Probing the spin-orbit Mott state in Sr3Ir2O7 by electron doping

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Probing the spin-orbit Mott state in $Sr_3Ir_2O_7$ by electron doping

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A dissertation submitted to the Faculty of the department of Physics in partial fulfillment of the requirements for the degree of Doctor of Philosophy

> Boston College Morrissey College of Arts and Sciences Graduate School

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Thomas C. Hogan

Advisor: Stephen D. Wilson, Ph.D.

Iridium-based members of the Ruddlesden-Popper family of oxide compounds are characterized by a unique combination of energetically comparable effects: crystalfield splitting, spin-orbit coupling, and electron-electron interactions are all present, and the combine to produce a $J_{\text{eff}} = 1/2$ ground state. In the bilayer member of this series, $\text{Sr}_3\text{Ir}_2\text{O}_7$, this state manifests as electrically insulating, with unpaired Ir^{4+} spins aligned along the long axis of the unit cell to produce a *G*-type antiferromagnet with an ordered moment of 0.36 μ_{B} .

In this work, this Mott state is destabilized by electron doping via La^{3+} substitution on the Sr-site to produce $(\text{Sr}_{1-x}\text{La}_x)_3\text{Ir}_2\text{O}_7$. The introduction of carriers initially causes nano-scale phase-separated regions to develop before driving a global insulator-to-metal transition at x = 0.04. Coinciding with this transition is the disappearance of evidence of magnetic order in the system in either bulk magnetization or magnetic scattering experiments. The doping also enhances a structural order parameter observed in the parent compound at forbidden reciprocal lattice vectors. A more complete structural solution is proposed to account for this previously unresolved distortion, and also offers an explanation as to the anomalous net ferromagnetism seen prior in bulk measurements.

Finally, spin dynamics are probed via a resonant x-ray technique to reveal evidence of spin-dimer-like behavior dominated by inter-plane interactions. This result supports a bond-operator treatment of the interaction Hamiltonian, and also explains the doping dependence of high temperature magnetic susceptibility.

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-Tom Hogan

November 29, 2016 Santa Barbara, California Make tiny changes to Earth.

– F.R.

Table of Contents

Ał	Abstract iii							
Ac	Acknowledgments v							
Lis	List of Tables xiii							
Li	st of	Figure	s	XV				
Lis	st of	Symbo	ols and Acronyms	xvii				
1 Ruddlesden-Popper Iridates 1.1 The Ruddlesden-Popper Series 1.2 Spin Orbit Coupling 1.3 Origin of the J _{eff} = 1/2 State 1.4 Bulk Magnetism and Static Spin Structure 1.5 Spin Dynamics 1.6 Relationship to the Cuprates References References								
2	Mea 2.1 2.2 2.3	Electric SQUID Neutro 2.3.1 2.3.2 2.3.3 2.3.4 2.3.5 2.3.6 X-Ray 2.4.1	ent Techniques cal Resistivity	31 . 32 . 33 . 35 . 35 . 36 . 42 . 46 . 48 . 51 . 52 . 55				

		2.4.2 Resonant Inelastic X-Ray Scattering (RIXS)
		2.4.3 Powder Diffraction and Reitveld Refinement
	Refe	rences
3	\mathbf{Syn}	thesis and Characterization 69
	3.1	Flux Growth of Single-Crystal $Sr_3Ir_2O_7$
	3.2	Doping The System
	3.3	Confirming Phase Purity
	3.4	Evaluating Chemical Composition
	Refe	rences
4	Cry	stal Structure of $Sr_3Ir_2O_7$ 81
	4.1	Previous Structural Reports
	4.2	Experimental and Computational Details
	4.3	Neutron Diffraction Results
	4.4	Point Group Measurement
	4.5	Proposed Structural Solution to $Sr_3Ir_2O_7$
	4.6	Discussion
	4.7	Conclusions
	Refe	rences
5	Pha	se Diagram of $(\mathbf{Sr}_{1-x}\mathbf{La}_x)_3\mathbf{Ir}_2\mathbf{O}_7$ 101
	5.1	Introduction
	5.2	Details of Methodology
	5.3	Bulk Probe Results
	5.4	Neutron and X-Ray Scattering
	5.5	Surface Probe and Thermodynamic Results
	5.6	La-doping Phase Diagram 115
	Refe	rences
6	Mag	gnetic Excitations in $(\mathbf{Sr}_{1-x}\mathbf{La}_x)_3\mathbf{Ir}_2\mathbf{O}_7$ 123
	6.1	Introduction
	6.2	Details of Methodology
	6.3	Dispersion Analysis
	6.4	Fitting the Dispersion
	6.5	REXS Investigation of Short Range Order 139
	6.6	Bulk Magnetization Evidence of Dimer Pairs
	Refe	rences

\mathbf{A}	Hund's Rules	149
	A.1 General Application	149
	A.2 Ir^{4+} in $Sr_3Ir_2O_7$	152
	References	153
В	Deriving Fine-Structure Corrections	155
	References	158
\mathbf{C}	Evaluating the Wilson ratio $R_{\mathbf{W}}$	159
	C.1 Evaluation with SI units	159
	C.2 Evaluation with CGS units	162
	References	163

List of Tables

1.1	d orbital wavefunctions expressed as spherical harmonics $Y_l^{m_l}$	11
3.1	Standard furnace heating profile	71
4.1	Lattice parameters for $Sr_3Ir_2O_7$ at 100 K , 300 K	91
4.2	Atomic positions and ADP for $Sr_3Ir_2O_7$ at $T = 300 \text{ K} \dots \dots \dots$	93
4.3	Atomic positions and ADP for $Sr_3Ir_2O_7$ at $T = 100 \text{ K} \dots \dots \dots$	94
6.1	Summary of refined magnetic exchange parameters for the parent and	1.40
	doped systems.	140
A.1	Spectroscopic notation for the quantum number $l. \ldots \ldots \ldots$	150

List of Figures

1.1	Unit cells of the strontium-iridate RP series	3
1.2	Octahedrally coordinated Ir^{4+} ion; d orbitals	7
1.3	Energy level splittings resulting in the $J_{\text{eff}} = \frac{1}{2}$ state.	12
1.4	Electrical transport and susceptibility of bulk $Sr_3Ir_2O_7$	13
1.5	The spin structure of $Sr_3Ir_2O_7$	17
1.6	Magnetic exchange coupling J 's nomenclature from J. Kim, et al	19
1.7	Generic phase diagram for the cuprates.	23
2.1	A four-probe lead configuration.	33
2.2	Real-space Scattering geometry illustrating the Bragg condition	40
2.3	Example triple-axis spectrometer geometry	47
2.4	The scattering geometry of the time-of-flight Laue method	49
2.5	X-ray optics configuration at APS Sector 27	62
2.6	X-ray diffraction data from a crushed $Sr_3Ir_2O_7$ single crystal	64
3.1	Schematic heating profile for flux growth	70
3.2	Typical layered powder charge for flux growth	72
3.3	$\theta - 2\theta$ XRD scan of a single crystal	75
3.4	Sample EDS Spectrum	78
4.1	Radial \mathbf{Q} scan through the (103) reflection	84
4.2	Unit cell of $Sr_3Ir_2O_7$	87
4.3	RA-SHG patterns measured from $Sr_3Ir_2O_7$	89
4.4	Local geometry of the IrO_6 octahedra.	92
5.1	La-doping dependence of electronic transport and magnetization. $\ .$.	106
5.2	Lattice parameter dependence on doping and temperature	107
5.3	Neutron scattering results tracking the evolution of $T_{\rm AF}$ with varying x.	109
5.4	Neutron scattering results tracking the evolution of $T_{\rm S}$ with varying x .	110
5.5	STM topography and associated $\frac{dI}{dV}$ spectra of $(\mathrm{Sr}_{1-x}\mathrm{La}_x)_3\mathrm{Ir}_2\mathrm{O}_7$	112
5.6	Heat capacity and magnetic susceptibility measurements for $x = 0.058$	
	$(\operatorname{Sr}_{1-x}\operatorname{La}_x)_3\operatorname{Ir}_2\operatorname{O}_7$	114

5.7	Electronic phase diagram of $(Sr_{1-x}La_x)_3Ir_2O_7$	116
6.1	Magnon dispersion of $Sr_3Ir_2O_7$ and modeling fits	125
6.2	Elastic line fits used to determine energy resolution in RIXS measure-	
	ments at APS beamline 27-ID-B	126
6.3	RIXS energy scans at (π, π) and $(\pi, 0)$.	129
6.4	RIXS energy scans at $(\pi/2, \pi/2)$ and $(0, 0)$.	131
6.5	Dispersion of M and M^* features in $(\mathrm{Sr}_{1-x}\mathrm{La}_x)_3\mathrm{Ir}_2\mathrm{O}_7$ for samples with	
	x = 0.02 and $x = 0.07$	133
6.6	Out-of-plane (L) dependence of RIXS spectra with $\boldsymbol{Q} = (0 0 L)$	134
6.7	Momentum dependence of M -peak widths associated with the inverse	
	lifetime of magnetic excitations in $(Sr_{1-x}La_x)_3Ir_2O_7$	135
6.8	Depiction of magnon gap value inequivalence at (π, π) and $(0, 0)$	136
6.9	RIXS spectral weight of M peaks across the AF zone; REXS data	
	showing the absence of AF correlations for an $x = 0.05$ sample	139
6.10	REXS scans demonstrating the absence of AF order for an $x = 0.05$	
	sample; comparison of weak structural and magnetic reflections ob-	
	served in an $x = 0.023$ sample	141
6.11	Curie-Weiss fits to high temperature susceptibility in various concen-	
	trations of $(\mathrm{Sr}_{1-x}\mathrm{La}_x)_3\mathrm{Ir}_2\mathrm{O}_7$	144

List of Symbols and Acronyms

2θ	scattering angle, page 36				
α	fine structure constant \sim 1/137, page 157				
x	dynamical structure factor (RIXS), page 60				
κ	momentum exchange vector, page 40				
au	reciprocal lattice vector, page 40				
$oldsymbol{M}(oldsymbol{\kappa})$	magnetic structure factor, page 45				
$oldsymbol{M}(oldsymbol{r})$	magnetization density, page 44				
χ	magnetic susceptibility, page 34				
Δ	crystal field splitting magnitude, page 8				
ϵ	x-ray polarization, page 53				
λ	wavelength, page 36				
$\stackrel{\leftrightarrow}{\sigma}$	conductivity tensor, page 56				
$ ho(oldsymbol{r})$	atomic electron density, page 53				
b	scattering length, page 38				
d	lattice plane spacing, page 36				
f	atomic scattering factor (x-rays), page 53				
f	flux ratio, page 71				
$f_{ m mag}$	magnetic form factor (x-rays), page 55				
f_j	magnetic form factor (neutrons), page 44				

$F_{ m N}$	nuclear unit-cell structure factor (neutrons), page 41
F_{hkl}	structure factor (x-rays), page 54
k	wavenumber, page 42
l	azimuthal quantum number, page 157
M	magnetization, page 34
n	Ruddlesden-Popper layer classification, page 2
n	principal quantum number, page 8
Р	atomic percentage, page 78
Р	integrated peak intensity, page 47
v_{λ}	neutron velocity, page 50
x	dopant concentration, page 73
AF	antiferromagnetic, page 15
ВО	bond-operator, page 125
CEF	crystal electric field, page 8
CW	Curie-Weiss, page 111
DFT	density functional theory, page 82
EDS	energy-dispersive x-ray spectroscopy, page 77
FWHM	full width at half maximum, page 128
ICP	inductively coupled plasma, page 77
INS	inelastic neutron scattering, page 18
LSW	linear spin wave, page 20
MIT	metal-insulator transition, page 107
RA-SHG	rotational anisotropy second harmonic generation, page 83
REXS	resonant elastic x-ray scattering, page 55
xviii	

- RIXS resonant inelastic x-ray scattering, page 59
- RP Ruddlesden-Popper, page 2
- SEM scanning electron microscope/microscopy, page 77
- SOC spin-orbit coupling, page 5
- SOM spin-orbit Mott state, page 12
- SQUID superconducting quantum interference device, page 34
- STS scanning tunneling spectroscopy, page 103
- TEM transmission electron microscopy, page 83
- XRD x-ray diffraction, page 52
- Z atomic number of an atom, page 4

Chapter 1

Ruddlesden-Popper Iridates

At the outset of this work, a discussion of the larger backdrop upon which this research was conducted is warranted. The bulk of the topic is concerned with the effect of doping a known system to perturb it into less well-known regions of a larger, more general phase diagram. The results of such work are only fully understood to the extent that they reveal some underlying commonality with the original system. Thus, a full understanding of the unperturbed physics becomes essential context. This chapter will discuss the larger class of materials $Sr_3Ir_2O_7$ belongs to, what attributes account for its unique electronic and magnetic properties, and the consensus understanding of this compound provided by published reports up until this point.

1.1 The Ruddlesden-Popper Series

The Ruddlesden-Popper (RP) series of compounds, named for the researchers who reported the first examples [1, 2] of this class of structures, describes a family of crystal structures which have been realized in a vast array of different compositions. The RP series can be thought of as a group of 'layered perovskites', referring to the hallmark pattern of perovskite-structure layers being stacked between 'rock salt'-like layers. Generally, the chemical form is given as $A_{n-1}A'_2B_nX_{3n+1}$, where the A and B-sites are cations and the X-sites are anions [3]. Here, n refers to the number of consecutive perovskite layers in the system, which serves to distinguish one member of a given RP series from another. Figure 1.1 shows the corresponding unit cells of the first three members of the series, as well as the $n \to \infty$ endpoint of a full perovskite structure.

Depending on the species of cations and anions populating the structures, a whole host of interesting electronic states can be realized, ranging from high-performance cathode materials (La₂NiO₄) [4] to unconventional chiral p-wave superconductivity (Sr₂RuO₄) [5–7], and even high-temperature superconductivity (La₂CuO₄) [8]. A myriad of diverse magnetic states can also emerge, including canted antiferromagnetism (Sr₂IrO₄) [9] and the giant magnetoresistance effect (Sr₃Fe_{2-x}Co_xO₇) [10]. Material properties can also evolve as a function of dimensionality- that is, even for fixed cation/anion types the perovskite layer thickness *n* can drive the evolution of material properties [11–15], such as a spin-flop transition observed when comparing Sr₂IrO₄ (*n* = 1) with Sr₃Ir₂O₇ (*n* = 2) [16]. Furthermore, there is a well-established relationship between phase transitions in perovskite-based materials and the asso-



Figure 1.1: Unit cells of the strontium-iridate RP series¹ $Sr_{n+1}Ir_nO_{3n+1}$ showing n = 1, 2 and 3 as well as the $n \to \infty$ limit. A-site Sr atoms shown in green, X-site O atoms in red, and B-site Ir atoms in tan at the center of the visualized octahedra.

ciated combinations of rotations of the constituent BX_6 octahedral cages, implying that the structure can play a dominant role in determining the electronic, thermodynamic, and magnetic properties of these systems [17–20].

Given the rich variety of physics manifest in these compounds, as well as the extent to which such systems are susceptible to chemical and structural tuning, it is clear the Ruddlesden-Popper family of compounds represent an ideal platform for

¹Two types of A-site cations are specified in the general definition: A atoms, which reside within the perovskite layers' interstitial sites, and A' atoms, which are the cations in the 'rock-salt'-type interface between perovskite layers. Such a distinction turns out to be unnecessary: both A and A'-sites are occupied by Sr atoms in this particular RP series (though these sites do remain crystalographically distinct; see Chapter 4).

investigating new frontiers of condensed matter physics.

1.2 Spin Orbit Coupling

With so many exotic RP-based compounds to choose from, investigating the iridates $(B \rightarrow \text{Ir}, X \rightarrow \text{O})$ specifically should be motivated. The reason is relatively straightforward: the unique physics of iridium-based complex oxides is chiefly defined by the presence of appreciable spin-orbit interactions. In such a system, the Schrödinger equation treatment of a simple central potential fails to accurately capture the correct energy landscape of the Ir 5*d* electron levels. The resulting 'fine-structure' of the energy levels emerges as a result of not only the spin-orbit interaction, but also relativistic corrections to the kinetic energy.²

To understand why these corrections are particularly relevant for an element like iridium, its helpful to understand their origin. Consider the situation of an electron in a circular orbit around some hydrogen-like nucleus with atomic number Z, but from the non-inertial frame of the electron. In that frame, it appears that the nucleus orbits the electron; from the Biot-Savart the 'current' of the rotating charged nucleus generates a magnetic field:

$$B = \frac{\mu_0 I}{2r} = \frac{\mu_0}{2r} \frac{Ze}{T} \Rightarrow \mathbf{B} = \frac{Ze\mu_0}{4\pi m} \frac{1}{r^3} \mathbf{L}$$
(1.1)

Where the substitutions I = Ze/T and $|\mathbf{L}| = r\left(m\frac{2\pi r}{T}\right)$ have been leveraged (where T is the period of rotation) to define the magnetic field in terms of the (orbital) an-

4

 $^{^{2}}$ A simultaneous derivation of both contributions to the fine structure (spin-orbit and relativistic corrections) using the Dirac equation can be found in Appendix B.

gular momentum of the electron. If we take as known the classical magnetic moment of the electron to be $\mu_e = -\frac{e}{2m}\mathbf{S}$ we can substitute these values into the Hamiltonian for the interaction between a magnetic moment and a magnetic field:³

$$H' = -\boldsymbol{\mu}_{\boldsymbol{e}} \cdot \mathbf{B} = -\frac{Ze^2 \mu_0}{8\pi m^2 r^3} \mathbf{S} \cdot \mathbf{L}$$
(1.2)

Eq. 1.2 is perhaps the clearest explanation for the moniker 'spin-orbit coupling' (SOC): it arises from the scalar product of \mathbf{S} , derrived from the intrinsic (spin) angular momentum, and \mathbf{L} , from the orbital angular momentum. Following through, if this is treated as a time-independent perturbation to the nominal central-potential hydrogen-like atom problem, it can be shown [21–23] that the resulting energy corrections are given by

$$E_{so} = -mc^2 \left(\frac{\alpha^2 Z^2}{2n^2}\right)^2 \left(\frac{n(j(j+1) - l(l+1) - 3/4)}{l(l+1/2)(l+1)}\right)$$
(1.3)

The salient feature to take away from Eq. 1.3 is that $E_{so} \propto Z^4$. This form finally lays bare in some crude way the cause for spin-orbit coupling's important role in iridate physics: the energy of such an interaction scales to the fourth power in atomic number Z. Recalling that $Z_{Ir} = 77$, heavy transition metals like Ir clearly represent an ideal regime for spin-orbit effects to potentially play a role. It is worth noting here that the expression given in Eq. 1.3 is only valid strictly in the case of a hydrogenlike atom (a single valence electron directly above a filled shell). Since Ir⁴⁺ has the

³To avoid unnecessary digressions into subtleties of electromagnetism here, we omit the modifications to the g-factor and the correction for our use of a non-inertial frame (Thomas precession). More detailed discussions of these effects can be found elsewhere [21, 22], and in Appendix B.

electronic structure [Xe] $4f^{14}$ $5d^5$, this is clearly not the case and some degree of screening of the full Z by core electrons must be considered. Estimating the degree of this screening to arrive an an effective atomic charge Z_{eff} can be accomplished by applying the so-called 'Slater rules' [24]. If Z_{eff} is taken to be a simple step function, a crude application of the Bohr treatment shows that for multi-electron atoms the energy splitting dependence is approximately $E_{so} \propto Z^2$ [25]. The absolute value of E_{so} in the RP-iridate systems is estimated to be $\approx 0.4 \text{ eV}$ [26].

1.3 Origin of the $J_{eff} = \frac{1}{2}$ State

Having established that the spin-orbit interaction is of a relevant energy scale in this system, a full evaluation of the other effects which define the electronic ground state in $Sr_3Ir_2O_7$ is in order. This begins with a basic question of the expected ground state of members of the strontium iridate RP-series. Given the strong oxidation states of Sr (+2) and O (-2), it is expected that Ir would exist in the +4 state. This results in an electronic configuration for Ir^{4+} of [Xe] $4f^{14}$ $5d^5$. Here, a simple band-based interpretation which assumes a free electron model would predict this compound to be a metal, with the odd number of electrons per unit cell resulting in a half-filled valence band [27]. The relatively large spatial extent of the 5d orbitals seems to qualitatively bolster such an argument as well.

The reader will then be shocked to find, however, that this is not the case! Both the n = 1 and 2 compounds are electrical insulators with resistivity values on the order of 10's of Ω cm at $T \approx 10$ K [29, 30]. The previous section already presents the case that SOC could be a likely culprit, but now too the validity of a free electron picture must also be called into question. A careful accounting of the effects such



Figure 1.2: At left, a schematic representation of the octahedral coordination of (blue) Ir^{4+} at the center of a 'cage' of (red) O^{2-} ions. At right, probability isosurfaces associated with the five 5*d* orbitals, from [28].

considerations have on the 5d energy levels is now made.

In a free Ir ion, the five 5d energy levels (meaning the energies of an electron occupying one of the associated orbitals: d_{z^2} , $d_{x^2-y^2}$, d_{xy} , d_{xz} , d_{yz}) are nominally degenerate. When the ion is evaluated in some non-spherically symmetric potential though, this is no longer necessarily the case. As the outermost electron shells, these d-orbitals are also the ones most readily affected by the surrounding electrostatic environment created by the neighboring ligands [31] as illustrated in Fig. 1.2. In the case of (d_{xy}, d_{xz}, d_{yz}) , the lobes corresponding to where an electron in this state would be most probably localized are positioned between the O²⁻ ions. Contrast this with $(d_{z^2}, d_{x^2-y^2})$ where these lobes directly overlap the O²⁻ sites.

From here, even a very coarse electrostatics argument is sufficient to explain the lifting of the degeneracy between these two groups of orbitals: electrons occupying the first group pay a lower energy cost, having minimized their Coulomb repulsion with the ligands, at least relative to the other pair [32]. For ease of reference, these two groupings are assigned the labels t_{2g} (d_{xy} , d_{xz} , d_{yz}) and e_g (d_{z^2} , $d_{x^2-y^2}$), a convention which originates from a group theory treatment describing irreducible representations.⁴ The degree of splitting is typically described relative to the energy of the *berycenter-* a hypothetical configuration in which the total charge of the ligands is distributed uniformly in a shell with a radius matching the average length of the metal-ligand bond. This provides a baseline scale for the energy increase from an average isotropic potential wherein the d states remain degenerate [34].

The impact of the octahedral coordination, with respect to the berycenter, is calculated to be energy shifts of $+(3/5)\Delta$ for the e_g orbitals and $-(2/5)\Delta$ for the t_{2g} set [35]. The absolute magnitude of Δ is based on the degree of orbital overlap and the atom type of the participating ion and ligands, but this splitting increases with increasing principal quantum number n when moving downward through the transition metal block of the periodic table (due to the increasing spatial extent of the d orbitals). This crystal electric field (CEF) splitting, measured to be about $\Delta = 3.6 \text{ eV}$ in Sr₃Ir₂O₇ [36], is sufficiently large (compared to the SOC $\approx 0.4 \text{ eV}$) to drive the electron configuration into the low-spin state,⁵ and will prove crucial to the formation of the $J_{\text{eff}} = \frac{1}{2}$ state.

To summarize, the effect of strong crystal field splitting is that the lower-energy t_{2g} orbitals are partially occupied with S = 1/2 and the e_g band remains empty.

⁴These labels are collectively referred to as Mulliken symbols. The first letter describes the degree of degeneracy ($e \rightarrow \times 2$; $t \rightarrow \times 3$), while the g indicates an wave function that is symmetric with respect to the inversion center (all d orbitals satisfy this condition). The 2 subscript indicates a wave function that is anti-symmetric with respect to a C_2 axis normal to the principle axis associated with the symmetry of the coordination, O_h , which is C_4 [33].

⁵So-called because the total intrinsic angular momentum S is reduced to S = 1/2 due to the CEF placing the e_g orbitals energetically 'out of reach' [37]. This is a direct result of the first Hund's Rule; see Appendix A for further discussion.

Before taking spin-orbit related effects into account, it is helpful to first simplify the orbital angular momentum picture: consider the generalized expression for an arbitrary matrix element of one of the three components of the orbital angular momentum operator \hat{L} as shown in Eq. 1.4. Indices i, j specify one of the d orbital wavefunctions, listed in Table 1.1 [38], and k denotes the component (x, y, z) of \mathbf{L} operating on the orbital state j.

$$\alpha_{i,j,k} = \langle d_i | L_k | d_j \rangle \tag{1.4}$$

Because there are five d orbitals, each of the L_x , L_y , and L_z matrices will have dimensions of 5 × 5. Recalling that $L_z |Y_l^{m_l}\rangle = m\hbar |Y_l^{m_l}\rangle$ and that the orthogonality of the spherical harmonics ensures $\langle Y_{l'}^{m'_l}|Y_l^{m_l}\rangle = \delta_{l',l} \ \delta_{m'_l,m_l}$, the elements of the L_z matrix are populated with relative ease. The remaining two, L_x and L_y are most easily described using the raising and lowering operators $L_{\pm} = L_x \pm i L_y^6$ and their associated eigenvalues of $L_{\pm} |Y_l^{m_l}\rangle = \hbar \sqrt{l(l+1) - m_l(m_l \pm 1)} |Y_l^{m_l \pm 1}\rangle$. Taken together, this information is summarized in Eq. 1.5.

$$L_{z} = \hbar \begin{pmatrix} 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & -2i & 0 & 0 \\ \hline 0 & 2i & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & i \\ 0 & 0 & 0 & -i & 0 \end{pmatrix}$$
(1.5a)

⁶Thus, $L_x = \frac{1}{2}(L_+ + L_-)$ and $L_y = \frac{1}{2i}(L_+ - L_-)$.

