A Systematic Study of the Effect of Spin-Orbit Interaction on Properties of Tetravalent and Pentavalent Iridate Compounds

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A systematic study of the effect of spin-orbit interaction on properties of tetravalent and pentavalent iridate compounds

DISSERTATION

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

By
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Lexington, Kentucky

Director: Dr. Gang Cao, Professor of Physics
Lexington, Kentucky
2016

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ABSTRACT OF DISSERTATION

A SYSTEMATIC STUDY OF THE EFFECT OF SPIN-ORBIT INTERACTION ON PROPERTIES OF TETRAVALENT AND PENTAVALENT IRIDATE COMPOUNDS

Previous studies of iridates have shown that an interplay of strong SOI, Coulomb interaction $U$, Hund’s rule coupling and crystalline electric fields result in unexpected insulating states with complex magnetic states. The novel $J_{\text{eff}} = 1/2$ insulating state first observed in Sr$_2$IrO$_4$ is a direct consequence of such an intriguing interplay and is one of the central foci of this dissertation study.

The work presented here consists of three projects: (1) Effects of Tb doping on Sr$_2$IrO$_4$ having tetravalent Ir$^{4+}$($5d^5$) ions; (2) Emergence of unexpected magnetic states in double-perovskite (Ba$_{1-x}$Sr$_x$)$_2$YIrO$_6$ with pentavalent Ir$^{5+}$($5d^4$) ions in the presence of strong SOI, and (3) The coexistence of a charge and magnetic order in a magnetic dimer chain system, Ba$_5$AlIr$_2$O$_{11}$, which has both tetravalent Ir$^{4+}$ ($5d^5$) and pentavalent Ir$^{5+}$ ($5d^4$) ions.

A significant portion of this dissertation will focus on Tb doped Sr$_2$IrO$_4$. A central finding of this work is that slight Tb doping (3%) readily suppresses the antiferromagnetic state but retains the insulating state, indicating an unusual correlation between the magnetic and insulating states as a result of the presence of the strong SOI.

However, SOI is not the only significant phenomenon. The study on the double-perovskite (Ba$_{1-x}$Sr$_x$)$_2$YIrO$_6$ revealed an exotic magnetic ground state, in sharp contrast to the anticipated singlet ground state in the strong SOI limit, raising an urgent question: is SOI as dominant as was initially anticipated in the iridates?

Finally, this study turns to a system containing both Ir$^{4+}$ and Ir$^{5+}$ ions, Ba$_5$AlIr$_2$O$_{11}$. This system features dimer chains of two inequivalent octahedra occupied by tetravalent Ir$^{4+}$ ($5d^5$) and pentavalent Ir$^{5+}$ ($5d^4$) ions respectively. Ba$_5$AlIr$_2$O$_{11}$ undergoes charge and magnetic order transitions at 210 K and 4.5 K, respectively.

SOI-driven physics is a rapidly evolving field with an ever growing list of theoretical proposals which have enjoyed very limited experimental confirmation thus far. This study has revealed a large range of interesting phenomena in the iridates that defy conventional theoretical arguments and that help to fill an experimental void in this field.

Keywords: spin-orbit interaction (SOI), iridates, double exchange, Mott insulator, Coulomb interaction, Hund’s rule coupling

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Date: December 1, 2016
A SYSTEMATIC STUDY OF THE EFFECT OF SPIN-ORBIT INTERACTION ON PROPERTIES OF TETRAVALENT AND PENTAVALENT IRIDATE COMPOUNDS

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Chapter 1. INTRODUCTION

1.1 Correlated Electron systems - Mott physics

Early theoretical descriptions based on the filling of electronic bands (band picture) were successful in explaining properties of metallic, insulating or transitioning materials using the weakly interacting or non-interacting electron model. In 1937, however, reports surfaced that a number of materials with partially filled d-electron bands like NiO exhibited insulating or poor conducting properties, which contradicted the expectations of metallic behavior based on the previously successful band picture [1]. Band theory relied on treating an electron as weakly interacting, embedded in the mean field produced by the other electrons where the electron kinetic energy was significantly larger than their electron-electron (Coulomb) energy. However, electron correlation has a much more substantial role with spin, charge, and orbital degrees of freedom having tremendous effects on material properties and a large number of unique behaviors. Electron correlation often leads to electron localization and is responsible for many phenomena such as ferromagnetism, antiferromagnetism, and superconductivity, including both insulating and metallic materials. Some of the more dramatic properties are significant responses to applied magnetic field (colossal magnetoresistance), large thermoelectric response, very high ordering temperatures and significant changes in resistivity across metal-insulator transitions [2]. Neville Mott was among the first who tried to explain the origin of insulating states in partially filled d- and f-orbitals as a result of strongly correlated electron interactions. He used a model with a single s-orbital at each lattice site where if fully occupied with spin up and spin down electrons, there would be strong Coulombic repulsion, which would open up a gap in the band that would be absent in the case of non-interacting electrons. This would result in splitting of the band into the Upper Hubbard Band (UHB), occupied by two electrons, and the Lower Hubbard Band (LHB) occupied by a single electron. In this case, even with one electron per site the LHB would result in an insulating state. Equation 1.1 is the simplest Hubbard Hamiltonian used to describe correlated electrons, taking into account only valence electrons near the Fermi level:

\[ H = \sum_{ij,\sigma} t_{ij} c_{i\sigma}^{\dagger} c_{j\sigma} + U \sum_i n_{i\uparrow} n_{i\downarrow} \]  

(1.1)

where first term represents kinetic energy, characterized by the hopping term \( t_{ij} \), and the second term local Coulomb repulsion (\( \sigma = \uparrow \) or \( \downarrow \) indicates spin direction with \( i \) and \( j \) representing lattice sites each with localized electrons) [2]. The \( t_{ij} \) hopping term is what determines the bandwidth \( W \) and it is the competition between the bandwidth \( W \) and Coulomb interaction \( U \) that determines the properties of these materials. The simplified model of the effect of the relation between the two onto the density of states in the case of half filling, one electron per lattice site, is represented in Figure 1.1.
Figure 1.1: The Density of States as a function of Coulomb Interaction $U$: (a) independent electron model with $U = 0$, Fermi level sits at the middle of the band resulting in metallic state, (b) when electrons weakly interact (small $U$) there is narrowing of the band however the DOS still resembles that of independent electrons, (c) for strongly correlated electrons $U > W$, the spectrum displays three peaks: two Hubbard bands and a quasiparticle peak at the Fermi level, (d) when electron correlation is strong enough to cause the quasiparticle peak to vanish, spectral weight is transferred to the two Hubbard bands, thereby causing a Mott metal-insulator transition. [2]

Although initially Mott didn’t associate the insulating state with magnetic ordering, Slater later attributed the insulating state and band gap to the long-range magnetic order, more
precisely antiferromagnetic (AFM) order. However, the appearance of an insulating state without magnetic order has contradicted Slater’s band picture and the presence of the spin and charge gap indicated the possibility of a continuum between the Mott and the band insulator.

1.2 Interplay of strong spin-orbit interaction and electron correlation

Spin-orbit interaction is a relativistic effect that links the electronic orbital and spin angular momenta. The effect of strong spin-orbit interaction (SOI) in semi-conductors, which have weak electron correlation, has led to numerous exciting phenomena, such as the Anomalous Hall Effect (AHE), and more recently, topological insulators and metals [3]. Nuclear charge can be suppressed by the fine structure constant. In the case of heavier atoms with large atomic number (and hence the large number of protons), the electric field produced by nuclear charge is significant and is substantial in iridates (Z = 77), which results in significant spin-orbit interaction. Atomic number increases as we move down the group in the periodic table, however at the same time for materials with large atomic number we observe more extended orbitals. In our case these are the d orbitals, and they cause an increase in radial separation between electrons, leading to a reduction in electron correlation U. The trend followed by electron correlation within the periodic table is opposite to that of atomic number, and increases as we move up the group in the periodic table Figure 1.2. Although most anomalous properties tend to be attributed to spin-orbit interaction in these materials, we will see that it is the competition between these relevant interactions that actually results in novel phases. These novel phases can be exquisitely sensitive to even slight perturbations induced by pressure, chemical doping and magnetic field.

![Periodic Table](image)

Figure 1.2: Periodic table with trend of increase in spin-orbit interaction and electron correlation as a result of change in atomic number (Z) and orbital size respectively
Along with spin-orbit interaction, electronic ground states are also determined by electron correlation, which leads to localization of the electronic states, and the hopping parameter \( t \), which represents kinetic energy of electrons hopping between atoms. There is an additional strong dependence of electronic states on the crystal structure, so its influence on the spin-orbit interaction and electron correlation need to also be investigated \[4\]. The effects of SOI and electron correlation have led to recent discoveries of new material phases \[5-6\]. Spin-orbit and Coulomb interaction values for transition metals have been tabulated for comparison and are summarized in Table 1.1. While the spin-orbit interaction \( \lambda_{so} \) for 3d-elements is so minor that it can act as perturbation in comparison to Coulomb interaction \( U \) as we move down the periodic table to 5d-elements, we see that the two interactions are comparable not just to each other, but also to several other relevant energies in these materials like Hund’s coupling \( J_H \) and crystal field \( \Delta \). As studies have been done on various 4d and 5d based oxides we could see that these energy scales vary slightly, resulting in a rich family of behavior \[3\].

<table>
<thead>
<tr>
<th>Electron type</th>
<th>( U ) (eV)</th>
<th>( \lambda_{so} ) (eV)</th>
<th>Interactions</th>
</tr>
</thead>
<tbody>
<tr>
<td>3d</td>
<td>5.0-7.0</td>
<td>0.01-0.1</td>
<td>( U &gt; CF &gt; \lambda_{so} )</td>
</tr>
<tr>
<td>4d</td>
<td>0.5-3.0</td>
<td>0.1-0.3</td>
<td>( U \sim CF &gt; \lambda_{so} )</td>
</tr>
<tr>
<td>5d</td>
<td>0.4-2.0</td>
<td>0.3-1.0</td>
<td>( U \sim CF \sim \lambda_{so} )</td>
</tr>
</tbody>
</table>

Table 1.1: Comparison of relevant d-electron energies \[14\]

1.3 Spin-orbit coupled Iridates

New phenomena observed in heavy transition metal oxides have attracted much of the attention due to the possibility of high temperature superconductivity, topological phases, quantum spin liquid, and other exotic states. These predicted new states are a result of the strong competition between Coulomb interactions, strong spin-orbit interaction, Hund’s rules and non-cubic crystal fields. As we will see when we look at the ground state of the compounds described in the following chapters, all iridates tend to be highly insulating, which as we discussed above, does not fit the conventional picture of materials with large extended d orbitals. In addition, the nature of extended 5d-orbitals in these materials should also result in fewer magnetic states compared to 3d based oxides. However, almost all iridates, particularly the layered Ruddlesden-Popper series \( \text{Sr}_{n+1}\text{Ir}_n\text{O}_{3n+1} \) and the hexagonal \( \text{BaIrO}_3 \) exhibit antiferromagnetic order with low ordering moments but high transition temperatures. For example, 240 K for the single layer \( \text{Sr}_2\text{IrO}_4 \), 285 K for the double layered \( \text{Sr}_3\text{Ir}_2\text{O}_7 \), 183 K for hexagonal \( \text{BaIrO}_3 \) and 185 K for orthorhombic \( \text{Sr}_{0.94}\text{Ir}_{0.78}\text{O}_{2.68} \) \[7-18\]. The magnetic structures closely track lattice distortions as a result of the strong SOI \[19-20\].

Collaborative research between the Cao group and others led to a discovery of the novel \( J_{eff} = \frac{1}{2} \) insulating state, a result of a combined effect of the electron-electron correlation and SOI \[7\]. A critical underlying mechanism for the novel states in iridates is
the SOI that vigorously competes with U, non-cubic crystalline electric fields, and Hund’s rule coupling. The net result of this competition is to stabilize ground states that have exotic behavior. Without inclusion of the spin-orbit interaction, two possibilities arise; firstly, on its own, the strong octahedral crystal field of 10 Dq splits the wide 5d band into \( t_{2g} \) (triplet) and \( e_g \) (doublet) orbital states, where five 5d electrons partially fill the \( t_{2g} \) band, leading to the metallic state depicted in Figure 1.3a. Since the energy gap between the \( t_{2g} \) and \( e_g \) states is too large, if electron filling is less than six we can ignore the \( e_g \) doublet. Since most of the iridates studied have four or five d electrons, this can safely be implemented. An alternative case is where electron correlation is significantly larger than the bandwidth to the extent of being able to sufficiently open the gap to result in the insulating \( S = \frac{1}{2} \) Mott ground state as shown in Figure 1.3b. Now, although the latter gives rise to an insulating state, the strength of the Coulombic interaction would have to be strong enough (\(-10 \text{ eV}\)) to overcome bandwidth, which as electron interaction is reduced for Ir atoms seems very unlikely (\( U \sim 0.4 \text{ - 2 eV}\)). The newly proposed model includes the effect of both the strong spin-orbit interaction as well as electron correlation, as shown in Figure 1.3c-e. The SOI is a relativistic effect proportional to \( Z^4 \) (\( Z = 77 \) for Ir), and has a strength of \( \sim 0.4 \text{ eV} \) in the iridates (compared to \( \sim 20 \text{ meV} \) in 3d materials), and splits the \( t_{2g} \) bands into states with the \( J_{\text{eff}} = 1/2 \) and \( J_{\text{eff}} = 3/2 \) character. Since \( \text{Ir}^{4+}(5d^5) \) ions provide five 5d-electrons to bonding states, four of them fill the lower \( J_{\text{eff}} = 3/2 \) bands, and one electron partially fills the \( J_{\text{eff}} = 1/2 \) band where the Fermi level \( E_F \) resides. The SOI yields a \( J_{\text{eff}} = 1/2 \) band that is so narrow that even a reduced \( U \) (\( \sim 0.5 \text{ eV} \)) operating within the extended 5d-electron orbitals is sufficient to open a gap \( \Delta \) that stabilizes an insulating state in the iridates.

