2006

A SYSTEMATIC STUDY ON THE THERMODYNAMIC AND TRANSPORT PROPERTIES OF LAYERED RUTHENATES

Xiunu Lin
University of Kentucky, xlin2@uky.edu

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ABSTRACT OF DISSERTATION

Xiunu Lin

The Graduate School
University of Kentucky
2007
A SYSTEMATIC STUDY ON
THE THERMODYNAMIC AND TRANSPORT PROPERTIES OF
LAYERED RUTHENATES

ABSTRACT OF DISSERTATION

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

By

Xiunu Lin
Lexington, Kentucky

Director: Dr. Gang Cao, Professor of Physics and Astronomy
Lexington, Kentucky
2007
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ABSTRACT OF DISSERTATION

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In the 4d transition metal oxides, the extension of the 4d orbitals leads to comparable and thus competitive kinetic and coulomb energies. As a result, small perturbations can induce significant changes in their physical properties, giving rise to a class of exotic phenomena that are rarely found in other materials. The ruthenates materials with readily tunable parameters open an avenue to study the strong electronic correlation in the rarely explored territory: the 4d transition metal oxides.

The bilayered system, \( \text{Ca}_3\text{Ru}_2\text{O}_7 \), belongs to the Ruddlesden-Popper series in which the physical properties are intimately linked to the lattice degrees of freedom. \( \text{Ca}_3\text{Ru}_2\text{O}_7 \), with its quasi-2D and severe structure distortion, is believed to be placed in a unique position at which the role of orbital degrees of freedom is highlighted. The system displays strikingly different behaviors when the field is applied along different crystalline axes. A ferromagnetic (FM) state with full spin polarization is achieved for \( B \parallel a \)-axis, but colossal magnetoresistance is realized only for \( B \parallel b \)-axis by avoiding the ferromagnetic state. In addition, for \( B \) rotating within the \( ac \)-plane, slow and strong SdH oscillations periodic in \( 1/B \) are observed for \( T \leq 1.5 \) K in the presence of metamagnetism. For \( B \parallel [110] \), oscillations are also observed but periodic in \( B \) (rather than \( 1/B \)) and persist up to 15 K. These properties together with highly unusual spin-charge-lattice coupling near the Mott transition (48 K) are driven by the orbital degrees of freedom.

Complex thermodynamic properties are also observed in the other ruthenates system such as \( \text{Sr}_4\text{Ru}_3\text{O}_{10} \) and \( \text{Pr}_3\text{RuO}_7 \). The \( \text{Sr}_4\text{Ru}_3\text{O}_{10} \) is a triple-layered system that shows a dedicate balance between fluctuations and order. Besides the anomaly at \( T_C = 102 K \), anomalous behavior at low temperatures are also observed in the thermal study, indicative of an unusual magnetic order in this material. The \( \text{Pr}_3\text{RuO}_7 \) shows one-dimensional structure with zig-zag chain of corner sharing \( \text{RuO}_6 \) octahedra running in parallel with the rows of edge-shared \( \text{PrO}_8 \) pseudo-cubes. Magnetic and thermal properties studies on its single crystals indicate that the exchange interaction is strongly anisotropic. A Schottky-type anomaly at low temperature suggests that the “ordered” chain \( \text{Pr} \) ions are still sensitive to a crystal field.
KEYWORDS: Transition Metal Oxides, Ruthenates, Quantum Oscillations, Colossal Magnetoresistance, strong electronic correlation

Xiunu Lin

March, 2007
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By
Xiunu Lin

Director of Dissertation: Dr. Gang Cao
Director of Graduate Studies Dr. Thomas H. Troland

March, 2007
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Dedicated to my Mother Liping Huang

献给母亲黄丽萍
ACKNOWLEDGMENTS

My first, and most earnest, acknowledgement must go to my advisor, Dr. Gang Cao. His support, guidance, and encouragement in the last three years have allowed me to develop experimental skills and to build up knowledge through conducting cutting edge researches at the University of Kentucky and national laboratories. In addition, his passion and enthusiasm for material science research have inspired me and lifted me up to a level higher than I could have imagined. In every sense, none of this work would have been possible without him. I am indebted to him more than he knows.

My special gratitude goes to Dr. Joseph Brill for his enlightened discussions, his expertise, and his beneficence. Without his insightful advice and his trust in my research capability, it could have been more difficult for me to struggle through this Ph. D. training.

There are numerous others that have assisted me in so many ways during my work at the University of Kentucky. In particular, I would like to thank Dr. Kwok-Wai Ng for introducing me to the field of condensed matter physics. I also want to thank my committee members Dr. Michael Cavagnero, Dr. Nancy Levenson, Dr. Stephen Holmes, and Dr. Bruce Hinds for their time and support in my final defense. Many thanks also go to the fellow graduate students in the department of Physics and Astronomy. Particularly, I would like to thank Vinobalan Durairaj, Esmat Elhami, Shalinee Chikara, and Angela Douglass for their helps and their sincere friendships.

I would like to thank Dr. Jack Crow, the preceding director of the National High Magnetic Laboratory, for inviting me to work in his lab in Tallahassee for three months. This experience has greatly enriched my experimental skills and knowledge in condensed matter physics. I also owe a debt of gratitude to my high school teacher Mengling Lin in China for his excellent instruction, which has inspired my interest in physics since then;

My deepest and most heartfelt thanks go to Paul. H. Xiong for always being there with me in times of struggle and joy. Without his continuous understanding, encouragement, and loving support, I could never be able to finish this work.
This dissertation is dedicated to my mother in China. Her unlimited love and faith in me is the original driving force that has kept me fighting toward this point of my life.
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Chapter 1  Introduction

The technology innovations based on electronic, optical, and magnetic materials have fundamentally changed the way we live. These technology revolutions would be impossible without continuous increase in our scientific understanding of materials, phenomena, and the processing and synthesis of these materials. Search for new materials is still the fundamental driving force for the continuous flourishing of modern technology.

In the last decade, extensive and intensive search for novel electronic materials has been carried out mainly in the 3\textit{d} Transition Metal Oxides (TMO), including the cuprates and manganites. This class of materials have created great sensation in condensed matter physics by exhibiting exotic electronic and magnetic phenomena, such as high T\textsubscript{C} superconductivity and Colossal Magnetoresistance (CMR). These phenomena are closely related to the strong electron-electron (\textit{el-el}) correlation, which originates from the on-site Coulomb repulsion between the localized 3d-orbitals electrons. The 4\textit{d} transition metal atoms have more extended orbitals compared with the 3\textit{d}-counterparts, and were thought to have smaller and insignificant \textit{el-el} correlation effects. Hence relatively less attention was paid to this class of materials.

However, with the observations of numerous intriguing properties, such as unconventional superconductivity\textsuperscript{3}, metal-insulator transition\textsuperscript{4,5}, and non-Fermi liquid behavior\textsuperscript{6}, new attentions are stimulated to the 4\textit{d} TMO. By investigating physical parameters such as \(\Delta_{pd}\) (charge transfer energy), \(U\) (Coulomb repulsion energy), and \(10D_q\) (crystal field splitting energy), it is found that although the \(U\) values of 4\textit{d} TMO are smaller than those of 3\textit{d} TMO, their \(\Delta_{pd}\) and \(10D_q\) values are relatively larger\textsuperscript{7}, so that the more extended 4\textit{d}-orbitals electrons have weaker on-site Coulomb repulsion energy, \(U\), (\(-1\) to \(2\text{eV}\)) but stronger hybridization energy, \(W\), (\(-2\) to \(5\text{eV}\)) with the neighboring O 2\textit{p}-orbitals. When the ratio of \(W/U\) is comparable, the competition between these two energies gives rise to rich and complex phases for this class of materials. In addition, due to the small value of \(U\), the roles 4\textit{d}-orbitals become more important and the spin-orbit coupling is then significant\textsuperscript{8,9}. So far, relatively few quantitative studies have been carried out on the 4\textit{d} TMO series and our understanding of this class of materials remains at a qualitative level. Ruthenates, the
ruthenium oxides, is one of the few classes of materials that provide us with a rare opportunity to study the strong correlation in the 4d TMO.

The ruthenate system has aroused a lot of attention since the discovery of $p$-wave superconductivity in Sr$_2$RuO$_4$, consequently inspiring great enthusiasm in exploring the Ru-based Ruddlesden-Popper (RP) series. This series has the general formula (Sr, Ca)$_{n+1}$Ru$_n$O$_{3n+1}$, with $n$ being the number of the coupled layers in one unit cell. They adopt layered perovskite structure (ABO$_3$) with the RuO$_6$ octahedra corner-share with each other to form planes, resembling a structure similar to that of the cuprate superconductors. In this series, as $n$ progresses from 1 to $\infty$, the number of nearest-neighbor RuO$_6$ octahedra increases from four to six, representing a systematic enhancement of the structure dimensionality. The series are then found to have an astonishing and distinctive dimensionality dependence of all physical properties due to the strong magnetoelastic interactions between the Ru ions. For example, as $n$ progresses from 1 to $\infty$, the antiferromagnetic ordering is systematically suppressed for the Ca$_{n+1}$Ru$_n$O$_{3n+1}$ system. In addition, since the ionic size of Ca$^{2+}$ ($r_{Ca}^{2+}=1.00\text{Å}$) is smaller than that of Sr$^{2+}$ ($r_{Sr}^{2+}=1.18\text{Å}$), replacing Sr with Ca generally induces structure distortion, leading to smaller bandwidth. This structural distortion induced by replacing Ca$^{2+}$ with Sr$^{2+}$ gives us extra choice to explore this class of materials. The systematic variances of properties with dimensionality and structure distortion make the RP series an excellent system to study the interplay between lattice, orbital, charges, and spin degrees of freedom in the 4d TMO.

Ca$_3$Ru$_2$O$_7$ ($n=2$) is a bilayered system intermediate between the Mott insulating antiferromagnet Ca$_2$RuO$_4$ ($n=1$) and the metallic paramagnet CaRuO$_3$ ($n=\infty$). It features a wide range of phenomena that are among the most important and interesting topics in the field of Condensed Matter Physics: Mott metal-insulator transition, metamagnetic transition, CMR, and Shubnikov-de Hass oscillations. The on-site Coulomb interaction $U$ is believed to be comparable with the kinetic energy $W$. As a result, any small perturbation such as external magnetic field can readily tune the physical properties in the ground state. This system has severe structure distortions due to the small ionic size of the Ca$^{2+}$, resulting in a rotation (on the $ab$ plane) and tilting (away from the $c$-axis) of the RuO$_6$ octahedra. The tilting projects primarily along the $bc$ plane rather than the $ac$ plane, leading to a strong anisotropy between the $a$- and $b$-axis. At low magnetic field, the system undergoes antiferromagnetic ordering at $T_N=56$K, followed by an abrupt metal-insulator transition at $T_{\text{MI}}=48$K.
The antiferromagnetic metallic phase intermediate between $T_N$ and $T_{MI}$ is rare for an undoped compound at ambient pressure. The isothermal magnetization measurement shows that for fields applied along the $b$- and $c$-axis, the system remains at antiferromagnetic state. But when a field $B$ of 6T is applied along the $a$-axis, the system shows a metamagnetic transition with a saturation moment of around 1.8$\mu_B$/Ru, indicating that more than 85% of the spins are polarized. This transition drives the system from the antiferromagnetic state to a ferromagnetic state, resulting in a resistivity reduction of around one order of magnitude. The strong coupling between lattice, spin, and orbital degrees of freedom is predominantly reflected in the properties of Ca$_3$Ru$_2$O$_7$, as revealed by the Raman studies. It was found that the metal-insulator transition at $T_{MI}$ is accompanied by a softening and broadening of the out-of-phase oxygen phonon mode. Ca$_3$Ru$_2$O$_7$ is certainly an important system that provides a precious opportunity for studying the strongly correlated interaction which is the central feature of the transition metal oxides.

Previous work on Ca$_3$Ru$_2$O$_7$ has revealed strong anisotropy in structural, magnetic, and transport properties of this system, showing intimate couplings between lattice, spin, and charge. However, the richness and complexity displayed in these properties indicate that the ground state of this system is still far from well understood. The study presented in this dissertation is then dedicated to further exploring its properties in great details. It was found that although the ferromagnetic state can reduce the $\rho_c$ (interplane resistivity or resistivity measured with both voltage and current running along the $c$-axis) by one-order of magnitude at 6T when $B||a$ (the magnetic easy-axis), the CMR with $\rho_c$ reduced by three-order of magnitudes is achieved only when $B||b$ (the magnetic hard axis) at 15T. It turns out that the ferromagnetic state is not the favorite state for electron hopping, making the Ca$_3$Ru$_2$O$_7$ a unique system that is different from the traditional magnetic materials where the CMR is achieved by stabilizing a ferromagnetic state. Parallel study between the $M$ and $\rho_c$, together with the comparison between properties for $a$-axis and $b$-axis suggest that the CMR could be intimately related to the orbital degrees of freedom. In addition, the orbital degree of freedom is apparently associated with unusual quantum oscillations. These oscillations are slow and strong; with their frequency strongly depend on the orientation of the applied field. They are all periodic in $1/B$ and occur only in the presence of metamagnetism, indicating a close
correlation between the construction of the Fermi surface and the spin-polarization of the Ferromagnetic state. However, when $B$ is along the [110] direction, the oscillations are observed to be periodic in $B$ and can persist to temperatures as high as 15K. Our investigations reveal strong evidences for the involvement of orbital degrees of freedom that is essentially a driving force for all novel phenomena observed.

The dissertation is organized as follows.

Chapter 2, **Theoretical Background**, presents theoretical concepts relevant to issues discussed in this thesis such as Mott transition, magnetoresistance, and quantum oscillations.

Chapter 3, **Experimental Techniques**, presents details on the crystal synthesis using both flux and floating zone techniques, sample characterization using various experimental probes in this work.

Chapter 4, **Results and discussion**, presents a series of measurements over wide temperature and magnetic field ranges. The magnetic and transport properties are mapped for $B$ ($\leq 7$T) along the $a$-, and $b$-axis. A parallel study between the magnetic and resistivity behaviors, together with the comparison between $a$-axis and $b$-axis are presented for further discussion. The transport properties as a function of magnetic field are measured for field up to 45T and temperature down to 0.5K. This measurement reveals unusual Colossal Magnetoresistance (CMR) for $B||b$ and quantum oscillations for $B$ rotating within the $ac$ plane. Oscillations periodic in $B$ are observed for $B \parallel [110]$ direction and persist up to 15K. All the data are presented, and discussed in this section. The last two sections of this chapter are developed for the thermodynamic study of other layered ruthenates, $Pr_3RuO_7$ and $Sr_4Ru_3O_{10}$. Both systems show strong competition between exchange interactions, resulting in complex magnetic and thermodynamic properties. The specific heat measurements on both systems show corresponding anomalies at the onset of magnetic ordering (102K for $Sr_4Ru_3O_{10}$ and 56K for $Pr_3RuO_7$). The experimental results are analyzed and then compared to the theoretical values. Detailed discussion about their thermodynamic properties can be found in this chapter.

Chapter 5: **Conclusions**, Summary of the phenomena observed on the ruthenates studied.
Chapter 2 Theoretical Background

2.1 Electronic correlations

After almost a century’s effort, the physical properties of some solids have been successfully explained with an independent particle picture, in which the interactions between the electrons can be ignored or well represented by an average potential. The macroscopic behavior of a system can then be understood starting from a detailed description of the individual particles and the way they interact. Band theory is one of the approximations that are built based on this picture. It provides a conceptually simple explanation for electron transport. This approximation has proven remarkably accurate for estimating electron flow in silicon chips and many other materials.

However, there are materials such as CoO whose transport behavior disobey the prediction from this theory. Mott insulator is one of these types of materials. They are fundamentally different from the conventional (band) insulators. The conductivity of the latter is blocked by the Pauli Exclusion principle. In a Mott insulator, the conductivity is blocked instead by the electron-electron Coulomb repulsion, or strong electronic correlation. To minimize the Coulomb repulsion energy, electrons have to stay away from each other as far as possible and tend to be localized. As a result, the electrons can “see” each other and the statistic correlations between the motions of individual electrons are important. In such cases, an independent particle picture is inappropriate and a many body model has to be considered.

Materials with strong electronic correlation generally display a broad range of interesting phenomena that show departure from the standard model of solids, such as metal-insulator transition, colossal magnetoresistance (CMR), and high $T_c$ superconductivity. Transition metal oxides (TMO) are this kind of materials that feature electronic correlation. These properties arise mainly due to the d-orbital wave functions which are confined more closely to the nucleus than for s or p states of comparable energy. As a result, the overlap between the transition metal ions and the neighboring metal ions is small and the electrons in this system can move only through the hybridization with oxygen. The electronic correlation usually involves the
interactions between the charge, spin, lattice, and orbital degrees of freedom in a nonlinear, synergetic manner, leading to an intrinsic complexity such as the co-existence of several competing states.

Theoretically, it has always been difficult to deal with strongly correlated electron systems. After several decades of efforts, even the basic properties of the strongly correlated electron system, such as linear temperature dependence of resistivity, are still beyond our understanding. The difficulty arises mainly from the wide range of energy scales involved and many competing orderings and instabilities that are associated with small differences in energy. One of the frontiers in strongly correlated electron physics, Dynamical Mean Field Theory (DMFT), is to develop new concepts and new computational methods to describe electronic states between the itinerant and localized states. DMFT has led to some significant advances in our understanding of strongly correlated systems. Different from the static mean field theory which could not describe the strong electronic correlation between the electrons, the DMFT is able to treat the many-body system both in momentum-space and in real-space, thus capable of describing both the wave-like and particle-like characters of the strongly correlated electrons. The DMFT has been very successful in reproducing complicated physical properties in a variety of materials and it would continue to be one of the most powerful tools that help us to better understand complicated phenomena in TMO.

2.2 Mott metal-insulator transition

The mott metal-insulator transition (MIT) is the central strong correlation effect because it addresses directly the competition between the Coulomb repulsion energy and the kinetic energy. It occurs when an onsite Coulomb repulsion energy $U$ exceeds the electronic bandwidth $W$, leading to the breakdown of independent electron pictures.

There are a variety of transition metal oxides that were predicted to be conductor by band theory turning out in fact to be insulators. For example, according to the band theory, for a material to be insulating, it is necessary to have an even number of electrons per unit cell in order to make its band fully occupied or empty. On the other hand, with an odd number of electrons per unit cell, we will necessarily
have a partially filled band, and the material must be metallic. But the prediction of the band theory fails in a number of cases. One of the oldest known and the clearest example is provided by the transition metal oxide CoO. The outer shell of Co has the configuration 3d⁷4s² and the oxygen has 2s²2p⁴. The number of electrons per unit cell is then 15, an odd number. According to band theory, CoO should be a metal. But in fact, CoO is one of the toughest insulators we have ever known.

