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2018

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Study of Three-Dimensional Kitaev Honeycomb Materials
 $\beta, \gamma\text{-Li}_2\text{IrO}_3$

by

Ramón Alejandro Ruíz Ramos

A dissertation submitted in partial satisfaction of the
requirements for the degree of
Doctor of Philosophy

in

Physics

in the

Graduate Division

of the

University of California, Berkeley

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Assistant Professor James G. Analytis, Chair
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Fall 2018

Study of Three-Dimensional Kitaev Honeycomb Materials
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Ramón Alejandro Ruíz Ramos

Abstract

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Transition metal oxides (TMO) are fascinating and complex materials that have puzzled condensed matter physicists for many years due to their many different electronically ordered ground states. Albeit separated by external or internal parameters, these nearly degenerate phases are sometimes intertwined in competition or coexistence, which can itself lead to further phase emergence.

A unique feature of the $5d$ iridium oxide materials is that spin-orbit λ_{SOC} and Coulomb interactions U are of comparable strength and therefore compete vigorously. In a honeycomb structure, this competition gives rise to strong magnetic frustration due to their edge-shared bonding environment, in which quantum interference of the two exchange paths favors a strongly anisotropic, Ising-like exchange between neighboring spin-1/2 moments. Such an interaction couples different orthogonal spin components for the three nearest neighbors and, as a consequence, no single exchange direction can be simultaneously satisfied, leading to strong frustration described by the Kitaev Hamiltonian. This model results in the infinitely degenerate and extremely exotic quantum spin liquid state, whose excitations range from being Majorana-like to fractionalized fermionic excitations.

In this thesis, I will discuss a range of physical properties resulting from the combine influence of charge, spin and orbital degrees of freedom. In the edge-sharing honeycomb iridates, the balance between U , SOC and CFE gives rise to a wealth of novel quantum phenomena, such as spin liquid and spin glass manifold states. In particular, I will study the three dimensional Kitaev candidate materials $\beta, \gamma\text{-Li}_2\text{IrO}_3$ using a combination of thermodynamics and resonant x-ray scattering techniques.

To my family and friends
for their love and support
through this the darkest of times.

“It was the best of times, it was the worst of times,
it was the age of wisdom, it was the age of foolishness,
it was the epoch of belief, it was the epoch of incredulity,
it was the season of Light, it was the season of Darkness,
it was the spring of hope, it was the winter of despair,
we had everything before us, we had nothing before us...”
Charles Dickens

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Acknowledgments

This dissertation is the result of more than a decade of work, and would not have been possible without the love and support of so many of my family, friends and collaborators. Born and raised in a small town in Guantánamo-Cuba, I never expected to be the first member of my family to complete a college education let alone a Physics PhD from one of the top institutions in the world. I took one step at a time with so many of you lifting me along the way. Thank you for that, and for comforting me when I was depressed. Thank you for taking care of me when I was seriously ill, and for lending me money when I didn't have enough to pay my rent. Thank you for your company, and for your inspiring words those days I felt like an impostor. In short, thank you for making this dream into a reality.

First and foremost, I would like to express my sincere gratitude to my very enthusiastic PhD supervisor **Prof. James G. Analytis** for his continuous support, patience, motivation, and immense knowledge; for giving me the opportunity to attend many scientific conferences and workshops; for helping develop my scientific writing, communication and computer skills; for introducing me to so many delightful labmates: Sylvia Lewin, Ian Hayes, Gilbert Lopez, Vikram Nagarajan, Robert Kealhofer, Mayia Vranas, Sooyoung Jang, Eran Mavic.

Secondly, I would like to express my gratitude to all the collaborators that helped with the collection and analysis of the data I presented here. Toni Helm for helping with the heat capacity measurements, **Nicholas P. Breznay** for his help with magnetization and REXS under pressure, **Alex Frañó** and **Zahir Islam** for their immense knowledge of REXS under applied field, **Ben Frandsen** for collaborations on μ SR measurements, **Gilbert Lopez** and **Mayia Vranas** for help with synthesis, powder diffraction and magnetic characterization, **Itamar Kimchi** for help with the theoretical understanding and symmetry analysis, **Vikram Nagarajan** for collection of torque data, and **Julia Y. Chang**, **Iain Oswald**, and **Gregory T. McCandless** for crystallographic analysis.

I would also like to thank my undergraduate mentors **Prof. Harriharan Srikanth** and **Manh Houng Phan**. Thank you for giving the opportunity to be a part of the Functional Materials Lab's family for over three years; your mentorship and dedication got me to where I am. Besides a very productive time, I also got the opportunity to work with a wonderful team of people: Kristen Repa, Paige Kelley, Jagannath Devkota, Anurag Chaturvedi and Jeff Wingo. I would also like to thank **Magaly Cortinas** and **Georgina López**, my high school Physics and Chemistry teachers who instigated my scientific aspirations.

A further shout-out to my fellow graduate school classmates for many stimulating discussions, for all the sleepless nights we were working together before a homework deadline, and for all the fun we have had in the last five years. In addition, I want to thank **Colette E. Patt**, **Ira Young** and **Prof. Steve Boggs** for supporting my interests outside the lab. They help me create and shape IGenSpectrum, and gave me the opportunity

to engage in countless community outreach programs which kept me sane during the rough times.

Most importantly, I would like to express my infinite gratitude to my family and friends to whom this work has been dedicated. To the best parents in the whole world, **Mabel Ramos** and **Felix Ruíz**, thank you for giving me an amazing life, for loving me as I am, for sacrificing your well-being with the hope that I may have a better future. To my brother **Felipe Ruíz**, thank you for giving me the opportunity to come to the US. To my family in Cuba, I miss you every single second; fun memories of our time together makes this separation bearable. To my loving fiancé **Desmond Richmond-Buccola** and our two adorable kitties, thank you for your love, patience and understanding all those nights I was away in beamtimes or conferences. To the **Aleman family**, thank you for making part of your wonderful family, and for feeding me for three and a half years. To my closest friends **Lilibeth Sosa**, **Marelys Mesa**, **Jorge Beccera** thank you for an amazing time together, for regularly visiting me after I moved away, for still making me part of your life even after eight years of separation. To my newest friends **Sylvia Lewin**, **Sam Kohn**, **Crystal Noel**, **Clio Sleator**, **Lily Hanson**, **Tess Schmidt**, **Vinay Ramasesh**, **Matt Gilbert**, **Claire Ziewitz**, **Mike Yen**, **Erik Copenhaver**, **Neil Goeckner-Wald** thank you for putting up with me the past five years, for letting cry in your shoulders when graduate school took the best of me, for teaching how to cook and eating my dinners, for many wonderful camping trips in California, and very exciting adventures around the world.

What an exciting journey this has been!

Chapter 1

Theoretical Background

In this thesis I will discuss a range of physical properties resulting from the combine influence of charge, spin and orbital degrees of freedom. The balance between electronic correlations (U), spin-orbit coupling (SOC) and crystal-electric field effects (CEF) gives rise to a wealth of novel quantum phenomena which can all be studied in transition metal oxide (TMO) materials.

Classical descriptions often fail to fully describe the behavior of quasi-particles in these TMO materials mainly because they are treated as independent particles. In reality, quasi-particles are correlated entities. This becomes very relevant in the case of localized $3d$ band which are insulating as a result of electron–electron interactions even though band structure calculations would describe them as metallic. In this case, Coulomb repulsion between electrons occupying the same orbital gives rise to unusual local moments, correlated metallic states, quantum criticality, unconventional superconductivity, colossal magneto-resistance etc.

On the other hand, spin-orbit coupling is a relativistic effect that combines the orbital angular momentum and the electron's spin in atoms. This interaction increases with the atomic number ($\sim Z^4$), being negligible for $3d$ TMO but very relevant for $5d$ materials. Strong SOC results in exotic new phases like topological band insulators and Weyl semi-metals even in the weakly correlated regime.

These two areas come together in the $5d$ TMO compounds, where the d orbitals become more extended and therefore, the electronic repulsion diminishes while the SOC increases dramatically. The interplay between them favours the emergence of new correlated states with the added ingredient of entangled spin and orbital moments. Our focus will be on the formation of novel types of Mott insulators in which the local moments are spin-orbit entangled $\mathcal{J} = 1/2$ Kramer doublets. These are formed for ions in a d^5 electronic configuration which includes most iridates with $Ir^{4+}(5d^5)$ and some ruthenates with $Ru^{3+}(4d^5)$ valency.

First, I will demonstrated how this $\mathcal{J} = 1/2$ entangled state arises in an octahedrally coordinated iridium ion. Then I will explore the relevant exchange interactions between neighboring IrO_6 octahedra, and their implications for the honeycomb lattice. Finally,

I will discuss potential materials for the study of the Kitaev honeycomb model, and in particular, how it relates to the physics of the Harmonic Honeycomb Li_2IrO_3 family.

1.1 Single Ion Physics

Iridium is the most corrosion-resistant metal, the second densest element and the third least-common element on Earth. It is a noble metal with chemical symbol Ir , atomic number $Z = 77$ and electronic configuration $[\text{Xe}]4f^{14}5d^76s^2$, which makes it a heavy transition metal.

A transition metal (TM) is characterized by a partially filled d -shell with total angular momentum $L = 2$ and five-fold degenerate orbitals: $d_{xy}, d_{yz}, d_{zx}, d_{x^2-y^2}, d_{3z^2-r^2}$ ($m_l = \pm 2, \pm 1, 0$). Using the $|l, m_l\rangle$ notation, the d -orbitals become:

$$\begin{aligned} d_{xy} &= \frac{i}{\sqrt{2}}(|2, -2\rangle - |2, 2\rangle) & d_{x^2-y^2} &= \frac{1}{\sqrt{2}}(|2, 2\rangle + |2, -2\rangle) \\ d_{xz} &= \frac{1}{\sqrt{2}}(|2, -1\rangle - |2, 1\rangle) & d_{3z^2-r^2} &= |2, 0\rangle \\ d_{yz} &= \frac{i}{\sqrt{2}}(|2, -1\rangle + |2, 1\rangle) \end{aligned}$$

When the TM is covalently bonded to a ligand oxygen atom (O^{2-}), a transition metal oxide compound forms. Therefore, iridates are loosely defined as ionic compounds containing an iridium oxide anion (IrO^-). These iridates can be found in different oxidation states ranging from -3 to $+6$. However, in the very common rutile structure (IrO_2), the iridium ion is trapped in an octahedral oxygen cage which reduces the Ir valency to Ir^{4+} ($5d^5$) by sharing 4 electrons with the oxygen p - orbitals [1].

In this section we will learn how the d -orbitals degeneracy of iridium oxide compounds is lifted by the combined influence of crystals electric field effects (Δ_{CEF}), spin-orbit coupling (λ_{SO}) and Coulomb interactions (U) to produced a novel $\mathcal{J} = 1/2$ Mott insulating state.

Crystal Field Effect: Δ_{CEF}

The hybridization between the transition metal d -orbitals and the ligand oxygen p -orbitals lifts the d -orbitals degeneracy due to the static electric field produced by the ligand's charge distribution. In the rutile structure case, the oxygen ligand has a negative valency so that the d -orbitals pointing towards the surrounding oxygen atoms have higher energy than orbitals pointing between ligand atoms. In group theory language, the anisotropic contributions from the octahedral crystal field (O_h) breaks the full rotational symmetry (SO_3) of the Ir d - orbitals and splits the energy levels into two irreducible representations of lower symmetry: e_g ($d_{x^2-y^2}, d_{3z^2-r^2}$) denoting two-dimensional representations, and t_{2g} (d_{xy}, d_{yz}, d_{zx}) denoting three- dimensional representations (Figure 1.1)[2].

The e_g states require higher energy to overcome the oxygen's electronegative repulsion, while the t_{2g} states sit between oxygens, avoiding some of the ligand's influence.

This CEF effect results on an energy splitting between the e_g and t_{2g} orbitals equal to:

$$\Delta_{CEF} = E(e_g) - E(t_{2g}) = 10Dq = \frac{5}{3} \frac{Ze^2}{a^5} \langle r^4 \rangle_{nd} \quad (1.1)$$

which actual strength depends on the potential generated by the ligands. This ionic model neglects any covalency in the bonds and, for the Ir case, results in $\Delta_{CEF} \sim 2.3$ eV. Nonetheless, it provides a good estimate for the CEF splitting experimentally measured in iridates to be ~ 3 eV [3, 4, 5, 6].

This large energy split leads to a low-spin configuration since Δ_{CEF} is larger than the Hund's coupling constant (J_H), which would otherwise decrease the inter-particle interaction by filling each orbitals with one electron of the same spin before filling orbitals with two electrons of opposite spin. As a result, e_g states are empty and all five electrons will occupy the t_{2g} states with total spin angular momentum $S = 1/2$ (Figure 1.1).

Furthermore, CEF quenches the orbital angular momentum $L = 2$ down to $L_{eff} = -1$. To see this, let us examine how $\mathbf{L} = (l_x, l_y, l_z)$ operates on the $|t_{2g}\rangle = (|d_{xy}\rangle, |d_{yz}\rangle, |d_{xz}\rangle)$ basis. By writing $l_x = 1/2(l_+ + l_-)$ and $l_y = 1/2i(l_+ - l_-)$ in terms of the ladder operators and using:

$$\begin{aligned} l_z |l, m_l\rangle &= m_l |l, m_l\rangle \\ l_{\pm} |l, m_l\rangle &= \sqrt{l(l+1) - m_l(m_l \pm 1)} |l, m_l \pm 1\rangle \end{aligned}$$

we notice that the matrix elements of $\langle t_{2g} | \mathbf{L} | t_{2g} \rangle$ correspond to the matrix elements for the $|p\rangle = (|p_x\rangle, |p_y\rangle, |p_z\rangle)$ orbital ($L = 1$) with the opposite sign, meaning that $\mathbf{L}(t_{2g}) = -\mathbf{L}(p)$ [7]. The total angular momentum vector becomes $\mathbf{L}_{eff} = -1$ and the $|l_{eff}, m_l\rangle$ states in the d -orbital basis become:

$$\begin{aligned} |1, 1\rangle &= \frac{1}{\sqrt{2}}(-|d_{yz}\rangle + i|d_{xz}\rangle) \\ |1, 0\rangle &= |d_{xy}\rangle \\ |1, -1\rangle &= \frac{1}{\sqrt{2}}(|d_{yz}\rangle + i|d_{xz}\rangle) \end{aligned} \quad (1.2)$$

To summarize, in an octahedral environment CEF splits the degeneracy of the iridium d -orbitals and creates a low-spin configuration with $S = 1/2$ and $\mathbf{L}_{eff} = -1$.

Spin-Orbit Coupling: λ_{SO}

The interaction between the electron's spin ($\mathbf{S}$) with its orbital momentum ($\mathbf{L}$) leads to further splitting of the atomic energy levels. SOC is a relativistic effect described by

$H_\lambda = \lambda_{SO} \sum_i S_i \cdot L_i$, where λ_{SO} denotes the coupling strength and it is proportional to atomic number Z ,

$$\lambda_{SO} = \frac{e^2}{4\pi\epsilon_0} \frac{\hbar^2}{m_e^2 c^2} \frac{Z^4}{l(l+1)(2l+1)n^3 a_o^3} \sim \frac{Z^4}{n^3} \quad (1.3)$$

Therefore, SOC can be treated as a small perturbation for $3d$ elements ($\lambda_{3d} \sim 20 - 40$ meV) [8] while it becomes very relevant for $5d$ TM ($\lambda_{5d} \sim 200 - 500$ meV) [9, 10]. In the presence of SOC, the total interaction Hamiltonian does not commute with S and L ; ergo, spin and orbital momenta are not separately conserved, and the total angular momentum $J = S + L$ becomes the good quantum number.

In the IrO_6 octahedral case, the energy eigen-states on equation. 1.2 will be described by $J = L_{eff} \pm S$ which corresponds to a doubly degenerate $J = 1/2$ and a quadruply degenerate $J = 3/2$ states. In the d -orbital basis, these states become[11]:

$$\begin{aligned} |1/2, \pm 1/2\rangle &= \frac{1}{\sqrt{3}}(|d_{yz}, \mp\rangle \pm i |d_{xz}, \mp\rangle \pm |d_{xy}, \pm\rangle) \\ |3/2, \pm 1/2\rangle &= \frac{1}{\sqrt{6}}(|d_{yz}, \mp\rangle \pm i |d_{xz}, \mp\rangle - 2 |d_{xy}, \pm\rangle) \\ |3/2, \pm 3/2\rangle &= \frac{1}{\sqrt{2}}(|d_{yz}, \pm\rangle \pm i |d_{xz}, \pm\rangle) \end{aligned} \quad (1.4)$$

where $\pm$ indicates the spin polarization. Notice that the wave-functions are given by a coherent superposition of different orbitals and spin states which leads to a peculiar distribution of spin densities in real space.

The half-filled $J = 1/2$ states are higher in energy due to the minus sign introduced by the total orbital momentum vector L_{eff} . The energy splitting between these states can be calculated by finding the difference between the eigenvalues of $S \cdot L = \frac{1}{2}(J^2 - L^2 - S^2)$ for the $J = 1/2$ and $J = 3/2$ states. Therefore,

$$\begin{aligned} \Delta E_{SO} &= \langle 1/2 | L \cdot S | 1/2 \rangle - \langle 3/2 | L \cdot S | 3/2 \rangle \\ &= \lambda_{SO} - (-1/2 \lambda_{SO}) \\ &= \frac{3}{2} \lambda_{SO} \end{aligned} \quad (1.5)$$

A direct consequence of SOC is that the valence electrons are in a state described by an entangled orbital and spin moment. Figure 1.1 shows the energy splitting and the occupancy of these energy levels in the ground state. The $J = 1/2$ state described thus far should give rise to an itinerant state since it is half-filled. However, we will learn in the next section that an localized state is observed as a consequence of the enhanced SOC.

