

NEUTRON SCATTERING STUDIES ON CORRELATED TRANSITION-
METAL OXIDES

By

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ABSTRACT

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We have explored the collective phenomena of correlated electrons in two different transition-metal oxides, Ruddlesden-Popper type ruthenates $(\text{Sr,Ca})_{n+1}\text{Ru}_n\text{O}_{3n+1}$ and inverse-trirutile chromates Cr_2MO_6 ($\text{M} = \text{Te, Mo and W}$), using neutron scattering in combination with various material characterization methods.

$(\text{Sr,Ca})_{n+1}\text{Ru}_n\text{O}_{3n+1}$ are $4d$ transition-metal oxides exhibiting competing magnetic and electronic tendencies. The delicate balance among the competing states can be readily tuned by perturbations, such as chemical doping and magnetic field, which gives rise to emergent phenomena. We have investigated the effects of $3d$ transition-metal doping on the magnetic and electronic properties of layered ruthenates. For instance, the single-layer ($n = 1$) Sr_2RuO_4 is an unconventional superconductor possessing an incommensurate spin density wave instability with a wave vector $\mathbf{q}_{ic} = (0.3 \ 0.3 \ L)$ driven by Fermi surface nesting. Upon Fe substitution, we have unveiled an unexpected commensurate spin density wave order with a propagation vector $\mathbf{q}_c = (0.25 \ 0.25 \ 0)$ in $\text{Sr}_2\text{Ru}_{1-x}\text{Fe}_x\text{O}_4$ ($x = 0.03$ and 0.05), despite the magnetic fluctuations persisting at $\mathbf{q}_{ic}$. The latter feature is corroborated by the first principles calculations, which show that Fe doping barely changes the nesting vector of the Fermi surface. These results suggest that in addition to the known incommensurate magnetic instability, Sr_2RuO_4 is also in proximity to a commensurate magnetic tendency that can be stabilized via Fe doping. We have also studied the effects of a magnetic field. For example, the bilayer ($n = 2$) $\text{Ca}_3(\text{Ru}_{1-x}\text{Ti}_x)_2\text{O}_7$ ($x = 0.03$) is a G-type antiferromagnetic Mott insulator. We have revealed that a modest magnetic field can lead to

colossal magnetoresistance arising from an anomalous collapse of the Mott insulating state. Such an insulator-to-metal transition is accompanied by magnetic and structural transitions. These findings call for deeper theoretical studies to reexamine the magnetic field tuning of Mott systems with magnetic and electronic instabilities, as a magnetic field usually stabilizes the insulating ground state in Mott-Hubbard systems.

Cr_2MO_6 ($\text{M} = \text{Te}, \text{W}$ and Mo) are spin dimer systems with the magnetic ions Cr^{3+} structurally dimerized favoring a singlet ground state. However, all three compounds investigated exhibit long-range antiferromagnetic orders at low temperature owing to the inter-dimer interactions. We have shown that the inter-dimer exchange coupling can be tuned from antiferromagnetic in Cr_2TeO_6 to ferromagnetic in Cr_2WO_6 and Cr_2MoO_6 , by altering the degree of d - p orbital hybridization between $\text{W}(\text{Mo})$ and O atoms. The tunability of the inter-dimer interactions without introducing additional complexities such as structural distortions and carrier doping offers a rare opportunity to drive the system toward the quantum critical point (QCP) separating the dimer-based quantum disordered state and the classical long-range antiferromagnetic order. Moreover, we have unraveled Higgs amplitude modes in the magnetic excitation spectra of Cr_2TeO_6 and Cr_2WO_6 , which are generally believed to survive only in systems close to the QCP where the ordered moment is suppressed significantly from its fully saturated value by quantum fluctuations. However, these two compounds are away from the QCP with the ordered moment reduced only by $\sim 24\%$. This study suggests that Higgs amplitude modes are not the privilege of ordered systems in the vicinity of the QCP, but may be common excitation modes in ordered spin dimer systems.

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Chapter 1

Introduction to correlated transition-metal compounds

1.1 Introduction and motivation

Electron-electron correlations in condensed matter can give rise to fascinating physical phenomena that are completely unexpected based on non-interacting electron pictures. A prototypical example is the correlation-driven metal-insulator transition (MIT), also known as the Mott transition [1]. Conventional band theory suggests that whether a material is a metal or insulator depends on whether the valence band is partially filled or fully occupied. However, many transition-metal oxides with partially filled d orbitals are insulating rather than metallic, which has been ascribed to the Coulomb repulsion between electrons occupying the same orbital. Other exciting discoveries in correlated electron systems include high- T_c superconductivity, colossal magnetoresistance (CMR) effect, multiferroicity and a diversity of charge, spin and orbital orders [2-7]. These findings are generally referred to as “emergent phenomena”, since they are very difficult to predict starting from the properties of their constituents [8]. Theoretical and experimental efforts in the past few decades have made dramatic progress in the understanding of the behaviors of correlated electrons. Nevertheless, many fundamental questions are still under intense investigations and remain challenging to the scientific community.

Transition-metal compounds offer an ideal playground for exploring the physics of emergent phenomena, owing to the strong correlations among the transition-metal d electrons. The complexity in the electronic properties arises from the fact that multiple degrees of freedom, such as charge, spin, orbital and lattice, are simultaneously active. For instance, here we consider a transition-metal oxide with a perovskite structure as shown in Fig. 1.1, the five-fold degenerate

atomic d orbitals split into the triply-degenerate t_{2g} orbitals and the doubly-degenerate e_g orbitals due to the crystal field produced by the octahedral coordination of oxygens. The electronic configuration is determined by the interplay of the crystal field splitting and the Hund's rule coupling. For example, while both Mn^{3+} ($3d^4$) and Ru^{4+} ($4d^4$) have three spin-up electrons occupying the t_{2g} orbitals, the fourth electron occupies one of the e_g orbitals in Mn^{3+} and gives rise to spin $S = 2$, whereas it occupies one of the t_{2g} orbitals in Ru^{4+} and leads to spin $S = 1$. In addition, the degeneracy of these electron orbitals can be further lifted by the coupling to the lattice. In an oxygen octahedron compressed along the z axis, the e_g electron in Mn^{3+} favors the occupation of the in-plane $d_{x^2-y^2}$ orbital. This effect, a distortion of the lattice dependent on the electronic state of the system, is called Jahn-Teller distortion and is prevalent in transition-metal compounds.

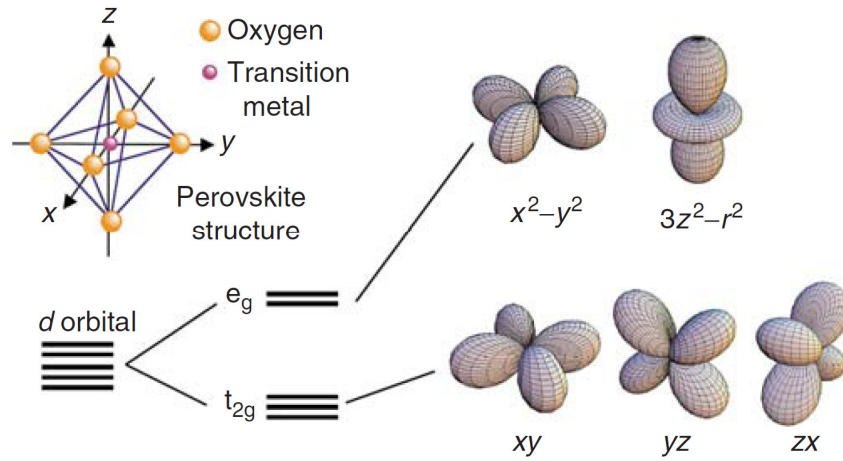


Figure 1.1: d -electron orbitals in an octahedral oxygen environment [8].

It is generally believed that the emergent states in correlated electron systems originate from the competition among various types of interactions, which establishes a delicate balance among the competing phases of comparable energy. Consequently, very small perturbations, such as variations in the chemical composition, magnetic field, electric field and structural change by applying pressure or strain, can dramatically alter the electronic properties of the entire system.

This is because the energy scale required to tip the balance is associated with the relative energy of the competing states and the intervening energy barriers, rather than that of melting the ordered state itself. The fundamental parameters (interactions) that are relevant in transition-metal compounds include the hopping amplitude (one-electron bandwidth), crystal field splitting, Hund's rule coupling, on-site Coulomb repulsion, exchange interaction, spin-orbit coupling and Jahn-Teller effect, etc.

In this chapter, we highlight some representative emergent phenomena that have been intensely studied in correlated transition-metal compounds, including high- T_c superconductivity in cuprates and iron-based superconductors, CMR in manganites and spin-orbit physics in iridates. As we shall see, the key ingredients in the physics of correlated electrons, such as phase competition, interplay among charge, spin, orbital and lattice degrees of freedom, and giant responses to perturbations, are ubiquitous in transition-metal compounds.

1.2 High- T_c superconductivity in cuprates and iron-based superconductors

High- T_c superconductivity is an archetype of the emergent phenomena in transition-metal compounds. It was first discovered in a hole-doped cuprate $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4$ in 1986 [9] and has attracted tremendous interest since then. The studies on high- T_c cuprates have not only unveiled many key aspects of the unconventional superconducting state, but also accelerated the development of condensed matter theories, which have drastically improved our understanding of complex correlated electron systems.

The nature of the high- T_c superconductivity in cuprates is fundamentally distinct from that of the conventional superconducting state. Conventional superconductivity was first observed by Onnes in Mercury in 1911 [10], which has been well described by the phenomenological Ginzburg-Landau theory [11] and the microscopic Bardeen-Cooper-Schrieffer (BCS) theory [12] developed

in the 1950s. The core idea of the BCS theory is that electrons pair into a spin-singlet state (“Cooper pairs”) at low temperature, and superconductivity arises from the Bose-Einstein condensation of the Cooper pairs. The attractive force that binds two electrons into a Cooper pair is the electron-phonon coupling, which limits the critical temperature T_c of conventional superconductors to be below 30 K. Nevertheless, the much higher T_c found in cuprates, such as $T_c = 90$ K in $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$ [13] and $T_c = 133$ K in $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+\delta}$ [14], cannot be explained by this scenario, as the electron-lattice coupling in real materials is not sufficiently strong. Thus far, the pairing mechanism in high- T_c cuprates remains an open question. In addition, the superconducting state is suggested to be a d -wave spin-singlet state, rather than an isotropic s -wave spin-singlet state as in conventional superconductors [15].

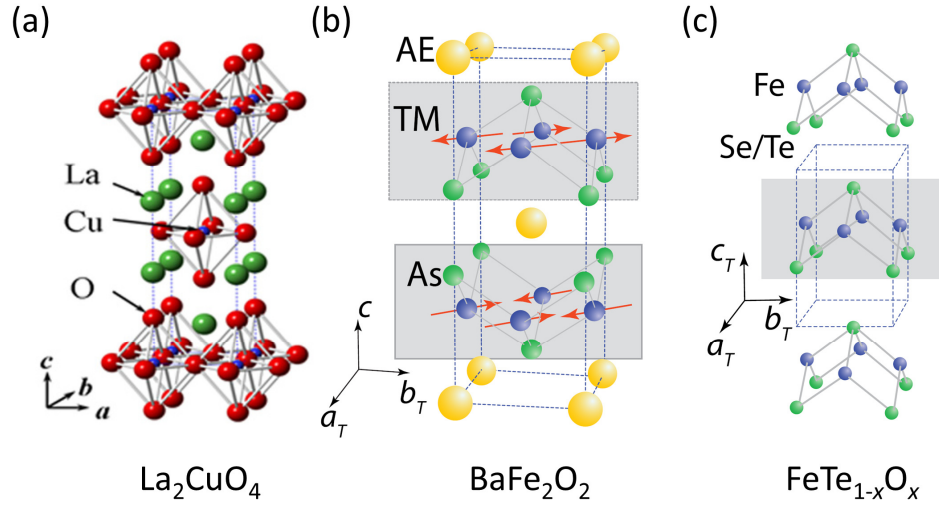


Figure 1.2: Schematics of the crystal structures of (a) cuprate La_2CuO_4 [16], (b) iron pnictide BaFe_2As_2 and (c) iron chalcogenide $\text{FeTe}_{1-x}\text{Se}_x$ [3].

Despite the various types of high- T_c cuprate compounds reported, there are many common features. First, all the cuprates have layered structures composed of CuO_2 planes where superconductivity emerges. For instance, the crystal structure of the parent compound of the first high- T_c superconductor La_2CuO_4 is sketched schematically in Fig. 1.2(a). It has a quasi-two-

dimensional layered perovskite structure where each Cu ion is centered in an oxygen octahedron. Second, the parent compounds of high- T_c cuprates are antiferromagnetic Mott insulators, and the superconducting state emerges as the antiferromagnetic order is suppressed by doping charge carriers, as shown in the phase diagrams in Fig. 1.3 [17]. Interestingly, on the hole-doped side, there exists a pseudogap phase in close proximity to the superconducting state, the origin of which is still unknown. Third, it is generally believed that understanding the normal state properties of high- T_c superconductors is essential to the theory of high- T_c superconductivity. However, the normal state of high- T_c cuprates exhibits a variety of unusual behaviors, which cannot be described in the framework of existing solid-state theories. Particularly, there has been growing experimental evidence showing that nanoscale inhomogeneity is responsible for the anomalous normal state properties [18]. To date, the mechanism of high- T_c superconductivity in cuprates is still a big mystery.

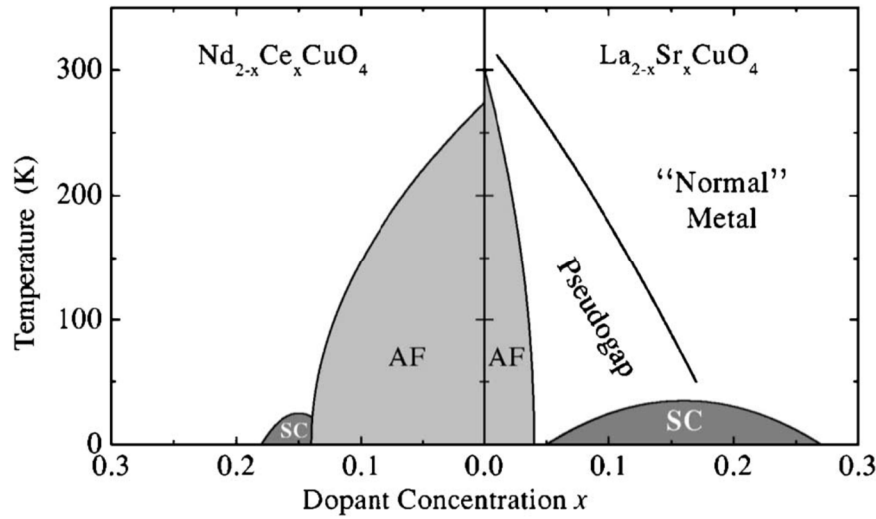


Figure 1.3: Phase diagrams of electron- and hole-doped high- T_c cuprates [17].

Intense experimental efforts have been devoted to searching for new high- T_c superconductors in other transition-metal compounds without copper. Great progress has been made in 2008, when high- T_c superconductivity was discovered in iron pnictides $\text{LaFeAsO}_{1-x}\text{F}_x$, $\text{A}_{1-x}\text{K}_x\text{Fe}_2\text{As}_2$ ($A = \text{Ca}$,

Sr and Ba), $\text{AFe}_{2-x}\text{B}_x\text{As}_2$ ($\text{B} = \text{Co}, \text{Ni}$ and Rh) and iron chalcogenides $\text{FeTe}_{1-x}\text{Se}_x$ [3]. Intriguingly, these iron-based superconductors share similar structures and properties and in many aspects resemble that of the high- T_c cuprates. For instance, iron-based superconductors also possess layered crystal structures consisting of Fe-As or Fe-Te/Se planes, as shown schematically in Fig. 1.2(b) and (c). The superconducting state, which appears as a dome in the phase diagram depicted in Fig. 1.4, emerges as charge carriers are doped into the antiferromagnetic parent compound, in analogy to the cuprates shown in Fig. 1.3. Nevertheless, the parent compounds of iron-based superconductors are often semimetallic rather than Mott insulating as in high- T_c cuprates, which suggests that itinerancy may be important.

In summary, the studies on the high- T_c cuprates and iron-based superconductors are still under way. They are believed to help improve our understanding of high- T_c superconductivity and eventually lead to technological applications.

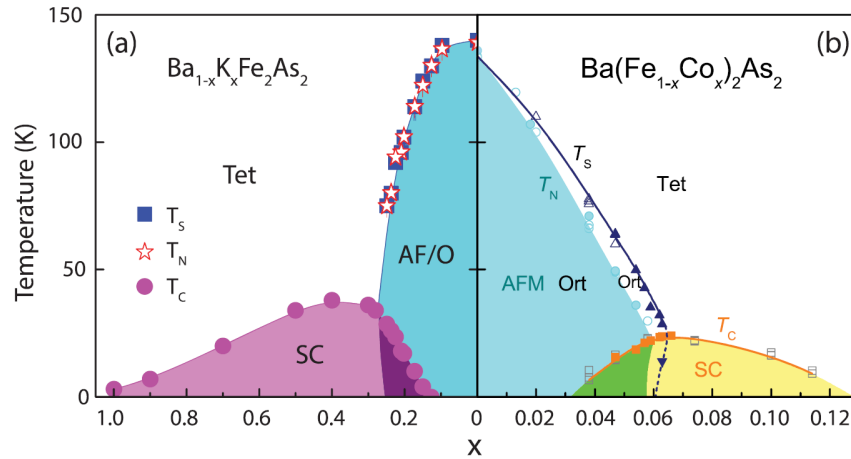


Figure 1.4: The structural and magnetic phase diagrams of electron- and hole-doped iron pnictide BaFe_2As_2 [3].

1.3 Colossal magnetoresistance in manganites

The perovskite manganites $(\text{RE}, \text{AE})_{n+1}\text{Mn}_n\text{O}_{3n+1}$ ($\text{RE} = \text{rare earth}$, $\text{AE} = \text{alkali earth elements}$, $n = 1, 2$ and ∞) are another typical correlated transition-metal oxides. Early studies on the

ferromagnetic metallic compounds have led to the development of the theory of double exchange interaction [19], which succeeds to account for the properties of manganites qualitatively. However, quantitative analysis suggests that the underlying physics is far more complicated. A rich variety of ordered phases can emerge in manganites upon varying the chemical composition. For instance, the structural and magnetic phase diagrams of the layered $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ ($n = 2$) is shown in Fig. 1.5. Many complex phases, such as ferromagnetic metallic state (FM), A-type, C-type and G-type antiferromagnetic insulating (AFI) phase, canted antiferromagnetic state (CAF) and charge-ordered (CO) state with different degrees of structural distortions are all possible in the same material system. This suggests that these distinct states are energetically close and can readily transform from one to another, which poses a great challenge to condensed matter theories. Moreover, multiple electronic degrees of freedom are intimately correlated, giving rise to complex charge-spin-orbital ordered states. The schematics of the spin-orbital orders in LaMnO_3 and BiMnO_3 are illustrated in Fig. 1.6 as examples. These observations suggest that phase competition is important in determining the physical properties of manganites.

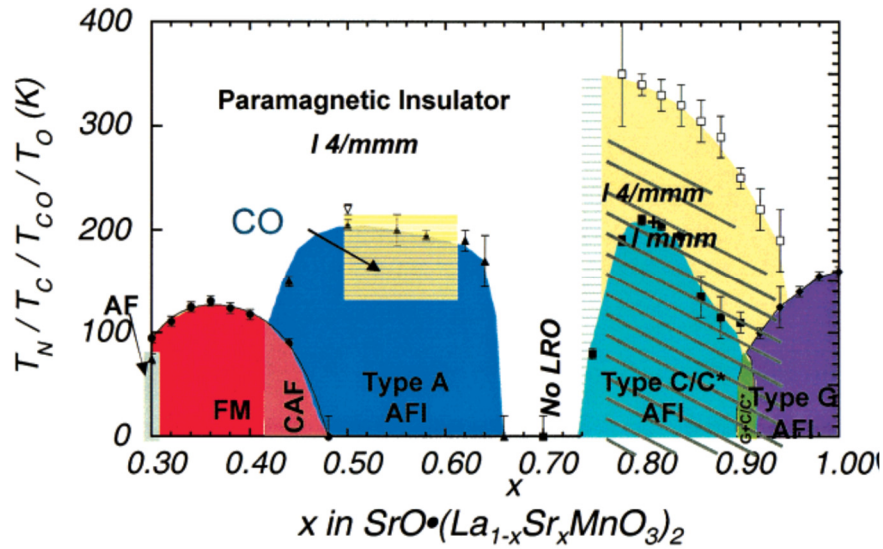


Figure 1.5: Structural and magnetic phase diagram of the layered manganite $\text{La}_{2-2x}\text{Sr}_{1+2x}\text{Mn}_2\text{O}_7$ as a function of temperature and chemical composition [20].

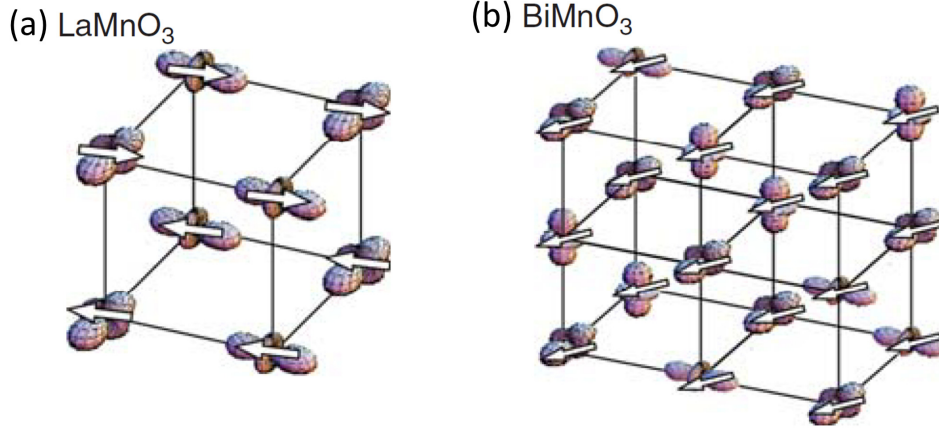


Figure 1.6: Spin-orbital orders in (a) LaMnO_3 and (b) BiMnO_3 [8].

Another striking emergent phenomenon in perovskite manganites is the CMR effects. In ordinary metals, the magnetoresistance is usually only a few percent, while in some artificial ferromagnetic multilayers it can be a few tens of percent due to spin-dependent scattering. Notably, in hole-doped manganites, the change in resistivity in a magnetic field can be as high as several orders of magnitude, which renders it promising for industrial applications. There are two main types of CMR effects observed in manganites. In ferromagnetic metallic compounds, the CMR effect is most remarkable near the Curie temperature T_c , as shown in Fig. 1.7(a). In contrast, in charge-ordered manganites, CMR occurs at low temperature via a melting of the charge order induced by a magnetic field, as shown in Fig. 1.7(b). In addition, electron-lattice coupling has been found to play an essential role. As we have discussed in Sec. 1.1, in Mn^{3+} the d electron occupying the e_g orbital is Jahn-Teller active, and a splitting of the in-plane $d_{x^2-y^2}$ and the out-of-plane $d_{3z^2-r^2}$ orbitals can occur provided the presence of structural distortions. Such electron-lattice coupling can give rise to novel physical properties. For example, the appearance of an insulating behavior near T_c of a ferromagnetic metal, as shown in Fig. 1.7(a), is quite unusual. Close examinations have revealed that a local structural distortion is induced as the conduction e_g

electron hops from one site to another, which leads to polaron formation and dominates the electrical transport in this temperature regime.

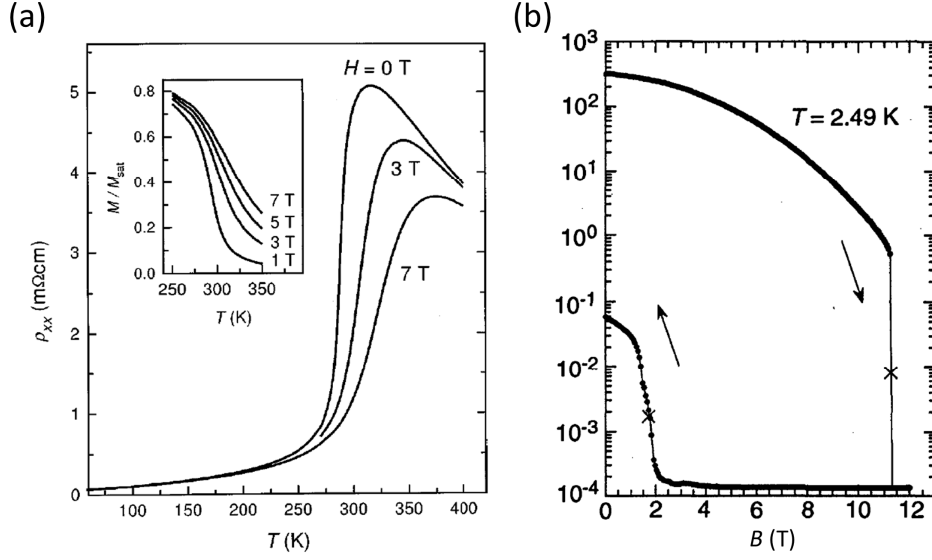


Figure 1.7: Magnetoresistance in (a) ferromagnetic metallic $Lr_{2/3}(Pb,Ca)_{1/3}MnO_3$ [21] and (b) antiferromagnetic charge-ordered $Nd_{0.5}Sr_{0.5}MnO_3$ [22].

Despite the extensive investigations that have been made on the physics of manganites, the story is still far from complete. Though the significance of the competition between two distinct ground states, i.e., the ferromagnetic metallic state and the antiferromagnetic insulating state, has been recognized, there is accumulating experimental evidence suggesting that a single-phase picture is not sufficient. Nanoscale phase separation is found to be prevalent in manganites, which is believed to be crucial to the realization of the CMR effect. Similar spatial inhomogeneity has been observed in many other transition-metal compounds, suggesting that it might be a universal element in the strongly correlated electronic systems [18].

1.4 Spin-orbit physics in iridates

Iridates are $5d$ transition-metal oxides characteristic of strong spin-orbit coupling (SOC), distinct from $3d$ and some $4d$ systems where SOC is usually considered as a perturbation. The

interplay of SOC and electron correlation has been proposed to lead to various types of novel phases, depending on their relative strength to the electron hopping amplitude t . A generic phase diagram established by theories is sketched in Fig. 1.8 [23]. In the weak correlation regime, topological insulators or semimetals have been discovered and intensely studied [23]. More complex phases arise in the strong correlation regime, such as Axion insulators, Weyl semimetals, Topological Mott insulators and spin liquids, which remain as a less explored territory in condensed matter physics.

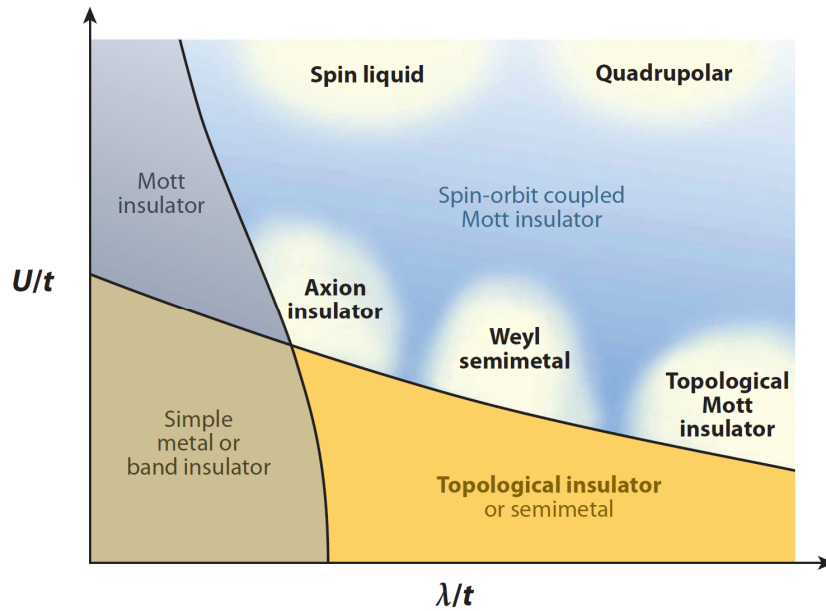


Figure 1.8: Generic phase diagram as a function of correlation strength U/t and SOC λ/t . t is the hopping amplitude [23].

In contrast to $3d$ transition-metal elements [Fig. 1.1], the strong SOC in $5d$ transition-metal ions results in a different multiplet structure of the electronic orbitals. For instance, Ir^{4+} possesses five electrons in the $5d$ orbitals, occupying the t_{2g} levels due to large crystal field splitting Δ_{O_h} generated by the octahedral oxygen coordination. SOC further lifts the degeneracy of the t_{2g} levels, leading to a $j = 3/2$ level and a $j = 1/2$ state, as shown in Fig. 1.9. The magnetism is

dominated by the singly occupied $j = 1/2$ electron. Thus, $5d$ iridates are excellent material systems to explore the physics dominated by both electron correlation and SOC. In the rest of this section, we outline a few examples.

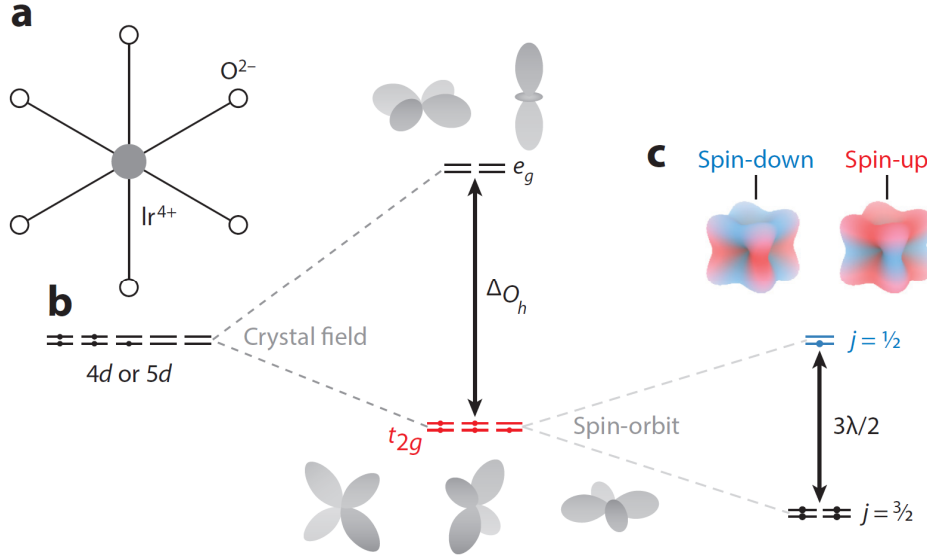


Figure 1.9: d -electron orbital splitting in an octahedral crystal field in the presence of strong SOC [24].

A natural extension of the studies on the perovskite high- T_c cuprates and CMR manganites is the Ruddlesden-Popper type perovskite iridates $\text{Sr}_{n+1}\text{Ir}_n\text{O}_{3n+1}$. Sr_2IrO_4 and $\text{Sr}_3\text{Ir}_2\text{O}_7$ are both antiferromagnetic spin-orbit Mott insulators, though $\text{Sr}_3\text{Ir}_2\text{O}_7$ is much weaker than Sr_2IrO_4 [25,26]. They serve as model compounds to study the exchange interaction and magnetic anisotropy in $5d$ magnetic systems. Furthermore, since Sr_2IrO_4 is isostructural to La_2CuO_4 , a very alluring idea is whether a superconducting state can be achieved by carrier doping. Such a superconducting state, if existing, is believed to be highly unconventional as pointed out by some theoretical proposals [27-29], which will to a great extent improve our understanding of unconventional superconductivity. Nevertheless, experimentally no superconductivity has been observed in this material so far.

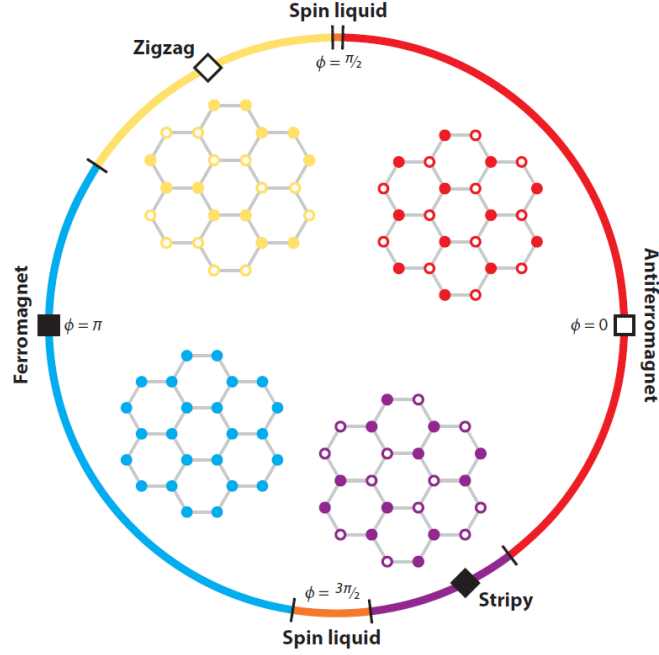


Figure 1.10: Phase diagram of the Heisenberg-Kitaev model [24].

In addition to the perovskite iridates, honeycomb iridates, such as Na_2IrO_3 and Li_2IrO_3 , have attracted great attention. It is suggested that a bond-dependent exchange interaction is symmetry-allowed, which provides a rare experimental realization of the celebrated Kitaev physics [30]. Figure 1.10 shows the phase diagram obtained by solving the Heisenberg-Kitaev model. Notably, quantum spin liquid states can stabilize in proximity to different types of magnetic ordered phases. Neutron and resonant x -ray scattering measurements have revealed that Na_2IrO_3 exhibits a zigzag magnetic order, which is likely to be close to the hypothetical quantum spin liquid phase [31,32].

To date, the studies on $5d$ transition-metal compounds in recent years have only uncovered a tip on the iceberg of the physics dominated by both electron correlations and SOC. Many opportunities and new frontiers are still waiting for further exploration.

1.5 Scope of this thesis

This thesis presents neutron scattering studies on two correlated transition-metal oxides, namely, Ruddlesden-Popper type ruthenates $(\text{Sr,Ca})_{n+1}\text{Ru}_n\text{O}_{3n+1}$ and inverse-trirutile chromates Cr_2MO_6 ($\text{M} = \text{Te, W and Mo}$). It is organized as follows:

Chapter 2 introduces the basics of neutron scattering, including nuclear and magnetic scattering, elastic and inelastic scattering, respectively, as well as different types of instruments used in the work presented in this thesis, such as triple-axis spectrometers, time-of-flight spectrometers, four-circle diffractometers and powder diffractometers.

Chapter 3 presents neutron scattering studies on the emergent states in Ruddlesden-Popper type ruthenates $(\text{Sr,Ca})_{n+1}\text{Ru}_n\text{O}_{3n+1}$, which are induced upon chemical doping or magnetic field.

Chapter 4 discusses neutron scattering studies on the inverse-trirutile chromates Cr_2TeO_6 , Cr_2WO_6 and Cr_2MoO_6 , where the magnetic properties are predominated by $S = 3/2$ spin dimers.

Chapter 5 summarizes all the work and the perspectives on future studies are given.

Chapter 2

Introduction to neutron scattering

2.1 Basic properties of neutrons

Neutron scattering is the most powerful technique to investigate both structural and magnetic properties of condensed matter. Thermal neutrons have the energy of $5 \sim 100$ meV and have been widely used in experiments. The de Broglie wavelength of thermal neutrons is of the same order as the interatomic distance, therefore interference effects are strong which provide valuable information on the microscopic structure of the system, in analogy to electron and x -ray scattering. Nevertheless, as neutrons have no charge, they can penetrate into the system deeply and be scattered by the nuclei through short-range nuclear forces. In addition, neutrons have spin $S = 1/2$ and can interact with the spin and orbital motion of the unpaired electrons, thus serve as ideal probes to the magnetic properties of the scattering system. Other than static structures, the dynamical properties of the scattering systems can also be studied as neutrons are scattered inelastically. Since the energy of thermal neutrons is of the same order as some of the elementary excitations in condensed matter, such as phonons and magnons, the energy of these excitations can be measured more accurately.

A typical geometry of neutron scattering experiments is sketched in Figure 2.1 [33]. A target is placed into the incident neutron beam and the number of neutrons scattered in the direction (θ, ϕ) in a small solid angle $d\Omega$ is measured by a neutron detector. The concept “cross section” is commonly used to analyze the neutron scattering data, as in many other scattering experiments. The “partial differential cross section” is defined by the equation

$$\frac{d^2\sigma}{d\Omega dE} = (\text{number of neutrons scattered per second into a solid angle } d\Omega$$

$$\text{in direction } (\theta, \phi) \text{ with final energy between } E \text{ and } E + dE) / \Phi d\Omega dE$$

where Φ is the flux of the incident neutrons, i.e. the number through unit area per second. The dimension of “cross section” is [area], as implied by its name.

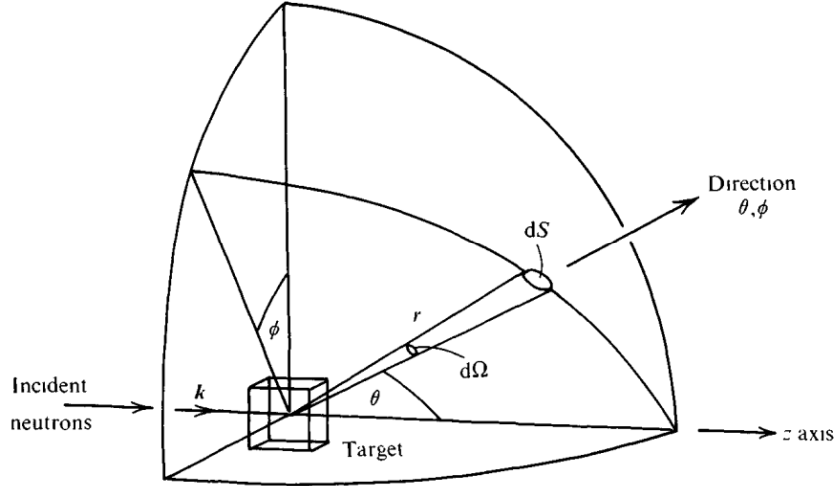


Figure 2.1: Typical geometry of a neutron scattering experiment [33].

Other useful quantities such as “differential cross section” $d\sigma/d\Omega$ and “total scattering cross section” σ_{tot} can be defined by the following equations

$$\frac{d\sigma}{d\Omega} = \int_0^\infty \left(\frac{d^2\sigma}{d\Omega dE} \right) dE$$

$$\sigma_{tot} = \int \left(\frac{d\sigma}{d\Omega} \right) d\Omega$$

Neutron scattering experiments measure the cross sections of different scattering processes. In the following sections, we give the formulae of the partial differential cross section derived in Ref. [33] for representative scattering processes concerned in this thesis, including nuclear and magnetic scattering. The nuclear scattering is a process where neutrons interact with the nuclei via

nuclear forces, whereas magnetic scattering is where neutrons couple to the magnetic moments of unpaired electrons, respectively.

2.2 Nuclear scattering

The basic expression of the partial differential cross section for nuclear scattering is

$$\frac{d^2\sigma}{d\Omega dE} = \frac{k'}{k} \frac{1}{2\pi\hbar} \sum_{jj'} b_j b_{j'} \int_{-\infty}^{+\infty} \langle \exp\{-i\boldsymbol{\kappa} \cdot \mathbf{R}_{j'}(0)\} \exp\{i\boldsymbol{\kappa} \cdot \mathbf{R}_j(t)\} \rangle \exp(-i\omega t) dt$$

where k and k' are the wave vectors of the incident and scattered neutrons, b_j and $b_{j'}$ the scattering lengths of the nuclei at sites j and j' , $\boldsymbol{\kappa} = \mathbf{k}_i - \mathbf{k}_f$ the change in the wave vectors, $\mathbf{R}_{j'}(0)$ and $\mathbf{R}_j(t)$ the positions of the nuclei at sites j and j' at time 0 and t , $\hbar\omega = E_i - E_f$ the change in the neutron energy, $\langle \dots \rangle$ denoting thermal average.

The scattering process can be classified into elastic scattering and inelastic scattering, depending on whether neutrons gain or lose energy. In the case of elastic nuclear scattering, the coherent differential cross section is

$$\left(\frac{d\sigma}{d\Omega}\right)_{coh\ el} = N \frac{(2\pi)^3}{v_0} \sum_{\boldsymbol{\tau}} \delta(\boldsymbol{\kappa} - \boldsymbol{\tau}) |F_N(\boldsymbol{\kappa})|^2$$

where

$$F_N(\boldsymbol{\kappa}) = \sum_d \bar{b}_d \exp(i\boldsymbol{\kappa} \cdot \mathbf{d}) \exp(-W_d)$$

N is the number of unit cells in the scattering system, v_0 the volume of the unit cell, $\boldsymbol{\tau}$ a vector in the reciprocal lattice, $F_N(\boldsymbol{\kappa})$ the structure factor, $\bar{b}_d$ the average scattering length of the d -th atom in the unit cell, $\mathbf{d}$ the equilibrium position of the d -th atom in the unit cell, $\exp(-W_d)$ the Debye-Waller factor. Thus, the scattering occurs only when

$$\boldsymbol{\kappa} = \mathbf{k} - \mathbf{k}' = \boldsymbol{\tau}$$

In the case of inelastic nuclear scattering, the coherent partial differential cross section for creating one phonon is

$$\begin{aligned} \left(\frac{d^2\sigma}{d\Omega dE}\right)_{coh+1} &= \frac{k'}{k} \frac{(2\pi)^3}{2v_0} \sum_s \sum_{\boldsymbol{\tau}} \frac{1}{\omega_s} \left| \sum_d \frac{\bar{b}_d}{\sqrt{M_d}} \exp(-W_d) \exp(i\boldsymbol{\kappa} \cdot \mathbf{d}) (\boldsymbol{\kappa} \cdot \mathbf{e}_{ds}) \right|^2 \\ &\times \langle n_s + 1 \rangle \delta(\omega - \omega_s) \delta(\boldsymbol{\kappa} - \mathbf{q} - \boldsymbol{\tau}) \end{aligned}$$

where ω_s is the angular frequency of a phonon for the s -th normal mode, M_d the mass of the d -th atom in the unit cell, $\mathbf{e}_{ds}$ the polarization vector, n_s the quantum number of the s -th mode, $\mathbf{q}$ the wave vector of the normal mode s . The energy and momentum conservation laws must be satisfied for the scattering to occur

$$E - E' = \hbar\omega_s$$

$$\mathbf{k} - \mathbf{k}' = \boldsymbol{\tau} + \mathbf{q}$$

The coherent partial differential cross section for annihilating one phonon is

$$\begin{aligned} \left(\frac{d^2\sigma}{d\Omega dE}\right)_{coh-1} &= \frac{k'}{k} \frac{(2\pi)^2}{2v_0} \sum_s \sum_{\boldsymbol{\tau}} \frac{1}{\omega_s} \left| \sum_d \frac{\bar{b}_d}{\sqrt{M_s}} \exp(-W_d) \exp(i\boldsymbol{\kappa} \cdot \mathbf{d}) (\boldsymbol{\kappa} \cdot \mathbf{e}_{ds}) \right|^2 \\ &\times \langle n_s \rangle \delta(\omega + \omega_s) \delta(\boldsymbol{\kappa} + \mathbf{q} - \boldsymbol{\tau}) \end{aligned}$$

Correspondingly, the momentum and energy conservation laws require

$$E - E' = -\hbar\omega_s$$

$$\mathbf{k} - \mathbf{k}' = \boldsymbol{\tau} - \mathbf{q}$$

2.3 Magnetic scattering

For a Bravais lattice with localized electrons, the differential cross section for elastic magnetic scattering is

$$\left(\frac{d\sigma}{d\Omega}\right)_{el} = (\gamma r_0)^2 N \left\{ \frac{1}{2} g F(\boldsymbol{\kappa}) \right\}^2 \exp(-2W) \sum_{\alpha\beta} (\delta_{\alpha\beta} - \hat{\boldsymbol{\kappa}}_\alpha \hat{\boldsymbol{\kappa}}_\beta) \sum_l \exp(i\boldsymbol{\kappa} \cdot \mathbf{l}) \langle \mathbf{S}_0^\alpha \rangle \langle \mathbf{S}_l^\beta \rangle$$

where $\gamma = 1.913$ is a constant, $r_0 = \frac{\mu_0 e^2}{4\pi m_e}$ the classical radius of electrons, N the number of unit cells, g the Landé g-factor, $F(\boldsymbol{\kappa})$ the magnetic form factor, $\exp(-2W)$ the Debye-Waller factor, $\delta_{\alpha\beta}$ the Kronecker delta, and α, β representing x, y, z , $\hat{\mathbf{r}}_\alpha$ and $\hat{\mathbf{r}}_\beta$ the unit vectors of $\boldsymbol{\kappa}$, $\mathbf{S}_l^\beta$ standing for the β -component of the spin angular momentum of atom at site l . Starting from this general formula, the expressions for different types of magnetic structures such as ferromagnets, antiferromagnets and noncollinear spin structures can be derived.

For ferromagnets, in a single domain the electron spins align in the same direction. The elastic differential cross section is

$$\left(\frac{d\sigma}{d\Omega}\right)_{el} = (\gamma r_0)^2 N \frac{(2\pi)^3}{v_0} \left\{ \frac{1}{2} g F(\boldsymbol{\kappa}) \right\}^2 \exp(-2W) (1 - \hat{\kappa}_z^2) \langle \mathbf{S}^z \rangle^2 \sum_{\boldsymbol{\tau}} \delta(\boldsymbol{\kappa} - \boldsymbol{\tau})$$

where $\boldsymbol{\tau}$ is a reciprocal lattice vector. Thus, the magnetic Bragg peaks occur at the same wave vectors in the reciprocal space as the nuclear Bragg peaks.

For simple antiferromagnets, the magnetic structure can be considered as two interpenetrating sublattices, where the spins on sublattice A are antiparallel to those on sublattice B. The expression for the differential cross section is

$$\left(\frac{d\sigma}{d\Omega}\right)_{el} = (\gamma r_0)^2 N_m \frac{(2\pi)^3}{v_{0m}} \sum_{\boldsymbol{\tau}_m} |F_M(\boldsymbol{\tau}_m)|^2 \exp(-2W) \{1 - (\hat{\boldsymbol{\tau}}_m \cdot \hat{\boldsymbol{\eta}})^2\} \delta(\boldsymbol{\kappa} - \boldsymbol{\tau}_m)$$

where

$$F_M(\boldsymbol{\tau}_m) = \frac{1}{2} g \langle \mathbf{S}^\eta \rangle F(\boldsymbol{\tau}_m) \sum_d \sigma_d \exp(i\boldsymbol{\tau}_m \cdot \mathbf{d})$$

N_m is the number of magnetic unit cells, v_{0m} the volume of the magnetic unit cell, $\boldsymbol{\tau}_m$ a vector in the magnetic reciprocal lattice, σ_d being +1 for an A ion and -1 for a B ion, respectively.

For noncollinear magnetic structures, for example, a helical structure in Au_2Mn as shown in Fig. 2.2, the elastic differential cross section is

$$\begin{aligned} \left(\frac{d\sigma}{d\Omega}\right)_{el} &= (\gamma r_0)^2 \frac{N (2\pi)^3}{4 v_0} \langle S \rangle^2 \left\{ \frac{1}{2} g F(\kappa) \right\}^2 \exp(-2W) (1 + \hat{\kappa}_z^2) \\ &\times \sum_{\tau} \{ \delta(\kappa + Q - \tau) + \delta(\kappa - Q - \tau) \} \end{aligned}$$

The magnetic Bragg peaks occur at

$$\kappa = \tau \pm Q$$

shown as a pair of satellite peaks around the nuclear Bragg peaks.

