DOUBLE PEROVSKITES WITH STRONG SPIN-ORBIT COUPLING

by

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Abstract

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We first present theoretical analysis of powder inelastic neutron scattering experiments in Ba$_2$FeReO$_6$ performed by our experimental collaborators. Ba$_2$FeReO$_6$, a member of the double perovskite family of materials, exhibits half-metallic behavior and high Curie temperatures $T_c$, making it of interest for spintronics applications. To interpret the experimental data, we develop a local moment model, which incorporates the interaction of Fe spins with spin-orbital locked magnetic moments on Re, and show that it captures the experimental observations.

We then develop a tight-binding model of the double perovskite Ba$_2$FeReO$_6$, a room temperature ferrimagnet with correlated and spin-orbit coupled Re $t_{2g}$ electrons moving in the background of Fe moments stabilized by Hund's coupling. We show that for such 3d/5d double perovskites, strong correlations on the 5d-element (Re) are essential in driving a half-metallic ground state. Incorporating both strong spin-orbit coupling and the Hubbard repulsion on Re leads to a band structure consistent with ab initio calculations. The uncovered interplay of strong correlations and spin-orbit coupling lends partial support to our previous work, which used a local moment description to capture the spin wave dispersion found in neutron scattering measurements.

We then adapt this tight-binding model to study $\{111\}$-grown bilayers of half-metallic double perovskites such as Sr$_2$FeMoO$_6$. The combination of spin-orbit coupling, inter-orbital hybridization and symmetry-allowed trigonal distortion leads to a rich phase diagram with tunable ferromagnetic order, topological $C = \pm 1, \pm 2$ Chern bands, and a $C = \pm 2$ quantum anomalous Hall insulator regime.

We have also performed theoretical analysis of inelastic neutron scattering (INS) experiments to investigate the magnetic excitations in the weakly distorted face-centered-cubic (fcc) iridate double perovskites La$_2$ZnIrO$_6$ and La$_2$MgIrO$_6$. Models with dominant Kitaev exchange seem to most naturally account for the neutron data as well as the measured frustration parameters of these materials, while the uniaxial Ising anisotropy does not. Our findings highlight how even seemingly conventional magnetic orders in oxide materials containing heavy transition metal ions may be driven by highly-directional exchange interactions rooted in strong spin-orbit coupling.

Motivated by experiments on the double perovskites La$_2$ZnIrO$_6$ and La$_2$MgIrO$_6$, we lastly study the magnetism of spin-orbit coupled $j_{\text{eff}} = 1/2$ iridium moments on the three-dimensional, geometrically frustrated, face-centered cubic lattice. The symmetry-allowed nearest-neighbor interaction includes Heisenberg, Kitaev, and symmetric off-diagonal exchange. A Luttinger-Tisza analysis shows a rich variety of orders, including collinear A-
type antiferromagnetism, stripe order with moments along the \{111\}-direction, and incommensurate non-coplanar spirals, and we use Monte Carlo simulations to determine their magnetic ordering temperatures.
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Chapter 1

Introduction

The discovery of high temperature superconductivity has focused considerable attention on transition metal oxides. They exhibit many other interesting phenomena due, in large part, to the dual nature of strongly correlated d-orbital electrons which exhibit both itinerant and localized behavior [1]. Such intermediate character is at the heart of much of the fascinating physics of the transition metal oxides, much of which continues to challenge the scientific community.

1.1 Double perovskites

Double perovskites are transition metal oxides with the structure $A_2BB'O_6$ [2]. The structure is a generalization of the perovskite structure $ABO_3$, which possesses a simple cubic lattice of B ions, with an A ion at the centre of each cube of B ions. Each B ion is also contained in an octahedral cage of oxygen ions. In an ideal double perovskite structure, in contrast, B and B' form interlocking face-centred cubic (f.c.c.) sublattices. An example of this structure is shown in Fig. 1.1

The phenomena present in a double perovskite depend strongly on the choice of A, B and B'. Smaller A ions, for instance, can lead to a partial collapse of the simple cubic lattice with B and B' ions at its vertices, resulting in monoclinic distortions. If B ions are magnetic and B' ions are not, completely different magnetic orders can be stabilized than when both B and B' ions are magnetic. With many options for A, B and B' that correspond to stable compounds, the double perovskite family allows for systematic study of many phenomena present in transition metal oxides.

1.1.1 Ordered double perovskites

Although the ideal double perovskite structure includes two interlocking face-centred cubic sublattices of B and B' ions, it is common for B and B' ions to switch places. Although this so-called anti-site disorder could in some situations enrich the physics of double perovskites, the work in this thesis focuses on phenomena of ordered double perovskites, where such disorder is absent in the ideal case and negligible in material samples, as this ordered form is preferred for the phenomena of interest in this work.

Anti-site disorder is typically less severe in double perovskites where the B site is a 3d ion and the B' site is a 4d or 5d ion, because the ionic size mismatch makes it less favourable for B and B' ions to switch places. In considering 4d/5d ions in double perovskites, however, spin-orbit coupling must be taken into account.
1.2 Spin-orbit coupling

An electron moving at a relativistic velocity sees a magnetic field $\vec{B}$ that can couple to its spin $\vec{S}$. For an electron in a crystal, movement about an ion with angular momentum $\vec{L}$ at relativistic velocities can generate this magnetic field $\vec{B}$, leading to a spin-orbit coupling term proportional to $\vec{L} \cdot \vec{S}$ [3]. The strength of this term is governed by the spin-orbit coupling strength $\lambda$, which increases in strength with atomic number. For a 3d ion, $\lambda \sim 10$ meV, while 4d ions can have $\lambda \sim 100$ meV, and spin-orbit coupling strength in 5d ions is on the scale of 400 meV.

1.3 Interplay between spin-orbit coupling and electron-electron correlations

In transition metal oxides, $\lambda$ for 4d/5d ions becomes comparable to the energy scale of electron correlations in the system, sometimes leading to novel phenomena [4]. Two manifestations of electron correlations that are particularly important to study in combination with spin-orbit coupling are magnetism and the Mott insulator phase. Magnetic order and spin-orbit coupling, for instance, can lead to the quantum anomalous Hall insulator and the Weyl semimetal, both of which will be introduced here.

1.3.1 Magnetism

Spontaneous magnetic order in materials is almost always a manifestation of strong electron-electron interactions, rather than a secondary effect due to a weak perturbation [3]. In becoming magnetic, a substance gets less metallic, but will not necessarily become an insulator. Systems with particular magnetic orders, strong spin-orbit coupling, and itinerant electrons are predicted to be candidates for exotic phases, including the quantum anomalous Hall insulator phase and the Weyl semimetal phase.
1.3.2 Quantum anomalous Hall insulators

Through a combination of ferromagnetic order in an itinerant magnet and spin-orbit coupling, a phase of matter closely-related to the integer quantum Hall effect, known as a quantum anomalous Hall insulator, can be realized in the absence of an applied magnetic field [5]. A quantum anomalous Hall insulator is a two-dimensional phase of matter that is insulating in the bulk but possesses chiral, metallic edge states. The edge states are topologically-protected, meaning that, so long as the bulk gap of the phase does not close, the edge states persist. Such edge states are furthermore dissipationless.

In both the quantum anomalous Hall insulator and the integer quantum Hall effect, Hall conductivity is quantized. One of the key differences between the two phases is that the integer quantum Hall effect is realized through application of an external magnetic field perpendicular to a two-dimensional electron gas. In the quantum anomalous Hall insulator, integer quantum Hall physics is realized by inducing the orbital motion of electrons of the integer quantum Hall effect through a combination of net magnetization - due to ordering of magnetic moments - out of the plane of the two-dimensional system, and spin-orbit coupling.

1.3.3 Weyl semimetals

The same ingredients that can lead to a quantum anomalous Hall insulator phase in a two-dimensional system can potentially lead to a Weyl semimetal phase in three dimensions [6]. It is possible to describe a three dimensional material’s Brillouin zone as a stack of 2D Brillouin zones, with each corresponding to a 2D system [7]. Each 2D system can be a topologically trivial or non-trivial quantum anomalous Hall insulator state, or intermediate between these two. There can be transition points in the Brillouin zone at which the topology changes, where band-touchings should occur. These band-touchings are themselves topologically-protected, exist in pairs, and can only be removed when the two band-touchings in a pair meet. If the chemical potential passes through one of these topologically-protected nodes in the Brillouin zone, the material’s low-energy physics is governed by the Weyl equation. That is, the material possesses emergent Weyl fermions.

1.4 Mott insulators

If correlations are strong enough and other requirements are met, electrons can also be localized by their mutual Coulomb repulsion to form materials known as Mott insulators. Although predicted by band theory to be metals, these materials are insulators as a result of strong correlations and can be modeled as localized spins in a lattice that interact with one another via exchange couplings.

1.5 Interplay between strong spin-orbit coupling, correlations, and geometric frustration

Mott insulators, when also possessed of spin-orbit coupling and geometric frustration (to be introduced in this section) can exhibit many properties thought to be important for realization of quantum spin liquid phases.

1.5.1 Geometric frustration

Geometric frustration, in combination with spin-orbit coupling and correlations, can also generate novel phenomena. If the B sublattice of a Mott-insulating double perovskite is non-magnetic, but the B’ sublattice is magnetic,
CHAPTER 1. INTRODUCTION

the system can be modeled as a face-centered cubic lattice of spins. As an f.c.c. lattice is an interlocking set of triangular, two-dimensional lattices, anti-ferromagnetic exchange couplings can potentially lead to geometric frustration of spins. If we consider a single triangle of spins with anti-ferromagnetic nearest-neighbour exchange couplings, for instance, we see that, if spin 1 points up, spin 2 wants to point down, and spin 3 prefers neither to point down or up.

1.5.2 Quantum spin liquid

The quantum mechanical uncertainty principle produces zero-point motions, which persist down to zero Kelvin in temperature. If these quantum fluctuations are strong enough relative to the size of spins in a Mott insulator, a superposition state in which spins simultaneously point in many different directions and are highly-entangled with one another may form, known as a quantum spin liquid [8].

The search for quantum spin liquids in material candidates has focused to a large extent on realizing a particular model for a quantum spin liquid known as the Kitaev model. It was realized certain superexchange pathways (with a superexchange pathway being a coupling between two iridium ions due to virtual electron hopping via an oxygen ion shared by the oxygen octahedra of these two iridium ions) in some Mott insulators could lead to weak Heisenberg exchange couplings relative to Kitaev exchange couplings [9]. More specifically, destructive interference between two superexchange pathways between edge-sharing octahedra in the honeycomb iridates can result in relatively weak Heisenberg couplings compared to Kitaev terms also allowed by symmetry.

The search for a quantum spin liquid continues, motivating exploration of Mott insulators with lattice geometries other than the honeycomb. Of particular interest is the face-centered cubic lattice.

1.6 Types of double perovskites studied in this thesis

This thesis focuses on two kinds of double perovskites in particular that exhibit physics governed by the interplay between strong spin-orbit coupling and strong correlations: Half-metallic, ferrimagnetic 3d/5d and 3d/4d double perovskites, and Mott-insulating iridate double perovskites.

1.6.1 Ferrimagnetic, half-metallic double perovskites

Ferrimagnetic double perovskites are double perovskites that exhibit ferrimagnetism, or net magnetization where not all moments contribute positively to this magnetization. This can emerge in double perovskites where the B site is magnetic, with moment length $M_B$, and the B’ site is also magnetic, with moment length $M_{B'}$, and $M_B \neq M_{B'}$. It can then be energetically-favourable for B moments to anti-align with B’ moments and generate a ferrimagnetic state (for instance, to maximize delocalization of electrons). Such double perovskites can exhibit itinerant electronic behaviour in combination with localized moments. Furthermore, depending on the moment sizes and other microscopic details, it is possible for one spin species to be localized by Pauli exclusion while the other still has a Fermi surface. This half-metallic character of some ferrimagnetic double perovskites is of considerable interest for spintronics applications, particularly in compounds with high Curie temperatures [2]. However, the ferrimagnetic order in some double perovskites, in combination with strong spin-orbit coupling and itinerant electronic behaviour, are also the basic ingredients for generating quantum anomalous Hall insulator phases in two dimensions and Weyl semimetal phases in three dimensions.

Double perovskite (DP) materials $A_2BB'O_6$, where the transition metal ions B and B’ reside on the two sublattices of a cubic lattice, can realize many complex phases.[118] Metallic variants, such as $Sr_2FeMoO_6$,
provide us with the simplest multi-orbital examples of ferrimagnetic order \[43\] kinetically stabilized by the Pauli exclusion principle.\[143, 144, 38, 59, 123, 40, 124\] Insulating variants where only the B'-site ion is magnetic, such as Ba$_2$YMoO$_6$ and La$_2$LiMoO$_6$, provide material examples of quantum mechanical moments living on the geometrically frustrated face-centered cubic lattice.\[62, 63, 262, 65, 26\] Metallic DPs, such as Sr$_2$FeMoO$_6$, are also of significant technological importance, being room temperature ferrimagnets with half-metallic band structures and a large spin polarization which is useful for spintronic applications.\[44, 129\] Metallic 3d/5d DPs are of particular interest in this regard since they appear to have strongly reduced B/B’ site mixing; samples of Ba$_2$FeReO$_6$ studied in previous work \[125\] have low < 1% anti-site disorder. Such anti-site disorder, which is common in other DPs and which is detrimental to spintronic applications, appears to be alleviated in 3d/5d DPs by the B/B’ ionic size mismatch suggesting that they might be better suited for applications. However, such 3d/5d DPs require us to confront the twin aspects of strong correlations and strong spin-orbit coupling, topics at the forefront of fundamental research \[68\] motivated by the possibility of stabilizing states such as fractionalized topological insulators (TIs).\[69, 70, 71, 72\] or Weyl semimetals.\[73, 74, 75, 76\]

### 1.6.2 Mott-insulating double perovskites

In this thesis, the Mott-insulating double perovskites La$_2$BIrO$_6$ (B = Mg/Zn) are studied. As Mg/Zn is closed shell but Ir is not, these double perovskites - neglecting small rotations of the oxygen octahedra and small distortions from the ideal cubic double perovskite structure - can be modeled as a face-centered cubic lattice of Ir magnetic moments. Strong correlations, strong spin-orbit coupling, and geometric frustration are each present in these compounds, making them interesting for study of the interplay of these phenomena, especially given many other opportunities to study this physics in other double perovskites \[10\].

Furthermore, however, couplings between magnetic moments of Ir ions arises from Ir-O-O-Ir superexchange: Such pathways - similar to Ir-O-Ir superexchange pathways between edge-sharing octahedra in honeycomb iridates - lead to weak Heisenberg exchange couplings through destructive interference along the two Ir-O-O-Ir paths between any two adjacent Ir ions. This means the La$_2$BIrO$_6$ double perovskites are furthermore promising materials in which to search for dominant Kitaev terms.

### 1.7 Inelastic neutron scattering

The neutron is a massive particle with zero charge. Because the neutron has no electric charge, it can penetrate deep into a sample, probing the bulk properties of a material. Neutrons also have a magnetic moment, which means that they may interact with both spin and orbital angular momentum associated with unpaired electrons in a material via a dipole-dipole interaction \[11\].

In time-of-flight inelastic neutron scattering, the kind of inelastic neutron scattering referred to in this thesis, the momentum of a pulse of neutrons and the time between its departure from a chopper to the sample is known, and the time of neutron flight from the sample to a detector is also known. The angle at which neutrons scatter off of the sample is then also measured. This may be used to calculate the momentum and energy transferred to the sample \[12\].

The scattering cross-section measured in such inelastic neutron scattering experiments may be shown to be proportional to the scattering function or dynamic structure factor $S(Q, \omega)$. The goal of a neutron scattering experiment is therefore to determine $S(Q, \omega)$. 
1.8 Layout of the thesis

The thesis is divided into two parts. Chapters 2 to 4 are on half-metallic, ferrimagnetic double perovskites, and Chapters 5 and 6 are on Mott insulating double perovskites. Each section begins with a joint theoretical and experimental study of some relevant compounds. Chapter 2, for instance, discusses an inelastic neutron scattering study of $\text{Ba}_2\text{FeReO}_6$ (BFRO), while Chapter 5 is an inelastic neutron scattering study of the compounds $\text{La}_2\text{MgIrO}_6$ and $\text{La}_2\text{ZnIrO}_6$ (collectively referred to as LBIO). Chapter 3 then discusses development of a tight-binding model of BFRO through comparison with experiment and ab initio. Chapter 4 covers adaptation of this tight-binding model to study of bilayers of another half-metallic, ferrimagnetic double perovskite, $\text{Sr}_2\text{FeMoO}_6$, grown in the $\{111\}$ crystallographic direction. Chapter 6, lastly, discusses study of the most general model allowed by symmetry for the LBIO compounds assuming an ideal f.c.c. lattice and restriction of the model to nearest neighbour exchange couplings only.

1.9 Publications and Contributions

Below are publications completed during the course of this doctoral thesis. A brief explanation of how each publication relates to the thesis is given.

1.9.1 Dominant Kitaev interactions on the fcc lattice in iridate double perovskites $\text{La}_2\text{BIrO}_6$ ($B = \text{Mg}, \text{Zn}$)

A. A. Aczel, A. M. Cook, T. J. Williams, S. Calder, A. D. Christianson, G.-X. Cao, D. Mandrus, Y. B. Kim, A. Paramekanti, arXiv:1507.07920 (Also accepted for publication in Physical Review B as an Editor’s Suggestion)

This paper constitutes chapter 5. I contributed to theory work on this paper, along with Y. B. Kim and A. Paramekanti. Experimental work was performed by A. A. Aczel, T. J. Williams, S. Calder, A. D. Christianson, G.-X. Cao, and D. Mandrus.

1.9.2 Design principles for shift current photovoltaics


This paper is not included in the thesis. I contributed to theory work on this paper, along with B. M. Fregoso, F. de Juan, and J. E. Moore.

1.9.3 Magnetism of $j=\frac{1}{2}$ moments on the fcc lattice in double perovskite Mott insulators


This paper is the basis of chapter 6. I contributed to theoretical work in this paper, along with S. Matern, C. Hickey, A. Paramekanti, and A. A. Aczel. A. A. Aczel also completed experimental work that is referenced in this paper and was the motivation for this work.

1.9.4 Emergent dome of nematic order around a quantum anomalous Hall critical point

This paper is not included in the thesis. I performed theoretical work for this paper, along with C. Hickey and A. Paramekanti.

1.9.5 Double Perovskite Heterostructures: Magnetism, Chern Bands, and Chern Insulators


This paper is chapter 3 of the thesis. I contributed to theory in the paper, along with A. Paramekanti.

1.9.6 Theory of metallic double perovskites with spin-orbit coupling and strong correlations: Application to ferrimagnetic Ba2FeReO6


This paper is the basis of chapter 2 of the thesis. I contributed to theory in this paper along with A. Paramekanti.

1.9.7 Neutron scattering study of magnetic excitations in a 5d-based double-perovskite Ba2FeReO6


This paper is the basis of chapter 1 of the thesis. I contributed to theory in this paper, along with A. Paramekanti. Experimental work was performed by K. W. Plumb, J. P. Clancy, A. I. Kolesnikov, B. C. Jeon, T. W. Noh, and Y.-J. Kim.
Chapter 2

Neutron scattering study of magnetic excitations in Ba$_2$FeReO$_6$

2.1 Introduction

Strong electronic correlations in the 3d and 4d transition metal oxides (TMOs) lead to such remarkable phenomena as high temperature superconductivity in the cuprates [13], colossal magnetoresistance in the manganites [14], and possible chiral superconductivity in the ruthenates [15]. In 5d-TMOs, the traditional viewpoint suggests that the larger spread of atomic wavefunctions leads to a smaller local Hubbard repulsion and a larger overlap between neighboring atomic orbitals, which cooperate to suppress strong correlation effects. Indeed, simple oxides like ReO$_3$ are good metals [16]. This traditional picture has been challenged by recent work on iridium-based complex oxides, which shows that the large spin-orbit (SO) coupling on Ir can split the $t_{2g}$ crystal field levels, yielding a reduced bandwidth for effective $j_{\text{eff}} = 1/2$ electrons and the re-emergence of strong correlations [17]. Iridates like Na$_2$IrO$_3$, Na$_4$Ir$_3$O$_8$, Eu$_2$Ir$_2$O$_7$ and Y$_2$Ir$_2$O$_7$, are of great interest since they may support correlated SO coupled magnetism or topological phases [18, 19, 20, 21, 22, 23, 76, 25].

Despite these remarkable developments in the iridates, there are good reasons to also explore spin-orbit coupling physics in other 5d TMOs. (i) In contrast to the iridates, where Ir is a strong neutron absorber, other TMOs such as those based on Re can permit a careful study of the spin-orbital dynamics via inelastic neutron scattering experiments. Such studies are valuable for an eventual complete understanding of the magnetism. (ii) While the iridates have been described by an effective one-band $j_{\text{eff}} = 1/2$ model with Hubbard correlations, other 5d elements may exhibit distinct phenomena associated with the regime where multi-orbital interactions and Hund’s coupling conspire with spin-orbit coupling to give rise to new physics. For example, there are two electrons in 5d orbitals ($d^2$) in Re$^{2+}$. Even in the presence of strong spin-orbit coupling and cubic crystal field, the electronic state is not described by simply filling $j_{\text{eff}} = 3/2$ single particle states with two electrons. We find that non-zero Hund’s coupling should be considered in addition to spin-orbit coupling,[26] and angular momentum in this case is described by a $j_{\text{eff}} = 2$ state. (iii) Some aspects of the iridates still appear to be controversial, for example whether the insulating states and magnetism in Na$_2$IrO$_3$ and Sr$_2$IrO$_4$ arise from $j_{\text{eff}} = 1/2$ Mott physics [17, 18, 19, 27] or from undergoing a Slater transition.[28, 29, 30] Exploring simpler 5d TMOs where one has a careful experimental and theoretical understanding of the SO coupled magnetism may provide a useful perspective on such issues.

Motivated by these considerations, we focus here on a 5d Re-based double perovskite material Ba$_2$FeReO$_6$. 

This general class of DP compounds \( A_2B'B'O_6 \) is also of great interest since materials like \( A_2FeReO_6 \) (\( A=Ca,Sr,Ba \)) \([31, 32, 33, 34, 35, 36, 37, 38, 39, 40]\), \( Sr_2FeMoO_6 \) \([2]\), and \( Sr_2CrOsO_6 \) \([41, 42]\), with a 3d magnetic B-ion and a 5d B’-ion, exhibit high ferromagnetic Curie temperatures. In addition, the half-metallic character and significant polarization of many DPs makes them ideal candidates for spintronic applications such as spin injection \([43, 44]\).

In this chapter, we analyze inelastic neutron scattering (INS) data on polycrystalline \( Ba_2FeReO_6 \) to study the magnetic excitations in its ferrimagnetic state, theoretically modeling the observed spectrum. The experimental data reported in this chapter were taken by the group of Young-June Kim. These results have been reported as a joint experiment and theory paper in \([125]\). The main results, which are summarized in Fig. 2.1, are as follows.

(i) The experimentalists who contributed to this work provided experimental evidence of two dispersive magnetic modes in the magnetic excitation spectrum, showing that Fe and Re electrons both exhibit strong correlations and contribute to the magnetization dynamics. (ii) Remarkably, there is evidence of nearly gapless magnetic excitations in the inelastic spectrum, indicating that despite the strong SOC, there is only a weak locking of Re-moments to the lattice in the ferrimagnetic state. (iii) We discuss a minimal local moment model of strongly coupled spin and orbital degrees of freedom on Re interacting with spins on Fe and show that this captures our experimental observations extremely well. (iv) We combine our results with published magnetization\([45]\) and X-ray magnetic circular dichroism (XMCD) data\([35]\) to obtain quantitative estimates of the Re and Fe moments and the effective Re-Fe exchange interaction. (v) We find evidence in the neutron scattering data which is suggestive of spin-phonon interactions, likely mediated by the strong spin orbit coupling. Such spin-phonon coupling has also been inferred in a recent Raman scattering study.\([37]\) Our combined experimental and theoretical work thus further opens up Re-based TMOs as model systems to study the interplay of spin orbit coupling and strong electronic correlations.

2.2 Experiments

Total 8.6g of polycrystalline \( Ba_2FeReO_6 \) sample was synthesized using the standard solid-state method reported previously \([36, 45]\). In some DPs, anti-site disorder (mixing of B and B’ site atoms) is significant, and suppresses saturated magnetic moments. However, for \( Ba_2FeReO_6 \), a large difference (\(~8\%) in the ionic radii of Fe\(^{3+}\) and Re\(^{5+}\) seems to mitigate this problem. From the structural refinement of x-ray powder diffraction data, we infer an anti-site disorder of \( \lesssim 1\% \), consistent with that reported by Winkler et al. \([46]\).

Neutron scattering measurements were carried out on the fine resolution Fermi-chopper spectrometer SEQUOIA\([47, 48]\) at the Spallation Neutron Source (SNS) at Oak Ridge National Laboratory (ORNL). Measurements were performed with Fermi chopper 1 rotating at a frequency of 300 Hz and phased for incident energies of 27 and 120 meV. A T0 chopper rotating at 180 Hz was used to eliminate a fast neutron background. The sample was sealed in an Al can and mounted on a closed cycle cryostat. Data were also collected for an empty Al sample can at \( T = 34 \) K, with an identical instrumental configuration. The absorption corrected empty can intensities were subtracted from the raw data at \( T = 34 \) K to remove scattering from the sample environment.