Coulomb Interactions: U

According to the single band Hubbard model [12, 13], two electrons occupying the same site experience the competition between the hopping energy (t) trying to delocalize

the electrons, and the electronic correlation energy (U) forcing the electrons to remain on site. This is described by the Hubbard Hamiltonian:

$$H_U = - \sum_{\langle i,j \rangle, \sigma} t_{ij} (a_{i\sigma}^\dagger a_{j\sigma} + a_{j\sigma}^\dagger a_{i\sigma}) + U \sum_i n_{i\uparrow} n_{i\downarrow}$$

where $a_{i\sigma}^\dagger$ ($a_{i\sigma}$) create (annihilate) an electron with spin $\sigma = \uparrow, \downarrow$ on lattice site i and $n_{i\uparrow} = a_{i\uparrow}^\dagger a_{i\uparrow}$ is the occupation number operator for such site.

If we considered a half-filled band, in the limit $U/t \rightarrow 0$, the system is metallic with bandwidth W , in agreement with band theory calculations. On the other hand, if $U/t \rightarrow \infty$, electronic correlations localize the electrons on a single site driving the system into an insulating state. Therefore, a metal-to-insulator transition is expected as a function of U/t , from a classical metal ($U/t=0$) to a Mott insulator ($U/t \gg 1$). In the correlated regime, the low energy physics is dictated by the super-exchange $J \sim t^2/U$ rather than by the hopping process t alone, and the interaction is described by the Heisenberg Hamiltonian:

$$H = \sum_{ij} J_{ij} S_i S_j = \frac{4t^2}{U} S_i S_j \quad (1.6)$$

This Mott insulating state is well-understood and experimentally observed in strongly correlated $3d$ TMO ($U \sim 5 - 10$ eV). However, in the weakly correlated $4d$ and $5d$ ($U \sim 1 - 2$ eV) [14] compounds a metallic state is expected due to the delocalized nature of these orbitals. Nonetheless, experimental results on complex iridates and osmates have observed insulating behavior. The formation of the Mott gap in these systems is counter-intuitive since the large overlap of these orbitals gives rise to a large electronic bandwidth and should lead to an itinerant state. It is only thanks to SOC that the effective bandwidth is reduced to a level where the weak electronic correlations can still drive the system into a Mott insulating state. In other words, U and λ_{SO} cooperate rather than compete in the iridate systems to form a " $\mathcal{J} = 1/2$ spin-orbit assisted Mott insulator" [15, 3].

Hund's Coupling: J_H

Hund's coupling is the energy scale associated with the intra-atomic exchange which lowers the cost of Coulomb repulsion when placing two electrons with parallel spins in different orbitals, as opposed to two electrons with in the same orbital [16].

Hund's rules specify the ground-state configuration of multi-electron atomic shells. For N electrons in an orbital with degeneracy $2L + 1$, the rules dictate:

1. First, the states are occupied to maximize the total spin S , meaning maximum electrons have their spins aligned. Electrons with parallel spins avoid each other which reduces the Coulomb repulsion. Hence the ground state of an incomplete shell in a free atom is that of a maximum spin.

2. Given S , the states are occupied to maximize the value of L , which means the subshells with maximum $|L|$ are preferential.
3. Finally, the total angular momentum J is obtained by combining L and S depending on the level the shell is filled:
 - less than half-filled, $J = |L - S|$
 - more than half-full, $J = |L + S|$
 - $L = 0$ and $J = S$ if exactly half-full

Typically, Ir^{+4} ions have $J_H \sim 0.2$ eV. Therefore, an octahedral environment results on a low-spin configuration since the crystal field energy is much stronger ($\Delta_{CEF} \gg J_H$). As we will see in the next section, the relevant spin interaction term between these $\mathcal{J} = 1/2$ isospins is strongly dependent on Hund's coupling.

The $\mathcal{J}$

$=1/2 \text{ state}$

In previous sections I described how a $\mathcal{J} = 1/2$ insulating pseudo-spin state arises in materials with a d^5 valency thanks to the combined influence of $\Delta_{CEF} \sim 2 - 3$ eV, $\lambda_{SO} \sim 0.5$ eV, $U \sim 1 - 2$ eV and $J_H \sim 0.2$ eV. This is best described by the Hamiltonian $H = H_o + H_\Delta + H_\lambda + H_U + H_{J_H}$, where H_o represents the spherically symmetric interaction, H_Δ is the crystal field effect, H_λ is the spin-orbit coupling, H_U is the Coulomb interaction and H_{J_H} is the Hund's coupling term.

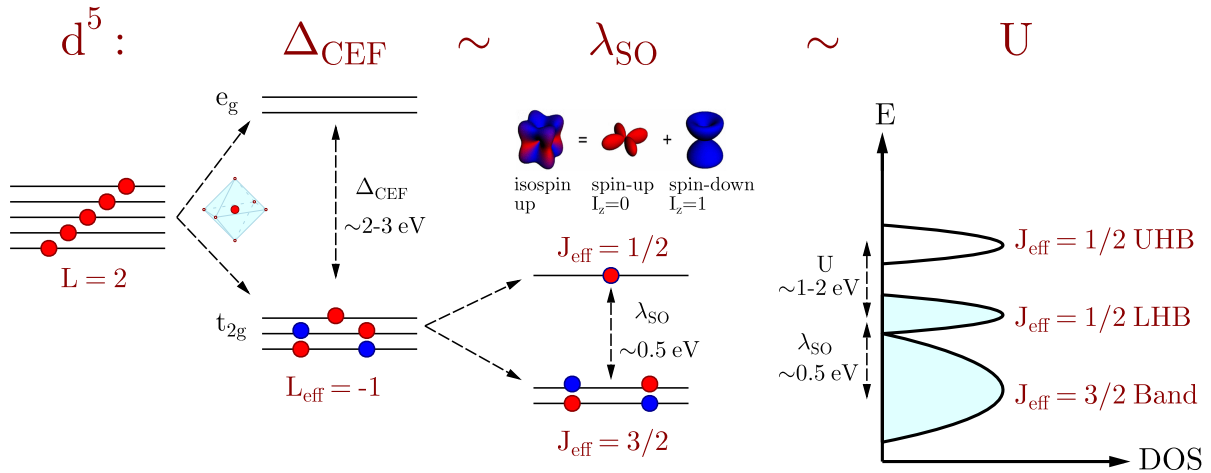


Figure 1.1: Formation of a spin-orbit entangled $\mathcal{J} = 1/2$ moment for ions in a d^5 electronic configuration thanks to the combined influence of $\Delta_{CEF} \sim 2 - 3$ eV, $\lambda_{SO} \sim 0.5$ eV and $U \sim 1 - 2$ eV.

The formation of such an insulating state was first observed on the layered perovskite Sr_2IrO_4 [17], and subsequently found on many others: $\text{Sr}_3\text{Ir}_2\text{O}_7$ [18], Ba_2IrO_4 [19], Na_2IrO_3 [20], etc. The SO assisted Mott insulator model was first proposed by B.J. Kim based on spectroscopic measurement on Sr_2IrO_4 [15]. The pure $\mathcal{J}$ state described by equation. 1.4, however, is only realized in perfect cubic symmetry. Tetragonal or trigonal distortions typical of octahedral environments can significantly change, or even destroy, the $\mathcal{J}$ state.

1.2 Bond Directional Interactions

These $\mathcal{J} = 1/2$ isospins are fundamentally different from pure $S = 1/2$ spins due to the admixture of spatially anisotropic orbitals. The interactions between them is best described by the multiorbital Hamiltonian [21]:

$$H = \sum_{\langle i,j \rangle, \sigma} t_{ij} (a_{i\sigma}^\dagger a_{j\sigma} + a_{j\sigma}^\dagger a_{i\sigma}) + \sum_i \left[\left(\frac{U - 3J_H}{2} \right) (n_i - 5)^2 - \lambda_{SO} S_i \cdot L_i - 2J_H S_i^2 - \frac{J_H}{2} L_i^2 \right] \quad (1.7)$$

where the hopping amplitudes (t_{ij}) have contributions from direct $d-d$ overlap, as well as processes through the intermediate oxygen atoms. Treating the kinetic term as a perturbation yields the complete spin Hamiltonian:

$$H = \sum_{ij} [J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j + \mathbf{D}_{ij} \cdot (\mathbf{S}_i \times \mathbf{S}_j) + \mathbf{S}_i \cdot \boldsymbol{\Gamma}_{ij} \cdot \mathbf{S}_j] \quad (1.8)$$

where J_{ij} is the isotropic Heisenberg coupling, $\mathbf{D}_{ij}$ is the Dzyaloshinskii-Moriya (DM) anti-symmetric vector, and $\boldsymbol{\Gamma}_{ij}$ is the symmetric pseudo-dipolar tensor [11]¹. The DM term favors spin canting of otherwise aligned magnetic moments, and it vanishes for inversion-symmetric bonds. Since $\boldsymbol{\Gamma}_{ij} \propto \mathbf{D}_{ij} \times \mathbf{D}_{ij}$, the $\boldsymbol{\Gamma}_{ij}$ term tends to be small when $D_{ij} \rightarrow 0$. This implies that inversion-symmetric bonds are typically dominated by the isotropic Heisenberg term $J_{ij} \sim t^2/U$, for both weak and strong SOC limits, unless special circumstances are achieved.

For d^5 filling, spin-orbit entanglement transfers the bond-directional nature of orbitals into that of pseudospins. The microscopic origin of such bond-directional interactions was worked out in pioneering work by Khaliullin [22] and later Jackeli and Khaliullin [23], in which two common cases of TM-O-TM bond geometries were studied: (A) 180°-bond formed by corner-sharing octahedra, and (B) 90°-bond formed by edge-shared ones (Figure 1.2).

(A) 180°-bond: This bonding geometry is found in perovskite Sr_2IrO_4 . The coupling between neighboring Ir ions have a single Ir-O-Ir exchange path and it is predominantly

¹Another way of thinking of this is that isotropic Heisenberg magnetism has $L = 0$ symmetry, DM has $L = 1$ symmetry, and Gamma has $L = 2$ symmetry.

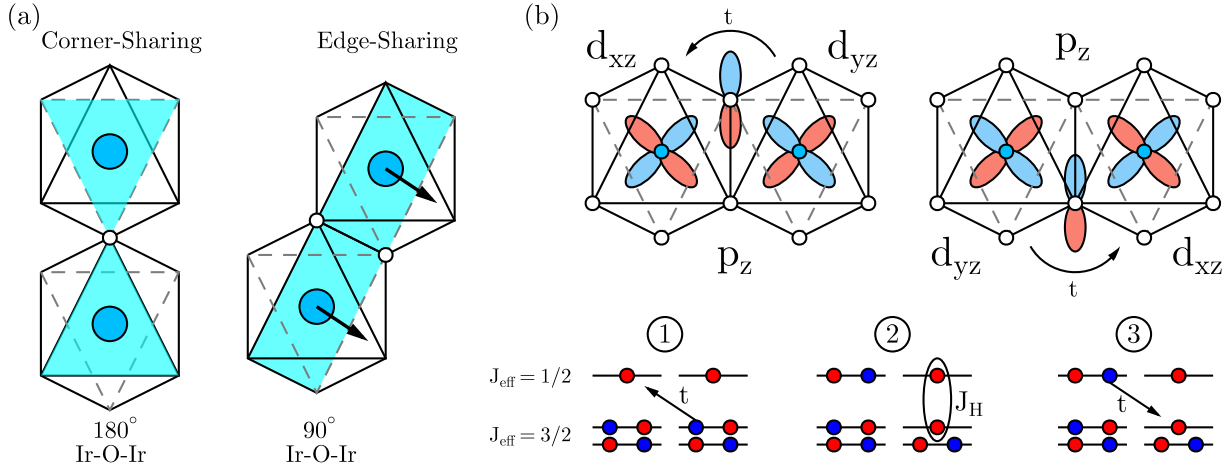


Figure 1.2: (a) Ir-O-Ir bond geometries: 180°-bond formed by corner-sharing octahedra (Sr_2IrO_4), and 90°-bond formed by edge-shared octahedra (A_2IrO_3). (b) Hopping paths in the idealized edge-sharing geometry and schematics of the virtual process that leads to the emergence of the bond directional Kitaev interactions [11].

described, despite the presence of strong SOC, by a symmetric Heisenberg exchange with a weak pseudo-dipolar anisotropic term [24]:

$$H_{ij} = J_1 \mathbf{S}_i \cdot \mathbf{S}_j + J_2 (\mathbf{S}_i \cdot \mathbf{r}_{ij})(\mathbf{r}_{ij} \cdot \mathbf{S}_j) \quad (1.9)$$

where $\mathbf{r}_{ij}$ is the unit vector along the ij bond, $S_{i,j}$ represent the entangled isospins ($\mathcal{J} = 1/2$), not to be confused with $J_{1(2)}$ coupling representing isotropic (anisotropic) interactions. The anisotropic term is controlled by J_H/U , the ratio of Hund's coupling and Coulomb repulsion. Therefore, in the strong SOC limit, magnetic interactions are governed by a nearly Heisenberg model (just as in the small SOC limit), and its anisotropy is entirely due to Hund's coupling (unlike conventional situations where J_H is unimportant).

(B) 90°-bond: This bonding geometry is found in the honeycomb $(\text{Na/Li})_2\text{IrO}_3$. The coupling between neighboring Ir ions have two Ir-O-Ir exchange path via upper and lower oxygen. Their transfer amplitudes destructively interference such that the symmetric Heisenberg exchange exactly vanishes and a finite anisotropic interactions appears due to the J_H multiplet of the excited states. In order words, all leading order contributions $\sim t^2/U$ vanish, and the only non-zero component of Γ_{ij} arises from higher order effects $\sim t^2 J_H/U^2$.

This can be seen if you consider the hopping between Ir sites occurring only via hybridization with the oxygen p -orbital. As seen in Figure 1.2a there are only two active orbital on a given bond. Hopping of holes between $\mathcal{J} = 1/2$ states vanishes, while the only relevant hopping takes a hole from a $\mathcal{J} = 1/2$ to an $m_j = \pm 3/2$ component of the

$\mathcal{J} = 3/2$ state on an adjacent site.

$$\begin{aligned}
& \left\langle \frac{1}{2}, -\frac{1}{2} \left| \hat{T}_{yz} p_{\uparrow}^z \right. \right\rangle \left\langle p_{\uparrow}^z \hat{T}_{zx} \left| \frac{1}{2}, -\frac{1}{2} \right. \right\rangle - \left\langle \frac{1}{2}, -\frac{1}{2} \left| \hat{T}_{xz} p_{\uparrow}^z \right. \right\rangle \left\langle p_{\uparrow}^z \hat{T}_{yz} \left| \frac{1}{2}, -\frac{1}{2} \right. \right\rangle \\
& \quad = -\frac{i}{3}t^2 + \frac{i}{3}t^2 = 0 \\
& \left\langle \frac{1}{2}, -\frac{1}{2} \left| \hat{T}_{yz} p_{\uparrow}^z \right. \right\rangle \left\langle p_{\uparrow}^z \hat{T}_{zx} \left| \frac{3}{2}, \frac{3}{2} \right. \right\rangle - \left\langle \frac{3}{2}, \frac{3}{2} \left| \hat{T}_{xz} p_{\uparrow}^z \right. \right\rangle \left\langle p_{\uparrow}^z \hat{T}_{yz} \left| \frac{1}{2}, \frac{3}{2} \right. \right\rangle \\
& \quad = -\frac{i}{\sqrt{6}}t^2 - \frac{i}{\sqrt{6}}t^2 = -\frac{2i}{\sqrt{6}}t^2
\end{aligned}$$

In such a virtual configuration, with two holes on a given site, Hund's coupling acts between the $\mathcal{J} = 1/2$ and the excited $\mathcal{J} = 3/2$ moments, ultimately generating ferromagnetic interactions in the ground state. Most importantly, since only the excited $m_j = \pm 3/2$ components contribute, the magnetic interactions depend on the spatial orientation of a given bond ij laying on the $\alpha\beta$ plane, and the magnetic easy-axis $\gamma = x, y, z$ is perpendicular to the plane of the bond. The strength of this bond-directional interaction can be described by the Hamiltonian² [25]:

$$H_{ij}^{\gamma} = -K_{\gamma} S_i^{\gamma} S_j^{\gamma} = -\frac{8t^2 J_H}{3U^2} S_i^{\gamma} S_j^{\gamma} \quad (1.10)$$

where t is the effective inter-orbital hopping mediated by the oxygen ions, J_H is the Hund's coupling and U is the electronic correlations. This bond-directional interaction leads to strong exchange frustration in a honeycomb lattice, as described by the Kitaev honeycomb model, which in turn leads to a spin liquid phase.

1.3 Kitaev Honeycomb Model

The Kitaev model [26] belongs to a larger class of so-called quantum compass Hamiltonian, in which the spin-spin interactions along each bond are highly anisotropic and depend on the spatial orientation of the bond. The model consists of a honeycomb lattice with SU(2) spins sitting on each of its vertices, and three different flavours of bonds emerging from each of these sites (see Figure 1.3(a,b)). This lattice consists of two simple sub-lattices, referred to as 'even' and 'odd', and three types of links: 'x,y,z-links'. These bonds host orthogonal Ising-like interactions which can be described using the spin operators S_i^{γ} where $\gamma = \{x, y, z\}$, i indexes the site, and K_{γ} is the spin coupling along a specific bond direction:

$$\begin{aligned}
H_K &= -K_{\gamma} \sum_{\langle ij \rangle} S_i^{\gamma} S_j^{\gamma} \\
&= -K_x \sum_{x\text{-link}} S_i^x S_j^x - K_y \sum_{y\text{-link}} S_i^y S_j^y - K_z \sum_{z\text{-link}} S_i^z S_j^z
\end{aligned} \quad (1.11)$$

²In fact, other terms are also possible in the hopping mechanism. For more details, see ref. [11]

This is a rare microscopic model that can be exactly solve by representing the spin operators in terms of Majorana particle operators (Figure 1.3 (c), so that the Hamiltonian reduces to a model of non-interacting Majorana fermions coupled to a static Z_2 gauge field. The solution to such model is a quantum spin liquid (QSL): a strongly correlated magnetic phase characterized by (1) the absence of spontaneous symmetry breaking, (2) the absence of long-range magnetic order, (3) the existence of long-range entanglement, and (4) the existence of fractionalized excitation and/or emergent gauge fields [27, 28]. Only nearest neighbors spin-spin correlations survive with gapless or gapped phases defined by the ratio of the Kitaev spin couplings.