	0	0	0	0	$-i\sqrt{3}$		0	0	0	$i\sqrt{3}$	0)	
	0	0	0	i	0		0	0	0	0	i	
$L_x = \hbar$	0	0	0	0	-i	$L_y = \hbar$	0	0	0	-i	0	
	0	-i	0	0	0		$-i\sqrt{3}$	0	i	0	0	
	$\sqrt{i\sqrt{3}}$	0	i	0	0		0	-i	0	0	0)	
											(1.5b)

There are two features of note in the preceding matrices: first, the elements of the submatrix spanning i, j = 1, 2 are zero for all k. Recall that these indices correspond to the unoccupied d_{z^2} and $d_{x^2-y^2}$ orbitals, which can now be safely ignored. The second notable feature is the submatrix associated with the t_{2g} states for L_z :

$$L'_{z} = \hbar \begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & i \\ 0 & -i & 0 \end{pmatrix}$$
(1.6)

Solving the eigenvalue problem for such a matrix yields $\epsilon = 0, \pm 1\hbar$, the expected result for l = 1. Thus, there is an *effective* angular momentum of $\tilde{l} = 1$. Since $m_l = \pm 2\hbar$ is not a solution, the orbital angular momentum is said to have been partially quenched. The spin-orbit calculation now involves an interaction with the form $H_{LS} = \tilde{\lambda}(\tilde{l} \cdot \mathbf{S})$ and in turn an associated effective total angular momentum given as $\tilde{J} = \tilde{l} + \mathbf{S} \equiv J_{\text{eff}}$. Solving the spin Hamiltonian for this configuration results in the t_{2g} triplet splitting into a $J_{\text{eff}} = \frac{3}{2}$ doublet and a $J_{\text{eff}} = \frac{1}{2}$ singlet, with an energy gap of $\frac{3}{2}\tilde{\lambda}$ [37, 39, 40]. The associated eigenvectors for the $J_{\text{eff}} = \frac{1}{2}$ state are given in Eq. 1.7 [41].

index	label	$Y_l^{m_l}$ basis expression
1	d_{z^2}	Y_2^0
2	$d_{x^2-y^2}$	$\frac{i}{\sqrt{2}}\left(Y_2^{\bar{2}} - Y_2^2\right)$
3	d_{xy}	$\frac{1}{\sqrt{2}}\left(Y_2^{\bar{2}}+Y_2^2\right)$
4	d_{xz}	$\frac{1}{\sqrt{2}}\left(Y_2^{\bar{1}} - Y_2^1\right)$
5	d_{yz}	$\frac{i}{\sqrt{2}}\left(Y_2^{\bar{1}}+Y_2^1\right)$

Table 1.1: d orbital wavefunctions in the basis of the spherical harmonics $Y_l^{m_l}$

$$|J_{\text{eff}} = \frac{1}{2}, \ m_{J_{\text{eff}}} = \pm \frac{1}{2} \rangle = \frac{1}{\sqrt{3}} \left(\pm |xy\rangle |\pm\rangle + |yz\rangle |\mp\rangle \pm i |xz\rangle |\mp\rangle \right)$$
(1.7)

Now, the $J_{\text{eff}} = \frac{3}{2}$ states are completely filled (4 e^-), and the problem is reduced to a single $J_{\text{eff}} = \frac{1}{2}$ band, which is half filled by the last electron. In spite of all the corrections from crystal fields and spin-orbit interactions, such a configuration still suggests a conductor, and so a final energy scale must be accounted for. Because only the single $J_{\text{eff}} = \frac{1}{2}$ band need be considered, the Hubbard model is applicable to treat electron-electron interactions. For purposes of illustration the one-dimensional Hubbard Hamiltonian in reproduced in Eq. 1.8 [42]:

$$H = H_t + H_U$$

$$H = -t \sum_{\langle ij \rangle} c^{\dagger}_{i,a} c_{j,a} + U \sum_i n_{i\uparrow} n_{i\downarrow}$$
(1.8)

From this expression the key feature of the Hubbard model can be inferred quite easily: namely, the competition between the band-like hopping term t (favoring a conducting state) and a correlation term scaled by U (favoring an insulating state). A rigorous application of the full Hubbard Hamiltonian to the $J_{\text{eff}} = \frac{1}{2}$ state is beyond



Figure 1.3: Energy level schematic demonstrating the various splittings of the 5*d* energy levels leading to the $J_{\text{eff}} = \frac{1}{2}$ state. Levels are populated with electrons in the final (farthest right) configuration.

the scope of this section, but it is the case [11, 26] that the $J_{\text{eff}} = \frac{1}{2}$ band is sufficiently narrowed (as a result of spin-orbit effects) that even quite modest U is enough to form an upper and lower Hubbard band. With the lower Hubbard band completely filled, and the upper Hubbard band empty, an insulating state is finally attained.

These various interactions and splittings are summarized schematically in Fig. 1.3. This model of a spin-orbit Mott (SOM) state, first proposed by Kim, et al. in their seminal work detailing the argument for this novel quantum state in Sr_2IrO_4 [26], has proven to be quite robust. In the years since, it has been employed as a theoretical framework for describing a number of iridates such as $Sr_3Ir_2O_7$ and $CaIrO_3$ [11, 43] as well as non-iridium-based compounds like α -RuCl₃ and Rb₂RhF₆ [44, 45].

Bulk electronic transport measurements, mentioned earlier [29, 30], reveal an



Figure 1.4: (a) Temperature dependence of the electrical resistivity and (b) irreversibility of magnetic susceptibility in $Sr_3Ir_2O_7$. Data in (b) collected under H = 800 Oe. (c) Magnetic molar susceptibility of $Sr_3Ir_2O_7$ showing a weak linear dependence above T_N . Data was collected while cooling under an applied H = 20 kOe.

insulating ground state in $Sr_3Ir_2O_7$ on the order of $10^2 \Omega$ m at low temperature ($\approx 10 \text{ K}$), an example of which can be found in Fig. 1.4 (a). There are two inflection points in resistivity, one near the onset of magnetic order at $T_N = 280 \text{ K}$, and a second at $T^* = 70 \text{ K}$. This second transition, seen in both conventional zero-field transport as well as magnetotransport under 9 T is consistent with a field-coupled order parameter freezing out below T^* [46].

1.4 Bulk Magnetism and Static Spin Structure

With the electronic configuration established, the question of magnetic properties in $Sr_3Ir_2O_7$ is next to be considered. Initial bulk magnetization reports describe the onset of some net ferromagnetic moment near T = 280 K, indicated by an increase from zero of the irreversibility (FC-ZFC) [30] as shown in a representative plot dataset in Fig. 1.4 (b). A second feature, a sharp change in the slope of magnetization, was observed near ≈ 220 K [46, 47]. The low temperature behavior (a positive slope in the irreversibility below 50 K) suggests diamagnetic behavior of some sort, but the slope in this regime can be made to change sign by the application of an ≈ 0.5 T magnetic field, indicating this behavior is only metastable. At the other extreme, magnetic susceptibility above T_N surprisingly does not show any Curie-like behavior, but instead a linear response with very small slope persists up to 400 K [48], and shown in Fig. 1.4 (c) (an explanation of which is offered in Chapter 6). There is also a strong anisotropy of the magnetization- when H is parallel to the long axis of the unit cell. An explanation for this anisotropy is posited in Chapter 4.

Under high field (7 T) though, a Curie-Weiss fitting of the susceptibility is possible and indicates an effective moment of $0.69 \,\mu_{\rm B} \,{\rm Ir}^{-1}$ [30], well short of the expected $1.73 \,\mu_{\rm B} \,{\rm Ir}^{-1}$ value for an $S = \frac{1}{2}$ system.⁷ A similar discrepancy is found in the measured ordered moment value of $0.037 \,\mu_{\rm B} \,{\rm Ir}^{-1}$ [47], a far cry from the $1 \,\mu_{\rm B} \,{\rm Ir}^{-1}$ for a single unpaired electron. These two observations are reminiscent of a canted anti-

⁷This expectation, expressed as $\mu_{\text{eff}} = g_J \sqrt{(J(J+1))} \mu_B$, derives from the Curie law [49] and yields 1.73 μ_B for $g_J=2$, $J=\frac{1}{2}$. That this is not the observed value is hardly surprising though- in reality the calculation should reflect the 'effective' nature of the total angular momentum by using a modified g-factor, namely $g_{\tilde{J}}$, discussed elsewhere [37].

ferromagnet, wherein much of the local moment is reduced due to antiferromagnetic (AF) ordering, but coordinated rotations of the moments result in a net moment. This is the case for Sr_2IrO_4 , where the direction of the Ir^{4+} moments are locked to the orientation of the oxygen octahedra in the limit of cubic symmetry [50, 51].

Scattering studies were undertaken to begin to identify the spin structure responsible for the bulk effects. Initial resonant elastic x-ray work and group theoretical treatments modeled a canted AF ordering with an in-plane moment (as is the case for Sr_2IrO_4 [47], but subsequent efforts revealed $Sr_3Ir_2O_7$ possesses a fundamentally different static spin structure. The additional application of polarization analysis to resonant x-ray scattering has yielded a wealth of information regarding the magnetic structure [16]. A number of crystallographically forbidden peaks, of the forms⁸ (10l)for even l and (01l) for odd l, were shown be temperature dependent order parameters with onsets corresponding to $T_{\rm N}$, suggesting they are magnetic Bragg peaks. By constraining the azimuthal angle such that the in-plane axis (100) is within the scattering plane and showing that all of the scattered intensity resides in 'flipped' polarization channel for a (10l) reflection, the magnetic moment is constrained to lie in the *ac*-plane. If instead the azimuthal angle constrains (010) to be in the scattering plane, a similar measurement of (01l) demands that the moment lie entirely in the *bc*-plane. Taken together, the only configuration which satisfies both of these conditions results in the Ir^{4+} moments pointing along the *c*-axis. The exact character of the magnetic coupling is implied by the nature of the observed bilayer structure

⁸Discussing scattering experiments performed on $Sr_3Ir_2O_7$ presents something of a challenge with regard to indexing, as the system has been described using tetragonal, orthorhombic, and monoclinic unit cells (see Chapter 4). Every effort will be made to specify which structure pertains to a given set of indices, though when in doubt the reader is encouraged to consult the referenced original work. For this section, indices correspond to the orthorhombic structural solution using *Bbcb* (space group No. 68).
factor in this system.

$$I = A|F_{\rm Ir}(Q)|^2 \sin^2\left(\frac{\pi ld}{c} + \phi\right) \tag{1.9}$$

Eq. 1.9 indicates that the intensity of a magnetic Bragg peak is weighted by an overall amplitude A, the magnetic form factor of iridium $F_{\rm Ir}$ at the corresponding Q, and the bilayer structure factor [52, 53]. This factor modulates the intensity of magnetic peaks with a periodicity of ld/c, where c is the length of the c-axis ($c \approx 20.9$ Å), and d is the distance between neighboring iridum atoms within a bilayer, along the c-axis ($d \approx 4.1$ Å). The additional phase ϕ takes only two values and determines the character of the interaction: $\phi = 0$ if the interaction between the constituent layers of the bilayer is antiferromagnetic, and $\phi = \pi/2$ if this interaction is ferromagnetic. A plot of magnetic Bragg peak intensities, measured by REXS, strongly aligns with the $\phi = 0$ version of Eq. 1.9, providing an unambiguous measure of the antiferromagnetic nature of Sr₃Ir₂O₇; specifically- a G-type antiferromagnet [16].

Further evidence of this spin structure is also observed via elastic neutron diffraction [46]. A survey of the magnetic Bragg peaks found signal at (10l) reflections for l =even and l =odd, the latter of which is crystallographically forbidden in *Bbcb*. Previous studies suggested the likely presence of multiple magnetic domains [16, 47], but such an picture fails to explain the temperature dependence observed by Dhital, et al. in which intensity at forbidden reflections persists *above* the Néel temperature $T_{\rm N}$. Polarized neutron diffraction was used in a separate work to show representative members of this group of forbidden peaks to be structural in their origin [54], and are in fact allowed under a more complete structural solution [55] detailed in Chapter 4. Nonetheless, if the difference in integrated intensities for the (10l) peaks at T = 315 K and T = 100 K is considered, the contribution purely from the magnetic



Figure 1.5: Diagram indicating the spin structure of G-type antiferromagnetic ordering of Ir^{4+} sites in $Sr_3Ir_2O_7$, adapted from [46].

ordering can be evaluated. These data were successfully fit using a two-domain model in which the Ir^4 + moments were oriented along the *c*-axis, offering further evidence that such a spin structure, depicted in Fig. 1.5, is correct.

1.5 Spin Dynamics

Attempting to probe magnetic excitations in the iridates presents several challenges, since the typical avenue for such pursuits has historically been inelastic neutron scattering. $Sr_3Ir_2O_7$ synthesis methods (detailed in Chapter 3) limit potential sample masses to just a few milligrams per crystal, while unfortunately INS can typically require several grams of material. Beyond this, neutron scattering with Ir samples is already especially challenging due to the element being one of the strongest absorbers of neutrons on the periodic table [56]. Even if sufficient material could be obtained, the energy scales of magnetic interactions in $Sr_3Ir_2O_7$ (~ 100 meV) are kinematically difficult to access given the neutron cross-section [57] and the nature of the Ir 5*d* form factor [58], as well as the small moment size further reducing absolute magnetic signal intensity.

Given this, recent advances in resonant inelastic x-ray scattering (RIXS) offer an attractive alternative (more details on the technique can be found in section 2.4.2). The first work on the RP iridates using RIXS was done for Sr_2IrO_4 to map the dispersion of magnons as well characterizing in further detail a more exotic so-called 'spin-orbit exciton' ascribed to excitations of holes between the $J_{\text{eff}} = \frac{1}{2}$ and $J_{\text{eff}} = \frac{3}{2}$ bands of a single Ir-site [59, 60]. Magnetic excitations in this system are quite well described by a pure Heisenberg model with coupling constants J = 60 meV, J' = -20 meV, J'' = 15 meV corresponding to the nearest, next-nearest, and next-



Figure 1.6: Diagram depicting magnetic exchange coupling J's included in the the Hamiltonian terms of Eq. 1.10. Figure adapted from [61].

next-nearest neighboring Ir-sites respectively. Similar measurements on Sr₃Ir₂O₇ are notable for their incompatibility with a Heisenberg description- here a significant magnon gap ($\approx 92 \text{ meV}$) is found despite the large magnon bandwidth ($\approx 70 \text{ meV}$). The gap is also notable in comparison to the energy scale of the bulk antiferromagnetic transition ($k_{\rm B}T_{\rm N} \approx 25 \text{ meV}$), suggesting that thermal fluctuations of the Ir⁴⁺ moments alone at this temperature would not be sufficient to completely disrupt the AF order [61]. The dispersion was modeled using a Hamiltonian which includes isotropic magnetic exchange terms associated with nearest neighbor couplings (see Fig. 1.6) as well as accounting for anisotropic superexchange interactions. The anisotropic superexchange interaction can be expressed as two terms, one symmetric and the other anitsymmetric. The symmetric contribution (Γ) is referred to as the pseudodipolar coupling,⁹ while the antisymmetric term (D) is known as the Dzyaloshinsky-Moriya interaction. Excitations in this model are characterized as a superposition of linear spin wave (LSW) modes. Due to the bilayer nature of the system terms weighting the strength of these interactions were included for both inand out-of-plane directions such that $H = H_{ab} + H_c$, the details of which are found in Eq. 1.10. The order of the brackets containing ij indicates a summation over nearest $\langle ij \rangle$, next-nearest $\langle \langle ij \rangle \rangle$, or next-nearest neighbors $\langle \langle \langle ij \rangle \rangle \rangle$, as seen in Fig. 1.6.

$$H_{ab} = \sum_{\langle ij\rangle} \left[J\vec{S}_i \vec{S}_j + \Gamma S_i^z S_j^z + D(S_i^x S_j^y - S_i^y S_j^x) \right] + \sum_{\langle \langle ij\rangle \rangle} \left[J_2 \vec{S}_i \vec{S}_j \right] + \sum_{\langle \langle ij\rangle \rangle \rangle} \left[J_3 \vec{S}_i \vec{S}_j \right]$$
$$H_c = \sum_i \left[J_c \vec{S}_i \vec{S}_{i+z} + \Gamma_c S_i^z S_{i+z}^z + D_c (S_i^x S_{i+z}^y - S_i^y S_{i+z}^x) \right] + \sum_{\langle ij\rangle} \left[J_{2c} \vec{S}_i \vec{S}_{j+z} \right]$$
(1.10)

The model successfully captures the general features of the magnon dispersion¹⁰ with magnetic exchange constants of J = 93 meV, $J_2 = 11.9 \text{ meV}$, $J_3 = 14.6 \text{ meV}$, and $J_c = 25.2 \text{ meV}$, while $\theta = 37^{\circ}$. The relative strengths of extracted values for the pseudodipolar terms ($\Gamma = 4.4 \text{ meV}$, $\Gamma_c = 34.3 \text{ meV}$) are offered both as the driving mechanism of c-axis magnetic anisotropy and the source of the anomalously large magnon gap in the system.

Nonetheless, several questions remain as to the validity of such a model. With nine free parameters (five J's, two Γ 's, and two D's, none of which are restrained by any applied theoretical limits in fitting) describing the general shape of the dispersion

⁹This nomenclature refers to the term's mathematical form being $\propto (\cos^2 \phi + \frac{1}{3})$, just as in a typical dipole-dipole interaction. In the case of the true antisymmetric superexchange interaction though, the scaling constant is between 100 and 1000 times stronger than the standard interaction between two magnetic dipoles, albeit with substantially shorter range [62].

¹⁰Dispersion data from [61] and a fit using the proposed model are both reproduced in Fig. 6.1 on page 125.

is to be expected, but a model of linear spin waves additionally enforces a symmetry of the dispersion about the in-plane momentum transfer $\mathbf{q} = (\pi/2, \pi/2)^{11}$ which is incongruous with measurement. Of further concern is that the model predicts two (optical and acoustic) magnon modes, yet only a single feature is observed in the spectra and is not well-matched by some supposed convolution of the two branches. A successive investigation also notes that at face value a dominant magnon mode in a bilayer-type structure has previously been ascribed to a system of weakly coupled spin dimers [63–66].

After separately calculating the RIXS scattering cross-section for different manifestations of the $J_{\text{eff}} = \frac{1}{2}$ state, Moretti Sala, et al. next applied a bond-operator mean-field theory approach to the problem of magnetic interactions in Sr₃Ir₂O₇ [63, 67]. The Hamiltonian is reproduced in Eq. 1.11, with the labeling convention of the isotropic J's remaining the same (Fig. 1.6), where indices are such that the first (l) designates which half of the bilayer the spin resides in, and the second (i, j) indexes a spin within a layer. The pseudodipolar and Dzyaloshinsky-Moriya terms are also included (the second and third terms in the J-weighted summation), and are indirectly scaled by θ , a parametrization of the relative strength of these anisotropic interactions.

$$H = J \sum_{\langle ij \rangle, l} \left[\cos\left(2\theta\right) \vec{S_{li}} \cdot \vec{S_{lj}} + 2\sin^2\left(\theta\right) S_{li}^z S_{lj}^z - \epsilon_i \epsilon_l \sin\left(2\theta\right) \left(\vec{S_{li}} \times \vec{S_{lj}}\right) \cdot \hat{e}_z \right] + J_2 \sum_{\langle\langle ij \rangle\rangle, l} \left[\vec{S_{li}} \cdot \vec{S_{lj}} \right] + J_3 \sum_{\langle\langle\langle ij \rangle\rangle\rangle, l} \left[\vec{S_{li}} \cdot \vec{S_{lj}} \right] + J_c \sum_i \left[\vec{S_{1i}} \cdot \vec{S_{2i}} \right]$$
(1.11)

¹¹For discussion of RIXS analysis, positions in momentum-space are indexed to a tetragonal setting scaled by π (for convenient comparison with cuprate RP compounds). Indices here are related to the previous orthorhombic setting by $H_t = \pi(H_o + K_o)$, $K_t = \pi(-H_o + K_o)$.

This treatment yields three (two degenerate transverse, one longitudinal) magnon modes whose shapes are not constrained to be symmetric about $(\pi/2, \pi/2)$. The researchers were able to successfully resolve both magnon branches and fits to the model¹² gave coupling constants of J = 26 meV, $J_2 = -15 \text{ meV}$, $J_3 = 6 \text{ meV}$, and $J_c = 90 \text{ meV}$. This is somewhat striking in a simplistic comparison between the dominant in- and out-of plane terms J/J_c . This ratio favors the inter-layer coupling here, yet surprisingly the prior work of Kim found that the intra-layer coupling was the primary driver of the large spin-gap and anisotropy.

With two different treatments of datasets derived from nearly identical chemical compounds, this proves a rather unsatisfying situation. The work comprising Chapter 6 represents an attempt to resolve this discrepancy by testing which model proves more descriptive of RIXS spectra collected from doped samples.

1.6 Relationship to the Cuprates

A common criticism of 'pure' research is that there is no terminal goal- no useful application resulting from the work. Often, unfortunately, knowledge for knowledge's own sake is insufficient justification for an enterprise. Following in this (somewhat cynical!) vein, one might level the question: *"What tangible benefit would be derived from a complete understating of the RP iridates?"* Aside from proving a rich and challenging intellectual pursuit, the RP iridates are very small, very costly to produce,¹³ and only exhibit their most interesting properties at liquid-He tempera-

 $^{^{12}\}mathrm{Again},$ dispersion data from [63] and a fit using the bond-operator model are both reproduced in Fig. 6.1 on page 125.

¹³Given the commercial price of IrO_2 at the time of press, it is estimated that each batch of $Sr_3Ir_2O_7$ crystals contains more than \$225 worth of materials and produces only 30-40 $\approx 1 \text{ mg}$ crystals.



Figure 1.7: Generic phase diagram of doping dependence in the cuprate family compounds. Figure reproduced directly from [70].

tures. Thus, such materials do not lend themselves well to any obvious engineering applications.

Study of the iridates is partially justified then, by virtue of their relationship to the cuprates. They are also members of the Ruddlesden-Popper class of materials, and ergo isostructural (to varying extents) to the iridates discussed in this work [68]. The un-doped parent compounds of the cuprates are also antiferromagnetic Mottdriven insulators and their electronic properties also derive from d orbitals. For the n = 1 case they are even well-described by the Heisenberg model, as is Sr₂IrO₄ [69]. A generic phase diagram for the cuprates is reproduced in Fig. 1.7, showing that upon chemical doping a host of interesting phases can be accessed, not least among them high- T_c superconductivity.

It follows then, at least in a hand-waving sense, that perhaps there may be

similarly exotic (perhaps even useful!) phases lurking somewhere within the doping/temperature phase diagram of the RP iridates. This is predicted more rigorously by a mapping of the $J_{\text{eff}} = \frac{1}{2}$ pseudospin space onto a variant of the Hubbard model used to describe the Cu-based family of high T_c materials [66]. The authors describe an analogy to be drawn between hole-doping in the cuprates and electron-doping in the iridates. It is the disappointing duty of this author to relate that at time of press no report of a bulk manifestation of superconductivity, be it resistance-free electrical transport or the Meissner effect, has yet emerged.

A complicating factor has been the RP iridates' resistance to electron doping via $La^3 + substitution$. Sr_2IrO_4 has been synthesized with concentrations as high as x = 0.06, while $Sr_3Ir_2O_7$ has been pushed in this work as high as x = 0.08 [71, 72] with no evidence of superconductivity. This is in contrast to compounds like $La_{2-x}Sr_xCuO_4$ where superconductivity has been observed with doping as low as $x \approx 0.025$ [73]. Even at the dopant levels already achieved in iridates however, the analogy between the two systems appears to hold strong. La-doped $Sr_3Ir_2O_7$ samples have been shown to exhibit characteristic photoemission spectra (Fermi-arcs) often associated with the pseudogap phase in the cuprates [74, 75]. Similar arcs have also been observed in surface doped Sr_2IrO_4 , and when driven to the highest doping concentrations using this technique, collapse into a *d*-wave point gap [76, 77].

The experimental realization of this *d*-wave gap has been met with much excitementits emergence is the spectroscopic signifier in the cuprates of the transition from the pseudogap phase (see Fig. 1.7) into the so-called 'superconducting dome'. It provides the strongest evidence yet that the high- T_c phenomenology may actually be realized in the iridate family. Obviously, a true thermodynamic measurement (resistivity, magnetization, heat capacity) would be preferable, but these techniques are inaccessible due to the nature of the doping mechanism. The surface-doping can only survive under ultra-high vacuum and low temperatures, and is easily destroyed by ambient temperatures, somewhat nullifying one of the key material properties of the oxides.

Considering this, pushing the boundaries of chemical doping and rigorously characterizing their effects still appear highly relevant pursuits. With a complete understanding of the true mechanism of high- T_c still outstanding, realizing this phase in a number of different systems will help to further narrow the list of explanatory variables.

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Chapter 2

Measurement Techniques

A wide array of experimental techniques and methods were employed to obtain the data presented in this work. Several are quite common in most experimental condensed matter physics laboratories and will be treated only very briefly here. The scattering techniques and motivating theory, however, will be described in greater detail as they are particularly powerful probes whose application is nontrivial, and the results of which provided crucial support to the conclusions of this work.

2.1 Electrical Resistivity

The humble electronic transport measurement is mentioned in passing here: a known excitation source of current I is applied to the sample, and the potential drop V across the sample is measured. Ohm's eponymous law is then leveraged to extract the resistance, R. Of more interest typically is the intrinsic quantity resistivity ρ , related to absolute resistance as shown in Eq. 2.1 by a geometric factor comprised of the length L of sample across which the voltage drop is measured, and the cross-sectional area A through which the current flows.

$$V = IR \qquad \qquad \rho = \frac{RA}{L} \tag{2.1}$$

Most often, the dependence of ρ on some external parameter is the true objective in such a measurement, such as the temperature dependence $\rho(T)$ or the magnetoresistance $\rho_T(B)$. Unlike a quick measurement with a multimeter, however, a precise measurement of resistivity requires a slightly more involved setup. A multimeter uses the same conductor to supply the excitation current and to measure the drop in potential. A quick application of Kirchhoff's circuit laws reveals such a measurement returns not only the resistivity of the sample in question, but also the wires used in series with the sample to perform the measurement. In the case that $R_{\text{samp}} \gg R_{\text{wire}}$, this is perfectly acceptable, but generally it is preferred to avoid this, as such a condition is not true generally.

A so-called 'four-probe' resistance measurement (schematic depicted in Fig. 2.1) neatly solves this problem by supplying the excitation current via separate terminals from the voltage drop measurement [1]. An adroit placement of the voltage leads



Figure 2.1: A four-probe lead configuration; for a known current source I, the resistance R can be determined by measuring the potential difference V across the distance L. The resistivity is computed as in Eq. 2.1 using L and the cross-sectional area $A = w \cdot t$ as depicted above.

directly *onto* the sample itself means no contribution to the drop from the resistance of the wires is measured- though care must be taken to correctly note the geometric factors L and A for the measurement to be accurate. For samples with ill-defined or arbitrary geometry, a van der Pauw measurement, detailed elsewhere [2], may be required.

2.2 SQUID Magnetometry

To gain insight into the behavior of the magnetic moments in a system, bulk magnetometry is often the first measurement attempted: sample preparation is relatively straightforward, the measurement is non-destructive, and many mature commercial magnetometry solutions are available. The principle of operation is basic enoughreproduced below are Faraday's law and the magnetic field produced by an ideal dipole moment m [3]:

$$\boldsymbol{\nabla} \times \boldsymbol{E} = -\frac{\partial \boldsymbol{B}}{\partial t} \qquad \qquad \boldsymbol{B}_{\text{dip}}(\boldsymbol{r}) = \frac{\mu_0}{4\pi} \frac{1}{r^3} [3(\boldsymbol{m} \cdot \hat{\boldsymbol{r}})\hat{\boldsymbol{r}} - \boldsymbol{m}] \qquad (2.2)$$

The magnetometer translates a sample through a fixed loop which induces voltage in said loop resulting from the change in magnetic flux as the field from the sample dipole moment m varies (at the site of the loop) in time. Measuring how the voltage changes and fitting the response curve allows the net ferromagnetic moment of the sample to be determined [4].

In the case of materials measured in this work, the net moment is quite smallon the order of 10^{-6} emu to 10^{-7} emu. The small induced voltages from such tiny moments are difficult to detect, and thus necessitate the sensitivity of a SQUID (Superconducting QUantum Interference Device)-based measurement loop to properly resolve.

A full-featured commercial system will not only automatically translate the sample and fit the response, but also provide environmental control of both applied magnetic field and temperature. Magnetometry measurements generally consist of collecting net-moment m(T) or m(H) curves and reconstructing quantities such as magnetization M or susceptibility χ .