Throughout this article we use pseudo-cubic notation \( a = b = c \approx 4.01 \) Å and index the momentum transfer \( Q \) in units of \( 1/a \) to aid comparison with theoretical calculations. In our magnetic model ferrimagnetism arises from G-type antiferromagnetic arrangement of inequivalent Fe and Re moments so that magnetic Bragg peaks occur at the antiferromagnetic wavevector \( Q_{AF} = (\pi, \pi, \pi) \) and the ferromagnetic wavevector \( Q_{FM} = (2\pi, 0, 0) \).

Maps of the inelastic neutron scattering intensity for 27 meV and 120 meV incident neutron energies are shown in Fig. 2.1 (a) and (b) respectively. An inelastic feature emanating from \( Q = 1.35 \) Å\(^{-1}\) corresponding to \( Q_{AF} \) is clearly resolved. The inelastic feature extends into two-bands of excitations with maximum intensities
Figure 2.1: Comparison of spin wave model and measured powder averaged magnetic scattering intensity for T = 34 K. An empty Al-Can background signal has been subtracted from the data. (a) and (b) are neutron scattering data for incident energies of 27 and 120 meV respectively. (c)-(d) Powder averaged dynamic structure factor calculated from the spin wave model with $6J_{\text{eff}}F = 39$ meV, and $6J_{\text{eff}}R = 25$ meV. Solid white lines in (a) and (b) show the dispersion relation from the spin wave model along $(0,0,0)$–$(\pi,\pi,\pi)$–$(3\pi/2,3\pi/2,3\pi/2)$.

near 25 meV and 39 meV. The scattering is strongest at low-Q and decays rapidly for increasing Q as is expected generally from the form factor dependence for magnetic scattering. Results from our theoretical model are shown in Fig. 2.1 (c)-(d) with the best-fit parameters.

The temperature and energy dependence of putative magnetic scattering in Ba$_2$FeReO$_6$ is presented in Fig. 2.2. Bragg peaks at $Q = 1.35$ Å$^{-1}$ corresponding to $Q_{\text{AF}}$, and $Q = 1.56$ Å$^{-1}$ corresponding to $Q_{\text{FM}}$ are shown in Fig. 2.2 (a). The elastic magnetic intensity decreases upon warming and the antiferromagnetic Bragg peak vanishes above 300 K, consistent with $T_c \approx 304$ K reported from uniform magnetization [45] and powder neutron diffraction measurements.[35] Magnetic elastic scattering at $Q_{\text{FM}}$ is superposed on a structural Bragg reflection so that it is more difficult to discern the temperature dependant intensity resulting from magnetic scattering at this Q position.

Constant momentum transfer cuts detailing the inelastic scattering emerging from the magnetic zone center are shown in Fig. 2.2 (b). The fluctuation-dissipation theorem $S(Q,E) = (n(E,T) + 1)\chi''(Q,E)$ relates the imaginary component of the dynamic susceptibility $\chi''(Q,E)$ to the dynamic structure factor measured by neutron scattering where $n(E,T)$ is the Bose thermal occupation factor. Correcting the INS intensity by the Bose factor allows for comparison of the inelastic scattering across the entire 400 K temperature range on a single intensity scale. Two strong inelastic features are visible near 25 meV and 39 meV which decrease in intensity upon increasing temperature. The temperature, momentum, and energy dependence of the low-Q inelastic scattering is entirely consistent with expectations for scattering from powder averaged spin-waves. Broader examination of the data reveals two bands of phonon scattering which partially obscures the magnetic signal above 3 Å$^{-1}$; however, the phonon and magnetic scattering are well resolved since the magnetic form factor rapidly attenuates the magnetic intensity with increasing Q while the phonon scattering intensity increases with Q (See Appendix).
Figure 2.2: Representative cuts through $S(Q,E)$. (a) Temperature dependence of magnetic Bragg peaks at $\{\pi, \pi, \pi\}$ and $\{2\pi, 0, 0\}$ determined by integrating the $E_i = 120$ meV data over the elastic line resolution $[-4 < E < 4 \text{ meV}]$. (b) Temperature dependence of Bose factor corrected inelastic scattering near the magnetic zone center. (c) Constant energy cuts from the $E_i = 27$ meV data at 34 K, each energy cut was integrated over $\pm 1 \text{ meV}$, the 7 meV cut is offset for clarity. (d) Bose factor corrected inelastic scattering at 34 K integrated over a magnetic Brillouin zone representing the magnetic density of states, the solid line is an equivalent cut from the spin wave model calculation. An empty can background has been subtracted from data in (c) and (d).

Constant energy cuts across the low energy magnetic scattering are shown in Fig. 2.2 (c). An inelastic feature emerging from the antiferromagnetic zone center is clearly resolved within our experimental resolution down to at least 3 meV. The scattering intensity is strongest near the antiferromagnetic wavevector at $Q = 1.35 \text{ Å}^{-1}$ — where the structure factor for magnetic scattering is maximized — and is small near the nuclear Bragg peak. This $Q$-dependence identifies the low energy inelastic scattering as magnetic in origin and places an upper bound of 3 meV for any gap in the spin wave dispersion. The $Q$-integrated inelastic intensity is peaked at the magnon zone boundary energy where the density of states for spin waves is maximized, enabling a precise determination of the zone-boundary energies from the powder averaged spectrum. The dynamic susceptibility integrated over the magnetic Brillouin zone is shown in Fig. 2.2 (d); scattering is strongly peaked at 25 meV and 39 meV. An equivalent cut from the powder averaged spin wave theory using the same parameters as in Fig. 2.1 (c) and (d) is also shown in the figure.1

1The different atomic form factors of Re and Fe have not been taken into account in the theoretical calculations; however, their form factors only differ by about 15% from the average form factor at the largest Q. Since the dispersing modes do not strictly have Re or Fe character, we expect taking form factors into account will slightly modify the intensities in our theoretical plots.
2.3 Theory and comparison with experiment

The two well-defined magnetic modes in Fig. 2.1, and the fact that the closely related material Ca$_2$FeReO$_6$ is an insulator, suggests that strong electronic correlations are important in Ba$_2$FeReO$_6$ on both Re and Fe. A local moment model thus provides a useful vantage point to describe its magnetic excitations.

2.3.1 Local Moment Model

On the Fe sites, a nominal valence assignment of Fe$^{3+}$ together with a strong Hund’s coupling leads to orbital moment quenching and a spin $F = 5/2$. On the Re sites, a nominal valence assignment of Re$^{5+}$ ($5d^2$) leads to two electrons in the $t_{2g}$ orbital. Thus, in contrast to the iridates, not only SOC but also Hund’s coupling ($J_H$) is important in determining the magnetic state on Re. [26] The atomic Hamiltonian, when projected to the $t_{2g}$ orbital [50], takes the form

$$H_{\text{Re}} = -2J_H \vec{S}^2 - \frac{J_H}{2} \vec{L}^2 - \lambda (\vec{\ell}_1 \cdot \vec{s}_1 + \vec{\ell}_2 \cdot \vec{s}_2),$$

(2.1)

where $\vec{S} = \vec{s}_1 + \vec{s}_2$ and $\vec{L} = \vec{\ell}_1 + \vec{\ell}_2$. The Hund’s coupling is expected to drive the two electrons into a spin symmetric state with $S = 1$ and an orbitally antisymmetric state with $L = 1$. Indeed, as shown in Fig. 2.3(a), $H_{\text{Re}}$ supports a 5-fold degenerate ground state over a wide range of $J_H/\lambda$ (see Appendix for details). For $J_H/\lambda \gtrsim 2$, which appears to be quite reasonable, we find as seen in Fig. 2.3(b) that this ground state manifold may be viewed as made up of $L = 1$ and $S = 1$ moments locked into a state with total angular momentum $\vec{R} = \vec{L} + \vec{S}$, with $R = 2$.\(^2\)

The simplest local moment Hamiltonian for Ba$_2$FeReO$_6$ is thus

$$H = J \sum_{<rr'>} \vec{S}_r \cdot \vec{F}_{r'} - \lambda \sum_{r \in \text{Re}} \vec{L}_r \cdot \vec{S}_r,$$

(2.2)

with a nearest neighbor antiferromagnetic exchange interaction between the Fe spin $\vec{F}$ and the Re spin $\vec{S}$ induced by intersite tunneling, and $\lambda$ denotes the spin-orbit coupling. This simple model should be more broadly applicable to many DPs A$_2$BB’O$_6$ with an orbitally nondegenerate magnetic B-site, and a magnetic B’-site with two electrons in an active $t_{2g}$ orbital.

For Ba$_2$FeReO$_6$, where spin-orbit coupling is expected to be strong, $\lambda \gg J$, and the local moment Hamiltonian simplifies to

$$H_{\text{eff}} = J_{\text{eff}} \sum_{<rr'>} \vec{R}_r \cdot \vec{F}_{r'},$$

(2.3)

yielding an effective Heisenberg model with moments $\vec{R}$, $\vec{F}$ on the Re and Fe sites, respectively. We find that

$$J_{\text{eff}} = J \frac{R(R+1) + S(S+1) - L(L+1)}{2R(R+1)}.$$

(2.4)

For $L=S=1$, and $R=2$, we obtain $J_{\text{eff}} = J/2$.

We expect that the metallic nature of Ba$_2$FeReO$_6$, and the concomitant carrier delocalization, will lead to a smaller effective value of $F$, $R$ compared to this highly localized viewpoint. This is borne out in our detailed comparisons with experiments discussed below.

\(^2\)Note that we use $R$ for the effective total angular momentum for a Re ion. $R = 2$ would correspond to $j_{\text{eff}} = 2$ if we borrow the notation commonly used in iridate literature.
assumption, however, yields a Fe spin
larger Fe moment. Our observations thus strongly suggest that we must have a naïve valence assignment of Fe.

For momenta with $Q = (2\pi, 0, 0)$ and in the (near) gaplessness of the lower energy mode. The ratio of the magnetic intensities at $Q = (\pi, \pi, \pi)$ to $Q = (2\pi, 0, 0)$ is given by $(S_+/S_-)^2$ which can be very large. As a result, the “antiferromagnetic” fluctuations near $Q = (\pi, \pi, \pi)$ are much more visible than the “ferromagnetic” fluctuations near $Q = (2\pi, 0, 0)$.

2.3.3 Spin-orbital locking on Re, moment sizes, exchange couplings

For momenta with $\gamma_Q = 0$, the spin wave dispersion yields $\Omega_+/\Omega_- = F/R$. Since these momenta dominate the magnon density of states, we can use the ratio of the observed peak positions in Fig. 2.2 (39 meV, 25 meV), to deduce that $F/R \approx 1.6$. If we assume that the Re moments have a pure spin origin, we have to set $R \lesssim 1$. This assumption, however, yields a Fe spin $F \lesssim 1.6$, which is anomalously low — first principles calculations [53, 36], a naïve valence assignment of Fe$^{3+}$, and the measured large saturation magnetization [45], all point to a much larger Fe moment. Our observations thus strongly suggest that we must have $R > 1$, indicating a nonzero orbital coupling.
contribution to the Re moment, in qualitative agreement with XMCD measurements.[35]

In order to obtain estimates of the moment sizes and the exchange coupling, we combine our INS results with previous XMCD[35] and magnetization [45] data. XMCD measurements[35] indicate a significant static orbital contribution to the magnetization on Re, with \( \mu^{\text{orb}}_{\text{Re}} / \mu^{\text{spin}}_{\text{Re}} \approx -0.3 \). This allows us to set \( L \approx 0.63S \), which yields \( S \approx 0.63R \) and \( L \approx 0.37R \). High field magnetization measurements on Ba\(_2\)FeReO\(_6\) indicate a saturation magnetization \( m_{\text{sat}} \approx 3\mu_B \). Together with the neutron data, this constrains the moment sizes to be \( R \approx 1.3 \) and \( F \approx 2.1 \), yielding an estimated exchange coupling \( J_{\text{eff}} \approx 3.1 \) meV, so that \( J \approx 6 \) meV.

We have checked that including a small direct Re-Re Heisenberg exchange \( \sim 0.1J_{\text{eff}} \) slightly modifies the spin wave dispersion and our exchange constant estimates, but does not significantly affect our estimate of \( R \). A large Re-Re exchange coupling \( \gtrsim 0.2 - 0.3J_{\text{eff}} \) leads to a dispersion which is not consistent with our data. The estimated magnitude of the exchange coupling and the absence of a strong frustrating Re-Re interaction, may have important implications for the theoretical modelling [2] of the closely related insulating DP, Sr\(_2\)CrOsO\(_6\). Thus, while previous XMCD measurements[35] on Ba\(_2\)FeReO\(_6\) have shown that there is a static orbital contribution to the ordered magnetic moment on Re in the ferrimagnetic state, our work shows that such SO locked moments on Re also play a role in the low energy magnetic excitations.

### 2.3.4 Structural transition and absence of spin gap

Ba\(_2\)FeReO\(_6\) has a weak tetragonal distortion, with \( c/a < 1 \), which onsets at the magnetic \( T_e \).[35] Since a Jahn-Teller distortion would lead to \( c/a > 1 \), not necessarily coincident with \( T_e \), we ascribe this distortion to SOC. Going beyond \( H_{\text{eff}} \), we expect a term \( -\epsilon \sum_i (R_{r,x} + 4R_{r,y} + 4R_{r,z}) \), arising from the cubic anisotropy, which locks the Re moment (and thus also the Fe spins) to the crystal axes. Such a magnetostructural locking term with \( \epsilon > 0 \) explains the observed tetragonal distortion at \( T_e \) as arising from weak orbital order, and would lead to a spin gap of order \( \epsilon \). This locking is expected to be small since it arises from a spin-orbit induced weak mixing of well-separated \( t_{2g} \) and \( e_g \) crystal field levels. [26] This is consistent with our experimental observations - we find no clear evidence of a spin gap down to \( \sim 1 \) meV. A very small magnetostructural locking term is also consistent with the measured weak coercive field \( \sim 0.2 \) Tesla.

### 2.3.5 Magnetic transition temperature

We use the above values of the moment sizes and exchange couplings to estimate the magnetic \( T_e \). The nearest neighbor classical Heisenberg model on a three-dimensional cubic lattice, with moments \( F, R \) on the two sublattices, has a mean field transition temperature \( 2J_{\text{eff}}FR \). Assuming a quantum renormalized \( T_e \approx 2J_{\text{eff}}\sqrt{FR(\sqrt{FR} + 1)} \), we estimate \( T_e \approx 315K \), in rough agreement with the measured \( T^{\text{expt}}_e \approx 304K \). If one takes the limit of fully localized moments, setting \( F = 2.5 \) and \( R = 2 \), one obtains \( T_e \approx 520 \) K, remarkably close to that of the insulating compound Ca\(_2\)FeReO\(_6\).

### 2.4 Summary

We have used theoretical modelling of inelastic neutron scattering data to study the magnetic excitations in Ba\(_2\)FeReO\(_6\), inferring the presence of strong correlations and spin orbit coupled moments on Re, and obtaining a broad understanding of the phenomenology in its ferrimagnetic state. Further efforts are necessary to synthesize single crystals or good quality thin films of Ba\(_2\)FeReO\(_6\) and other DPs. In Chapter 3, we will turn to a more microscopic model of BFRO retaining itinerant electrons.
2.5 Interaction effects - atomic limit

For the \(d^{(2)}, d^{(3)}, d^{(4)}\) configuration of electrons in the \(t_{2g}\) orbital, we have to consider matrix elements of the Coulomb interaction on the same footing as the spin orbit coupling. The interaction Hamiltonian projected to the \(t_{2g}\) orbitals is given by \cite{54}

\[
H_{\text{int}} = U \sum_\alpha n_\alpha n_\alpha + (U - \frac{5J_H}{2}) \sum_{\alpha<\beta} n_\alpha n_\beta - 2J_H \sum_{\alpha<\beta} \vec{S}_\alpha \cdot \vec{S}_\beta + J_H \sum_{\alpha \neq \beta} d^\dagger_\alpha \alpha d_{\beta \uparrow} \beta. \tag{2.6}
\]

After some algebra, this can be reexpressed in terms of rotationally invariant operators as

\[
H_{\text{int}} = \frac{U - 3J_H}{2} n_{\text{tot}}^2 - 2J_H \vec{S}^2 - \frac{J_H}{2} \vec{L}^2 - \lambda (\vec{\ell}_1 \cdot \vec{s}_1 + \vec{\ell}_2 \cdot \vec{s}_2) \tag{2.7}
\]

where we assume the normal ordered form of these operators. For a \(d^{(2)}\) configuration, \(n_{\text{tot}} = 2\). Including the spin orbit coupling term leads to the effective atomic Hamiltonian for \(\text{Re}\)

\[
H_{\text{Re}} = -2J_H \vec{S}^2 - \frac{J_H}{2} \vec{L}^2 - \lambda (\vec{\ell}_1 \cdot \vec{s}_1 + \vec{\ell}_2 \cdot \vec{s}_2) \tag{2.8}
\]

where \(\vec{L} = \vec{\ell}_1 + \vec{\ell}_2\) and \(\vec{S} = \vec{s}_1 + \vec{s}_2\).

2.6 Appendix A: Hamiltonian diagonalization

To diagonalize this Hamiltonian \(H_{\text{Re}}\) for a \(d^{(2)}\) configuration, we write the full Hamiltonian in the basis \(|L, m_\ell, S, m_s\rangle\) corresponding to total orbital and total spin angular momentum. Since the individual orbital angular momenta \(\ell_1 = \ell_2 = 1\) and individual spin angular momenta are \(s_1 = s_2 = 1/2\), we use a shorthand for the Clebsch-Gordan coefficients, defining them via

\[
|L, m_\ell, S, m_s\rangle = |L, m_\ell\rangle \otimes |S, m_s\rangle \tag{2.9}
\]

\[
|L, m_\ell\rangle = \sum_{m_{1, m_2}} C_{L m_\ell}^{m_{1, m_2}} |m_1, m_2\rangle \tag{2.10}
\]

\[
|S, m_s\rangle = \sum_{s_1, s_2} C_{S s_1, s_2}^{m_s} |s_1, s_2\rangle \tag{2.11}
\]

in terms of which the full Hamiltonian becomes

\[
\langle L', m'_\ell, S', m'_s |H_{\text{at}}^{(2)} |L, m_\ell, S, m_s\rangle \equiv H_{L, m_\ell, S, m_s}^{L', m'_\ell, S', m'_s} \tag{2.12}
\]

where

\[
H_{L, m_\ell, S, m_s}^{L', m'_\ell, S', m'_s} = \delta_{L, L'} \delta_{S, S'} \delta_{m_\ell', m_\ell} \delta_{m_s', m_s} E_{L, S} - \lambda \sum_{m_{1, m_2}, s_1, s_2} C_{L m_\ell}^{m_{1, m_2}} C_{S s_1, s_2}^{m_s} (2m_1 s_1 C_{m_1, m_2}^{L'm'_\ell} C_{s_1, s_2}^{S'm'_s} + \sqrt{2} C_{m_1 + 1, m_2}^{L'm'_\ell} C_{s_1 - 1, s_2}^{S'm'_s} + \sqrt{2} C_{m_1 - 1, m_2}^{L'm'_\ell} C_{s_1 + 1, s_2}^{S'm'_s}) \tag{2.13}
\]
2. Neutron scattering study of magnetic excitations in Ba$_2$FeReO$_6$

Figure 2.4: (a) Neutron scattering intensity at 34 K for an incident energy of 120 meV. An empty Al can background has been subtracted from the data. (b)–(d) Constant energy cuts across bands of inelastic scattering at 70, 40 and 25 meV respectively. Solid black lines are a fit to $I(Q) = A(E) + BQ^2$ delimiting the $Q$-dependent contribution of phonon scattering at each energy.

and

$$E_{L,S} = \left[ -2J_H S(S+1) - \frac{J_H}{2} L(L+1) \right]$$

Here, we must restrict ourselves to totally antisymmetric electronic states; $(L, S) = (0,0), (1,1), (2,0)$ yield the allowed 15 basis states.

When $J_H = 0$, we find eigenstates at three distinct energies corresponding to filling two electrons into single-particle states corresponding to a low energy $j = 3/2$ manifold or a higher energy $j = 1/2$ doublet. On the other hand, when $\lambda = 0$, we find $H_{Re}$ has, in increasing order of energy, total angular momentum eigenstates $^3P, ^1D$, and $^1S$.

The numerically computed spectrum of $H_{Re}$ is shown in Fig. 4 of this chapter. Over a wide range of $J_H/\lambda$, we find a 5-fold degenerate ground state when spin-orbit coupling competes with $J_H$. For $J_H/\lambda \gg 1$, we can show that the $^3P$ ground states at $\lambda = 0$ split into spin-orbit coupled states which may be labelled by total angular momentum $L+S = 2,1,0$ in increasing order of energy. (corresponding to $^3P_2, ^3P_1, ^3P_0$ states with degeneracies 5, 3, 1). This shows that a local $-\lambda \vec{L} \cdot \vec{S}$, with $L = S = 1$, is a good description of the lowest energy manifold of states when $J_H/\lambda \gtrsim 2$. However, when $J_H \lesssim \lambda$, this sequence changes to 5, 1, 3 (in ascending order) suggesting that such a simple description fails.

2.7 Appendix B: Phonon background

The measured scattering intensity consists of a number of components including coherent nuclear and magnetic scattering, as well as incoherent processes. Additional background scattering originating from the sample environment, and detector dark current is eliminated by subtracting the signal measured for an empty Al sample can using identical instrumental configuration. The signal of interest is coherent scattering from magnons, which has a momentum dependent intensity dominated by the magnetic form factor. In general, the magnetic form-factor
rapidly decays as a function of $Q$, thus the magnetic INS intensity will decrease with increasing $Q$. In contrast, both coherent scattering from phonons and incoherent nuclear scattering intensities increase quadratically with $Q$ in a powder averaged measurement [55]. Any periodic modulations of the coherent phonon scattering arising from the structure factor should also increase in intensity with $Q$.

A map of the inelastic neutron scattering at 34 K, for 120 meV incident energy is shown in Fig. 2.4 (a). There are three bands of inelastic scattering, around 25, 40, and 70 meV which increase in intensity with increasing $Q$. We associate each of these with three phonon bands. The magnetic signal emerges from the antiferromagnetic zone center at $Q = 1.35 \, \AA^{-1}$ and extends into two bands with maximum intensities at 25 meV and 39 meV.

To highlight the momentum dependence of the scattering intensities constant energy cuts through each band of inelastic scattering are shown in Fig. 2.4 (b) – (d). Around 70 meV, [Fig. 2.4 (b)], the scattering is dominated by phonons, here the momentum dependence of scattering intensity is entirely described by the quadratic form $I(Q) = A(E) + BQ^2$, where $A$ is a constant function of $Q$ parameterizing background originating from the small multiple scattering contributions to the inelastic scattering. On average $A$ is a decaying function of energy. In Fig. 2.4 (c) and (d) the overall intensity increases with increasing $Q$ at high $Q$, and above $Q = 3 \, \AA^{-1}$ the scattering is dominated by phonons, as can be seen from the fits to $I(Q)$ (solid black lines). However, below $Q = 3 \, \AA^{-1}$ the INS intensity clearly increases above the phonon background with decreasing $Q$. Furthermore in Fig. 2.4 (d) the low $Q$ scattering intensity modulation is consistent with the magnetic Brillouin zone. Thus, the magnetic scattering is well separated in $Q$ from the phonon scattering, and the magnetic scattering is clearly identified through momentum, and temperature dependencies (see Fig. 3 of the main text). We note that the two lower phonon modes, which are common to many perovskite materials, are at energies which are not far from the zone-boundary magnon mode energies. Further single crystal inelastic neutron scattering measurements are required to determine whether this is a mere coincidence, or a result of magnon-phonon coupling in this material.
Chapter 3

Theory of metallic double perovskites with spin orbit coupling and strong correlations

3.1 Introduction

In this chapter, we focus on metallic ordered DPs with mixed 3d/5d transition metal ions on the B/B’ sites, specifically the Ba$_2$FeReO$_6$ material,[77, 45] with the structure as shown in Fig.4.1. we obtain the following main results. (i) We consider a model of the ordered double perovskite Ba$_2$FeReO$_6$ (see Fig.4.1) retaining the relevant electronic states in the vicinity of the Fermi level. This model, after taking spin-orbit coupling as well as correlations effects into account within a self-consistent mean field theory, is shown to reproduce previous ab initio electronic structure results [36] in the ferrimagnetic ground state. Our model accounts for the dominant energy scales in this material: (a) the strong Hund’s coupling on Fe, the Hubbard repulsion on Re, and the Fe-Re charge transfer energy (all on the scale of $\sim$ 1eV), (b) the strong spin-orbit coupling on Re ($\sim$0.5eV), and (c) the nearest neighbor Re-Fe hopping terms which leads to electron itinerancy ($\sim$ 0.3eV). In addition, we include weaker terms such as inter-orbital mixing and second neighbor hopping which are required to reproduce the band degeneracies at high symmetry points in the Brillouin zone found in earlier ab initio studies. (ii) Our theory accounts semi-quantitatively for the measured saturation magnetization [134], as well as X-ray magnetic circular dichroism (XMCD) experiments which find a significant orbital contribution to the Re magnetization in the ordered state.[35, 120] (iii) Based on the orbital occupations in the magnetically ordered state, we predict a tetragonal distortion, with c-axis compression accompanying magnetic order, in agreement with experimental data.[35, 120] We also predict a specific doping dependence to this orbital order and distortion which could be tested in future experiments. (iv) The strong correlations on Re, inferred from our study, lends partial support to earlier work which showed that a local moment description of the ferrimagnetic state provides a reasonably good description of the magnetic dynamic structure factor obtained using inelastic neutron scattering experiments. [125] This importance of strong correlation effects and local moment physics on the 5d element is in agreement with previous ab initio studies [124] that discussed the emergence of local moments of closely related Cr-based 3d/5d DPs Sr$_2$CrB’O$_6$ upon progressing through the series with B’=W,Re,Os. (v) From our computed band dispersion, we show the appearance of Weyl nodes in such metallic ferrimagnetic DPs. This is in line with the general understanding that in the presence of spin-orbit coupling, such Weyl nodes are expected to be induced by breaking of time-reversal symmetry or inversion symmetry.[80, 81] (vi) Using the Kubo formula for the spin-orbit coupled bands, we find that Ba$_2$FeReO$_6$ itself appears to have only a small intrinsic anomalous Hall effect (AHE)
in the ordered ferrimagnetic state at low temperature, but the AHE is significant in hole doped systems, and we speculate that it might also be significant at intermediate temperatures below the ferrimagnetic $T_c$ in Ba$_2$FeReO$_6$.