Nevill Mott and R. Peierls then proposed that the strong correlations between electrons can be responsible for the insulating character of these materials. The theory they proposed addresses directly the competition between kinetic energy and Coulomb repulsion energy (or correlation energy) and is the central issue of strong correlation electrons. Different from the conventional insulators which can be predicted by band theory, a Mott insulator arises due to the correlation between electrons instead of incomplete filling of the d-bands.

The Hubbard model is one of the simplest approximations that describe the Mott insulator. It is built on two assumptions. First, only a single band has to be taken into account; second, the interaction is purely local, or in other words, we will consider only the on-site or intra-atomic Coulomb interaction between electrons. The Hubbard model relies on the tight-binding model to describe the itinerant tendency for electrons to jump between neighboring atoms, and also considers the localized tendency with on-site electron-electron repulsion that is not usually considered in regular band theories. These two tendencies, represented by W and U, compete to determine whether the materials is conducting or insulating and will drive the materials through Mott transition from a metallic state to insulating state. The Hamiltonian for this model is then expressed as the sum of the band energy and Coulomb interaction energy, representing the itinerant tendency and the localization tendency. The Hubbard gap is usually defined as the difference between U and W. The two bands that are separated by the Hubbard gap are called the “upper Hubbard band” and “lower Hubbard band” respectively. These two sub-bands may look like the valence and conduction band of a semiconductor, but in fact they are not the same. For a valence of a conduction band, each band can hold up to 2L (L is the number of the lattice sites) electrons, while the Hubbard sub-bands can contain not more than L electrons. The splitting into two Hubbard bands is a correlation effect that could not be described by independent electron theories.
Figure 2.1 shows how the local density of states varies as the ratio of U/W increases. For independent electrons without correlation effect, the corresponding density of state (DOS) is a half filled ellipse with the Fermi energy lies in the middle of the band (see Figure 2.1.a). As the Coulomb repulsion joins in the interacting picture and gives the system a weak correlation, the ratio U/W increases from zero and the bandwidth becomes narrower. In this case, the electrons can be described as quasiparticle and its DOS retains the metallic characteristic (see Figure 2.1.b). For strong correlated system with large U/W ratio (see Figure 2.1.c), the spectrum is characterized by a three-peak structure: the lower and upper Hubbard bands and the quasiparticle peak. The Hubbard bands extend away from the Fermi level due to the hopping of the electrons and the quasiparticle peak centers near the Fermi level. The Mott metal-insulator transition occurs when the correlation effect (or Coulomb repulsion) is sufficiently strong to cause a band gap between the Hubbard bands with the vanishing of the quasiparticle peak, making the system transfers from Figure 2.1.c to Figure 2.1.d.

Figure 2.1. Adopted from the journal article “strongly correlated materials: insight from dynamical mean-field theory” published in PHYSICS TODAY, march 2004. (Quoted from ref. 45)
Nevertheless, not all the unpredicted insulators can be treated with Hubbard band model. According to Zaanen, Sawatzky, and Allen’s picture\textsuperscript{51}, if the energy of the oxygen 2\textit{p} band is higher than that of the Hubbard lower band, then \( \Delta_{pd} \), (the energy for charge to transfer between different atoms (oxygen and transition metal atoms for the case of TMOs)), is smaller than \( U \) (the Coulomb repulsion energy between the Hubbard sub-bands). In such case, the charge excitation, or the elevation of electrons/holes in energy level, is between the transition metal atom and the oxygen atom. The system should then be treated in the charge transfer regime with an ionic model\textsuperscript{2, 52}. On the other hand, if the energy of the Hubbard lower band is higher than that of the O 2\textit{p} band, then \( U > \Delta_{pd} \). The charge excitation is between the Hubbard sub-bands and the system can be treated with a Mott-Hubbard model. Ruthenates, compared with the early 3d TMO which are classified to be in the Mott Hubbard regime, have smaller \( U \) (\(~1.8\text{eV}\)) and larger \( \Delta_{pd} \) (\(~3.2\text{eV}\)) (for the case of SrRuO\textsubscript{3}) and should be treated with the Mott-Hubbard model as well\textsuperscript{7, 53, 54}.

Since the discovery of high temperature superconductivity in layered cuprates, the issue of the Mott transition in a quasi two-dimensional system has become especially important. Layered ruthenium oxides (Sr/Ca)\textsubscript{n+1}Ru\textsubscript{n}O\textsubscript{3n+1} are similar to the cuprates in terms of structure. The bandwidth \( W \) of this system can be well tuned by varying the dimensionality and the Sr/Ca ratio, giving rise to the different Mott parameter \( U/W \). Varying the transition element itself can induce a greater change due to the different ability of the transition elements to overlap with their surroundings. Dimensionality is another important parameter that is found to be effective in the alteration of \( W/U \) ratio\textsuperscript{2}. These factors are subtle and interweave with different kinds of couplings, making the study of the Mott transition even more challenging and interesting as well.

### 2.3 Crystal field and Jahn-Teller theorem

The correlation effect would not be so rich and complex without the involvement of the lattice degree of freedom\textsuperscript{14}. The structure configuration adopted by each system creates a corresponding crystal field through which lattice degree of freedom plays an important role in the correlation picture.
The Crystal field effect primarily arises from the electronic repulsion between the negatively charged electrons of the $d$-orbitals of the transition metal cations and the $p$-orbitals from oxygen ligands. The crystal field theory is mainly developed to describe how the ligands affect the $d$-orbital electrons’ energies. The electrons in a $d$-orbital that is closer to the ligands (larger overlap between $p$-$d$ orbitals) will have a higher energy than those further away (smaller overlap between $p$-$d$ orbitals) because they feel more repulsion. Thus, the $d$-orbitals will split in energy. It then follows that an important aspect of crystal field theory is the orientation of the $d$-orbital lobes with respect to the position of the surrounding oxygen ligands.

To be able to understand the crystal field effect, it is essential to have a clear picture of the shapes (angular dependence functions) of the $d$ orbitals. For the free transition metal atoms, there is a set of five degenerate $d$-orbitals: $d_z^2$, $d_{x^2}-y^2$, $d_{xy}$, $d_{xz}$, $d_{yz}$ as illustrated in Figure 2.2. The $d_{xy}$, $d_{xz}$, $d_{yz}$ orbitals are grouped together as $t_{2g}$ orbitals because their lobes all point away from the $x$, $y$, and $z$ axes. The $d_z^2$, $d_{x^2}-y^2$ orbitals are grouped together as $e_g$ levels because their lobes point along $x$, $y$, and $z$ axes. The crystal field crucially depends on the symmetry of the local environment. For transitional metal cations sitting in an octahedral environment with the oxygen ligands sitting at the points ($\pm r$, 0, 0), (0, $\pm r$, 0) and (0, 0, $\pm r$), the $t_{2g}$ orbitals with lobes pointing between the $x$, $y$ and $z$ axes will be decreased in energy because these orbitals have small direct overlap with the neighboring $p$-orbitals, whereas the $e_g$ orbitals with lobes pointing along the axes will be raised in energy because the orbitals have larger overlap with the $p$-orbitals. As a result, the originally fivefold degenerate $d$-orbitals split into two set of levels: the threefold $t_{2g}$ orbitals lowered in energy and the twofold $e_g$ orbitals higher in energy. In the case of a tetrahedral local environment, the lower energy levels will be the $e_g$ orbitals and the higher energy levels will be $t_{2g}$ orbitals.
Figure 2.2. Five d orbitals. In an octahedra crystal field, these fivefold degenerate orbitals are split into two $e_g$ orbitals ($x^2-y^2$ and $3z^2-r^2$) and three $t_{2g}$ orbitals ($xy$, $yz$, and $zx$).

The size of the crystal field splitting energy $10D_q$ between these two sets of energy level, $t_{2g}$ and $e_g$, depends on several factors: the nature of the metal ion, the metal’s oxidation state, and the arrangement of the ligands around the metal ion. How the spins fill these orbitals depends on the competition between the crystal field splitting gap $10D_q$ and the Coulomb repulsion energy $U$ (which determines the energy cost for two electrons to sit in the same orbital). For $10\Delta_q$ higher than $U$, the spins will doubly occupy the lower energy before filling the higher energy orbitals (low spin case or strong field case). On the other hand, if $10\Delta_q$ is smaller than the Coulomb repulsion energy, the spins will first singly fill all energy orbitals before filling any orbitals doubly (high spin case or weak field case). Take the Fe$^{4+}$ and Ru$^{4+}$ ions for example. They both loose four electrons and have four electrons in the outer orbitals. The Fe$^{4+}$ follow the high spin case and has $S=2$ because the splitting between $t_{2g}$ and $e_g$ is small ($10\Delta_q \sim 1.2$eV), whereas the Ru$^{4+}$ follow the low spin case and has $S=1$ because the splitting between $t_{2g}$ and $e_g$ is large ($10\Delta_q \sim 3$eV). In the system we
studied, the Ru$^{4+}$ shows low spin state with its four $d$ electrons filling in the $t_{2g}$ orbitals. In such case $S=1$, assuming that the orbital moment are all quenched.

For an ideal octahedra or tetrahedral structure, the $t_{2g}$ and the $e_g$ levels are 3-fold and 2-fold degenerate respectively. However, this degeneracy can be lifted when the ideal structure is distorted. It all occurs because in some circumstances it is energetically favorable for the crystal structure to spontaneously distort to save energy, as predicted in the Jahn-Teller Theorem. In this case, the electronic energy gain will balance the elastic energy cost due to this distortion. This effect further changes the local environment symmetry of the transition cations and thus disturbs the energy of relevant orbitals and can be very significant in the case of partially filled orbitals. For example, in the case of an collapsed octahedral along the c axes, the shortening of c-axes lattice parameter increases the overlap between $d_{yz}$ / $d_{xz}$ orbitals and the $p$-orbital but reduce the overlap between $d_{xy}$ orbital and the $p$-orbital, resulting in increased $d_{yz}$ and $d_{xz}$ energy level and decreased $d_{xy}$ energy level. The $t_{2g}$ level is no longer degenerate but splits into two levels: degenerate $d_{xz}$ and $d_{yz}$ levels and the $d_{xy}$ level as illustrated in Figure 2.3. The result is then reversed if the octahedron is elongated.

\[ \text{Figure 2.3. The effect of Jahn-Teller distortion on the } d \text{ orbitals in an octahedral environment.} \]
The orbital degeneracy is commonly lifted by the crystal field effect or by the Jahn-Teller distortion. In both cases the orbital order can be deduced from the crystal structure. As a result, the Jahn-Teller distortion is intimately coupled with orbital degrees of freedom in some materials.

2.4 Orbital physics

Electrons bounded to atoms can be characterized by three quantum states: spin, charge, and orbital. In the strongly correlated electron system, the internal degree of freedoms, spin and orbital, still survive and play important roles in determining their physical properties. The role played by the spin degree of freedom has been well recognized. For example, it is now understood that the exchange interactions between the spins give rise to rich and complex magnetic behaviors in TMO. However, the orbital degree of freedom is generally ignored and only a single correlated orbital is taken into consideration in most situations. In fact, there are many unusual phenomena that can not be explained if the orbital degree of freedom is not taken into account.

Classically, the orbital represents the shape of the electron cloud in solid as illustrated in Figure 2.2. When the crystal field is strong, the orbital degeneracy can be removed and the orbital degree of freedom is quenched. However, when the d-orbitals are left degenerate, the electrons can choose between different orbitals or linear combination of these orbitals. The role played by the orbital is then very similar to that of spin, because the electron chooses between spin up and spin down state or a combination of both. Theoretically, the possible choices of the orbitals can be treated as pseudospin. Since the space extension orientation for each d-orbital is different, the magnitude and sign of the interactions, such as electron transfer interactions and magnetic exchange interaction, between the neighboring electrons depend on which orbitals the electrons occupy. Thus, the orbital degree of freedom is activated and can play an important role in strongly correlated electron system through strong coupling with charge, spin and lattice dynamics.

The prototype case of orbital ordering is observed in the manganese oxides with perovskite structure. In these compounds, the spins may favor ferromagnetic interaction or antiferromagnetic interaction depending on which orbital they are occupying, resulting in a complex spin-orbital coupled state. For example in
LaMnO$_3$, the in-plane orbital ordering of alternative $(3x^2-r^2)/(3y^2-r^2)$ orbitals favors ferromagnetic ordering in-plane and antiferromagnetic ordering between the plane$^{59,60}$. However, the most fascinating features of the manganese is the colossal magnetoresistance phenomena that is relevant to the orbital ordering due to the Jahn-Teller distortion and double exchange due to the mixed valance states$^{61,62}$. It is found that the insulating phase that contribute to the CMR near $T_C$ may be related with the striped features which are induced by orbital ordering$^{54,63}$.

Besides the manganese, orbital physics are also observed in other transition metal oxides$^{64-67}$. Recently, evidence, both experimentally$^9$ and theoretically$^{53,68}$, has been mounting for the importance of orbital physics in the 4$d$ transition metal ruthenium in the perovskite structure. Generally for the ruthenates, the splitting energy between the $e_g$ and $t_{2g}$ orbitals is larger than the Coulomb repulsion energy. As a result, all the spins will be placed in the $t_{2g}$ orbitals and the $e_g$ orbitals is irrelevant in this system. For example, in Ca$_3$Ru$_2$O$_7$, the Ru$^{4+}$ has a d$^4$ configuration, so that there are three majority spin (either all spin up or all spin down) electrons and one minority spin electron in the $t_{2g}$ orbitals. For Ru$^{4+}$ sitting in a perfect octahedral, the minority spin is shared by all three degenerate $t_{2g}$ orbitals and the orbital degrees of freedom are then active$^{68}$. Take Sr$_{2-x}$Ca$_x$RuO$_4$ as an example: the ending member, Sr$_2$RuO$_4$, is believed to be a triplet superconductor$^{12}$. When the Sr is replaced by Ca, the superconductivity is rapidly destroyed and a paramagnetic phase appears. Further substitution of Sr by Ca drives the system into an antiferromagnetic insulator$^{69}$. This immediate phase transition is argued to be associated with a lattice distortion which leads to a complex ordering among $d_{xy}$, $d_{yz}$, and $d_{xz}$ orbitals$^{54}$.

Despite the intriguing phenomena that can be associated with the orbital ordering, so far there are no direct experimental tools to measure orbital ordering. However, evidence of orbital ordering/disordering can still be collected from Raman scattering study and resonant X-ray scattering studies$^{40,70}$.

2.5 Landau Level Quantization and Shubnikov de-Haas Effect

The Fermi surface is the surface of constant energy that separates the unfilled energy states and the filled ones in $k$ space. Mapping the Fermi topography is always
an important work in condensed matter physics not only because the shape of the Fermi surface yields important information about the magnetic, electronic and optical properties of the materials but also because it is an irreplaceable approach to test the validity of many models.

There are several techniques that can yield such Fermi surface information: anomalous skin effect, cyclotron resonance, magneto-acoustic geometric effect, the Shubnikov-de Haas (SdH) effect, the de Haas-van Alphen effect, or any techniques that probe parameters that are related to Fermisurface. All these techniques require high quality single crystals in order to reduce the Dingle temperature, a measure of scattering from defects. When the magnetic field applied on the crystals, the electrons will accelerate around an orbit on the plane perpendicular to the applied magnetic field. According to the Bohr-Sommerfeld relation \[ \oint P \cdot dr = (n + \gamma)2\pi\hbar \] (\( \gamma \) is the phase correction, \( \gamma = 1/2 \) for free electron), the orbits are quantized under the field in real space and the flux through any orbit is \( \Phi_n = (n + \gamma) \frac{2\pi\hbar c}{e} \). It then follows that the magnetic flux through the corresponding area in \( k \) space is \[ \Phi_n = \left( \frac{\hbar c}{e} \right)^2 \frac{1}{B} S_n = (n + \gamma) \frac{2\pi\hbar c}{e} \], hence \( S_n = (n + \gamma) \frac{2\pi e}{\hbar c} B \).

This implies that with the application of the magnetic field, the original quantization scheme is broken and the new states are now condensed on the quantized orbits. For example, at zero magnetic fields, the energy states are uniformly distributed under the Fermi level. When the magnetic field is applied to this system, the original energy states condensed to the new quantized orbits. The area between successive orbits is \( \Delta S = S_n - S_{n-1} = \frac{2\pi e B}{\hbar c} \). In Figure 2.4, at B=B_1, the total energy of the electrons is unchanged since equal amount of electrons have their energies raised and decreased at B_1. Increasing B from B_1 to B_2 will increase the total energy as well as the density of state (DOS) on the Fermi surface. Further increasing B from B_2 to B_3 leads to the evacuating of electrons from the highest level and the electrons then condenses to another new set of quantized orbits, resulting in the decrease of the total energy and the DOS on the Fermi level.
As the applied field $B$ increased, the quantized orbits expand and are then drawn out through the Fermi surface with the population of orbits on or near the Fermi surface oscillates. For two successive orbits ($n$ and $n+1$) that moving out through the same Fermi surface in $k$ space, $S = S_n = (n + \gamma) \frac{2\pi e}{h c} B_n$ and $S = S_{n+1} = (n + 1 + \gamma) \frac{2\pi e}{h c} B_{n+1}$, it then follows that $S \left( \frac{1}{B_{n+1}} - \frac{1}{B_n} \right) = \frac{2\pi e}{hc}$, indicating that equal increment of $1/B$ produces similar orbits and that the magneto oscillatory effect occurs with $1/B$ periodicity. It also follows that since $\Delta \left( \frac{1}{B} \right) = \frac{2\pi e}{hcS}$, the oscillation frequency $\Delta B$ is proportional to $S$, which is the extremal area of the Fermi surface normal to the direction of the applied magnetic field\textsuperscript{71}.

Figure 2.4. The quantization of Landau Levels under the application of magnetic fields. Here $B_1 < B_2 < B_3$. 
The oscillation of the DOS or the electronic energy results in several striking effects on the physical properties of the materials at low temperatures: the oscillation of resistivity, susceptibility, and heat capacity. The oscillation of resistivity with changing magnetic field is generally called Shubnikov de-Haas (SdH) oscillation. The temperature dependence of SdH-oscillation amplitude can be described by a Lifshitz-Kosevich relationship: 

\[ A_T = \frac{\pi \lambda}{\sinh \pi \lambda} \] 

Here \( \lambda = \frac{2 \pi k_B T}{\beta H} \), \( \beta = \frac{e \hbar}{m_c c} \) (\( A_T \): oscillation amplitude, \( m_c \), cyclotron effective mass, \( \hbar \), plank constant) \(^{72,73}\). Fitting this formula to the temperature dependence of oscillations amplitude, we can then calculate the cyclotron mass \( m_c \), an important parameter that is considered to be related to electron correlation. Generally, the strong correlation tends to enhance the effective mass of the quasiparticles as have been proved in the cuprates and heavy fermion system \(^{74,75}\). The effective mass can also be determined using the coefficient \( \gamma \) of the linear term in the low-temperature specific heat. Generally, these two values are expected to be equal. However, since the cyclotron effective mass \( m_c \) is defined by the main cyclotron resonance in SdH oscillations and the other cyclotron resonances with different frequencies may be neglected, the higher effective masses may not be detected by this technique \(^{76}\). The \( m_c \) and the \( m^* \) from the specific heat measurement may not be equal.

