Emergent phenomenon in Jeff=1/2 iridate

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PREFACE

The following presented in this dissertation has been published or in preparation of publishing

Chapter Two

Chapter Three


Chapter Four

ABSTRACT

Recent work on various quantum materials has led to fruitful results including unconventional magnetic states, topological properties, and exotic emergent phenomena. High Tc superconductivity is one of the prominent properties discovered in quantum materials like strong correlated systems. Though the efforts on understanding this exotic behavior have lasted for years, the mechanism remains elusive owing to the many-body nature of the system and the research scope limitation within cuprates. Recent unravel of J_{eff}=1/2 state in the iridate square lattice offers alternative to study the complicated many body physics and potentially achieve high Tc superconductivity. In addition, the combination of electron correlation and strong spin-orbital coupling makes iridate a promising material to explore diverse exotic behaviors beyond cuprates.

This dissertation work utilizes the epitaxial heterostructure engineering to construct various J_{eff}=1/2 iridate thin films under different effective dimensionality to study both fundamental physics and explore new emergent phenomenon. Following a detailed survey of thermodynamic stability of Sr_{n+1}Ir_nO_{3n+1} thin films, the argon gas is found to be helpful in stabilizing Sr_{n+1}Ir_nO_{3n+1} under intermediate dimensionality. Epitaxial strain can be applied to stabilize chemical substituted SrIrO_3 thin film where no bulk single crystal sample has been synthesized so far. Moreover, epitaxial strain is used to tune the correlation in a pseudospin-1/2 iridate superlattice within a Slater-Mott crossover regime. The physical properties of iridate superlattice is shown to be highly susceptible to structural modulation with observation that is rarely found in 3d transition metal oxides. The structural modulation on iridate thin film under 3D limit also successfully induces exotic transport properties which may originate from Berry curvature.
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CHAPTER 1 INTRODUCTION

Modern condensed matter physics research shows a strong interest in both understanding and designing quantum materials where interactions among constituent electrons and strong quantum-mechanical effects lead to various emergent phenomena, like topological properties [1], quantum spin liquid [2], and superconductivity [3]. The collective behavior under different interactions can hardly be explained from the properties of individual electrons. The study of quantum materials can help on both fundamental scientific understanding and future engineering applications. On the other hand, due to the complexity of the system, it requires both good material platform and advanced probing techniques. One of the prominent quantum materials is the 5d transition metal oxides (TMOs). In 5d TMOs, the similar energy scale between different interactions makes the interplay among different degree of freedom stronger than materials like 3d transition metal oxides (Figure. 1.1(a)). The small on-site Columbo repulsion makes it possible to explore the weak and intermediate correlation regime and the larger spin-orbit coupling (SOC) also indicates the possibility for various topological properties. With advanced techniques like heterostructure engineering and x-ray scattering, the iridate can be used as a platform to explore correlation physics beyond 3d TMOs. In addition, by varying strength between different interactions, a lot of exotic states can be potentially realized (Figure. 1.1(b)) [4].

1.1 Strong correlated system

Interacting many-body systems come in various forms ranging from the network for embryonic stem cell development [5] to the highly dynamic human collective behavior [6]. The number of constituents in the systems is often extremely large and the interactions between the constituents are strong. Though the nature of its many-body interaction often makes it extremely difficult to obtain an exact solution for the systems, various exotic phenomenon emerges. In the past decades, the intense study of strong correlated systems has result in fruitful results, including high-Tc superconductors [7], multiferroics [8] and metal-insulator transition [9]. One of the most fascinating examples is the discovery of superconductivity in cuprates. Superconductivity is a quantum state of materials formed by the condensation of paired conduction electrons [3, 10] and its exotic properties like zero resistance shows great potential in applications. While experimental observation of $T_C$ in conventional superconductor has not yet exceeded 39 K at ambient pressure [11], the highest critical temperature achieved in the cuprate high $T_c$ superconductors is 133 K at ambient pressure [12]. These high $T_c$ superconductors cannot be well explained by BCS theory and thus distinguish themselves from conventional superconductors. Even though intensive theoretical and experimental research have been carried out, the origin of the
Figure 1.1 (a) Comparison between 3d and 4d/5d electrons. [13] (b) Sketch of generic phase diagram for electronic materials in terms of interaction $U/t$ and $\lambda/t$. [4]
superconductivity in these materials remain elusive [3, 10, 14-17]. The discovery of cuprate high T_c superconductors [7] also remarks the emergence of strongly correlated electron systems as the centerpiece of solid state physics and the rejuvenation of the field once thought to be reaching the maturity [18]. In addition to the exotic superconductivity phenomenon, the parent compound of cuprates is also important in the study of strong correlated systems. The understanding the role of correlation in its parent compound not only helps find out the origin of superconductivity but also deepens knowledge of the interplay between electronic and magnetic interactions under correlation.

### 1.1.1 Cuprates and Iridates

The high T_c superconducting phenomenon in cuprates is discovered in Ba–La–Cu–O system [7]. It is remarkable that the cuprate high T_c superconductor has a record high critical temperature. Moreover, its parent compound La$_2$CuO$_4$ is a magnetic insulator while most conventional superconductors are either single element or metal alloy [19] (Figure. 1.2(a)). La$_2$CuO$_4$ has a layered perovskite structure where the CuO$_2$ plane forms a square lattice (Figure. 1.2(b)). The electronic configuration of Cu$^{2+}$ is 3d$^9$ which leaves only one hole on its d-orbital states. The d-orbital states of Cu$^{2+}$ in LaCuO$_4$ is split into two degenerate e$_g$ ($d_{3z^2-r^2}, d_{x^2-y^2}$) and three degenerate t$_{2g}$ ($d_{xy}, d_{xz}, d_{yz}$) orbitals states due to the cubic crystal field. In addition, the Jahn-Teller distortion lifts the degeneracy in the e$_g$ orbital states and thus makes it possible to use a half-filling single band to capture the low energy physics in La$_2$CuO$_4$. Single electron approximation would predict La$_2$CuO$_4$ to be a metal; however, the strong electron correlation results a charge gap opening which marks La$_2$CuO$_4$ a Mott insulator [14, 20]. La$_2$CuO$_4$ is a spin-1/2 antiferromagnetic (AFM) insulator with a square lattice structure. The understanding of high T_c superconductivity phenomenon remains elusive, attributed to both the complicated many-body effects, and limited experimental systems. To deepen the understanding this exotic phenomenon, it is necessary to have more experimental systems. Though high T_c superconductivity is also observed in pnictide [21], its antiferromagnetism in its parent compound is very different from the parent compound of cuprates [22, 23].

It begins with searching for materials analogous to La$_2$CuO$_4$ in hope to shred the light on criteria of high T_c superconductor. The search lasts for a long time until recently Sr$_2$IrO$_4$ emerges a strong potential candidate for high T_c superconductor [24]. The layered perovskite structure in the Sr$_2$IrO$_4$ was characterized in the 50s [25] (Figure. 1.3(a)) and it was regarded to have a S=1/2 ground state due to the half-filled d$_{xy}$ orbital state in the 90s [26]. Early transport measurement shows the resistivity of singe crystal sample increases as temperature decrease indicating it is an insulator (Figure. 1.3(b)). The magnetometry
Figure 1.2 (a) Phase diagram of cuprates. (b) Schematic structure of La$_2$CuO$_4$
Figure 1.3 (a) Schematic diagram of layered structure of Sr$_2$IrO$_4$. (b) Temperature dependence of resistivity of Sr$_2$IrO$_4$. (c) Temperature dependence of the magnetic moment of Sr$_2$IrO$_4$. (d) Schematic diagram of spin canting of an S-1/2 antiferromagnetic square lattice system.
measurement observes a weak ferromagnetism under 240 K [26] (Figure. 1.3(c)). The observed weak ferromagnetism is later understood as a result of spin canting [27]. The spin couples antiferromagnetically in Sr$_2$IrO$_4$; on the other hand, the existence of strong spin orbit coupling (SOC) locks the spin degree of freedom with lattice degree of freedom. The octahedral rotation eventually leads to the canting of spin; thus, a non-zero net moment rises from an antiferromagnetic ordering (Figure. 1.3(d)).

Despite of the structural, electronic, and magnetic similarity between two compounds, the S-1/2 state in iridate remains debatable. Recent discovery of the pseudo-spin ½ state (J$_{\text{eff}}$=1/2 state) in Sr$_2$IrO$_4$ then establishes a strong connection to La$_2$CuO$_4$ and it also explains various observed phenomenon [28]. In Sr$_2$IrO$_4$, the t$_{2g}$ state resulted from cubic crystal field splitting is further split into doublet J$_{\text{eff}}$=1/2 state and quadlets J$_{\text{eff}}$=3/2 state under SOC (Figure. 1.4(a)). The J$_{\text{eff}}$=1/2 is a Kramer doublet where it can be written in $|L_{Z}, S_{Z}\rangle$ basis as [29]

$$
|\uparrow\rangle = \frac{1}{\sqrt{3}} |0, \uparrow\rangle - \frac{\sqrt{2}}{\sqrt{3}} |1, \downarrow\rangle
\tag{1.1}
$$

$$
|\downarrow\rangle = -\frac{1}{\sqrt{3}} |0, \downarrow\rangle + \frac{\sqrt{2}}{\sqrt{3}} |1, \uparrow\rangle
\tag{1.2}
$$

where $|0, \downarrow\rangle = |xy, \downarrow\rangle$ and $|\pm, \downarrow\rangle = \frac{1}{\sqrt{2}} (|yz, \downarrow\rangle \pm i|xz, \downarrow\rangle)$. Since there are 5 electrons on the d-shell of Ir ion in Sr$_2$IrO$_4$, the J$_{\text{eff}}$=3/2 state is filled and J$_{\text{eff}}$=1/2 state is half-filled. This J$_{\text{eff}}$=1/2 state has a much narrow bandwidth compared to original t$_{2g}$ state; thus, a moderate Coulomb interaction is sufficient to open a charge gap [28, 30] (Figure. 1.4(b)). Therefore, Sr$_2$IrO$_4$ is often regard as a SOC Mott insulator. Despite of good analogy between Sr$_2$IrO$_4$ and La$_2$CuO$_4$, no high T$_c$ superconductivity was yet observed with carrier doping [31, 32]. While the search for high T$_c$ superconductivity is still on going, the combination of on-site Coulomb interaction, crystal field splitting and SOC at the similar energy scale in iridate shows a promising path to realize various exotic emergent phenomenon like topological effect and unconventional magnetism [4, 33, 34].

In addition, Sr$_2$IrO$_4$ belongs to Sr$_{n+1}$Ir$_n$O$_{3n+1}$ Ruddlesden-Popper series where Sr$_2$IrO$_4$ is under quasi-2D limit (n=1) within this series (Figure 1.5). As the dimensionality increases within this series, the system goes from an antiferromagnetic insulating to a nonmagnetic semimetal [35]. While Sr$_2$IrO$_4$ is a potential candidate to realize superconductivity, Sr$_3$Ir$_2$O$_7$ (n=2) also shows a lot of interesting properties. One of the interesting phenomena observed in this compound is the spin-flop transition. While the spin aligns antiferromagnetically within ab plane in Sr$_2$IrO$_4$ (n=1), it becomes a c-axis colinear antiferromagnetic magnetic structure in Sr$_3$Ir$_2$O$_7$ (n=2) [36]. Recent study also
Figure 1.4 (a) Schematic diagram of $J_{\text{eff}}$ picture. (b) Schematic diagram of $J_{\text{eff}}=1/2$ Mott state [27].
Figure 1.5 (a)(b)(c) Schematic diagram of the structural of $\text{Sr}_{n+1}\text{Ir}_n\text{O}_{3n+1}$ series[33].
reveals an antiferromagnetic excitonic insulator state within Sr$_3$Ir$_2$O$_7$ [37]. As the dimensionality increases to 3D, SrIrO$_3$ ($n=\infty$) is found to be non-magnetic semi-metal. The semi-metallicity is considered to be deeply connected to the band topology [38]. The abundant emergent phenomena in Sr$_{n+1}$Ir$_n$O$_{3n+1}$ series also show the rich physics to be explored beyond cuprates.

In addition to Sr$_{n+1}$Ir$_n$O$_{3n+1}$ series, recent progress of heterostructure engineering has created a series mSrIrO$_3$/nSrTiO$_3$ thin films that mimic the Sr$_{n+1}$Ir$_n$O$_{3n+1}$ series [39] (Figure 1.6). The layered perovskite Sr$_2$IrO$_4$ can be considered as a stacking between one layer of SrIrO$_3$ and one layer of SrO. The heterostructure synthesis method is applied to replace the SrO layer with SrTiO$_3$ layer. The SrTiO$_3$ layer acts as a blocking layer that separates the nearest two SrIrO$_3$ layers. The SrTiO$_3$ is also considered to be relatively inert as Ti$^{4+}$ ion has a 3d$^0$ electronic configuration. The mSrIrO$_3$/nSrTiO$_3$ superlattice which mimics Sr$_{n+1}$Ir$_n$O$_{3n+1}$ also shows a similar electronic and magnetic behavior with respective [39-41]. The quasi-2D SrIrO$_3$/SrTiO$_3$ superlattice (1/1-SL) shows an insulating behavior under (Figure 1.7 (a)) and a clear kink is observed around 135K (Figure. 1.7 (b)). Further magnetometry measurement also shows a weak ferromagnetism below 150 K which is slightly lower than the Sr$_2$IrO$_4$ (Figure. 1.7(c)). On the other hand, the 2SrIrO$_3$/SrTiO$_3$ superlattice (2/1-SL), which mimics Sr$_3$Ir$_2$O$_7$, shows a weaker insulating behavior compared to 1/1-SL which is consistent with the observation in the Sr$_{n+1}$Ir$_n$O$_{3n+1}$ series (Figure 1.7 (a)). A kink can still be observed in 2/1-SL (Figure 1.7 (b)). However, a weak ferromagnetism is observed for 2/1-SL below 120 K, indicating the artificial superlattice is not a complete replicate of Sr$_{n+1}$Ir$_n$O$_{3n+1}$ series. In addition to mimic the Sr$_{n+1}$Ir$_n$O$_{3n+1}$ series, the heterostructure engineering allows one to further control the dimensionality of the iridate superlattice. By controlling the number of inserted SrTiO$_3$ layers, one can further weaken the interlayer coupling between two SrIrO$_3$ layers. By having 2 SrTiO$_3$ layers, the resistivity of the SrIrO$_3$/2SrTiO$_3$ superlattices (1/2-SL) increases compared to 1/1-SL. For 1/2-SL, no kink is observed in the resistivity vs temperature. Moreover, the weak ferromagnetism is only observed below 40 K indicating the suppression of magnetic ordering. With further increase of SrTiO$_3$ layers, the change of both insulating behavior and magnetic ordering becomes insignificant. The introduce of mSrIrO$_3$/nSrTiO$_3$ superlattices not only provides an alternative iridate square lattice systems but also allows one to have a higher structural tunability which can be used to further explore the interesting physics.

**1.1.2 Slater-Mott crossover regime**

The low energy physics in the La$_2$CuO$_4$ can be captured by a single band half-filling
Figure 1.6 Schematic diagram of mSrIrO$_3$/SrTiO$_3$ superlattice [39].
Figure 1.7 (a) Temperature dependent resistivity of the SLs. The arrows indicate the position of the resistivity anomaly in 2/1- and 1/1-SLs. (b) $d(ln \rho)/d(1/T)$ shown as a function of $T$. (c) The remnant magnetization plotted against temperature. Before measurements under the zero-field condition, all the samples were cooled from room temperature to 2 K with application of a 5 kOe in-plane magnetic field. The dashed lines are guides to the eye [41].
Hubbard model which is a simple, approximate model for the interaction of electrons in narrow energy bands [42]. The corresponding Hamiltonian is

\[ H = t \sum_{i,j,\sigma} (c_{i\sigma}^\dagger c_{j\sigma} + h. c.) + \frac{1}{2} U \sum_{i,\sigma} n_{i,\sigma} n_{i,-\sigma} - \sum_{i,\sigma} v_{i,i} n_{i,\sigma} \]  

1.3

where \( n_{i,\sigma} = c_{i\sigma}^\dagger c_{i\sigma} \) and the last term is equal to \(-\frac{1}{2} INn^2\) which is a constant. This Hamiltonian seems simple since it only has two terms: electron hopping (t) and on-site Coulomb repulsion (U). Though it only takes the onsite Coulomb interaction from electrons with different spins into account, the introduction of the correlation effect has made it a truly many-body problem. The model successfully explains insulating state in various 3d transition metal compounds [9]. La\(_{2}\)CuO\(_4\) is a good example where strong effective correlation (U\(>>t\)) opens a charge gap and thus makes it a Mott insulator [42, 43]. In the case of strong correlation, one can consider the extreme case where t=0. In this case, the electrons are localized, and each site is single occupied for a square lattice at half filling. A double occupied states and an empty state will require a higher energy equal to U compared to two single occupied state. In order for an electron to be able to hop from one site to another one, it needs to overcome U which can be hardly. In addition to La\(_{2}\)CuO\(_4\), other 3d TMOs like V\(_2\)O\(_3\), LaTiO\(_3\) and NiO\(_2\) are also considered to be Mott insulators.

To have a better understanding of the insulating states in this strong correlated limit, one can take a theoretical approach by employing the Green function techniques [42, 44].

\[ G_{jk}^\sigma(E) \sim \int \langle c_{i\sigma}(E) c_{k\sigma}^\dagger(E) \rangle e^{iEt} dt \]  

1.4

where E is in the unit of frequency \( \omega \). In the atomic limit and half filling one band model, it is found by Hubbard that

\[ G_{ij}^\sigma(E) = \frac{1}{2\pi} \delta_{ij} \left[ \frac{1}{2} \left( \frac{1}{E-T_0} + \frac{1}{E-T_0-U} \right) \right] \]  

1.5

For the one-particle Green function it is possible to retrieve the density of pseudo-particle states which turns out to be,

\[ \rho_\sigma(E) = \frac{i}{N_0} \lim_{\epsilon \to 0^+} \sum_{j|i} [G_{jj}^\sigma(E + i\epsilon) - G_{jj}^\sigma(E - i\epsilon)] = \frac{1}{2} [\delta(E - T_0) + \delta(E - T_0 - U)] \]  

1.6

From this result, it is clear that the system will behave like if there are only two energy levels with energy T\(_0\) and T\(_0\)+U (Figure. 1.8).