Taking a broader viewpoint, Re-based layered quasi-two-dimensional oxides or heterostructures may be more strongly correlated than the three-dimensional DPs, and may lead to interesting Mott physics [262, 26] beyond the iridates due to the local competition between interactions and spin-orbit coupling due to the d$_{2}$ configuration of Re$^{5+}$. Furthermore, one can carry out detailed inelastic neutron scattering studies in Re-based oxides, thus allowing for the possibility to explore the magnetism in more detail than in the iridates. This may prove to be useful in future studies of exotic variants of Re-based oxides.

### 3.2 Model

The simple charge counting for Ba$_2$FeReO$_6$ suggests Re$^{5+}$ and Fe$^{3+}$ valence states on the transition metal ions. In this state, the five 3d-electrons on Fe are expected to be locked into a spin-$5/2$ moment due to strong Hund’s coupling in the half-filled d-shell. Here, we will treat this magnetic moment as a classical vector. The two 5d-electrons in the Re $t_{2g}$ orbital are mobile, able to hop on and off the Fe sites subject to a charge transfer energy $\Delta = E_{Fe} - E_{Re} > 0$, and Pauli exclusion which constrains electrons arriving on Fe to be antiparallel to the direction of the local Fe moment. For a general direction of the Fe moment, $\vec{F} = (\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta)$ at a given site, we must project the added electrons onto the allowed direction to satisfy Pauli exclusion, locally setting $f_{\uparrow} = \sin \frac{\theta}{2} e^{-i\phi/2} f$ and $f_{\downarrow} = -\cos \frac{\theta}{2} e^{i\phi/2} f$, effectively “stripping” the electron of its spin degree of freedom. Such models have been proposed for other DP materials,[143, 144, 38, 59, 123, 40?] and shown to capture the phenomenology of Sr$_2$FeMoO$_6$ including thermal phase transitions and disorder effects. [2, 82, 83]

However, most of these previous studies, with the notable exception of Ref. [124] have ignored spin-orbit coupling effects, which are expected to be extremely important for 5d transition metal oxides.

Our model does not explicitly account for additional superexchange interactions between the Fe local moment and the emerging local moments on the Re sites which is explicitly taken into account as a separate term in some previous studies (for example, Ref. [124]); however, we think such terms should emerge more naturally from an
effective tight-binding model when strong correlations are incorporated, as might be relevant to Mott insulating oxides like \( \text{Sr}_2\text{CrOsO}_6 \). Fe-Fe superexchange terms which we omit, since they are not necessary to drive the ferrimagnetic state observed in \( \text{Ba}_2\text{FeReO}_6 \), may prove to be important in understanding the complete magnetic phase diagram as a function of doping which is not addressed in this chapter. However, they are likely to be small given the Fe-Fe separation in the DP structure. Further differences between the results of Ref. [124] and our work stem from the fact that their model is for \( \text{d}^3 \) configuration of Cr, as opposed to our \( \text{d}^5 \) state on Fe; while both spin components of the itinerant electrons are permitted on Cr (since the \( \text{e}_g \) orbital is available), only one spin projection is allowed for itinerant electrons on Fe due to the Pauli exclusion.

### 3.2.1 Non-interacting tight binding model

The model describing Re electrons moving in the presence of Fe moments then takes the form

\[
H_0 = H_{\text{hop}} + H_{\text{so}} + H_{\text{cl}}.
\]

Here, the Hamiltonian \( H_{\text{hop}} \) describes intra-orbital hopping of electrons on the lattice, from Re to Fe (nearest-neighbor) and from Re to Re (next-neighbor), as well as inter-orbital hopping of electrons between next-neighbor Re sites; \( H_{\text{so}} \) is the atomic spin-orbit coupling on Re, projected to the \( \text{e}_g \) manifold, of strength \( \lambda \); finally, \( H_{\text{cl}} \) describes the charge transfer energy offset \( \Delta \) between Re and Fe sites. For simplicity, we only focus on the case of a uniform magnetization on the Fe site, with one Re and one Fe atom, as shown in Fig. 4.1 to study the model Hamiltonian; however in order to facilitate a comparison with published \textit{ab initio} electronic structure calculations, we will later assume a body-centered tetragonal unit cell containing two Re and two Fe atoms, with lattice constants \( d_a = d_b = d_c / \sqrt{2} \) as shown in Fig. 4.1, and use orthorhombic notation to plot the band dispersion of the eighteen bands in the Brillouin zone.

We label the electrons on the Fe and Re sites by \( f_\ell \) and \( d_\ell \sigma \) respectively, with \( \ell = (1 \equiv yz, 2 \equiv zx, 3 \equiv xy) \) denoting the orbital, and \( \sigma = \uparrow, \downarrow \) being the spin. The Hamiltonian takes the following form in momentum space, where we assume implicit summation over repeated spin and orbital indices,

\[
\begin{align*}
H_{\text{hop}} &= \sum_k \left( \eta_\ell(k) g_\sigma(\theta, \phi) d_\ell^{\dagger \sigma}(k) f_\ell(k) \right. + \text{h.c.} \\
&+ \sum_k \epsilon_\ell(k) (d_\ell^{\dagger \sigma}(k) d_\ell^{-\sigma}(k) + \alpha_f f_\ell^{\dagger}(k) f_\ell(k)) \\
&+ \sum_{k(\ell \neq \ell')} \gamma_{\ell \ell'}(k) (d_\ell^{\dagger \sigma}(k) d_{\ell'}^{-\sigma}(k) + \alpha_f f_\ell^{\dagger}(k) f_{\ell'}(k)) \tag{3.1}
\end{align*}
\]

\[
\begin{align*}
H_{\text{so}} &= i \frac{\lambda}{2} \sum_k \varepsilon_{\ell mn} \tau_{\sigma \sigma'}^m d_\ell^{\dagger \sigma}(k) d_{\ell'}^{-\sigma'}(k) \tag{3.2}
\end{align*}
\]

\[
\begin{align*}
H_{\text{cl}} &= \Delta \sum_k f_\ell^{\dagger}(k) f_\ell(k) \tag{3.3}
\end{align*}
\]

Here, in light of our previous discussion, we have only retained a single spin projection on the Fe site, with \( g_\uparrow(\theta, \phi) = \sin \frac{\theta}{2} e^{-i\phi/2} \) and \( g_\downarrow(\theta, \phi) = -\cos \frac{\theta}{2} e^{i\phi/2} \). The various hopping processes are schematically illustrated in Fig. 3.2. The first term in \( H_{\text{hop}} \) describes nearest-neighbor intra-orbital hopping from Re to Fe, parameterized by \( t_\sigma, t_\delta \). The next two terms in \( H_{\text{hop}} \) characterize next-neighbor hopping processes, with the ratio of Fe-Fe hoppings to Re-Re hoppings being \( \alpha_f \); we will fix \( \alpha_f = 0.5 \). While the second term captures intra-orbital hopping between closest pairs of Re atoms or Fe atoms (parameterized by \( t', t'' \)), the third term captures inter-orbital hopping between closest pairs of Re atoms or Fe atoms (parameterized by \( t_m \)). Many of these hopping
Figure 3.2: Symmetry-allowed hopping matrix elements for double perovskites $A_2B'B'O_6$ (e.g., $Ba_2FeReO_6$), indicated for a few orbitals. $t_\pi$, $t_\delta$ are $B$-$B'$ ($Fe$-$Re$) intraorbital hoppings, $t'$, $t''$ are $B'$-$B'$ ($Re$-$Re$) intraorbital hoppings, and $t_m$ denotes the interorbital $B'$-$B'$ ($Re$-$Re$) hopping. All processes related to these by cubic symmetry are allowed. The Fe-Fe hoppings are identical to Re-Re hoppings, but scaled by a factor $\alpha_f = 0.5$. Also shown are the rotated axes (compass) for the tetragonal unit cell of $Ba_2FeReO_6$, with $x'$-$y'$ (dashed lines) being the original cubic axes for defining the orbitals.

processes ($t_\delta, t_m, t''$) have a small energy scale; however they are important to reproduce the band degeneracies found in $ab$ $initio$ calculations at high symmetry points in the Brillouin zone. The explicit momentum dependence of the dispersion coefficients appearing in $H_{\text{hop}}$ is given in Appendix A.

### 3.2.2 Interaction effects

Electron-electron interactions are partially accounted for by $H_0$ in the previous section — in part, by the charge transfer gap $\Delta$, and, in part, by the implicit Hund’s coupling which locks the Fe electrons into a high-spin state. However, electronic interactions on Re have been omitted in $H_0$. We next include these local Hubbard interactions on Re. The interaction Hamiltonian in the $t_{2g}$ orbitals of Re takes the form [84]

$$H_{\text{int}} = U \sum_{i\ell\alpha} n_{i\ell\uparrow} n_{i\ell\downarrow} + (U - 5J_H/2) \sum_{\ell < \ell'} n_{i\ell\uparrow} n_{i\ell'\downarrow}$$

$$- 2J_H \sum_{\ell < \ell'} \vec{S}_{i\ell} \cdot \vec{S}_{i\ell'} + J_H \sum_{\ell \neq \ell'} d_{i\ell\uparrow} d_{i\ell'\downarrow} d_{i\ell'\uparrow} d_{i\ell\downarrow}$$

(3.4)

where $i$ labels the Re sites, and $\vec{S}_{i\ell} = \frac{1}{2} d_{i\ell\alpha} \sigma_{\alpha\beta} d_{i\ell\beta}$ is the spin at site $i$ in orbital $\ell$. We wish to then study the full Hamiltonian $H = H_0 + H_{\text{int}}$. For simplicity, we only retain only the dominant intra-orbital Coulomb repulsion, treating it at mean field (Hartree) level, as

$$H_{\text{int}} \approx U \sum_{i\ell} \left[ \frac{\rho_{\ell}}{2} (n_{i\ell\uparrow} + n_{i\ell\downarrow}) - 2\vec{m}_{\ell} \cdot \vec{S}_{i\ell} - \frac{\rho_{\ell}^2}{4} + \vec{m}_{\ell} \cdot \vec{m}_{\ell} \right]$$

(3.5)
where $\rho_\ell = \langle n_{i\ell \uparrow} + n_{i\ell \downarrow} \rangle$, $\vec{m}_\ell = \langle \vec{S}_{i\ell} \rangle$, and we set $\vec{m}_\ell = -m_\ell (\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta)$, with $m_\ell > 0$, so that $\vec{m}_\ell$ is anti-parallel to the Fe moment $\vec{F}$. For simplicity, we only focus on the case $\theta = \phi = 0$, so the Fe sites can only accommodate itinerant spin-$\downarrow$ electrons. We then numerically determine $m_\ell$ and $\rho_\ell$ in a self-consistent fashion, using the non-interacting ground state as the starting point for the iterative solution, while ensuring that the choice of the chemical potential lead to a total of two electrons per unit cell (i.e., per Re atom). Such a mean field treatment of electron-electron interactions does not capture all aspects of the strong correlation physics, e.g. bandwidth renormalization and mass enhancement. Nevertheless, recognizing this caveat, we use the self-consistent solution of the mean field equations to study the effects of interactions and spin-orbit coupling on the reorganization of the nine electronic bands, compare the physical properties with experimental results, and make qualitative predictions for future experiments.

### 3.3 Physical properties

We begin by discussing the effect of electronic correlations in the DPs in the absence of spin-orbit coupling. We show that such correlation effects appear to be crucial to stabilize a half-metallic state with complete polarization in the 5d perovskites, due to the large second-neighbor Re-Re hopping which otherwise prevents a half-metallic state. We then turn to the effect of spin-orbit coupling, and show that it reorganizes the band structure, yielding results which are in reasonable agreement with previous ab initio electronic structure studies.\[36\] (As pointed out earlier, the band dispersions discussed below are plotted using the orthorhombic notation with an enlarged unit cell containing two Fe and two Re atoms, leading to eighteen electronic bands instead of nine.) Finally, we compare the mean field result for the saturation magnetization with experiments, and the spin and orbital magnetization on the Re site with previous XMCD data, and discuss other physical properties such as tetragonal lattice distortion and predictions for the AHE. Throughout this discussion, we will assume a ferromagnetic order of the Fe moments - a more complete study of the magnetic phase diagram as a function of doping and temperature will be the subject of future numerical investigations.

#### 3.3.1 Correlations stabilize a half-metal

If we ignore Re correlations entirely, setting $U = 0$, and also ignore spin-orbit coupling by setting $\lambda = 0$, the band structure shown in Fig.3.3(a) has decoupled spin-$\uparrow$ and spin-$\downarrow$ bands. The twelve spin-$\downarrow$ bands corresponding to electrons which can delocalize on Re and Fe. By contrast, the six spin-$\uparrow$ bands corresponds to purely Re states. Working in units where $t \pi = 1$, we find that to make a reasonable comparison with the ab initio calculations, we have to choose a significant $t' = 0.3$ (Re-Re hopping), but all other hoppings can be assumed to be small; for simplicity, we fix $t_5 = t'' = t_m = 0.1$. Finally, we have to assume a moderate charge transfer energy $\Delta = 3$ which splits the spin-$\downarrow$ states into two groups: 6 lower energy Re-Fe hybridized spin-$\downarrow$ states (dominant Re character) which form a broad band, and 6 higher energy dominantly Re-Fe hybridized spin-$\downarrow$ states (dominant Fe character) which form a narrow band. Finally, the remaining 6 Re-$\uparrow$ states form a narrow dispersing band, crossing the chemical potential and overlapping in energy with the broad spin-$\downarrow$ band. For $U = 0$, the system thus contains both spin states at the Fermi level. When we incorporate a Hubbard repulsion $U = 8t_\pi$ at mean field level, we see from Fig. 3.3(b) that its main effect is to self-consistently shift the spin-$\uparrow$ bands higher in energy, leaving only spin-$\downarrow$ states at the Fermi level. The resulting band dispersion is in reasonably good agreement with LDA+U calculations. Although we have not attempted a detailed quantitative fitting to the LDA+U band structure, the features noted below are robust. (i) A rough comparison with the overall bandwidth in the ab initio
3.3.2 Spin-orbit coupling: Band reconstruction, spin/orbital magnetization, and comparison with magnetization and XMCD experiments

We next turn to the effect of incorporating both spin-orbit coupling and Hubbard interactions on Re, solving the mean field equations in case of a nonzero $U$. From Fig.3.3(c) and (d), where we have set $\lambda = 2t_\pi$ ($\approx 660$ meV), we find decoupled spin-$\uparrow$ (red, solid) and spin-$\downarrow$ (blue, dashed) states. Comparing (a) and (b), we see that correlations on Re push the spin-$\uparrow$ states to higher energy, leading to the stabilization of a half-metal ground state. An effective spin-orbit coupling, (c) $U = 0$ and $\lambda = 2t_\pi$, and (d) $U = 8t_\pi$ and $\lambda = 2t_\pi$, leads to mixed-spin states and splits degeneracies, but for a physically reasonable value $U = 8t_\pi$ preserves significant spin polarization $\sim 90\%$ for states at the Fermi level.

To summarize, we have obtained a tight-binding description including interactions of DPs with spin-orbit coupling. In contrast to 3d/4d DP materials like $\text{Sr}_2\text{FeMoO}_6$, we find that 3d/5d DPs have a significant second neighbor hopping; strong correlations on the 5d element (Re) therefore play a crucial role in stabilizing a half-metallic ground state in the 3d/5d DPs.

Figure 3.3: Band dispersion in the orthorhombic notation for the Re and Fe electronic states for different choices of Hubbard interaction $U$ and spin-orbit coupling $\lambda$, with energy on the $y$-axis in units of $t_\pi$. The solid black line indicates the chemical potential. For no spin-orbit coupling, (a) $U = 0$ and $\lambda = 0$ and (b) $U = 8t_\pi$ and $\lambda = 0$, we find decoupled spin-$\downarrow$ (red, solid) and spin-$\uparrow$ (blue, dashed) states. Comparing (a) and (b), we see that correlations on Re push the spin-$\uparrow$ states to higher energy, leading to the stabilization of a half-metal ground state. A nonzero spin-orbit coupling, (c) $U = 0$ and $\lambda = 2t_\pi$, and (d) $U = 8t_\pi$ and $\lambda = 2t_\pi$, leads to mixed-spin states and splits degeneracies, but for a physically reasonable value $U = 8t_\pi$ preserves significant spin polarization $\sim 90\%$ for states at the Fermi level.

Calculations without spin-orbit coupling [36] suggests that $t_\pi \approx 330$ meV. This is somewhat larger than estimates for $\text{Sr}_2\text{FeMoO}_6$ in the literature [143, 144] ($\approx 270$ meV). (ii) We estimate the interaction energy scale on Re to be $U \approx 2.5$ eV, smaller by a factor of two compared with typical values for 3d transition metals. (iii) There is a significant Re-Re hopping, $t'/t_\pi \sim 0.3$, we need to include in order to be able to capture the bandwidths of the spin-$\uparrow$ and spin-$\downarrow$ bands. All these observations are reasonable given the more extended nature of Re orbitals when compared with 3d or 4d transition metal ions. The presence of appreciable Re-Re hoppings has been pointed out in previous work, [85, 59] although they did not take correlation effects on Re into account. More recent work has also arrived at similar conclusions regarding significant Re-Re hoppings.[124]
for our estimated $t_z$), we see that spin-orbit coupling clearly eliminates the degeneracies occurring at the $\Gamma$-point for $\lambda = 0$. It also significantly reconstructs the dispersion of the eighteen bands, leading to reasonably good agreement with published ab initio calculations which include spin-orbit coupling.[36] In the next section, we will discuss the resulting appearance of Weyl nodes in the band dispersion and the intrinsic anomalous Hall effect in the ordered state. Here, we will use the mean field solution to estimate the average Fe valence, the Fe ordered moment, and the spin and orbital contributions to the Re moment. In the ground state with correlations, we find that the average valence of Fe shifts from the naive charge counting value Fe$^{3+}$ to Fe$^{2.6+}$, and the Fe moment is lowered to an effective value $F_z \approx 2.3$ (corresponding to $4.6 \mu_B$). Quantum spin fluctuations beyond the mean field result might further slightly suppress this value. On Re, we find an ordered spin moment $S_z \approx 0.78$ and an orbital moment $L_z \approx 0.48$; taking the $g$-factor into account, and undoing the sign change of the orbital angular momentum which appears upon projection to the $t_{2g}$ Hamiltonian, this implies a ratio of magnetic moments $\mu_{\text{Re}}^{\text{orb}} / \mu_{\text{Re}}^{\text{spin}} \approx -0.31$, remarkably close to the experimentally measured XMCD result $\approx -0.29$. We find that the actual value of the spin magnetic moment, $\mu_{\text{Re}}^{\text{spin}} \approx 1.56 \mu_B$, is larger than the experimentally reported XMCD value $\approx 1.08 \mu_B$. This discrepancy might be partly due to the fact that (i) the experimental results are on powder samples, and hence might appear to be smaller simply due to averaging over grain orientations, and (ii) the method to extract the individual spin or orbital magnetic moments relies on additional assumptions, while the ratio is apparently more reliable.[35] We must contrast these results with the case where we ignore Re correlations entirely; in that case, the Fe moment is not much affected, $F_z^{U=0} \approx 2.4$, but the Re moments are strongly suppressed, yielding $S_z^{U=0} \approx 0.15$ and an orbital moment $L_z^{U=0} \approx 0.09$ which would lead to a much smaller $\mu_{\text{Re}}^{\text{spin}} (U = 0) \approx 0.3 \mu_B$ than is experimentally estimated, as well as a much larger saturation magnetization, $4.6 \mu_B$, than the measured value [45, 134] which is $\approx 3.2-3.3 \mu_B$. Our estimates in the presence of correlations, by contrast, yield $m_{\text{sat}} \approx 3.5 \mu_B$, in much better agreement with the data. Finally, we use our solution to estimate the polarization, defined as the degree of magnetization for states near the Fermi level. We find that while the correlated half-metal state in the absence of spin-orbit coupling exhibits (obviously) 100% polarization, using $\lambda = 2t_z$ reduces the polarization to $\approx 90\%$. However, if we only take spin-orbit coupling into account and ignore strong correlations, the states near the Fermi level are nearly unpolarized.

In 3d/5d DP materials, spin orbit coupling and strong correlations are both crucial to obtain the experimentally observed spin and orbital magnetization and their locking, and to explain the experimentally observed saturation magnetization and XMCD signal. Spin-orbit coupling leads to a slight decrease of the correlation-induced spin polarization at the Fermi level.

### 3.3.3 Orbital order, tetragonal distortion in ferrimagnetic state, and doping dependence

In the converged mean field state, with the magnetization along the $z$-axis, we find that the density on Re in the three orbitals are different, with $\rho_{xy} \approx 0.60$ and $\rho_{xz} = \rho_{yz} \approx 0.53$. This orbital imbalance is induced in the $z$-ferrimagnetic state due the spin-orbit coupling. The larger extent of the $xy$-orbital in the $xy$-plane, compared with its smaller extent along the $z$-direction, implies that this orbital charge imbalance would lead to a tetragonal distortion of the lattice, to occur coincident with ferrimagnetic ordering and with a shrinking of the $c$-axis, as has indeed been observed to occur experimentally. The precise extent of this distortion, which is observed [35] to be $\sim 0.1\%$, depends on details such as the lattice stiffness, and is beyond the scope of our calculation.

When we solve the self-consistent equations at various dopings $\delta$ (excess electrons per Re) assuming persistent ferrimagnetic order, the extent of this orbital imbalance, characterized by a tetragonal order parameter $\eta_{\text{tet}} = \frac{1}{p} (\rho_{xy} - \rho_{xz}/2 - \rho_{yz}/2)$, changes systematically as shown in Fig. 3.4(a). Light electron doping leads to a slightly larger orbital population imbalance and should enhance the $c$-axis compression, while a larger electron doping...
leads to a gradual decrease of $\eta_{tet}$. Hole doping beyond $\gtrsim 0.25$ holes/Re leads to $\eta_{tet} < 0$, which should cause elongation along the c-axis. The spin contribution to the magnetization on Re, arising from the different orbitals, also shows a similar doping trend as seen from Fig. 3.4(b), while the orbital contribution to the magnetization on Re has the largest magnitude at zero doping. These results could be possibly be explored experimentally by partially substituting Ba by trivalent La (electron doping), or by Cs or other monovalent ions (hole doping).

Thus, in 3d/5d DP materials, spin orbit coupling and the ferrimagnetic order of itinerant electrons leads to orbital ordering. This, in turn, should lead to a compression along the c-axis, consistent with the experimentally observed tetragonal distortion, and we predict a specific doping dependence to this structural distortion.

### 3.3.4 Doping-dependent anomalous Hall effect

We next turn to the intrinsic AHE in the ferrimagnetic state of such 3d/5d DPs. As pointed out in recent work, for pyrochlore iridates with all-in-all-out order under uniaxial pressure,[75] as well the ferromagnetic infinite-layer ruthenate SrRuO$_3$, [86] this intrinsic AHE contains two contributions: (i) a surface contribution arising from Fermi arc states [73] associated with Weyl nodes in the dispersion, and (ii) a bulk contribution from carriers near the Fermi surface. A pair of such Weyl nodes for Ba$_2$FeReO$_6$ is shown in Fig. 3.5 obtained from the interacting band dispersion.  

