mean field theory there is a discontinuity in the specific heat at critical point. The specific heat is higher in the ordered state than in the disordered state. For higher Sr doping, \( x = 0.58 \), only a single broadened mean-field anomaly is observed at \( T_N \sim 53\)K, with \( \Delta C_p \sim 0.4R \) and no specific heat signatures corresponding to \( T_{MI} \). The decrease in the magnitude of the \( C_p \) anomalies at \( T_N \) is consistent with the magnetization anomalies, suggesting that introducing Sr in the system either decreases the magnitude or the average density of the ordering moments.

The magnetic field dependence, \( M(B) \) (Figure 4.44) shows that the metamagnetic transition occurs at \( T \leq 40 \) K for \( M_b \) whereas, the hint of an emerging metamagnetic transition can be seen in \( M_a \) for \( T \geq 40 \) K. For pure \( \text{Ca}_3\text{Ru}_2\text{O}_7 \) the metamagnetic transition occurs in \( M_b \) at low temperatures. This reversal in magnetic anisotropy by Sr substitution is similar (although weak compared to) Cr and suggests that the easy axis is rotating from \( b \)-axis towards the \( a \)-axis. This is reflected in the \( M(T) \) data as well (Figure 4.42) where \( a \)-axis magnetization develops an anomaly corresponding to \( T_{MI} \).

Figure 4.45 shows the field dependence of the magnetoresitivity ratio, \( \frac{\rho_c(B) - \rho_c(0)}{\rho_c(0)} \) as a function of magnetic field, \( B \). Although \( M_a \) is smaller than \( M_b \), the at \( T \leq 40 \) K magnetization \( M(B, T) \) also depicts the inverse relation like \( \text{Ca}_3(\text{Ru}_{1-x}\text{Cr}_x)_2\text{O}_7 \) between
magnetization and magnetoresistance. Although $M_a(B)$ is much smaller in magnitude than $M_b(B)$ as shown in Figure 4.44, the magnetoresistance ratio is stronger along $b$-axis, Figure 4.45. This scenario is similar to the Cr doped Ca$_3$Ru$_2$O$_7$ but it is interesting to note that the spin-valve behavior in Sr doped system is not as robust as in Cr substituted Ca$_3$Ru$_2$O$_7$

As mentioned in the earlier section an increase in magnetization with increasing field is usually accompanied by reduction in spin scattering but this have contradicted our results
in both the doped system so far. Magnetoresistance for Sr doped system peaks at $T = 45$ K and this peak occurs at a critical field $B_{c2}$, which also corresponds to the critical field in metamagnetic transition as shown in Figure 4.46(a). Unlike Cr where $\rho_c(B)$ maximizes via two transitions, $B_{c1}$ and $B_{c2}$ (Figure 4.38), for Sr the transition are much smoother (although smaller in magnitude) and have a sharp change in slope. The spin valve like behavior in Sr doped $\text{Ca}_3\text{Ru}_2\text{O}_7$ may be explained by a similar scenario as $\text{Ca}_3(\text{Ru}_{1-x}\text{Cr}_x)_2\text{O}_7$. Sr$^{+2}$ introduced in the Ca-O planes with a bigger ionic radius than Ca$^{+2}$ increases the “thickness” of the insulating spacer layers between the two FM bilayers, this in turn weakens the antiferromagnetic exchange coupling.

4.6.2 $(\text{Ca}_{1-x}\text{Ba}_x)_3\text{Ru}_2\text{O}_7$

This section focuses on the impact of Ba, specifically, of 2% Ba doping on $\text{Ca}_3\text{Ru}_2\text{O}_7$. Ba has an ionic size of 1.35 Å much bigger than that for Sr$^{+2}$ (ionic size = 1.12 Å). This difference in ionic sizes is manifest in the fact that very light doping of only 2% Ba concentration is enough to drive the system to a beautifully robust spin-valve behavior, much larger than achieved by even 15% Sr substitution and quite comparable to 17% Cr substitution in $\text{Ca}_3\text{Ru}_2\text{O}_7$.

![Figure 4.47](image.png)

Figure 4.47: The magnetization, $M_a$ and $M_b$ for $(\text{Ca}_{0.98}\text{Ba}_{0.02})_3\text{Ru}_2\text{O}_7$ as a function of temperature $T$. Right scale: $C/T$ as a function of $T$ for $x = 0.02$
Figure 4.47 shows the magnetization as a function of temperature for \((\text{Ca}_{1-x}\text{Ba}_x)\text{Ru}_2\text{O}_7\) for \(x = 0.02\) for both \(a\)- and \(b\)-axis. Also shown is the specific heat \(C\), as a function of temperature. Substituting Ba in \(\text{Ca}_3\text{Ru}_2\text{O}_7\) increases the AFM-M region to about 32 K temperature range as opposed to only 8 K for pure \(\text{Ca}_3\text{Ru}_2\text{O}_7\). For \(M_b\) the metal to insulator transition, \(T_{MI} = 40\) K is considerably lowered and Néel temperature, \(T_N = 72\) K is pushed towards much higher temperature in comparison to pure \(\text{Ca}_3\text{Ru}_2\text{O}_7\). In addition, the \(a\)-axis magnetization develops an anomaly corresponding to \(T_{MI}\). The magnetization also has an upturn for \(T \leq T_{MI}\) possibly due to spin canting. The specific heat, \(C(T)\) exhibits a mean-field like second order phase transition slightly lower than \(T_N\) but there is no transition observed corresponding to \(T_{MI}\). Low temperature data, \(2K < T < 30K\) fitted to \(C = \gamma T + \beta T^3\) gives the coefficient of electronic contribution to specific heat, \(\gamma \sim 112\) mJ/mol-K\(^2\) and the coefficient of phonon contribution, \(\beta \sim 4.24 \times 10^{-4}\) mJ/mol-K\(^3\). The coefficient for electronic contribution to the specific heat, \(\gamma\), is largely enhanced compared to the values in the pure system \([69, 94]\), suggesting an increased density of states (DOS) at the Fermi energy.

![Image](image1.png)  
(a) Left scale: \(\rho_c\) for \(x = 0.02\) and Right scale: \(\rho_c\) for \(x = 0\)

![Image](image2.png)  
(b) Left scale: \(\rho_a\) and Right scale: \(\rho_b\)

Figure 4.48: Zero field resistivity as a function of temperature of \((\text{Ca}_{1-x}\text{Ba}_x)\text{Ru}_2\text{O}_7\) for \(x = 0\) and \(x = 0.02\) for \(a\)-, \(b\)- and \(c\)-axis.