Another important information about the Fermi surface that can be extracted from the SdH oscillations is the relaxation time \( \tau(k) \), or the mean free time between collisions of charge carriers (electrons or holes) in metals. To exhibit oscillatory behavior, the tested sample should be pure so that the charge carriers have long enough mean-free-path to finish at least one cyclotron. Dingle temperature, \( T_D = \frac{\hbar}{4 \pi^2 k_B \tau} \), is inversely proportional to the relaxation time and is an important index for the purity of samples \(^{77}\). From the oscillations amplitude as a function of \( B^{-1} \), one can extract the Dingle temperature from the Dingle damping factor \( R_D = \exp(-14.69 \mu_c c / T_D B) \) (\( \mu_c = m_c / m_0 \)) \(^{14}\). The Dingle temperature for flux-grown \( \text{Ca}_3\text{Ru}_2\text{O}_7 \) single crystals varies from 1.5 to 3.0K, which is comparable to good organic metals with \( T_D \) varying from 0.5~3.5K.
2.6 Magnetoresistance

Many materials exhibit a change in their resistance on the application of a magnetic field. This phenomenon is generally referred to as magnetoresistance and usually estimated by a parameter - magnetoresistance ratio $MR = \frac{\Delta \rho}{\rho} = \frac{\rho(H) - \rho(0)}{\rho(0)}$, with $\rho(H)$ being the resistivity at high magnetic field, $H$, and $\rho(0)$ being the resistivity at zero field. The effect includes giant magnetoresistance (GMR), colossal magnetoresistance (CMR) and magnetic tunnel effect (TMR). The mechanisms of both behaviors are based on spin-dependent scattering.

The GMR behavior can be well explained by the two-current model. Based on this model, the scattering between the electrons with parallel spins is smaller compared with the scattering of the electrons with antiparallel spins. As illustrated in Figure 2.5, if the spins in both the first and second magnetic layers are aligned in the same direction with the application of a magnetic field, one of the spin channel (up spins) can easily pass through both of these two layers, thus the resistance is low. If the spins in these two magnetic layers are misaligned, then none of the spin channels can get through the structure easily and the electrical resistance is then high.

![Figure 2.5](image.png)

*Figure 2.5. The schematic graph for the two-current model. The resistance is small if the spins in the magnetic layers are parallel; resistance is large if the spins of the magnetic layers are antiparallel.*
GMR generally occurs in layered system with at least two ferromagnetic layers and one metallic intermediate layer. The magnetoresistance ratio, $M$, may be as much as 50%, and the effect is termed “GIANT”.\cite{79-81} GMR can also be observed in a junction between two ferromagnet layers in which electrons undergo quantum tunneling through a thin insulating layer. This type of magnetoresistance is usually specified as Tunneling Magnetoresistance (TMR)\cite{78}.

CMR generally refers to an extremely large magnetoresistive effect that was predominantly discovered in the manganese-based oxides with the perovskite structure. The resistance changes by orders of magnitudes particularly at temperatures near Curie temperature $T_C$\cite{82,83}. Different from GMR, CMR is generally associated with a resistivity peak in the vicinity of $T_C$\cite{84}. As the applied field $B$ increased, both the height and the width of the peak diminish. CMR observed in manganese is traditionally associated with a double exchange mechanism. The manganese exhibit mixed valence state $\text{Mn}^{3+}$ and $\text{Mn}^{4+}$. In $\text{Mn}^{5+}$, the electron in $e_g$ is itinerant and the electrons in $t_{2g}$ are localized. In $\text{Mn}^{4+}$, only $t_{2g}$ orbitals are occupied by 3 electrons and the $e_g$ is empty. Because of the Pauli principle, the electron in $e_g$ orbital can only delocalize into an orbital containing the same spin electron since it doesn’t involve spin flips which costs energy. The application of magnetic field helps to align the core spins and therefore decreases the resistivity, especially around $T_C$\cite{56}.

However, Recently there are discovery of CMR in some other compounds which can’t be well explained by the double exchange model\cite{30,85,86}. It was pointed out by many experimental evidences that the orbital degree of freedom is also involved in the CMR effect\cite{87}. However, due to the complexity, a clear understanding of this mechanism is still unsatisfied.

### 2.7 Magnetism

In an atom, when the electrons occur in pairs, the oppositely aligned spins will cancel each other in the magnetic field, thus there is no net magnetism. Alternately, atoms with unpaired electrons in their outer orbits will show net magnetism. For the TMO, since the outer orbital, $d$-orbital, has five levels to fill, the chance of getting unpaired electrons is higher. In addition, since the $d$-orbitals are contracted, the $d$-orbital electrons tend to show localized tendency which generally favors magnetism.
For these reasons, the TMO shows rich and complex magnetic behaviors like paramagnetism, antiferromagnetism, and ferromagnetism depending on the interactions between the unpaired local moments\textsuperscript{56}.

In pure paramagnetism, there is no interaction between the unpaired spins and the spins are randomly oriented in the absence of an external field, resulting in zero net moment\textsuperscript{56}. Materials showing paramagnetism generally exhibit small and positive susceptibility to the external field and are slightly attracted by it. Under relatively low magnetic field, paramagnetic materials show magnetic behavior that obeys the Curie-Weiss law $\chi = \chi_0 + \frac{C}{T - \theta}$. Here $\chi$ is the magnetic susceptibility which is defined as $\chi = M/H$ for fields within linear $M(H)$ dependence; $\chi_0$ is the temperature independent susceptibility and is expected to be proportional to the density of state at the Fermi Surface; $C$ is the curie constant and $\theta$ is the Curie-Weiss temperature. Generally, $C = (N\mu_{\text{eff}}^2)/3k$. Rearranging this formula gives $\mu_{\text{eff}} = \sqrt{(3kC/N)/2} = 2.82C^{1/2}$. Theoretically, $\mu_{\text{eff}}$ is expected to be $2[S(S+1)]^{1/2}\mu_B$, assuming all the orbital angular momentums are completely quenched.

For the unpaired electrons that do interact with each other, the spins can spontaneously anti-align or align, resulting in antiferromagnetism or ferromagnetism respectively. The Hamiltonian that describes the exchange interactions between these local moments is: $H = -\sum_{ij} J_{ij} S_i \cdot S_j + g\mu_B \sum_j S_j \cdot B$ (here $J$ is the spin exchange parameter which defines the magnitude of this interaction. The first term represents the Heisenberg exchange energy and the second term represent Zeeman energy)\textsuperscript{56}. If the exchange interaction is positive, $J>0$, the local moments tend to line up in a unique direction to minimize the exchange energy, and the system shows ferromagnetism for temperature lower than $T_C$, the Curie temperature. One of the characteristics of ferromagnetic materials is the existence of magnetic domains (or Weiss domains). Within the domains, the local magnetic moments align parallel with each other. But at longer range, the domains tend not to be aligned. In some ferromagnetic materials, the domains can be easily aligned by a small magnetic field ($\sim 10^{-6}$ T). Another important feature of the ferromagnetic materials is the hysteresis loop that is observed in the $M(B)$ plot. If an external field is applied to the ferromagnetic materials, the magnetization $M$ grows with the increase of magnetic field $B$ non-linearly and then achieves a limit values $M_s$, the magnetic saturation moment. When the applied field is
reduced to zero, the magnetization reduces to the remnant magnetization Mr instead of zero. To reduce the magnetization to zero, an external field applied in the opposite direction is required and the system then shows hysteresis in the M(B) plot. The magnetic hysteresis observed in the ferromagnetic materials is partially decided by the magnetic domains.  

If the exchange interaction is negative, J<0, it is then favorable for the neighboring moments to align antiparallel to each other and the system shows antiferromagnetism. Generally, materials exhibit antiferromagnetism at low temperatures and become paramagnetic for temperatures higher than TN, the Neel temperature. Antiferromagnetic materials response differently for magnetic fields applied along different orientations. For field applied perpendicular to the spins, the magnetization is expected to increase linearly with field as the spins gradually bend towards the direction of the magnetic field. For field applied parallel to the spins, interesting phenomena occurs. At small magnetic field, the spins don’t rotate and stay lining up along opposite direction. However, when a critical field Bc is reached, the system suddenly switch into a different configuration with all the spins align along the direction of the external field. With this sudden transition, the system is driven from the antiferromagnetic state to ferromagnetic state. This transition is generally called spin-flop transition or metamagnetic transition.  

For temperatures well above the characteristic temperature TC (or TN), both ferromagnet and antiferromagnet becomes a paramagnet obeying the Curie-Weiss law \( \chi = \chi_0 + \frac{C}{T - \theta} \). The sign of \( \theta \) depends on the nature of the magnetic interaction (ordering). For ferromagnetic interaction, \( \theta = T_C > 0 \) whereas for antiferromagnetic interaction, \( \theta = T_N < 0 \). Fitting this formula to the experimental data taken highly above the critical temperatures will thus give us additional information about the magnetic interaction.
Chapter 3  Experimental Techniques

In this chapter, a thorough discussion of single crystal synthesis is presented and discussed along with characterization techniques.

3.1 Single crystal synthesis

Single crystals are critical to materials research as they possess the most intrinsic properties of the materials. However, synthesis of single crystals of complex materials has been a deep challenge. In the following, we describe sophisticated procedures developed during the course of our studies on the ruthenates.

3.1.1 Flux technique

The flux technique is a high temperature solution growth method which allows the synthesis of single crystals with sufficiently large size using less sophisticated equipment and information. This growth is carried out in a crucible (e.g., Pt, Ir, Au crucibles). Components of the desired materials are dissolved in a flux which permits the growth to occur at temperatures well below the melting point of the solute phase. This technique also results in well-formed crystals due to the absence of steep temperature gradient and mechanical or thermal strain. In order to achieve supersaturation, which helps the growth of single crystals of a large size, different kinds of techniques are taken, such as slow cooling technique, flux evaporation technique and temperature gradient technique\(^8\).

The \(\text{Ca}_3\text{Ru}_2\text{O}_7\) and the \(\text{Sr}_4\text{Ru}_3\text{O}_{10}\) crystals were firstly grown with the flux technique\(^23, 89\). To grow \(\text{Ca}_3\text{Ru}_2\text{O}_7\), an off-stoichiometric ratio of \(\text{CaCO}_3\), \(\text{RuO}_2\), and self flux \(\text{CaCl}_2\) were mixed and loaded in Pt crucible with a Pt cap. The Ca:Ru ratio is around 7:1 and the \(\text{CaCO}_3: \text{CaCl}_2\) ratio is approximately 1:12. These mixtures were heated to 1500 °C and then soaked for 25 hours. After that, they were slowly cooled at 2 °C/h to 1350 °C and then rapidly quenched to room temperature at a rate of around 100°C/h. The samples obtained from this technique are usually of \(1\times1\times0.4\)mm\(^3\) in size with the c axis being along the shortest dimension. Similar approach can be followed to grow the single crystals of \(\text{Sr}_4\text{Ru}_3\text{O}_{10}\). The starting mixtures include...
SrCO$_3$, RuO$_2$, and SrCl$_3$ of nonstoichiometric ratio. After being thoroughly ground, they are placed in Pt crucibles and heated to 1500°C for 24 hours, then cooled slowly to 1350°C at a cooling rate of 2-5°C/h, and finally quenched to room temperature to avoid twinning. Crystals obtained from this method are generally of 1×1×0.4mm$^3$ in size.

3.1.2 Floating zone technique

Ca$_3$R$_2$O$_7$, Sr$_4$Ru$_3$O$_{10}$, and Pr$_3$RuO$_7$ can also be synthesized by floating zone (FZ) technique using a NEC SCII-MDH-11020 image furnace. The furnace is a focus-heating furnace with rotary double ellipsoidal mirrors as illustrated in Figure 3.1.

![Figure 3.1. Schematic diagram of floating zone furnace with double ellipsoidal mirrors. (Quoted from website: people.deas.havard.edu)](image_url)
In this furnace, each of these ellipsoidal mirrors is equipped with a halogen lamp located at one of the focal points. The infrared rays emitted from the lamps are then reflected by the gold-plated mirrors towards the other focal point, which is arranged to sit at the center of these two mirrors. Generally, with two 1.5kW halogen lamps, the ultimate temperature the apparatus can reach at the central focus zone is around 2050 °C. The temperature at the central focus point can then be adjusted by tuning the power of the lamps. With a transparent quartz tube, we can manipulate the growing atmosphere, and at the same time observe the growing condition through a camera. The furnace is also equipped with water-cooling system to prevent overheating on the mirrors and the whole system.

The polycrystalline rods for the crystal growth are prepared by a standard solid-state reaction method. To start with, CaCO$_3$ and RuO$_2$ compounds are cooked separately at 400°C for 5 hours to get rid of moisture. Then, they are mixed, ground in an agate mortar and cooked at 900°C for 15 hours. To ensure a uniform mixing of these two materials, the mixtures are reground and cooked again at 900°C for another 15 hours. After that, the mixtures are filled into a clean cylinder-like rubber balloon and compressed under a pressure of around 35Mpa. The compressed rod is then removed from the balloon and sintered at 1000°C in air for another 20 hours. A similar procedure can be followed to grow Sr$_4$Ru$_3$O$_{10}$ and Pr$_3$RuO$_7$ but with different starting materials. For Sr$_4$Ru$_3$O$_{10}$, SrCO$_3$ and RuO$_2$ mixtures, the ratio is 1:0.9; For Pr$_3$RuO$_7$, the Pr$_6$O$_{11}$ and RuO$_2$ ratio is 2.7:1. Both mixtures are then treated thermally with a similar procedure.

The rods used in the floating zone synthesis are about 4-6 mm in diameter and 4-5 cm in length. The feed rod was hung from the upper shaft using Platinum wire, and the seed rod was fastened to the sample holder on the top of the lower shaft. To start with, tips of the feed rod and seed rod are brought together to the central focal zone, melted and then connected to form a molten zone (Figure 3.2.a). During the growing of the crystal, both the upper and the lower shaft move down inside sealed quartz tube, driving the polycrystalline rod through the central focus zone. The crystallization occurs as the molten zone of the materials move vertically away from the central focal zone (Figure 3.2.b-c). At the end of the growth (Figure 3.2.d), the upper rod and the crystallized rod are separated and the system is cooled down at a rate of 1V/h. During the growth, both rods are kept rotating at opposite directions for the following purposes: 1). In cases when the rods are not thoroughly melted, they
will knock each other off the center. The opposite rotation can then make sure that the rods in the molten zone are properly melted into liquid. 2). In cases when the heat inside the molten zone is not uniformly distributed, the rotation helps the rods to be melted equably. A smooth growth of the crystal is achievable by carefully adjusting the following parameters: pressure of the gas, mixture gas ratio, lamp voltage, main shaft speed, gap speed. Because of volatile RuO\(_2\) for temperature above 1100º, a Ru-rich feed rod is used instead of a stoichiometric one. The excess RuO\(_2\) compensates the loss of RuO\(_2\) at high temperatures.

Figure 3.2 Demonstration of crystal growth. (a) Beginning of the growth, the seed rod and the feeding rod are melted and connected to form a molten zone. (b-c) Middle of the growth, the whole rod moves vertically through the focus zone and the materials crystallizes. (d) Ending of the growth, the rods separated and system cooled.

Despite of the success of the FZ technique in growing Sr\(_2\)RuO\(_4\), growing high-quality Ca\(_3\)Ru\(_2\)O\(_7\) has been a major challenge. This is because the free energies of its sister compounds such as Ca\(_2\)RuO\(_4\) and CaRuO\(_3\) are rather close to that of Ca\(_3\)Ru\(_2\)O\(_7\). As a result, this unfavorable feature requires a subtle growth condition that can avoid any inclusion of unwanted phase. The high volatility of Ru required excess Ru in the polycrystalline rod, but too much Ru in the polycrystalline rod will increase the melting temperature and result in loosing more Ru and getting unwanted phase. Increasing the crystal growth speed can effectively reduce the loss of Ru in the crystal, but higher growing speed also means higher melting temperature and unstable growing status. Using inert gas as growing mediate is another way of keeping Ru in
the crystal but the mixture ratio and gas pressure has to be well controlled in order to get the optimal growth condition. Generally, oxygen is needed to melt the rods, but oxygen in the atmosphere may react to the Ru and generate RuO$_2$, removing more Ru away from the feed rod. All these issues require a delicate and well-balanced approach for the crystal growth.

One unique difficulty arising in the Ca$_3$Ru$_2$O$_7$ synthesis is the twinning between a-axis and b-axis crystalline. Since the physical properties of this system are highly anisotropic as will be discussed in chapter 4, the twinning can produce serious problem in characterizing the physical properties of the sample. Table 1 shows the crystal growth conditions and their corresponding crystal qualities. One of the measures in evaluating sample quality for this particular system is by testing its saturation moment $M_S$. The more $M_S$ is close to $2\mu_B$/Ru, the better quality. The table indicates that the atmosphere is a key parameter in determining the crystal quality. For example, when we use feed rods with $n=1.39$ (F139-F140), decreasing the O$_2$ ratio in the mixed gas helps to keep more Ru in the crystal. Lower the gas pressure from 3.0bar to 2.0bar (F140-F143) may help reduce the intensity of O$_2$ in the atmosphere and thus the chance for O$_2$ to react with RuO$_2$ is less. Another important parameter that shows pronounced effect in the crystal quality is the crystal growth speed $V_1$. Generally, it is desirable to keep the speed $V_1$ as low as possible in order to stabilize the growing condition. However, the slower the speed the longer the melted materials stay in the molten zone. As a result, more RuO$_2$ will be released from the solvent. In this case, we have to keep the growth at relatively “high” speed-around 35mm/h. An intuitive way to keep Ru in the crystal would be to start with Ru-rich raw materials: meaning larger $n$. However, when more Ru is included in the materials, the melting temperature will increase as well and this in turn releases more RuO$_2$ into the air. For example, from Table 1 we can tell that increasing $n$ doesn’t necessarily leads to higher-quality crystals. However, it is always difficult to estimate the effect of $n$ when the growth condition changes from one growth to another. A successful growth of Ca$_3$Ru$_2$O$_7$ can be achieved after several trials by delicately balancing different effects coming from different controlling parameters.
Table 1

Summary of crystal quality in various growth conditions.