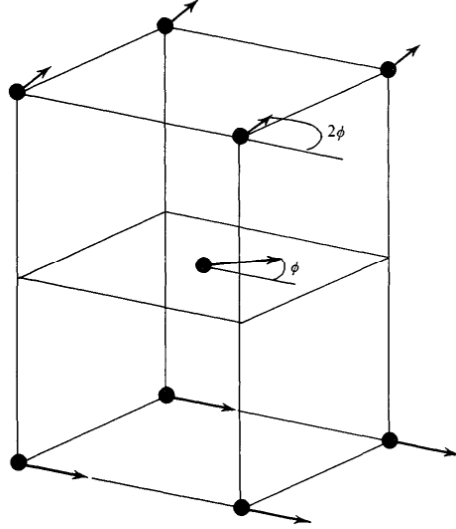


Figure 2.2: Magnetic structure of Au_2Mn [33].

In analogy to the coherent one-phonon scattering, inelastic magnetic scattering can probe the spin dynamics by the creation or annihilation of magnons. The partial differential cross section of coherent one-magnon scattering for a single domain is

$$\frac{d^2\sigma}{d\Omega dE} = (\gamma r_0)^2 \frac{k'}{k} \frac{(2\pi)^3}{v_0} \frac{1}{2} S (1 + \hat{\kappa}_z^2) \left\{ \frac{1}{2} g F(\kappa) \right\}^2 \exp(-2W)$$

$$\times \sum_{\tau, q} \{ \delta(\boldsymbol{\kappa} - \mathbf{q} - \boldsymbol{\tau}) \delta(\hbar\omega_q - \hbar\omega) \langle n_q + 1 \rangle \\ + \delta(\boldsymbol{\kappa} + \mathbf{q} - \boldsymbol{\tau}) \delta(\hbar\omega_q + \hbar\omega) \langle n_q \rangle \}$$

The thermal average of n_q is

$$\langle n_q \rangle = \{ \exp(\hbar\omega_q \beta) - 1 \}^{-1}$$

where $\beta = 1/k_B T$. The first term represents the creation of one magnon, whereas the second one stands for the annihilation of one magnon. The energy and momentum conservation laws are reflected in the delta functions

$$\mathbf{k} - \mathbf{k}' = \boldsymbol{\tau} \pm \mathbf{q}$$

$$\frac{\hbar^2}{2m} (k^2 - k'^2) = \pm \hbar\omega_q$$

2.4 Neutron scattering instrumentation

The neutron scattering experiments presented in this thesis are mainly carried out using the national facilities in High Flux Isotope Reactor (HFIR) and Spallation Neutron Source (SNS) in Oak Ridge National Laboratory (ORNL).

HFIR is a reactor-based neutron source, where neutrons are produced by the spontaneous fission of ^{235}U . In contrast, SNS is built with an accelerator, and neutrons are produced by bombarding a heavy target (e.g., mercury) with high-energy protons. The difference is that the neutron beam is continuous at HFIR, whereas it is pulsed at SNS. Several different types of instruments have been used for neutron scattering experiments, including triple-axis spectrometers, time-of-flight spectrometers, four-circle diffractometers and powder diffractometers.

2.4.1 Triple-axis spectrometer

Triple-axis spectrometers are one of the most versatile instruments designed for both elastic and inelastic neutron scattering experiments. In the work presented in this thesis, the HB-1A fixed-

incident-energy triple-axis spectrometer and CG-4C cold neutron triple-axis spectrometer (CTAX) at HFIR are two triple-axis spectrometers used. The schematic of the CTAX spectrometer is sketched in Fig. 2.3.

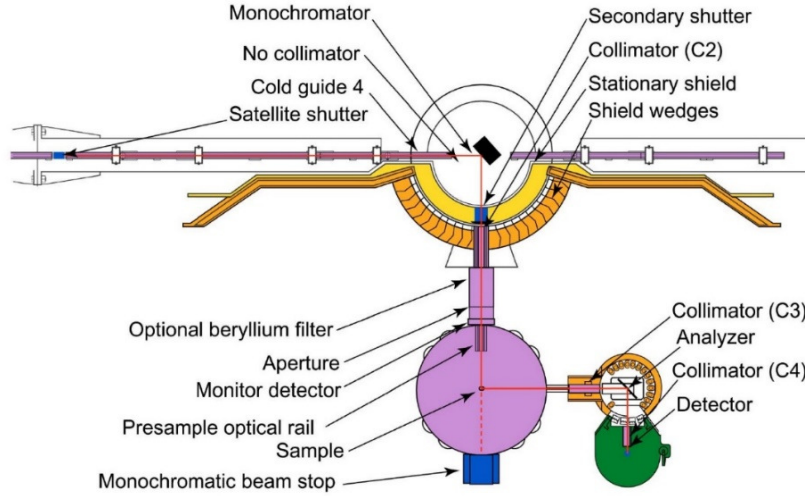


Figure 2.3: Schematic of the CG-4C cold neutron triple-axis spectrometer (CTAX) in HFIR, ORNL.

The name “triple-axis” refers to the monochromator axis, the sample axis and the analyzer axis, respectively. The monochromator is a single crystal which selects the energy of the incident neutrons by the Bragg reflection. The analyzer is also a single crystal that selects the energy of the scattered neutrons counted by the detector. Using a triple-axis spectrometer, the scans can be conveniently made either along a certain direction in the momentum transfer axis at a fixed energy transfer E (constant- E scan), or along the energy transfer axis at a fixed $\mathbf{Q}$ vector (constant- $\mathbf{Q}$ scan), which enables the measurements of the scattering function $S(\mathbf{Q}, \omega)$ in a controlled fashion.

2.4.2 Time-of-flight spectrometer

Time-of-flight spectrometers are another type of widely used neutron scattering instruments that are usually built with a spallation neutron source. For instance, the schematic of the SEQUOIA time-of-flight spectrometer at SNS in ORNL is shown in Figure 2.4. In sharp contrast to the triple-

axis spectrometers, time-of-flight spectrometers are equipped with arrays of detectors covering a large area of the momentum transfer space. The energy of the incident neutrons is selected by a set of Fermi choppers (e.g., “ T_0 choppers”, “Fermi choppers”), and that of the scattered neutrons is determined by the time it takes for the neutrons to arrive at the detectors. Time-of-flight spectrometers have the advantage of measuring large regions of energy transfer $\hbar\omega$ and momentum transfer $\mathbf{Q}$ space simultaneously, thus are particularly efficient for inelastic neutron scattering measurements. In the work presented in this thesis, the SEQUOIA and HYSPEC time-of-flight spectrometers at SNS are used.

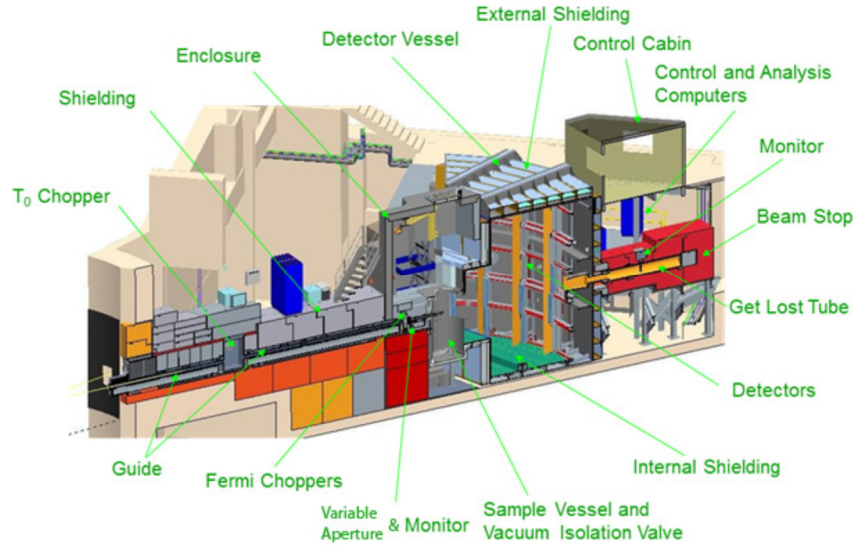


Figure 2.4: Schematic of the SEQUOIA time-of-flight spectrometer in SNS, ORNL [34].

2.4.3 Four-circle diffractometer

Four-circle diffractometers are designed for the determination of nuclear and magnetic structures of single crystals. For example, the picture of the HB-3A four-circle diffractometer at HFIR is shown in Fig. 2.5 [35] and the schematic representation of the angles defining the scattering geometry is shown in Fig. 2.6 [36].



Figure 2.5: HB-3A four-circle diffractometer in HFIR, ORNL [35].

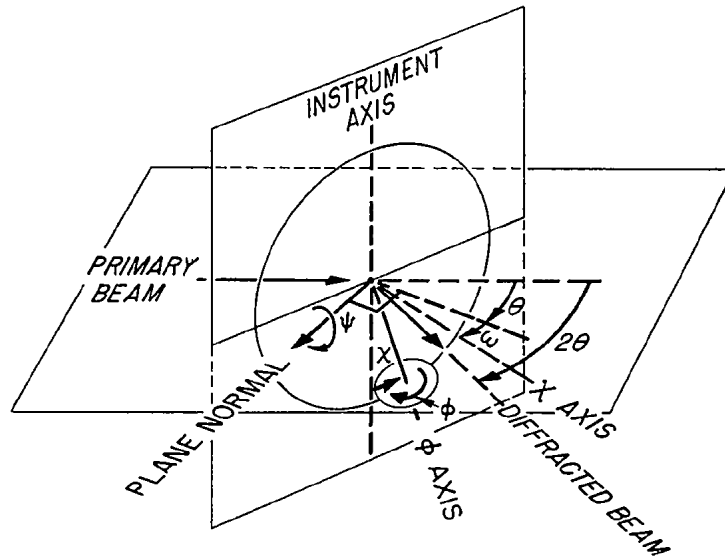


Figure 2.6: Schematic representation of the angles in four-circle diffractometry [36].

The scattering plane defined by the incident (primary) and diffracted beams is horizontal, and the “instrument axis” is vertical passing through the center of the instrument where the samples are mounted. The orientation of the sample is defined by a set of angles θ , ω , χ and ϕ . The scattering angle 2θ is the angle between the incident and diffracted beams. The angle θ denotes a

rotation of the sample about the instrument axis when the detector rotates by 2θ . The sample can also rotate by an additional angle ω about the same axis. The χ -axis is in the scattering plane, perpendicular to the χ -circle (vertical circle containing the instrument axis). And the angle between the χ -axis and the incident beam is $\theta + \omega$. The angle χ is then defined as a rotation about the χ -axis. The ϕ -axis is along the radial direction of the χ -circle forming an angle χ with respect to the “instrument axis”. The angle ϕ defines a rotation about the ϕ -axis [36].

Compared with triple-axis spectrometers where only momentum transfer $\mathbf{Q}$ in a given scattering plane can be reached, four-circle diffractometers provide much more degrees of freedom for sample rotations. Thus, a larger portion of the momentum transfer space can be measured without remounting the sample.

2.4.4 Powder diffractometer

Powder diffractometers are designed for investigating the structural and magnetic properties of polycrystalline samples. The picture and schematic of the HB-2A powder diffractometer at HFIR is shown in Fig. 2.7 and 2.8, respectively [37]. The energy of the incident neutron beam is selected by the monochromator crystal utilizing Bragg conditions. The elastic scattering cross section is measured for a broad range of momentum transfer $\mathbf{Q}$ by a detector bank consisting of a variety of ^3He counting tubes.



Figure 2.7: HB-2A powder diffractometer in HFIR, ORNL [37].

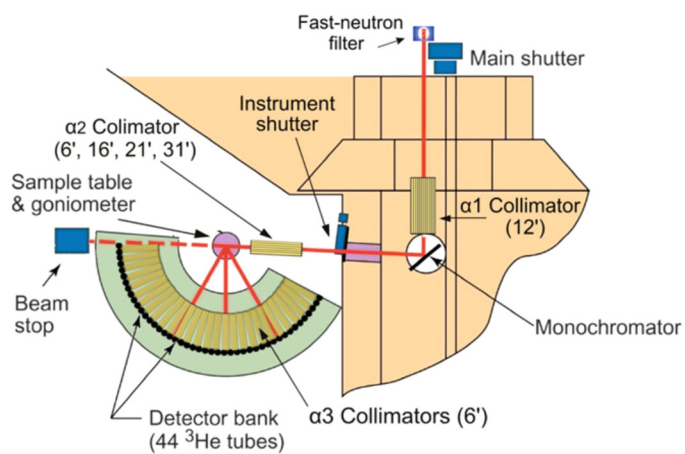


Figure 2.8: Schematic of the HB-2A powder diffractometer in HFIR, ORNL [37].

Chapter 3

Neutron scattering studies on Ruddlesden-Popper type ruthenates

3.1 Introduction and motivation

The $4d$ transition-metal oxides, particularly the Ruddlesden-Popper type ruthenates $(\text{Sr,Ca})_{n+1}\text{Ru}_n\text{O}_{3n+1}$, provide excellent playgrounds for exploring the emergent phenomena in correlated electron systems. Owing to the more extended $4d$ electron orbitals, the correlation effect is weaker than that in $3d$ transition-metal oxides, whereas the SOC is not as strong as that in $5d$ materials. In analogy to the high- T_c cuprates and CMR manganites, the electronic charge, spin, orbital and lattice degrees of freedom are all active. Thus, the magnetic and electronic ground states are very susceptible to perturbations, such as chemical doping, magnetic field and pressure, due to the competition of various interactions of comparable energy scale.

$(\text{Sr,Ca})_{n+1}\text{Ru}_n\text{O}_{3n+1}$ crystallizes in a Ruddlesden-Popper type perovskite structure consisting of RuO_2 planes separated by $(\text{Sr,Ca})\text{O}$ layers. The schematics of the crystal structures of Sr_2RuO_4 ($n = 1$), $\text{Sr}_3\text{Ru}_2\text{O}_7$ ($n = 2$) and SrRuO_3 ($n = \infty$) are depicted in Fig. 3.1. The Ru^{4+} ($4d^4$) magnetic ions are centered in the oxygen octahedra, with four electrons occupying the t_{2g} levels ($S = 1$). While the Sr-based compounds tend to be ferromagnetic and metallic as n increases, substituting Ca for Sr leads to additional structural distortions and drives the system toward antiferromagnetic and nonmetallic phases. Moreover, a diversity of exotic emergent properties have been discovered in $(\text{Sr,Ca})_{n+1}\text{Ru}_n\text{O}_{3n+1}$, including unconventional superconductivity [38-40], Mott transitions [41], metamagnetic quantum critical point (QCP) [42] and orbital order [43,44], etc.

In this chapter, using neutron scattering technique together with magnetic susceptibility, specific heat and electrical transport measurements, we show that the magnetic and electronic properties of Ruddlesden-Popper type ruthenates can be readily tuned by $3d$ transition-metal doping and magnetic field. In Section 3.2 and 3.3, we present the studies on the effects of Fe doping on Sr_2RuO_4 ($n = 1$) and $\text{Sr}_3\text{Ru}_2\text{O}_7$ ($n = 2$). In Section 3.4 and 3.5, we discuss the studies on the effects of magnetic field on $\text{Ca}_3(\text{Ru}_{0.97}\text{Ti}_{0.03})_2\text{O}_7$ and $\text{Ca}_3(\text{Ru}_{0.95}\text{Fe}_{0.05})_2\text{O}_7$ ($n = 2$). The doping effects of Mn on $\text{Ca}_3\text{Ru}_2\text{O}_7$ and the magnetic-field-induced phase transitions are described in Section 3.6. In Section 3.7, we investigate the magnetic transitions of $\text{Sr}_4\text{Ru}_3\text{O}_{10}$ ($n = 3$) driven by temperature and magnetic field.

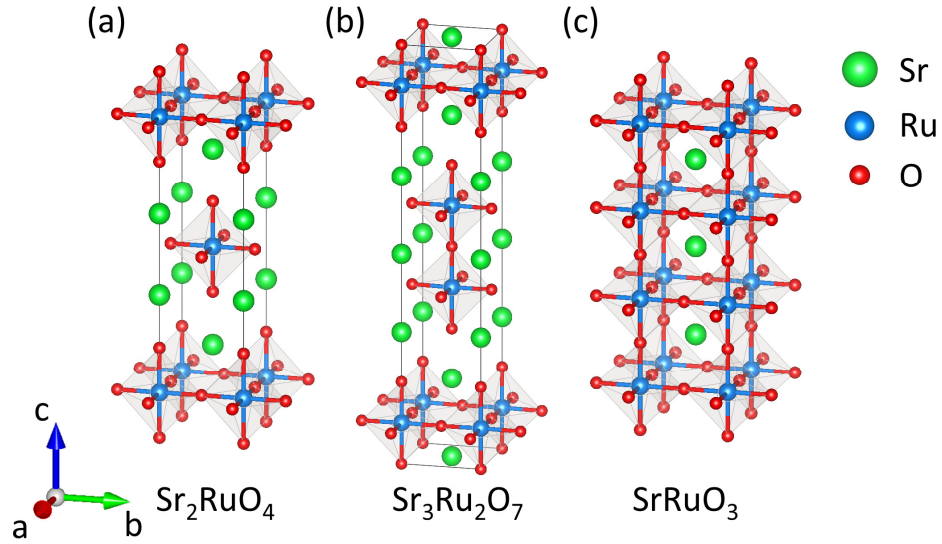


Figure 3.1: Crystal structure of Ruddlesden-Popper type ruthenates $\text{Sr}_{n+1}\text{Ru}_n\text{O}_{3n+1}$ ($n = 1, 2$ and ∞).

3.2 Non-Fermi surface nesting driven spin density wave order in $\text{Sr}_2(\text{Ru,Fe})\text{O}_4$

The single-layer Sr_2RuO_4 ($n = 1$) is isostructural to the parent compound of the high- T_c cuprate La_2CuO_4 . Unconventional superconductivity has been discovered in this material with $T_c = 1.5$ K [45], which is proposed to be chiral p -wave different from the s -wave superconductivity in conventional superconductors or the d -wave spin-singlet one in high- T_c cuprates [46]. Although a variety of experiments have substantiated the unconventional character of the superconducting state and examined the symmetry of the order parameter as well as the structure of the superconducting gap [38-40], the pairing mechanism and the nature of the superconductivity in Sr_2RuO_4 are still open questions. For instance, the absence of topologically protected edge currents [47] is not in line with the time-reversal symmetry breaking p -wave superconductivity [48,49]. Recently it is argued that the superconducting Cooper pairs in Sr_2RuO_4 cannot be described in terms of pure singlets or triplets, but are spin-orbit entangled states due to spin-orbit coupling [50,51].

Furthermore, as in other unconventional superconductors, the correlation between superconductivity and magnetism in Sr_2RuO_4 is of particular interest. That is, the superconducting state is close to magnetic instabilities, and spin fluctuations may be responsible for the superconducting pairing mechanism [52]. While the normal state of Sr_2RuO_4 shows Fermi liquid behavior below $T = 25$ K [53], the system exhibits strong magnetic instabilities with ferromagnetic and antiferromagnetic fluctuations coexisting and competing [54,55]: The Fermi surface nesting of the quasi-one-dimensional α/β bands leads to antiferromagnetic fluctuations, whereas the close proximity of the Fermi level to a Van Hove singularity of the quasi-two-dimensional γ band gives rise to ferromagnetic fluctuations [56,57]. Ferromagnetic correlations have been corroborated by

nuclear magnetic resonance measurements [58], and are suggested to be responsible for the p -wave superconductivity [59]. However, neutron scattering experiments found prominent incommensurate antiferromagnetic fluctuations at $\mathbf{q}_{ic} = (0.3 \ 0.3 \ L)$, arising from Fermi surface nesting of the α/β bands [54]. Such incommensurate antiferromagnetic fluctuations along with strong anisotropy have been proposed to account for the unconventional superconductivity in Sr_2RuO_4 [60]. Additionally, recent theoretical and experimental studies have also suggested that the superconductivity in Sr_2RuO_4 may be generated by the Cooper pairs on the α/β bands but not on the γ band [61,62].

A fundamental challenge to the understanding of unconventional superconductivity is how the tendency towards magnetic ordering is suppressed while strong magnetic fluctuations are maintained that may lead to superconductivity. Intriguingly, for Sr_2RuO_4 , at the bare density functional level the incommensurate magnetic instability at $\mathbf{q}_{ic}$ is sufficiently strong so that ordering would be expected [63]. This ordering is presumably suppressed by spin fluctuations, possibly associated with competing orders [55], which is a characteristic common to unconventional superconductors. A powerful means of exploring the competing magnetic tendencies in Sr_2RuO_4 is chemical doping. For instance, moderate substitutions of Ca for Sr sites, and Ti or Mn for Ru sites have been shown to give rise to static spin density wave (SDW) ordering with the propagation vector associated with the nesting Fermi surface [64-66]. In contrast, carrier doping via La substitution for Sr sites enhances ferromagnetic fluctuations by elevating the Fermi level closer to the Van Hove singularity of the γ band [67]. These studies attest that the magnetic ground state of Sr_2RuO_4 is in the vicinity of the antiferromagnetic and ferromagnetic instabilities.

In this section, we present a commensurate, quasi-two-dimensional SDW ordering in Sr_2RuO_4 induced by Fe doping for Ru. This magnetic ordered state is characterized by a wave vector $\mathbf{q}_c =$

(0.25 0.25 0), in contrast to the incommensurate ones in Ti- and Mn-doped compounds [65,66]. Intriguingly, the incommensurate magnetic excitations at $\mathbf{q}_{ic} = (0.3 \ 0.3 \ 0)$ associated with Fermi surface nesting in the pristine Sr_2RuO_4 persist in the Fe-doped compounds. This suggests that the induced static ordered state is not driven by Fermi surface nesting, which has been corroborated by *ab initio* electronic structure calculations. These results imply that, in addition to the known incommensurate magnetic instability, Sr_2RuO_4 is also in proximity to a commensurate magnetic tendency which may facilitate the suppression of static magnetic order and give rise to unconventional superconductivity.

3.2.1 Materials and methods

Single crystals of $\text{Sr}_2\text{Ru}_{1-x}\text{Fe}_x\text{O}_4$ ($x = 0.03$ and 0.05) samples were grown using the Floating Zone method [66]. Magnetization, specific heat and electrical resistivity were measured using the Physical Property Measurement System (PPMS, Quantum Design). Neutron diffraction experiments were performed using the HB-1A thermal neutron triple-axis spectrometer at HFIR in ORNL, with fixed incident neutron energy $E_i = 14.6$ meV and the collimation setting of $40'-40'$ -sample- $40'-80'$. The samples were oriented in the $(H \ K \ 0)$ and $(H \ H \ L)$ scattering planes, respectively, where $(H \ K \ L)$ are in reciprocal lattice units $2\pi/a$, $2\pi/b$ and $2\pi/c$ ($a = b = 3.868$ Å and $c = 12.684$ Å at 5 K in the tetragonal space group $I4/mmm$). Magnetic excitations were measured using the HB-1 triple-axis spectrometer at HFIR and the HYSPEC, CNCS and SEQUOIA time-of-flight spectrometers [68] at SNS in ORNL with samples co-aligned in the $(H \ K \ 0)$ plane. The incident neutron energy was set as $E_i = 13$ meV at HYSPEC and 3.32 meV at CNCS, respectively. *x*-ray absorption spectroscopy (XAS) measurements were carried out on the beamline 4-ID-C at the Advanced Photon Source (APS) in Argonne National Laboratory (ANL).

3.2.2 Magnetic susceptibility, specific heat and resistivity

The main panel of Fig. 3.2(a) shows the temperature dependence of the DC magnetic susceptibility χ_c of $\text{Sr}_2\text{Ru}_{1-x}\text{Fe}_x\text{O}_4$ ($x = 0.05$) measured with $B = 1$ T applied along the c axis. There are three remarkable features. (i) Compared to the weak temperature dependence associated with the Pauli paramagnetism in the parent compound [53], the Fe-doped compound exhibits enhanced Curie-Weiss susceptibility, which implies the formation of localized moments induced by Fe doping. The Curie-Weiss fit on the susceptibility at elevated temperatures gives rise to an effective magnetic moment $\mu_{\text{eff}} \sim 1.8 \mu_B$ per Ru. (ii) A paramagnetic-antiferromagnetic phase transition is observed at $T_N \sim 64$ K, as evidenced by the peak in the magnetic susceptibility data. (iii) Upon further cooling, a bifurcation between the zero-field-cooled (ZFC) and field-cooled (FC) data emerges below $T_g \sim 16$ K, characteristic of a spin-glass-like state.

The inset of Fig. 3.2(a) shows the isothermal magnetization measurements performed at $T = 2$ K and 20 K. Hysteresis is observed at 2 K which is consistent with the fact that ferromagnetic correlations develop in the spin-glass-like state. The spin-glass-like state below T_g is also supported by the frequency dependence of the AC magnetic susceptibility data plotted in Fig. 3.2(b), where one can see that the peak around 16 K weakly shifts to higher temperatures with increasing measurement frequency. Note that such a bifurcation between FC and ZFC data and the hysteretic behavior in magnetization are absent for the in-plane magnetic susceptibility measurements where the antiferromagnetic phase transition is also observed, as shown in Fig. 3.3(a) and (b), indicating that the spin-glass-like state presumably arises from the development of short-range ferromagnetic correlations between RuO_2 layers. Furthermore, the magnetic moments induced by Fe doping exhibit magnetic anisotropy with the ordered moment along the c axis. Similar features have been observed in the Ti- and Mn-doped Sr_2RuO_4 [69,66].

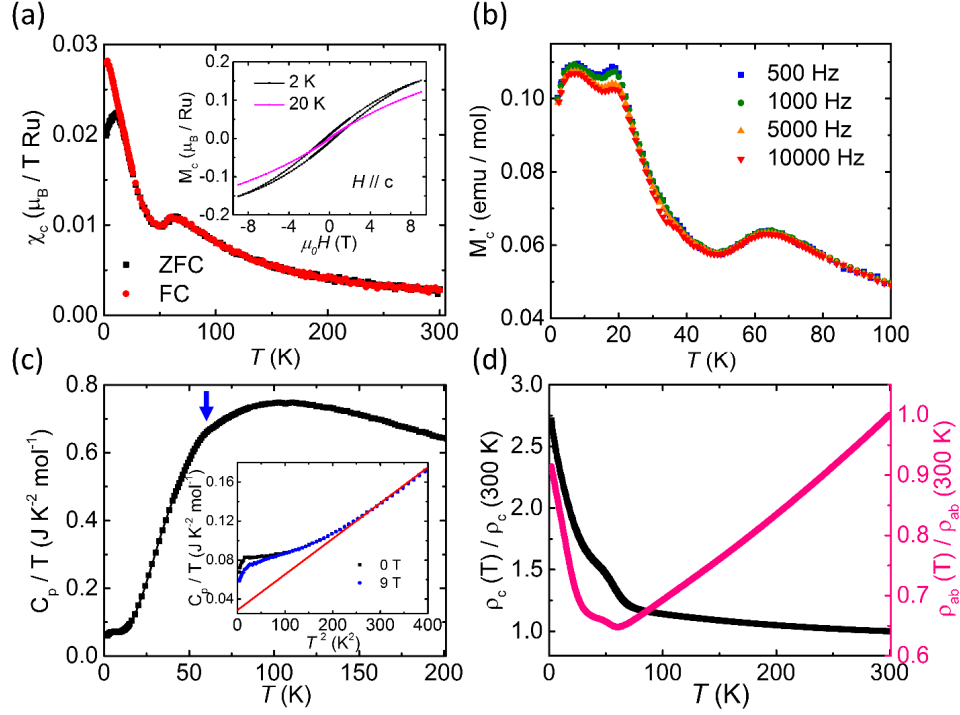


Figure 3.2: (a) Temperature dependence of out-of-plane DC susceptibility χ_c of $\text{Sr}_2\text{Ru}_{0.95}\text{Fe}_{0.05}\text{O}_4$ after ZFC and FC, respectively. Inset shows the isothermal magnetization as a function of field at $T = 2$ and 20 K after ZFC. (b) Temperature dependence of AC susceptibility measured with $h = 10$ Oe. (c) Temperature dependence of specific heat at zero field. Inset shows the expanded view of the low-temperature region with the data measured at 9 T included for comparison. The solid red line is a linear fit for $16 \text{ K} < T < 30 \text{ K}$. (d) In-plane and out-of-plane resistivity as a function of temperature.

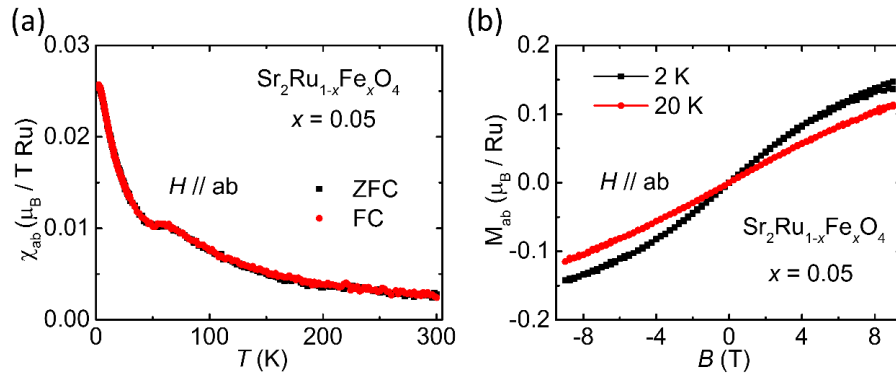


Figure 3.3: (a) Temperature dependence of in-plane DC susceptibility χ_{ab} of $\text{Sr}_2\text{Ru}_{0.95}\text{Fe}_{0.05}\text{O}_4$ after ZFC and FC, respectively. (b) Magnetization as a function of magnetic field at $T = 2$ K and 20 K.

Figure 3.2(c) presents the temperature dependence of the specific heat measured at zero field. An anomaly is observed around T_N , corresponding to the onset of antiferromagnetic ordering. The small change in specific heat at T_N might be due to the small magnetic moment size associated with this spin ordered state. It is worth noting that a specific heat anomaly is not convincingly observed in the Ti- and Mn-doped compounds, even though a static magnetic order develops at low temperature in both systems [66,70]. The inset of Fig. 3.2(c) shows the plot of C_p/T vs T^2 and the extracted Sommerfeld coefficient is in the range of $27 \sim 35 \text{ mJ mol}^{-1} \text{ K}^{-2}$, depending on the temperature fitting regime, which is slightly smaller than the one obtained from the parent compound [53], presumably due to the reduced carrier density upon the formation of the SDW order [66,70]. Interestingly, as seen in the inset, the specific heat at low temperature is enhanced and can be suppressed upon applying a 9-T magnetic field, which is most probably ascribable to the magnetic contribution associated with the spin-glass-like state. Temperature dependence of the out-of-plane and in-plane resistivity ρ_c and ρ_{ab} are shown in Fig. 3.2(d). Both ρ_c and ρ_{ab} exhibit anomalies at T_N and close to T_g . Particularly, the increase in ρ_{ab} below T_N implies a partial gap opening on the Fermi surface arising from the formation of the antiferromagnetic order.

3.2.3 Neutron diffraction

In order to determine the magnetic structure of Sr_2RuO_4 induced by Fe doping, we performed neutron diffraction measurements. Fig. 3.4(a) shows the scans along the $[1\ 0\ 0]$ direction over $\mathbf{q}_c = (0.25\ 0.25\ 0)$ at $T = 4, 50$ and 100 K measured on $\text{Sr}_2\text{Ru}_{0.95}\text{Fe}_{0.05}\text{O}_4$. A Gaussian-shaped Bragg peak is clearly observed at 4 and 50 K but vanishes at 100 K , indicating the magnetic origin of this peak. In addition, the full width at half maximum (FWHM) is found to be determined by the instrument resolution, which implies the formation of a long-range commensurate magnetic order in the ab plane. On the contrary, the scans around $\mathbf{q}_{ic} = (0.3\ 0.3\ 0)$ and $(0.3\ 0.3\ 1)$ do not give

discernible magnetic intensity. Fig. 3.4(b) shows the scans along the $[0\ 0\ 1]$ direction across the magnetic Bragg peak $\mathbf{q}_c = (0.25\ 0.25\ 0)$ measured at various temperatures. Distinct from the scans along the $[1\ 1\ 0]$ direction, these curves can be fitted using a Lorentzian function implying a correlation length of about $20\ \text{\AA}$ along the c axis at $T = 4\ \text{K}$. This suggests that the magnetic ordering induced by Fe doping is nearly two-dimensional, with very short correlation length along the c axis. Additionally, the strongest magnetic Bragg peak is observed at $\mathbf{q}_c = (0.25\ 0.25\ L)$ with $L = 0$ instead of $L = 1$, indicating the absence of the phase shift between neighboring RuO_2 layers [64]. These results are in sharp contrast to the earlier studies on Ti- and Mn-doped Sr_2RuO_4 , where short-range incommensurate SDW order with the propagation vector $\mathbf{q}_{ic} = (0.3\ 0.3\ 1)$ originating from the nesting Fermi surface are reported [65,66]. This suggests that the mechanism for the emergence of the commensurate magnetic order in Fe-doped Sr_2RuO_4 is different.

The temperature dependence of the magnetic intensity at $\mathbf{q}_c$, which is proportional to the square of the staggered magnetization of the antiferromagnetic order, is shown in Fig. 3.4(c). A well-defined phase transition is readily seen at $T_N = 64\ \text{K}$, consistent with the magnetic susceptibility and specific heat measurements. It is worth noting that for the 3% Fe-doped compound ($x = 0.03$), the magnetic Bragg peaks are also observed at $\mathbf{q}_c$ and other equivalent wave vectors, but not at $\mathbf{q}_{ic}$, as presented in the contour map in Fig. 3.4(d). The observation of both magnetic reflections associated with the magnetic propagation vectors $\mathbf{q}_c = (0.25\ 0.25\ 0)$ and $(0.25\ -0.25\ 0)$ implies the existence of magnetic twin domains due to the tetragonal symmetry of the crystal structure. The intensity of the corresponding magnetic reflections is comparable, indicating that the population of these two magnetic twin domains are nearly equal.

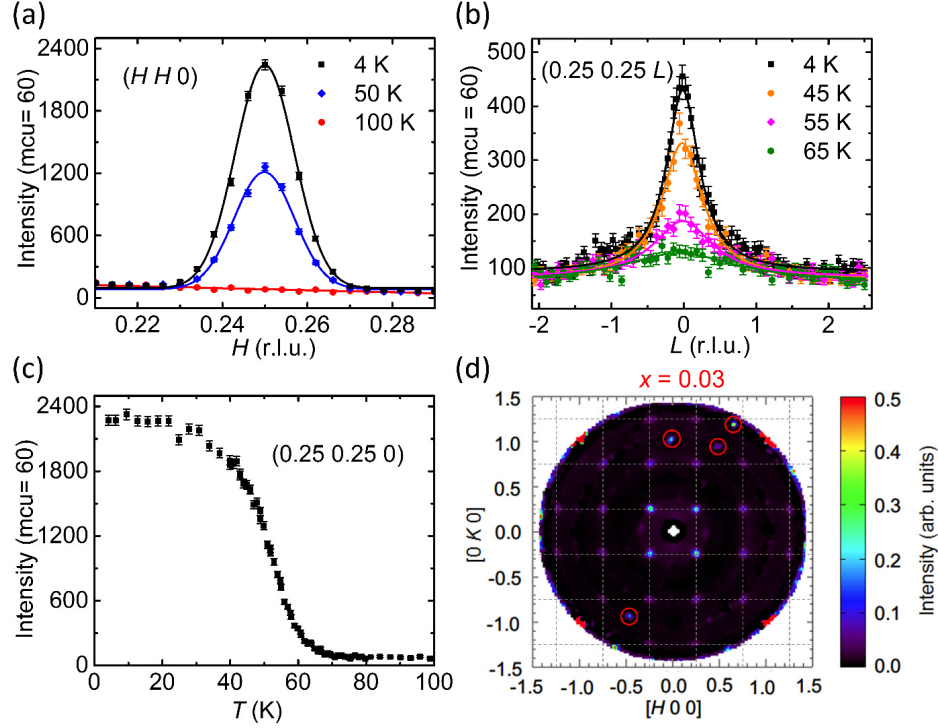


Figure 3.4: (a) Scans across $\mathbf{q}_c = (0.25\ 0.25\ 0)$ along the $[1\ 1\ 0]$ direction at $T = 4, 50$ and 100 K measured on $\text{Sr}_2\text{Ru}_{0.95}\text{Fe}_{0.05}\text{O}_4$. (b) Scans across $\mathbf{q}_c = (0.25\ 0.25\ 0)$ along the $[0\ 0\ 1]$ direction at selected temperatures. (c) The intensity of magnetic Bragg peak $\mathbf{q}_c = (0.25\ 0.25\ 0)$ as a function of temperature. Note that the sample measured for (b) is smaller than that for (a,c). (d) Contour map of elastic magnetic scattering intensity of $\text{Sr}_2\text{Ru}_{0.97}\text{Fe}_{0.03}\text{O}_4$ at $T = 1.6$ K after subtracting the background measured at 80 K. Spurious peaks are denoted by red circles. The residue intensity near the nuclear peaks $(\pm 1\ \pm 1\ 0)$ is presumably due to the thermal shift in the lattice parameters.

Possible models of the magnetic structure have been explored by the magnetic representational analysis using the program BASIREPS in the FULLPROF suite [71] and by the magnetic symmetry approach using the tools at the Bilbao Crystallographic Server [72]. The crystal symmetry of $\text{Sr}_2\text{Ru}_{1-x}\text{Fe}_x\text{O}_4$ ($x = 0.03$ and 0.05) is assumed to be the same as that of the parent compound (No. 139, $I4/mmm$), as discussed in Appendix A. The maximal magnetic space groups compatible with the space group of the crystal structure and the propagation vector $\mathbf{q}_c = (0.25\ 0.25\ 0)$ require the magnetic moments to be oriented either along the c axis or in the ab plane. We find that our data are best described by the SDW models with the moments parallel to the c axis, in

agreement with the magnetic susceptibility measurements. Since the moment distribution of the SDW order can be described as a cosine modulation $\mu_l = S \cos(\mathbf{q} \mathbf{R}_l + \delta)$, there are two possible spin configurations that depend on the choice of the initial phase δ : (i) $S (+, 0, -, 0)$ when $\delta = 0$ (magnetic group C_{cmcm}), or (ii) $1/\sqrt{2}S (+, +, -, -)$ when $\delta = (2n + 1)\pi/4$, in which n is an integer (magnetic group C_{cmca}). The parameter S represents the amplitude of the magnetic moment which has been estimated from the diffraction data to be about $0.4 \mu_B$. The schematics of these two magnetic structure models are illustrated in Fig. 3.5(a) and (b), respectively. Note that these two models give rise to identical neutron diffraction patterns and are different only in the size of the local moment by a factor of $\sqrt{2}$. The corresponding magnetic twin domain with $\mathbf{q}_c = (0.25 -0.25 0)$ is shown in Fig. 3.5(c) and (d).

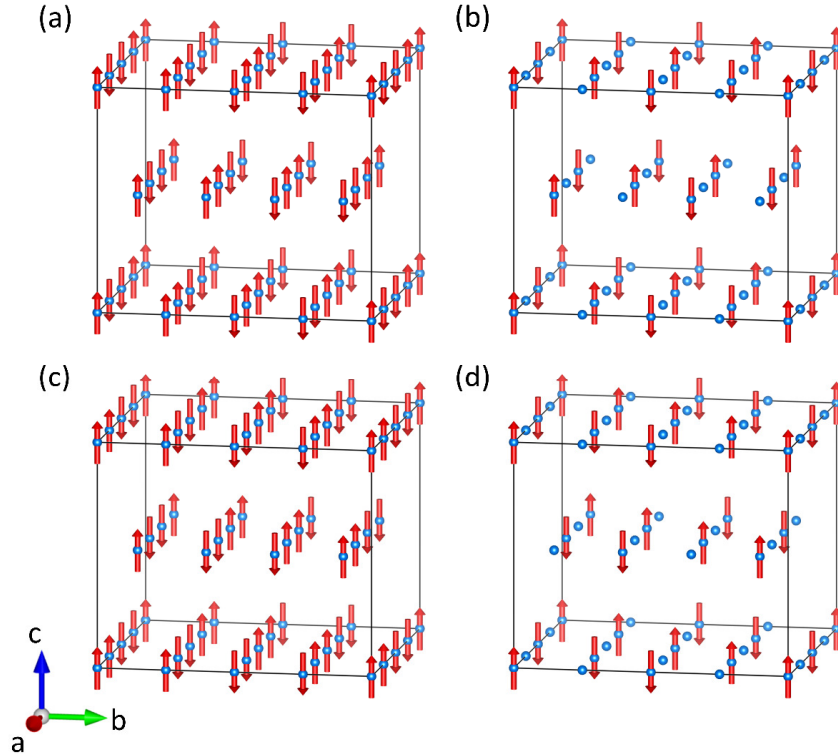


Figure 3.5: Schematics of the SDW order of two magnetic twin domains in $\text{Sr}_2\text{Ru}_{1-x}\text{Fe}_x\text{O}_4$. (a),(b) SDW with $\mathbf{q}_c = (0.25, 0.25, 0)$. (c),(d) SDW with $\mathbf{q}_c = (0.25, -0.25, 0)$.

3.2.4 Density functional theory calculations and x-ray absorption

The fact that the commensurate magnetic order with a propagation vector $\mathbf{q}_c = (0.25 \ 0.25 \ 0)$ emerges in Fe-doped Sr_2RuO_4 is very intriguing, considering that both the strong magnetic fluctuations in the pristine compound and the static incommensurate magnetic order in the Ti- and Mn-doped compounds occur at the same wave vector $\mathbf{q}_{ic} = (0.3 \ 0.3 \ L)$, which are ascribed to the Fermi surface nesting of the quasi-one-dimensional α/β bands [54,65,66]. This raises an important question: Does the commensurate magnetic order originate from the change in the nesting vector of the Fermi surface upon Fe substitution?

To address this question, in collaboration with Dr. D. J. Singh and Dr. K. V. Shanavas in University of Missouri, we performed density functional theory (DFT) calculations for both the pristine and Fe-doped Sr_2RuO_4 , using the generalized gradient approximation of Perdew, Burke and Ernzerhof (PBE-GGA) [73] and the projector augmented plane wave method [74] as implemented in the VASP code [75]. We used an energy cut-off of 450 eV and a k -point sampling of $22 \times 22 \times 13$ for the single unit cell of Sr_2RuO_4 and $7 \times 7 \times 13$ for a $3 \times 3 \times 1$ supercell to obtain a similar density of k -points. The structures were fully optimized. We also checked by performing calculations for the $3 \times 3 \times 1$ supercell containing one Fe using the all electron general potential linearized augmented plane wave method [74] as implemented in the WIEN2k code [76] and relaxing only the internal atomic coordinates. The calculation yielded essentially the same results as the VASP calculations.

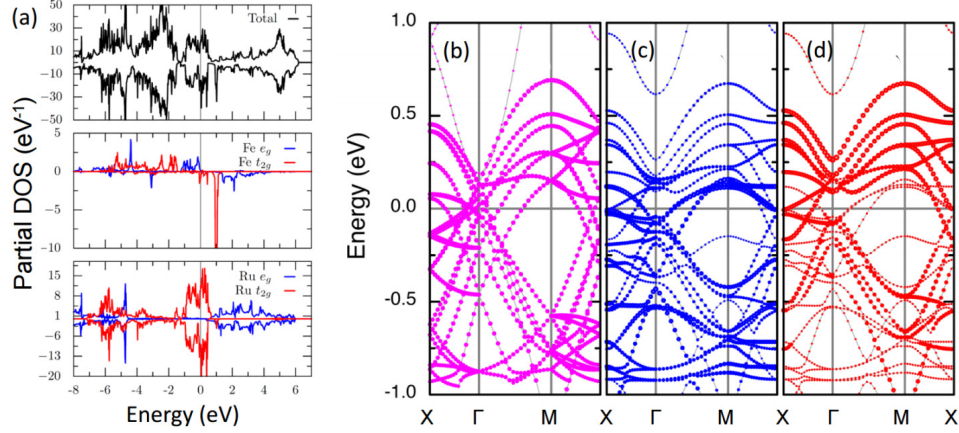


Figure 3.6: Electronic structure for a $3 \times 3 \times 1$ supercell of Sr_2RuO_4 containing one Fe substitution. (a) Density of states and projections showing majority spin as positive and minority spin as negative. (b) Fat band plot of the band structure showing Ru character for the unsubstituted supercell (heavier symbols represent higher Ru character), in comparison with the Fe substituted cell, emphasized by heavier symbols. (c) Ru character from Ru neighboring Fe and (d) Ru not neighboring Fe.

The Fermi surfaces and other properties of bulk Sr_2RuO_4 were similar to the prior reports [59]. All calculations with Fe spin polarized were performed. The density of states (DOS) and projections of a $3 \times 3 \times 1$ supercell, which contains one Fe atom replacing the Ru in Sr_2RuO_4 , is shown in Fig. 3.6 along with a band structure plot for the folded zone. The majority spin of the Fe *d* orbitals is fully occupied, as shown in Fig. 3.6(a), suggesting that Fe enters as the high-spin configuration Fe^{3+} which is in agreement with the XAS measurements presented in Fig. 3.7(a). The calculated multiplet splitting of the Fe 3*s* core level in our DFT calculation is 4.45 eV, consistent with this high-spin state. Thus, the introduction of Fe results in an electron deficiency of $1 e / \text{Fe}$ for the host lattice. It is important to note that the Fermi surfaces are large and by Luttinger's theorem, a change of $0.03 e \sim 0.05 e$ per cell leads to a change in the Fermi surface volume of $0.015 \sim 0.025$ of the Brillouin zone volume, consistent with the small shifts (~ 0.1 eV near E_F) along with distortions in the band structure for 11% Fe doping [Fig. 3.6(b)-(d)]. These small changes resulting from 3% and 5% Fe doping cannot explain the large shift in the magnetic

ordering vector, thus a simple itinerant electron explanation in terms of band filling is not operative. However, in addition to the Fe moments, we find a strong back polarization of the Ru neighboring Fe amounting to more than $1 \mu_B / \text{Ru neighbor}$ ($1.08 \mu_B$ as obtained by integrating the spin density over a sphere of radius 2 Bohr around the Ru). We infer that this strong local magnetic coupling of Fe and Ru frustrates the incommensurate nesting and leads to the commensurate order observed in our experiments.

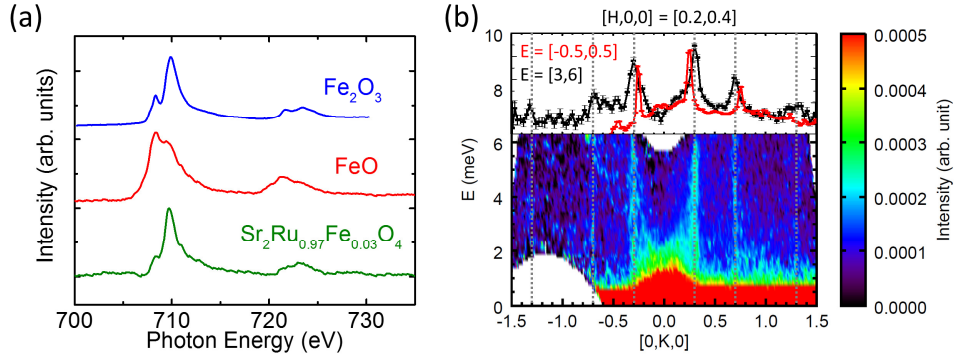


Figure 3.7: (a) x-ray absorption spectra of Sr₂Ru_{0.97}Fe_{0.03}O₄ near the Fe *L* edge in comparison with FeO and Fe₂O₃. (b) Lower panel: contour map of inelastic neutron scattering intensity as a function of *E* and *K*, *H* integrated from 0.2 to 0.4. Upper panel: cuts along [0 1 0] with *E* integrated from 3 to 6 meV (black) and from -0.5 to 0.5 meV (red), respectively. *H* is integrated from 0.2 to 0.4. Note that the intensities of these two curves are scaled. Data were measured on Sr₂Ru_{0.97}Fe_{0.03}O₄.