Figure 4.48(a) shows the \(c\)-axis resistivity for \((\text{Ca}_{1-x}\text{Ba}_x)\text{Ru}_2\text{O}_7\) for \(x = 0.02\) as a function of temperature in the AFM-M region. Despite the enhanced DOS suggested by an enhanced specific heat coefficient, \(\gamma\), which should normally lead to an even more insulating state due to increases scattering, Ba substitution surprisingly makes the system very conducting over the entire temperature range. The conducting behavior of \(c\)-axis...
resistivity in AFM-M region for Ba is in sharp contrast to that of (Ca_{0.85}Sr_{0.15})_3Ru_2O_7 and (Ca_{0.83}Cr_{0.17})_3Ru_2O_7 (Figure 4.43(a) and Figure 4.35). The anisotropic character of the Ba doping is evident in the fact that $\rho_a$ and $\rho_b$ are less conducting and still preserves the AFM-M region as shown in Figure 4.48(b) with $T_N = 46$ K (a little higher compared to magnetization data) and $T_N = 72$ K.

Figure 4.49: Magnetization, $M$ as a function of magnetic field, $B$ for (Ca$_{1-x}$Ba$_x$)$_3$Ru$_2$O$_7$ for $x = 0.02$ for at various temperatures for both $a$-axis and $b$-axis.

Figure 4.50: The field dependence of MR, $[\rho_c(B) - \rho_c(0)]/\rho_c(0)$ for (Ca$_{1-x}$Ba$_x$)$_3$Ru$_2$O$_7$ for $x = 0.02$ for $40 \leq T \leq 60$ K

Figure 4.49(a) and 4.49(b) shows the magnetization for (Ca$_{1-x}$Ba$_x$)$_3$Ru$_2$O$_7$ for $x = 0.02$ as a function of magnetic field.
Figure 4.50 shows the field dependence of magnetoresitivity ratio (MR) defined as 
\[
\frac{\rho_c(B) - \rho_c(0)}{\rho_c(0)}
\] for B \parallel a-axis and B \parallel b-axis and for 40 \leq T \leq 60 K. And Figure 4.49 shows magnetization as a function of magnetic field for a- and b-axis for T = 2 K and T = 45 K. For B \parallel b-axis, M for T = 2 K shows a metamagnetic transition which the hysteresis behavior similar to that for the pure (x = 0) system but a lowered saturated ordered moment \(M_s \sim 1.7 \mu_B/Ru\) and a lower critical field \(B_C(\sim 4T)\). This transition weakens as T rises and disappears before T = 45 K. For B \parallel a-axis, M shows a metamagnetic transition at T = 45 K, also with a much lower critical field \(B_c \sim 3 T\) and a saturation moment \(1.5 \mu_B\). This suggests a rotation of easy axis similar to Cr and Sr substituted Ca\(_3\)Ru\(_2\)O\(_7\). The change in magnetic structure is accompanied by a marked reduction in c-axis resistivity and \(M_a\) maximizes with a sharp peak at 45 K with the corresponding saturation magnetization of \(1.5 \mu_B\), Figure 4.51. The figure correlates how the metamagnetic transition correlates with the sharp peak in magnetoresistance.

![Figure 4.51: Field dependence of \(\frac{\rho_c(B) - \rho_c(0)}{\rho_c(0)}\) and M (right scale) for the B \parallel b axis at T = 43 K for x = 0 and T = 45 K for x = 0 Ca\(_3\)Ru\(_2\)O\(_7\)](image)

To understand the spin valve behavior in Sr and Ba substituted Ca\(_3\)Ru\(_2\)O\(_7\) one possibility is the Tunneling magnetoresistance effect. The magnetization of each bilayer in pure Ca\(_3\)Ru\(_2\)O\(_7\) is pinned due to strong exchange coupling within the bilayer. One of the characteristics of TMR is that the external magnetic field required to rotate the magnetization is sufficiently low. This is because there is almost no exchange coupling between the magnetization of the two layers as a result of the insulating barrier inserted between them. The
antiparallel and parallel alignment of the magnetization are realized by using a small difference in the coercive force between the two ferromagnet. This is achieved by introducing a dopant in the spacer layer that relaxes the crystal structure of the distorted Ca$_3$Ru$_2$O$_7$ and hence changing the density of states for the majority and minority spin electrons at the Fermi surface. By introducing Sr or Ba in the Ca-O layers, we are effectively changing the thickness of the insulating spacer layer and consequently the exchange coupling within the bilayer. This scenario is consistent with weaker magnetoresistance in Sr (smaller ionic size than Ba) compared to Ba. Ba ionic size provides with an optimized thickness so that the exchange coupling is minimum.

The Slonczewski model for TMR includes two identical FM layers with exchange split bands, separated by a rectangular potential barrier. This leads, for a thick barrier, to a conductance that is a linear function of the cosine of the angle between the magnetization.

\[ G(\theta) = G_0 (1 + P^2 \cos \theta) \]  

where \( P \) is the effective spin polarization of the tunneling electrons.

With the increasing field the relative orientation of the now softened bilayers change, that is \( \theta \) changes with increasing B and achieve AFM alignment at the critical field. The
probabilities of scattering for both majority and minority spin electrons are enhanced since majority spins will now tunnel to minority spin states and vice versa which leads to higher resistance and a peak in magnetoresistance ratio. The remaining antiparallel spins also switch with increasing magnetic field an spin disorder scattering is reduced by field induced magnetization. Scattering is now zero for majority spin electrons and still finite for minority spin. The total resistivity is now primarily from majority spin carriers and drops dramatically.

4.6.3 Summary

In summary, we have uncovered a novel bulk spin valve behavior in doped Ca$_3$Ru$_2$O$_7$ utilizing the naturally engineered layered structure of the Ca$_3$Ru$_2$O$_7$ system as opposed to the artificially made complicated multilayer heterostructure. The spin valve behavior results from the elegant physics underlying the Antiferromagnetic-Metallic region and the half-metallic behavior predicted in the pure system. This study gives a handle on exploiting the above mentioned characteristic and altering the exchange coupling via two directions - either by introducing a dopant on the magnetic site or introducing the dopant in the rock salt Ca-O layer. Both lead to a change in the exchange coupling and/or the coercivities of the Ferromagnetic layers. This provides a valuable insight into the future direction of exploiting spintronics direction in the bulk single crystals.
CHAPTER 5: NOVEL MAGNETISM IN LAYERED IRIDATES, SR_{N+1}IR_{N}O_{3N+1}

5.1 Magnetism and strong magnetoelectric effects in Sr_{2}IrO_{4}

Figure 5.1: Crystal structure of single layered Sr_{2}IrO_{4}
The spin, orbital and lattice degrees of freedom and their interplay have revealed rich underlying physics and many interesting phenomena such as superconductivity, colossal magnetoresistance, Mott transition and spin, charge and orbital ordering in 3d TMOs. Despite a wide array of interesting physics found in these materials, little is known about similar behavior in 4d and 5d TMOs for which the d orbitals are more spatially extended and spin-orbit coupling is almost an order of magnitude larger than the 3d TMOs. Moreover, because the 4d and 5d were thought to be weakly correlated, they are expected to be more metallic and less magnetic than their 3d and 4f counterparts.