Despite the ease with which such data is collected, the interpretation is often nontrivial. While relatively simple magnetic systems such as ferromagnets, antiferromagnets, paramagnets have well-defined signatures in the temperature dependence of their bulk susceptibility or M(H) curves, they are the exception. For systems that are not well-characterized, bulk susceptibility on its own can present something of a mystery since it only relates the behavior of the *net* moment. Systems like canted antiferromagnets with (seemingly!) anomalously low net moments, or disordered glassy systems for example are difficult to identify by bulk magnetometry alone.

In such cases, additional measurements can be necessary. Often a local probe such as μ SR (where the data correspond to the magnitude and direction of the *local* magnetic field at a particular muon stopping site within the crystal structure) can be a helpful compliment to magnetometry in order to construct a more complete description of a magnetic state. Conversely, other bulk probes can serve this function as well, as will be discussed in subsequent sections on x-ray and neutron scattering.

2.3 Neutron Scattering

2.3.1 Introduction to Neutron Scattering

The discovery of the neutron in 1932 opened the door to a vast array of invaluable experimental techniques capable of probing the structure and dynamics of matter across a wide range of length scales. Some words are spent here discussing how such an unassuming particle ends up proving so useful. As an uncharged particle, neutrons can penetrate deep into materials because there is no Coulomb repulsion from either the protons or electrons- thus, the scattering mechanism is due instead to nuclear forces. On the other hand, the neutron does possess a spin ($s = \frac{1}{2}$), and thus interacts with magnetic materials possessing unpaired electrons [5].

Because the energy of a neutron is given by $E = \hbar^2 k^2/2m$, thermal neutrons (where $E_n \approx k_B \cdot 300 \text{ K}$) have wavelengths on the order of just a few Angstrom (Å) [6]. Recall that Bragg's Law relates the scattering angle θ and the spacing d between regular planes of atoms to the wavelength λ of the incident radiation by $n\lambda = 2d\sin(\theta)$, for comparable λ and d. Since the typical length-scale of inter-atomic distances in most condensed matter systems is on the order of a few Å, thermal neutrons clearly are an ideal probe to leverage scattering techniques to study such systems.¹

2.3.2 Nuclear Bragg Scattering

A neutron scattering experiment, at its most simplistic, consists of placing a sample within a neutron beam, and counting how many neutrons are scattered from the sample. For a given incident beam flux density of Φ ,² we can already define the *total* scattering cross-section σ_{total} as

$$\sigma_{\text{total}} = \frac{\text{total no. of neutrons scattered per 1s}}{\Phi}$$
(2.3)

This counting is accomplished by various types of detectors, but most detectors can not simultaneously measure the full solid angle Ω , so it falls to the experimenter to decide where (in space) to place the detector and commence counting. Taking the sample as the origin, such a detector position can be defined in standard polar coordinates r, θ , and ϕ . For sufficiently large r, the coverage area of the detector is just $d\Omega$, some fraction of the full solid angle. Now the *differential cross-section* can be defined:

$$\frac{d\sigma}{d\Omega} = \frac{\text{no. of neutrons scattered into } d\Omega \text{ per 1 s}}{\Phi \ d\Omega}$$
(2.4)

¹The discussion which follows roughly tracks the first few chapters of Ref. [5] and to a lesser extent Ref. [6] to quickly build up the fundamental theory of neutron scattering.

²Neutron flux density Φ has units of ['number of neutrons' / (area · time)], thus all the crosssections presented here have units of area.

If the detector has some means of energy discrimination, a final cross-section called the *partial differential cross-section* is given as

$$\frac{d\sigma^2}{d\Omega \ dE'} = \frac{\text{no. of neutrons scattered into } d\Omega \text{ per 1 s having } E' < E < E' + dE'}{\Phi \ d\Omega \ dE'}$$
(2.5)

Clearly these quantities are related to one another- integrating Eq. 2.5 with respect to energy recovers Eq. 2.4, where all energies contribute:

$$\int_0^\infty \left(\frac{d\sigma^2}{d\Omega \ dE'}\right) dE' = \frac{d\sigma}{d\Omega} \tag{2.6}$$

...and integrating Eq. 2.4 over the full solid angle Ω yields Eq. 2.3.

$$\int_{\text{all space}} \left(\frac{d\sigma}{d\Omega}\right) d\Omega = \sigma_{\text{total}} \tag{2.7}$$

The cross-sections are defined here to connect the somewhat involved mathematics which follow to the real quantities measured in a laboratory setting. Efforts will be made to periodically draw attention to important features as the cross-sections are now developed. An application of Fermi's Golden rule [5], which provides an expression for the probability of an incident neutron with wave vector \mathbf{k}' scattering into a state with wave vector \mathbf{k} , gives the differential cross-section the form

$$\frac{d\sigma}{d\Omega} = \left| \langle \boldsymbol{k}' | \, \hat{V} \, | \boldsymbol{k} \rangle \right|^2 \tag{2.8}$$

It is known empirically that scattering of neutrons from nuclei is an isotropic process [6]. The form of \hat{V} which satisfies this condition for a single neutron-nucleus scattering event is a scaled delta-function, referred to as the Fermi pseudo-potential: $\hat{V} \propto b \ \delta(\boldsymbol{r} - \boldsymbol{R})$, where \boldsymbol{R} is the position of the nucleus and b is a complex constant, independent of energy, called the scattering length.

The expression given in Eq. 2.8 can now be evaluated for scattering from a single, fixed nucleus at $\mathbf{R} = 0$. The incoming neutron beam, directed along the z-axis, is treated as a plane wave with wavenumber k, such that $\psi_{\text{inc.}} = e^{i\mathbf{k}\cdot\mathbf{r}}$ and similarly, $\psi_{\text{scat.}} = e^{i\mathbf{k}\cdot\mathbf{r}}$. This then yields,

$$\frac{d\sigma}{d\Omega} = \left| \int_{\text{all space}} \left(e^{-i\boldsymbol{k}'\cdot\boldsymbol{r}} \left(b \ \delta(\boldsymbol{r}) \right) \ e^{i\boldsymbol{k}\cdot\boldsymbol{r}} \right) d\boldsymbol{r} \right|^2 = |b|^2 \tag{2.9}$$

It follows then from Eq. 2.7 that the total cross section in this simple case is just

$$\sigma_{\text{total}} = 4\pi |b|^2 \tag{2.10}$$

The complex component of b is relevant for absorption processes, but for the treatment here, this is assumed to be small. It should be noted that b is not easily calculated for a given nucleus from first principles- it varies somewhat randomly as a function of atomic number and even between various isotopes of the same element.³ Given the abundance of natural occurring isotopes, a reasonable question would be to ask how a distribution of b_i 's within a sample would impact the cross-section.

In this case, the Fermi pseudo-potential is simply modified to be a summation

³While a somewhat unsatisfying situation from the prospective of a complete nuclear forces theory, the 'random' variance of scattering lengths is that gives neutron scattering such a high degree of elemental and isotropic contrast, a very useful experimental result.

over all the nuclei (indexed by l) in the in the sample

Where $\kappa = k - k'$. The resulting differential cross-section for such a pseudo-potential can be reduced to the following

$$\frac{d\sigma}{d\Omega} = \sum_{l,l'} e^{i\boldsymbol{\kappa}\cdot(\boldsymbol{R}_l - \boldsymbol{R}_{l'})} \overline{b_{l'}^* b_l}$$
(2.12)

A careful consideration of the last term in the expression, the average product of two arbitrary scattering lengths, finds $\overline{b}_{l'}^* \overline{b}_l = |\overline{b}|^2 + \delta_{l,l'} \left(\overline{|b|^2} - |\overline{b}|^2 \right)$, which in turn gives the differential cross-section the form-

$$\frac{d\sigma}{d\Omega} = \sum_{l,l'} e^{i\boldsymbol{\kappa}\cdot(\boldsymbol{R}_l - \boldsymbol{R}_{l'})} \left|\bar{b}\right|^2 + \sum_{l,l'} e^{i\boldsymbol{\kappa}\cdot(\boldsymbol{R}_l - \boldsymbol{R}_{l'})} \delta_{l,l'} \left(\overline{|b|^2} - \left|\bar{b}\right|^2\right)$$
(2.13)

The term associated with $|\bar{b}|^2$ is the scattering expected from a uniform system of nuclei each with the same $b_l = \bar{b}$, and is referred to as *coherent* scattering. The second term is the *incoherent* contribution to the cross-section which arises as a result of the random distribution of b_l 's within a sample. Since the b's are constants and their various averages not dependent on any index of the summation, total scattering cross-sections can be defined for each (via Eq. 2.10) as

$$\sigma_{\rm coh} = 4\pi \left(\overline{b}\right)^2 \quad \sigma_{\rm incoh} = 4\pi \left(\overline{(b)^2} - (\overline{b})^2\right) \tag{2.14}$$



Figure 2.2: The scattering geometry for a generic reciprocal lattice illustrating the Bragg condition between incident and scattered wave vectors \mathbf{k}' , \mathbf{k} and the reciprocal lattice vector $\boldsymbol{\tau}$.

Skipping forward, the differential cross section for coherent, elastic $(E_i = E_f)$ scattering from a crystal lattice (comprised of N unit cells, each with volume v_0) at a given reciprocal lattice vector $\boldsymbol{\tau}$ is given by

$$\left(\frac{d\sigma}{d\Omega}\right)_{\text{coh, elst}} = N \; \frac{(2\pi)^3}{v_0} \; \sum_{\boldsymbol{\tau}} \delta(\boldsymbol{\kappa} - \boldsymbol{\tau}) |F_{\text{N}}(\boldsymbol{\kappa})|^2 \tag{2.15}$$

First, it is clear from Eq. 2.15 that the only terms which contribute to this crosssection are those for which $\kappa = \tau$. That is, only momentum exchanges $\kappa = k - k'$ matching a reciprocal lattice vector τ produce a non-zero cross-section. For elastic scattering, the constraint k = k' sets up a simple geometric equality that $\tau = 2k \sin(\theta)$ (see Fig. 2.2). The absolute length of τ is defined in terms of the associated real-space distance d between lattice planes by $\tau = n \frac{2\pi}{d}$ [7], and the wave number k is related to the wavelength λ by $k = \frac{2\pi}{\lambda}$. Substituting these in for the previous expression of τ ...

$$\tau = 2k\sin(\theta)$$

$$n\frac{2\pi}{d} = 2\left(\frac{2\pi}{\lambda}\right)\sin(\theta) \qquad (2.16)$$

$$\Rightarrow n\lambda = 2d\sin(\theta)$$

...recovers the familiar form of Bragg's law.

The other notable feature from Eq. 2.15 is the function $F_{\rm N}(\boldsymbol{\kappa})$, known as the nuclear unit-cell structure factor; it is defined as

$$F_{\rm N}(\boldsymbol{\kappa}) = \sum_{l} \bar{b}_{l} \exp\{i\boldsymbol{\kappa} \cdot \boldsymbol{l}\} \exp\{-W_{l}\}$$
(2.17)

where l denotes the real-space position of an atom, and l indexes all the atoms in the unit cell (the other exponential term, the Debye-Waller factor, accounts for thermal oscillations of the atoms at finite temperatures). It is worth noting that despite the fact that any κ which is equivalent to some τ will satisfy the Bragg condition and produce a non-zero cross-section (that is, non-zero counts registered by a detector oriented in the appropriate geometry), this contribution is *scaled* by the nuclear structure factor, which is generally not the same for every valid κ . Thus, the rate of counts expected to be observed for any valid scattering geometry depends on the specific choice of τ used to satisfy the delta function. This mechanism of scattering from atomic nuclei is how neutrons are used to probe a crystal lattice in order to determine a structural solution for a system of interest.

2.3.3 Magnetic Bragg Scattering

As mentioned previously, the neutron's spin also means it participates in magnetic interactions with unpaired electrons in a sample placed in a neutron beam. A sketch of how this mechanism functions now follows:⁴ The potential of a neutron experiencing the magnetic field from an unpaired electron in the scattering system can be written as the sum of two different components, owing to the intrinsic (spin) and orbital contributions to the total angular momentum of the electron:

$$V_m = -\boldsymbol{\mu}_n \cdot \boldsymbol{B} \propto \boldsymbol{\sigma} \cdot (\boldsymbol{W}_S + \boldsymbol{W}_L)$$
(2.18)

A general form of the partial differential cross-section (Eq. 2.5) can be written in terms of neutron state (denoted by spin state σ and wavenumber k), as well as the energy state of the scattering system (λ):

$$\left(\frac{d^2\sigma}{d\Omega \ dE'}\right)_{\sigma\lambda\to\sigma'\lambda'} = \frac{k'}{k} \left(\frac{m}{2\pi\hbar^2}\right)^2 \left|\langle \boldsymbol{k}', \sigma', \lambda' \right| V_m \left|\boldsymbol{k}, \sigma, \lambda \rangle\right|^2 \delta(E_\lambda - E_{\lambda'} + \hbar\omega) \quad (2.19)$$

Treating just the integration of the spatial coordinate, it can be shown that the contribution from all unpaired electrons in the scattering system (indexed by i) is given by

$$\sum_{i} \langle \boldsymbol{k}' | \boldsymbol{W}_{\mathrm{S}} + \boldsymbol{W}_{\mathrm{L}} | \boldsymbol{k} \rangle = (4\pi) \sum_{i} \exp\{i\boldsymbol{\kappa} \cdot \boldsymbol{r}_{i}\} \left[\hat{\boldsymbol{\kappa}} \times (\boldsymbol{s}_{i} \times \hat{\boldsymbol{\kappa}}) + \frac{\mathrm{i}}{\hbar\kappa} (\boldsymbol{p}_{i} \times \hat{\boldsymbol{\kappa}}) \right]$$
(2.20)
= $(4\pi) \boldsymbol{Q}_{\perp}$

⁴Again, this line of inquiry is sourced from Refs. [5], [8], and [9]- specifically in this case the chapters discussing elastic magnetic scattering.

$$\Rightarrow \left(\frac{d^2\sigma}{d\Omega \ dE'}\right)_{\sigma\lambda\to\sigma'\lambda'} = (\gamma r_0)^2 \ \frac{k'}{k} \left|\langle\sigma',\lambda'\right| \boldsymbol{\sigma}\cdot\boldsymbol{Q}_{\perp} \left|\sigma,\lambda\rangle\right|^2 \delta(E_{\lambda} - E_{\lambda'} + \hbar\omega) \quad (2.21)$$

Where $\gamma = 1.913$, and r_0 is the classical radius of the electron, and Q_{\perp} is the component of the magnetic interaction operator normal to κ . To continue evaluating this expression the sum over the final (σ', λ') states is taken, and this result is averaged over the initial states (σ, λ) , which yields

$$\left(\frac{d^{2}\sigma}{d\Omega \ dE'}\right) = (\gamma r_{0})^{2} \frac{k'}{k} \sum_{\alpha\beta} (\delta_{\alpha\beta} - \hat{\kappa}_{\alpha}\hat{\kappa}_{\beta}) \\
\times \sum_{\lambda\lambda'} p_{\lambda} \langle\lambda| Q_{\alpha}^{+} |\lambda'\rangle \langle\lambda'| Q_{\beta} |\lambda\rangle \ \delta(E_{\lambda} - E_{\lambda'} + \hbar\omega)$$
(2.22)

Here, α , β refer to components of σ and p_{λ} represents the probability associated with the system initially being in state λ . If the assumption of unpolarized neutrons scattering from spin-only unpaired moments in a scattering system is made, the elastic differential cross-section, obtained by taking the thermal average $(t \to \infty)$, is

$$\left(\frac{d\sigma}{d\Omega}\right)_{\text{elastic}} = (\gamma r_0)^2 \sum_{\alpha\beta} (\delta_{\alpha\beta} - \hat{\kappa}_{\alpha}\hat{\kappa}_{\beta}) \left\langle Q_{\alpha}(-\boldsymbol{\kappa}) \right\rangle \left\langle Q_{\beta}(\boldsymbol{\kappa}) \right\rangle$$
(2.23)

A moment is now taken to consider the operator Q. It is related to the quantity appearing in Eq. 2.21, Q_{\perp} , by

$$\boldsymbol{Q}_{\perp} = \hat{\boldsymbol{\kappa}} \times (\boldsymbol{Q} \times \hat{\boldsymbol{\kappa}}) \tag{2.24}$$

Q-proper is of general interest because it is essentially a Fourier transform (to within

a constant) of the magnetization density $M(\mathbf{r})$ as see in Eq. 2.25.

$$\boldsymbol{Q} = -\frac{1}{2\mu_{\rm B}}\boldsymbol{M}(\boldsymbol{\kappa}) = -\frac{1}{2\mu_{\rm B}}\int \boldsymbol{M}(\boldsymbol{r})\exp\{i\boldsymbol{\kappa}\cdot\boldsymbol{r}\}d\boldsymbol{r}$$
(2.25)

Since the spins themselves are assumed here to be only from localized electrons, the magnetization density can be represented as a simple summation over the contribution from atomic sites indexed by j located at positions \mathbf{R}_{j} :

$$\boldsymbol{M}(\boldsymbol{R}) = \sum_{j} \boldsymbol{M}(\boldsymbol{R}_{j} + \boldsymbol{r}_{j})$$
(2.26)

Combining this with Eq. 2.25,

$$2\mu_{\rm B}\boldsymbol{Q} = \sum_{j} \exp\{i\boldsymbol{\kappa}\cdot\boldsymbol{R}_{j}\} \int \boldsymbol{M}(\boldsymbol{R}_{j}+\boldsymbol{r}_{j}) \exp\{i\boldsymbol{\kappa}\cdot\boldsymbol{r}_{j}\}d\boldsymbol{r}_{j}$$
(2.27)

If the magnetism at a given site arises purely from spin, the total magnetic moment M_j is proportional to the spin operator S_j , and equal to the integration over all space of the magnetization density,

$$\boldsymbol{M}_{j} = 2\mu_{\rm B}\boldsymbol{S}_{j} = \int \boldsymbol{M}(\boldsymbol{R}_{j} + \boldsymbol{r}_{j})d\boldsymbol{r}_{j}$$
(2.28)

Now a quantity, labeled the *magnetic form factor*, at the jth site, can be defined simply as the Fourier transform of the magnetization density:

$$f_j(\boldsymbol{\kappa}) = \frac{\int \boldsymbol{M}(\boldsymbol{R}_j + \boldsymbol{r}_j) \exp\{i\boldsymbol{\kappa} \cdot \boldsymbol{r}_j\} d\boldsymbol{r}_j}{\int \boldsymbol{M}(\boldsymbol{R}_j + \boldsymbol{r}_j) d\boldsymbol{r}_j}$$
(2.29)

...which allows the $M(\kappa)$ to be written in the form,

$$\boldsymbol{M}(\boldsymbol{\kappa}) = 2\mu_{\rm B} \sum_{j} \boldsymbol{S}_{j} f_{j}(\boldsymbol{\kappa}) \exp\{i\boldsymbol{k} \cdot \boldsymbol{R}_{j}\}$$
(2.30)

This is a generalized form of the magnetic structure factor [10], analogous to the nuclear structure factor shown in Eq. 2.17. Consider, finally, and alternative form of the differential cross-section Eq. 2.23, obtained via Eqs. 2.25, 2.24, and 2.21:

$$\left(\frac{d\sigma}{d\Omega}\right)_{\text{elastic}} = \left(\frac{\gamma r_0}{2\mu_{\text{B}}}\right)^2 |\hat{\boldsymbol{\kappa}} \times (\boldsymbol{M}(\boldsymbol{\kappa}) \times \hat{\boldsymbol{\kappa}})|^2$$
(2.31)

The notation of Eq. 2.31 explicitly demonstrates two important results: first, in an elastic neutron scattering experiment, the contribution to the differential cross-section due to magnetic scattering alone is proportional to the component of magnetization which is normal to $\hat{\kappa}$, squared. It is this mechanism which permits the determination of spin structures, which describe the position and orientation of magnetic moments in the sample and their associated symmetry with respect to the crystal lattice. Second, due to the composition of the magnetic structure factor, namely that it contains the magnetic form factor, the intensity of a given magnetic reflection falls off sharply with an increasing scattering vector. Typically, magnetic Bragg scattering is weaker (by between two to three orders of magnitude) in intensity as compared with nuclear scattering.

A final note: the discussion above treated scatting from moments resulting only from the intrinsic angular momentum of unpaired electrons in the scattering system. As discussed in Chapter 1 however, the RP iridate system is not so simply described. Here, both spin and angular momentum contribute to the $J_{\text{eff}} = \frac{1}{2}$ state. In this case, the elastic differential cross-section, generalized to include scattering from both spin and orbital angular momentum contributions to the total angular momentum, can be written as,

$$\left(\frac{d\sigma}{d\Omega}\right)_{\text{elastic}} = (\gamma r_0)^2 N \left|\frac{1}{2}gF(\boldsymbol{\kappa})\right|^2 \exp\{-2W\} \sum_{\alpha\beta} (\delta_{\alpha\beta} - \hat{\kappa}_{\alpha}\hat{\kappa}_{\beta}) \sum_{l} \exp\{i\boldsymbol{\kappa} \cdot \boldsymbol{l}\} \langle S_0^{\alpha} \rangle \langle S_l^{\beta} \rangle$$
(2.32)

The magnetic form factor, here as $F(\boldsymbol{\kappa})$, is now defined as

$$\frac{1}{2}g F(\boldsymbol{\kappa}) = \frac{1}{2}g_S \mathcal{J}_0 + \frac{1}{2}g_L (\mathcal{J}_0 + \mathcal{J}_2)$$
(2.33)

The spin and orbitals contributions to the Landé splitting factor are listed below, as is the definition for \mathcal{J}_n in terms of the spherical Bessel functions $j_n(\kappa, r)$ and the previously mentioned magnetic density function $\mathbf{M}(\mathbf{r})$.

$$g = g_{S} + g_{L}$$

$$g_{S} = 1 + \frac{S(S+1) - L(L+1)}{J(J+1)}$$

$$g_{L} = \frac{1}{2} + \frac{L(L+1) - S(S+1)}{2J(J+1)}$$

$$\mathcal{J}_{n} = 4\pi \int j_{n}(\kappa, r) \ M(r)r^{2} \ dr$$
(2.34)

2.3.4 Triple-Axis Geometry

The functional form of the nuclear (2.17) and magnetic (2.30) structure factors is belabored in the previous section because of the critical role they play in the ability of an experimenter to resolve a Bragg peak during a scattering experiment.

For the 'rotating crystal' method, the experimental setup is designed to rotate the



Figure 2.3: Example triple-axis spectrometer geometry. Arrow indicates the direction of source beam from the source. Monochromator and analyzer crystals shown in black, research sample in blue, and the detector in red. Base image sourced from the Canadian Neutron Beam Centre [11], which depicts the N5 instrument where much of the work presented in subsequent chapters was conducted.

crystal in a monochromatic beam about an axis $\hat{\psi} \parallel \hat{k}' \times \hat{k}$, with the scattering angle 2θ satisfying the Bragg condition (2.16) while the detector is fixed. Adding up all the counts seen by the detector during this rocking curve is equivalent to integrating the differential cross-section over the bounds of the rotation and produces

$$P = N \frac{V}{v_0^2} \Phi |F(\boldsymbol{\tau})|^2 \frac{\lambda^3}{\sin \theta}$$
(2.35)

Where the subscript of F is intentionally omitted, as this applies to either typical nuclear or magnetic scattering processes, and one need only drop in the appropriate structure factor as required.

A common setup to conduct such a measurement is a triple-axis spectrometer.

To meet the monochromatic beam requirement, a highly ordered crystalline material which the full white-beam (so-called because it contains neutrons of many wavelengths) encounters first is employed (the monochromator). Leveraging the Bragg condition for the lattice spacing of the monochromating crystal, a scattered beam with a narrow distribution of energies can be directed at the sample. This beam scatters from the sample then, as previously described.

An experimenter *could* now choose to measure the flux directly from the sample with their detector, but interpreting such data would be difficult: various inelastic processes (excitation of phonons, magnons, etc.) can also produce scattered neutrons in addition to the elastic ones (and recall that all forms employed for the differential cross-section previously assumed elastic scattering). Thus, it is necessary to exclude neutrons with energies not matching those of the incident beam. This is accomplished with a similar setup to the monochromator, but is labeled as the analyzer to avoid confusion. This experimental design is depicted schematically in Fig. 2.3; the term 'triple-axis' is derived from the three separate scattering configurations required by the measurement. Other neutron optics (such as collimators, filters, and beam-forming slits) are included between the sample and monochromator/analyzer to reduce noise and optimize scattering signal.

2.3.5 Time-of-Flight Technique

Another common scattering technique is the 'Laue method', in which the scattering crystal is stationary but the incident neutrons (originating from a fixed direction) arriving at the sample are of a large continuum of wavelengths. There is a Bragg condition for each family of planes within the sample associated the incident \hat{k} that is



Figure 2.4: Scattering geometry in a time-of-flight Laue implementation. Neutrons represented as colored circles where the shade gives a relative sense of neutron wavelength. The detector is depicted as a point detector, but in a true Laue setup, area detectors covering a significant portion of the full solid angle are employed.

not met in general for a given neutron of wavelength λ . In Laue scattering however, the continuous distribution of incident λ 's containing wavelengths which do satisfy many of these Bragg conditions. The scattered radiation is typically measured by an area-based method of detection (rather than a 'point' detector as is typical in the previously described triple-axis geometry) in order to capture many of the Bragg spots simultaneously; a greater number of diffraction spots permit structural determinations to be executed with greater certainty.

With a polychromatic incident beam however, a problem quickly arises: how to determine which reflection condition to associate with a given Bragg spot on the area detector? One solution to this problem employs time-of-flight neutron scattering. A short, well-defined (in time) pulse of polychromatic neutrons is formed by a 'chopper' at time $t = t_0$ and continues down a known flight path (chopper-to-sample) of length L. Recall that the velocity of an individual neutron within this pulse is related to its de Broglie wavelength [5] by

$$v_{\lambda} = \sqrt{\frac{2E_{\lambda}}{m_n}} = \sqrt{\frac{2}{m_n} \frac{h^2}{2m_n \lambda^2}} = \frac{h}{m_n \lambda}$$
(2.36)

As the neutron pulse travels down the path, the spatial separation between two neutrons of wavelengths λ and λ' after some time t is given by

$$\Delta L_{\lambda,\lambda'} = v_{\lambda'}t - v_{\lambda}t = t\frac{h}{m_n}\left(\frac{1}{\lambda'} - \frac{1}{\lambda}\right)$$
(2.37)

Since the 'cooler' neutrons move more quickly, those with the shortest wavelengths remain at the leading edge of the bunch as it becomes more extended in space while traveling along the flight path. This simple result actually grants energy resolution to the experiment if care is taken to note the time t_1 that the neutron arrives at the detector, and the sample-to-detector distance L_1 . An elastically scattered neutron detected at time t_1 had to travel a distance of $L + L_1$ in time $t_1 - t_0$, which determines its velocity as $v_1 = (L+L_1)/(t_1-t_0)$. Eq. 2.36 can be used to back out the wavelength. This information, along with the known geometry (depicted in Fig. 2.4) for a given position on an area detector, allows the lattice spacing d associated with this reflection to be determined via Eq. 2.16.

If enough of these reflections are collected, they can be systematically processed and the unit cell parameters algorithmically determined. Such a dataset is well-suited for a full structural refinement, particularly in oxides due to the appreciable scattering length of oxygen in neutron scattering. Magnetic scattering is more challenging given the generally weaker intensity of most magnetic peaks (due to the magnetic form factor suppressing peaks with larger scattering vectors) and the resolution limits inherent to the Laue geometry (set by the physical pixel size of the area detectors used). This technique is employed for the analysis discussed in Chapter 4.