![Graph showing the relationship between doping and magnetization on Re](image_url)

Both contributions to the intrinsic AHE are captured by the momentum-dependent Berry curvature [87, 88] of the spin-orbit coupled bands, which is, in turn, obtained from the Kubo formula

$$
\sigma_{xy} = e^2 \hbar \int \frac{d^3k}{(2\pi)^3} \sum_{m \neq n} \frac{f(\varepsilon_{km}) - f(\varepsilon_{kn})}{(\varepsilon_{km} - \varepsilon_{kn})^2} \text{Im}(\mu^x_{nm} \nu^y_{nm}). \tag{3.6}
$$

Here, $\varepsilon_{km}$ is the single-particle energy at momentum $k$ and band $m$, $\nu^\alpha = \frac{1}{\hbar} (\partial H_{mf}/\partial k_\alpha)$ are components of the velocity operator with $H_{mf}$ being the self-consistently determined mean-field Hamiltonian matrix, and $f(.)$ is the Fermi function.  

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1The full set of Weyl nodes - their location, charges, and dependence on the direction of the magnetization vector - will be discussed elsewhere. (A. M. Cook, A. A. Burkov, and A. Paramekanti, work in progress)

2An equivalent route to computing $\sigma_{xy}$ is to view the 3D band dispersion $\varepsilon_{k3}$ as a sequence of 2D band structures parameterized by the momentum $k_3$ along one direction,[74, 86] writing it as $\varepsilon_{k3}^{[k_1,k_2]}(k_3, k_2)$. Each such 2D band can have a momentum dependent Berry curvature and a nonzero Chern number, thus yielding a quantum Hall insulator for a filled band. Weyl nodes, which act as ‘monopoles’ in momentum space - sources or sinks of integer quanta of Berry flux [73, 75, 74] - correspond to quantum Hall transitions in momentum space where the Chern number jumps as a function of $k_3$. Integrating the Berry curvature, obtained by using gauge invariant plaquette products of
Ba$_2$FeReO$_6$, we find that $\sigma_{xy}$ at zero temperature is small, $\sigma_{xy} \sim 10^{-3} \frac{e^2}{\hbar d_c}$ where $d_c \approx 8\AA$ is the lattice constant in Fig. 4.1. This translates into $\sigma_{xy} \sim 5 \Omega^{-1} \text{cm}^{-1}$.

In order to explore $\sigma_{xy}$ over a larger space of parameters, we consider its variation with doping. Rather than simply shifting the chemical potential, we solve the Hartree mean field equations over a range of electron densities, and then compute $\sigma_{xy}$ in the resulting self-consistent band structure. We find that electron doping does not significantly enhance the AHE, but a hole doping of about 0.5-0.8 holes/Re leads to a larger AHE $\sigma_{xy} \sim -100 \Omega^{-1} \text{cm}^{-1}$ to $-250 \Omega^{-1} \text{cm}^{-1}$. Even this significant AHE is small in natural units ($\sim 0.1 \frac{e^2}{\hbar d_c}$) at $T = 0$, which we attribute to the large spin polarization in the completely ordered ferromagnet. It is possible that the AHE is a non-monotonic function of temperature, peaked at some intermediate temperature below the magnetic $T_c$, even in the undoped compound.

Thus, in 3d/5d DP materials, spin orbit coupling and the ferrimagnetic order is expected to lead to an intrinsic AHE. The AHE appears likely to be larger for hole doped systems compared to an expected small value for Ba$_2$FeReO$_6$ and is likely, in Ba$_2$FeReO$_6$, to be peaked at intermediate temperatures below $T_c$.

### 3.4 Conclusion

We have obtained a tight-binding description of the metallic DPs, including spin-orbit coupling and strong correlation effects. Although we have here only applied it to Ba$_2$FeReO$_6$, finding good agreement with a broad variety of experiments and with electronic structure calculations, our work should be broadly applicable to other 3d/4d and 3d/5d DP materials as well. Our finding that strong correlation effects are needed to explain many of the experimental observations also lends partial justification to our previous theoretical work which modelled the measured spin wave spectrum using a local moment model. Further theoretical work is needed to study the thermal fluctuation effects of the Fe moments, clarify what factors control the doping dependence of $\sigma_{xy}$, and to separate the bulk and surface contributions to the AHE. Furthermore, it would be useful to investigate if ferrimagnetic order in fact survives over a wide range of doping using an unbiased numerical approach. In future experiments, it would be useful to test our predictions for the doping dependence of the structural distortion and the AHE. Given that most DP materials are in the form of powder samples, measuring the AHE and separating the intrinsic contribution from extrinsic contributions would be experimentally challenging; nevertheless systematic doping studies of the various properties of such 3d/5d DPs would be valuable. Finally, it appears extremely

wavefunction overlaps,[89, 86] over all the $k_3$ slices yields the total $\sigma_{xy}$. 

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Figure 3.5: (a) Band dispersion of Ba$_2$FeReO$_6$ in the presence of interactions and spin-orbit coupling plotted along $k_z$ at fixed ($k_x = 0.0393, k_y = 1.9242$), showing the nine bands and a pair of Weyl nodes (with energy on $y$-axis in units of $t_\pi$). The parameters used are the same as those for Fig. 3.3(b), namely $U = 8t_\pi$ and $\lambda = 2t_\pi$. (b) Doping dependence of the intrinsic anomalous Hall conductivity $\sigma_{xy}$. 

In order to explore $\sigma_{xy}$, we find that $\sigma_{xy}$ at zero temperature is small, $\sigma_{xy} \sim 10^{-3} \frac{e^2}{\hbar d_c}$ where $d_c \approx 8\AA$ is the lattice constant in Fig. 4.1. This translates into $\sigma_{xy} \sim 5 \Omega^{-1} \text{cm}^{-1}$.

In order to explore $\sigma_{xy}$ over a larger space of parameters, we consider its variation with doping. Rather than simply shifting the chemical potential, we solve the Hartree mean field equations over a range of electron densities, and then compute $\sigma_{xy}$ in the resulting self-consistent band structure. We find that electron doping does not significantly enhance the AHE, but a hole doping of about 0.5-0.8 holes/Re leads to a larger AHE $\sigma_{xy} \sim -100 \Omega^{-1} \text{cm}^{-1}$ to $-250 \Omega^{-1} \text{cm}^{-1}$. Even this significant AHE is small in natural units ($\sim 0.1 \frac{e^2}{\hbar d_c}$) at $T = 0$, which we attribute to the large spin polarization in the completely ordered ferromagnet. It is possible that the AHE is a non-monotonic function of temperature, peaked at some intermediate temperature below the magnetic $T_c$, even in the undoped compound.

Thus, in 3d/5d DP materials, spin orbit coupling and the ferrimagnetic order is expected to lead to an intrinsic AHE. The AHE appears likely to be larger for hole doped systems compared to an expected small value for Ba$_2$FeReO$_6$ and is likely, in Ba$_2$FeReO$_6$, to be peaked at intermediate temperatures below $T_c$. 

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$\frac{e^2}{\hbar d_c}$.
important to find ways to synthesize bulk single crystals or high quality thin films of such DP materials which
would greatly open up the exploration of their physical properties and applications.

3.5 Appendix A: Tight binding coefficients

When we work with the triclinic unit cell, there is one Fe atom and one Re atom in each unit cell. Going to
momentum space, the coefficients of the tight-binding hopping Hamiltonian

$$H_{\text{hop}}$$

in Eq. 3.1 have intra-orbital terms given by

$$\epsilon_{xy} = -2t'(\cos k_xa + \cos k_ya)$$

(3.7)

$$+ 8t'' \cos(\frac{k_xa}{2}) \cos(\frac{k_ya}{2}) \cos(\frac{k_zc}{2})$$

(3.8)

$$\epsilon_{xz} = 2t''(\cos k_xa + \cos k_ya) + 4t'' \cos(\frac{k_xa-k_ya}{2}) \cos(\frac{k_zc}{2})$$

(3.9)

$$- 4t' \cos(\frac{k_xa+k_ya}{2}) \cos(\frac{k_zc}{2})$$

$$\epsilon_{yz} = 2t''(\cos k_xa + \cos k_ya) + 4t'' \cos(\frac{k_xa+k_ya}{2}) \cos(\frac{k_zc}{2})$$

(3.10)

and

$$\eta_{xy} = 4t_\pi \cos(\frac{k_xa}{2}) \cos(\frac{kya}{2}) - 2t_\delta \cos(\frac{k_zc}{2})$$

(3.11)

$$\eta_{xz} = 2t_\pi \cos(\frac{k_xa+k_ya}{2}) + 2t_\pi \cos(\frac{k_zc}{2})$$

(3.12)

$$- 2t_\delta \cos(\frac{k_xa-k_ya}{2})$$

$$\eta_{yz} = 2t_\pi \cos(\frac{k_xa-k_ya}{2}) + 2t_\pi \cos(\frac{k_zc}{2})$$

(3.13)

$$- 2t_\delta \cos(\frac{k_xa+k_ya}{2}).$$

(3.14)

The intra-orbital terms take the form

$$\gamma_{xz,yz} = -2t_m(\cos k_xa - \cos k_ya)$$

(3.16)

$$\gamma_{xy,yz} = -4t_m \sin(\frac{k_xa + k_ya}{2}) \sin(\frac{k_zc}{2})$$

(3.17)

$$\gamma_{xy,xz} = 4t_m \sin(\frac{k_xa - k_ya}{2}) \sin(\frac{k_zc}{2}).$$

(3.18)
Chapter 4

Double perovskite bilayers: Magnetism and non-trivial topology

4.1 Introduction

The discovery of two-dimensional (2D) tunable and conducting electronic states at transition metal oxide interfaces [90] holds great promise for oxide electronics [91, 92]. The rapid experimental advances in oxide heterostructures [93, 94, 95, 96, 97] have led to the finding that these interface states host coexisting superconductivity and magnetism driven by electronic correlations [98, 99, 100]. Transport studies on epitaxial thin films of 5d transition metal oxides with strong spin-orbit coupling have revealed strain as a powerful tool to control their electronic properties [101, 102]. These experiments have motivated significant work on understanding the interplay of correlations, quantum confinement, and spin orbit coupling in transition metal oxides such as cubic perovskites, pyrochlores, and oxide interfaces [103, 104, 105, 106, 107, 108, 109, 110, 111, 112, 113, 114, 115, 116].

Recently, \((\text{LaNiO}_3)_n-(\text{LaMnO}_3)_n\) oxide superlattices have been grown along the \{111\} direction [117], and found to display an unusual exchange bias effect. The infinite \((1, 1)\) superlattice with alternating triangular layers of Ni and Mn ions corresponds to a “double” perovskite \(\text{La}_2\text{NiMnO}_6\). Such double perovskites (DPs) are complex oxides, \(\text{A}_2\text{BB’O}_6\), with transition metal ions B and B’ residing on the two sublattices of a 3D cubic lattice [118] as shown in Fig. 4.1(a). Theoretical calculations [119] suggest multiferroic behavior in the series \(\text{R}_2\text{NiMnO}_6\) (R being a rare-earth element). Other important bulk DP materials include \(\text{Sr}_2\text{FeMoO}_6\) (SFMO) [43], \(\text{Ba}_2\text{FeReO}_6\), and \(\text{Sr}_2\text{FeReO}_6\) [45, 120] which support half-metallic ferrimagnetism [143, 144, 38, 123, 2, 124, 125, 126, 127, 128] with potential for spintronic applications [44, 129], as well as ferromagnetic Mott insulators like \(\text{Sr}_2\text{CrOsO}_6\) [130, 131].

Motivated by these developments, we study the magnetism and spin-orbit coupled electronic bands in a \{111\} bilayer film of such DPs sandwiched between inert oxide band insulators, focusing on the 3d/4d material SFMO as a prototypical example. As shown in Fig. 4.1(b), such a \{111\} DP bilayer has Fe and Mo ions living on the two sublattices of a (buckled) honeycomb lattice. The system consists of spin-orbit coupled \(t_{2g}\) electrons on the triangular lattice formed by Mo, coupled to local moments on the triangular Fe lattice. Our central result is the emergence, in such a bilayer, of tunable \(\pm 1, \pm 2\) Chern bands and Chern insulators with a quantized anomalous Hall effect driven by spontaneous kinetic ferrimagnetism of Fe moments.

Our study of the magnetism and electronic states in the SFMO bilayer reveals the following. Among a large variety of magnetically ordered or disordered states we have examined, the ferromagnetically ordered state of the
Figure 4.1: (a) Crystal structure of Sr$_2$FeMoO$_6$. Arrows depict bulk ferrimagnetic ground state configuration of spins on the Fe and Mo sites. (b) $\{111\}$ view of a bilayer, showing buckled honeycomb lattice with Fe and Mo ions on the two sublattices.

Fe moments has the lowest energy. This is consistent with experimental results on bulk SFMO [43] and theoretical studies of bulk SFMO in the absence of spin-orbit coupling [2]. The magnetic anisotropy arising from electronic energies is governed by the interplay of spin-orbit coupling, interorbital hybridization, and a symmetry-allowed trigonal distortion. Depending on parameters, this interplay is found to favor various orientations of the local moments. For the $\{110\}$ orientation of magnetic order, we find electronic bands with Chern numbers $C = \pm 1$. For the $\{111\}$ ordered state, with Fe moments perpendicular to the bilayer, we find that the Mo $t_{2g}$ electrons display bands with Chern numbers $C = \pm 2$; we present an effective two-band triangular lattice model of Zeeman-split $j = 3/2$ states which correctly captures the emergence of this nontrivial band topology. These bands have a direct gap, but typically overlap in energy leading to a metallic state. In the presence of a symmetry-allowed trigonal distortion, we find a regime of a $C = \pm 2$ Chern insulator, $\mathcal{C}L$, i.e., a quantum anomalous Hall insulator with a pair of chiral edge modes, having a gap $\sim 75$K.

4.2 Model

Strong Hund’s coupling on Fe$^{3+}$ locks the 3d$^5$ electrons into a large $S_F = 5/2$ local moment, which we treat as a classical spin similar to Mn spins in the colossal magnetoresistive manganites [132]. The 4d$^1$ electron on Mo$^{5+}$ hops on or off Fe, subject to a charge-transfer energy $\Delta$. Pauli exclusion on Fe forces the spin of the arriving electron to be antiparallel to the underlying Fe moment. This leads to kinetically stabilized ferromagnetic order of the Fe moments in bulk SFMO [143, 144, 38, 123, 2, 124]. However, previous work on SFMO has not considered the effect of quantum confinement or spin-orbit coupling on these electronic states. Here, we consider $\{111\}$ bilayers which confines electrons to a two-dimensional (2D) honeycomb lattice geometry as shown in Fig. 1. The $t_{2g}$ orbitals on Mo act as effective $L = 1$ angular momentum states, and experience local spin-orbit coupling $-\lambda \mathbf{L} \cdot \mathbf{S}$, with $\lambda > 0$, which should lead to a low energy $j = 3/2$ quartet and a high energy $j = 1/2$ doublet. Finally, the reduced symmetry of the honeycomb bilayer in a thin film grown along $\{111\}$ permits a trigonal distortion [112] $H_{\text{tri}} = \chi_{\text{tri}} (\mathbf{L} \cdot \mathbf{n})^2$, where $\mathbf{n}$ is a unit vector perpendicular to the bilayer; $\chi_{\text{tri}} > 0$ corresponds to compressing the Mo oxygen octahedral cage [133]. Incorporating these new ingredients, we arrive at the model
Hamiltonian

\[ H = \sum_{\langle ij \rangle, \ell, \sigma} \left[ t^{ij}_{\ell} g_{\sigma}(j) d^\dagger_{i \ell \sigma} f_{j \ell} + H.c. \right] + \Delta \sum_{\ell} f^\dagger_{\ell \tilde{\ell}} f_{\ell \tilde{\ell}} + H_{\text{tri}} \]

\[ + \sum_{\langle \langle ij \rangle \rangle, \ell, \sigma} \eta^{ij}_{\ell \tilde{\ell}} d^\dagger_{i \ell \sigma} d_{j \ell \sigma} + \frac{i}{2} \lambda \sum_{i} \varepsilon_{\ell m n} \tau^m_{\sigma \sigma'} d^\dagger_{i \ell m \sigma} d_{i \ell m \sigma'} \]  

Here \( d(f) \) denotes electrons on Mo (Fe), \( i \) labels sites, \( \sigma \) is the spin label, \( \ell = 1, 2, 3 \) (\( \equiv yz, zx, xy \)) is the orbital index, and \( \varepsilon \) is the totally antisymmetric tensor. With \( \tilde{F} = (\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \theta) \) denoting the Fe moment direction, Pauli exclusion leads to a single spin projection [2] (antiparallel to \( \tilde{F} \)) for electrons on Fe, with \( g_{\sigma}(j) = \sin \frac{\theta}{2} e^{-i\phi_\sigma/2} \) and \( g_{\sigma}(j) = -\cos \frac{\theta}{2} e^{i\phi_\sigma/2} \). Matrix elements \( t^{ij}_{\ell} \) correspond to intra-orbital Mo-Fe hoppings \( t_\pi, t_\delta \), while \( \eta^{ij}_{\ell \tilde{\ell}} \) encodes Mo-Mo intra-orbital hopping amplitudes \( t', t'' \) and an inter-orbital hopping amplitude \( t_m \) (see Supplementary Material for details of hopping processes). Such a model Hamiltonian, with strong spin-orbit coupling and \( H_{\text{tri}} = 0 \), has been previously shown [126] to successfully capture the phenomenology of the ferrimagnetic state of bulk Ba₂FeReO₆, quantitatively explaining its \textit{ab initio} band dispersion [36], saturation magnetization [45, 134], the spin and orbital polarizations measured using X-ray magnetic circular dichroism (XMCD) [35], and spin dynamics observed using neutron scattering [125]. Our model captures the key energy scales in SFMO: (i) the implicit strong Hund’s coupling on Fe (\( \sim 2 \text{eV} \)), (ii) the Fe-Mo charge transfer energy (\( \Delta \sim 0.5 \text{eV} \)), (iii) the nearest neighbor intra-orbital Mo-Fe hopping which leads to electron itinerancy (\( t^{ij}_{\ell} \sim 0.25 \text{eV} \)), and (iv) the spin-orbit coupling on Mo (\( \lambda \sim 0.12 \text{eV} \)). Second neighbor intra-orbital and inter-orbital hoppings \( (\eta^{ij}_{\ell \tilde{\ell}} \sim 0.025 \text{eV}) \) are much weaker. However, we retain them since they play a role in pinning the Fe moment direction in the ferrimagnetic state, leading to well-defined Chern bands and a nonzero ferromagnetic \( T_c \) in 2D.

### 4.3 Magnetism in the bilayer

The ground state of bulk SFMO is a ferrimagnet. In order to explore the magnetic structure of the \{111\} SFMO bilayer, we have computed the electronic energies of a wide range of magnetic configurations of Fe moments for \( \chi_{\text{tri}} = 0 \), including (i) ferrimagnetic configurations with different spin orientations, (ii) period-2 stripe-like configurations with different spin and stripe orientations, and (iii) random configurations.

Fig. 4.2(a) compares these energies per Fe site, plotted in units of \( t_\pi = 250 \text{meV} \) which is the nearest neighbor.
Mo-Fe hopping amplitude, showing that the ferromagnetic states have the lowest energy, consistent with the kinetic energy lowering due to maximal electronic delocalization. The energy difference between the ferromagnetic and disordered or stripe configurations allows us to infer an exchange energy between neighboring Fe moments on the triangular lattice, \( J_{\text{FF}} \approx 1.5 \text{meV} \). This value is close to the bulk 3D value, \( \approx 3 \text{meV} \), estimated from theoretical calculations [2]; our slightly smaller value might stem from the different lattice geometry and the inclusion of spin-orbit coupling.

Unlike previous work, which had Heisenberg symmetry for the magnetism, the inclusion of spin-orbit coupling also leads to energy differences between different ferromagnetic orientations of the Fe moments; see Fig. 4.2(b). With no trigonal distortion, \( \chi_{\text{tri}} = 0 \), the six \{110\} orientations with Fe moments lying in the bilayer plane have the lowest energy. As seen from Fig. 4.2(c), other high symmetry orientations are higher in energy by \( \delta E \sim 1 \text{meV} \).

We have also explored the effect of trigonal distortion on the energy of different ferromagnetic orientations. For \( \chi_{\text{tri}} < 0 \), we expect \( \vec{L} \parallel \hat{n} \) in order to minimize the energy. This favors the \{111\} orientation of \( \vec{L} \), and spin-orbit coupling then forces the spins to also point out of the bilayer plane. For \( \chi_{\text{tri}} > 0 \), it is energetically favorable to have \( \vec{L} \perp \hat{n} \), so the \{110\} orientations remain favorable. We have numerically confirmed these expectations. The combination of spin-orbit coupling and trigonal distortion can thus favor a variety of “Ising” or “clock” ferromagnetic ground states; we therefore expect a nonzero magnetic \( T_c \) even in the bilayer. For \{111\} ordering, we expect an Ising transition temperature \( T_c = \alpha S_F \sqrt{J_{\text{FF}}} \delta E \), where \( \delta E \) is the anisotropy energy (i.e., the characteristic cost for rotating spins away from the Ising axis), and we estimate the numerical prefactor \( \alpha \sim 4 \) (see Supplementary Material for details). Using a typical anisotropy energy \( \delta E \sim 0.2 \text{meV} \), and setting \( S_F = 5/2 \) and \( J_{\text{FF}} = 1.5 \text{meV} \), this yields \( T_c \sim 65 \text{K} \), although \( T_c \) might be much higher than this crude estimate suggests. When the ground state favors one of the six \{110\} orientations, we expect a slightly reduced transition temperature, as well as an intermediate phase with power law magnetic order. These \( T_c \) values are substantially lower than \( T_c^{\text{bulk}} \sim 400 \text{K} \) but still easily accessible in experiments. A full Monte Carlo study of the thermal fluctuation effects and finite temperature transitions will be discussed elsewhere. We next turn to the ground state electronic properties of this SFMO bilayer, focusing on the Berry curvature of electronic bands induced by the spontaneous ferromagnetism of Fe moments.
Figure 4.4: Spectrum of the Chern insulator, CI, in a cylinder geometry, in units of $t_\pi = 250\text{meV}$, against momentum $k$ along the periodic direction. Here, $t_m = -0.11t_\pi$ and $\chi_{\text{tri}} = -0.15$. We find a pair of chiral edge modes at the top and bottom edges, consistent with $C = 2$. In addition, we find a nonchiral edge mode which is, however, not topologically protected. The estimated bulk gap is $0.03t_\pi \sim 75\text{K}$.

4.4 Chern bands and phase diagram

In order to explore the dependence of band topology on the Hamiltonian parameters, for a filling of 1-electron per Mo, we have computed the magnetization direction and Chern number $C$ of the relevant low-lying bands as a function of the trigonal distortion parameter, $\chi_{\text{tri}}$ and the second neighbor interorbital hopping $t_m$. Even this limited exploration of the full parameter space yields a rich phase diagram, shown in Fig. 4.3, with several magnetic phases and emergent band topologies, illustrating that the \{111\} grown DPs may be particularly useful systems to study topological phases of correlated oxide materials. We find that the electronic states show the following phases depending on the magnetization direction: (i) normal metal (NM) where the lowest pair of bands overlap in energy and they are both topologically trivial; (ii) a normal insulator (NI) phase where a full gap opens up between these topologically trivial bands; (iii) A Chern metal (CM) where the lowest pair of bands have (opposite) nontrivial Chern numbers as indicated, yet overlap in energy leading to a metallic state with a non-quantized anomalous Hall response; (iv) a $C = \pm 2$ Chern insulator (CI) where a full gap opens up between the two lowest topologically nontrivial bands leading to a quantized anomalous Hall conductance $\sigma_{xy} = 2e^2/\hbar$ and a pair of chiral edge modes. Fig. 4.4 shows the spectrum of the CI state in a cylinder geometry, depicting a pair of chiral modes at each edge, which cross from the valence to the conduction band. We estimate the bulk gap of the CI state to be $0.03t_\pi \sim 75\text{K}$.

4.5 Effective model for $C = 2$ Chern bands

Chern bands with $C = 2$ are unusual [135, 136, 137, 138] and differ from conventional Landau levels or Hofstadter bands with $C = 1$. How can we understand the emergence of this nontrivial band topology? Since the $C = \pm 2$ bands arise for magnetization perpendicular to the bilayer, we begin by studying the phase diagram with Fe moments constrained to point along \{111\}. As shown in Fig. 4.5(a), this leads to a wide swath of the phase diagram where the lowest two bands possess $C = \pm 2$. We find that this lowest pair of bands remains separated from the higher bands. The CI state then appears from opening up a full band gap between these lowest two nontrivial bands.

We next focus on constructing an effective model for the emergence of $C = \pm 2$ bands for $\chi_{\text{tri}} = 0$, as we
increase $t_m$ beyond a critical value (see trajectory shown in Fig. 4.5(a)). At the atomic level, the ferromagnetically aligned Fe moments produce an exchange field on the states of neighboring Mo atoms, leading to Zeeman splitting of the spin-orbit coupled $j = 3/2$ states on Mo. The two relevant lowest bands arise from the lowest Zeeman split $j_n = +3/2, +1/2$ levels where $j_n = \mathbf{\hat{n}} \cdot \mathbf{\hat{n}}$ and $\mathbf{\hat{n}}$ is a unit vector along \{111\}. With the spin-quantization axis along $\mathbf{\hat{n}}$, these atomic wavefunctions are $|j_n = 3/2\rangle = \frac{1}{\sqrt{3}}(|yz\rangle + \omega|xz\rangle + \omega^2|xy\rangle)|\uparrow\rangle$ and $|j_n = 1/2\rangle = -\frac{\sqrt{2}}{3}(|yz\rangle + |zx\rangle + |xy\rangle)|\uparrow\rangle + \frac{1}{3}(|yz\rangle + \omega|xz\rangle + \omega^2|xy\rangle)|\downarrow\rangle$ where $\omega = e^{i2\pi/3}$. We project the Mo-Mo intra-orbital hoppings and the inter-orbital hopping ($t_m$) onto these two Zeeman split states (see Supplementary Material for details). For sufficiently large $t_m$, the resulting two-band Hamiltonian displays a skyrmion with winding number 2 in the hexagonal Brillouin zone as shown in Fig. 4.5(b), thus accounting for $C = 2$ Chern bands. For small $t_m$, we find it leads to topologically trivial bands. This simple effective model thus captures our numerical results and explains the formation of $C = \pm 2$ bands.