The larger spatial extent of the orbitals results in increased hybridization between the
metal cation $d$ and the oxygen $p$ orbitals. $4d/5d$ systems have a larger crystal field splitting compared to the $3d$ compounds and are usually in the low-spin state. $4d/5d$ systems lie in the “intermediate-coupling regime” where the on-site coulomb repulsion and the bandwidth are comparable, that is, $U/W \sim 1$.

In marked contrast to expected metallic behavior, many iridates display highly unusual behavior. For example, layered BaIrO$_3$ [16, 19, 67], Sr$_{n+1}$Ir$_n$O$_{3n+1}$ (n=1 and 2) [14, 25] and Ba$_2$NaOsO$_6$ [34] are magnetic insulators. SrIrO$_3$ [17] shows non-Fermi liquid behavior, Na$_4$Ir$_3$O$_8$ [79] has a spin liquid ground state. The spin-orbit coupling (SOC) is crucial in explaining the anomalous behavior observed in these systems. The unusual insulating state of Sr$_2$IrO$_4$ could be explained by cooperative interaction between electron correlation and spin orbit coupling. The spin-orbit coupling constant of 5$d$ TMOs is about 0.3 eV to 0.4 eV which is much larger than that of 3$d$ TMOs ($\sim$ 20 eV). The underlying physics of 5$d$ TMOs is not a simple adiabatic continuation of the 3$d$ TMO physics to a small $U$ regime, and a new paradigm is required for understanding their unique novel phenomenon.

This work is further motivated by a combination of recent findings in optical and theoretical studies [52, 73, 72, 51]. Single-layer Sr$_2$IrO$_4$ exhibits the novel Mott state driven by a spin-orbit interaction comparable to $U$. As shown in Figure 5.3, the octahedral crystal field splits the Iridium 5$d$ bands in Sr$_2$IrO$_4$ into $t_{2g}$ and $e_g$ orbital states. Usually, the crystal field is large enough to yield a $t_{2g}$ low spin state for Sr$_2$IrO$_4$ and since the system has a partially filled $t_{2g}$ band, it is expected to be a metal. An unrealistically large Coulomb interaction, $U \gg W$, where $W$ is the bandwidth, could lead to a typical spin $S = 1/2$ system. On the other hand, a reasonable $U$ value cannot give an insulating state as observed in Sr$_2$RhO$_4$, which is a normal metal [95]. In the strong spin-orbit coupling case, the degeneracy in the $t_{2g}$ states are lifted to yield $J_{eff} = 1/2$ and $J_{eff} = 3/2$ bands. $J_{eff} = 1/2$ lies higher in energy, seemingly against Hund’s rule. $J_{eff} = 1/2$ actually branches off from the $J_{5/2}$ state due to a large crystal field. With the lower lying $J_{eff} = 3/2$ completely filled, the system is an effectively half-filled $J_{eff} = 1/2$ single narrow band system so that even a small $U$ opens a Mott gap, making it a $J_{eff} = 1/2$ insulator [52, 73, 72, 51].

The $J_{eff} = 1/2$ bandwidth (0.48 eV) is so narrow that even a weakened $U$ is sufficient to further split the $J_{eff} = 1/2$ band into upper and lower Hubbard bands split by a Mott gap $\Delta_0$ eV [51, 73], a circumstance that favors a recently predicted mechanism of Giant Magnetolectric Effect (GME) [42]. The GME is an established feature of 3$d$
multiferroics but previously unobserved in 5$d$ perovskites. Moreover, the traditional view is that GME depends only on the magnitude and spatial dependence of magnetization, whereas the mechanism suggests a critical role of an effective spin-orbit gap $\Delta_S$\cite{12}. Our results indicate this mechanism is realized in Sr$_2$IrO$_4$.

I report the data for electrical resistivity $\rho$, magnetization $M$, ac susceptibility $\chi'$, heat capacity $C$, thermoelectric power $S$ and dielectric constant $\epsilon$ measurements on single crystal Sr$_2$IrO$_4$ as a function of temperature $T$, magnetic field $H$ and frequency $\omega$. The experimental results lead to the following scenario:

- Near a newly observed magnetic phase transition $T_M \sim 100$ K, the dielectric constant
\( \epsilon(T) \) rises abruptly by more than two orders of magnitude,

- A large magnetodielectric shift that occurs near a low-field metamagnetic transition and,

- \( T_M \) separates two temperature regions with vastly different frequency dependence of \( \epsilon \) and, therefore, defines a drastic change in spin dynamics that couples to the dielectric response.

### 5.1.1 Single Crystal growth and Structure

![Figure 5.4: Field-cooled magnetization \( M(T) \) and inverse susceptibility \( \Delta \chi^{-1}(T) \) (right scale) at applied field \( \mu_0 H = 0.2 \, \text{T} \) for Sr\(_2\)IrO\(_4\)](image)

Single crystals were grown in Pt crucibles using self-flux techniques from off-stoichiometric quantities of IrO\(_2\), SrCO\(_3\), and SrCl\(_2\) \[14, 25\]. The resulting shapes of Sr\(_2\)IrO\(_4\) are plate-like with an average size of \( 0.8 \times 0.7 \times 0.05 \, \text{mm}^3 \) with the shortest dimension along the \( c \)-axis. Sr\(_2\)RuO\(_4\) crystallizes in a K\(_2\)NiF\(_4\) type layered perovskite structure [5.1]. The x-ray diffraction data and neutron diffraction measurements indicate the IrO\(_6\) octahedra are rotated about the crystallographic \( c \)-axis by about \( 11^\circ \), reducing the space group symmetry from \( I4/mmm \) to \( I4_1/acd \) with an enlarged unit cell. This rotational distortion breaks the inversion center existing between the Ir ions along the \( (100) \) and \( (010) \) directions for \( I4/mmm \) symmetry [30], and distortion increases with decreasing temperature. The rotation of the
IrO$_6$ octahedra changes from 11.36° at room temperature to 11.72° at 10 K [43]. The Ir-O-Ir bond angle decreases from 157.28° to 156.56° and is an important parameter in the study of Sr$_2$IrO$_4$ as it controls the hopping of the 5$d$ electrons and superexchange interaction between Ir atoms via the bridging O sites.