In the Mott’s picture, the emergence of magnetism can be viewed because of charge gap opening; on the other hand, there is a different picture where the relation between magnetism and gap opening is indistinguishable. Materials under this picture are Slater
Figure 1.8 Schematic diagram of two separate bands under strong correlated limit.
insulator and the effective correlation in these materials is weak ($U\ll t$) [45]. In the Slater’s picture, gap opening which is a result of translation symmetry breaking is connected to spin order [45] (Figure. 1.9). Therefore, the system is metallic above the transition temperature while it becomes AFM insulating below the transition temperature. Unlike Mott insulator, Slater insulator is extremely rare. One of a candidate for Slater insulator is NaOsO$_3$ where research shows the metal-insulator transition temperature in the material is the same as its $T_N$ [46]. To illustrate the origin of insulating behavior due to AFM order, one can consider a simple theoretical approach. One can take the tight binding approximation for a 1D half filling case and perform the discrete Fourier transform of the creation and annihilation operator with

$$c_{i\sigma} = \frac{1}{\sqrt{N}} \sum_k c_{k\sigma} e^{ikx_i}$$

So that the Hubbard Hamiltonian with $U=0$ will become

$$H = \sum_{k,\sigma} (-2t\cos(kr)) c_{k\sigma}^\dagger c_{k\sigma}$$

where $r$ is the space between two nearest neighbors. In this case, the system will behave like a metal. The introduction of antiferromagnetic ordering will break the translation symmetry; thus, opens a gap in 1.8. To realize it, a trick that changes the tunneling parameter is introduced as

$$t_{j,j+1} = -t[1 + \Delta(-1)^j]$$

where $\Delta$ depends on the displacement of the position of the ion. By introduce this displacement of ion, the translation symmetry is broken. Now the unit cell will have size $2r$ instead of $r$. If we define the creation and annihilation operator on the odd sites as $(a_{j\sigma}, a_{j\sigma}^\dagger)$ and $(b_{j\sigma}, b_{j\sigma}^\dagger)$ on the even sites, the Hamiltonian is then written as

$$H = -t \sum_{j,\sigma} [1 + \Delta(-1)^j](a_{j\sigma}^\dagger b_{j\sigma} + a_{j+1\sigma}^\dagger b_{j\sigma} + \text{h.c.})$$

The Fourier transform of the Hamiltonian will give

$$H = -t \sum_{k,\sigma} \tilde{c}_{k\sigma}^\dagger \begin{pmatrix} 0 & 1 - \Delta + (1 + \Delta)e^{-i2kr} \\ 1 - \Delta + (1 + \Delta)e^{i2kr} & 0 \end{pmatrix} \tilde{c}_{k\sigma}$$

where $\tilde{c}_{k\sigma} = (a_{k\sigma}, b_{k\sigma})$. The diagonalization of the Hamiltonian will give the solution as

$$E_k = \pm 2t \sqrt{1 - (1 - \Delta^2 \sin^2(kr))}$$

Therefore, the band will be split into two with a gap of $2\Delta$ and a half filling system is now an insulator instead of a metal.
Figure 1.9 Schematic diagram of gap opening under the translation symmetry breaking in the Slater insulator. [47]
Though, mechanism behind the emergence of insulating states under these two limits are very different, they both leads to an antiferromagnetic insulating state on a S-1/2 square lattice system. Moreover, the strong and weak correlation regimes can be connected through a smooth crossover region called Slater-Mott crossover regimes (Figure. 10). The Slater-mott crossover regime corresponds to the region with an intermediate coupling. As the correlation approaches one limit from the other limit, the electronic and magnetic properties of the correlated system evolve correspondingly. It is particularly intriguing to consider evolution of the physical properties of the system at finite temperature. One of the macroscopic distinctions between the two limit is that the Slater insulator becomes metallic above $T_N$ while Mott insulator remains to be an insulator since the charge gap is independent of magnetic ordering. On the other hand, the many-body nature of the correlated system makes it extreme difficult to solve it even for a simple single band Hubbard Hamiltonian. The small perturbation approximation can be applied to study both correlation limit, but such approach is no longer valid when the coupling is intermediate. In order to study this intermediate coupling regime, it is necessary to have both a good experimental or material platform with an intermediate coupling and some tools to effectively tune the correlation of the system. Not only is this crossover regime being interesting in understanding the cooperative behavior of spin and charge, one can also make an analogy to the BCS-BEC crossover in the Hubbard model with an attractive interaction [48-50].

Though materials within this crossover regime is rare, some optical spectroscopy and STM measurements have suggested the co-existence of both Mott and Slater insulator behaviors in $\text{Sr}_2\text{IrO}_4$ [51, 52]. On the other hand, both single crystal and epitaxial thin film $\text{Sr}_2\text{IrO}_4$ shows its insulating behavior persists under external pressure and epitaxial strain [53, 54]. The robustness of the insulating behavior shows that $\text{Sr}_2\text{IrO}_4$ is not an ideal candidate. In addition to $\text{Sr}_2\text{IrO}_4$, the $\text{SrIrO}_3/\text{SrTiO}_3$ superlattice is also an alternative candidate to study this crossover regime. The $\text{SrIrO}_3/\text{SrTiO}_3$ superlattice is an pseudospin-1/2 square lattice system with antiferromagnetic insulating state while heterostructure engineering provides a higher capability in structural modulation over superlattices.

1.1.3 Heisenberg picture

For a single band half-filling Hubbard model under strong onsite Coulomb repulsion, instead of considering interactions between electrons, one can further simplify Hamiltonian by considering the interactions between spins. In this case, the hopping term in Hubbard Hamiltonian is considered as a small perturbation since $U<<<t$. The second order approximation is given as
Figure 1.10 Slater-Mott crossover regime [55].
where }c_i^\sigma, c_j^{\sigma'}\rangle \text{ state denotes the }i\text{th site with spin }\sigma\text{ and }j\text{th site with spin }\sigma'. |n\rangle \text{ is the }n\text{th excited states with energy }E_n. \text{ The energy between }E_0 \text{ and }E_n \text{ is }U \text{ as shown in previous section. In this case, if the two spins are aligned in the same direction, then the }E_{2\text{nd}} \text{ will be zero since the Pauli exclusive principle forbids a doubly occupied states with the spin in the same directions. If the spins are aligned in the opposite direction, then there are two scenarios. The first scenario can be considered as the }|c_i^\sigma, c_j^{\sigma'}\rangle \text{ state remains after exchange which will corresponds to}

\[ E_{2\text{nd}}^2 = \frac{2t^2}{U} \sum_{<i,j>} \langle c_i^\sigma, c_j^{\sigma'} | c_i^\sigma c_j^{\sigma'} | c_i^\sigma, c_j^{\sigma'} \rangle \]  

where \( c_i^\sigma, c_j^{\sigma'} \) denotes the state of the }i\text{th site with spin }\sigma\text{ and }j\text{th site with spin }\sigma'. |n\rangle \text{ is the }n\text{th excited states with energy }E_n. \text{ The energy between }E_0 \text{ and }E_n \text{ is }U \text{ as shown in previous section. In this case, if the two spins are aligned in the same direction, then the }E_{2\text{nd}} \text{ will be zero since the Pauli exclusive principle forbids a doubly occupied states with the spin in the same directions. If the spins are aligned in the opposite direction, then there are two scenarios. The first scenario can be considered as the }|c_i^\sigma, c_j^{\sigma'}\rangle \text{ state remains after exchange which will corresponds to}

\[ E_{2\text{nd}}^2 = \frac{2t^2}{U} \sum_{<i,j>} \langle c_i^\sigma, c_j^{\sigma'} | c_i^\sigma c_j^{\sigma'} | c_i^\sigma, c_j^{\sigma'} \rangle \]  

The second scenario can be considered as the }|c_i^\sigma, c_j^{\sigma'}\rangle \text{ state changes to }|c_i^{\sigma'}, c_j^{\sigma}\rangle \text{ after exchange which will corresponds to}

\[ E_{2\text{nd}}^{\text{as}} = -\frac{t^2}{U} \sum_{<i,j>} \langle c_i^{\sigma'}, c_j^{\sigma} | c_i^\sigma c_j^{\sigma'} c_i^{\sigma'} c_j^{\sigma} | c_i^{\sigma'}, c_j^{\sigma} \rangle \]  

The spin operator can also be represented as

\[ S_i = \sum_{\alpha\beta} c_{i\alpha} \sigma_{\alpha\beta} c_{i\beta} \]  

where \( \sigma_{\alpha\beta} \) is the Pauli matrix. Now the exchange operator in both (1.14) and (1.15) can be replaced with the spin operator which gives rise to an effective Hamiltonian

\[ H_{\text{eff}} = \frac{4t^2}{U} [S_i^zS_j^z + \frac{1}{2} (S_i^+S_j^- + S_i^-S_j^+) - 1/4] \]  

This leads to the Heisenberg Hamiltonian (dropping the constant term) [56]

\[ H = \frac{1}{2} \sum_{i,j} S_i S_j \]  

In this simplified Hamiltonian, only spin exchange interaction is considered, and Hamiltonian appears to have an isotropic form. This Hamiltonian can be used to characterize the magnetic long-range order of the system for which it explains AFM in La\textsubscript{2}CuO\textsubscript{4}. The isotropic Heisenberg Hamiltonian also can be used to characterize the exchange coupling in layered perovskite iridate like Sr\textsubscript{2}IrO\textsubscript{4} [29, 57]. The pseudo-spin \( \frac{1}{2} \) state has mixed both spin and orbital so it generally makes the total pseudo-spin \( \frac{1}{2} \) not conserved in the exchange process. However, in a 180 degree bonding geometry the
hopping arises only between orbitals of the same symmetry, i.e., \(xz\) to \(xz\), etc., which implies that not only spin but also the orbital, and hence the total pseudospin, are conserved during the exchange process [30]. By neglecting Hund’s coupling, one can use an effective S-1/2 Heisenberg Hamiltonian to characterize the interaction between \(J_{\text{eff}}=1/2\) on a square lattice in \(\text{Sr}_2\text{IrO}_4\). Once the Hund’s coupling \((J_H/U)\) is turned on, virtue excitation to \(J_{\text{eff}}=3/2\) state allows spin flip and can lead to anisotropic interactions [29, 30]. Thus, pseudo-spin Hamiltonian becomes

\[
H = \sum_{i,j} (J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j + D_{ij} \mathbf{S}_i \times \mathbf{S}_j + \Gamma_{ij} S_i^z S_j^z)
\] 1.19

The first term is the isotropic Heisenberg exchange interaction. The second term is the Dzyaloshinskii-Moriya (DM) interaction which is a result of spin-orbit coupling. The spin-orbit coupling is relatively weak in the 3d TMOs like \(\text{La}_2\text{CuO}_4\) so that the DM interaction is often neglected in this case. The DM interaction will favor a spin canting in a magnetic ordered system. Therefore, a weak ferromagnetism is often observed in layered iridate systems. The third term is symmetric anisotropy where \(\Gamma\) is a function of \(\theta\) and \(J_H/U\). This pseudo-spin ½ model is not only useful in \(\text{Sr}_2\text{IrO}_4\) but also other iridate square lattice system like artificial iridate superlattice [39, 58].

One of the key feature in the pseudospin-1/2 square lattice system is the existence of hidden SU(2) symmetry under the unfrustrated condition [59]. The unfrustrated condition refers to the case where the summation of the DM vector within a closed loop vanishes. The Hidden SU(2) symmetry can be uncovered by perform a staggered rotation transformation of the spin operator in (1.19) (Figure. 1.11). Under the transformation the spin operator can be written as

\[
\hat{\mathbf{S}}^x = S^y \sin \varphi + S^x \cos \varphi \tag{1.20}
\]

\[
\hat{\mathbf{S}}^y = S^y \cos \varphi - S^x \sin \varphi \tag{1.21}
\]

If one writes down the isotropic Heisenberg interaction of \(\hat{\mathbf{S}}\) operator between two neighboring sites as

\[
\hat{\mathbf{S}}_i \hat{\mathbf{S}}_j = \cos (2\varphi)\mathbf{S}_i \cdot \mathbf{S}_j + \sin (2\varphi) \mathbf{2} \cdot [\mathbf{S}_i \times \mathbf{S}_j] + [1 - \cos (2\varphi)]S_i^z S_j^z \tag{1.22}
\]

It is clear that (1.19) can now be written in the isotropic Heisenberg term as

\[
H = \sum_{i,j} J_{ij} \hat{\mathbf{S}}_i \cdot \hat{\mathbf{S}}_j \tag{1.23}
\]

More importantly, the Zeeman energy term \(h \sum_i S_i^x\) under this transformation is then given as

\[
H_{\text{Zeeman}} = h \cos \varphi \sum_i \hat{S}_i^x + h \sin \varphi \sum_i e^{i \varphi \cdot r} \hat{S}_i^y \tag{1.24}
\]
Figure 1.11 Schematic diagram of staggered rotation transformation of spin operator [59].
It manifests the linear coupling of external field with AFM order parameter $M_s = \sum_i e^{iQ \cdot r_i} \hat{S}_i^y$.

This SU(2) hidden symmetry enabled linear coupling between external field and AFM order parameter not only exists under the Heisenberg picture, but it also exists in a more general Hubbard picture. In this case, the effective single band Hubbard Hamiltonian for a pseudospin-1/2 square lattice is given as [40]

$$
H = -t \sum_{i,j} \sum_{\alpha,\beta} [c_{i\alpha}^+ (e^{i\phi^{\exp}_{Q - r_i})} \sigma^\alpha \sigma^\beta c_{j\beta} + h. c.] + U \sum_j n_{j,\uparrow} n_{j,\downarrow} - h \cdot \sum_j \mathbf{s}_j \tag{1.25}
$$

where external field $h$ couples with the electron spin $s_j = \frac{1}{2} \sum_{\alpha,\beta} c_{i\alpha}^\sigma c_{j\beta}$.

The most important thing here is the consideration of spin dependent hopping represented by the phase factor $e^{i\phi^{\exp}_{Q - r_i})} \sigma^z$. This spin dependent hopping is enabled by the strong SOI and lattice octahedra rotation. Unlike the usual spin-half Hubbard model, this phase factor renders complex hopping integrals for different spins due to the spin–orbit entangled $J_{eff} = 1/2$ wavefunctions. It is important to note that the in-plane spin canting in the AFM ground state is ultimately driven by this spin-dependent hopping and the angle $\phi$ of the phase factor determines the canting angle $\phi$ at zero field [60, 61]. To illustrate the linear coupling between the external field with the staggered moment, a staggered reference frame transformation can be taken as $\tilde{c}_{j\alpha} = \sum_{\beta} [e^{i\phi^{\exp}_{Q - r_i})} ]_{\alpha\beta} c_{j\beta}$ to convert the global spin reference frame into a local spin reference frame (Figure. 1.12).

Then the Hamiltonian is given as

$$
H = -t \sum_{<i,j,\sigma>}[\tilde{c}_{i,\sigma}^+ \tilde{c}_{j,\sigma} + h. c.] + U \sum_j \tilde{n}_{j,\uparrow} \tilde{n}_{j,\downarrow} - h^z \sum_j \tilde{s}_j^z - \cos \phi h^\perp \cdot \sum_j \tilde{s}_j^\perp + 
$$

$$
\sin \phi (i \sigma^y h^\perp) \cdot \sum_j \tilde{s}_j^\perp e^{iQ \cdot r_j} \tag{1.26}
$$

where $\tilde{s}_j^z$ and $\tilde{s}_j^\perp$ are the out-of-plane and in-plane component of the transformed spin $\tilde{s}_j = \frac{1}{2} \sum_{\alpha,\beta} c_{i\alpha}^\sigma c_{j\beta}$, and $h^z$ and $h^\perp$ are the out-of-plane and in-plane component of the external field. The transform uncovers the spin-independent hopping in the Hubbard Hamiltonian and shows a linear coupling between the external field and staggered magnetization. This indicates a potential strong interplay between charge and spin degree of freedom can be observed in the pseudospin-1/2 iridate superlattice.
Figure 1.12 Charge hopping in spin-up (red) and spin-down channels (blue) in different spin frames. In the global spin frame (left panel), charge hopping bears an alternating phase factor when circling around the square lattice. This phase factor is gauged away in the rotated local spin frame (right panel), leading to an isotropic Hubbard model. The annihilation operators $\tilde{c}_{j,\alpha}$, in the local frame are transformed from $c_{j,\beta}$ in the global frame according to the shown transformation [40].
1.2 Band topology and transport properties

Topology is long time study subject in the mathematics which focus on the geometric properties of systems preserved under continuous deformation. Topology has also been intensively studied in the physics research, particular in the study of fluid mechanics [62]. Recently, the application of topology in condensed matter physics has led to fruitful results [1]. In addition to the discovery of new topological properties, the application of topology also gives us some new insight in the novel phenomenon. The geometric phase in quantum physics can be obtained by considering a time dependent Schrodinger equation under adiabatic process. The time dependent Schrodinger equation is given as

\[ i\partial_t \Psi(t) = H(t)\Psi(t) \]  

1.27

The adiabatic theorem states that a physical system remains in its instantaneous eigenstate if a given perturbation is acting on it slowly enough and if there is a gap between the eigenvalue and the rest of the Hamiltonian’s spectrum [63]. Under adiabatic process there exists a set of instantaneous eigenstates which are the solution of the Hamiltonian

\[ H(t)\psi_n(t) = E_n(t)\psi_n(t) \]  

1.28

These instantaneous eigenstates \( \psi_n(t) \) is not the real solution of the time dependent Schrodinger equation \( \Psi(t) \). Now, the real wavefunction of time-dependent Schrodinger equation can be expressed in these instantaneous eigenstates

\[ \Psi(t) = e^{i\gamma(t)} e^{i\theta(t)} \psi_n(t) \]  

1.29

\[ \theta_n(t) = \int_0^t E_n(t') dt' \]  

1.30

\[ \gamma_n(t) = i \int_0^t (\psi_n(t') | \dot{\psi}_n(t') \rangle) dt' \]  

1.31

where \( \theta_n(t) \) is the dynamical phase and \( \gamma_n(t) \) is the geometric phase. The concept of geometric phase is very important in physics as many interesting phenomena can be explained by it. One of the examples is the Aharonov-Bohm effect as shown by Berry [64]. Considering two charged particles moving in two closed loops in the space and the starting and ending points for those two closed loops are the same. There is no magnetic flux inside either closed loop, but the vector potential is non-zero. In classical physics those two particles moving in those two closed loops should be the same. However, in quantum physics regime, the two particles will pick up two different phases depends on the trajectory [65]. The picked-up phase is given as

\[ \gamma = q \oint_C A \, dx \]  

where A is the vector potential. This phase is essentially a geometrical phase. Depending on the trajectory of each particle, the phase difference can go from 0 to \( 2\pi \). In the experiments, this effect can be observed
through the interference of two electrons passing through a double slit around a solenoid (Fig. 1.13) [66].