Figure 1.3: Graphical representation for 5d electron energy: (a) wide \( t_{2g} \) band without SOI and U, (b) wide \( t_{2g} \) band without SOI but unrealistically large U opening the gap, (c) with SOI but no U, (d) with both SOI and U resulting in \( J_{\text{eff}} = \frac{1}{2} \) insulating state, (e) 5d electron splitting by SOI and crystal field [7].
1.4 Sr$_2$IrO$_4$

1.4.1 Underlying observations

Sr$_2$IrO$_4$ is a single-layer member of the Ruddlesden-Popper series Sr$_{n+1}$Ir$_n$O$_{3n+1}$, where n is the number of Ir-O layers in unit cell. It crystallizes as a reduced tetragonal structure (space-group I4$_1$/acd) due to rotation of the IrO$_6$ octahedra by about 11° about the c-axis, also confirmed by neutron study of Sr$_2$IrO$_4$ [9-11, 21]. This crystal structure is similar to those of two known superconductors Sr$_2$RuO$_4$ and La$_2$CuO$_4$, drawing even more attention to a single-layer iridate. As mentioned earlier, most 5d electron based compounds, notably Sr$_2$IrO$_4$ and Sr$_3$Ir$_2$O$_7$ tend to order at high temperatures, and the former is a weak ferromagnet, ordering with a Curie temperature of T$_c$ = 240 K. Besides the ordering temperature at 240 K, we can observe in Figure 1.4 the additional two anomalies: one at T$_{M1}$ ≈ 100 K and the other at T$_{M2}$ ≈ 25 K, noticeable in both M$_a$ and M$_c$ measurements. Two anomalies have also been observed in our ac susceptibility data, which shows a frequency dependent peak at ~100K that could indicate magnetic frustration [9-11, 22-25]. We indeed see a decrease in magnetic anisotropy with the weakening of the signal in temperature dependence along the M$_a$ direction and enhancement of the M$_c$ signal, which indicates a changing magnetic structure below transition temperature.

Figure 1.4: Sr$_2$IrO$_4$ temperature dependence of: (a) the magnetization (left scale) and Curie-Weiss fitting (right scale), (b) the a- and c- axis resistivity
Although, as we will see in next section, that Sr$_2$IrO$_4$ can be easily driven to a metallic state by chemical doping, the pure compound electrical transport data shows a very insulating state for the whole temperature range from 1.7 K - 600 K. There are three distinct temperature regions closely following the regions bounded by transition temperatures in magnetic susceptibility data. When fitted to the activation law

$$\rho(T) \sim e^{\frac{\Delta}{2k_B T}}$$

(1.2)

each region energy gap is as follows:

- a) region I: 19 K < T < 26 K gives energy gap $\Delta = 18.4$ meV
- b) region II: 26 K < T < 85 K gives energy gap $\Delta = 45.2$ meV
- c) region III: 85 K < T < 350K gives energy gap $\Delta = 107.2$ meV

where the region III value of $\Delta = 107.2$ meV closely resembles the value measured optically 0.1 eV [7].

### 1.4.2 Chemical doping

Sr$_2$IrO$_4$, as mentioned above, crystallizes as a tetragonal structure with IrO$_6$ octahedra that rotate about the c-axis, resulting in a larger unit cell volume by a factor of $\sqrt{2} \times \sqrt{2} \times 2$. There is a distortion of the in-plane Ir1-O2-Ir1 bond angle $\theta$, which is very sensitive and critical for electron hopping, as slight changes to the bond angle can drive the very insulating Sr$_2$IrO$_4$ into a metallic state. One of the methods to alter the lattice distortion and bond angle is by chemical doping. Two very prominent examples are light doping with K$^+$ and La$^{3+}$ for Sr$^{2+}$ at the A site. Besides the obvious doping with electrons and holes during this substitution, there are also significant differences in ionic size, which causes substantial changes in lattice parameters as K$^+$ has an ionic radius of 1.38 Å, La$^{3+}$ is 1.03 Å and Sr$^{2+}$ is 1.18 Å. Changes in the bond angle as the doping level is increased can be seen in Figure 1.5.

![Figure 1.5: Phase diagram of Ir-O-Ir bond angle $\theta$ as function of La and K doping concentration in (Sr$_{1-x}$A$_x$)$_2$IrO$_4$ [24]](image-url)
These changes in lattice parameters are directly reflected in electronic properties, where resistivity drops by a factor of $10^{-8}$ for La$^{3+}$, and $10^{-10}$ for K$^+$ as the doping level is increased to 4 and 2% respectively as shown in Figure 1.6. As the La$^{3+}$ concentration is increased, the magnetic transition temperature decreases and fully vanishes while at the same time the metallic state is realized at 4%. However, the K$^+$ doped sample although it reaches a metallic state at $x = 0.02$, the magnetically ordered state still persists at the same time (see Figure 1.6c) [24,26]. As we have seen in the parent compound, the magnetic transition temperature $T_C = 240$ K does not show any anomaly in the electronic properties in this temperature region [27], which indicates that there is no strong correlation between the electronic and magnetic properties, as anticipated. Similarly, decoupling between magnetic and transport properties is observed in (Sr$_{0.98}$K$_{0.02}$)$_2$IrO$_4$, where the metallic state is not accompanied by changes in magnetic state initiating more in depth look at the dependence of charge gap formation on magnetic interaction [28-29]. In the inset of Figure 1.6b there is an apparent drop below 10 K in resistivity which could imply sharp decrease in inelastic scattering below this temperature.

![Figure 1.6: The a-axis resistivity $\rho_a$ (a) and (b) the c-axis resistivity $\rho_c$ for (Sr$_{1-x}$La$_x$)$_2$IrO$_4$, (c) the a-axis resistivity $\rho_a$ and magnetization $M_a$ for (Sr$_{1-x}$K$_x$)$_2$IrO$_4$ [24]](image)
Unlike the tuning of lattice parameters and electron/hole doping we examined in the case of \((\text{Sr}_{1-x}\text{A}_x)\text{IrO}_4\) with \(\text{A} = \text{K}, \text{La}\), we have also attempted to study the effect that the strength of SOI has on physical properties. To study this effect of altered strength of SOI, on the Ir site we have doped \(\text{Rh}^{4+} (4d^5)\), and for comparison \(\text{Ru}^{4+} (4d^4)\), which both have reduced SOI with the pure \(\text{Sr}_2\text{RhO}_4\), which is a paramagnetic correlated metal with SOI of about \(0.16 \text{ eV} [31]\). Since it is well known that \(\text{Sr}_2\text{RuO}_4\) is a p-wave superconductor, we can see that the effect of strength of SOI is dependent on the electronic structure, lattice distortion, and Coulomb interaction. \(\text{Sr}_2\text{RhO}_4\) is both electronically and structurally analogous to \(\text{Sr}_2\text{IrO}_4\), including the rotation of the \(\text{RhO}_6\)-octahedra about the \(c\)-axis but with smaller rotation of \(\sim 9.7^\circ\) compared to \(11^\circ\) for \(\text{Sr}_2\text{IrO}_4\). Since the ionic radius is significantly smaller for \(\text{Rh}^{4+} (0.600 \text{ Å})\) compared to \(0.625 \text{ Å}\) for \(\text{Ir}^{4+}\), it is no surprise that in Figure 1.7 we observe systematic changes in lattice parameters as the concentration changes in \(\text{Sr}_2\text{Ir}_{1-x}\text{Rh}_x\text{O}_4\) where \((0 \leq x \leq 1)\).

**Figure 1.7:** Lattice parameter changes as function of Rh concentration in \(\text{Sr}_2\text{Ir}_{1-x}\text{Rh}_x\text{O}_4\): (a) \(a\)- and \(c\)-axis, (b) unit cell volume and Ir/Rh-O-Ir/Rh angle [34]

Although SOI is reduced as the Rh concentration is increased, no significant change in band filling is to be expected because the reduced SOI only reduces the band splitting, while the Fermi energy still lies between the \(J_{\text{eff}} = \frac{1}{2}\) and \(J_{\text{eff}} = 3/2\) bands, and as result of disorder, easily leads to electron scattering [30-33]. Similar behavior is expected from \(\text{Sr}_2\text{Ir}_{1-x}\text{Ru}_x\text{O}_4\), however, unlike the Rh doping, instead of five 4d electrons Ru provides only four 4d electrons, resulting in additional hole doping into the \(t_{2g}\) band as well as a reduction in SOI. This hole doping shifts the Fermi energy within the now reduced splitting between
$J_{\text{eff}} = \frac{1}{2}$ and $\text{Jeff} = 3/2$ bands, placing the Fermi energy just inside the lower band and easily driving the system into a metallic state \cite{34-35}. The density of states is increased at the Fermi energy and the scattering due to disorder has no significant consequence. Now, while the Ru doped system can easily be driven into a robust metallic state, Rh substitution features three distinct regions differing by Rh concentration in $\text{Sr}_2\text{Ir}_{1-x}\text{Rh}_x\text{O}_4$:

Region I: $0 \leq x \leq 0.24$ features reduction in resistivity by six orders of magnitude and even exhibits a metallic state above 50 K in a-axis resistivity. While the c-axis is reduced, it still demonstrates insulating behavior over the whole temperature range. In this range the magnetic order is reduced, and fully vanishes at $x = 0.16$.

Region II: $0.24 \leq x \leq 0.85$ unexpectedly exhibits an increase in insulating state as the magnitude rises up to $10^7 \Omega \text{cm}$ until it drops again at $x = 0.75$. In the temperature range between 2 K and 100 K, data can be fitted to the variable range hopping (VRH) model which describes low temperature conductivity in strongly disordered systems where $\rho \sim \exp\left(\frac{1}{T}\right)^{1/2}$, indicating presence of Anderson localization due to disorder.

Region III: $0.85 \leq x \leq 1$ close to $x=1$ we observe the metallic state.

Figure 1.8 presents the phase diagram of the $\text{Sr}_2\text{Ir}_{1-x}\text{Rh}_x\text{O}_4$ as a function of Rh concentration $x$, and its variation with temperature based on the results briefly discussed above. Rh doping effectively reduces SOI and enhances Hund’s rule coupling, which in turn competes with SOI. Although, the decrease in SOI brings on the decrease in resistivity and the vanishing of the magnetic transition temperature at $x = 16 \%$, continued increase in Rh results in disorder on the Ir/Rh site and the mismatch between the energies of the Ir and Rh site in the octahedron impedes the hopping of the electrons between the two.
1.4.3 Remarkable effect of Tb doping: $\text{Sr}_2\text{Ir}_{1-x}\text{Tb}_x\text{O}_4$

In our interest to study the effect of reduction of SOI on tetravalent $\text{Sr}_2\text{IrO}_4$, as well as the interaction between 4f and 5d electrons we have comprehensively studied the single crystals of $\text{Sr}_2\text{Ir}_{1-x}\text{Tb}_x\text{O}_4$ ($0 \leq x \leq 0.03$). Our initial anticipation was for tetravalent Tb$^{4+}$ ($4f^7$) to occupy the $\text{Sr}^{2+}$ site, however extended measurements using X-ray absorption spectra have proved that the Tb instead occupies the Ir$^{4+}$ site and reduces SOI and tetragonal crystal electric field while enhancing Hund’s rule coupling. Although, it is no surprise that the slight doping of just 3% of Tb has already succeeded in full suppression of magnetic order, since this was already observed at 4% La$^{3+}$ doping. What is unlikely is the persistent insulating state that seems to be decoupled from the antiferromagnetic order, and is unaffected by full AFM state suppression. One potential reason for preventing the metallic state from forming might be due to mismatch in energy levels between Ir and Tb ions. However, as described later in Chapter 4, that in addition to this decoupling of AFM order and the insulating state is the new spiral incommensurate magnetic order at just 3%, which is supported both by neutron measurements as well as by the large specific heat at low temperatures. More generally, this behavior manifests once again an unusual correlation between the magnetic and insulating states in the iridates.