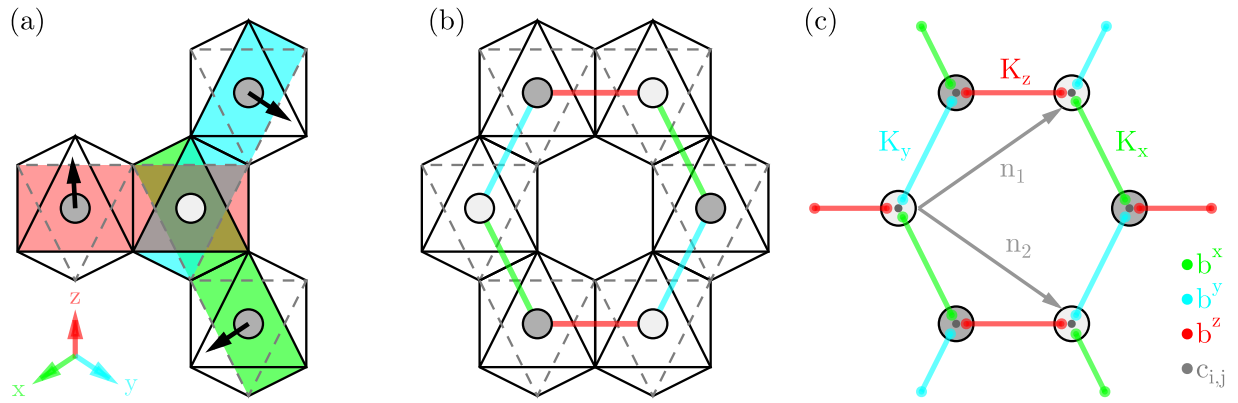


Figure 1.3: (a) The Kitaev model's building-block is composed of four edge-sharing octahedra. Bond-directional coupling between each pair of neighboring octahedra create three orthogonal planes of interactions which can not be simultaneously satisfied giving rise to exchange frustration. (b) Honeycomb lattice with bond-directional couplings K_x, K_y, K_z can be analytically solved. (c) Each Ir isospin site can be represented in terms of four Majorana particles (b^x, b^y, b^z, c_{ij}).

Conservation Laws

The analytical solution of this Hamiltonian is only possible because of an infinite number of conserved quantities associated with the loops (plaquettes) of the lattices. Kitaev showed that all terms on the Hamiltonian commute with the flux operator $\hat{W}_p = 2^6 S_1^x S_2^y S_3^z S_4^x S_5^y S_6^z = \prod_{i=1}^6 S_i^\gamma S_{i+1}^\gamma$, where p denotes the plaquette (hexagons) and 1...6 label the sites on each plaquette. Since $\hat{W}_p^2 = 1$, its eigenvalues are ± 1 . Furthermore, the loop operators commute with each other and with the Hamiltonian ($[\hat{W}_p, \hat{W}_p'] = [H_K, \hat{W}_p] = 0$); however, it does not commute with the local spin operators ($[S_i, \hat{W}_p] \neq 0$). As a consequence, the Hilbert space decomposes into subspaces (one for each flux configuration) and restricts the problem to a single flux sector [27].

Solution and Excitations

An exact solution of this model can be obtained through direct mapping of the Pauli spins operators $\{S^x, S^y, S^z\}$ to four types of Majorana operators $\{b_i^x, b_i^y, b_i^z, c_i\}$ (see Figure 1.3(c) so that:

$$\begin{aligned} b^x &= a_\uparrow + a_\downarrow^\dagger & S^x &= \frac{i}{2} b^x c \\ b^y &= -i(a_\uparrow - a_\downarrow^\dagger) & S^y &= \frac{i}{2} b^y c \\ b^z &= a_\downarrow + a_\uparrow^\dagger & S^z &= \frac{i}{2} b^z c \\ c &= -i(a_\downarrow - a_\uparrow^\dagger) \end{aligned}$$

and $(a/a^\dagger)_\uparrow$ are the fermion creation/annihilation operators, which leads to a representation defined by the configuration of “flux” variables $\hat{u}_{jk} = ib_j^\gamma b_k^\gamma$ (also Z_2 gauge field or bond operator) and “matter” fermions c_j :

$$H = \frac{i}{4} \sum_{\langle jk \rangle} \hat{A}_{jk} c_j c_k \quad (1.12)$$

$$\hat{A}_{jk} = \begin{cases} 2K_\gamma \hat{u}_{jk} & \text{if } (j, k) \text{ are connected} \\ 0 & \text{otherwise} \end{cases}$$

The b^γ fermions are completely local entities, since bonds of any given type are disconnected from other bonds of the same type. Therefore, the bond operators $\hat{u}_{jk}$ are a constant of motion with eigenvalues ± 1 . The plaquette operator becomes $\hat{W}_p = u_{21}u_{23}u_{43}u_{45}u_{65}u_{61}$ such that each plaquette has a flux degree of freedom. The configuration $W_p = +1$ is called flux-free and $W_p = -1$ has flux. The flux can be thought of as artificial magnetic field through the plaquette.

The most interesting choice is the one that minimizes the ground state energy (flux-free condition with $W_p = +1$ on each hexagon); thus we assume their self-consistently determined expectation values $u_{jk} = +1$ for all links (j, k) (a procedure Kitaev called “removing hats”) where j belongs to the even sub-lattice, and k belongs to the odd sub-lattice. Since W_p does not commute with the local spin operators, this “flux-ordered” ground state cannot exhibit any long range spin order, and instead is a Z_2 spin-liquid with only short-range nearest neighbors spin-spin correlations [11].

This flux-free configuration preserves translational symmetry so that the resulting quadratic Hamiltonian can be exactly diagonalized using Fourier transform. Let’s represent the site j as (s, λ) where s refers to the unit cell and λ to the position type inside the

cell.

$$\begin{aligned}
 H &= \frac{i}{4} \sum_{s,\lambda,t,u} A_{s,\lambda,t,u} c_{s,\lambda} c_{t,u} \\
 H_q &= \frac{1}{2} \sum_{\mathbf{q},\lambda,u} (i\tilde{A}_{\mathbf{q},\lambda,u}) a_{-\mathbf{q},\lambda} a_{\mathbf{q},u}
 \end{aligned} \tag{1.13}$$

The energy spectrum $\epsilon_{\mathbf{q}}$ is given by the eigenvalues of the matrix $i\tilde{A}_{\mathbf{q}}$. In the $(\mathbf{n}_1, \mathbf{n}_2)$ basis, we obtain $\epsilon_{\mathbf{q}} = \pm |f_{\mathbf{q}}|$ since:

$$\begin{aligned}
 i\tilde{A}_{\mathbf{q}} &= \begin{pmatrix} 0 & if_{\mathbf{q}} \\ -if_{\mathbf{q}}^* & 0 \end{pmatrix} \\
 f_{\mathbf{q}} &= 2(K_x e^{i\mathbf{q} \cdot \mathbf{n}_1} + K_y e^{i\mathbf{q} \cdot \mathbf{n}_2} + K_z)
 \end{aligned} \tag{1.14}$$

where $\mathbf{n}_1 = (1/2, \sqrt{3}/2)$ and $\mathbf{n}_2 = (-1/2, \sqrt{3}/2)$ in the standard xy -coordinates.

The Hamiltonian in equation 1.13 is similar to the p-wave BCS mean-field Hamiltonian describing superconductivity in the square lattice. The ground state is fermion free $a_{\mathbf{q}} |0\rangle = 0$ with ground-state energy depending on the anisotropy of the Kitaev couplings. The excitations, on the other hand, are matter fermions $a_{\mathbf{q}}^\dagger$ with dispersion given by $E_{\mathbf{q}}$. It is easy to verify that if the magnitude of any coupling is greater than the sum of the other two ($|K_i| \geq |K_j| + |K_k|$), then the quasi-particle spectrum is gapped.

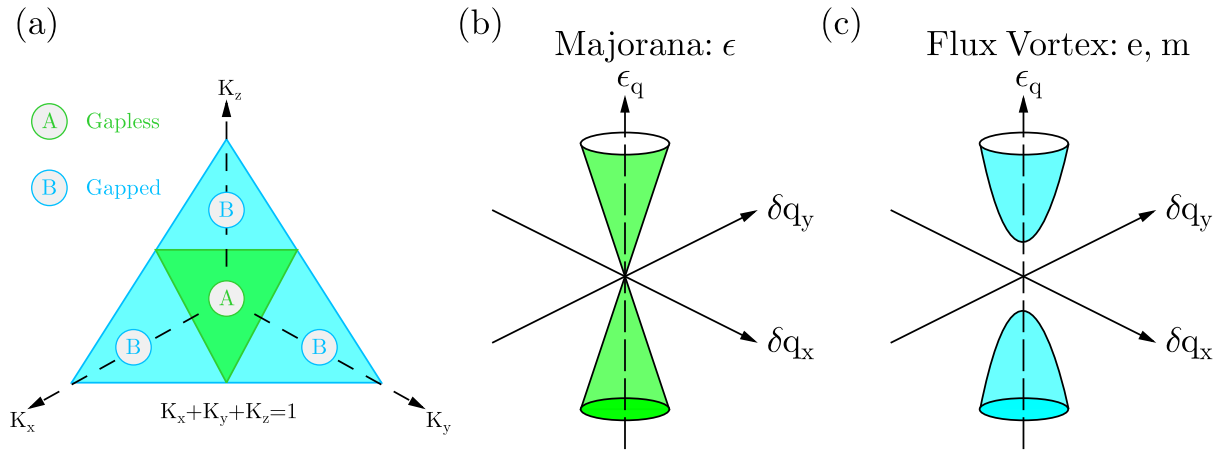


Figure 1.4: (a) Phase diagram of the Kitaev model defined in the parameter space by the triangular equality $K_x + K_y + K_z = 1$. Depending on the coupling anisotropy, the matter fermion excitations can be either: (b) gapless or (c) gapped phases.

Let's consider the plane defined by $K_x + K_y + K_z = 1$ in the parameter space, with $K_{x,y,z} \geq 0$. In this region, a gapless phase can be found if and only if the equation

$K_x e^{i\mathbf{q}\cdot\mathbf{n}_1} + K_y e^{i\mathbf{q}\cdot\mathbf{n}_2} + K_z = 0$ satisfy the triangular inequalities:

$$|K_x| \leq |K_y| + |K_z|, \quad |K_y| \leq |K_x| + |K_z|, \quad |K_z| \leq |K_x| + |K_y|$$

Therefore, we define a phase diagram with one gapless phase A and three symmetry-related gapped phases B. In phase A, the Majorana fermions (ϵ) remain itinerant and form a gapless state with a Dirac cone dispersion around the point of equal coupling (Figure 1.4 (b)). If one of the coupling dominates, the system undergoes a phase transition into a gapped spin liquid phase B with flux excitations. This latter state exhibit a static Z_2 gauge field which orders at zero temperature and has massive elementary excitations called vison (e, m) (Figure 1.4 (c)).

Gapless QSL

In the gapless phase, there are exactly two real, inequivalent momenta with zero energy: $\mathbf{q} = \pm\mathbf{q}^*$. If we represent the momentum space by the parallelogram spanned by $(\mathbf{q}_1, \mathbf{q}_2)$, the basis dual to $(\mathbf{n}_1, \mathbf{n}_2)$, then $\mathbf{q}^* = 1/3 \mathbf{q}_1 + 2/3 \mathbf{q}_2$ and $-\mathbf{q}^* = 2/3 \mathbf{q}_1 + 1/3 \mathbf{q}_2$. In the symmetric case ($K_x = K_y = K_z$) the solutions are given by:

$$\epsilon_{\mathbf{q}} \approx \pm \sqrt{\delta q_x^2 + \delta q_y^2} \quad (1.15)$$

Therefore, the spectrum has conic singularities at $\pm\mathbf{q}^*$ (see Figure 1.4 (b)). As the anisotropy of the coupling constants increases, the two Dirac points veer towards one another until they merge at the boundary between the gapless and gapped phases. In the gapped phase there are no real vector $\mathbf{q}$ for which $\epsilon_{\mathbf{q}} = 0$.

It turns out that the application of a magnetic field h along the 111- direction results on an even more exotic spin liquid with non-Abelian topological order. The gap is of the form $\Delta = h_x h_y h_z / K^2$, where $K = K_{x,y,z}$ has been assumed for simplicity, and $\epsilon_{\mathbf{q}} \approx \pm \sqrt{\delta q_x^2 + \delta q_y^2 + \Delta^2}$. This state is identical to that of the $p_x + ip_y$ superconductor [29], the Moore-Read $\nu = 5/2$ fractional quantum Hall state [30], and other systems of interest for fault-tolerant topological quantum computing.

Gapped QSL

In the gapped phase, one coupling constant dominates such that the Hamiltonian can be solved using perturbation theory to find that the excitation gap is of the form $\Delta = K_x^2 K_y^2 / (16|K_z|^3)$ [31].

In this phase, spin correlations decay exponentially with distance, therefore, spatially separated quasiparticle cannot interact directly. Nonetheless, they interact topologically if they move around each other. In this case, the particles excitations, or *superselection sectors* are: vacuum (1), bosonic electric charge (e), bosonic magnetic vortex (m) and fermionic Majorana particles ($\epsilon = e \times m$). These excitations exhibit Abelian (Z_2) topological order and macroscopic entanglement similar to the toric model [31]. The e -particles

and m -particles are vortices with the same energy that live on alternating rows of hexagons, yet they cannot be transformed into one another without creating or destroying a fermion.

1.4 Realization of Kitaev Model

The 2D Kitaev honeycomb model studied thus far does not exhibit a finite-temperature phase transition, but instead undergoes a thermal crossover into an infinitely degenerate spin liquid phase at $T = 0$. A 3D extension of the Kitaev model is defined on the hyper-honeycomb and harmonic honeycomb lattices which will be discussed in the next chapter [32, 33]. Many fundamental aspects in the 3D Kitaev model are inherited from the original 2D one, including the exact solvability and the ground state phase diagram. However, a finite temperature phase transition into the QSL state is anticipated in the 3D lattices [34]. The fractionalization of spins into Majorana fermions is not just a mathematical tool but physically important in the Kitaev model. Since the isospin $1/2$ fractionalizes into four Majorana fermions: three of them form localized bond fluxes and the fourth one forms itinerant Majorana bands which determine the excitation spectrum, a material realization of this model could lead to the experimental discovery of Majorana fermions and offer a way to directly probe the underlying Z_2 gauge field.

Thermal fractionalization

Most recently, experimental and theoretical work have started to shed a light as to how the high temperature paramagnetic spins with magnetic entropy $S_m = R \ln 2$, fractionalize into Majorana fermions upon cooling [35, 34]. Nevertheless, the relevance of fractionalization to the experimentally observable quantities remains a topic of debate. To study this thermal fractionalization of the quantum spin, the partition function is found:

$$Z = \text{Tr}_{u_{ij}} \text{Tr}_{c_i} e^{\hat{H}_K / \beta}$$

where $\text{Tr}_{u_{ij}}$ and Tr_{c_i} are the traces for localized and itinerant Majorana fermions, $\hat{H}_K$ is the Kitaev Hamiltonian operator in equation. 1.12 and $\beta = 1/k_B T$ is the temperature. Using this partition function, other thermodynamic quantities can be obtained such as heat capacity and entropy:

$$C_v = \frac{1}{NT^2} \left(\langle \epsilon^2 \rangle - \langle \epsilon \rangle^2 - \left\langle \frac{\partial \epsilon}{\partial \beta} \right\rangle \right)$$

$$S = \ln 2 - \int_T^{T_m} \frac{C_v}{T} dT$$

where ϵ is the energy of the itinerant Majorana fermions. These calculations showed that localized and itinerant Majoranas release their entropy at two well-separated temperature scales, with each crossover having an impact on the experimental observables like

heat capacity or thermal conductivity. Itinerant Majoranas release $1/2R \ln 2$ at $T_H \sim K$, marking the development of spin correlations between nearest neighboring sites. Above this temperature, the system obeys Curie behavior, however, below T_H the spin correlations show deviations from Curie behavior and quickly saturates to the expected ground state value [36]. Localized Majoranas release the other $1/2R \ln 2$ at $T_L \sim K/100$ when the Z_2 fluxes freeze and a QSL is obtained. Therefore, the paramagnetic spin fractionalizes at T_H but the QSL state is not obtained until T_L is reached. These crossover temperatures, therefore, define three very different regions shown in Figure 1.5 (b):

- $T > T_H$: The high-temperature paramagnetic (PM) region, where the magnetic susceptibility obeys Curie-Weiss behavior.
- $T_H > T > T_L$: The correlated paramagnetic region, where the magnetic susceptibility strongly deviates from Curie-Weiss, the magnetic specific heat is linear in temperature ($\sim T$) and the transport of Majorana fermions is completely coherent, although the Z_2 fluxes are thermally disordered.
- $T < T_L$: The QSL region where the flux excitations ($W_p = -1$) freeze until a coherent flux-free ground state ($W_p = +1$) is reached. In this QSL region, the heat capacity has a quadratic temperature dependence ($\sim T^2$).