3.2.5 Inelastic neutron scattering

The robustness of the nesting vector of the α/β bands on the Fermi surface with respect to Fe doping is corroborated experimentally by the magnetic excitation spectra measured using the time-of-flight inelastic neutron scattering technique. The lower panel of Fig 3.7(b) shows the contour map of the scattering intensity of Sr₂Ru_{1-*x*}Fe_{*x*}O₄ (*x* = 0.03) as a function of *E* (i.e., energy transfer) and *K*. Surprisingly, the dominant magnetic excitations above *E* = 3 meV are well centered at the incommensurate wave vectors $\mathbf{q}_{ic} = (0.3 \ 0.3 \ 0)$ and $(0.3 \ 0.7 \ 0)$ [black curve in the upper panel of Fig. 3.7(b)], which is different from the elastic magnetic reflections (red curve) centered at the

commensurate wave vectors $\mathbf{q}_c = (0.25 \ 0.25 \ 0)$ and $(0.25 \ 0.75 \ 0)$. In addition, the magnetic fluctuations barely show any energy dependence, similar to that in both the pristine and the Ti-doped compounds [54,77]. While the magnetic excitations related to this ordered state warrant further investigation, the coexistence of the commensurate magnetic order at $\mathbf{q}_c = (0.25 \ 0.25 \ 0)$ and the dynamic spin fluctuations at $\mathbf{q}_{ic} = (0.3 \ 0.3 \ 0)$ in Fe-doped Sr_2RuO_4 implies that the magnetic order is not driven by the Fermi surface nesting as in the Ti- and Mn-doped compounds [65,66]. Thus, Fe doping reveals a previously unanticipated commensurate magnetic instability in Sr_2RuO_4 at $\mathbf{q}_c = (0.25 \ 0.25 \ 0)$, which competes with the known incommensurate one. These results suggest that the tendency toward magnetic ordering in Sr_2RuO_4 is suppressed by quantum fluctuations associated with competing magnetic instabilities, while strong spin fluctuations are maintained and may give rise to the unconventional superconducting state.

3.2.6 Summary

We have unraveled a commensurate SDW order with a propagation vector $\mathbf{q}_c = (0.25 \ 0.25 \ 0)$ in Sr_2RuO_4 upon Fe doping for Ru, whereas the incommensurate magnetic fluctuations at $\mathbf{q}_{ic} = (0.3 \ 0.3 \ L)$ in the pristine compound persist. This suggests that this commensurate ordered state does not arise from Fermi surface nesting, in contrast to the previous studies on Ti-, Mn- and Ca-doped Sr_2RuO_4 [64-66]. This study indicates that the unconventional superconducting state in Sr_2RuO_4 is not only adjacent to the known incommensurate magnetic order, but also to a commensurate one.

3.3 Magnetic order and metal-insulator transition in $\text{Sr}_3(\text{Ru,Fe})_2\text{O}_7$.

The bilayer $\text{Sr}_3\text{Ru}_2\text{O}_7$ ($n = 2$) exhibits a Fermi liquid ground state that is close to a ferromagnetic instability [78]. More intriguingly, it possesses a magnetic-field-tuned QCP, where non-Fermi liquid behavior [42] and highly anisotropic magnetoresistance [79] emerge. Recently neutron diffraction measurements have identified two different magnetically ordered phases close to the QCP [80]. Furthermore, it is revealed that ferromagnetic and antiferromagnetic spin fluctuations coexist in this system [81], and the latter is suggested to be dominant near the critical field, which is unexpected for a metamagnetic transition [82].

Chemical doping is an effective approach to tailor the materials' properties by stabilizing one of the competing phases while suppressing others. In contrast to Sr_2RuO_4 , Ti and Mn dopants have different effects on the physical properties of $\text{Sr}_3\text{Ru}_2\text{O}_7$. While both Ti and Mn doping lead to insulating electronic transport behaviors at low temperature, Ti doping gives rise to an incommensurate SDW order with a propagation vector $\mathbf{q}_{\text{ic}} = (0.24 \ 0.24 \ 0)$ [83,84], but Mn-doped $\text{Sr}_3\text{Ru}_2\text{O}_7$ exhibits a commensurate E -type antiferromagnetic order characterized by $\mathbf{q}_c = (0.25 \ 0.25 \ 0)$ [85,86]. In both cases, the static magnetic orders do not reflect the dominant dynamical magnetic correlations at $\mathbf{q} = (0.09 \ 0 \ 0)$ and $(0.25 \ 0 \ 0)$ in the pristine $\text{Sr}_3\text{Ru}_2\text{O}_7$ [81], distinct from those in Ti- and Mn-doped Sr_2RuO_4 [65,66]. In addition, synchrotron XAS measurements have found that Mn dopants in $\text{Sr}_3\text{Ru}_2\text{O}_7$ display a valence value of Mn^{3+} , and show an inversion of the conventional crystal-field level hierarchy, which is suggested to be due to the hybridization between the Ru-O $4d$ - $2p$ bands and the Mn $3d$ orbitals [87]. Inspired by the discovery of the commensurate SDW order in Fe-doped Sr_2RuO_4 , it would be interesting to study the effects of Fe doping on the ground state properties of $\text{Sr}_3\text{Ru}_2\text{O}_7$.

In this section, we present the magnetic and electronic properties of Fe-doped $\text{Sr}_3\text{Ru}_2\text{O}_7$. In contrast to the paramagnetic metallic state in the parent compound, $\text{Sr}_3(\text{Ru}_{1-x}\text{Fe}_x)_2\text{O}_7$ ($x = 0.01$) shows a metallic spin-glass-like ground state, whereas for $x = 0.03$ an insulating phase with a quasi-two-dimensional E -type antiferromagnetic order with the propagation vector $\mathbf{q}_c = (0.25 \ 0.25 \ 0)$ is observed below $T_N \sim 40$ K. These features are similar to that in Mn-doped $\text{Sr}_3\text{Ru}_2\text{O}_7$ [88], which suggests that the magnetically ordered state induced upon Fe and Mn doping originates from the intrinsic instability of $\text{Sr}_3\text{Ru}_2\text{O}_7$.

3.3.1 Materials and methods

Single crystals of $\text{Sr}_3(\text{Ru}_{1-x}\text{Fe}_x)_2\text{O}_7$ ($x = 0.01$ and 0.03) were grown using the Floating Zone method. Magnetization, specific heat and resistivity measurements were performed using PPMS. Neutron diffraction experiments were carried out using the HB-1A thermal neutron triple-axis spectrometer at HFIR in ORNL. The energy of the incident neutrons is fixed as $E_i = 14.6$ meV. The single crystals were oriented in the $(H \ K \ 0)$ and $(H \ H \ L)$ scattering planes, and were mounted in an aluminum sample can and cooled using a closed-cycle helium refrigerator down to 4 K. For convenience, we describe our neutron diffraction data using the tetragonal lattice symmetry $I4/mmm$ with $a = b = 3.874$ Å and $c = 20.69$ Å. The neutron intensity was presented in the unit of counts per monitor count unit (mcu), with 1 mcu corresponding to approximately 1 second. Synchrotron XAS experiments were performed using the beamline 4-ID-C at APS in ANL to measure the valence state of the Fe dopants.

3.3.2 Magnetic susceptibility, specific heat and resistivity

The main panels of Fig. 3.8(a) and (b) show the temperature dependence of the magnetic susceptibility χ_c of $\text{Sr}_3(\text{Ru}_{1-x}\text{Fe}_x)_2\text{O}_7$ ($x = 0.01$ and 0.03) after ZFC and FC, respectively. In the pristine $\text{Sr}_3\text{Ru}_2\text{O}_7$, the magnetic susceptibility is nearly isotropic with a pronounced peak at $T = 16$

K in both χ_c and χ_{ab} [78], which is ascribable to the crossover of the nature of the dominant magnetic fluctuations from ferromagnetic to antiferromagnetic upon cooling [81]. No hysteresis effect is observed between the ZFC and FC data [78]. In contrast, for $x = 0.01$, the peak at 16 K is completely suppressed in both χ_c and χ_{ab} . Instead, χ_c (T) shows a maximum at $T_g \sim 4$ K, below which a bifurcation between the ZFC and FC data is clearly seen, characteristic of a spin-glass-like state. Figure 3.8(c) displays the magnetization as a function of the magnetic field applied along the c axis at $T = 2$ and 6 K, respectively. The hysteretic behavior observed at 2 K indicates that short-range ferromagnetic correlations develop between the neighboring RuO₂ layers along the c axis below T_g . On the contrary, as shown in the inset of Fig. 3.8(a), the in-plane magnetic susceptibility χ_{ab} shows a paramagnetic behavior down to 2 K, and there is no bifurcation between the ZFC and FC curves. These results suggest that Fe doping in Sr₃Ru₂O₇ induces strong magnetic anisotropy with the easy axis along the c direction, similar to Fe-doped Sr₂RuO₄ [89]. Furthermore, the metamagnetic transition observed in the parent compound has been completely smeared out, as shown in the inset of Fig. 3.8(c), which implies that Fe doping drives the system away from metamagnetism, as reported in Ti-doped Sr₃Ru₂O₇ [83].

Interestingly, for $x = 0.03$, a sharp peak in magnetic susceptibility develops in both χ_c and χ_{ab} at $T_N \sim 40$ K, suggestive of the onset of a paramagnetic-antiferromagnetic phase transition. Neither the bifurcation in the magnetic susceptibility curves $M(T)$ measured with ZFC and FC histories nor the hysteresis in the isothermal magnetization $M(H)$ is observed. In addition, it is noteworthy that at 9 T, the magnetization at 2 K is much smaller than that at 50 K. These results suggest that the nature of these peaks in the magnetic susceptibility data is fundamentally different from that in the $x = 0.01$ compound, which implies that 3% Fe dopants lead to the formation of a long-range antiferromagnetic ordering.

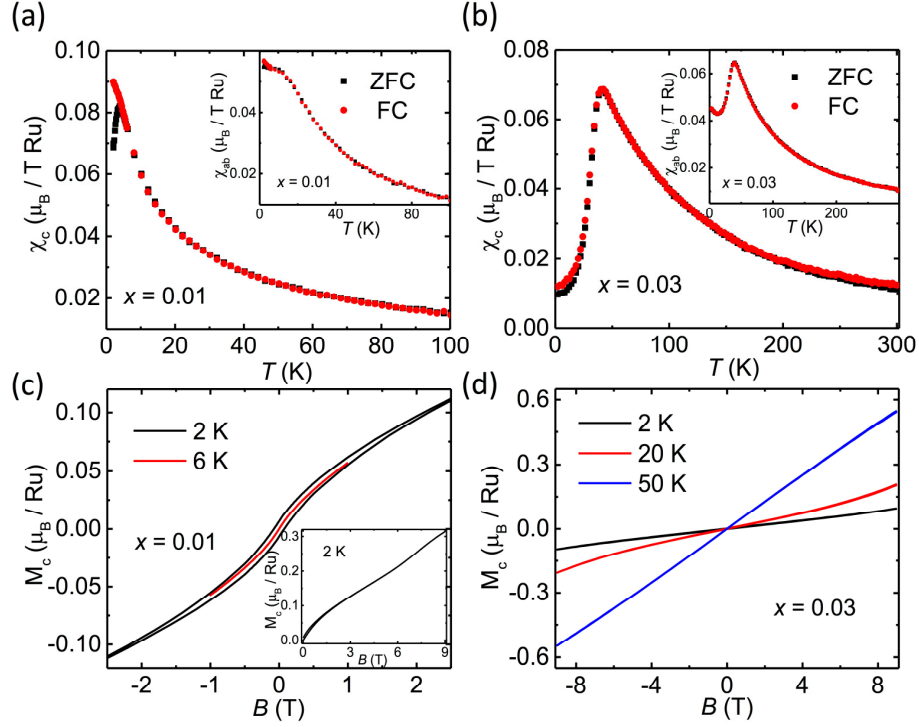


Figure 3.8: (a),(b) Temperature dependence of magnetic susceptibility χ_c of $\text{Sr}_3(\text{Ru}_{1-x}\text{Fe}_x)_2\text{O}_7$ ($x = 0.01$ and 0.03) after ZFC and FC. Insets show the in-plane magnetic susceptibility χ_{ab} as a function of temperature after ZFC and FC. (c),(d) Isothermal magnetization as a function of magnetic field of $\text{Sr}_3(\text{Ru}_{1-x}\text{Fe}_x)_2\text{O}_7$ ($x = 0.01$ and 0.03), respectively. The field is applied along the c axis. Inset shows the data of the $x = 0.01$ compound at 2 K up to 9 T.

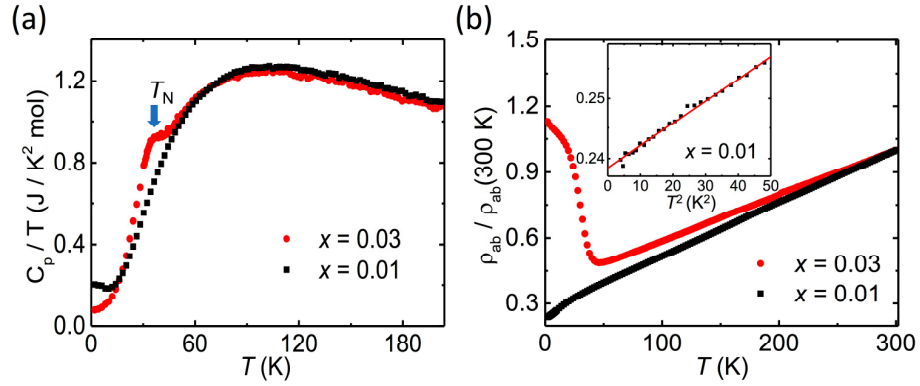


Figure 3.9: (a) Specific heat of $\text{Sr}_3(\text{Ru}_{1-x}\text{Fe}_x)_2\text{O}_7$ ($x = 0.01$ and 0.03) as a function of temperature. The blue arrow denotes T_N obtained from magnetic susceptibility measurements. (b) In-plane resistivity ρ_{ab} of $\text{Sr}_3(\text{Ru}_{1-x}\text{Fe}_x)_2\text{O}_7$ as a function of temperature. Inset shows ρ_{ab} vs T^2 in the low-temperature regime for $x = 0.01$. The red line is a fit using linear function.

Figure 3.9(a) shows the temperature dependence of the specific heat for $\text{Sr}_3(\text{Ru}_{1-x}\text{Fe}_x)_2\text{O}_7$ ($x = 0.01$ and 0.03). It is worth pointing out two distinctive features. First, for the $x = 0.03$ compound, an anomaly is clearly observed close to $T_N \sim 40$ K, which is indicative of the formation of a long-range antiferromagnetic order. In contrast, no anomaly in specific heat has been observed in the $x = 0.01$ compound in this temperature range. Second, the $x = 0.01$ compound exhibits an upturn below $T \sim 10$ K, which is presumably of magnetic origin. Note that C_p/T measured at the lowest temperature (~ 0.21 J / K² mol) is much larger than that for the $x = 0.03$ compound (~ 0.06 J / K² mol). Similar behaviors have been observed in Ti-doped $\text{Sr}_3\text{Ru}_2\text{O}_7$ [84], which has been suggested to be associated with the spin fluctuations. The increase of the specific heat in the low-temperature limit in the disordered state (e.g., $x = 0.01$) can be ascribed to the softening of the magnetic fluctuations when being closer to the magnetically ordered state induced upon doping, whereas the suppression of the value of C_p/T in the antiferromagnetically ordered phase for the $x = 0.03$ compound is due to the opening of the gap in the spin excitation spectrum [84].

The temperature dependence of the in-plane resistivity ρ_{ab} of Fe-doped $\text{Sr}_3\text{Ru}_2\text{O}_7$ is presented in Fig. 3.9(b). Similar to the pristine $\text{Sr}_3\text{Ru}_2\text{O}_7$, the $x = 0.01$ compound exhibits metallic behavior down to 2 K. At low temperature, $\rho_{ab}(T)$ shows T^2 dependence as shown in the inset, which is characteristic of the Fermi liquid behavior. However, the field-induced anisotropic and highly resistive state in the parent compound [79] is completely suppressed in the $x = 0.01$ compound, consistent with the absence of the metamagnetic transition in the magnetic susceptibility data shown in the inset of Fig. 3.8(c). In contrast, a metal-insulator transition (MIT) is observed in the $x = 0.03$ compound at $T_{\text{MIT}} \sim 44$ K, similar behaviors have been observed in Ti- and Mn-doped $\text{Sr}_3\text{Ru}_2\text{O}_7$ [84,86]. It has been suggested that the MIT in the Mn-doped compound is Mott type, induced by electron correlations instead of Slater type due to the formation of the antiferromagnetic

order [85]. As T_{MIT} of the $x = 0.03$ compound of Fe-doped $\text{Sr}_3\text{Ru}_2\text{O}_7$ is very close to the antiferromagnetic transition temperature $T_{\text{N}} \sim 40$ K, it might be helpful to study this material system with higher Fe doping concentrations to resolve the nature of this MIT.

3.3.3 Neutron diffraction

In order to determine the spin structure of the antiferromagnetically ordered phase in $\text{Sr}_3(\text{Ru}_{0.97}\text{Fe}_{0.03})_2\text{O}_7$, we have carried out neutron diffraction measurements. The magnetic Bragg peaks were observed at $\mathbf{q}_c = (0.25 \ 0.25 \ 0)$ and the equivalent wave vectors in the reciprocal space, such as $(0.75 \ 0.75 \ 0)$ and $(1.25 \ 1.25 \ 0)$, etc. Figure 3.10(a) shows the scans along the $[1 \ 1 \ 0]$ direction across $\mathbf{q}_c$ at representative temperatures. The data are well fitted by Gaussian functions and the peak width is resolution limited, indicating a long-range ordering in the ab plane.

Temperature dependence of the peak intensity of $\mathbf{q}_c$ is shown in Fig. 3.10(b). The magnetic intensity starts to increase at $T \sim 40$ K on cooling, consistent with T_{N} obtained in the magnetic susceptibility measurements. Figure 3.10(c) shows the scans along the $[0 \ 0 \ 1]$ direction across $\mathbf{q}_c$ at selected temperatures. These curves are best fitted by Lorentzian functions, in contrast to Gaussian for the scans along the $[1 \ 1 \ 0]$ direction, which indicates short-range magnetic correlations ($1 / \text{FWHM} = 1.2c$, $c = 20.69$ Å at $T = 4$ K) along the c axis. These results suggest that the magnetic ordering is quasi-two-dimensional, similar to that in Ti- and Mn-doped $\text{Sr}_3\text{Ru}_2\text{O}_7$ [84,88]. Figure 3.10(d) displays the same scan across $\mathbf{q}_c = (0.25 \ 0.25 \ 0)$ and $(0.75 \ 0.75 \ 0)$ for a wider L range at $T = 4$ K. It is worth noting that the magnetic intensities are only observed at even values of L . Furthermore, while the intensity of $(0.25 \ 0.25 \ L)$ with $L = 0$ and 2 is much greater than that of $(0.75 \ 0.75 \ L)$, at $L = 4$ and 6 the intensities of these two types of magnetic Bragg peaks are comparable.

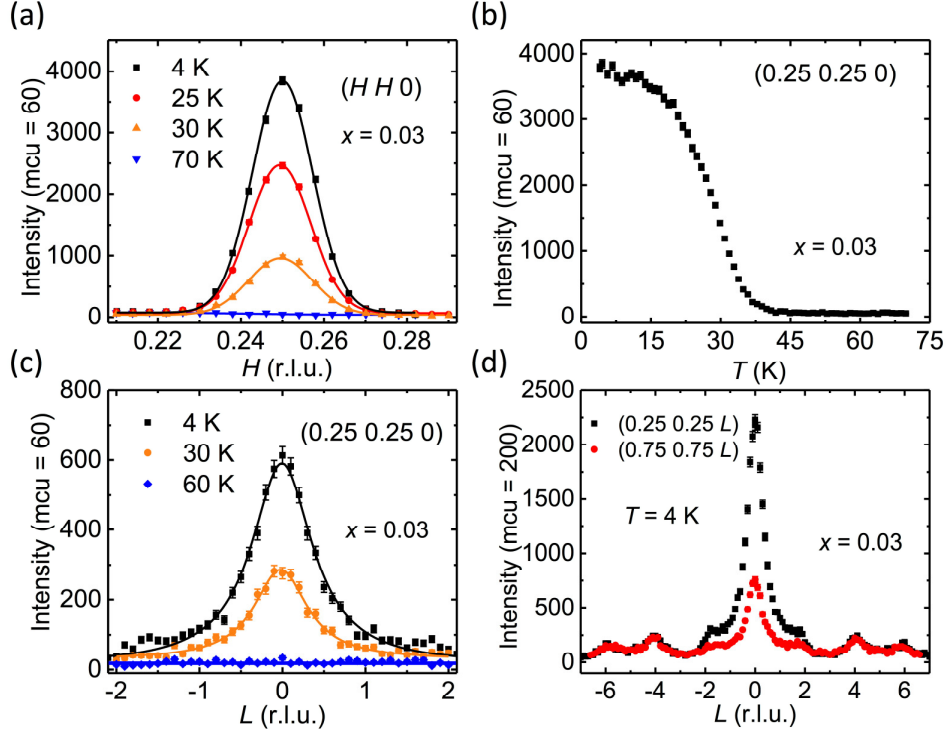


Figure 3.10: Neutron diffraction data of $\text{Sr}_3(\text{Ru}_{1-x}\text{Fe}_x)_2\text{O}_7$ ($x = 0.03$). (a) Scans around $\mathbf{q}_c = (0.25, 0.25, 0)$ along the $[1\ 1\ 0]$ direction at representative temperatures. (b) Temperature dependence of the peak intensity of $\mathbf{q}_c = (0.25, 0.25, 0)$. (c), (d) Scans around $\mathbf{q}_c = (0.25, 0.25, 0)$ and $(0.75, 0.75, 0)$ along the $[0\ 0\ 1]$ direction, respectively.

Possible magnetic structure models have been explored by the magnetic representational analysis using FULLPROF [71] and the magnetic symmetry analysis using the programs at Bilbao Crystallographic Server [72]. The results obtained are in agreement with each other. Due to the orthorhombic crystal symmetry and the propagation vector $\mathbf{q}_c = (0.25, 0.25, 0)$ (i.e., $(0.5, 0, 0)$ in orthorhombic symmetry notation [88]), our data are best described by the *E*-type antiferromagnetic structure with zigzag spin chains in the *ab* plane, as shown in Fig. 3.11(a). The magnetic moments in a bilayer are ferromagnetically aligned, similar to that in Mn-doped $\text{Sr}_3\text{Ru}_2\text{O}_7$ [88]. For this magnetic structure model, the squared structure factors of the magnetic reflections $\mathbf{q}_c = (0.25, 0.25, L)$ and $(0.75, 0.75, L)$ are nonzero only for even values of L :

$$|S(0.25, 0.25, L)|^2 = |S(0.75, 0.75, L)|^2 \sim \cos^2(2\pi\Delta L)$$

where $2\Delta \sim 0.20$ is the separation between neighboring RuO_2 planes. This is in line with the data shown in Fig. 3.10(d). In addition, the comparison of the intensity of $(0.25 \ 0.25 \ L)$ and $(0.75 \ 0.75 \ L)$ also provides clues on the spin orientation. The cross section of the magnetic neutron diffraction is given by

$$\sigma(\mathbf{q}) \propto |F(\mathbf{q})|^2 [1 - (\hat{\mathbf{q}} \cdot \hat{\mathbf{M}})^2] |S(\mathbf{q})|^2$$

where $F(\mathbf{q})$ is the magnetic form factor, $S(\mathbf{q})$ the magnetic structure factor, and $\hat{\mathbf{q}}$, $\hat{\mathbf{M}}$ the unit vectors of the wave vector $\mathbf{q}$ and the magnetic moment $\mathbf{M}$. The fact that the intensity of $(0.25 \ 0.25 \ L)$ and $(0.75 \ 0.75 \ L)$ for $L = 4$ is comparable suggests that the magnetic moments are along the c axis, such that the polarization factor $[1 - (\hat{\mathbf{q}} \cdot \hat{\mathbf{M}})^2]$ is greater for the latter, since the structure factors $S(\mathbf{q})$ are equal for these two reflections and the magnetic form factors $F(\mathbf{q})$ decrease rapidly with the increasing modulus of $\mathbf{q}$. Similar argument holds for the $L = 6$ case. The ordered moment is estimated to be $\sim 0.5 \mu_B$ for the $x = 0.03$ compound, which is much smaller than $2 \mu_B$ expected for fully localized Ru^{4+} magnetic moments.

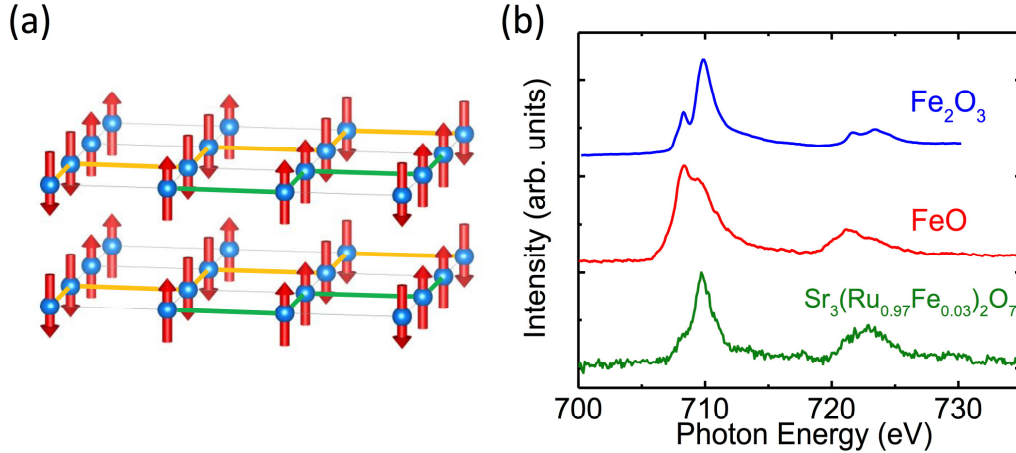


Figure 3.11: (a) Schematic of the *E*-type antiferromagnetic order of one bilayer in $\text{Sr}_3(\text{Ru}_{0.97}\text{Fe}_{0.03})_2\text{O}_7$. (b) Synchrotron XAS measurements on $\text{Sr}_3(\text{Ru}_{0.97}\text{Fe}_{0.03})_2\text{O}_7$ and the reference samples FeO (Fe^{2+}) and Fe_2O_3 (Fe^{3+}).

3.3.4 Discussions

There are several remarkable features observed in Fe-doped $\text{Sr}_3\text{Ru}_2\text{O}_7$ that may help to elucidate the effects of $3d$ transition-metal dopants on this system.

First of all, the magnetic structure of $\text{Sr}_3(\text{Ru}_{0.97}\text{Fe}_{0.03})_2\text{O}_7$ is very similar to that in the Mn-doped compound, which is independent on the Mn doping concentration [86]. This suggests that the magnetic ordering is an inherent instability of the system and the role of Fe and Mn dopants is to tip the balance between the competing magnetic tendencies.

Second, the propagation vectors of the magnetic orders induced by $3d$ transition-metal doping, e.g., Ti [84], Mn [86] and Fe in this study, do not correspond to the dominant spin fluctuations in the pristine $\text{Sr}_3\text{Ru}_2\text{O}_7$, which are centered on the principal axes of the tetragonal Brillouin zone at $\mathbf{q} = (0.09 \ 0 \ 0)$ and $(0.25 \ 0 \ 0)$ [81]. It has been reported that these incommensurate antiferromagnetic fluctuations originate from the nesting of the Fermi surface [81]. Therefore, the observation of a commensurate E -type antiferromagnetic order with the propagation vector distinct from the wave vectors of the spin fluctuations in the pristine $\text{Sr}_3\text{Ru}_2\text{O}_7$ suggests that the impurity-induced magnetic order in this bilayer ruthenate system is not due to Fermi surface nesting, a feature different from that in Ti- and Mn-doped Sr_2RuO_4 [65,66].

Third, it is well-known that the magnetism in layered ruthenates is strongly correlated with structural transitions. In Mn-doped $\text{Sr}_3\text{Ru}_2\text{O}_7$, a change in the lattice constants of $\sim 0.1\%$ has been reported at T_N by x -ray diffraction measurements [86]. However, no change in the lattice constants at either T_N or T_{MIT} was convincingly observed in Fe-doped $\text{Sr}_3\text{Ru}_2\text{O}_7$ via single-crystal neutron diffraction measurements, although we cannot exclude the possibility that the change is too small to be seen within the instrumental resolution. Since the ionic radius of the Fe dopants is important to the structural distortions of the RuO_6 octahedra, we have performed synchrotron XAS

measurements on the $x = 0.03$ compound at the Fe $L_{2,3}$ edge at room temperature to determine the valence value of Fe. Two reference samples, FeO and Fe₂O₃, with well-defined valence values were measured simultaneously. As shown in Fig. 3.11(b), the peak position and the line shape of the data suggest that the Fe dopants are in the Fe³⁺ valence state, the same as Mn³⁺ in Mn-doped Sr₃Ru₂O₇ [87]. Since the ionic radii of Fe³⁺ and Mn³⁺ are the same and are slightly larger than that of Ru⁴⁺ [90], we expect that Fe dopants give rise to similar structural effects as Mn. It has been reported that Mn doping reduces the rotation of the RuO₆ octahedron and enhances the octahedral flattening via a reduction in the apical Ru-O bond length in the magnetically ordered state [91]. Theoretical studies on the correlation between structure and magnetism have been performed on Ca_{2-x}Sr_xRuO₄ and are valuable references to the Ruddlesden-Popper type perovskite ruthenates. It is revealed that the rotation of the RuO₆ octahedron favors ferromagnetism and the subsequent tilting leads to antiferromagnetism, while the flattening of the octahedron is essential to stabilize the ferromagnetic or antiferromagnetic state [92]. However, the observed *E*-type antiferromagnetic order in Fe- and Mn-doped Sr₃Ru₂O₇ is not in line with this picture that the magnetic order is due to the doping-induced changes in the structural distortions discussed above.

Finally, the interplay between the 3*d* orbitals of the dopants and the Ru 4*d* orbitals might be essential to the impurity-induced magnetic ordering and MIT. For instance, it has been reported that the hybridization between the Mn 3*d* and Ru-O orbitals can reverse the conventional hierarchy of the crystal-field levels of the half-filled Mn *e_g* orbital in Mn-doped Sr₃Ru₂O₇ [87]. Recent studies on Fe-doped Sr₂RuO₄ has found a commensurate magnetic ordering characterized by the propagation wave vector $\mathbf{q}_c = (0.25 \ 0.25 \ 0)$. DFT calculations show that Fe doping barely changes the Fermi surface but induces strong back polarization on the Ru neighboring Fe, which may lead to the formation of the commensurate magnetic order [89]. Considering the similarity between the

electronic structures of Sr_2RuO_4 and $\text{Sr}_3\text{Ru}_2\text{O}_7$ [87], it is very likely that a similar scenario holds true for the Fe-doped $\text{Sr}_3\text{Ru}_2\text{O}_7$, though first principles calculations are highly desired to examine this conjecture.

3.3.5 Summary

We have studied the magnetic and electronic properties of the bilayer ruthenate $\text{Sr}_3\text{Ru}_2\text{O}_7$ doped by Fe. We find that in contrast to the Fermi liquid ground state in the pristine compound, 1% Fe substitution leads to a metallic spin-glass-like state, whereas an insulating *E*-type antiferromagnetic ordered phase is induced below $T_N \sim 40$ K in the 3% Fe-doped compound. This magnetic ordering is quasi-two-dimensional with short correlation length along the *c* direction, similar to that in Mn-doped $\text{Sr}_3\text{Ru}_2\text{O}_7$. These results suggest that this doping-induced ordered state is associated with the intrinsic magnetic instability of the pristine compound, which can be readily tuned via the local exchange coupling between the magnetic dopants and the Ru hosts.

3.4 Field-induced insulator-metal transition and colossal magnetoresistance in $\text{Ca}_3(\text{Ru,Ti})_2\text{O}_7$

The bilayer $\text{Ca}_3\text{Ru}_2\text{O}_7$ ($n = 2$) crystallizes in an orthorhombic structure with the space group $Bb2_1m$ (No. 36) [93]. Upon cooling, it undergoes an antiferromagnetic transition at $T_N = 56$ K and a MIT at $T_{\text{MIT}} = 48$ K [94]. Below 30 K, the material exhibits quasi-two-dimensional metallic behavior [95] due to small un-nested Fermi surface pockets surviving through the MIT [96]. Neutron diffraction measurements have revealed that the magnetic moments in the bilayer are aligned ferromagnetically, and the bilayers are stacked antiferromagnetically along the c axis. The magnetic moments are along the a axis (AFM-a) at $T_{\text{MIT}} < T < T_N$ but are along the b axis (AFM-b) below T_{MIT} [97].

Previous studies have shown that $3d$ transition-metal doping for Ru can dramatically change the magnetic and electronic properties of ruthenates. In $\text{Ca}_3\text{Ru}_2\text{O}_7$, a Mott insulating state can be achieved by doping as low as $\sim 3\%$ Ti into the Ru sites. The Mott character of the charge gap has been confirmed by the recent hard x -ray photoemission measurements [98]. Concomitantly, the ground state magnetic structure transforms from AFM-b to G-type with the nearest-neighbor spins coupled antiferromagnetically (G-AFM). The major effect of Ti substitution is to disrupt carrier hopping and narrow the bandwidth [99]. The phase diagram of $\text{Ca}_3(\text{Ru}_{1-x}\text{Ti}_x)_2\text{O}_7$ as a function of temperature T and Ti doping concentration x is shown in Fig. 3.12(a).

3.4.1 Materials and methods

$\text{Ca}_3(\text{Ru}_{0.97}\text{Ti}_{0.03})_2\text{O}_7$ single crystals were grown using the Floating Zone method. The Ti doping concentration was verified using the energy dispersive spectroscopy (EDS). Magnetoresistance and magnetic susceptibility measurements were done using PPMS. Neutron diffraction experiments were performed at Helmholtz Zentrum Berlin (HZB) using the E4 two-axis diffractometer equipped with a $20 \times 20 \text{ cm}^2$ position-sensitive detector. The neutron incident wavelength was $\lambda = 2.434 \text{ \AA}$. The sample of $\sim 100 \text{ mg}$ was aligned in the $(H 0 L)$ scattering plane and cooled by a helium cryostat. The magnetic field was applied along the b axis, while the Bragg reflections were measured up to 14.5 T.

3.4.2 Magnetoresistance

Figure 3.13(a) and (b) show the temperature dependence of the out-of-plane resistivity ρ_c and the in-plane resistivity ρ_{ab} of $\text{Ca}_3(\text{Ru}_{0.97}\text{Ti}_{0.03})_2\text{O}_7$ measured with a magnetic field of 0 T and 9 T applied along the b axis. At zero field, $\text{Ca}_3(\text{Ru}_{0.97}\text{Ti}_{0.03})_2\text{O}_7$ undergoes a MIT on cooling, with a sharp increase in ρ_c and ρ_{ab} by ~ 5 and ~ 3 orders of magnitude, respectively, at T_{MIT} . In contrast, at $B = 9 \text{ T}$, both ρ_c and ρ_{ab} gradually increase at low temperature by only a smaller factor, attributable to disorder scattering. Such a dramatic magnetoresistive effect is also observed in the isothermal resistivity measurements at $T = 10 \text{ K}$ shown in Fig. 3.13(c) and (d). With increasing magnetic field applied along the b axis, both ρ_c and ρ_{ab} decreases sharply at a critical field $B_c \sim 8.5 \text{ T}$ and show a hysteresis with decreasing field, indicating a first-order insulator-to-metal transition (IMT). On the other hand, both resistivity values decrease slightly with the field applied along the a axis, which is close to the magnetic hard axis.

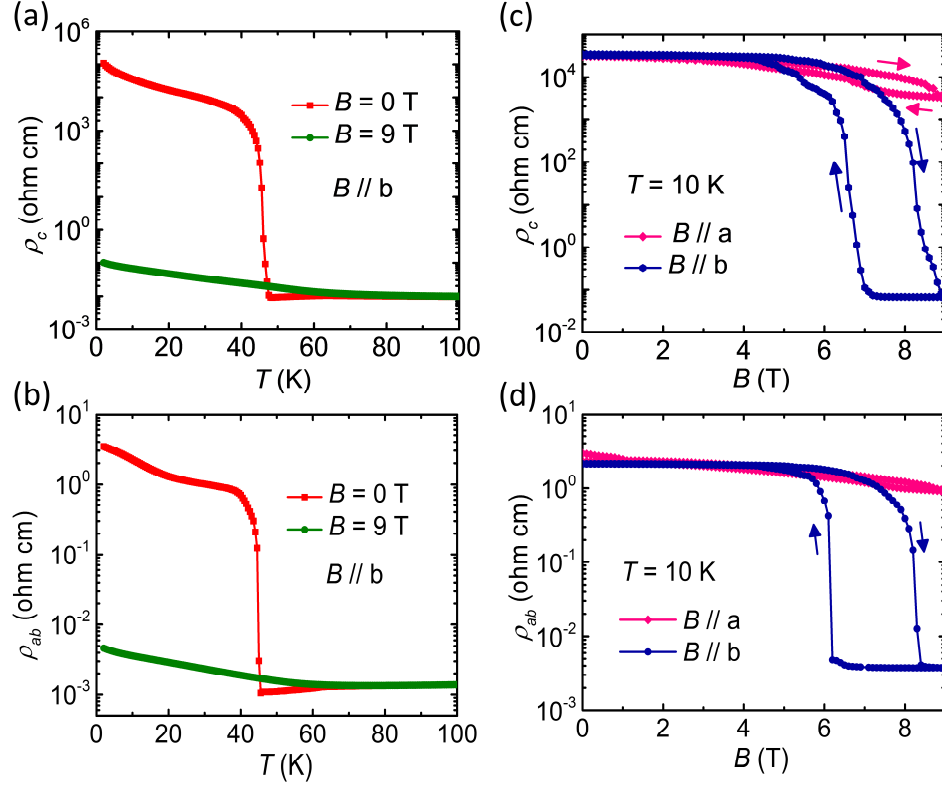


Figure 3.13: (a),(b) Temperature dependence of resistivity ρ_c and ρ_{ab} measured at $B = 0$ and 9 T applied along the b axis. The magnetic field was applied at $T = 100$ K and the measurements were taken while cooling. (c),(d) Magnetic field dependence of ρ_c and ρ_{ab} at $T = 10$ K.

3.4.3 Neutron diffraction

To obtain a deeper insight into the magnetic-field-induced IMT in $\text{Ca}_3(\text{Ru}_{0.97}\text{Ti}_{0.03})_2\text{O}_7$, we performed single-crystal neutron diffraction measurements at $T = 10$ K with the field applied along the b axis. Interestingly, the lattice parameters of $\text{Ca}_3(\text{Ru}_{0.97}\text{Ti}_{0.03})_2\text{O}_7$ change drastically when the magnetic field approaches the critical value where the resistivity drops significantly. As shown in Fig. 3.14(a), the lattice constant c increases by $\sim 0.78\%$. Similar behavior has been observed by heating the sample at zero magnetic field from low temperature to above T_{MIT} [99]. These observations demonstrate that the Mott insulating ground state of $\text{Ca}_3(\text{Ru}_{0.97}\text{Ti}_{0.03})_2\text{O}_7$ is stabilized by a strong coupling to the lattice distortions, in analogy to the bandwidth-controlled Mott system $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$ [41,101]. In both cases, the emergence of the Mott insulating state is accompanied

by a structural transition from a long c axis to a short one [99,102]. The enhanced RuO_6 octahedral flattening and tilting below T_{MIT} reduce the bandwidth [103] and change the occupancy of the t_{2g} orbitals [92,104], leading to a MIT [103,105,106].

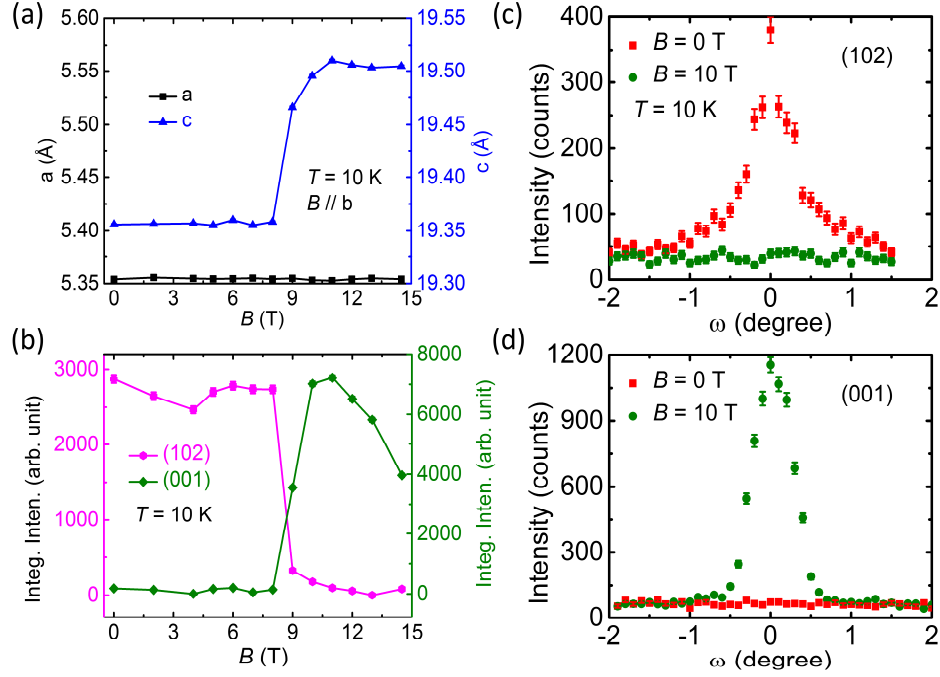


Figure 3.14: (a) Field dependence of lattice parameters. Statistical errors from the fitting procedure are smaller than the symbol size. (b) Field dependence of the integrated intensity of magnetic Bragg peaks (1 0 2) and (0 0 1), respectively, measured at $T = 10$ K. The magnetic field was increased for both nuclear and magnetic Bragg peak scans. (c),(d) Rocking curves of (1 0 2) and (0 0 1) measured at $B = 0$ T and 10 T applied along the b axis, $T = 10$ K.

The remarkable lattice structure and resistivity changes in $\text{Ca}_3(\text{Ru}_{0.97}\text{Ti}_{0.03})_2\text{O}_7$ induced by a magnetic field are accompanied by a magnetic structure transition. Fig. 3.14(c) and (d) show the rocking curves of (1 0 2) and (0 0 1) magnetic Bragg peaks, respectively, measured at $T = 10$ K, $B = 0$ T and 10 T after the sample was cooled down in zero magnetic field. Note that the (1 0 2) magnetic Bragg peak refers to G-AFM magnetic structure as in Ti-doped $\text{Ca}_3\text{Ru}_2\text{O}_7$ [99], while (0 0 1) corresponds to AFM-b or AFM-a type magnetic structures as in the pristine $\text{Ca}_3\text{Ru}_2\text{O}_7$ [97]. The disappearance of (1 0 2) and the emergence of (0 0 1) at $B = 10$ T indicate a field-induced

magnetic structure transition from G-AFM to one similar to AFM-a (or AFM-b). However, the field-induced state is not a collinear magnetic structure but a canted antiferromagnetic phase (denoted as CAFM), i.e., a vector superposition of AFM-a and a ferromagnetic component along the b axis, as discussed in Appendix B. The strong coupling between the field-induced structural transition and the magnetic transition can be readily seen. The integrated intensity of (1 0 2) and (0 0 1) magnetic Bragg peaks measured at $T = 10$ K as a function of increasing magnetic field is shown in Fig. 3.14(b). The intensity of (0 0 1) increases significantly at B_c where that of (1 0 2) has a sharp drop, indicative of a magnetic phase transition. Clearly, the critical field of the magnetic transition coincides with that of the structural transition. These observations are similar to those observed in the temperature-dependent studies on the same compound but in the absence of a magnetic field, reinforcing the presence of strong spin-lattice coupling in this system [99]. The peak intensities of (1 0 2) and (0 0 1) as a function of magnetic field at representative temperatures are shown in Fig. 3.15. The sample was initially cooled down to 10 K at zero field and the peak intensities were measured with the field increasing first, followed by the field decreasing, prior to warming up to the next measurement temperature. The hysteresis observed at low temperature indicates the first-order nature of the field-induced transition between G-AFM and CAFM. The CMR effects are observed only accompanying the field-driven G-AFM to CAFM transition below T_{MIT} . On the contrary, the resistivity shows little change at $T_{MIT} < T < T_N$, where (0 0 1) is suppressed as the magnetic field increases until the magnetic moments are fully polarized by the magnetic field.

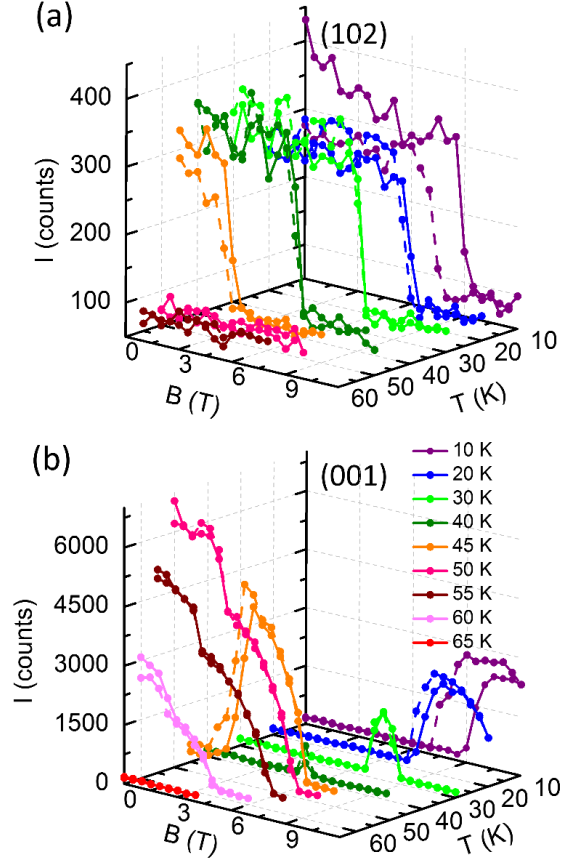


Figure 3.15: (a),(b) Neutron intensity of the (1 0 2) and (0 0 1) magnetic Bragg peaks as a function of magnetic field measured at different temperatures. The solid curve is for increasing field and the dashed one is for decreasing field.

Figure 3.16 presents the $T - B$ phase diagram which summarizes our electronic transport and neutron diffraction measurements. At $T_{\text{MIT}} < T < T_{\text{N}}$, upon applying the magnetic field along the b axis, $\text{Ca}_3(\text{Ru}_{0.97}\text{Ti}_{0.03})_2\text{O}_7$ undergoes a magnetic phase transition from AFM-a to CAFM, and finally to a fully spin polarized paramagnetic state (PM), a feature similar to that in the parent compound [97]. In contrast, below T_{MIT} , $\text{Ca}_3(\text{Ru}_{0.97}\text{Ti}_{0.03})_2\text{O}_7$ exhibits a magnetic phase transition from G-AFM to CAFM, which occurs simultaneously with the electronic structure changing from an insulating state to a weakly localized state, implying the strong correlation between the field-induced IMT and magnetic phase transition.