<table>
<thead>
<tr>
<th>Batch no.</th>
<th>n</th>
<th>O₂/(Ar+O₂)</th>
<th>P(bar)</th>
<th>V₁ (mm/h)</th>
<th>V₂ (mm/h)</th>
<th>PC</th>
<th>Mₛ (μB/Ru)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F143</td>
<td>1.39</td>
<td>30%</td>
<td>2.0</td>
<td>35</td>
<td>0.5</td>
<td>Ca₃₂₇</td>
<td>1.87</td>
</tr>
<tr>
<td>F140</td>
<td>1.39</td>
<td>30%</td>
<td>3.0</td>
<td>34</td>
<td>1</td>
<td>Ca₃₂₇+Ca₂₁₄</td>
<td></td>
</tr>
<tr>
<td>F130</td>
<td>1.39</td>
<td>50%</td>
<td>3.0</td>
<td>34</td>
<td>1</td>
<td>Ca₂₁₄</td>
<td></td>
</tr>
<tr>
<td>F94</td>
<td>1.46</td>
<td>70%</td>
<td>3.0</td>
<td>34</td>
<td>1</td>
<td>Ca₃₂₇</td>
<td>1.56</td>
</tr>
<tr>
<td>F92</td>
<td>1.67</td>
<td>80%</td>
<td>4.0</td>
<td>33</td>
<td>1.5</td>
<td>Ca₃₂₇+Ca₂₁₄</td>
<td>0.15</td>
</tr>
<tr>
<td>F91</td>
<td>1.67</td>
<td>65%</td>
<td>3.2</td>
<td>32</td>
<td>1</td>
<td>Ca₃₂₇ (T)</td>
<td>1.3</td>
</tr>
<tr>
<td>F88</td>
<td>1.30</td>
<td>65%</td>
<td>3.7</td>
<td>32</td>
<td>1</td>
<td>Ca₃₂₇ (T)</td>
<td>1.25</td>
</tr>
<tr>
<td>F87</td>
<td>1.30</td>
<td>100%</td>
<td>4.5</td>
<td>30</td>
<td>1</td>
<td>Ca₃₂₇ (T)</td>
<td>0.05</td>
</tr>
<tr>
<td>F70</td>
<td>1.58</td>
<td>100%</td>
<td>3.5</td>
<td>29</td>
<td>1.5</td>
<td>Ca₃₂₇ (T)</td>
<td>1.2</td>
</tr>
<tr>
<td>F58</td>
<td>1.35</td>
<td>100%</td>
<td>2.5</td>
<td>25</td>
<td>2.7</td>
<td>Ca₃₂₇+Ca₂₁₄</td>
<td>0.442</td>
</tr>
</tbody>
</table>

n=1.5N(Ru)/N(Ca): ratio of the polycrystalline feed rod; O₂/(Ar+O₂): percentage of oxygen in the mixed gas; P: the total pressure of the mixed gas; V₁: shaft speed of both feed and seed rod (or crystal growth speed); V₂: compensating feed speed of the upper rod; PC: phase constitution of the crystal rod detected by powder X-ray diffraction, T indicates twinning crystals.

One major advantage of floating zone technique is its capability to grow large single crystals, which may not be possible by conventional methods such as flux technique. The diameters of the single crystals that can be grown by floating zone technique are limited only by the surface tension of the molten zone. Usually the crystals can be as large as 60mg in mass and 4×3×1×mm³ in dimensionality as shown in Figure 3.3.
The growth of Sr$_4$Ru$_3$O$_{10}$ and Pr$_3$RuO$_7$ are carried out in O$_2$ gas with growing rate, $V_1$, of 19mm/h and 20mm/h respectively. Powder X-ray diffraction indicates that both samples show the desired phase Sr$_4$Ru$_3$O$_{10}$ and Pr$_3$RuO$_7$. However, the susceptibility and specific heat measurements show trace of heterogeneity in both samples. More systematic and delicate sequence needed to be developed in order to grow single crystals of Sr$_4$Ru$_3$O$_{10}$ and Pr$_3$RuO$_7$ with better quality.

### 3.2 Crystalline structure characterization

The knowledge of crystalline structure is essential for an understanding of the physical properties of materials. X-ray powder diffraction is one of the methods that have been widely applied in condensed matter physics to study crystalline structure.

X-rays are in fact electromagnetic radiations with wavelength around 1 Å. Since their wavelengths are comparable with the size of an atom, they are used to explore within crystals. The diffraction pattern of x-ray reveals critical information about the structure of the materials. The target we use for our x-ray diffractometer is copper that emits a wavelength of 1.54184 Å. X-rays are usually generated in an x-ray tube, in which there is a cathode and an anode. A large voltage difference (40-60kV) is placed between the cathode and the anode, causing the electrons to move at high velocity from the filament to the anode target. X-rays are generated at the point when the high speed electrons hit the anode and radiate in all directions. The output of the radiation from the target consists of a series of intense sharp maxima and usually one particular peak is selected for exploring the crystals.
These output X-rays are reflected from the material powder and then detected by an X-ray detector. In the normal scanning, the detector scans around the sample along the circumference of a circle, giving us the intensity of the X-rays as a function of the detector angle \( \theta \). Positions of the peaks determined by the Bragg law reflect the crystal structure. The combination of peak positions and the intensity is unique for different types of crystal structures\(^94\).

To characterize the samples, a single piece of single crystal is selected and crashed into powder in a small mortar and then placed on the center of a quartz plate. A standard scan usually runs from \( 10^\circ < \theta < 70^\circ \) at a rate of \( 0.02^\circ \) per step. When a spectrum is collected, it can be quickly compared to the Powder Diffraction Files in a database of known structures. Using an orthorhombic symmetry with space group \( A2Ima \)\(^{23, 34}\), we are able to estimate the crystalline lattices to be \( a=5.3720(6)\text{Å} \), \( b=5.55305(6)\text{Å} \), and \( c=19.572(2)\text{Å} \). Figure 3.4 shows the X-ray spectrum for flux and floating zone samples of \( \text{Ca}_3\text{Ru}_2\text{O}_7 \) respectively. We notice that the common impurity phase such as \( \text{Ca}_2\text{RuO}_4 \) (with a characteristic peak at 14) is absent in the diffraction patterns. The peaks numbers and positions of the floating zone grown samples are identical to those of the flux samples, as illustrated in Figure 3.4, indicating that the directions of the diffracted beams coming from both samples are identical. Since the orientations of the diffracted beams are generally determined by the shape and size of the crystals’ unit cell, we can then conclude that the symmetries in both samples are the same. However, a closer comparison between these two diffraction patterns shows that the intensities of the peaks are different. For example, for the flux grown samples, the highest peaks locates at \( 2\theta=18.0\); whereas for the floating zone grown samples, the highest peaks is at \( 2\theta=32.4\). The difference in diffraction intensities is possibly due to the variance in the positions of the atoms within the unit cell of each sample\(^95\). Considering the fact that the crystallization is realized through the surface tension of the molten rod in the floating zone growth, we suspect that the variance in atomic position might have been induced by the external tension of the rod. Other growing conditions like high \( \text{O}_2/\text{N}_2 \) mixture pressure and fast crystallization speed might also have contributed to the difference in diffraction intensities. Nevertheless, no prominent difference in the physical properties has been detected so far in the flux and floating zone samples.
3.3 Magnetic property measurement

The magnetic susceptibilities of the samples are measured using a Quantum Design SQUID (Superconducting Quantum Interference Device) with MPMS (Magnetic Property Measurement System) XL 7. The core of this set up is a sensitive
SQUID sensor which can be used to measure magnetic moments with a range of sensitivity from about $10^{-8}$ emu to 2 emu. The high performing capability of a SQUID is attributed to the quantized state of the superconducting ring and the extraordinary non-linear behavior of the Josephson junction. Because of its extreme sensitivity to fluctuations in magnetic fields, the sensor is screened from field fluctuations with a superconducting shield. The sensor is then connected to a superconducting detection coil with superconducting wire. In the measurement, the sample moves step by step through the detection coil, generating change of magnetic flux in the detection coil. Since the detection coil, the connecting wires and the SQUID sensor form a closed superconducting loop, any change of magnetic flux in the detection coils will produce a change in the persistent current in the detection circuit, which is proportional to the change in the magnetic flux. Here the SQUID functions as a highly linear current-voltage convertor. The output voltage of the SQUID is proportional to the magnetic moment of the sample. The MPMS is also equipped with temperature control and magnet control system. The sample temperature can be precisely controlled from 1.7K to 400K. And a magnetic field as high as 7 Tesla is achievable by applying current to superconducting solenoid.

In the routine measurements, a single crystal is weighted with an electronic weight and glued to a magnetically inert quartz rod with GE varnish. Since all systems under study are highly anisotropic, extra attention is paid to the orientation of the samples when gluing them to the quartz rod. This quartz is then fixed to the end of the SQUID drive rod and inserted into the cryostat’s sample chamber. Since the calibration software has assumed that the sample is at the center of the sample chamber, for every measurement we center our sample not only along the z-axis but also radially in the sample chamber as well.

3.4 Transport properties

3.4.1 Transport properties measurement at low fields

The magnetometer in Dr. Cao’s lab is also equipped with a transport function. Both the resistivity and magnetoresistance can be measured by applying standard four-point-probe technique. This technique is chosen over a two-point-probe method.
because it eliminates the probe resistance, contact resistance, and spreading resistances that are generally unavoidable with the two-point-probe method. As illustrated in Figure 3.5, four probes (probes 1, 2, 3, and 4) are brought into contact with a tested sample at known distance and geometry. Current can be driven into the sample through probe 1 and probe 4, and the voltage drop over probe 2 and probe 3 can be measured using a very high Ohmic measurement device so that the current flowing through probe 2 and 3 is negligible. Since the resistance, \( R \), of a sample is defined as \( R = \rho \cdot \frac{L}{A} \) (\( L \): the distance between probe 2 and 3, \( A \): the area of the cross section, \( \rho \): the resistivity), \( \rho \) can then be found to be \( \rho = \frac{R \cdot A}{L} \). To make a solid contact between the probe and the sample, two EPOXYs (model H20E) of same amount are mixed and used as glue to attach leads to the sample. Four 1 milli- inch gold wires are attached to the sample with the EPOXY mixture and then baked at 150° for 5 to 20 minutes to ensure good contact points. Since the studied crystals are highly anisotropic, special attention are paid when putting the leads on the samples. For \( a \)-axis resistivity measurement, the contact points are arranged linearly along \( a \)-axis. For \( c \)-axis resistivity measurement, due to the small sample dimension, two contact points are arranged on the surface of the same side and are arranged as close as possible, the other two contact points are arranged on the corresponding positions of the other side of the sample. The sample with the leads was then glued to the probe with GE varnish. The gold wires are then attached to the probe leads with silver paint. The transport property measurement is then carried out with a Linear Research and also Keithely meters.
3.4.2 Transport properties measurement at high magnetic fields

The measurements of transport properties at high magnetic field were carried out at the National High Magnetic Field Laboratory (NHMFL) in Tallahassee, Florida. Very often, a rotating probe is used in order to map the anisotropy of the transport properties at high magnetic fields. This probe has proper string and spring set up that can rotate the sample platform along an axis that is perpendicular to the long probe axis as illustrated in Figure 3.6. The magnetic field is always applied along the probe. To measure the transport properties with magnetic field applied along $a-/b$- axis, the sample was placed on the surface of the sample station with $a-/b$-axis orientated along the long probe axis. Such an arrangement allows the sample to rotate in the $ac/bc$ plane. To measure the transport properties with the sample rotating in the $ab$ plane, an L-shape copper stand was glued on the surface of the sample station in such a way that the other half part of the L-shape copper stood vertically on the surface of the sample station. The sample was then placed on this half part of the copper with the $c$-axis perpendicular to the long probe axis. An arrangement like this allows the sample to be rotated in the $ab$ plane. To prevent the magnetic sample from being peeled off from the platform due to the high magnetic field (as high as 45T), extra attention has to be taken to hold the sample in position. Besides the GE varnish
that has been used to glue the sample to the sample station, another layer of GE varnish was applied on the top of the sample to hold the sample on its desired position.

Figure 3.6. The sketch for the rotation probe used in high field measurement

The rotation probe was inserted into a He\(^3\) vacuum jacket, which was then placed in a pre-cooled Dewar sitting inside the 45T hybrid magnet. The He\(^3\) vacuum jacket, which has been pumped to ultrahigh vacuum, is then connected to a He\(^3\) recycling system. When cooling down the whole system, He\(^3\) was guided into the He\(^3\) vacuum jacket and played a role as exchange gas to help the cooling down. The sample temperature can be further cooled from 4.2K to 1.5K by pumping the liquid He\(^4\). During this process, more liquid He\(^3\) was guided into the He\(^3\) jacket and then condensed inside the He\(^3\) jacket. When enough He\(^3\) was collected in the jacket, the He\(^3\) jacket was pumped to further cool the sample down to 0.5K.

The 45T magnetic field is the strongest, sustained magnetic field in the world. It is achieved by combining a superconducting magnet (outsert) and a conventional electromagnet (insert) which sits inside the superconducting magnet. The outer superconducting coil generates static field of around 11 Tesla. The rest of the field is
generated by the water-cooled resistive magnet. With such a strong magnetic filed, we were able to observe Quantum Oscillations and other phenomena in high fields.

### 3.5 Heat capacity measurement

The heat capacity of single crystals (Sr₄Ru₃O₁₀ and Pr₃RuO₇) were measured using the ac calorimetry technique that was introduced by Sulivan and Seidel⁹⁷. This technique allows one to measure small samples with high precision. It applied oscillating heat to a sample coupled thermally to the heat bath, resulting in a measurable temperature oscillation with magnitude inversely proportional to the heat capacity⁹⁸.

For measurements taken at temperatures above 15K, the crystal was attached to a pair of flattened, crossed Chromel-Constantan thermocouple junctions with GE7031 varnish (or silver paint). For measurements taken at temperatures between 3K and 20K, the crystals are attached to Cernox bolometers⁹⁹, ¹⁰⁰. Both the thermocouple and the Cernox bolometer function as sample holder and temperature change detector in the measurement. The whole assembly was then sealed inside copper tubing which was filled with helium gas (typically 500 millitorr at room temperature) in the measurement. The helium gas is the main medium that keeps the thermal contact between the sample and the heat sink. A quartz halogen lamp provided the heating source, light, chopped at certain frequency $\omega$. The oscillation induced on the sample temperature due to the modulated light was then measured by the thermocouple, whose signal was amplified by a ratio of 100 using a low-noise transformer before measured by a lock-in amplifier. The other thermocouple was then used to measure the average increase in temperature over the heat bath⁹³, ¹⁰¹.

The key procedure that determines the success of this experiment is to find the proper chopping frequencies in different temperature ranges. There are two important characteristic time constants that determine the appropriate chopping frequency: the external relaxation time constant $\tau_1$ and the internal relaxation time constant $\tau_2$. $\tau_1$ characterizes the time for the sample temperature to come to equilibrium with the heat bath. $\tau_2$ characterizes the time for the sample to come to a uniform temperature after the application of the external heating. The chopping frequency has to chosen in such a way so that it is slow enough to allow the sample temperature to become uniform.
yet fast enough to avoid energy from dissipating away from the sample to the heat bath. This means the reasonable frequency should satisfy: $\tau_2 << 1/\omega << \tau_1$. This condition will be satisfied if the chopping frequency lies within the horizontally flat part of a graph of $f \cdot V_{ac}$ vs. $f$. Since both the helium gas conductance and the heat capacity of the crystals change with temperature, the upper and lower limit of the chopping frequency is temperature dependent. Experimentally, the sample temperature has to be stabilized at different temperatures with the frequency dependence checked.

Since the absorbed power is unknown, this ac calorimetry technique can only determine the relative value of the heat capacity. We have to rely on published data or heat capacity determined by another technique (e.g. on larger samples of powders), such as differential scanning calorimetry (DSC) to find its absolute values. The temperature dependence of heat capacity was then obtained by normalizing the relative value to the absolute heat capacity value at high temperatures.
Chapter 4  Results and Discussions

The Ruddlesden-popper series (Sr, Ca)$_{n+1}$Ru$_n$O$_{3n+1}$ ($n=$number of Ru-O layers in one unit cell) are perovskite based systems sharing the same Ru$^{4+}$ in an octahedral environments with corner sharing topology. However, despite the structure similarity, magnetic and electronic properties revealed in these series are extraordinarily diverse. These properties include superconductivity in single layer Sr$_2$RuO$_4$, which appears to have p-wave spin-triplet pairing$^{3, 103, 104}$, the Mott metal-insulator transition in antiferromagnet Ca$_2$RuO$_4$,$^{22, 32}$, itinerant ferromagnetism in SrRuO$_3$$^{17, 105}$, paramagnetic behavior in “bad” metals CaRuO$_3$$^{17}$, and metamagnetic quantum critical behavior in Sr$_3$Ru$_2$O$_7$$^{20, 106}$. The diversity exhibited in this series mainly arises from the strong dependence of the physical properties on dimensionality and structure distortion, i.e., the lattice degree of freedom. As $n$ increases from 1 to 2 to 3 and to infinity, the number of Ru neighbors per ion increases from four for $n=1$, to 5 for $n=2$, to $16/3$ for $n=3$, and to six for $n=\infty$. Accordingly, the dimensionality is raised from 2D, to quasi-2D, to quasi-3D and finally to 3D. In addition, although the Sr$^{2+}$ and Ca$^{2+}$ are isovalent ions, the difference in their ionic sizes leads to significant difference in structural distortions between the Ca and Sr series. As a result, the Ca series and Sr series exhibit entirely different physical properties: the Sr series is metallic and tends to be ferromagnetic but the Ca series is inclined to be insulating and antiferromagnetic. Such features strongly suggest that the properties of this series of materials are intimately correlated with the lattice degree of freedom.

For Ca$_2$RuO$_4$$^{21, 22}$, since the exchange interaction is limited to be within the ab plane, the lattice distortion induced by the Ca ions turns out to be one of the dominant energy terms in the interaction pictures, resulting in severe structure transition at 357K. However for CaRuO$_3$, when the dimensionality is higher, the structural distortions are not that important, as indicated by the similar resistivity behaviors between SrRuO$_3$ and CaRuO$_3$$^{33, 107, 108}$. As a bilayered system which lies between $n=1$ and $n=\infty$, Ca$_3$Ru$_2$O$_7$ is believed to be placed in a unique position at which the orbital degree of freedom plays a critical role in determining the physical properties. The orbital degree of freedom is sensitive to lattice distortion via orbital-lattice coupling,
and to the magnetic field via strong spin-orbital coupling. In this chapter, we are going to probe the orbital physics through magnetic field tuning.