Sr$_2$IrO$_4$ reveals weak ferromagnetic ordering along both the crystallographic directions with $T_C$=240 K as shown in Figure 5.4. Sr$_2$IrO$_4$ also features a low-field metamagnetic transition with a small saturation moment $\mu_s < 0.13\mu_B$/Ir, which has some sample dependence along the easy $a$-axis. The high temperature data, $270 < T < 350$ K is fitted to the Curie-Weiss law. The Curie-Weiss temperature $\theta_{CW} = +236$ K extrapolated from the inverse susceptibility $\Delta\chi^{-1}$ ($\Delta\chi = \chi(T) - \chi(0)$, where $\chi_0$ is the temperature independent contribution) confirms ferromagnetic exchange coupling. Also, the Arrott plots corroborate the existence of weak FM order with $T_c \sim 240$ K. The effective paramagnetic moment $\mu_{eff} (= 0.5\mu_B)$ and the saturation moment $\mu_s (< 0.13\mu_B$/Ir) at 1.7 K are substantially smaller for those expected for a $S = 1/2$ system.

![Figure 5.5: Specific heat $C(T)$ for single layered Sr$_2$IrO$_4$](image)

Figure 5.5 shows the specific heat measurements for Sr$_2$IrO$_4$. The specific heat measurements $C$ at low temperatures ($3 < T < 11$ K) fits a predominantly $T^3$ at $\mu_0H = 0$ and $9$ T [Figure 5.5(b)] due to the contribution by either phonons or magnons for an antiferromagnetic ground state, in apparent conflict with the weak FM behavior seen in Figure 5.4. $C(T)$ in this temperature range changes considerably with magnetic field. For example,
\[ \frac{C(T, H) - C(T, 0)}{C} \sim 16\% \text{ at } 9\ T \text{ and retains the } T^3 \text{ dependence. This dependence indicates a significant magnetic contribution to } C(T) \text{ and suggests that a competition between AFM and FM exchange produces a low temperature } C(T) \text{ consistent with antiferromagnetic magnons. An antiferromagnetic ground state is also consistent with previously reported results } [30] \text{ which suggests that the weak ferromagnetism is a result of spin canting motivated by the Dzyaloshinsky-Moriya interaction. The relative strength of antiferromagnetic and ferromagnetic coupling might be responsible for the complex magnetic ground state. The balance of these couplings clearly shifts to drive different ground state at high and low temperatures. There is only a very tiny anomaly in } C(T) \ (\Delta C \sim 4 \text{ mJK/mole K}) \text{ observed near } T_C \text{ indicating a very small change in entropy near the Curie temperature, Figure } 5.5(b). \text{ The absence of an anomaly in specific heat } C(T) \text{ near } T_C \text{ is also noted by other groups } [56]. \]

Figure 5.6: Resistivity log\(\rho(T)\) for Sr\(_2\)IrO\(_4\) as a function of temperature for \(T \leq 600\ K\) in both \(a\) and \(c\) axis.

The most remarkable feature in Sr\(_2\)IrO\(_4\) is the fact that the anomaly corresponding to \(T_C(=240\ K)\) in magnetization has no signature in resistivity \(\rho(T)\) and Seebeck coefficient \(S(T)\) [Figures 5.6 and 5.7]. This suggests that there is no change in the density of states and spin orbit coupling near the Curie temperature expected for a well established magnetic phase transition. This in turn suggests that the driving physics behind the thermal properties is not the same as the mechanism for magnetic properties. Also to be noted is that the transport properties of Sr\(_2\)IrO\(_4\) are extremely sensitive to oxygen content, but the magnetism is not \([51, 58]\). Introducing very dilute oxygen vacancies into single crystal Sr\(_2\)IrO\(_4\)-\(\delta\) with \(\delta \leq 0.04\) leads to significant changes in the lattice parameters and an
Figure 5.7: Thermoelectric power $S(T)$ for Sr$_2$IrO$_4$ as a function of temperature $T \leq 600$ K for both $a$ and $c$ axis insulator-to-metal transition at $T_{MI}=105$ K. For $\delta \approx 0.04$, the bond angle increases with decreasing temperature from $157.028^\circ$ at 295 K to $157.072^\circ$ at 90 K. The change in the bond angle $\Delta \theta = 0.792^\circ$ is remarkably large for such a small oxygen depletion. Dilute oxygen vacancies relax the bond angle and reverse its temperature dependence with increasing $\delta$ while significantly reducing the structural distortion at low $T$. The $a$-axis resistivity is reduced by a factor of $10^{-9}$ with doping at $T = 1.8$ K as $\delta$ changes from 0 to $\sim 0.4$. The $c$-axis resistivity changes by a factor of $10^{-7}$. For $\delta \approx 0.04$, there is a sharp insulator-to-metal transition near $T_{MI}=105$ K \cite{58}.

Figure 5.8: (a) Real part of ac susceptibility $\chi'(T, \omega)$ along the $a$-axis at $\mu_0 H = 0.1$ T and frequencies $\omega = 8$ and 80 Hz. (b) $\chi'(T)$ for $\omega = 8$ Hz at $\mu_0 H = 0.01$ and 0.1 T.

Figure 5.8: ac susceptibility for Sr$_2$IrO$_4$ at different magnetic fields and frequencies.
The absence of a phase-transition signature in $\rho(T \approx T_C)$ and $S(T \approx T_C)$ could reflect a spin-glass state. One of the signatures of spin glass behavior is a sharp peak close to spin freezing point that is frequency-dependent in the real part of the ac magnetic susceptibility, $\chi'(T, \omega)$ shown in Figure 5.8(b). The figure shows $\chi'(T)$ for $\omega = 0.8$ and 80 Hz with a driving field magnitude of 1 Oe and a dc field of 0.1 T. It shows only a gradual slope change well below $T_C=240$ K, but a pronounced peak in the vicinity of 135 K. $\chi'(T)$ demonstrates no detectable frequency dependence, thus providing no apparent evidence for spin glass behavior near the ordering temperature. However, the temperature dependence of $\chi'$ is highly susceptible to a dc magnetic field. As exhibited in Figure 5.8(a), the onset of $T_C$ is better defined at a weaker field of $\mu_0H = 0.01$ T, but it readily evolves into two distinct peaks at a stronger magnetic field of $\mu_0H = 0.1$ T. This behavior is in marked contrast to dc magnetization $M(T)$ that changes with $H$ only slightly near $T_C$ but considerably below 135 K as seen in Figures 5.9(a) and 5.9(b).