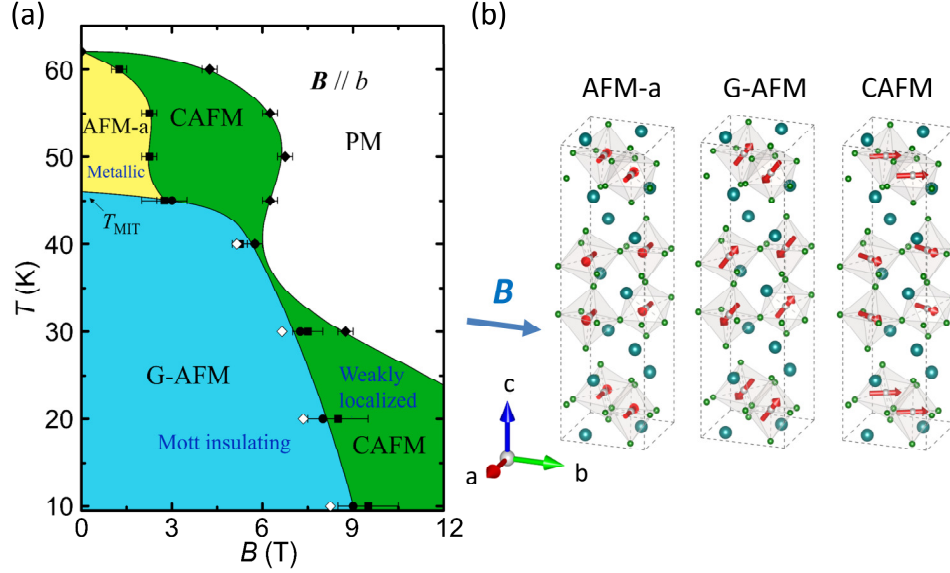


Figure 3.16: (a) T - B phase diagram of $\text{Ca}_3(\text{Ru}_{0.97}\text{Ti}_{0.03})_2\text{O}_7$ in a magnetic field along the b axis. The solid squares, circles and diamonds are phase boundaries determined by neutron diffraction measurements: solid squares denote the points where $(0\ 0\ 1)$ shows up, and solid circles represent where $(1\ 0\ 2)$ disappears. The solid diamonds stand for the points where $(0\ 0\ 1)$ disappears completely. The open diamonds are the phase boundaries determined by the resistivity measurements. (b) Schematics of spin structures of AFM-a, G-AFM and CAFM phases.

3.4.4 Density functional theory calculations

To understand the CMR phenomena we observed in Ti-doped $\text{Ca}_3\text{Ru}_2\text{O}_7$, we have carried out DFT calculations in collaboration with Dr. G.-Q. Liu in Ningbo Institute of Material Technology and Engineering. The calculations were performed with the full-potential linear augmented plane wave (FLAPW) within the local spin density approximation (LSDA) which is implemented in WIEN2K package [76]. The irreducible Brillouin zone was sampled with 100 k -points. To investigate the interplay of structural, magnetic and electronic properties, we assumed that the Ti induced change in electron count is very small. Thus, the calculations were done for the parent $\text{Ca}_3\text{Ru}_2\text{O}_7$. Below are three major findings from our calculations.

(i) The role of electron correlation: In agreement with Ref. [99], at the bare density functional level the low-temperature crystal structure and G-AFM magnetic structure give rise to a metallic

state shown in Fig. 3.17(a). This is inconsistent with the experimental observations, implying the essential role of electron correlations to stabilize an insulating ground state. Taking into account an on-site Coulomb repulsion $U = 2$ eV [104,105] leads to the opening of an electronic band gap of ~ 0.2 eV, as shown in Fig. 3.17(b).

(ii) The spin-charge-lattice interplay: In contrast to the insulating behavior [Fig. 3.17(b)] in the low-temperature G-AFM state with a larger RuO_6 octahedral flattening, Fig. 3.17(c) shows a metallic character for the field-induced AFM-a type magnetic structure accompanied by a suppressed octahedral flattening, which agrees with our experimental observation. This drastic change in the nature of the ground state suggests strong interplay among spin, charge and lattice degrees of freedom.

(iii) The importance of electronic orbital polarization: In the insulating state, the electronic orbitals are polarized with the spin-down channel of the d_{xy} orbital almost fully occupied while the d_{xz}/d_{yz} orbitals are nearly empty, as shown in Fig. 3.17(b). This arises from a larger octahedral flattening that lifts the degeneracy of the t_{2g} orbitals (d_{xy} and d_{xz}/d_{yz}). In contrast, in the metallic state [Fig. 3.17(c)], the reduced structural distortion gives rise to a suppression of the d_{xy} orbital occupancy and a drastic reduction of the orbital polarization. These results suggest that the field-induced orbital depolarization in this multiband system may play an important role in the collapse of the Mott insulating ground state.

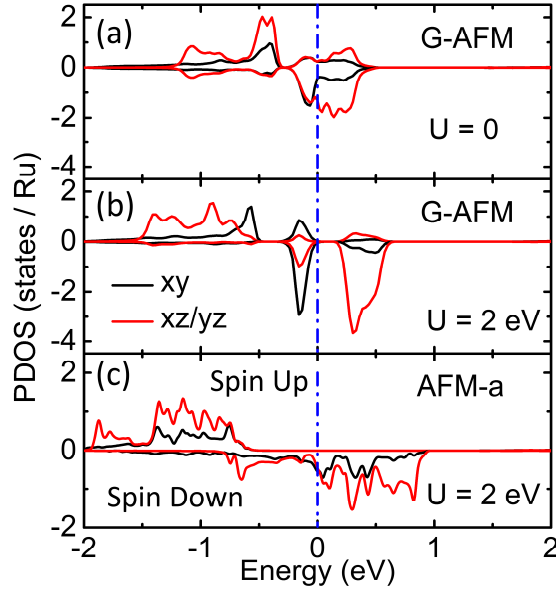


Figure 3.17: Projected density of states (PDOS) of the Ru d_{xy} and d_{xz}/d_{yz} orbitals. (a) PDOS calculated using the low-temperature crystal structure and G-AFM magnetic structure with the on-site Coulomb interaction $U = 0$. (b) PDOS calculated using the low-temperature crystal structure and G-AFM magnetic structure with $U = 2$ eV. (c) PDOS calculated using the high-temperature crystal structure and AFM-a magnetic structure with $U = 2$ eV.

3.4.5 Comparison with early theories

In Mott insulators, the insulating ground state is stabilized by Coulomb repulsion. Generally, there are two fundamental tuning parameters in Mott systems, i.e., bandwidth and band filling [1], which can be controlled experimentally by varying pressure, carrier concentration and electric field, etc [107-110]. However, a collapse of the Mott gap induced by a magnetic field is rarely observed. Theoretical studies based on a half-filled single-band Hubbard model predicted a magnetic-field-driven first-order metamagnetic localization transition from a strongly correlated metallic paramagnetic state to an insulating state via a competition between the local antiferromagnetic exchange and the Zeeman energy [111-113]. This prediction has been suggested to account for the field-induced Mott transition in a quasi-two-dimensional organic conductor κ -(BEDT-TTF)₂Cu[N(CN)₂]Cl [114]. However, the observation of a collapse of the Mott gap in Ti-

doped $\text{Ca}_3\text{Ru}_2\text{O}_7$ is not in line with this simple picture. Instead, the Mott insulating state in $\text{Ca}_3(\text{Ru}_{0.97}\text{Ti}_{0.03})_2\text{O}_7$, as in various other material systems, is much more complicated. It is often antiferromagnetic and the MIT is accompanied by lattice distortions [99]. Hence, the observation of a collapse of the Mott insulating state in Ti-doped $\text{Ca}_3\text{Ru}_2\text{O}_7$ induced by a magnetic field implies that the coupling among lattice, spin and orbital degrees of freedom is crucial to the understanding of the Mott insulating states and the associated phase transitions, which has not been explored in great depth theoretically.

3.4.6 Comparison with CMR manganites

We would like to point out that the physical origin of the CMR effect observed in Ti-doped $\text{Ca}_3\text{Ru}_2\text{O}_7$ is fundamentally distinct from that in the hole-doped manganites. The canonical CMR effect is observed in manganites that become ferromagnetic at low temperature via the double exchange mechanism [115], such as $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ($x = 0.175$) [4]. The application of a magnetic field leads to large magnetoresistance near the transition temperature, which has been ascribed to the reduction in spin scattering and the polaron effects due to strong electron-lattice interactions. The occurrence of CMR in manganites can also originate from the field-induced melting of the charge-ordered state, for example, in $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ and $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ with the ratio of Mn^{3+} to Mn^{4+} being commensurate with the crystalline lattice [116,22]. However, neither of these two mechanisms can be applied to account for the observations in $\text{Ca}_3(\text{Ru}_{0.97}\text{Ti}_{0.03})_2\text{O}_7$, considering the fact that the CMR effect emerges only at low temperature below T_{MIT} and the single valence state of Ru ions (Ru^{4+}). Furthermore, the CMR effect in manganites can be explained using the one- e_g orbital model [117], although a later study using the two- e_g orbital model explains the first-order CMR transition for some manganites [118]. In contrast, it is essential to take into account the

multiband (t_{2g} orbitals) structure of Ti-doped $\text{Ca}_3\text{Ru}_2\text{O}_7$ in order to understand the field-induced IMT, as discussed in Section 3.4.4.

3.4.7 Comparison with the parent compound

The magnetoresistive effect in $\text{Ca}_3(\text{Ru}_{0.97}\text{Ti}_{0.03})_2\text{O}_7$ is also distinct from that in the parent compound.

(i) The pristine $\text{Ca}_3\text{Ru}_2\text{O}_7$ exhibits a metallic ground state. Thus, no magnetic-field-induced transition in the electronic structure occurs as in $\text{Ca}_3(\text{Ru}_{0.97}\text{Ti}_{0.03})_2\text{O}_7$.

(ii) When the magnetic field is applied along the magnetic easy axis (b axis), an enhancement in the conductivity by ~ 1 order of magnitude has been observed at $B = 6$ T (4 K), which is accompanied by a first-order metamagnetic transition. Based on neutron diffraction measurements, this magnetoresistive effect has been attributed to a bulk spin-valve effect associated with spin scattering [97].

(iii) A reduction in the resistivity in the metallic ground state (AFM-b) has been observed with a field of 15 T applied along the magnetic hard axis (a axis), which is argued to originate from the suppression of orbital ordering at high fields [119]. However, no orbital ordering in $\text{Ca}_3\text{Ru}_2\text{O}_7$ at zero field has been convincingly detected in resonant x -ray scattering experiments [120].

In contrast to the parent compound, the CMR effect observed in $\text{Ca}_3(\text{Ru}_{0.97}\text{Ti}_{0.03})_2\text{O}_7$ cannot be interpreted in the framework of a spin-valve mechanism. Instead, it suggests a magnetic-field-induced change of the electronic ground state from a Mott insulator to a weakly localized state, i.e., a collapse of the Mott state.

3.4.8 Discussions

In addition to the spin-lattice-orbital coupling and the field-induced orbital depolarization discussed above, we would like to underline the essential role of phase competition on the collapse

of the Mott gap in a magnetic field in $\text{Ca}_3(\text{Ru}_{0.97}\text{Ti}_{0.03})_2\text{O}_7$. It is noteworthy that the closure of the Mott gap in $\text{Ca}_3(\text{Ru}_{0.97}\text{Ti}_{0.03})_2\text{O}_7$ by a modest magnetic field is quite unexpected, considering that the upper limit of the associated Zeeman energy per Ru^{4+} spins is about 1.4 meV, much smaller than the Mott gap of ~ 120 meV estimated from the optical conductivity measurements [121]. However, due to the proximity to the phase boundary [Fig. 3.12], two dramatically different states, one a weakly localized state with AFM-a or AFM-b spin structure and the other a Mott insulating state with G-AFM magnetic structure, are close in energy. Owing to the phase competition, the energy required to trigger the transition is associated with the difference between the energies of these two states and the height of the intervening energy barriers, thus is much smaller than that needed to melt the order completely. This idea is in analogy to the CMR effects in manganites [122], though the microscopic mechanisms are very different as discussed above. The significance of the delicate competition is also manifested by the fact that for materials slightly away from the phase boundary, for example $x = 0.05$, no magnetic-field-induced IMT is observed up to 9 T [Fig. 3.18].

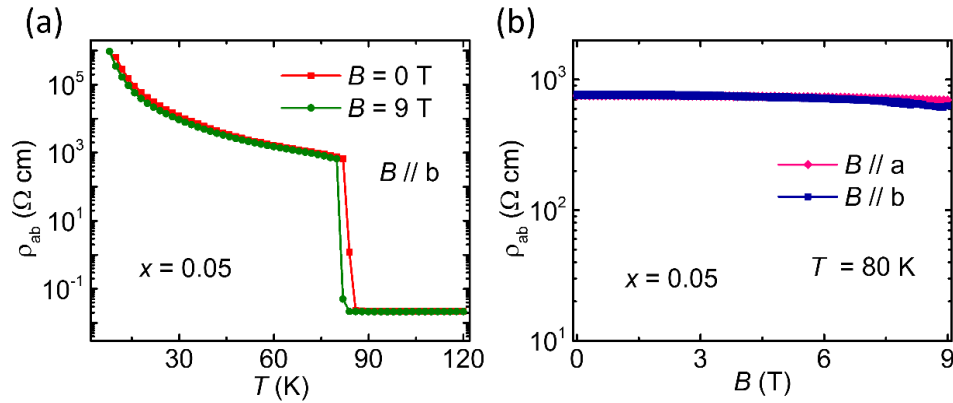


Figure 3.18: (a) Temperature and (b) magnetic field dependence of the in-plane resistivity of $\text{Ca}_3(\text{Ru}_{0.95}\text{Ti}_{0.05})_2\text{O}_7$.

3.4.9 Summary

The presence of electronic and magnetic instabilities with strong spin-lattice-charge couplings and potential changes in the orbital occupancy, enables a drastic change in the electronic structure of $\text{Ca}_3(\text{Ru}_{0.97}\text{Ti}_{0.03})_2\text{O}_7$ by a modest magnetic field, leading to a collapse of the Mott insulating ground state. Thus, $\text{Ca}_3(\text{Ru}_{0.97}\text{Ti}_{0.03})_2\text{O}_7$ serves as a rare example among the antiferromagnetic Mott insulators whose electronic ground state can be tuned using the magnetic field as a controlling parameter. This study would stimulate future theoretical studies on the field-induced IMT in Mott systems with multiband electronic structure, strong magnetic and electronic instabilities, as well as subtle interplay of various degrees of freedom.

3.5 Field-induced incommensurate-commensurate magnetic transitions in $\text{Ca}_3(\text{Ru,Fe})_2\text{O}_7$

Upon Fe doing for Ru, $\text{Ca}_3(\text{Ru}_{1-x}\text{Fe}_x)_2\text{O}_7$ ($x = 0.05$) exhibits the coexistence of the commensurate AFM-b and an incommensurate magnetic soliton lattice below $T_{\text{MIT}} \sim 43$ K, in addition to the metallic state with AFM-a type magnetic structure at $T_{\text{MIT}} < T < T_{\text{N}}$, $T_{\text{N}} \sim 83$ K. The incommensurate magnetic soliton lattice is a distorted cycloidal structure propagating along the a axis [Fig. 3.19(c)], with a nearly temperature-independent propagation wave vector $\mathbf{q}_{\text{ic}} = (\delta \ 0 \ 1)$, $\delta \sim \pm 0.017$, as evidenced by the observation of the third-order harmonics of the magnetic Bragg reflections $\mathbf{q}_{\text{ic}}$ in the neutron diffraction measurements [123]. Owing to the non-centrosymmetric crystal symmetry, Dzyaloshinskii-Moriya (DM) interaction is expected to play an essential role in the formation of the incommensurate magnetic soliton lattice [124]. The incommensurability δ of $\text{Ca}_3(\text{Ru}_{0.95}\text{Fe}_{0.05})_2\text{O}_7$ is rather small, indicating a long period of the incommensurate phase of ~ 58 unit cells or ~ 315 Å along the a axis, which is typical for incommensurate magnetic structures stabilized by DM interactions.

The evolution of the magnetic soliton lattice phase in the presence of magnetic field is an intriguing problem to investigate, as it essentially reflects the interplay among exchange interactions, magnetic anisotropy, Zeeman interaction and DM interaction in this system. In this section, we study the field-induced spin structure transitions of $\text{Ca}_3(\text{Ru}_{0.95}\text{Fe}_{0.05})_2\text{O}_7$ upon applying the magnetic field both parallel and perpendicular to the spin propagation direction (i.e. a axis). First-order incommensurate-to-commensurate magnetic transitions have been observed for both $B \parallel a$ and $B \parallel b$ axes. Intriguingly, the field-induced magnetic phase transitions display irreversible behaviors, where metastable states with different ordering wave vectors have been observed upon decreasing the magnetic field. The metastable states persist below a characteristic temperature T_{g}

~ 37 K, above which the equilibrium ground state is restored, which implies that thermal fluctuations play a crucial role.

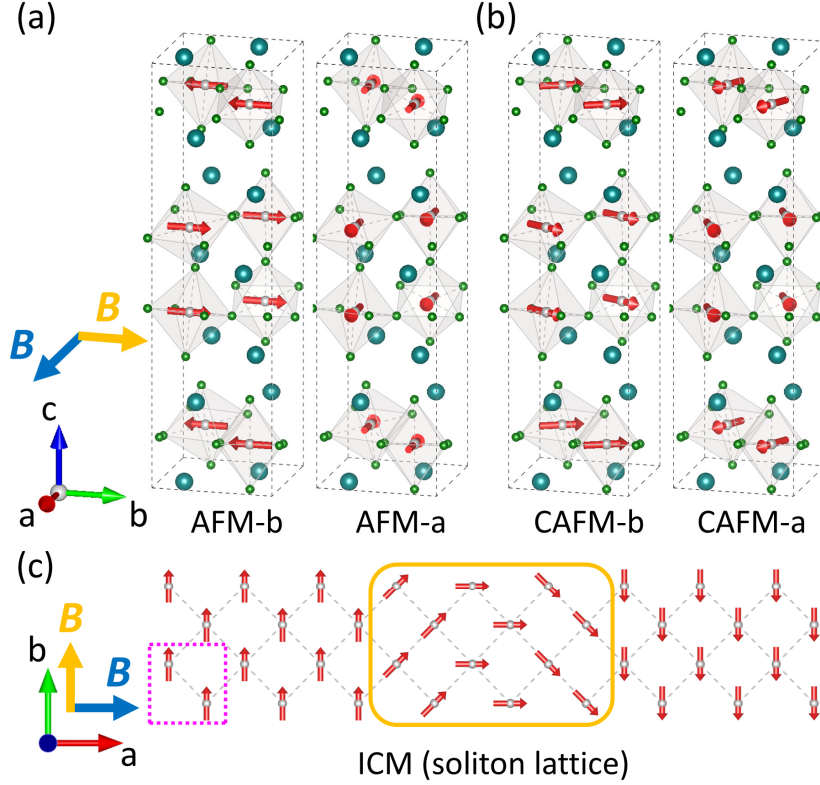


Figure 3.19: Schematic diagrams of the magnetic structures in $\text{Ca}_3(\text{Ru}_{0.95}\text{Fe}_{0.05})_2\text{O}_7$. (a) AFM-a and AFM-b: collinear antiferromagnetic structures with the magnetic moments along the *a* and *b* axis, respectively. (b) CAFM-b (CAFM-a): canted antiferromagnetic structures consisting of an AFM-a (AFM-b) component and a ferromagnetic one along the *b* (*a*) axis. (c) In-plane view of one of the bilayers of the incommensurate magnetic soliton lattice. The dashed square in magenta represents one unit cell. The orange rectangle with rounded corners encloses the domain wall. The blue and orange arrows represent the direction of the magnetic field to be along either the *a* or *b* axis.

3.5.1 Materials and methods

Single crystals of $\text{Ca}_3(\text{Ru}_{0.95}\text{Fe}_{0.05})_2\text{O}_7$ were synthesized by the Floating Zone method. Magnetotransport measurements were performed using PPMS. Neutron diffraction experiments were carried out using the E4 two-axis diffractometer in HZB and the CG-4C cold neutron triple-axis spectrometer (CTAX) at HFIR in ORNL. The wavelength of the incident and scattered

neutrons is $\lambda = 2.434 \text{ \AA}$ at E4 and is chosen as $4.045 \text{ \AA}$ at CTAX to have better resolution in the momentum transfer. The single-crystal sample was aligned in the horizontal ($H \ 0 \ L$) scattering plane, where H and L are in the reciprocal lattice units (r.l.u.). At E4, the sample was mounted inside a vertical-field cryomagnet with the magnetic field applied along the b axis, while at CTAX it was loaded into a similar vertical-field cryomagnet as well as a horizontal-field one where the magnetic field was applied along the a axis up to 4 T, respectively. The horizontal-field cryomagnet contains two pairs of windows for the incident and outgoing neutron beams. Constraint by the scattering geometry and the size of the window, only magnetic reflections around $\mathbf{q}_c = (0 \ 0 \ 1)$ are accessible in the neutron diffraction study for $B \parallel a$ axis. The neutron intensity is presented in the unit of counts per monitor count unit (mcu), where 1 mcu corresponds to ~ 1 second.

3.5.2 Neutron diffraction for $B \parallel b$ axis

In this section, we present the neutron diffraction study as the magnetic field is applied along the b axis, perpendicular to the spin propagation axis as indicated by the orange arrow in Fig. 3.19(a) and (c). Figure 3.20(a) and (b) show the contour maps of the neutron intensity of scans along the $[1 \ 0 \ 0]$ direction across the magnetic Bragg peak $\mathbf{q}_c = (0 \ 0 \ 1)$ at $T = 15 \text{ K}$ after ZFC the sample. At zero field, both commensurate and incommensurate magnetic peaks are observed at $\mathbf{q}_c = (0 \ 0 \ 1)$ and $\mathbf{q}_{ic} = (\delta \ 0 \ 1)$, $\delta \sim \pm 0.017$, respectively. There is sizable diffuse scattering intensity centered at the commensurate peak $\mathbf{q}_c$, in agreement with the previous report [123]. As the magnetic field increases, the intensity of the incommensurate magnetic Bragg peaks at $\mathbf{q}_{ic}$ is suppressed and vanishes at the critical field $B_c^\uparrow = 4.7 \pm 0.1 \text{ T}$. Concomitantly, the commensurate peak centered at $\mathbf{q}_c$ gets enhanced and the intensity due to diffuse scattering disappears. This observation clearly suggests a first-order magnetic-field-driven incommensurate-to-commensurate phase transition with an abrupt change in the magnetic wave vector. Note that the width of these

magnetic Bragg peaks is not resolution limited, indicating a correlation length of $\sim 370a$ for the commensurate state and $\sim 340a$ for the incommensurate phase at zero field, and $\sim 580a$ for the commensurate phase at $B = 9$ T, $T = 1.5$ K, where a is the lattice constant. Since the reflection condition due to the symmetry of the crystal structure requires that either both H and L are even, or the sum of H and L is even, the enhancement in the intensity of $(0\ 0\ 1)$ suggests the formation of an antiferromagnetic phase at $B > B_c^\uparrow$. We have observed a series of magnetic Bragg peaks in the reciprocal space at $(0\ 0\ 3)$, $(0\ 0\ 5)$ and $(0\ 0\ 7)$, etc. The analysis of the spin structure of the field-induced commensurate phase at $B > B_c^\uparrow$ in $\text{Ca}_3(\text{Ru}_{0.95}\text{Fe}_{0.05})_2\text{O}_7$ is very similar to that of the pristine and Ti-doped $\text{Ca}_3\text{Ru}_2\text{O}_7$ as described in Appendix B. It is determined to be a canted antiferromagnetic structure (CAFM-b), as shown in Fig. 3.19(b). Such a field-induced incommensurate-to-commensurate transition may arise from the competition among Zeeman energy, exchange energy and DM interaction [125], a mechanism similar to that reported in a DM-induced spin spiral $\text{Ba}_2\text{CuGe}_2\text{O}_7$ [126].

At $T_{\text{MIT}} < T < T_{\text{N}}$, in a magnetic field along the b axis, the system transforms from AFM-a to CAFM-b, and finally to a fully spin polarized state (PM). The magnetic phase diagram established by the neutron diffraction data collected at E4 and CTAX is shown in Fig. 3.21.

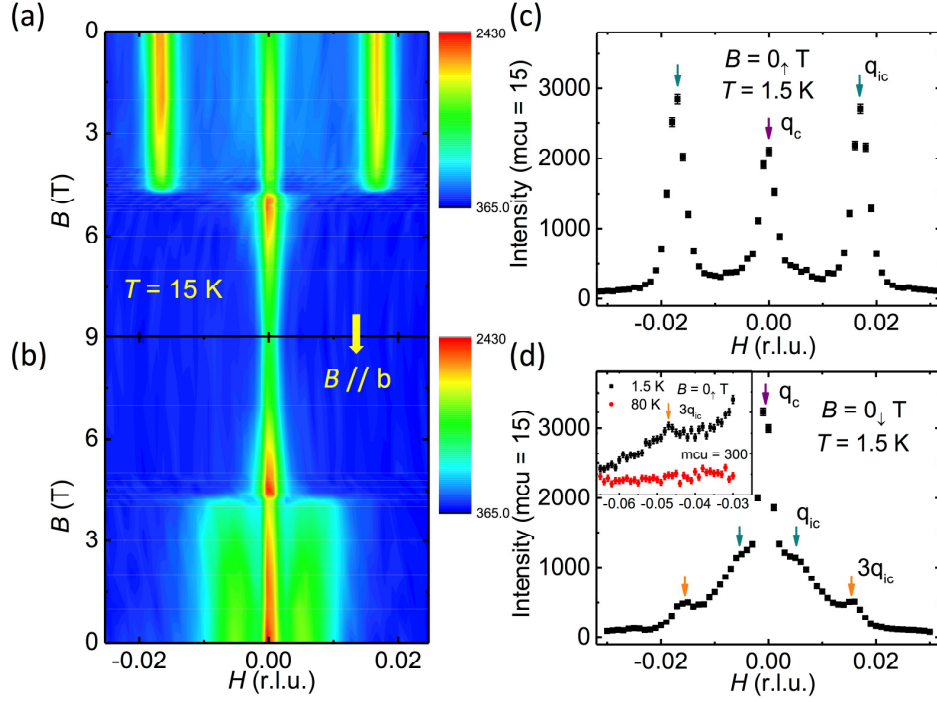


Figure 3.20: (a),(b) Contour maps of the intensity of scans along the $[1\ 0\ 0]$ direction across $\mathbf{q}_c = (0\ 0\ 1)$ in a magnetic field applied along the b axis at $T = 15$ K. The light gray grids denote the measurement fields. (c),(d) Scans along the $[1\ 0\ 0]$ direction across $\mathbf{q}_c = (0\ 0\ 1)$ in the $0_{\uparrow}T$ and $0_{\downarrow}T$ phases at $T = 1.5$ K, respectively. The dark green and orange arrows mark the first-order incommensurate magnetic Bragg peaks and their third-order harmonics, respectively, while the purple ones mark the commensurate reflections. Inset shows the zoom-in view of the third-order harmonics at $T = 1.5$ K and 80 K, $B = 0_{\uparrow} T$. The data were taken at CTAX.

Very intriguingly, as the magnetic field decreases, the system cannot restore to its original zero-field state. As shown in Fig. 3.20(b), the commensurate CAFM- b spin structure transforms into the coexistence of commensurate and incommensurate ones below the critical field $B_c^{\downarrow} = 4.3 \pm 0.5$ T, corroborating the first-order character of the field-induced magnetic phase transition. While the commensurate magnetic peak is still located at $\mathbf{q}_c = (0\ 0\ 1)$, the incommensurate ones are centered at $\mathbf{q}_{ic} = (\pm 0.005\ 0\ 1)$, in contrast to $(\pm 0.017\ 0\ 1)$ prior to applying the magnetic field. As the magnetic field decreases further down to 0 T, this new incommensurability remains unchanged and does not restore to the initial values, i.e., $\mathbf{q}_{ic} = (\pm 0.017\ 0\ 1)$.

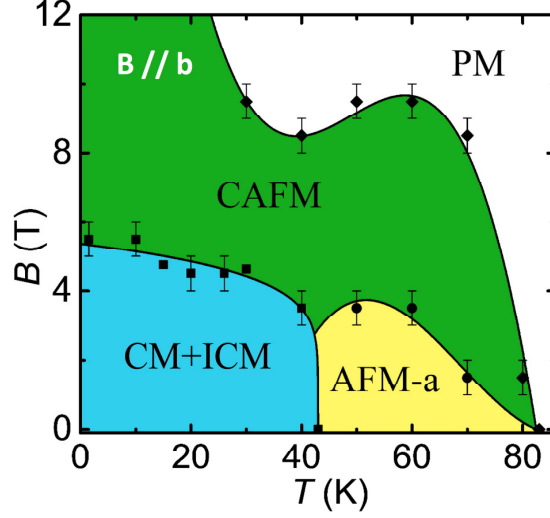


Figure 3.21: Phase diagram of $\text{Ca}_3(\text{Ru}_{0.95}\text{Fe}_{0.05})_2\text{O}_7$ in a magnetic field along the b axis for field ramping up. Note that the error bars of the data points at 15 K and 30 K are smaller than the size of the symbol.

Figure 3.20(c) and (d) present the scans measured at $T = 1.5$ K and $B = 0$ T before (denoted as $0_{\uparrow}T$) and after ($0_{\downarrow}T$) ramping the magnetic field up to 9 T. We have observed several remarkable features. (i) In addition to the first-order incommensurate magnetic reflections (green arrows) discussed above, the third-order harmonic peaks (orange arrows) are also observed for both $0_{\uparrow}T$ and $0_{\downarrow}T$ states. This feature suggests that the magnetic soliton lattice reemerges in the $0_{\downarrow}T$ state, but with a much longer periodicity (~ 200 unit cells or ~ 1100 Å along the a axis). (ii) The intensity ratio of the third- to the first-order harmonic peaks I_3/I_1 is much larger at $B = 0_{\downarrow}$ T, suggesting that the incommensurate magnetic structure is more distorted from the uniform cycloidal structure with narrower domain wall width. (iii) While the FWHM of the commensurate peak remains nearly unchanged compared to the one in the $0_{\uparrow}T$ state, the FWHM of the incommensurate magnetic peaks in the $0_{\downarrow}T$ state becomes broader, implying a shorter correlation length of the magnetic soliton lattice in the $0_{\downarrow}T$ state. It is worth noting that such a $0_{\downarrow}T$ phase is rather persistent and a subsequent magnetic field cycling between 0 and 9 T shows a reversible behavior with the

magnetic wave vector transforming between the incommensurate $\mathbf{q}_{ic} = (\pm 0.005 \ 0 \ 1)$ and the commensurate $\mathbf{q}_c = (0 \ 0 \ 1)$, unless the temperature is raised high enough. These results suggest that the system could not restore to its equilibrium ground state after the field-induced incommensurate-to-commensurate phase transition. Instead, it forms a persistent metastable state at low temperature, leading to the irreversible behavior of the modulation wave vector in the field-induced magnetic phase transition.

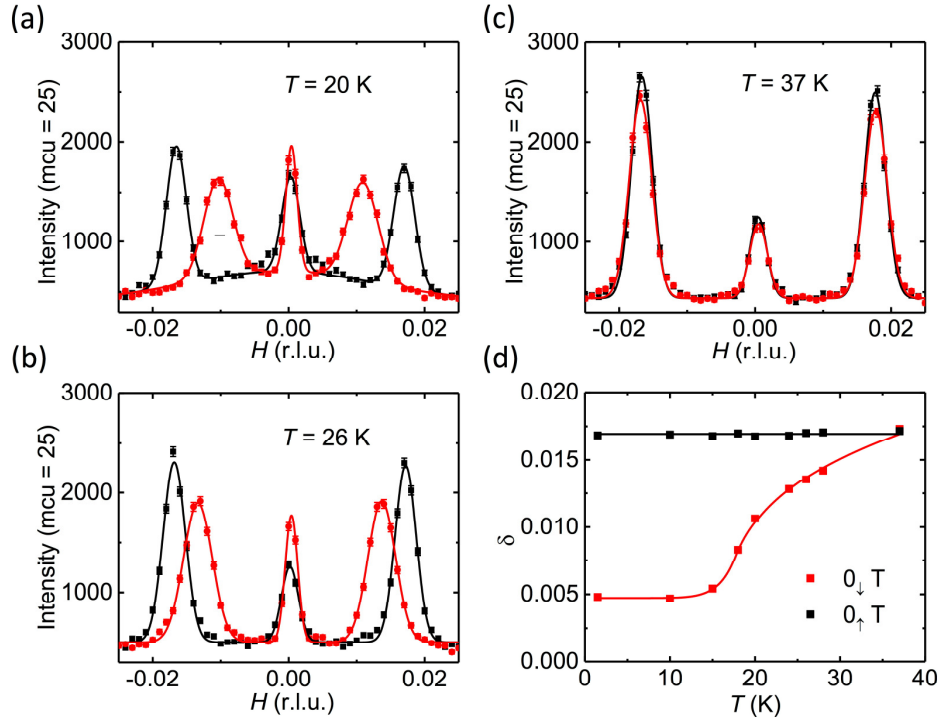


Figure 3.22: (a)-(c) Scans along the $[1 \ 0 \ 0]$ direction across $\mathbf{q}_c = (0 \ 0 \ 1)$ in the $0_{\uparrow}T$ (black) and $0_{\downarrow}T$ (red) phases at representative temperatures. The magnetic Bragg peaks are fitted using Gaussian functions (solid curves). The gray horizontal line indicates the instrument resolution. (d) Incommensurability δ of the first-order incommensurate magnetic wave vector $\mathbf{q}_{ic} = (\pm\delta \ 0 \ 1)$ in the $0_{\uparrow}T$ and $0_{\downarrow}T$ phases at different temperatures. The error bars obtained from Gaussian fitting are smaller than the symbol size. The solid curves are guides to the eye. The data were taken at CTAX.

Figure 3.22(a)-(c) present the irreversibility of the field-driven incommensurate-commensurate magnetic structure transition at representative temperature. The scans along the $[1$

$0\ 0]$ direction were performed at zero field under different histories following the aforementioned procedure, one right after ZFC to the designated measurement temperature ($0_{\uparrow}T$) and the other after ZFC and applying the magnetic field up to 9 T, then removing the magnetic field ($0_{\downarrow}T$). One can see that the wave vector $\mathbf{q}_{ic}$ of the incommensurate magnetic reflection in the $0_{\uparrow}T$ state stays almost constant below T_{MIT} , consistent with the previous report [123]. However, the $0_{\downarrow}T$ state behaves in a completely different way where $\mathbf{q}_{ic}$ of the incommensurate peaks is dependent on the measurement temperature. A summary of the zero-field incommensurability δ measured in both $0_{\uparrow}T$ and $0_{\downarrow}T$ states is presented in Fig. 3.22(d). In contrast to the constant $\delta = 0.017$ in the $0_{\uparrow}T$ state, δ in the $0_{\downarrow}T$ state is relatively smaller and remains unchanged below 18 K, above which δ increases monotonically and gradually reaches the value of the equilibrium state. This indicates that a complete recovery of the equilibrium ground state at $B = 0_{\downarrow}$ T takes place at a characteristic temperature $T_g \sim 37$ K that is slightly lower than T_{MIT} . In addition, it is noteworthy that the incommensurate peaks in the $0_{\downarrow}T$ state, for example at 20 K, are much broader than that in the equilibrium $0_{\uparrow}T$ state, implying that the $0_{\downarrow}T$ state has a shorter correlation length. These features suggest that the emergence of the field-induced metastable $0_{\downarrow}T$ state at low temperature is due to the fact that the system gets trapped at a local minimum in the free energy landscape. As a result, the transformation to the equilibrium ground state is kinetically prohibited by the energy barriers unless thermal fluctuations are strong enough to overcome this barrier.

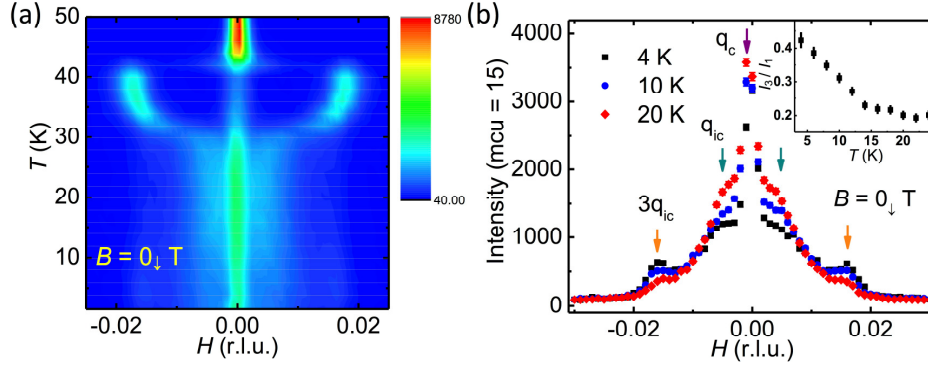


Figure 3.23: (a) Contour map of the intensity of scans along the $[1\ 0\ 0]$ direction over $\mathbf{q}_c = (0\ 0\ 1)$ while warming up in the metastable $0_\downarrow T$ phase. The measurement temperatures are denoted by the light gray grids. (b) Scans along the $[1\ 0\ 0]$ direction over $\mathbf{q}_c = (0\ 0\ 1)$ at representative temperatures. The third-order harmonics of the incommensurate magnetic reflections are denoted by orange arrows. Inset shows the temperature dependence of the intensity ratio I_3/I_1 in the $0_\downarrow T$ phase. The data were taken at CTAX.

To further understand the temperature evolution of the field-induced metastable state, we prepared the initial $0_\downarrow T$ state at $T = 1.5$ K, then performed the measurements at various temperatures while warming up. The data are shown in Fig. 3.23(a) (2 K / step). The incommensurate wave vector $\mathbf{q}_{ic} = (\pm 0.005\ 0\ 1)$ remains almost unchanged until $T \sim 31$ K, then starts to evolve gradually toward the equilibrium state with $\mathbf{q}_{ic} = (\pm 0.017\ 0\ 1)$, which is eventually reached at $T_g \sim 37$ K. In the meantime, the intensity of the commensurate peak $\mathbf{q}_c = (0\ 0\ 1)$ gets much weaker and the peak width becomes narrower, due to the phase transformation from the metastable state toward the equilibrium phase. Notably, the temperature where $\mathbf{q}_{ic}$ starts to deviate from that of the low-temperature $0_\downarrow T$ state is sensitively dependent on the measurement procedures, as shown in Fig. 3.22(d) and 3.23(a), i.e., the former at $T \sim 18$ K and the latter at $T \sim 31$ K, indicating that the incommensurability of the $0_\downarrow T$ state obtained using different measurement protocols can be quite different for $18\text{ K} < T < 31\text{ K}$. This implies that a mechanism which is sensitively dependent on both temperature and magnetic field history has to be invoked in order to explain this irreversible behavior. Fig. 3.23(b) shows the evolution of the third-order

harmonics measured in the 0 T state at representative temperatures. The temperature dependence of the intensity ratio I_3/I_1 is shown in the inset. As the temperature increases, I_3/I_1 decreases indicating that the incommensurate magnetic soliton lattice evolves toward the uniform cycloidal spin structure with broader domain wall width at elevated temperatures, similar to the zero-field study reported previously [123].

3.5.3 Magnetoresistance and neutron diffraction for $B \parallel a$ axis

It is well-known that the magnetic phase transitions of DM helimagnets are rather complicated, depending on the orientation of the external magnetic field. In this section, we present the studies on the field-induced spin structure transitions of $\text{Ca}_3(\text{Ru}_{0.95}\text{Fe}_{0.05})_2\text{O}_7$ upon applying the magnetic field along the a axis, parallel to the propagation direction of the incommensurate magnetic soliton lattice, as denoted by the blue arrows in Fig. 3.19(a) and (c).

Figure 3.24(a) shows the normalized out-of-plane resistivity ρ_c as a function of magnetic field at $T = 15\text{ K}$, as the magnetic field is applied along the a and b axis, respectively. The measurements were performed after the sample was initially cooled in zero magnetic field for each case. For $B \parallel b$, the magnetoresistance displays a minimum at $B_c^\uparrow = 5 \pm 0.25\text{ T}$ as the magnetic field increases, corresponding to the incommensurate-to-commensurate spin structure transition to CAFM-b as revealed by neutron diffraction measurements [127]. The transition is of first order, as indicated by the appearance of hysteresis as the magnetic field increases and decreases ($B_c^\downarrow = 4.5 \pm 0.25\text{ T}$). Intriguingly, when the magnetic field is applied along the a axis, a first-order transition is also observed at $B_c^\uparrow = 2.25 \pm 0.25\text{ T}$, in sharp contrast to the parent compound where no anomaly is observed in this field range [128,129]. This transition is likely to be associated with a field-induced spin structure transition as well. For comparison, Figure 3.24(b) shows the data taken at $T = 55\text{ K}$, where the material displays a metallic state with the AFM-a type magnetic structure at zero field

[123,127]. One can see that the features are completely different from that observed at 15 K. The magnetoresistance increases continuously as the magnetic field is along the b axis, whereas it exhibits a sudden jump for $B \parallel a$. In the AFM- a phase, one would expect a first-order spin-flop or spin-flip transition when the magnetic field is applied along the easy axis (a axis), but a continuous transformation into the fully polarized state (PM) if the magnetic field is applied along the hard axis (b axis) [97]. The observations at 55 K seem to be well explained by this scenario.

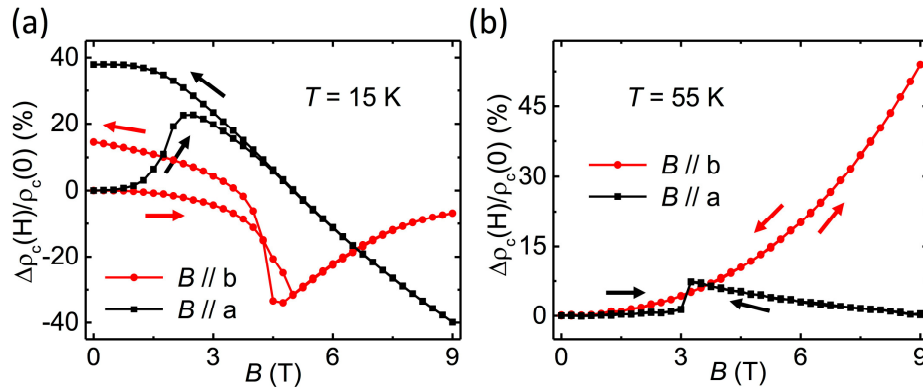


Figure 3.24: (a) Normalized out-of-plane resistivity ρ_c of $\text{Ca}_3(\text{Ru}_{0.95}\text{Fe}_{0.05})_2\text{O}_7$ as a function of magnetic field at (a) $T = 15$ K and (b) $T = 55$ K. The magnetic field is applied along the a and b axis, respectively.

Interestingly, the magnetoresistance data [Fig. 3.24(a)] for both $B \parallel a$ and $B \parallel b$ axes, which are essentially dominated by the spin scattering process of different magnetic structures, also exhibit irreversible behaviors. The zero-field resistance in the $0_\downarrow T$ state is much greater than that measured in the $0_\uparrow T$ phase ($0_\uparrow T$ and $0_\downarrow T$ are defined in Sec. 3.5.2). The emergence of such hysteresis implies the formation of metastable magnetic phases when the magnetic field decreases, as discovered by the neutron diffraction study described above [127]. Similar to the one induced with the magnetic field applied along the b axis, the metastable phase induced for $B \parallel a$ is also quite persistent. The change in the resistance is found to be less than $\sim 0.1\%$ in the time scale up to $\sim 10^4$ seconds, and further cycling the magnetic field between 0 and 9 T gives rise to reversible

phase transitions between the low-field metastable phases and the high-field states. Such a magnetic memory effect can be erased only by heating the material up to a high enough temperature, which suggests that thermal fluctuations play an essential role.

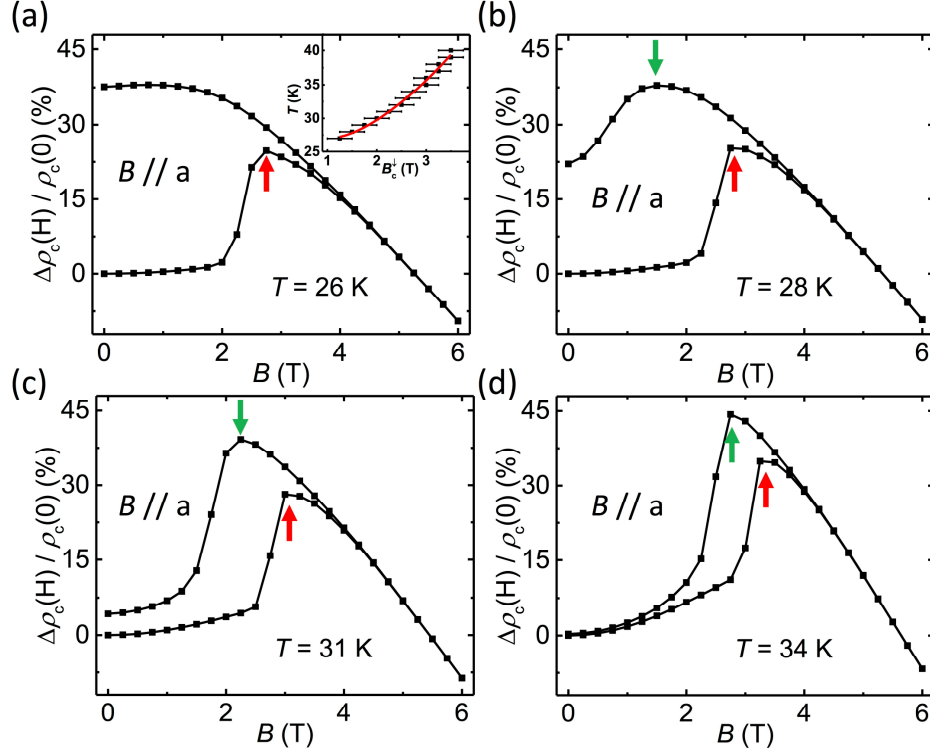


Figure 3.25: Normalized out-of-plane resistivity ρ_c of $\text{Ca}_3(\text{Ru}_{0.95}\text{Fe}_{0.05})_2\text{O}_7$ as a function of magnetic field at representative temperatures. The upper and lower critical fields are denoted by red and green arrows, respectively. Inset shows the lower critical field $B_c^\downarrow$ as a function of temperature. The red solid line is a fit using power law. The magnetic field is along the a axis.

Figure 3.25(a)-(d) shows the irreversible field-induced phase transitions for $B \parallel a$ at representative temperatures. Because of the history effect, each measurement was done after heating the sample to a temperature above T_N then ZFC to the measurement temperature to clean up the magnetic memory. Below 26 K, as the magnetic field decreases from 9 T, the magnetoresistance monotonically increases and becomes saturated, giving rise to a large open hysteresis. On the contrary, at $T > 26$ K, the magnetoresistance [Fig. 3.25(b)-(d)] shows a decrease at the critical field $B_c^\downarrow$ (marked by green arrows) as the magnetic field decreases, suggesting that

the phase transformation starts to occur. In addition, the remnant magnetoresistance at zero field ($0\downarrow T$) decreases with increasing temperature, and finally disappears at $T \sim 34$ K [Fig. 3.25(d)], which may suggest that the equilibrium phase (coexistence of commensurate and incommensurate spin structures with $\delta \sim \pm 0.017$) has been recovered.

In order to determine the magnetic structure of the field-induced phase below T_{MIT} and the metastable phase at $B < B_c^\downarrow$, we have carried out neutron diffraction measurements with the magnetic field applied along the a axis. Due to the limited access to the reciprocal space with the horizontal-field cryomagnet, we only focus on the magnetic reflections around $\mathbf{q}_c = (0\ 0\ 1)$. Figure 3.26(a) and (b) show the contour maps of the neutron intensity of scans across $\mathbf{q}_c = (0\ 0\ 1)$ along the $[1\ 0\ 0]$ direction at $T = 15$ K (every 0.5 T from 0 to 4 T). At zero field, the system exhibits coexistence of the commensurate magnetic peak $\mathbf{q}_c = (0\ 0\ 1)$ and incommensurate ones $\mathbf{q}_{\text{ic}} = (\delta\ 0\ 1)$, $\delta = \pm 0.017$, in agreement with the previous study [123]. As the magnetic field increases, the incommensurate peaks are suppressed at a critical field $B_c^\uparrow = 2.25 \pm 0.25$ T (defined as the point where the incommensurate peaks are gone completely), much smaller than that when $B \parallel b$, and the incommensurability δ keeps nearly constant during the phase transition. In the meantime, the intensity of the commensurate one is enhanced, and the peak width becomes broader. As the magnetic field increases further, the $(0\ 0\ 1)$ peak intensity gets stronger and the peak width becomes narrower. However, the integrated intensity decreases slightly, implying that the antiferromagnetic staggered magnetization is gradually suppressed by the magnetic field. Note that the reflection condition of the crystal symmetry of $\text{Ca}_3(\text{Ru}_{0.95}\text{Fe}_{0.05})_2\text{O}_7$ ($Bb2_1m$, No. 36) requires that both H and L are even, or the sum $H + L$ is even [93]. The emergence of Bragg reflections at $(0\ 0\ 1)$ suggests that the system is in an antiferromagnetic phase, similar to the field-induced states in the pristine and other doped $\text{Ca}_3\text{Ru}_2\text{O}_7$ [97,130,131]. Although only one magnetic reflection is

available in this experiment, considering that in all other related studies on $\text{Ca}_3\text{Ru}_2\text{O}_7$ this magnetic reflection corresponds to an AFM-a or AFM-b type spin structure [97,127,130], we propose that the field-induced magnetic structure is CAFM-a, a superposition of AFM-b and a ferromagnetic component along the a axis, as shown in Fig. 3.19(b).