4.1 Basic features of \( \text{Ca}_3\text{Ru}_2\text{O}_7 \)

4.1.1 Crystal structure

\( \text{Ca}_3\text{Ru}_2\text{O}_7 \) shows perovskite-like structures with double layers of \( \text{RuO}_6 \) octahedra corner-sharing with each other. The double-layered \( \text{RuO}_6 \) forms planes with the \( \text{Ca}-\text{O} \) layers intervening within and between them. The \( \text{Ca}-\text{O} \) layer helps stabilize the perovskite structure without contributing to the total spins of this system. Since no oxygen ions within the intervening \( \text{Ca}-\text{O} \) layer are shared by the Ru ions of the adjacent double layers, the exchange interactions and conductivity perpendicular to the \( \text{RuO} \) planes would be weaker compared with those within the \( \text{RuO} \) planes. Compared with the ionic size of \( \text{Sr}^{2+} (r_{\text{Sr}}=1.18\text{Å}) \), the ionic size of \( \text{Ca}^{2+} (r_{\text{Ca}}=1.00\text{Å}) \) is smaller, resulting in an orthorhombic distortion with \( a=5.3720(6)\text{Å}, \) \( b=5.55305(6)\text{Å}, \) and \( c=19.572(2)\text{Å} \). This corresponds to a space group of either \( \text{A}_2\text{ma} \) (with \( a \) being the short axis) or \( \text{Cmc2}_1 \) (with \( a \) being the long axis)\(^{16, 34} \). In this thesis, we take \( a \)-axis as the short axis with space group \( \text{A}_2\text{ma} \).

The distortion exhibits itself as a rotation (around the \( c \)-axis) and a tilting (away from the \( c \)-axis) of the \( \text{RuO}_6 \) octahedra as clearly illustrated in Figure 4.1\(^{28} \). The tilting projects primarily along the \( ac \) plane, giving rise to an orthorhombic structure with anisotropic \( a- \) and \( b- \) lattice parameters. It is estimated that the \( \text{Ru-O-Ru} \) bond angles, which reflect the distortion effect, differ considerably from 180°. Within the \( ab \) plane, the \( \text{Ru-O-Ru} \) bond angles alternate between 149.87° and 150.47°, whereas for the Ru ions in the double layers the \( \text{Ru-O-Ru} \) bond angle is 152.13°. The tilting and rotation of \( \text{RuO}_6 \) octahedra are so severe that even the individual octahedron is contorted\(^{16} \). Within the octahedra, the \( \text{O-Ru-O} \) bond angles are distorted away from 180°: around 177° for \( \text{O-Ru-O} \) bond angles along the \( c \)-axis, between 179.42° and 179.53° for \( \text{O-Ru-O} \) bond angles perpendicular to the \( c \)-axis. Compared with the \( \text{Ru-O} \) bonds (\( \sim 1.9910\text{Å} \)) sandwiched between the \( \text{RuO}_6 \) plane, the other \( \text{Ru-O} \) bonds are longer (\( \sim 1.9914 \text{Å} \)).
The single crystals of Ca$_3$Ru$_2$O$_7$ were grown by the self-flux technique with typical dimension size of about $0.5 \times 0.4 \times 0.3$ mm$^3$. According to the TEM (Transmission Electron Microscopy) studies, the crystallographic c-axis is along the shortest dimension whereas the a-axis and b-axis are about 45° away from the rectangular edges.

### 4.1.2 Magnetic properties

Although the crystal distortions illustrated in the previous section are subtle, the impact they have on the magnetic properties is profound. The temperature dependence of magnetization for magnetic fields applied along different lattice crystallines clearly demonstrates the magnetic anisotropy even on the $ab$ plane. At $B=0.5$T, $M_a$ (magnetization for $B||a$-axis) features two transitions in cooling down the system. The first transition occurs at Neel temperature, $T_N=56$K, going from a paramagnetic state to antiferromagnetic state. When further cooled down, the system shows a plateau, followed by a precipitous drop of magnetization at the metal – insulator transition temperature $T_{MI}=48$K$^{23}$. As $B$ increases, $T_{MI}$ shifts slightly with $T_N$.
transition getting rounded and then disappearing. In the isothermal magnetization measurement, the magnetic state is driven from antiferromagnetic state to ferromagnetic state through a first-order metamagnetic transition upon \( B=6T \). The saturation moment reaches as high as \( 1.8\mu_B/Ru \) for \( B>6T \), suggesting more than 85% of the expected saturation moment (assuming \( M_S=2\mu_B/Ru \) for an \( S=1 \) system).

For \( B\parallel b \)-axis, the \( M_b \) (magnetization for \( B\parallel b \) axis) shows only a single peak at \( T_N=56K \) and no transition at \( T_{MI} \). As \( B \) increases, \( T_N \) decreases but the antiferromagnetic state remains. Similar to \( M_a \), \( M_c \) also features two transitions at \( T_N \) and \( T_{MI} \) but with smaller magnitudes. But as \( B \) increases, system retains its antiferromagnetic state for \( B \) as high as 7T.

This anisotropy in magnetization is better illustrated in the angular dependence of magnetization with \( B \) (6.5T) rotates on the ab plane at \( T=10K \). For \( B \parallel a \) with \( \theta=0 \) (0 is the angle between the a-axis and B), the system shows a saturation moment of about \( 1.8\mu_B/Ru \). This moment drops abruptly as \( B \) rotates away from a-axis, followed by a broad and short peak centered at \( \theta=90^\circ \), the b-axis. This angular dependence does not resemble those of conventional ferromagnets such as CrO\(_2 \) whose angular dependence follows a sinusoidal function \( M = F(\cos \theta) \). Instead, it displays a sharp distinction between the magnetic easy and hard axis, signaling an unusual anisotropy that has not been observed before. This transition in the angular dependence pattern suggests a rotation of magnetic easy axis from the a-axis to the b-axis as temperature increases from 46K to 56K.

### 4.1.3 Transport properties

Corresponding to the magnetic anomalies, the resistivity measurement at zero field features two transitions at \( T_N(56K) \) and \( T_{MI}(48K) \). At \( T_N=56K \), resistivity drops abruptly, followed by a sharp Mott metal-insulator transition at \( T_{MI} \) with resistivity increasing by a factor of 20 for the c-axis. Between 48K and 56K there is an unusual antiferromagnetic metallic state which intermediates between the antiferromagnetic insulating state and the paramagnetic metallic state.

X-ray diffraction studies reveal a shrinkage of the c-axis lattice parameter at around \( T_{MI}=48K \) when cooling down, but no significant changes in the \( a \) axis and \( b \) axis lattices are observed. The shortening of the c-axis suggests the Jahn Teller...
effect\textsuperscript{65}, which lifts the degeneracy of the $t_{2g}$ orbitals by lowering $d_{xy}$ level relative to $d_{xz}$ and $d_{yz}$ energy levels. As a result, orbital ordering may occur, weakening the mobility of conduction electrons. The simultaneous magnetic, structural, and metal-insulator transition strongly indicates a magnetoelastic effect\textsuperscript{38,39}.

For $B\parallel a$-axis, the interplane resistivity $\rho_c$ drops abruptly by one order of magnitude, corresponding to the first-order metamagnetic transition which leads to 85% spin polarization along the $a$-axis. The resistivity reduction achieved by this metamagnetic transition can be associated with a tunneling magnetoresistance. When $B (>6T)$ is applied along the $a$-axis, the system is driven to ferromagnetic state. Because of the layered nature, the insulating Ca-O plane and the spin-polarized Ru-O planes form the FM-insulator-FM junction which facilitates coherent motion of the electrons along the $c$-axis\textsuperscript{15}. The magnetoresistance mechanism is similar to the traditional magnetic materials like the Fe/Ge/Fe multilayers\textsuperscript{78}.

### 4.1.4 Thermal properties

Heat capacity measurement has always been an instructive probe in describing the low temperature properties of materials. It can provide very rich quantitative information on the distribution of electron, phonon, and magnon states. The specific heat measurement for $\text{Ca}_3\text{Ru}_2\text{O}_7$ was carried out on a parquet of carefully aligned single crystals by McCall et. al. using a quasiadiabatic heat pulse method\textsuperscript{110,111}. Since $\text{Ca}_3\text{Ru}_2\text{O}_7$ shows strong anisotropy in structural, magnetic, and transport properties, the specific heat measurement was carried out with $B$ applied along $a$- and $b$-axis respectively.

For $B\parallel a$, the low-temperature measurement was taken for $B=0$ and 8 T respectively\textsuperscript{111}. The results in the range of $2<T<13K$ are plotted as $c/T$ vs $T^2$ and then fitted to a linear formula: $c/T=\gamma+\beta T^2$. The fitting results in $\beta$ values that give rise to Debye temperature of $\theta_D=480K$ and $\theta_D=465K$ for $B=0T$ and 8T respectively, similar to those obtained in a two-layer ruthenates\textsuperscript{31}. The $\gamma$ value, which is proportional to the density of states (DOS) at the Fermi level, is determined to be $44 \pm 2 \text{ mJ/mole K}^2$ for $B=0T$ from the linear fitting, suggesting either high electronic correlation or partially localized states near the Fermi surface. This value is comparable to those for the metallic member of the RP ruthenates\textsuperscript{17,18,22}, even though the system is observed to
be non-metallic at low-temperature. As B increased to 8T, $\gamma$ remains the same, signaling that there is no change in DOS through the metamagnetic transition. The constant $\gamma$ value over the metamagnetic transition suggests an A-type antiferromagnetic ordering. This argument agrees with the neutron scattering study and the density functional calculation, both supporting an A-type antiferromagnetism with ferromagnetic order within the plane\textsuperscript{112,113}.

Even though the $\gamma$ remains constant over the metamagnetic transition at B=6T, latent heat was released when magnetic field was increased and decreased through the critical fields, resulting in spontaneous increase of sample temperature of around 5K. This observation is consistent with the fact that the transition itself is a first-order transition, as indicated by the hysteresis in the isothermal magnetization curve. However, since the transition occurs between two isentropic states - from antiferromagnetic state to ferromagnetic state, the latent heat could not have come from the magnetocaloric effect. (The magnetocaloric effect occurs only for the paramagnetic state to ferromagnetic state transition, in which the alignment of the magnetic moments reduces the entropy. The reduced entropy is then released through increasing the temperature of the materials.) However, it may suggest that when the system undergoes the metamagnetic transition, there are large electronic and/or structure changes due to the spin-orbital or spin-lattice coupling.

Corresponding to the transitions that were observed in magnetic and transport properties at T=48K and 56K, for B=0T, the specific heat also shows anomalies at both temperatures. The anomaly exhibited at 48K is a narrow and highly symmetric peak, suggesting that the transition is first order. The entropy removal calculated under the peak is only 2.7±0.15 J/mole K, which is much smaller than the expected value 2Rln(3)=18.25 J/mole K for an S=1 system. However, since the transition at 48K is between an antiferromagnetic insulating state and an antiferromagnetic metallic state, no much spin-orientating activity is involved in this transition and the $\Delta S$ is then reasonable to be much smaller than the expected value. However, for the transition at 56K that involves magnetic ordering, the peak is much smaller with an almost negligible entropy removal of $\Delta S=0.3J$/mole K (compared with the expected value18.25 J/mole K). Both anomalies are smaller than what would be expected for magnetic (spins) ordering, indicating that their sources are other than spins.
As the applied field along the a-axis increases, the peak at 48K shrinks and shifts to lower temperature. At B~5.5T, the entropy removal under the peak is suppressed to zero. For B∥b, the entropy removal decreases linearly with increasing field for 6<B<12T. A fitting to the field dependence of entropy removal, ΔS(B), predicts the vanishing of ΔS at around 15T, which happen to coincide with the observed critical field that is responsible for the CMR when B∥b. The CMR for B∥b is believed to be associated with orbital degree of freedom. In this case, the coincidence between these two critical fields (the critical field for CMR and the critical field for the vanishing of ΔS) may indicate that the anomaly at 48K is also associated with orbital degree of freedom.

The observations from this specific heat study strongly indicate that the thermal property of Ca$_3$Ru$_2$O$_7$ couldn’t be well explained solely by spin degree of freedom. The strong spin-orbit coupling or spin-lattice coupling has to be considered in order to understand the anomalies and first order transitions in this system.

### 4.2 Anomalous Colossal Magnetoresistance

Shown in Figure 4.2 is the field dependence of the resistivity for the c axis (interplane) $\rho_c$ (right scale) for $T=0.4$ K and $0\leq B\leq 45$ T with $B||a, b, c$ axes. $\rho_c$ is extraordinarily sensitive to the orientation of $B$. For the $B||a$ axis (magnetic easy axis), $\rho_c$ shows an abrupt drop by an order of magnitude at 6 T, corresponding to the first-order metamagnetic transition leading to the spin-polarized or ferromagnetic (FM) state with a saturated moment $M_s$ of 1.8$\mu_B$/Ru or more than 85% polarized spins (see left scale in Figure 4.2). The reduction of $\rho_c$ is attributed to the coherent motion of electrons between Ru-O planes separated by insulating Ca-O planes, a situation similar to spinfilters where the probability of tunneling depends on the angle between the spin magnetization of adjacent ferromagnets. The fully spin-polarized state can lower the resistivity by at most a factor of 10. As $B$ is increased further from 6 to 45 T, $\rho_c$ increases linearly with $B$ by more than 30%, which is interesting in its own right since a quadratic dependence is expected for regular metals. Because spin scattering is already reduced to its minimum at B=6 T, the linear increase can arise only from orbital degrees of freedom that via spin-orbit coupling hinder the electrons from hopping.
Figure 4.2. (color online). Isothermal magnetization $M$ for the $B \parallel a$, $b$, and $c$ axes at $T=2K$ (left scale). Magnetic field dependence of the $c$-axis resistivity $\rho_c$ for the $B \parallel a$, $b$, and $c$ axes at $T=0.4K$ (right scale). Note that the magnetic easy axis is along the $a$-axis with spin polarization of more than 85%. Inset: $B$ dependence of the $a$-axis resistivity $\rho_a$ for the $B \parallel a$, $b$, and $c$ axes at $T=0.4K$.

For the $B \parallel b$ axis (magnetic hard axis), there is no spinflop transition and the system remains AFM. In sharp contrast with $\rho_c$ for the $B \parallel a$ axis, $\rho_c$ for the $B \parallel b$ axis rapidly decreases by as much as 3 orders of magnitude at $B_c = 15$ T, 2 orders of magnitude more than that for $B \parallel a$, where spins are fully polarized. For the $B \parallel c$ axis, on the other hand, $\rho_c$ displays Shubnikov–de Haas (SdH) oscillations with low frequencies of 28 and 10 T$^{115}$. (The SdH effect reappears with vastly different behavior when $B$ rotates within the $ac$ plane$^{30}$.) Remarkably, $\rho_c$ for $B \parallel c > 39$ T is much smaller than $\rho_c$ for $B \parallel a$. From 0 to 45 T, $\rho_c$ decreases by a factor of 7 and 40 for $B \parallel a$ and $B \parallel c$, respectively.

Since the fully polarized state for $B_{||a} > 6$ T can reduce $\rho$ by only 1 order of magnitude, so even the $b$-axis $M$ were fully polarized at high fields, it still cannot account for the 3 orders of magnitude decrease in $\rho_c$ when $B_{||b} > 15$ T, indicating that the spin degree of freedom alone is not at all enough to explain the behavior observed.
in Figure 4.2. It is striking that a fully spin-polarized state, which is essential for magnetoresistance in all other magnetoresistive materials\textsuperscript{116,117}, is the least favorable for conduction in Ca\textsubscript{3}Ru\textsubscript{2}O\textsubscript{7}. It deserves mentioning that the resistivities $\rho_a$ (resistivity measured with both voltage and current running along the a-axis) and $\rho_c$ behave very similarly, as shown in the inset. For $B \parallel a$, the decrease in $\rho_a$ is also 1 order of magnitude, the same as that of $\rho_c$, suggesting that the reduction in both $\rho_a$ and $\rho_c$ is driven by the same in-plane spin polarization. For $B \parallel b$, $\rho_a$ decreases by 2 orders of magnitude when $B>B_c$, confirming that the spin-polarized state is indeed not favorable for electron hopping. The striking behavior is that $\rho_a$ (~$10^{-3}$ $\Omega$cm) is larger than $\rho_c$ (~$10^{-4}$ $\Omega$cm) when $B>B_c$, although the opposite is true when $B < B_c$. There may be a change in effective dimensionality driven by $B$ that results in incoherent-coherent and dimensional crossover and thus smaller interplane $\rho_c$ when $B>B_c$. The crossover, if any, has a lesser impact on the intraplane $\rho_a$. This behavior driven by $B$ could be analogous to that driven by temperature discussed in Ref.\textsuperscript{118}.

Shown in Figure 4.3 are $M$ and $\rho_c$ as functions of $B$ for the $B \parallel a$ and $b$ axes for $40 \leq T < 56$ K. The advantage of this temperature range is that $B_c$, along both the $a$- and the $b$-axis, falls within the range of 7 T, so that $M$ can be fully characterized using a SQUID magnetometer. A direct comparison of $\rho$ and $M$ allows to further probe correlations and the role of OO. Figure 4.3 (a) displays $M$ as a function of $B$ for the $B \parallel a$ axis. At 40 K, $M(B)$ is still very similar to $M(B)$ at low temperatures (see Figure 4.2) but with slightly lower $M_s$ (=1.6$\mu_B$/Ru) and $B_c$ (=5.8 T). For $41 \leq T \leq 45$ K, a second transition develops at $B^* > B_c$, suggesting an intermediate FM state for $B_c < B < B^*$, which is not fully polarized along the $a$ axis. A possible interpretation is that the spins are rotating away from the $a$ axis due to a shortening of the $c$ axis near $T_{MI}$, and hence a stronger field ($B^*$) is required to realign these spins along the $a$ axis. Since the spin rotation tends to become stronger as $T$ approaches $T_{MI}$, $B^*$ increases with $T$. $M$ is about 1$\mu_B$/Ru at $B_c$ and increases by 0.6$\mu_B$/Ru at $B^*$. Only half of the ordered spins are thus aligned with the $a$ axis in the spin reorientation (SR) region for $B_c < B < B^*$, $B_c$ decreases with $T$ and vanishes near $T_N$ (=56 K). Unlike $M$ for the $B \parallel a$ axis, $M$ for the $B \parallel b$ axis is unsaturated at $B>B_c$ and rounded at $B_c$ without hysteresis, suggesting a second-order transition [see Figure 4.3 (b)]. Noticeably, the $b$-axis $M$ at 7 T always converges to $\sim$1$\mu_B$/Ru, which is corresponding to 50% spin polarization and
is independent of $T$. Clearly, $M_s$ for the $B \parallel b$ axis is always smaller than that for the $B \parallel a$ axis in spite of the spin reorientation that partially enhances $M$ for the $B \parallel b$ axis.

Figure 4.3. Field dependence of $M$ and $\rho_c$ for $B \parallel a$ axis [panel (a) and panel (c)] and for $B \parallel b$ axis [panel (b) and panel (d)] for temperature range $40K \leq T \leq 52K$. $B^*$ indicates the second magnetic transition for $B \parallel a$ axis. $B_{c1}$ (solid arrows pointing down) and $B_{c2}$ (open arrows pointing up) represent the beginning and the ending of the resistivity valleys.