A key feature revealed in Figures 5.9(a) and 5.9(b) is the newly observed magnetic anomaly, denoted as $T_M$. $T_M$ is clearly highly sensitive to $H$, which might be a result of gradual spin canting due to the rotation of IrO$_6$ octahedra. As mentioned earlier, IrO$_6$ octahedra is rotated by 0.36° from room temperature to 10 K accompanied by a significant reduction of Ir-O-Ir bond angle from 157.28 to 156.56° and increase in the c-axis parameter. The data in Figure 5.9 suggests that $T_M$ marks a crossover of the dominant exchange coupling from FM to AFM with a reduction in the Ir-O-Ir bond angle. Increased spin canting, or an AFM state at low $T$ is also consistent with the downturn in $M$, substantial rise in $\rho(T < T_M)$, and $C(T)$ seen at low temperatures in Figure 5.4. A strong temperature dependence of bending modes associated with the Ir-O-Ir bond angle was observed [72], which in turn influences the magnetic exchange interaction. It is not surprising that the magnetic properties are highly sensitive to impurity doping on either the Sr or Ir site. As shown in Figure 5.9(c), 2% Ba substitution for Sr in Sr$_2$IrO$_4$ completely eliminates all major magnetic features of the pure Sr$_2$IrO$_4$, mostly noticeably, $T_M$ and low $-T$ downturn in $M$ that are critical to the GME.

The stronger spin canting clearly causes a sizable rise in the resistivity near $T_M$ as shown in Figure 5.6. Another interesting aspect of this magnetic anomaly is it’s association with the dielectric response. Figure 5.10(a) shows the c-axis dielectric constant $\epsilon_c(T)$ along with the c-axis magnetization $M_c(T)$ (right scale) as a function of $T$ for a few representative
Figure 5.9: dc magnetization $M(T)$ for $\text{Sr}_2\text{IrO}_4$ and $(\text{Sr}_{1-x}\text{Ba}_x)_2\text{IrO}_4$ for different magnetic fields for $a$ and $c$-axis. The arrows in figures (a) and (b) $H$–dependent anomaly at $T_M$. 

(a) Magnetization $M_a(T)$ for different magnetic fields for $a$-axis

(b) Magnetization $M_c(T)$ for different magnetic fields for $c$-axis

(c) dc magnetization $M(T)$ for $(\text{Sr}_{1-x}\text{Ba}_x)_2\text{IrO}_4$ for different magnetic fields for $a$ and $c$-axis
frequencies. Two key features in Figure 5.10(a) are (1) A striking two orders of magnitude rise in $\epsilon(T)$ and a peak near $T_M$, to some extent is similar to La$_2$CuO$_4$ as reported in [24]. The enhancement in dielectric constant $\epsilon(T)$ observed in Sr$_2$IrO$_4$ is much larger than that in some well known magnetoelectric systems such as BaMnF$_4$ [86], BiMnO$_3$, [54], HoMnO$_3$ and YMnO$_3$ [64] and, (2) the peak in $\epsilon(T)$ that corresponds to $T_M$ divides the plot into two distinct regions - one with a weak frequency dependence and the other with a stronger frequency dependence, marked as region I and II respectively in figure 5.10(a).

In region I, $\epsilon(T)$ behaves more like a ferroelectric, which is frequency independent but in region II, $\epsilon(T)$ shows a characteristic of a relaxor that exhibits strong frequency dispersion, due chiefly to frustration and disorder or soft-mode lattice. However, in a conventional relaxor, frequency dependence diminishes and eventually vanishes at higher temperatures when thermal fluctuations breaks the dispersive relaxor state. The observed frequency dependence of region II behaves otherwise.

$T_M$ clearly defines a drastic change in spin dynamics that couples the dielectric response. It seems that in region II, there exists a strong competition between the ferromagnetic and antiferromagnetic couplings that may result in some degree of frustration or even an incommensurate state, and the spin-lattice coupling or the lack of it in turn may give rise to a soft-mode lattice. The slight but visible frequency dependence of $\chi'$ near 135 K might be such an indication (Figure 5.8(b)). With decreasing temperature, the rotational disorder further develops, hence straightening the antiferromagnetic coupling. Near $T_M$, the antiferromagnetic coupling becomes dominant, and spins are thus “locked in” with the lattice, forming a rigid (spin) lattice in region I. This explains not only the rise of $\rho(T)$ near the anomaly $T_M$ but also why magnetodielectric effect $\Delta\epsilon/\epsilon(0)$ is 75% at 50 K but only 17% at 110 K, as illustrated in Figure 5.12(a), because $\epsilon$ in region I can better respond to $H$ via the stronger spin-lattice coupling.

Also, shown in Figure 5.12(b) is that the onset of the magnetodielectric effect $\Delta\epsilon/\epsilon(0)$ occurs near $H_c$, the metamagnetic transition [14]. The large value of $\Delta\epsilon/\epsilon(0)$ is remarkable considering the exceptionally weak $M(< 0.1\mu_B/Ir)$, to which $\Delta\epsilon$ is expectedly to be proportional ($\Delta\epsilon \sim M^2$). In fact, the observed $\Delta\epsilon/\epsilon(0)$ is much greater than that of currently studied systems, e.g. BiMnO$_3$, HoMnO$_3$ and YMnO$_3$ etc. It is also to be noted that the magnetoresistance in Sr$_2$IrO$_4$ is negligible even at much higher $H$ [14, 56] and the observed magnetodielectric effect is thus intrinsically due to the strong magnetoelectric
(a) Real part of the $c$-axis dielectric constant $\epsilon'_c(T)$ for representative frequencies $\omega$ (left scale), and $c$-axis magnetization $M_c(T)$ (right scale). Also shown is the schematic change of O-Ir-O bond angle from region I to region II.

(b) Real part of the $a$-axis dielectric constant $\epsilon'_a(T)$ for representative frequencies $\omega$ (left scale), and $a$-axis magnetization $M_a(T)$ (right scale).