Other Interaction Terms

This model is only applicable under very special circumstances. For a pair of ideal edge-shared octahedra, the bond symmetry allows two additional terms [37, 21] and the anisotropic magnetic interactions between sites i and j can be described more generally by the JKT Hamiltonian³ [39]:

$$\begin{aligned}
 H &= \sum_{ij} \left[J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j + K_{ij} S_i^\gamma S_j^\gamma + \Gamma_{ij} (S_i^\alpha S_j^\beta + S_i^\beta S_j^\alpha) \right] \\
 &= \sum_{ij} [J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j + K_{ij} (\mathbf{S}_i \cdot \boldsymbol{\gamma}_{ij})(\mathbf{S}_j \cdot \boldsymbol{\gamma}_{ij}) + \Gamma_{ij} \{(\mathbf{S}_i \cdot \boldsymbol{\alpha}_{ij})(\mathbf{S}_j \cdot \boldsymbol{\beta}_{ij}) + (\mathbf{S}_i \cdot \boldsymbol{\beta}_{ij})(\mathbf{S}_j \cdot \boldsymbol{\alpha}_{ij})\}]
 \end{aligned} \tag{1.16}$$

where $\alpha, \beta \perp \gamma$ and $\boldsymbol{\gamma}_{ij} \propto \hat{r}_{Ir-O_1} \times \hat{r}_{Ir-O_2}$ [24]. These unit vectors emphasize that only a particular component of the total spin contributes to the anisotropic interaction. The isotropic Heisenberg coupling J describes the strength of the direct Ir–Ir interaction, while the bond-directional couplings K, Γ represent indirect exchange through the oxygen ligands. The symmetric off-diagonal exchange Γ couples the two orthogonal spin

³Another form of the Hamiltonian was described by Kimchi et. al. [38] where Γ is replaced in favor of a distinct Ising coupling of the spin components parallel to the bond orientation, I_c .

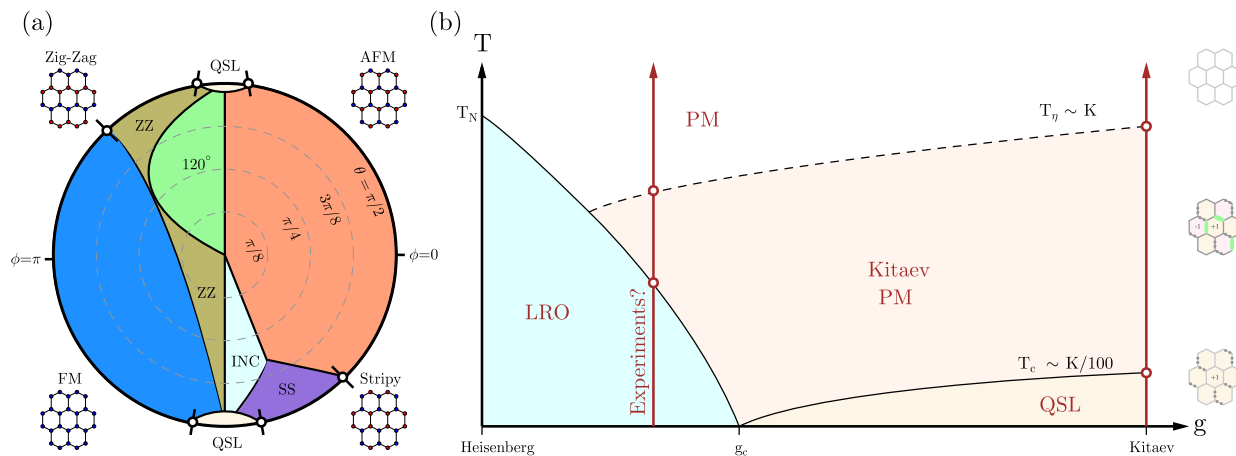


Figure 1.5: (a) Generic classical phase diagram of the JKT model defined in the parameter space θ and ϕ , where $(J, K, \Gamma) = (\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \phi)$ such that $g = \sqrt{J^2 + K^2 + \Gamma^2} = 1$. [37] Besides the quantum spin liquid phase (QSL), other magnetic states are possible depending on the relative ratio between the coupling constants. Most importantly, the zig-zag (ZZ) order found in Na_2IrO_3 and $\alpha\text{-RuCl}_3$, and the incommensurate spiral (INC) found in the $\alpha, \beta, \gamma\text{-Li}_2\text{IrO}_3$. (b) Temperature as a function of coupling constant g . In the purely Heisenberg limit, the disorder paramagnetic spins magnetically order at T_N . In the Kitaev limit, the paramagnetic spins fractionalize into itinerant and localized Majoranas at $T^* \sim K$. In the Kitaev paramagnet region, short-range nearest neighbor correlations develop thanks to the itinerant Majoranas, although the localized Majoranas form disordered fluxes. At T_C , flux excitations freeze and a coherent QSL state is observed.

components α, β for a Kitaev interaction along the γ direction. For lower symmetry local environments, further terms may be required to fully parameterize the interactions.

The spin Hamiltonian 1.16 hosts, in addition to the Kitaev QSL phase, a wealth of unusual magnetically ordered ground states. A generic classical phase diagram of this model is represented in Figure 1.5 (a) [37] where the exchange have been parameterized using angles θ and ϕ as $(J, K, \Gamma) = (\sin \theta \cos \phi, \sin \theta \sin \phi, \cos \phi)$ such that the energy scale was fixed by $\sqrt{J^2 + K^2 + \Gamma^2} = 1$. In the boundary, the off-diagonal term vanishes ($\Gamma = 0$) and the resulting Heisenberg-Kitaev model host four classical ground state phases: antiferromagnetic (AFM), zig-zag (ZZ), ferromagnetic (FM), and stripy (SS) [40, 41]. As the Γ interactions are turned on, other exotic phases appear: 120° order and incommensurate spiral order (INC) [37]. The resulting phase diagram of equation 1.16 has been extensively studied at the classical and quantum levels, both at zero and finite temperature, as well as finite magnetic field and pressure.

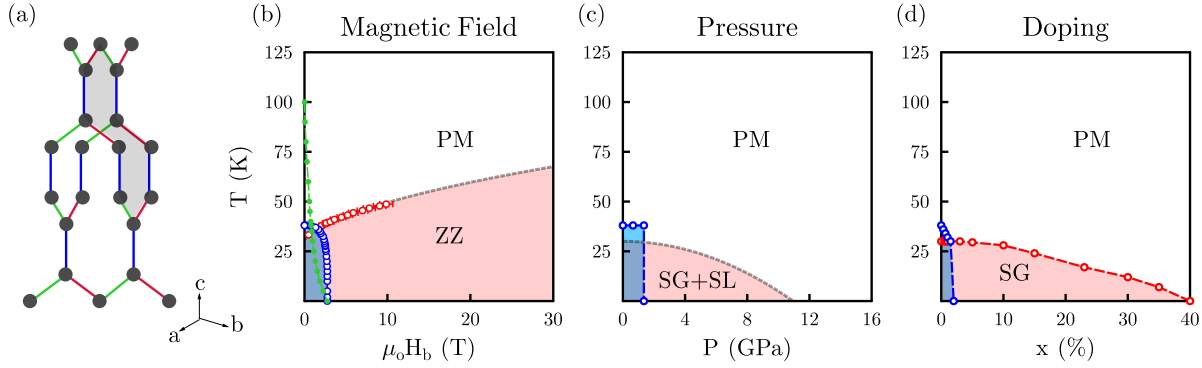


Figure 1.6: **Summary of the main results which will be presented in this dissertation for the three dimensional Kitaev materials β, γ - Li_2IrO_3 .** (b) Chapter 2,3,5 will study the effect of an applied magnetic field using magnetometry, heat capacity and resonant scattering techniques. (c) Chapter 6 will explore the consequences of applied hydrostatic pressure. (d) Chapter 7 will be devoted to the study of the effect of non-magnetic chemical substitution.

1.5 Thesis Overview

The material presented in this dissertation explores the main properties of the three dimensional Mott-Kitaev candidates β, γ - Li_2IrO_3 . The chapters follow a logical progression in the investigation of their structural and magnetic properties, under normal conditions, as well as external perturbations such as applied magnetic field, hydrostatic pressure and non-magnetic doping.

- **Chapter 1:** In this chapter, I discussed the theoretical background relevant to the physics of iridium ions in a cubic environment. In particular, we were interested in the interaction between different edge-sharing iridium octahedra and their possible connection to the Kitaev honeycomb model. We concluded with a complete description of this model's ground state, excitations as well as the expected behavior of different thermodynamic quantities.
- **Chapter 2:** In the following chapter, I will describe in details the synthesis procedure and the structural properties of these materials. I will also explore their highly anisotropic magnetic response in the high temperature paramagnetic region ($T > 100$ K) and the low temperature order state ($T < 38$ K). I will show that the high temperature anisotropy follows what is expected from the geometry of the local moments, while the low temperature response of the magnetically special $\hat{b}$ -axis reflects the bond-directional exchange anisotropy of the Kitaev type.
- **Chapter 3:** The subsequent chapter will be devoted to the study of their magnetic properties in the intermediate temperature region ($38 \text{ K} < T < 100 \text{ K}$). I will show

that a new phase transition with extraordinary magnetic anisotropy onsets at $T_\eta = 100$ K which may be a manifestation of the novel excitations proposed to exist in the Kitaev spin liquid (see figure 1.5(c)).

- **Chapter 4:** In this chapter I will briefly described the general formalism of the Resonant X-ray Scattering technique. I will show how the scattering cross-section is enhanced when the incident x-ray energy is tuned to an absorption transition energy. This will then allow us to investigate electronic orders which are otherwise undetectable. Moreover, I will show that for iridates in the dipole approximation, the magnetic scattering intensity depends on the polarization of the incoming and scattered x-ray beams as well as the magnetic moment.
- **Chapter 5:** In this chapter I will use resonant scattering to study the effect of an applied magnetic field along the magnetically special $\hat{b}$ -axis of β -Li₂IrO₃. I will show that the critical field H^* complete suppresses the low temperature incommensurate order, a direct measurement of the smallness of the Heisenberg term. I will also show that a commensurate zig-zag component growth with the applied magnetic field, and it is strongly intertwined with the INC order below H^* . The sum of the INC and COM intensities remains constant, and independent signature of the smallness of J .
- **Chapter 6:** The next chapter will track the evolution of the incommensurate order of γ -Li₂IrO₃ under an applied hydrostatic pressure. I will show that the INC order abruptly disappears at a critical pressure P_c , which provides strong evidence for the tunability of the exchange couplings.
- **Chapter 7:** This chapter will explore the effect of non-magnetic chemical substitution in the Ir site of β -Li₂IrO₃. I will shows that less than 2% Ru doping destroys the low temperature magnetic ground state and stabilizes a correlated spin glass state.
- **Chapter 8:** In the final chapter, I will summarize the main findings of this study and give some examples for possible future experiments.

The main experimental techniques used throughout this dissertation will be described as follows:

- **Magnetometry and Heat capacity:** Appendix C and Appendix D.
- **Torque:** Chapter 3.
- **Resonant Elastic/Inelastic x-ray Scattering:** Chapter 4.
- **Muon Spin Resonance and Energy dispersive x-ray Spectroscopy:** Chapter 7

Chapter 2

High and Low Temperatures Properties

The work described in this chapter has been published as Ref. [42].

The bond-directional interactions described by Jackeli and Khaliullin in 2009 [23], can be naturally found in the two-dimensional A_2MO_3 type compound, where octahedrally coordinated M^{+4} ions form honeycomb planes interleaved by A^+ ions. Therefore, they proposed that Kitaev physics could be studied by placing a spin 1/2 on the M site, such as in A_2IrO_3 compounds. The first of the iridium-based honeycomb systems to be studied in this context were the layered honeycomb materials α - Na_2IrO_3 and α - Li_2IrO_3 , both of which exhibit low temperature magnetic order. Single crystal measurements of α - Na_2IrO_3 have shown that this system orders in a zig-zag staggered structure [43, 44, 45, 46], where the moment is co-linear in the direction of the zig-zag honeycomb chains, but staggered between chains. Recent measurements of α - Li_2IrO_3 revealed a non-coplanar incommensurate magnetic order [47], where the Ir moments counter-rotate on next nearest-neighbor sites. Three-dimensional generalizations of the Kitaev model have been discovered, namely the γ - Li_2IrO_3 [32] and the β - Li_2IrO_3 [33] systems. Both crystallize with a similar orthorhombic structure and contain the same kind of structural building blocks - edge sharing IrO_6 octahedra, where the $\hat{c}$ -axis octahedra connect zig-zag diagonal chains that propagate in two directions, approximately 70° to each other (Figure 2.1 (a, b)). Alternating the number of these building blocks effectively changes the dimensionality of these materials[32]. These 3D systems also show long-range magnetic order at low temperatures [48, 49]. This suggests that there are non-Kitaev terms in the Hamiltonian, relieving the frustration and obscuring any low-energy signature of the Kitaev physics [38, 23, 39]. The relative strength and sign of the coupling constants (J, K, Γ) vary between the different Kitaev candidate materials. However, the Kitaev coupling is always found to be the dominant exchange with similar ratio $|K/J| \approx 4$ [25].

In this chapter, I will discuss the main thermodynamic properties of β, γ - Li_2IrO_3 in the high-temperature paramagnetic region and the low-temperature magnetic order state. I will particularly emphasize the differences in the anisotropic response in these regions, where the high-temperature susceptibility reflects the g-factor anisotropy, while the low-

temperature susceptibility has been attributed to the spin anisotropic Kitaev exchange. The properties of the correlated paramagnet region will be discussed in the following chapter.

2.1 Structural Characterization

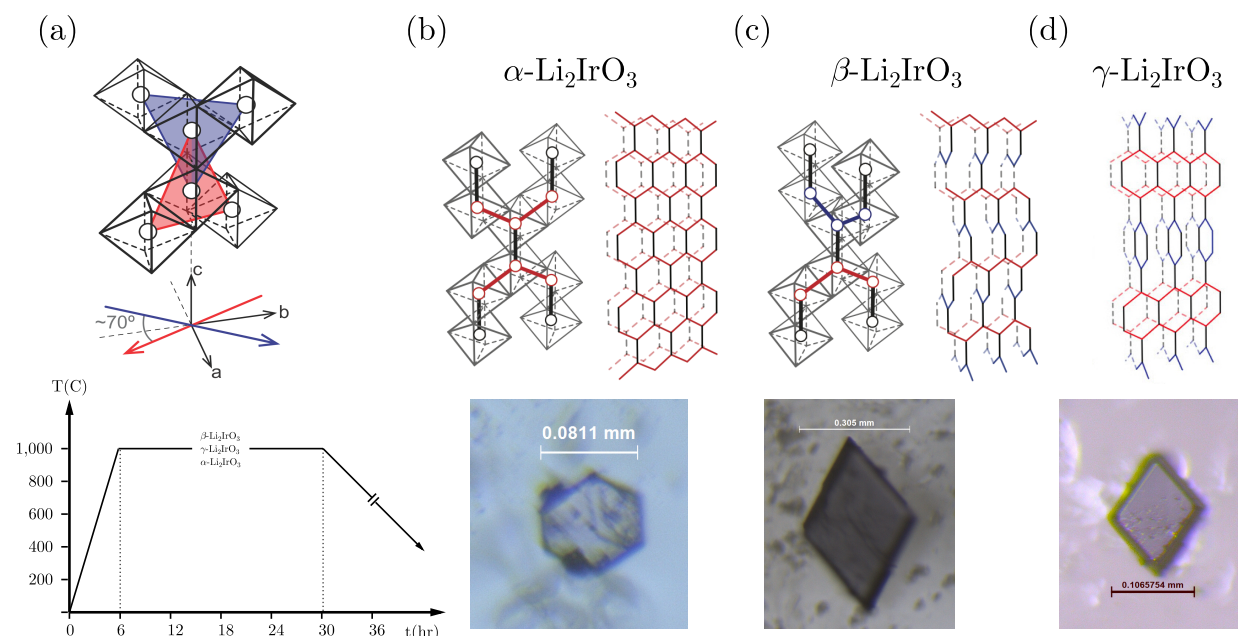


Figure 2.1: **Crystal structure and morphology of the Harmonic Honeycomb Family** α , β , γ - Li_2IrO_3 . (a) Each Ir moment is surrounded by one of two planar, triangular environments indicated by blue and red shaded triangles, located at either side of the $\hat{b}$ -axis. The two choices of edge shared bonds give rise to two kinds of links that are locally indistinguishable and define two bonding planes 70° apart. Links along the $\hat{c}$ -axis can either keep the same (S-links) or rotate (R-links) the honeycomb planes which gives rise to many structures. The known members of this family of compounds α , β , γ - Li_2IrO_3 (b, c, d) grow in a narrow margin of temperatures. Adapted from [32]

The structural building unit that supports Kitaev interactions in the honeycomb materials is doubly degenerate, and therefore, can be the basis for a family of structures henceforth called the *Harmonic Honeycomb Family* [32]. This structural degeneracy can be seen by defining a planar, triangular environment around each Ir atoms delimited by its three nearest Ir neighbors (Figure 2.1 (a)). This then allows two kinds of locally indistinguishable c -axis bonds, one that preserves the same orientation (S-link) as the previous honeycomb strip and one that rotates it (R-link) by $\phi \sim 70^\circ$. In the case that all

the bonds preserve the same plane, the resulting structure is the layered honeycomb system (α -Li₂IrO₃). If on the other hand, every honeycomb strip switches orientation, the hyper-honeycomb structure (β -Li₂IrO₃) is obtained. In this manner, further polytypes can be envisioned by tuning the vertical bonds (c-axis) of the honeycomb plane with different combinations of S- and R-links. This poses a way to tune the global dimensionality and alternate the symmetry of the materials that are otherwise locally indistinguishable. Finally, we note that S- and R-links differ in another important regard: S-links are inversion symmetric while R-links are not. For structures containing the latter, this may lead to magnetic components in the Hamiltonian that break inversion symmetry, for example the Dzyaloshinsky-Moriya term. Note this is a local property in that the total space group for the systems may remain inversion symmetric.