### 1.2.1 Berry Phases and transport properties

The geometrical phase is often called as Berry phase in condensed matter physics as Berry is one of the pioneers in applying geometrical phase in solving quantum physics [64]. It has since become an important concept in understanding the intrinsic mechanism in several topological properties. One of the most well-known application of Berry phase is in the understanding of Hall effect [67, 68]. Hall effect occurs when electric potential builds up along the transverse direction when a current is applied in the material. The ordinary hall effect is discovered in 1879 [69] and it is a useful tool to measure the carrier density and carrier type of the material. The ordinary hall coefficient of the materials can be written as $R_H = \frac{1}{ne}$, where n is the carrier density of the material. Depends on the carrier type the coefficient can be either positive or negative. In addition to ordinary hall effect, subsequent research has discovered various type of new hall effect (Figure. 1.14).

The ordinary hall effect can be understood classically. The carrier moving under a magnetic field will experiences the Lorentz force which is orthogonal to the moving direction of the carrier. Therefore, carriers will accumulate on the transverse direction and thus a hall voltage is built up and the hall voltage linearly depends on the applied field. However, a nonlinear field dependence of Hall voltage is also observed in some ferromagnetic materials. This phenomenon is also referred as anomalous Hall effect (AHE). Since AHE is mostly observed in ferromagnetic materials in the early days, it is long thought that ferromagnetism is the primary reason behind AHE [67]. Later research has found that the mechanism behind AHE is more complicated. The mechanism of AHE can be divided into extrinsic contribution and intrinsic contribution. The extrinsic contribution of AHE includes the skew-scattering and side jump [67]. The skew-scattering contribution to the AHE can be sharply defined; it is simply the contribution which is proportional to the Bloch state transport lifetime [67]. Skew scattering is due to chiral features which appear in the disorder scattering of spin-orbit coupled ferromagnets [67]. On the other hand the definition of side jump contribution is not straightforward. A semiclassical description of side-jump contribution is given as when considering the scattering of a Gaussian wave packet from a spherical impurity with spin-orbit interaction $H_{SO} = (1/2m^2c^2)(r^{-1}\partial V/\partial r)S_z L_z$, a wave packet with incident wave vector $k$ will suffer a displacement transverse to $k$ equal to $1/6k \hbar^2/m^2c^2$ [67]. In addition to the two extrinsic contributions, there is an intrinsic contribution which has only been recognized recently by
Figure 1.13 Schematic of the Aharonov-Bohm (AB) and Ehrenberg-Siday two-slit interference experiments, where the magnetic field $B$ is zero in the region outside the solenoid.
Figure 1.14 Schematic diagram of different hall effect. (a) Ordinary hall effect. (b) Quantum hall effect. (c) Anomalous Hall effect (d) Quantum anomalous hall effect [70].
theoretical and experimental efforts and the Berry phase is the mechanism behind the intrinsic AHE [67].

The intrinsic contribution to the AHE conductivity only depends on the band structure and it can be calculated directly from Kubo formula on an ideal lattice [67].

\[
\sigma_{ij}^{AH} = e^2 \hbar \sum_{n} \int \frac{d\mathbf{k}}{(2\pi)^2} \left[ f(\varepsilon_n(k)) - f(\varepsilon_{n'}(k)) \right] \times \text{Im} \left( \frac{\langle n, k | \mathbf{v}_i(k) | n', k \rangle \langle n', k | \mathbf{v}_j(k) | n, k \rangle}{\varepsilon_n(k) - \varepsilon_{n'}(k)} \right)
\]

where \( \varepsilon_n(k) \) is the eigenvalue of the eigenstate \(| n, k \rangle\) Bloch Hamiltonian H. The velocity operator in (1.32) is defined as \( \mathbf{v}(k) = \frac{1}{\hbar} \nabla_k H(k) \). Here the imaginary part in (1.32) is also referred as Berry curvature and it can be written as

\[
\Omega_n(k) = \nabla_k \times a_n(k)
\]

where \( a_n(k) = i(n, k | \nabla_k | n', k) \) is also referred as Berry connection. The anomalous hall conductivity can be expressed as

\[
\sigma_{ij}^{AH} = e^2 / \hbar \int \frac{d\mathbf{k}}{(2\pi)^2} f(k) \Omega_n(k)
\]

The Berry phase not only contributed to the electric transport properties; it also contributes to thermoelectric transport properties. The Berry phase can also contribute the intrinsic anomalous Nernst effect (ANE). The Nernst effect is phenomenon observed when a sample allowing electrical conduction is subjected to a magnetic field and a temperature gradient normal (perpendicular) to each other. Like the AHE the conductivity of intrinsic ANE can be expressed as

\[
S_{ij}^{AN} = e^2 k_B / h \int \frac{d\mathbf{k}}{(2\pi)^2} s(k) \Omega_n(k)
\]

where \( s(k) = f(k) \ln(f(k)) - (1 - f(k)) \ln(1 - f(k)) \).

1.2.2 Band structure of Iridates

Considerable attention has been devoted to the non-trivial physics arising from large spin-orbit coupling in recent years [1]. Among various materials, iridate shows to be a promising candidate for realization of different topological properties [38, 71-73]. One of the most known examples is the 3D perovskite SrIrO\(_3\) which is a nonmagnetic semimetal. SrIrO\(_3\) is the 3D limit in the Ruddlesden-Popper series Sr\(_{n+1}\)Ir\(_{n}\)O\(_{3n+1}\). While Sr\(_2\)IrO\(_4\) (n=1) is an antiferromagnetic insulator, the semi-metallicity observed in SrIrO\(_3\)
(n=∞) is initially understood as a result of bandwidth broaden due to the increase of dimensionality [35]. Subsequent research work has shown the semi-metallicity originates from the Dirac nodal line [38]. The tight-binding model is constructed by Carter et al which only considers the nearest and next nearest neighboring hopping between the $J_{\text{eff}}=1/2$ orbits. The calculated band structure shows a line nodal near the U point (Figure.1.10) [38]. This nodal line is understood as a result of the glide symmetry plane in its Pbnm space group.

### 1.3 Experimental Technique

The heterostructure engineering is applied to achieve atomically flat thin films. The ability of control each atomic layer makes it possible to construct new materials with desired structure to achieve the goal of the study. The physical properties of thin films are characterized through various in-house and on-site techniques. The evolution of electronic and magnetic properties of the thin films are studied under structural modulations.

#### 1.3.1 Pulsed Laser Deposition

Pulsed Laser Deposition (PLD) is one of the prime epitaxial growth methods to synthesis high quality single crystal thin films. Features like stoichiometric transfer, excited oxidizing species and simplicity in initial setup make PLD a very competitive oxide synthesis method among others [74]. Particularly, PLD has been widely used in synthesizing iridate thin film [39, 75-77]. In PLD, a pulsed laser is focused onto a material to be deposited and each pulsed laser is going to ablate a small amount of the material creating plasma plume (Figure. 1.16 (a)). The ablated material is ejected from the target in a highly forward directed plume which provides the material flux for film growth [74]. Depends on the laser frequency and ablation speed, one can use PLD to achieve very fast growth rate. The atomic layer precision control is achieved through monitoring the surface of the sample using reflectivity high energy electron diffraction (RHEED). RHEED utilize the diffraction of electrons on the surface which provides the information of periodic arrangement of the surface atoms. The intensity oscillation of the specular spot-on diffraction pattern shows how layer-by-layer growth is proceeded with each oscillation represents one atomic layer (Figure. 1.16 (b)).

#### 1.3.2 Synchrotron based X-ray scattering technique

To characterize the crystal and magnetic structures of nanometer films are very
Figure 1.15 Underlying band structure of orthorhombic perovskite SrIrO3 obtained by a tight binding model including only Ir-Ir direct hopping. The unit of energy is $t$ [38].
Figure 1.16 (a) Schematic diagram of Pulsed Laser Deposition system. (b) RHEED intensity oscillations of the specular spot during the growth of a thin film. Inset: RHEED pattern at the surface.
challenging. In-house measurements will not provide important information like magnetic structure, staggered moment, octahedra rotation and electronic structure. To achieve these goals, synchrotron-based x-ray scattering, and absorption techniques are applied in this dissertation.

One of the important crystal structural properties of perovskite oxides is the octahedral tilting [78, 79]. When the octahedron in the perovskite structure is tilted then it will cause the neighboring octahedron to be tilted. Considering an octahedron is tilted along a particular axis with magnitude of \( \alpha \), then the next octahedron that is on the axis perpendicular to this particular axis will also tilt with \(-\alpha\). Therefore, the unit cell along the perpendicular axis will be doubled (Figure. 1.17 (a)). For the next octahedron on this particular axis, it can tilt with \( \alpha \) or with \(-\alpha\). If the two octahedrons tilt with the same angle, then it is often referred as in-phase rotation; whereas it is out-of-phase rotation if the angle is opposite. The out-of-phase rotation will result in a double of the unit cell. Since the octahedral tilting result in doubling of the unit cell, additional reflections are produced on the half integer reciprocal lattice planes (Figure. 1.17 (b)) [80, 81]. The intensity of these half integer reflections is often much smaller compared to those integer peaks; in addition, the thin films are only less than micrometer thickness. Therefore, this weak intensity is very difficult to pick up in the in-house XRD measurement due to the low flux of x-ray source. On the other hand, synchrotron-based XRD has a very high brilliance; thus, it can be used to identify the octahedral tilting in perovskite thin films.

In addition, synchrotron-based x-ray scattering has high energy tunability and monochromatic; thus, one can fine tune the energy across the absorption edge of a select element. The x-ray absorption spectroscopy is a powerful tool which provides the useful information about the electronic structure of the system. The x-ray photon is absorbed by the material to excite a core electron to an empty state which is above fermi level. By tuning the x-ray energy, a spectrum is obtained which surveys the empty states of the system. Only when the photon energy is large than the binding energy of a core electron at specific state will one see a sharp increase in the spectrum and the energy is corresponds to a specific absorption edge (Figure. 1.18 (a)). The integrated intensity of the spectrum corresponds to the number of empty states and the absorption edge can be used to analyze the electronic state of the element in the materials. For instance, in a Fe\(_2\)O\(_3\) compound, the Fe K-edge edge jump occurs at 7.13 keV for a Fe\(^{2+}\) and at 7.134 keV for a Fe\(^{3+}\) [82]. The electronic state of the Fe element can be identified by performing a XAS and compare the position of observed absorption edge. The transient rate between the initial core electron state and final empty state can be expressed through Fermi golden rule:

\[
W_{if} \propto |\langle i | H | f \rangle|^2 n_f
\]

\[1.36\]
Figure 1.17 (a) Octahedral tilting result in double unit cells in perovskite. (b) A half integer Bragg peak due to octahedral tilting.
Figure 1.18 (a) XAS of O K-edge of an iridate superlattice. (b) Schematic diagram of XLD measurement of p orbital state in a thin film sample. (c) The orbitals that are probed by x-ray with different polarizations.
where $|i\rangle$ is the initial state, $|f\rangle$ is the final state, $H$ is the light matter interaction operator 

$$H = \vec{p} \cdot \vec{\epsilon} e^{i\vec{k} \vec{r}}$$

and $n_f$ is the density of final state.

The XAS can also be used to study the anisotropy of the system by utilizing the polarization of the x-ray. The incident x-ray photon is used to excite the core electron to fill the empty states. Depending on the polarization direction of photon, the spectrum maybe different, in other words, the density of empty states probed by x-ray may be different. For instance, for X K-edge, an x-ray with in-plane polarization probes the empty $p_x, p_y$ states while an out-of-plane polarization probes the empty $p_z$ state (Figure. 1.18 (b)). The obtained XAS could be different with those two different polarizations (Figure. 1.19(a)) and this is x-ray linear dichroism (XLD). If there is no difference between the two XAS, this indicates the empty states are equal. In a d-orbital transition metal oxides, this also means there is no charge anisotropy between these two directions since the charge anisotropy can be projected as the hole occupation rates in d-orbitals. To probe the charge anisotropy of transition metal oxides, one can directly probe the L-edge of the material. An alternative way to achieve this goal is to probe at O K-edge. There is a strong hybridization between the d-orbital of transition metal and p-orbital of oxygen in the oxides; thus, one can probe the difference in empty states in d orbital states (Figure 1.18 (c)).

Moreover, the x-ray scattering can be used to identify the magnetic structure of thin films. Though neutron scattering is considered by many as a primary technique to study the magnetic structure of the materials, it is found to be difficult to study the magnetic structure of thin films using neutron sources. The neutron flux is relatively low compared to synchrotron x-ray source which implies it requires larger volume of sample which is difficult to achieve in thin film samples. On the other hand, the high absorption of some isotopes also makes it difficult to study certain materials using neutron. To overcome these difficulties in studying magnetic structure of thin films, resonant elastic x-ray scattering (REXS) is introduced. The REXS takes advantage of the resonant effect when the incident photon energy is tuned near the absorption edge, the scattering signal is largely enhanced at the resonant energy. Due to the high flux of synchrotron x-ray source, it is possible to measure a thin film with even nanometer thickness. Moreover, the element selectivity of absorption edge means the only the corresponding electronic state at the absorption edge will contributed to enhanced signal. Therefore, it is possible to study the contribution of magnetic properties from each element. One of examples in applying REXS is the study of magnetic properties of iridate thin films [39]. The 5d valence electrons in Ir ions are mainly responsible for the magnetic and electronic properties in iridate thin film. The study is usually carried out at the Ir L-edge where a strong dipole transition between 2p orbital state
and 5d orbital state occurs. The transition from 2p_{1/2} to 5d is the Ir L_{3}-edge while 2p_{3/2} to 5d is the Ir L_{2}-edge.

The x-ray resonant scattering is a second order process as it takes two steps. A photon of energy \( \hbar \omega_k \) is initially absorbed by the materials to excite the core electron above Fermi level. An intermediate state is created but it is very unstable. Therefore, this state will decay within its lifetime and emits a photon with energy \( \hbar \omega_{kr} \). The scattering cross-section of x-ray scattering can be found in Boseggia’s work [83].

\[
\frac{d^2\sigma}{d\Omega dE'} = \left( \frac{e^2}{mc^2} \right)^2 \frac{\omega_{kr}}{\omega_k} |A_0 + A_{\text{nonres}} + A_{\text{res}}|^2 \delta(E_a - E_b + \hbar \omega_k - \hbar \omega_{kr})
\]

where

\[
A_0 = \langle b | \sum_j e^{iK \cdot r_j} | a \rangle e' \cdot \epsilon
\]

\[
A_{\text{nonres}} = -i \frac{\hbar \omega_k}{mc^2} \left( \sum_j L(Q) \cdot A'' + S(Q) \cdot B' \right)
\]

\[
A_{\text{res}} \approx -\frac{1}{m} \sum_c \sum_{ij} \frac{E_a - E_c}{\hbar \omega_k} \left( \frac{b[(\epsilon' \cdot p_i) \Sigma_i e^{-iK \cdot r_i} | c \rangle \langle c' \cdot p_j) \Sigma_j e^{iK \cdot r_j} | a \rangle}{E_a - E_c + \hbar \omega_k - i\Gamma_c/2} \right)
\]

where \( A'', B' \) are beam dependent factors, \( L(Q) \) and \( S(Q) \) are the Fourier transform of the orbital and spin magnetization density. \( i\Gamma_c / 2 \) term is used to avoid any nonphysical divergence in the denominator and to consider the finite lifetime the intermediate \( | c \rangle \) states. In the case of elastic scattering \( | a \rangle \equiv | b \rangle \) and \( \hbar \omega_k = \hbar \omega_{kr} \). In this dissertation the focus is iridate L-edge where the dipole transition occurs and the resonant scattering, so the amplitude of resonant scattering part can be rewritten as

\[
A_{\text{res}} \approx m \sum_c \sum_{ij} \frac{(E_a - E_c)^3}{\hbar^2 \omega_k} \left( \frac{b[(\epsilon' \cdot p_i) \Sigma_i e^{-iK \cdot r_i} | c \rangle \langle c' \cdot p_j) \Sigma_j e^{iK \cdot r_j} | a \rangle}{E_a - E_c + \hbar \omega_k - i\Gamma_c/2} \right)
\]

In most of REXS measurement, only the dependence of the REXS cross-section on the polarization of the photons and the direction of the magnetic moment is the focus so that an expression derived by Hannon et al. [84] is applied. The amplitude of resonant scattering cross-section is then given as

\[
A_j = (\epsilon' \cdot \epsilon) F^0 - i(\epsilon' \times \epsilon) \cdot Z_j F^1
\]

where \( F^0 \) are the factors that determine the strength of the resonance based on the atomic properties in the unit of wave vector \( k \) and \( Z_j \) is the direction of the magnetic moment of the \( j \)th ions. The first term contains no dependence on the magnetic moment and the second
term is linear in the magnetic moment direction and produces first harmonic magnetic satellites in antiferromagnetic [83]. The higher order terms that correspond to the high order terms in magnetic satellites are ignored since it is not observed in iridate thin films in this dissertation. The polarization of the photon in the REXS experiments are usually projected onto an orthogonal two vector basis \( \sigma \) (perpendicular to scattering plane) and \( \pi \) (parallel to scattering plane). The dependence of the polarization can then be expressed in a 2-by-2 matrix in \((\sigma, \pi)\) basis. Thus, the amplitude can be written as

\[
A_j = \begin{pmatrix} 1 & 0 \\ k' \cdot k \end{pmatrix} F^0 - i \begin{pmatrix} 0 & k \cdot \hat{z}_j \\ -k' \cdot \hat{z}_j & (k' \times k) \cdot \hat{z}_j \end{pmatrix} F^1
\]

The first term connects incident and reflected wave without changing its polarization. The second term mixed the polarization between two polarizations \((\sigma, \pi)\). In this dissertation, the resonant magnetic scattering measurement is carried out at Ir L\(_3\)-edge. The amplitude of each channel of iridate at L\(_3\)-edge is given by Boseggia [83]

\[
A_{\sigma\sigma'} = \frac{2(1+A+A^2)}{2+A^2}
\]

\[
A_{\sigma\pi'} = \frac{i[(A-2)(A-2)]\cos\theta'}{2+A^2}
\]

\[
A_{\pi\sigma'} = \frac{i[(A-2)(A-2)]\cos\theta}{2+A^2}
\]

\[
A_{\pi\pi'} = \frac{6\sin\theta \sin\theta - 2(1+A+A^2)\cos\theta \cos\theta}{2+A^2}
\]

In the experiment, if the magnetic Bragg peaks are at the same position of structure peaks, then the \(\sigma-\sigma'\) channel and \(\pi-\pi'\) channel will contain signal from both crystal and magnetic structure. For instance, a half integer peaks occurs under out-of-phase octahedral tilting while an antiferromagnetic magnetic structure peak will occur at the same position. Since the structural Bragg peaks are normally much stronger compared to magnetic Bragg peaks, most of the measured intensity in these two channels will be from structure. Therefore, in this thesis, the REXS measurement is carried out in \(\sigma-\pi'\) channel. The chosen of each specific channel is achieved through putting a polarization filter in front of the detector. In this case, a graphite polarization filter is used. Though a filter is applied, a portion of intensity from structure Bragg peaks is still allowed. Thus, two sets measurement at different energy are carried out in each Bragg peak measurement. One is carried out at resonant energy which will contains both largely enhanced magnetic peak signal and
structural peak signal. The other one is carried out below the resonant energy which should only include the intensity from structural Bragg peaks. The scattering geometry in given in Figure 1.19.