Interestingly, we find a direct transition between the normal insulator and the CI with $C = \pm 2$ in our phase diagrams in Fig. 4.3(a) and Fig. 4.5(a). If such a transition occurred via a gap closing and reopening at the Brillouin zone corners, the critical theory would have massless Dirac fermions, with interactions being perturbatively irrelevant at the transition. Such transitions have also been discussed recently for integer quantum Hall plateau transitions of bosons [139]. However, we find the gap closing at the NI-CI transition occurs at the zone center, leading to a quadratic band touching (with $2\pi$ Berry phase) at the critical point. Such a quadratic band touching point is protected by $C_6$ symmetry in the noninteracting theory [140]; interactions, which are marginally relevant, may lead to intermediate spontaneous nematic phases [140, 141, 142].

**4.6 Discussion**

We have shown that simple double perovskite materials can exhibit a rich phase diagram with various ferromagnetic orders and band topologies in a bilayer grown along \{111\}. Such Chern bands emerging from half-metallic states have also been discussed recently at CrO$_2$-TiO$_2$ interfaces [111]. Going beyond our simple model, the inclusion of electron-electron interaction effects on the Mo atom might expand the CI regime. Such correlation effects may be studied in the full model as well as the reduced two-band model of Chern bands which may be amenable to exact diagonalization studies. Such studies might also shed further light on the CI-NI transition.
and intermediate phases driven by a quadratic band touching instability. The broken inversion symmetry in the bilayer is expected to lead to a Rashba interaction; while the unusual topological phases we have uncovered are stable to a small Rashba coupling, a sufficiently strong Rashba interaction might drive spin spirals of Fe moments \cite{104, 116} and suppress the topological Chern bands. Further work is necessary to understand the competition between the Rashba and correlation effects. In future work, we also plan to study similar physics in bilayers of 5d-based double perovskites such as Ba$_2$FeReO$_6$ which have a $d^2$ configuration and stronger spin-orbit coupling, which could stabilize more robust quantum anomalous Hall phases.
δ the presence of a typical anisotropy energy cost $\delta E \sim T$ yields the temperature $\xi$ moments away from the Ising axis over a correlated domain of area

\[ \text{state along } \{ \text{misalignment of spins away from the Ising axis is not thermally possible. Using } J \text{ is broken to a discrete symmetry, allowing for a nonzero} \]

\[ \text{Heisenberg symmetry, leading to} \]

\[ \text{can have moments pointing in any direction in spin-space. The resulting effective model for Fe moments will have} \]

\[ \text{formation of a ferromagnetic state on the triangular lattice} \]

\[ \text{coupling } \lambda \text{ hopping term} \]

\[ \text{dimensional space of parameters, we vary just the strength of the trigonal distortion} \]

\[ \chi \text{ modified due to the trigonal distortion in the bilayer geometry. To simplify the exploration of the full multi-} \]

\[ \text{hopping parameters provide a good description of the bulk properties; however, they might get slightly} \]

\[ \text{modified due to the trigonal distortion in the bilayer geometry. To simplify the exploration of the full multi-} \]

\[ \text{similar to values in the literature [143, 144, 2]. We expect a similarly small interorbital hopping} \]

\[ \text{strength.} \]

\[ \text{The Chern bands are robust to slight variations in these hopping parameters and tuning of the spin orbit coupling} \]

\[ \text{strength.} \]

\[ \text{Appendix A: Parameters in the tight binding model.} \]

\[ \text{We consider symmetry allowed nearest neighbor Mo-Fe intra-orbital hoppings. For next neighbor Mo-Mo hopp-} \]

\[ \text{ings, intra-orbital as well as inter-orbital terms are allowed by symmetry, and we retain both processes. The} \]

\[ \text{intra-orbital hopping terms are shown in Fig. 4.6(a)-(c) for } d_{xy}, d_{yz}, d_{xz} \text{ orbitals. The two nearest neighbor intra-} \]

\[ \text{orbital hoppings are denoted by } t_\pi \text{ and } t_\delta. \text{ The next-neighbor intra-orbital hoppings are denoted by } t', \text{ and } t''. \text{ Finally, Fig. 4.6(d) depicts the inter-orbital hopping, with coupling } t_m, \text{ between different indicated orbitals on nearest pairs of Mo sites. In our computations, with } t_\pi = 1, \text{ we set } \delta = -0.11, t' = -0.09, t'' = 0.1, \text{ which are} \]

\[ \text{similar to values in the literature [143, 144, 2]. We expect a similarly small interorbital hopping } t_m \sim -0.1t_\pi. \text{ These hopping parameters provide a good description of the bulk properties; however, they might get slightly} \]

\[ \text{modified due to the trigonal distortion in the bilayer geometry. To simplify the exploration of the full multi-} \]

\[ \text{dimensional space of parameters, we vary just the strength of the trigonal distortion } \chi_{\text{tri}} \text{ and the inter-orbital} \]

\[ \text{hopping term } t_m, \text{ keeping } t_\delta, t', \text{ and } t'' \text{ fixed. We fix the charge transfer energy } \Delta = 2.5t_\pi \text{ [2], and the spin orbit} \]

\[ \text{coupling } \lambda = 0.5t_\pi. \text{ We fix } t_\pi = 250\text{meV, close to values used in earlier studies [143, 2]. We have checked that} \]

\[ \text{the Chern bands are robust to slight variations in these hopping parameters and tuning of the spin orbit coupling} \]

\[ \text{strength.} \]

\[ \text{Appendix B: Estimate of ferromagnetic } T_c. \]

\[ \text{In the absence of spin-orbit coupling, the Fe moments which form a ferromagnetic state on the triangular lattice} \]

\[ \text{can have moments pointing in any direction in spin-space. The resulting effective model for Fe moments will have} \]

\[ \text{Heisenberg symmetry, leading to } T_c = 0 \text{ for the 2D bilayer. With spin-orbit coupling, this Heisenberg symmetry} \]

\[ \text{is broken to a discrete symmetry, allowing for a nonzero } T_c. \text{ Below, we estimate } T_c \text{ in the case of the Ising ordered} \]

\[ \text{state along } \{111\} \text{ which supports interesting } C = \pm 2 \text{ Chern bands.} \]

\[ \text{We start from the isotropic 2D Heisenberg model, where the correlation length diverges as } \xi(T) \sim e^{2\pi\rho_s/T} \]

\[ [145], \text{ with the spin stiffness } \rho_s \sim 2J_{\text{FF}}S_F^2. \text{ For weak Ising anisotropy } \delta E, \text{ the energy cost of misaligning} \]

\[ \text{moments away from the Ising axis over a correlated domain of area } \xi^2(T) \text{ is } \delta E \times \xi^2(T). \text{ Equating this with } T \]

\[ \text{yields the temperature } T_c \text{ below which we must view the Heisenberg model as an effective Ising model, where misaligment of spins away from the Ising axis is not thermally possible. Using } J_{\text{FF}} = 1.5\text{meV, } S_F = 5/2, \text{ and} \]

\[ \delta E \sim 0.2\text{meV, this yields an estimate } T_c \sim 200\text{K, which is only logarithmically sensitive to } \delta E. \]

\[ \text{Next, staying at } T \ll T_c, \text{ we consider the effective domain wall energy cost of a } \{111\} \text{-}\{111\} \text{ boundary in} \]

\[ \text{the presence of a typical anisotropy energy cost } \delta E \text{ to turn the Fe spin away from the Ising axis. For small } \delta E, \text{ we} \]

\[ \text{Figure 4.6: Intra-orbital hopping amplitudes } t_\pi, t_\delta, t', t'' \text{ for different orbitals: (a) } xy-\text{orbital, (b) } yz-\text{orbital, (c) } xz-\text{orbital. (d) Inter-orbital hopping amplitude between pairs of indicated orbitals on Mo sites.} \]
can optimize the domain wall size $\ell_{dw}$ by minimizing, with respect to $\ell_{dw}$, the energy per unit length of a straight domain wall on the triangular lattice,

$$E = \frac{1}{2} 2 J_{FP} S_F^2 (\frac{\pi}{\ell_{dw}})^2 \ell_{dw} + \frac{1}{2} (\delta E) \ell_{dw},$$

where the first term is the gradient cost and the second term is the average ‘misalignment’ energy. This leads to $\ell_{dw} = \pi S_F \sqrt{2 J_{FP}/\delta E}$, and to the optimal energy of the domain wall per unit length $E_{opt} = \pi S_F \sqrt{2 J_{FP} \delta E}$.

We can view $E_{opt}/4$ as being the exchange coupling $J_{eff}$ of an effective 2D triangular lattice Ising model. The exact transition temperature of the Ising model on the 2D triangular lattice is $T_c = 4 J_{eff}/\ln 3 \sim 0.9 E_{opt}$. This yields a rough estimate $T_c = \alpha S_F \sqrt{J_{FP} \delta E}$, with $\alpha \approx 4$. Using $J_{FP} = 1.5\text{meV}$, $S_F = 5/2$, and $\delta E \sim 0.2\text{meV}$, yields $T_c \sim 65\text{K}$. The argument leading to this estimate appears to be internally consistent, with Ising-like moments forming at $T_c$ and ordering at $T_c < T_s$.

In fact, our crude estimate might be significantly underestimating $T_c$, and the ordering is likely to occur at somewhat higher temperatures. Numerical studies of anisotropic Heisenberg models [146] find a much higher transition temperature, about 60% of the Ising model transition temperature, even for extremely weak anisotropies ($\sim 10^{-3}$). In our case, using this numerical result would suggest $T_c \sim 220\text{K}$. Thus magnetic ordering might occur quite close to the Heisenberg-Ising crossover temperature $T_s$ estimated above.

### 4.9 Appendix C: Effective two-orbital model of $C = \pm 2$ Chern bands.

The spin-orbit coupled atomic wavefunctions corresponding to $j = 3/2$ states with projection $j_n = 3/2, 1/2$ are respectively given by

$$|j_n = 3/2\rangle = \frac{1}{\sqrt{3}}(|yz\rangle + \omega |zx\rangle + \omega^2 |xy\rangle) \uparrow,$$

and

$$|j_n = 1/2\rangle = -\frac{\sqrt{2}}{3}(|yz\rangle + |zx\rangle + |xy\rangle) \uparrow + \frac{1}{3}(|yz\rangle + \omega |zx\rangle + \omega^2 |xy\rangle) \downarrow,$$

where $\omega = e^{2\pi i/3}$. Here $j_n \equiv \vec{j} \cdot \hat{n}$ with $\hat{n}$ along \{111\}, and the Fe moments are assumed to point along \{111\}. Due to the Fe ordering, there is an effective Zeeman field experienced by the Mo sites which leads to a Zeeman splitting $B_z$ between the $j_n = 3/2$ and $j_n = 1/2$ states. Since SFMO is half-metallic, we make the simplifying assumption that the relevant bands near the Fermi level are well described by considering only hopping of the $\uparrow$ spins, and focusing on only the Mo sites due to the charge transfer energy $\Delta = 2.5 t_{\sigma}$ which suppresses occupation on Fe sites. The Mo-Mo hopping has two dominant contributions: (i) the inter-orbital term $t_m$ in the original Hamiltonian; (ii) an effective $t'_{eff}$ hopping, which includes the direct $t'$ hopping between Mo-Mo as well as (possibly more significant) indirect Mo-Fe-Mo hoppings which can occur at $O(t_{\sigma}^2/\Delta)$. These are schematically depicted in Fig. 4.7.

We can project both hopping processes onto the $j_n = 3/2, 1/2$ atomic states, which leads to a 2-orbital triangular lattice Hamiltonian. In momentum space, this takes the form

$$H(k) = \left(\begin{array}{cc}
-\frac{2}{3}(t'_{eff} - t_m)\gamma_k - B_z & \frac{2\sqrt{2}}{3} (t'_{eff} - \omega t_m) \beta_k^* \\
\frac{2\sqrt{2}}{3} (t'_{eff} - \omega^2 t_m) \beta_k & -\frac{4}{3}(t'_{eff} + 2 t_m) \gamma_k
\end{array}\right)$$

Let us define $\hat{a} = \hat{\alpha}, \hat{b} = -\hat{x}/2 + \gamma \sqrt{3}/2, \hat{c} = -\hat{x}/2 - \gamma \sqrt{3}/2$. In terms of these, the matrix elements are given by $\gamma_k = \sum \delta \cos k \cdot \hat{\delta}$ with $\delta \equiv \hat{a}, \hat{b}, \hat{c}$, and $\beta_k = \omega \cos k \cdot \hat{a} + \omega^2 \cos k \cdot \hat{b} + \cos k \cdot \hat{c}$. We expect $B_z \sim t'_{eff}$.
Fixing $B_z, t'_{\text{eff}}$ and varying $t_m$ leads to a transition between (i) a topologically trivial state where both bands have Chern number zero and (ii) a topologically nontrivial state where bands have Chern numbers $C = \pm 2$. This topologically nontrivial state is characterized in momentum space by the development of a winding number 2 skyrmion texture as shown in Fig. 5(b) of the paper, where the arrows represent the ‘effective magnetic field’ direction in the $2 \times 2$ space of Eq. 4.5.
Chapter 5

Strong directional exchange on the fcc lattice in La$_2B$IrO$_6$ ($B = \text{Mg, Zn}$)

5.1 Introduction

Magnetic materials with strongly-anisotropic exchange interactions often display exotic magnetic properties and allow fundamental theories of quantum magnetism to be tested in the laboratory [147, 148, 149]. Many interesting studies on these topics have concentrated on systems based on rare earths or 3$d$ transition metals with unquenched orbital angular momentum. For example, the classical spin ice pyrochlores Dy$_2$Ti$_2$O$_7$ and Ho$_2$Ti$_2$O$_7$ with net ferromagnetic nearest neighbor exchange and dipole interactions are well-described by an Ising Hamiltonian with the moments constrained to lie along the local $\langle 111 \rangle$ directions [150]. Recent studies have shown that such classical spin-ice materials, with ‘two-in, two-out’ magnetic ground states, support emergent monopole excitations [151], and there is ongoing work aimed at understanding ‘quantum spin-ice’ physics in materials such as Yb$_2$Ti$_2$O$_7$ [152].

Recently, a novel family of magnetic materials based on strong spin-orbit coupling (SOC) and the $d^5$ electron configuration, so-called $j_{\text{eff}} = 1/2$ Mott insulators, have been attracting great interest [153], as the relativistic entanglement of the orbital and spin degrees of freedom leads to unusual single ion wavefunctions [? ?]. Two different types of interactions for these wavefunctions have been considered in the ideal limit of a local cubic environment: superexchange mediated by a single anion via (a) a 90° bond (e.g. edge-sharing octahedra) and (b) a 180° bond (e.g. corner-sharing octahedra).

Superexchange through a 180° bond leads to a Hamiltonian with Heisenberg and anisotropic pseudodipolar terms [? ]. Resonant inelastic x-ray scattering (RIXS), performed to probe magnons in the single layer iridate Sr$_2IrO_4$, shows that its magnetic excitations are consistent with a dominant Heisenberg interaction [154], with a small gap induced by spin-orbit induced anisotropic couplings. However, RIXS on the bilayer iridate Sr$_3$Ir$_2$O$_7$ provides evidence for a large spin gap ascribed to a significant interplane pseudodipolar term for spins within the bilayer, leading to the spin gap and bandwidth of the magnons having comparable values of 92 and 70 meV respectively [155]. Such a pseudodipolar (Ising-like) term is symmetry-allowed in a tetragonal crystal. Its magnitude is thought to be large due to the proximity to a metal-insulator transition and a sizable tetragonal distortion of the IrO$_6$ octahedra, which together increase both the impact of the Hund’s coupling on intermediate states in the superexchange process as well as the mixing of $j_{\text{eff}} = 1/2$ and $j_{\text{eff}} = 3/2$ states [155].

Superexchange through a 90° bond is even more intriguing. In this geometry, there are two different ex-
change paths connecting magnetic ions that can interfere in a destructive manner, leading to a Hamiltonian where anisotropic exchange terms dominate [9]. For the special case of the two-dimensional (2D) honeycomb lattice, the resulting Hamiltonian is called the ‘Kitaev model’ [156] and it is exactly solvable, with a quantum spin liquid ground state and emergent Majorana fermion excitations.

A true example of a Kitaev spin liquid has, however, remained elusive, as experimental realizations of the 2D honeycomb lattice such as \( \alpha \)-Li\(_2\)IrO\(_3\) [157] Na\(_2\)IrO\(_3\) [158], and \( \alpha \)-RuCl\(_3\) [159] are characterized by magnetically ordered ground states [160, 161] due to non-negligible Heisenberg, off-diagonal, or further neighbor exchange couplings [162, 163, 164, 165]. On the other hand, recent Raman scattering [166, 167] and inelastic neutron scattering (INS) [168, 169] measurements have found evidence for strong Kitaev interactions in \( \alpha \)-RuCl\(_3\), suggesting the ordered ground state may be proximate to a quantum phase transition into the Kitaev spin liquid ground state. Finally, recent experiments on the 3D honeycomb polymorphs \( \beta/\gamma \)-Li\(_2\)IrO\(_3\) [170, 171] have uncovered complex spiral orders [172, 173] ascribed to significant Kitaev exchange [174, 175].

While the quest to find an experimental example of a Kitaev spin liquid continues, a parallel effort is underway to characterize the magnetic properties of other \( j_{\text{eff}} = 1/2 \) Mott insulators. Systems of particular interest have superexchange mediated by anions through 90° bonds, as they are prime candidates to host Kitaev-type exchange interactions [176]. Exploring cases in which the magnetic ion coordination number is different from the three-fold coordination of the honeycomb motif in previously studied materials should yield further insights into the role of Kitaev interactions in quantum magnetism on other lattices.

Motivated by this background, in this work we study the \( j_{\text{eff}} = 1/2 \) Mott insulating double perovskites (DPs) \( \text{La}_2\text{B}\text{IrO}_6 \) \( (B = \text{Mg, Zn}) \) [177, 178, 179], with Ir\(^{4+}\) ions on the quasi-face-centered cubic (quasi-fcc) lattice. Experimental data reported in this chapter were obtained by A. A. Aczel and coworkers at ORNL. These results have been reported as a joint experimental/theory paper. In these materials, the local octahedral environment of the Ir\(^{4+}\) ions is very close to the cubic limit, and the larger Ir-Ir distance compared with \( ABO_3 \) perovskites leads to a strong Mott insulator, thus suggesting that the \( j_{\text{eff}} = 1/2 \) description is appropriate. Although the DP structure does not feature direct edge-sharing \( \text{IrO}_6 \) octahedra, interference between multiple Ir-O-Ir paths can still suppress oxygen-mediated Heisenberg superexchange [180]. This would lead to a Hamiltonian with a dominant, highly-anisotropic, Kitaev exchange. Indeed, the fcc lattice has been theoretically proposed as a potential venue for hosting Kitaev interactions [176].

The DP fcc structure has new features beyond previous, experimentally-studied, candidate Kitaev materials - twelve-fold coordinated Ir sites, strong geometric frustration, and a larger Ir-Ir distance weakening direct Heisenberg exchange. This motivates us to explore the nature of magnetism in these materials in detail. The significance of the Kitaev interactions in \( \text{La}_2\text{B}\text{IrO}_6 \) is not at all evident from the observed magnetic ordering. Indeed, as explained in detail below, both materials exhibit A-type (Type-I) antiferromagnetic (AFM) ordering, with transition temperatures \( T_N = 12 \) K for \( \text{La}_2\text{Mg}\text{IrO}_6 \) and 7.5 K for \( \text{La}_2\text{ZnIrO}_6 \) [178, 179, 181]. It is interesting to note that the corresponding frustration parameters \( f \), defined as the ratio of the Curie-Weiss temperature \( \theta_{\text{CW}} \) to the AFM ordering temperature \( T_N \), were found to be quite small (2 and 0.4 respectively) [178]. Such commonly observed magnetic order on the fcc lattice has been traditionally ascribed to first and second neighbor Heisenberg exchange interactions [267, 268]. However, as shown in recent work, just the simplest, symmetry-allowed, nearest neighbor AFM Kitaev coupling on the fcc lattice can stabilize A-type AFM with low \( f \) values [186], warranting a further exploration of the role played by spin-orbit induced exchange on quantum magnetism in double perovskites.

The smoking gun signature of any strong anisotropic couplings is most clearly encoded in the quantum spin fluctuations, and it reveals itself in the magnon spectrum. In this chapter, we present results from an INS study of the magnetic excitations in \( \text{La}_2\text{B}\text{IrO}_6 \). Typically, INS is the most powerful technique to probe magnetic
excitations in crystals. However, INS generally has severe limitations in most iridates due to an unfavorable magnetic form factor and the strong neutron absorption cross-section of the Ir nuclei, rendering RIXS as the tool of choice to study magnons [154, 155, 187]. Remarkably, as shown in Fig. 5.1, we find that La$_2$BIrO$_6$ exhibit a clearly observable INS signal, revealing gapped, highly non-dispersive magnons. It is likely that the non-dispersive nature of the magnons is what leads to a higher intensity over a small energy window, rendering them clearly visible in the INS measurements unlike for most other iridates. Our INS work is important since RIXS does not yet possess the meV resolution to study low energy magnons in a strong Mott insulator.

A comparison of our INS results with theoretical calculations shows that we can describe the data using either dominant Kitaev interactions, symmetry-allowed even on the ideal fcc lattice, or models with conventional Heisenberg interactions and uniaxial Ising anisotropy which are disallowed on the ideal fcc lattice, but may be induced by distortions away from the ideal cubic limit. However, a dominant uniaxial Ising exchange appears difficult to reconcile with the weak non-cubic distortions in La$_2$BIrO$_6$, while a moderate uniaxial Ising exchange does not simultaneously explain the measured frustration parameters in La$_2$BIrO$_6$. Our work thus favors the Kitaev exchange as a more natural explanation for the INS observations since it also simultaneously explains the frustration parameter in these materials. Our study suggests that even the conventional A-type AFM order in these geometrically-frustrated materials is ultimately driven by directional Kitaev exchange couplings resulting from strong spin-orbit coupling of heavy transition metal ions.

This chapter is organized as follows: We begin with a discussion of the crystal structure and magnetic ordering patterns for La$_2$BIrO$_6$ in Sections II and III. We then present the INS data on these materials in Section IV which show evidence for gapped spin waves, followed by a description of the most likely phenomenological spin wave models needed to describe these results in Section V. Section VI discusses a comparison of the various models to the neutron scattering data, while Section VII discusses the qualitative effects of octahedral rotations and $B/B'$ site disorder. Section VIII concludes with a summary of our work and implications for other materials.

### 5.2 Crystal structure

Ordered double perovskites with the general formula $A_2BB'O_6$ ideally crystallize in a cubic structure, with the $B$ and $B'$ ions occupying two interpenetrating fcc sublattices. La$_2$MgIrO$_6$ and La$_2$ZnIrO$_6$ crystallize in the lower symmetry, monoclinic space group $P2_1/n$, arising from small structural distortions to the cubic structure. The unit cell associated with the $P2_1/n$ space group is a superstructure of the primitive cubic unit cell, which can be approximately indexed in tetragonal notation due to the extremely weak monoclinic distortions. Assuming that $\hat{x}$, $\hat{y}$, and $\hat{z}$ are aligned with the three fcc crystallographic directions, the relationships between the tetragonal and fcc lattice constants are as follows: $a_t = a_{fcc}(\hat{x} \pm \hat{y})/2$ and $c_t = a_{fcc}\hat{z}$. For La$_2$BIrO$_6$, previous x-ray diffraction studies [178] have shown that $a_{fcc} \approx 7.9 \, \text{Å}$.