Material	Harmonic-Honeycomb #	Lattice Name	Dimensionality
α -Li ₂ IrO ₃	$N = \infty$	Honeycomb	2D
β -Li ₂ IrO ₃	$N = 0$	Hyper-honeycomb	3D
γ -Li ₂ IrO ₃	$N = 1$	Stripy-honeycomb	3D

Table 2.1: The *Harmonic Honeycomb Family* was defined by Modic et. al. [32] as ${}^{\mathcal{H}}\langle N \rangle$ -Li₂IrO₃ where ${}^{\mathcal{H}}\langle N \rangle$ refers to the number of complete honeycomb rows along the c -axis before rotation into the next configuration. The end members of this series are the 3D hyperhoneycomb structure with ${}^{\mathcal{H}}\langle 0 \rangle$ and 2D layered honeycomb with ${}^{\mathcal{H}}\langle \infty \rangle$ [50].

Synthesis of α , β , γ -Li₂IrO₃

Single crystals of Li₂IrO₃ were synthesized using an isothermal vapor transport technique. Ir (99.9% purity, BASF) and Li₂CO₃ (99.999 % purity, Alfa-Aesar) powders were ground in the molar ratio of 1:1.05 and pelletized at approximately 3000 psi. It is important to notice that the starting reagent must be very pure and finely grinded to maximize surface area during the reaction. For all synthesis, 5% excess Li₂CO₃ was added to compensate for the high-temperature lithium volatility [51]. The pellets were placed on a closed alumina crucible (Al₂O₃), reacted in air for 24 h, and then cooled-down to room temperature at 2 °C/h to yield single crystals of either β -Li₂IrO₃ or γ -Li₂IrO₃. The distinction between the growths is the dwelling temperature: reacting the pellet at 1,050 °C yields single crystals of β -Li₂IrO₃, while 1,000 °C yields γ -Li₂IrO₃.

The temperature gradient plays only a minor role in the process driving the crystal growth [52]. Instead, it is the formation of the crystals themselves that facilitates the transport by maintaining a concentration gradient. The single crystalline Li₂IrO₃ form

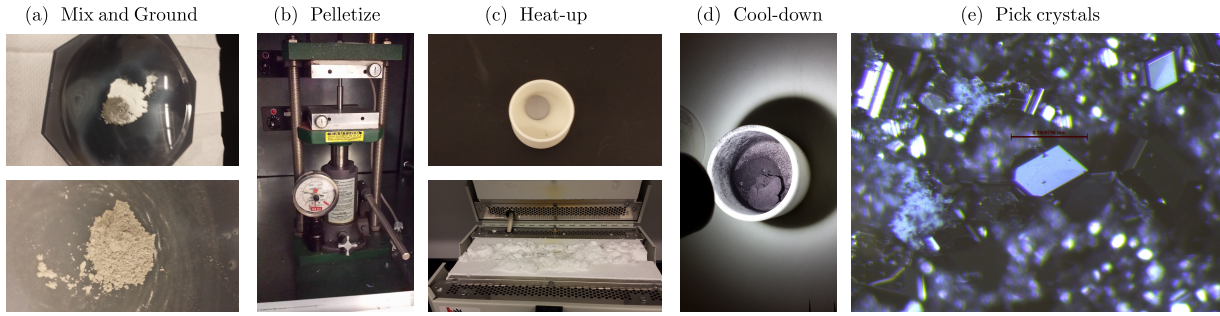
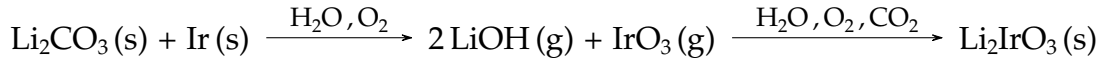


Figure 2.2: Pictures describing every step on the synthesis process of both β , γ - Li_2IrO_3 . The reagents are ground and pelletized before being reacted on an alumina crucible. After cool-down, single crystals can be pick up from the powder.

from gaseous LiOH and IrO_3 and the mechanism describing the transport process, can be summarized with the following equilibrium equation:



	α - Li_2IrO_3	β - Li_2IrO_3	γ - Li_2IrO_3
Space Group :	C2/m (#12)	Fddd (#70)	Cccm (#66)
Bravais lattice:	monoclinic	orthorhombic	orthorhombic
Z :	4	16	16
a (Å):	5.1633(2)	5.9101(1)	5.9119(3)
b (Å):	8.9294(3)	8.4622(1)	8.4461(5)
c (Å):	5.1219(2)	17.857(6)	17.8363(1)
α, β, γ (°) :	90, 109.759, 90	90, 90, 90	90, 90, 90
Volume (Å ³) :	222.24(1)	893.0(5)	890.6(1)
ρ (g/cm ³) :	7.594(4)	7.565(6)	7.578(8)

Table 2.2: Room Temperature Structural Parameters of α , β , γ - Li_2IrO_3 [32, 33, 42, 52].

Structural Properties

Both $\beta, \gamma\text{-Li}_2\text{IrO}_3$ form into a very similar diamond (rhombus) faceted crystals (Figure 2.1). These 3D structures, have local Ir-Ir bonds that are identical to the 2D honeycomb lattice, $\alpha\text{-Li}_2\text{IrO}_3$, in which each IrO_6 octahedron shares an edge with three neighboring octahedra, giving rise to three orthogonal Ir-O₂-Ir planes. The difference between the polymorphs arises because the Ir ions can form two types of links that are locally indistinguishable (S- and R-links). These two kinds of links are connected along the $\hat{c}$ -axis and define two bonding planes separated by $\sim 70^\circ$: one propagating along the $\hat{a} + \hat{b}$ and the other along the $\hat{a} - \hat{b}$ direction. Each $\hat{c}$ -axis bond can either preserve (S-link) or rotate (R-link) away from the previous bond, which results in a 3D network of Ir moments. $\alpha\text{-Li}_2\text{IrO}_3$ preserves all the same $\hat{c}$ -axis bond, $\beta\text{-Li}_2\text{IrO}_3$ rotates all nearest-neighbor, and $\gamma\text{-Li}_2\text{IrO}_3$ rotates all next nearest-neighbor $\hat{c}$ -axis bond.

The room temperature x-ray diffraction pattern for $\beta\text{-Li}_2\text{IrO}_3$ along 4 different planes is shown in Figure 2.3, and the structural parameters for all member of the Harmonic honeycomb family are listed in table ?? . Temperature dependent structural characterization of $\beta\text{-Li}_2\text{IrO}_3$ were performed at 90, 120, and 273 K through the SCrALS project (Service Crystallography at the Advanced Light Source) and no structural transition was observed.

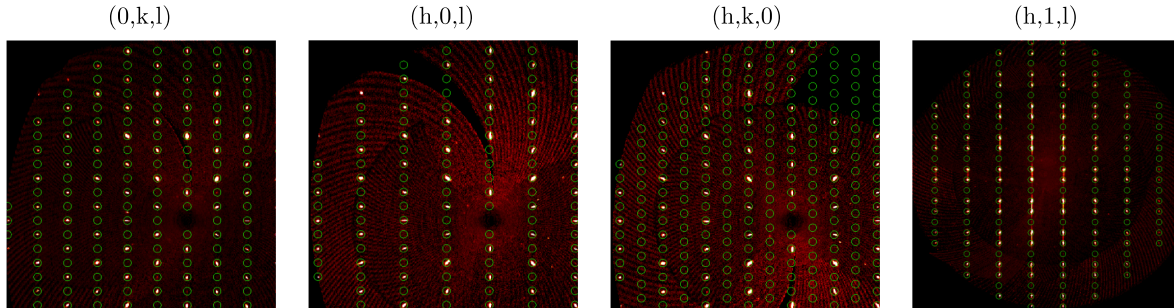


Figure 2.3: X-ray diffraction pattern of $\beta\text{-Li}_2\text{IrO}_3$ in the $(0, k, l)$, $(h, 0, l)$, $(h, k, 0)$ and $(h, 1, l)$ planes. The raw data (bright points) is well reproduced by the calculation (green circles) for the $Fddd$ structure.

The atomic fractional coordinates for these orthorhombic structures are listed in table 2.3. In $\beta\text{-Li}_2\text{IrO}_3$ iridium occupy a single crystallographic site while $\gamma\text{-Li}_2\text{IrO}_3$ has two iridium sublattices. These structures can be easily distinguish experimentally since they have different symmetries, and as a consequence, different diffraction patterns. The allowed structural reflections listed in table 2.3 demonstrate that the $Fddd$ space group (lower-symmetry structure) has a much more restricted selection rule compared to $Cccm$. For example, in the $(hk0)$ plane $h + k$ is required to be a multiple of 4 and both h and k to be even, as opposed to the less restrictive $h + k$ even for $Cccm$. In addition to sharp Bragg

$\beta\text{-Li}_2\text{IrO}_3$					$\gamma\text{-Li}_2\text{IrO}_3$			
Atom	site	x	y	z	site	x	y	z
Ir1	16g	1/8	1/8	0.7085(4)	8k	1/4	1/4	0.0836(2)
Ir2	-	-	-	-	8i	1/2	1/2	0.1670(3)
Li1	16g	1/8	1/8	0.04167	8j	0	1/2	0.3333
Li2	16g	1/8	1/8	0.875	8k	3/4	1/4	0.25
Li3	-	-	-	-	8k	3/4	1/4	0.91667
Li4	-	-	-	-	4c	1/2	1/2	0.50
Li5	-	-	-	-	4d	1/2	0	0
O1	16e	0.8572	1/8	1/8	16m	0.77(1)	0.515(3)	0.087(4)
O2	32h	0.6311	0.3642	0.0383	8g	0.72(2)	1/2	1/4
O3	-	-	-	-	8l	0	0.262(8)	0
O4	-	-	-	-	16m	0.49(1)	0.262(8)	0.163(3)
hkl:		h+k, h+l, k+l=2n				h+k=2n		
0kl:		k,l=2n, k+l=4n				k,l=2n		
h0l:		k,l=2n, h+l=4n				h,l=2n		
hk0:		k,k=2n, h+k=4n				h+k=2n		
h00:		h=4n				h=2n		
0k0:		k=4n				k=2n		
00l:		l=4n				l=2n		

Table 2.3: Atomic fractional coordinates and Reflection Conditions for $\beta, \gamma\text{-Li}_2\text{IrO}_3$ [49, 48, 53].

peaks, the x-ray diffraction pattern also revealed the presence of weak, but clearly visible diffuse scattering in the form of “rods” of scattering intensity in-between Bragg peaks along the l -direction, sharply defined in the h and k directions. This diffuse scattering most likely originates from occasional structural faults in the nominal atomic stacking sequence along the c -axis.

2.2 Magnetic Characterization

Magnetic susceptibility measurements show that both β -Li₂IrO₃ and γ -Li₂IrO₃ magnetically order at $T_I = 38$ K. Resonant elastic x-ray scattering (more information in chapter 4) revealed that a very similar incommensurate spiral magnetic structure with counter-rotating moments and propagation vector $q = (0.571, 0, 0)$ sets in at this temperature in both polytypes [48, 49]. However, we have found that the magnetic anisotropies are quite different between the two, suggesting that subtle structural differences can strongly affect the magnetic response. As can be seen in Figure 2.4 (a), the low-temperature $\hat{b}$ -axis magnetic susceptibility is much larger in β -Li₂IrO₃ than in γ -Li₂IrO₃ such that the magnetic anisotropy are quite different: $\chi_b/\chi_a(\beta) \sim 22$ and $\chi_b/\chi_a(\gamma) \sim 10$.

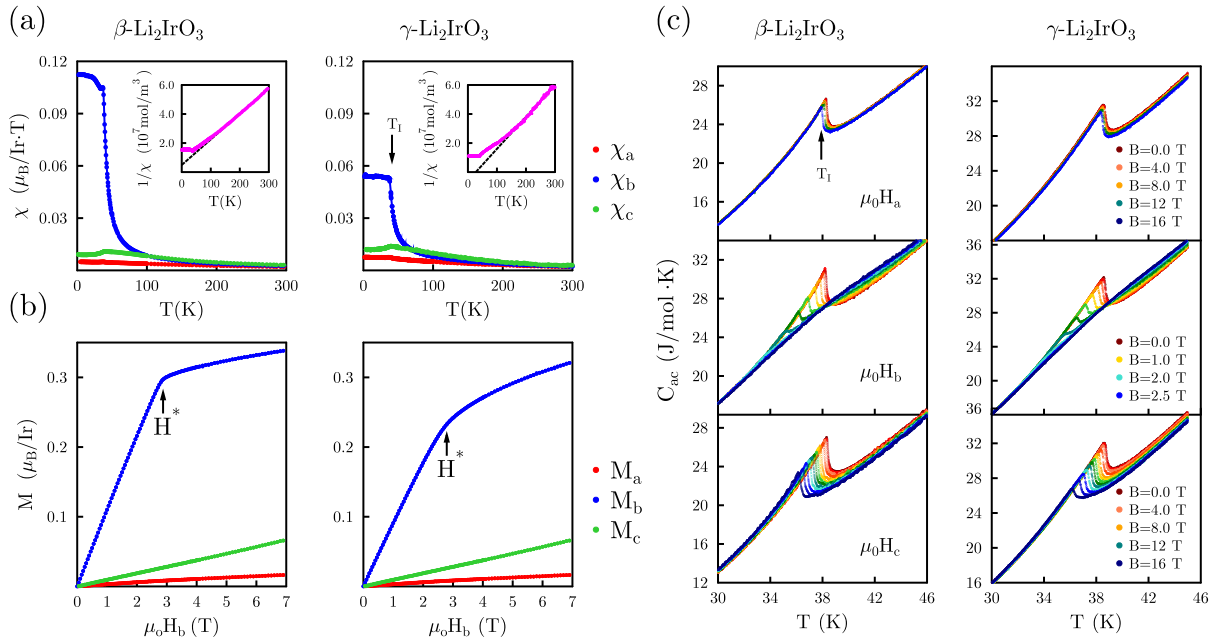


Figure 2.4: Comparing the thermodynamic properties of β and γ -Li₂IrO₃. (a) Temperature dependent susceptibility shows that both structures magnetically order at $T_I = 38$ K. The low-temperature magnetic anisotropy ratio is very different between them: $\chi_b/\chi_a(\beta) \sim 22$ and $\chi_b/\chi_a(\gamma) \sim 10$. The inset shows a Curie-Weiss behavior above ~ 150 K. (b) Field dependent magnetization along the principle axes taken at 2 K shows the extreme anisotropic response of both materials. The b-axis magnetization responds linearly to an applied field up to a kink field $H^* = 2.8$ T. (c) The magnetic anisotropy is also evident in the temperature dependence of the *ac* heat capacity: the cusp around T_I barely shifts when a 16 T field is applied along $\hat{a}$ while it is reduced to 36 K when applied along $\hat{c}$. On the other hand, 3 T along $\hat{b}$ is enough to completely suppress the magnetic transition.

The inset in Figure 2.4(a) shows that the average susceptibility $(\chi_a + \chi_b + \chi_c)/3$ fits a Curie-Weiss model for temperatures above 100 K, yielding effective moments very close to the value $\mu_{\text{eff}} \sim 1.73 \mu_B/\text{Ir}$ expected for the ideal $\mathcal{J} = 1/2$ moment. The overall Curie-Weiss temperature $\Theta_{\text{CW}} \sim |T_I|$ (Table 2.4), naïvely suggest that the interactions are mean field-like. However, given that we know the order is complex incommensurate state and that each principal axis has a different Θ_{CW} ranging from positive to negative values, this equivalence is likely to be a coincidence resulting from cancellations of opposing interactions along the different principal axes. Hence the frustration parameter $f = \Theta_{\text{CW}}/T_I$ underestimates the true degree of frustration in these materials. Moreover, below 100 K the data strongly deviate from a linear behavior (This is the subject discussed in chapter 3).

Figure 2.4(b) displays the field dependent magnetization for both β , γ - Li_2IrO_3 taken

	β - Li_2IrO_3	γ - Li_2IrO_3
	1.87 ± 0.2	1.67 ± 0.2
	$\hat{a} : 1.87 \pm 0.1$	1.86 ± 0.1
$\mu_{\text{eff}} (\mu_B/\text{Ir})$	$\hat{b} : 1.76 \pm 0.1$	1.74 ± 0.1
	$\hat{c} : 1.99 \pm 0.1$	1.89 ± 0.1
	-28 ± 5	$+34 \pm 5$
	$\hat{a} : -94 \pm 5$	$+18 \pm 5$
$\Theta_{\text{CW}} (\text{K})$	$\hat{b} : +10 \pm 5$	$+14 \pm 5$
	$\hat{c} : +0 \pm 5$	-61 ± 5
$\mu_0 H_b^* (\text{T})$	2.80 ± 0.05	2.80 ± 0.05
$M_b^* (\mu_B/\text{Ir})$	0.31 ± 0.05	0.23 ± 0.05
$\Delta S_m (\% R \cdot \ln 2)$	22.5 ± 0.5	13.5 ± 0.5

Table 2.4: Curie-Weiss fitting parameters and thermodynamic properties. Summary of the effective moment and Curie-Weiss temperature obtained for β - Li_2IrO_3 and γ - Li_2IrO_3 along the principle axes. The kink field H^* is the same for both system with different values of the induced moment M^* . The magnetic entropy change associated with T_I and the approximate Debye temperatures are also given.

at 2 K. The $\hat{a}$, $\hat{c}$ -axis magnetic response is linear to the applied field, $M = \chi H$. However, the $\hat{b}$ -axis magnetization is linear in H until a kink is observed at $\mu_0 H^* \sim 2.8$ T. Above H^* , the magnetization gradually increases with a smaller, non-linear slope. The induced moment at H^* , although different for both polymorphs (see Table 2.4), is far from the expected $\sim 1.0 \mu_B$ saturation magnetization for an effective spin $1/2$ moment. It should be also noted that the sharpness of the feature at H^* is qualitatively different. While the kink in β -Li₂IrO₃ occurs very abruptly, the kink in γ -Li₂IrO₃ is more gradual. It has been suggested that H^* defines the boundary of a high-field phase¹ [33, 32, 42] and so the similar responses of β and γ compounds, implies that the field induced phase is likely the same.