### 1.3.3 Electric and thermoelectric measurement

To characterize the electronic properties of the system, the transport measurement is carried out the system through both electric and thermoelectric methods. The evolution of resistivity under different control parameter reflects the change of insulating behavior in the system which is correlated with the change of the bandgap. The transverse transport measurement not only provides the carrier density of the system but also provides the way to characterize the electronic properties driven by topological properties.

The electric transport measurement is carried out in four-point probe geometry (Figure. 1.21). The external current is applied through current channel (I+, I-) and the voltage is measured on the voltage channel (V+, V-). The four-point probe measurement is applied to eliminate the contact resistance between the probe and wire. The change of voltage from the voltage channel (V+, V-) is only contributed from the voltage change of the sample between these two probes while the contact resistance should not contribute. The resistivity measurement is carried out under different temperature and field. The sample is mounted on a bridge puck and put into a commercial Physical Properties Measurement Systems from Quantum Design. The temperature dependent measurement is carried out under vacuum condition. The resistivity will increase as temperature decreases if the sample is an insulator and if the resistivity decreases as temperature increases then the sample is a metal. The resistivity under different magnetic field is measured by rotating the sample into different direction while keeping the current flowing direction fixed. The different geometry in the field dependence measurement can give rise to artificial errors for the experiments. For instance, when the carrier is moving parallel to the field direction it does not experience Lorentz force. On the other hand, when the carrier is moving perpendicular to the field, the Lorentz effect must be taken into consideration. However, in this thesis, it is found that the errors caused by geometry difference is negligible; thus, the current flow direction is unchanged during the measurement. The Hall measurement is carried out in a four-point Hall bar geometry. The current is applied through current channel (I+, I-) while the transverse voltage due to the Hall effect is measured on voltage channel (V+, V-).

The thermoelectric measurement is carried out in a similar geometry (Figure. 1.20). In the thermoelectric measurement both the thermopower and Nernst effect of the samples
Figure 1.19 Scattering geometry and coordinates of the system [83].
Figure 1.20 Schematic diagram of transport measurement
are measured. In the thermoelectric measurement a carrier flow is created by temperature difference between two ends of the sample. The sample is placed on a bridge puck with each end attaching to a copper plate. One end of the copper plate is attached with a resistivity heater. By applying dc current on the resistivity heater, the copper plate is heated up and thus the temperature on the one end of sample increases. A heat flow is subsequently created which goes from high temperature end to the low temperature end. The high temperature end will have more thermal excited electrons in the valence states. Because of the density difference between the hot end and cold end, the carriers will thus drift from high density ends to the lower density ends. Depends on the carrier type, it could be either electrons or holes. Two thermocouples are attached to each copper plates to measure the temperature difference between the two ends. It is assumed that the heat loss between the copper plate and sample is negligible so that the temperature difference between two ends is the same as the temperature difference between two copper plates. In the thermopower measurement, the build-up the voltage between the hot and cold ends is measured and this is also called Seebeck effect. In addition, another set of thermoelectric measurement is carried out in this thesis which measures the build-up transverse voltage under the out-of-plane magnetic field. It is the Nernst effect measurement which is analogous to Hall effect measurement.
CHAPTER 2
EPITAXIAL STABILIZATION OF IRIDATE THIN FILMS

Ruddlesden-Popper type \( \text{Sr}_{n+1}\text{Ir}_n\text{O}_{3n+1} \) compound is a major focus of condensed matter physics where the subtle balance between electron-electron correlation, spin-orbit interaction and crystal field effect brings a host of emergent phenomena. While it is understandable that a canted antiferromagnetic (AFM) insulating state with an easy-plane anisotropy is developed in \( \text{Sr}_2\text{IrO}_4 \) as the 2D limit of the series, it is intriguing that bilayer \( \text{Sr}_3\text{Ir}_2\text{O}_7 \), with slightly higher effective dimensionality, stabilizes c-axis collinear antiferromagnetism. As the dimensionality further increases, \( \text{SrIrO}_3 \) turns out to be a nonmagnetic semimetal where the crystal symmetry result in an intriguing Dirac nodal ring on its band structure. In this chapter, the work will mainly focus on synthesis.

2.1 Introduction

Layered compounds of Ruddlesden-Popper (RP) oxides \( A_{n+1}B_nO_{3n+1} \) are a fertile playground to study and engineer the interplay of electronic and magnetic properties with crystal lattice dimensionality [4, 27, 28, 33]. The crystal structure of the RP series can be viewed as \( n \) consecutive \( ABO_3 \) perovskite layers sandwiched by rock-salt \( AO \) layers along the c-axis. When \( n \) varies from 1 to infinity, the lattice undergoes an evolution from the quasi-two-dimensional (2D) limit to the three-dimensional (3D) limit, leading to a dimensional crossover of electronic and magnetic interactions [12, 28, 31, 35, 78, 85-87]. For example, the 2D limit of the iridate RP family, \( \text{Sr}_2\text{IrO}_4 \) (Fig. 2.1(a)), represents a spin-orbit coupled Mott insulator [27]. The subtle balance between spin-orbit coupling, onsite Coulomb repulsion, and crystal field effect leads to a pseudospin \( J_{\text{eff}} = 1/2 \) moment on each Ir site that orders antiferromagnetically within the 2D perovskite layer with an easy ab-plane anisotropy and spin canting [12, 29, 88]. The magnetic structure is extremely sensitive to the dimensionality as slight increase of \( n \) to 2 stabilizes a c-axis collinear antiferromagnetic (AFM) insulating state in \( \text{Sr}_3\text{Ir}_2\text{O}_7 \) (Fig.2.1.1(a)), rendering a dimensionality-controlled spin flop transition [36]. When further moving toward the 3D limit, the insulating ground state melts into a topological semimetallic state in paramagnetic \( \text{SrIrO}_3 \) (Fig. 2.1.1(a)) [38, 71, 89, 90].

To study and control the emergent phenomena within the dimensional crossover, epitaxial growth of the RP series is a particularly appealing route due to additional tunability of the lattice structure, such as imposing epitaxial strain [90-92]. However, while epitaxial thin films of \( \text{Sr}_2\text{IrO}_4 \) and \( \text{SrIrO}_3 \) can be readily obtained and have been characterized by many techniques [53, 77, 90, 92], epitaxial growth of \( \text{Sr}_3\text{Ir}_2\text{O}_7 \) is much
more challenging. It was reported that by using a single SrIrO$_3$ target, Sr$_3$Ir$_2$O$_7$ phase can be obtained through carefully control of the oxygen pressure and the temperature within a small region of the parameter space [93]. The low thermodynamic stability and the narrow growth window of the Sr$_3$Ir$_2$O$_7$ phase were later confirmed by using a target of the Sr$_3$Ir$_2$O$_7$ phase [94]. On the other hand, the magnetic ordering of the Sr$_3$Ir$_2$O$_7$ thin films remains unclear.

In this section, a systematic investigation of the thermodynamic stability of the iridate RP series in relation to the growth atmosphere is performed. By using a target of the Sr$_2$IrO$_4$ phase, high-quality thin films of single Sr$_2$IrO$_4$, Sr$_3$Ir$_2$O$_7$ and SrIrO$_3$ phase are obtained by varying pure oxygen pressure. Sr$_{n+1}$Ir$_n$O$_{3n+1}$ thin films with thickness around 100 nm were deposited on SrTiO$_3$ (001) (STO, $a_{pc} = 3.905$ Å) single crystal substrates by using a pulsed laser deposition system (KrF excimer laser). During deposition, the laser fluence was kept 3 J/cm$^2$. Growth temperature was chosen to be 850°C in order to maximize the synthesis window of the Sr$_3$Ir$_2$O$_7$ phase based on a previous report [93]. Two independent experiments were performed in pure oxygen and argon-mixed oxygen atmosphere with varying growth pressure from 1 mTorr to 120 mTorr. Crystal structure and crystallinity of the thin films were investigated by X-ray diffraction (XRD) measurements on a Panalytical X’Pert MRD diffractometer using Cu Kα radiation (1.5406 Å). Magnetic properties measurements were carried out on a Vibrating Sample Magnetometer (Quantum Design). The dc resistivity was measured by using the standard four-point probe on a Physical Property Measurement System (Quantum Design). Synchrotron X-ray resonant magnetic scattering experiments were performed at NSLS-II beamline 4-ID, at Brookhaven National Laboratory.

2.2 Result and Discussion

Figure 2.1(b) shows representative XRD patterns of thin films grown in pure oxygen atmosphere but with different pressures. At the lowest pressure value used in this study (1 mTorr), only a set of (0 0 $L$) Bragg reflections that corresponds the Sr$_2$IrO$_4$ phase can be seen. The observation indicates epitaxial growth of Sr$_2$IrO$_4$ on the SrTiO$_3$ substrate along the [001] direction without observable impurity phases. The single Sr$_2$IrO$_4$ phase is also observed at 10 mTorr and 20 mTorr, which is consistent with previous reports [93]. At 80 mTorr and 100 mTorr, a different phase appears with all the film peaks can be indexed as the (0 0 $L$) Bragg reflections of the Sr$_3$Ir$_2$O$_7$ phase. Further increasing the growth pressure to 120 mTorr suppresses the Sr$_3$Ir$_2$O$_7$ phase and leaves only a set of film peaks near the substrate (0 0 $L$) peaks, characteristic of a single SrIrO$_3$ perovskite phase [95]. The Bragg reflections of the Sr$_3$Ir$_2$O$_7$ phase are broader than those of the Sr$_2$IrO$_4$ and SrIrO$_3$
phases, indicating possible presence of stacking faults in the \( \text{Sr}_3\text{Ir}_2\text{O}_7 \) phase and consistent with previous reports \cite{93}. These results indicate that not only the \( n = 1 \) and \( n = \infty \) structures of the RP series can be epitaxially grown by using a \( \text{Sr}_2\text{IrO}_4 \) target, the \( n = 2 \) structure can also be stabilized by carefully varying the atmosphere pressure.

To further elucidate on this point, we performed detailed physical properties measurements. Figure 2.2(a) displays the temperature dependent resistivity of the \( \text{Sr}_3\text{Ir}_2\text{O}_7 \) and \( \text{Sr}_2\text{IrO}_4 \) films. The monotonic increase of resistivity with decreasing temperature reveals the insulating state of both thin films. The \( \text{Sr}_3\text{Ir}_2\text{O}_7 \) film is evidently less insulating than the \( \text{Sr}_2\text{IrO}_4 \) film considering the smaller room-temperature resistivity and the relatively weaker insulating temperature dependence, consistent with the reports on the bulk counterparts \cite{87, 96, 97}. The observation indicates that the dimensionality evolution of the electronic ground state of the iridate RP phases was preserved in the thin films. A resistivity anomaly was also observed for the \( \text{Sr}_3\text{Ir}_2\text{O}_7 \) thin film at \( T \sim 250 \) K. From the relation between \( d \left( \ln \rho \right)/d \left( 1/T \right) \) and \( T \) (inset of Fig. 2.2(a)), a \( \lambda \) -like cusp can be clearly seen, suggesting a significant change in the electronic properties. Figure 2.1.2(b) shows the film magnetization as a function of temperature measured under an in-plane magnetic field. The \( \text{Sr}_2\text{IrO}_4 \) film displays a weak but non-zero magnetization when temperature cools below 210 K. Note that the net magnetization of \( \text{Sr}_2\text{IrO}_4 \) is due to spin-canting of the antiferromagnetically coupled \( J_{\text{eff}} = 1/2 \) moments \cite{28, 29, 57, 88}. The magnetic measurement thus implies an antiferromagnetic transition of the \( \text{Sr}_2\text{IrO}_4 \) film with the Neel transition temperature \( T_N = 210 \) K. In contrast, there is no comparable jump in magnetization in the \( \text{Sr}_3\text{Ir}_2\text{O}_7 \) film even down to the base temperature of 10 K.

While the absence of net magnetization along with the resistivity kink observed in the thin film are compatible with a collinear antiferromagnetic configuration as reported for \( \text{Sr}_3\text{Ir}_2\text{O}_7 \) single crystals \cite{36}, direct verification of the antiferromagnetic ordering is usually highly challenging for thin film samples. To this end, we exploited x-ray magnetic resonant scattering, which has been proven to be a powerful probe of magnetic structure of iridates due to the element selectivity and resonant enhancement \cite{36}. By tuning the x-ray photon energy to the Ir \( L_3 \)-edge, we performed magnetic resonant scattering measurements on the \( \text{Sr}_3\text{Ir}_2\text{O}_7 \) film at 10 K. The \((-0.5 0.5 24)\) AFM Bragg peak was clearly identified by the \( L \)-scan, as shown in Fig. 2.2(c), directly demonstrating that the Ir moments are antiferromagnetically ordered within each IrO\(_2\) plane. Fig. 2.2(d) shows the energy profile at the representative magnetic reflection across the Ir \( L_3 \)-edge. A clear resonant effect can be seen at energy slightly lower than the Ir \( L_3 \) white line similar to other iridium compounds \cite{88, 98}, confirming the dominant role of Ir ions in developing the long-range magnetic ordering. This observation agrees well with the G-type AFM structure as reported in a \( \text{Sr}_3\text{Ir}_2\text{O}_7 \) single crystal \cite{36, 99, 100}. Along with the structural analysis, we conclude that
Figure 2.1 (a) Schematic crystal structures of Sr$_2$IrO$_4$, Sr$_3$Ir$_2$O$_7$ and SrIrO$_3$. (b) X-ray Diffraction $\theta - 2\theta$ plots of representative samples with distinct RP phases. An offset is added to each plot for better presentation.
Figure 2.2 (a) Temperature dependent resistivity of Sr$_2$IrO$_4$ (circle) and Sr$_3$Ir$_2$O$_7$ (triangle) thin films. The resistivity kink of the Sr$_3$Ir$_2$O$_7$ thin film is indicated with a blue arrow. Inset shows the temperature dependence of $d \ln \rho / d (1/T)$ of the Sr$_3$Ir$_2$O$_7$ thin film. A clear $\lambda$-like cusp can be observed. (b) Temperature dependence of magnetic moment per Ir of Sr$_2$IrO$_4$ and Sr$_3$Ir$_2$O$_7$ thin films measured under a 0.5 T in-plane magnetic field. (c) $L$-scan around the (-0.5 0.5 24) magnetic reflection of the Sr$_3$Ir$_2$O$_7$ thin film at 10 K at the Ir $L_3$-edge. (d) Energy profile of the (-0.5 0.5 24) Bragg reflection peak across the Ir $L_3$-edge at 10 K. The error bars denote the statistic error.
the as-obtained film under the intermediate pressure indeed has a single Sr$_3$Ir$_2$O$_7$ phase.

The growth evolution of the RP phases as a function of oxygen atmosphere pressure is summarized in the left panel of Fig. 2.3(a). As oxygen pressure increases from 1 mTorr to 100 mTorr, the obtained thin film evolves from a single Sr$_2$IrO$_4$ phase to a single Sr$_3$Ir$_2$O$_7$ phase. Between these two single phases, there is an intermediate region where a mixed phase is observed. The growth window of the pure Sr$_3$Ir$_2$O$_7$ phase is relatively narrow and spans a range of ~ 20 mTorr only. To enlarge the growth window, we systematically tuned the oxygen partial pressure while fixing the total atmosphere pressure to be 100 mTorr by introducing different amount of argon into the chamber. Five oxygen partial pressure of 80 mTorr, 50 mTorr, 20 mTorr, 10 mTorr and 0 mTorr were selected for this study. Starting from high oxygen partial pressure $P_0 = 80$ mTorr ($P_{Ar} = 20$ mTorr), the obtained thin film displays a single Sr$_3$Ir$_2$O$_7$ phase (Fig. 2.3(b)), which is the same as that in pure oxygen atmosphere with $P_0 = 80$ mTorr. With decreasing $P_0$ down to 50 mTorr ($P_{Ar} = 50$ mTorr), interestingly, the obtained thin film still only shows the set of Bragg reflections that characterizes a Sr$_3$Ir$_2$O$_7$ single phase. This is in sharp contrast with the mixed phase film synthesized under pure oxygen atmosphere of the same $P_0 = 50$ mTorr (Fig. 2.3(c)). As $P_0$ further decreases down to 20 mTorr ($P_{Ar} = 80$ mTorr) and 10 mTorr ($P_{Ar} = 90$ mTorr), Sr$_3$Ir$_2$O$_7$ phase remains robust though the Bragg reflections are broadened (Figs. 2.3(c) and (d)). In other words, the thermal stability of the Sr$_3$Ir$_2$O$_7$ phase has been significantly enhanced by introducing argon. On the other hand, in a pure argon atmosphere, i.e., $P_0 = 0$ mTorr, none of the above RP phases can be synthesized, highlighting the critical role of oxygen in stabilizing a Sr$_{n+1}$Ir$_n$O$_{3n+1}$ phase. The growth evolution as a function of $P_0$ within mixed atmosphere is sketched in the right panel of Fig. 2.3(a). As compared to that obtained in pure oxygen atmosphere, it is clear that the growth window of the Sr$_3$Ir$_2$O$_7$ phase has been greatly expanded after introduction of argon.