The corresponding $\rho_c$ as a function of $B$ for the $B \parallel a$ and $b$ axes is displayed in Figure 4.3 (c) and (d), respectively. For the $B \parallel a$ axis, $\rho_c$ at 40 K shows an abrupt drop at $B_c$ similar to that at low temperatures with a magnetoresistance ratio $\Delta \rho/\rho(0) = 58\%$, where $\Delta \rho=\rho(7T)−\rho(0)$. In the range $41 \leq T \leq 45 K$, $\rho_c$ for $B \parallel a$ decreases initially at $B_{c1}$, and then further at $B^*$ with a total $\Delta \rho/\rho(0)$ similar to that at 40 K. Clearly, for $T \leq 45 K$, $\rho_c$ perfectly mirrors the behavior of $M$ for the $B \parallel a$ axis, suggesting a strong spin-charge coupling in this region. However, for $T < 46 K$, a
valley develops in $\rho_c$; the beginning and the end of this valley define two fields, $B_{c1}$ ($B_{c1} = B_c$ for $T < 46$ K) and $B_{c2}$. The valley broadens with increasing $T$ ($B_{c1}$ decreases with $T$, while $B_{c2}$ increases) and changes its shape for $T \geq 48.2$ K, where the slope at $B_{c1}$ is now positive and $B_{c1}$ increases with $T$. An important point is that the field dependence of $\rho_c$ for $46 \leq T \leq 52$ K does not track the field dependence of $M$ [compare Figure 4.3(a) and (c)]. This lack of parallel behavior of $M$ and $\rho_c$ is precisely a manifestation of the crucial role of the orbital degrees of freedom that dictate electron hopping for $B \parallel a$.

Furthermore, the reduction in $\rho_c$ for the $B \parallel b$ axis [Figure 4.3 (d)] is always much larger than that for the $B \parallel a$ axis [Figure 4.3 (c)], and yet $M_s$ for the $B \parallel b$ axis is always smaller than $M_s$ for the $B \parallel a$ axis. For example, at 42 K and 7 T, $\Delta \rho/\rho(0) = 50\%$ with $M_s = 1.52\mu_B$/Ru for $B \parallel a$, and $\Delta \rho/\rho(0) = 80\%$ with $M_s = 1.03\mu_B$/Ru for $B \parallel b$. Note that the difference in both $M_s$ and $\Delta \rho/\rho(0)$ between the $B \parallel a$ and $b$ axes is $\sim 35\%$. The temperature dependence of $M(7$ T) (left scale) and $\Delta \rho/\rho(0)$ at 7 T (right scale) for the $B \parallel a$ and $b$ axes is summarized in Figure 4.4(a). Such an inverse correlation between $M$ and $\Delta \rho/\rho(0)$ suggests that the spin-polarized state is indeed detrimental to the CMR. For $T > T_{MI}$, the metallic state is recovered for $B < B_{c1}$. However, applying $B$ along the $a$ axis leads to a rapid increase in $\rho_c$ with positive $\Delta \rho/\rho(0)$ reaching as high as $112\%$ for $B > B_{c2}$, whereas applying $B$ along the $b$ axis results in essentially no changes in $\rho_c$. 
Figure 4.4. (a) Temperature dependence of $M$ (triangles) and $\Delta \rho/\rho(0)$ (solid circles, right scale) at 7T for the $B||a$ and $b$ axes. (b), (c) Phase diagrams plotted as $B$ vs $T$ summarizing various phases for the $B \parallel a$ and $b$ axes, respectively. Note that in (b) $B_{c1}(\rho)$ and $B_{c2}(\rho)$ indicate the curves generated based on $\rho$, and $B_c(M)$ on $M$.

As is known, for $B<6$ T, the Mott-like state is due to the OO facilitated by the $c$-axis shortening at $T_{MI}^{27,37}$. When $B_{||a} > 6$ T, the magnetic state becomes FM with the OO remained and stabilized by the FM state. The orbital order is either a ferro-orbital (FO) or an antiferro-orbital (AFO) configuration. Hence the system is in either
a FM-FO or a FM-AFO state. The former inhibits the hopping of the $4d$ electrons because of the Pauli Exclusion Principle, while the latter permits intersite transitions but at the expense of the Coulomb energy. Therefore, despite an order of magnitude drop in $\rho_c$ due to the spin polarization when $B>6$ T, a fully metallic state can never be reached for the $B \parallel a$ axis. In fact, the linear increase in $\rho_c$ with increasing $B$ for $B_{[a]} > 6$ T, as shown in Figure 4.2, may manifest a strengthened OO via the enhanced FM state. Conversely, applying $B$ along the $b$ axis steadily suppresses the AFM state $^{27}$, removing the orbital order through spin-orbit interaction when $B>B_c$. Such an orbitally disordered (OD) state drastically increases the electron mobility, therefore leading to CMR. On the other hand, applying $B$ along the $c$ axis has a noticeable impact on spin and orbital configurations when $B>B_c$. For $48.2 < T < 56$ K, the system changes from an AFM-OD to an AFM-OO phase when $B>B_{c1}$. The evolution of the magnetic-orbital configuration is associated with the Jahn-Teller coupling, which appears in the vicinity of $T_{\text{MI}}$.

This phase diagram is remarkable consistent with rapid changes of Ru-O phonon frequency with $B$ seen in Raman scattering experiments. The Raman scattering studies the vibrational, rotational and other low-frequency modes in a system. In contrast to magnetic and transport measurements, it allows us to directly probe the evolution of the orbital configuration, spin dynamics, and structural properties of Ca$_3$Ru$_2$O$_7$ as functions of temperature, magnetic fields, and pressure$^{37}$.

The Raman scattering experiment was carried out by Karpus et. al.$^{37, 40, 41}$. It studied the spin and orbital dynamics by tracking two frequency modes: (a) a low frequency mode near 56cm$^{-1}$ which is associated with spin wave (magnon) excitation.
of the antiferromagnetic ground state (This mode is used to monitor the spin configuration in Ca$_3$Ru$_2$O$_7$)\textsuperscript{38, 39}; (b) the Ru-O phonon near 416 cm$^{-1}$ which is sensitive to the RuO$_6$ octahedra structure and orbital population. The shifting of this mode generally indicates the variance of electrons population in the d-orbital.

From the Raman studies, Karpus and his collaborators observed that the metal-insulator transition and the spontaneous collapse of the c-axis lattice at $T_{MI}=48^\circ$ are accompanied with the softening and broadening of a Ru-O phonon mode\textsuperscript{37-39}, indicating an orbital-configuration reconstruction around this temperature. Further exploration in the field-induced spin and orbital configuration in the vicinity of $T_{MI}=48K$ reveals the following phenomena due to the transitions between complex orbital and magnetic phases (see Fig. 2(b) in Ref.37).

For $B \parallel a$, the system is observed to evolve from an OO (orbital-ordered) state for $B < B_{c1}$ to an OD (orbital-disordered) state for $B_{c1} < B < B_{c2}$ and finally to a reentrant OO state as $B$ increases ($B_{c1}$ and $B_{c2}$ are the critical fields where the OO-OD transitions occur).

(a) AF/OO regime ($T < T_{MI}$ and $B < B_c=6T$, AF: antiferromagnetic; OO: orbital-ordered) Here the magnon modes for the antiferromagnetic ordering are clearly observed whereas the Ru-O phonon mode is shifted to frequency value smaller than 418 cm$^{-1}$. The softening of this phonon mode indicates that the RuO$_6$ octahedra are compressed and the orbital ordering persists in this regime: the $d_{xy}$ orbital is lowered relative to the $d_{yz}$ and $d_{xz}$ orbitals and the orbital occupancy is $(n_{yz/zx}, n_{xy}) \sim (2, 2)$. This analysis is consistent with the insulating behavior that has been observed in the transport property measurements in which the resistivity increases by a factor of 20 as temperature decreases\textsuperscript{27, 29, 111}.

(b), Orbital-degenerate regime ($T_{MI}<T<T_N$ and $B_{c1}<B<B_{c2}$,) In this phase regime, the phonon energy modes increase to higher than 418 cm$^{-1}$ as the field increases, indicating that the RuO$_6$ octahedra are gradually undistorted and the three d-orbitals are approximately degenerate with electron population $(n_{yz/zx}, n_{xy})=8/3, 4/3)$\textsuperscript{41}. As a result, the three d-orbitals are degenerate and the orbital-ordered state is removed. The system shows more conductive behavior in this regime as illustrated in Figure 4.3 (b).

(c) FM/OO regime ($B>B_{c2}$; FM: ferromagnetic) - In this phase only a single-magnon mode is observed, signaling a FM state that is realized by metamagnetic
transition. The phonon mode shifts back to around 418 cm$^{-1}$, indicating a compressed RuO$_6$ octahedra with electron population ($n_{yz/zx}$, $n_{zr}$) $\sim$ (2, 2), and the system is back to its orbital-ordered state. This explains why the system remains at its insulating state even though the spins are polarized$^{27}$.

For $B \parallel b$, the Ru-O phonon energy systematically increases as $B$ increases, accompanied with a diminution of the magnon intensity. This transformation, together with the unexpected magnetoresistance observed along this direction$^{29}$, indicates a field-tuned transition from the AF-OO phase [($n_{yz/zx}$, $n_{zr}$) $\sim$ (2, 2)] for $B<\text{Bc}$ to an OD phase [($n_{yz/zx}$, $n_{xy}$) = 8/3, 4/3] for $B>\text{Bc}$.

The complex phases revealed by the Raman study are remarkably consistent with our parallel magnetic and transport properties studies$^{29}$, providing complementary evidence for the importance of the orbital degrees of freedom in this system.

From the evidence and discussion presented here, it is obvious that the orbital degree of freedom and its coupling to spin and lattice play a critical role in Ca$_3$Ru$_2$O$_7$. As a consequence, applying $B$ along the $a$, $b$, and $c$ axes leads to novel and vastly different properties. Most notably, CMR achieved by avoiding the FM state is fundamentally different from that of all other magnetoresistive materials.

4.3 Anomalous quantum oscillations

From the Colossal Magnetoresistance studies, it is obvious that the transport property of Ca$_3$Ru$_2$O$_7$ is extremely sensitive to the orientation of $B^{30}$. A resistivity reduction of one order of magnitude is observed for $B$ applied along the magnetic easy axis-a axis, but a three order of magnitudes drop in resistivity is observed for $B$ applied along the hard axis–b axis. For $B$ applied along the c axis, system shows slow yet strong quantum oscillations. It is then of great interest to explore how the transport property evolves as the orientation of $B$ varies with respect to the crystalline direction.

The field dependence of $\rho_c$ (on a logarithmic scale) for $B$ rotating in the $ac$ plane ($B \parallel a$ axis $\theta = 0^\circ$ and $B \parallel c$ axis $\theta = 90^\circ$) at $T=0.4$ K is shown in Figure 4.5 (a) for $B$ ranging from 11 to 45 T. $B_c$ occurs at 6 T for the $B||a$ axis, and increases with increasing $\theta$, i.e., as $B$ rotates towards to the $c$ axis. The striking finding is that strong SdH oscillations are qualitatively different for $11^\circ \leq \theta \leq 56^\circ$ and $56^\circ < \theta \leq 90^\circ$. It is
then likely that the vicinity of $\theta=56^\circ$ marks the onset of the melting of the OO state as $B$ rotates further away from the easy axis of magnetization ($a$ axis). This destabilizes the FM state, and thus the OO state via direct coupling to the field or the spin-orbit interaction. (This is only possible perturbatively, because the spin-orbit interaction is quenched by crystalline fields.) Consequently, the electron mobility increases drastically, explaining the largely enhanced conductivity for $56^\circ < \theta \leq 90^\circ$.

Figure 4.5. (a) $\rho_c$ for $B$ rotating in the ac plane with $\theta=0$ and $90^\circ$ corresponding to $B||a$ and $B||c$, respectively. (b) Enlarged $\rho_c$ on a linear scale for clarity. Note that the range of $B$ is from 11 to 45T in (a) and (b).
For $0<56^\circ$ the strong oscillations occur only for $B>B_c$ and with frequencies significantly larger than the ones previously observed for the $B \parallel c$ axis. For clarity, Figure 4.5 (b) exhibits $\rho_c$ on a linear and enlarged scale for $B > B_c$. For $0^\circ < \theta < 56^\circ$ and $B > B_c$, $\rho_c$ increases with both $B$ and $\theta$, and displays oscillatory behavior only for $11^\circ \leq \theta < 56^\circ$. While the extremal orbits responsible for the oscillations are facilitated by the FM state, it is remarkable that no oscillations are seen when $\theta = 0$ ($B \parallel a$ axis), where the FM state is fully established at $B_c=6$ T. In contrast, no oscillations were discerned for $B$ rotating within the $bc$ plane at $B$ up to 45 T\textsuperscript{119}. The bumps seen in $\rho$ for $B \parallel b$ [Figure 4.5 (a)] are not oscillatory at higher $B$. The $bc$ plane is perpendicular to the easy axis of magnetization and has no FM component\textsuperscript{14, 15, 119}, suggesting a critical link of the SdH oscillations to the fully polarized FM state. The FM and the different projections of the tilt angles of the RuO$_6$ octahedra onto the $ac$ and $bc$ planes\textsuperscript{16} are expected to affect the Fermi surface.

On the other hand, for $56^\circ < \theta = 90^\circ$, the oscillations disappear for $B>B_c$ but are present for $B<B_c$, accompanying the much more conducting phase at high fields, as shown in Figure 4.5 (a) and (b). The frequency of the oscillations seen for $B<B_c$ remains essentially unchanged with $\theta$ for $65^\circ < \theta < 90^\circ$. Since the $d_{xy}$ orbitals are believed to be responsible for the oscillations $B \parallel c$ axis, the nearly constant frequency upon tilting of $B$ suggests that the oscillations in the absence of the metamagnetism originate from a nearly spherical pocket of the same $d_{xy}$ orbitals. Conversely, the oscillations for $11^\circ \leq \theta < 56^\circ$ and $B > B_c$ could be associated with a configuration of the FM state and ordered $d_{z^2}$ and/or $d_{x^2-y^2}$ orbitals. These orbitals offer only limited electron hopping (as confirmed by a larger $\rho_c$), and thus lower density of charge carriers and longer mean free path which in turn facilitates electrons to execute circular orbits.

Figure 4.6\textsuperscript{30} shows the amplitude of the SdH oscillations as a function of $1/B$ for several representative $\theta$ at (a) $T=0.4$ K and (b) 1.5 K. The SdH signal is defined as $\Delta \rho/\rho_{bg}$, where $\Delta \rho = (\rho_c - \rho_{bg})$ and $\rho_{bg}$ is the background resistivity. $\rho_{bg}$ is obtained by fitting the actual $\rho_c$ to a polynomial. The Fast Fourier Transformation (FFT) yields the same frequencies as those determined from Figure 4.6 (a) and (b). The result from the FFT is shown as Figure 4.6. (c) for a representative $\rho_c$ at $T=1.5$ K and $\theta = 26^\circ$. Clearly, the oscillations are strong and slow, and their phase and frequency shift systematically with changing $\theta$. The oscillations vanish for $\theta > 56^\circ$, suggesting that
the extremal cross section responsible for the oscillations is highly susceptible to the orientation of $B$. SdH oscillations are usually rather weak in metals\textsuperscript{114}, the remarkably strong oscillatory behavior for $11^\circ \leq \theta < 56^\circ$ may arise from an extremal orbit with a flat dispersion perpendicular to the cross section, so that a large constructive interference can occur. It is also noted that the $1/\cos\theta$-like behavior seen in Figure 4.6 (a) and (b) may imply the cylindrical Fermi surface elongated along the $c$ axis, which favors the two-dimensional conductivity. With further increasing $\theta$ ($=56^\circ$), the impact of $B$ on the Fermi surface becomes even more dramatic and the closed orbit is no longer observed. The closed orbit is possibly replaced by open ones that do not contribute to oscillations.
Figure 4.6. The amplitude of the SdH oscillations defined as $\Delta \rho / \rho_{bg}$ as a function of inverse field $B^{-1}$ for various $\theta$ and for (a) $T=0.4$ K and (b) 1.5 K; (c) The SdH amplitude as a function of frequency, $f$, obtained from the fast Fourier transformation for a representative $\rho_c$ at $T=1.5$ K and $\theta=26^\circ$.

Figure 4.7$^{30}$ illustrates the angular dependence of the SdH frequency for $T=0.4$ and 1.5 K (left scale) and $B_c$ (right scale). The unusual feature is that the frequency is temperature dependent, increasing about 15% when $T$ is raised from 0.4 to 1.5 K. The frequency for $B>B_c$ rapidly decreases with increasing $\theta$ and reaches about 45 T in the vicinity of $\theta=56^\circ$, whereas the frequency for $B<B_c$ stays essentially constant for
$\theta > 56^\circ$. The oscillations become difficult to measure in the vicinity of $B_c$. This is expected if $B_c$ is associated with the melting of OO. The frequencies for $B>B_c$ are significantly larger than those for $B<B_c$, suggesting the former oscillations either originate from different electron orbits or a restructured Fermi surface. The angular dependence of $B_c$, on the other hand, is rather weak for $\theta < 56^\circ$ but becomes much stronger for $\theta > 56^\circ$. Note that $\rho_c$ displays a weak plateau at high magnetic fields and $\rho$ approaching $90^\circ$, which disappears for the $B||c$ axis because the FM state is no longer energetically favorable. Such an inverse correlation between the frequency and $B_c$ reinforces the point that the FM state reconstructs the Fermi surface and facilitates the oscillatory effect. It is evident that the vicinity of $\theta = 56^\circ$ or $52^\circ < \theta < 65^\circ$ marks a crossover region between the FM-OO state and the orbital degenerate (OD) state as shown in Figure 4.7.

Figure 4.7. The angular dependence of frequency for $T=0.4K$ and $1.5K$ (left scale, circles) and $B_c$ (right scale, squares) for $T=0.4K$. Note that the frequency is indicated with solid circles for $B>B_c$ and with empty circles for $B<B_c$. The shaded area in the vicinity of $56^\circ$ marks the melting of OO as $\theta$ increases.
For $B \parallel [110]$, $\rho_c$ also shows oscillations in the magnetoresistance as displayed in Figure 4.8\(^{30}\). The striking behavior is that these oscillations are periodic in $B$, instead of $1/B$, with a period of $\Delta B = 11$ T and persistent up to 15 K. This highly unusual observation is corroborated by plotting the data both as a function of $1/B$ [Figure 4.8 (a) and (b)] and $B$ [Figure 4.8 (c) and (d)]. The oscillations die off rapidly if $B$ slightly departs from the [110] direction (within $\pm 5^\circ$).