We now turn our attention to the field and temperature response of the heat capacity of β , γ -Li₂IrO₃ (Figure 2.4(c)). The temperature dependence of the ac specific heat, C_p , were measured with different values of magnetic field applied along the main crystal axes. These data show a sharp cusp-like anomaly at T_I , indicative of a second order phase transition into the magnetically ordered phase. The anisotropy observed on the susceptibility measurements is also seen here: when $\mu_0 H = 16$ T is applied along the $\hat{a}$ -axis, the heat capacity cusp barely shifts, when applied along $\hat{c}$, the transition is reduced to ~ 36 K. On the other hand, $\mu_0 H = 2.8$ T applied along the $\hat{b}$ -axis, is enough to completely suppress the transition. To quantify the change in magnetic entropy change at T_I , we calculate the difference in the total entropy for data taken at $\mu_0 H = 0$ T and 16 T for field along the $\hat{b}$ -axis². The values obtained are far smaller than the expected $\Delta S_m = R \cdot \ln(2J + 1) = R \cdot \ln 2$ for a $J = 1/2$ isospin (See Table 2.4).

Furthermore, we notice that the heat capacity response for $T > T_I$ is different for field along the $\hat{a}$ and $\hat{c}$ when compared to field applied along the $\hat{b}$ -axis. When the magnetic field is applied along $\hat{a}$ and $\hat{c}$ -axes, the heat capacity is suppressed, due to a suppression of entropy-carrying magnetic fluctuations. However, when the magnetic field is applied along $\hat{b}$, the heat capacity is enhanced. This may be due to presence of field-induced carriers of entropy, associated with a field-induced phase at low-temperature.

Similarities: The primary structural difference between β -Li₂IrO₃ and γ -Li₂IrO₃ is in the nature of the next nearest neighbor bonds along the $\hat{c}$ -axis. However, this does not lead to significant differences in their magnetic structure: the incommensurate state has the same periodicity ($q = (0.571, 0, 0)$) [48, 49], which sets in at the same temperature ($T_I = 38$ K) [32, 33], it is suppressed by a similar magnetic field ($\mu_0 H^* \sim 2.8$ T) [32, 33, 42] and isostatic pressure ($P_c = 1.4$ GPa) [33, 54]. This strongly suggests that the minimal Hamiltonian describing these materials is the same [39, 38], and mainly depends on nearest neighbor interactions, which sensitively depend on the Ir-O₂-Ir bond angle, which are almost identical in these compounds.

Differences: There are, however, subtle differences between them: the susceptibility anisotropy ratios $\chi_b/\chi_a(\beta) \sim 2 \chi_b/\chi_a(\gamma)$, the magnitude of the induced moment at the

¹For more details see chapter 5

²No non-magnetic iso-structure is currently available to subtract the lattice contribution.

critical field $M^*(\beta) \sim 3/2 M^*(\gamma)$, and the entropy associated with the heat capacity jump $\Delta S_m(\beta) \sim 2\Delta S_m(\gamma)$. This later discrepancy may suggest that the incommensurate transition in the γ compounds freezes out fewer spin degrees of freedom. Though this may arise from an enhanced frustration in γ systems, this interpretation seems at odds with the fact that T_I is unchanged. There is a possibility that there are more disorder sites in γ than in β somewhat suppressing long-range order. However, one might expect a paramagnetic enhancement in the susceptibility from the defects at low temperature, which we do not observe. Finally, it may be that the γ system is closer in energy to other nearby broken symmetry states (as suggested by theory [38]), which may lead to more degrees of freedom available at T_I and a smaller magnetic anisotropy (depending of course on the magnetic response of these nearby ordered states), but without strongly affecting the transition temperature. Certainly, high resolution resonant magnetic scattering measurements as a function of field, or inelastic measurements (like neutron or resonant inelastic x-ray scattering) could be used to resolve the origin of the subtle difference between β and γ .

In the next sections, we will separately study the high- and low-temperature magnetic behaviors.

2.3 High temperature: g-factor anisotropy.

In the harmonic honeycomb series each iridium atom occupies a local environment with uniaxial g-factor anisotropy that can be captured by a magnetic susceptibility $\chi_{\parallel}$, parallel to and $\chi_{\perp}$, perpendicular to the plane defined by its three nearest neighbor iridium atoms. For the 3D structures, two such local planes exist (red and blue planar, triangular environments in Figure 2.5(a) such that the total magnetization can be derived from a superposition of both local magnetization:

$$\begin{aligned} M_a &= M_{\perp} \cos \phi/2 + M_{\parallel} \sin \phi/2 \\ M_b &= M_{\perp} \sin \phi/2 - M_{\parallel} \cos \phi/2 \\ M_c &= M_{\parallel} \end{aligned}$$

where ϕ is the angle between the planes, and the magnetization parallel, $M_{\parallel}$, and perpendicular, $M_{\perp}$, to each of the planes can be written as:

$$\begin{aligned} M_{\perp} &= \chi_{\perp} H_{\perp} = \chi_{\perp} (H_a \cos \phi/2 + H_b \sin \phi/2) \\ M_{\parallel} &= \chi_{\parallel} H_{\parallel} = \chi_{\parallel} (H_a \sin \phi/2 - H_b \cos \phi/2) \end{aligned}$$

Therefore, the geometric relation between the underlying pair of honeycomb planes results in three components of magnetization (M_a , M_b , M_c) determined by only two mi-

croscopic parameters ($M_{\parallel}$, $M_{\perp}$):

$$M_a = H_a[\chi_{\perp} \cos^2 \phi/2 + \chi_{\parallel} \sin^2 \phi/2]$$

$$M_b = H_b[\chi_{\perp} \sin^2 \phi/2 + \chi_{\parallel} \cos^2 \phi/2]$$

$$M_c = H_c \chi_{\parallel}$$

The anisotropic susceptibility of this family of structures can be simplified using $\chi_{\pm} = (\chi_{\parallel} \pm \chi_{\perp})/2$ such that:

$$\chi_a = \chi_+ - \chi_- \cos \phi$$

$$\chi_b = \chi_+ + \chi_- \cos \phi$$

$$\chi_c = \chi_+ + \chi_-$$

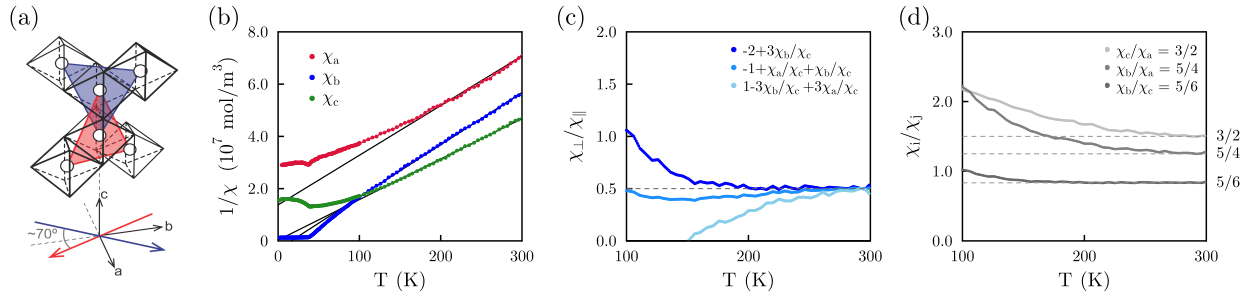


Figure 2.5: High temperature: g-factor anisotropy. (a) Each Ir moment is surrounded by one of two planar, triangular environments indicated by blue and red shaded triangles, separated by 70° . (b) Inverse magnetic susceptibility along the principle axes shows that the high temperature data follows the expected g-factor anisotropy ordering of the local Ir environment: $\chi_c > \chi_b > \chi_a$. The Curie-Weiss fitting results are summarized in table 2.4. (c) The high-temperature local susceptibility ratio $\chi_{\perp}/\chi_{\parallel} = 1/2$ can be found using the global magnetic susceptibility. The figure inset shows the relationship between the global magnetic susceptibilities $2\chi_b = \chi_a + \chi_c$. (d) At high-temperatures, the global susceptibility ratio approaches the values dictated by g-factor anisotropy. These geometric constraints are temperature independent so that the softening of χ_b and the reordering of the principle axes at low-temperature cannot be explained by g-factor anisotropy alone.

Furthermore, the geometry of the undisturbed, edge-sharing, cubic octahedra constrains the angle separating these two planes to be $\cos \phi = 1/3$. As a consequence, at high temperature where g-factor anisotropy dominates, all three principal components of the

magnetic susceptibility must be equally spaced with ordering given by $\chi_c > \chi_b > \chi_a$:

$$\begin{aligned}\chi_a &= \chi_+ - 1/3\chi_- \\ \chi_b &= \chi_+ + 1/3\chi_- \\ \chi_c &= \chi_+ + \chi_-\end{aligned}$$

We can algebraically manipulate these expressions to find: (i) the expected relationship between the total susceptibilities ($2\chi_b = \chi_a + \chi_c$), (ii) the local anisotropic ratio in terms of the measured total magnetic susceptibilities (Figure 2.5 (c):

$$\begin{aligned}\chi_{\parallel} &= \chi_c \\ \chi_{\perp} &= 3\chi_b + 2\chi_c \\ &= 3/2\chi_a + 1/2\chi_c \\ &= \chi_a + \chi_b - \chi_c\end{aligned}$$

Figure 2.5 (c) shows that at 300 K, the local anisotropy ratio is $\chi_{\perp}/\chi_{\parallel} = 1/2$. Notably, this is the opposite of the anisotropy observed for the layered Na_2IrO_3 in which $\chi_{\perp}/\chi_{\parallel} = 2$ (Data shown at the end of chapter 3). Furthermore, using this local anisotropy ratio, we can expect the room temperature susceptibility ratios to be:

$$\frac{\chi_c}{\chi_a} = \frac{3}{2} \qquad \frac{\chi_b}{\chi_a} = \frac{5}{4} \qquad \frac{\chi_b}{\chi_c} = \frac{5}{6}$$

as observed experimentally (Figure 2.5 (d))³. The low temperature $\chi_{\parallel}/\chi_{\perp}$ deviates from this simply geometrical consideration. This happens because the equidistant model breaks down at low temperatures where we need to include exchange anisotropy.

2.4 Low temperature: Exchange anisotropy.

The Kitaev Hamiltonian can be relabeled using the crystallographic directions of the 3D orthorhombic honeycomb iridates, and it becomes:

$$H_K = -K^c \sum_{\langle ij \rangle \in \mathbf{c}} S_i^b S_j^b - K^h \sum_{\langle ij \rangle \in (\mathbf{a}+\mathbf{c})} S_i^{a+c} S_j^{a+c} - K^h \sum_{\langle ij \rangle \in (\mathbf{a}-\mathbf{c})} S_i^{a-c} S_j^{a-c} \quad (2.1)$$

where $S^{\hat{b}}$ and $S^{\hat{a}\pm\hat{c}} = (S^{\hat{a}} \pm S^{\hat{c}})/\sqrt{2}$ are the spin operators in a set of orthogonal directions, with $\{\hat{a}, \hat{b}, \hat{c}\}$ being unit vectors along the orthorhombic crystal axes. The conversion between the Cartesian and crystallographic axes is $\{\hat{x}, \hat{y}, \hat{z}\} = \{1/\sqrt{2}(\hat{a}+\hat{c}), 1/\sqrt{2}(\hat{c}-\hat{a}), -\hat{b}\}$.

³This susceptibility ratios can also be obtained from the effective moments and Weiss temperatures listed in table 2.4 as $\frac{\chi_i}{\chi_j} = \frac{\mu_i}{\mu_j} \frac{T - \Theta_j}{T - \Theta_i}$ where $T=300$ K

Each $\langle ij \rangle$ bond is defined by the axis perpendicular to its Ir–O₂–Ir plane which lies along one of the directions $\{(\hat{a} + \hat{c}), (\hat{a} - \hat{c}), \hat{b}\}$. All the nearest neighbor Ir–Ir bonds can be divided into three classes, one for each component of spin: the $\hat{b}$ component from the $\hat{c}$ –axis bonds, and the $\hat{a} \pm \hat{c}$ components from the h bonds defining each honeycomb plane. The exchange couplings K^h are constrained by the symmetry of the space group to be the same on the $(\hat{a} \pm \hat{c})$ bonds, but K^c , the coefficient of S^b coupling, is symmetry-distinct from K^h . The $\hat{c}$ –bonds carry Kitaev coupling of spin component $\hat{b} = \hat{z}$ as seen in figure 2.6 (a). Therefore, the $\hat{b}$ –axis is the only crystallographic axis that coincides with a symmetry-distinct exchange direction in the Kitaev Hamiltonian ($\hat{z}$), making it magnetically special. For the stripy honeycomb lattice, the c –bonds are further distinguished into two types: bonds within the hexagons and bonds between rotated hexagons, which are not related to each other by symmetry.

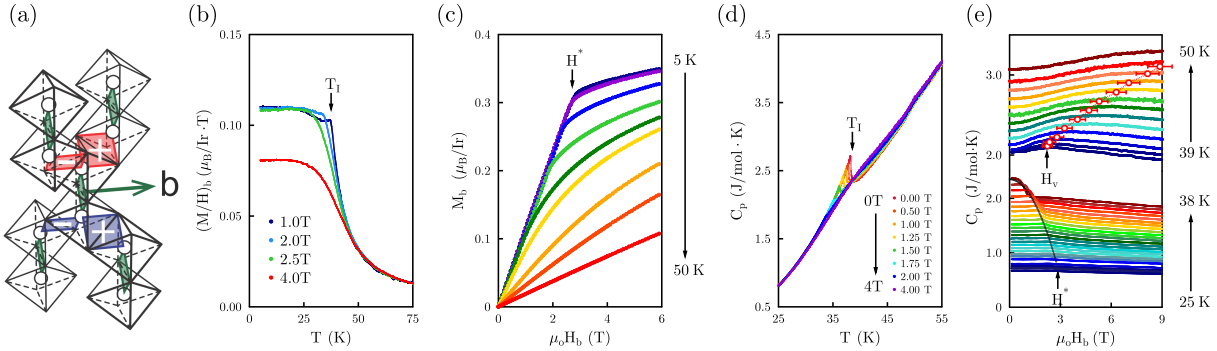


Figure 2.6: Low temperature: exchange anisotropy. (a) The Ir–O₂–Ir planes define three orthogonal directions of the spin-exchange: the $\hat{b}$ component of the c –axis bonds and the $\hat{a} \pm \hat{c}$ components from the bonds defining the honeycomb rows. The exchange couplings along the $\hat{a} \pm \hat{c}$ direction are the same but the $\hat{b}$ coupling is symmetry-distinct, making the $\hat{b}$ axis magnetically special. (b) Susceptibility as a function of temperature for $\mu_0 H = 1, 2, 2.5$ & 4 T. (c) The field dependent magnetization along the $\hat{b}$ –axis shows a linear response to the applied field up to a kink field $H^* = 2.8$ T which we will show on Chapter 5, it corresponds to the suppression of the incommensurate state and the development of a zig-zag component. (d) Heat capacity as a function of temperature for fields up to 4 T. The data shows a triangular anomaly around the transition at T_I . (e) Field dependence of the ac heat capacity for temperatures above and below the magnetic transition. When $T < T_I$, a sharp step occurs while crossing the phase boundary defined by H^* . Within the boundary, the response to the applied field is almost constant. For $H > H^*$, the specific heat decreases with applied field. When $T > T_I$, a broad hump is observed in the specific heat data which moves to higher field as the temperature increases.

On these grounds, the $\hat{b}$ –axis response to an applied magnetic field has been extensively studied [42, 55, 32, 33], and it has been established that many interesting behaviors

Curie-Weiss fitting for multiple fields along $\hat{b}$ -axis.			
	1.0T	2.0T	4.0T
$\mu_{\text{eff}} (\mu_B/\text{Ir})$	1.76 ± 0.1	1.73 ± 0.1	1.76 ± 0.1
$\theta_{\text{CW}} (\text{K})$	18 ± 5	20 ± 5	18 ± 5

Table 2.5: Curie-Weiss Parameters of $\beta\text{-Li}_2\text{IrO}_3$ fitted for $T > 100$ K.

emerge. The minimal Hamiltonian for the experimental systems takes the form:

$$H = H_K + H_J + H_\Gamma + \mu_o H^b \sum_i g_i \cdot S_i \quad (2.2)$$

where H_K is the bond-directional Kitaev exchange given by equation 2.1, H_J is the Heisenberg interaction term, H_Γ is the off-diagonal symmetric anisotropy exchange, and H^b is the magnetic field applied along the $\hat{b}$ -axis.