Figure 5.10: Real part of the dielectric constant $\epsilon'(T)$ and Magnetization (right scale) for $\text{Sr}_2\text{IrO}_4$ for different frequencies for $c$ and $a$-axis.

coupling. The magnetoelectric coupling is an intriguing phenomenon that has been studied in the last few decades, particularly in recent years, for example as reported in these papers [41, 44, 33, 53, 84, 42]. Almost all magnetoelectric and multiferroic materials that have
been investigated so far are 3d-based compounds. is the first compound to depict the magnetoelectric effect in the 5d based system. The GME in Sr$_2$IrO$_4$ is unique because it is driven by spin-orbit gapping of 5d bands rather than the magnitude and spatial dependence of magnetization, as traditionally accepted. In summary, a dominant spin-orbit coupling in Sr$_2$IrO$_4$ shifts the balance of competing magnetic, dielectric and lattice energies, generating a type of Giant Magnetoelectric effect that is not dependent on the magnetization, but nevertheless, is intimately linked with the complex magnetic order emerging from an exotic Mott insulating state. In essence, there exists a novel type of magnetoelectric phenomenon where the ferroelectric moment $P$ is closely associated with an effective Mott gap $\Delta_s$ in the presence of strong SOC rather than the magnitude of magnetization ($P \sim \Delta_s$) [42].

5.2 Comparison to Sr$_3$Ir$_2$O$_7$

The primary focus of this chapter is the $J_{eff,1/2}$ novel Mott-insulator Sr$_2$IrO$_4$, its sister compound Sr$_3$Ir$_2$O$_7$ ($n = 2$) as a comparison and for gainful insight into the dimensionality dependence of layered Ruddlesden-Popper series Sr$_{n+1}$Ir$_n$O$_{3n+1}$. Sr$_3$Ir$_2$O$_7$ belongs to the class of iridates that exhibits unconventional and unexpected behaviors. It shows anomalous diamagnetic behavior among other interesting properties discussed in the next section.
5.3 Physical properties of Sr$_3$Ir$_2$O$_7$

Single crystals were grown in Pt crucibles using self-flux techniques from off-stoichiometric quantities of IrO$_2$, SrCO$_3$, and SrCl$_2$ [14, 25]. These mixtures were heated to 1480°C in Pt crucibles, fired for 20 h, cooled at 5°C/h to 1440°C, and then rapidly quenched to room temperature. The quenching process is critical to ensure an exclusion of precursor phases such as Sr$_2$IrO$_4$, which is a stronger magnet with $T_C=240$ K. A slight inclusion of the Sr$_2$IrO$_4$ phase could fully overshadow the diamagnetic response, or eliminate the negative magnetization by lifting the magnetic background, although temperature dependence remains unchanged below 50 K. A good indication of the inclusion of Sr$_2$IrO$_4$ in Sr$_3$Ir$_2$O$_7$ is
an anomaly near $T_C=240$ K in ZFC magnetization. ZFC magnetization for pure Sr$_3$Ir$_2$O$_7$ shows no features in that temperature range. The resulting shapes of Sr$_3$Ir$_2$O$_7$ are plate-like with an average size of $0.6 \times 0.5 \times 0.1$ mm$^3$ with the shortest dimension along the $c$-axis.

The crystal structure of Sr$_3$Ir$_2$O$_7$ like its sister compound Sr$_2$IrO$_4$ is characterized by the reduced space-group symmetry, and is $Bbca$ for Sr$_3$Ir$_2$O$_7$ [25]. The IrO$_6$ octahedra is rotated about the $c$-axis $\sim 11^\circ$. Like Sr$_2$IrO$_4$, Sr$_3$Ir$_2$O$_7$ shows an elongation in the $c$-axis with decreasing temperature. Within a layer the rotations of the IrO$_6$ octahedra alternate in sign, leading to a staggered structure such that the two layers in the double layer are out of phase [25].

Figure 5.13: Field-cooled magnetic susceptibility $\chi(T)$ at $\mu_0 H = 0.1$ T for Sr$_3$Ir$_2$O$_7$ for both $a$- and $c$-axis

Sr$_2$IrO$_4$ and share some similarities but it is their pronounced dissimilarities that highlight the intriguing physics. As reported by Cao et.al [25], Sr$_3$Ir$_2$O$_7$ is a magnetic insulator with a transition to weak ferromagnetism at $T_C=285$ K. The magnetic moment at $T = 1.7$ K and an applied magnetic field of 7 T is only $0.037 \mu_B$/Ir, that is, less than 4% of the moment expected for a localized spin system $S = 1/2$ (expected moment is $1 \mu_B$/Ir). The most remarkable phenomenon is a magnetization reversal in the basal plane below $T_D = 20$ K for field-cooled system. Hence, Sr$_3$Ir$_2$O$_7$ has anomalous *diamagnetic* response, with the magnetization pointing opposite to the magnetic field as shown in Figure 5.13.

Although there is no theoretical explanation available for the magnetization reversal, this behavior is believed to be primarily driven by spin-orbit coupling [25], once again,
emphasizing the importance of spin-orbit coupling in this class of materials. Nevertheless, the specific heat has a weak but well defined anomaly corresponding to $T_C$ as shown in Figure 5.14. This is despite the fact that phonon contribution $\sim \beta T^3$, where $\beta$ value yields a Debye temperature $\theta_D$ of 310 K, predominates, thus often masking phase transitions at high temperatures. Also the resistivity data shown in Figure 5.15 displays simultaneous magnetic anomalies at both $T_C$ and $T_D$ along both $a$-axis $\rho_a$ and $c$-axis $\rho_c$.

![Figure 5.14: Specific heat $C(T)$ as a function of temperature for single crystal Sr$_3$Ir$_2$O$_7$. Inset: Enlarged $C(T)$ near the Curie-temperature $T_C$](image)