1.5 Breakdown of $J_{\text{eff}} = 0$ singlet ground state

The properties of iridates have been driven by the distinctive combination of strong SOI, electron correlation, and crystal electric fields. This interplay of very comparable interaction energies has led to exotic complex magnetic states, and as a result, was the basis for the origination of $J_{\text{eff}} = ½$ Mott insulating state model which successfully described properties seen in most of the iridates thus far. Even though most of the studies were done on tetravalent Ir$^{4+}$ ion based compounds, the few pentavalent compounds, such as nonmagnetic NaIrO$_3$, also satisfied this model as the four 5d electrons available in pentavalent ion, in a strong SOI regime, would fill the lower band resulting in a $J_{\text{eff}} = 0$ singlet ground state. Recent work has shown that magnetic states in pentavalent Ir can arise due to competition between noncubic crystal fields, SOI, singlet-triplet splitting and exchange interactions [36-37]. However, as we will see in more detail in Chapter 4, our own study of double perovskite iridates, encompassing pentavalent Ir ions $\text{Sr}_2\text{YIrO}_6$ and ($\text{Ba}_{1-x}\text{Sr}_x$)$_2\text{YIrO}_6$, both of which show exotic magnetic states at low temperatures indicate breakdown of the $J_{\text{eff}} = 0$ singlet ground state. The $\text{Sr}_2\text{YIrO}_6$ magnetic state below 1.3 K was attributed to the non-cubic crystal field due to strong distortion in the crystal structure which was not accounted for in the initial $J_{\text{eff}} = ½$ Mott state model. Nevertheless since we studied cubic ($\text{Ba}_{1-x}\text{Sr}_x$)$_2\text{YIrO}_6$, which also orders magnetically, we suspected other possible origins to the magnetic moment in the pentavalent Ir systems: (1) possibility of overlap between the $J_{\text{eff}} = ½$ and $J_{\text{eff}} = 3/2$ bands due to increased electron hopping, (2) independent electron picture for SOI, electron hopping and crystal fields and (3) band structure effects where $e_g$ orbitals play no role, resulting in breakdown of the $J_{\text{eff}} = 0$ state in cubic $\text{Ba}_2\text{YIrO}_6$. More details and discussion on this will be presented in Chapter 4.
1.6 Wide gap between experimental observation and theoretical proposals

Since the first discovery of iridates and the first observation of their unconventional properties, there has been extended theoretical work predicting possible exotic phases, of which most are yet to be experimentally realized. Due to competition between SOI and electronic correlations, many interesting properties are to be expected, including phases with unusual topological properties and exotic surface states, unconventionally magnetically ordered states and quantum spin liquids [38-44]. In addition, in layered cuprates charge doping to Mott insulators has induced high-temperature superconducting states, and theoretical predictions have already been made that similar high-temperature superconductivity could be realized in doped Sr$_2$IrO$_4$ or other iridates [45-47]. However, even though there has been successful doping to Sr$_2$IrO$_4$ and the system has been driven to metallic state, no superconducting state has yet been realized. Charge doping, both La and K into polycrystalline Ba$_2$IrO$_4$, in attempts to achieve superconductivity has also been unsuccessful. However, a semi-metallic state at above 15% La and K doping has been observed, as well as a pressure induced metallic state down to 4.2 K [48], while pressure even as high as 55 GPa has failed to induce any metallic state in Sr$_2$IrO$_4$ [49-51].

Additionally, complex magnetic behavior can be observed due to the combined effects of SOI and crystal-field stabilizing spin-orbit entangled magnetic moments, like those for Ir$^{4+}$ ions at the center of IrO$_6$ octahedra. These have been theoretically proposed to interact via strong-anisotropic exchange interaction, leading to large frustration effects forming new magnetic states, such as the quantum spin liquid, which led to extended experimental study of Na$_2$IrO$_3$ and Li$_2$IrO$_3$ as a potential candidates for the Kitaev model [52-54]. The study of Dirac fermions has led to new research areas such as Weyl semi-metals and topological insulators. Since these require strong SOI for stability, there have been extended questions as to whether they could be observed in iridates or other electron-correlated materials. Of these, two have already been proposed as potential candidates as topological insulator Sr$_2$IrRhO$_6$ [55] and pyrochlore iridates as Weyl semi-metals [56]. However, most of the proposed candidate physical properties have yet to confirm theoretical predictions as direct observation of the proposals hasn’t been realized yet. The gap between experimental results and theoretical prediction has yet to be overcome.
Chapter 2. EXPERIMENTAL METHODS

2.1 Single crystal synthesis

Single crystals are arrays of a well-defined chemical motif that are periodic in three dimensions. Although their growth is generally much more difficult and time consuming than for poly-crystalline materials, there are many advantages - from uniformity in composition and anisotropy present in single crystals to the absence of grain boundaries which are obviously present in poly-crystalline samples. Besides these advantages in terms of physical properties measurement, high-quality single crystals are a must in many technological applications. There are various methods for single crystal growth, each with its own advantages for growth of certain type of materials. Some of the methods we used to grow single crystals are:

a) Growth from solution (flux method)
b) Growth from the liquid phase (floating zone method, Bridgman, etc.) and
c) Growth from gas phase (chemical vapor deposition, pulsed laser deposition, etc.).

All three of these methods are different in their own way and produce single crystals of various sizes. Figure 2.1 shows some of the single crystals grown by flux method. The spatial extent for these single crystals is in millimeter range while for poly-crystalline samples, individual grain size tends to be in the micrometer range.

![Flux grown single crystals: (a) Sr$_2$IrO$_4$ and (b) Ba$_5$AlIr$_2$O$_{11}$](image)

Figure 2.1: Flux grown single crystals: (a) Sr$_2$IrO$_4$ and (b) Ba$_5$AlIr$_2$O$_{11}$

2.1.1. Flux method for single crystal growth

The flux method is solution growth at very high temperatures, close to and above 2000° C, hence it is suitable for growth of congruently as well as incongruently melting materials. Due to the high growth temperature, crucibles are chosen that can withstand high temperatures, have low reactivity with most fluxes and are highly resistive to most chemical attacks. Most commonly used crucibles for the flux method are high alumina ($99.8\%$ Al$_2$O$_3$) or platinum crucibles. The method for flux growth entails heating of the crucible containing flux mixed with solute to high enough temperature until all the solute materials have fully dissolved. Materials are held at this final temperature for several hours and then very slowly cooled down to room temperature. Single crystals grown by this method tend to be small in size but have very few impurities. Most issues arising from growth using the flux method is related to flux becoming embedded inside the crystals or
due to difficulty retrieving or separating grown single crystals from the flux. In order to prevent or remedy these obstacles, selection of proper flux choice is crucial. Besides the low melting temperature, the chosen flux should not form stable compounds with the solute and should be easily separated from the single crystals. The two most important advantages are that the range of materials that can be grown via the flux method is very large and flux grown crystals tend to show natural surfaces. Examples of single crystals studied in this work, Sr$_2$IrO$_4$ and Ba$_5$AlIr$_2$O$_{11}$, are shown in Figure 2.1. The method for growth of each of these materials are explained below:

Sr$_2$Ir$_{1-x}$Tb$_x$O$_4$ - single crystals were grown from non-stoichiometric quantities of SrCl$_2$, SrCO$_3$, IrO$_2$ and Tb$_2$O$_7$ using a self-flux variation of the technique. The constituents in powder form were ground together and placed in a platinum crucible in preparation for single crystal growth. The mixture was heated to 1470° C, to melt all the material, and it was maintained at the same temperature for over 20 hours. It was then cooled down to 1400° C at the rate of 2° C/hr and then cooled quickly to room temperature.

(Ba$_{1-x}$Sr$_x$)$_2$YIrO$_6$ - single crystals were grown using the self-flux technique from non-stoichiometric quantities of IrO$_2$, BaCO$_3$ and SrCO$_3$, and Y$_2$O$_3$. The mixture of powdered constituents was heated up to 1440° C, where it was maintained for five hours and then slowly cooled down at 2° C/hr. Typical single crystals were approximately 1.0 x 1.0 x 0.5 mm$^3$.

2.1.2 Floating zone method for single crystal growth

![A diagram showing optical floating zone furnace operation](image-url)
The floating zone method is another frequently used technique in our laboratory, using an NEC two-mirror model SCII-MDH-11020 floating-zone optical furnace. One of the most beneficial aspects of this method is successful growth of very large single crystals, as well as the exceptional purity of single crystals grown. The growth technique involves:

(1) Initial preparation of several grams of polycrystalline material that we intend to grow in single crystal form. Stoichiometric amounts of the main constituents for the growth of desired compound are mixed and ground in powder form. The mixture is then placed into an alumina crucible and sintered to produce the polycrystalline form of the single crystal we intend to grow. At this point, most often methods like powder x-ray diffraction are used to ensure that the correct phase, free of impurities, has been produced.

(2) This polycrystalline powder is then pressed into a long rod using commercial latex balloons and sintered into a long rod, whose uniform density, shape and thickness are crucial for successful single crystal growth. The sintered rod, averaging about 7-8 cm in length is then cut into two parts. The longer part is hung on the upper shaft of the furnace (feed) and shorter one (seed) is attached to the bottom shaft (see Figure 2.2)

(3) A small uniform molten zone is maintained by surface tension between the feed material and the seed. The feed material rod is lowered at a very slow rate into the molten zone while both upper and lower shaft are slowly lowered out of the zone to facilitate cooling and single-crystal growth. Stability of the molten zone is critical to maintain uniform phase growth, limit defects, and suppress twinning in the crystal.

Figure 2.3: Floating zone furnace during operation
The growth atmosphere within the FZ furnace can be adjusted from vacuum to inert or to oxygen-rich to provide environmental control necessary for the materials to grow. One downside of the floating zone method is that for materials that have high vapor pressure it can be difficult to control loss of the material as high temperature is approached. One way to remedy this is to add excess material to compensate for the loss during growth, since the pressure that we can apply only reaches 0.97 MPa and this is often not enough to control the loss of high vapor materials. The most beneficial feature of the FZ method is that any impurity will prefer to stay in the molten zone, and will be pushed to the end of the feed material resulting in highly pure single crystals. There are several variables that can influence the quality of the grown single crystals besides the quality of the rod, which is often most critical parameter. Some of the others are (1) the rate at which the material is crystallized, as slow rates tend to yield large single crystals, but are not always favorable in the case of materials with high vapor pressure constituents (vide supra), (2) large temperature gradients that lead to cracks due to thermal stress and (3) rotation and the temperature of the molten zone. While rotation is necessary for uniform mixing, it can cause cracking if not well controlled; and although the temperature in the molten zone needs to be high enough to ensure full melting of the rod in the zone, if too high, it can cause cavitation in the zone and frequent discontinuities due to liquid material loss and bubbling, which causes deformities in the single crystals.

2.2 Materials structural characterization

2.2.1 Powder X-ray diffraction

In order to have a more comprehensive understanding of synthesis, structure and properties of materials it is important to know the arrangement of atoms inside the crystal structure of a material. There are many different methods that deliver structural information over varying distance scales, but the most comprehensive and detailed information is provided by methods which involve diffraction. In a diffraction experiment, an incident wave is directed onto the material while a detector collects sufficient diffraction maxima to either solve the structure or to act as a fingerprint via pattern matching. Since a diffraction pattern represents the range of periodicities in the material, at low angles we are able to observe diffraction peaks corresponding to long range periodic arrangement of atoms, while short-range periodic arrangement is observed at high angles. The incident wave in a diffraction experiment must have a wavelength comparable to spacing between atoms, i.e., of the order of an ångström. Crystals that have unambiguous and precise atomic arrangements give sharp diffraction peaks. In addition to X-ray diffraction, there are also electron and neutron diffraction, which operate by different physical mechanisms, however, they all have one common requirement, and that is the fulfilment of the Bragg’s law:

\[ 2dsin(\theta) = n\lambda \]  \hspace{1cm} (2.1)
In order to briefly describe derivation of Bragg’s law and to derive the conditions necessary to observe interference of waves scattered by the two planes as shown in Figure 2.4 it is instructive to look at the geometric construction of a simple structure consisting of two atomic planes separated by distance \( d \).

![Diagram of Bragg's law](image)

As we can see from the image above, the incident angle for both parallel rays is \( \theta \), and the plane separation \( d \) determines the difference in path length between the two scattered rays. This path difference equals \( 2d \sin \theta \), corresponding to the left hand side of the Bragg’s law, and to observe constructive interference this path difference needs to be equal to \( n\lambda \), where \( n \) is an integer. Most of the diffraction patterns contain numerous diffraction peaks with different peaks corresponding to different inter-planar spacing, \( d \).

In cases where powder polycrystalline samples are measured, there are randomly oriented crystals in large quantities in the sample, so all Bragg peaks are observed. From the diffraction peaks and angle \( \theta \) we could determine the inter-planar spacing for each diffraction peak. Some of the more simple equations for the lattice parameters are presented below, corresponding to cubic, orthorhombic, and tetragonal crystal systems:

\[
\frac{1}{d^2} = \frac{h^2 + k^2 + l^2}{a^2} \quad \text{(Cubic crystal system)}
\]

\[
\frac{1}{d^2} = \frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2} \quad \text{(Orthorhombic crystal system)}
\]

\[
\frac{1}{d^2} = \frac{h^2 + k^2}{a^2} + \frac{l^2}{c^2} \quad \text{(Tetragonal crystal system)}
\]
Even though determining lattice parameters for some crystals could be done by hand, most samples with large number of atoms, especially for lower symmetry, cannot. The easiest way to determine the majority or any impurity phase, is by comparing the obtained diffraction pattern to a database, which contains diffraction patterns for most crystalline materials made to date. One of the most common uses of powder X-ray diffraction method is for determining if there are any unknown crystals/phases within the sample. Discovering any additional peaks not corresponding to the known database pattern could indicate an impurity phase or additional crystals present in the material. One of the powder diffraction patterns from a polycrystalline Sr$_2$IrO$_4$ sample intended for use as a target in a pulsed laser deposition experiment is pictured below in Figure 2.5, with red lines indicating peaks from the database pattern.

![Powder diffraction pattern for Sr$_2$IrO$_4$](image)

Figure 2.5: Powder diffraction pattern for Sr$_2$IrO$_4$ obtained using Bruker D8 Advance Diffractometer

### 2.2.2 Single crystal X-ray diffraction

Although powder X-ray diffraction is frequently used in our laboratory, to get the most information from crystal and molecular structure, symmetry and packing, the use of single crystal x-ray diffraction is essential. For our single crystal structure determination we have used two different facilities, one at the University of Kentucky Chemistry Department X-
ray Facility, which has a Nonius Kappa CCD diffractometer with Mo Kα X-ray source and the Rigaku X-ray diffractometer equipped with a PILATUS 200 K hybrid-pixel-array detector at Oak Ridge National Laboratory.