Below 100 K, a striking reordering of the principle components of susceptibility occurs, with χ_b becoming an order of magnitude larger than its expected geometric value ($\chi_b/\chi_a(300\text{ K}) = 5/4$ to $\chi_b/\chi_a(5\text{ K}) = 22$). This is in stark contrast to spin-isotropic Heisenberg exchange systems where the low-temperature susceptibility reflects the g-factor anisotropy observed at high temperature, even in the presence of spatially anisotropic exchange. The observed increase in χ_b cannot be driven by the temperature independent g-factor, and it is therefore, attributed to spin-anisotropic exchange described by equation 2.1. At low temperature, the susceptibility ratios become:

$$\begin{array}{lll} \frac{\chi_c}{\chi_a}(\beta) \sim \frac{3}{2} & \frac{\chi_b}{\chi_a}(\beta) = 22 & \frac{\chi_b}{\chi_c}(\beta) = 12.5 \\ \frac{\chi_c}{\chi_a}(\gamma) \sim \frac{3}{2} & \frac{\chi_b}{\chi_a}(\gamma) = 7.5 & \frac{\chi_b}{\chi_c}(\gamma) = 4.5 \end{array}$$

Figure 2.6 shows the main thermodynamics results for $\beta\text{-Li}_2\text{IrO}_3$ with field along $\hat{b}$ -axis (very similar results were also obtained for $\gamma\text{-Li}_2\text{IrO}_3$). The normalized magnetization M/H remains constant for $H < 2.8$ T (the non-linearity at low fields will be studied in the next chapter). Above the critical field H^* , magnetization gradually increases with a small slope (Figure 2.6 (b)). The kink field H^* moves to lower values with increasing temperature (Figure 2.6 (c)) which manifests itself as a break on the slope of the low-temperature field dependent specific heat (Figure 2.6 (e)).

Furthermore, field scans of the specific heat, $C_p(H)$, at different temperatures show that for $T > T_I$, a broad hump (H_v) is observed in the specific heat data which moves to higher field as the temperature increases. The behaviors observed above and below T_I

are illustrated in Figure 2.6 (d, e). For $T < T_I$, the incommensurate phase transition can be easily resolved as a sharp step on the $C_p(H)$ slope. As the temperature is lowered, there is almost no difference as one crosses H^* , indicating that the phase boundary is almost vertical (consistent with our $M(H)$ data). This step-like feature evolves into a broad hump for $T > T_I$. A dashed line in Figure 2.6 (e) serves as a guide to the eye denoting the maximum $C_p(H)$ at each temperature. The similarity in the evolution of C_p with applied field between β and γ compounds, again suggests that the high field nature is likely to be the same.

Chapter 3

Intermediate Temperatures Properties

Since Khaliullin and Jackeli [23, 40] first pointed out that Kitaev's frustrated compass model[56] on a honeycomb lattice could be realized in 4d and 5d transition metal systems, these materials have become one of the most promising routes to experimentally realizing a quantum spin liquid. The ground state itself, first described by Kitaev [56], is characterized by the long range order of flux degrees of freedom, emerging from the fractionalization of the local spins into Majorana excitations. Because all of the candidate materials, including the 2D Na_2IrO_3 and RuCl_3 , magnetically order at low temperature [46, 57, 48, 49, 47] most recent research has been targeted at finding high temperature signatures of these exotic states or proximity thereto. Recent spectroscopic and thermodynamic studies of RuCl_3 [58, 59, 60, 61] for example, have reported evidence for the onset of nearest-neighbor Kitaev correlations, consistent with a proposal by Motome and co-authors of a thermal crossover from a paramagnet to a spin-“fractionalized” state [62]. Similar studies have been extended these conclusions to Li_2IrO_3 and Na_2IrO_3 systems [63, 64]. In this work I focus specifically in this region of temperature, finding that in the case of the three-dimensional $\beta, \gamma\text{-Li}_2\text{IrO}_3$ materials, this crossover into the “fractionalized” state is accompanied by a true phase transition at $T_\eta = 100$ K as seen in Figure 3.1. The signatures of this transition are subtle, hence eluding detection in previous measurements, but also very unusual, pointing to the presence of an exotic order parameter. As H_{app} increases, this transition becomes less visible, explaining why it has been undetected until now. Figure 3.1 (c) shows that the field dependent magnetization is linear just above T_η , and becomes non-linear just below it.

Although Kitaev's proposed ground state does not break time reversal symmetry, the application of magnetic fields has nevertheless proven a useful probe of its signatures. Kitaev showed that when a field is applied along one of the compass axes, the system retains its spin-liquid nature, allowing chiral 3-spin terms. In a remarkable experiment on RuCl_3 , Kasahara *et al.* recently discovered the presence of a half integer quantum thermal Hall effect in applied fields which are apparently strong enough to suppress the magnetic order, but not so strong as to compromise the spin liquid state that harbors the chiral Majorana edge modes [65]. There are few generalizations of the consequences of

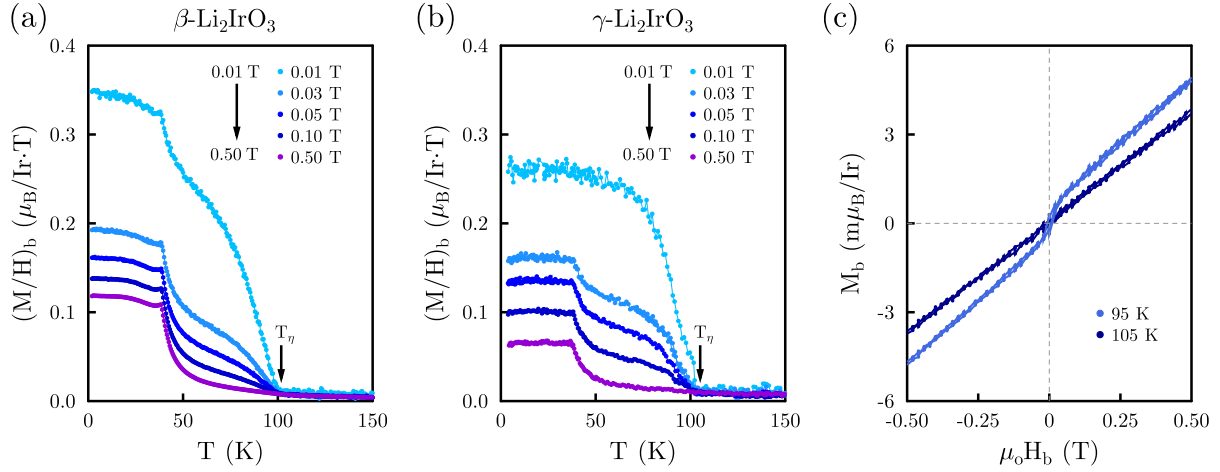


Figure 3.1: **100 K magnetic phase in β, γ - Li_2IrO_3 .** (a, b) As H_{app} increases, the 100 K transition becomes less noticeable. (c) The field dependent magnetization is linear right above T_η and becomes non-linear for small field below T_η .

an applied field to a three dimensional Kitaev network, though several unusual properties have already been detected; the incommensurate order is suppressed by $\sim 2.8 \text{ T}$ [42], and an unusual magnetic anisotropy detected in sawtooth-like features in the torque (which choose the crystallographic b direction as an easy-axis). It was recently suggested that the origin of this anomaly could originate from a scalar chiral spin order of the form $\mathbf{S}_i \cdot (\mathbf{S}_j \times \mathbf{S}_k)$, which arises when magnetic flux penetrates the loop formed by the i, j, k sites of the triangular sublattice [66]. However, a recent study showed that the saw-tooth torque could be explained without the need to invoke such an exotic order parameter, but by simply considering the role of exchange and g -factor anisotropy near a phase boundary [67]. It was also calculated that the scalar chiral order, should it exist, would be fairly small in magnitude, coupling to the field with around $1 \text{ m}\mu_B$ per site, varying in space depending on the anisotropy of the spin-spin interactions [67]. Interestingly, the b -axis is the only crystallographic direction that coincides with one of the Kitaev compass directions, and the temperature scale for the onset of the torque anomaly, overlaps the region of thermal “fractionalization” discussed above.

3.1 Magnetic Characterization

Figure 3.2 shows that the three-dimensional Kitaev candidates β - Li_2IrO_3 , undergoes a phase transition at $T_\eta = 100 \text{ K}$, characterized by a tiny magnetic moment but with unusual anisotropies which suggest spin and orbital degrees of freedom are strongly entwined by Kitaev-like correlations. This transition precedes the known incommensurate state that sets in at $T_I = 38 \text{ K}$ and shares the same ordering (anisotropy) of the principle

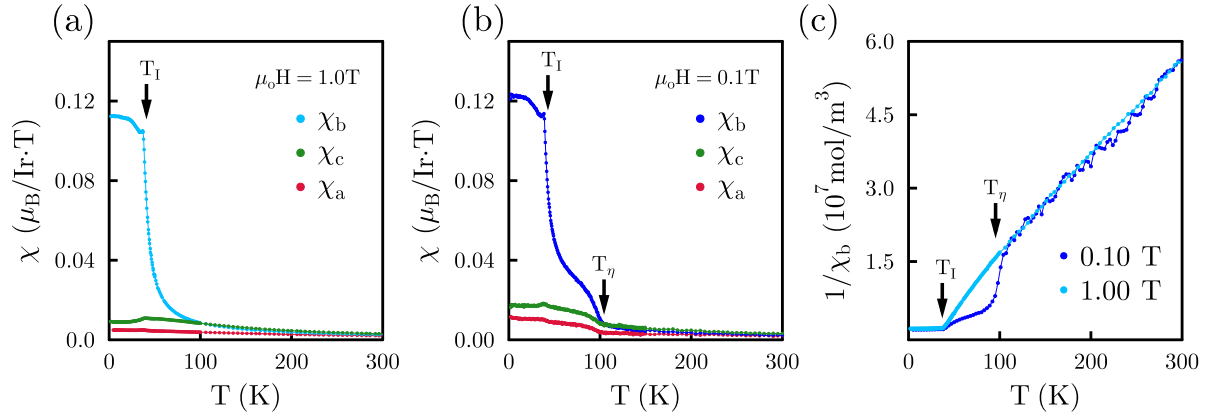


Figure 3.2: **Anisotropic magnetic susceptibility of $\beta\text{-Li}_2\text{IrO}_3$, taken using:** (a) 1.0 T and (b) 0.1 T. At $T_I = 38 \text{ K}$, the system transitions into an incommensurate spiral state with non-coplanar, counter-rotating moments. When a small magnetic field is applied ($H < 0.5 \text{ T}$), a separate transition is also observed at 100 K. (c) Curie-Weiss fitting for data taken at 1.0 T and 0.1 T. The low-field data shows two distinct behaviors: a linear response above 100 K and a strong deviation from Curie-Weiss behavior $100 > T > 40 \text{ K}$.

axes. To understand its behavior, we study the field-cooled (FC) and zero field-cooled (ZFC) magnetization. First, the system is cooled from room temperature to 2 K at a rate of 20 K/min in zero magnetic field. Then a 0.1 T field was applied and magnetization was measured on warming (M_{ZFC}). The second curve corresponds to a protocol where the system was cool-down under a constant magnetic field, and magnetization was measured on reheating (M_{FC}).

In Figure 3.2 (a,b) we contrast the anisotropic magnetization measured at 1 T and 0.1 T, respectively. The measurements agree at high and low temperature limits; at high temperatures $T \gg 100 \text{ K}$, the magnetization anisotropy follows the g -factor anisotropy discussed in the last chapter. The effective spin $\mathcal{J}$ is extracted from the high temperature slope of the inverse susceptibility, shown in Figure 3.2 (c), and can be completely understood as $\mathcal{J} = 1/2$ paramagnetic spins coupled to their orbital environment. At low temperatures the system orders into an incommensurate state $T_I = 38 \text{ K}$ [49, 48]. The deviations, however, occur at intermediate temperatures, below $T_\eta = 100 \text{ K}$ where we see a subtle but clear feature in the magnetization indicative of a phase transition, hidden from previous measurements. The transition temperature is conspicuously close to the temperature window under intense study in the 2D Kitaev candidate systems, where there is thought to be evidence of emergent, fractional excitations.

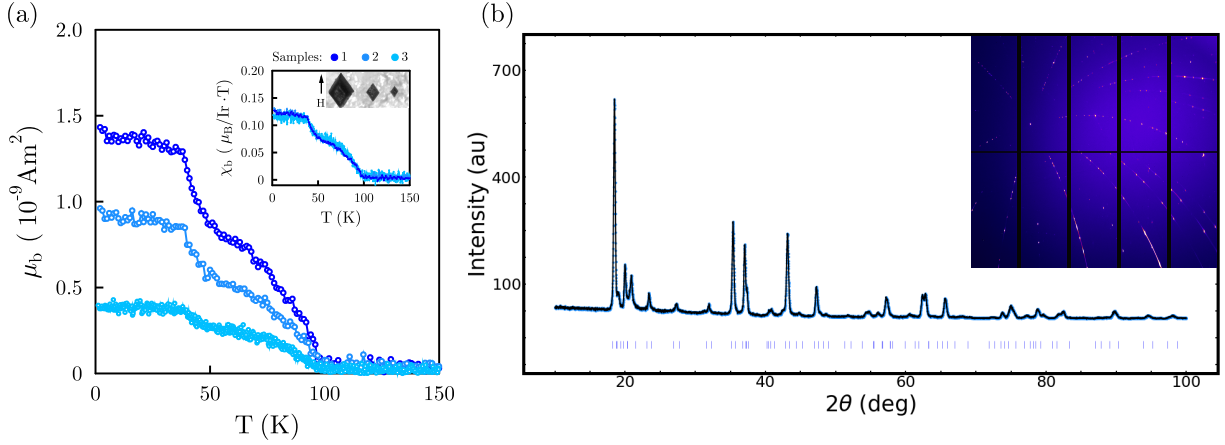


Figure 3.3: (a) Field-cooled magnetic moment of three samples of different volumes measured using a 0.01 T field applied along the b-axis. The inset demonstrate the intrinsic nature of the observed high temperature phase since the volume fraction is the same for all measured samples. (b) The powder x-ray diffraction data (blue) can be exactly modeled (black) by a combination of $\beta\text{-Li}_2\text{IrO}_3$ and $\gamma\text{-Li}_2\text{IrO}_3$ structures. Laue diffraction on single crystals show a homogeneous single phase structure.

Impurity phases

A possible explanation for the observation of the 100 K transition is the existence of an impurity phase. The common impurities of IrO_2 and elemental Ir can be ruled out since they are known paramagnets [68], as can any lithium based oxides which are non-magnetic. Note that the susceptibility itself is consistent with a $\mathcal{J} = 1/2$ moment, consistent with an Ir^{4+} magnetic ion in an octahedral environment, expected in $\beta\text{-Li}_2\text{IrO}_3$. It is possible that there exist more complex lithium based iridates of an unknown structure, but we exclude these for the following reasons. Firstly, extensive Laue diffraction on our single crystals show peaks that can all be indexed with the $\beta\text{-Li}_2\text{IrO}_3$ structure. Secondly, the volume fraction of an impurity phase will likely vary from sample to sample, but we have no evidence of such variation in our experiments. Over the ≥ 20 samples measured, the volume has varied by a factor of three or more, but in each case the ferromagnetic moment scales to the same value (see Figure 3.3(a)). Thirdly, the magnetic anisotropy of the 100 K magnetic phase is the same as that of the incommensurate phase intrinsic to $\beta\text{-Li}_2\text{IrO}_3$. This would be highly unusual for an impurity phase since the magnetic anisotropy of these systems does not follow their structural anisotropy, so that even oriented impurity phases would have to coincidentally have the same magnetic anisotropy. The smaller induced magnetic moment in $\gamma\text{-Li}_2\text{IrO}_3$ allows us to see the order parameter-like behavior of the transition at T_η without the influence of the incommensurate state. While this may suggest that the 100 K state is independent of the incommensurate state, it also emphasizes that it orders the same moment in different crystal

structures. Finally, we note that the low-temperature susceptibility in $\beta\text{-Li}_2\text{IrO}_3$ at low magnetic fields matches perfectly the high-field susceptibility, which is dominated by the intrinsic $\beta\text{-Li}_2\text{IrO}_3$. This is not be expected if the magnetic moment of an impurity phase is additive, since it will be present at all temperatures. We conclude that the weak ferromagnetism cannot arise from an impurity phase, but rather is intrinsic to these materials.

3.2 Anisotropy of the 100 K transition

With an impurity phase ruled out, there are a number of possible origins that could arise in these systems. Figure 3.4(a-c) shows that M_{FC} continuously increases below T_η as temperature decreases while M_{ZFC} shows a cusp with a maximum at a temperature smaller than T_η . This cusp occurs because the applied field is smaller than the anisotropy field ($H_{app} < H_a = 2K_u/M_s$) which aligns the spins in a preferred direction determined by uniaxial anisotropy (K_u). During ZFC, the magnetic domains are locked in random directions. When a small magnetic field is applied at the lowest temperature, far below T_η , the magnitude of the resultant magnetization will depend on the anisotropy of the system. If the system is highly anisotropic, the small applied field will not be sufficient to rotate the spins in the direction of the applied field and, therefore, the magnetization will be very small [69]. As we approach T_η from below, thermal energy softens the spins so that the small applied field is able to rotate them in the field's direction, which shows up as a cusp near T_η . If on the other hand, the sample is cooled through T_η in a magnetic field, the magnetic domains will be locked in a particular direction dictated by the competition between H_{app} and H_a . Therefore, M_{FC} increases with decreasing temperature for a highly anisotropic material.

Figure 3.4(d-f) shows the field dependent magnetization below T_η , illustrating clear hysteresis behavior along every crystallographic axis, and a coercive field that increases with decreasing temperature (in our case we actually measure the anisotropy field H_a). The insets show the hysteresis curve after a linear background was subtracted, determined from the high field susceptibility in Figure 3.2(a). Surprisingly, the anisotropy field is independent of crystallographic direction, while the saturation moment M_s varies by a factor of ~ 10 , mirroring the susceptibility anisotropy. In typical magnetically ordered systems, or even in spin glasses, the behavior is usually the other way around, where the saturation moment is isotropic (since it is related to the local moment), while the coercive field is anisotropic (since it is related to the anisotropy of the free energy).