Figure 4.8. The amplitude of the oscillations for $B \parallel [110]$ and $T=0.5K$ as a function of (a) $B^{-1}$ and (c) $B$. The amplitude of the oscillations for various temperatures (from 0.5K to 15T) plotted as a function of (b) $B^{-1}$ and (d) $B$. (e) The temperature dependence of oscillations amplitude.
Oscillations in the magnetoresistivity periodic in $1/B$ (SdH effect) are a manifestation of the constructive interference of quantized extremal orbits of Fermi surface cross sections perpendicular to the field. Due to the Pauli principle the electrons are bound to follow the Fermi surface. The projection of the real space trajectory of a free electron onto a plane perpendicular to $\mathbf{B}$ reproduces the $k$-space trajectory rotated by $\pi/2$ and scaled by a factor $c \hbar /|e|B$. Hence, trajectories with constructive interference in real space are expected to be periodic in $B$ rather than $1/B$ (the frequency is proportional to the cross-sectional area in reciprocal space, so that the relation to the real space is $B^2$). Oscillations in the magnetoresistivity periodic in $B$ are realized in some mesoscopic systems and always related to finite size effects. Examples are (i) the Aharonov-Bohm (AB) effect, (ii) the Sondheimer effect, and (iii) the edge states in quantum dot. Each of the cases involves a geometrical confinement. The AB interference occurs when a magnetic flux threading a metallic loop changes the phase of the electrons generating oscillations in the magnetoresistance and is observed only in mesoscopic conductors, but not in bulk materials. The Sondheimer effect requires a thin metallic film with the wave function vanishing at the two surfaces. The thickness of the film has to be comparable with the mean free path. This gives rise to boundary scattering of the carriers that alters the free electron trajectories and the possibility of interference. Finally, the edge states require a quantum Hall environment with real space confinement.

Since the bulk material has no real space confinement for the orbits of the carriers, the most likely explanation for the periodicity as a function of $B$ is a Fermi surface cross section that changes with field. The $t_{2g}$ orbitals have off-diagonal matrix elements with the orbital Zeeman effect, and hence couple directly to the magnetic field. Consequently, the magnetic field could lead to a dramatic change of the Fermi surface if it points into a certain direction. Note that the pockets involved are very small (low frequencies as a function of $1/B$) and susceptible to external influences. If there is more than one conducting portion of the Fermi surface, occupied states can be transferred from one pocket to another with relatively small changes in the external parameters. This is also consistent with the 15% of change in the frequency when $T$ is raised from 0.4 to 1.5 K shown in Figure 4.7. Indeed, the amplitude of the oscillations follows the Lifshitz-Kosevich behavior expected for SdH oscillations [see Figure 4.8 (c)]. It is noted that the AB effect at finite $T$ would show the same amplitude.
dependence. What is still perplexing is that the cross section of the observed pocket is only 0.2% of the Brillouin zone, so the position of the Fermi energy is fixed at the nonquantized level of other Fermi surface branches. In such a situation, the density of states oscillates only against $1/B$. In addition, if the origin of the oscillations periodic in $B$ is ascribed to the Landau quantization, it is then perplexing as to why there is no SdH oscillations in the [110] direction, together with the oscillations periodic in $B$.

The observations of the magnetoresistance oscillations in $\text{Ca}_3\text{Ru}_2\text{O}_7$ periodic both in $B$ and $1/B$ reflect the crucial dependence of the quantized orbits on the orientation of $B$. The novel phenomena highlight the critical role of the orbital degrees of freedom embodied via the coupling of the $t_{2g}$ orbitals to the magnetic field and certainly merit more experimental and theoretical efforts.

4.4 Studies of the other layered ruthenates

4.4.1 Thermal properties of $\text{Sr}_4\text{Ru}_3\text{O}_{10}$

$\text{Sr}_4\text{Ru}_3\text{O}_{10}$ is another member of the RP series, $(\text{Ca}, \text{Sr})_{n+1}\text{Ru}_n\text{O}_{3n+1}$, with $n=3$. This system features a complex competition between intraplane antiferromagnetic and interplane ferromagnetic interactions. The magnetization measurement shows a sharp ferromagnetic order along c-axis (perpendicular to the RuO$_6$ planes) at $T_C=105\text{K}$, followed by an anomaly at $T_M=50\text{K}$ with the moment further increased. However, the temperature dependence of magnetization for ab plane exhibits only a weak cusp at $T_C$ and a pronounced peak at $T_M$, resembling behavior of enhanced paramagnet. Isothermal magnetization saturates at $B=0.2\text{T}$ for $B||c$ but shows a sharp metamagnetic transition at $2.5\text{T}$ for $B||ab$. The saturation moment achieved for $B||c$ is less than what we would expect from Ru$^{2+}$ ions (Ms=2$\mu_B$/Ru for a S=1 system). All these results suggest an exotic ground state with complex magnetic interactions. Several efforts have been made to probe the properties of this system, but a clear picture is still unrevealed.

Thermal properties were studies using ac-calorimetry, using typical frequencies of 2Hz at high temperatures and 20Hz at low temperatures. The relative specific heat data are then normalized to an absolute value measured by differential scanning calorimetry (DSC) at 200K. For comparison, the specific heat of $\text{Sr}_4\text{Ru}_3\text{O}_{10}$
is measured on crystals grown by both flux (FX) and floating zone (FZ) techniques. Overall, both samples show similar temperature dependence of the specific heat as displayed in Figure 4.9.

![Figure 4.9. The temperature dependence of specific heat for floating zone (FZ) samples and flux (FX) samples. For clarity, the data for FZ sample are shifted up by five. Note that the specific heat data are all normalized to the gas constant, R=8.31 J/(mole K).](image)

However, the results shown in Figure 4.10 indicate a better quality of FX sample than the FZ sample. The FX sample exhibits a sharp mean-field-like step in the specific heat at $T_C=102K$, whereas the anomaly exhibited by FZ sample is less pronounced and broader. This observation is consistent with the susceptibility measurement in which the FZ sample is less anisotropic than the FX samples, showing a transition at $T_C$ that is not as sharp as that of FX sample. The reason for the difference between FZ and FX samples might be due to inter-growths between $ab$ and c-axis direction and possible inclusions of small amounts of other ruthenate phases in the FZ sample.
The anomaly at 102K shows a sharp mean-field-like step, signaling a collective ordering of spins upon $T_C$. One can evaluate the extent of this ordering from the entropy reduction $\Delta S$ induced by spin ordering. The entropy removal we would expect from one ordering spin is $R\ln(2S+1)$. For a system like Sr$_4$Ru$_3$O$_{10}$ with $S=1$, if all the three spins in one formula unit are ordered, the expected entropy removal would be $\Delta S=3R\ln(2S+1)=3.3R$. With the correct baseline behavior...
unknown, it is not easy to calculate the exact entropy removal. However, we can still estimate a lower limit of $\Delta S$ to be $\sim 0.02R$ by fitting the specific heat away from the transition to a smooth curve as indicated in Figure 4.11. On the other hand, the upper limit of $\Delta S$ can be estimated to be $\Delta S \sim \Delta C \sim 0.4R$, as expected from a mean-field anomaly. As a result, the entropy removal at $T_c$ is estimated to be $0.02R < \Delta S < 0.4R$. These values are significantly smaller than what we would have expected (3.3R), indicating that only a small amount of the spins are ordered. It is possible that at zero magnetic field, the competition between antiferromagnetic and ferromagnetic interactions generate a strong spin fluctuation in the system, making the system difficult to order at zero field and resulting in a small entropy removal\textsuperscript{128,129}. In fact, spin fluctuations can be strong even in the high magnetic field region, leading to a saturation moment of only $1.13\mu_B$/Ru, which is less than 60% of the full spin ordering. Taking this consideration into account, the maximum $\Delta S$ we would expect for this system at zero field is $1.86R$ with $B (>0.2T)$ applied along the c-axis.

**Figure 4.11.** The temperature dependence of $C/R$ for FX samples near $T_c=102K$ and the fitting curve of a quadratic function. Inset: The specific heat minus the fitting background.
Figure 4.12 shows the temperature dependence of the specific heat at around 50K. No thermal anomaly corresponding to the magnetic and transport anomalies at $T_M$ can be detected in both FZ and FX samples, suggesting that these anomalies result from gradual “cross-over” behavior rather than a thermodynamic phase transition at zero field. A gradual “cross-over” behavior in magnetic, thermodynamic, and transport properties can possibly arise from the coherence-incoherence and dimensional crossover that is typical to the layered strongly correlated metals\textsuperscript{118}.

![Figure 4.12. The temperature dependence of specific heat around 50K for both samples. For clarity, the specific heat data of FZ sample is shifted up by one.](image)

The specific heat at low temperatures is plotted as $C/T$ vs. $T^2$ in Figure 4.13. Since we normalize the specific heat data at high temperature 200K, any small difference between the FZ and FX samples can be magnified at low temperatures, resulting in the seeming difference between them in this plot. Nonetheless, both samples display deviation from the expected $C/T=\gamma+\beta T^2$ behavior by showing a
negative curvature downturn for T<9K. In other words, besides the electronic contribution \( C_e = \gamma T \) and the phonon contribution \( C_{ph} = \beta T^3 \), there may be contributions coming from the spin excitations. Since at low temperatures, the specific heat deviate below the \( C/T = \gamma + \beta T^2 \) line and has positive slope when decreasing towards zero, we estimate the magnon contribution to be \( C_s = \eta T^p \) with \( 1 < p < 3 \). However, to get a reasonable Debye temperature \( \Theta < 500 \text{ K} \), close to that of \( \text{SrRuO}_3 \) and \( \text{Sr}_3\text{Ru}_2\text{O}_7 \), we have to set \( p \) to be \( 1 < p < 2 \). Our fitting, with \( p = 3/2 \), then yields a set of parameters that are listed in Table 2. The values of \( \beta \) obtained from this fit are 0.012 and 0.017mJ Ru\(^{-1}\) K\(^{-4}\) for FX and FZ samples respectively, giving rise to an average Debye temperature \( \sim 423\text{K} \). The \( \gamma \) values are 23 and 15 mJ Ru\(^{-1}\) K\(^{-2}\) for the FX and FZ samples respectively. Combined with the susceptibility measurement\(^{11}\), this give rise to a Wilson ratio \( \sim 4.5 \), implying a significant electron correlation in this system. However, our \( \gamma \) is considerably smaller than the values observed for \( \text{SrRuO}_3 \) (\( \sim 30 \) mJ Ru\(^{-1}\) K\(^{-2}\)) and \( \text{Sr}_3\text{Ru}_2\text{O}_7 \) (110 mJ Ru\(^{-1}\) K\(^{-2}\)).
Figure 4.13. (a) The temperature dependence of specific heat at low temperatures for both FZ and FX samples. For clarity the data for FZ sample have been shifted up by one. (b) C/RT as a function of $T^2$ for both samples. Both sets of data are fitted to $C = \gamma T + \beta T^3 + \eta T^{3/2}$ and $C = \beta T^3 + \eta T \ln (T/T_0)$. 
The fitting also generates some valuable information about the magnetic ordering and deserve some elaboration here. First of all, both FX and FZ samples shows good fitting with \( p=3/2 \), which however suggests a three-dimensional ferromagnetic order. For a three-dimensional ferromagnet, with three spins/formula unit, \( \eta/R=3(0.040)\times(SJ_{\text{eff}})^{-3/2} \), where \( J_{\text{eff}} \) is the effective exchange interaction averaged over nearest neighbors. Hence, taking \( S=1 \), our fit gives \( SJ_{\text{eff}}=8K \). This small value suggests that is there is residual three dimensional ferromagnetic order, it affects only a small component of the spins. (Note that a \( T^{3/2} \) term with such a small value of \( J_{\text{eff}} \) cannot be associated with inclusions of ferromagnetic \( \text{SrRuO}_3 \), for which such a contribution was not observed). On the other hand, for a system showing two-dimensional antiferromagnetic ordering with an easy axis for spin polarization in addition to one-dimensional ferromagnetic ordering, the low-temperature \( (k_B T<<\varepsilon_A) \) magnon contribution to the specific heat will be activated as \( C_S\sim T^{1/2}\exp(-\varepsilon_A/k_B T) \), where \( \varepsilon_A \) is the antiferromagnetic magnon energy gap and the prefactor is the contribution from ferromagnetic spin-waves. On the other hand, for \( k_B T>>\varepsilon_A \), the antiferromagnetic gap becomes irrelevant and \( C_S\sim T^{3/2} \). The existence of specific heat contribution \( C_S\sim T^{5/2} \) may signal a cross-over behavior between these two limits when the temperature is comparable to the antiferromagnetic anisotropy, e.g. \( \varepsilon_A/k_B\sim5K \). However, the magnetization measurement suggests a planar isotropy associated with a metamagnetic transition that is achieved by a large magnetic field, adding to the difficulty to explain these behaviors.

<table>
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<th>Parameters</th>
<th>( \gamma ) (mJ Ru(^{-1}) K(^{-2}))</th>
<th>( \beta ) (mJ Ru(^{-1}) K(^{-4}))</th>
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The low temperature specific heat can also be fitted with another function \( C_S=\eta T\ln(T/T_0) \), which indicates ferromagnetic fluctuations near a quantum critical point. However, the exhibition of ferromagnetic interplane order in this system again makes it difficult to explain such dependence. In a word, our measurement data suggest an unusual magnetic order including both ferromagnetic and...
antiferromagnetic order. A more thorough understanding of this interaction requires measurements with the application of field along different orientations.

In conclusion, we have presented specific heat measurement on both a floating zone grown (FZ) sample and a flux grown (FX) sample. Similar temperature dependence of specific heat was observed for both samples except that the flux grown sample has a sharper anomaly at 102K. The anomaly observed for FX is smaller than what we will expect for complete spin ordering. No anomaly is observed at 50K for either sample, indicating that the changes observed in magnetic and transport properties may be a crossover behavior in nature rather than a phase transition. Interestingly, both samples display an extra specific heat term that is $T^{3/2}$ dependent, which has never been observed in the other strontium ruthenate systems. Although a thorough interpretation for this dependence is still unavailable, it certainly indicates an unusual magnetic order in this material.

4.4.2 Magnetic and thermal properties of Pr$_3$RuO$_7$

Besides the RP series, ruthenate-based oxides can also be formed with different crystalline structures. For example, the ruthenates Ln$_3$RuO$_7$ (Ln is lanthanides) can be crystallized with either orthorhombic or disordered fluorite structure (depending on the ionic size of the Ln cations). Here Ru ions are pentavalent instead of tetravalent.

In the case of the Pr$_3$RuO$_7$ system, the unit cell is orthorhombic with $a=10.974$ (13) Å, $b=7.376$ (11) Å, and $c=7.528$ Å, corresponding to a space group of Cmcm. Ru$^{5+}$ is octahedrally coordinated and the octahedra are corner sharing with each other, forming a zig-zag chain along the c-axis as illustrated in Figure 4.14. Flanking the chain RuO$_6$ octahedra on the bc plane are the chains of distorted PrO$_8$ edge-sharing cubes along the c-axis. The RuO$_6$ and the PrO$_8$ chain then form layers along the a-axis, leaving the other two-third of the Pr ions, which are coordinated by seven fold oxygen, sitting between the layers. The interlayer separation (5.5Å) is larger than the intralayer separation (3.7Å), leaving the system with a one-dimensional configuration which may be reflected in its magnetic and electronic properties. In addition, the unpaired 4f electron from the Pr$^{3+}$ can interact with the
unpaired d electrons from the Ru$^{5+}$ sides, providing a precious chance for studying the coupling between electrons of two different magnetic cation constituents$^{131,132,134}$. 

*Figure 4.14. Crystal structure of Ln$_3$RuO$_7$. Here Ln=Pr (Quoted from Ref.132).*

Shown in Figure 4.15 is the magnetic susceptibility as a function of temperature with B (=0.01T) parallel ($\chi_\parallel$) and perpendicular ($\chi_\perp$) to the c-axis. Consistent with the pervious measurements on powder samples, the system shows very anisotropic susceptibility with $\chi_\parallel$ much stronger than $\chi_\perp$ at high temperatures, indicating a magnetic easy-axis along the RuO$_6$ chain or the PrO$_8$ chain. Our measurements also detect an antiferromagnetic ordering at $T_N$=54K, with polarization
(approximately) along c, but no second anomaly is observed at 35K as indicated in the previous measurements on polycrystalline samples. It is possible that this anomaly (at 35K) is not an intrinsic phenomenon but simply arises from the crystalline defects in polycrystalline samples.

Fitting for the high temperature (150-350K) susceptibility to the Curie-Weiss law $\chi = \chi_0 + C/(T-\theta_C)$ is displayed in the inset of Figure 4.15. The parameters obtained from the fitting are listed in Table 3. The temperature-independent susceptibilities, $\chi_0$, are 1.74emu/mole and 2.29emu/mole respectively for c-axis and its perpendicular directions. The Curie constant is 4.21emu K/mole for both directions, corresponding to an effective moment $\mu_{\text{eff}}$ of around 5.81$\mu_B$. Our Curie constant is smaller than those calculated from the polycrystalline samples, which might be due to the difference on
the fitting temperature ranges between these two analyses. Finally, the curie temperatures $\theta_c$ are +48K for the c-axis and -21K for the perpendicular direction as displayed in the Figure 4.15, implying antiferromagnetic coupling for the perpendicular direction and twice as strong ferromagnetic coupling for the c-axis.

Table 3 Comparison between different studies

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</table>

The isothermal magnetization measurement in Figure 4.16 for T=2K clearly illustrates the anisotropy of the single crystal by showing a metamagnetic transition at 3.5T for $B_\parallel$c, but no transition for $B_\perp$c. The application of field helps to align moments along c-axis but leaves the system at paramagnetic state when $B_\perp$c. The saturation moment $M_S$ reached for $B_\parallel$c is $4.8\mu_B$/f.u at 2K and it decreases gradually as temperature increases. It is worth pointing out that for La$_3$RuO$_7$ that includes only a single magnetic species, Ru$^{5+}$, no metamagnetic transition is detected$^{135}$. This observation suggests the involvement of Pr moments (including angular moments and spin moments) that affect the magnetic properties of this system series.
In the Pr$_3$RuO$_7$, both the RuO$_6$ octahedra chain and the PrO$_8$ cubic chain run along the c-axis by either corner-sharing or edge-sharing, thus greatly enhances the coupling interaction along the c-axis. Reflected in the susceptibility measurement, the magnitude of $\chi$ along c-axis is larger than $\chi$ in the perpendicular direction. In addition, since the superexchange interactions always favor 180° bond angle rather than 90° bond angle, the exchange interaction is expected to be stronger for d electrons (couple through the 180° Ru-O-Ru bond) than the f electrons (couple through the 90° Pr-O-Pr bond). In fact, it has been proved that doping on the ruthenium sites has a stronger effect on magnetic property than doping on the praseodymium sites$^{131}$. It is then very likely that the Néel transition is mainly driven by the Ru moments. Although the interaction from the chain Pr ions is not as strong as that from chain Ru, they still can be sensitive to the exchange field built up by the ruthenium ordering and order correspondingly. The exchange interaction from

Figure 4.16. The isothermal magnetization $M$ as a function of $B$ at $T=2K$ for $M_{\perp}$ and $M_{||}$.
interchain Pr ions is expected to be even weaker due to the large layer separation and
the lack of oxygen in between. However, it is hard to rule out the possibility that they
may take part in affecting the phase transition.