In order to obtain enough information to solve the single-crystal structure several hundred to a few thousand images are obtained from various single crystal orientations. To be able to obtain all the images classical single crystal x-ray diffractometers used a four-circle goniometer. These four circles refer to four independent angles as seen in Figure 2.6 below. However, our single crystal x-ray diffraction measurements have been taken by the use of Kappa-type goniometer, where χ is replaced by κ which is coupled with Ω and φ in a three circle stage.

ϕ – angle of rotation about goniometer head axis
χ – angle of inclination of the φ axis
Ω – angle of rotation of single crystal with respect to principal axis of goniometer
2θ – the swing angle of the detector

Figure 2.6: Classical single crystal diffractometer four circle operational schematic

The data collection process collects large number of diffraction peak images, most commonly using a CCD camera as a detector to collect all symmetrically inequivalent diffraction peaks and their intensities. These peaks/diffraction spots carry contribution from the atoms in the original object so it is necessary to collect all unique diffraction spots out to sufficient resolution in order to complete structural refinement. Based on the intensity of the diffraction patterns, information about electron density can be obtained. Atom locations correspond to electron density maxima.

The process of single crystal structure determination involves selection of a single crystal of regular shape (most preferred spherical) and small in size about 50 - 150 μm to ensure
absorption of x-rays within the single crystal is minimized. Visual inspection of several images of the diffraction pattern is usually sufficient to determine the quality of the sample and the possible presence of twinning inside the crystal. If the single crystal is of high enough quality, a full data set is collected. The number of images and angular rotation necessary depends on the symmetry of the crystal. Initial structure solution is typically done using SHELXS, SHELXT (or some other program), or by comparison to a related known structure. The final structure model is refined by full-matrix least-squares using programs such as SHELX-97 [57].

2.2.3 Energy Dispersive X-ray Spectroscopy

Unlike powder and single-crystal X-ray diffraction, which mainly focus on structure determination, energy dispersive x-ray spectroscopy (EDX) centers more on elemental analysis of the material. In this work, a Hitachi/Oxford 3000 EDX instrument was used. The technique entails charged electrons or X-rays being directed at the sample with enough energy to excite one of the bound electrons. This leaves an empty hole, which is subsequently filled by an electron from a higher energy level. As the electron from the higher energy level fills the hole, the energy difference can be released in form of an X-ray [58]. An energy dispersive spectrometer can thus be used to determine the energy and the number of emitted X-rays, and since each element has its own characteristic set of peaks in electromagnetic atomic spectra, we can obtain information about the elemental composition of the sample. A schematic representation of the process is shown in Figure 2.7.

![Diagram of EDX process]

Moseley’s relation (Equation 2.2) is often used to relate the transitions (in the relation represented by constants B and C) to the atomic number Z and the wavelength of the
characteristic X-ray beam. The subscripts $\alpha$ and $\beta$ in the Figure 2.7 represent different families of transitions and the sample EDX spectrum is shown in Figure 2.8.

$$\lambda = \frac{B}{Z - C^2} \quad (2.2)$$

Figure 2.8: EDX spectrum of single crystal Sr$_2$Ir$_{1-x}$Rh$_x$O$_4$ discussed in this work

2.3 Magnetic property measurements

For most materials, the orbital angular momentum and its intrinsic spin are reflected in the temperature or field dependent magnetic signature. Certain materials, such as permanent magnets, can produce magnetic fields in the absence of external magnetic fields. Depending on the existence and alignment of magnetic moments with the applied external field, we can define three most commonly encountered types of magnetism: diamagnetism, paramagnetism, and ferromagnetism. Magnetic properties are a crucial component in the determination of the ground state of a material under study, and in addition to the other physical properties, they define the characteristics of a material.

Magnetization measurements performed in this work were taken using a Quantum Design MPMS-7T SQUID Magnetometer with a Helium-3 system, capable of reaching temperatures down to 0.44K. Some of the advantages of using the MPMS system are ease of temperature and magnet control, as well as the use of a unique superconducting SQUID amplifier system. The procedure for DC magnetization measurements includes sample mounting onto the quartz rod, which is located at the bottom of the measurement probe that is subsequently installed into the sample chamber. Upon proper loading, the sample is centered with respect to the pickup coils and is ready for measurements.

As the sample moves through the pickup coils, the SQUID measures the change in flux and converts the flux directly to voltage (see Figure 2.9). For our measurements, a 7 Tesla superconducting magnet is used to magnetize the sample while the pickup coils detect the sample magnetic moment.
The illustration of the DC SQUID pickup coils in Figure 2.9 shows the set of four superconducting coils. One set of two (center) are wound clockwise, while the two single coils, one each at bottom and the top of the pickup coils, are both wound counterclockwise. The rationale behind the specific winding order is to cancel the contribution from the MPMS superconducting magnet or any other contribution not coming from the sample. As the sample is moved through the pickup coils, magnetization of the sample induces an electromotive force inside the pickup coils and the amplified signal is detected by the SQUID electronics. The high sensitivity of the pickup coils of $10^{-8}$ emu enables measurement of very small single crystals in the temperature range of 1.7 K to 400 K, with an added low temperature option (iHelium-3 system), which supports temperatures down to 0.44 K [59].

### 2.4 Transport properties measurements

The transition metal oxides (TMO) studied in this work (see introductory Chapter) cover a wide range of electrical transport properties from insulators to metals and superconductors, all of which have been observed in TMO. A Quantum Design MPMS-7T has been used for our transport measurements to enable characterization in high magnetic field, and in the range 1.7 K to 400 K, with the electrical resistivity measurement facilitated by a Linear Research 700 AC bridge and the combined 2400 Keithley Sourcemeter and 2182 Keithley Nanovoltmeter for DC current measurements. For high temperature measurement up to 900 K we have used a Displex closed cycle Helium cryostat by Advanced Research System again in combination with set of Keithley meters.

Electrical resistivity was measured using the four-probe method, which relative to the more common two-probe method has the advantage of eliminating contribution from contact and wire resistance. The method includes two current leads attached such that the current passes fully through the cross sectional area, thus ensuring the same current, $I$, through the sample. Then the two adjacent voltage leads can be applied to measure potential difference without the inclusion of the contact or wire resistance, as no current passes through these voltage leads. From the voltage drop measured and the input current, $I$, we can determine sample resistance via Ohm’s law.
$$R = \frac{V}{I} \quad (2.3)$$

However, in order to characterize how strongly a sample opposes the flow of electrons as its intrinsic bulk property, we need to calculate electrical resistivity using the sample dimensions via the relation for electrical resistivity defined by

$$\rho = R \frac{A}{l} \quad (2.4)$$

where $A$ is the cross sectional area of the sample, and $l$ distance between the two voltage probes.

For our measurements, gold wires of 0.001 inch diameter were used for contact probes, with the contacts made using two component epoxy H20E. The sample is then secured to the measurement probe in the desired direction relative to the magnetic field by using GE varnish.

This has been the standard procedure used for all our measurements, but with the addition of using a high temperature ceramic to secure the sample to the measurement probe in the case of high temperature measurements, as GE varnish cannot withstand such high temperatures.

### 2.5 Thermal properties measurements

Heat capacity measurements historically have not been so common because they were much more difficult to execute, and less reliable compared to electrical transport. However, these days heat capacity measurements are fairly common due to the advent of instruments such as the Quantum Design Physical Property Measurements Systems (PPMS), which offers dilution refrigerator options for measurement from 400 K down to 0.05 K in magnetic fields of up to 14 T. The benefits of heat capacity measurement range from the ability to extract information about the magnetic, electronic and lattice properties, as well as information about density of states and energy levels when measured at low temperatures [60].
The measurement procedure involves sample attachment to the sample platform using thermal conducting Apiezon grease: type H for high and type N for low-temperature measurements. Prior to sample measurement, an addenda is measured with just grease applied to the sample platform to assess heat capacity of the system without the sample, and this is later subtracted from the experimental signal to ensure that the final sample measurement does not include any contribution from the grease. The QD Heat Capacity option uses a relaxation technique to fit the response of a measurement cycle of heating followed by a cooling period to the model that accounts for thermal relaxation of sample platform, as well as the sample itself. The response can be fitted to two different models:

1. Simple model: this assumes that the sample and sample platform are in good contact and at the same temperature during measurement.

2. Two-tau model: this is used when the sample has poor contact with the sample platform, resulting in a temperature difference between the two. This model accounts for any difference by simulating heat flow between the sample and sample platform, as well as sample platform and sample puck [60].

2.6 Dielectric measurements

A material is categorized as dielectric if the material has a propensity to store energy when an external electric field is applied. For example, if a DC voltage source is placed across a parallel plate capacitor, more charge is stored when a dielectric is placed between the plates compared to a capacitor with vacuum between the plates [61]. The relation between capacitance and dielectric constant is

$$C = \frac{\kappa \varepsilon_0 A}{d} \quad (2.5)$$
where $C$ is capacitance, $A$ is the area of the plates, $d$ distance between the plates and $\kappa$ dielectric constant ($\varepsilon_0$ is the permittivity of free space). Since in an ideal capacitor the area of the plates is significantly larger than the plate separation, most of our measurements have been done on either cleaved or polished single crystals, so as to ensure small $d$. In addition, to ensure no gap between the sample and the plates, we used silver paint to cover the plates, and gold wire to connect the plate to the electrodes. Measurements were done using a QuadTech 7600 LCR meter with frequency range of 10 Hz to 2 MHz and temperature from room temperature down to 5 K in a PPMS 9T sample chamber. There are several mechanisms that can contribute to dielectric response, each having a certain cutoff frequency:

(1) Dipole orientation and ionic conduction, which interact strongly at microwave frequencies
(2) and atomic and electronic mechanisms, which are relatively weaker, all shown in Figure 2.11.

![Figure 2.11: Frequency response of dielectric mechanisms](image)

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CHAPTER 3. THEORETICAL METHODS

3.1 Crystal Electric Field Environment

Crystal field theory is a model that describes how transition metal ions with $d^n$ configuration are perturbed by their environment. We already know that $s$ orbitals have spherical distribution, but $p$ and $d$ orbitals have angular dependence, as shown in Figure 3.1 for $d$-orbitals.

![Angular dependence of d-orbitals](image)

Figure 3.1: Angular dependence of d-orbitals

As we can see in the image above, the $t_{2g}$ orbitals are directed between the $x$, $y$, and $z$ axes while the $e_g$ orbitals are directed along those axes. When the metal ion is found in vacuum, although the spatial distribution of the five orbitals are different, their energies are all same (i.e., they are degenerate). However, this is not the case when the metal ion is found in an octahedral environment. In such a case, the energies are split due to the so-called 'crystal field', which results in $e_g$ orbitals having higher energy and $t_{2g}$ orbitals being lower in energy. The reason for the splitting in energy is that the higher energy orbitals are those that directly face near-neighbor ligands while the lower energy orbitals have nodal planes in the direction of near-neighbor ligands, which partially splits the degeneracy of the $5d$ orbitals. Initially the crystal field model relied on a purely ionic model, which assumed that the energy splitting was caused by electrostatic perturbation of transition metal ion by the surrounding anions. However, this approach has been abandoned as a result of ab initio calculations of crystal field splitting that have shown that the splitting can be interpreted in terms of orbital overlap [62]. The amount of crystal field splitting $\Delta$ is dependent on the type of metal ion, the octahedral complex, and the charge on the metal ion. Figure 3.2 shows the splitting of the degenerate $d$-orbital energies.
Consequently, the arrangement of electrons is governed by the strength of the crystal field splitting relative to exchange interactions, which results in either high- or low-spin configurations being observed. A high-spin configuration involves filling of orbitals by single electrons, which results in parallel spins in cases where exchange interaction is strong, while the low-spin configuration favors the strong crystal field splitting regime and results in filling of low energy orbitals starting from $t_{2g}$ orbitals with double electrons before populating higher energy orbitals reducing overall spin [62].

3.2 Spin Orbit Coupling

Spin-orbit coupling is the interaction between electron spin and the orbital angular momentum, and results in a shift of electronic energy levels in an atom or solid. For a general potential $V(r)$, spin orbit coupling is given by

$$\hat{\mathcal{H}} = \frac{1}{2m^2c^2r} \left( \frac{\partial V}{\partial r} \right) \mathbf{L} \cdot \mathbf{S}$$  \hspace{1cm} (3.1)

and for the case of a hydrogen-like atom potential, the new Hamiltonian is

$$V(r) = -\frac{1}{4\pi \epsilon_0} \frac{Ze^2}{r}$$  \hspace{1cm} (3.2)

$$\hat{\mathcal{H}} = \frac{1}{2m^2c^2} \frac{1}{4\pi \epsilon_0} \frac{Ze^2}{r^3} \mathbf{L} \cdot \mathbf{S}$$  \hspace{1cm} (3.3)

Here, the Hamiltonian no longer commutes with $\mathbf{L}$ and $\mathbf{S}$ as they are no longer conserved on their own when spin-orbit coupling is present. In this case, states that do commute with the Hamiltonian are $\mathbf{L}^2$, $\mathbf{S}^2$, $\mathbf{J} = \mathbf{L} + \mathbf{S}$ and $\mathbf{J}^2$. In the new basis, $\mathbf{L} \cdot \mathbf{S}$ is diagonal, i.e.

$$\mathbf{L} \cdot \mathbf{S} = \frac{1}{2} (J^2 - \mathbf{L}^2 - \mathbf{S}^2) = \frac{1}{2} (j(j+1) - l(l+1) - s(s+1))$$  \hspace{1cm} (3.4)
where the right hand side gives the eigenvalues of $L \cdot S$. Since spin-orbit interaction is represented by $\lambda \, L \cdot S$, the estimate of the expected value for spin orbit interaction and $1/r^3$ term are

$$\langle \lambda L \cdot S \rangle = \frac{\lambda}{2} \left( j(j + 1) - l(l + 1) - s(s + 1) \right)$$  \hspace{1cm} (3.5)$$

$$\left\langle \frac{1}{r^3} \right\rangle = \frac{Z^3}{n^3 a^3 l(l + 1)(l + 1/2)}$$ \hspace{1cm} (3.6)$$

Combining the two terms we find

$$\langle \hat{H}_{SO} \rangle = \frac{Z^4 e^2}{8\pi \epsilon_0 m^2 c^2} \left[ \frac{2(j(j + 1) - l(l + 1) - s(s + 1))}{2(j(j + 1) - l(l + 1) - s(s + 1))} \right]$$ \hspace{1cm} (3.7)$$

As discussed in Chapter 1, spin-orbit interaction has significant consequences for materials with large atomic number $Z$, which from Equation 3.7 we see is proportional to $Z^4$. For 5d transition metal oxides, the value of SOI is 0.3 - 0.4 eV, which is comparable to Coulomb interaction, and leads to new $J_{\text{eff}} = \frac{1}{2}$ Mott state in Sr$_2$IrO$_4$.