2.3.6 Neutron Source Generation Methods

With the reader hopefully now convinced of the utility of the neutron as a scientific tool of investigation into condensed matter systems, a brief moment is taken to discuss the practical matter of how a source of neutrons is obtained. The earliest sources of neutrons were reactor-based due to the excess produced in common fission reactions such as

$${}^{235}_{92}\text{U} + {}^{1}_{0}\text{n} \longrightarrow {}^{139}_{56}\text{Ba} + {}^{94}_{36}\text{Kr} + 3 {}^{1}_{0}\text{n}$$
(2.38)

If the fission reactor vessel has some aperture in it, this would allow some portion of these liberated neutrons ($E \approx 2 \,\text{MeV}$ / neutron) [12] to escape. This raw source can be further conditioned using moderators (to shift the energy distribution of the neutrons) and optics to create a well-defined beam. Absolute beam flux at such facilities is on the order of 10^{14} to 10^{15} (neut. cm⁻² s⁻¹) [12]. For a number of obvious safety reasons, as well as more subtle political ones, nuclear fission reactors are not the most ideal neutron sources. The currently emerging generation of sources is instead based on proton accelerators.

These accelerator-based sources, often referred to as *spallation* sources, produce neutrons via a completely different mechanism. Despite the complex infrastructure required to achieve the result, the concept is simple enough to explain: protons are accelerated to high energies (GeV) and collided with a target composed of some material with heavy nuclei.⁵ The resulting nuclear reactions cause tens of neutrons

⁵For the work discussed in Chapter 4 the source target was composed of mercury atoms.
per incident proton to be ejected.⁶ As before, this raw source can then be optimized for any number of experiments.

The spallation technique has several advantages, chief among them that the same time-averaged flux of the reactor sources can be achieved while requiring an order of magnitude less energy to be dissipated as heat [12]. The pulsed nature of the method also allows the target time to dissipate heat between pulses, and lends itself well to time-of-flight implementations discussed earlier. Despite persisting engineering challenges (particularly with regard to target failure) accelerator-based spallation sources represent a promising next-generation neutron source technology.

2.4 X-Ray Scattering

The motivation for employing x-ray diffraction (XRD) in the study of condensed matter systems stems partially from the difficulty encountered in generating neutrons, described briefly in the previous section. The absolute flux of even the most prolific neutron sources pales in comparison to that of synchrotron x-ray sources. Synchrotron x-ray generation is also a very mature technology, with the newest facilities coming online designated as 'fourth generation light sources' [13]. Synchrotrons leverage the fact that as charged particles experience an acceleration, radiation is emitted. Electrons are given energy via a linear accelerator, and then contained in a storage ring. Bending magnets needed to steer the electrons in a circular path are one means of accelerating the electron bunches to produce radiation, but the more extreme the acceleration, the greater the number of photons emitted. A variety of insertion

⁶These liberated neutrons are referred to as 'spall', after the geological term which referrs to flakes of material chipped off from a larger chunk of a mineral.

devices (undulators, wigglers) are employed to create complex magnetic fields for the electron bunches to traverse, such that they experience rapid oscillations thus and produce even more photon flux.

Fundamentally, x-ray scattering differs from its neutron counter-part by virtue of the scattering mechanism. Whereas neutrons interact with the nuclei via nuclear forces, x-rays interact with the electric fields resulting from the charge distributions of valence electrons in solids. For coherent, elastic scattering of x-rays a quantity called the *atomic scattering factor* given by f can be defined as

$$f = \frac{\text{amplitude of photons scattered by an atom}}{\text{amplitude of photons scattered by a single electron}}$$
(2.39)

This expression is calculated by summing the contribution to the amplitude of scattered radiation from all Z electrons of the in question, expressed mathematically, the (non-resonant) atomic scattering factor associated with classical Thompson scattering [14] is given in Eq. 2.40

$$f_0(\boldsymbol{\kappa}) = \epsilon_s^* \cdot \epsilon_i \int_{\text{all space}} \rho(\boldsymbol{r}) \exp\{i(\boldsymbol{\kappa} \cdot \boldsymbol{r})\} d\boldsymbol{r}$$
(2.40)

Here, $\rho(\mathbf{r})$ is the atomic electron density summed over all occupied electrons states for the atom, and ϵ_i , ϵ_s denote the polarization of the incident and scattered radiation. It is notable that for charge-scattering f is maximized when the incident and scattered polarizations are parallel, as well as that f's absolute magnitude is expected to be proportional to Z in some monotonic fashion based on the contribution of $\rho(\mathbf{r})$.⁷ This is in marked contrast to the seemingly random variance of the atomic scattering

⁷An exact linear proportionality is found in the limit of only forward scattering: $f_0 = \epsilon_s^* \cdot \epsilon_i Z$.

length b seen in neutron scattering. The atomic scattering factor's dependence in this way on atomic number is what makes x-ray scattering more sensitive to atoms of higher Z. The steepness with which f falls off with scattering angle depends on the size of the ion- spatially larger ions induce more destructive interference, and thus decrease more precipitously [15].

Just as for neutrons (Eq. 2.17), there is an analogous structure factor for x-ray scattering:

$$F_{hkl} = \frac{\text{amplitude scattered by atoms in a unit cell}}{\text{amplitude scattered by a single electron}}$$
(2.41)

Which can be defined in terms of the atomic scattering factors of Eq. 2.40, the Miller indices h, k, and l, of the reflection in question, and the fractional coordinates within the unit cell of the atom contributing to the sum, as follows

$$F_{hkl} = \sum_{n=1}^{n=N} f_n(\boldsymbol{\kappa}) \exp\{2\pi i (hx_n + ky_n + lz_n)\}$$
(2.42)

Again, it is the case that scattered beam intensity is proportional to the magnitude of the structure factor squared

$$I_{hkl} \propto |F_{hkl}|^2 \tag{2.43}$$

...thus the utility of classical x-ray scattering for probing the atomic structure of a unit cell (for atoms of appreciable Z, recall) is now apparent. With neutrons however, scattering processes are also sensitive to the total angular momentum of unpaired electrons in magnetic species of atoms; the form of Eq. 2.40 seems to imply that x-ray scattering has no such sensitivity. As it turns out, x-rays can in fact be used to probe magnetism in a materials. At sufficiently high energies a magnetic x-ray form factor, arising from the interaction between the magnetic field of the incoming radiation and the spin and angular momentum of the electrons comprising the scattering system, is given by [16]:

$$f_{\rm mag}(\boldsymbol{\kappa}, \hbar\omega) = (ir_0) \frac{\hbar\omega}{mc^2} \left(\frac{1}{2} \boldsymbol{L}(\boldsymbol{\kappa}) \cdot \boldsymbol{a} + \boldsymbol{S}(\boldsymbol{\kappa}) \cdot \boldsymbol{b} \right)$$
(2.44)

Here, $S(\kappa)$ is a familiar quantity: the Fourier transform of the spin density (2.29) which appeared in the neutron magnetic structure factor. $L(\kappa)$ is an analogous term related to the Fourier transform of the angular momentum density. a, b are vectors whose direction depends on the incident and scattered wave vectors as well as the corresponding polarizations of the radiation and are described elsewhere [14, 17]. Unfortunately, the magnetic scattering due to this mechanism alone is extremely weak, and not an ideal probe. There are other methods by which the incident radiation can couple to unpaired spins in a sample, though. To accomplish this, experiments must be conducted using a particular incident energy, said to be 'on-resonance'. The theory of resonant elastic x-ray scattering is outlined next.

2.4.1 Resonant Elastic X-Ray Scattering (REXS)

In the context of scattering, resonance refers to the capture of some particle in a bound, metastable state which eventually decays, and releases the particle. Obviously in this case the capture is of a photon: when the incident photon's energy matches that of the ΔE between a ground and excited state of some electron in the scattering system, the photon is absorbed and the electron raised to the excited state. Such a configuration is unstable though, and eventually the electron decays back to its ground state, and the photon is emitted. The Hamiltonian associated with this process [18] is given by

$$H = \frac{-e}{mc} \boldsymbol{p} \cdot \boldsymbol{A} + \frac{-e\hbar}{mc} \boldsymbol{S} \cdot (\boldsymbol{\nabla} \times \boldsymbol{A})$$
(2.45)

To properly derive the full resonant elastic x-ray scattering cross-section from Eq. 2.45 is unfortunately beyond the scope of this chapter. Instead, some important results are presented⁸ as motivation for the use of the technique.

First, it must be stated explicitly that the atomic scattering factor presented previously (2.40) is actually but one component of a more general expression [19]:

$$f^{\text{full}}(\boldsymbol{\kappa}, \hbar\omega) = f_0(\boldsymbol{\kappa}) + f'(\hbar\omega) + if''(\hbar\omega) + f_{\text{mag}}(\boldsymbol{\kappa}, \hbar\omega)$$
(2.46)

The first term is that associated with classical Thompson scattering from Eq. 2.40; the second accounts for the varying responses of electrons with different binding energies throughout the occupied shells, and the imaginary term encapsulates the effects of these binding energies dampening the otherwise free electron density; the contribution from Eq. 2.44 is also included for completeness. The sum of the two middle terms is proportional to the conductivity tensor $\overleftrightarrow{\sigma}$ (and the factors themselves related to each other by the Kramers-Kronig relations). The importance of these terms is best understood in the context of the intensity of diffracted radiation measured via REXS:

$$I_{\text{REXS}}(\hbar\omega) \propto \left| \hat{\epsilon}_s^* \cdot \overset{\leftrightarrow}{\sigma} \cdot \hat{\epsilon}_i \right|^2 \tag{2.47}$$

Eq. 2.47 motivates the experimenter to calculate the matrix elements of $\overleftrightarrow{\sigma}$. These can be expressed, for a resonance condition exciting a bound electron from state $|i\rangle$

⁸This section roughly follows the proper derivation and discussion of Ref. [18].

to state $|j\rangle$ with energy difference ω_0 , as

$$\sigma_{i,j} = \frac{e}{2\pi m^2} \left(\frac{1}{\omega + \omega_0 + i\Gamma/2} + \frac{1}{\omega - \omega_0 + i\Gamma/2} \right)$$
(2.48)

...where Γ is a width parameter,⁹ and the expression in parentheses is sometimes called the *resonant prefactor* [20]. From this functional form of $\sigma_{i,j}$, the role of the incident energy becomes clear: this matrix element diverges in the limit $\omega \to \omega_0$. This has striking implications in the context of Eq. 2.47, since the square of the diverging $\sigma_{i,j}$ is what is measured in an experiment. Thus far, these results are generically true of all scattering on-resonance: what is the impact on magnetic scattering¹⁰ of this enhancement effect?

This is answered by solving for the form of the scattering tensor in the presence of a moment $\boldsymbol{m} \parallel \hat{z}$, notated as $\overrightarrow{F_{\hat{z}}^{\mathrm{m}}}$, and generalizing this for any orientation of the moment $(\overrightarrow{F^{\mathrm{m}}})$. It can be shown [19] that this generalized scattering tensor takes the form

$$\overset{\leftrightarrow}{F^{\mathrm{m}}} = \overset{\leftrightarrow}{F^{\mathrm{0}}} \left(\hat{\epsilon}_{s}^{*} \cdot \hat{\epsilon}_{i} \right) + \overset{\leftrightarrow}{F^{\mathrm{1}}} \left(\hat{\epsilon}_{i} \times \hat{\epsilon}_{s}^{*} \right) \cdot \hat{\boldsymbol{m}} + \overset{\leftrightarrow}{F^{\mathrm{2}}} \left(\hat{\epsilon}_{s}^{*} \cdot \hat{\boldsymbol{m}} \right) \left(\hat{\epsilon}_{i} \cdot \hat{\boldsymbol{m}} \right)$$
(2.49)

The proportionality factors \overrightarrow{F}^{n} are defined elsewhere [17]; the most important features of Eq. 2.49 can be found in the polarization dependence of the terms which comprise it. The first expression has no dependence on the direction of the moment, and the factor $(\widehat{\epsilon}_{s}^{*} \cdot \widehat{\epsilon}_{i})$, as in Eq. 2.50, indicates this is only contributes to charge scattering. The second term, however, finally shows the conditions necessary to discriminate a magnetic Bragg peak from charge scattering via resonant elastic x-ray scattering: the

⁹This lifetime broadening is attributed to the many non-radiative effects which make the intermediate excited state unstable. Mathematically, it arises from the substitution of a Dirac-delta with a Lorentzian to accommodate the realities of a physical system [20].

¹⁰Recall that the enhancement only applies to the contribution from f' + if'' in Eq. 2.46, and not the explicitly magnetic f_{mag} .

term is maximal when $\hat{\epsilon}_i \perp \hat{\epsilon}_s^*$. Thus, for a known incident polarization, the character of a reflection (charge or magnetic in origin) can be determined by analyzing the polarization of scattered radiation to see if it has been rotated into the opposite channel. This, combined with the vector nature of $(\hat{\epsilon}_i \times \hat{\epsilon}_s^*)$ with respect to the moment direction, indicates magnetic REXS is also a viable tool for the determining spin structures.

The final term, quadratic in its dependence on $\hat{\boldsymbol{m}}$, is also sensitive to magnetism, but less helpful since it would not be sensitive to an antiferromagnetic system (where (-) signs from each would cancel). Eq. 2.47 is modified now, with \vec{F}^{m} playing a role similar to the magnetic structure factor, to give

$$I_{\text{REXS}}^{\text{mag}}(\hbar\omega) = \left|\sum_{i} \exp\{i\boldsymbol{\kappa}\cdot\boldsymbol{r}_{i}\} \ \hat{\epsilon}_{s}^{*}\cdot \overrightarrow{F^{\text{m}}} \cdot \hat{\epsilon}_{i}\right|^{2}$$
(2.50)

It is clear now that resonant elastic x-ray scattering- leveraging the inherent flux advantage of a synchrotron source, along with the resonant enhancement to magnetic peaks resolved using polarization analysis, is a powerful tool for magnetic studies of condensed matter materials. Thus far, however, both this and the previous section have limited the discussion to the case of elastic scattering- when an analyzer is used to exclude all scattered intensity where $E_s \neq E_i$. This restriction is necessary for a tractable approach to solving static nuclear and spin structures, but if the data collection is expanded to include any E_s , information regarding the dynamics of the system can also be revealed. Just this type of analysis is treated next, when the resonant condition is applied to an inelastic x-ray study.

2.4.2 Resonant Inelastic X-Ray Scattering (RIXS)

Given the discussion in previous sections, it should come as no surprise that the scattered intensity in a resonant inelastic x-ray scattering process, exciting an electron from a ground state E_g to the higher energy state E_f , can be represented in the general form

$$I_{\text{RIXS}}(\omega, \boldsymbol{k}_{i}, \boldsymbol{k}_{s}, \boldsymbol{\epsilon}_{i}, \boldsymbol{\epsilon}_{s}) = \sum_{f} |\mathcal{F}_{f,g}(\omega_{\boldsymbol{k}}, \boldsymbol{k}_{i}, \boldsymbol{k}_{s}, \boldsymbol{\epsilon}_{i}, \boldsymbol{\epsilon}_{s})|^{2} \delta(E_{f} + \hbar\omega_{\boldsymbol{k}_{s}} - E_{g} - \omega_{\boldsymbol{k}_{i}})$$
(2.51)

...where the summation runs over all possible excited states. The factor $\mathcal{F}_{f,g}$ contains information with regard to which excitations contribute to the scattering amplitude at a given energy and momentum exchange, as well as the dependence on polarization [20].¹¹

For the purposes of this discussion, direct RIXS is assumed, as it is the dominant process in the study detailed subsequently in Chapter 6. In this process, a core electron is initially excited to the empty valence state, and a *different* electron from the valence band decays to fill the hole, leaving behind an electron-hole excitation in the valence band. Such an excitation carries momentum $\hbar \kappa$ and energy $\omega(\kappa)$, and can propagate throughout the system.¹² In the case of direct RIXS, $\mathcal{F}_{f,g}$ can be expressed as the expectation value of the operator shown in Eq. 2.52 [22], for given final and initial states, $|f\rangle$, $|i\rangle$,

$$\mathcal{F}_{f,g} = \langle f | \hat{O} | i \rangle = \langle f | (W^c_{\epsilon} \rho_{\kappa} + \boldsymbol{W}^s_{\epsilon} \cdot \boldsymbol{S}_{\kappa}) | i \rangle$$
(2.52)

¹¹This sectional generally follows the discussion from relevant sections of a review of the RIXS technique, found in Ref. [20]. The use of any additional references is notated explicitly.

¹²This very excitation has, in fact, been experimentally observed in the RP iridates [21].

Two familiar quantities comprise this operator: the charge (ρ_{κ}) and spin (S_{κ}) density operators for the conduction electrons in the system; the relative weighting by the RIXS form factors (W_{ϵ}) depend on the species of atom, the geometry of the experiment, and the incident/scattered polarization directions. Thus, the intensity from Eq. 2.51 can be represented as

$$I_{\text{RIXS}} = |W_{\epsilon}^{c}|^{2} \boldsymbol{\chi}^{c}(\boldsymbol{\kappa}, \omega) + |\boldsymbol{W}_{\epsilon}^{s}|^{2} \boldsymbol{\chi}^{s}(\boldsymbol{\kappa}, \omega)$$
(2.53)

...where the χ 's are termed the *dynamical structure factors* associated with charge and spin. The exact form and evaluation of these functions is the subject of considerable interest [22–24], but is not treated here.

Instead, satisfied with a general sense of what comprises the RIXS cross-section, the application of this technique to magnetism is discussed. Leveraging resonant x-rays to probe magnetic excitations is a somewhat recent trend- the first reports focused on magnon dispersions in the cuprates [25–27] were published only about five years prior to the work discussed later in Chapter 6. As was the case for elastic resonant x-ray scattering, the theoretical treatment of the effective magnetic interaction in the case of RIXS is similarly non-trivial. The optical dipole transition inherent to the technique does not induce spin-flip excitations- these are instead the result of core-hole spin-orbit coupling occurring in the intermediate state [28].

$$R_{\omega_i,j}^{\epsilon_i,\epsilon_s} = \overset{\leftrightarrow}{\sigma}^{(0)}(\epsilon_i \cdot \epsilon_s^*) + \frac{\overset{\leftrightarrow}{\sigma}^{(1)}}{s}(\epsilon_s^* \times \epsilon_i) \cdot \boldsymbol{S}_j + \cdots$$
(2.54)

An expression is defined by Haverkort [28] in Eq. 2.54 to provide an exact form of the RIXS transition operator for magnetic excitations truncated to single site transitions (an unwieldy third term is omitted as it does not contribute at all in the case of s = 1/2). It is related to the conductivity tensor introduced in Eq. 2.47 by $\epsilon_s^* \cdot \overleftrightarrow{\sigma} \cdot \epsilon_i = \langle i | R_{\omega_i,j}^{\epsilon_i,\epsilon_s} | j \rangle$. This expression bears some resemblance to the result found in the elastic case (Eq. 2.49), and provides a tractable, effective description for the magnetic interaction for transitions associated with spin flips. It thus allows magnon excitations to be resolved with RIXS in a similar fashion to how magnetic Bragg peaks were analyzed with REXS.

In addition to magnetic excitations, predicted to have significant intensity at the $\text{Ir-}L_3$ edge, direct RIXS spectra reveal quasiparticle modes associated with various other phenomena as well. Among these are orbitons, in which optically forbidden dd transitions are accessed by coupling to the lattice, as well as the observation of spectral lines associated with transitions between the crystal-field-split t_{2g} and e_g levels have been reported [20, 21].

A final comment on the experimental geometry of the scattering experiment: even in lieu of the high flux provided by synchrotron sources, magnetic excitations probed in small sample volumes, themselves characterized by small magnetic moments, necessitate an efficient collection of photons during energy scans to construct a series of spectra.¹³ The analyzer of the MERIX spectrometer at the Advanced Photon Source employed in this study uses a unique geometry to aid in the timely collection of these data. Instead of rotating a single analyzing crystal to isolate a given scattered energy E_s as is used for the elastic case and iterating this one step in energy at a time, a unique diced spherical analyzer is utilized.

This analyzer is composed of several hundred independent segments of a highly

¹³To give the reader a sense of the timescale involved: even in the optimized configuration described here, collection of a single RIXS spectrum for $(Sr_{1-x}La_x)_3Ir_2O_7$ as seen in Figs. 6.3 and 6.4 takes on the order of 3-4 hours. The dispersions shown in Chapter 6 each include ≈ 30 such scans.



Figure 2.5: Top: X-ray optics configuration at APS Sector 27; figure sourced from [20]. Bottom: Detail of the optical paths for scattered x-rays of various energies incident on the diced spherical analyzer (A); figure from [29]. The detector (Det) and sample (S) positions are also indicated.

crystalline material of known orientation, all positioned with faces tangent to some sphere with radius R_A as depicted in the lower detail of Fig. 2.5. The result is that energies within an appreciable span ΔE can be simultaneous collected in batches; further, since the geometry of the diced spherical analyzer spatially separates x-rays of different energies on the strip detector, energy resolution is simultaneously achieved. Depending on the incident energy, different materials comprising the analyzer are required to permit the required energy resolution- most edges are adequately covered by Si or Ge analyzer crystals [29].

2.4.3 Powder Diffraction and Reitveld Refinement

A few brief comments are made here regarding laboratory applications of x-ray scattering techniques (in contrast to synchrotron sources). As mentioned in Section 2.3.5, a Laue scattering geometry permits the collection of many peaks by using an area detector and a polychromatic source to meet the various Bragg conditions of a fixed sample. To some extent, the triple-axis method (2.3.4) represents the inverse, in which a monochromatic beam scatters from a sample with variable orientations, chosen to satisfy a single Bragg condition. In the case of the latter, an effort to collect peak positions and intensities en masse for a structural study clearly represents a time-consuming endeavor.

Consider instead, if the crystal in question is ground into a fine 'powder' of microscale crystallites. In this case, assuming there is no strong preferred orientation, the powder consists of a (huge!) collection of randomly oriented crystallites. For a given scattering angle 2θ associated with plane-spacing d_{hkl} there is a reasonable expectation that some non-zero fraction of the population of crystallites are oriented



Figure 2.6: X-ray diffraction data from a crushed $Sr_3Ir_2O_7$ single crystal using a Cu-K_{α} laboratory radiation source. Selected reflections indexed in the *Bbcb* (space group No. 68) structural solution are also shown.

relative to k_i such that the resulting k_f is scattered into the detector. There are geometric arguments [15], as well as the Ewald formalism [30] which show this more rigorously, but the eventual outcome is the same: that all possible reflections can be accessed by varying a single parameter, the scattering angle 2θ . An example dataset is shown in Fig. 2.6. The raw data reveals peak positions and in turn provides some indication of the relevant *d*-spacings, but to generate a complete indexing of the peaks, the structure must be solved. That is, the size of the unit cell and the position and types of atoms comprising it must be known to reconstruct the diffraction pattern. In practice, arriving at a full structural solution from powder XRD alone, for a previously unknown structure, is non-trivial and not described here (guides can be found elsewhere [30, 31]). If the researcher has a reasonable guess as to the sample content though, the data can be easily compared to a known structure.

A technique called Rietveld refinement takes this known structure (comprising the

space group, lattice parameters, and unit cell contents) and attempts to reconcile it with the observed data by varying atom positions, displacement factors, peak shape parameters, and a number of other factors by means of a least-squares algorithm. The quantity to be minimized is given by R

$$R = \sum_{i} w_i (Y_{io} - Y_{ic})^2 \tag{2.55}$$

...where the summation is over the discrete data points in 2θ , and the Y's correspond to the observed and calculated intensities at that particular point. w_i is a weighting factor, which accounts for the reduced counting error the greater the observed intensity [30]. The Rietveld method alone will not solve a structure, but it provides a quantitative measure of the extent to which observed data is described by a given structural model of one or several phases present in the measured powder. Often, the precise manner in which a refinement fails is the best indicator of how to improve a model: additional peaks can suggest the presence of an impurity phase, peak splittings can imply a reduction in symmetry, etc.

The Rietveld method alongside other techniques such as Le Bail fitting (which can extract unit cell parameters independent of any information regarding the contents) are indispensable analysis tools for preliminary sample characterization. Using laboratory x-ray sources to ensure sample quality is critical for efficient use of more scarce resources such as allotted time at user facilities which is competitively awarded.

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Chapter 3

Synthesis and Characterization

Before any serious investigation can be made into a given material of interest, high quality samples must first be grown. Here, the procedure used to grow single crystals of $Sr_3Ir_2O_7$ is discussed. Single crystals, as apposed to polycrystalline or amorphous compounds, have a number of key advantages, such as preserving details of anisotropic properties, largely avoiding problems associated with grain boundaries, and requiring smaller total amounts of material for scattering experiments, to name a few. The utility of measurements performed on the newly synthesized compound and the ease of analytical treatment are both directly linked to how well the sample was grown, and so a series of metrics to evaluate crystal quality is also delineated in this chapter.



Figure 3.1: Schematic heating profile for a generic crystal growth utilizing the flux method as implemented here.

3.1 Flux Growth of Single-Crystal $Sr_3Ir_2O_7$

Crystal growth of $Sr_3Ir_2O_7$ for this work was accomplished exclusively via the flux growth technique, first reported to be viable for this system by Subramanian, et al. in 1994 [1]. This synthesis method is particularly useful for reactions where the constituent materials melt incongruously due to the flux aiding reaction by functioning as a solvent as well as lowering the overall melting temperature [2]. The compounds are placed inside a container and heated until all the material has completely dissolved into a molten solution. The entire system is then cooled slowly- as the temperature falls below the saturation point, a precipitate of the reactants begins to form. Crystals spontaneously nucleate from defects on the container walls and their growth is fed by further precipitation as the temperature slowly ramps down (a representative heating profile is shown schematically in Fig. 3.1). Care is taken not to exhaust the flux during this process to ensure maximum yield of the reaction and size of the crystals.

Segment No.	Start Temp. (°C)	End Temp. (°C)	Ramp Time (h)
1	25	1000	4
2	1000	1300	3
3	1300	1300	5
4	1300	850	125
5	850	25	3

Table 3.1: Details of the standard furnace heating profile used to grow the single crystals for this work.

To synthesize $Sr_3Ir_2O_7$, the reactants employed are strontium carbonate $(SrCO_3)^1$ and iridium oxide $(IrO_2)^2$, and a strontium chloride salt $(SrCl_2)^3$ is utilized as a flux. As a precaution, the powders are all dried initially to minimize the presence of moisture during the reaction: $SrCl_2$ and $SrCO_3$ at 300 °C, IrO_2 at 900 °C, both for a minimum of 12 h. Once dried, stoichiometric amounts (using the chemical reaction depicted in Eq. 3.1) of the reactants are weighed out along with a known molar ratio f of flux material. A typical flux ratio for $Sr_3Ir_2O_7$ growth was f = 15, implying 15 mol of $SrCl_2$ per mole of $Sr_3Ir_2O_7$.

$$3 \operatorname{SrCO}_3 + 2 \operatorname{IrO}_2 \xrightarrow{f \operatorname{SrCl}_2} \operatorname{Sr}_3 \operatorname{Ir}_2 \operatorname{O}_7 + 3 \operatorname{CO}_2$$
 (3.1)

These powders are placed within a container whose chemical composition is carefully chosen so as to not participate in the reaction; for this work 10 ml Pt crucibles⁴ were used. Materials are layered from the bottom up in order of decreasing melting point, as indicated in Fig. 3.2 and a Pt lid is placed on top to act as a partial seal during reaction. This entire container is then placed inside an alumina (Al₂O₃) cru-

¹Alfa Aesar SrCO₃, 99.99% (Metals Basis).