Figure 5.15 displays the thermoelectric power for both $a$-axis $S_a$ and $c$-axis $S_c$ is weakly temperature-dependent and small ($25 - 30 \mu$V/K) above $T_C$, but as temperature decreases, both $S_a$ and $S_c$ rises sharply near $T_C$ and peak near 150 K. This reveals a few interesting aspects in Sr$_3$Ir$_2$O$_7$. The positive value of $S$ indicates that charge carriers are primarily holes, which can be qualitatively explained by the $c$-axis elongation that lifts the degeneracy in $t_{2g}$ orbitals, resulting in the $d_{xy}$ orbital slightly higher than the $d_{yz}$ and $d_{xz}$. Due to a large crystal field the system is in low spin state so that the lower $d_{yz}$ and $d_{xz}$ orbitals are fully populated with four of five $d$ electrons and the $d_{xy}$ orbital with one only, thus leaving a hole. It is this hole that is responsible for the positive $S$. Secondly, the sharp feature near $T_C$ mirrors the onset in resistivity near $T_C$, where the system becomes more insulating with decreasing temperature. Since thermoelectric power probes the derivative of the density
of states, the drastic behavior near $T_C$ clearly indicates the change of scattering rates in different bands and a gap opening corresponding to the weak ferromagnetic transition. Thirdly, the temperature derivatives of thermoelectric power and resistivity are similar, that is, $dS/dT \sim d\rho/dT$, over a wide temperature range (see Figure 5.16). This is unusual because $dS/dT \sim d\rho/dT$ usually occurs in the vicinity of magnetic ordering temperature. This characteristic observed here implies that the leading temperature dependences of $S$ and $\rho$ are the same over a wide range of temperature. Another puzzling aspect is the reversed anisotropies of thermoelectric power and resistivity below $T_C$, for instance, $S_a (150)$ K = 210 $\mu$V/K > $S_c (150)$ K = 90 $\mu$V/K, but $\rho_a < \rho_c$, or $\rho_c/\rho_a \sim 7$. This behavior has been verified in four different crystals. It may not be entirely coincident that the magnetic ordering along the $c$-axis seems never fully established as shown in Figure 5.13 and as reported in [25]. Of all the complex phenomenon exhibited by Sr$_3$Ir$_2$O$_7$, one is particularly intriguing, that is, the magnetic ordering at $T_C$=285 K in $\chi_a(T)$, although weak, represents a robust phase transition strongly correlated with $S(T)$, $C(T)$ and $\rho(T)$. Considering Sr$_2$IrO$_4$ is the closest neighbor of Sr$_3$Ir$_2$O$_7$, it is particularly striking when such a correlation is absent in Sr$_2$IrO$_4$ and indicates to a profound dimensionality dependence in the layered iridates.
Figure 5.16: Thermoelectric power $S(T)$ as a function of temperature for $a$- and $c$-axis for Sr$_3$Ir$_2$O$_7$. Inset: $dS/dT$ and $d\rho/dT$ vs $T$ to illustrate $dS/dT \sim d\rho/dT$. 
CHAPTER 6: CONCLUDING REMARKS

6.1 Summary

In this work, I aimed to study the structural, thermodynamic and transport properties of the 4\textit{d} layered ruthenates - Sr$_4$Ru$_3$O$_{10}$, impurity doped bilayer Ca$_3$Ru$_2$O$_7$ and 5\textit{d} layered iridates with focus on Sr$_2$IrO$_4$. It is clearly evident from the data and discussions presented in Chapter 4 and Chapter 5 that the 4\textit{d} and 5\textit{d} electron systems provide an indispensable insight into the understanding of the strongly correlated electron physics. For these materials, both the larger spatial extend of \textit{d} orbitals and stronger spin-orbit coupling reveal a rich, often unexpected and intriguing variety of physical phenomena. On the one hand, the more spatially extended orbitals lead to larger bandwidths $W$ and smaller on-site Coulomb interaction and Stoner parameter. On the other hand, the more extended active orbitals make it more likely for itinerant physics to be important and stronger spin-orbit effects lead to novel states, for instance, in Sr$_2$IrO$_4$.

The magnetization, resistivity and specific heat results presented in Chapter 4 for pure Sr$_4$Ru$_3$O$_{10}$ and impurity doped Sr$_4$Ru$_3$O$_{10}$ are not characteristic of any obvious ground state and points to a delicate balance between fluctuations and order. Sr$_4$Ru$_3$O$_{10}$ is host to interesting phenomena such as quantum oscillations, tunneling magnetoresistance, unusually low temperature specific heat as discussed in section 4.3, and strong spin-lattice coupling, section 4. The key feature pertaining to this system is the borderline magnetism, see section 4.1.3. Sr$_4$Ru$_3$O$_{10}$ displays spontaneous ferromagnetism along the $c$-axis (perpendicular to the layers), while for magnetic field within the $ab$-plane it features a pronounced peak in the magnetization and a first order metamagnetic transition shown in section 4.1.3. The ferromagnetism along the $c$-axis indicates that the Stoner criterion is satisfied, $Ug(E_F) \geq 1$, where $U$ is an exchange interaction and $g(E_F)$ the density of states at the Fermi surface.

The response to a field in the plane, however, is strikingly similar to Stoner enhanced paramagnetism and metamagnetism with $Ug(E_F) < 1$. The instabilities and the anisotropy may arise from the two-dimensional Van Hove singularity (logarithmic divergence) close to the Fermi level in conjunction with the coupling of the spins to the orbital states of Ru$^{4+}$. This also seem evident from La doping on Sr$_4$Ru$_3$O$_{10}$ discussed in section 4.2.2. The coexistence of the interlayer ferromagnetism and the intralayer metamagnetism makes
Sr$_4$Ru$_3$O$_{10}$ crucially different from Sr$_3$Ru$_2$O$_7$, where spontaneous ferromagnetism is absent. Itinerant ferromagnetism and metamagnetism depend sensitively on $U$ and $g(E_F)$, and are not expected to coexist. But Sr$_4$Ru$_3$O$_{10}$ under La and Ca doping defiantly shows the coexistence of both as discussed in section 4.2.2. The structural distortions caused by Ca doping leads to larger anisotropy, however, magnetism in Sr$_4$Ru$_3$O$_{10}$ turns out to be highly sensitive to the band filling (La doping) than to structural distortions.

The low temperature experimental results for Sr$_4$Ru$_3$O$_{10}$ in section 4.3 reveal a host of anomalous properties, namely, a growing specific heat $C$ with increasing magnetic field $B$, a $\log(T)$ contribution to $C/T$ at low temperatures, an abrupt jump and anomaly in $C/T$ at $B_c = 2.90$ T and $B_c = 7$ T for $B \parallel ab$-plane and $B \parallel c$-axis, respectively, and corresponding changes in the power law of the resistivity between $T^2$ and $T^{3/2}$. The novelty of this work lies in the fact that the quantum fluctuations occur in a system where both interlayer spontaneous ferromagnetism and intralayer field-induced metamagnetism coexist, a feature distinctively different from all other systems involving a Quantum Critical Point.

It would be helpful to further study the unusual ground state in Sr$_4$Ru$_3$O$_{10}$ by applying pressure along $c$-axis and in the $ab$-plane. In light of the above results, it might further reveal the nature of the highly anisotropic properties in this system. Preliminary studies on Cr doped Sr$_4$Ru$_3$O$_{10}$ reveal a spin-valve like behavior similar to that seen in impurity doped Ca$_3$Ru$_2$O$_7$, see section 4.3. It will be interesting to study this phenomenon in detail.