### 3.3 Hund’s rule

Formulated by Friedrich Hund around 1927, Hund’s rules govern the electron filling of degenerate electronic orbitals to represent the ground state of a multi-electron atom. When obeyed, the electron configuration best agrees with quantum mechanical calculations. Such a configuration results in the least electron repulsion since each electron in degenerate orbitals has the same unpaired spin but is forbidden to occupy any other of the degenerate orbitals [63]. The reason for this forbidden occupation of the other degenerate orbitals is governed by the Pauli Exclusion Principle, which states that no two electrons having the same set of quantum numbers: $n$ (principle quantum number), $l$ (orbital quantum number), $m_l$ (orbital magnetic quantum number) and $m_s$ (spin magnetic quantum number) can occupy the same orbital. Thus a maximum of two paired electrons can occupy an orbital, with requirement that one electron has $m_s = +1/2$ and the other $m_s = -1/2$. Note that the two electrons are assigned opposite spins of magnitude 1/2. The set of guidelines called Hund’s rules are summarized below:

1. For the partially filled shell, one way that $n$ electrons can be arranged into $2(2l+1)$ levels, is to have the lowest lying energy levels be those with highest
spin \( S \), which translates into highest value \( S_z \) can have. If \( n \leq 2l + 1 \), \( S \) is equal to \( n/2 \) where if \( n = 2l + 1 \), the maximum value of \( S \) becomes \( l + \frac{1}{2} \).

(2) Total orbital angular momentum \( L \) has largest value for the lowest lying states, and to find that value similarly to the First rule, it is the maximum value \( L_z \) can have. For shells that are less than half filled, \( L = l + (l - 1) + \ldots + (l - (n - 1)) \), and for the exact half-filled shell \( L = 0 \).

(3) For the atoms with outermost shell less than half filled, the lowest energy is that with the lowest total orbital angular momentum, \( J = |L - S| \), while a more than half-filled shell has lowest energy level with highest value of \( J = L + S \).

The spin-orbit interaction, represented by \( \lambda(L \cdot S) \) can lift the degeneracy of the \((2L+1)(2S+1)\) states and prefers maximum \( J \) for negative \( \lambda \) (shells more than half filled) and minimum \( J \) for positive \( \lambda \) (shells less than half filled). This leads to:

\[
\begin{align*}
J &= |L - S| & \text{for} & \quad n \leq (2l + 1) \\
J &= L + S & \text{for} & \quad n \geq (2l + 1) [63].
\end{align*}
\]

3.4 The Jahn-Teller Effect

Named after Hermann Arthur Jahn and Edward Teller, the Jahn-Teller theorem states that any nonlinear molecule with a spatially degenerate electronic ground state that cannot be stable will undergo a geometrical distortion to remove the degeneracy, and thereby lower the symmetry and energy of the system [64]. Even when not under the influence of Jahn-Teller effects, very rarely are perfectly regular octahedral sites found in crystal. Most commonly they are found with somewhat reduced symmetry. There are specific electron configurations, like \( d^4 \) high spin configuration that prefer a distorted environment. Two of the common configurations that prefer distorted environments, \( d^4 \) and \( d^9 \), and this could be due to uneven occupation of \( e_g \) orbitals, tend to give tetragonal distortion with two lengthened metal - ligand bonds [62].
Uneven occupation of $e_g$ orbitals, i.e., neither half nor full orbitals, leads to further splitting, shown in Figure 3.3, in order for a stable state to be achieved. Although it is expected that Jahn-Teller theory should also satisfy the symmetry lowering for the uneven filled $t_{2g}$ orbitals as well, in practice, the stabilization energy is too low to compete with the spin-orbit interaction, and is often an order of magnitude weaker than the crystal field effect [62].

3.5 Exchange Interactions

Exchange interaction most often depends on chemical bonding effects, such that if no interaction between magnetic moments is present, materials tend to be diamagnetic or paramagnetic. However, if there is an overlap of electrons combined with Pauli’s exclusion principle, magnetic moments couple to one another and form magnetically ordered states, i.e., either ferromagnetically or antiferromagnetically aligned states. Application of Hund’s rule by itself is not always reliable in solids and molecules where the neighboring atom spins may prefer either parallel or antiparallel alignment.

3.5.1 Direct Exchange
For example [62], if we have two weakly interacting atoms with a single unpaired electron, the energy difference between $S = 0$ singlet and $S = 1$ triplet states of the combined system can be expressed as

$$\Delta E = 2K - 4St$$ \hspace{1cm} (3.8)

First term, $2K$, represents potential exchange that happens between two electrons in an atom in different orbitals, leading to Hund’s rules and high-spin ground states. The electron repulsion in the two states is due to the Pauli Exclusion Principle requirement for antisymmetric states in the case of electron interchange. Although the contribution is quite small when atoms are well separated, it is always ferromagnetic. The second term is a kinetic exchange term, $4St$, which depends on $S$, i.e., the overlap integral of the two orbitals and the hopping integral, $t$, which represents the effective interaction between neighboring atoms that determine band width. Since these overlapping orbitals are more stable for antiparallel arrangements, the kinetic exchange term is antiferromagnetic, and depends directly on chemical bonding. There are two circumstances. If the orbitals on different magnetic ions are orthogonal, only the potential exchange term contributes and ferromagnetic order is expected. On the other hand, if there is significant orbital overlap, the kinetic exchange term dominates and antiferromagnetic order is anticipated. The alternative, more commonly used term for this antiferromagnetic interaction is the Heisenberg exchange parameter

$$J = \frac{-2t^2}{U}$$ \hspace{1cm} (3.9)

The Bethe-Slater curve gives the strength of the direct exchange interaction as a function of interatomic distances (Figure 3.4).

![Figure 3.4: The Bethe-Slater curve for direct exchange interaction](image)

3.5.2 Indirect Exchange

Indirect exchange is able to couple moments over significantly large distances by using conduction electrons as intermediaries in metals where there is dominant exchange, due to lack of overlap between neighboring electrons. This indirect exchange occurs because depending on the separation of the pair of ions, we could have either ferromagnetic
or antiferromagnetic coupling, and the indirect nature comes from the magnetic ion inducing spin polarization in conduction electrons in its neighborhood, which is felt by the surrounding magnetic ions that are in close proximity. Indirect exchange is often called RKKY exchange after Ruderman, Kittel, Kasuya, and Yoshida. The exchange integral is represented by

\[ J \propto \frac{\cos(2k_Fr)}{r^3} \]  

(3.10)

and has oscillatory dependence on the distance between magnetic ions.

![Coefficient of indirect exchange as function of interatomic distance](image)

Figure 3.5: The coefficient of indirect exchange as function of interatomic distance \( a \)

### 3.5.3 Superexchange

Another indirect exchange with large distances between atoms, but this time for insulating materials, is often called superexchange. It involves two metal ions that are separated by intervening non-magnetic anion. In case of the linear metal-oxygen-metal grouping, ground states can mix the two types of excited configurations if they are antiparallel, otherwise it would be prevented by the exclusion principle. In such a case, the Hubbard parameter \( J \) is altered due to not only being dependent on the Hubbard energy \( U \), but also by the charge transfer gap between the valence oxygen band and the empty d level, which takes the form

\[ J = -2t^2 \left[ \frac{1}{U} + \frac{1}{E_{CT}} \right] \]  

(3.11)

The charge transfer gap \( E_{CT} \) decreases as the nuclear charge in the metal increases. One consequence of which is that we see an increase in Néel temperature as we move down the series of MnO, FeO, CoO, … This occurs because as the gap is narrowed there is more covalent bonding between metal and oxygen, leading to larger overlap between the metal ions [62].
3.5.4 Double Exchange

In cases where a compound has multiple oxidation states present, double exchange can occur. Here, an electron from the $e_g$ level can hop to a neighboring atom if both are ferromagnetically aligned, otherwise in case of antiferromagnetic alignment Pauli Exclusion Principle would forbid such hopping from occurring. The ability to hop without having to change direction of spin (to obey the Hund’s rule) would lower the kinetic energy, as shown in Figure 3.6.

Figure 3.6: Double exchange mechanism between ions with different oxidation states and ferromagnetic coupling
CHAPTER 4. RESULTS AND DISCUSSION

4.1 Decoupling of the Antiferromagnetic and Insulating States in Tb doped Sr$_2$IrO$_4$

4.1.1 Introduction

As mentioned earlier in Chapter 2, Sr$_2$IrO$_4$ exhibits unconventional decoupling between its magnetic and transport properties in such a way that the magnetic ordering transition at 240 K is not observed in transport properties. From study of variously doped Sr$_2$IrO$_4$ we have seen that the charge gap opening, about 0.62 eV in the parent compound, due to strong SOI can easily be overcome, and as a result of even light chemical doping can drive the system to a metallic state. This induced metallic state is often, but not always, accompanied by the disappearance of antiferromagnetism. This is in contrast to other iridates such as BaIrO$_3$ and Sr$_3$Ir$_2$O$_7$, where magnetic and transport properties are closely correlated. Comprehensive study of single crystals of Sr$_2$Ir$_{1-x}$Tb$_x$O$_4$ confirms our earlier findings, as even light Tb doping of 3% of tetravalent Tb$^{4+}$ ($4f^7$) substituting for Ir$^{4+}$ suppresses the AFM ordering while the system persists in an insulating state.

The single crystals studied were grown using the flux method from non-stoichiometric quantities of SrCl$_2$, SrCO$_3$, IrO$_2$ and Tb$_4$O$_7$, and resulted in crystals as large as 2.0 x 2.0 x 0.2mm$^3$. Since the Tb$^{4+}$ ionic radius in octahedral environments is 0.13 Å larger than the Ir$^{4+}$ ionic radius (Ir$^{4+}$ is 0.625 Å, while Tb$^{4+}$ is 0.755 Å), we observe significant changes in lattice parameters and reduced distortion, even though the tetragonal crystal structure is still preserved. Figure 4.1 tracks the changes in lattice parameters as the Tb concentration is increased. Unit cell volume obtained from single crystal x-ray diffraction seem to closely track the changes in lattice parameters, however, there is an unusual drop in the lattice

![Figure 4.1: The Tb concentration dependence of (a) a- and c-axis lattice parameters and unit cell volume V (right scale) and (b) c/a ratio and Ir-O-Ir bond angle $\theta$ (right scale)](image)
parameters until at about 3% the expected increase is observed. Reduced distortion can be observed from the changes in the Ir-O-Ir bond angle, as can be seen in Figure 4.1b, where the angle increases to 160.05° for x = 0.02 but unusually drops again at x = 0.03 to 158.60° (at x = 0, the bond angle is 156.47°). As a result of the strong magnetoelastic coupling, lattice parameter changes have significant impact on magnetic properties, as will become clear in the discussion of magnetic properties (vide infra) [65].

4.1.2 X-ray absorption spectroscopy

X-ray absorption spectroscopy is most often used for determination of electronic or geometric structure of matter. The experimental data presented here employed the techniques of X-ray absorption near-edge structure (XANES), which was used to determine the valence state of Tb, and X-ray absorption fine structure (XAFS) for Tb site occupancy determination. These experiments were performed at Argonne National Laboratory. Many of the rare earth ions are commonly trivalent. Although mixed or other valence states are possible, e.g., for Tb, they are not very common. To determine Tb valence state, we have compared the XANES Tb L₃ absorption edge data with those of the already known Tb valence states like Tb₄O₇ (Tb³⁺), BaTbO₃ (Tb⁴⁺) and our own 2% and 3% Tb doped Sr₂IrO₄.