²Alfa Aesar IrO₂, Premion 99.99% (Metals Basis).

³Alfa Aesar SrCl₂, 99.5% (Metals Basis)

⁴Heraues Group



Figure 3.2: Typical layered powder charge for flux growth.

cible/lid which is itself in turn placed in a high-temperature furnace.⁵ The alumina crucible serves to protect the internal surfaces of the furnace and elements from the flux and reactants. The details of a 'standard' heating profile for growth of $Sr_3Ir_2O_7$ are outlined in Table 3.1.

Once the heating sequence is complete the grown crystals at the bottom of the Pt crucible remain encased in the remainder of the now-solid $SrCl_2$ flux. They are extracted by soaking the crucible in water, which dissolves the $SrCl_2$ over time with repeated flushings. With the flux removed, the material can be extracted most easily with the aid of a stereo-microscope to avoid damaging the delicate, larger single crystals. Typical crystal sizes can be as large a $1 \text{ mm} \times 1 \text{ mm} \times 0.25 \text{ mm}$, with masses usually between 0.5 mg to 2 mg. The crystal habit is that of a thin platelet; in the vast majority of samples, the direction normal to the plate coincides with the long axis of the unit cell, and the stright edges with the two shorter dimensions (a detailed treatment of the structure can be found in Chapter 4). Often a residual layer of flux

 $^{^5 \}mathrm{SentroTech}$ ST-1600C Box Furnace

is retained on the surface- this is removed by again soaking in water, or with the use of adhesive office tape to cleave this dirty top layer off to obtain a relatively pristine interface for surface-based probes.

3.2 Doping The System

Much of this work focuses on the role played by dopants- where an atom of a different type is substituted on a given site of the lattice. $Sr_3Ir_2O_7$ will be referred to as the 'parent' compound to distinguish it from doped systems which have a chemical formula appearing as $(Sr_{1-x}La_x)_3Ir_2O_7$. In the case of doped compounds, these are identified by the concentration of the dopant, that is, the value of x in the previous formula, for example. Despite the wide array of physical states observed in doped samples however, their synthesis is essentially the same as that of the parent.

When doping the system on the A-site (referencing the generic chemical formula for members of the Ruddlesden-Popper series given by $A_{n+1}B_nO_{3n+1}$) with La, lanthanum oxide $(La_2O_3)^6$ is also dried at 300 °C for a minimum of 12 h along with the SrCl₂ and SrCO₃. Again stoichiometric amounts are massed out, now in order to balance the chemical equation given by Eq. 3.2. Before layering in the Pt crucible, the two compounds contributing atomic species that will share a site, here SrCO₃ and La₂O₃, are mixed thoroughly (15 min) using an agate mortar and pestle.

⁶Alfa Aesar La₂O₃, REacton 99.99% (REO)

$$3(1-x)\operatorname{SrCO}_3 + \frac{3x}{2}\operatorname{La}_2\operatorname{O}_3 + 2\operatorname{IrO}_2 \xrightarrow{f \operatorname{SrCl}_2} \operatorname{Sr}_{3(1-x)}\operatorname{La}_{3x}\operatorname{Ir}_2\operatorname{O}_7 + \dots$$
(3.2)

To optimize parameters for La-doped sample growth sequences, it was often necessary to modify the standard heating profile as listed in Table 3.1. Specifically, increasing the ramp time in segment 4 to as high as 158 h was found to be more advantageous for growing crystals in the highest doping ranges (x > 0.04). Attempts to modify the flux ratio were made, but f = 15 was still found to remain the most ideal.

3.3 Confirming Phase Purity

With crystals now in hand the task moves to characterizing the quality of the samples to determine their suitability for further measurements. Upon recovery of crystals from a flux growth, the first and most obvious question is if the crystals grown are of the intended phase, or if the possesses some known or unknown impurity phase as well. The crystal habit is a decent first clue- $Sr_3Ir_2O_7$ proper grows as small platelets, whereas the $n \to \infty$ member of the Ruddlesden-Popper series $SrIrO_3$ grows with an octahedral habit. Unfortunately though, the most common impurity phase, Sr_2IrO_4 , *also* grows as small platelets, so no cursory visual examination of a given sample can discriminate between one or the other, or as it more common- a crystal containing both. Thus, a more thorough accounting of crystal phase must be made.



Figure 3.3: $\theta - 2\theta$ scan of a single crystal oriented to probe (00l)-type refelctions. Indexing is correct for an assignment of space group *Bbcb* (No. 68). Schematic of the radiation (yellow) scattering from a crystal (black) is shown as an inset.

As discussed in Section 2.4.3, x-ray diffraction is a powerful tool for probing crystal structure and could reveal key information with respect to a given crystal's phase purity. Unfortunately, this requires the crushing of the single crystal to collect a full dataset upon which to execute a proper refinement, and thus even if the crystal was phase-pure, it was destroyed in the process of confirming that fact. While this initially appears as a frustrating catch-22 [3], a rather simple solution exists. Since the long axis of the unit cell (assigned the label c here, for argument's sake) points normal to the plate-like surface of the crystal, a typical $\theta - 2\theta$ scan in a powder XRD instrument of the crystal sitting on a flat surface will reveal reflections of the type (00l) as shown in Fig. 3.3.

Consider the nature of the impurity phase Sr_2IrO_4 : as the single-layer (n = 1)member of the Ruddlesden-Popper series it is 'compatible' with the same stacking sequence that defines the bilayer compound, and hence intergrowths of the two phases are relatively common. Necessarily though, this means any impurity volume is oriented such that our x-ray scan will also reveal $(0\ 0\ l)$ -type reflections of the of Sr₂IrO₄ phase. In particular, a simulated diffraction pattern (for Cu-K_{α} radiation) generated using the reported Sr₂IrO₄ structure[4] reveals a primary peak near 13.5°.

Empirically, such a feature has been seen in many of these 'single-crystal powder scans', and a full refinement of such a sample (once ground up and properly measured) in fact reveals the presence of Sr_2IrO_4 . Thus, the presence or absence of this signature peak at 13.5° (provided, of course, that the standard $Sr_3Ir_2O_7$ peaks are accounted for) serves as a reliable proxy for the most common impurity phase. To preclude the possibility of mixed-phase samples as an explanatory factor in subsequent results, each crystal used for these measurements was measured in this way to confirm relative phase purity.

3.4 Evaluating Chemical Composition

Since the presence of dopants in the small concentrations treated here does not drastically alter the structure of $Sr_3Ir_2O_7$ the above technique remains a valuable tool for assessing phase purity. With a doped sample though, there is an additional degree of information required: how to determine x, the dopant concentration. Many mature quantitative techniques, for example inductively coupled plasma atomic emission spectroscopy (ICP-AES), offer this functionality, but require the destruction of the material to be analyzed. This is perfectly acceptable if the variation of dopant concentration within a batch is always small: characterizing a few representative samples would sufficient to describe the batch as a whole, in that case. Alternatively, if individual crystals are very large, a small piece can be sacrificed as a metric of the remainder.

In the case of $Sr_3Ir_2O_7$, however, neither use-case is acceptable. The distribution of dopant levels from crystal to crystal within a batch is quite wide- on the order of several percent in x. Thus, the concentration of any measured representatives is a poor predictor of the actual concentration of another crystal within the batch. Furthermore, single crystals are of such small mass that they would need to be sacrificed in their entirety to characterize chemical content via ICP.

Thus, it is necessary to obtain a measure of the elemental composition with a non-destructive probe for every crystal to be used in further measurements. The probe of choice in this case is energy-dispersive x-ray spectroscopy (EDS), measured within a scanning electron microscope (SEM). In the process of generating an image of the sample, the SEM bombards the crystal with high-energy (20 keV) electrons. Incoming 'beam' electrons can eject electrons from the core of given species of atom in the sample to create a hole; when an electron from a higher energy level in that same atom decays to fill the hole radiation is emitted. The frequency of this radiation is determined by the spacing between the high and low energy levels in the atom. Since these level spacings are characteristic of a given type of atom, the frequency of observed radiation indicates the atomic species of the material being probed.

With a beam incident on a sample comprised of multiple types of atoms, a spectrum is produced with peaks corresponding to energy-level-transitions of the constituent elements (as shown in Fig. 3.4). Software can be used to fit this spectrum,



Figure 3.4: A portion of an EDS spectrum for a $(Sr_{1-x}La_x)_3Ir_2O_7$ sample. The blue curve is a rough fit of the background signal, with the teal curve the fit of the complete spectrum. Data is presented as a counts historgram with very fine energy binning (units of keV) in dull gray-green. Families of peaks are labeled with their respective element symbols.

and the atomic percentage P of each atom comprising the probed volume can be calculated from the peak intensities. For a given crystal, 5 to 10 spectra with a typical area of $\approx 50 \,\mu\text{m}^2$ were collected and analyzed. Dopant concentration is defined as shown in Eq. 3.3. The standard deviation of this (admittedly small) population of measurements gives a rough sense of the homogeneityty of the crystal, and the mean provides a center value. Given that EDS is a surface probe, the best results (narrow distribution of x across a sample, absence of signal from Cl due to remnant flux) are achieved when the surface is cleaved before measurement.

$$x = \left(\frac{P_{Dopant}}{P_{Dopant} + P_{Host}}\right) \times 100 \tag{3.3}$$

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Chapter 4

Crystal Structure of $Sr_3Ir_2O_7$

As mentioned in Chapter 1, several outstanding questions regarding observed bulk and scattering results in $Sr_3Ir_2O_7$ remain. Among them- what is the origin of the net ferromagnetic signal observed in susceptibility? The solution of the spin structure, in which moments point parallel to the long axis, precludes the known in-plane rotation of IrO_6 octahedra as a solution, as is the case for Sr_2IrO_4 . Also unexplained is the weak structural reflection seen in both neutron and x-ray scattering which violates the orthorhombic structural solution. Both of these questions may potentially be answered by a more complete structural solution, the construction of which is detailed in this chapter.

4.1 Previous Structural Reports

The spin-orbit Mott state as realized in the Ruddlesden-Popper (RP) strontium iridates $(Sr_{n+1}Ir_nO_{3n+1})$ remains of considerable interest due to the unique physics arising from the confluence of comparable strong spin-orbit coupling and electronelectron interactions in the presence of a strong cubic crystal field [1–3]. Subtleties in the lattice structures of these systems are of critical importance in determining both the spin-orbital content of the ground state wave function [3], the resulting magnetic ground state [4], and details within the electronic band structure [5]. In particular, for the n = 2 member of the RP series (Sr₃Ir₂O₇) both density functional theory (DFT) [6–8] and models of magnetic order [9] and dynamics [10, 11] are sensitive to subtleties in the local crystal fields at Ir sites.

The structure of $Sr_3Ir_2O_7$ was originally reported as a distorted bilayer perovskite variant described by the tetragonal space group I_4/mmm (No. 139) with unit cell dimensions a = 3.896 Å, c = 20.879 Å [12]. In initial studies, evidence of an in-plane rotation (along the unique tetragonal c axis) of the octahedral cages surrounding the Ir atoms was observed via x-ray scattering; however this was refined within a disordered I_4/mmm model, where the phasing of the octahedral rotations from site to site is random. Other subsequent x-ray investigations have also observed incoherent rotations among the oxygen octahedra [13]—potentially arising from compositional disorder.

A separate x-ray study put forward an orthorhombic unit cell (a = 5.522 Å, b = 5.521 Å, c = 20.917 Å) indexed with an improper Hermann-Mauguin symbol *Bbca* [14] (space group No. 68) and modeled using coherent intralayer counterrotations of neighboring octahedra along the *c*-axis. Additional support for this orthorhombic model with coherent octahedral rotations was provided by a transmission electron microscopy (TEM) study of the reflection conditions observed in electron diffraction patterns [15]. Here the reciprocal lattices of both *Bbcb-* and *Acaa-*type structures, each an alternate setting of the *Ccce* space group (No. 68), were superimposed to match the observed patterns—demonstrating that this system is prone to twinning. This TEM-derived structural solution parallels that of the analogous ruthenate compound $Sr_3Ru_2O_7$ [16], where all modes of octahedral rotation about their symmetry axes were considered as candidate structures.

Even when accounting for the coherent phasing of octahedral rotations, *Ccce* still fails to completely describe some subtle aspects of $Sr_3Ir_2O_7$'s lattice structure. Neutron diffraction measurements [17] have observed peaks in the $[H \ 0 \ L]$ zone (*Bbcb* setting) that violate the reflection condition H, L = 2n imposed by the space group [18]. One such reflection at $\mathbf{Q} = (1 \ 0 \ 3)$ is shown in Fig. 4.1. These weak violations were later confirmed to be of structural origin via a polarized neutron scattering study [19] and are reminiscent of those observed within the n = 1 system Sr_2IrO_4 (also via neutron diffraction) [20, 21]. While in Sr_2IrO_4 two unique Ir environments were ultimately refined [22, 23], the origin of the Bragg violations in $Sr_3Ir_2O_7$ and their implication for the lattice structure remains an open question.

Single crystal neutron scattering and rotational anisotropy second harmonic generation (RA-SHG) measurements are utilized here to resolve the structure of $Sr_3Ir_2O_7$. The point group for the lattice is constrained via RA-SHG measurements to be either 4/m or 2/m or one of even lower symmetry, which when combined with single crystal neutron data identifies the monoclinic space group C2/c as the correct structural symmetry. Density functional theory calculations were used to guide the space group



Figure 4.1: Radial \mathbf{Q} scan at T = 315 K through the (1, 0, 3) reflection demonstrating a violation of the general reflection condition H,L = 2n for the orthorhombic *Bbcb* space group. Data reproduced from Ref. [17]

search and identify the most energetically favored mode of lattice distortion. In addition to in-plane rotations, oxygen octahedra in this new lower symmetry can tilt off-axis, suggesting that the anomalous, weak in-plane ferromagnetism of $Sr_3Ir_2O_7$ originates from these tilts combined with strong spin-lattice coupling. Using probes sensitive to both oxygen sites as well as point group symmetry, our measurements ultimately provide a foundation for understanding the further structural distortions observed in this system during metallization via pressure [24] and electron substitution [25].

4.2 Experimental and Computational Details

The method for growing the $Sr_3Ir_2O_7$ single crystals used in our study is reported elsewhere [25] (also see Chapter 3). Neutron scattering measurements were conducted by measuring a small single crystal (mass 5.6 mg, dimensions 1.25 mm × 1.13 mm × 0.1 mm) in the time-of-flight single crystal Laue diffractometer TOPAZ at Oak Ridge National Laboratory. Sample orientations were optimized with the CRYSTALPLAN software [26] for an estimated coverage of 99.8% of equivalent reflections for the nominal orthorhombic cell for this system. Reduction of the raw data, including accounting for Lorentz corrections, absorption, the time-of-flight spectrum, and detector efficiency were carried out with ANVRED3 [27]. The raw peaks were integrated using a 3-D ellipsoidal routine [28], and the reduced dataset was refined using SHELXL [29].

To guide the search for the correct space group, density functional theory was employed to compare several potential solutions.¹ Of the resulting relaxed structural geometries, those that did not display the correct antiferromagnetic ordering of the Ir 5d moments in the simulated structures could be discarded. Structures which remained served as initial conditions for refinement to the neutron diffraction dataset. The calculations were performed using the projector augmented-wave method [31] in the Vienna Ab initio Simulation Package (VASP) [32, 33]. The PBE functional [34] was used with a screened on-site Coulomb repulsion parameter U of 2 eV on the Ir d orbitals, with spin-orbit coupling taken into account. Taken together, the +Uinteraction and SOC open up a Mott-Hubbard gap within the Ir 5d band. Since the material is layered, Van der Waals interactions are accounted for via Becke-Johnson damping [35], as implemented in VASP. For the 48-atom unit cell, a plane-wave cutoff

¹DFT calculations were conducted by L. Bjaalie and C. G. Van de Walle [30].

of 500 eV and $4 \times 4 \times 1$ Γ -centered k-point mesh were used.

Determining the point group of $Sr_3Ir_2O_7$ was accomplished through the use of RA-SHG techniques.² These data were acquired using the rotating scattering plane based technique (described in Ref. [36]) from cleaved surfaces of $Sr_3Ir_2O_7$ with the long cell axis parallel to the surface normal. Incident light was provided by a Ti:sapph regenerative amplifier (800 nm center wavelength, 60 fs pulse duration, 10 kHz repetition rate) and focused to a spot size less than 100 µm on the crystal with a fluence less than 1 mJ cm⁻². The linear polarization of the incident (in) and reflected (out) light was selected to be either in (P) or out of (S) the scattering plane. The orientation of the two in-plane crystallographic axes were determined independently by x-ray Laue diffraction.

4.3 Neutron Diffraction Results

The refined results from single crystal diffraction data collected from $Sr_3Ir_2O_7$ are discussed first. Diffraction data were collected and patterns refined both at 100 K and 300 K. As a starting procedure for refinement, the undistorted tetragonal parent I_4/mmm structure was transformed into candidate lower-symmetry space groups [37– 40] corresponding to pure rotations about axes of high symmetry [16]. Distortions of the octahedra were introduced using the relaxed structures from DFT calculations as initial positions. These structures were then refined to the single crystal neutron diffraction data at T = 300 K to evaluate which set of octahedral rotations most faithfully reproduced the observed pattern. Neutron scattering as a probe is particularly well-suited to this task as, compared to synchrotron radiation, it is more

²RA-SHG measurements were conducted by L. Zhao, C. Belvin, and D. Hsieh [30].



Figure 4.2: Refined lattice structure of $Sr_3Ir_2O_7$. Red atoms denote oxygen sites, blue atoms within octahedra denote iridium sites, and green atoms denote strontium sites. (a) The in-plane oxygen octahedral rotations as viewed along the *a*-axis. (b) Out-of plane oxygen octahedral tilt mode, viewed along the *b*-axis. c) Off-axis view of the chemical unit cell. Atom positions are those of the T = 300 K refinement to the C2/c space group.
sensitive to the oxygen comprising the octahedra. Similar to $Sr_3Ir_2O_7$'s ruthenate analog, all tetragonal subgroups rendered poor fits and the two best models which emerged were refined within space groups No. 68 (*Ccce*) and No. 15 (*C2/c*).

The former group *Ccce* is consistent with the previously reported structure [14, 15], and represents the coordinated rotation of in-plane octahedra with the rotational sense about the long (here, b) axis for intralayer neighboring cages being opposite. However this structure fails to account for the weak Bragg violations (> 10³ times weaker than primary peaks) known to exist in this system, implying that there may be a further distortion into a lower symmetry. Alternatively, the latter C2/c monoclinic group, related to *Ccce* by the transformation matrix $-b+\frac{1}{4}$, $a+\frac{1}{4}$, c, can account for these violations and represents a combination of the previous in-plane octahedral rotation with an additional octahedral tilt mode [16], as seen projected separately in panels (a) and (b) of Fig. 4.2. Taken blindly however, the *R*1 values resulting from refinement of the time-of-flight data alone were comparable for each candidate group, mandating further constraints to determine the correct solution.

4.4 Point Group Measurement

To further distinguish between the two possible solutions, rotational anisotropy second harmonic generation measurements were taken. RA-SHG is a technique capable of directly determining the crystallographic point group symmetry of a material. In these experiments, light of frequency ω is obliquely incident on the surface of a crystal and the intensity of light reflected at 2ω is measured as a function of the angle (ϕ) between the scattering plane and some in-plane crystalline axis [36]. By performing these measurements using different combinations of incident and outgoing light po-



Figure 4.3: RA-SHG patterns (open circles) from $Sr_3Ir_2O_7$ acquired under (a) $S_{in}-P_{out}$, (b) $P_{in}-P_{out}$, (c) $S_{in}-S_{out}$ and (d) $P_{in}-S_{out}$ polarization geometries at T = 295 K. The intensities of all patterns are normalized against the PP trace. Red lines overlaid on the data are best fits to bulk electric quadrupole induced RA-SHG calculated using either of the centrosymmetric 4/m or 2/m point groups. The bottom row (e)–(h) shows the corresponding best fits to bulk electric-quadrupole induced RA-SHG from the centrosymmetric 4/mmm (green) and mmm (blue) point groups as well as to bulk electric-dipole induced RA-SHG from the non-centrosymmetric 2mm point group (orange). Responses that are absent in the plots are forbidden by symmetry.

larization, the entire nonlinear optical susceptibility tensor can be determined, which embeds all the point group symmetries of the material. This technique has recently been used to help identify subtle structural distortions in Sr_2IrO_4 that lower the point group symmetry from 4/mmm to 4/m [22, 41].

Fig. 4.3 shows RA-SHG patterns from $Sr_3Ir_2O_7$ acquired under all four linear polarization geometries at room temperature (> T_N). The bottom row shows best fits to calculations based on the three crystallographic point groups that have been proposed for $Sr_3Ir_2O_7$: tetragonal 4/mmm (*I4/mmm*) [12], orthorhombic mmm (*Bbcb*) [14, 15], and orthorhombic 2mm (*Bb2*₁*m*) [19]. For the non-centrosymmetric 2mm point group, it is assumed that the dominant contribution to SHG to be of bulk electricdipole origin. For the centrosymmetric 4/mmm and mmm point groups on the other hand, bulk electric-dipole SHG is forbidden, and instead the dominant contribution is presumed to be of bulk electric-quadrupole origin, consistent with the case for Sr_2IrO_4 [22, 41]. It is clear from Figs. 4.3 (e)–(h) that none of these three proposed point groups can describe the RA-SHG data. On the other hand, by assuming bulk-electric quadrupole induced SHG from a centrosymmetric 4/m point group, excellent agreement with the data is obtained, as shown in Figs. 4.3 (a)–(d) (Note that bulk magnetic dipole induced SHG from a 4/m point group does not qualitatively match the data). Any sub-group of 4/m (such as 2/m) fits the data equally well since it naturally contains all elements of the 4/m electric-quadrupole susceptibility tensor. Taken together with the diffraction data presented in Section III, these results suggest that $Sr_3Ir_2O_7$ crystallizes in a 2/m point group but is very close to being 4/m.

4.5 Proposed Structural Solution to $Sr_3Ir_2O_7$

With the RA-SHG analysis unambiguously ruling out the orthorhombic point group mmm associated with *Ccce*, we exclude space group No. 68 as a possible solution and focus exclusively on No. 15 (C2/c). Tables 4.2 and 4.3 list the complete refinement results obtained at T = 300 K and T = 100 K respectively. The relative atomic positions reported correspond to the standard setting of space group C2/c (No. 15), wherein the unique axis (associated with the single oblique angle β) is *b*, and the long axis is *a*. Atomic displacement factors were also refined with all U_{ij} matrices passing

	T = 300 K	T = 100 K
a	$20.935(4){ m \AA}$	$20.917(3)\text{\AA}$
b	$5.5185(13)\text{\AA}$	$5.5080(10){ m \AA}$
c	$5.5099(9){ m \AA}$	$5.4995(7){ m \AA}$
β	90.045(18)°	$90.069(15)^{\circ}$
V	$636.6(2) \text{ Å}^3$	$633.60(17)\text{\AA}^3$

Table 4.1: Refined lattice parameters and unit cell volumes for $Sr_3Ir_2O_7$ at measured temperatures using space group C2/c (No. 15), Z = 4.

a check for positive definiteness. Each atomic site within the cell refined to be fully occupied within error. Associated unit cell parameters are listed in Table 4.1.

To converge, fits require refining the structure as a twin and obtain final R1 values of 5.7% (300 K) and 5.9% (100 K). Our choice of twin law is informed by the 'accidental' pseudosymmetry of the unit cell. Previously, the unit cell parameters comprising the basal plane (b and c for C2/c) have been consistently reported as identical to within experimental precision; furthermore, no measurable obliquity of the cell has been previously reported. As no tetragonal space groups produce a satisfactory solution the conditions $b \approx c$, $\beta \approx 90^{\circ}$ instead represent an effective tetragonal metric of the system. The twin law which permits the refinement to converge is a symmetry operator of the tetragonal point group 4/mmm: a two-fold rotation about the [0 1 1] direction (basal plane diagonal). In real space, for a small deviation from the condition $\beta = 90^{\circ}$, this is tantamount to an altering of the rotational phasing of the octahedra (along the long axis) at the twin boundary. The twin scale factor was refined to 0.497, very near the ideal 'perfect twin' value of 0.5. We note that because the twin law is not a symmetry operator of the point group of the individual's lattice (2/m), this is classified as twinning by pseudo-merohedry [42].



Figure 4.4: Refined T = 300 K geometry of the IrO₆ octahedra in Sr₃Ir₂O₇ showing relevant bond lengths and their uncertainties. Oxygen atoms are depicted in red, with the central iridium atom in blue.

A representative oxygen octahedral cage surrounding each Ir site is depicted in Fig. 4.4. The full refinement reveals only a slight tetragonal distortion in the apical direction (\hat{a} , for the standard setting used here), with a distortion parameter [43] of only $\Delta_d = 1.10 \times 10^{-4}$. In comparing this new model at 300 K with previous reports, two distinguishing attributes should be highlighted: first, the in-plane rotation angle of 11.5° closely matches previous measurements [14]. Next, in contrast to *Ccce*, the out-of-plane tilt (now permitted) refines to a value of 0.23°. At 100 K, the in-plane rotation angle increases to 11.8° and the tilt to 0.33°. Representative projections of both features, alongside the full unit cell, are seen in Fig. 4.2. The presence of a tilt angle representing only a $\approx 0.3\%$ deviation from the orthorhombic model with

Atom	Wyckoff Site		х	У		Z
Ir	8f		0.59755(4)	0.7	495(5)	0.7500(4)
Sr(1)	$4\mathrm{e}$		0.500000	0.2	489(11)	0.750000
Sr(2)	8f		0.68747(7)	0.7	507(9)	0.2494(5)
O(1)	$4\mathrm{e}$		0.500000	0.7	480(14)	0.750000
O(2)	8f		0.69414(8)	0.7487(9)		0.7496(7)
O(3)	8f		0.09674(14)	0.4499(9)		0.4490(5)
O(4)	8f		0.09610(14)	0.9488(9)		0.5507(5)
Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ir	0.00670	0.00800	0.00210	-0.00030	-0.00170	-0.00040
Sr(1)	0.01010	0.00700	0.01200	0.00000	-0.00100	0.00000
Sr(2)	0.00930	0.01200	0.01100	0.00190	-0.00190	-0.00170
O(1)	0.00460	0.02100	0.02200	0.00000	-0.00230	0.00000
O(2)	0.00400	0.00700	0.02100	0.00130	-0.00180	-0.00050
O(3)	0.01450	0.01120	0.00700	-0.00010	-0.00040	0.00290
O(4)	0.01650	0.01040	0.00840	0.00060	-0.00100	-0.00270

Table 4.2: Results of refinement of T = 300 K neutron diffraction data to the C2/c model. Wyckoff site labels, relative atomic coordinates and anisotropic displacement factor matrices U_{ij} are included. R1 = 0.057

a nearly identical in-plane rotation at these temperatures is consistent with the fact that, by merit of diffraction data refinement alone, C2/c and Ccce describe the single crystal diffraction data equally well.