For each free Pr$^{3+}$ ($L=3$, $S=1$ and $J=4$), the expected effective moment is
$\mu_{\text{eff}}=g(J(J+1))^{1/2}=3.54\mu_B$ if the orbital moments are not quenched. Then $C=(\mu_{\text{eff}}/2.82)^2$
=1.58 emu K/mole. For orbitally quenched Ru$^{5+}$ ($S=3/2$), the expected Curie constant
is 1.87$\mu_B$. All the possible Curie constants and the expected saturation moments
coming from possible moments configurations are listed in Table 4. The Curie
constant calculated from case 4 ($C=4.87$ emu K/mole) is close to our experimental
value 4.2 emu K/mole, indicating that all Pr orbital moments are quenched before the
Néel transition. In addition, at low temperatures and high magnetic fields ($B>3.5T$),
the experimental saturation moment $4.8\mu_B$/f.u is close to $M_s$ in case 6 ($M_s=5\mu_B$/f.u),
which suggests that only the chain Pr spin moments and the Ru spin moments
contribute to the total saturation moments. Hence our magnetic property measurement
suggests that the interlayer praseodymium ions are in singlet states.

Table 4. Possible configurations of the magnetic moments

<table>
<thead>
<tr>
<th>configuration of moments</th>
<th>C from Chain Pr (×1)</th>
<th>C from Interlayer Pr (×2)</th>
<th>C from Ru (×1)</th>
<th>Total C</th>
<th>$M_s(\mu_B$/f.u.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. All Pr moments are unquenched</td>
<td>1.58</td>
<td>1.58×2</td>
<td>1.87</td>
<td>6.6</td>
<td>12.6</td>
</tr>
<tr>
<td>2. Interlayer Pr moments are quenched</td>
<td>1.58</td>
<td>0</td>
<td>1.87</td>
<td>3.5</td>
<td>6.2</td>
</tr>
<tr>
<td>3. Chain Pr moments are quenched</td>
<td>0</td>
<td>1.58×2</td>
<td>1.87</td>
<td>5.03</td>
<td>9.4</td>
</tr>
<tr>
<td>4. All the Pr orbital moments are quenched</td>
<td>$J=S=1$, $C=1$</td>
<td>$J=S=1$, $C=1×2$</td>
<td>1.87</td>
<td>4.87</td>
<td>9</td>
</tr>
</tbody>
</table>
Table 4 (Continued)

<table>
<thead>
<tr>
<th></th>
<th>J=0, C=0</th>
<th>J=S=1, C=-1 \times 2</th>
<th>1.87</th>
<th>3.87</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>5. Only the interlayer Pr's spin moment unquenched</td>
<td>J=S=1, C=1</td>
<td>J=0, C=0</td>
<td>1.87</td>
<td>2.87</td>
<td>5</td>
</tr>
</tbody>
</table>

The measurement of magnetic properties has illustrated the one-dimensional feature of this system and the possible spin configuration. We then measured the thermal properties of this system using DSC and ac calorimetry\textsuperscript{102, 136}, hoping that more detail about the interactions can be brought out from this measurement. The typical chopping frequency for our ac-calorimetry sample (m=21mg) was 4Hz for the thermocouple measurement and 10Hz for the bolometer measurement, with both frequencies appropriate over wide temperature ranges. Figure 4.17 (a) shows the temperature dependence of the specific heat normalized to the gas constant (R=8.31 J/(mole K)). As expected, the specific heat at high temperature is close to $c=3NR=3\times(3+1+7)R=33R$. Figure 4.17 (b) is the specific heat for temperatures between 20K and 80K. Corresponding to the Néel transition observed in the susceptibility measurement, the specific heat displays an anomaly at 54K with $\Delta c_p \sim 2R$. Surprisingly, this anomaly is vertical on the high temperature side and can be extrapolated to its background value at $T\sim T_N/2$, a very “mean field” like shape that is generally not typical to insulating materials. This “mean field” character might be due to the Ru-Pr interchain interaction, which includes more distant ruthenium moments into the interaction picture and results in long range coupling between rutheniums.
Figure 4.17. (a) The temperature dependence of specific heat (normalized to gas constant $R=8.31 \text{ J/(mole K)}$) over the whole temperature range. Note that the low temperature data measured by ac calorimetry are normalized to the high temperature data measured by DSC calorimetry at around 120K. (b) The temperature dependence of specific near $T_N$. The solid line is a third-order polynomial fitting curve that provides the background for estimating entropy change. The inset shows the specific heat minus the fitting background.
The specific heat at low temperatures is plotted as $c/R$ vs. $T$ and $c/RT$ vs. $T^2$ in Figure 4.18 (a) and Figure 4.18 (b). The specific heat between 12 and 20K can be well fitted by $c_p = \gamma T + \beta T^3$, generating a slope $\beta = 1.2\text{mJ/(mole K}^4)$. This corresponds to a Debye temperature $\theta_D$ of around 300K, if we assume that the contribution comes only from phonons. However it is also possible that there might be a contribution from antiferromagnetic spinwaves (which also has a $T^3$ dependence in three dimensions). In this case, the Debye temperature would be larger. The fitting also yields $\gamma$ of ~ 160 mJ/(mole K$^2$), which is even larger than the coefficient observed in the highly correlated metallic ruthenates in the RP series. In fact, the temperature-independent susceptibility $\chi_0$ is also very close to that of those materials. Both values suggest that there is a considerable density of state in Pr$_3$RuO$_7$. The observation of large $\gamma$ in an insulating material has also been reported in Gd$_2$RuO$_5$. It is suggested that the insulating character might arise from the strong scattering rather than a band or correlation gap.
Figure 4.18. (a) The low temperature specific heat plotted as C/R vs. T. (b) The low temperature specific heat plotted as C/RT vs. $T^2$. The solid curves are the Schottky anomaly fittings. (c) A sketch for the proposed model that illustrates how the $\Gamma_3$ split as temperature change: The red lines represent the Kramer’s doublet and the blue line represents the singlet.
The specific heat shows a plateau for temperatures lower than 10K. A similar but smaller increase (without γT term) has also been reported by Zhou et. al\textsuperscript{131}. This plateau can be fitted as a Schottky anomaly with excitation of a two-level system: \(c_p = \beta T^3 + \nu g R(\delta/T)/[1 + g \exp(\delta/T)]^2\). Here \(\delta\) is the excitation energy, \(g\) the ratio between the ground-state degeneracy and the excited state degeneracy, and \(\nu\) the number of excitations per formula unit. Fits are shown for two sets of parameters (\(\nu, g\)), both giving an excitation energy \(\delta\sim 14\)K.

Here we provide a model that explains the Schottky anomaly in terms of crystal-field excitation of the chain praseodymium. For Pr ions in a cubic crystal field, its ground state is a \(\Gamma_5\) triplet consisted of a Kramer’s doublet degenerated with a singlet as illustrated in Figure 4.18(c). For \(T>54\)K, the \(\Gamma_5\) can be treated as a triplet with degeneracy three although there might be a small gap between the Kramer’s doublet and the singlet due to the distorted cubic environment. Further splitting within the Kramer doublet degeneracy is rendered by the exchange field that is established by the antiferromagnetic ordering of the ruthenium at \(T=54\)K, leaving an excitation energy \(\delta\) between the singlet state and the “spin up” member of the doublet as indicated in Figure 4.18(c). The set up of the exchange field by Ru makes approximately half of the chain Pr hop to the spin up state, leaving the others in singlet state. However further decrease temperature below \(\delta/k\) drives all the spins to the spin up state. Our fitting to the Schottky anomaly (using formula \(c_p = \beta T^3 + \nu g R(\delta/T)/[1 + g \exp(\delta/T)]^2\)) gives rise to \(g/\nu=2\). If \(g=1\) then \(\nu\sim 1/2\), indicating the existence of a supercell which has not yet been observed. On the other hand, if \(\nu=1\), then \(g=2\), implying a degenerate ground state. In addition, the inconsistency between our fitting and the proposed model could not be improved by including a \(\gamma T\) term.

Despite the problems with the fitting, we can still use explain the specific heat anomaly at \(T_N\) by applying the basic idea of our model, i.e., the \(\Gamma_5\) triplet can be split by the exchange field and small crystal field. We assume that at the Néel transition, the degeneracy of the chain Pr goes from 3 to 2. Harada et al have argued that in the \(\text{Ln}_3\text{RuO}_2\) compounds, the Ru ground state is also reduced to a Kramer’s doublet due to the crystal field\textsuperscript{133,138}. Based on these two arguments, the estimated \(\Delta c\) from mean
field theory should be \( \Delta c_{\text{MF}} = (5R/2) \sum [((\Gamma_j^2 - 1)/(\Gamma_j^2 + 1))] = 2.5R \), which is close to our experimental value \( \Delta c = 2R \) (Here \( \Gamma_j \) is the ratio of degeneracy above and below the transition. they are 3/2 for chain Pr and 2 for Ru respectively). It is then also possible to estimate the entropy change by \( \Delta S = R \sum \ln(\Gamma_j) = 1.1R \), somewhat larger than the entropy change estimated with the baseline shown in Figure 4.16, \( \Delta S \sim 0.5R \). However Hinatsu estimated a much larger entropy change (\( \sim 3R \)) with a questionable phonon background\(^{134}\).

In conclusion, \( \text{Pr}_3\text{RuO}_7 \)'s magnetic and thermal properties are dominated by its one-dimensional features and further complicated by multiple contributions of moments from both Pr and Ru sites. At 54K, the system goes through a Néel transition, which is accompanied by a “mean field” like anomaly. No anomaly is observed at 35K in both magnetic and thermal measurements. Both the magnetic and thermal measurements indicate that the interchain Pr are not actively involved in the exchange coupling and only the chain Pr order with Ru at \( T_N \). The establishment of the exchange field from Ru moments further splits the degeneracy of chain Pr and leads to a low temperature Schottky anomaly in the specific heat measurement.
Chapter 5  Conclusions

This study has been centered on the structural, transport and thermodynamic properties of the bilayered Ca$_3$Ru$_2$O$_7$ and other ruthenate systems.

A primary characteristic of the 4d- and 5d-electron elements is that their d-orbitals are more extended compared to those of their 3d-electron counterparts. Stronger $p$-$d$ hybridization and electron-lattice coupling, along with reduced intra-atomic Coulomb interaction $U$, are thus anticipated in these systems. Consequently, the 4d- and 5d-transition metal oxides have comparable $U$ and bandwidth $W$, and are on the border between metallic and insulating behavior, and small perturbations can induce drastic changes in the ground state. From the theoretical point of view, 4d and 5d transition metal compounds, with strong competing interactions, are in a regime difficult to explain using traditional approaches developed for conventional itinerant metals. Moreover, these systems exhibit nearly every collective state known for solids, e.g., ferroelectricity, ferromagnetism, antiferromagnetism, metamagnetism, ferromagnetic semiconducting behavior, superconductivity, orbital ordering, colossal magnetoresistance including inter-plane tunneling magnetoresistance.

The novelty of these materials is highlighted by the unusual colossal magnetoresistivity (CMR) that is attained by avoiding ferromagnetic state. A CMR normally occurs for the field applied along the easy axis of magnetization, where a FM polarization is achieved. In Ca$_3$Ru$_2$O$_7$, which we first discovered, an unusual CMR is realized only when $B$ is perpendicular to the easy axis of magnetization ($a$-axis) or when the FM state is avoided. This CMR phenomenon is fundamentally different from those of all other magnetoresistive systems that are primarily driven by spin polarization. For $B \parallel a$-axis (magnetic easy-axis) $\rho_c$ shows an abrupt drop by an order of magnitude at 6 T, signaling a first-order metamagnetic transition to a spin-polarized or FM state with a saturated moment $M_s$ of 1.8 $\mu_B$/Ru, corresponding to more than 85% saturation. The reduction of $\rho_c$ is attributed to the coherent motion of electrons between Ru-O planes separated by insulating Ca-O planes, a situation similar to spin-filters (FM/I/FM) where the probability of tunneling depends on the angle between the spin magnetizations of the flanking FM regions. Clearly, the fully polarized state can lower the resistivity by at most a factor of 10. For $B \parallel b$-axis (hard-axis), there is no spin-flop transition and the system remains AFM. In sharp contrast
to $\rho_c$ for $\mathbf{B} \parallel a$-axis, $\rho_c$ for $\mathbf{B} \parallel b$-axis rapidly decreases by as much as three orders of magnitude at $B_c = 15$ T, two orders of magnitude more than that for $\mathbf{B} \parallel a$, where spins are fully polarized. For $\mathbf{B} \parallel c$-axis, on the other hand, $\rho_c$ displays Shubnikov-de Haas oscillations with low frequencies of 28 T and 10 T.

Since the fully polarized state for $\mathbf{B}(> 6$ T) $\parallel a$ can reduce $\rho$ by only one order of magnitude, even if the $b$-axis $\mathbf{M}$ were fully polarized at high fields, it could not account for the three orders of magnitude decrease in $\rho_c$ when $\mathbf{B}(>15$ T) $\parallel b$. This indicates that the spin degree of freedom alone is not at all enough to explain the behavior observed. All results provide a coherent picture illustrating that the FM state, which is essential for magnetoresistance in all other magnetoresistive materials, is the least energetically favorable for electron hopping due to the orbital ordering that is facilitated by the FM state through spin-orbit coupling in this ruthenate. Applying $\mathbf{B}$ along the $b$-axis effectively destabilizes the FM state and resulting orbital ordering, thereby drastically increasing the electron hopping amplitude leading to the CMR, as illustrated. These phenomena reveal that that orbital order and its coupling to lattice and spin degrees of freedom drive the exotic properties in $\text{Ca}_3\text{Ru}_2\text{O}_7$.

The dramatic and varied physics of these materials revealed in studies by us and others clearly identifies a class of highly correlated electron materials rich with novel physical properties that not only span almost every ordered state known in condensed matter physics, but includes unusual phenomena not found in other materials. It has become increasingly clear that the orbital degrees of freedom drive the complex phase diagram via couplings of the orbital degrees of freedom to the spin (spin-orbit interaction) and lattice (Jahn-Teller effect) degrees of freedom.

The specific heat measurements on $\text{Sr}_4\text{Ru}_3\text{O}_{10}$ and $\text{Pr}_3\text{RuO}_7$ yield very interesting results that indicate complicated spin ground states for both systems. For $\text{Sr}_4\text{Ru}_3\text{O}_{10}$, a sharp mean-field-like anomaly was observed at the onset of ferromagnetic ordering at $T_C=102$K. However, the anomaly is much smaller than we would expect for complete ordering of the spins. No anomaly can be detected at 50K, suggesting a spin crossover behavior instead of phase transition. At low temperatures, a specific heat contribution from magnons is observed, showing a temperature dependence of $\sim T^{3/2}$ whose origin is still unclear. Our measurement on a single crystal of $\text{Pr}_3\text{RuO}_7$ reveals some intrinsic properties of this system that have not been observed in polycrystalline samples. The susceptibility suggests that the exchange
interaction is strongly anisotropic. The competition between the ferromagnetic interaction and the antiferromagnetic interaction gives rise to the metamagnetic transition (with saturation moment of 4.8μB/f.u) for $B||c$, the chain direction. The specific heat anomaly at 54K is mean field in shape and probably arises from the magnetic ordering of the Ru and the chain Pr. The interlayer Pr appears to be inactive in the magnetic ordering. At $T_N$, the establishment of the exchange field from Ru moments further splits the degeneracy of chain Pr, resulting in a low temperature Schottky anomaly, suggesting that the “ordered” chain Pr are still sensitive to a crystal field.

The Ph.D. education has afforded me the opportunity to develop my knowledge and understanding of diverse subjects, preparing me with diverse background for independent research in future. I was exposed to various subjects in physics: quantum mechanics, electromagnetic, solid state physics, atomic physics, nuclear physics, and so on. The broadness of the knowledge gives me a platform based on which I am able to continue accumulating more knowledge in the future. My understanding of the condensed matter physics was gradually deepened by practicing the knowledge of this subject in my Ph.D. graduate training. Being equipped with this knowledge and understanding, I am now in a better position to explore the unknown world of physics.

My capability to explore the unknown world of physics was developed in my Ph.D. graduate training. During this period, I was able to not only grasp some experimental skills that are fundamental in conducting research, but also collect some ideas on research methods, i.e., how to detect an unsolved problem and how to tackle the problem by trying different kinds of methods. For example, in growing the single crystals of $\text{Ca}_3\text{Ru}_2\text{O}_7$, I always ended up with unwanted phases such as $\text{Ca}_2\text{RuO}_4$ and $\text{CaRuO}_3$. A thorough review of the crystal-growth process and literature studies help me find out the possible reasons for this problem and solve it.

The Ph.D. training has endowed me with not only research skills but also personal characters which I think are essential to an experimentalist: patience, persistence, hard work and carefulness. The hardships I have experienced in this training have tested not only my research capability but also my will to commit myself to scientific research. By overcoming these hardships, I have grained personality maturity which will benefit me in my career and my personal life as well.
I have accumulated some knowledge of the condensed matter physics through this training, but the completion of my Ph. D. training marks not an ending but a new beginning of a long trip to the unknown world.
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Vita

Xiunu (Sophie) Lin

Date of Birth: September 21\textsuperscript{st}, 1979,
Place of Birth: Kuibi, Hui'an, Fujian, P. R. China.

Education

- **Ph. D.** in Physics 5/2007
  - Thesis title: “A systematic study on the thermodynamic and transport properties of layered ruthenates”
  - Advisor: Gang Cao
  - Institute: University of Kentucky, United States

- **M. S.** in Physics (GPA 3.8/4.0) 09/2003
  - Institute: University of Kentucky, United States

- **B. S.** in Physics (GPA 3.5/4.0) 07/2000
  - Institute: Xiamen University, P.R. China

Conference Presentations

- “Observation of oscillatory magnetoresistance periodic in 1/B and B in Ca\textsubscript{3}Ru\textsubscript{2}O\textsubscript{7}, APS March Meeting, Baltimore, United States 03/2006

- “Orbitally driven behavior-Mott transition, quantum oscillations and colossal magnetoresistance in bilayered Ca\textsubscript{3}Ru\textsubscript{2}O\textsubscript{7}, APS March Meeting, Los Angeles, United States 03/2005

- “Competing Ground States in Triple-layered Sr\textsubscript{4}Ru\textsubscript{3}O\textsubscript{10}: Verging on itinerant ferromagnetism with critical fluctuations”, APS March Meeting, Montreal, Canada 03/2004
Publications
10. G. Cao, L. Balicas, W. H. Song, Y.P. Sun, Y. Xin, V.A. Bondarenko, J.W.