From the chemical formula $A_{n+1}B_nO_{3n+1}$ of the RP oxides, it can be seen that the $B/A$ cation ratio increases from 0.5 for $n = 1$ to 1 for $n = \infty$. The Sr$_2$IrO$_4$ and Sr$_3$Ir$_2$O$_7$ phases can be considered as variants of SrIrO$_3$ with different degrees of Ir-deficiency. It is indeed possible for SrIrO$_3$ to decompose into the various RP members with the byproduct of Ir and O$_2$, or vice versa. As shown by the previous studies [93], such a controllability of the thermodynamic stability of the three RP phases can be achieved during the growth by varying the ambient pressure of pure oxygen, which is also observed in our study. On the other hand, the background pressure of pulsed laser deposition is also known to strongly influence the plasma plume dynamics, including the ratio and energetics of different ions [74, 101]. This effect may also have significant impact on the growth kinetics, such as the sticking coefficients of different ions and species, especially when the pressure is tuned by more than two orders of magnitudes [74]. Such impact is confirmed by the observed
Figure 2.3 (a) Growth phase diagram of $\text{Sr}_{n+1}\text{Ir}_n\text{O}_{3n+1}$ thin films. The left panel summaries the results under pure oxygen atmosphere and the dashed rectangle highlights the oxygen partial pressure range of interest, from 10 to 80 mTorr. The right panel shows results under argon-mixed oxygen atmosphere. The black, red, and blue regions denote, respectively, where a single phase of $\text{SrIrO}_3$, $\text{Sr}_3\text{Ir}_2\text{O}_7$ and $\text{Sr}_2\text{IrO}_4$ is observed. The $\text{Sr}_2\text{IrO}_4$ and $\text{Sr}_3\text{Ir}_2\text{O}_7$ phases-mixed region is drawn as pink. Batwing markers label synthesized thin films. X-ray Diffraction $\theta - 2\theta$ plots for thin film samples synthesized under $P_O = 80$ mTorr (b), 50 mTorr (c), 20 mTorr (d) and 10 mTorr (e) in pure oxygen and argon-mixed oxygen atmosphere. Plots of samples grown in mixed atmosphere are vertically shifted for clarity.
expansion of the growth window of the Sr$_3$Ir$_2$O$_7$ phase when the overall pressure is maintained by introducing argon. In other words, when reducing the pressure under a pure oxygen atmosphere, the changes in the thermodynamic phase stability and the plume dynamic both favor the conversion from the Ir-rich to Ir-deficient phases. This combination results in a sharp evolution between the two end members, the Sr$_2$IrO$_4$ and SrIrO$_3$ phases with a narrow window of the Sr$_3$Ir$_2$O$_7$ phase in between. Indeed, the previous and our studies all found a remarkably similar phase dependence on the oxygen pressure from the level of 1 mTorr to 100 mTorr regardless of the target stoichiometry. Such a phase evolution is significantly slowed down when the plume dynamics is stabilized by introducing argon to maintain the total pressure, extending the growth window of the Sr$_3$Ir$_2$O$_7$ phase.

2.3 Conclusion

In conclusion, we systematically investigated the effect of growth atmosphere on the epitaxial growth of Sr$_{n+1}$Ir$_n$O$_{3n+1}$ series. The magnetic scattering measurements in combining with structural analysis and physical properties measurement enable us to draw the growth phase diagram as a function of oxygen pressure, upon which the narrow growth window of the Sr$_3$Ir$_2$O$_7$ phase is highlighted. We demonstrated that this growth window can be greatly expanded through introducing argon in the growth chamber. Known that pure oxygen is widely used during oxide synthesis process, the present study affords an efficient route to synthesize a metastable phase during epitaxial growth.
CHAPTER 3 STRAIN-MODULATED SLATER-MOTT CROSSOVER OF PSEUDOSPIN-HALF SQUARE-LATTICE

3.1 Introduction

Electron-electron interaction holds the key to numerous emergent phenomena of modern condensed matter physics, such as superconductivity, insulator-to-metal transition, quantum magnetism, colossal magnetoresistance, stripe order, and spin liquid phases [9, 14, 102-104]. The idea that a sufficiently large Coulomb repulsion triggers collective localization of the electrons and opens a correlated charge gap in an otherwise metallic system, has been widely used to account for intriguing insulating states in a huge variety of quantum materials. Such a correlated gap opening is often accompanied with the emergence of magnetism [9, 105]. A prominent example is the Mott insulating parent compound of high-$T_c$ cuprates [106, 107], where the localized electrons interact with each other through superexchange interactions and form antiferromagnetic (AFM) order below the Néel temperature $T_N$. The key physics of such many-body behavior is well captured by the single-band two-dimensional (2D) Hubbard Hamiltonian on a square lattice [108-112]. While this picture essentially maps the half-filled Hubbard Hamiltonian to the Heisenberg Hamiltonian in the limit of strong Coulomb repulsion [106, 107], it is known treating the Hubbard Hamiltonian in the weak Coulomb repulsion limit also stabilizes an insulating ground state simply driven by the AFM order, i.e., the so-called Slater insulator [45]. Despite yielding the same ground state, these two perturbative approaches at the two opposite limits predict drastically different behaviors in the paramagnetic state: a Slater insulator is metallic above $T_N$, whereas a Mott insulator remains insulating. This distinction highlights the fact that solving the 2D Hubbard Hamiltonian is highly challenging, despite its simple form, especially in the regime of intermediate interaction and finite temperatures, where there is no small control parameter and unlike the Slater and Mott approaches. It is thus crucial to obtain and drive real 2D systems across this regime in experiments.

The recent advances in the field of 5$d$ iridates have led to new opportunities with the so-called $J_{\text{eff}} = 1/2$ electrons, which can also be described by an effective spin-half Hubbard Hamiltonian [4, 27, 113]. The local $J_{\text{eff}} = 1/2$ Kramer doublet is stabilized by strong spin-orbit coupling (SOC) under an octahedral crystal field and is half-filled under the Ir$^{4+}$ 5$d^2$ low-spin configuration [26-29, 57, 88, 114]. The resulting $J_{\text{eff}} = 1/2$ band on a square lattice indeed exhibits an AFM insulating ground state in Sr$_2$IrO$_4$ [26, 88, 96, 115] and Ba$_2$IrO$_4$ [116-118]. Both systems share similar structural motifs to the cuprate parent compound La$_2$CuO$_4$ [106]. But the larger spatial extension of the 5$d$ orbitals also has reduced correlation from that of 3$d$ orbitals, implying that iridates may fall into the
intermediate-coupling regime \([52, 119]\). Indeed, resistivity and optical conductivity measurements have suggested a much smaller charge gap in the iridates \([35, 120]\), opening the door to driving and examining a 2D half-filled single-band system across the intermediate interaction regime. The insulating behavior of \(\text{Sr}_2\text{IrO}_4\) turns out to be fairly robust against high pressure applied up to 55 GPa \([54, 121]\). \(\text{Ba}_2\text{IrO}_4\), on the other hand, was found to become metallic around 13 GPa \([122]\). However, the crucial response of the AFM order remains unclear in both cases, although the weak ferromagnetism of \(\text{Sr}_2\text{IrO}_4\) due to spin canting disappears around 20 GPa \([54]\).

In this section, a systematic investigation of the stability of the AFM order and the electronic modulation of the \(J_{\text{eff}} = 1/2\) square lattice in \((\text{SrIrO}_3)_1/(\text{SrTiO}_3)_1\) superlattice (SL) by varying epitaxial strain is presented. As shown in Fig. 3.1(a), this SL structure is effectively an artificial crystal of \(\text{Sr}_2\text{IrTiO}_6\) \([120, 123, 124]\), where the square lattice of IrO\(_6\) octahedra is separated by a \(\text{SrTiO}_3\) monolayer, mimicking the quasi-2D \(\text{SrIrO}_3\) layers in the Ruddlesden-Popper structures \([33, 87, 125-127]\). The SLs were fabricated by pulsed laser deposition with \textit{in-situ} reflection high energy electron diffraction. We tune the epitaxial strain by growing the SL on three different substrates [Fig. 3.1(b)]: \(\text{SrTiO}_3\) (001) (STO, \(a_{pc} = 3.905\) Å), \((\text{LaAlO}_3)_{0.3}(\text{Sr}_2\text{TaAlO}_6)_{0.7}\) (001) (LSAT, \(a_{pc} = 3.868\) Å) and \(\text{NdGaO}_3\) (001) (NGO, \(a_{pc} = 3.863\) Å). During the growth, all the SLs were kept in the same stacking sequence with a thickness of 30 supercells by \textit{in-situ} monitoring the deposition process. X-ray diffraction (XRD) measurements were performed on a Panalytical X’Pert MRD diffractometer to verify the crystalline quality as well as the epitaxial relationship. Synchrotron XRD measurements and x-ray resonant magnetic scattering (XRMS) experiments were performed at beamlines 33BM and 6IDB, respectively, at the Advanced Photon Source of the Argonne National Laboratory. A crystal analyzer was adopted during the XRMS measurement to improve the magnetic signal-to-noise ratio. X-ray absorption spectroscopy (XAS) experiments at the Ir L-edge were performed at beamline 4IDD at the Advanced Photon Source of the Argonne National Laboratory. These measurements confirm that the picture of the half-filled pseudospin-half state is valid for our samples \([128]\). Linear polarization-dependent XAS experiments at the O K-edge were performed at beamline 4.0.2, at the Advanced Light Source of the Lawrence Berkeley National Laboratory. First-principle density functional theory calculations were performed using the projector augmented wave technique as implemented in Vienna \textit{ab-initio} Simulations Package \([129]\). Due to the large SOC of Ir, we have carried out non-collinear spin-dependent calculations to determine the electronic properties.
Figure 3.1 (a) A schematic of the (SrIrO$_3$)$_1$/(SrTiO$_3$)$_1$ superlattice grown on a substrate with compressive epitaxial strain. Because of the in-plane compression, the lattice structure is elongated along the out-of-plane [001] direction. The black arrow denotes the spin. Top view of the square lattice of IrO$_6$ octahedra. Rotation around the $c$-axis causes a $\sqrt{2}\times\sqrt{2}$ cell expansion of the square lattice. (b) - (d) XRD patterns along the (0 0 $L$) direction for SLs grown on STO, LSAT and NGO, respectively. The supercell $a\times a\times 2c$ ($a$ and $c$ are pseudo-cubic in-plane and out-of-plane lattice parameters, respectively) is used for the notation. The blue, green, and red dashed lines represent the (0 0 4) film peak position of SL-NGO, SL-LSAT and SL-STO, respectively. (e) - (g) Reciprocal space mappings around the film (106) or (116) reflection of SL-STO, SL-LSAT and SL-NGO. The same in-plane Q-vectors of the SLs and the corresponding substrates demonstrates that all the SLs are fully strained within the experimental resolution.
3.2 Result and Discussion

Figure 3.1(b) to (d) show the representative XRD \( \theta-2\theta \) scans for the SLs grown on the three substrates, respectively. Clear \((0\ 0\ \text{even})\) reflections with pronounced Kiessig fringes can be seen on all the SLs, indicating high epitaxial quality and sharp film-substrate interface. In addition, we observed clear \((0\ 0\ \text{odd})\) peaks that come from the alternating SIO-STO growth mode of the SLs, confirming the realization of the as-designed stacking pattern along the \(c\)-axis. Since the applied strain is expected to be increasingly compressive from STO, to LSAT, and to NGO, it is important to verify the strain state of the SL. We performed reciprocal space mapping (RSM) to measure the in-plane lattice parameters. As shown in Figure. 3.1(e) to (g), the Bragg peaks of all SLs are fully aligned with that of the underlying substrates along the in-plane direction with no observable asymmetric intensity distribution, demonstrating the fully strained state. Therefore, the in-plane lattice parameter of the SLs decreases monotonically going from STO to LSAT, and NGO substrates. Correspondingly, the \((0\ 0\ L)\) peak positions of the SLs are systematically shifted to lower angles, indicative of an expansion along the \(c\)-axis. The extracted pseudocubic \(c\)-axis lattice parameter of the SLs increases from 3.954 Å on STO (SL-STO) to 3.980 Å on LSAT (SL-LSAT) and 3.988 Å on NGO (SL-NGO).

An important structural distortion in the physics of the 2D \( J_{\text{eff}} = 1/2 \) electrons is the octahedral rotation/tilting \([29, 38, 72]\). We performed synchrotron-based XRD to measure the corresponding half-order structural peaks. The results show that SL-LSAT and SL-NGO only have octahedral rotation with respect to the \(c\)-axis while octahedral tilting with respect to the \(a\)- or \(b\)-axis is not observable \([128]\). This 2D IrO\(_6\) octahedral structure leads to a \(\sqrt{2} \times \sqrt{2}\) cell expansion within the \(ab\)-plane (Fig. 3.1 (b)), similar to that in Sr\(_2\)IrO\(_4\) \([130]\). SL-STO also has a significant octahedral rotation, but a small octahedral tilting is observable as well \([128]\), consistent with the previous reports \([131, 132]\). The disappearance of the octahedral tilting in SL-LSAT and SL-NGO indicates that the planar oxygen ions, while displaced, remain in the same plane as the Ir sites and the Ir-O-Ti bond is straightened by compressive strain \([133]\).

The SL-STO shows an insulating behavior with an AFM order in previous section \([40]\). Despite the characteristic AFM Mott insulating ground state, the charge transport reveals an anomalous T-dependence that cannot be explained within the Mott-Heisenberg scheme. In particular, the insulating behavior is clearly enhanced upon cooling below \(T_N\) in comparison to the data above \(T_N\) (Fig. 3.3 (a)). More interestingly, the resistance can be significantly enhanced near \(T_N\) under an in-plane magnetic field (inset of Fig. 3.3 (a)). This positive MR is in stark contrast to conventional AFM semiconductors and other Mott insulators, where a negative MR is usually observed due to the field-induced suppression
Figure 3.2 Room-temperature $L$-scan across the $(0.5\ 1.5\ 5)$ Bragg reflection of SL-STO (a), SL-LSAT (b) and SL-NGO (c). (d) $L$-scan across the $(0.5\ 0.5\ 5)$ reflection for all the SLs. The Bragg reflection of the SLs were defined using the $a \times a \times 2c$ ($a$ and $c$ are the in-plane and out-of-plane lattice parameters of a pseudo-cubic unit cell, respectively) supercell. The error bar denotes statistical error.
Figure 3.3 (a) T-dependence of the normalized in-plane resistance (solid). It can be well described by the thermal activation model (dash) above \( T_N \) (200–300 K), which is extrapolated below \( T_N \). Inset shows measurements with and without an in-plane 8 T magnetic field. (b) Temperature dependence of MR under different field. (c) In-plane uniform susceptibility \( \chi \) extracted from the in-plane field-induced XMCD difference. (d)-(f) Cartoons of a half-filled Hubbard system. (d) Coulomb potential (upward curve) confines one electron–hole pair on each lattice site in an AFM insulating ground state. (e) Magnetic moments decrease with expanded electron-hole pairs or disappear with excitations into the electron–hole continuum. (f) A staggered magnetic field reinforces the staggered moments and the electron–hole pairing.
of transverse spin fluctuations. Figure 3.3 (b) shows the T-dependent MR defined as $\frac{[R(B) - R(B = 0T)]}{R(B = 0 T)}$ under different field strengths. The MR is always positive and displays a strong anomalous behavior where the MR above $T_N$ rapidly increases upon cooling and reaches a maximum around $T_N$, indicative of a large field-induced enhancement of the paramagnetic insulating state. The magnitude of the positive anomalous MR is indeed remarkably large, reaching 14% at 14 T or equivalently $\sim$1%/T, considering the absence of spontaneous long-range magnetic order above $T_N$. In other materials, MR of this magnitude in the paramagnetic state is usually negative and relates to insulator-to-metal phase transition, highlighting the unusual combination of robust insulating/semiconducting behavior and large positive MR that is present in the SL.

To reveal the role of the external field, we measured x-ray magnetic circular dichroism (XMCD) at the Ir L3-edge. XMCD measures the uniform magnetization, which at zero magnetic field characterizes the canted component of the spontaneous AFM order parameter (OP). The field-induced XMCD variation is thus proportional to the uniform susceptibility $\chi$, which indeed displays a clear maximum around $T_N$ (Fig. 3.3 (c)). The similar T-dependence of $\chi$ and MR suggests that the external field triggers the anomalous charge response near $T_N$ via the large staggered susceptibility. This can be understood by considering a half-filled single band Mott insulator where charge is relatively localized, each local magnetic moment due to charge localization can be considered as an electron–hole pair (Figure. 3.3(d)). The local moment interacts antiferromagnetically below $T_N$. Correspondingly, fluctuations that excite localized charges into the electron–hole continuum above the Mott gap would lead to spatial fluctuations in the size of the magnetic moments, and vice versa (Figure. 3.3 (e)). The external field acts like staggered field on these antiferromagnetic coupled local moment under the hidden SU(2) symmetry (Figure 3.3 (f)). Therefore, the electron-hole pair is enforced by the external field and the resistance increases under external field. The MR above $T_N$ is the charge response to the large relative increase of the staggered magnetization induced by the external field. The large positive MR in above $T_N$ is incompatible with Mott physics since charge degree of freedom is frozen in Mott insulator. The fact that charge gap depends on $M_s$ renders the weakly coupling regime, but the SL remains insulating above $T_N$. The coexistent characteristics of the Slater and the Mott regimes indicate that the observed behavior can only be consistent with the crossover regime.

Since SL-STO is shown to be within the crossover regime, the evolution of its physical properties under epitaxial strain is furtherly studied. With increasing compressive strain, the SLs show a systematic suppression of resistivity and insulating behavior. Figure 3.4 (a) compares their temperature dependent resistivity from 300 K to 10 K. As can be seen, the resistivity of the SL-STO increases by about two orders of magnitude upon
Figure 3.4 (a) Temperature dependent resistivity of SL-STO (red circles), SL-LSAT (green diamonds) and SL-NGO (blue triangles). (b) Temperature dependent resistivity of SL-NGO with different thickness.
cooking to the base temperature, whereas the SL-LSAT increases only about one order. When further increasing the compressive strain, the resistivity of SL-NGO was further reduced. More importantly, its temperature dependence displays a metallic behavior at high temperatures. As shown in the Figure. 3.4(b), the resistivity monotonically decreases with temperature in the high-temperature region until reaching a minimum around 180 K, below which the resistivity slowly increases for only three times down to 10 K. This observation suggests an emerging “bad metallicity” [134] of the $J_{\text{eff}} = 1/2$ electrons in the SL under large compressive strain, which is in contrast to the robust insulating behavior in Sr$_2$IrO$_4$ under high pressure [54, 121] or compressive strain [53, 92, 135]. The observed metallic behavior does not change with different thickness of the superlattice indicating the observation is robust and repeatable (Figure. 3.4 (b)).

Upon the suppression of the insulating state and the emergence of metallicity, the fate of the AFM order is crucial for revealing the underlying mechanism. While AFM order is often probed by neutron scattering in bulk crystals, it is highly challenging for ultrathin films due to the small sample volume. Instead, we performed XRMS measurements at the Ir L$_3$-edge on the SLs to directly monitor the AFM Bragg peak. A clear resonant effect can be seen at energies slightly lower than the Ir L$_3$-edge white line, a common feature in magnetic iridate compounds [39, 117, 136-139], demonstrating the dominant role of iridium ions in developing the magnetic long-range order (Figure. 3.5 (a)). In the subsequent measurements, the x-ray energy was fixed at the value that maximizes the resonant effect. Figures 3.5 (b-d) show L-scan around the (0.5 0.5 2) magnetic reflections for the SL-STO, SL-LSAT and SL-NGO, respectively. The observation of (0.5 0.5 2) magnetic reflections at 7 K in all three SLs demonstrating the persistence of the AFM ground state. The AFM structure of the SLs is determined to be C-type, where the Ir moments order antiferromagnetically within the square lattice and the adjacent Ir layers order ferromagnetically (Fig. 3.1(a)). It is also conspicuous that the intensity of magnetic peaks decreases as the compressive strain increases. In addition, the integrated intensity of the AFM Bragg peak ($I_{\text{AFM}}$) at 7 K decreases by about 75% from SL-STO to SL-LSAT and by about another 75% from SL-LSAT to SL-NGO. Since the AFM Bragg peak is proportional to the staggered magnetization square ($M_s^2$), this measurement allows quantifying the strain dependence of the AFM order parameter, which drops by half from SL-STO to SL-LSAT and by another half from SL-LSAT to SL-NGO.