![Figure 4.2: (a) XANES results for x = 0.02 and 0.03 compared to previously studied Tb³⁺ and Tb⁴⁺ ions; (b) magnitude of complex Fourier transformation of the XAFS data (black line) and fit (red line); (c) real part of complex Fourier transformation of the XAFS data (black line) and fit (red line) [66]](image-url)
As can be seen in Figure 4.2a, the energy difference between the Tb$^{3+}$ and Tb$^{4+}$ ions for a core level electron 2p$_{3/2}$ to be excited into the empty 5d states is about 8 eV, so the energy spectra peaks are notable. When compared to the XANES results of the known valence Tb states measured before, [67-68] we can see that our two doped samples (green and blue line in Figure 4.2a) both align with the Tb$^{4+}$ peak. This indicates that the majority of the Tb doped in Sr$_2$Ir$_{1-x}$Tb$_x$O$_4$ is tetravalent, with radius 0.76 Å [69], and this is reflected in the increase in bond distances between Tb-O, Tb-Sr and Tb-Ir by 0.10(1), 0.12(4) and 0.05(3) Å, respectively, compared to the parent compound. In order to determine the Tb occupying site, XAFS measurements were fitted to the FEFF 6.0 theoretical standards [70] produced using the single-crystal structure of Sr$_2$IrO$_4$ at room temperature [11]. The XAFS results in Figure 4.2b-c show how the fitting (red line) almost identically resembles that of the measured data, indicating Tb doping at the Ir site in the Sr$_2$Ir$_{1-x}$Tb$_x$O$_4$. For comparison, measured data has also been fitted for the case of Tb replacing the Sr site for x = 0.03 doped single crystals, shown in Figure 4.3 and the disagreement between the data and the fitting (green line) is obvious.

Figure 4.3: XAFS data for discovery of Tb site substitution: (a) the magnitude of the complex Fourier transform in real space, (b) the real part of the complex Fourier transform in real space, (c) XAFS in photoelectron momentum space, and (d) the back Fourier transform in photoelectron momentum space: (all panels black dots and lines represent XAFS data and simulations by red/green lines for Tb at Ir/Sr site) [66]
4.1.3 Incommensurate magnetic order

Tetravalent Tb\(^{4+}\) has seven 4f electrons (4f\(^7\)). Unlike the 5d electrons, 4f electrons are localized and have no crystal field splitting, giving the system a total spin of S = 7/2 and angular momentum L = 0. Due to doped impurities, it is expected to have a disturbance in the Ir spins. As we can see in Figure 4.4a-b, Tb has already destroyed the long range AFM order at x = 0.03, which can be observed in a- and c- axis magnetization data.

Figure 4.4: (a) M\(_a\) temperature dependence at \(\mu_0H = 0.1\) T for 0 \(\leq x \leq 0.03\) and (b) M\(_c\) temperature dependence at \(\mu_0H = 0.1\) T for 0 \(\leq x \leq 0.03\) [66]

Although magnetic order fully vanishes at 3\% Tb doping, there is magnetic hysteresis in the a-axis magnetization for the same sample in zero-field-cooled and field-cooled measurements, with a small anomaly around 10 K (see Figure 4.5), which could indicate an incommensurate magnetic order that has also been confirmed by neutron diffraction data.

Figure 4.5: The temperature dependence for x = 0.03 of \(\chi_a\) and \(\chi_c\); for \(\chi_c^{-1}\) on right scale: (enlarged FC and ZFC low temperature region for \(\chi_0\)) [66]
Curie-Weiss law fitting for \( x = 0.03 \) in Figure 4.5 (right scale) gives a negative Curie-Weiss temperature \( \theta_{CW} = -1.5 \text{ K} \), which as we have discussed earlier, differs from the parent compound, which has a positive Curie-Weiss temperature of +240 K. The transition from the magnetically ordered parent compound to a fully suppressed magnetic state is closely followed by the Curie-Weiss temperature (see Figure 4.6a), indicating transition from the AFM state to a new state with possible ferromagnetic order. It is not a surprise that we observe an increase in effective moment \( \mu_{\text{eff}} \) but for the tetravalent \( \text{Tb}^{4+} \) with \( S = \frac{7}{2} \) it is likely that the interaction with Ir 5d electrons is quite significant, as the 1.85 \( \mu_{B} \)/f.u. for \( x = 0.03 \) in Figure 4.6b (right scale) is quite weak from the expected effects of Tb doping, as the tetravalent ion has an effective moment of 7.94 \( \mu_{B}/\text{Tb} \).

Figure 4.6: (a) The temperature dependence of \( \Delta \chi^{-1} \) for \( 0 \leq x \leq 0.03 \), (b) Curie-Weiss temperature dependence on Tb concentration and effective moment dependence on Tb concentration (right scale) [66]

This strong correlation between the 4f and 5d electrons is evident in isothermal magnetization (see Figure 4.7) and its effect is displayed through the magnetic anisotropy and the ordered moment. With Tb doping, the c-axis magnetization, \( M_{c} \), is enhanced and overcomes \( M_{a} \) even at \( x = 0.01 \). This is different from \( \text{Sr}_2\text{IrO}_4 \), where \( M_{a} \) is almost twice \( M_{c} \) due to moments lying in the plane [21]. For the parent compound, magnetization saturates even before reaching 2 T, while even a magnetic field of 14 T does not result in saturation for the \( x = 0.03 \) single crystals measured at 1.8 K, suggesting ferromagnetic behavior in the doped compound. There is also a significant increase in the moment if estimated for zero applied field \( H = 0 \) for the c-axis measurement, which for the pure compound is about 0.02\( \mu_{B} \)/Ir, whereas for the \( x = 0.03 \) sample it is one order of magnitude stronger at 0.25\( \mu_{B}/\text{f.u.} \).
As mentioned earlier, the anisotropy between the ZFC and FC data for a-axis magnetic susceptibility in Figure 4.5 is supported by neutron diffraction measurements. From the earlier studies we are familiar with the signature $(1,0,2)$ peak for the AFM state of pure $\text{Sr}_2\text{IrO}_4$ [21,71], which following the increased Tb doping and vanishing of AFM order, is reflected directly in the reduction of the signature peak (see Figure 4.8) at $x = 0.005$ until it fully vanishes at $x = 0.03$. In accordance with the observation of an anomaly around 10K in susceptibility measurements, there is a new magnetic peak observed at wave vectors $q_m = (0.95,0,0)$ and $(0,0.95,0)$ in Figure 4.8b, confirming the incommensurate magnetic order, which becomes more pronounced as the Tb doping is increased. The appearance of the pair of peaks could be indicative of the spiral order with moments along the c axis, which would justify the observed increase in c-axis magnetization. There are several reasons that show this spiral magnetic order along the c-axis to be an energetically favorable condition:

a) Stronger tetragonal crystal field effect as a result of enhancement of c/a ratio supported by the larger Tb$^{4+}$ ion causing c-axis to be preferred orientation for Ir moment.

b) Enhancement of Hund’s rule coupling on Tb sites, favoring FM interactions along the c-axis.
c) Disappearance of the AFM state could be due to competition between FM out-of-plane and AFM in-plane moments

Figure 4.8: (a) Temperature dependence of the peak (1,0,2) for x = 0 and 0.005, inset: the rocking curve of the (1,0,2) peak for x = 0.005 at 5 K and 250 K, (b) Temperature dependence of the peaks (0.95,0,0) and (0,0.95,0) [66]

4.1.4 Anderson localization (variable range hopping)

The Ir-O-Ir bond angle is proportional to the electrical resistivity as we have seen in previous chemically doped Sr$_2$IrO$_4$ systems. When highly insulating Sr$_2$IrO$_4$ is driven into metallic state, the metallic state most of the time follows the increase in the bond angle due to favorable condition for easy electron hopping. Figure 4.1b (right scale) tracks the changes in Ir-O-Ir bond angle $\theta$ and as the angle increases it is reflected in electrical transport data for both a-axis $\rho_a$ and c-axis $\rho_c$ with the enormous reduction in electrical resistivity of about four orders of magnitude as can be seen in Figure 4.9a-b. Electrical resistivity data in Figure 4.9c fits the VRH data very well, indicating that the Anderson localization may significantly affect electron hopping with long range Coulomb repulsion, and structural distortion may contribute to the electrical resistivity, as the doped Sr$_2$Ir$_1$. 
$x$-Tb$_4$O$_4$ fits the VRH model much better compared to the pure compound [72-74]. Anderson localization, which is most often associated with disorder could be due to the incompatibility of energy levels of Ir and Tb sites, which weakens electron hopping, that in turn leads to the continued presence of the insulating state.

![Figure 4.9](image)

Figure 4.9: The temperature dependence of (a) the a-axis resistivity $\rho_a$ and (b) the c-axis resistivity $\rho_c$, (c) $\ln(\rho_a)$ vs $T^{-1/2}$ for $x = 0, 0.02$ and $0.03$ [66]

Considering the persistent insulating state, it is unusual that the specific heat data when fitted to the expression for electron ($\gamma$) and phonon ($\beta$) contribution:

$$C(T) = \gamma T + \beta T^3$$  \hspace{1cm} (4.1)

has a value of $\gamma$, usually indicator of the density of states near the Fermi level, that is unusually large for an insulating state [66]. The increase in $C(T)/T$ with the Tb concentration is due to Tb$^{4+}$ spins, since we see the upturn in the $C(T)/T$ at low temperatures below 5K, which is most likely due to the spin of the Tb$^{4+}$ S = 7/2 states (Figure 4.10). The linear dependence of heat capacity could be due to light disorder, which causes two level tunneling between two atomic positions [75]. The low temperature upturn
observed in the whole series of $\text{Sr}_2\text{Ir}_{1-x}\text{Tb}_x\text{O}_4$ is highly sensitive to the applied magnetic field, with a peak forming at 1 T for $x = 0.03$, which shifts to higher temperature as the field is increased (see Figure 4.11a).

![Figure 4.10](image)

**Figure 4.10:** The specific heat $C(T)/T$ vs $T^2$ over temperature range $1.7 \, K < T < 18 \, K$ for $0 \leq x \leq 0.03$ [66]

This shift in the peak is as expected with weakly correlated Tb$^{4+}$ ion in a magnetic field since the zero-field entropy when calculated for the entropy per Tb$^{4+}$ spin comes to be $2.53k_B$, which is very close to the entropy of the $S = 7/2$ system of 2.08$k_B$.

![Figure 4.11](image)

**Figure 4.11:** (a) The specific heat $C(T)/T$ vs $T$ for $x = 0.03$ at fields up to 14 T, (b) The specific heat $C(T)/T$ vs $\mu_0H$ at $T = 1.8 \, K$ and 4 K [66]
4.2 Breakdown of the spin-orbit imposed $J_{\text{eff}} = 0$ singlet state in double-perovskite iridates with $\text{Ir}^{5+}$ ($5d^4$) ions

4.2.1 Introduction

In Chapter 1 we reviewed the novel $J_{\text{eff}} = \frac{1}{2}$ Mott state that has been observed in layered iridates with tetravalent $\text{Ir}^{4+}$ ions such as $\text{Sr}_2\text{IrO}_4$, $\text{Na}_2\text{IrO}_3$, $\text{Sr}_3\text{Ir}_2\text{O}_7$ in which the one electron partially occupies the $J_{\text{eff}} = \frac{1}{2}$ band, and governs the new physics as it is closest to the Fermi energy [76]. Commonly seen in these materials is an insulating state that order antiferromagnetically at high temperatures. However, for pentavalent iridates with $\text{Ir}^{5+}$ ($5d^4$) ions, strong SOI is expected to impose a nonmagnetic singlet ground state $J_{\text{eff}} = 0$. Recent studies on $\text{NaIrO}_3$ [77-78] provide an example of this as it shows no magnetic state. However, our study on $\text{Sr}_2\text{YIrO}_6$, as well as several other, experimental and theoretical works, recently have reported the appearance of a new magnetic state and contradictions to the expected $J_{\text{eff}} = 0$ state [79-81]. There are several different possible explanations for the reason of the observed magnetic state:

1. Non-cubic crystal fields on the $J_{\text{eff}} = \frac{1}{2}$ and $J_{\text{eff}} = 3/2$ states

2. Overlap between $J_{\text{eff}} = \frac{1}{2}$ and $J_{\text{eff}} = 3/2$ bands due to large band width as a result of electron hopping

3. Two-site picture having different interactions couple at separate sites

4. Magnetic order as a result of a band structure effect, instead of non-cubic crystal effects in these double perovskites

Our initial work on $\text{Sr}_2\text{YIrO}_6$ [79], where magnetic state is observed below 1.3 K, was attributed to the effects of non-cubic crystal field due to structural distortions. However, a band structure study on $\text{Ir}^{5+}$ double perovskites has shown that the reason for the magnetic state is due to band structure effects and not the non-cubic crystal field [81], and has predicted the magnetic state in $\text{Ba}_2\text{YIrO}_6$, which has not yet been observed in recent experimental studies [82-83]. Nevertheless, our study of single crystals of $\text{Ba}_2\text{YIrO}_6$ and Sr doped $\text{Ba}_2\text{YIrO}_6$ confirms predictions made by band structure calculations and the exotic magnetic ground state is observed below 1.6 K.

4.2.2 Crystal structure of (Sr,Ba)$_2\text{YIrO}_6$

Growth of $(\text{Ba}_{1-x}\text{Sr}_x)\text{YIrO}_6$ single crystals ($x = 0, 0.37$ and $1$) was done using the self-flux method from non-stoichiometric quantities of $\text{IrO}_2$, $\text{BaCO}_3$ (and $\text{SrCO}_3$) and $\text{Y}_2\text{O}_3$ with successful growth of single crystals of approximate size 1.0 x 1.0 x 0.5 mm$^3$. For single crystals $\text{Ba}_2\text{YIrO}_6$ and $(\text{Ba}_{0.63}\text{Sr}_{0.37})\text{YIrO}_6$, they both crystallize as cubic structures, with space group Fm-3m (No. 225), in which every other Ir is replaced by nonmagnetic Y. All
the Ir\(^{5+}\) ions form a network of edge-sharing tetrahedra, resulting in a FCC structure shown in Figure 4.14c.