We now make an effort here to quantify the magnitudes of the monoclinic structural distortions for the IrO$_6$ octahedra of La$_2$BIrO$_6$. The distortions have two main effects: the rotation of the octahedra about both the cubic [110] and c-axes, and the deformation of the Ir$^{4+}$ local environment away from ideal cubic. The rotation angles of the IrO$_6$ octahedra can be determined according to Ref. [188] by using the refined atomic fractional coordinates and the Glazer notation discussed in Refs. [189, 190]. We find that the IrO$_6$ octahedra have global rotations of 13$^\circ$ and 14$^\circ$ for the Mg and Zn systems respectively about the cubic [110] axis, and rotations of 9$^\circ$ and 11$^\circ$ respectively about the c-axis that are staggered between adjacent ab-layers. The deformation of the IrO$_6$ octahedra can be quantified by considering the different Ir-O bond lengths and O-Ir-O bond angles. From the structural refinements reported in Ref. [178], we find that the six Ir-O bond lengths are within 1% of each other.
CHAPTER 5. STRONG DIRECTIONAL EXCHANGE ON THE FCC LATTICE IN La₂BIrO₆ (B = Mg, Zn) 41

Figure 5.1: (Color online) Color contour plots of the coarse energy resolution HYSPEC data for (a) La₂MgIrO₆ and (b) La₂ZnIrO₆ with $E_i = 15$ meV and $T = 1.5$ K. Inelastic modes with weak dispersion are clearly observed for both materials. The color contour plots with $E_i = 15$ meV and $T = 20$ K shown in panels (c) and (d) indicate that these modes disappear above the respective $T_N$’s of 12 K and 7.5 K for the Mg and Zn systems respectively, which suggests that they have a magnetic origin. Panels (e) and (f) depict similar color contour plots for La₂MgIrO₆ and La₂ZnIrO₆ at $T = 1.5$ K, but with better energy resolution arising from the choice of $E_i = 7.5$ meV. The same excitations are visible in these inelastic spectra. Note that the lowest-$Q$ regions in the color contour plots show no intensity; this issue results from a background oversubtraction of the direct beam, which is a consequence of the strong neutron absorption of Ir in the samples. Panels (g) and (h) show constant-$\hbar\omega$ cuts through the $T = 1.5$ K fine-resolution datasets with an integration range of [0.6, 1] meV. The lack of increased intensity near the magnetic zone center $Q = 0.79 \text{ Å}^{-1}$ for each system indicates that the magnetic excitations are fully-gapped.

for both materials, and all O-Ir-O bond angles are within 3.5° (1.5°) of 90° and 180° for the Mg (Zn) system. This implies a nearly-ideal local cubic environment for the Ir⁴⁺ ions, which is consistent with $j_{\text{eff}}=1/2$ single ion ground states for La₂BIrO₆.

5.3 Magnetic ordering

For La₂MgIrO₆, magnetization measurements show no evidence for a net ferromagnetic (FM) moment, while neutron powder diffraction work [178] finds a magnetic Bragg peak at $Q = 0.79 \text{ Å}^{-1}$ corresponding to A-type AFM order. These combined results are consistent with a magnetic propagation vector of $\vec{k} = (0.5 0.5 0)_t$, indicative of FM planes stacked along the [$11\bar{0}$]ₜ direction. Although the data do not determine the moment direction unambiguously, electronic structure calculations [178] predict that the moments lie predominantly in the FM planes (A-II type AFM in the notation of Ref. [186]).

For La₂ZnIrO₆, magnetization measurements find evidence for a net FM moment, while neutron diffraction again detects [178] a magnetic Bragg peak at $Q = 0.79 \text{ Å}^{-1}$. These findings are consistent with a canted A-type AFM characterized by a $\vec{k} = 0$ propagation vector, which defines the c-axis as the FM plane stacking direction. The magnetic Bragg peak is then uniquely indexed as (001)ₜ. The observation of this peak, combined with the absence of the (100)ₜ and (011)ₜ peaks, strongly implies that the ordered moments lie in the FM planes. Thus, the A-type AFM in this system also corresponds to A-II. The spin canting in La₂ZnIrO₆ arises from the small, staggered IrO₆ octahedral rotations ($\sim 11°$).
Figure 5.2: (Color online) (a), (b) Constant-$Q$ cuts through the HYSPEC data shown in Fig. 5.1(a) and (b), integrated over $Q = [0.6, 1] \text{Å}^{-1}$. These cuts clearly show that the inelastic modes are gapped in each case. Gaussian fits are superimposed on the data, which were used to determine the peak positions. For La$_2$MgIrO$_6$, the mode is centered at $\hbar \omega = 2.57(4)$ meV, and for La$_2$ZnIrO$_6$, it is centered at 2.09(3) meV. (c), (d) HB-3 constant-$Q$ scans with $Q = 0.79 \text{Å}^{-1}$ for La$_2$MgIrO$_6$ and La$_2$ZnIrO$_6$ at selected temperatures. The spin gaps close around $T_N$ for each compound, indicating that the modes have a spin wave origin. Note that 1 mcu (monitor count unit) ≈ 10000 and 11000 monitor counts for the Mg and Zn data respectively.

5.4 Inelastic neutron scattering results

We next discuss experimental results on the magnetic excitations associated with the ordered phases of these materials. Inelastic neutron scattering data were collected on previously synthesized [178] powder samples of La$_2$BIrO$_6$ at the HYSPEC spectrometer of the Spallation Neutron Source, Oak Ridge National Lab (ORNL). The powder samples were loaded in Al annular cans to minimize neutron absorption. All data were collected using incident energies of $E_i = 7.5$ and 15 meV, with corresponding Fermi chopper frequencies of 240 and 300 Hz, resulting in instrumental energy resolutions of 0.3 and 0.7 meV (Gaussian full-width half-maximum [FWHM]) respectively at the elastic line. A He cryostat was used to achieve a base temperature of 1.5 K. Empty Al annular can measurements were subtracted from all the HYSPEC data presented in this work, so the Al scattering contribution to the sample spectra would be minimized. INS data for these systems were also collected using a He cryostat on the thermal triple axis spectrometer HB-3 at the High Flux Isotope Reactor of ORNL. A collimation of 48°-60°-60°-120° and a fixed final energy of $E_f = 14.7$ meV were used to achieve an energy resolution of 1.2 meV at the elastic line (Gaussian FWHM).

Fig. 5.1(a) and (b) depict color contour plots of the coarser energy resolution $E_i = 15$ meV HYSPEC data at $T = 1.5$ K, where a nearly-dispersionless excitation band is visible for both materials. Note that the lowest-$Q$ regions in these plots show no intensity; this issue results from a background oversubtraction of the direct beam, which is a consequence of the strong neutron absorption of Ir in the samples. The observed excitations are clearly magnetic in origin, as they decrease in intensity with increasing $Q$. They are also no longer visible above $T_N$, with only quasi-elastic scattering remaining, as shown in panels (c) and (d). Color contour plots of the finer energy resolution $E_i = 7.5$ meV HYSPEC data are presented in Fig. 5.1(e) and (f). The same excitations are still present
in the data, which indicates that they are not spurious in nature. Fig. 5.1(g) and (h) show constant-$h\omega$ cuts through the fine-resolution data for the two materials, with an integration range of [0.6, 1] meV. We find no evidence for enhanced intensity near the $Q = 0.79$ Å$^{-1}$ magnetic Bragg peaks, which suggests that these excitations are fully gapped. Finally, as shown in Fig. 5.2(a) and (b), a low-$T$ constant-$Q$ cut through the fine-resolution data centered about the magnetic zone center $Q = 0.79$ Å$^{-1}$ reveals that the central position of the mode is 2.57(4) meV for La$_2$MgIrO$_6$ and 2.09(3) meV for La$_2$ZnIrO$_6$, with a FWHM in each case of $\sim$ 1 meV.

We have also carried out detailed temperature-dependent measurements on the thermal triple axis spectrometer HB-3. Fig. 5.2(c) and (d) present constant-$Q$ scans at a magnetic zone center ($Q = 0.79$ Å$^{-1}$) for La$_2$MgIrO$_6$ and La$_2$ZnIrO$_6$ respectively. The two panels provide strong evidence that the spin gaps close around $T_N$ in each case, with spectral weight shifting down to lower energies with increasing $T$. This observed temperature-dependence of the modes indicates that they correspond to spin waves. Furthermore, a crystal field interpretation can be ruled out by considering the typical single ion energy level scheme for $j_{\text{eff}} = 1/2$ Mott insulators. For this class of materials, the lowest-lying excited state to the $j_{\text{eff}} = 3/2$ band is separated from the $j_{\text{eff}} = 1/2$ ground state by $3\lambda_{SO}/2$, where $\lambda_{SO}$ is the spin-orbit coupling constant. The typical energy scale for this crystal field excitation is on the order of 100’s of meV due to large $\lambda_{SO}$ [191, 192, 169], which is certainly incompatible with the energy scale of the magnetic modes observed here. With the magnetic excitations for La$_2$BIrO$_6$ now unambiguously identified as spin waves, we turn to a theoretical modeling of these results.

## 5.5 Theoretical Models

A-type AFM order of fcc lattice magnets can be accounted for by mean field theory [268] using a nearest-neighbor AFM exchange and stabilizing second neighbor ferromagnetic exchange. We therefore begin by plotting $S(Q, \omega)$ in Fig. 5.3 for a $J_1$-$J_2$ Heisenberg model with nearest AFM exchange $J_1 > 0$, and next-neighbor FM exchange $J_2 < 0$, with $\Theta_{\text{CW}} = -3J_1 - 3J_2/2$. We fix $J_2 = -0.5J_1$ in our model. Although the sign of $J_2$ does not agree with predictions from ab initio calculations [184] or recent experiments [185] on double perovskites, we make this choice because it supports A-type AFM with a small $f \approx 2$ (the experimental value found for La$_2$MgIrO$_6$). Despite powder averaging, we see that the gapless Goldstone mode is clearly visible; such a Heisenberg model is clearly ruled out by our INS data. The observed spin gap and weakly-dispersive spectra, with the gap being comparable to or even larger than the magnon bandwidth, are instead suggestive of a nearly Ising-like exchange. Below, we examine the possible origins of this large exchange anisotropy which is responsible for the magnon gaps observed in La$_2$BIrO$_6$.

The strategy we follow to construct the spin model is very similar to that for other perovskite iridates: namely, we start by assuming an ideal fcc lattice and considering all possible symmetry-allowed exchange couplings, and next incorporate octahedral rotations by making suitable local spin rotations on the $j_{\text{eff}} = 1/2$ moments. In the ideal fcc limit, the uniaxial Ising exchange interaction, which is the simplest anisotropic exchange interaction typically used to model such gapped magnon spectra, is symmetry-forbidden. However, even in this ideal limit, the highly-directional Kitaev interaction and an off-diagonal symmetric (ODSE) are allowed by symmetry [186]. In previous work, we have shown that an AFM Kitaev exchange favors A-type AFM order with moments aligned along the Ir-O bond directions [186], consistent with neutron diffraction results [178] for La$_2$BIrO$_6$. On the other hand, ODSE favors spins pointing along the (111) axes. In addition, we have previously suggested, based on thermodynamic considerations such as the frustration parameter, that this highly directional Kitaev exchange interaction might be relevant to understanding magnetism in La$_2$BIrO$_6$. Here, we explore the impact of such Kitaev exchange interactions on the spin dynamics, uncovering a quantum order-by-disorder effect with a spin
Next, we turn to the possible effects of lattice distortions away from the ideal fcc limit. The weak mono-
clinic distortions leading to the $P2_1/n$ structure of $La_2BiO_6$ allow for a large variety of new exchange terms on
symmetry grounds. A set of such exchange couplings induced by non-cubic distortions have been discussed in
previous work in the context of double perovskites [193, 194]. However, given the large number of new terms
and the limited data, it is not clear that we can extract anything useful from this most general analysis. We thus
focus on the simplest case of a tetragonal crystal distortion [194] which allows for only a subset of all the terms;
in particular, we focus on two new anisotropies which are symmetry-allowed under such a distortion. First, the
tetragonal distortion allows for the Kitaev interaction to be different in one crystal plane compared with the other
two orthogonal planes. Second, the tetragonal distortion picks a unique axis, thus permitting a uniaxial Ising
interaction. We show that such phenomenological models provide a reasonably good description of the INS data.
Note that in the limit of extreme anisotropy, the former leads to a 2D square lattice classical Ising model with
neighboring planes being weakly coupled by quantum effects, while the latter leads to a 3D nearly-classical Ising
AFM on the fcc lattice.

5.5.1 Kitaev Model on the ideal fcc lattice

We have previously studied the classical phase diagram for ideal $j_{\text{eff}} = 1/2$ fcc magnets [186], keeping all
symmetry-allowed nearest neighbor (NN) interactions including Heisenberg, Kitaev, and off-diagonal symmetric
exchange [195]. A key finding, relevant to $La_2BiO_6$, was that while the simple NN AFM Heisenberg model
exhibits A-type AFM order, the exact same order is also favored by just the AFM Kitaev exchange. One might
distinguish between these two microscopic mechanisms for the observed order using the frustration parameter,
f. For the NN Heisenberg model on the fcc lattice, we estimated $f \approx 9$ for spin-$1/2$ moments [186]. However,
these iridates exhibit robust AFM order, with experimental values for $f \leq 2$, suggesting that SOC-induced Kitaev
interactions are large, suppressing frustration and enhancing $T_N$. This led us to propose a minimal Kitaev model
on the ideal fcc lattice,

$$H_K = J_K \sum_{\langle rr' \rangle_{yz}} S_x^r S_x^{r'} + J_K \sum_{\langle rr' \rangle_{xz}} S_y^r S_y^{r'} + J_K \sum_{\langle rr' \rangle_{xy}} S_z^r S_z^{r'}$$

(5.1)
as a better starting point to describe the magnetism in $La_2BiO_6$. Here, $\langle rr' \rangle_{yz}$ denotes nearest neighbors in the
$yz$-plane (similarly for $xz, xy$). This model has $\Theta_{\text{CW}} = -J_K$, so $J_K > 0$ is consistent with the reported $\Theta_{\text{CW}} < 0$
for $La_2BiO_6$ [178]. A classical Monte Carlo study [186] of $H_K$ showed that $f \approx 2$, in good agreement with
the data on $La_2MgIrO_6$. Here, we focus on the effects of quantum spin fluctuations and the resulting dynamic
structure factor of such Kitaev models.

1. Quantum order-by-disorder

The AFM Kitaev model with $J_K > 0$ on the fcc lattice leads to A-type AFM, with spins in the FM plane (A-II
AFM), consistent with the discussed magnetic order of $La_2BiO_6$. However, the classical Kitaev model does not
select any special direction in the plane, leading to an accidental XY degeneracy. We study the effect of quantum
fluctuations around the ordered A-II AFM state at $T = 0$, using Holstein-Primakoff (HP) bosons. Considering
FM $xy$-planes stacked antiferromagnetically along $\hat{z}$, and spins making an angle $\phi$ with the $\hat{x}$-axis (Ir-O bond
direction), we carry out a standard linear spin-wave analysis. Assuming that the spins in the AFM A-II state lie
in the cubic $xy$ plane, and make an angle $\phi$ with the $x$-axis, the classical ground state energy is independent of $\phi$. 

Figure 5.3: (Color online) Dynamical structure factor $S(Q,\omega)$ for the $J_1$-$J_2$ Heisenberg model on the fcc lattice with $J_2 = -0.5J_1$. Note that instrumental energy resolution, appropriate for HYSPEC with $E_i = 7.5$ meV, is incorporated here.

Figure 5.4: Plot of the $\phi$-dependent zero point energy contribution $E_{zp}$ (in units of $J_K$) for the Kitaev model, showing minima at discrete values of $\phi = n\pi/2$ ($n = 0, 1, 2, 3$) which leads to quantum order-by-disorder with spins pointing along the Ir-O bond directions.

We evaluate the contribution from zero point fluctuations using a standard Holstein-Primakoff expansion, setting:

$$S_x^r = (-1)^z(\frac{1}{2} - a_r^\dagger a_r) \cos \phi - \frac{1}{2}(a_r + a_r^\dagger) \sin \phi$$  \hspace{1cm} (5.2)

$$S_y^r = \frac{1}{2}(a_r + a_r^\dagger) \cos \phi + (-1)^z(\frac{1}{2} - a_r^\dagger a_r) \sin \phi$$  \hspace{1cm} (5.3)

$$S_z^r = (-1)^z \frac{1}{2i}(a_r - a_r^\dagger)$$  \hspace{1cm} (5.4)

This leads to a spin wave energy:

$$\omega_\phi(k) = 2J_K \left[ (1 + C_{xy}^k)(1 + C_{xz}^k \cos^2 \phi + C_{yz}^k \sin^2 \phi) \right]^{1/2}$$  \hspace{1cm} (5.5)

with $C_{ij}^k = \cos k_i \cos k_j$ ($i = x, y, z$). The zero-point energy of quantum fluctuations is $E_{zp}(\phi) = \frac{1}{2} \int \omega_\phi(k) \, dk$ per spin. We plot $E_{zp}(\phi)$ in Fig. 5.4, showing that it has discrete minima at $\phi = n\pi/2$ ($n = 0, 1, 2, 3$). Quantum fluctuations in the presence of SOC thus break the accidental degeneracy in $\phi$ of the classical Kitaev model,
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Figure 5.5: (Color online) Theoretical powder-averaged $S(Q, \omega)$ for the Kitaev models considered in the text for various degrees of spatial anisotropy $\lambda_K$. (a-e) Kitaev model within linear spin wave theory (i.e., no magnon interactions) for cases ranging from the ideal fcc limit ($\lambda_K = 0$, no spin gap) to large anisotropy ($\lambda_K = 4$). The corresponding frustration parameters $f_K$ are also shown, and range from $f_K \approx 2$ for the ideal fcc lattice to smaller values with increasing anisotropy. (f-j) Kitaev models with spatial anisotropy and magnon interactions. Here, magnon interactions induce an order-by-disorder spin gap even for $\lambda_K = 0$, while they lead to a slight enhancement of the spin gap for $\lambda_K > 0$. Note that instrumental energy resolution, appropriate for HYSPEC with neutron incident energy $E_i = 7.5$ meV, is incorporated in all panels.

2. Gapped Magnons

Since quantum fluctuations lift the classical XY degeneracy of the Kitaev model, we expect the concomitant development of a magnon gap. To see this in a transparent manner, we expand the above expression for the zero point energy, $E_{zp}(\phi) \approx E_{zp}(\phi = 0) + \frac{1}{2} \gamma \phi^2$, where:

$$\gamma = J_K \int_\mathbf{k} \sqrt{1 + \frac{C_{xy}^2}{1 + C_{xz}^2} (C_{yz}^2 - C_{xz}^2)}.$$ (5.6)

This leads to a pinning field $2\gamma \approx 0.2J_K$ in the ordered state, opening up a magnon gap. Such an order-by-disorder gap was discussed within different models for $LaTiO_3 [196]$ and the rare-earth pyrochlore $Er_2Ti_2O_7 [197]$. In $LaTiO_3$, the SOC is weak, leading to a tiny gap for highly-dispersive magnons. In $Er_2Ti_2O_7$, this leads to an extremely small order-by-disorder gap, which was recently resolved [198] in INS to be $\approx 0.053$ meV. This gap is about an order of magnitude smaller than the observed energy scale ($\sim 0.5$ meV) of zone boundary magnetic excitations in this material [197, 198].

The magnon gap appears naturally upon incorporating magnon interactions at higher order in the Holstein-Primakoff expansion (see Appendix), which leads to the self-consistent mean field Hamiltonian:

$$H_{mf} = \sum_{\mathbf{k} > 0} \left( a_{\mathbf{k}}^\dagger a_{-\mathbf{k}} \right) \begin{pmatrix} A_k & B_k \\ B_k & A_k \end{pmatrix} \begin{pmatrix} a_{\mathbf{k}} \\ a_{-\mathbf{k}}^\dagger \end{pmatrix}.$$ (5.7)
with \( A_k = (2+C_{xy}+C_{zz}) + \delta A_k \), \( B_k = (C_{zz}-C_{xy}) + \delta B_k \), and

\[
\begin{align*}
\delta A_k &= 2(\tilde{F}_{xy} - \tilde{F}_{xz}) + \tilde{F}(C_{xy}-C_{zz}) - 2\tilde{G}(C_{xy}+C_{zz}) \\
&- 2(G_{xy} + G_{xz}) - 4\tilde{G}y_{yz}C_{yz} \\
\delta B_k &= (\tilde{G}_{xy} - \tilde{G}_{xz}) + 2\tilde{G}(C_{xy}-C_{zz}) - \tilde{F}(C_{xy}+C_{zz}) \\
&- (\tilde{F}_{xy} + \tilde{F}_{xz}) - 4\tilde{F}y_{yz}C_{yz}.
\end{align*}
\] (5.8)

\[
\begin{align*}
\tilde{F} &= \int F_k \, F_k', \quad \tilde{F}_{ij} = \int C_k^j C_k'^i \Psi_k, \quad \text{and similarly for } \tilde{G}, \quad \text{with } F_k = \sinh 2\varphi_k, \quad G_k = (\cosh 2\varphi_k - 1)/2, \\
\text{the renormalized dispersion } \Omega_k = \sqrt{A_k^2 - B_k^2}, \quad \cosh 2\varphi_k = A_k/\Omega_k, \quad \text{and } \sinh 2\varphi_k = -B_k/\Omega_k. \quad \text{We determine } F_k, G_k \\
\text{self-consistently. The resulting powder averaged dynamic structure factor } S(Q, \omega) \text{ (see Appendix) is plotted in} \\
\text{Fig. 5.5(f), and shows clear evidence of gapped magnons.}
\]

### 5.5.2 Spatially-anisotropic Kitaev exchange

We have computed the magnon gap arising from spin-wave interactions in the ideal fcc lattice Kitaev model. However, since La\(_2\)Bi\(_2\)O\(_6\) exhibit weak monoclinic distortions, magnon gaps may also be generated from inequivalent Kitaev couplings in different planes \((yz, zx, xy)\). This leads to:

\[
H_K = J_k^x \sum_{(rr')_yz} S^x_r S^x_{r'} + J_k^y \sum_{(rr')_{xz}} S^y_r S^y_{r'} + J_k^z \sum_{(rr')_{xy}} S^z_r S^z_{r'}. \tag{5.10}
\]

The self-consistent mean field Hamiltonian becomes:

\[
H_{\text{mft}} = \sum_{k>0} \left( a_{-k}^\dagger a_{-k} \right) \left( \begin{array}{cc} A_k & B_k \\ B_k & A_k \end{array} \right) \left( \begin{array}{c} a_{+k}^\dagger \\ a_{-k} \end{array} \right), \tag{5.11}
\]

with \( A_k = (2J_k^x + J_k^z C_{xy} + J_k^y C_{xz}) + \delta A_k \), \( B_k = (J_k^y C_{zz} - J_k^z C_{xy}) + \delta B_k \), and

\[
\begin{align*}
\delta A_k &= 2(J_k^x \tilde{F}_{xy} - J_k^y \tilde{F}_{xz}) + \tilde{F}(J_k^z C_{xy} - J_k^y C_{zz}) \\
&- 2\tilde{G}(J_k^x C_{xy} + J_k^y C_{xz}) - 2(J_k^x \tilde{G}_{xy} + J_k^y \tilde{G}_{xz}) \\
&- 4J_k^x \tilde{G}y_{yz}C_{yz} \\
\delta B_k &= (J_k^x \tilde{G}_{xy} - J_k^y \tilde{G}_{xz}) + 2\tilde{G}(J_k^z C_{xy} - J_k^y C_{zz}) \\
&- \tilde{F}(J_k^x C_{xy} + J_k^y C_{xz}) - (J_k^x \tilde{F}_{xy} + J_k^y \tilde{F}_{xz}) \\
&- 4J_k^x \tilde{F}y_{yz}C_{yz}. \tag{5.13}
\end{align*}
\]

For the simplest case of tetragonal symmetry, we can set \( J_k^y = J_k^z \equiv J_k \) and \( J_k^x = (1 + \lambda_K)J_k \). Choosing \( \lambda_K > 0 \) then leads to moments ordered along \( S_x \). We plot the corresponding powder-averaged dynamic structure factors in Fig. 5.5 for various values of \( \lambda_K \). Here, panels (a)-(e) in Fig. 5.5 ignore magnon interactions, while panels (f)-(j) include magnon interactions. We see that for \( \lambda_K > 0 \), a spin gap is already present in linear spin wave theory ignoring magnon interactions, while magnon interactions lead to a slight enhancement of the spin gap. Thus, unlike the isotropic limit where magnon interactions are crucial for the ‘order-by-disorder’ spin gap, here the magnon interactions do not lead to any qualitatively new physics. Nevertheless, it is reassuring to observe that the dispersion for the weakly-anisotropic Kitaev case is not too different from the dispersion of the ideal fcc Kitaev model including magnon interactions, since both effects essentially lead to pinning of moments. We
Figure 5.6: (Color online) Theoretical powder-averaged $S(Q, \omega)$ for the Heisenberg-Ising models considered in the text within linear spin-wave theory with fixed AFM Heisenberg $J_1 = 1$, second neighbor AFM exchange $J_2 = 0, 0.5$, and varying degrees of uniaxial anisotropies $\lambda_{1,2}$ in the first and second neighbor exchanges, such that $J_1' = J_2' = J_{1,2}$ and $J_2'' = (1 + \lambda_{1,2})J_{1,2}$. (a-d) Models with only first neighbor exchange, with $J_2 = 0$. The corresponding frustration parameters $f_H$ are also shown, and range from $f_H \approx 9$ for the isotropic case with $\lambda_1 = 0$ to $f_H \approx 2$ for extreme anisotropy $\lambda_1 \gg 1$. (e-h) Models with $J_2 = 0.5$ and varying degrees of anisotropy. Note that instrumental energy resolution, appropriate for HYSPEC with $E_i = 7.5$ meV, is incorporated in all panels.

have also computed the frustration parameter $f_K$ for this series of models, determined from the powder-averaged $\theta_{CW} = -J_K(1 + \lambda_K/3)$ and $T_N$ obtained from classical Monte Carlo simulations with scaling by $S(S+1)$ to account for quantum effects. As indicated, $f_K$ is within the range of experimental values $\sim 0.4-2$.