4.6 Discussion

As a separate metric aiding in the differentiation among possible space groups for $Sr_3Ir_2O_7$, density functional theory calculations were employed. Atom positions in the two models for C2/c and Ccce were allowed to relax, subject to symmetry constraints, and the total energies of the resulting configurations were compared. The energy

Atom	Wyckoff Site		х	У		\mathbf{Z}
Ir	8f		0.59754(4)	0.7	502(11)	0.7504(2)
Sr(1)	$4\mathrm{e}$		0.500000	0.2	490(2)	0.750000
Sr(2)	8f		0.68756(7)	0.7	491(16)	0.2505(4)
O(1)	$4\mathrm{e}$		0.500000	0.7	481(16)	0.750000
O(2)	8f		0.69432(8)	0.7	0.7490(10)	
O(3)	8f		0.09592(14)	0.4	0.4460(9)	
O(4)	8f		0.09688(16)	0.9	0.9476(10)	
Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ir	0.00720	0.00930	0.00240	0.00140	0.00060	-0.00060
Sr(1)	0.00890	0.00300	0.00800	0.00000	0.00310	0.00000
Sr(2)	0.01070	0.00300	0.01100	0.00000	0.00610	-0.00260
O(1)	0.00700	0.00400	0.01900	0.00000	0.00800	0.00000
O(2)	0.00510	0.00700	0.01000	0.00100	0.00180	0.00320
O(3)	0.01130	0.00620	0.00390	0.00020	-0.00080	-0.00040
O(4)	0.01140	0.01160	0.00790	0.00000	-0.00060	-0.00460

Table 4.3: Results of refinement of T = 100 K neutron diffraction data to the C2/c model. Wyckoff site labels, relative atomic coordinates and anisotropic displacement factor matrices U_{ij} are included. R1 = 0.059

associated with the monoclinic group C^2/c was calculated to be 26 meV lower than that of *Ccce*, supporting the notion that the activation of the octahedral tilt mode permits a slight reduction of the overall energetics.

Based on the combination of neutron diffraction, RA-SHG data, and DFT analysis, the C2/c model is a more complete structural solution as it also resolves previous anomalies in reported neutron diffraction data. General reflection conditions for space group No. 15 (in the standard C2/c setting) impose the condition H + L = 2n [18]; now the weak 'violations' of the orthorhombic solution observed previously [19] are allowed reflections in C2/c. Structure factors corresponding to these reflections, calculated from the refined atomic positions in the monoclinic cell reported here, predict relative intensities of the order matching those observed in earlier triple-axis neutron studies [17, 19].

The C2/c model also offers a microscopic explanation of the anomalous presence of a net ferromagnetic moment in the basal plane of $Sr_3Ir_2O_7$ as seen in prior bulk susceptibility measurements [14, 25]. The solution of the magnetic structure depicts antiferromagnetically ordered moments aligned out-of-plane, along the \hat{a} -direction [13, 17, 44]; however scattering would be unable to resolve small (< 1°) projections of the moment away from this axis. Assuming a mechanism of spin-locking to octahedral orientation [4] similar to that observed in Sr_2IrO_4 [23, 45], the ordered moment in the C2/c setting would project a small component into the *b*-*c* plane below $T_N = 280$ K, resulting in a net ferromagnetic moment. To quantify this, the tilt angle observed at 100 K in conjunction with the reported ordered moment size of $0.36 \,\mu_{\rm B} \,\mathrm{Ir}^{-1}$ [17, 25] would imply an in-plane ferromagnetic moment of $\approx 1 \times 10^{-3} \,\mu_{\rm B} \,\mathrm{Ir}^{-1}$, in relatively good agreement with *b*-*c* plane magnetization data previously reported in this system [14, 46].

4.7 Conclusions

The measurements outlined here provide a comprehensive, multi-probe study arriving at the structural solution of the bilayer iridate system $Sr_3Ir_2O_7$. The assignment of the monoclinic space group C2/c (No. 15) readily accounts for previously reported rotations of the in-plane octahedra while at the same time enabling a subtle octahedral tilt mode distortion not resolved in previous studies of this system. This tilt breaks the nominal orthorhombic symmetry, lowering the point group from mmm to 2/m as seen in the RA-SHG data, and permits scattering at previously observed Bragg violations of *Ccce*. Including this further distortion in the structural model is supported by DFT calculations, which demonstrate that such a tilt represents a lowering of the overall lattice energy. Our data provide the needed foundation for understanding how the lattice distorts and its subsequent role as this spin-orbit Mott system is driven toward the metallic state via doping or pressure.

Publication

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Chapter 5

Phase Diagram of $(\mathbf{Sr}_{1-x}\mathbf{La}_x)_3\mathbf{Ir}_2\mathbf{O}_7$

With the basic electronic, magnetic, and structural properties of $Sr_3Ir_2O_7$ established, it is of interest to attempt to destabilize the spin-orbit aided Mott state by means of carrier doping (electrons, in this case). A systematic mapping of the evolution of magnetic and transport properties as a function of doping concentration allows a preliminary phase diagram to be constructed. The phase diagram is a helpful tool in evaluating the strength of competing interactions in $(Sr_{1-x}La_x)_3Ir_2O_7$, and provides context within which subsequent doping-dependence studies leveraging alternate probes might be understood. It also serves to contrast alternate methods of carrier insertion, such as chemical substitution of holes or surface doping of ions.

5.1 Introduction

As outlined in Chapter 1, the seminal examples of the spin-orbit Mott state were reported in the n = 1 and n = 2 members of the $\mathrm{Sr}_{n+1}\mathrm{Ir}_n\mathrm{O}_{3n+1}$ Ruddlesden-Popper series [1, 2], where Ir^{4+} cations, in the limit of a cubic crystal field, realize a $J_{eff} = 1/2$ antiferromagnetic ground state [3, 4]. Realizing new electronic phases in close proximity to this SOM state is a subject of considerable theoretical work [5], and recent experiments have begun to suggest exotic properties present in nearby metallic states [6, 7]. However, the central task of understanding the mechanism of the Mott state's collapse in these 5*d*-electron Mott systems remains an open question, where, for instance, the roles of competing phases and additional modes of symmetry breaking remain unaddressed. This chapter outlines a rigorous investigation of the phases accessed by doping elections (via La^{3+}) into $\mathrm{Sr}_3\mathrm{Ir}_2\mathrm{O}_7$.

The bilayer (n = 2) material Sr₃Ir₂O₇ is an excellent test system for exploring carrier substitution in a spin-orbit Mott material [8, 9]. The reduced short-range Coulomb interaction, U, attributable to its 5d valence states and the increased bandwidth inherent to Sr₃Ir₂O₇'s bilayer structure lead to a marginally stable insulating state [10]. As a result, the Mott insulating state manifests in the weak limit where the charge gap is of the same order as the nearest neighbor Heisenberg exchange coupling J [11, 12]. This provides a unique platform for exploring the collapse of the Mott phase, where relatively small perturbations (e.g. changes in carrier concentration) can affect dramatic changes in the stability of the insulating state, and one where the mechanism of the gap's collapse can be explored in the limit of dilute substitution.

Consistent with the idea of a delicate Mott state, $Sr_3Ir_2O_7$ has recently been

shown to manifest metallic behavior under small levels of La-substitution (electrondoping) [13]. However, little remains understood regarding the nature of the metallic state realized upon carrier substitution and the means through which the parent $J_{\text{eff}} = \frac{1}{2}$ Mott state collapses. For instance, once the Mott state is destabilized, conflicting reports have suggested both an unusual metallic state with a negative electronic compressibility [7] as well as a surprisingly conventional, weakly correlated metal [14]. Notably lacking is a detailed understanding of the structural and electronic responses of this prototypical weak SOM system as electrons are introduced. This remains an essential first step toward developing a deeper understanding of the interactions remaining after the parent SOM state is quenched.

Here the results of bulk transport/magnetization, neutron/x-ray scattering, and scanning tunneling spectroscopy (STS) measurements are presented in order to map the evolution of the antiferromagnetic SOM state in $(Sr_{1-x}La_x)_3Ir_2O_7$ upon electron substitution. Light electron doping initially drives the weak SOM state to fragment into nanoscale regions of mixed metallic and insulating character that eventually collapse into a uniform metallic regime beyond x = 0.04. The addition of donors to the system causes a swelling of the unit cell volume, and a parallel suppression of magnetostriction effects associated with the onset of Ising-like magnetic order [15]. Once in the globally metallic phase, the long-range G-type Néel state remnant from the parent Mott phase vanishes, and a metallic state with an enhanced susceptibility and Wilson ratio emerges. Our aggregate data demonstrate the doping-driven, firstorder, melting of a weak spin-orbit Mott phase into a correlated metal.

5.2 Details of Methodology

Single-crystal samples of $(Sr_{1-x}La_x)_3Ir_2O_7$ were grown via techniques similar to earlier reports [9, 16], with complete details provided in Chapter 3. Electronic transport measurements were carried out using a four-probe contact configuration and measured with a Lakeshore 370 AC Resistance Bridge. Measurements were performed in a Janis Research Company CCR with a base temperature of 3 K. Magnetization measurements were collected with Quantum Design Magnetic Property Measurement System (MPMS) 5XL SQUID and MPMS3 SQUID-VSM magnetometers. Heat capacity measurements were collected within a Quantum Design Physical Property Measurement System (PPMS).¹

Structural determination was carried out on crystals previously characterized for dopant concentration via EDS which were ground to a fine powder and measured in Bruker D2 Phaser and PANalytical Empyrean XRD machines at room temperature. No impurity phases were observed within instrument resolution. Lattice parameters and unit cell volumes were refined within the *Bbcb* space group (No. 68), shown in Fig. 5.2 (a). Data below x = 0.045 was binned into 0.01 wide bins centered at integer concentrations. Error bars about the refined lattice parameter value correspond to the estimated standard deviation output of the PANalytrical HighScore software package (errors were propagated for points representing bins of more than one measurement).

Neutron experiments were performed at the N5 triple-axis spectrometer at the Canadian Neutron Beam Centre, Chalk River Laboratories. Samples were mounted to thin (0.4 mm) Al plates with a drop of CYTOP fluoropolymer, cured at 100 °C for one hour. Sample orientation is known to have the *c*-axis perpendicular to the

¹Additional information regarding each of the probes listed here can be found in Chapter 2.

face of these small platelets, and the *a*-axis is often found parallel to a long, regular edge of the sample. Samples were aligned within a CCR in the $(H \ 0 \ L)$ plane using the orthorhombic *Bbcb* structural solution. Experiments were performed with PG monochrometer and analyzer using the $\mathbf{Q} = (0\ 0\ 2)$ reflection. The incident wavelength was 14.58 meV (2.370 51 Å) and collimations of 0' - 36' - 33' - 144' were used before the monochromator, sample, analyzer, and detector, respectively.

Resonant x-ray measurements were performed on beam line 6-ID-B at the Advanced Photon Source at Argonne National Lab and X22C at the NSLS at Brookhaven National Lab. The radiation source was an undulator insertion device at 6-ID-B and a bending magnet at X22C. Samples were mounted using a small spot of GE varnish to a small copper mount. This mount was connected to the cold head of a CCR using Be domes for the radiation shield and vacuum shroud. Samples were aligned in the (H 0 L) plane on (0 0 20) and (2 0 10) Bragg reflections (again, indexed in *Bbcb*). Data was collected with incident energy tuned to the resonant peak corresponding to the Ir L_3 edge (11.22 keV). Experiments on X22C utilized a Si(111) analyzer. 6-ID-B utilized a PG-008 crystal for polarization analysis.

Scanning tunneling microscopy/spectroscopy (STM/S) measurements² were performed at 4 K using etched W tips, on samples cleaved at ≈ 77 K in UHV. Cleavage was found to occur between SrO layers and, consistent with earlier reports [12], the atoms imaged in STM topographies belong to the Sr sublattice of the exposed SrO plane. dI/dV spectra were taken by the usual lock-in technique with tip height fixed in constant-current mode at +330 mV and -300 mV for maps shown later in Figs. 5.5 (c) and (d) respectively. Individual La dopants appear as squares in the topography (Figs. 5.5 (a) and (b)). In electronically phase-separated samples den-

²STM/S measurements were conducted by D. Walkup and V. Madhavan [17].



Figure 5.1: (a) Resistivity as a function of temperature $\rho(T)$ for $(\mathrm{Sr}_{1-x}\mathrm{A}_x)_3\mathrm{Ir}_2\mathrm{O}_7$, A=La and Ca. (b) Magnetization data for $(\mathrm{Sr}_{1-x}\mathrm{La}_x)_3\mathrm{Ir}_2\mathrm{O}_7$. Data plotted is fieldcooled (FC) minus zero-field cooled (ZFC) data under 800 Oe applied parallel to the c-axis.

sity fluctuations of La-dopants were not strongly correlated with the metal/insulator nature of the dI/dV spectra- that is, the spatial location of La-dopants was not correlated with the location of metallic puddles. The evolution of this effect and the role of surface and subsurface La dopants in destroying the insulating state locally is discussed elsewhere [18].

5.3 Bulk Probe Results

Immediately upon introducing La into $\text{Sr}_3\text{Ir}_2\text{O}_7$ a dramatic drop in the low temperature resistivity $\rho(T)$ is observed for concentrations as low as x = 0.01, as shown in Fig. 5.1 (a). Using the naïve metric of $\frac{\partial\rho}{\partial T} < 0$ as $T \to 0$ to define an "insulating" phase, the system is found to remain in an insulating state until $x_{\text{MIT}} \approx 0.04$ is



Figure 5.2: (a) Powder x-ray data showing the *a*-axis and unit cell volume as a function of La- and Ca-substitution in $\text{Sr}_3\text{Ir}_2\text{O}_7$. (b) Neutron scattering data showing relative shifts in lattice constants for $(\text{Sr}_{1-x}\text{La}_x)_3\text{Ir}_2\text{O}_7$. Values are the fractional change of lattice values from 225K, e.g. *a*-axis $\Delta\% = 100(\frac{a(T)-a(225K)}{a(225K)})$

reached. Upon further doping, a change in the sign of the low temperature $\frac{\partial \rho}{\partial T}$ occurs, which is hereafter denote for simplicity as the metal-insulator transition (MIT). Doping beyond this level results in the vanishing of the irreversibility in the static spin susceptibility, emblematic of AF ordering in Sr₃Ir₂O₇, as shown in Fig. 5.1 (b). This rapid quenching of the parent system's weak net ferromagnetism is coincident with the onset of the metallic phase and suggests the suppression of the Néel state in the metallic regime.

As electrons are introduced into the system, the in-plane lattice parameters expand (Fig. 5.2 (a)) while the *c*-axis remains unchanged within resolution. This results in a swelling of the lattice volume that continues with increased La-concentration, reminiscent of the lattice swelling observed in La-doped $SrTiO_3$ [19] where correlation effects enhance the destabilization/expansion of the lattice driven by adding conduction electrons into antibonding orbitals. This combined effect competes with steric effects and, if correlation effects are strong enough, can drive lattice expansion even at small doping levels. The relative magnitude of the volumetric expansion $\Delta V/V \approx 0.03\%$ per percentage of La-dopant is nearly identical for both $(Sr_{1-x}La_x)_3Ir_2O_7$ and La-doped SrTiO₃—suggesting a comparable role played by correlations. The magnitude of this effect can be demonstrated by alloying comparablysized, isovalent Ca²⁺ (180 pm)³ instead of La³⁺ (195 pm) into the system, where purely steric effects instead drive a lattice contraction (Fig. 5.2 (a)).

An additional structural response to the MIT is shown in Fig. 5.2 (b), which reveals that the anisotropic thermal contraction of the parent system upon cooling vanishes as it is doped into the metallic phase. Namely, both parent and lightly Ladoped $Sr_3Ir_2O_7$ samples possess a *c*-axis lattice constant that expands upon cooling while the basal plane lattice constants contract. The magnitude of this effect gradually switches to a conventional, uniform, thermal contraction as the MIT is traversed, and the doping-driven switch in behavior tracks the disappearance of irreversibility in the static spin susceptibility. This suggests that the expansion of the *c*-axis upon cooling for $x \leq x_{\text{MIT}}$ is driven by strong magnetoelastic coupling where magnetostriction between the Ising-like, *c*-axis oriented, moments and their local lattice environment drive an anisotropic distortion of the lattice.

5.4 Neutron and X-Ray Scattering

The disappearance of irreversibility in magnetization measurements, however, is not a rigorous metric for determining the doping evolution of the magnetic order in a

³Radii taken from [20]. For reference, the radius of Sr is 200 pm.



Figure 5.3: (a) Background subtracted magnetic order parameter measurements for $(Sr_{1-x}La_x)_3Ir_2O_7$. Data was collected at the $\mathbf{Q}=(102)$ position and normalized to a sample-dependent scale factor. (b) AF-ordered moment and relative weight of forbidden structural peak (109), representative of T_S for $(Sr_{1-x}La_x)_3Ir_2O_7$. Data for x=0 is taken from [16].

canted AF. To further investigate the evolution of AF order as the metallic state is approached, neutron scattering measurements were performed. For samples with $x \leq x_{\text{MIT}}$, magnetic scattering remained consistent with the G-type spin structure of the parent material [15, 16]. Scattering results plotted in Figs. 5.3 (a) and (b) show that the ordered AF moment rapidly collapses as x_{MIT} is approached, yet the ordering temperature remains only weakly affected. This contrasts the percolative MIT realized in Ru-doped $\text{Sr}_3\text{Ir}_2\text{O}_7$, where AF order survives into the metallic regime and remains coherent across electronically phase separated patches [21]. Instead, Lasubstitution rapidly quenches spin order associated with $\text{Sr}_3\text{Ir}_2\text{O}_7$'s G-type structure, which vanishes with the stabilization of the low temperature metallic state.

An additional order parameter also develops as a function of La-doping below a characteristic temperature $T_{\rm S}$. This distortion appears in the form of a weak, tem-



Figure 5.4: (a) Background subtracted neutron scattering data showing select $T_{\rm S}$ order parameters at the (109) wave vector. Intensity of the scattering has been normalized via a sample dependent scale factor. (b) Radial scans through the (107) reflection in both $\sigma - \sigma$ and $\sigma - \pi$ scattering channels for $(\mathrm{Sr}_{1-x}\mathrm{La}_x)_3\mathrm{Ir}_2\mathrm{O}_7 x = 0.058$ showing significant signal only from charge scattering.

perature dependent, superlattice at *Bbcb* forbidden $\mathbf{Q}=(odd\ 0\ odd)$ positions. Despite being a crystallographically forbidden position, polarization analysis for an x = 0.058 $(\mathrm{Sr}_{1-x}\mathrm{La}_x)_3\mathrm{Ir}_2\mathrm{O}_7$ sample at 6 K shows the superlattice to be nonmagnetic in origin. Fig. 5.4 (b) shows scans through (107) in the $\sigma - \sigma$ (charge) and $\sigma - \pi$ (magnetic) channels reveal a $\sigma - \pi$ peak intensity of just $\approx 2.4\%$ of the $\sigma - \sigma$ peak. This signal arises simply from bleed-through from $\sigma - \sigma$ due to inherent limits of the polarization analysis, and confirms the origin of the reflection to be via charge scattering. Figs. 5.3 (b) and 5.4 (a) show the evolution of this structural distortion as a function of increasing La-content. The relative weights of Bragg reflections associated with this distortion are plotted in Fig. 5.3 (b), and the corresponding temperature evolution of the order parameters are plotted in Fig. 5.4 (a). As La content is increased, both $T_{\rm S}$ and its relative scattering weight increase, seemingly saturating across $x_{\rm MIT}$.

5.5 Surface Probe and Thermodynamic Results

One explanation for the trade-off in scattering weight between this new structural order parameter and AF order, along with the relatively weak doping dependence of $T_{\rm S}$ and $T_{\rm AF}$ away from the critical regime, is that light electron-doping generates a phase separated ground state. To test this notion, STS measurements were performed on samples residing on both sides of the MIT. The resulting spectra of samples in the insulating x = 0.035 and metallic x = 0.048 regimes are plotted in Fig. 5.5 where electron-doping with $x \leq x_{\rm MIT}$ results in a nanoscale phase separated ground state with distinct insulating and gapless regions. Upon continued doping to x = 0.048, a homogenous, globally gapless, ground state is observed and is consistent with the metallic transport observed for $x > x_{\rm MIT}$.

Beyond $x_{\rm MIT}$, static spin susceptibility data for a metallic sample with x = 0.058are plotted in the Fig. 5.6 inset. The data, fit to a Curie-Weiss (CW) model with an additional temperature independent Pauli term, give $\Theta = -69 \pm 9 \,\mathrm{K}$ and $\mu_{\rm eff} = 0.51 \pm 0.02 \,\mu_{\rm B}$. This Curie-Weiss behavior can be shown to originate from metallic (electronically gapless) regions of the sample, and not from rare-region spin clusters with a spectral gap, by comparing the static spin susceptibility data with spectroscopic results. These two scenarios can be discriminated as follows: first, consider the requisite volume fraction of hypothetical clusters of local moments within the sample that would produce the effective Curie-Weiss observed in the inset of Fig. 5.6, recalling that the parent $\mathrm{Sr}_3\mathrm{Ir}_2\mathrm{O}_7$ material does not show high-temperature CW behavior above $T_{\rm N} \approx 280$ [22] (as depicted in Fig. 1.4; see Chapter 6 for further discussion of this behavior). In hypothesizing what the local moments of Ir⁴⁺ ions



Figure 5.5: STM topography of $(Sr_{1-x}La_x)_3Ir_2O_7$ at 300 mV bias for (a) insulating x=0.035 and (b) metallic x=0.048 samples. $\frac{dI}{dV}$ spectra obtained on a grid in each topograph are plotted in panels (c) for x=0.035 and (d) for x=0.048. Representative numbered points are highlighted in each map and the corresponding $\frac{dI}{dV}$ spectra are emphasized as solid lines in spectral histograms. Fully gapped and gapless spectra are observed in the x=0.035 sample while a homogenous, gapless state appears across spectra in x=0.048.

in the clusters could be, the strictest scenario is considered by using the full S=1/2 local moment $\mu_{\text{local}} = 1.73 \ \mu_{\text{B}}$ as the nominal Ir local moment. This local impurity moment can only generate the observed/apparent CW behavior of $0.51 \ \mu_{\text{B}} \ \text{Ir}^{-1}$ if full 1.73 μ_{B} moments occupied $\approx 9\%$ of the sample volume.

It can be shown that the STM data preclude this possibility. Fig. 5.5 (b) shows a 15 nm x 15 nm topographic map of the sample, whose spectral histogram is plotted in Fig. 5.5 (d). Within this map, no gapped regions were observed. This corresponds to a 22 500 Å² area map and a survey of 1480 unit cells (with a = b = 3.897 Å). The tetragonal unit cell has 3.897 Å as the nearest neighbor Ir-Ir distance, and there is one Ir-cation per 3.897 Å × 3.897 Å square. The positional binning of the spectral histogram is 2.4 Å × 2.4 Å. That no gapped regions were observed within the STS spectra therefore means that the upper limit for the volume fraction of gapped regions (presumably with clustered magnetic moments) is 0.07%. This is two orders of magnitude smaller than what is necessary to account for the local moment cluster explanation of susceptibility data. Hence, rare, gapped regions with local moments cannot account for the observed susceptibility.

Similarly, if a second scenario is considered where clusters of ferromagnetic spins saturate under the applied *H*-field and, via disorder, mimic a CW response. If once again the strictest case where full moments of $1 \mu_{\rm B} \, {\rm Ir}^{-1}$ occupy the polarized clusters is assumed, the volume fraction of the sample needed to host these polarized clusters (again presumably with an accompanying spectral gap) can be calculated. The measured $\chi(T)$ and applied field given in Fig. 5.6 imply a lower limit on the volume fraction of such clustered regions of 0.36% of the sample volume. This worst-case estimate is excluded by the gapless sample volume fraction surveyed in Figs. 5.5 (b) and (d) as detailed above. Additionally, larger STS maps surveying 562 500 Å² were



Figure 5.6: Heat capacity $c_v(T)$ data for x = 0.058 La. Dashed line is a fit to the form $c_v(T) = \gamma T + \beta T^3$ with $\gamma = 19.88 \pm 0.30$ [mJ mole⁻¹ K⁻²] and $\beta = 0.409 \pm 0.007$ [mJ mole⁻¹ K⁻⁴]. Inset shows $\chi(T)$ for this same sample with $H = 20kOe \parallel ab$ -plane with dotted line denoting the Curie-Weiss fit discussed in the text.

also collected and spectral histograms analyzed on this same sample [18]. These also revealed no gapped spectra, which further reduces the possible volume fraction of gapped regions to be smaller than 0.003% of the sample volume. Assuming that the surface electronic states probed by STS data are reflective of the bulk, the combined analysis of the susceptibility and STS data mandates the survival of a local moment response within gapless regions of the sample.

Heat capacity data from this same x = 0.058 concentration (Fig. 5.6) obtain a

Sommerfeld coefficient $\gamma = 19.88 \pm 0.30 \text{ [mJ mol}^{-1} \text{ K}^{-2}\text{]} (\gamma = 9.94 \text{ [mJ mol}^{-1} \text{ K}^{-2}\text{]}),$ also reflecting a metal with enhanced correlation effects. Low temperature $\chi(T)$ from this same sample shows $\chi = 0.0229 \text{ [J T}^{-2} \text{ mol}^{-1}\text{]}$ at T = 2 K, leading to a Wilson ratio⁴ of $R_W = \frac{\pi^2 k_B^2 \chi}{3 \mu_B^2 \gamma} \approx 8.4$. This enhanced R_W is consistent with a system near an instability [23] and suggests that the state realized for $x > x_{\text{MIT}}$ is a correlated metal with an enhanced spin susceptibility that retains remnant correlations from the SOM parent phase.

5.6 La-doping Phase Diagram

The electronic phase diagram summarizing the evolution of the SOM phase upon electron-doping is plotted in Fig. 5.7. Immediately upon doping electrons into the parent Sr₃Ir₂O₇, a regime of phase separation appears—one where nanoscale AF ordered insulating regions segregate from gapless metallic regions that stabilize a global structural distortion below $T_{\rm S}$. For $x < x_{\rm MIT}$, $T_{\rm S}$ increases in parallel to the growth of the volume fraction of the sample hosting the metallic phase. Similarly, the combined neutron/STM data of Figs. 5.3, 5.4 and 5.5 demonstrate that the apparent reduction in the AF moment under light electron doping largely arises from electronic phase separation of the sample into AF ordered insulating and paramagnetic metallic regions. Upon doping beyond the critical concentration of $x \approx 0.04$, a first-order line appears where AF order collapses and the system becomes globally metallic.

Earlier reports of persistent AF order in metallic concentrations of $(Sr_{1-x}La_x)_3Ir_2O_7$ were unable to discern whether this coexistence was intrinsic to the physics of a doped SOM insulator or extrinsic due to macroscopic sample inhomogeneity [13]. Our ob-

⁴For details concerning the evaluating the Wilson ratio see Appendix C, page 159.