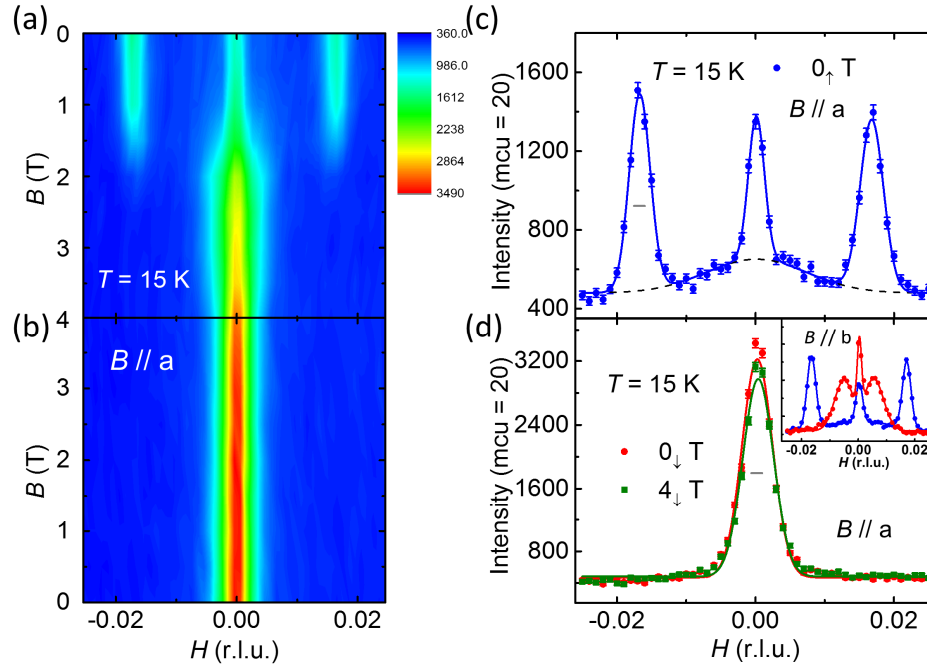


Figure 3.26: Contour maps of the neutron intensity of scans across $\mathbf{q}_c = (0 \ 0 \ 1)$ along the $[1 \ 0 \ 0]$ direction at $T = 15$ K as (a) the magnetic field increases from 0 to 4 T and (b) the magnetic field decreases from 4 to 0 T. (c),(d) Cuts of the scans taken at $B = 0 \uparrow$, $4 \downarrow$ and $0 \downarrow$ T. The solid and dashed lines are fitted curves using Gaussian functions. The gray line denotes the instrument resolution. The magnetic field is applied along the a axis. Inset shows the scans at $B = 0 \uparrow$ T (blue) and $0 \downarrow$ T (red) when the magnetic field is along the b axis at $T = 15$ K.

The irreversibility of the field-induced magnetic transition is clearly observed in the neutron diffraction measurements. As the magnetic field decreases, surprisingly, both the peak width and peak intensity of the commensurate $(0 \ 0 \ 1)$ magnetic reflection stay nearly unchanged and the incommensurate ones do not reemerge down to 0 T at $T = 15$ K. This agrees well with the magnetoresistance measurements, where the critical field $B_c^\downarrow$, i.e. the phase transformation into the equilibrium phase (coexistence of commensurate and incommensurate spin structures with $\delta \sim$

± 0.017), is absent [Fig. 3.24(a)]. This observation is different from that for $B \parallel b$, where the system transforms into a metastable state with much smaller incommensurability $\delta \sim \pm 0.004$ ($T = 15$ K) [127]. Figure 3.26(c) and (d) show the scans at $B = 0_{\uparrow}$, $4_{\downarrow}$ and $0_{\downarrow}$ T. Inset shows the scans at $B = 0_{\uparrow}$ T and $0_{\downarrow}$ T as the magnetic field is applied along the b axis for comparison. All the incommensurate and commensurate magnetic peaks can be well fitted by Gaussian functions (a broad peak is added in Fig. 3.26(c) to account for the broad diffuse scattering intensity, as discussed in Ref. [127]). The widths of all the peaks are not resolution limited (the resolution is denoted by the short gray line). Particularly the width of $(0\ 0\ 1)$ at $B = 4$ T is much broader than that in the $0_{\uparrow}T$ phase, which suggests a much shorter correlation length $\sim 210a$ in the field-induced CAFM-a phase and the metastable state at $B = 0_{\downarrow}$ T.

We also performed the same neutron diffraction measurements at a higher temperature $T = 34$ K, where a critical field $B_c^{\downarrow}$ is seen in the magnetoresistance measurements [Fig. 25(b)-(d)], as shown in Fig. 3.27(a) and (b). Similarly, the incommensurate-to-commensurate magnetic transition occurs at $B_c^{\uparrow} = 2.75 \pm 0.25$ T, close to that shown in the magnetoresistance data [Fig. 3.25(d)]. However, as the magnetic field decreases, at $B_c^{\downarrow} = 2$ T the commensurate $(0\ 0\ 1)$ peak becomes weaker and two incommensurate peaks appear at $\mathbf{q}_{ic} = (\delta\ 0\ 1)$, $\delta \sim \pm 0.01$. Upon further reducing the magnetic field, the incommensurability δ gradually evolves toward that of the equilibrium state, which indicates a decrease in the period of the incommensurate magnetic structure. Nevertheless, the equilibrium value of the incommensurability $\delta \sim \pm 0.017$ cannot be reached down to 0 T at this temperature. A complete recovery of the initial incommensurability occurs in the measurements done at $T_g = 37$ K, the same as that when the magnetic field is along the b axis [127]. The small discrepancy in T_g where the equilibrium state is recovered determined by neutron diffraction and magnetotransport measurements might be due to the fact that the

incommensurability can be better resolved by neutron diffraction. Figure 3.27(c) and (d) show the representative scans at $B = 0_{\uparrow}, 4_{\uparrow}$ T and $1.5_{\downarrow}, 0_{\downarrow}$ T respectively. The peak width of $(0\ 0\ 1)$ at $B > B_c^{\uparrow}$ (CAF_M-a) is not resolution limited, corresponding to a correlation length of $\sim 450a$. In the metastable state at $B < B_c^{\downarrow}$, the correlation length of the commensurate phase is comparable to that of the CAF_M-a phase, but the incommensurate peaks are broader and become slightly narrower as the magnetic field decreases.

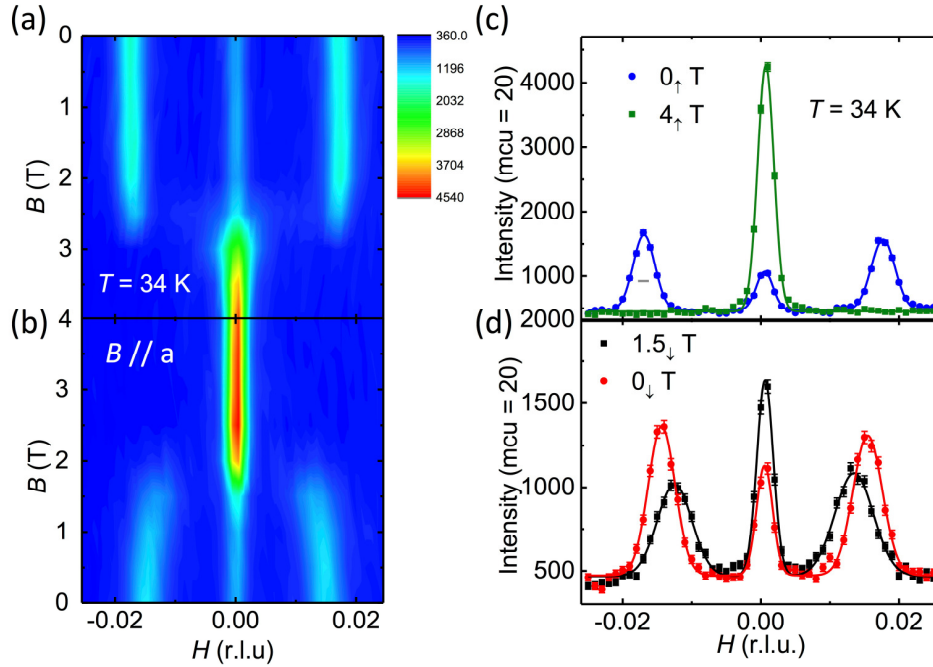


Figure 3.27: Contour maps of the neutron intensity of scans across $\mathbf{q}_c = (0\ 0\ 1)$ along the $[1\ 0\ 0]$ direction at $T = 34$ K as (a) the magnetic field increases from 0 to 4 T and (b) the magnetic field decreases from 4 to 0 T. (c),(d) Cuts of the scans taken at $B = 0_{\uparrow}, 4_{\uparrow}$ T and $1.5_{\downarrow}, 0_{\downarrow}$ T. The solid lines are fitted curves using Gaussian functions. The gray line denotes the instrument resolution. The magnetic field is applied along the a axis.

To make a further comparison with the $B \parallel b$ case, we also studied the evolution of the $0_{\downarrow}T$ metastable phase as a function of temperature. The metastable state was obtained using the same procedure as the $0_{\downarrow}T$ phase shown in Fig. 3.26(b). Namely, we first ZFC the sample to 15 K and applied 4 T magnetic field along the a axis. The magnetic field was then reduced to zero. Figure

3.28(a) shows the contour map of the neutron intensity obtained by scanning across $\mathbf{q}_c = (0\ 0\ 1)$ along the $[1\ 0\ 0]$ direction at various temperatures (every 2 K from 15 to 50 K). Upon warming the magnetic reflection $(0\ 0\ 1)$ almost doesn't change until $T = 31$ K, where the incommensurate peaks start to appear and move towards the equilibrium state with $\mathbf{q}_{ic} = (\delta\ 0\ 1)$, $\delta \sim \pm 0.017$. As soon as the incommensurate peaks show up, the intensity of the commensurate $(0\ 0\ 1)$ peak becomes much weaker, indicating that the commensurate magnetic structure (CAF_{FM}-a) transforms into the incommensurate ones. Fig. 3.28(b) shows the scans at selected temperatures $T = 15, 34$ and 37 K. One clearly see that the equilibrium states is reached at $T_g = 37$ K, similar to the study for $B \parallel b$ [127]. In addition, the peak width of $(0\ 0\ 1)$ at $T = 34$ K is much narrower than that at 15 K, which implies that the correlation length becomes much longer ($\sim 440a$). In contrast, the peak width of the incommensurate peaks is broader and corresponds to a correlation length of $\sim 230a$. For $T > 37$ K, the behavior of the magnetic Bragg peaks is the same as that of the equilibrium $0_\uparrow T$ phase [123].

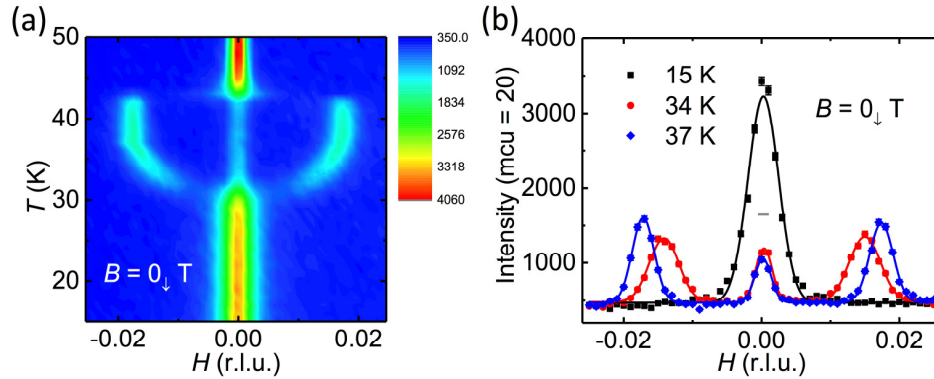


Figure 3.28: (a) Contour map of the neutron intensity of scans across $\mathbf{q}_c = (0\ 0\ 1)$ along the $[1\ 0\ 0]$ direction in the $0_\downarrow T$ phase at various temperatures. (b) Cuts of the scans taken at $T = 15, 34$ and 37 K in the $0_\downarrow T$ phase. The solid lines are fitted curves using Gaussian functions. The gray line represents the instrument resolution.

3.5.4 Discussions

In $\text{Ca}_3(\text{Ru}_{0.95}\text{Fe}_{0.05})_2\text{O}_7$, due to the non-centrosymmetric crystal symmetry, it is convenient to

ascribe the formation of incommensurate magnetic structures to the DM interaction [124]. In fact, incommensurate magnetic structures have been observed in Ti- and Mn-doped $\text{Ca}_3\text{Ru}_2\text{O}_7$, but only in a small temperature window near the MIT [100,131]. These results suggest that the incommensurate magnetic structures are close in free energy to AFM-b or AFM-a, thus can be readily induced by light chemical doping. Owing to the noncollinear, long-period incommensurate magnetic structures, first-order spin structure transitions have been observed as the magnetic field is applied along both the a and b axis, which is in sharp contrast to the parent compound [132,129]. In the pure $\text{Ca}_3\text{Ru}_2\text{O}_7$, below T_{MIT} , the material displays a collinear AFM-b type magnetic structure, with the staggered magnetization along the b axis [97]. The magnetic field leads to a first-order spin-flop transition at $B_c = 6$ T ($T = 4$ K) only when the magnetic field is applied along the b axis [129]. On the contrary, as the magnetic field is applied along the a axis, the system continuously evolves toward the fully spin polarized state (PM) and no first-order spin structure transition is observed [97]. Note that although a field-induced transition is seen at 15 T, it is attributed to a change in the orbital occupancy [129]. As a DM helimagnet, the stabilization of the incommensurate magnetic soliton lattice in $\text{Ca}_3(\text{Ru}_{0.95}\text{Fe}_{0.05})_2\text{O}_7$ and its evolution as a function of temperature and magnetic field are governed by the competition among Zeeman interaction, exchange interaction, DM interaction and magnetocrystalline anisotropy [133], a mechanism that accounts for different types of spin structure transitions in various other DM magnets such as $\text{Ba}_2\text{CuGeO}_7$ [134,135] and FeGe [136-138], etc. However, a more detailed theory is required to interpret these observations quantitatively.

The irreversibility in the incommensurate-to-commensurate magnetic phase transitions driven by a magnetic field in $\text{Ca}_3(\text{Ru}_{0.95}\text{Fe}_{0.05})_2\text{O}_7$ is characteristic of a metastability phenomenon. The supercooling and superheating phases associated with first-order transitions are prototypical

metastable states [139]. Metastability often emerges when the phase transformation to the thermodynamic equilibrium state is kinetically prohibited, particularly at low temperature where thermal fluctuations are not sufficiently strong to overcome the intervening energy barriers in the free energy landscape. It has been observed in different systems regardless of the microscopic details, such as the field-induced magnetic transitions in phase-separated manganites [22,140-142] and the field-induced metastable vortex lattices in superconducting MgB_2 [143,144]. A common feature among these metastable states is that the history effect can be erased by heating up the system to a high enough temperature, which suggests that thermal fluctuations are essential in the emergence of metastability.

Metastability concerning incommensurate magnetic structures, especially on the modulation wave vectors, have been observed in other magnetic systems such as TbMnO_3 [145], DyMn_2O_5 [146], UNiAl [147], where a different incommensurability or even an alternative modulation wave vector emerges as the magnetic field decreases. In some other cases, the systems maintain the pressure- or field-induced state upon releasing the pressure or removing the magnetic field, for example, Cr in a pressure-induced transition [148], $\text{Ba}_{0.5}\text{Sr}_{1.5}\text{Zn}_2(\text{Fe}_{1-x}\text{Al}_x)_{12}\text{O}_{22}$ [149] and $\text{NaFe}(\text{WO}_4)_2$ [150] in the magnetic-field-driven phase transitions. A plausible qualitative explanation for the field-induced irreversibility in the magnetic modulation vector in $\text{Ca}_3(\text{Ru}_{0.95}\text{Fe}_{0.05})_2\text{O}_7$ may be given from the perspective of the free energy landscape as a function of thermodynamic variables. Upon decreasing the magnetic field, due to the first-order nature of the phase transition, the nucleation of the new phase requires an activation energy in order to overcome the intervening energy barriers between the local minima. However, thermal fluctuations at low temperature are not strong enough, which prevents the formation of large enough nucleus of the stable phase [139]. The critical field $B_c^\perp$ signifies the magnetic field at which the strength of

the thermal energy $\sim k_B T$ and the height of the energy barrier U between CAFM and the metastable phase become comparable. Such a mechanism has been applied to account for the irreversibility observed in phase-separated manganites $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ and $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$, where large hysteresis is seen in the phase transition between a ferromagnetic metallic state and an antiferromagnetic charge-ordered phase driven by a magnetic field [22,140]. Following the analysis in Ref. [22], the temperature dependence of $B_c^\downarrow$ obtained by magnetoresistance measurements as summarized in the inset of Fig. 3.25(a), can be approximately scaled using an empirical function $T \propto |B - B_c^{(0)}|^\beta$, where $B_c^{(0)}$ is the critical field when U becomes zero [22]. The fact that $B_c^\downarrow$ becomes greater as the temperature increases suggests that the height of the energy barrier U decreases as the magnetic field is swept down, in analogy to that in the manganite systems. The value of the critical exponent β is sensitively dependent on the choice of $B_c^{(0)}$. In the inset of Fig. 3.25(a), the solid line represents the fit with $\beta = 1.5$.

The microscopic origin of the metastability in the modulation wave vector of the incommensurate magnetic structures in $\text{Ca}_3(\text{Ru}_{0.95}\text{Fe}_{0.05})_2\text{O}_7$ remains elusive. One may be tempted to attribute the irreversibility to the coupling between the commensurate AFM-b and the incommensurate magnetic structures, since they coexist in this material. However, such a scenario might not be valid since no convincing evidence that suggests any correlation between the intensity, correlation length, or the diffuse scattering intensity of the commensurate peak and the modulation wave vector $\mathbf{q}_{\text{ic}}$ is seen in the neutron diffraction experiment, as discussed in Ref. [127]. In spite of the absence of a unifying microscopic theory to address this irreversibility problem, the phenomenological theories proposed to account for the metastability in Cr might shed light on the underlying mechanism [151,152]. First, we discuss spin-lattice coupling. It has been suggested that the lattice distortions induced by the SDW ordering in Cr have negative free energy, which

results in the persistence of the domain walls when ramping down the pressure and leads to the metastability in the modulation wave vector [151]. Nevertheless, this is not likely the origin of the metastability observed in $\text{Ca}_3(\text{Ru}_{0.95}\text{Fe}_{0.05})_2\text{O}_7$, since no lattice modulation peaks at $2\mathbf{q}_{ic}$ displaced from the nuclear peak (0 0 4) are convincingly observed, as shown in Fig. 3.29, in contrast to those in Cr indicating the presence of strong exchange striction. Second, we discuss domain wall pinning. It has been proposed that the metastability in Cr can also stem from the pinning of domain walls by nonmagnetic impurities [152]. In Fe-doped $\text{Ca}_3\text{Ru}_2\text{O}_7$, we speculate that the interaction between the magnetic Fe dopants and the domain walls might be responsible for the metastability. Although these randomly doped magnetic impurities can enhance the heterogeneous nucleation process of the magnetic domain walls during the commensurate-to-incommensurate transition when the magnetic field ramps down, they also pin the domain walls thus create energy barriers and prevent the domain wall density from reaching the equilibrium value, leading to the observed metastability [152]. However, a more comprehensive theoretical study is desired to account for this metastability phenomenon.

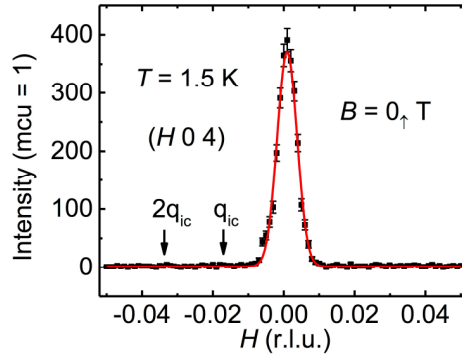


Figure 3.29: Scan along the $[1\ 0\ 0]$ direction across the nuclear Bragg peak (0 0 4) at $T = 1.5$ K in the $0_{\uparrow}T$ phase.

3.5.5 Summary

We have investigated the magnetic-field-induced phase transitions of $\text{Ca}_3(\text{Ru}_{1-x}\text{Fe}_x)_2\text{O}_7$ ($x =$

0.05) with the field applied both along and perpendicular to the propagation direction of the incommensurate magnetic soliton lattice. First-order incommensurate-to-commensurate magnetic transitions into canted antiferromagnetic structures (CAF_M-a or CAF_M-b) have been observed. In addition, the field-induced transitions display distinct irreversible behaviors below a characteristic temperature T_g and give rise to persistent metastable states, where the system either maintains the high-field phase or transforms into an intermediate incommensurate state with smaller incommensurability. These observations can be qualitatively described in the framework of frozen kinetics at low temperature, which prevents the system from overcoming the energy barriers and reaching the equilibrium state. Therefore, Fe-doped $\text{Ca}_3\text{Ru}_2\text{O}_7$ provides an ideal material system to study the metastability problem of the magnetic soliton lattice, which deserves further theoretical investigations.

3.6 Tuning the competing states in $\text{Ca}_3\text{Ru}_2\text{O}_7$ by Mn doping

In the previous two sections, we have shown that nonmagnetic Ti and magnetic Fe impurities substituted for Ru in $\text{Ca}_3\text{Ru}_2\text{O}_7$ give rise to significantly different doping effects. An interesting question arises: What is the role of the $3d$ transition-metal dopants in determining the magnetic and electronic states? In this section, we discuss the doping effects of another magnetic impurity Mn on the spin structure of $\text{Ca}_3\text{Ru}_2\text{O}_7$. We find that Mn induces an incommensurate cycloidal spin structure in a narrow temperature range close to T_{MIT} for $x \leq 0.03$, while the ground state magnetic structure is the same as that of the parent compound. However, the system exhibits a G-AFM Mott insulating state with a simultaneous change in the lattice parameters at T_{MIT} for $x \geq 0.04$. Furthermore, in $\text{Ca}_3(\text{Ru}_{0.96}\text{Mn}_{0.04})_2\text{O}_7$ that is close to the phase boundary [153], a magnetic field applied along the b axis drives a spin structure transition from G-AFM to CAFM below T_{MIT} , which is accompanied by an IMT and a drastic change in the lattice constants. In contrast, at $T_{\text{MIT}} < T < T_{\text{ICM}}$, an incommensurate-to-commensurate magnetic transition has been observed without any detectable structural change in the neutron diffraction measurements. Our results show that the effects of the magnetic Mn doping is very similar to the nonmagnetic Ti but is different from the magnetic Fe.

3.6.1 Materials and methods

The single-crystal samples of $\text{Ca}_3(\text{Ru}_{1-x}\text{Mn}_x)_2\text{O}_7$ with doping concentrations ranging from $x = 0$ to 0.1 were grown by the Floating Zone technique. The magnetization and resistivity measurements were performed using PPMS. Neutron diffraction experiments were carried out using the HB-1A and CG-4C triple-axis spectrometer at HFIR in ORNL. The energy of the incident neutrons of HB-1A and CG-4C was fixed as $E_i = 14.6$ meV and 5 meV, respectively. During the measurements on the materials of different doping concentrations at zero field, the samples were

oriented in the $(H\ 0\ L)$ and $(0\ K\ L)$ scattering planes and mounted in an aluminum can which is cooled using a closed-cycle helium refrigerator down to 4 K. To study the magnetic-field-induced transitions, the $\text{Ca}_3(\text{Ru}_{0.96}\text{Mn}_{0.04})_2\text{O}_7$ sample was aligned in the horizontal $(H\ 0\ L)$ scattering plane and loaded into a vertical-field cryomagnet such that the magnetic field was applied along the b axis up to 8 T.

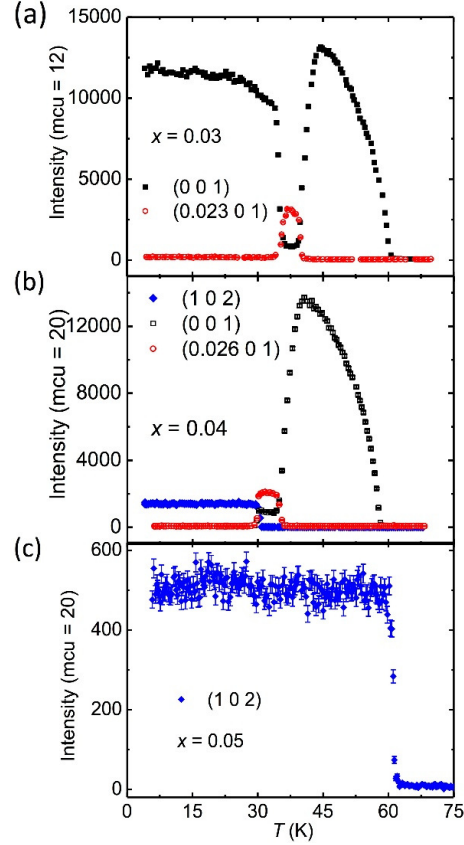


Figure 3.30: Temperature dependence of the intensity of representative magnetic Bragg peaks $(1\ 0\ 2)$, $(0\ 0\ 1)$ and $(\delta\ 0\ 1)$ of $\text{Ca}_3(\text{Ru}_{1-x}\text{Mn}_x)_2\text{O}_7$ ($x = 0.03, 0.04$ and 0.05), $\delta = 0.023$ and 0.026 for $x = 0.03$ and 0.04 , respectively.

3.6.2 Magnetic properties of $\text{Ca}_3\text{Ru}_2\text{O}_7$ upon Mn doping at zero field

Figure 3.30 shows the temperature dependence of the intensity of the representative magnetic peaks for $\text{Ca}_3(\text{Ru}_{1-x}\text{Mn}_x)_2\text{O}_7$ with different doping concentration x . For $x = 0.03$, at $T_N \sim 61$ K the magnetic peaks show up at the nuclear-forbidden wave vectors $\mathbf{q} = (0\ 0\ 1)$ and other equivalent

positions in the reciprocal space, for example (0 0 5) and (0 0 7), etc. The intensity keeps increasing until $T_{\text{ICM}} \sim 42$ K, where the incommensurate magnetic Bragg peak $\mathbf{q}_{\text{ic}} = (\delta \ 0 \ 1)$ emerges while the commensurate ones get suppressed. This incommensurate magnetic structure exists only in a very narrow temperature range $T_{\text{CM}} (\sim 34 \text{ K}) < T < T_{\text{ICM}}$, below which the intensity of the commensurate magnetic peaks is enhanced and persists down to the lowest temperature measured. For $x = 0.04$, the high-temperature magnetic phases are similar to those in the $x = 0.03$ compound. However, at $T_{\text{MIT}} \sim 30$ K the intensity of both (0 0 1) and $(\delta \ 0 \ 1)$ disappears completely, and new magnetic peaks show up at (1 0 2), (1 0 4) and (1 0 6), etc., which suggests that the ground state spin structure is different from that of the parent compound and the $x = 0.03$ one. For $x = 0.05$, only one first-order magnetic transition is observed at $T_{\text{N}} \sim 60$ K, and the low-temperature magnetic structure is characterized by the magnetic peak $\mathbf{q} = (1 \ 0 \ 2)$.

To determine the spin structures of different magnetic phases in Mn-doped $\text{Ca}_3\text{Ru}_2\text{O}_7$, we have collected a series of nuclear and magnetic Bragg peaks in the $(H \ 0 \ L)$ and $(0 \ K \ L)$ scattering planes for each Mn doping concentration. Figures 3.31(a)-(d) show the scans along the $[1 \ 0 \ 0]$ direction across the magnetic reflections (0 0 5) and (0 0 1) for $x = 0.03$ and 0.04 at representative temperatures. The rocking curve scans over (1 0 2) for $x = 0.04$ and 0.05 are shown in Fig. 3.31(e) and (f), respectively. We have performed magnetic representational analysis to explore the possible magnetic structures using FULLPROF [71]. We find that the strongest (0 0 1) peak corresponds to AFM-a or AFM-b where the magnetic moments are aligned parallel to each other within the bilayer but are antiparallel between adjacent bilayers [97]. The strongest (1 0 2) peak represents G-AFM with all nearest-neighbor magnetic moments aligned antiparallel to each other [99]. The incommensurate magnetic phase characterized by $\mathbf{q}_{\text{ic}} = (\delta \ 0 \ 1)$ is a cycloidal magnetic structure propagating along the a axis, with the period determined by the incommensurability δ . It

is worth noting that the magnetic wave vectors of the incommensurate magnetic structures are strongly temperature-dependent, as shown in Fig. 3.31(c) and (d). No higher-order harmonics are observed, suggesting that the incommensurate magnetic phase is uniformly modulated, in contrast to the magnetic soliton lattice in Fe-doped $\text{Ca}_3\text{Ru}_2\text{O}_7$ [123]. For $x = 0.03$, similar to the parent compound, the $(2\ 0\ 1)$ magnetic peak is present at $T = 4\text{ K}$ but is absent at 50 K , which suggests that at $T < T_{\text{CM}}$, the magnetic moments are along the b axis (AFM-b). In contrast, in the high-temperature phase at $T_{\text{ICM}} < T < T_{\text{N}}$, the moments are along the a axis (AFM-a) [97], which is also the case for the $x = 0.04$ compound.

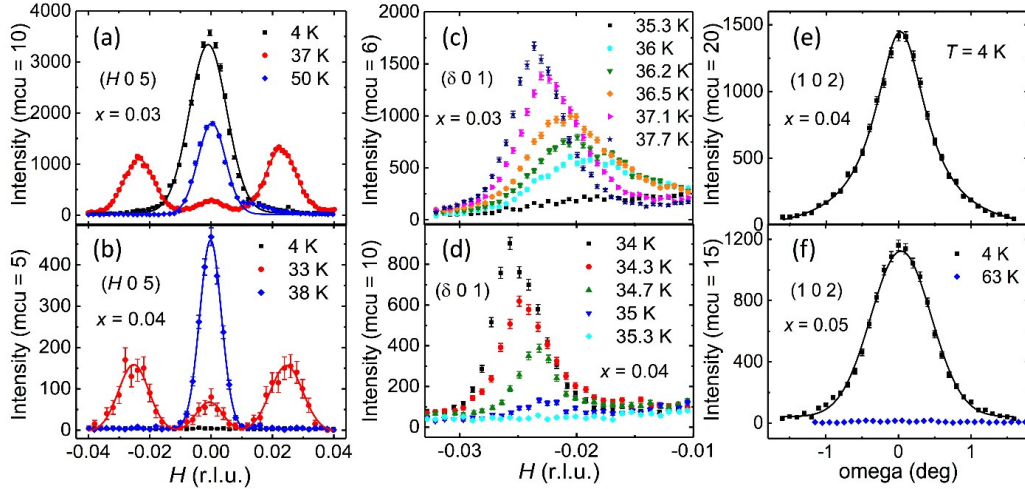


Figure 3.31: (a),(b) Scans along the $[1\ 0\ 0]$ direction across the magnetic wave vector $(0\ 0\ 5)$ at representative temperatures. (c),(d) Scans across the magnetic wave vector $(0\ 0\ 1)$ in the incommensurate magnetic phase. (e),(f) Rocking curve scans across the magnetic wave vector $(1\ 0\ 2)$ at representative temperatures.

Very intriguingly, the magnetic transition to the low-temperature G-AFM state is accompanied by a dramatic change in the lattice constants. Figure 3.32 shows the lattice constants a , b and c as a function of temperature. For $x = 0.03$, there is no observable anomaly in all the lattice constants throughout the temperature range measured. In contrast, for $x = 0.04$ upon cooling the lattice constant b increases discontinuously by $\sim 0.98\%$, while c decreases by $\sim 0.71\%$ at $T_{\text{MIT}} \sim 30\text{ K}$,

which is much more pronounced compared with that in the parent compound ($\sim 0.1\%$) [93]. The shortening along the c axis and the expansion in the in-plane b axis imply a flattening of the RuO_6 octahedron, similar to that in Ca_2RuO_4 , which may lead to a change in the orbital occupancy of the Ru t_{2g} electrons [92,102]. For $x = 0.05$, a structural change of comparable magnitude is also observed at the magnetic transition T_N .

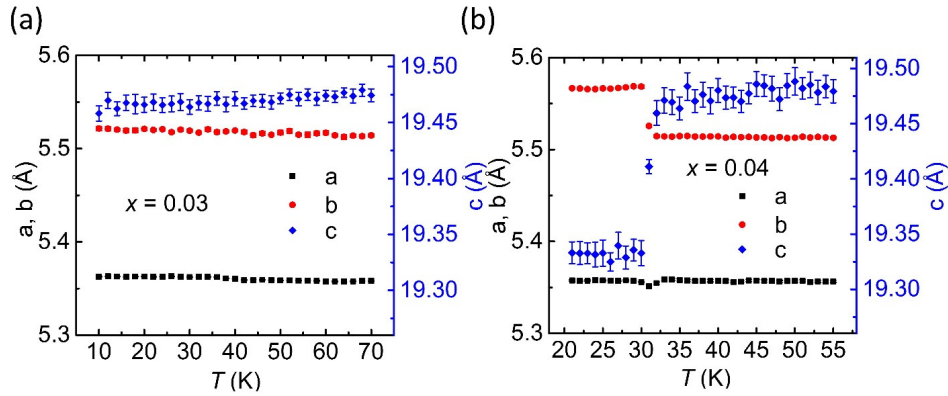


Figure 3.32. Lattice parameters of $\text{Ca}_3(\text{Ru}_{1-x}\text{Mn}_x)_2\text{O}_7$ ($x = 0.03$ and 0.04) as a function of temperature.

3.6.3 Magnetic and transport properties of $\text{Ca}_3(\text{Ru}_{1-x}\text{Mn}_x)_2\text{O}_7$ ($x = 0.04$) in a magnetic field

We have further investigated the effects of the magnetic field on the magnetic and electronic properties of Mn-doped $\text{Ca}_3\text{Ru}_2\text{O}_7$. Note that since the ground state magnetic structure of the $x = 0.03$ compound is similar to the parent compound (AFM-b), applying a magnetic field along the b axis is expected to lead to a transition to CAFM [97]. In contrast, no field-induced transition (up to 9 T) is observed in the resistivity measurements on the $x = 0.05$ sample. Notably, the $x = 0.04$ compound is close to the phase boundary [153], bridging the correlated AFM-b phase and the Mott insulating G-AFM state. Therefore, we have performed single-crystal neutron diffraction, magnetization and resistivity measurements on Mn-doped $\text{Ca}_3\text{Ru}_2\text{O}_7$ of this doping concentration ($x = 0.04$).

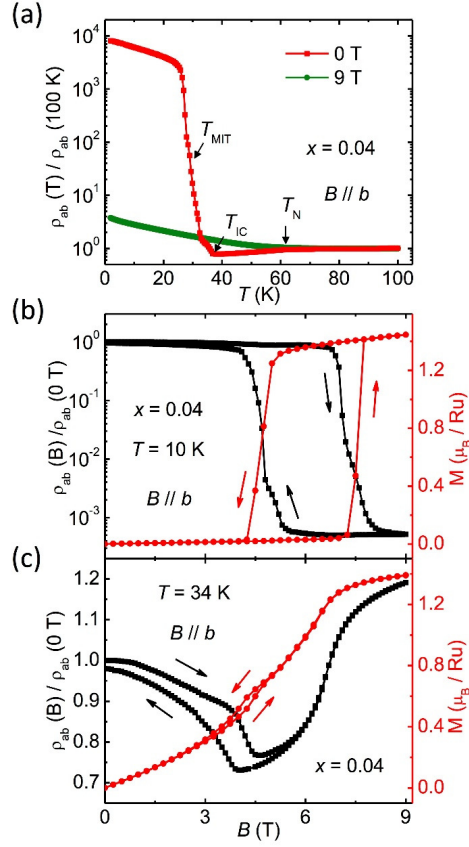


Figure 3.33: (a) Temperature dependence of the in-plane resistivity ρ_{ab} at $B = 0\text{ T}$ and 9 T , $B \parallel b$ axis. (b),(c) Field dependence of the in-plane resistivity ρ_{ab} and magnetization M at $T = 10\text{ K}$ and 34 K , $B \parallel b$ axis.

Figure 3.33(a) shows the temperature dependence of the in-plane resistivity ρ_{ab} of $\text{Ca}_3(\text{Ru}_{0.96}\text{Mn}_{0.04})_2\text{O}_7$ at $B = 0$ and 9 T applied along the b axis, respectively. In contrast to the zero-field data where a series of transitions have been observed, in a magnetic field of 9 T , the system displays a localized behavior throughout the entire temperature range measured, suggesting a dramatic change in the electronic structure. In addition, the field-induced IMT is accompanied by the magnetic transitions. Figure 3.33(b) and (c) show the isothermal magnetoresistance and magnetization as a function of magnetic field at $T = 10$ and 34 K , respectively. At $T = 10\text{ K}$, the Mott insulating ground state is suppressed by a magnetic field at $B_c^\uparrow = 7.2\text{ T}$ with a change in the resistivity by ~ 3 orders of magnitude. Concurrently, a large change in the magnetization is

observed, indicating a field-induced spin structure transition. This field-induced phase transition is of first order, which is manifested by the large hysteresis loops as the magnetic field increases and decreases. At $T = 34$ K where the zero-field state shows the coexistence of commensurate and incommensurate magnetic structures, the magnetic field can also drive a first-order magnetic transition, as shown in both magnetoresistance and magnetization measurements. However, a much smaller change in resistivity is observed upon applying the magnetic field, presumably related to the spin scattering associated with a magnetic structure transition, which is distinct from the 10 K data that arise from the change in the electronic structure.

In order to determine the spin structure of the field-induced state in $\text{Ca}_3(\text{Ru}_{0.96}\text{Mn}_{0.04})_2\text{O}_7$, we performed neutron diffraction measurements. Figure 3.34(a) and (b) show the rocking curve scans across the magnetic wave vectors $\mathbf{q} = (1\ 0\ 2)$ and $(0\ 0\ 1)$ at $T = 10$ K, $B = 0$ T and 8 T, respectively. One clearly sees that $(1\ 0\ 2)$ is suppressed completely at 8 T, while an alternative magnetic Bragg peak $(0\ 0\ 1)$ appears. Figure 3.34(c) and (d) show the intensity of $(1\ 0\ 2)$ and $(0\ 0\ 1)$ magnetic peaks as a function of magnetic field at $T = 10$ K. A field-induced magnetic structure transition is observed at $B_c^\uparrow = 7.3 \pm 0.1$ T. The large hysteresis loop observed when the magnetic field increases and decreases indicates the first-order nature of the field-induced spin structure transition, in agreement with both magnetoresistance and magnetization measurements. We have collected a series of magnetic Bragg peaks such as $(0\ 0\ 3)$, $(0\ 0\ 5)$ and $(2\ 0\ 1)$, etc. at $B = 8$ T, and performed representational analysis using FULLPROF [71]. The antiferromagnetic structure that best describes the neutron diffraction data is of AFM-a type, where the staggered magnetic moments are along the a axis, perpendicular to the applied magnetic field. In combination to the ferromagnetic component along the b axis revealed in the magnetization measurements, the resultant field-induced magnetic state is CAFM, which is a vector sum of AFM-a and a

ferromagnetic component ($\sim 1.4 \mu_B$ at $B = 8$ T, 10 K) along the b axis, similar to the field-induced state in the parent and Ti-doped compounds discussed in Appendix B. It is worth noting that above $B_c^\uparrow$, the intensity of (0 0 1) starts to decrease as the magnetic field increases further, which can be ascribed to the fact that CAFM transforms toward the fully spin polarized state (PM) with a decrease in the staggered antiferromagnetic moment.

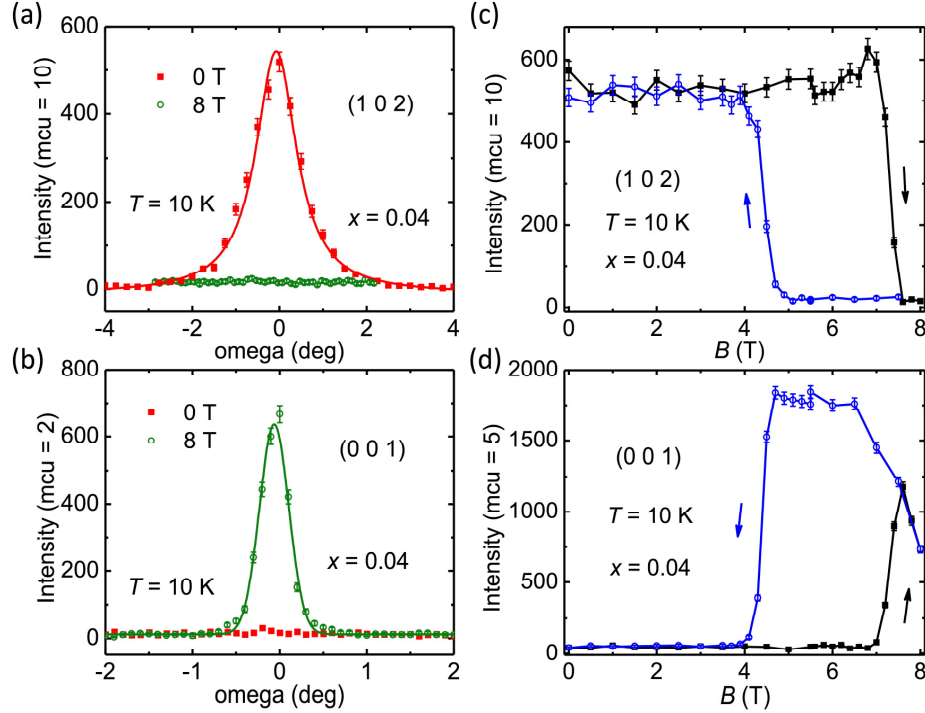


Figure 3.34: Rocking curve scans on $\text{Ca}_3(\text{Ru}_{0.96}\text{Mn}_{0.04})_2\text{O}_7$ across (1 0 2) and (0 0 1) at $B = 0$ T and 8 T, respectively, $T = 10$ K. (c),(d) The intensity of (1 0 2) and (0 0 1) as a function of magnetic field, $T = 10$ K.

We have also studied the field-induced magnetic transition of the incommensurate magnetic structures at $T_{\text{MIT}} < T < T_{\text{ICM}}$. Figure 3.35(a) and (b) show the scans along the $[1\ 0\ 0]$ direction across the magnetic wave vector $\mathbf{q} = (0\ 0\ 1)$ at $T = 34$ K. At zero field, the magnetic structure exhibits the coexistence of commensurate and incommensurate phases. However, at $B = 5$ T, the incommensurate peaks are suppressed, and the intensity of the commensurate peak becomes much stronger, indicating an incommensurate-to-commensurate magnetic transition. Similar

enhancements in the magnetic intensity are also observed at the wave vectors (0 0 3), (0 0 5) and (0 0 7), etc. Figure 3.35(c) and (d) show the field dependence of the magnetic intensity of (0 0 1) and (0.0245 0 1) at $T = 34$ K. The system undergoes an incommensurate-to-commensurate magnetic transition at $B_{c1}^\uparrow = 4.4 \pm 0.1$ T, where the (0.0245 0 1) peak is suppressed completely while the (0 0 1) peak increases then stays almost constant. This field-induced incommensurate-commensurate magnetic transition is also of first order in nature, as the hysteresis loops are clearly seen when the magnetic field increases and decreases. By performing an analysis similar to that at $T = 10$ K, we conclude that the field-induced magnetic state at $B_{c1}^\uparrow$ is CAFM as well. In addition, as the magnetic field increases further, the intensity of the (0 0 1) peak starts to decrease and finally disappears at $B_{c2}^\uparrow = 6.6$ T, which indicates that the AFM-a component of the CAFM state is completely suppressed and the system is in a fully spin polarized state (PM).

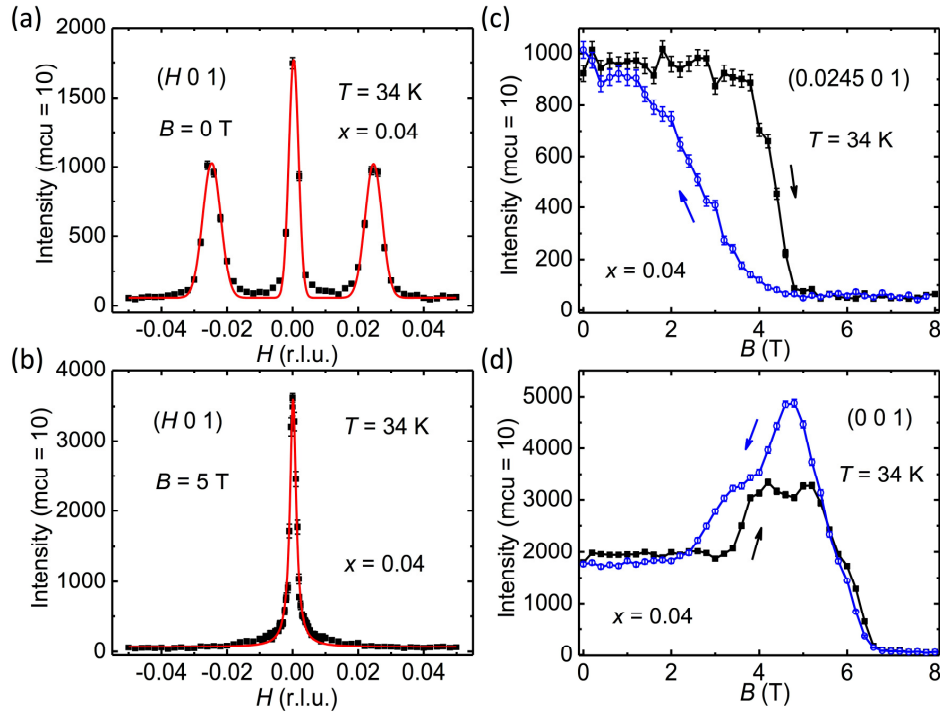


Figure 3.35: (a),(b) Scans on $\text{Ca}_3(\text{Ru}_{0.96}\text{Mn}_{0.04})_2\text{O}_7$ along the [1 0 0] direction across (0 0 1) at $B = 0$ T and 5 T, $T = 34$ K. (c),(d) The intensity of (0 0 1) and (0.0245 0 1) magnetic Bragg peaks as a function of magnetic field, $T = 34$ K.

The field-induced IMT of the G-AFM Mott insulating state is accompanied by a simultaneous change in the lattice parameters. As shown in Fig. 3.36(a), at $T = 10$ K the lattice parameter c increases at $B_c^\uparrow$ by nearly $\sim 1\%$, while the lattice parameter a remains unchanged across the transition. The magnetoelastic coupling is similar to that observed at zero field, where the Mott insulating state is accompanied by a flattening of the RuO_6 octahedra. On the contrary, no structural change is observed for the field-induced magnetic transition at $T = 34$ K, as shown in Fig. 3.36(b).