![Figure 4.14c: FCC structure](image)

**Figure 4.12: The double perovskite Ba\(_2\)YIrO\(_6\) crystal structure**

Although the ionic size of Y\(^{3+}\) and Ir\(^{5+}\) are significantly different, 0.900 Å and 0.570 Å respectively, there is no inter-site disorder. The structural parameters are presented in Table 4.1 and Table 4.2 for Ba\(_2\)YIrO\(_6\) and (Ba\(_{0.63}\)Sr\(_{0.37}\))\(_2\)YIrO\(_6\) respectively. Both compounds are cubic with no significant distortion and their lattice parameters change very slightly with temperature. However, in case of Sr\(_2\)YIrO\(_6\), octahedra are tilted and rotated as can be seen in Figure 4.14. Lattice parameters and unit cell volume for both pure and doped Ba\(_2\)YIrO\(_6\) at 100K are \(a = 8.348\) (5) Å, \(V = 581.85\) (78) Å\(^3\) and \(a = 8.280\) (4) Å, \(V = 567.74\) (75) Å\(^3\) respectively.

<table>
<thead>
<tr>
<th>Site</th>
<th>x</th>
<th>Y</th>
<th>Z</th>
<th>Occupancy</th>
<th>(U_{eq}(\text{Å}^2))</th>
</tr>
</thead>
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<tr>
<td>Ba</td>
<td>8c</td>
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<td>0.25</td>
<td>1</td>
<td>0.0063(5)</td>
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<tr>
<td>Y</td>
<td>4a</td>
<td>0</td>
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<td>0.0049(6)</td>
</tr>
<tr>
<td>Ir</td>
<td>4b</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.0059(4)</td>
</tr>
<tr>
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<td>0</td>
<td>0</td>
<td>1</td>
</tr>
</tbody>
</table>

*Table 4.1: Ba\(_2\)YIrO\(_6\) structural parameters at 100 K*
<table>
<thead>
<tr>
<th>Site</th>
<th>x</th>
<th>Y</th>
<th>Z</th>
<th>Occupancy</th>
<th>Ueq(Å²)</th>
</tr>
</thead>
<tbody>
<tr>
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<td>0.25</td>
<td>0.63(2)</td>
<td>0.0072(4)</td>
</tr>
<tr>
<td>Sr</td>
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<td>0.25</td>
<td>0.25</td>
<td>0.37(2)</td>
<td>0.37(2)</td>
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<tr>
<td>Y</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0.0049(4)</td>
</tr>
<tr>
<td>Ir</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>1</td>
<td>0.0056(3)</td>
</tr>
<tr>
<td>O</td>
<td>0.2632(7)</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>0.027(2)</td>
</tr>
</tbody>
</table>

Table 4.2: \((\text{Ba}_{0.63}\text{Sr}_{0.37})_2\text{YIrO}_6\) structural parameters at 100 K

Changes in lattice parameters are shown as a function of temperature for both pure and Sr doped \(\text{Ba}_2\text{YIrO}_6\).

srIrO₆ crystallizes as a monoclinic structure that can be derived from the parent perovskite SrIrO₃ by replacing every other Ir by a nonmagnetic Y, such that the remaining magnetic Ir⁵⁺ ions form a FCC structure with lattice parameters elongated. Figure 4.14 shows the unit cell where the tilt and rotation in octahedra are obvious, especially Figure 4.14b where the flattening of the octahedra is significant due to the shorter bond distance compared to in plane bond distance where Ir-O3 bond distance is 1.9366 Å, while for Ir-O1 is 1.9798 Å and for Ir-O2 it is 1.9723 Å. This flattening is the cause of the increase in non-cubic crystal electric field.
<table>
<thead>
<tr>
<th>Structure</th>
<th>Space Group</th>
<th>$a$ (Å)</th>
<th>$b$ (Å)</th>
<th>$c$ (Å)</th>
<th>$\beta$ (°)</th>
<th>IrO$_6$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sr$_2$YIrO$_6$</td>
<td>Monoclinic</td>
<td>P2$_1$/n</td>
<td>5.7751</td>
<td>5.7919</td>
<td>8.1704</td>
<td>90.22</td>
</tr>
</tbody>
</table>

Table 4.3: Sr$_2$YIrO$_6$ lattice parameters

Figure 4.14: (a) The crystal structure of double perovskite Sr$_2$YIrO$_6$, (b) flattened IrO$_6$ octahedra, (c) replacement order of Y ions for Ir ions leads to face centered cubic with geometrically frustrated edge-sharing tetrahedra [79]

4.2.3 Magnetic order in spite of expected J$_{\text{eff}}$=0 singlet ground state

Both Ba$_2$YIrO$_6$ and (Ba$_{0.63}$Sr$_{0.37}$)$_2$YIrO$_6$ display paramagnetic behavior above 1.6 K. For the temperature range 50 K < T < 300 K, magnetic susceptibility data fit the Curie-Weiss
law, giving an effective moment of $\mu_{\text{eff}} = 1.44 \mu_B$/Ir and a Curie-Weiss temperature of $\theta_{\text{CW}} = -149$ K for the pure compound. For the Sr doped single crystal, these values are significantly lower, where effective moment $\mu_{\text{eff}} = 0.64 \mu_B$/Ir and Curie-Weiss temperature of $\theta_{\text{CW}} = -18$ K shown in Figure 4.15a. The large negative Curie-Weiss temperature for the compound indicates strong antiferromagnetic coupling, while the effective moment is significantly smaller compared to the anticipated $2.83 \mu_B$/Ir for spin only $S=1$ 5$d^4$ electrons, which is often seen in iridates as a result of strong spin orbit interaction. The frustration parameter $|\theta_{\text{CW}}|/T_N = 97.3$ is very large and it is the geometrical frustration of the FCC lattice combined with strong SOI that is suppressing the long range magnetic order above 1.6 K by strong quantum fluctuations. Figure 4.15b shows the enlarged low temperature magnetic susceptibility measurement with evident AFM transition temperature $T_N = 1.48$, with an additional magnetic anomaly around $T = 0.6$ K. However, the AFM state does not seem to be fully ordered due to the very weak ordered moment at highest measured field $\mu_0H = 7$T, which is just below $0.12 \mu_B$/Ir in Figure 4.15c. Although weakly ordered, as the temperature is lowered, the field dependent magnetization is lower, indicating stronger AFM order. At this lower temperature of $T = 0.5$ K, although very weak there is a slope change around 4.5 T that is not observed at the higher temperature.
Figure 4.15: Ba$_2$YIrO$_6$ temperature dependence of (a) magnetic susceptibility and $1/\Delta\chi$ (right scale) at $\mu_o H = 1$ T and (b) low temperature susceptibility for $0.44 \, K \leq T \leq 4 \, K$, (c) the isothermal magnetization at $T = 0.5$ and $0.8 \, K$

In comparison to the magnetic properties of pure Ba$_2$YIrO$_6$, the doped (Ba$_{0.63}$Sr$_{0.37}$)$_2$YIrO$_6$ shows very similar behavior, but with reduced Curie-Weiss temperature $\theta_{cw} = -18 \, K$ and effective moment $\mu_{eff} = 0.64 \, \mu_B$/Ir. We can still observe the
strongly field dependent AFM transition temperature, just at the slightly lower temperature with the low temperature anomaly now occurring around $T = 1$ K shown in Figure 4.16b. The slope change in isothermal magnetization is more evident as the magnetization almost reaches saturation around 2.5 T before it starts to rise again with higher field. This transition from saturation to the increase at critical field was also observed in Sr$_2$YIrO$_6$ [79].

Figure 4.16: The (Ba$_{0.63}$Sr$_{0.37}$)$_2$YIrO$_6$ temperature dependence of (a) magnetic susceptibility and $1/\Delta \chi$ (right scale) at $\mu_0 H = 1$ T and (b) low temperature susceptibility for $0.44 \leq T \leq 4$ K, (c) the isothermal magnetization at $T = 0.5$ and 0.8 K
Figure 4.17: Ba$_2$YIrO$_6$ and Ba$_{1.26}$Y$_{0.74}$IrO$_6$ thermal properties temperature dependence: (a) the specific heat $C(T)$ and (b) the entropy removal $S(T)$ for Ba$_2$YIrO$_6$; (c) specific heat $C(T)$ and (d) the entropy removal $S(T)$ for Ba$_{1.26}$Y$_{0.74}$IrO$_6$.

The low-temperature specific heat data confirms the long range magnetic order in Figure 4.17a, c, where both pure and Sr doped double perovskites exhibit a commencement of the peak around the transition temperatures $T_N$. To measure the magnetic transition, entropy removal was calculated from the experimental data and compared to the expected
value for $S = 1$ system. The measured entropy removal in Figure 4.17b, d for \( \text{Ba}_2 \text{YIrO}_6 \) was 0.07 J/mole K and for \((\text{Ba}_{0.63} \text{Sr}_{0.37})_2 \text{YIrO}_6 \) it was 0.08 J/mole K, which are both are significantly lower than the expected value $R \ln(2S+1) = R \ln(3) = 9.13$ J/mole K. The reason for such low entropy removal could be due to frustration, in which magnetic ions have already lost their entropy at higher temperatures since the pure \( \text{Sr}_2 \text{YIrO}_6 \) compound has even lower entropy removal of 0.025 J/mole K, which could be a norm among these double perovskites.

The magnetic susceptibility of the whole series \((\text{Ba}_{1-x} \text{Sr}_x)_2 \text{YIrO}_6 \) is shown in Figure 4.18 with the systematic shift in the transition temperature as $T_N$ decreases linearly as Sr concentration is increased.

![Figure 4.18](image.png)

Figure 4.18: The low temperature dependence of magnetic susceptibility for whole double perovskite series \((\text{Ba}_{1-x} \text{Sr}_x)_2 \text{YIrO}_6 \)

That the whole series exhibit similar magnetic behavior indicates the presence of the same AFM ground state. This evolves as the Sr concentration is altered, and is reflected in lattice parameters as well as the amount of distortion present. Although in our initial study of \( \text{Sr}_2 \text{YIrO}_6 \), we assumed that the distortion was an indicator for latent electron hopping, however, recent band structure calculations on double perovskites have negated that, suggesting that band structure was the leading cause for the observed behavior.
Figure 4.19: Isothermal magnetization at $T = 0.5$ K for the $(Ba_{1-x}Sr_x)_2YIrO_6$
4.3 Coexisting charge and magnetic orders in the dimer-chain iridate Ba$_5$AlIr$_2$O$_{11}$

4.3.1 Introduction

Chapter 1 introduced the strong competition between relevant energies of Coulomb interaction (~0.5 eV) and spin-orbit interaction (~0.4 eV), which in 5d electron based iridates are comparable to each other, as well as to Hund’s coupling (~0.5 eV) and the crystal electric field. This delicate balance between competing energies leads to ground states that are highly sensitive to small perturbations, as well to different degrees of freedom, with strong coupling to lattice degrees of freedom. Due to strong SOI and the formation of $J_{\text{eff}}=3/2$ and $J_{\text{eff}}=1/2$ states (Figure 1.2), very little work has been done on pentavalent Ir$^{5+}$ (5d$^4$) iridates, since the four d-electrons would completely fill the lower $J_{\text{eff}}=3/2$ band, resulting in a nonmagnetic, singlet $J=0$ ground state. Nevertheless, due to competition between SOI, noncubic crystal field, exchange interaction, and singlet-triplet splitting, recent theoretical and experimental works have shown that magnetic order can be observed in pentavalent iridates.

Ba$_5$AlIr$_2$O$_{11}$ is one of the compounds that display new magnetic states as a result of the competition between SOI and charge ordering. This system is different from most studied iridates, as unlike other two- and three-dimensional systems, it is a quasi one-dimensional dimer chain system. The unique aspect of this new compound is the presence of both tetravalent Ir$^{4+}$ and pentavalent Ir$^{5+}$ ions inside the dimers, which lie along the b axis and are connected via AlO$_4$ tetrahedra shown in Figure 4.20.

Figure 4.20: The single crystal structure of Ba$_5$AlIr$_2$O$_{11}$: (a) ac plane, (b) ab plane and (c) characteristic single crystal with labeled b-axis [84]
These dimers have been studied before in other transition metal oxides, and they most frequently house non-integer average number of electrons per transition metal, and double exchange plays an important role in properties observed in these systems. As explained earlier in Chapter 3, this occurs when an “extra” electron hops between neighboring transition metal ions with localized spin, and the Hund’s rule coupling stabilizes the state. However, in the iridate based material, we have an additional influence of the strong SOI onto the new magnetic and dielectric state.

4.3.2 Crystal structure of Ba$_5$AlIr$_2$O$_{11}$

Ba$_5$AlIr$_2$O$_{11}$ single crystals were grown via the flux method, and averaged approximately 2 x 1 x 1mm$^3$ in size. The crystal structure as well as a representative single crystal are shown in Figure 4.20a-c. The crystal structure is orthorhombic, space group Pnma (No. 62), with lattice parameters at room temperature $a = 18.7630(38)$ Å, $b = 5.7552(12)$ Å and $c = 11.0649(22)$ Å. Each dimer contains two face-sharing IrO$_6$ octahedra, but have different Ir1 and Ir2 octahedral sites, which house pentavalent and tetravalent ions respectively. A subtle structural change occurs at $T_S = 210$K, which can be observed in the lattice parameters/unit cell volume in Figure 4.21a and b, and in the Ir1-Ir2 bond length and thermal displacement in Figure 4.21c and d, with the more significant change observed in the latter two.