Figure 3.6 (a) compares the temperature dependence of the integrated intensity of the (0.5 0.5 2) AFM Bragg peak for the SLs. The magnetic peak of SL-STO disappears above 150 K, which is consistent with the previous reports [39, 40]. As the compressive strain increases, the magnetic peak for SL-LSAT and SL-NGO vanishes at 75 K and 55 K, respectively, demonstrating a systematic decrease of $T_N$. In addition, the magnetization of
Figure 3.5 (a) The energy profile at the (0.5 0.5 2) Bragg reflection across the Ir $L_3$-edge for the SL-STO at 7 K. L-scan (Ir $L_3$-edge) across the (0.5 0.5 2) magnetic reflection of SL-STO (b), SL-LSAT (c), and SL-NGO (d) at 7 K. The peak intensities of SL-LSAT and SL-NGO were plotted in the same scale as SL-STO for comparison and scaled by two and three times, respectively, for better visibility. The error bar denotes statistical error. The dash line serves a guide to the eyes.
Figure 3.6 (a) Temperature dependence of magnetic peaks (0.5 0.5 2) for SL-NGO, SL-LSAT and SL-STO (b) Temperature dependence of the in-plane remnant magnetization of SL-LSAT and SL-STO. The remnant magnetization was measured under zero field after cooling down in a 0.5 T in-plane magnetic field.
SL-LSAT and SL-STO are measured. Figure 3.6 (b) shows the temperature dependence of the remnant magnetization of SL-LSAT and SL-STO. An in-plane net magnetization is observed when temperature is below 75 K for SL-LSAT and 150 K for SL-STO. The remnant magnetization (ReM) at 10 K for SL-LSAT is about 50% of that in SL-STO, consistent with the estimated AFM order parameter reduction from the magnetic resonant scattering experiments. On the other hand, we were not able to characterize the remnant magnetization of SL-NGO, because of the difficulty in eliminating the paramagnetic contribution from the NGO substrate that dominates the total signal in magnetization measurements.

Figure 3.7 (a) summarizes the evolution of the electronic and magnetic properties of the SLs by comparing the AFM order parameter (\( \sqrt{I_{AFM}} \)) and the logarithm of the resistivity increase, which characterizes the strength of the insulating behavior, as functions of the Néel temperature. In particular, the fact that \( T_N \) is suppressed in accordance with the weakening of the insulating behavior demonstrates the dominant role of charge fluctuations in controlling the thermal stability of the quasi-2D AFM order. This is consistent with the observed amplitude reduction of the ground state staggered magnetization, which also signifies enhanced charge fluctuations due to delocalization. The fact that \( M_s \) was reduced simultaneously with \( T_N \) can be understood in the weak coupling limit of the 2D Hubbard model, where both the mean-field ordering temperature and the staggered magnetization are proportional to the ground state charge gap induced by AFM pairing. This is essentially the picture of the Slater insulating state [45]. This picture is however clearly inconsistent with the experimental observations above \( T_N \). Specifically, a metallic state is necessary in the Slater picture in the absence of magnetic order, whereas all three SLs show insulating behavior above \( T_N \), as summarized in Figure 3.7 (b). Such an observation indicates a charge gap already exists before the AFM order sets in, reminiscent of the Mott insulating state in the strong coupling limit.

The blend of the behaviors characteristic of the weak and strong coupling limits clearly suggests that the system should be instead considered in the Slater-Mott crossover regime or the intermediate-coupling regime, which is the most challenging one for solving the 2D Hubbard model, especially at finite temperatures [109]. While the AFM insulating ground states of the two limits can be continuously connected [109, 140], one of their key differences is the size of the magnetic moment [141]. The observed variation of the base-temperature staggered magnetization of the SLs shows a strain-driven modulation of the pseudospin-half square lattice within the crossover regime. At temperatures above \( T_N \), our results indicate that the Mott gap remains finite but is relatively small, especially under a large compressive strain. The local moment is thus expected to be small and fluctuates.
Figure 3.7 (a) The evolution of staggered moment and resistivity increases are plotted against the Néel temperature $T_N$. (b) A summary diagram of the phase evolution of the SL with respect to temperature and in-plane lattice constant. The green region denotes antiferromagnetic (AFM) insulating state with the green dashed line being the phase boundary, while the white and red regions represent non-magnetic (NM) insulating and metallic states, respectively.
strongly with temperature due to significant thermal excitation of the charge carriers. When temperature is comparable with the charge gap; the moment will be completely annihilated with the emergence of metallicity. This corresponds to temperatures that are usually unpractically high but could be reached in the Slater-Mott crossover regime, such as the thermal evolution of SL-NGO from the AFM ground state to the weakly insulating paramagnetic state and eventually to the weakly metallic state (Figure 3.7 (b)). The results of our study reveal the unique character of the crossover regime unexpected in both the Mott and Slater pictures.

To shed additional light on the strain-induced variation in the underlying electronic structure, a series of x-ray absorption spectroscopy (XAS) experiments are carried out. First, we measured valence state of Ir through XAS experiments at the Ir L-edge. As shown in Figure 3.8, the XAS line shapes of SL-STO and SL-NGO are similar and there is no observable energy shift between them at the L3-edge. Furthermore, the nominal Ir$^{4+}$ valence state in the SLs can be concluded because of the same XAS line shapes of the SLs and IrO$_2$, and an Ir$^{3+}$ valence state will cause a large energy shift of 2 eV as that observed in IrCl$_3$. Due to the strong fluorescence signal from the LSAT substrate around the Ir edge, however, we are not able to measure XAS of the SL-LSAT. Nevertheless, given that all the SLs were prepared under the same condition and the compressive strain of SL-LSAT is in between SL-STO and SL-NGO, we expect the same Ir$^{4+}$ valence state in the SL-LSAT. In addition, we are able to estimate the expectation value for spin-orbit coupling \( \langle L \cdot S \rangle \) based on the XAS branching ratio (BR) of the L3-edge and L2-edge [142]. The BR, which is the ratio between the integrated while line intensities at the L3-edge and L2-edge, is obtained for both SL-STO and SL-NGO [142, 143]. Then, we can relate the BR to the \( \langle L \cdot S \rangle \) of the holes on Ir 5d orbital states: \( BR = (2 + r) / (1 - r) \) where \( r = \langle L \cdot S \rangle / \langle n_h \rangle \) [54, 142]. Thus, for SL-STO, we obtained \( \langle L \cdot S \rangle = 2.65 \ (h^2) \) and \( \langle L \cdot S \rangle = 2.40 \ (h^2) \) for SL-NGO. These values are similar to other iridate compounds with an Ir$^{4+}$ valence state under an octahedral crystal field [54, 117, 143], confirming the picture of a half-filled pseudospin half state. The difference between the two samples is within the error of the analysis.

In addition, we performed linearly polarized XAS experiments at the O K-edge, which probes the unoccupied states projected onto the O 2p-orbitals (Figs. 3.9(a)-(c)). Figure 3.9(d) displays the polarization dependent spectra near the absorption edge for all the SLs. The pre-edge (527-529 eV) feature is characteristic of the \( J_{\text{eff}} = 1/2 \) state hybridized with the O 2p orbitals, whereas the higher-energy (529-534 eV) peak represent the Ir \( e_g \) band and the Ti \( t_{2g} \) band [92]. We observed a clear difference of the pre-edge intensities between the in-plane and out-of-plane polarization channels, implying an anisotropic hybridization of the Ir \( J_{\text{eff}} = 1/2 \) state and the O 2p-orbitals. In the out-of-plane channel, the x-ray probes the hybridization of the 2p$_z$ orbitals of the four planar oxygen
Figure 3.8 XAS of SL-NGO (blue), SL-STO (red), IrO$_2$ (black) and IrCl$_3$ (pink) at the Ir L$_3$-edge and L$_2$-edge. The absorption is shifted vertically for clarity.
Figure 3.9 Schematic diagram of linearly dependent XAS measurement at O K-edge. (a) Out-of-plane channel. (b) and (c) In-plane channel. (d) Polarization dependent O K-edge x-ray absorption (XAS) spectra of SL-STO (red), SL-LSAT (green) and SL-NGO (blue). The solid/dashed line denotes XAS from out-of-plane/in-plane measurement. The absorption is shifted vertically for clarity. (e) X-ray linear dichroism extracted from (d).
sites with the Ir $d_{yz}$ and $d_{xz}$ orbitals (Figure. 3.9 (a)). On the other hand, the in-plane channel is sensitive to the hybridization of the Ir $d_{xy}$ orbital with the two planar oxygen $2p_y$ orbitals (Figure. 3.9 (b)) and the Ir $d_{yz}$ orbital with the two apical oxygen $2p_y$ orbitals (Figure. 3.9 (c)). Therefore, the larger spectral intensity in the out-of-plane channel from Figure. 3.9 (d) indicates a stronger hybridization between the Ir ions with the planar oxygens in all the SLs. Figure 3.9 (e) illustrates the difference spectra between the out-of-plane and in-plane channels, i.e., x-ray linear dichroism (XLD). A systematic enhancement of the XLD signal can be seen from the SL-STO to SL-NGO. This observation indicates that the overall hybridization with the planar oxygen increases with increasing compressive strain, which could lead to reduction of the effective correlation of the 2D $J_{eff} = 1/2$ band and the observed modulation within the Slater-Mott crossover regime.

For comparison, we performed first-principles calculations on the whole series of SL [128]. To assess the native influence of the structural strain on the electronic hybridization, we set $U$ to zero in all the calculations. The density functional theory (DFT) calculations are performed using the projector augmented wave (PAW) technique as implemented in Vienna ab-initio Simulations Package (VASP) [144]. The Perdew-Burke-Ernzerhof (PBE) functional revised for solids (PBEsol) [145] is used. Plane wave basis set, which are expanded until the cut-off energy of 600 eV, is used to represent the Kohn-Sham wave functions. In the superlattice (SL), since there is a high spin-orbit coupling (SOC) element (Ir), we have included SOC in the calculations. The in-plane pseudocubic lattice parameters of the three SLs at room temperatures are the same as that of the three substrates according to the fully strained state. We scale them by a factor of 0.9982 for the calculations since the equilibrium lattice parameter of STO obtained by DFT calculation is 3.898 Å instead of 3.905 Å [146]. The experimental c/a ratios are used for calculations of SLs. The pseudocubic c- and a-axis lattice parameters of the SLs represent the Ir-Ti and Ir (Ti)-Ir(Ti) interatomic distances, respectively. The atomic positions of the SLs are relaxed in the calculations to find the lowest-energy state. Additionally, to avoid the complications associated with the choice of $U$ [39, 120, 124, 147], we set $U$ to zero in all the calculations. In the calculated structures, the Ir-O-Ti bond angle, which represents the octahedra tilting with respect to the in-plane pseudocubic axes, is 178.4° for SL-STO, 179.8° for SL-LSAT, and 179.8° for SL-NGO. The latter two mean the bond angle is effectively 180° within computational error and there is no octahedral tilt, which is consistent with the experimental observation. The Ir-O-Ir bond angle, which is predominantly caused by octahedral rotation with respect to the c-axis, is 151.6° for SL-STO, 150.6° for SL-LSAT and 150.1° for SL-NGO. The Ti-O-Ti bond angle is 173.9° for SL-STO, 171.8° for SL-LSAT and 170.4° for SL-NGO.
Figure 3.10 (a) and 3.10 (b) presented the density of states (DOS) of the planar oxygen as well as the apical oxygen within ±0.4 eV from the Fermi level, where the $J_{\text{eff}} = 1/2$ band is located. One can see that the overall DOS of planar oxygen ions is indeed increased from SL-STO to SL-LSAT and SL-NGO, whereas the overall DOS of apical oxygen ions has been systematically reduced with increasing compressive strain, as expected from the elongated lattice along the $c$-axis. We further extracted the $p_z$ and $p_y$ components of the DOS of both oxygen ions and took a difference following the similar rule in XLD measurement. This difference of the projected DOS is shown in Figure 3.9(c), where a systematic increase with compressive strain can be seen for the unoccupied states above the Fermi level, similar to the XLD result.

3.3 Conclusion

In conclusion, we investigated the epitaxial strain-induced electronic and magnetic evolution of (SrIrO$_3$)$_1$(SrTiO$_3$)$_1$ SL. By increasing compressive strain, we efficiently reduced the effective correlation strength of the $J_{\text{eff}} = 1/2$ electrons. Correspondingly, the staggered magnetization and the Néel temperature are systematically and significantly suppressed though AFM structure remains robust within the range of applied strain. The insulating behavior was also strongly suppressed with the emergence of metallicity at high temperatures. When lowering the temperature, the metallic state crossovers into a weak insulating state before the AFM order kicks in. We argue this evolution of the low-temperature ground state in conjunction with the emerging high-temperature excited state is characteristic of modulation of the interaction coupling within the Slater-Mott crossover regime of a half-filled spin-half Hubbard system on a square lattice. Given the possibility of direct probe of the AFM order and epitaxial engineering, the SL represents an excellent model system for exploring the emergent phenomena in this intriguing regime.
Figure 3.10  Density of states (DOS) of the planar oxygen ions (a) and apical oxygen ions (b). (c) The projected DOS difference (PDOS Diff.) extracted from (a) and (b).
CHAPTER 4 STRUCTURAL MODULATED PHYSICAL PROPERTIES OF J$_{\text{EFF}}$=1/2 IRIDATE THIN FILMS IN 3D LIMITS

4.1 Introduction

In the past decades, study of strong correlated systems has led to many emergent phenomena like metal-to-insulator transition [9], exotic magnetism [2] and superconductivity [14]; meanwhile, a great interest has developed recently on the system with the combination of the electron correlation and strong spin-orbit coupling (SOC) [4]. The presence of strong SOC not only couples the orbital degree freedom with spin degree of freedom but also promotes the occurrence of inverted bands which leads to the non-trivial band topology [148, 149]. In addition to non-trivial topological states, the band inversion could potentially generate region of divergence of Berry curvature in Brillouin zone which could lead to largely enhanced charge transport properties like intrinsic anomalous hall effect (AHE) [150, 151]. The intrinsic AHE is a result of combination of electronic band topology in momentum space and magnetic structure in real space. It is often observed in ferromagnetic materials and is recently seen in some non-collinear antiferromagnetic materials where time-reversal symmetry (TRS) breaking ensures a non-vanishing Berry phase in both cases [152]. Thus, a giant AHE can be realized in a magnetic system with strong SOC while AHE itself also serves a good probe to study the effects of topology on the correlated electrons.

The SOC is often treated as a small perturbation in 3d transition metal oxides; whereas 5d transition metal oxides have a relatively weak Coulomb interaction and strong SOC [13]. The comparable energy scale among different interaction has led to some unique emergent states like J$_{\text{eff}}$=1/2 state in the iridates [88]; in addition, it makes the system highly susceptible to small perturbation. The iridate is not only a great platform to explore the Mott-Hubbard physics but also a good candidate to realize various intriguing topological properties [4, 33]. For instance, the bulk SrIrO$_3$ has a ring-shaped Fermi surface which is protected by its crystalline symmetry [38, 71]. The existence of Dirac nodal ring prevents the system collapse into a magnetic insulator while lifting the degeneracy is predicted to be able to realize various topological states [73, 153]. In fact, through interfacial engineering, various exotic properties like topological hall effect is observed in quasi-2D SrIrO$_3$ heterostructure [58]. On the other hand, though epitaxial strain is shown to be sufficient to break the symmetry and opens a Dirac gap in SrIrO$_3$ neither magnetic ordering nor topological state is observed in the SrIrO$_3$ thin films so far [90, 154, 155]. On the other hand, it was found that magnetic transitions could be triggered through partial chemical substitutions of the Ir site with various ions in perovskite SIO [156, 157]. While the Ir valence is altered in many of these cases, one outstanding example is a near-room-temperature weak ferromagnetism that was discovered in isovalent nonmagnetic Sn$^{4+}$-substituted perovskite SrIr$_{1-x}$Sn$_x$O$_3$, which also becomes insulating in contrast to SIO [158, 159]. While these emergent behaviors render this substitution series as promising
functional magnetic materials, only polycrystalline samples can be synthesized in the bulk [158], which requires high pressure synthesis similar to the parent compound SIO [86, 95, 160]. The lack of single-crystalline samples hinders further exploration of the magnetic structure and the underlying mechanism of magnetism induced by the nonmagnetic substitutions. Furthermore, epitaxial strain can be applied as an effective tool for one to further explore the strong SOC related emergent phenomenon.

In this section, the antiferromagnetic SISO thin film is synthesized on different substrates with different orientations where both anisotropic magnetoresistance and anomalous Hall effect is also observed. SISO thin films were deposited from a polycrystalline target of nominal SISO composition [158] on STO(001)-orient, TSO (001)-oriented and TSO(110)-oriented single crystal substrates by using a pulsed laser deposition system (KrF excimer laser) equipped with a reflection high-energy electron diffraction (RHEED) unit. During deposition, the substrate temperature and laser fluence were kept as 700 °C and 2 J/cm², respectively, with a constant oxygen pressure of 115 mTorr. Crystal structure and crystallinity of the thin films were investigated by x-ray diffraction (XRD) measurements on a Panalytical X’Pert MRD diffractometer using Cu Kα radiation (1.5406 Å). The surface quality was characterized by atomic force microscopy. The composition was checked through energy dispersive spectroscopy (EDS). Sample resistivity was measured by using the standard four-point probe on a Physical Property Measurement System (Quantum Design). Synchrotron x-ray diffraction measurements were carried out at room temperature at beamline 33-BM, and x-ray resonant magnetic scattering experiments were performed at beamline 6-ID-B at the Advanced Photon Source of the Argonne National Laboratory.