The bilayer Ca$_3$Ru$_2$O$_7$ is a truly unique material as seen in the physical properties it shows. It is highly anisotropic as seen in the magnetic and transport properties, it undergoes an antiferromagnetic (AFM) phase transition at $T_N = 56$ K in low fields, followed by a Mott-like metal-insulator transition at $T_{MI} = 48$ K. As a result of strong spin-orbit coupling, an external magnetic field $B$ leads to novel magnetoresistive properties including Shubnikovde Haas oscillations within a partially-gapped Mott state, and oscillatory magnetoresistance that is periodic in magnetic field $B$ (not $1/B$). In particular, colossal magnetoresistance (CMR), which is driven by ferromagnetism in all other known materials, is attained in Ca$_3$Ru$_2$O$_7$ by avoiding a FM state, hinting at a novel mechanism based upon orbital ordering within a highly anisotropic, antiferromagnetic metallic (AFM-M) state.

Ca$_3$Ru$_2$O$_7$ is then a truly unique material for further study and indeed under impurity doping reveals spin valve behavior in bulk single crystals as presented in section 4.4. Thus far, the spin valve behavior has only been realized in magnetic multilayers and heterostruc-
ture. Cr doping on Ru site in Ca$_3$Ru$_2$O$_7$ first revealed the spin-valve behavior in bulk single crystals. Interestingly, Ba doping on Ca site also reveal a robust spin valve behavior. Spin valve effect is also seen in Sr doping albeit weaker than Ba, which indicates the effect of ionic size on the variation of exchange coupling and hence the coercive strength of the different layers. Impurity substitution apparently alters the density of states in the AFM-M state and creates soft and hard bilayers having antiparallel spin alignments that induce spin-valve behavior for the magnetic field parallel to $a$-axis.

Chapter 5 presented the structural, thermodynamic and transport properties of layered iridates Sr$_{n+1}$Ir$_n$O$_{3n+1}$ ($n = 1, 2$ and $\infty$). Due to the most extended orbitals in the $d$ block, the 5$d$ systems are expected to show minimal correlation. However, the change of bandwidth with increasing $n$ (number of Ir-O layers) show a distinct change in the properties of this series as seen in the experimental data presented in Chapter 5. This is also supported by the results from optical spectroscopy and first principle calculation. An insulator-metal transition driven by the bandwidth change is observed as $n$ increases: Sr$_2$IrO$_4$ showed a finite size optical gap; for Sr$_3$Ir$_2$O$_7$ the optical gap is almost zero and the gap finally disappeared for SrIrO$_3$. Sr$_3$Ir$_2$O$_7$ is a magnetic insulator with a transition to weak ferromagnetism at $T_C=285$ K. This is reflected in the the thermopower, specific heat and resistivity measurements. However, for Sr$_3$Ir$_2$O$_7$ sister compound Sr$_2$IrO$_4$ no signature of $T_C=240$ K is found in the transport and thermal measurements. This absence of correlation in Sr$_2$IrO$_4$ is rather remarkable. A dominant spin-orbit coupling in Sr$_2$IrO$_4$ has a novel $J_{eff} = 1/2$ state and a novel Giant Magnetoelectric effect that is not dependent on the magnetization.

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BIBLIOGRAPHY


125
[43] Q. Huang, J. Soubeyroux, O. Chmaissem, I. Sora, A. Santoro, R. Cava, J. Krajewski,
and W. P. Jr. Neutron powder diffraction study of the crystal structures of and at
room temperature and at 10 k. *Journal of Solid State Chemistry*, 112(2):355 – 361,
1994.

reversal and memory in a multiferroic material induced by magnetic fields. *Nature*,

in $\text{Sr}_3\text{Ru}_2\text{O}_7$: Fermi liquid close to a ferromagnetic instability. *Phys. Rev. B*,

[46] M. Iliev, V. Popov, A. Litvinchuk, M. Abrashev, J. Bckstrm, Y. Sun, R. Meng, and
C. Chu. Comparative raman studies of $\text{Sr}_2\text{RuO}_4$, $\text{Sr}_3\text{Ru}_2\text{O}_7$ and $\text{Sr}_4\text{Ru}_3\text{O}_{10}$. *Physica

instabilities
Effects of Zero-Point Fluctuations. *Journal of the Physical Society of Japan*,


$(\text{La}_{0.5}\text{Na}_{0.5})\text{RuO}_3$ and $(\text{Ca}_{1-x}\text{A}_x)\text{RuO}_3$ (A=Mg, Sr). *Journal of the Physical


et al. Novel $j_{\text{eff}} = 1/2$ mott state induced by relativistic spin-orbit coupling in .

\[ J_{\text{eff}} = \frac{1}{2} \text{ mott state induced by relativistic spin-orbit coupling in } \text{Sr}_2\text{IrO}_4. \]  


[58] O. Korneta, T. Qi, S. Chikara, S. Parkin, L. De Long, P. Schlottmann, and G. Cao. Electron-doped \( \text{Sr}_2\text{IrO}_4-\delta \) \( 0 \leq \delta \leq 0.04 \) : Evolution of disordered \( j_{\text{eff}} = 1/2 \) mott insulator into an exotic metallic state. *Physical Review B*, 82(11):115117, 2010.


transition and correlated metallic state in 5d transition metal oxides $\text{Sr}_{n+1}\text{Ir}_n\text{O}_{3n+1}$ ($n = 1, 2, \text{ and } \infty$). *Phys. Rev. Lett.*, 101:226402, Nov 2008.


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5. G. Cao, V. Durairaj, S.Chikara, S. Parkin and P. Schlottmann, Partial antiferromagnetism in spin chain Sr\(_5\)Rh\(_4\)O\(_{12}\),Ca\(_5\)Ir\(_4\)O\(_{12}\) and Ca\(_4\)IrO\(_6\), \textit{Phys. Rev. B} \textbf{75}, 134402 (2007)

7. V. Varadarajan, S. Chikara, V. Durairaj, X.N. Lin, G. Cao, J.W. Brill Specific heat of (Ca$_{1-x}$Sr$_x$)$_3$Ru$_2$O$_7$ single crystals, Solid State Communications **141**, 402 (2007)


11. G. Cao, S. Chikara, E. Elhami, X.N. Lin and P. Schlottmann, From Itinerant Ferromagnetism to Insulating Antiferromagnetism: a Magnetic and Transport Study of single Crystal SrRu$_{1-x}$Mn$_x$O$_3$ ( 0 $\leq$ x $<$ 0.60 ), *Phys. Rev. B* **71**, 035104 (2005)


14. G. Cao, S. Chikara, X. N. Lin, E. Elhami and V. Durairaj, High-Temperature