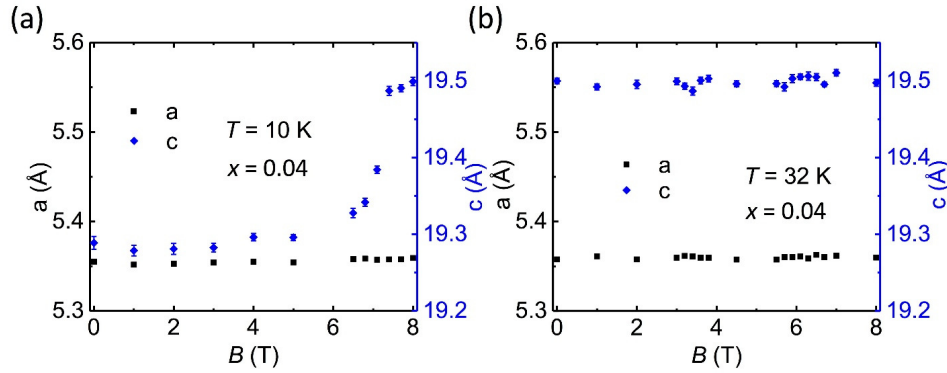


Figure 3.36: Lattice constants a and c of $\text{Ca}_3(\text{Ru}_{0.96}\text{Mn}_{0.04})_2\text{O}_7$ as a function of magnetic field at (a) $T = 10$ K and (b) $T = 32$ K.

3.6.4 Discussions

Very surprisingly, the effects of the magnetic Mn doping on $\text{Ca}_3\text{Ru}_2\text{O}_7$ resemble that of the nonmagnetic Ti substitution [99,100], but are in contrast to the magnetic Fe doping [123]. This suggests that these emergent states are related to the intrinsic instabilities of the Ru-O network and the role of $3d$ transition-metal dopants is to tip the balance between competing tendencies that already exist in this bilayer ruthenate system.

The scenarios proposed in the studies on Ti-doped $\text{Ca}_3\text{Ru}_2\text{O}_7$ are likely to be applicable to the Mn-doped compounds. The electron correlation, the strong coupling between spin and lattice

degrees of freedom, the flattening of the RuO_6 octahedra which is expected to change the orbital occupancy of the Ru t_{2g} levels, and the phase competition are the key ingredients to understand the emergence of the G-AFM Mott insulating state and the field-induced IMT in $\text{Ca}_3(\text{Ru}_{1-x}\text{Mn}_x)_2\text{O}_7$. The mechanism underlying the similarity in the doping effects of nonmagnetic Ti and magnetic Mn on $\text{Ca}_3\text{Ru}_2\text{O}_7$, which are significantly different from that of the other magnetic dopants Fe, is an intriguing but challenging question to investigate. In a recent work, J. Peng et al. [153] find that the MIT temperatures T_{MIT} of $\text{Ca}_3\text{Ru}_2\text{O}_7$ with different 3d transition-metal dopants are predominated by the structural parameter $c/\sqrt{ab}$ not only in the low-temperature ordered phase, but also in the high-temperature paramagnetic state. It is proposed that the magnetic and electronic states of 3d transition-metal doped $\text{Ca}_3\text{Ru}_2\text{O}_7$ are determined by lattice-orbital coupling, i.e. the G-AFM Mott insulating state can stabilize only below a critical value of this structural control parameter, where orbital polarization is expected based on first principles calculations. Therefore, due to the larger structural distortions induced by Ti and Mn dopants compared to that of the Fe dopant, Ti- and Mn-doped $\text{Ca}_3\text{Ru}_2\text{O}_7$ exhibit G-AFM Mott insulating state, whereas Fe-doped compound shows incommensurate magnetic structures resulting from the competition among DM interaction, exchange interactions and magnetic anisotropy. Furthermore, it has been suggested that the structural distortions caused by 3d transition-metal impurity is dominated by the electronic scattering rather than the difference in the ionic radius or the magnetic moments [153].

3.6.5 Summary

We have investigated the magnetic properties of the emergent phases in the bilayer ruthenate $\text{Ca}_3\text{Ru}_2\text{O}_7$ induced by Mn doping. The system shows an incommensurate magnetic structure for $x \leq 0.03$, where the ground state magnetic structure is the same as the parent compound. For $x \geq 0.04$, the ground state changes to a G-AFM Mott insulator. We have also investigated the magnetic-

field-induced phase transitions in $\text{Ca}_3(\text{Ru}_{0.96}\text{Mn}_{0.04})_2\text{O}_7$ that is positioned at the phase boundary of the $T - x$ phase diagram. Upon applying a magnetic field along the b axis, the G-AFM ground state transforms into CAFM through a first-order transition, together with a collapse of the Mott insulating state and drastic changes in the lattice constants. Our results unambiguously demonstrate the presence of competition among various states in this bilayer ruthenate system, which can be tuned by $3d$ transition-metal doping and external magnetic field.

3.7 Temperature- and field-driven spin reorientations in triple-layer ruthenate $\text{Sr}_4\text{Ru}_3\text{O}_{10}$

To date, compared to the intense efforts invested on the single-, double-layer and three-dimensional ruthenates ($n = 1, 2$ and ∞), there have been much fewer studies on the triple-layer ($n = 3$) compounds. $\text{Sr}_4\text{Ru}_3\text{O}_{10}$ crystallizes in an orthorhombic space group $Pbam$ [154], as shown in Fig. 3.37(a), which displays interesting but perplexing magnetic properties. From the magnetic susceptibility measurements, it has been reported that $\text{Sr}_4\text{Ru}_3\text{O}_{10}$ undergoes a paramagnetic-ferromagnetic transition at $T_c = 105$ K, below which the easy axis is along the c direction [154]. Intriguingly, while an additional transition has been found in the magnetic susceptibility at $T^* = 50$ K [154,155], no anomaly is revealed in the specific heat measurements [156]. Although several distinct scenarios have been proposed to account for the feature at T^* , its intrinsic character remains an open question. On the one hand, below T^* a canted antiferromagnetic structure with a ferromagnetic component along the c axis and an antiferromagnetic component in the ab plane has been proposed [155,157]. Nevertheless, no evidence of antiferromagnetism has been observed via neutron diffraction experiments [158,159]. On the other hand, previous neutron diffraction measurements have yielded contradictory results regarding the direction of the ferromagnetic moments in $\text{Sr}_4\text{Ru}_3\text{O}_{10}$ [158,159]. It is initially argued that the spins are aligned in the ab plane based on the observation of $(0\ 0\ L)$ -type magnetic Bragg peaks and no anomaly has been observed at T^* [158]. As a result, the feature at T^* in the magnetic susceptibility measurements is ascribed to a magnetic domain process [158]. In contrast, a distinct magnetic easy axis has been proposed more recently, where the magnetic moments are determined to be along the c axis since the $(0\ 0\ L)$ -type magnetic Bragg peaks are found to be absent. In addition, a kink-like feature has been reported in the temperature dependence of the Bragg reflection $(2\ 0\ 0)$ at T^* , which is also claimed

to be observed in all other reflections [159]. Therefore, the easy axis of the ferromagnetic moments and the nature of the anomaly at T^* of $\text{Sr}_4\text{Ru}_3\text{O}_{10}$ remain elusive.

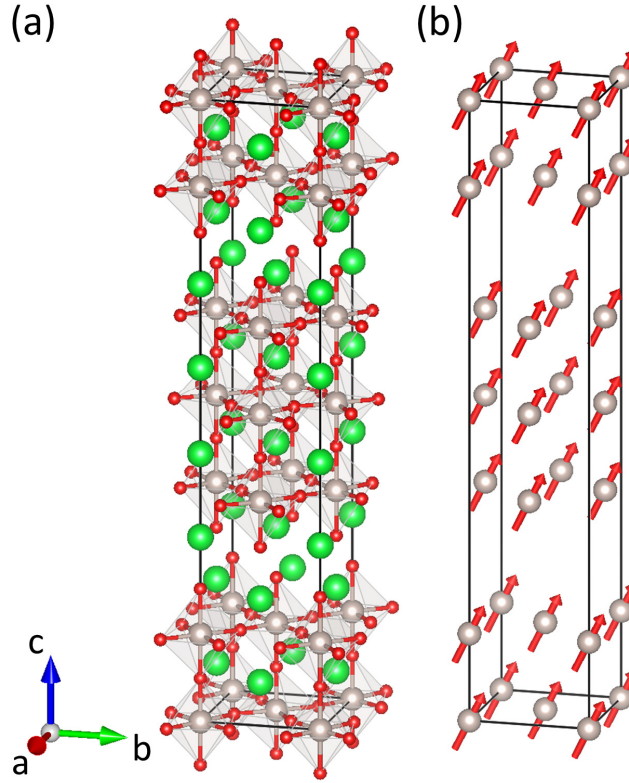


Figure 3.37: (a) The crystal structure of $\text{Sr}_4\text{Ru}_3\text{O}_{10}$. (b) The magnetic structure of $\text{Sr}_4\text{Ru}_3\text{O}_{10}$. Note that both moment size and spin direction cannot be uniquely determined due to the lack of enough Bragg peaks with reasonably good magnetic intensity.

Another intriguing property of $\text{Sr}_4\text{Ru}_3\text{O}_{10}$ is the field-induced metamagnetic transition. While a typical magnetic hysteresis loop of ferromagnets is observed as the magnetic field is applied along the c axis, a first-order metamagnetic transition is seen below T^* for the field applied in the ab plane [154,155]. Experimental signatures of the electronic phase separation during the phase transition have been observed [160]. Nevertheless, previous neutron diffraction studies reveal controversial features regarding this metamagnetic transition. Across the critical field, while no anomaly has been observed in the field dependence of the magnetic reflection $(0\ 0\ 8)$ in Ref. [158], a field-induced transition at the same wave vector is reported in Ref. [159]. In addition, it has been

revealed that the metamagnetic transition is accompanied by a change in the lattice, as evidenced in the Raman scattering [157], neutron diffraction [159] and magnetostriction studies [161], which suggests the presence of strong spin-lattice coupling in this system. To date, the nature and the origin of this metamagnetic transition are yet to be resolved.

In this section, we present a single-crystal neutron diffraction study on the magnetic order and the metamagnetic transition in $\text{Sr}_4\text{Ru}_3\text{O}_{10}$. We find that the material orders ferromagnetically at $T_c \sim 100$ K without any signature of antiferromagnetic components, in agreement with the previous studies [158,159]. However, the magnetic moments are found to possess both in-plane and out-of-plane components below T_c , in contrast to the previous neutron diffraction studies where the spins are proposed to align either in the ab plane [158] or along the c axis [159]. In addition, we have observed spin reorientations below $T^* \sim 50$ K, where the magnetic moments incline toward the out-of-plane direction. Furthermore, we show that while the magnetic moments are nearly along the c axis at $T = 1.5$ K, a magnetic field applied along the in-plane $[1 -1 0]$ direction gives rise to a spin reorientation at a critical field B_c , above which there exists a spin component perpendicular to the plane defined by the field direction and the c axis, in accordance to the metamagnetic transition. This observation is distinct from the previous studies, where the metamagnetic transition is ascribed to the magnetic domain processes [158] or the coexistence of zero-field c -axis component and the field-induced in-plane spin polarization [159]. Both temperature- and magnetic-field-driven spin reorientations are presumably ascribable to the change in the magnetocrystalline anisotropy that is strongly correlated with the RuO_6 octahedral distortion. Our results reconcile the inconsistency among previous neutron diffraction studies on the magnetic easy axis of $\text{Sr}_4\text{Ru}_3\text{O}_{10}$, resolve the puzzling character of the transition at T^* , and elucidate the nature of the field-induced metamagnetic transition.

3.7.1 Materials and methods

The single-crystal $\text{Sr}_4\text{Ru}_3\text{O}_{10}$ was grown by the Floating Zone method [162]. The lattice constants are $a = 5.5280 \text{ \AA}$, $b = 5.5260 \text{ \AA}$ and $c = 28.651 \text{ \AA}$. The phase and quality of the crystal have been verified by x -ray diffraction measurements. The magnetization as a function of both temperature and magnetic field has been measured using SQUID, and the results are in agreement with previous studies [154,155]. A very small amount of SrRuO_3 intergrowth has been revealed in the magnetic susceptibility measurements, which is easy to be separated in the neutron diffraction measurements due to its very different lattice parameter c ($c = 7.8446 \text{ \AA}$ in the orthorhombic unit cell). Zero-field and field-dependent neutron diffraction measurements were performed using the HB-3A four-circle diffractometer ($\lambda = 1.5426 \text{ \AA}$) and the HB-1A triple-axis spectrometer ($\lambda = 2.36 \text{ \AA}$), respectively, at HFIR in ORNL. At HB-3A, the sample was mounted on an aluminum stick and loaded into a closed-cycle Helium displacer. At HB-1A, the sample was oriented in the horizontal ($H H L$) scattering plane and loaded into a vertical-field cryomagnet such that the magnetic field was applied along the $[1 -1 0]$ direction. The Bragg reflections ($H K L$) were in the reciprocal lattice units $2\pi/a$, $2\pi/b$ and $2\pi/c$ of the orthorhombic space group $Pbam$ (No. 55) [154].

3.7.2 Temperature-driven spin reorientations at zero field

We start with the zero-field neutron diffraction data collected at the HB-3A four-circle diffractometer. Figure 3.38(a) and (b) present the rocking curves of the nuclear Bragg reflections $(0 0 2)$ and $(1 1 1)$ at $T = 8, 50$ and 100 K , respectively. The intensity of $(0 0 2)$ shows a non-monotonic behavior, which is significantly enhanced at 50 K compared to that measured at 8 K and 100 K . In contrast, the $(1 1 1)$ intensity becomes stronger with decreasing temperature. These observations suggest that there is magnetic intensity superimposed on the nuclear Bragg peaks. To further elucidate the non-monotonic temperature dependence of the magnetic intensity, Figure

3.38(c) and (d) present the peak intensity of (0 0 2) and (1 1 1) Bragg reflections as a function of temperature, respectively. Upon cooling, additional reflection intensity in both peaks emerges below 100 K. Similar enhancement has been observed in other nuclear Bragg peaks including (0 0 6) and (0 0 8), indicating the development of a ferromagnetic ordering below $T_c \sim 100$ K in line with the magnetic susceptibility measurements [154]. Consistent with Fig. 3.38(a), the intensity of the (0 0 L)-type magnetic reflections with $L = 2, 6$ and 8 , exhibits non-monotonic temperature dependence, with a maximum at $T^* \sim 50$ K that is reminiscent of the anomaly at T^* in the magnetic susceptibility data [154,155]. In accordance to Fig. 3.38(b), the magnetic intensity of (1 1 1) emerges at T_c and continues to increase below T^* . On the one hand, the observation of the (0 0 L)-type magnetic reflections in our study is in agreement with the previous neutron diffraction experiments reported in Ref. [158], but is different from that in Ref. [159] where they are found to be absent. On the other hand, we have revealed distinct temperature-dependent behaviors in the intensity of (0 0 L) and (1 1 1) in our experiment, which is in sharp contrast to the previous studies where either no anomaly was observed [158], or a kink feature was claimed to exist in the temperature dependence of all the reflections [159]. Note that the HB-3A diffractometer is equipped with a two-dimensional neutron detector, from which the change in the scattering angle 2θ of the diffracted neutrons at different temperatures is found too small to be resolved due to the instrumental resolution limitation. This is in agreement with a change in the lattice constants of only $\sim 0.04\%$ upon cooling observed in the previous studies [159]. Therefore, the variation in the peak intensity of these Bragg peaks cannot be ascribed to the structural change, but is magnetic in origin.

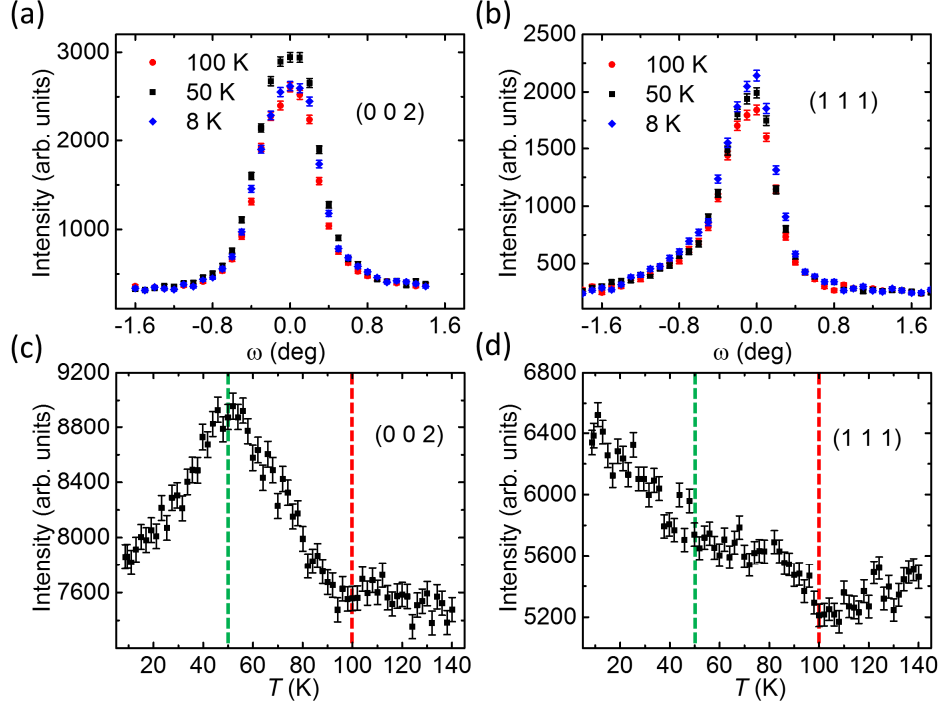


Figure 3.38: (a),(b) Rocking curve scans across (0 0 2) and (1 1 1) Bragg reflections at $T = 8, 50$ and 100 K, respectively. (c),(d) Temperature dependence of the peak intensity of (0 0 2) and (1 1 1) at $B = 0$ T. The red and green dashed lines denote T_c and T^* , respectively.

In order to explore the possible magnetic configurations in $\text{Sr}_4\text{Ru}_3\text{O}_{10}$, we carried out the magnetic representational analysis using the program SARAH [163]. The space group of the crystal structure is No. 55 *Pbam* and the propagation vector is $\mathbf{k} = (0\ 0\ 0)$. There are four inequivalent Ru atoms in a chemical unit cell which are located at Ru1 (0 0 0), Ru2 (0 0 0.1402), Ru3 (0.5 0 0.3598) and Ru4 (0.5 0 0.5). The analysis shows that an in-plane antiferromagnetic component would give rise to strong magnetic reflections at (1 0 0), (1 0 1) or (0 1 1), which, nevertheless, are all absent in our measurements. Therefore, the feature at T^* in the magnetic susceptibility cannot be ascribed to the formation of antiferromagnetic components in the *ab* plane that was claimed previously [155,157]. As a result, the only symmetry-allowed magnetic configuration in $\text{Sr}_4\text{Ru}_3\text{O}_{10}$ is the ferromagnetic structure with the magnetic moments either along the *c* axis or in the *ab* plane. Since neutrons couple to the magnetic moment perpendicular to the

momentum transfer $\mathbf{q}$, the observation of magnetic intensities at $(0\ 0\ L)$ with $L = 2, 6$ and 8 at $T^* < T < T_c$ suggests the development of a magnetic order with the spins aligned in the ab plane. This, combined with the magnetic susceptibility measurements which show an easy axis closer to the c axis, suggests that the ferromagnetic moments have both in-plane and out-of-plane components in this temperature regime. Note that at $T^* < T < T_c$, the intensity of $(0\ 0\ 2)$ increases more rapidly than that of $(1\ 1\ 1)$, implying that the magnetic moments incline toward the ab plane, though the easy axis is always closer to the c axis. Below T^* , the decrease in the intensity of the $(0\ 0\ L)$ -type magnetic peaks suggests that the in-plane ferromagnetic moment reduces, and the spins incline continuously toward the out-of-plane direction upon cooling. This speculation is supported by the observation of an increase in the intensity of the $(1\ 1\ 1)$ Bragg peak below T^* , as the direction of the $(1\ 1\ 1)$ wave vector is almost perpendicular to the c axis (note that $a^* \approx b^* \approx 1.137\ \text{\AA}^{-1}$, $c^* \approx 0.219\ \text{\AA}^{-1}$). We have collected the nuclear and magnetic Bragg peaks at 8 K, 50 K and 100 K, and attempted to perform Rietveld analysis using the program FULLPROF [71]. It is worth noting that the magnetic moments of the outer-layer Ru ions (Ru1 and Ru4) and the central-layer ones (Ru2 and Ru3) can be different, owing to the difference in the direction and magnitude of the RuO_6 octahedral rotation [154]. At $T = 8\ \text{K}$, due to the very weak intensity of the $(0\ 0\ L)$ peaks, the spins are nearly aligned along the c axis. Since only the $(1\ 1\ 1)$ peak is associated with this spin component, the magnitude of the magnetic moments of the outer- and central-layer Ru ions cannot be exclusively determined at this temperature. Similarly, more magnetic reflections are required in order to determine the moment sizes and the canting angles quantitatively at T^* . The schematic of the magnetic structure of $\text{Sr}_4\text{Ru}_3\text{O}_{10}$ at zero field is plotted in Fig. 3.37(b).

3.7.3 Field-driven spin reorientations

Next, we discuss the neutron diffraction measurements using the HB-1A triple-axis spectrometer with the magnetic field applied along the in-plane $[1\ -1\ 0]$ direction, where a first-order metamagnetic transition is observed in the magnetic susceptibility measurements [154]. Figure 3.39(a) and (b) display the peak intensity of the $(0\ 0\ 2)$ and $(1\ 1\ 1)$ Bragg peaks as a function of the magnetic field at $T = 1.5\text{ K}$. It is remarkable that the intensity of $(0\ 0\ 2)$ increases significantly at $B_c = 1.5\text{ T}$, whereas that of $(1\ 1\ 1)$ decreases. These observations are distinct from the previous study where no anomaly has been observed in the intensity of the magnetic reflections as a function of magnetic field [158]. It is worth noting that in another neutron diffraction study, a similar trend to $(0\ 0\ 2)$ shown in Fig. 3.39(a) has been observed in the field dependence of the intensity of $(0\ 0\ 8)$ [159]. However, a slight reduction in the scattering intensity of the $(H\ K\ 0)$ reflections was claimed and suggested to be associated with the ferromagnetic moment along the c axis, which led the authors to argue that the field-induced transition is due to the coexistence of the initial zero-field ferromagnetic order with a field-induced in-plane spin polarization [159]. If this were the case, one would expect a slight increase in the magnetic intensity of the $(1\ 1\ 1)$ reflection above the critical field B_c , as $(1\ 1\ 1)$ is perpendicular to the $[1\ -1\ 0]$ direction but is about 82.2° with respect to the $[0\ 0\ 1]$ direction. This is not in line with our observation of a field-induced decrease in the intensity of the $(1\ 1\ 1)$ reflection, which suggests that the applied magnetic field gives rise to a spin component perpendicular to the plane defined by the field direction and the c axis. This is supported by a recent study which, by measuring the magnetic moment vectors, reports the existence of a magnetic moment component that is perpendicular to the field rotation plane [164]. Note that the slight difference in the critical field compared with that in the magnetic susceptibility data may arise from the different applied field directions in the ab plane. To further support the

variation of the magnetic intensity below and above B_c , Figure 3.39(c) and (d) plot the θ - 2θ scans over the (0 0 2) and (1 1 1) Bragg peaks measured at $T = 1.5$ K with $B = 0$ and 3.5 T, respectively. We can clearly see that above B_c the intensity of the (0 0 2) peak becomes enhanced while that of the (1 1 1) peak is suppressed. Furthermore, there is no noticeable change in the 2θ values of both peak positions across the field-induced magnetic transition, which is consistent with the previous study that the lattice constants a and c change only by $\sim 0.04\%$ at the critical field that is beyond the instrumental resolution in our study [159]. For comparison, in the inset of Fig. 3.39(d), we present the θ - 2θ scan of a high- $|\mathbf{Q}|$ nuclear peak (0 0 16), where the magnetic intensity is expected to be very weak due to the small magnetic form factor. The very little difference in the intensity of (0 0 16) at $B = 0$ and 3.5 T further substantiates that the field-induced intensity variation of the low- $|\mathbf{Q}|$ peaks (0 0 2) and (1 1 1) is magnetic in origin, rather than due to a structural change.

Figure 3.40(a) and (b) show the θ - 2θ scans of the (0 0 2) and (1 1 1) Bragg peaks measured at $T = 50$ K with $B = 0$ and 3.5 T, respectively. The intensity of both (1 1 1) and (0 0 2) displays negligible changes upon applying the magnetic field. These results, combined with the features observed at low temperature shown in Figure 3.39, are in agreement with the magnetic susceptibility measurements that the metamagnetic transition only occurs below $T^* \sim 50$ K.

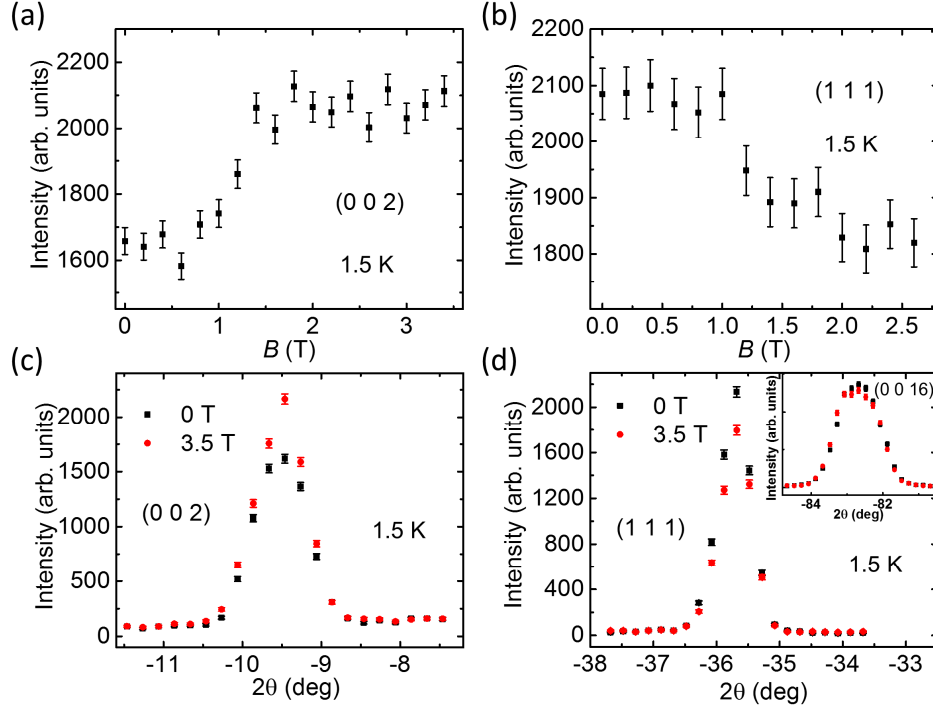


Figure 3.39: (a),(b) Field dependence of the peak intensity of (0 0 2) and (1 1 1) at $T = 1.5$ K. (c),(d) θ - 2θ scans across (0 0 2) and (1 1 1) at $B = 0$ and 3.5 T, $T = 1.5$ K. Inset shows the θ - 2θ scan over (0 0 16) at $B = 0$ and 3.5 T, $T = 1.5$ K.

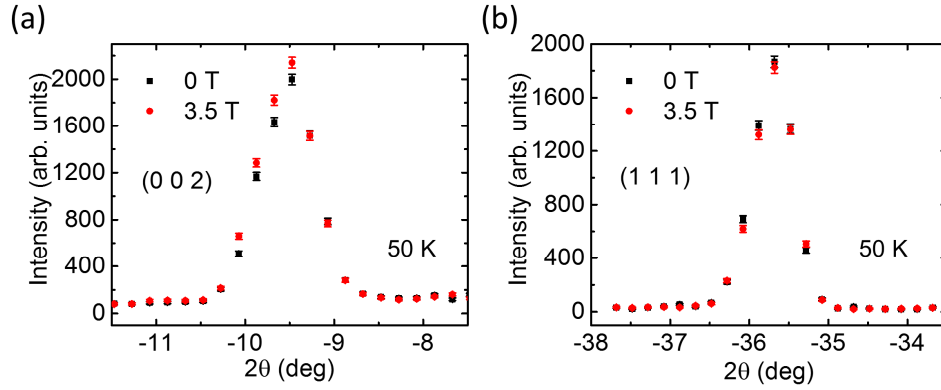


Figure 3.40: θ - 2θ scans across (0 0 2) and (1 1 1) at $B = 0$ and 3.5 T, $T = 50$ K.

3.7.4 Discussions

The observation of a spin reorientation at T^* in $\text{Sr}_4\text{Ru}_3\text{O}_{10}$ at zero field has elucidated the long-standing puzzle on the anomaly in the magnetic susceptibility measurements [154]. This spin

reorientation suggests a change in the magnetic easy axis as a function of temperature. This feature is reminiscent of the widely studied spin reorientation transitions in rare earth magnets and orthoferrites [165], which are ascribed to the change in the magnetic anisotropy constants as a function of external parameters, such as temperature, magnetic field and pressure, etc [166]. Our finding raises an intriguing question: What is the underlying mechanism responsible for the change in the magnetic easy axis in $\text{Sr}_4\text{Ru}_3\text{O}_{10}$? It is known that in Ruddlesden-Popper type ruthenates, the magnetic anisotropy is strongly coupled to the structural distortions of the RuO_6 octahedra. For instance, the magnetocrystalline anisotropy has been extensively investigated in SrRuO_3 thin films, where the magnetic anisotropy and the saturated magnetic moments can be readily tuned by controlling the RuO_6 octahedral distortion via the epitaxial strain imposed by substrates [167]. Considering the fact that the ferromagnetic state with $T_c \sim 100$ K in the triple-layer ($n = 3$) $\text{Sr}_4\text{Ru}_3\text{O}_{10}$ bridges the physics between the double-layer ($n = 2$) $\text{Sr}_3\text{Ru}_2\text{O}_7$ (Fermi liquid, ferromagnetic instability) [78] and the three-dimensional ($n = \infty$) SrRuO_3 (ferromagnetic, $T_c = 160$ K) [168], the change in the magnetocrystalline anisotropy in $\text{Sr}_4\text{Ru}_3\text{O}_{10}$ across T^* may arise from the corresponding changes in the lattice structures. Indeed, anomalies in the lattice constants with c expanding while a contracting below T^* at zero field have been observed previously [159,161]. These changes in lattice parameters are expected to alter the occupancy of the Ru t_{2g} orbitals in this multiband system, which consequently affects the magnetic anisotropy through spin-orbit coupling [169].

The nature of the in-plane field-induced metamagnetic transition in $\text{Sr}_4\text{Ru}_3\text{O}_{10}$ below T^* , which has been an unresolved puzzle, can now be readily understood. It is also due to a spin reorientation where the magnetic moments reorient from the nearly c axis toward the ab plane. Intriguingly, we find that there exists a magnetic moment component perpendicular to the plane defined by the field

direction and the c axis above the critical field, which is consistent with the observation of a recent study where it has been ascribed to the Dzyaloshinskii-Moriya interaction assuming that the easy axis is along the c direction [164]. On the other hand, it is worth noting that across the field-induced metamagnetic transition below T^* the lattice parameter a expands while c shrinks [159], a trend which is opposite to the lattice change observed upon cooling through T^* at zero field discussed above [159,161]. This suggests that the magnetic anisotropy is altered above the critical field due to strong spin-lattice coupling, which needs to be taken into account in the future theoretical modeling.

3.7.5 Summary

The magnetic structure and the metamagnetic transition in the triple-layer ruthenate $\text{Sr}_4\text{Ru}_3\text{O}_{10}$ ($n = 3$) are revisited by neutron diffraction measurements. The magnetic order below $T_c \sim 100$ K is found to be ferromagnetic with both in-plane and out-of-plane spin components, and the ferromagnetic moments evolve toward the c axis below $T^* \sim 50$ K. These findings elucidate the long-standing puzzle on the nature of the magnetic transition at T^* in $\text{Sr}_4\text{Ru}_3\text{O}_{10}$. Below T^* , in a magnetic field applied along the in-plane $[1 -1 0]$ direction, the ferromagnetic moments undergo a spin reorientation from the c axis toward the ab plane with a spin component perpendicular to the plane defined by the magnetic field direction and the c axis. Both temperature- and field-induced spin reorientations can be attributed to a change in the magnetocrystalline anisotropy due to the change in the RuO_6 octahedral distortion.

Chapter 4

Neutron scattering studies on inverse-trirutile chromates

4.1 Introduction and motivation

Inverse-trirutile compounds $A_2^{3+}B_2^{6+}O_6$ ($A = \text{Ga, V, Cr, Mn and Fe}$; $B = \text{Te, W}$) crystallize in a tetragonal structure characterized by a tripling of the rutile unit cell along the c axis. The crystal structure is composed of chains of edge-sharing AO_6 octahedra separated by a BO_6 octahedron. The materials of interest in this chapter are the chromates Cr_2MO_6 ($M = \text{Te, W and Mo}$). The crystal and magnetic structures of Cr_2TeO_6 and Cr_2WO_6 were first reported in the late 1960s, as sketched in Fig. 4.1(a) and (b) [170]. The nearest-neighbor Cr^{3+} ions with $S = 3/2$, separated by a distance of $\sim 3 \text{ \AA}$, are coupled antiferromagnetically ($J_1 > 0$) which is much stronger compared to the next-nearest-neighbor interaction J_2 ($\sim 3.8 \text{ \AA}$). Thus, the two nearest-neighbor Cr^{3+} spins are expected to form a $S = 3/2$ spin dimer, with the dominant exchange interactions between Cr^{3+} spins illustrated in Fig. 4.1(c). Both compounds exhibit long-range antiferromagnetic orders with the Neel temperature $T_N = 93 \text{ K}$ for Cr_2TeO_6 and $T_N = 45 \text{ K}$ for Cr_2WO_6 , respectively [171].

Interestingly, even though the lattice parameters ($a = b = 4.545 \text{ \AA}$ and $c = 8.995 \text{ \AA}$ for Cr_2TeO_6 ; $a = b = 4.583 \text{ \AA}$ and $c = 8.853 \text{ \AA}$ for Cr_2WO_6), bond lengths and bond angles are very close in these two materials, their ground state magnetic structure are very distinct [170]. The inter-dimer interaction in Cr_2TeO_6 is antiferromagnetic ($J_2 > 0$), whereas that in Cr_2WO_6 is ferromagnetic ($J_2 < 0$). It is important to emphasize that the difference in the inter-dimer superexchange interaction J_2 , which is mediated by the intervening oxygen ions, cannot be explained by the Goodenough-Kanamori rules based on the symmetry consideration of the occupied electron orbitals [172,173]. Thus, understanding the nature of the inter-dimer exchange interactions in these

isostructural inverse-trirutile compounds is of fundamental importance to elucidate the origin of different types of magnetic orderings observed.

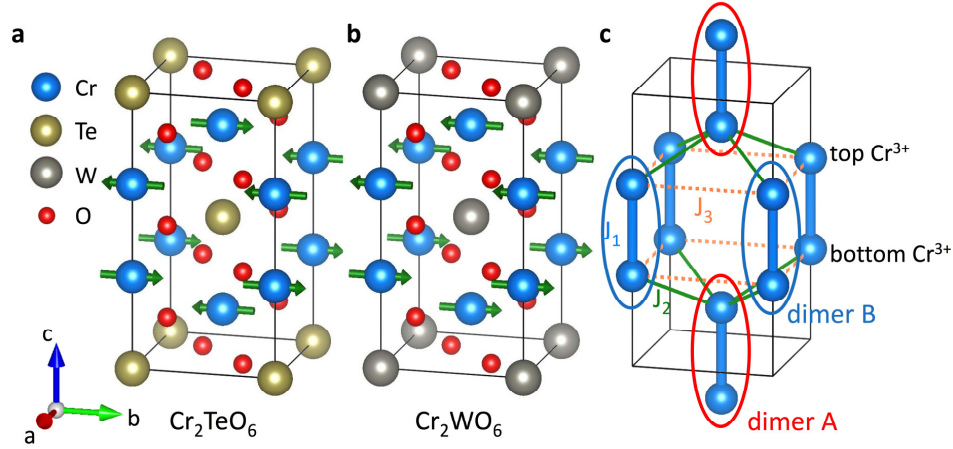


Figure 4.1: Schematics of the crystal and magnetic structures of (a) Cr_2TeO_6 and (b) Cr_2WO_6 . (c) Dominant exchange interactions between Cr^{3+} ions. The black line represents a unit cell. There are two dimer sites (A and B) in a unit cell. Each dimer consists of two spins at the top and bottom sides strongly coupled by an antiferromagnetic exchange interaction ($J_1 > 0$). The dimers interact with each other by inter-dimer interactions (J_2 and J_3); J_2 connects different dimers (A-B) and J_3 connects the same dimer sites (A-A; B-B). The magnetic structure in the ordered phase indicates that $J_3 < 0$ (ferromagnetic) in both Cr_2WO_6 and Cr_2TeO_6 , while J_2 is ferromagnetic ($J_2 < 0$) in Cr_2WO_6 and antiferromagnetic ($J_2 > 0$) in Cr_2TeO_6 , respectively. We find that $J_1 \gg |J_2|, |J_3|$.

The magnetic excitations of the inverse-trirutile compounds are also of particular interest. For classical long-range ordered spin systems, the magnetic excitations are generally well described by the linear spin wave (LSW) theory, which gives rise to transverse Nambu-Goldstone modes arising from the phase fluctuations of the order parameter. Nevertheless, for spin dimer systems, the LSW theory does not always work well. With a dominant antiferromagnetic intra-dimer exchange interaction, the system forms a singlet ground state ($S_{tot} = 0$) with a gapped triplet first excited state ($S_{tot} = 1$). As the inter-dimer interactions become stronger, it undergoes a phase transition from the quantum disordered state to a long-range ordered state. Such a long-range magnetic order can be induced via applying pressure to enhance the inter-dimer interactions, or via applying magnetic field to split the spin-triplet state by the Zeeman term in the Heisenberg

Hamiltonian. Intriguingly, in the ordered phase close to the quantum critical point (QCP), in addition to the gapless transverse Goldstone modes, the longitudinal fluctuations in the magnitude of the sublattice magnetization are expected to give rise to Higgs amplitude modes, which are in analogy to Higgs bosons in high energy physics [174,175]. However, to date, the experimental realizations and observations of Higgs amplitude modes in quantum spin systems are rather rare, particularly limited to quasi-one-dimensional $S = 1$ spin chains [176-178], two-dimensional coupled $S = 1/2$ two-leg spin ladders [179] and spin dimer systems with $S = 1/2$ [180-182]. This is in part because it is rare to find spin systems with the ground state close to a QCP and excitations within an appropriate energy range that is approachable using spectroscopic probes, and in part because the Higgs amplitude modes have a finite life time, decaying into a pair of transverse Goldstone modes which makes the observation difficult [183-185].

In this chapter, we explore the nature of the exchange interactions as well as the magnetic excitations of the inverse-trirutile chromates. In Sec. 4.2, we show that the inter-dimer interactions in $\text{Cr}_2(\text{Te}_{1-x}\text{W}_x)\text{O}_6$ can be tuned from antiferromagnetic to ferromagnetic via mixing the nonmagnetic Te and W ions. Our density functional theory (DFT) calculations suggest that the hybridization between the W $5d$ and O $2p$ orbitals plays an essential role in the observed ferromagnetic inter-dimer interactions in Cr_2WO_6 . To substantiate this idea, in Sec. 4.3 we investigate the magnetic and electronic structures of another isostructural inverse-trirutile Cr_2MoO_6 , and we find that the orbital hybridization between Mo $4d$ and O $2p$ indeed leads to a ferromagnetic inter-dimer coupling. Finally, in Sec. 4.4, we present the observation and explanation of Higgs amplitude modes in the magnetic excitation spectra of Cr_2TeO_6 and Cr_2WO_6 via inelastic neutron scattering and extended spin wave (ESW) theory calculations.

4.2 Tuning the exchange interaction in $\text{Cr}_2(\text{Te,W})\text{O}_6$ via orbital hybridization

As soon as the magnetic structures of Cr_2TeO_6 and Cr_2WO_6 are determined, it is pointed out that the magnetic coupling in these materials is strongly influenced by the nonmagnetic Te and W ions [173]. The implications of these observations are remarkable: one may tune the inter-dimer exchange interactions in a spin dimer system without introducing severe structural distortions or adding additional charge carriers. In this section, we present the magnetic phase diagram and the electronic structure of $\text{Cr}_2(\text{Te}_{1-x}\text{W}_x)\text{O}_6$ system ($0 < x < 1$) obtained via neutron powder diffraction measurements and first principles calculations, respectively. We observe a crossover in the sign of the inter-dimer exchange interaction at $x_c \sim 0.7$, where both the transition temperature T_N and the sublattice magnetic moment M_s reach the minimum values. Our *ab initio* electronic structure calculations show that the presence of the low-lying W 5*d* states and their hybridization with the O *p* states play an important role in the exchange interaction between Cr 3*d* moments. However, a quantum phase transition to the quantum disordered spin-singlet state cannot be achieved by the chemical substitution of Te and W.

4.2.1 Materials and methods

Polycrystalline samples of $\text{Cr}_2(\text{Te}_{1-x}\text{W}_x)\text{O}_6$ with various x values were synthesized using the solid-state chemistry reaction method. The mixtures of Cr_2O_3 , TeO_2 and WO_3 were grounded together and annealed in air around $700 \sim 1000$ °C for 40 hours. The magnetization was measured using the Superconducting Quantum Interference Device (SQUID) magnetometer and the specific heat was measured using PPMS. Neutron powder diffraction measurements on each sample of ~ 4 grams were performed using the HB-2A neutron powder diffractometer at HFIR in ORNL. The

data were taken with the incident neutron wavelength $\lambda = 2.41 \text{ \AA}$ using the collimation of 12'-open-6'.

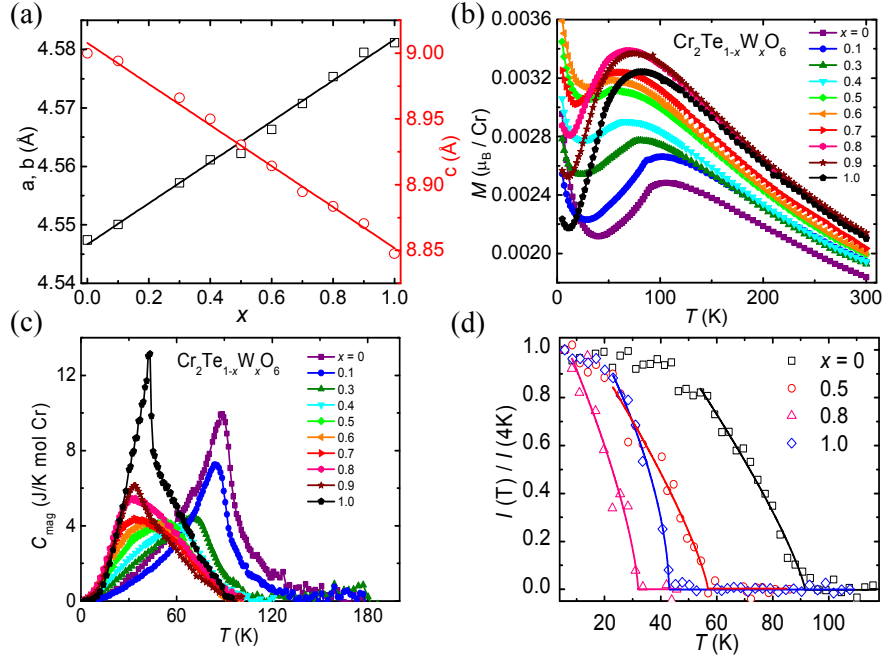


Figure 4.2: (a) x dependence of lattice parameters measured at $T = 4 \text{ K}$. (b),(c) Temperature dependence of magnetic susceptibility and magnetic specific heat, respectively. (d) Normalized neutron intensity of order parameters, (1 0 1) for $x = 0, 0.5$ and (0 0 1) for $x = 0.8, 1$, as a function of temperature. Solid lines are guides to the eye.

4.2.2 Magnetic susceptibility, specific heat and powder neutron diffraction

Figure 4.2(a) presents the lattice parameters at $T = 4 \text{ K}$ for $\text{Cr}_2(\text{Te}_{1-x}\text{W}_x)\text{O}_6$, which are obtained by refining the neutron powder diffraction data using FULLPROF [71]. The in-plane lattice expands while the c axis contracts slightly with increasing W concentration. The linear relationship of a and c as a function of x suggests a homogenous solid solution of the Te and W mixture. The temperature dependence of the magnetic susceptibility measured with an applied field $H = 3000 \text{ Oe}$ is shown in Fig. 4.2(b). There are two noteworthy features: (i) All the samples display a broad peak with the peak position T_p evolving non-monotonically with x . (ii) As to be shown later, the antiferromagnetic transition temperature T_N of these compounds is smaller than the corresponding

T_p , implying the development of strong low-dimensional correlations prior to forming the three-dimensional long-range magnetic order. The increase in the magnetic susceptibility at low temperature presumably originates from the paramagnetic impurities.

The non-monotonic dependence of T_N on x is corroborated by the temperature dependence of the magnetic specific heat shown in Fig. 4.2(c). The magnetic specific heat is obtained by subtracting the phonon contribution from the total heat capacity, using the scaled specific heat of an isostructural nonmagnetic compound Ga_2TeO_6 . Compared with the relatively sharp drop in the heat capacity at $T > T_N$ in both end members, the magnetic heat capacity of $\text{Cr}_2(\text{Te}_{1-x}\text{W}_x)\text{O}_6$ with nonzero x , particularly for $0.3 \leq x \leq 0.8$, exhibits broad peaks reminiscent of a spin-glass-like transition. However, no difference is found in the temperature dependence of the DC magnetic susceptibility measured under ZFC and FC conditions. In addition, the AC magnetic susceptibility measurements reveal nearly frequency-independent ($f = 10 \sim 10\text{kHz}$) signal even for $x = 0.5$ at which the compound shows the strongest chemical site disorder. This excludes the occurrence of a spin-glass transition. Instead, all the compounds display long-range antiferromagnetic orders as revealed by the neutron powder diffraction measurements discussed next. On the other hand, the integrated magnetic entropy is in the range of $4.43 \sim 9.53 \text{ J / (K mol Cr)}$, much smaller than the theoretical value ($11.5 \text{ J / (K mol Cr)}$) for Cr^{3+} ions with $S = 3/2$. Thus, the broadening of the magnetic heat capacity suggests that in $\text{Cr}_2(\text{Te}_{1-x}\text{W}_x)\text{O}_6$ the low-temperature long-range ordered antiferromagnetic state coexists with strong magnetic fluctuations.

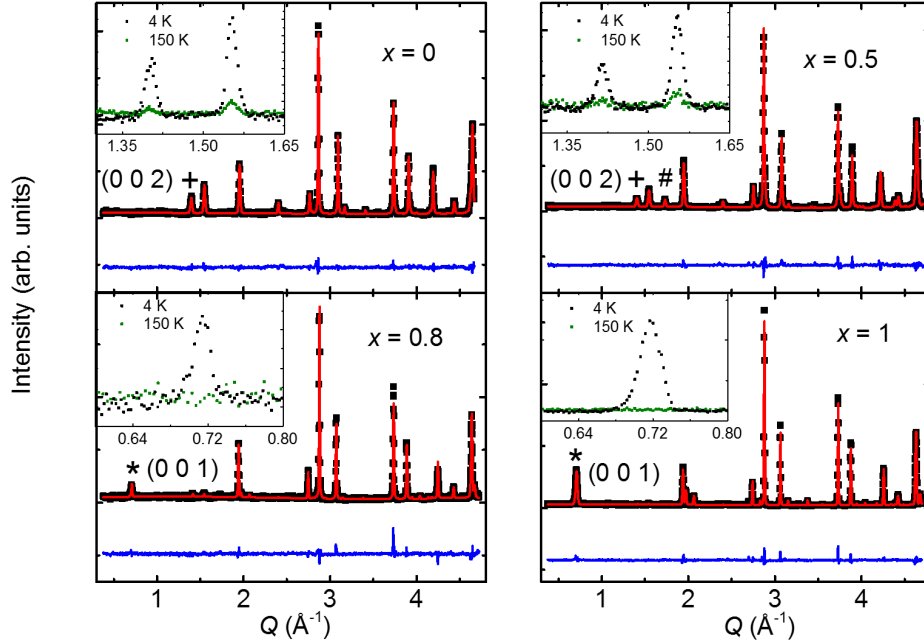


Figure 4.3: Neutron powder diffraction measurements with $x = 0, 0.5, 0.8$ and 1.0 at $T = 4$ K. Black symbols are the experimental data, red curves for fits and the difference between these two are represented by the blue curves. For $x = 0.5$, there is a minor impurity phase Cr_2O_3 ($< 1\%$) as denoted by #. Symbols of + and * denote the magnetic Bragg peaks for AFM-I and AFM-II, respectively. Insets show the expanded view of the low-angle magnetic Bragg peaks at $T = 4$ K (black) and 150 K (dark green).