4.2 Result and Discussion

4.2.1 SISO on STO(001)

The epitaxial deposition process is controlled by in-situ monitoring the RHEED intensity of the specular reflection. As shown in Fig. 4.1(a), we observed well-defined RHEED oscillations over the whole growth process, indicating a stable layer-by-layer growth mode of SISO on the STO substrate. The RHEED pattern recovers the bright spots of both specular and off-specular reflections lying on the zeroth Laue circle after the growth of each layer as demonstrated in the inset of Fig. 4.1(a), indicating a smooth surface. Shown in Fig. 4.1(b) is a representative XRD θ−2θ scan of the obtained SISO films along the STO (001) direction, from which clear film Bragg reflections are observed next to the STO substrate peaks. No impurity phase reflection is found, confirming the single perovskite phase of the samples. The out-of-plane lattice constant can be determined as 4.028 Å which is significantly larger than the bulk (~3.966 Å) [158]. The out-of-plane elongation can be explained as a direct response to the ~−1.6% in-plane compressive strain of SISO when growing on STO (3.905 Å). In addition, high-contrast fringes are observed around the film
Figure 4.1 (a) RHEED oscillation pattern during the thin film growth. The inset is the RHEED image after growth. (b) XRD $\theta - 2\theta$ scan along the STO (001) direction. The pseudo-cubic unit cell $a \times a \times c$ is used for the notation. The inset is the surface morphology map by atomic force microscopy. (c) Reciprocal space mapping around the SISO (013) plane.
reflection suggesting a coherent and sharp film-substrate interface. From the size of the fringes, we obtained a thickness of ~18 nm for this particular sample shown in Fig. 4.1(b), which is consistent with the estimation based on the number of RHEED oscillations, confirming the layer-by-layer growth control with a growth rate about one unit cell per 5 seconds. Clear terraces because of the substrate miscut can be seen on the sample surface, and the surface roughness with the terrace is ~0.1 nm (Fig. 4.1(b) inset). From reciprocal space mapping measurement, we confirmed that the SISO thin film has the same in-plane lattice parameter with that of the STO substrate and therefore is fully strained (Fig. 4.1(c)). The volume of the pseudocubic cell obtained from the measured lattice parameter is ~61.42 Å³, which is ~1.6% smaller than the bulk [158] due to the compressive strain.

To further resolve the epitaxial crystalline structure of the SISO thin film beyond the lattice constants measurements, we investigated the octahedral rotation pattern via synchrotron XRD measurements. Bulk SrIr₁₋ₓSnₓO₃ was previously found to be orthorhombic with the Pbam space group due to the a' a c' perovskite octahedral rotation pattern [158], where the pseudocubic c'-axis is parallel to the orthorhombic [001]or direction. The superscript "+ (−)" here from the Glazer notation [78] denotes an in-phase (out-of-phase) rotation manner of successive octahedra in a projection view. Since octahedral rotation shifts oxygen ions away from the centrosymmetric positions and expands the primitive unit cell, the rotation pattern can be characterized by a set of half-integer Bragg reflections. Following Glazer’s method [78, 79], we performed a broad survey to find the in-phase rotation axis of the SISO thin film (Fig. 4.2(a)). There is no observable peak at (1.5 0.5 2) which indicates that film c-axis is not an in-phase rotation axis. In contrast, a clear (1 0.5 1.5) peak is observed, suggesting that the a-axis is the in-phase rotation axis. Additionally, we also observed a (0.5 1 1.5) peak, pointing to a b-axis in-phase octahedral rotation. Since bulk orthorhombic cell has only one in-phase rotation axis, the coexistence of the two in-phase rotation axes suggests that the [001]or axis is within the film plane with a twin domain structure, as schematically shown in Fig. 4.2(c). In other words, the SISO thin film has a mixed a' b' c' and a' b' c' rotation pattern when grown on the cubic STO substrate. This scenario can be further verified by measuring the associated out-of-phase rotation peaks shown in Fig. 4.2(b). We found the (0.5 1.5 1.5) peak corresponding to b'/c' rotation, the (1.5 0.5 1.5) peak corresponding to a'/c' rotation, and the (0.5 0.5 1.5) peak corresponding to a'/b' rotation. The observation of all these three peaks demonstrates out-of-phase rotations along all three axes, consistent with the picture of the 90°-rotated orthorhombic twin domains shown in Fig. 4.2(c). The rotation angles of the two out-of-phase axes cannot be quantified here but are likely to be different due to epitaxial strain [154, 161].

Next, we show electronic and magnetic properties of the obtained SISO thin film. As shown in Fig. 4.3(a), the room-temperature resistivity of the SISO thin film is about 2 mΩ·cm, similar to the SIO thin films grown on STO [90, 91]. However, in contrast to the weak temperature dependence of the semimetallic resistivity of SIO, the resistivity of SISO thin film increases by more than two orders of magnitude when cooling from room temperature to 10 K. This indicates an insulating nature of SISO, which is consistent with the bulk polycrystalline sample [158]. In addition, we also observed a clear resistivity kink...
Figure 4.2 Synchrotron XRD measurements. (a) In-phase rotation Bragg peaks. (1.5 0.5 2), (1 0.5 1.5) and (0.5 1 1.5) correspond to $c^+$, $a^+$ and $b^+$ octahedral rotations, respectively. (b) Out-of-phase rotation Bragg peaks. (0.5 0.5 1.5), (0.5 1.5 1.5) and (1.5 0.5 1.5) corresponds to $a/b^-$, $b/c^-$ and $a/c^-$ octahedral rotations, respectively. (c) Schematic diagrams of twin crystal domains of the SISO thin film. The grey zone denotes the $a^+b^-c^-$ rotation pattern while the brown zone represents the $a^+b^+c^-$ rotation pattern.
Figure 4.3 (a) Representative temperature dependence of the SISO thin film resistivity. Inset shows the temperature dependence of \(d \left( \ln \rho \right)/d(1/T)\). (b) Temperature dependence of remnant moment per Ir (ReM) within the \(ab\)-plane (red) and along the \(c\)-axis (blue). (c) Resonant x-ray magnetic scattering measurements (red circles) along the \((0.5\ 0.5\ L)\) truncation rod at 10 K (Ir \(L_3\)-edge). Data collected at off-resonant condition (blue triangles) is also shown for comparison. (d) Energy profile of the \((0.5\ 0.5\ 2.5)\) Bragg reflection peak across the Ir \(L_3\)-edge at 10 K. The dashed line served as a guidance. (e) Temperature evolution of the magnetic Bragg peak \((0.5\ 0.5\ 2.5)\) (Ir \(L_3\)-edge). The dashed line serves as a guideline. The error bars denote the statistic error.
around 200 K, which can be further seen in the plot of $d \ln(\rho) / d(1/T)$ as a function of temperature as a $\lambda$-shape cusp peaks at 185 K (inset of Fig. 4.3(a)). This behavior was also reported in the bulk and associated with a magnetic transition [158]. To shed light on the magnetic state of the SISO thin film, we measured the temperature dependent remnant magnetization. As shown in Fig. 4.3(b), the in-plane remnant magnetization (ReM$/ab$-plane) sharply increases when temperatures cooled down below 200 K, and saturates at $\sim 0.043 \ \mu_B$/Ir at the base temperature, close to the reported value in the bulk counterpart [158]. Meanwhile, no significant remnant magnetization along the out-of-plane direction (ReM$/c$-axis) was observed. The onset temperature of the weak FM transition is similar to the onset temperature of the resistivity kink, confirming a strong coupling between electronic transport and magnetic ordering in the SISO film.

The origin of the weak ferromagnetism of SISO is believed to be associated with spin canting of a G-type AFM order of the $J_{\text{eff}} = 1/2$ moments on Ir sites [158], but the AFM structure has yet to be resolved completely. While neutron scattering is often used to probe magnetic structure, the limited sample volume of such thin films with the small $J_{\text{eff}} = 1/2$ moment of the neutron-absorbing Ir ion precludes the feasibility of this route. Instead, we performed resonant x-ray magnetic scattering measurements around the Ir $L_3$-edge, which is an element-selective technique with resonant enhancement of the magnetic signal. The magnetic contribution to the scattering intensity was further extracted by suppressing the charge contribution through the $(\sigma - \pi)$ channel of a pyrolytic graphite analyzer. Shown in Fig. 4.3(c) is a representative Bragg reflection with magnetic contribution found at (0.5 0.5 2.5) at 10 K. The peak intensity drops by about half when the photon energy is tuned away from the Ir $L_3$-edge, indicating significant resonance with the Ir 5$d$ state. The off-resonance intensity at this position is a structural peak from the out-of-plane octahedral rotation discussed earlier and remains detected here because of a combination of its strong intensity and the incomplete efficiency of the analyzer in blocking the $(\sigma - \pi)$ channel. Since the octahedral rotation peak is not supposed to have structural contribution from the Ir sublattice, the observed resonance is likely to due to magnetic order. This is confirmed by the energy profile shown in Fig. 4.3(d), which maximizes the peak intensity at the energy slightly lower than the Ir $L_3$ white line with a typical magnetic line shape [28, 88, 131, 138]. The fact that the magnetic Bragg peak appears at the (0.5 0.5 2.5) position directly demonstrates that Ir magnetic moment is antiferromagnetically coupled with all six nearest-neighboring sites, forming a G-type AFM structure. This can be further verified from the absence of any (0.5 0.5 $\text{integer}$) magnetic reflection as shown in Fig. 4.3(c). When warming the sample, the magnetic component starts to decrease above 100 K as shown in Fig. 4.3(e) and eventually disappears around 200 K, above which only the non-resonant structural component remains. This temperature dependence is consistent with that of the magnetization and resistivity kink, demonstrating a canted G-type AFM insulating ground state of SISO.

In the G-type AFM order, each Ir moment is antiparallel aligned with all six neighboring Ir moments regardless of whether the neighbor’s octahedron is rotated in-phase or out-of-phase. The antiferromagnetic interaction can be considered as Heisenberg-like superexchange, and it is not expected to be very sensitive to the 90$^\circ$-rotated
orthorhombic domain boundary, unlike the antiphase domains [162, 163]. On the other hand, since the octahedral rotation introduces Dzyaloshinskii–Moriya interactions [57], magnetic anisotropy could be influenced and the AFM axis may change direction across the orthorhombic domain wall. In addition, given that the strong in-plane remnant magnetization is consistent with shape anisotropy of thin film, it is unclear whether the intrinsic magnetic anisotropy favors spin-canting in the plane or out of the plane. Finally, we noticed the AFM ordering temperature is lower than the bulk. We checked the Sn concentration of the film by EDS, which shows a 1:3 atomic ratio between Sn and Ir but with significant error due to the small film signal. Although the deviation from the nominal Sn concentration could be related to the nonequilibrium process of the deposition, this result suggests that the lower ordering temperature is not due to Sn-deficiency. Other effects, such as epitaxial strain, could be in play. All these open questions are interesting directions for future investigations, given the possibility of directly probing the AFM order in such thin films by resonant x-ray.

4.2.2 SISO on TSO(001)

Figure 4.4 (a) show the representative XRD θ – 2θ scans for the SISO on TSO(001). Clear (0 0 even) reflections are observed for SISO on TSO(001), with pronounced Kiessig fringes can be seen, indicating high epitaxial quality and sharp film-substrate interface. No impurity phase reflection is found, confirming the single perovskite phase of the samples. The c-axis lattice constant is 0.398 nm for SISO on TSO(001). Reciprocal space mapping measurement confirmed that the SISO thin films are fully strained. The alignment of the substrate and film along the same Q is indicative of the coherent matching of the in-plane film and substrate lattice parameters (Figure. 4.4 (b)).

To further resolve the epitaxial crystalline structure of the SISO thin film, we performed synchrotron XRD measurements to study the IrO₂ octahedral rotation. Bulk SrIr₁₋ₓSnₓO₃ was previously found to be in Pbnm space group with an a’b’c’ octahedral rotation pattern where the pseudocubic c’ axis is parallel to the orthorhombic [0 0 1] direction. Thin film SISO on SrTiO₃ (001) is revealed to have two c’ rotation axis along in-plane direction of the substrate which corresponds to a 90° twinned crystal domain. We performed a similar broad survey on both SISO on TSO(001) to identify its octahedra rotation and titling. Figure 4.5 (a) shows the room temperature L-scan around (1 2 6), (0.5 1.5 3) and (-0.5 1.5 3). The existence of in-phase rotation along a will result in a Bragg peak at (-0.5 1.5 3). The existence of in-phase rotation along b will result in a Bragg peak at (0.5 1.5 3). The existence of in-phase rotation along c will result in a Bragg peak at (1 2 6). Only one Bragg peak is observed around (1 2 6) indicating there is only a c’ rotation axis. Compared to result in the previous section, the twinned crystal domains are reduced to a single domain if the Pbnm symmetry is still preserved. By applying epitaxial strain, the in-plane rotation axis of SISO is now tilted from in-plane direction to the out-of-plane direction. In addition, Figure 4.5 (b) shows the room temperature L-scan around (1 0 3) and (0 1 3). The existence of (0 1 3) Bragg reflection indicates the existence of a’/b’ rotations. For a crystal in Pbnm space group, the (0 1 3) Bragg reflection is forbidden due to the
Figure 4.4 (a) XRD $\theta - 2\theta$ scan along TSO(001) direction. (b) Reciprocal space mapping around SISO (106) plane.
Figure 4.5 (a) Room temperature L-scan around (0.5 1.5 3), (-0.5 1.5 3) and (1 2 6). The black circle denotes (1 2 6) peak, the blue triangle denotes (0.5 1.5 3), and red square denotes (-0.5 1.5 3) peaks. (b) Room temperature L-scan around (1 0 3) and (0 1 3). Red cross denotes the (0 1 3) peak and blue circle denotes the (1 0 3) peak.
existence of b-glide symmetry plane while only (1 0 3) Bragg reflection is allowed. In this case, a weak and broad Bragg peak with well-defined fringes is observed around (1 0 3); on the other hand, no Bragg reflection from thin film is observed. The sharp peak at (0 1 3) is from the substrate TSO since it is also in the Pbnm space group. This indicates the b-glide symmetry plane of thin film is perpendicular to the b-glide symmetry plane for substrates and this also shows that there exists only one orthorhombic structure domain.

While SISO thin film is observed to have a G-type AFM magnetic structure, the direction of AFM spin is not resolved due to lack of single crystal in bulk and the existence of twinned domains in the SISO on STO(001). Here, we performed XRMS measurements at the Ir L3 edge on single domain SISO thin films to directly study its AFM order. While AFM order is often probed through neutron scattering in bulk crystals, it is highly challenging for ultrathin films due to the small sample volume. We observed (0 -1 7) magnetic reflection for SISO on TSO(001) at 7K (Figure 4.6 (a)). The observation of (H, K, L=odd) Bragg peak, while no magnetic peak is observed at (H, K, L=even), indicates G-type AFM magnetic structure for SISO on TSO(001). The temperature dependence of magnetic peak is also studied (Figure 4.6 (b)). As the temperature increases from base temperature, the intensity of magnetic peak vanishes above 250 K indicating the vanishing of AFM order.

In order to resolve the AFM spin direction, we perform a systematic azimuthal dependence of the AFM Bragg peaks, as was done for various iridates. For SISO on TSO(001), SISO(001) aligns perpendicular to the film surface and the SISO(010) lies in the vertical scattering plane at the azimuthal origin. The sample was rotated about the scattering vector Q (0 1 7) by an angle $\phi$ and its intensity was measured (Figure 4.7 (a)). The integrated intensity of the Bragg peak is proportional to the $|M_s \cdot k_f|^2$ where $M_s$ is staggered moment and $k_f$ is the diffraction vector. Thus, when the spin aligns perpendicular to the scattering plane of (0 1 7), the intensity of Bragg peak is zero. On the other hand, a maximum occurs when the spin aligns within the scattering plane. Figure 4.7 (b) shows the Lscan of magnetic peak (0 1 7) at different azimuth angles. As the azimuth angle changes from 0 to 90 degree, the intensity of the magnetic peaks increases respectively. The integrated intensity of (0 1 7) as function of azimuthal angle $\phi$ is shown in Figure 4.7 (c) where the integrated intensity shows a minimum at $\phi$ equal to 0 and a maximum at $\phi$ equal to 90. Thus, spin aligns perpendicular to SISO(010) and parallel to SISO(100). Our calculated azimuth dependence of the integrated intensity with spin aligns along [100] direction (blue line in Figure 4.7 (c)) matches our experimental observation.

The magnetic and electronic properties of SISO are further studied through various transport measurement. The SISO on TSO(001) shows an insulating behavior where the longitudinal resistivity increases monotonically as temperature decreases from 300 K down to 100 K (Figure 4.8 (a)). The magnetoresistance (MR) is measured where anomalous MR is observed for both SISO on TSO(001) near $T_N$. Figure 4.8 (b) shows the temperature dependence of MR of SISO on TSO(001) under 8T field. The MR is defined as $[R(H=8T)-R(H=0T)]/R(H=0T)$ with field applied along different direction. The MR for field applied
Figure 4.6 (a) On resonant and off resonant Bragg reflection around (0 -1 6) and (0 -1 7) for SISO on TSO(001). The red circle denotes the Lscan on resonant at energy 11.217 keV. The blue circle denotes the Lscan off resonant at energy 11.19 keV.
Figure 4.7 (a) Schematic diagram of azimuth measurement on SISO on TSO(001). The blue arrow denotes the direction of spin. (b) Lscan around (0 -1 7) at different azimuth angle. The dash line serves as a guideline. (c) Azimuth dependence of the integrated intensity of Bragg peak (0 -1 7). The triangular is the experiment results from (b). The solid line is the simulated azimuth dependence of (0 -1 7) with spin aligns along [1 0 0].
Figure 4.8 (a) Temperature dependence of resistivity of SISO on TSO(001) (b) Temperature dependence of magnetoresistance of SIOSn on TSO(001) with field applied along different direction. (c) The field dependence of the magnetoresistance at 243 K. (d) Angle dependence of magnetoresistance when 8T external field is applied. The field is applied along [001] direction at angle equals to zero. The sample is rotated along [010] under 8T.
along SISO(001) is significantly larger than the field applied along SISO(100) and SISO(010). The MR remains positive in the measured temperature region with a maximum around T_N. The MR above the T_N rapidly increases upon cooling and reaches a maximum of 12% around T_N. The MR also shows a linear dependence as field increases from 0 to 8T at 243 K (Figure. 4.8 (c)). Figure 4.8 (d) shows the angular dependence of AMR of SISO on TSO (001).

The occurrence of anomaly in MR with maximum around T_N indicates SISO could be within the Slater-Mott crossover regime. The anomalous positive MR is observed in the quasi-2D pseudospin-1/2 square lattice system within the Slater-Mott crossover regime. Within this crossover regime, due the strong interplay between spin and charge, the external field is able trigger an anomalous charge response near T_N via staggered susceptibility. Moreover, the spin dependent hopping is subject to the spin canting of the system due to the SOC, and this is in align with the observed anisotropic MR. SISO on TSO(001) has the G-type AFM structure with spin ordering along SISO(100) as well as a - b c^t octahedral rotation pattern. The structural distortion results in a spin canting along SISO(001) direction; thus, only when external field applied along SISO(001) direction, a strong charge response is expected.