5.5.3 Alternative models with uniaxial Ising exchange anisotropies

Finally, we turn to the case where we ignore all Kitaev interactions, but instead use a phenomenological, and more conventional, view that the spin gaps simply arise from uniaxial Ising interactions. We thus introduce such Ising couplings in addition to a Heisenberg coupling. Such uniaxial Ising couplings are symmetry-forbidden on the ideal fcc lattice, but permitted in the presence of distortions away from the ideal fcc limit. Limiting ourselves to short-range exchange, such a Heisenberg-Ising Hamiltonian, where different spin components interact with different strengths, is given by

$$H_{HI} = \sum_{\langle rr' \rangle} J_{1,2}^{\mu} S_\mu^r S_\mu^{r'} + \sum_{\langle\langle rr' \rangle\rangle} J_{2}^{\mu} S_\mu^r S_\mu^{r'} \quad (5.14)$$

where $\langle \cdot \rangle$ and $\langle\langle \cdot \rangle\rangle$ refer to nearest and next-nearest neighbor sites. Setting $J_{1,2}^y = J_{1,2}^z = J_{1,2}$ and $J_{1,2}^x = (1 + \lambda_{1,2})J_{1,2}$, we find within linear spin-wave theory,

$$H_{HI} = \sum_{k>0} \left( a_k^+ a_{-k} \right) \begin{pmatrix} A_k & B_k \\ B_k & A_k \end{pmatrix} \begin{pmatrix} a_k \\ a_{-k}^+ \end{pmatrix} \quad (5.15)$$

with $A_k = 2J_1 (1 + \lambda_1 + C_{xy}) - J_2 (3 + 3\lambda_2 - C_{2x} - C_{2y} - C_{2z})$ and $B_k = 2J_1 (C_{yz} + C_{xz})$, where we have defined $C_{2x} = \cos 2k_x$ and similarly for $C_{2y}, C_{2z}$. 

\[ \]
The powder-averaged dynamic structure factors \( S(Q, \omega) \) for this case are shown in Fig. 5.6 for \( J_2/J_1 = 0.0, 0.5 \) and various values of anisotropy \( \lambda_{1,2} \), along with the corresponding frustration parameters \( f_H \) determined using \( T_\lambda \) from Monte Carlo simulations and \( \theta_{CW} = -J_1(3 + \lambda_1) - J_2(3 + \lambda_2)/2. \) We select \( \lambda_1 > 0 \) and \( \lambda_2 < 0 \) which have been shown [185] to stabilize A-II type AFM when the anisotropy is strong enough to overcome the AFM \( J_2 \). It is clear from Fig. 5.6 that \( S(Q, \omega) \) exhibits a high intensity band of gapped dispersionless excitations which resembles the INS data, for various values of the anisotropy. We note that the frustration parameter \( f_H \) for these models is large (\( f_H \sim 4-9 \)) for modest anisotropy values \( \lambda_{1,2} \sim 1 \), approaching \( f_H \sim 2 \) for large uniaxial anisotropy.

### 5.6 Comparison with experiments

Both \( \text{La}_2\text{MgIrO}_6 \) and \( \text{La}_2\text{ZnIrO}_6 \) show a gapped and weakly-dispersive magnetic mode in the INS data. Based on our theoretical calculations above, the simplest description of the INS data is in terms of a spin model with a large uniaxial Ising-like exchange component. Indeed, the simple nearest neighbor Heisenberg-Ising model with large \( \lambda \), as seen in Fig. 5.6, can potentially describe the spin gap revealed by INS as well as the modest frustration parameter. However, is it reasonable to assume such a large uniaxial Ising anisotropy?

To answer this question, we begin by noting that models with large uniaxial Ising exchange anisotropy adequately describe qualitatively-similar INS spectra in certain 3d-transition metal ion based magnets such as \( \text{CsCoCl}_3 \) and \( \text{CsCoBr}_3 \) [199, 200]. In these two \( \text{Co}^{3+} \) systems, the comparable values for SOC (\( \sim 28 \) meV for \( \text{CsCoCl}_3 \) [201]) and the non-cubic crystal field distortion parameter \( \delta \) in the single ion Hamiltonian lead to the large uniaxial Ising anisotropies (\( \lambda = 7-8 \) [199]). In \( \text{La}_2\text{BiRO}_6 \), a similarly large uniaxial Ising anisotropy with a single ion origin should result in the complete breakdown of the \( j_{\text{eff}}=1/2 \) description, significantly modifying the isotropic single ion ground state wavefunctions. However, this is unlikely, as the SOC scale is expected to be on the order of 100’s of meV and much larger than \( \delta \). Indeed, the \( \text{Ir}^{4+} \) local octahedral environments in \( \text{La}_2\text{BiRO}_6 \) are amongst the closest to ideal cubic of any \( j_{\text{eff}} = 1/2 \) Mott insulating candidates [191]. Furthermore, recent RIXS measurements have validated a \( j_{\text{eff}}=1/2 \) ground state for \( \text{Na}_2\text{IrO}_3 \) [192], which exhibits much larger \( \text{IrO}_6 \) octahedral distortions.

Among other iridates, RIXS work on the stacked bilayer material \( \text{Sr}_3\text{Ir}_2\text{O}_7 \), which has staggered \( \text{IrO}_6 \) octahedral rotations about the c-axis of \( \sim 12^\circ \) [202], has shown that the spin waves exhibit a significant magnon gap [155]. This has been understood as a result of significant uniaxial Ising exchange (\( \lambda \sim 1.4 \)) between spins on adjacent planes in the bilayer which is comparable to the Heisenberg exchange [155]. We note that such a pseudodipolar interaction is indeed symmetry-allowed in \( \text{Sr}_3\text{Ir}_2\text{O}_7 \) even in the absence of octahedral rotations. It has been suggested that the large magnitude of this term in \( \text{Sr}_3\text{Ir}_2\text{O}_7 \) might be due to the sizable tetragonal distortions of the \( \text{IrO}_6 \) octahedra, and the proximity to a metal-insulator transition [155] which leads to increased mixing of \( j_{\text{eff}} = 1/2 \) and \( j_{\text{eff}} = 3/2 \) states and a more significant impact of Hund’s coupling on intermediate states in the superexchange process. Neither of these effects, the strong tetragonal distortions or proximity to a metal-insulator transition, are applicable for the double perovskites since they are deep in the Mott insulating regime and have nearly cubic \( \text{IrO}_6 \) octahedra. Furthermore, even in \( \text{Sr}_3\text{Ir}_3\text{O}_7 \), it is important to note that there are no entirely new exchange interactions not already allowed in the absence of octahedral rotations which are thought to become significant simply from the staggered octahedral rotations [155]. Thus, although \( \text{La}_2\text{BiRO}_6 \) have comparable \( \text{IrO}_6 \) octahedral rotations (albeit about two different crystallographic axes), these rotations alone cannot be responsible for any large new exchange couplings which are not already symmetry-allowed in the ideal fcc lattice.

The above arguments suggest that the regime of very large uniaxial Ising anisotropies (\( \lambda_{1,2} \gg 1 \)) is unlikely.
for La$_2$BIrO$_6$. Therefore the most plausible scenario is that the weak symmetry-lowering in La$_2$BIrO$_6$ leads to small values for non-cubic exchange couplings, and small deviations from the $j_{\text{eff}}=1/2$ picture. It is clear that the Heisenberg-Ising models yield gapped spin wave excitations as expected. Indeed, the conventional Heisenberg-Ising models in Fig. 5.6(e)-(h) with $J_2 > 0$ and $\lambda_{1,2} \sim \mathcal{O}(1)$ appear to do a reasonable job of describing the non-dispersive magnon band seen in the INS data (although they exhibit weaker dispersive features at higher energies). However, such Heisenberg-Ising models even with anisotropies of order unity yield frustration parameters, $f_H \sim 5-9$, significantly larger than the measured frustration parameters $f \sim 0.4-2$ [178], since an AFM second-neighbor exchange tends to frustrate A-type AFM order. This means that while we can choose couplings in such magnetic models to reproduce the approximate center of the magnon band and the transition temperature $T_N$, they overestimate $\Theta_{CW}$ by at least a factor of two. By contrast, the Kitaev models with small anisotropies $\lambda_K = 0-0.2$ yield frustration parameters in the range of experimental values. Thus, it appears to be a reasonable conclusion that such Kitaev models, possibly supplemented by small additional terms, most naturally explain both the INS data as well as the frustration parameter.

Fig. 5.7(a) shows an illustrative plot of $S(Q, \omega)$ for the Kitaev model with weak anisotropy $\lambda_K = 0.2$ supplemented by a small AFM second-neighbor Heisenberg coupling, $J_2 = 0.2 J_K$. For La$_2$MgIrO$_6$, a choice of $J_K = 1.7$ meV leads to reasonable agreement between the center of the computed magnon band and the magnon band observed in the INS data shown in Fig. 5.1(e). We have included a white dashed curve on the plot corresponding to the kinematic cutoff arising from an incident neutron energy $E_i = 7.5$ meV, which is applicable to the particular dataset that we are modeling. Using these parameters for La$_2$MgIrO$_6$, we find $\Theta_{CW} \approx -27K$ and $T_N \approx 14K$; both these results are in very good agreement with the experimental data [178]. For La$_2$ZnIrO$_6$, we suggest that a weak ferromagnetic second neighbor exchange might be a plausible route to the smaller frustration ratio, although we do not have a clear microscopic understanding for the difference in sign of $J_2$ when compared with La$_2$MgIrO$_6$. As shown in Fig. 5.7(b), we can get a reasonable description of the magnon dispersion with $J_K \approx 0.7$ meV, $\lambda_K = 0.2$, and $J_2 = -0.2 J_K$. In this case, we find $T_N = 8K$ and $\Theta_{CW} = -6K$, again in very good agreement with the experimental data.
5.7 Discussion

We note that even in the ideal cubic fcc limit, the most general symmetry-allowed Hamiltonian includes an off-diagonal symmetric exchange (ODSE) term \[164, 186\]. However, a small ODSE does not significantly affect our results, while a dominant ODSE leads to ordered moments pointing along the \(\langle 111 \rangle\) direction \[186\] which does not agree with previous neutron diffraction work for \(\text{La}_2\text{B}_{\text{Ir}}\text{O}_6\) \[178\].

A more complete theory \[203, 194\] for the magnetic excitations of \(\text{La}_2\text{B}_{\text{Ir}}\text{O}_6\) must incorporate antisymmetric Dzyaloshinskii-Moriya (DM) interactions arising from octahedral rotations. However, previous work on \(\text{Sr}_2\text{IrO}_4\) shows that the effect of octahedral rotations in these \(j_{\text{eff}} = 1/2\) Mott insulators may be largely accounted for by making local unitary rotations on the Heisenberg model \[?\], so the Ir moments track the local octahedral rotations \[204\]. This leads to a ‘hidden’ Heisenberg symmetry \[? 205\], which explains the existence of highly dispersive and nearly-gapless magnetic excitations in \(\text{Sr}_2\text{IrO}_4\) \[154, 206, 207\]. Thus, the observed weakly dispersive and gapped magnon band in \(\text{La}_2\text{B}_{\text{Ir}}\text{O}_6\) cannot simply be attributed to DM terms arising from octahedral rotations in the P2\(\_1/n\) structure.

Our theoretical modeling above has considered the ideal fcc lattice or weak anisotropies induced by small non-cubic distortions. However, it is well known that \(B/B'\) site mixing may play an important role in DPs \[208, 209\]. The density of antisite defects \(n_d\) is commonly estimated from structural refinements of DP diffraction data, although it was previously assumed that this effect is negligible for \(\text{La}_2\text{B}_{\text{Ir}}\text{O}_6\) in Ref. \[178\]. We have therefore revisited the x-ray diffraction data presented in that paper and performed new structural refinements, with the site mixing included as a fitting parameter. We estimate a \(B/B'\) site mixing value of \(\leq 8\%\) and \(\leq 5\%\) for the Mg and Zn systems respectively, with lattice constants and atomic fractional coordinates essentially identical to the values reported in Ref. \[178\]. Magnons can scatter off such defects, leading to momentum broadening. With a magnon mean free path \(\ell \sim n_d^{-1/3}\), this will lead to momentum broadening with \(\Delta Q \sim 1/\ell\). Such disorder broadening may smear some of the sharp features in the theoretical \(S(Q, \omega)\). Such disorder scattering, as well as the momentum broadening arising from finite instrument resolution, also not considered in the modeling, may lead to improved agreement between theory and experiment.

5.8 Conclusions

In conclusion, we have carried out a joint experimental and theoretical investigation of the spin dynamics in the \(j_{\text{eff}} = 1/2\) Mott insulators \(\text{La}_2\text{B}_{\text{Ir}}\text{O}_6\). Taken together, our INS data, spin wave calculations, and thermodynamic considerations suggest that \(\text{La}_2\text{B}_{\text{Ir}}\text{O}_6\) are likely to be rare examples of materials with significant Kitaev exchange. This unconventional interaction on the fcc lattice leads to AFM order, rather than an exotic quantum spin liquid. Nevertheless, our work suggests that studying materials with multiple Ir-O-O-Ir superexchange pathways between the same two magnetic ions is a promising design principle to search for other Kitaev materials. Our work also points to the possibility that such SOC-induced directional exchange couplings may be the driving force responsible for the gapped A-type AFM states found in a variety of other 4\(d/5d\)-based DPs \[210, 211, 185, 212, 213\]. In future work, it would be useful to synthesize small single crystals of \(\text{La}_2\text{B}_{\text{Ir}}\text{O}_6\) and other DPs. This would serve to distinguish models with dominant Kitaev exchange which would have only very small anisotropies in \(\Theta_{\text{CW}}\) from competing models with large uniaxial exchange anisotropies which would exhibit a highly anisotropic \(\Theta_{\text{CW}}\).
Beyond linear spin waves, we set:

\[ S_r^x = (-1)^2 \left( \frac{1}{2} - a_r^\dagger a_r \right) \]  
\[ S_r^y = \frac{1}{2} (a_r + a_r^\dagger) - \frac{1}{4} (a_r^\dagger a_r + a_r a_r^\dagger) \]  
\[ S_r^z = (-1)^2 \left[ \frac{1}{2i} (a_r - a_r^\dagger) - \frac{1}{4i} (a_r a_r^\dagger - a_r^\dagger a_r) \right] \]

and expand the Hamiltonian, only keeping terms to quartic order, which we decouple using mean field parameters \( F_k = \langle a_k^\dagger a_{-k} \rangle \) and \( G_k = \langle a_k^\dagger a_k \rangle \). This leads to the Hamiltonian:

\[ H_{mft} = \sum_{k>0} \left( a_k^\dagger \ a_{-k} \right) \left( \begin{array}{cc} A_k & B_k \\ B_k & A_k \end{array} \right) \left( \begin{array}{c} a_k^\dagger \\ a_{-k} \end{array} \right) \]  

with \( A_k = (2 + C_{xy} + C_{xz}) + \delta A_k \), \( B_k = (C_{xz} - C_{xy}) + \delta B_k \), and

\[ \delta A_k = 2(F_{xy} - F_{zz}) + F(C_{xy} - C_{xz}) - 2G(C_{xy} + C_{zz}) \]
\[ - 2(G_{xy} + G_{xz}) - 4G - 4G_{yz} C_{yz} \]  
\[ \delta B_k = (G_{xy} - G_{zz}) + G(C_{xy} - C_{xz}) - F(C_{xy} + C_{zz}) \]
\[ - (F_{xy} + F_{zz}) - 4F_{yz} C_{yz}. \]

Here, we have defined averages \( \bar{F} = \int_k F_k \), \( \bar{F}_{ij} = \int_k C_k^{ij} F_k \), and similarly for \( G_k \). Requiring self-consistency, we set \( F_k = \sinh 2\varphi_k \) and \( G_k = (\cosh 2\varphi_k - 1)/2 \), with the renormalized dispersion \( \Omega_k = \sqrt{A_k^2 - B_k^2} \), \( \cosh 2\varphi_k = A_k/\Omega_k \), and \( \sinh 2\varphi_k = -B_k/\Omega_k \).

To solve these equations, we begin with a guess for the Hamiltonian matrix of the form \( \delta A_k = \gamma \), and \( \delta B_k = 0 \), where \( \gamma \) represents the effect of the pinning field arising from order-by-disorder as described in the text. We then iterate the mean field equations to achieve self-consistency.

Using the converged result, we compute the renormalized staggered magnetization, and find \( m_{AF} \approx 0.46 \) in the ideal fcc lattice Kitaev model, leading to \( \sim 8\% \) suppression of the classical \( j_{eff} = 1/2 \) order parameter due to quantum fluctuations. Taking into account the staggered octahedral rotation \( \approx 11^\circ \) in La$_2$ZnIrO$_6$ this 0.92\( \mu_B \) staggered magnetization translates into a uniform magnetization \( \approx 0.18\mu_B \), which roughly agrees with the measured value \( \approx 0.22\mu_B \) in La$_2$ZnIrO$_6$.

We can use these converged results to also compute the resulting dynamic structure factor, which has components:

\[ S_{xx}(\mathbf{q}, \omega) = \frac{1}{4} \int \frac{d^3p}{(2\pi)^3} (\sinh 2\varphi_p \sinh 2\varphi_{p+\mathbf{G}} + 4\cosh^2 \varphi_p \sinh^2 \varphi_{p+\mathbf{G}}) \delta(\omega - \Omega_p - \Omega_{p+\mathbf{G}}) \]
\[ S_{yy}(\mathbf{q}, \omega) = (\cosh 2\varphi_q + \sinh 2\varphi_q)(1 - 2G - \bar{F}) \delta(\omega - \Omega_q) \]
\[ S_{zz}(\mathbf{q}, \omega) = (\cosh 2\varphi_q - \sinh 2\varphi_q)(1 - 2G + \bar{F}) \delta(\omega - \Omega_{q+z}) \]

where the first term corresponds to longitudinal fluctuations while the latter two correspond to transverse fluctuations. We find, numerically, that the longitudinal fluctuations make a very small contribution to the structure.
factor, and can be ignored in practice. Powder averaging leads to $S(Q, \omega)$, with $Q = |\vec{q}|$, which we convolute with a Gaussian function representing the instrumental energy resolution, and plot in Fig. 5.5(f) above.
Chapter 6

Spin-orbit coupled $j_{\text{eff}} = 1/2$ iridium moments on the fcc lattice

6.1 Introduction

Heavy atoms with strong spin-orbit coupling (SOC) and electronic correlations are predicted to form exotic quantum phases [214]. Rare-earth ions with strong SOC on the frustrated pyrochlore lattice can yield local moments with unusual exchange couplings, leading to ‘quantum spin ice’, as in Yb$_2$Ti$_2$O$_7$ [215, 216, 217, 218, 219]. Another exciting proposal is to realize the Kitaev Hamiltonian, with a spin liquid ground state and Majorana fermion excitations [220], in iridium oxides with edge-sharing octahedra, such as the two-dimensional (2D) honeycomb iridates Na$_2$IrO$_3$ and Li$_2$IrO$_3$ [217, 222]. Doping such Mott insulators has been predicted to lead to topological superconductivity [223, 224, 225, 226, 227]. Experimentally, in both Na$_2$IrO$_3$ and Li$_2$IrO$_3$, the spin liquid state is preempted by magnetic order [228, 229] induced by interactions beyond the Kitaev model. Nevertheless, extensive work on these materials [230, 231, 232, 233, 234, 235], and 3D harmonic honeycomb iridates $\beta$, $\gamma$-Li$_2$IrO$_3$ [236, 237, 238, 239, 240, 241, 242, 243], ascribes their complex order to large Kitaev couplings. Kitaev interactions in the triangular iridate Ba$_3$IrTi$_2$O$_9$ may lead to vortex crystals or gauge-like degeneracies [244, 245, 246].

In light of these studies, we explore the following important issues. What kinds of phases does the Kitaev interaction support in 3D lattices with geometric frustration? Do experiments suggest dominant Kitaev interactions in any geometrically frustrated materials? Here, we address these questions in the context of ordered double perovskite (DP) compounds, a large class of materials with the chemical formula $A_2BB'O_6$, where B and B’ ions occupy the two sublattices of a 3D cubic crystal. Metallic DPs such as Sr$_2$FeMoO$_6$ [247] are of great interest as half-metallic ferromagnets [248, 249? , 250, 2]. Recent work on metallic DPs has examined the role of SOC on bulk spin dynamics [251], and Chern bands in ultrathin films [252, 253, 254, 255, 256]. On the other hand, DPs where B is an inert filled-shell ion, and B’ is a heavy 4d/5d ion, form Mott insulators with local moments on the frustrated fcc lattice of B’ ions [257, 258, 259, 260, 261, 262, 263, 26, 264]. Our work is motivated by the recent synthesis of La$_2$ZnIrO$_6$ and La$_2$MgIrO$_6$ [265]. Structurally, both materials have nearly undistorted oxygen octahedra. A nominal valence Ir$^{4+}$ (5d$^5$), together with the strong SOC and larger spacing between Ir ions compared to perovskites, suggests that these materials behave as effective $j_{\text{eff}}=1/2$ Mott insulators [265].

In the previous chapter, we argued, based on neutron scattering and thermodynamic measurements, that the Kitaev interaction could play an important role in the iridate Mott insulators La$_2$BIrO$_6$. Here, we turn to an analysis of the phase diagram of the most general nearest neighbor model on the f.c.c. lattice.
In this chapter, we focus on the broad aspects of magnetism in an ideal fcc lattice, highlighting the rich physics of strong SOC in a canonical frustrated 3D lattice. Our key results are the following. (i) We show that even the nearest-neighbor symmetry-allowed Hamiltonian on the fcc lattice, which includes Heisenberg, Kitaev, and symmetric off-diagonal exchange couplings, leads to rich magnetic phases such as collinear antiferromagnetism, stripes, or multimode spirals. Indeed, previous work [266] has suggested that strong Kitaev interactions should be present in a large class of 2D and 3D lattices, including the fcc lattice, but did not study the most general symmetry-allowed Hamiltonian. (ii) We find that strong SOC can also stabilize a regime of robust A-type antiferromagnetism (AFM), also called Type-I AFM, which is observed in neutron diffraction on La\(^2\)ZnIrO\(_6\) and La\(^2\)MgIrO\(_6\) [265]. Our results challenge the conventional wisdom which ascribes robust A-type antiferromagnetism in many fcc magnets to further neighbor Heisenberg exchange [267, 268], and suggests that anisotropy due to SOC may be crucial in 5d oxides. Indeed, a recent ab initio study of Sr\(_2\)CrSbO\(_6\) [269] finds next-neighbor interactions are negligible, \(\lesssim 5\%\) of the first neighbor interactions. (iii) In certain regimes with A-type AFM, we uncover a residual accidental XY degeneracy of collinear states. Thermal order by disorder pins the moments along the Ir-O bond directions. (iv) We argue that thermodynamic data on La\(^2\)ZnIrO\(_6\) and La\(^2\)MgIrO\(_6\) [265], i.e., their ordering pattern and small frustration parameter, indicate a dominant antiferromagnetic Kitaev coupling. Microscopically, this may arise from the near-cancellation of Heisenberg interactions, from multiple Ir-O-O-Ir superexchange paths [222, 266, 245], and the smaller direct exchange for well-separated Ir atoms in the DP structure. We argue that a subtle difference in magnetic orders can reconcile ‘weak’ ferromagnetism in La\(^2\)ZnIrO\(_6\) with its absence in La\(^2\)MgIrO\(_6\). These compounds thus realize a new class of ‘Kitaev materials’. Ultrathin films of La\(^2\)BiIrO\(_6\), grown along \{111\}, could realize the triangular lattice AFM Kitaev model.