Some representative neutron powder diffraction data for $x = 0, 0.5, 0.8$ and 1.0 measured at $T = 4$ K (and 150 K shown in the insets) are shown in Fig. 4.3. For $x = 0$ and 0.5 , the magnetic Bragg peaks show up at $\mathbf{q} = (0\ 0\ 2)$, and the refined spin structure is with antiferromagnetic inter-dimer exchange interaction (AFM-I), as shown in Fig. 4.1(a); For $x = 0.8$ and 1 , the magnetic Bragg peaks occur at $\mathbf{q} = (0\ 0\ 1)$, and the corresponding magnetic structure is with ferromagnetic inter-dimer interaction (AFM-II), as shown in Fig. 4.1(b). It is noteworthy that the FWHM of the magnetic Bragg peaks of all the samples is determined by the instrumental resolution according to the Rietveld refinement, confirming the existence of a long-range magnetic order at low temperature. Temperature dependence of the order parameters of these four samples is plotted in

Fig. 4.2(d), which shows a non-monotonic dependence of T_N on x , as discussed previously, with T_N for $x = 0.8$ smaller than the others.

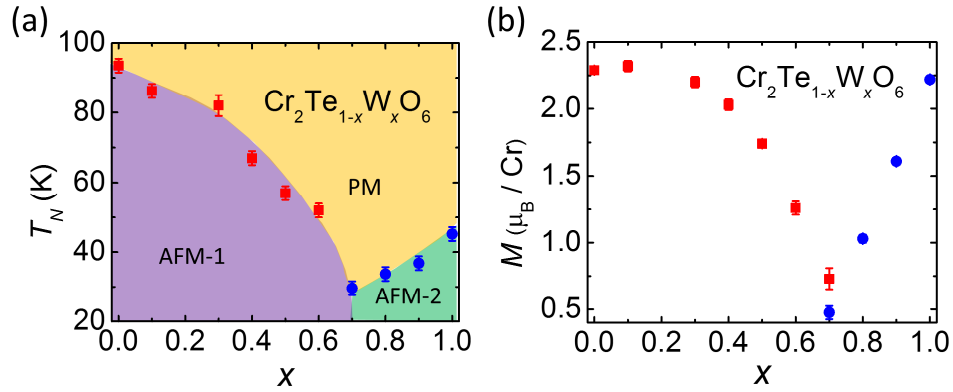


Figure 4.4: (a) $T_N - x$ phase diagram of $\text{Cr}_2(\text{Te}_{1-x}\text{W}_x)\text{O}_6$. PM represents the paramagnetic phase. (b) Sublattice magnetization as a function of x obtained from neutron powder diffraction measurements.

The $T_N - x$ phase diagram of $\text{Cr}_2(\text{Te}_{1-x}\text{W}_x)\text{O}_6$ is shown in Fig. 4.4(a). Interestingly, the system displays a crossover of the magnetic state at $x_c \sim 0.7$. The compounds with $x < 0.7$ exhibit an AFM-I type magnetic structure, whereas those with $x > 0.7$ show an AFM-II type magnetic structure. Accordingly, T_N varies non-monotonically as a function of x and reaches the minimum value ($T_N \sim 29.6$ K) at x_c . At the crossover point ($x_c \sim 0.7$), both AFM-I and AFM-II types of magnetic structures coexist, as shown in Fig. 4.5. Intriguingly, the sublattice magnetization M_s of $\text{Cr}_2(\text{Te}_{1-x}\text{W}_x)\text{O}_6$ obtained from the data refinement at $T = 4$ K also displays a non-monotonic dependence on x and reaches a minimum at x_c , as shown in Fig. 4.4(b). All M_s values are smaller than the expected value $3 \mu_B$ for fully localized Cr^{3+} ions (with negligible SOC).

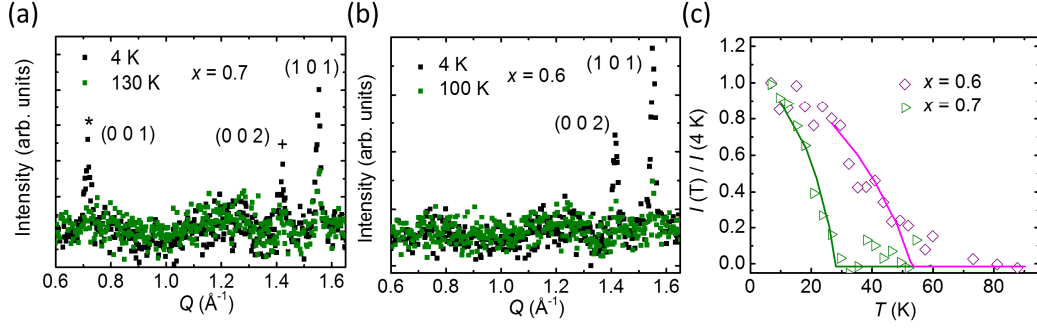


Figure 4.5: (a),(b) Expanded view of low-angle neutron powder diffraction data of $\text{Cr}_2(\text{Te}_{1-x}\text{W}_x)\text{O}_6$ with $x = 0.6$ and 0.7 . Both $(0\ 0\ 1)$, $(0\ 0\ 2)$ and $(1\ 0\ 1)$ magnetic Bragg peaks are observed at $T = 4$ K for the $x = 0.7$ sample indicating the coexistence of AFM-I and AFM-II, while only $(0\ 0\ 2)$ and $(1\ 0\ 1)$ appear for the $x = 0.6$ sample corresponding to AFM-I. (c) Temperature dependence of the $(1\ 0\ 1)$ magnetic Bragg peak of these two samples.

These experimental observations bring out several interesting questions: (i) What are the underlying mechanisms that determine the magnetic ground states of the end members? Because of very similar crystal structures and lattice parameters of Cr_2TeO_6 and Cr_2WO_6 , the difference in their magnetic structures cannot be explained simply by the Goodenough-Kanamori rules based on superexchange interactions. Thus, one has to understand the differences in the electronic structures of these materials. (ii) Why do both T_N and M_s depend non-monotonically on x and display the minimum values at $x_c \sim 0.7$?

4.2.3 Density functional theory calculations

In order to understand the ground state magnetic structures and the nature of the intra- and inter-dimer exchange interactions, we have carried out DFT calculations within the generalized gradient approximation (GGA) and GGA+ U [186] as implemented in the Vienna *ab initio* simulation package (VASP) [186,187,75], using the projector-augmented wave method [188,74] and Perdew-Burke-Ernzerhof exchange-correlation functional [73] in collaboration with Dr. S. D. Mahanti and Dr. D. Do in Michigan State University. We have chosen four different long-range ordered magnetic states denoted as A-B (AFM-AFM = AFM-I, AFM-FM = AFM-II, FM-AFM

and FM-FM), where A refers to intra-dimer and B refers to inter-dimer magnetic coupling. In all the calculations, the structural parameters and ionic positions are allowed to relax. The plane-wave energy cutoff and the total energy accuracy are set as 400 eV and 10^{-3} eV, respectively. To sample the Brillouin zone, we use the Monkhorst-Pack schemes with the k -mesh of $14 \times 14 \times 7$ for self-consistent calculations and $20 \times 20 \times 10$ to get the density of states (DOS).

Table 4.1: (top) Total energy (eV/unit cell) of different [intra]-[inter] dimer magnetic configurations. (bottom) Calculated and experimental values of intra- (J_1) and inter- (J_2) dimer exchange parameters as in the model proposed by Drillon et al [189] using GGA.

Configuration		AFM-AFM	AFM-FM	FM-AFM	FM-FM
GGA	Cr ₂ TeO ₆	-131.711	-131.547	-131.634	-131.411
	Cr ₂ WO ₆	-159.930	-160.002	-159.854	-159.815
GGA+ U , $U=4$	Cr ₂ TeO ₆	-122.603	-122.572	-122.583	-122.561
	Cr ₂ WO ₆	-150.714	-150.768	-150.701	-150.750

Compound		Cr ₂ TeO ₆		Cr ₂ WO ₆	
Parameter		J_1 (meV)	J_2 (meV)	J_1 (meV)	J_2 (meV)
Theo.	GGA	-4.3	-2.3	-10.4	1.0
	GGA+ U , $U=4$ eV	-1.12	-0.46	-1.0	0.75
Ref. [189]		-2.9	-0.4	-3.8	0.12

In Table 4.1 (top), we give the GGA energies (per magnetic unit cell containing four Cr atoms). The ground state is AFM-AFM (AFM-I) for Cr₂TeO₆ and AFM-FM (AFM-II) for Cr₂WO₆, in agreement with the neutron diffraction results. The magnetic moments are nearly the same for all four Cr atoms and lie in the range of $2.6 \sim 2.8 \mu_B$, lower than $3.0 \mu_B$ for the Cr³⁺ spin, indicating the hybridization between Cr d and O p , Te s and W d states. Since GGA generally does not adequately describe the d electrons in transition-metal atoms, we have also done GGA+ U calculations [190,191]. In the same table, we give the energies for $U = 4$ eV (this incorporates both intra-site Coulomb repulsion and exchange through a single parameter [186]). The lowest energy states are consistent with those obtained in the GGA calculations. The major effect of U is to

reduce the splitting between the ground state and the excited states, indicating a reduction in the strength of the effective exchange coupling between the Cr moments. At the same time, the magnetic moments of Cr ions increase to $\sim 3.0 \mu_B$.

To understand the nature of the exchange couplings between different Cr moments, we look at the geometry and local coordination of the intra- and inter-dimer Cr^{3+} pairs. The distance between the intra-dimer Cr atoms (Cr1 and Cr3 in Fig. 4.6) is $\sim 3 \text{ \AA}$, whereas that between the inter-dimer Cr atoms (Cr1 and Cr2, or Cr3 and Cr4 in Fig. 4.6) is $\sim 3.6 \text{ \AA}$. The exchange interaction between Cr1 and Cr3 is dominated by the Anderson antiferromagnetic (A-AFM) kinetic exchange [192] ($\sim 2t^2/U$ in the Hubbard model representation where t is the hopping between the d orbitals of Cr and U is an effective intra-atomic Coulomb repulsion). The direct A-AFM exchange between the inter-dimer Cr atoms is likely to be negligible because the distance is $\sim 3.60 \text{ \AA}$ and t falls off exponentially. On the other hand, for both intra- and inter-dimer, one has to consider the superexchange via the O atom which is bonded to either a Te or W atom. Since the Cr1-O-Cr3 angle is close to 90° , we expect the strength of the Cr1-Cr3 superexchange to be weak. Thus, A-AFM exchange dominates leading to an antiferromagnetic alignment. In contrast, the Cr1-O-Cr2 angle is $\sim 130^\circ$ thus superexchange should be appreciable. In Cr_2TeO_6 , this superexchange is antiferromagnetic, consistent with the filled oxygen states providing the superexchange path. On the contrary, in Cr_2WO_6 the Cr1-O-Cr2 coupling is ferromagnetic whose origin may be attributed to the low-lying unoccupied W d state that hybridizes with the O p and mediates this ferromagnetic exchange, as to be discussed next.

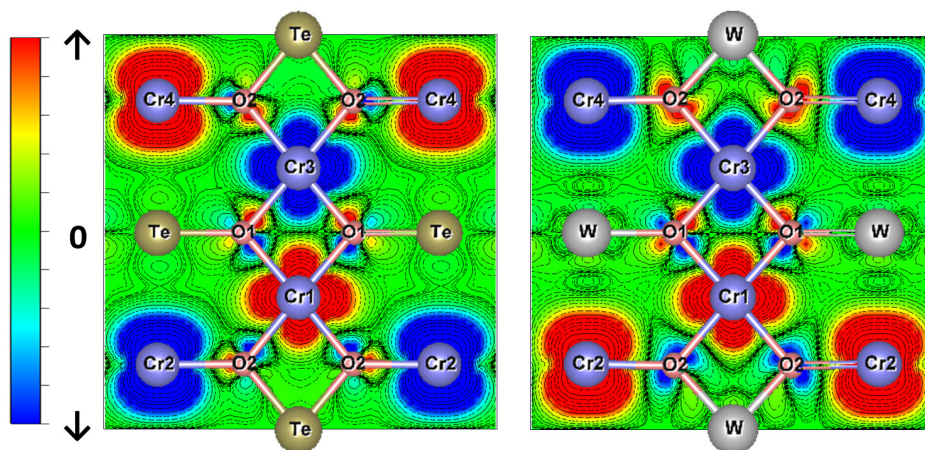


Figure 4.6: Spin densities on the (1 1 0) plane of Cr_2TeO_6 (left) and Cr_2WO_6 (right) where red represents spin up and blue stands for spin down.

In Fig. 4.6, we give the ground state spin densities for the two compounds. The spin densities associated with Cr1 and Cr3 (intra-dimer coupling) and the nearest oxygen (O1) are very similar in the two compounds. The superexchange through these oxygen atoms is very weak due to the nearly 90° exchange path (as one can see in Fig. 4.6), where different O p orbitals hybridize with Cr1 and Cr3. In contrast, the spin densities associated with the inter-dimer exchange between Cr1 and Cr2 differ dramatically. In Cr_2TeO_6 this coupling is dominated by the O2 induced superexchange ($\sim 130^\circ$ path) with very little Te s or p state mixing, whereas in Cr_2WO_6 the O2 charge and spin distributions are strongly altered by the W d states. This hybridization (and the basic difference between Cr_2TeO_6 and Cr_2WO_6) is also seen in the projected density of states (PDOS) given in Fig. 4.7. One can see that both Te p and W d hybridize with O2 p , but the latter is more strongly. This is due to the fact that the W d states are closer in energy to the O2 p band. The difference in the strength of this hybridization also shows up clearly in the O2 p partial DOS, which consequently affects the hybridization between the Cr1, Cr2 d states and the O2 p states. Why the difference in the Cr d and O2 p hybridization gives a ferromagnetic inter-dimer coupling for Cr_2WO_6 is more subtle. A simple pictorial (and perturbative) way of thinking about this is as

follows: O2 p and W d (or Te p) hybridization creates a virtual hole in the O2 p band (which can be either spin up or spin down). This virtual hole can mediate a ferromagnetic double exchange between Cr1 and Cr2. For W d this hybridization is much stronger, and the resultant ferromagnetic coupling strength is larger than the usual antiferromagnetic superexchange. Therefore, the net effect is a weak ferromagnetic exchange. In Cr₂TeO₆ the ferromagnetic coupling is much weaker and the antiferromagnetic superexchange wins. This underlying physics is somewhat similar to that proposed by Kasuya to explain the ferromagnetic coupling between the rare-earth moments in EuS [193].

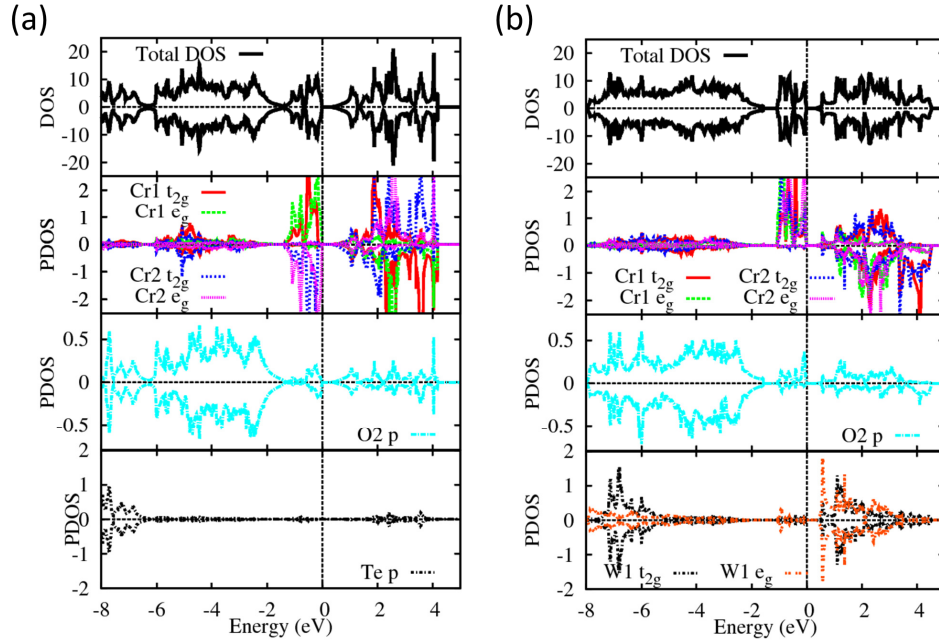


Figure 4.7: Projected density of states of Cr₂TeO₆ (left) and Cr₂WO₆ (right). Cr1 and Cr2 are two inter-dimer Cr ions. O2 mediates the exchange coupling between Cr1 and Cr2 and hybridizes with Te and W.

In Table 4.1 (bottom), we give the values of the intra-dimer (J_1) and inter-dimer (J_2) exchange obtained by fitting the energies of different spin configurations obtained within GGA to an $S = 3/2$ Heisenberg model. Clearly, the intra-dimer exchange is antiferromagnetic in both compounds, while the inter-dimer one is antiferromagnetic in Cr₂TeO₆ but ferromagnetic in Cr₂WO₆.

Introduction of the intra-site Coulomb repulsion U reduces the strength of the exchange, particularly the antiferromagnetic exchange. These results are in qualitative agreement with the values extracted from the high-temperature susceptibility measurements by Drillon et al [189], although there are quantitative differences.

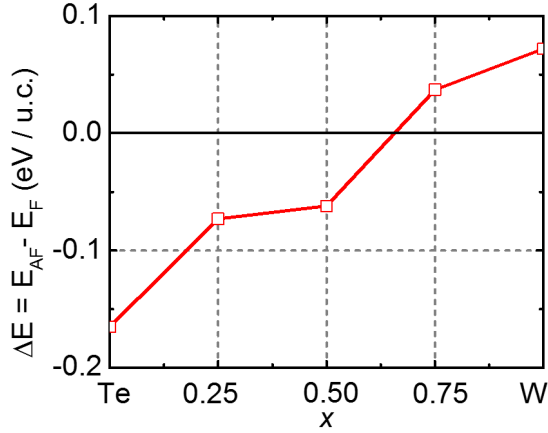


Figure 4.8: Energy difference between antiferromagnetic and ferromagnetic inter-dimer magnetic configurations with antiferromagnetic configuration fixed for the intra-dimer interaction.

Finally, to understand the magnetic structures of $\text{Cr}_2(\text{Te}_{1-x}\text{W}_x)\text{O}_6$ with different x , we have used the virtual crystal approximation (VCA) and GGA to calculate the energies of the AFM-I and AFM-II magnetic structures. The energy difference between these two magnetic configurations is plotted in Fig. 4.8. We find that the ground state switches from AFM-I to AFM-II when $x \sim 0.7$, consistent with the experimental results. Although VCA addresses the problem in an average way (it does not probe the effects of local fluctuations caused by disorder, clustering, etc.), the results suggest that by controlling the effective coupling between Cr $3d$ and W $5d$ states (indirectly through intervening O) through the substitution of W into Te sites, we can indeed tune the competition of the magnetic interactions between the inter-dimer Cr spins, i.e., antiferromagnetic superexchange and ferromagnetic exchange induced by the orbital hybridization. At $x \sim 0.7$, these

two magnetic interactions are comparable in strength, leading to the strongest spin fluctuations thus the minimum values in both M_s and T_N .

4.2.4 Summary

We have discovered a crossover of the magnetic ground states in isostructural $\text{Cr}_2(\text{Te}_{1-x}\text{W}_x)\text{O}_6$ compounds at $x_c \sim 0.7$ where both the Neel temperature T_N and the sublattice magnetization M_s reach the minimum. These phenomena have been attributed to the competition between the antiferromagnetic superexchange and an unusual ferromagnetic exchange that arises from the orbital hybridization between the unoccupied W $5d$ orbitals and the O $2p$ states which provide the exchange path between two Cr moments. This work highlights a new approach to tune the magnetic exchange via chemical doping without introducing additional charge carriers or structural distortions.

4.3 Ferromagnetic inter-dimer interaction in Cr_2MoO_6

To further substantiate the proposed orbital hybridization effect of the nonmagnetic ions with empty d orbitals in determining the nature of the exchange interaction, we have studied the magnetic properties and the electronic structure of another inverse-trirutile compound Cr_2MoO_6 . In this system, the presence of the low-lying unoccupied Mo $4d$ orbitals hybridizing with the occupied $2p$ orbitals of the oxygen atom in the Cr-O-Cr superexchange path would give rise to a ferromagnetic coupling between the inter-dimer Cr moments, as in Cr_2WO_6 . This is exactly what we have observed.

4.3.1 Materials and methods

Polycrystalline samples of Cr_2MoO_6 were synthesized [194] under high-pressure and high-temperature conditions using a cubic anvil system. The mixtures of Cr_2O_3 and MoO_3 in the stoichiometric ratio were grounded thoroughly and reacted at 1000 °C for 30 min under 4 GPa. Phase purity of the obtained product was first examined at room temperature using the powder x -ray diffraction. The magnetic susceptibility was measured using the SQUID magnetometer and the specific heat was characterized using PPMS. Neutron powder diffraction measurements on the sample of ~ 1 gram were performed on the HB-2A neutron powder diffractometer at HFIR in ORNL. The data were taken with the neutron wavelength $\lambda = 2.41$ Å and a collimation of 12'-open-6', and were analyzed using FULLPROF [71].

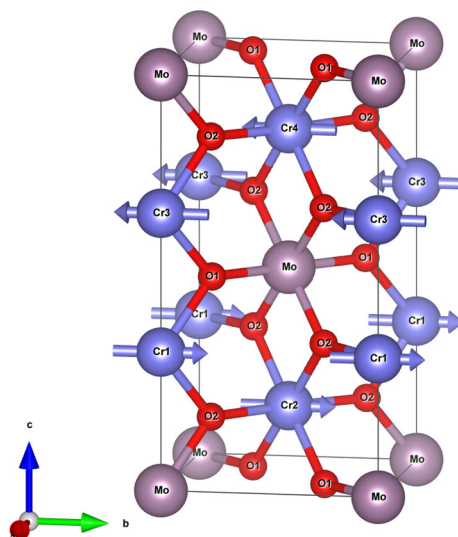


Figure 4.9: Schematic of the crystal and magnetic structure of Cr_2MoO_6 . The intra-dimer interaction is antiferromagnetic, whereas the inter-dimer exchange is ferromagnetic.

4.3.2 Magnetic susceptibility, specific heat and powder neutron diffraction

The schematics of both crystal structure and the obtained magnetic structure of Cr_2MoO_6 are shown in Fig. 4.9. It has an inverse-trirutile structure with the tetragonal space group $P4_2/mnm$, and the lattice parameters are $a = b = 4.58717(9) \text{ \AA}$ and $c = 8.81138(22) \text{ \AA}$ at $T = 4 \text{ K}$. As seen in Table 4.2, the Cr-O-Cr bond angles and bond lengths are close to those of Cr_2WO_6 and Cr_2TeO_6 due to the similar ionic radii of Mo^{6+} , Te^{6+} and W^{6+} . As to be shown later, Cr_2MoO_6 undergoes a paramagnetic-antiferromagnetic transition at $T_N = 93 \text{ K}$ with the same spin order as Cr_2WO_6 . The Cr^{3+} spins are aligned in parallel within the ab plane but are antiparallel within the dimer (Cr1-Cr3 and Cr2-Cr4). The inter-dimer coupling (Cr1-Cr2 and Cr3-Cr4) is ferromagnetic, the same as that in Cr_2WO_6 but is in contrast to the antiferromagnetic coupling in Cr_2TeO_6 [170,195]. The close similarity in the crystal structures of these compounds with dramatically distinct magnetic structures underscores the limitations of the Goodenough-Kanamori rules [172,173] in predicting the nature of the exchange interaction in these complex systems with competing exchange

mechanisms. The role of other nonmagnetic ions (e.g., Mo, Te and W) in the superexchange mechanism has to be reexamined.

Table 4.2: Structural parameters of Cr_2TeO_6 , Cr_2WO_6 and Cr_2MoO_6 at $T = 4$ K, including lattice parameters, bond lengths and bond angles.

		Cr_2TeO_6	Cr_2WO_6	Cr_2MoO_6
Lattice Parameters (Å)	a	4.54472(8)	4.58346(5)	4.58717(9)
	b	4.54487(8)	4.58346(5)	4.58717(9)
	c	8.99539(21)	8.85319(13)	8.81138(22)
Bond Length (Å)	Cr3-Cr1	2.968(14)	2.930(13)	2.78(3)
	Cr3-Cr4	3.559(7)	3.558(6)	3.603(8)
	Cr3-Cr3	4.54487(8)	4.58346(5)	4.58717(9)
Bond angle (degree)	Cr3-O1-Cr1	98.3(3)	97.6(3)	96.65(16)
	Cr3-O2-Cr4	127.0(4)	128.6(3)	130.3(3)

Figure 4.10(a) shows the temperature dependence of the magnetic susceptibility measured in an external field $H = 1000$ Oe. A broad peak is observed at $T_p \sim 98$ K, implying the presence of short-range antiferromagnetic correlations near and above this temperature. Inset displays the inverse susceptibility and a Curie-Weiss fit that is performed in the temperature range $200 \sim 300$ K. The fitting gives a Weiss temperature $\Theta_w \sim -254.4$ K and an effective magnetic moment $\mu_{\text{eff}} \sim 2.92 \mu_B / \text{Cr}$. The negative Θ_w is consistent with the dominance of antiferromagnetic correlations in Cr1-Cr3 and Cr2-Cr4 dimers [189] in this system. The increase in the susceptibility at low temperature is presumably due to paramagnetic impurities [171,195]. The magnetic heat capacity as a function of temperature $C_{\text{mag}}(T)$ is shown in Fig. 4.10(b) with the phonon contribution subtracted by the scaled heat capacity of an isostructural nonmagnetic compound Ga_2TeO_6 from the total heat capacity measured [inset of Fig. 4.10(b)]. The sharp peak at $T_N \sim 93$ K in $C_{\text{mag}}(T)$ indicates a transition into a long-range ordered antiferromagnetic state. It is noteworthy that the transition temperature T_N is slightly lower than T_p determined from the broad peak in the magnetic susceptibility, which seems to be a common feature in the inverse-trirutile compounds such as

Cr_2TeO_6 , Cr_2WO_6 and Fe_2TeO_6 [171,195]. Such a feature is associated with the presence of short-range low-dimensional magnetic fluctuations prior to entering a three-dimensional long-range antiferromagnetic state.

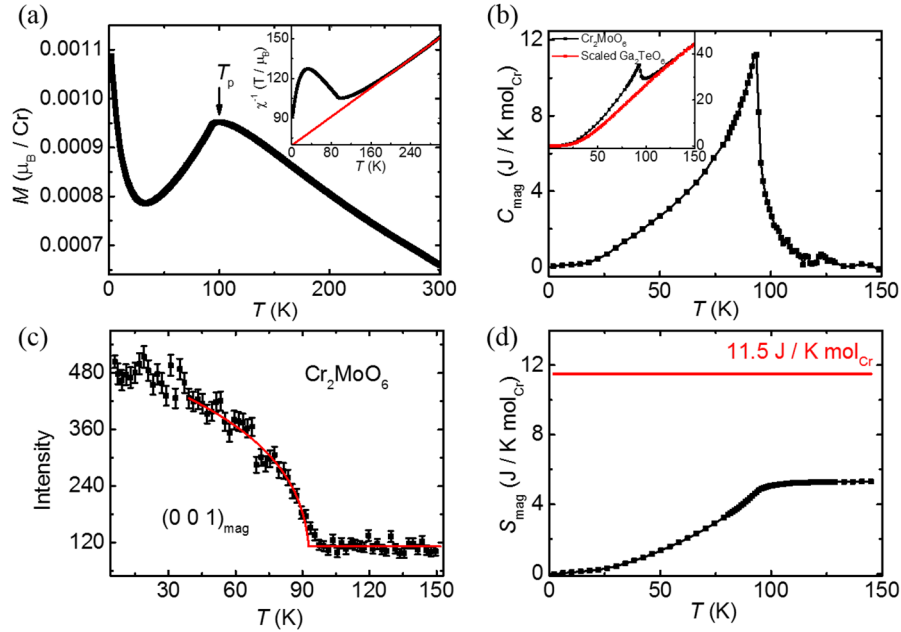


Figure 4.10: (a) Temperature dependence of magnetic susceptibility. Inset shows the inverse susceptibility and the Curie-Weiss fit. (b) Temperature dependence of magnetic heat capacity. Inset shows the subtraction of the phonon contribution using the scaled heat capacity of Ga_2TeO_6 . (c) Intensity of $(0\ 0\ 1)_{\text{mag}}$ magnetic Bragg peak as a function of temperature. The solid line is a guide to the eye. (d) Temperature dependence of the integrated magnetic entropy. The horizontal red line denotes the theoretical value for $S = 3/2$.

The integrated magnetic entropy is shown in Fig. 4.10(d) with a saturated value of 5.30 J / (K mol Cr), which is about ~50% of the theoretical value (11.5 J / (K mol Cr)) for the $S = 3/2$ Cr^{3+} ions. The presence of the resultant residual magnetic entropy implies the existence of magnetic correlations in the system above T_N . Note that the residual magnetic entropy (6.20 J / (K mol Cr)) is nearly half of the maximum value which has been commonly observed in low-dimensional or frustrated magnetic systems with competing interactions. It has also been seen in the isostructural compounds $\text{Cr}_2(\text{Te}_{1-x}\text{W}_x)\text{O}_6$ [195].

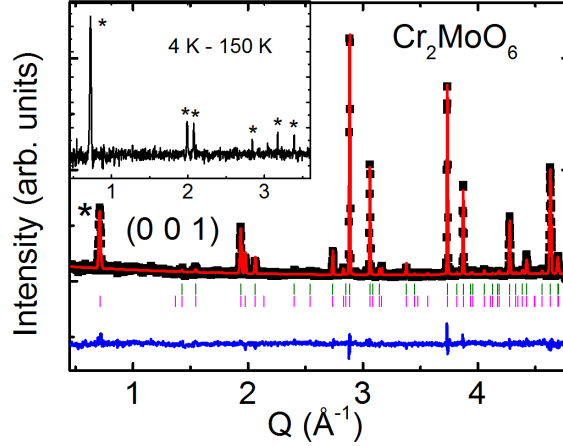


Figure 4.11: Neutron powder diffraction data of Cr_2MoO_6 at $T = 4$ K. The black symbols are experimental data and the red curve is the Rietveld refinement fit. The difference is represented by the blue. The positions of the nuclear and magnetic peaks are marked by the green and magenta lines, respectively. Inset shows the difference between the low- and high-temperature data with the positions of magnetic Bragg peaks denoted by the symbol “*”.

The neutron powder diffraction data measured at $T = 4$ K are shown in Fig. 4.11. The magnetic propagation vector is determined to be $(0\ 0\ 0)$. Representational analysis using the *BasIreps* program in FULLPROF [71] suggests that the magnetic structure shown in Fig. 4.9 is symmetry compatible and the most plausible fit to the data. This magnetic structure is identical to that of Cr_2WO_6 , that is, the inter-dimer coupling is ferromagnetic. Note that the in-plane spin direction could not be unambiguously determined because of the tetragonal structure of the system and the nature of the neutron powder diffraction data. The FWHM of the magnetic Bragg peaks is determined by the instrumental resolution according to the refinement, confirming the long-range character of the magnetic order. Inset shows the zoom-in view of the magnetic Bragg peaks after subtracting the 150 K neutron diffraction data from the 4 K one. The temperature dependence of the intensity of the $(0\ 0\ 1)$ magnetic Bragg peak is presented in Fig. 4.10(c) with the solid curve as a guide to the eye. The magnetic signal disappears at the antiferromagnetic transition temperature $T_N \sim 93$ K, consistent with the specific heat measurement. Note that the magnitude of the static

magnetic moment ($\sim 2.47 \mu_B / \text{Cr}$) extracted from the neutron powder diffraction measurements is smaller than the theoretical value of $3.0 \mu_B / \text{Cr}$, which is attributed to quantum spin fluctuations as well as the covalency [196-198].

4.3.3 Density functional theory calculations

The observed ferromagnetic inter-dimer coupling in Cr_2MoO_6 is consistent with a mechanism we proposed earlier for Cr_2WO_6 [195]. The nearby unoccupied Mo $4d$ orbitals (W $5d$) play an essential role in determining the sign of the Cr-Cr exchange by hybridizing with the intervening filled O p orbitals. That is, the $d - p$ hybridization induced ferromagnetic exchange dominates the usual antiferromagnetic superexchange interaction in Cr_2MoO_6 and Cr_2WO_6 . In contrast, in Cr_2TeO_6 , a compound with a similar crystal structure but without the empty Te d orbitals, the superexchange interaction between two inter-dimer Cr moments is antiferromagnetic. However, in spite of the similarity, i.e. the presence of the empty d orbitals, the Neel temperature of Cr_2MoO_6 is considerably higher than that of Cr_2WO_6 ($T_N \sim 45 \text{ K}$).

To understand the electronic structure and the magnetic properties of Cr_2MoO_6 , we have carried out first principles calculations for four different intra-dimer and inter-dimer magnetic configurations, i.e., AFM-AFM, AFM-FM, FM-AFM and FM-FM, where AFM and FM denote antiferromagnetic and ferromagnetic alignments, respectively. DFT calculations were done in a similar way to that described in Sec. 4.2.3. According to the total energies of different magnetic configurations listed in Table 4.3, we can see that GGA and GGA+ U calculations give the same magnetic ground state AFM-FM (AFM-II), consistent with the experimental results. However, in contrast to Cr_2WO_6 and Cr_2TeO_6 [195], GGA gives a small negative band gap in Cr_2MoO_6 , while the experiment shows an insulating behavior. Note that GGA usually underestimates the band gap

in semiconductors [199] and the problem is severe in systems containing 3d electrons such as Cr. This problem can be partially corrected through the GGA+ U approximation [190,191].

Table 4.3: Total energy (in eV) per magnetic unit cell containing four Cr^{3+} ions of different magnetic configurations.

Configuration	AFM-AFM	AFM-FM	FM-AFM	FM-FM
GGA	-153.325	-153.520	-153.457	-153.422
GGA+ U	-143.649	-143.671	-143.562	-143.635

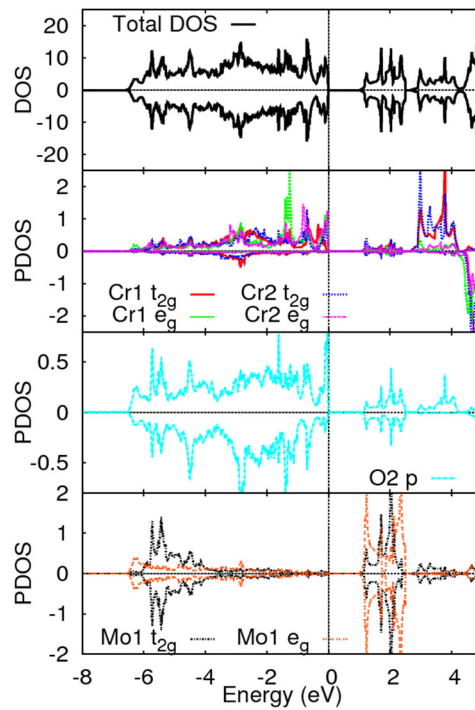


Figure 4.12: Density of states (DOS) in the unit of number of states / (eV u.c.) and projected density of states (PDOS) in the unit of number of states / (eV atom) of Cr_2MoO_6 calculated by GGA+ U .

Figure 4.12 presents the density of states (DOS) and projected density of states (PDOS) of Cr_2MoO_6 calculated using GGA+ U with $U = 4$ eV. GGA+ U indeed opens up a band gap and increases the Cr^{3+} magnetic moment from $\sim 2.5 \mu_B$ for GGA to $\sim 2.9 \mu_B$ for GGA+ U . The reduction from $3.0 \mu_B$ to $2.9 \mu_B$ is due to the covalency, and a comparison with the experimental value $2.47 \mu_B$ suggests that the effect of quantum spin fluctuations is important in this system [196-198]. Note

that in our electronic structure calculations, the principal axis is along the tetragonal axes, which are not aligned with the cubic axis of the local crystal field of the CrO_6 octahedra, giving rise to the mixture of both t_{2g} and e_g states in the former coordinate system for Cr $3d$ orbitals. Also note that the Mo $3d$ orbitals were treated as core states and were not a part of the manifold of active orbitals because of the large energy difference ($\sim 235.45\text{eV}$) between O $2p$ and Mo $3d$. Therefore, the notation of d orbitals of Mo hereafter refers to its $4d$ orbitals. The projected DOS shows that there is strong hybridization between Mo d and O p near the bottom of the O p band (-4 to -6.5 eV), and the hybridization also shows up in the lower part of the conduction band [200]. This strong hybridization is due to the small distance between Mo and O atoms (~ 1.9 Å). The Cr d states, which are mainly in the energy range 0 to -4 eV, do not hybridize strongly with the Mo d states due to the large Cr-Mo distance (~ 3.0 and ~ 3.5 Å). However, the perturbed (by mixing with Mo d) O p bands hybridizing with the Cr d states (Cr-O distance is ~ 1.9 Å) lead to a ferromagnetic interaction between the inter-dimer Cr spins. This physics is very similar to what we found in Cr_2WO_6 [195]. As elaborated in the cartoon shown in Fig. 4.13, a simple perturbative way of understanding this ferromagnetic coupling is that the hybridization of O p with the empty Mo d orbitals creates a virtual hole in the O p band. This hole leads to a ferromagnetic coupling between two Cr^{3+} d spins, which flank this oxygen atom. In this sense, the empty $4d$ orbitals of Mo are responsible for the observed ferromagnetic coupling between inter-dimer Cr spins, similar to what happens in the Cr_2WO_6 compound.

To visualize the magnetic ordering and the orbital hybridization effect, we show the spin densities projected onto the $(1\ 1\ 0)$ plane in Fig. 4.14. We can see that the inter-dimer (Cr1-Cr2, Cr3-Cr4) Cr spin densities are the same (ferromagnetic, blue-blue or red-red) and the intra-dimer (Cr1-Cr3, Cr2-Cr4) spin densities are opposite (antiferromagnetic, red-blue), which is very similar

to that of Cr_2WO_6 but in contrast to Cr_2TeO_6 [195]. The remarkable difference is seen in the spin density associated with the oxygen atom (O2), which mediates the inter-dimer exchange. In Cr_2WO_6 and Cr_2MoO_6 both lobes are of the same polarization, whereas in Cr_2TeO_6 they have opposite polarizations [195], characteristic of the ferromagnetic and antiferromagnetic coupling between Cr1 and Cr2, respectively.

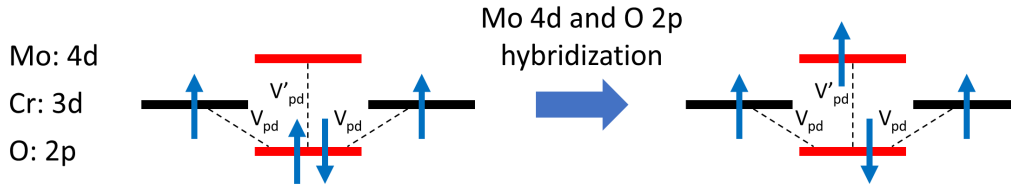


Figure 4.13: A cartoon illustrating the ferromagnetic coupling between two Cr 3d moments via the orbital hybridization between O 2p and Mo empty 4d orbitals leading to a virtual electron transfer leading to a ferromagnetic coupling between two Cr moments via Cr 3d-O 2p hybridization.

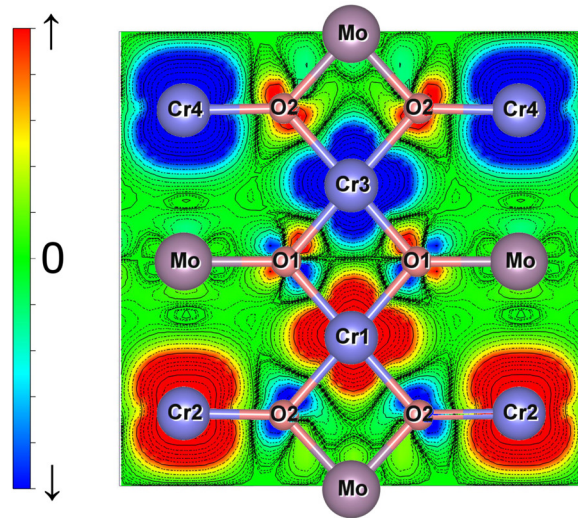


Figure 4.14: Spin density projected on the (1 1 0) plane of Cr_2MoO_6 calculated using GGA+ U where red and blue indicate spin up and spin down, respectively. Since the local cubic axes of the CrO_6 octahedra are rotated from the chosen tetragonal x - y - z coordinates (Fig. 4.9), in the latter coordinate system Cr d - t_{2g} and d - e_g states are mixed.

We have calculated the sign and strength of the intra-dimer (J_1 , Cr1-Cr3 distance ~ 2.780 Å) and inter-dimer (J_2 , Cr3-Cr4 distance ~ 3.604 Å) exchange interactions between Cr moments using

a simple nearest-neighbor Heisenberg model $H = -2 \sum_{\langle i,j \rangle} J_{ij} \vec{S}_i \cdot \vec{S}_j$ for Cr_2WO_6 and Cr_2MoO_6 within GGA and GGA+ U . The respective values are given in Table 4.4. Note that compared to J_1 and J_2 , further-neighbor interactions (J_3 , Cr3-Cr3 distance within the ab plane ~ 4.587 Å) are much weaker thus are neglected here. A similar approximation was made previously in Ref. [189]. As seen in the table, the introduction of U reduces the strengths of the exchange couplings in general. However, because of the competition between ferromagnetic and antiferromagnetic contributions to a given exchange parameter, the introduction of U affects J_1 and J_2 differently, not only for a given system but also between different systems. The precise quantitative values should not be taken seriously but the qualitative trends are consistent with the experiments. The smaller J_2 value of Cr_2MoO_6 than that of Cr_2WO_6 given by GGA+ U is consistent with the scenario that the Mo $4d$ orbital is less extended than the W $5d$ one, which is expected to contribute a weaker ferromagnetic interaction induced via a less extent of d - p orbital hybridization. More careful calculations of the total energy using improved approximations to the exchange correlation potential within DFT are needed to pin down the parameters of the exchange Hamiltonian. Also, magnon dispersion measurements and theoretical calculations will help us understand the nature of the magnetic exchange in these interesting systems.

Table 4.4: Exchange parameters J_1 and J_2 obtained from the simple isotropic Heisenberg model $H = -2 \sum_{\langle i,j \rangle} J_{ij} \vec{S}_i \cdot \vec{S}_j$; $J_{ij} = J_1$ for intra-dimer and $J_{ij} = J_2$ for inter-dimer exchange. Values with superscript * are obtained using GGA based on a model proposed in Ref. [189].

Compound	Cr_2MoO_6		Cr_2WO_6	
Parameter	J_1 (meV)	J_2 (meV)	J_1 (meV)	J_2 (meV)
Theo. (GGA)	-5.4	2.7	-10.4	1.0
Theo.(GGA+ U)	-1.9	0.15	-1.0	0.75
Ref. [189]			-3.8*	0.12*

4.3.4 Summary

We have studied the magnetic and electronic properties of an inverse-trirutile compound Cr_2MoO_6 to examine the idea that the low-lying empty d bands associated with Mo can induce a ferromagnetic coupling between two Cr moments by perturbing the p orbitals of the O atom that mediates the exchange interaction. The underlying physics is similar to the one we have suggested for Cr_2WO_6 with low-lying empty W $5d$ bands. GGA+ U appears to give a better description of this system. However, for a quantitative understanding of the exchange parameters more theoretical work is necessary. Also, inelastic neutron scattering measurements on the magnon spectra will be helpful in pinning down the exchange parameters to validate the theoretical predictions.

4.4 Higgs amplitude modes in the magnetic excitation spectra of Cr_2TeO_6 and Cr_2WO_6

In this section, we present the magnetic excitations of Cr_2TeO_6 and Cr_2WO_6 measured by inelastic neutron scattering on polycrystalline samples. Longitudinal Higgs (amplitude) modes have been observed, together with transverse Goldstone (phase) modes, which can be well described using the extended spin wave (ESW) theory. Although these two compounds are not close to a QCP, the large spin quantum number ($S = 3/2$) in combination with the narrow bandwidth of the amplitude modes, makes the detection of the Higgs amplitude modes feasible in the polycrystalline samples. This work provides new insights into the search for the amplitude fluctuations in condensed matter systems, particularly in spin dimers beyond $S = 1/2$.

4.4.1 Materials and methods

The growth of the polycrystalline samples of Cr_2TeO_6 and Cr_2WO_6 has been described in Sec. 4.2.1. The quality of the samples has been verified by the powder x -ray and powder neutron diffraction measurements. Inelastic neutron scattering measurements were performed using the SEQUOIA time-of-flight spectrometer at SNS in ORNL. The incident neutron energy was fixed as $E_i = 65$ meV in order to cover a large enough area in the energy and momentum transfer ($E - |\mathbf{Q}|$) space. Samples of ~ 4 grams each were loaded in a standard aluminum sample can with helium exchange gas and mounted onto a closed-cycle refrigerator. At each temperature, an identical empty sample can was used for background subtraction.

4.4.2 Inelastic neutron scattering

Figure 4.15(a) and (b) show the powder-averaged magnetic excitation spectra as a function of energy transfer E (in meV) and momentum transfer $|\mathbf{Q}|$ (in $\text{\AA}^{-1}$) at $T = 4$ K. In Cr_2WO_6 , for $|\mathbf{Q}| = 0.72 \text{ \AA}^{-1}$ corresponding to the magnetic Bragg reflection (0 0 1) and the equivalent $|\mathbf{Q}|$ positions in

the reciprocal space, gapless excitations have been observed in the energy range of $0 < E < 10$ meV. The intensity of these excitations is strongest around $|\mathbf{Q}| \sim 1.27 \text{ \AA}^{-1}$ and $E \sim 9$ meV. The magnetic dispersions below 10 meV energy transfer can be well described by the LSW theory taking into account three exchange interactions J_1, J_2 and J_3 presented in Fig. 4.1(c), where the powder-average of two branches of the magnetic excitations accounts for the observed spectra. Thus, the excitations in the energy range $0 < E < 10$ meV are transverse Goldstone modes originating from the spontaneously broken rotational symmetry in the magnetically ordered state. Very strikingly, an additional gapped mode centered at $E \sim 12$ meV is also observed. This mode is less dispersive than the transverse modes, and the dependence of its intensity on $|\mathbf{Q}|$ indicates that it is also associated with the long-range magnetic order. Furthermore, there is another excitation mode around $E \sim 21$ meV, although it is not obvious in the intensity map [Fig. 4.15(a)].