Further Hall measurement revealed an anomalous hall effect (AHE) for SISO on TSO(001). A clear hysteresis of ρ_{xy} (B) as a function of magnetic field perpendicular to the film is observed only below T_N (Figure. 4.9). The coercive field increases as temperature decreases. In addition, the hall resistivity at zero field ρ_{xy} (H=0, T) increases as temperature decreases and reaches 8*10^{-6} Ω ∙ cm at 190K. The AHE observed in SISO on TSO(001) could be driven by the intrinsic Berry curvature. For SrIrO_3 bulk materials, theoretical band calculation has suggested existence of band crossing in the U-R-X plane while experiment observation also shows a divergent behavior. Even if symmetry breaking lifts the degeneracy around these points, the Bloch wave function still experiences a rapid change which result in a sizable Berry. The TRS breaking introduced by the AFM ordering provides the necessary condition for AHE as it breaks the mirror symmetry so that the summation of Berry curvature of all the occupied states becomes non-zero.

In addition, the Berry curvature could also result in an anomalous Nernst effect (ANE) in the thermoelectric transport correspondingly; thus, thermoelectric transport measurement is also applied on SISO on TSO(001). While Berry curvature driven AHE accounts for the contribution from all the occupied states, the ANE is only sensitive to the states near Fermi levels. The temperature dependence of thermopower or Seebeck coefficient of SISO on TSO(001) is measured (Figure. 4.10 (a)). The thermopower −S_{xx} increases as temperature decreases. The temperature dependence of thermopower under different external field is measured. The external field is applied along TSO(001) direction. The magnetic thermopower is extracted from Figure. 4.10 (a) and an anomaly is observed in the temperature evolution of magnetic thermopower (Figure. 4.10 (b)). As the temperature approaches T_N, the magnetic thermopower increases and reaches a maximum around T_N. The magnetic thermopower decreases as the temperature decreases below T_N.
Figure 4.9 The field dependence of hall resistivity at different temperature.
Figure 4.10 (a) Temperature dependence of Seebeck coefficient of SISO on TSO(001) with different field applied. The red line denotes 0.1T field applied. The blue line denotes the 3T field applied along TSO(001) (b) The magnetic Seebeck coefficient extract from (a). The \( M_{Sxx} \) is defined as \( (S_{xx}(3T) - S_{xx}(0.1T))/S_{xx}(0.1T) \). (c) Field dependence of \( -S_{xy} \) of SISO on TSO(001) at different temperature. The magnetic field is applied along TSO(001). (d) Temperature variation of staggered moment, hall resistivity at zero field and Nernst effect at zero field. The circle denotes the staggered moment. The square denotes the anomalous Nernst effect at zero field. The triangular denotes the anomalous hall effect at zero field.
This magneto-thermoelectric effect is consistent with the observation in the MR measurement. This renders the strong interplay between spin and charge degree of freedom within the sample. In addition, the Nernst effect is investigated on SISO on TSO(001) where the heat flow is applied along SISO(100), and the transverse voltage is measured along SISO(010) while external field is applied along SISO(001). In Figure. 4.10 (c), the field-dependence of Nernst thermopower is measured at different temperature where a clear anomalous Nernst effect (ANE) is observed below \(T_N\). As the temperature decreases, the coercive field gradually increases; in addition, the Nernst signal at both zero field increases as temperature increases and it reaches 2 uV/K at 200 K. Compared to the observation in the hall measurement, the coercive field is almost the same for AHE and ANE at the same temperature. Moreover, both \(\rho_{xy}\) and \(-S_{xy}\) increases as temperature decreases below \(T_N\) and this is consistent with the temperature evolution of staggered moment (Figure 4.10 (d)).

### 4.2.3 SISO on TSO(110)

Figure. 4.11 (a) show the representative XRD \(\theta - 2\theta\) scans for the SISO on TSO(110). Clear (even even 0) reflections are observed for SISO on TSO(110), with pronounced Kiessig fringes can be seen, indicating high epitaxial quality and sharp film-substrate interface. No impurity phase reflection is found, confirming the single perovskite phase of the samples. The c-axis lattice constant is 0.400 nm for SISO on TSO(110). Reciprocal space mapping measurement confirmed that the SISO thin films are fully strained. The alignment of the substrate and film along the same \(Q_x\) is indicative of the coherent matching of the in-plane film and substrate lattice parameters (Figure. 4.11 (b)).

To further resolve the epitaxial crystalline structure of the SISO thin film, we performed synchrotron XRD measurements to study the \(\text{IrO}_2\) octahedral rotation. We followed the methods in the last section and performed a similar broad survey on SISO on TSO(110) to identify its octahedra rotation and titling. Figure 4.11 (c) shows the room temperature HKLscan around (1 2 -2), (-0.5 -1.5 1) and (-1.5 0.5 3). The existence of in-phase rotation along \(a\) will result in a Bragg peak at (-0.5 -1.5 1). The existence of in-phase rotation along \(b\) will result in a Bragg peak at (-1.5 0.5 3). The existence of in-phase rotation along \(c\) will result in a Bragg peak at (1 2 -2). Only one Bragg peak is observed around (1 2 -2) indicating there is only a \(c^+\) rotation axis. In addition, Figure 4.11 (d) shows the room temperature HKLscan around (3 0 1) and (0 3 1). The observation of Bragg reflection at (3 0 1) indicates the existence of \(a/b\). For SISO on TSO(110), Bragg reflection is only observed around (3 0 1) indicating there is only one orthorhombic structural domain; moreover, the b-glide symmetry plane of thin film aligns in the same direction of the b-glide symmetry plane of substrate. For both SISO on TSO(001) and SISO on TSO(110), the thin film is fully strained, and the thin film follows the crystal orientation of the TSO substrate (Figure 4.12).

Though SISO is fully strained on TSO(110), we want to see if the magnetic
Figure 4.11 (a) XRD $\theta - 2\theta$ scan along TSO(001) direction. (b) Reciprocal space mapping around SISO (106) plane. (c) Room temperature Lscan around (0.5 - 1.5 1), (1.5 - 0.5 3) and (1 - 2 2). The black circle denotes (1 - 2 2) peak, the blue triangle denotes (-0.5 - 1.5 1), and red square denotes (1.5 - 0.5 3) peaks. (d) Room temperature HKLscan around (3 0 1) and (0 3 1). Red cross denotes the (3 0 1) peak and blue circle denotes the (0 3 1) peak.
Figure 4.12 Schematic diagram of SISO thin film on TSO(001) and TSO(110).
structure remains the same, so we carried out the XRMS on this sample. Here, we performed XRMS measurements at the Ir L₃ edge on single domain SISO thin films to directly study its AFM order. We observed (5 0 1) magnetic reflection for SISO on TSO(110) at 7K (Figure. 4.13 (a)). The observation of (H, K, L=odd) Bragg peak, while no magnetic peak is observed at (H, K, L=even), indicates G-type AFM magnetic structure for SISO on TSO(110). The temperature dependence of magnetic peak (3 2 1) is also studied (Figure. 4.13 (b)). As the temperature increases from base temperature, the intensity of magnetic peak decreases. The intensity of magnetic peak vanishes above 240 K indicating the vanishing of AFM order.

In order to resolve AFM spin direction, we perform a systematic azimuthal dependence of the AFM Bragg peaks, as was done for various iridates. For SISO on TSO(110), SISO(1-10) aligns perpendicular to the film surface and the SISO(110) lies in the vertical scattering plane at the azimuthal origin. The sample was rotated about the scattering vector Q (3 2 1) by an angle $\phi$ and its intensity was measured. Figure 4.13 (c) shows the HKL-scan of magnetic peak (3 2 1) at different azimuth angles. As the azimuth angle varies, the intensity of the magnetic peaks varies respectively. The integrated intensity of (3 2 1) as function of azimuthal angle $\phi$ is shown in Figure 4.10 (d) where the integrated intensity shows two minimums at $\phi$ equal to 50 and 165 and also two maximums at $\phi$ equal to 115 and 285. Thus, spin aligns perpendicular to SISO(010) and parallel to SISO(100). Our calculated azimuth dependence of the integrated intensity with spin aligns along [100] direction (blue line in Figure. 4.13 (d)) matches our experimental observation.

The magnetic and electronic properties of SISO are further studied through various transport measurement. The SISO on TSO(110) shows an insulating behavior where the longitudinal resistivity increases monotonically as temperature decreases from 300 K down to 100 K (Figure 4.14 (a)). The magnetoresistance (MR) is measured where anomalous MR is observed for both SISO on TSO(110) near $T_N$. Figure. 4.14 (b) shows the temperature dependence of MR of SISO on TSO(110) with 8T field applied along different direction. The MR for field applied along SISO(001) is significantly larger than the field applied along SISO(110) and SISO(1-10). The MR remains positive in the measured temperature region with a maximum around $T_N$. The MR above the $T_N$ rapidly increases upon cooling and reaches a maximum of 8% around $T_N$. The MR also shows a linear dependence as field increases from 0 to 8T at 225 K (Figure. 4.14 (c)).

The transverse transport measurement is further carried out. Figure. 4.15 (a) shows the field dependence of hall resistivity of SISO on TSO(110). The $\rho_{xy}$ increases linearly as field increase and no AHE is observed for SISO on TSO(110). In addition, the Nernst effect of SISO on TSO(110) is also measured. Figure. 4.15 (b) shows the field dependence of the Nernst effect of SISO on TSO(110) at 190 K and no ANE is observed for the sample. The obscene of AHE and ANE can be understood as a result of the absence of canted moment along out-of-plane direction. The SISO on TSO(110) has a G-type AFM magnetic structure with spin along a direction. Since SISO is fully strained and follows the crystal
Figure 4.13 (a) HKL scan around (5 0 1) and (5 0 2) on resonant and off resonant. The red circle denotes the HKL scan around (5 0 1) on resonant at 11.217 keV. The black triangle denotes the HKL scan around (5 0 2) on resonant at 11.217 keV. The blue circle denotes the HKL scan around (5 0 1) off resonant at 11.19 keV. (b) Temperature dependence of intensity of Bragg peak (3 2 1). (c) The HKL scan around (3 2 1) at different azimuth angle. (d) Azimuth dependence of the integrated intensity of Bragg peak (3 2 1). The red circle is the experiment results from (c). The solid line is the simulated azimuth dependence of (3 2 1) with spin aligns along [1 0 0].
Figure 4.14 (a) Temperature evolution of the $\rho_{xx}$ of SISO on TSO(110). (b) Temperature dependence of magnetoresistance of SIOSn on TSO(110) with field applied along different direction. (c) The field dependence of the magnetoresistance at 225 K.
Figure 4.15 (a) Field dependence of the hall resistivity of SISO on TSO(110) at 210 K. (b) Field dependence of Nernst effect of SISO on TSO(110) at 190 K.
of the TSO(110) substrate, the canted moment which is along [001] direction is then within the plane. This is consistent with the MR measurement where the in-plane MR is much larger than the out-of-plane direction. Though it is possible to have AHE/ANE for colinear AFM samples, the anomalous hall conductivity only exists for $\sigma_{xy}$. For a Pbnm group sample with spin aligns perpendicular to its glide plane, the off-diagonal term in its hall conductivity tensor $\sigma_{ij}$ vanishes except for $\sigma_{xy}$.

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4.3 Conclusion

We have synthesized SISO on STO substrate and TSO substrates with different orientation. The SISO is fully epitaxial grown on all different substrate with same structure while further magnetic scattering measurements revealed that they both have G-type AFM. SISO on STO(001) shows two structural twinned domains while SISO on TSO(001) and TSO(110) only shows one structural domain. The scattering measurement on SISO on STO(001) and TSO(110) both revealed the same magnetic structure with spin axis along [1 0 0] direction. The magnetoresistance measurement unfolded a large positive anisotropic anomalous behavior around $T_N$ which is a characteristic of Slater-Mott crossover regime. Hall measurement shows only SISO on TSO(001) holds an AHE while it is absent in SISO on TSO(110). The thermoelectric measurement shows a corresponding magnetothermoelectric effect and ANE. The result shows that transport properties like AHE and ANE can be induced in the non-magnetic semimetal with large spin orbit coupling through non-magnetic ion doping. Moreover, through epitaxial engineering one can control the AHE and ANE by controlling the orientation of the plane of the materials through synthesis on the substrate with different orientation. This provides more opportunities in design and control new spintronic devices.
CHAPTER 5 CONCLUSION AND OUTLOOK

In this work, a series of iridate thin films have been synthesized. Through study of different iridate thin films, several new emergent phenomena are observed. One of the main ideas in this work is to take advantage of the intermediate coupling and the high tunability in the iridate thin films to realize a platform in the Slater-Mott crossover regime. Another goal is to explore emergent phenomena in the iridate because of the strong SOC.

The synthesis of iridate superlattice shows that it can be used as a platform to explore this intermediate regime. Two perovskite SIO and STO are combined to create a superlattice with each one of them stacking alternative respectively. The epitaxial strain is used to stabilize this superlattice and it also serves as the main control parameter in this study. By synthesize superlattice on different substrate with different lattice mismatch, different epitaxial strain is applied to the superlattice. The structural characterization through XRD confines the lattice expansion along c-axis and RSM ensures the thin film is fully strained. The subsequent characterization of magnetic and electronic properties not only shows systematic change of physical properties of system under strain but also confirms that the system is in the intermediate regime. The applied compressive epitaxial strain effectively makes system less insulating; moreover, the system even shows metallic behavior under largest compressive strain. On the other hand, REXS measurement on these superlattices shows that even though the AFM ordering is suppressed under compressive strain, the ground state of the superlattices remains to be AFM. Further XLD measurement shows that the compressive strain indeed modulates the electron correlation within the $J_{\text{eff}}=1/2$ electronic state. The suppression of both insulating behavior and AFM ordering renders that epitaxial strain is an effective tool to control the physical properties of the system. More importantly, under largest compressive strain, the superlattice shows metallic behavior above 180 K while AFM ordering only emerges below 55 K. This is contrast to either the Mott insulator or Slater insulator. The observation renders the complexity of the system within Slater-Mott crossover regime under finite temperature.

The synthesis of chemical substituted iridate thin films shows that anomalous transport properties can be realized by epitaxial strain. The non-magnetic semi-metallic SIO is chemical substituted with Sn. The epitaxial strain is used to stabilize the SISO thin films. Structural, electronic, and magnetic characterization of SISO on STO shows that the thin film has an AFM insulating ground state with an Pbnm structure. The successful synthesis of single crystal epitaxial thin film of SISO can help in studying this material since there is only polycrystal bulk samples. With different epitaxial strain applied, it is shown that the magnetic properties can be tuned and thus result in the occurrence of both AHE and ANE. For SISO on TSO(001), physical properties characterization shows that the system remains to be AFM insulator. The azimuthal dependence in the REXS measurement shows that the staggered moment aligns along [001]-direction which result in a canted moment along out-of-plane direction. The electric transport measurement then revealed an anisotropic magnetoresistance behavior and AHE. The thermoelectric measurement also shows a magneto-Seebeck effect as well as ANE. In addition, SISO is
also synthesized on TSO(110). Though the substrate has different orientation and applies different epitaxial strain on SISO, the SISO thin film fully follows the orientation of the substrate with its crystal and magnetic structure remains the same compared to SISO on TSO(001). Though the anisotropic magnetoresistance behavior is observed in SISO on TSO(110), both AHE and ANE are absent in the sample. The absence anomalous behavior in the transverse transport measurement is likely due to the symmetry.

Overall, both works have shown that iridate thin films are good platform to study fundamental physics and explore emergent new phenomenon. In addition, the epitaxial strain plays an important role in both cases as it serves as a good tool to tune the physical properties of the system. There are a lot of work can be done following these two works.

First, the epitaxial strain has shown to be an effective tool to modulate the iridate superlattice in the Slater-Mott crossover regime. In this work, the maximum compressive strain that is applied is about 1% and a metallicity is already observed above 180 K. Then, if a larger compressive is applied, how will the properties of the system changes. It is known that a Slater insulator ought to be metallic above $T_N$ and AFM insulator below it. A larger compressive strain should tune the system more towards the Slater limit. Based on current observation the compressive strain intends to suppress both AFM order and insulating behavior. If the larger compressive strain is applied, then will the system become a Slater insulator or a non-magnetic metal. There is still a lot of blank space between the current experimental point and the Slater limit. It also applies to the tensile strain. If a tensile strain is applied the system ought to go towards the Mott limit. The system will become more insulating, and the transition temperature may increase as well but it requires experiments to verify. By tuning the system within this Slater-Mott crossover regime, one would know more about the role of correlation in the electronic and magnetic properties of the system, particularly at finite temperature. This is a difficult task to achieve by theoretically calculate the single band Hubbard Hamiltonian. With a detailed mapping within this intermediate regime, it can also help the theoretical work.

Second, the initial proposal in study the pseudospin-1/2 iridate square lattice is to mimic the work done in the cuprate, to realize the high-$T_c$ superconductivity. The iridate superlattice is an AFM insulator which is analogous to the parent compound of cuprates. The carrier doping in other iridate compound like Sr$_2$IrO$_4$ where it has already result in some interesting discovery like fermi arc and pseudo gap are observed. On the other hand, iridate superlattice as a pseudospin-1/2 square lattice system also has the potential to be the parent compound of a new superconductor. Thus, carrier doping iridate superlattice may result in some interesting phenomenon. In addition to superconductivity, carrier doping with different concentration may result in different phases or states in the iridates. Because of the existence of strong SOC, the exotic phases on the phase diagram of iridate superlattice s may be more abundant compared to 3d TMOs. The carrier doping can also be applied to the SISO sample. While iridate superlattice can be viewed as a system in quasi-2D limit, the SISO is system in 3D limit. The dimensionality has been shown in various work to play an import role in the properties of the system. Thus, carrier doping a
spin-orbit Mott insulator in 3D limit may result in some unexpected result compared to the case in 2D limit.

Third, the observation of AHE and ANE in SISO also raise the question if it is possible to realize the quantum version of these properties in the iridate superlattice. The anomalous transport properties have been realized in quasi-2D iridate superlattice by combing the iridate layer with a magnetic material layer. The topological hall effect is also observed in combining 4d TMOs with iridate. Therefore, it leaves one wonder if it is possible to realize the quantum hall effect and quantum anomalous hall effect in the iridate superlattices. To achieve this goal, one may need to apply various heterostructure engineering techniques like finding the right insertion layer and using epitaxial strain to break the right symmetry. Though some of the theoretical calculation indicates it is possible to realize these properties, research so far has not been able to achieve so.

There is still a lot one can explore in these iridate thin films. The strong interplay between different degrees of freedom in the iridate makes it has a lot of potential. The work so far has only revealed a corner of an iceberg. Many interesting properties like superconductivity, topological properties and unconventional magnetism await to be discovered.
22. de la Cruz, C., et al., *Magnetic order close to superconductivity in the iron-based


Boseggia, S., *Magnetic order and excitations in perovskite iridates studied with resonant X-ray scattering techniques*, in Faculty of Maths and Physical Sciences. 2015, University of College London: UCL Discovery.


Kini, N.S., et al., *Transport and thermal properties of weakly ferromagnetic


128. See Supplemental Materials for detailed characterization and calculation.


VITA

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