### 6.2 Model

To construct a minimal model on the fcc lattice of Ir moments, we consider the ideal cubic DP structure, and focus on nearest neighbor terms which are expected to dominate. We appeal to symmetry arguments to write down all possible terms, based on the fact that the effective \(j_{\text{eff}} = 1/2\) angular momentum operator is a pseudovector (axial vector). Requiring invariance of the Hamiltonian under lattice rotational and mirror symmetries [270] constrains the Hamiltonian coupling nearest-neighbor Ir sites to be of the form \(H = H_H + H_K + H_{OD}\),

\[
H_H = J_H \sum_{\langle rr' \rangle} \vec{S}_r \cdot \vec{S}_{r'} \tag{6.1}
\]

\[
H_K = J_K \left( \sum_{\langle rr' \rangle_{xy}} S_{x}^{r} S_{y}^{r'} + \sum_{\langle rr' \rangle_{yz}} S_{x}^{r} S_{z}^{r'} + \sum_{\langle rr' \rangle_{xz}} S_{y}^{r} S_{z}^{r'} \right) \tag{6.2}
\]

\[
H_{OD} = \Gamma \sum_{r} \left[ \left( S_{x}^{r} S_{y}^{r+x+y} + S_{y}^{r} S_{x}^{r+y+x} - S_{x}^{r} S_{y}^{r-x-y} \right) - S_{y}^{r} S_{x}^{r+x+y} \right] + (x, y \leftrightarrow y, z) + (x, y \leftrightarrow x, z). \tag{6.3}
\]

Here, \(\langle rr' \rangle\) denotes all first-neighbor pairs, while \(\langle rr' \rangle_{xy}\) denotes first-neighbors restricted to the \(xy\)-plane (similarly for \(yz, xz\)). \(H_H\) is the Heisenberg term, \(H_K\) is the Kitaev interaction, and \(H_{OD}\) is a symmetric off-diagonal exchange term. Antisymmetric Dzyaloshinskii-Moriya interactions are forbidden here by inversion symmetry. A dominant \(J_H < 0\) leads to ferromagnetism; this is incompatible with the ordering observed in La\(^2\)BiIrO\(_6\) (B=Mg,Zn), so we assume \(J_H > 0\).
6.3 Luttinger-Tisza analysis

To determine the preferred magnetic orders, we use the Luttinger-Tisza (LT) method which considers the spins to be classical moments, and replaces the constant length spin vectors by unconstrained vector fields $\vec{\phi}_r$. The classical spin Hamiltonian written in momentum space then takes the form

$$H_{LT} = 2J_H \sum_k \phi_k^\mu M_{\mu\nu}(k) \phi_k^\nu,$$

with

$$M(k) = \begin{pmatrix}
A_k + \alpha C_{kx}^{yz} & -\gamma S_{ky}^{yz} & -\gamma S_{kz}^{yz} \\
-\gamma S_{kx}^{yz} & A_k + \alpha C_{ky}^{xz} & -\gamma S_{kz}^{xz} \\
-\gamma S_{kx}^{xz} & -\gamma S_{ky}^{xz} & A_k + \alpha C_{kz}^{xy}
\end{pmatrix}. \tag{6.4}
$$

Here, $A_k = (\cos k_x \cos k_y + \cos k_x \cos k_z + \cos k_y \cos k_z)$, $C_{ij}^{kl} = \cos k_i \cos k_j$, and $S_{ij}^{kl} = \sin k_i \sin k_j$, and we have defined $\alpha = J_K / J_H$ and $\gamma = \Gamma / J_H$. Here, $k_i$ (with $i = x, y, z$) denote components of the momentum along the cubic Ir-O axes, and we have set the Ir-O-B bond length (B=Zn,Mg) to unity. Diagonalizing $H_{LT}$ for $J_H > 0$, and looking for the lowest energy eigenvalue in $k$, we find the rich variety of magnetic orders shown in Fig. 6.1.

Magnetic orders. — The LT analysis yields collinear as well as spiral antiferromagnetic (AFM) states. We describe these phases below, and compare their energy with numerical simulated annealing results.

A-I AFM: This is an A-type collinear AFM (also referred to as a Type-I AFM in the literature) which consists of ferromagnetically ordered spins in the cubic ab-plane layered antiferromagnetically along the c-axis. The spins point along the c-axis, perpendicular to the ferromagnetic planes as shown in Fig. 6.2. There are six symmetry related A-I AFM ground states, associated with a three-fold choice of the layering direction and a two-fold choice of the Ising AFM order. Although these are the lowest energy collinear states, there is an accidental classical degeneracy, where one can form multimode states leading to coplanar or even noncoplanar states with the same classical ground state energy. This degeneracy is expected to be broken in favor of collinear states by fluctuation effects, and our simulated annealing finds the above collinear states to be stabilized by thermal order by disorder.
A-II AFM: This is also an A-type collinear antiferromagnet; however spins lie in the ferromagnetic planes as in Fig. 6.2. In addition to collinear states, there are again multimode coplanar or noncoplanar states with the same classical ground state energy; we expect and observe numerically that thermal fluctuations favor the collinear orders. However, the ground state energy is independent of the precise angle in the plane so that there is an accidental XY degeneracy of collinear states. Our simulated annealing results show that this degeneracy is also broken by thermal fluctuations, with ‘order by disorder’ favoring spins along the Ir-O bond direction. There are twelve symmetry related A-II ground states favored by fluctuations, arising from a three-fold choice of the layering direction and a four-fold choice of the spin axis. Remarkably, the A-II AFM order persists even in the pure Kitaev limit with $J_K > 0$.

Stripe: The collinear stripe state has spins pointing along the $\{111\}$ and $\{\bar{1}\bar{1}\bar{1}\}$ directions arranged as shown in Fig. 6.3 for $(k_x, k_y, k_z) \equiv \pm (\pi/2, \pi/2, \pi/2)$; symmetry related orders are degenerate. Ordering with this wavevector is also referred to as a Type-II AFM. The ordering wavevector determines the direction of the spins, so that flipping one of the momentum components also flips the corresponding spin component; ordering at $\pm (\pi/2, -\pi/2, \pi/2)$ leads to spins along $\{1\bar{1}1\}$ and $\{\bar{1}1\bar{1}\}$. This leads to a total of eight ground states.

Incommensurate Spiral (IC-1, IC-2): In these regimes, the LT analysis suggests an incommensurate coplanar spiral order with wavevector $(k_x, k_y, k_z) \equiv (\pi, Q, Q)$, and symmetry related equivalents. With $\alpha = J_K/J_H$ and $\gamma = \Gamma/J_H$, minimizing the LT energy leads to $Q = \cos^{-1}(1 + \alpha/2)\cos 2Q - \gamma \sin 2Q - \sqrt{D}$

$$D \equiv [\alpha (\cos P - \cos Q)\cos Q - \gamma \sin^2 Q]^2 + 8\gamma^2 \sin^2 P \sin^2 Q \quad (6.5)$$

Again, a single mode spiral does not satisfy the spin constraint, and our simulated annealing numerics show noncoplanar multimode spiral order in this regime.
Figure 6.3: Real space spin configurations in the collinear stripe state, showing moments pointing along the diagonal \{111\} and \{-1-1-1\} directions for \((k_x, k_y, k_z) \equiv (\pi/2, \pi/2, \pi/2)\).

6.4 Monte Carlo results

To complement the LT analysis, we have used simulated annealing numerics, which preserves the spin constraint, to find the classical ground states. Fig. 6.4(a) compares the numerically computed ground state energy per spin to the Luttinger-Tisza result, for \(J_K/J_H = 1.5\) and varying \(\Gamma/J_H\). The agreement between the two is excellent in the A-II AFM and Stripe states, where the collinear order is precisely recovered. Our result that the A-II AFM state appears even for large \(J_K\) differs from an earlier study [266] which proposed a spiral ground state based on a Luttinger-Tisza analysis which did not take into account thermal fluctuations and order-by-disorder. For IC-1/IC-2, the simulations indicate multimode order, and lead to an energy per spin (for \(36^3\) lattice) which is only slightly higher by \(\lesssim 2\%\).

In order to determine the magnetic ordering temperature in the various phases, we have carried out Monte Carlo simulations on system sizes with up to \(24^3\) spins. Fig. 6.4 shows the magnetic \(T_c\) as determined from the specific heat singularity, along various cuts through the Luttinger-Tisza phase diagram. The Heisenberg limit in the absence of SOC \((J_K = 0, \Gamma = 0)\) is the most fragile state with the lowest \(T_c \approx 0.44J_H S^2\); our results here agree with previous work on the fcc Heisenberg model [271], where thermal order by disorder leads to a nonzero \(T_c\). The A-I AFM, A-II AFM, and stripe phases appear most robust with high \(T_c\), since SOC enhances the pinning of the moment direction. Thus, although the exchange interactions induced by SOC are frustrated on the fcc lattice, the SOC nevertheless enhances \(T_c\) by favoring certain spin orientations, thus reducing the effects of thermal disordering.

6.5 Comparison with experiments

La$_2$ZnIrO$_6$ and La$_2$MgIrO$_6$ are A-type AFMs. Combined \textit{ab initio} and neutron diffraction studies [265] suggest that the Ir spins lie predominantly in the ferromagnetic planes, viz. the A-II AFM state. This is consistent with \(J_K > 0\) and \(|\Gamma| < J_K/2\). Order by disorder pins moments along the Ir-O bond directions.

The Curie-Weiss temperature of \(j_{\text{eff}} = 1/2\) moments on the ideal fcc lattice is \(\Theta_{CW} = -(3J_H + J_K)\), independent of \(\Gamma\). However, both La$_2$ZnIrO$_6$ and La$_2$MgIrO$_6$ have a monoclinic P2$_1$/n structure, arising from small IrO$_6$ octahedral rotations — an octahedral rotation \(\phi\) about the cubic \(c\)-axis which is staggered between adjacent \(ab\) layers, and a global tilt about the cubic \(\{110\}\) axis. In the strong SOC limit, the Ir moments track the octahedral rotation, as shown for Sr$_2$IrO$_4$ [272]. A high temperature expansion yields a powder averaged \(\Theta_{CW} = -J_H - \frac{1}{7}(2J_H + J_K)(1 + 2 \cos 2\phi)\). If the axis along which the ferromagnetic planes are stacked in staggered fashion coincides with the axis of the staggered octahedral rotations, it leads to a net ferromagnetic moment \(\approx m \sin \phi\) in the A-II AFM state, where \(m\) is the ordered moment. Equivalently, we may start with the Hamilto-
Figure 6.4: (a): Comparison of the ground state energy per spin $E_\text{gs}$ obtained within LT method (solid line) and simulated annealing (dots). (b),(c): Magnetic transition temperature $T_c$ of the classical model (in units of $J_H S^2$, for spin length $S$) vs. $\Gamma/J_H$, obtained using Monte Carlo simulations for cuts through the phase diagram (Fig. 6.1) at $J_K/J_H = -1.0, +1.5$. (d) Plot of the “frustration parameter”, the ratio of the $T_c \equiv T_c(1+1/S)$ to $\Theta_{CW}$; the rescaling of $T_c$ by $(1+1/S)$ accounts for the classical $S^2$ being replaced by the quantum $S(S+1)$. The dark square shows the result at $J_K/J_H \rightarrow \infty$.

nian in the ideal cubic limit, and construct the Hamiltonian for the case with octahedral rotations by making local unitary rotations on the $j=1/2$ spins which induces Dzyaloshinskii-Moriya interactions, leading to an AFM with ‘weak’ ferromagnetism [272].

In La$_2$MgIrO$_6$, ab initio studies predict a ‘weak’ ferromagnetic moment $\approx 0.3\mu_B$ in the monoclinic P2$_1$/n structure; however, experiments do not detect any ferromagnetic moment in the ordered phase. To understand this discrepancy we propose that the axis of the staggered octahedral rotations and the stacking direction of the ferromagnetic planes are along orthogonal cubic axes (see Fig. 6.5), and ab initio results may have missed the correct ordering due to subtle energy differences. This can be tested if additional magnetic Bragg peaks can be resolved using high resolution X-ray diffraction. If we ignore SOC ($J_K = 0, \Gamma = 0$), and note that $\phi \approx 9^\circ$ from the structural data is small, the measured $\Theta_{CW} \approx -24K$ yields $J_H \approx 8K$. Our Monte Carlo simulations at $J_K = 0, \Gamma = 0$ show $T_c \approx 0.44J_H S^2$, consistent with previous work on the fcc Heisenberg model [271]. Heuristically replacing the classical $S^2$ by $S(S+1)$ for quantum spins leads to a renormalized $\tilde{T}_c = T_c(1+1/S)$. This is a good approximation for the 3D cubic lattice $S = 1/2$ Heisenberg model [273]. Here, on the fcc lattice, with $J_H = 8K$ and $S = 1/2$, we find $\tilde{T}_c \approx 2.6K$, much smaller than $T_c^{\text{exp}} = 12K$. With $\Gamma \neq 0$, but keeping $J_K = 0$, $T_c$ hardly changes or even gets suppressed. This hints at a significant $J_K > 0$. Indeed, the “frustration parameter” $f = -\Theta_{CW}/T_c$, plotted in Fig. 6.4(d) for $\Gamma = 0$, shows that recovering the experimentally observed small $f \approx 2$ needs a large Kitaev exchange $J_K/J_H \gg 1$.

Thus, we suggest that a model with a dominant Kitaev term $J_K > 0$, perturbed by a weak Heisenberg exchange coupling $J_H \ll J_K$, is a good starting point to understand $j_{\text{eff}} = 1/2$ magnetism in La$_2$MgIrO$_6$; we estimate this dominant coupling $J_K \approx 24K$. These estimates do not shed much light on the off-diagonal symmetric exchange since the powder averaged $\Theta_{CW}$ is independent of $\Gamma$, and $T_c$ is not very sensitive to $\Gamma$ (see Fig. 6.4(c)). However $|\Gamma| > J_K/2$ is precluded by the observed order. Traditionally, in fcc magnets, robust A-type order is ascribed to second-neighbor Heisenberg interactions [267, 268]. For heavy oxides, however, our results show that the A-type AFM, and the small frustration parameter, is due to SOC-induced Kitaev interactions.
Figure 6.5: Conjectured alignment of staggered octahedral rotations and the ferromagnetic planes in the A-II AFM state for \( \text{La}_2\text{ZnIrO}_6 \) (top) and \( \text{La}_2\text{MgIrO}_6 \) (bottom), with the spins shown on Ir octahedra (yellow). We have picked the \( z \)-axis as the direction along which the octahedral rotations are staggered for the Ir octahedra, and shown only \( z = 0, 1 \) planes. For \( \text{La}_2\text{ZnIrO}_6 \), the FM planes are the \( xy \)-planes stacked antiferromagnetically along \( z \), leading to a net ‘weak’ ferromagnetic moment along \( -\hat{y} \), while for \( \text{La}_2\text{MgIrO}_6 \) the FM planes are \(xz\)-planes stacked antiferromagnetically along \( y \) leading to no net ferromagnetic moment. The uniform Ir octahedral tilts are unimportant for this discussion and is not shown.

In \( \text{La}_2\text{ZnIrO}_6 \), there is a measured ‘weak’ ferromagnetic moment \( \approx 0.22 \mu_B \); thus, the axis along which the ferromagnetic planes are stacked in staggered fashion must coincide with the axis of the staggered octahedral rotations (see Fig. 6.5). Setting \( \phi \approx 11^\circ \), consistent with structural data, we expect a moment \( \approx 0.19 \mu_B \), close to the measured value. This is smaller than the \textit{ab initio} prediction \( \approx 0.5 \mu_B \). Based on the smaller \( T_{\text{expt}} \approx 7.5 K \) in \( \text{La}_2\text{ZnIrO}_6 \), and assuming similar ratios of exchanges, \( J_H/J_K \ll 1 \), we estimate the dominant \( J_K \approx 15 K \), and \( \Theta_{CW} \approx -15 K \); however, experiments report \( \Theta_{CW} \approx -3 K \) [265]. This discrepancy remains to be resolved.

In summary, DP Mott insulators are a distinct class of materials which host strong Kitaev exchange interactions. Our study calls for a microscopic understanding of the AFM Kitaev exchange, motivates a search for DPs with large \( \Gamma \), which can stabilize stripes or complex spiral orders.
Chapter 7

Conclusion

7.1 Overview

In this thesis, an introduction to the interplay between strong correlations and spin-orbit coupling is provided and studied in a particular class of materials known as double perovskites. The thesis is divided into two sections – one on ferrimagnetic, half-metallic double perovskites from chapters 2 to 4 and one on Mott-insulating double perovskites covering chapters 5 and 6 – each section starting with a joint theoretical and experimental study of some relevant compounds. Chapter 2 discusses an inelastic neutron scattering study of Ba$_2$FeReO$_6$ (BFRO). Chapter 3 discusses development of a tight-binding model of BFRO through comparison with experiment and ab initio. Chapter 4 covers adaptation of this tight-binding model to study of bilayers of another half-metallic, ferrimagnetic double perovskite, Sr$_2$FeMoO$_6$, grown in the \{111\} crystallographic direction. Chapter 5 is an inelastic neutron scattering study of the compounds La$_2$MgIrO$_6$ and La$_2$ZnIrO$_6$ (collectively referred to as LBIO). Chapter 6, lastly, discusses study of the most general model allowed by symmetry for the LBIO compounds assuming an ideal f.c.c. lattice and restriction of the model to nearest neighbour exchange couplings only.

Each chapter contains discussion and conclusions based on the results in that section. A brief summary of key points is included here as well:

7.2 Chapter 2

Motivated by exploring spin-orbit coupled magnetism in 5d-based transition metal oxides (TMOs) beyond the iridates, we present a powder inelastic neutron scattering study of magnetic excitations in Ba$_2$FeReO$_6$ - a member of the double perovskite family of materials which exhibit half-metallic behavior and high Curie temperatures $T_c$. We find clear evidence of two well-defined dispersing magnetic modes in its low temperature ferrimagnetic state. We develop a local moment model, which incorporates the interaction of Fe spins with spin-orbital locked magnetic moments on Re, and show that it captures our experimental observations. This allows us to extract moment sizes and exchange couplings, explain the magnitude of $T_c$, and to infer that magneto-structural locking terms are weak. Our study further opens up Re-based compounds as model systems to explore the interplay of strong correlations and spin-orbit coupling in 5d TMOs.

We consider a model of the double perovskite Ba$_2$FeReO$_6$, a room temperature ferrimagnet with correlated and spin-orbit coupled Re $t_{2g}$ electrons moving in the background of Fe moments stabilized by Hund’s coupling. We show that for such 3d/5d double perovskites, strong correlations on the 5d-element (Re) are essential in driving
a half-metallic ground state. Incorporating both strong spin-orbit coupling and the Hubbard repulsion on Re leads to a band structure consistent with ab initio calculations. Using our model, we find a large spin polarization at the Fermi level, and obtain a semi-quantitative understanding of the saturation magnetization of Ba$_2$FeReO$_6$, as well as X-ray magnetic circular dichroism data indicating a significant orbital magnetization. Based on the orbital populations obtained in our theory, we predict a specific doping dependence to the tetragonal distortion accompanying ferrimagnetic order. Finally, the combination of a net magnetization and spin-orbit interactions is shown to induce Weyl nodes in the band structure, and we predict a significant intrinsic anomalous Hall effect in hole-doped Ba$_2$FeReO$_6$. The uncovered interplay of strong correlations and spin-orbit coupling lends partial support to our previous work, which used a local moment description to capture the spin wave dispersion found in neutron scattering measurements. Our work is of interest in the broader context of understanding metallic double perovskites which are of fundamental importance and of possible relevance to spintronic applications.

### 7.3 Chapter 3

We consider a model of the double perovskite Ba$_2$FeReO$_6$, a room temperature ferrimagnet with correlated and spin-orbit coupled Re $t_{2g}$ electrons moving in the background of Fe moments stabilized by Hund’s coupling. We show that for such 3d/5d double perovskites, strong correlations on the 5d-element (Re) are essential in driving a half-metallic ground state. Incorporating both strong spin-orbit coupling and the Hubbard repulsion on Re leads to a band structure consistent with ab initio calculations. Using our model, we find a large spin polarization at the Fermi level, and obtain a semi-quantitative understanding of the saturation magnetization of Ba$_2$FeReO$_6$, as well as X-ray magnetic circular dichroism data indicating a significant orbital magnetization. Based on the orbital populations obtained in our theory, we predict a specific doping dependence to the tetragonal distortion accompanying ferrimagnetic order. Finally, the combination of a net magnetization and spin-orbit interactions is shown to induce Weyl nodes in the band structure, and we predict a significant intrinsic anomalous Hall effect in hole-doped Ba$_2$FeReO$_6$. The uncovered interplay of strong correlations and spin-orbit coupling lends partial support to our previous work, which used a local moment description to capture the spin wave dispersion found in neutron scattering measurements. Our work is of interest in the broader context of understanding metallic double perovskites which are of fundamental importance and of possible relevance to spintronic applications.

### 7.4 Chapter 4

Recent experiments have demonstrated the controlled layer-by-layer growth of oxide heterostructures. This leads to the exciting prospect of tuning magnetism and topological states of correlated electrons in low dimensions. Here, we model \{111\}-grown bilayers of half-metallic double perovskites such as Sr$_2$FeMoO$_6$, which form a buckled honeycomb lattice, with a triangular lattice of Fe moments interacting with spin-orbit coupled Mo electronic $t_{2g}$ states. The combination of spin-orbit coupling, inter-orbital hybridization and symmetry-allowed trigonal distortion leads to a rich phase diagram with tunable ferromagnetic order, topological $C = \pm 1, \pm 2$ Chern bands, and a $C = \pm 2$ quantum anomalous Hall insulator regime. An effective two-band model of Zeeman-split $j = 3/2$ states captures this emergence of $C = \pm 2$ band topology.
7.5 Chapter 5

We have performed inelastic neutron scattering (INS) experiments to investigate the magnetic excitations in the weakly distorted face-centered-cubic (fcc) iridate double perovskites La$_2$ZnIrO$_6$ and La$_2$MgIrO$_6$, which are characterized by A-type antiferromagnetic ground states. The inelastic neutron scattering data on these geometrically frustrated magnets provide clear evidence for gapped spin wave excitations with very weak dispersion. The INS data can be reproduced by models with uniaxial Ising anisotropy or highly-directional Kitaev exchange couplings. The uniaxial Ising exchange model is symmetry-forbidden on the ideal fcc lattice, although it might arise from the interplay of lattice distortions and spin-orbit coupling. However, this model appears to be inappropriate for these double perovskite iridates, since a large uniaxial Ising term is at odds with their weak non-cubic distortions, while a moderate uniaxial exchange is unable to explain their small frustration parameters. By contrast, models with dominant Kitaev exchange naturally account for the neutron data as well as the measured frustration parameters of these materials. The Kitaev model is symmetry-allowed on the ideal fcc lattice and has a magnon gap induced by quantum order-by-disorder. Weak anisotropies of the Kitaev couplings, generated by the symmetry-lowering due to lattice distortions, can pin the order and enhance the magnon gap. Our findings highlight how even seemingly conventional magnetic orders in oxide materials containing heavy transition metal ions may be driven by highly-directional exchange interactions rooted in strong spin-orbit coupling.

7.6 Chapter 6

Motivated by experiments on the double perovskites La$_2$ZnIrO$_6$ and La$_2$MgIrO$_6$, we study the magnetism of spin-orbit coupled $j_{\text{eff}} = 1/2$ iridium moments on the three-dimensional, geometrically frustrated, face-centered cubic lattice. The symmetry-allowed nearest-neighbor interaction includes Heisenberg, Kitaev, and symmetric off-diagonal exchange. A Luttinger-Tisza analysis shows a rich variety of orders, including collinear A-type antiferromagnetism, stripe order with moments along the $\{111\}$-direction, and incommensurate non-coplanar spirals, and we use Monte Carlo simulations to determine their magnetic ordering temperatures. We argue that existing thermodynamic data on these iridates underscores the presence of a dominant Kitaev exchange, and also suggest a resolution to the puzzle of why La$_2$ZnIrO$_6$, but not La$_2$MgIrO$_6$, exhibits ‘weak’ ferromagnetism.

7.7 Future work

These results highlight the value of double perovskites with strong spin-orbit coupling as test-beds of exotic physics emerging from strong spin-orbit coupling and strong correlations, but further investigations of these compounds are necessary. Future work is warranted to fully understand the roles correlations can play in the physics of half-metallic, ferrimagnetic double perovskites, for instance. As fabrication of double perovskite thin films advances, more will need to be done to explore their potential for various applications given their promise for realizing useful and interesting topological phases of matter. Similarly, the phase diagram of the local moment model for $j_{\text{eff}} = 1/2$ pseudospins on the f.c.c. lattice discussed here is rich, and remains largely unexplored. Further experimental work and accompanying theoretical study of Mott-insulating double perovskites such as La$_2$MgIrO$_6$ and La$_2$ZnIrO$_6$ is also important to further understanding their potential for harboring quantum spin liquid phases and providing further support for the claim that Kitaev exchange couplings are dominant in these compounds. This will be especially true when single-crystal samples of these double perovskites large enough for inelastic neutron scattering become available.
Perhaps the most important thing to take away from this thesis is that the double perovskites are a vast family of transition metal oxides, themselves a massive field of study at the heart of many great challenges of modern condensed matter physics. The perovskite structure is one of the most widespread in nature, incredibly versatile and capable of richness not only through options for the constituents of the compounds, which imbue the compounds with oftentimes competing phenomena, but also via deviations from the ideal perovskite structure such as octahedral rotations, other lattice distortions, and disorder. There is much work to be done to learn the secrets of these compounds in all their forms and use these to make the world a better place.
Bibliography


[49] The different atomic form factors of Re and Fe have not been taken into account in the theoretical calculations; however, their form factors only differ by about 15% from the average form factor at the largest Q. Since the dispersing modes do not strictly have Re or Fe character, we expect taking form factors into account will slightly modify the intensities in our theoretical plots.

[50] When projected to $t_{2g}$ subspace, the effective orbital angular momentum becomes $L_{eff} = 1$ with opposite sign. We drop the subscript and use this $L$ in the following discussions.

[51] Note that we use $\mathcal{R}$ for the effective total angular momentum for a Re ion. $\mathcal{R} = 2$ would correspond to $j_{eff} = 2$ if we borrow the notation commonly used in iridate literature.


[133] For the Mo 4d$^1$ configuration, this trigonal distortion could occur as a spontaneous Jahn-Teller effect.


[181] Ref. [179] suggests that there are actually two different magnetic transition temperatures in close proximity for La$_2$ZnIrO$_6$ ($T_1 = 7.3$ K and $T_2 = 8.5$ K), but this finding is not important for the results presented in our work.