Figure 4.21: The lattice parameters temperature dependence: (a) a, b and c-axis, (b) the unit cell volume V, (c) Ir1-Ir2 bond distance and (d) the Ir1 thermal displacement $U$ [84]
The ionic radii $r$ for $\text{Ir}^{4+}$ (5d$^5$) and $\text{Ir}^{5+}$ (5d$^4$) are 0.625 Å and 0.570 Å, respectively. This significant difference is evident in the different volume for the two inequivalent octahedra within the dimers. Below the temperature of the structural change, at $T = 100\text{K}$, the average bond distance $d$ are: $d_{[\text{Ir1-O}]} = 1.997$ Å, $d_{[\text{Ir2-O}]} = 2.013$ Å, and $d_{[\text{Ir-Ir}]} = 2.7204(5)$ Å. These bond distances exhibit dramatic slope change at the structural change temperature, $T = 210\text{K}$, as can be seen in Figure 4.21a-d. Ir-O dimers are corner connected through AlO$_4$ tetrahedra to form dimer chains along the b axis, but the dimer chains are not connected in the a- and c-axis directions. This results in weak intrachain interactions and very small interchain interactions, primarily due to the lack of pathways between chains.

### 4.3.3 Existence of charge order in $\text{Ba}_5\text{AlIr}_2\text{O}_{11}$

The difference in Ir-O bonds lengths between the two types of octahedra indicate two different oxidation states, leading to the conclusion that charge order is present in the system and has significant effects on physical properties of $\text{Ba}_5\text{AlIr}_2\text{O}_{11}$.

![Figure 4.22: The temperature dependence of (a) b-axis resistivity $\rho_b$, inset: ln $\rho_b$ vs 1/T; (b) a and b-axis dielectric constant, inset: b-axis low temperature dielectric constant]([84])
We observe a very large, almost nine orders of magnitude, increase in resistivity along the dimer chain direction when the temperature is decreased from 750K to 80K. The activation law fits the data in this temperature range well, giving an activation energy gap of \( \Delta_a \approx 0.57 \text{ eV} \). In addition, we observe a distinct slope change at \( T_s = 210\text{K} \), and this slope is much steeper below the structural transition temperature. This is indicative of localization of electronic states accompanying the structural transition.

Figure 4.23 shows a schematic of the anticipated orientation of the dipoles created within each dimer as a result of charge ordered state, predicting that dipoles are parallel to each other within each dimer chain, but antiparallel between dimer chains, in order to minimize electrical energy.

![Figure 4.23: The illustration of proposed electrical dipoles, E and magnetic moments, M in ac- and ab-plane](84)

Structural transitions are often accompanied by lattice softening, and this might be the cause for the peak, sharp transition, and two order of magnitude increase in dielectric constant, as can be seen in Figure 4.22b for both directions \( \varepsilon'_a \) and \( \varepsilon'_b \). The dielectric peak is larger than even well-known ferroelectrics like \( \text{BaMnF}_4 \) and \( \text{BiMnO}_3 \) [85-87]. The strong frequency dependence of the dielectric constant could be an indicator of relaxor behavior.

### 4.3.4 Magnetic order in \( \text{Ba}_5\text{AlIr}_2\text{O}_{11} \)

Even though we are able to observe a structural transition in electrical transport as well as dielectric and thermal properties, we were unable to observe any obvious anomaly in the magnetization curve, as can be seen from inset of Figure 4.24. We do, however, observe
magnetic order at $T_M = 4.5K$, which is conveyed as a peak in the b-axis magnetization, while along the a- and b-axis we can only observe an upturn below this transition temperature. This temperature is fairly low, but this is expected due to the quasi-one-dimensional structure of this material. Large magnetic anisotropy might be an indicator that SOI is significantly stronger than any noncubic crystal field, which would be able to weaken SOI and cause more isotropic magnetic behavior. Figure 4.23 shows the proposed alignment of magnetic moments with ferromagnetically aligned moments within each dimer, but antiferromagnetically alignment between dimer chains in order to minimize dipole energy. This proposed alignment does not include any possible canting, which from magnetization data, we would suspect to have some canting towards the a-axis because $M_a$ is significantly larger than $M_c$.

![Figure 4.23: The temperature dependence of a-, b- and c-axis magnetization at $\mu_oH = 7T$ and $1/\Delta\chi_b$ (right scale) [84]](image)

Curie-Weiss law data fitting demonstrates a negative Curie-Weiss temperature $\theta_{CW} = -14K$ for the temperature range $50 < T < 320K$, and indicates antiferromagnetic coupling with the effective moment $\mu_{\text{eff}} = 1.04\mu_B$/dimer. However, calculation of the expected effective moment in Equation 4.2 for $S=3/2$ system is $3.88\mu_B$, which is significantly smaller than the experimentally determined effective moment. This reduced moment could be due to SOI and electron hopping between the two Ir sites, Ir1 and Ir2.

$$\mu_{\text{eff}} = 2\sqrt{S(S+1)}\mu_B$$  \hspace{1cm} (4.2)
As the magnetic field is increased up to 12T, magnetic susceptibility \( \chi_b \) is reduced along the b-axis, which could indicate enhancement of antiferromagnetic compensation, while the field only slightly shifts the transition temperature even though the high field of 12T would be expected to fully remove the transition at \( T_M = 4.5 \) K.

![Figure 4.25: The temperature dependence of (a) the b-axis magnetic susceptibility and (b) b-axis magnetization for various pressures][84]

The transition temperature, \( T_M \), at 4.5 K tends to be more sensitive to applied hydrostatic pressure, and it shifts upwards to 5 K at 8.2 kbar, indicating increased interaction between magnetoelastic effects and 5d electrons. Specific heat also confirms the long-range magnetic order onset at \( T_M = 4.5 \) K in Figure 4.26a, evidenced by the lambda peak, which like magnetization data, is also insensitive to the application of high field. Entropy removal found from analysis of specific heat data is approximately 1.00 J mole\(^{-1}\) K\(^{-1}\), which is also much smaller than the expected entropy removal for \( S = 3/2 \), which is 11.37 J mole\(^{-1}\) K\(^{-1}\). Due to structural transition at \( T_S = 210 \) K, some of the entropy may have been removed,
thereby compensating for the dramatic difference between the experimental and calculated entropy values.

Figure 4.26: Thermal properties temperature dependence of (a) specific heat $C(T)$ and (b) specific heat for structural transition temperature range [84]
CHAPTER 5 CONCLUSION

In this dissertation I have reviewed the role of spin-orbit interaction and the accompanying new phenomena in several 5d transition metal oxides with spin-orbit interaction as an essential component in determining electronic and magnetic ground states of these materials. The large spin-orbit interaction in iridates dramatically enriches the effect of electron correlation by forming a $J_{\text{eff}} = \frac{1}{2}$ band near the Fermi level, thus bringing iridates into Mott instability. Since the high temperature superconductivity in 3d transition metal oxides (cuprates) was achieved by carrier doping in single-band Mott insulators, the $J_{\text{eff}} = \frac{1}{2}$ band could be viewed as equivalent, and has anticipated the formation of high $T_c$ superconducting state in iridates via charge doping. I have briefly reviewed several cases of carrier doping of which none have fulfilled this expectation, but have shown that the $J_{\text{eff}} = \frac{1}{2}$ insulating state can be readily driven to a metallic state by chemical doping. Furthermore, we have observed that transport properties are strongly coupled to local distortions or disorder in iridates, and can be easily tuned by changes in lattice parameters or by light chemical doping. Unlike the rest of the iridates, the archetype of $J_{\text{eff}} = \frac{1}{2}$ insulating state (i.e., Sr$_2$IrO$_4$) shows no apparent correlation between magnetic and transport properties, as no anomaly corresponding to the magnetic ordering temperature is observed in the transport data. However, as it is chemically doped, suppression of the antiferromagnetic state is almost always accompanied by the emergence of a metallic state. The sole exception being Tb, which although fully suppressed magnetically, still preserves its insulating state, as was discussed in more detail above. It appears that spin-orbit interaction is the driving force, as it either competes or cooperates with the other comparable interactions (i.e., crystal field energy, Hund’s rule coupling and electron correlation) in bringing about the novel exotic magnetic and insulating ground states. However, our study of pentavalent Ir$^{5+}$ based double perovskites shows that spin-orbit interaction may not be as important as it has been presumed so far. The reason being that the anticipated $J = 0$ singlet ground state in the strong spin-orbit interaction regime is not realized, and the magnetically ordered state has been experimentally observed. For these reasons, study of the effect of spin-orbit interaction on the tetravalent Ir$^{4+}$ and pentavalent Ir$^{5+}$ based compounds has formed the foundation of the work in this dissertation. I have mainly used the methods of measurement of electrical transport, magnetic and thermodynamic properties as the main characterization techniques in determining the major findings of this work which include:

- Tb$^{4+}$ when substituted for Ir$^{4+}$ in Sr$_2$Ir$_{1-x}$Tb$_x$O$_4$ alters the relative strength of the spin-orbit interaction and the tetragonal crystal electric field, but enhances the Hund’s rule coupling which competes with the SOI that ultimately result in the complete suppression of antiferromagnetic state at 3% Tb doping. At the same time, the energy mismatch between the Tb and Ir site might impede carrier hopping, leading to a persistent insulating state;
• Even though the $J_{\text{eff}} = \frac{1}{2}$ insulating state model driven by strong spin-orbit interaction was successful in describing the new physics observed in many of the iridates, it may not be sufficient in the case where spin-orbit interaction competes with comparable strength of exchange interactions and electron hopping, as we have observed in the series of $(\text{Ba}_{1-x}\text{Sr}_x)_2\text{YIrO}_6$, which feature a magnetic ground state, indicating breakdown of the $J = 0$ state anticipated in strong spin-orbit interaction regime; and

• Observed coexistence of charge and antiferromagnetic order in a quasi-one-dimensional dimer system $\text{Ba}_5\text{AlIr}_2\text{O}_{11}$, which features both tetravalent and pentavalent Ir ions in inequivalent octahedra as a result of the presence of charge disproportionation, formation of molecular orbitals, double exchange mechanism and spin-orbit interaction.

The work presented in this dissertation is just a part of contribution to the vast arena that the field of iridates has become since the emergence of first iridate compounds with some of the more intensively studied iridates listed below:

<table>
<thead>
<tr>
<th>Structure</th>
<th>Compound</th>
<th>Physical Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Layered perovskite</td>
<td>$\text{Sr}_3\text{Ir}_2\text{O}_7$</td>
<td>$J_{\text{eff}} = \frac{1}{2}$ Mott insulator, complex magnetism, Lattice-driven Magnetoresistance, Giant Magneto-electric Effect, Anomalous Magnetism, Non-Ohmic Behavior, …</td>
</tr>
<tr>
<td></td>
<td>$\text{Sr}_2\text{IrO}_4$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Doped $\text{Sr}<em>{\text{n+1}}\text{Ir}</em>\text{n}\text{O}_{3\text{n+1}}$</td>
<td></td>
</tr>
<tr>
<td>Hexagonal Perovskite</td>
<td>$\text{BaIrO}_3$</td>
<td>$J_{\text{eff}} = \frac{1}{2}$ Mott insulator, Coexistence of FM and Charge Density Wave, Quantum Critical point, Geometric Frustration, …</td>
</tr>
<tr>
<td></td>
<td>$\text{SrIrO}_3$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\text{Ca}_5\text{Ir}<em>3\text{O}</em>{12}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\text{Ca}_4\text{IrO}_6$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Doped $\text{BaIrO}_3$</td>
<td></td>
</tr>
<tr>
<td>Pyrochlore</td>
<td>$\text{Bi}_2\text{Ir}_2\text{O}_7$</td>
<td>Metallic states; Strong magnetic Instability, …</td>
</tr>
<tr>
<td></td>
<td>$\text{Pb}_2\text{Ir}_2\text{O}_7$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Doped $\text{Bi}_2\text{Ir}_2\text{O}_7$</td>
<td></td>
</tr>
<tr>
<td>Honeycomb</td>
<td>$\text{Na}_2\text{IrO}_3$</td>
<td>Zig-Zag Magnetic Order</td>
</tr>
<tr>
<td></td>
<td>Doped $\text{Na}_2\text{IrO}_3$</td>
<td></td>
</tr>
<tr>
<td>Hexagonal Perovskite</td>
<td>$\text{Sr}_3\text{LiIrO}_3$</td>
<td>Correlated Insulator</td>
</tr>
<tr>
<td>Double Perovskite</td>
<td>$\text{Sr}_2\text{YIrO}_6$</td>
<td>Correlated Insulator</td>
</tr>
<tr>
<td></td>
<td>$\text{Sr}_2\text{GdIrO}_6$</td>
<td></td>
</tr>
</tbody>
</table>

There have been extensive studies on many of the existing iridates, and many interesting phenomena have been experimentally observed, including lattice-driven
magnetoresistance, giant magneto-electric effect, coexistence of ferromagnetic order and charge density wave, and $J_{\text{eff}} = \frac{1}{2}$ Mott insulating state. However, many of the theoretical predictions or proposals have yet to be observed. Some of those predicted properties are superconductivity in Sr$_2$IrO$_4$, expected to be achieved by doping higher levels of carriers past the doping levels that drive the system into a metallic state; topological Mott insulators or various other topological phases, as well as Weyl semimetals. Since so many predictions have been made it is clear that the work on the iridates has a long way to go, both theoretically in describing some of the observed properties that do not fit the long-standing models we currently rely upon, and experimentally in making materials that reflect or possess theoretically predicted exotic states.
REFERENCES


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