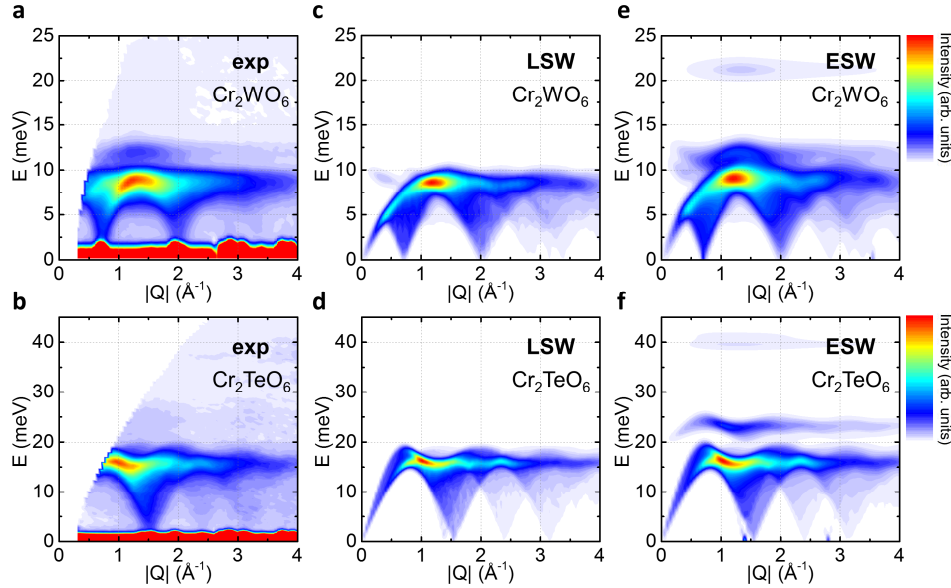


Figure 4.15: (a),(b) Powder-averaged magnetic excitation spectra as a function of energy transfer E and momentum transfer $|\mathbf{Q}|$ of Cr_2TeO_6 and Cr_2WO_6 at $T = 4$ K, respectively. The background measured using an empty sample can has been subtracted. (c),(d) Powder-averaged magnetic excitation spectra calculated by the LSW theory. (e),(f) Powder-averaged magnetic excitation spectra calculated by the ESW theory.

To better visualize these two additional modes discussed above, Fig. 4.16(a) shows the cuts of the neutron intensity as a function of E , with $|\mathbf{Q}|$ integrated from 1.2 to 1.5 $\text{\AA}^{-1}$. At $T = 4$ K, three distinct modes are observed at $E \sim 9$, 12 and 21 meV, respectively. In contrast, at $T = 60$ K which is slightly above $T_N = 45$ K, while a broad peak associated with the transverse modes is still present due to the short-range correlations of the magnetic order surviving above T_N (also see Fig. 4.17(a)), the latter two modes at $E \sim 12$ meV and 21 meV are completely suppressed, affirming the magnetic character of these two modes. It is important to point out that these two additional modes cannot be captured by the LSW theory calculation, as shown in Fig. 4.15(c).

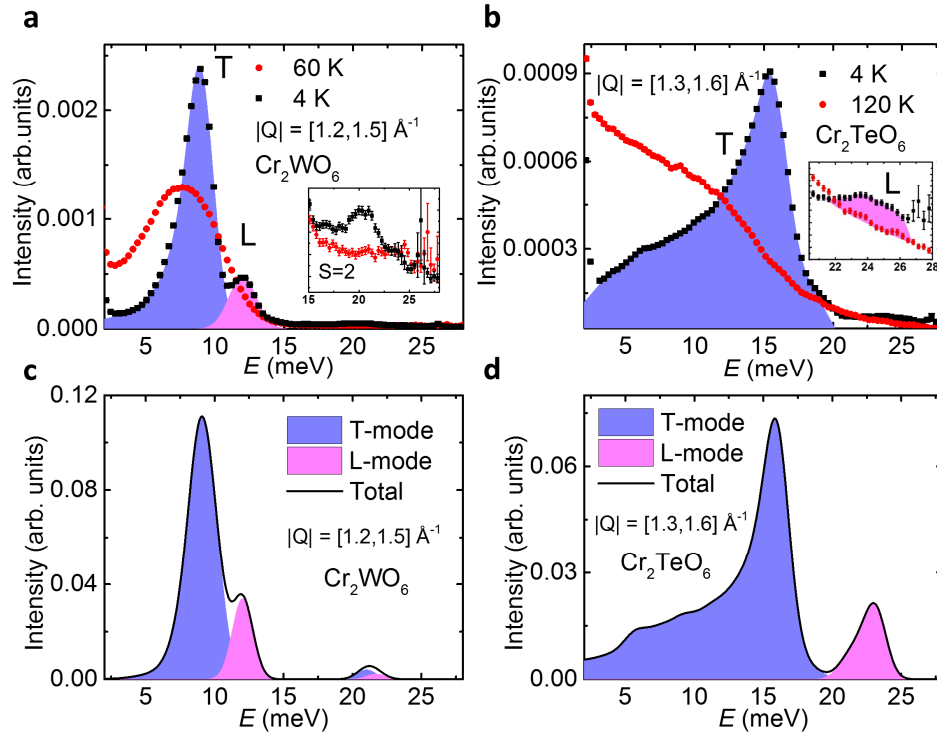


Figure 4.16: (a),(b) Inelastic neutron scattering intensity as a function of E at $T = 4$ K collected at SEQUOIA, $|\mathbf{Q}|$ integrated from 1.2 to 1.5 $\text{\AA}^{-1}$ for Cr_2WO_6 and 1.3 to 1.6 $\text{\AA}^{-1}$ for Cr_2TeO_6 . Insets display the zoom-in view of E between 15 meV and 28 meV for Cr_2WO_6 , and between 20.5 meV and 28 meV for Cr_2TeO_6 . (c),(d) Inelastic neutron scattering intensity as a function of E calculated by the ESW theory at $T = 0$ K, $|\mathbf{Q}|$ integrated from 1.2 to 1.5 $\text{\AA}^{-1}$ for Cr_2WO_6 and 1.3 to 1.6 $\text{\AA}^{-1}$ for Cr_2TeO_6 .

Similarly, in Cr_2TeO_6 , there are transverse modes in the magnetic excitation spectra but in the energy range $0 < E < 19$ meV, higher compared with that in Cr_2WO_6 , which can also be adequately described by the LSW calculations. Intriguingly, in spite of the difference in the sign of J_2 in these two compounds, a gapped mode is also observed at $E \sim 23$ meV in Cr_2TeO_6 , which disappears above T_N as shown in the E -cut plots at $T = 4$ and 120 K presented in Fig. 4.16(b). As in the case of Cr_2WO_6 , this additional mode cannot be explained using the LSW theory [Fig. 4.15(d)].

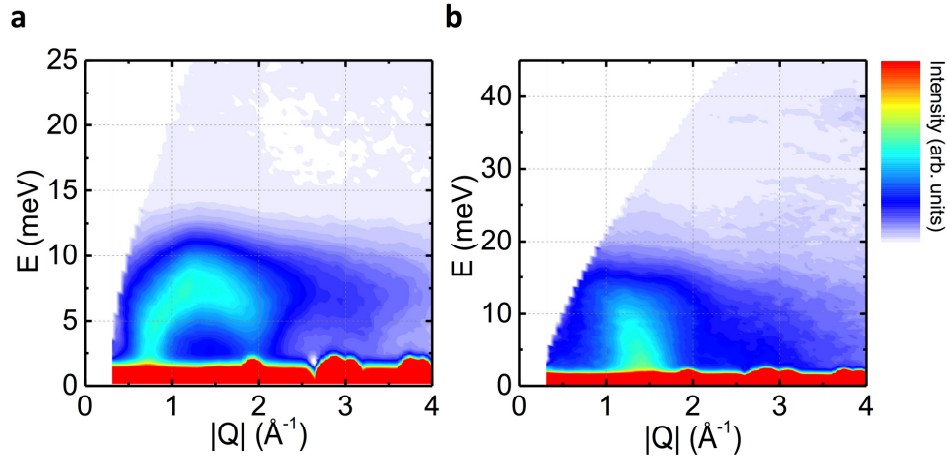


Figure 4.17: Powder-averaged magnetic excitation spectra above T_N in (a) Cr_2WO_6 at $T = 60$ K, and (b) Cr_2TeO_6 at $T = 120$ K, respectively, measured with the incident neutron energy $E_i = 65$ meV.

4.4.3. Linear spin wave theory calculations

The spin wave dispersions of Cr_2WO_6 and Cr_2TeO_6 have been calculated using the LSW theory in collaboration with Dr. S. D. Mahanti in Michigan State University. The dispersion relation for Cr_2TeO_6 is

$$\omega = \pm S J_2 (4 + \eta) \sqrt{(1 + \gamma_{3k})^2 - |\gamma_{1k} \pm \gamma_{2k}^*|^2}$$

and that for Cr_2WO_6 is

$$\omega = \pm S J_2 (4 + \eta) \sqrt{(1 + \gamma_{3k})^2 + |\gamma_{1k}|^2 - |\gamma_{2k}|^2 \pm X^{\frac{1}{2}}}$$

where

$$\gamma_{1\mathbf{k}} = \frac{4}{4 + \eta} e^{ik_z(\frac{c}{2} - \delta)} \cos(k_x a/2) \cos(k_y a/2)$$

$$\gamma_{2\mathbf{k}} = \frac{\eta}{4 + \eta} e^{ik_z \delta}$$

$$\gamma_{3\mathbf{k}} = \frac{4\eta'}{4 + \eta} \left[1 - \frac{1}{2} (\cos(k_x a) + \cos(k_y a)) \right]$$

$$X = [4(1 + \gamma_{3\mathbf{k}})^2 - 2|\gamma_{2\mathbf{k}}|^2]|\gamma_{1\mathbf{k}}|^2 + (\gamma_{1\mathbf{k}}^2 \gamma_{2\mathbf{k}}^2 + \gamma_{1\mathbf{k}}^{*2} \gamma_{2\mathbf{k}}^{*2})$$

η and η' are defined as $\eta = J_1/|J_2|$ and $\eta' = |J_3|/|J_2|$, respectively. δ is the separation between two Cr^{3+} spins in a dimer: $\delta = c/3$. The calculated spin wave dispersions are shown in Fig. 4.18, and the associated powder-averaged spectra are shown in Fig. 4.15(c) and (d). The exchange parameters used are tabulated in Table 4.5.

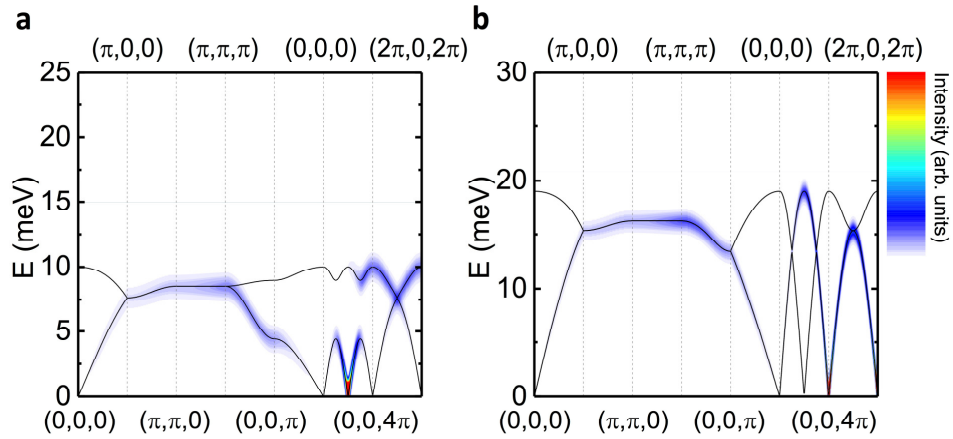


Figure 4.18: Spin wave dispersions and intensity of inelastic neutron scattering of (a) Cr_2WO_6 and (b) Cr_2TeO_6 calculated by SpinW code using the LSW theory.

Table 4.5: Exchange parameters for Cr_2WO_6 and Cr_2TeO_6 used for the LSW calculations.

	J_1 [meV]	J_2 [meV]	J_3 [meV]
Cr_2WO_6	5.80	-0.38	-0.10
Cr_2TeO_6	11.5	0.87	-0.10

4.4.4 Extended spin wave theory calculations

Since the weakly dispersing high-energy modes (gapped modes) in the magnetic excitation spectra of both Cr_2WO_6 and Cr_2TeO_6 cannot be explained within the LSW approximation where only phase fluctuations are included, these gapped modes can potentially be attributed to the amplitude modes associated with the fluctuations in the magnitude of the magnetic moments. In order to better understand the nature of these magnetic excitations, we have extended the LSW calculations for interacting spin dimer systems in collaboration with Dr. M. Matsumoto in Shizuoka University [201]. Extended spin wave (ESW) theory was introduced to study the multipole dynamics of the quadrupole ordered phases in CeB_6 [201] and $\text{PrOs}_4\text{Sb}_{12}$ [202], and was also applied to interacting spin dimer [203], spin trimer [204] and spin tetramer systems [205,206]. It is equivalent to the bond operator formulation introduced to study the excited states in bilayer spin systems [207] and interacting spin dimer systems [208,209]. The present formulation has an advantage for investigating the magnetic excitations in complicated systems such as $S = 3/2$ spin dimers, where there are 16 local states of a dimer.

Starting from the crystal structure of Cr_2WO_6 and Cr_2TeO_6 shown in Fig. 4.1(c), the Hamiltonian for the interacting $S = 3/2$ spin dimer systems is given by the following general form:

$$H = \sum_i \sum_{\mu} H_{intra}(i, \mu) + \sum_{\langle i, \mu, j, \mu' \rangle} H_{inter}(i, \mu, j, \mu') \quad (1)$$

The first term $H_{intra}(i, \mu)$ represents the Hamiltonian of a dimer on the $\mu (= A, B)$ sublattice (see Fig. 4.1(c)) in the i^{th} unit cell. It can be written as

$$H_{intra} = J_1 \mathbf{S}_{i\mu l} \cdot \mathbf{S}_{i\mu r} \quad (2)$$

$\mathbf{S}_{i\mu\gamma}$ represents the $S = 3/2$ spin operator at the $\gamma (= l, r)$ which are equivalent to the top and bottom spins of the dimer in Fig. 4.1(c)) site in a dimer on the $\mu (= A, B)$ sublattice in the i^{th} unit cell. The

second term $H_{inter}(i, \mu, j, \mu')$ in Eq. (1) is the Hamiltonian for the inter-dimer interaction between dimers on the μ and μ' sublattices in the i^{th} and j^{th} unit cell, respectively. It is expressed as

$$H_{inter}(i, \mu, j, \mu') = \sum_{\gamma, \gamma' = l, r} J_{i\mu\gamma, j\mu'\gamma'} \mathbf{S}_{i\mu\gamma} \cdot \mathbf{S}_{j\mu'\gamma'} \quad (3)$$

where $J_{i\mu\gamma, j\mu'\gamma'}$ represents the exchange coupling constant. In Eq. (1), the summation $\sum_{\langle i\mu j\mu' \rangle}$ is taken over the pairs of interacting spins by the J_2 and J_3 interaction shown in Fig. 4.1(c).

First, we solve the Hamiltonian under a mean-field approximation on the basis of the dimer states. For weak inter-dimer interactions, we obtain a singlet ($S_{\text{tot}} = 0$) local ground state with no magnetic moment. When the inter-dimer interactions are increased, the magnetic ($S_{\text{tot}} \neq 0$) states of a dimer participate in the ground state and finite magnetic moments appear. The ordered phase is realized for

$$20(|J_2| + |J_3|) \geq J_1 \quad (4)$$

and a QCP is obtained when

$$20(|J_2| + |J_3|) = J_1 \quad (5)$$

The finite Neel temperatures of Cr_2WO_6 and Cr_2TeO_6 indicate that these two compounds satisfy Eq. (4). On the basis of a dimer lattice, the ordered moment is staggered in Cr_2WO_6 . The ordering wave vector is expressed by $\mathbf{Q} = (0 \ 0 \ 1)$ in the reciprocal lattice unit. In Cr_2TeO_6 , the ordered moment is uniform on the dimer lattice and the ordering wave vector is expressed by $\mathbf{Q} = (0 \ 0 \ 0)$.

The detailed ESW calculations can be found in the Supplemental Materials of Ref. [210]. Figure 4.15(e) and (f) show the calculated powder-averaged magnetic spectra based on the ESW theory for Cr_2WO_6 and Cr_2TeO_6 , respectively. They are in very good agreement with the experimental results presented in Fig. 4.15(a) and (b). The exchange parameters used to obtain the best fit between the experimental and calculated spectra are tabulated in Table 4.6, together with

the calculated magnetic moments that are consistent with the experimental values. As shown in Fig. 4.19 and 4.20, the observed gapless magnetic excitations in both compounds are indeed the transverse Goldstone modes, which can be well described by both LSW and ESW calculations. The additional gapped modes observed in both compounds are however captured only in the ESW theory, as illustrated in both the calculated contour map [Fig. 4.15(e) and (f)] and the E -cut plots [Fig. 4.16(c) and (d)]. Specially, we would like to stress that the features at $E \sim 12$ meV in Cr_2WO_6 and $E \sim 23$ meV in Cr_2TeO_6 with narrow bandwidth are ascribed to the amplitude modes, which stem from the fluctuations in the magnitude of the magnetic moment in the ordered state (with the ground state a mixture of both $S_{\text{tot}} = 0$ spin-singlet state and $S_{\text{tot}} = 1$ spin-triplet state) – the Higgs amplitude modes. Note that the intensity of the longitudinal modes relative to the transverse modes is weaker in the experimental data compared to the calculated value. The overestimated intensity of the longitudinal modes is due to the fact that the ESW calculations are done on the basis of a harmonic theory where the magnon-magnon interaction is not taken into account. In reality, the presence of this interaction would lead to the decay of the longitudinal mode into a pair of transverse modes, resulting in broadened linewidth and reduced intensity of the longitudinal modes.

Table 4.6: Exchange parameters and magnetic moment for Cr_2WO_6 and Cr_2TeO_6 obtained by the ESW calculations. The magnetic moment is normalized to the saturated value (full moment).

	J_1 [meV]	J_2 [meV]	J_3 [meV]	M/M_s
Cr_2WO_6	5.25	-0.475	-0.10	0.794
Cr_2TeO_6	9.4	1.035	-0.10	0.820

Another interesting point is that there are additional higher energy modes around 21 meV and 40 meV in Cr_2WO_6 and Cr_2TeO_6 , respectively, predicted in the calculations. These are attributed to the $S_{\text{tot}} = 2$ excited state, although their intensities are weak in the inelastic neutron scattering measurements. In spite of this, the $S_{\text{tot}} = 2$ excitation mode is convincingly observed in Cr_2WO_6 ,

as shown in Fig. 4.16(a), which in turn unambiguously supports the scenario of an $S = 3/2$ spin dimer and the resultant observation of the amplitude modes in this system. We also tried to look for the $S_{\text{tot}} = 2$ excitation mode in Cr_2TeO_6 using an incident neutron energy $E_i = 90$ meV, but the phonons around 40 meV mask this weak magnetic signal, as shown in Fig. 4.21.

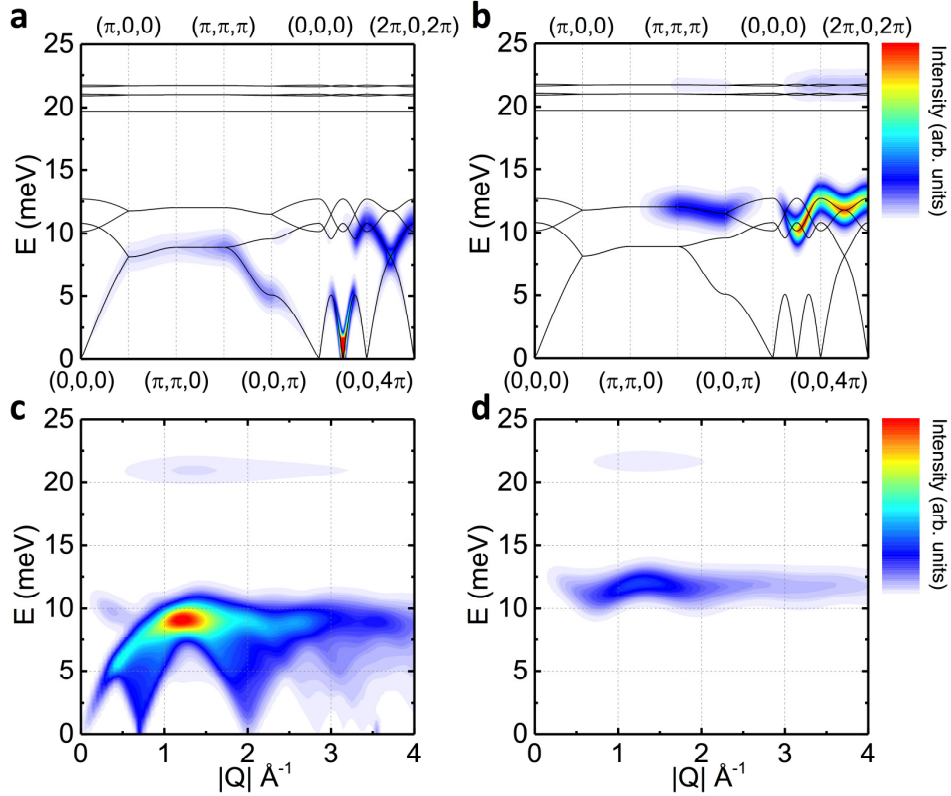


Figure 4.19: The spin wave dispersion and intensity of inelastic neutron scattering of the (a) transverse and (b) longitudinal modes in Cr_2WO_6 , respectively, calculated using the ESW theory. (c) and (d) are the powder-averaged magnetic excitation spectra for the transverse and longitudinal modes, respectively. The broadening factor is chosen as $\Gamma = 1.0$ meV that is close to the instrumental energy resolution.

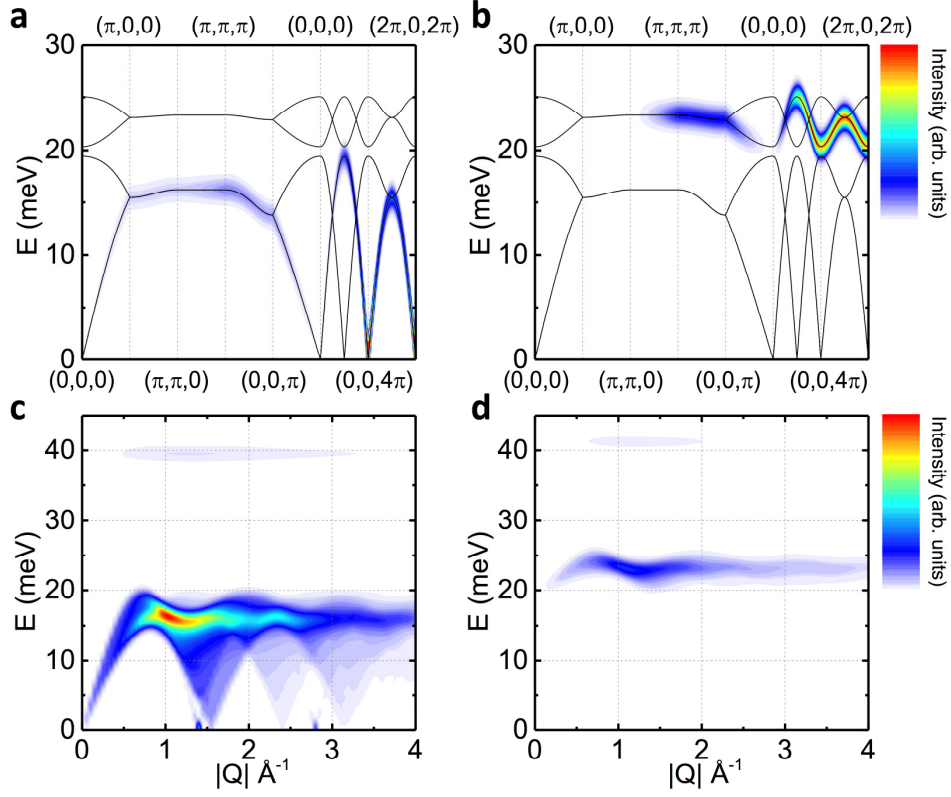


Figure 4.20: The spin wave dispersion and intensity of inelastic neutron scattering of the (a) transverse and (b) longitudinal modes in Cr_2TeO_6 , respectively, calculated using the ESW theory. (c) and (d) are the powder-averaged magnetic excitation spectra for the transverse and longitudinal modes, respectively. The broadening factor is chosen as $\Gamma = 1.0$ meV that is close to the instrumental energy resolution.

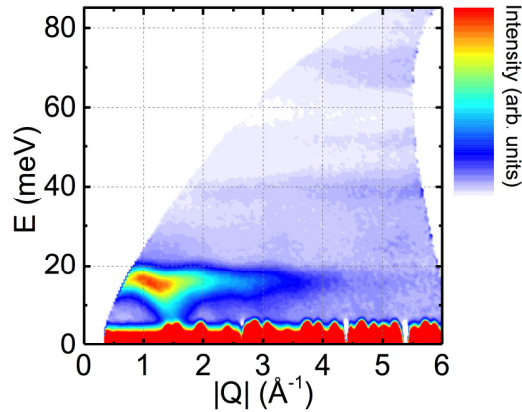


Figure 4.21: Powder-averaged magnetic excitation spectrum of Cr_2TeO_6 at $T = 4$ K measured with the incident neutron energy $E_i = 90$ meV at $T = 4$ K.

It is known that in quantum antiferromagnets the amplitude excitations may emerge when the ground state of the system is in the vicinity of a QCP where the ordered moment is reduced significantly by quantum fluctuations. The observation of Higgs amplitude modes in the magnetic excitation spectra of Cr_2WO_6 and Cr_2TeO_6 even in the polycrystalline samples is quite striking, considering that their ordered moments are reduced by only $\sim 24\%$. A natural question arises: Are the ground states of both compounds close to the QCP? To quantitatively evaluate the exchange parameters of Cr_2WO_6 and Cr_2TeO_6 with respect to the QCP, in Fig. 4.22(a) and (b) we show the $|J_2|/J_1$ dependence of the excitation gap and the magnetic moment with the values of J_1 and J_3 fixed as listed in Table 4.6. The magnetic moment increases with $|J_2|/J_1$ in the ordered phase, as illustrated by the magenta curves in Fig. 4.22. The black line represents the excitation gap in the disordered phase, which is threefold degenerate. The excitation gap is located at $\mathbf{Q} = (0\ 0\ 1)$ and $(0\ 0\ 0)$ for Cr_2WO_6 and Cr_2TeO_6 , respectively, and it is analytically given by

$$E_{gap} = \sqrt{J_1^2 - 20J_1(|J_2| + |J_3|)}$$

in the disordered phase. In the ordered phase, the excitation modes split into two transverse modes and one longitudinal mode. The transverse mode (*T*-mode) stays gapless, reflecting the global rotational symmetry of the spin Hamiltonian. The gap of the Higgs amplitude mode (*L*-mode) scales with $|J_2|/J_1$. This excitation gap corresponds to the Higgs mass in high-energy physics. According to Eq. (5), the QCP is located at $|J_2|/J_1 = 0.031$ and 0.040 for Cr_2WO_6 and Cr_2TeO_6 , respectively. The estimated values of this ratio are $|J_2|/J_1 = 0.0905$ and 0.101 for Cr_2WO_6 and Cr_2TeO_6 , respectively, as indicated by the vertical green dashed lines. Correspondingly, the calculated ordered moments normalized to the fully saturated value for Cr^{3+} are consistent with the observed reduction in the ordered moment of $\sim 24\%$.

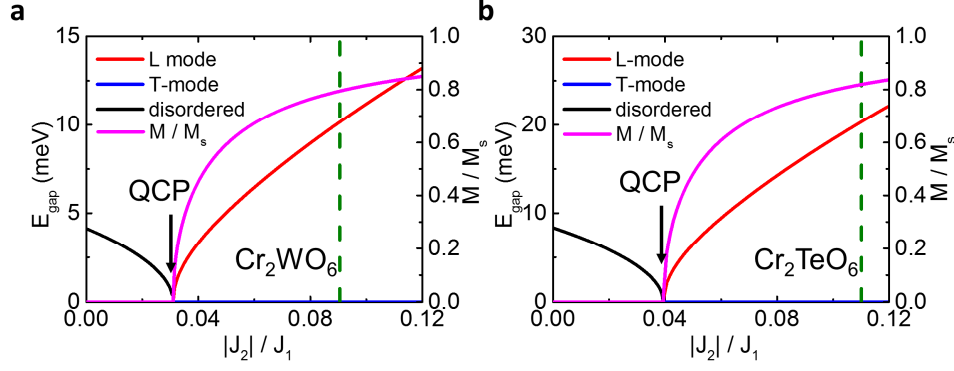


Figure 4.22: (a),(b) $|J_2|/J_1$ dependence of the ordered moment M/M_s and the excitation gaps. The black line represents the excitation gap in the disordered state. The excitation gaps of the longitudinal modes (L -mode) and the transverse modes (T -mode) in the ordered state are plotted by red and blue solid lines, respectively. The exchange parameters of Cr_2TeO_6 and Cr_2WO_6 are denoted by green dashed vertical lines. The ordered moments are represented by magenta lines.

4.4.5 Discussions

As the system goes away from the QCP, the energy of the amplitude mode increases and the neutron scattering intensity weakens. This, together with the tendency of decaying into transverse modes, makes it difficult to detect Higgs amplitude modes. Thus, our observation brings about another intriguing question: What makes it feasible to observe the longitudinal excitation modes in these two compounds? There are several contributing factors. i) These compounds are spin dimers with $S = 3/2$. Similar to the $S = 1/2$ spin dimer systems, the low-lying states here are $S_{\text{tot}} = 0$ singlet and $S_{\text{tot}} = 1$ triplet, suggesting a similar low-energy structure. However, the matrix elements of the spin operators (between the singlet and triplet states) are different between $S = 3/2$ and $S = 1/2$ dimer systems, with the matrix element enhanced by $\sqrt{5}$ for the $S = 3/2$ dimer. As a result, the intensity of the amplitude mode is enhanced relative to the transverse mode in the case of the $S = 3/2$ dimer. ii) Interestingly, as shown in Fig. 4.19 and 4.20, the dispersion of the amplitude modes in both Cr_2WO_6 and Cr_2TeO_6 is weak and the inelastic neutron scattering intensity stays in a narrow energy region separated from the transverse modes, which enables us

to distinguish these two modes even with polycrystalline samples. Our results suggest that Higgs amplitude modes are not the privilege of the ordered quantum spin dimers in the vicinity of a QCP, but may be common excitation modes that can survive even away from it.

Finally, we would like to point out that the inverse-trirutile systems composed of dimerized edge-sharing octahedra, such as Cr_2WO_6 and Cr_2TeO_6 in this study, provide substantial opportunities to search for and tune Higgs amplitude modes in quantum antiferromagnets. First, as both the intra-dimer interaction J_1 and inter-dimer interaction J_2 can be effectively tuned by varying the concentration of the nonmagnetic atoms in $\text{Cr}_2(\text{Te}_{1-x}\text{W}_x)\text{O}_6$, one can anticipate the presence of the amplitude modes in the whole series of compounds. In particular, J_2 changes its sign at $x \sim 0.7$, giving rise to minimum values of both the Neel temperature T_N and the ordered moment $M/M_s \sim 15\%$, as shown in Fig. 4.4 [195]. The small ordered moment suggests that the ordered phase is very close to the QCP at $x \sim 0.7$ that would yield stronger intensity of the amplitude modes. Second, the availability of various isostructural inverse-trirutile compounds consisting of edge-sharing $(\text{M}_2\text{O}_{10})^{14-}$ ($\text{M} = \text{Cr}, \text{Fe}, \text{Mn}$ and V , etc.) entities with reduced ordered moments and low Neel temperatures, enables the exploration of a wider range in the exchange parameter space that may lead to the observation of Higgs amplitude modes in other interacting spin dimer systems beyond $S = 1/2$.

4.4.6 Summary

We present the observation of the Higgs amplitude modes in the inelastic neutron scattering measurements on polycrystalline Cr_2TeO_6 and Cr_2WO_6 compounds with interacting $S = 3/2$ spin dimers that are away from a QCP. The measured magnetic excitation spectra, both the longitudinal and transverse modes, agree well with the extended spin wave (ESW) calculations. This study suggests that Higgs amplitude modes may be common excitation modes in quantum spin dimers

instead of being limited to a few exceptional systems close to a QCP, thus paving a new avenue to search for and understand the physics of Higgs-like quasiparticles in condensed matter systems.

Chapter 5

Summary and perspectives

Collective behaviors of correlated electrons are one of the mysteries in condensed matter physics even after decades of intense investigations. Studies on transition-metal oxides, where the effects of electron correlations are essential, have contributed tremendously to the development of this field. In this thesis, we have presented neutron scattering studies on Ruddlesden-Popper type ruthenates $(\text{Sr,Ca})_{n+1}\text{Ru}_n\text{O}_{3n+1}$ and inverse-trirutile chromates Cr_2MO_6 ($\text{M} = \text{Te, W and Mo}$).

Perovskite $(\text{Sr,Ca})_{n+1}\text{Ru}_n\text{O}_{3n+1}$ is a prototypical $4d$ correlated electron system ideal for exploring the physics of emergent phenomena. Owing to the strong coupling among charge, spin, orbital and lattice degrees of freedom, the magnetic and electronic properties are very susceptible to perturbations, such as chemical doping and magnetic field. For instance, upon 3% $\sim$ 5% Fe doping we have unraveled a commensurate SDW order with the propagation vector $\mathbf{q}_c = (0.25 \ 0.25 \ 0)$ in Sr_2RuO_4 ($n = 1$), which cannot be ascribed to Fermi surface nesting as suggested by inelastic neutron scattering measurements and electronic structure calculations. For $\text{Sr}_3\text{Ru}_2\text{O}_7$ ($n = 2$) we have found that Fe doping leads to an E -type antiferromagnetic insulating state distinct from the Fermi liquid ground state in the parent compound. In the presence of a magnetic field, we have observed a field-induced collapse of the Mott gap in $\text{Ca}_3(\text{Ru}_{0.97}\text{Ti}_{0.03})_2\text{O}_7$ accompanied by changes in the spin structure and the lattice, which results in a CMR effect that is fundamentally different in nature from that in phase-separated manganites. For $\text{Ca}_3(\text{Ru}_{0.95}\text{Fe}_{0.05})_2\text{O}_7$, the magnetic field drives an incommensurate-to-commensurate magnetic transition when applied either along the crystallographic a or b axis. The magnetic phase transitions are found to be irreversible when

removing the magnetic field, leading to history-dependent metastable states that transform into the equilibrium one only upon warming up the system above a characteristic temperature T_g .

Cr_2MO_6 ($M = \text{Te}$ and W) have inverse-trirutile structures with structurally dimerized Cr^{3+} magnetic moments. We show that the nature and strength of the inter-dimer interaction can be effectively tuned by mixing Te and W in the solid solution $\text{Cr}_2(\text{Te}_{1-x}\text{W}_x)\text{O}_6$. The sign of the inter-dimer exchange interaction changes at $x_c \sim 0.7$, where the Neel temperature T_N and the sublattice magnetization M_s reach the minimum. Our DFT calculations suggest that the hybridization between the $\text{W } 5d$ and $\text{O } 2p$ orbitals in the Cr-O-Cr exchange path might play a crucial role. To further validate this idea, we have also studied the magnetic structure of another isostructural compound Cr_2MoO_6 and found that the inter-dimer interaction is indeed ferromagnetic as expected from the $\text{Mo } 4d\text{-O } 2p$ hybridization. The magnetic excitation spectra of Cr_2TeO_6 and Cr_2WO_6 measured by the inelastic neutron scattering also exhibit intriguing physics. In addition to the transverse Goldstone modes, we have observed longitudinal modes, also known as Higgs amplitude modes, that arise from the fluctuations in the magnitude of the ordered moment. It is generally believed that Higgs amplitude modes are only observable when the system is close to a QCP separating the dimer-based quantum disordered phase and the long-range ordered state, where the ordered moment and the transition temperature are strongly suppressed by quantum fluctuations. Intriguingly, our ESW calculations have shown that these two materials are away from the QCP, which is highly unexpected according to the conventional wisdom.

A number of intriguing questions remain open and are worth further experimental and theoretical investigations. Here we give a few examples. (i) What is the microscopic origin of the commensurate SDW order in Sr_2RuO_4 ; and more importantly, does it have any correlation with the p -wave unconventional superconductivity? (ii) The spin wave excitations of this commensurate

SDW order are not well captured in the current inelastic neutron scattering measurements. Is it because of its low energy scale? (iii) What are the roles of the 3d transition-metal dopants? Why is the effect of Ti and Mn similar in Sr_2RuO_4 but different from that of Fe, whereas in $\text{Sr}_3\text{Ru}_2\text{O}_7$, Mn and Fe give rise to similar effects which are different from Ti. (iv) Is the insulating state in Fe-doped $\text{Sr}_3\text{Ru}_2\text{O}_7$ a Mott type originating from electron correlations, or Slater type arising from the magnetic order? (v) Is the collapse of the Mott insulating state in a magnetic field a universal phenomenon? (vi) Is it possible to experimentally verify the presence of orbital order in the Mott insulating ground state of Ti-doped $\text{Ca}_3\text{Ru}_2\text{O}_7$? (vii) What's the origin of the irreversibility in the field-induced transitions in Fe-doped $\text{Ca}_3\text{Ru}_2\text{O}_7$?

There are still ample opportunities in Ruddlesden-Popper type ruthenates and inverse-trirutile compounds for exploring the collective behaviors of correlated electrons. Other than chemical doping and magnetic field, applying hydrostatic or uniaxial pressure is also quite effective in tuning the magnetic and electronic properties of ruthenates. Recent studies on $\text{Ca}_3(\text{Ru}_{0.97}\text{Ti}_{0.03})_2\text{O}_7$ have shown that the G-AFM Mott insulating ground state collapses with a very low hydrostatic pressure, which is ascribed to the coupling between the lattice distortions and the orbital polarization by DFT calculations [211]. In addition, the electric field is also a promising tuning parameter. Researchers have found that an insulator-to-metal transition can be induced in Ca_2RuO_4 , which is accompanied by a structural transition [212]. Moreover, the photo-doping effects have been studied on some Mott insulators using femtosecond lasers. Upon exciting the charge carriers across the Mott gap, transient novel phases may emerge [109]. The relaxation process from the excited states to the equilibrium one may provide valuable information on the electron correlations. The idea is likely to be applicable to correlated ruthenates. Another emerging field that has been developing rapidly in recent years is the transition-metal oxide thin films and heterostructures

[213]. It has been demonstrated that the physical properties can be tailored by epitaxial strains imposed by different substrates or substrate orientations. SrRuO_3 is a rare $4d$ ferromagnetic metal with a Curie temperature $T_c = 160$ K and strong magnetocrystalline anisotropy, and it has been widely used as the conducting layer in heterostructures [167]. Prototypical interfacial phenomena such as exchange bias effects have been observed in $\text{SrRuO}_3 / \text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ bilayers grown on SrTiO_3 substrates [214]. Furthermore, more exotic phenomena can occur at the interface. For instance, highly confined two-dimensional electron gas and superconductivity have been observed in $\text{SrTiO}_3 / \text{LaAlO}_3$ [215,216]. While a similar two-dimensional electron gas has been theoretically predicted in $\text{SrRuO}_3 / \text{SrTiO}_3$ superlattices [217], it has not been observed experimentally.

For the inverse-trirutile compounds, the availability of isostructural materials consisting of different magnetic ions (e.g. Fe, Mn and V) enables further studies regarding the dependence of Higgs amplitude modes on the spin quantum numbers and the ratio of the inter- and intra-dimer interactions $|J_2|/J_1$. Further experiments, such as magnetic-field-dependent measurements and polarized neutron scattering studies, will indeed provide more information once high-quality single-crystal samples are synthesized successfully.

In conclusion, though understanding the electron correlations remains challenging for condensed matter physicists, transition-metal compounds have offered an important stage where new discoveries are always expected. Further experimental and theoretical efforts are still highly desired.

APPENDICES

APPENDIX A: Crystal symmetry of $\text{Sr}_2\text{Ru}_{1-x}\text{Fe}_x\text{O}_4$ ($x = 0.03$ and 0.05)

The symmetry of the crystal structure is an important starting point to explore the symmetry-allowed magnetic structure models. In addition, the assignment of the observed $\mathbf{q}_c = (0.25 \ 0.25 \ 0)$ peak to a magnetic Bragg peak, rather than a nuclear one arising from a change in the crystal symmetry, requires a determination of the space group. Here, the space group of $\text{Sr}_2\text{Ru}_{1-x}\text{Fe}_x\text{O}_4$ ($x = 0.03, 0.05$) is assumed to be the same as that of the parent compound (No. 139 $I4/mmm$). The rationales are as follows:

(i) The ionic radii of Fe^{3+} (0.645 Å) and Ru^{4+} (0.62 Å) are very close, similar to $\text{Sr}_2\text{Ru}_{1-x}\text{Ti}_x\text{O}_4$ where the ionic radius of Ti^{4+} is 0.605 Å. In fact, the space group of the end members of all three compounds are the same, i.e. $I4/mmm$.

(ii) In spite of the significant difference in the ionic radii of Sr^{2+} (1.31 Å) and Ca^{2+} (1.18 Å), the space group of $\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$ remains the same as Sr_2RuO_4 for $1.5 < x \leq 2$ (i.e., within 25% of Ca substitution for Sr) [102].

Therefore, due to the low doping concentration 3% ~ 5% and the similar ionic radii of Fe^{3+} and Ru^{4+} , the crystal symmetry of Fe-doped Sr_2RuO_4 is not likely to change. In fact, even assuming that there were structural distortions such that the space group changed to $I4_1/acd$ ($\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$, $0.5 < x < 1.5$ due to RuO_6 rotation) or $Pbca$ ($\text{Ca}_{2-x}\text{Sr}_x\text{RuO}_4$, $x < 0.2$ due to rotation, tilting and flattening), the wave vector $\mathbf{q}_c = (0.25 \ 0.25 \ 0)$ in tetragonal notation becomes $\mathbf{q}_c = (0.5 \ 0 \ 0)$ in orthorhombic notation, which still cannot be assigned as a nuclear Bragg peak. Therefore, the emergence of this new Bragg peak must be associated with the formation of a magnetic order, rather than related to the structural change that does not actually take place in $\text{Sr}_2\text{Ru}_{1-x}\text{Fe}_x\text{O}_4$. (Note that all the ionic radius data are taken from Ref. [90])

APPENDIX B: Determination of magnetic structures by neutron diffraction

In this section, we describe the details on determining the different magnetic structures in $\text{Ca}_3\text{Ru}_2\text{O}_7$ and Ti-doped $\text{Ca}_3\text{Ru}_2\text{O}_7$ based on neutron diffraction measurements. The AFM-a/AFM-b and G-AFM type magnetic structures have been reported previously by W. Bao et al [97] and X. Ke et al [99], respectively. The determination of the CAFM phase above the critical field B_c at $T < T_{\text{MIT}}$ is presented as follows. The space group of $\text{Ca}_3(\text{Ru}_{1-x}\text{Ti}_x)_2\text{O}_7$ ($x = 0.03$) is $Bb2_1m$ (No. 36), and the magnetic propagation vector for the CAFM phase is $(0\ 0\ 1)$. We performed magnetic representational analysis using FULLPROF [71]. According to this symmetry analysis, only four types of collinear antiferromagnetic structure models are possible, as shown in Fig. B1(a). Since the L index of the observed magnetic reflections $(0\ 0\ L)$ is odd, model 3 and 4 can be ruled out immediately as the squared magnetic structure factor $|F(h0l)|^2 = 0$. In both model 1 and 2, the magnetic moments in the RuO_2 plane are coupled parallel to each other.

In model 1, the magnetic moments are parallel with the bilayer and antiparallel between adjacent bilayers (AFM-a or AFM-b).

In model 2, within the bilayer the spin configuration of two RuO_2 layers is antiparallel and the bilayers are coupled antiparallel along the c axis.

The squared magnetic structure factor is $|F(h0l)|^2 = 64\cos^2(2\pi l\epsilon)$ for model 1 and $|F(h0l)|^2 = 64\sin^2(2\pi l\epsilon)$ for model 2, where $2\epsilon = 0.1978$. Since we have observed sizable magnetic intensity at $(0\ 0\ 5)$ at $T = 10\text{ K}$ and $B = 10\text{ T}$ [Fig. B1(b)], model 2 can be readily excluded as $|F(005)|^2 = 64\sin^2(2\pi l\epsilon) \approx 0$. In addition, the magnetic reflections $(0\ 0\ 1)$ and $(2\ 0\ 1)$ have the same structure factor $|F(h01)|^2 = 64\cos^2(2\pi l\epsilon) \approx 0.6610$. Thus, the absence of the $(2\ 0\ 1)$ magnetic reflection suggests that the staggered antiferromagnetic moment is aligned along the a axis, since neutrons couple to the moments perpendicular to the momentum transfer $\mathbf{q}$.

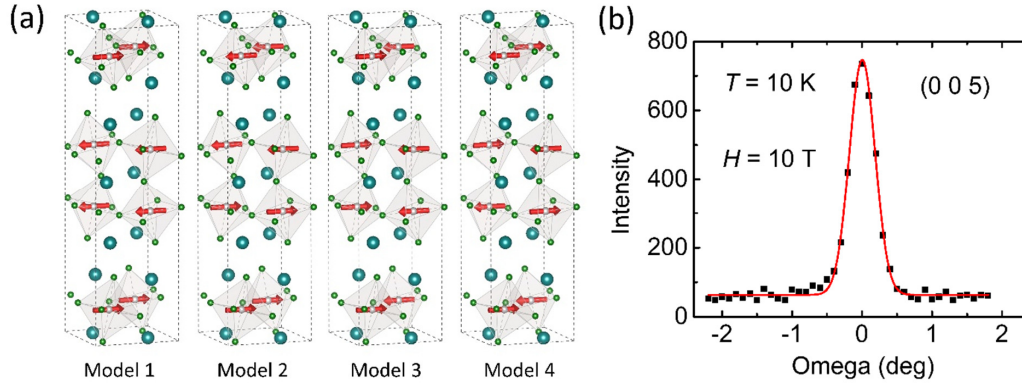


Figure B1: (a) Schematics of possible magnetic structures. (b) Rocking curve scan across (0 0 5) magnetic Bragg peak at $T = 10$ K and $B = 10$ T, $B \parallel b$ axis.

The evidence to the presence of spin canting is the following:

(i) As shown in Fig. 3.15(b), the intensity of the field-induced (0 0 1) peak at $T = 10$ K is weaker than the intensity of (0 0 1) at $T = 50$ K and $B = 0$ T.

(ii) The isothermal magnetization measurements [Fig. B2] with the magnetic field applied along the b axis yield a metamagnetic transition and the field-induced phase has a large ferromagnetic moment. Hence, the field-induced magnetic structure below T_{MIT} is a canted antiferromagnetic phase (CAFM): a superposition of AFM-a and a ferromagnetic component along the b axis. For instance, at $T = 20$ K, the canted spins above the critical field (~ 9 T) have an antiferromagnetic component of $\sim 0.71 \mu_B$ and a ferromagnetic component of $\sim 1.76 \mu_B$ along the b axis.

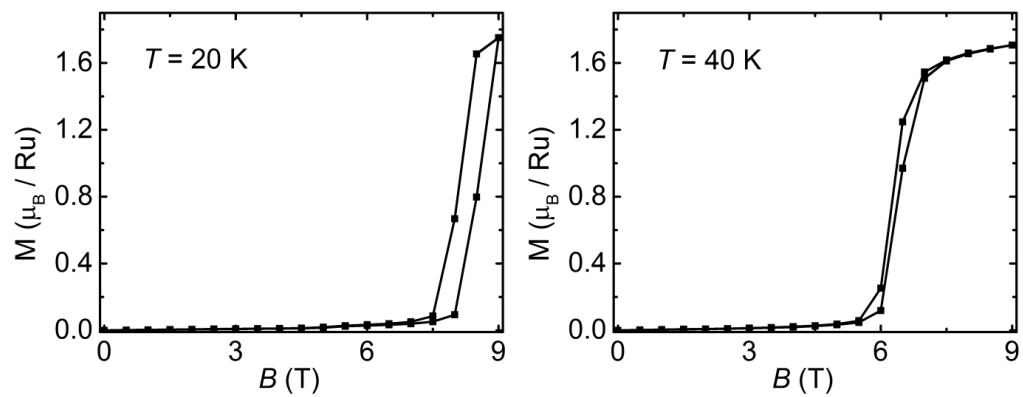


Figure B2: Magnetization of $\text{Ca}_3(\text{Ru}_{0.97}\text{Ti}_{0.03})_2\text{O}_7$ as a function of magnetic field at selected temperatures.

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