Figure 5.7: Electronic phase diagram of $(Sr_{1-x}La_x)_3Ir_2O_7$. Open symbols denote neutron scattering measurements and closed symbols denote x-ray data. Black triangles denote scattering measurements of T_{AF} and red squares denote measurements of T_S . The dashed line marks the MIT measured via charge transport and the first-order line where the Néel state vanishes. The hatched region marks the electronically phase separated region where T_S and T_{AF} , AF-I denotes antiferromagnetic insulating state, and PM-M marks the paramagnetic metallic phase. Data for x = 0 taken from [16].

servation of an abrupt, first-order, collapse of the $Sr_3Ir_2O_7$ parent material's Néel state upon entering the metallic regime resolves this open question and demonstrates the instability of long-range AF order once the weak SOM state inherent to $Sr_3Ir_2O_7$ is tuned beyond half-filling. Since strong in-plane AF superexchange masks the local moment behavior above T_{AF} in undoped $Sr_3Ir_2O_7$ [11, 22], the doping-induced collapse of AF beyond the MIT ultimately allows for the Ir local moments to be observed in the correlated metallic regime.

Our measurements depict the destruction of the parent state's Néel order upon entering the metallic regime and are consistent with recent theoretical work demonstrating the filling-tuned, first-order MIT of a weak Mott state in the intermediate coupling regime [24, 25]. The first order nature of the MIT is demonstrated explicitly by the phase coexistence for $x \leq x_{\text{MIT}}$ plotted in Fig. 5.5. As the system is driven across the MIT phase boundary, the development of a structural symmetry breaking transition suggests a multicritical point driven by a competing energy scale, T_{S} , near the parent SOM phase.

As one test of whether $T_{\rm S}$ is endemic to the metallic state, additional neutron scattering measurements were performed on isovalent-substituted $({\rm Sr}_{0.93}{\rm Ca}_{0.07})_{3}{\rm Ir}_{2}{\rm O}_{7}$. This system remains an insulator (Fig. 5.1 (a)) and bulk irreversibility measurements show $T_{\rm N} \approx 270$ K, close to that of the unalloyed parent material. Still, the reduced cation size drives a low temperature structural distortion along the identical (odd, 0, odd) wave vectors as in La-substituted ${\rm Sr}_{3}{\rm Ir}_{2}{\rm O}_{7}$ (Fig. 5.4 (a)). $T_{\rm S}$ for this Ca-doped sample, however, occurs at a reduced energy scale relative to its Ladoped counterpart. This reduced $T_{\rm S}$ at a comparatively higher Ca-dopant concentration (larger steric perturbation) suggests that the electronic contribution to the lattice deformation enhances $T_{\rm S}$ and drives the metallic state. This is also consistent with reports of a structural distortion appearing near the pressure-driven MIT of $Sr_3Ir_2O_7$ [13, 26].

In summary, our data demonstrate the carrier-driven first-order melting of the SOM phase in $(Sr_{1-x}La_x)_3Ir_2O_7$, consistent with the predictions of an electronically phase separated state intermediate to the complete collapse of the Mott phase in the weak limit. Beyond the critical $x_{MIT} = 0.04$ concentration, the SOM state collapses into a metallic state with enhanced spin susceptibility and local moment behavior. Ascertaining whether the lattice distortion emergent at the onset of the metallic state is purely a structural effect or a secondary consequence of a competing electronic instability is an interesting avenue for future exploration.

Publication

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Chapter 6

Mapping the Evolution of Magnetic Excitations in $(\mathbf{Sr}_{1-x}\mathbf{La}_x)_3\mathbf{Ir}_2\mathbf{O}_7$

Now that the rudimentary phase diagram for $(\mathrm{Sr}_{1-x}\mathrm{La}_x)_3\mathrm{Ir}_2\mathrm{O}_7$ has been established, the impact of this carrier doping on spin dynamics is evaluated. Mentioned previously, two prior studies of the parent compound $\mathrm{Sr}_3\mathrm{Ir}_2\mathrm{O}_7$ arrived at somewhat conflicting conclusions regarding the strength of the magnetic exchange constants. These two models are evaluated via RIXS in the context of doping levels above and below x_{MIT} and complemented with additional bulk magnetization work in an effort to determine which more accurately describes the observed excitation spectra.
6.1 Introduction

Models of Heisenberg antiferromagnets on a bilayer square lattice have generated sustained theoretical and experimental interest due to their rich variety of ground states [1–5]. In zero field, an instability occurs above a critical ratio of interlayer to intralayer magnetic exchange that transitions spins from conventional antiferromagnetism into a dimer state comprised of spin singlets [1, 6]. These singlets may interact and form the basis for numerous unconventional ground states such as valence bond solids [7, 8], quantum spin liquids [4], Bose-glasses [9], and other quantum disordered states [8]. Realizations of bilayer systems inherently near the critical ratio of interlayer to intralayer coupling however are rare, primarily due to orbital/exchange anisotropies strongly favoring either interplane or intraplane exchange pathways in accessible compounds [10–12].

 $J_{\text{eff}} = \frac{1}{2}$ moments are arranged onto a bilayer square lattice within the n = 2member of the $\text{Sr}_{n+1}\text{Ir}_n\text{O}_{3n+1}$ Ruddlesden-Popper series, $\text{Sr}_3\text{Ir}_2\text{O}_7$ [13]. The strong spin-orbit coupling inherent to the Ir^{4+} cations in cubic ligand fields renders a largely three dimensional spin-orbit entangled wave function [14, 15]. This combined with the extended nature of its 5*d* valence electrons presents $\text{Sr}_3\text{Ir}_2\text{O}_7$ as an interesting manifestation of the bilayer square lattice—one where appreciable interlayer coupling potentially coexists with strong intralayer exchange inherent to the single layer analogue $\text{Sr}_2\text{Ir}\text{O}_4$ [16].

While its ground state is antiferromagnetic [19–21], measurements of magnetic excitations in $Sr_3Ir_2O_7$ observe anomalous spectra with large spin gaps ($\Delta E \approx 90 \text{ meV}$) whose values exceed that of the single magnon bandwidth [17, 18]. This has led to



Figure 6.1: Magnon dispersion relations for Sr-327 plotted for (a) LSW model of Kim *et al.*, with data reproduced at L = 26.5 r.l.u. from Ref. [17] and (b) the BO model of Moretti Sala *et al.*, with data reproduced at L = 28.5 r.l.u. from Ref. [18]. (c) Exchange terms within the Heisenberg models of the square lattice bilayer with dimer outlined by dashed red line (d) Illustration of momentum cuts in panels (a) and (b) across the AF zone

models shown in Figs. 6.1 (a) and (b) that cast the underlying exchange into two extremes: A linear spin wave approach with a large anisotropy gap and predominantly intraplane exchange [17] versus a bond operator (BO) mean field approach [22] with a dominant interplane, dimer-like, exchange [18, 23]. Recently, an additional excitation attributed to a longitudinal mode associated with triplon excitations was observed supporting the latter approach [24].

The comparable ability of both LSW and BO approaches to capture major fea-



Figure 6.2: Pseudo-Voight fits of incoherent elastic scattering after spectrometer alignment at the start of experiments measuring the x = 0.07 (left panel) x = 0.02(right panel) samples. The shape parameter is denoted as μ , the center as x_c , and the width of the peaks by Γ .

tures of the magnetic spectra of $Sr_3Ir_2O_7$ invites further study. In particular, considerable insight can be gained by probing the evolution of spin dynamics as static AF order is suppressed. Recent work has shown that, unlike Sr_2IrO_4 , $Sr_3Ir_2O_7$ can be driven into a homogenous metallic state with no static spin order via La-substitution [25, 26]. Local moment behavior, notably absent in parent $Sr_3Ir_2O_7$ [27], appears in these electron-doped samples and hints at an unconventional metallic state [25].

Here resonant inelastic x-ray scattering (RIXS) is utilized to explore the spin dynamics of $(Sr_{1-x}La_x)_3Ir_2O_7$ as it transitions from an AF insulator into a paramagnetic metal. Beyond x = 0.04 (6% electrons/Ir), AF order vanishes, yet robust magnetic excitations persist deep into the metallic regime. Excitations become overdamped as carriers are introduced, yet the large spin gap inherent to the AF parent state survives into the disordered regime. The spectral weight of magnons in the metallic state becomes nearly momentum independent and exhibits a dispersion best described using the BO representation appropriate for a dimer state [18]. Supporting this, static spin susceptibility measurements resolve the emergence of local moments which grow with increasing La-content and are consistent with a picture where each electron doped breaks a dimer and creates an uncompensated moment. Our aggregate data are best understood in the framework of a disordered dimer state emergent upon electron substitution in La-doped $Sr_3Ir_2O_7$.

6.2 Details of Methodology

Resonant elastic x-ray scattering (REXS) data were collected on the bending magnet beamline C1 at the Cornell High Energy Synchrotron Source (CHESS) at Cornell University. The sample was mounted to a copper post with a small amount of GE varnish, which was then connected to a 4K CCR employing Be domes for the radiation shield and vacuum shroud. Scattering measurements were conducted in the (H H L) scattering plane, and samples aligned using the (0010) and (1110) Bragg reflections.¹ Elastic data reported here was collected at the Ir L₃ edge (11.218 keV) utilizing a PG-006 crystal for polarization analysis and a NaI detector.

Resonant inelastic x-ray scattering (RIXS) measurements were performed at 27-ID-B at the Advanced Photon Source at Argonne National Laboratory. Samples were mounted to an aluminum fixture with a small amount of GE varnish, which was then connected to a closed cycle refrigerator (CCR). In order to maximize signal intensity a radiation shield was not used. Instead, only a Be-domed vacuum shroud was used which limited the base temperature to 40 K. Scattering measurements were conducted primarily within the (H K 26.5) plane, with the crystal aligned via the $\mathbf{Q} = (0\,0\,20)$ and $\mathbf{Q} = (1\,1\,20)$ Bragg reflections.²

¹Reflections here are indexed in the I_4/mmm tetragonal space group (No. 139).

²See Footnote 1.

A double crystal diamond-111 monochromator was positioned before a channel cut Si-448 monochromator, with E_i set to the Ir L₃ edge value (11.215 keV). E_f was measured with a diced spherical Si-448 analyzer and a DECTRIS MYTHEN detector. After alignment of the incident optical components, the sample scattering angle 2θ was set to 20° (vertical), and an energy scan was taken to measure the elastic line from two pieces of scotch tape. The full width at half maximum (FWHM) of the resulting peak provides a metric for the energy resolution of the measurement ($\Delta E_{\rm res} = 32 \,{\rm meV}$). Fits of the elastic line with a pseudo-Voight function are shown in Fig. 6.2.

RIXS spectra were collected at T = 40 K for two La-doped Sr-327 concentrations: x = 0.02, an AF insulator ($T_{AF} \approx 240$ K) and x = 0.07, a paramagnetic metal [25]. Momentum positions are denoted using the in-plane (H, K) wave vectors in the approximate tetragonal unit cell ($a \approx b \approx 3.90$ Å) and, unless stated otherwise, momentum scans were collected at L = 26.5 [r.l.u.]. Representative spectra for both x = 0.02 and x = 0.07 samples are shown in Fig. 6.3. Cuts taken at zone center $Q = (\pi, \pi)$ and zone boundary $Q = (\pi, 0)$ positions³ are shown with the elastic line (E), single magnon (M), proposed multimagnon (M^*), and d - d excitations (D) shaded. Individual excitations were fit to as a Lorenztian $L_Q(E)$ multiplied by the Bose population factor $B_T(E)$ (Eq. 6.1). The inverse lifetime values Γ_Q for all excitations were substantially greater than the instrumental resolution.

$$I_Q(E) = L_Q(E) \cdot B_T(E) = \left(\frac{2A}{\pi} \frac{\Gamma_Q}{4(E - E_Q)^2 + \Gamma_Q^2}\right) \left(1 - e^{\frac{-E}{k_B T}}\right)$$
(6.1)

³In discussing the dispersion, tetragonally indexed momenta coordinates are scaled by an additional factor of π , in the fashion of notation used in similar studies on cuprate materials.



Figure 6.3: Representative energy scans collected at 40 K at fixed **Q** for samples with x = 0.02 and x = 0.07. Panels (a) and (b) show scans performed at the AF zone center (π, π) and zone boundary $(\pi, 0)$ for AF insulating x = 0.02 respectively while panels (c) and (d) show the same scans for paramagnetic, metallic x = 0.07. Features labeled E, M, M^* , and D denote scattering from the elastic line, single magnon, multimagnon, and d - d excitations respectively.

Full energy spectra were fit using the following components: an overall constant background term, an elastic line fit to a pseudo-Voigt function, a small linear background on the x-ray energy loss side typically associated with a particle-hole continuum, and a series of four peaks associated with magnetic (M, M^*) and d - dexcitations (D) modeled as shown in Eq. 6.1. These peaks were symmetrized to the energy gain side of the spectrum using detailed balance, however their contributions are drastically suppressed due to weighting by the Boltzmann factor (where $T_{\text{meas.}} = 40 \text{ K} \ll \Delta E_{\text{res}}/k_{\text{B}} = 371 \text{ K}$).

The fitting routine was executed in four steps, the first three of which identified a workable set of starting parameters for a full fit to the data. These steps were:

- 1. The energy gain side of the spectrum was fit to a pure pseudo-Voight function and constant background term to extract the elastic line's profile.
- 2. Parameters associated with features in the region $-1500 \text{ meV} < \Delta E < -500 \text{ meV}$ were then added to the refinement. This consisted of d-d excitations (*D*-peaks) as well as a small linear background term.
- 3. These high energy and elastic peak parameters were then fixed, and the low energy M and M^* peaks $-500 \text{ meV} < \Delta E < 0 \text{ meV}$ were added and allowed to refine.
- 4. Having identified these parameters as a starting point, as a final step, all parameters are then refined simultaneously for the final spectra fits shown throughout.

Fits assumed that the M^* peak was present in all spectra, that its amplitude should be less than that of the M peak, and that its width should be of the same order of the M peak. Besides the examples of spectra fits shown in Fig. 6.3, fits



Figure 6.4: Additional energy scans collected at 40 K at fixed **Q** for samples with x = 0.02 and x = 0.07. Panels (a) and (b) show scans performed at $(\pi/2, \pi/2)$ and (0, 0) for AF insulating x = 0.02 respectively while panels (c) and (d) show the same scans for paramagnetic, metallic x = 0.07. Features labeled E, M, M^* , and D denote scattering from the elastic line, single magnon, multimagnon, and d - d excitations respectively.

at the remaining high symmetry points are shown in Fig. 6.4 to show the routine is robust across the dispersion.

6.3 Dispersion Analysis

The dispersions of the M and M^* peaks along the high symmetry directions illustrated in Fig. 6.1 (d) are plotted for both samples in Fig. 6.5. Energies of M (squares) and M^* (circles) peaks are shown with the Γ_Q associated with M peaks illustrated via the larger shaded regions. Only one feature associated with a single magnon excitation could be identified, and no additional acoustic/optical branches associated with spin waves from a bilayer or longitudinal modes associated with triplon excitations were isolated.

In order to investigate the out-of-plane (*L*-dependent) dispersion of the magnon feature, a series of spectra were collected for various *L* values at a fixed in-plane momentum transfer of $\mathbf{Q} = (0,0)$. This in-plane position also corresponds to the wave vector where the longitudinal mode in the parent material had dispersed far away from the principal magnetic peak, representing the most ideal conditions under which to resolve the reported longitudinal mode [18]. Spectra collected at $\mathbf{Q} = (00 L)$ positions for various *L* in the x = 0.07 sample are shown in Fig. 6.6 (a).

Aside from the increase in the elastic peak (ascribed to an increase in Thompson scattering caused by the scattering angle deviating from the near-90° condition at L = 26.5) it should be noted there is no additional feature resolved that may be attributed to a longitudinal branch. Subsequent fitting of these spectra (Fig. 6.6 (a)) demonstrate that the data are fully reproduced by fits employing only the E, M, M^* and D features described previously. The resulting fit peak areas and energies of the



Figure 6.5: Dispersion of M and M^* features for (a) x = 0.02 and (b) x = 0.07 samples. M and M^* peaks are plotted as squares and circles respectively, each with accompanying errors. The larger shaded regions about the M-dispersion are the excitations' FWHM. Solid lines denote fits to the transverse modes using the BO model and dashed lines denote the predicted positions of longitudinal modes.



Figure 6.6: (a) Raw data and fits of energy scans collected at various L values along fixed $\mathbf{Q} = (00 L)$ for the x = 0.07 sample at 40 K. (b) Calculated L-dependence for intensities of the transverse (red) and longitudinal (blue) modes at fixed momentum transfer $\mathbf{Q} = (00 L)$. Dashed lines indicate calculation for the parent using parameters reported in [18]; solid lines were calculated using exchange constants derived from fits to the M-dispersion of the x = 0.07 sample shown in Fig. 6.5. Black squares are the spectral weight of the M feature in (a), normalized to the model curve at L=26.5 for clarity. Green squares, corresponding to the right axis, indicate the center of the M peak.

M peaks are plotted in Fig. 6.7 (b). Both are L-independent within error for the zones explored, as in the parent compound [17].

Any weak additional modes are obscured due to the overdamping of the M excitations as carriers are introduced—an effect which partially convolves the M and M^* features. The rapid decrease in excitation lifetimes (shown in Fig. 6.7) with increasing La-content precludes any subtle features from being conclusively extracted from the data. The predicted intensity of the longitudinal mode relative to transverse modes [18] is illustrated in Fig. 6.6 (b). The lifetime broadening of the M peaks as



Figure 6.7: *M*-peak widths as a function of in-plane momentum transfer (Q_c fixed at L = 26.5). Red symbols show fit values for the x=0.07 sample and blue symbols show values for the x = 0.02 sample. The inverse lifetimes of the *M*-excitations have a weak momentum dependence and increase from an average value of $\Gamma_{avg} = 75$ meV for x = 0.02 to $\Gamma_{avg} = 124$ meV for x = 0.07.

La content is increased from the insulating x=0.02 sample to the metallic x=0.07 sample (Fig. 6.7).

Despite the absence of this second mode, tests can still be made using the collected RIXS spectra regarding the suitability of the LSW and BO approaches to the bilayer square lattice Heisenberg Hamiltonian, described by in-plane exchange constants J_1 , J_2 , J_3 , interplane exchange J_c , and an anisotropy term θ as illustrated in Fig. 6.1 (c) [17, 18]. Specifically, the data show that the gap energies of M-peaks at the (π, π) and (0, 0) positions become increasingly inequivalent upon doping. For the x = 0.07 sample, the AF zone center (π, π) gap value decreases to $E_{\pi,\pi} = 73 \pm 4$ meV whereas the Γ -point (0, 0) gap remains nearly unchanged from the parent system at $E_{0,0} = 89 \pm 4$ meV as shown in Fig. 6.8. The differing energies of the M



Figure 6.8: Zoom in of raw RIXS data collected at $\mathbf{Q} = (\pi, \pi)$ (blue squares) and $\mathbf{Q} = (0, 0)$ (red squares). Solid lines are full spectra fits described previously. Dashed vertical lines denote the energy centers for M peaks in each scan.

peaks at these two points suggest that a simple LSW model cannot account for the dispersion [17]. In a naive LSW approach, the combined optical plus acoustic spectral weight should remain degenerate at the (π, π) and (0, 0) positions, which for the x = 0.07 sample would violate the assumption that both an acoustic and optical mode are convolved within the largely *L*-independent *M* excitations [17]. The BO approach however allows for nondegenerate spectral weight at these positions through inequivalent transverse mode $E_{\pi,\pi}$ and $E_{0,0}$ gap values whose ratio is governed by the anisotropy term $\cot(\theta) = E_{0,0}/E_{\pi,\pi}$. Therefore, to parameterize the dispersion in electron-doped Sr₃Ir₂O₇ samples, the BO model was utilized [18, 23].

6.4 Fitting the Dispersion

For completeness, we reproduce the spin Hamiltonian and bond operator derived dispersion relation from Moretti Sala et al. [18]:

$$H = J \sum_{\langle ij \rangle, l} \left[\cos\left(2\theta\right) \vec{S_{li}} \cdot \vec{S_{lj}} + 2\sin^2\left(\theta\right) S_{li}^z S_{lj}^z - \epsilon_i \epsilon_l \sin\left(2\theta\right) \left(\vec{S_{li}} \times \vec{S_{lj}}\right) \cdot \hat{e}_z \right] + J_2 \sum_{\langle\langle ij \rangle\rangle, l} \left[\vec{S_{li}} \cdot \vec{S_{lj}} \right] + J_3 \sum_{\langle\langle\langle ij \rangle\rangle\rangle, l} \left[\vec{S_{li}} \cdot \vec{S_{lj}} \right] + J_c \sum_i \left[\vec{S_{1i}} \cdot \vec{S_{2i}} \right]$$
(6.2)

The exchange constants J_1 , J_2 , J_3 , and J_c are depicted in Fig. 6.1 (c). The second and third terms in the *J*-weighted summation are contributions resulting from anisotropic superexchange interactions (pseudodipolar and Dzyaloshinsky-Moriya terms, respectively); the parameter θ governs the degree of anisotropy characterizing the interactions ($\theta \to 0 \Rightarrow$ fully isotropic). The dispersion relation associated with the BO treatment of the above Hamiltonian is given by:

$$\omega_{\boldsymbol{q},\alpha} = \sqrt{A_{\boldsymbol{q},\alpha}^2 + |B_{\boldsymbol{q},\alpha}|^2} \tag{6.3}$$

Where α indicates the longitudinal (z) and degenerate transverse $(\tau = x, y)$ modes. The functions A and B are defined for the longitudinal mode $(\alpha = z)$ as,

$$A_{q,z} = 4J_1 \left[\sin^2(2\chi) \left(1 - \frac{J_2}{J_1} - \frac{J_3}{J_1} \right) + \frac{J_c}{4J_1} \cos(2\chi) \right] + \frac{J_1}{2} \left[\cos^2(2\chi)\gamma_q + \frac{J_2}{J_1}\delta_q + \frac{J_3}{J_1}\phi_q \right]$$
(6.4)
$$B_{q,z} = \frac{J_1}{2} \left[\cos^2(2\chi)\gamma_q + \frac{J_2}{J_1}\delta_q + \frac{J_3}{J_1}\phi_q \right]$$

...and for the transverse modes ($\alpha = \tau$) by Eq. 6.5:

$$A_{q,\tau} = 2J_1 \left[\frac{J_c}{2J_1} \cos^2(\chi) + \sin^2(2\chi) \left(1 - \frac{J_2}{J_1} - \frac{J_3}{J_1} \right) \right] + \frac{J_1}{2} \left[\cos(2\theta) \cos(2\chi) \right] \gamma_q + \frac{J_2}{2} \delta_q + \frac{J_3}{2} \phi_q$$
(6.5)
$$B_{q,\tau} = \frac{J_1}{2} \left[\cos(2\theta) - i \sin(2\theta) \sin(2\chi) \right] \gamma_q + \frac{J_2}{2} \cos(2\chi) \delta_q + \frac{J_3}{2} \cos(2\chi) \phi_q$$

Further parametrizations of these functions are as follows:

$$\gamma_{q} = 2 \left[\cos(q_{x}) + \cos(q_{y}) \right]$$

$$\delta_{q} = 2 \left[\cos(q_{x} + q_{y}) + \cos(q_{x} - q_{y}) \right]$$

$$\phi_{q} = 2 \left[\cos(2q_{x}) + \cos(2q_{y}) \right]$$

$$\chi = \frac{1}{2} \cos^{-1} \left(\frac{J_{c}}{4(J_{1} - J_{2} - J_{3})} \right)$$

(6.6)

Fits using the BO generated dispersion relations along the pathways illustrated in Fig. 6.1 (d) are shown as solid lines in Figs. 6.5 (a) and (b). Due to the suppressed spectral weight expected for the longitudinal mode [18] and the broadened Γ values inherent to doped samples, the predicted longitudinal branches lie convolved either within the FWHM of the M mode or M^* feature. Fits were therefore performed only to the transverse modes' dispersion, and the predictions for the accompanying longitudinal modes are plotted for reference. Using this parameterization, the coupling constants are found to evolve with La-content as indicated in Table 6.1.

While electron-doping drives a subtle shift in the M dispersion, the bandwidth is largely unaffected upon transitioning from the AF insulating regime (x = 0.02) into the paramagnetic, metallic state (x = 0.07). This is striking, in particular due to the reported absence of magnetic order in the x = 0.07 sample [25]. The distribution



Figure 6.9: (a) Energy integrated spectral weight of M peaks across the AF zone. Data for x = 0.02 (blue circles) show a maximum at the zone center consistent with its AF ordered ground state. Data for x = 0.07 (red circles) show a nearly Q-independent response. (b) REXS data showing the absence of AF correlations in the x = 0.05 sample. Black circles denote H-scans through the AF position $(\frac{1}{2}, \frac{1}{2}, 18)$ in the $\sigma - \pi$ channel. Red circles denote the structural reflection at $(\frac{1}{2}, \frac{1}{2}, 19)$ in the $\sigma - \sigma$ channel scaled by 1/50 for clarity. Background has been removed from the data.

of the spectral weights of M peaks in both samples further reflect this fact and are plotted in Fig. 6.9 (a). In the AF x = 0.02 sample, the energy integrated weight is maximal at the magnetic zone center (π, π) as expected [28]; however this zone center enhancement vanishes with the loss of AF order in the x = 0.07 sample.

6.5 **REXS** Investigation of Short Range Order

In order to further search for signatures of remnant short-range order in the metallic regime, REXS measurements were collected at 7 K on an x = 0.05 crystal. Data collected at the Ir L_3 edge are plotted in Fig. 6.9 (b) showing *H*-scans through the

	Ref. [18]	This Work	This Work	
	x = 0	x = 0.022	x = 0.071	Units
J_1	26	37.7 ± 0.4	29.1 ± 0.7	meV
J_2	-15	-14.0 ± 0.3	-17.0 ± 0.6	meV
J_3	6	4.8 ± 0.3	5.2 ± 0.6	meV
J_c	90	87.6 ± 1.1	80.1 ± 2.3	meV
θ	37	41.2 ± 0.7	37.2 ± 1.7	degrees (°)

Table 6.1: Summary of refined magnetic exchange parameters for x = 0.02 and x = 0.07 samples compared with the parent x = 0 system as reported in Ref. [18]. Note that errors are extracted from the non-linear least squares fitting routine and are artificially low; an alternate empirical uncertainty bound is $\approx 5\%$ of the exchange constant.

magnetic $(\frac{1}{2} \frac{1}{2} 18)$ and structural $(\frac{1}{2} \frac{1}{2} 19)$ reflections in the $\sigma - \pi$ and $\sigma - \sigma$ channels respectively. No signal was found in the $\sigma - \pi$ channel at the nominal magnetic wave vector $\mathbf{Q} = (\frac{1}{2} \frac{1}{2} 18)$, and so additional wider scans along high-symmetry directions were made in an attempt to perform a broader search of alternate positions in reciprocal space. In Fig. 6.10 (a) these scans have been normalized to a monitor, background subtracted, and offset from zero for clarity in order to demonstrate that no magnetic correlations were observed. Despite the lack of any magnetic signal, a weak, non-resonant (Fig. 6.10 (b)) structural reflection was observed in the $\sigma - \sigma$ channel at $(\frac{1}{2} \frac{1}{2} 19)$; shown at (1/50) scale in Fig. 6.9 (b).

These same reflections ($\mathbf{Q} = (\frac{1}{2} \frac{1}{2} 18)$ and $\mathbf{Q} = (\frac{1}{2} \frac{1}{2} 19)$ in the $\sigma - \pi$ and $\sigma - \sigma$ scattering channels respectively) were also measured via REXS in an AF ordered x = 0.023 sample at 7K. Data were normalized to a common monitor, and constant background terms were subtracted; see Fig. 6.10 (c). For x = 0.023, both the antiferromagnetic Bragg reflection at $(\frac{1}{2} \frac{1}{2} 18)$ and the weak structural peak at $(\frac{1}{2} \frac{1}{2} 19)$ are apparent. These data give a relative measure of the intensities of the $(\frac{1}{2} \frac{1}{2} 19)$ and $(\frac{1}{2} \frac{1}{2} 18)$ peaks in a control sample whose ordered moment is known to



Figure 6.10: (a) Scans along high symmetry directions of the magnetic zone. Curve colors correspond to the direction of the cut shown in the inset map of reciprocal space using the dispersion momentum notation. Data points represent count times of at least three minutes per point. (b) Energy scan in the $\sigma - \sigma$ channel at the Q = (0.50.519) peak position showing a signature of the Ir-L₃ (11.215 keV) absorption edge and no resonant enhancement. (c) $\theta - 2\theta$ scans of the (0.50.518) and (0.50.519) features in their respective scattering channels for a doped sample where both are present (x = 0.023). Solid lines depict Lorentzian fits of the peaks.

be $m_{\rm AF} \approx 0.31 \ \mu_{\rm B} \ [25]$.

The corresponding scans performed on an x = 0.05 sample (plotted in Fig. 6.9 (b)) can be compared with this x = 0.023 data to generate an estimate of the measurement's sensitivity. To give an initial sense of scale, the scattering volumes of the two samples were comparable and the x = 0.023 sample's magnetic peak at $(\frac{1}{2}, \frac{1}{2}, 18)$ in Fig. 6.10 (c) was collected at count times of 10 s per point whereas the flat data for the x = 0.05 sample in Fig. 6.9 (b) was collected at 270 s per point. Using the normalized peak intensities and assuming the same theoretical spin structure for both x = 0.023 and x = 0.05, the upper bound for the AF ordered moment in the x = 0.05sample becomes $m_{\rm AF} < 0.06 \ \mu_{\rm B}$. This number also accounts for the changes in the relative intensities of the weak $(\frac{1}{2}, \frac{1}{2}, odd)$ structural peaks induced via La-substitution (a factor of $\approx 3.4 \times$ enhancement for x = 0.05).

The absence of static antiferromagnetism in samples with x > 0.04 is consistent with earlier neutron diffraction measurements [25] and render it distinct from its single layer analogue, Sr₂IrO₄. In electron-doped Sr₂IrO₄, short-range AF order survives to the highest doping levels explored $\approx 12\%$ electrons/Ir [26, 29] and can account for a magnon dispersion with slightly renormalized magnetic exchange [30]. In contrast, electron-doping Sr₃Ir₂O₇ reveals gapped spin excitations that persist beyond the disappearance of AF order. While a slight increase in J_c/J_1 from 2.32 to 2.75 accompanies the disappearance of AF order and is naively consistent with predictions for the formation of a dimer state beyond a critical ratio of $J_c/J_1 \approx 2.5$ [1, 6], the extended in-plane exchange and anisotropy terms used in the BO approach of Ref. [18] as well as the presence of doped carriers necessarily modify this critical threshold [31].

6.6 Bulk Magnetization Evidence of Dimer Pairs

Although doping complicates models of dimer excitations, it also provides a further test for a hidden dimer state in $Sr_3Ir_2O_7$. In the simplest picture, adding an electron to the IrO_2 planes creates a nonmagnetic Ir^{3+} site within a sea of $J = \frac{1}{2}$ moments. For a ground state composed of uncorrelated dimers, this nonmagnetic site should break a dimer and leave an uncompensated $J = \frac{1}{2}$ moment behind. Hence, doping the dimer state with electrons should simultaneously seed nonmagnetic Ir^{3+} sites and an increasing fraction of weakly coupled, uncompensated spins within the sample. An order by disorder transition should eventually follow among these unfrustrated local moments in the T = 0 limit [32–34].

Intriguingly, previous magnetization measurements reported an unusual Curie-Weiss (CW) response in electron-doped Sr₃Ir₂O₇ [25]. This fact combined with the absence of CW behavior in the high temperature susceptibility of the parent system (see Fig. 1.4, page 13) suggests a dopant induced local moment behavior. To explore this further, magnetization measurements were performed on a series of $(Sr_{1-x}La_x)_3Ir_2O_7$ samples with varying levels of La-content. The high temperature CW susceptibilities for each sample are plotted in Fig. 6.11 (a) and the local paramagnetic moments (μ_{eff}) are plotted as a function of La-concentration in Fig. 6.11 (b). The μ_{eff} extracted from CW fits grows with increasing doping, and the μ_{eff} induced per La-dopant approaches that of uncompensated $J = \frac{1}{2}$ local moments. The absence of static AF order combined with the growth of local moments in the presence of significant AF exchange supports the notion of an underlying disordered dimer state in metallic Sr₃Ir₂O₇.



Figure 6.11: (a) Curie-Weiss fits to high temperature susceptibility with a temperature independent χ_0 term removed and collected under H = 5 kOe. (b) Local moments $\mu_{\text{eff}}/\text{La}$ extracted from fits in panel (a).

The nearly Q-independent energy-integrated spectral weight of the M-excitations in the metallic regime is also consistent with a dimer state where the intradimer coupling (J_c) approaches the excitation bandwidth. The small increase in the J_c/J_1 ratio as doping is increased from x = 0.02 and x = 0.07 samples is however not the likely driver for the dimer state's stabilization, in particular given that $J_c/J_1 \approx 3.5$ reported for the AF ordered parent system [18] exceeds the ratios for both of the doped compounds. Additionally, structural changes driven by electron doping in Sr₃Ir₂O₇ are relatively small, and the nearly cubic ligand field of Sr₃Ir₂O₇ ($\Delta_d =$ 1.10×10^{-4} [35]) does not change appreciably with electron doping [25]. Rather, a dimer state is likely stabilized by the critical threshold for dimer formation being driven downward via electron-doping similar to t - J models of hole-doping in bilayer cuprates [31, 36, 37].

In summary, RIXS data reveal spin excitations in $(Sr_{1-x}La_x)_3Ir_2O_7$ that persist

across the AF insulator to paramagnetic metal transition. Across the insulator-metal transition, static AF correlations vanish and extended LSW models fail to describe the surviving spin spectra with nondegenerate excitations at the two-dimensional AF zone center and Γ points. Instead, a BO-based mean field approach, reflective of strong interplane dimer interactions, captures the observed dispersion and suggests a disordered dimer state in the metallic regime. The presence of a hidden, disordered dimer state is supported by bulk magnetization data which reveal the emergence of anomalous local moments in $(Sr_{1-x}La_x)_3Ir_2O_7$ and are consistent with dopant-induced creation of uncompensated spins from broken dimer pairs. Our results point toward an unconventional metallic state realized beyond the collapse of spin-orbit Mott state in Sr_3Ir_2O_7.

Publication

This chapter is based largely on a publication titled *Disordered Dimer State in Electron-Doped* $Sr_3Ir_2O_7$, which appeared in Physical Review B [38]. Acknowledgments and funding sources contributing to this research are reproduced below.⁴

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Appendix A

Hund's Rules

A.1 General Application

Hund's rules provide an algorithm which minimizes the relevant interaction energies (Coulomb and spin-orbit) in a given electronic structure to provide an estimate as to the ground state configuration of a given free ion. In the case of L-S spin-orbit interaction (Russell-Saunders coupling [1]), the ion's Hamiltonian commutes with L and S, and thus J as well. Therefore, L, L_z , S, S_z , J, and J_z are all good quantum numbers and Hund's rules typically apply [2].

An example is first considered for an Ir^{2+} ion,¹ and the quantum numbers describing the state of the electrons in the unfilled d shell are identified. The structure of this ion is given by [Xe] $4f^{14}$ $5d^7$, so the principal quantum number n = 5 can be read explicitly. Using Table A.1, the angular momentum quantum number l is easily discerned from the spectroscopic shell labeling convention.

Thus for a free Ir^{4+} ion l = 2. The (2l + 1) allowed m_l states are spanned by

¹Note that this first example is *not* the 4+ oxidation state of Ir in Sr₃Ir₂O₇.

orbital	s	р	d	f	g	h	i	k	1
l =	0	1	2	3	4	5	6	7	8

Table A.1: Spectroscopic labeling scheme for the azimuthal quantum number *l*.

 $\pm l$, and so the allowed m_l are 2, 1, 0, -1, -2. Since these are electrons, $m_s = 1/2$. Hund's rules are now applied in order of *decreasing* priority- that is, satisfying the condition of Rule 1 takes precedence over Rule 2, and likewise Rule 2 over Rule 3.

Rule 1: Maximize S

The total intrinsic angular momentum S is given by the summation

$$S = \sum m_s = \frac{1}{2} \left(N_{\rm up} - N_{\rm down} \right) \tag{A.1}$$

This total spin angular momentum is just the number of unpaired electrons multiplied by m_s . To maximize S is essentially to minimize the Coulomb potential by partially filling all the orbitals with a single electron first, and only then adding a second electron of opposite spin (in keeping with the Pauli exclusion principle) to assign the remainder. The five different d orbitals are represented schematically below, where the arrows represent electrons whose spin is indicated by the arrow direction:

$$\uparrow \uparrow \downarrow \uparrow \uparrow \uparrow \uparrow \downarrow$$

The choice of which orbitals to double-occupy is 'random' above to emphasize that without considering angular momentum, they are all degenerate, and so any choice is valid with regard to the first Hund's rule of maximizing S. In this example, applying Eq. A.1 to the above gives S = (5-2)/2 = 3/2.

Rule 2: Maximize L

As just mentioned, however, the orbitals are not strictly degenerate in the presence of spin-orbit coupling. Instead, they should be distinguished using the associated m_l value:

$$\overline{2}$$
 $\overline{1}$ $\overline{0}$ $\overline{-1}$ $\overline{-2}$

But now the choice of which orbitals to doubly occupy is non-trivial. It is Hund's second rule which guides this decision- the configuration is chosen such that the orbital angular momentum is maximized, where L is given by

$$L = \sum m_l \tag{A.2}$$

Clearly L is maximized when the band is near quarter-filling $(L = l + l - 1 + \dots + 0)$, and at half-filling it is zero $(L = l + \dots + -l = 0)$. Beyond half-filling, the highest m_l orbital is doubly occupied first, and then $m_l - 1$ and so on. In the Ir²⁺ example, this looks like

$$\frac{\uparrow\downarrow}{2} \stackrel{\uparrow\downarrow}{\frac{1}{1}} \stackrel{\uparrow}{\frac{1}{0}} \stackrel{\uparrow}{\frac{1}{-1}} \stackrel{\uparrow}{\frac{1}{-2}}$$

Where a maximal value of L = 2(2) + 2(1) + 1(0) + 1(-1) + 1(-2) = 3 is obtained.

Rule 3: Minimize J

The final rule aids in determining the value of $J = |L \pm S|$, which is to be minimized. In the case that the shell is less than half-filled, J = |L - S|. In the case that it is greater than half-filled, J = |L + S| (one can verify easily that for the case of exactly half-filling J = S, and represents the absolute maximum for either choice of sign). For the example, J = |3 + 3/2| = 9/2.

A.2 Ir⁴⁺ in $Sr_3Ir_2O_7$

Consider now the case of Ir^{4+} ([Xe] $4f^{14}$ $5d^5$), the actual oxidation state present in $Sr_3Ir_2O_7$. Applying Hund's rules yields the half-filling configuration just described:

$$\frac{\uparrow}{2} \quad \frac{\uparrow}{1} \quad \frac{\uparrow}{0} \quad \frac{\uparrow}{-1} \quad \frac{\uparrow}{-2}$$

Where S = 5/2, L = 0, and J = 5/2. This high-spin state (wherein S is maximal) clearly does not match the final result of Section 1.3. The reason for this is two-fold: first, recalling at the outset of this appendix the statement that Hund's rules apply to *free* ions. This simplified analysis ignores the ligand-derived crystal electric field in which the Ir⁴⁺ ion resides in the Sr₃Ir₂O₇ system. The effect of that crystal field, shown by an explicit calculation of the matrix elements of the angular momentum operator \hat{L} , is to map the system to an effective $\tilde{l} = 1$ state. Demonstrating this schematically,

$$\begin{array}{c} \overline{2} \quad \overline{-2} \\ \uparrow \\ \Delta_{\rm CFS} \\ \downarrow \\ \overline{1} \quad \overline{0} \quad \overline{-1} \end{array}$$

The crystal field splits the relative energies of the nominally degenerate d orbitals to such an extent (Δ_{CFS} , in fact) that it becomes energetically preferable to violate Hund's first rule and populate the lower t_{2g} orbitals first. Following through with the second Hund's rule though yields the low-spin state where the total intrinsic angular momentum is now only S = 1/2.

$$\frac{\uparrow\downarrow}{1}\;\frac{\uparrow\downarrow}{0}\;\frac{\uparrow}{-1}$$

The second caveat which prevents a direct application of Hund's rules to Ir^{4+} in $Sr_3Ir_2O_7$ is the presence of strong spin-orbit coupling (not well described by the L-S coupling formalism, which treats the spin-orbit interaction as a perturbation). In this case, the depicted low spin configuration of the t_{2g} manifold (naïvely with all electrons having J = |1 + 1/2| = 3/2, as per the third Hund's rule) is further energetically split into a $J_{\text{eff}} = \frac{3}{2}$ doublet and the $J_{\text{eff}} = \frac{1}{2}$ singlet, themselves linear superpositions of the $|m_l\rangle$ states.

Only when treating the spin-orbit interaction as the dominant effect (j-j coupling) is the correct ground state derived theoretically. Unfortunately, there is no similarly simple set of rules $a \ la$ Hund's which accomplish this for elements with high Z, because L and S are no longer good quantum numbers [1]. Despite this, the problem is well defined and can be treated in a general way, albeit at the cost of some notational complexity [3].

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Appendix B

Deriving Fine-Structure Corrections via the Dirac Equation

Consider first the relativistic correction to the kinetic energy, derived using timeindependent perturbation theory for a hydrogenic atom.¹ This energy term arises from the inclusion of an associated perturbative term in the Hamiltonian, both of which are are given by

$$H_r = \frac{-p^4}{8m^3c^2} \implies E_r = \frac{E_n^2}{2mc^2} \left(\frac{4n}{l+\frac{1}{2}} - 3\right) Z^4$$
 (B.1)

Further, consider a second correction which comes about from the spin-orbit interaction H_{so} . Here, the perturbation arises from the interaction of the electron magnetic moment μ with the apparent magnetic field it observes as the nucleus 'orbits' around it, as introduced in Section 1.2 (Eq. 1.1). If the correct relativistic expression for the

¹The details to arrive at Eqs. B.1 are worked out in many graduate texts on quantum mechanics [1-3] and not reproduced here for the sake of brevity.

magnetic moment is used, this interaction term H'_{so} can be written as

$$H'_{so} = -\boldsymbol{\mu} \cdot \boldsymbol{B} = -g\left(\frac{e}{2m}\right)\boldsymbol{S} \cdot \left(\frac{Ze\mu_0}{4\pi m}\right)\frac{1}{r^3}\mathbf{L}$$
(B.2)

...but this is not rigorously correct. The frame of the electron (from which the B of Eq. 1.1 was derived) is *non-inertial*. The cost associated with working in an accelerating frame comes in the form of a kinematic correction called the Thomas precession, whose effect is to amend the gyromagnetic ratio [4] such that $g \to g - 1$, so the correct interaction Hamiltonian now reads

$$H'_{so} = -(g-1)\left(\frac{Ze^2\mu_0}{8\pi m^2}\right)\frac{1}{r^3}\boldsymbol{S}\cdot\boldsymbol{L}$$
(B.3)

This perturbation results² in an energy correction of the form

$$E_{so} = \frac{E_n^2}{mc^2} \left(\frac{n(j(j+1) - l(l+1) - \frac{3}{4})}{l(l+\frac{1}{2})(l+1)} \right) Z^4$$
(B.4)

Immediately, it is somewhat striking that both E_r and E_{so} are scaled by the same factor $(E_n^2 Z^4)/(mc^2)$. If sum $E_r + E_{so}$ is evaluated a more compact expression for these two comparable energy corrections is given by,

$$E_{so} + E_r = \frac{E_n^2 Z^4}{2mc^2} \left(3 - \frac{4n}{j + \frac{1}{2}}\right)$$
(B.5)

That these two corrections reduce to the result in Eq. B.5 is satisfying on its own merits, but this same expression can be arrived at by leveraging an inherently relativistic treatment of quantum mechanics instead of perturbation theory.

²See Footnote 1, re: Eq. B.3. Note also that for the electron, $g \approx 2$.

The Dirac equation is exactly solvable for a particle interacting with a hydrogenlike atom having Coulomb potential $V = -Ze^2/r$ [1], and has an energy spectrum as shown in Eq. B.6:

$$E_{n,j} = mc^2 \left[1 + \left(\frac{Z\alpha}{n - (j + \frac{1}{2}) + [(j + \frac{1}{2})^2 - (Z\alpha)^2]^{1/2}} \right)^2 \right]^{-1/2}$$
(B.6)

Here, m is the reduced mass of the electron, c is the speed of light, n is the principal quantum number, j is the azimuthal quantum number (associated with angular momentum), Z is the atomic number of the nucleus in question, and α is the finestructure constant. It is a very revealing exercise to perform a power series expansion of this expression in $(Z\alpha)$ which yields:

$$E_{n,j} = mc^2 (Z\alpha)^0 + -\frac{mc^2}{2n^2} (Z\alpha)^2 + \frac{mc^2}{8n^4} \left(3 - \frac{4n}{j + \frac{1}{2}}\right) (Z\alpha)^4 + O[Z\alpha]^6 + \dots$$
(B.7)

Immediately, some familiar expressions can be identified. The first term mc^2 is just the rest-mass energy of the electron, and the following term is the energy dependence of the so-called 'gross structure':

$$-\frac{mc^2}{2n^2}(Z\alpha)^2 = -\frac{me^4}{2\hbar^2 n^2}Z^2 = E_n Z^2$$
(B.8)

The third term, which quantifies the lifting of degeneracy between states possessing different j values, gives rise to the 'fine-structure' and can be represented as:

$$E_{fs} = \frac{E_n^2}{2mc^2} \left(3 - \frac{4n}{j + \frac{1}{2}}\right) Z^4$$
(B.9)

...which is actually an identical expression to Eq. B.5. This treatment is advantageous

because there was no need for the *ad hoc* insertion of the correction due to Thomas precession to arrive at an exactly correct result. That said, it is impossible to separate back out in any intuitive fashion the independent terms for the relativistic and spinorbit corrections; but that is perhaps that is the point: in a fully relativistic treatment, both effects should be treated on equal footing.

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Appendix C

Evaluating the Wilson ratio $R_{\mathbf{W}}$

The Wilson ratio, briefly discussed in Section 5.5, provides a rough metric for the importance of electron-electron interactions [1]. In particular, it is expected to take the value of $R_{\rm W} = 1$ in a non-interacting system, and for the Kondo model $R_{\rm W} = 2$ [2]. Thus, as an easily calculated value potentially signifying the importance of correlations in a system, it is of general interest. Evaluating the expression can prove somewhat treacherous though, being a scaled ratio between Sommerfeld's γ (more commonly measured in SI units) and magnetic susceptibility (typically measured in CGS/EMU). The details of the numeric value reported in the main text are outlined here with annotations to draw the reader's attention to important details.

C.1 Evaluation with SI units

The Wilson ratio can be expressed as:

$$R_{\rm W} = \frac{4\pi^2 k_{\rm B}^2 \chi_{\rm m}}{3(g\mu_{\rm B})^2 \gamma_{\rm m}} \tag{C.1}$$
If the g-factor is taken to be 2, the expression can be slightly simplified,

$$R_{\rm W} = \frac{\pi^2 k_{\rm B}^2 \chi_{\rm m}}{3\mu_{\rm B}^2 \gamma_{\rm m}} \tag{C.2}$$

Choosing to work in SI units, the fundamental constants are given as

$$\mu_{\rm B} = 9.274 \times 10^{-24} \,\mathrm{J}\,\mathrm{T}^{-1}$$

 $k_{\rm B} = 1.380 \times 10^{-23} \,\mathrm{J}\,\mathrm{K}^{-1}$

Thus Eq. C.2 can be further simplified to just

$$R_{\rm W} = 7.29 \; \frac{[{\rm T}^2]}{[{\rm K}^2]} \; \frac{\chi_{\rm m}}{\gamma_{\rm m}} \tag{C.3}$$

The final step is to insert the measured values for molar susceptibility and the Sommerfeld coefficient (taken from Fig. 5.6). The latter takes units of heat-capacityover-temperature since it represents the slope of the linear contribution to low temperature specific heat $c_V(T)$ [3]. This quantity was measured in SI [J K⁻²] and thus needs only be scaled by the moles of sample (n).

$$\gamma_{\rm m} = \frac{\gamma}{n} = \frac{0.011\,68 \times 10^{-6}\,\mathrm{J\,K^{-2}}}{6.248 \times 10^{-7}\,\mathrm{mol}} = 0.0187\,\,\frac{[\mathrm{J}]}{[\mathrm{K}^2\,\mathrm{mol}]} \tag{C.4}$$

Treating the susceptibility, however, requires a little more care. Starting with the fundamental definition of molar magnetic susceptibility

$$\chi_{\rm m} = \frac{m}{H \cdot n} \tag{C.5}$$

Where m is the total magnetic moment, H is the applied magnetic field, and n is the number of moles of material in question. In the MPMS m is measured in the nonunit of [emu] [4]. This can be converted to the correct expression for magnetization in the SI system with the relation $10^{-3} \text{ J T}^{-1} \equiv 1$ emu.

$$m = 2.865 \times 10^{-5} \text{ emu} = 2.865 \times 10^{-5} \text{ emu} \left(10^{-3} \frac{\text{J T}^{-1}}{\text{emu}} \right)$$
 (C.6)

Similarly, the applied magnetic field H is often measured in the CGS unit [Oe]. We must leverage the fact that in CGS both H and B actually have the same dimensions-

$$G \equiv \sqrt{\frac{g}{cm}} \cdot \frac{1}{s} \equiv Oe$$
 (C.7)

-to arrive at the following conversion:¹

$$H = 20\,000 \text{ Oe} \to 20\,000 \text{ G} = 20\,000 \text{ G} \cdot \left(10^{-4} \frac{\text{T}}{\text{G}}\right)$$
 (C.8)

Which can be substituted back into Eq. C.5 along with Eq. C.6 to yield

$$\chi_{\rm m} = \frac{m}{H \cdot n} = \frac{2.865 \times 10^{-5} \, \mathrm{emu} \left(10^{-3} \frac{\mathrm{J} \, \mathrm{T}^{-1}}{\mathrm{emu}} \right)}{20\,000 \, \mathrm{G} \cdot \left(10^{-4} \frac{\mathrm{T}}{\mathrm{G}} \right) \cdot n}$$

$$\chi_{\rm m} = 0.0229 \, \frac{[\mathrm{J}]}{[\mathrm{T}^2] \cdot [\mathrm{mol}]}$$
(C.9)

If this is substituted back into the expression for R_W (Eq. C.3) along with γ_m (Eq. C.4), the final value is found to be

$$R_{\rm W} = 7.29 \ \frac{[{\rm T}^2]}{[{\rm K}^2]} \ \frac{\chi_{\rm m}}{\gamma_{\rm m}} = 7.29 \ \frac{[{\rm T}^2]}{[{\rm K}^2]} \ \frac{0.0229 \ \frac{[{\rm J}]}{[{\rm T}^2] \cdot [{\rm mol}]}}{0.0187 \ \frac{[{\rm J}]}{[{\rm K}^2] \cdot [{\rm mol}]}}$$
(C.10)
$$R_{\rm W} = 8.93$$

¹The rationale for this is tied up in the differences of how the two unit systems are defined. A more exhaustive discussion on the pitfalls of magnetic units can be found in Appendix A of [5].

While little quantitative meaning can be culled from the numeric expression itself, the point is to illustrate another measure which suggests that electron-electron interactions are significant for highly-doped $(Sr_{1-x}La_x)_3Ir_2O_7$.

C.2 Evaluation with CGS units

For the satisfaction of both the reader and the author, an alternate evaluation is presented here using the CGS system of units. Since the Wilson ratio is unitless, correct application of both unit systems should yield the same result. In CGS, the values of the fundamental constants are given by

$$\mu_{\rm B} = 9.274 \times 10^{-21} \,\rm erg \, G^{-1}$$
$$k_{\rm B} = 1.380 \times 10^{-16} \,\rm erg \, K^{-1}$$

The effect of which is to converts Eq. C.3 into CGS

$$R_{\rm W} = 7.29 \times 10^8 \; \frac{[{\rm G}^2]}{[{\rm K}^2]} \; \frac{\chi_{\rm m}}{\gamma_{\rm m}}$$
 (C.11)

Most of the remaining work now comes in converting the measured SI units of γ_m into CGS using 1 erg $\equiv 10^{-7}$ J,

$$\gamma_{\rm m} = \frac{\gamma}{n} = \frac{0.011\,68 \times 10^{-6}\,\mathrm{J\,K^{-2}} \cdot \left(\frac{1\,\mathrm{erg}}{10^{-7}\,\mathrm{J}}\right)}{6.248 \times 10^{-7}\,\mathrm{mol}}$$

$$\gamma_{\rm m} = 1.87 \times 10^{5}\,\frac{[\mathrm{erg}]}{[\mathrm{K}^{2}] \cdot [\mathrm{mol}]}$$
(C.12)

All of our magnetic units were already in CGS, so $\chi_{\rm m}$ need not be modified

$$\chi_{\rm m} = \frac{m}{H \cdot n} = \frac{2.865 \times 10^{-5} \text{ emu}}{20\,000 \text{ G} \cdot 6.248 \times 10^{-7} \text{ mol}} = 0.002\,29\,\frac{[\text{emu}]}{[\text{G}] \cdot [\text{mol}]} \tag{C.13}$$

Substituting Eqs. C.12 and C.13 into Eq. C.11 for the final evaluation,

$$R_{\rm W} = 7.29 \times 10^8 \; \frac{[{\rm G}^2]}{[{\rm K}^2]} \; \frac{\chi_{\rm m}}{\gamma_{\rm m}} = 7.29 \times 10^8 \; \frac{[{\rm G}^2]}{[{\rm K}^2]} \; \frac{0.002\,29 \; \frac{[\rm emu]}{[{\rm G}] \cdot [\rm mol]}}{1.87 \times 10^5 \; \frac{[\rm erg]}{[{\rm K}^2] \cdot [\rm mol]}}$$
(C.14)
$$R_{\rm W} = 8.93 \; \frac{[{\rm G}] \cdot [\rm emu]}{[\rm erg]}$$

The final piece of the puzzle is the definition of 1 emu \equiv 1 erg G⁻¹, making this expression unitless as well. That the ratios match regardless of the unit system is a trivial result, but given the potential confusion with the units of magnetic properties involved it is worth showing explicitly.

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When we have found all the mysteries and lost all the meaning we will be alone, on an empty shore

– T. Stoppard, Arcadia