In Figure 3.5(a), we show zero field cooled (ZFC) and field cooled (FC) magnetization curves (inset), and their difference. The latter shows the natural form expected of a magnetic order parameter growing below T_η . Figure 3.5(b) shows the zero-field (AC) heat capacity response of $\beta\text{-Li}_2\text{IrO}_3$, showing a clear kink at $T_\eta = 100$ K. This confirms the presence of phase transition, and indicates that the fraction of system's degrees of freedom that are frozen must be very small. The anisotropy field H_a , where the moment associated with the hidden phase is saturated is plotted as part of the phase diagram and

appears to be indifferent to the phase boundary as the system crosses into the incommensurate phase marked by H^* . On the other hand, H_a terminates at the zero temperature at $H_a(0) \sim H^*(0)$ within experimental error, suggesting the incommensurate and hidden phase might share a common energy scale.

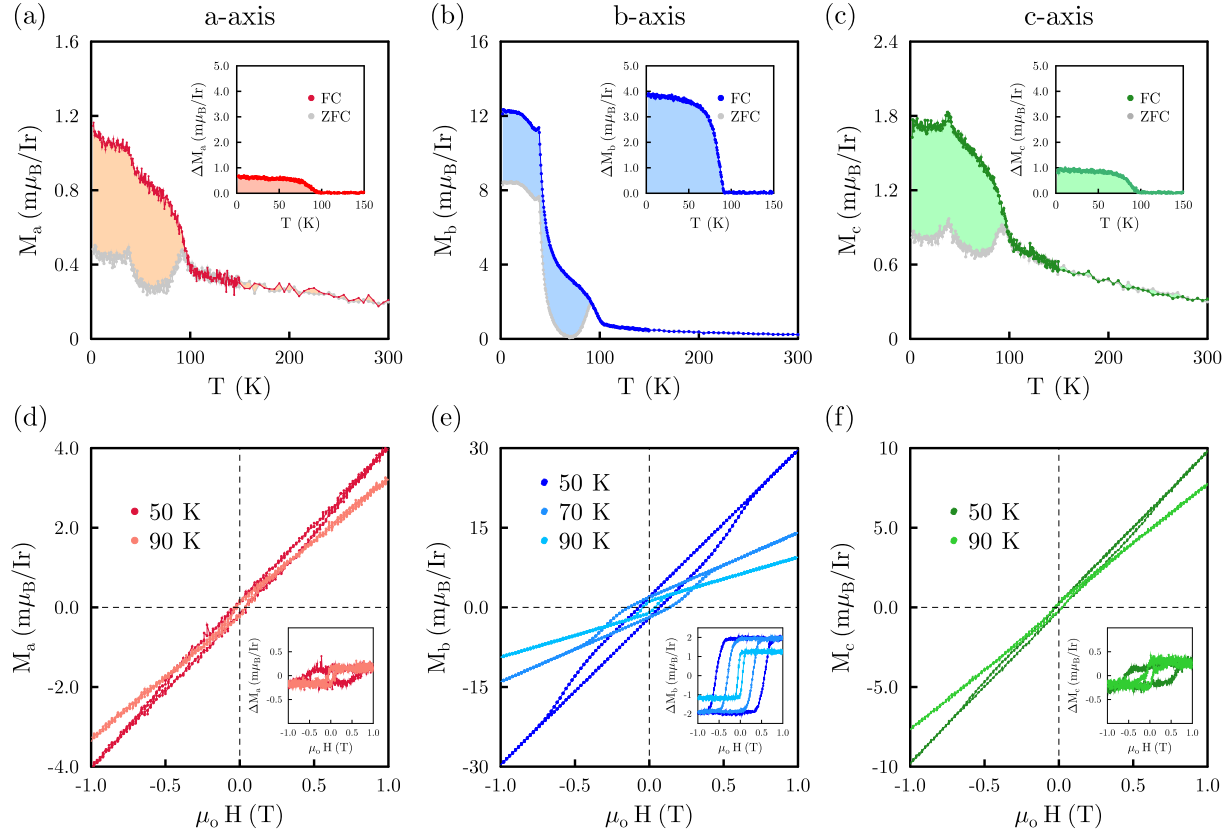


Figure 3.4: **Characterizing the magnetic anisotropy of the 100 K transition.** (a-c) Field-cooled and zero field-cooled magnetization of $\beta\text{-Li}_2\text{IrO}_3$ (M_{FC} , M_{ZFC}). The inset shows the difference between these two curves $\Delta M = M_{FC} - M_{ZFC}$. (d-f) Variable-field magnetic response of $\beta\text{-Li}_2\text{IrO}_3$ along the three principle axes. Hysteresis behavior was observed below $T_\eta = 100$ K. The inset shows the data after the high field linear response was subtracted.

Recently, a number of experimental studies have reported evidence for the freezing of itinerant Majorana degrees of freedom, consistent with a crossover transition predicted by Motome *et al.* [36, 35] to occur as a precursor to a low temperature Kitaev spin liquid state. In principle, there is an onset of short range correlations, at a temperature comparable to the energy scale of the Kitaev term itself, K . Experimentally, this apparently manifests as strong deviations from Curie-Weiss-like magnetic susceptibility and a slow freezing of the magnetic entropy, observed to occur at ~ 100 K in $\alpha\text{-Na}_2\text{IrO}_3$ and $\alpha\text{-Li}_2\text{IrO}_3$, and ~ 85 K

in RuCl_3 [70, 60, 64]. The present observation of a WFM transition at 100K could be a coincidence, but it is suspiciously similar; deviations in the susceptibility observed by other authors are very similar in 3D and 2D materials, as are deviations in the heat capacity [71, 63]. The distinction is that in the 3D case, as we have shown, there is a true WFM phase transition. Such a difference may arise naturally, simply due to the dimensionality of the system, since 3D systems are more unstable to phase transitions on general grounds [72], so that while an onset of magnetic correlations leads to a crossover in the α structures, it leads to an instability in the β and γ systems, even though the origin is the same. In this picture, instead of the WFM arising from $\mathcal{H}_I$, it would be connected to the ferromagnetic Kitaev term itself. Interestingly, previous studies of RuCl_3 have observed a phase transition at around 100K-150K, with a strongly sample dependent transition temperature [1]. It seems possible that the onset of this transition depends on defects that form links between the 2D layers, rendering the systems effectively more three-dimensional, facilitating a (sample dependent) phase transition at the onset of the correlations. Systematic disorder studies are necessary to further investigate this possibility.

Finally, we comment on a further intriguing possibility, which would answer why the magnetic moment is so small, is that the WFM phase originates from dilute magnetic defects. Chalker and Moessner [73, 74] have shown that site dilution in Kitaev systems can lead to the formation of strong local moments. These moments have long range interactions arising from non-local correlated excitation arising from the Kitaev spin liquid. In the present systems, site dilution would correspond to iridium vacancies, a natural defect in these systems. Such local moments may always be present, but at a temperature scale corresponding to the onset of strong correlations (perhaps similar scale to the model of Motome *et al.*), they may freeze into a spin glass. The WFM behavior we observe would in this case be a Kitaev spin glass in the presence of strong magnetic anisotropy, which leads to hysteresis in the magnetization, as expected in a ferromagnet.

Another possibility is that the WFM phase arises from intrinsic impurities in the materials themselves, that give rise to randomly distribute dilute magnetic moments.

Torque

Magnetic anisotropy can be characterized by measuring magnetic torque since an anisotropic material experiences torque when the magnetic easy axis is not aligned with the applied magnetic field, such that:

$$\tau = \mathbf{M} \times \mathbf{H} \quad (3.1)$$

In the linear response region (typically small fields), the magnetic anisotropy ($M_i = \chi_{ij} H_j$) is captured by the susceptibility tensor χ_{ij} , which is diagonal in the basis of the principle magnetic axes. For our orthorhombic crystals, the magnetic axes coincide with the crystallographic axes ($\hat{a}, \hat{b}, \hat{c}$) and define the principle susceptibilities ($\chi_{a,b,c}$). Therefore, for rotations in the bc -plane, the anisotropic magnetization gives rise to a torque along the $\hat{a}$

direction defined as:

$$\tau_a = M_a H_c - M_c H_b = (\chi_b - \chi_c) H_b H_c \quad (3.2)$$

This expression can be re-written in terms of the magnetic susceptibilities by defining a rotation angle θ between the $\hat{c}$ -axis and the applied magnetic field:

$$\tau_a = (\chi_b - \chi_c) H^2 \sin \theta \cos \theta = \frac{1}{2} (\chi_b - \chi_c) H^2 \sin 2\theta \quad (3.3)$$

Therefore, we can expect the amplitude of the torque signal to change sign since the principle axes susceptibility $\hat{b}$ and $\hat{c}$ reorder around 100 K.

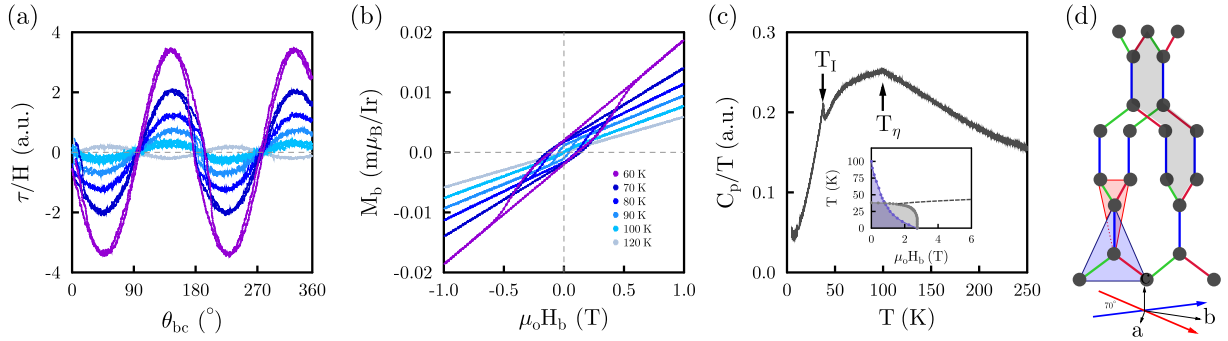


Figure 3.5: (a) Angular dependent torque $\tau_a = 1/2(\chi_b - \chi_c)H^2 \sin 2\theta$ for rotations in the bc plane shows a change in sign as we cross T_η . Hysteresis in the torque data is observed below T_η , and the $\hat{b}$ axis anisotropy field corresponds to that observed on the magnetization measurements. (c) Heat capacity response of hyperhoneycomb β -Li₂IrO₃ measured using the AC technique. A triangular cusp at $T_I = 38$ K shows the transition into the incommensurate spiral state while a small kink was observed at $T_\eta = 100$ K. The figure inset shows the updated T-H phase diagram where the blue dots represent the anisotropy field H_a . (d) Three dimensional structure of β -Li₂IrO₃, where colors correspond to orthogonal compass directions of the Kitaev model. In addition, it shows the two triangular environments possible for a magnetic ion in β -Li₂IrO₃, and determines the g -factor anisotropy.

3.3 Discussion

The anisotropic magnetic susceptibility of β -Li₂IrO₃ is quite well understood at high temperature, behaving like paramagnetic spins in an orbital environment that reflects the local symmetry of the structure [32], illustrated in Figure 3.5 (c). As the temperature approaches the incommensurate transition from above, the magnetic principal axes undergo a substantial reordering, which is thought to reflect a strong Kitaev-like term in the minimal Hamiltonian [38]. The details of the incommensurate magnetic ordered

of $\beta\text{-Li}_2\text{IrO}_3$, can be captured by including extra terms $\mathcal{H}_\delta$, which constitute a deviation from the ideal Kitaev model:

$$\mathcal{H} = K \sum_{\langle ij \rangle} S_i^\gamma S_j^\gamma + \mathcal{H}_\delta \quad (3.4)$$

where $\gamma = x, y, z$ specify the three compass directions of the Kitaev exchange, K . In the zig-zag ordered systems, like Na_2IrO_3 and RuCl_3 for example, [43, 44], $\mathcal{H}_\delta$ can be captured by a Heisenberg term $\mathcal{H}_J = -J \sum_{\langle ij \rangle} \mathbf{S}_i \cdot \mathbf{S}_j$. [40] In the incommensurate ordered systems $\alpha, \beta, \gamma\text{-Li}_2\text{IrO}_3$ [49, 48], it is thought that Heisenberg coupling is small and the dominant non-Kitaev interaction is something more peculiar; Kimchi *et al.* suggested a c -axis Ising term coupling spin components parallel to the bond direction, while Lee *et al.* have suggested a symmetric off-diagonal interaction that is present on all bonds. The latter is known as the Γ term $\mathcal{H}_\Gamma = \Gamma \sum_{\langle ij \rangle} S_i^\alpha S_j^\beta + S_i^\beta S_j^\alpha$ and couples different components of spin orthogonal to the Kitaev compass direction γ . [39] Rousohatzakis and Perkins [75] recently applied this model to give a complete picture of the field dependent behavior of $\beta\text{-Li}_2\text{IrO}_3$, notably suggesting that there exists a small zig-zag component at zero field arising from a correspondingly small Heisenberg interaction [48, 42]. It is tempting to think that the 100K transition reported here is the onset of a zig-zag transition, but several of its features seem inconsistent with this picture; the energy scale is nearly an order of magnitude larger than the Heisenberg term described in Ref. [75], the moment along the b -axis is two orders of magnitude smaller than expected for a zig-zag state [42], and the isotropic hysteresis field with an anisotropic saturation moment is very difficult to imagine in this scenario. Detailed resonant magnetic x-ray scattering experiments have shown that the incommensurate state orders around half the total moment available, while the remainder remains fluctuating and no evidence at zero field for the presence of any other magnetic order. These observations make it unlikely that the moment of the hidden axial phase presently measured reflects the canted moment of some other long range order, but rather the frozen moment that is intrinsic to the phase itself.

It is clear from Figure 3.5 (b) that the hidden phase evolves like an order parameter in temperature in all crystallographic directions, and in almost all respects seems independent of the incommensurate order at low temperature; the hysteresis field does not show evidence of any jump as the system crosses into temperatures and fields where the incommensurate phase is present (inset Figure 3.5 (a) and its magnetic contribution seems perfectly separable (Figure 3.5 (b)). On the other hand, within the resolution of our measurements, the anisotropy field $H_a(T = 0)$ appears to intercept critical field $H^*(T = 0)$ at which the incommensurate state is completely suppressed [42], and this seems like a surprising coincidence. More importantly, the saturation magnetization of the hidden phase follows almost exactly the anisotropy of the magnetic susceptibility, varying by a factor of 10 between crystallographic directions. Anisotropic saturation moments are common to rare-earth magnets where $M_s = g\mu_B \mathcal{J}$, following the g -factor anisotropy which can vary between different crystallographic directions due to strong spin-orbit coupling. However, the degree of anisotropy is very difficult to explain, and moreover, the anisotropy does

not follow the local structural environment (as would be expected if the origin was from the g -factor alone). Most remarkably of all is that in contrast with the anisotropic M_s , the anisotropy field H_a is completely isotropic, within error.

In a ferromagnet with uniaxial anisotropy, the anisotropy field H_a is proportional to $\sim K_a/M_s$, where K_a is the constant describing the anisotropic free energy $F = K_a \sin^2 \theta$, with θ taken with respect to an easy axis. Within the hidden phase of β -Li₂IrO₃, H_a is isotropic (it is in this sense “pan-axial”), implying that M_s reflects the anisotropy of the free energy, in contrast to the usual case where it reflects the local moment. Given this anisotropy is determined by Kitaev exchange interaction [38, 39], it follows that the moment of the hidden phase is coupled to these interactions; the moment is itself emergent.

The recent observations of the “fractionalization” of magnetic degrees of freedom due to the onset of Kitaev-like correlations in a number of Kitaev candidate materials, may be directly related to our observations. These studies have focused largely on two-dimensional candidates, where this transition appears as a crossover. On general grounds, fluctuations in two-dimensions may suppress a phase transition [72], that might otherwise occur in 3D, so it may be that the hidden phase is connected to this short range correlated phase. One possibility, is that defects form moments that order into a spin glass. While these are not in general expected to have anisotropic saturation moment, it is known that in Kitaev systems can have special kinds of defects; site vacancies can trap flux degrees of freedom in the spin liquid, forming large local moments,[73] as shown schematically in Figure 3.5(d). In principle, these could form in the same temperature range where the thermal fractionalization seen in related materials takes place, and these could form a spin glass whose local moment is connected to the Kitaev correlations; a Kitaev spin glass.

Finally, we comment on the recent argument for the existence of scalar chiral spin order, characterized by a time reversal symmetry breaking order parameter $\mathbf{S}_i \cdot (\mathbf{S}_j \times \mathbf{S}_k)$. Although originally invoked to explain the saw-tooth torque anisotropy seen in γ -Li₂IrO₃ and RuCl₃, recent calculations appear to show that magnitude of the 3-spin coupling terms is too small to explain the data. Nevertheless, the hidden phase measured here may have some key features that are consistent with the chiral spin order picture; the phase is breaks time reversal symmetry, and the magnitude of M_s may be comparable to the scale of the 3-spin terms calculated in Ref. [67], of order $\sim 1 \text{ m}\mu_B$. This may naturally explain the anisotropy of the saturation moment, which in this picture may follow the anisotropy of the spin-spin correlations; the anisotropic exchange interactions from which 3-spin order originates, has an emergent moment that inherits this anisotropy.

Whatever the origin of the hidden phase, the presence of a phase transition, as well its extraordinary magnetic anisotropies, suggest a novel ground state that onset at relatively high temperatures, comparable to the Kitaev exchange scale. This ground state may be a manifestation of the novel excitations purported to exist in the Kitaev spin liquid, suggesting that room-temperature manifestations and, therefore, applications are at least possible.

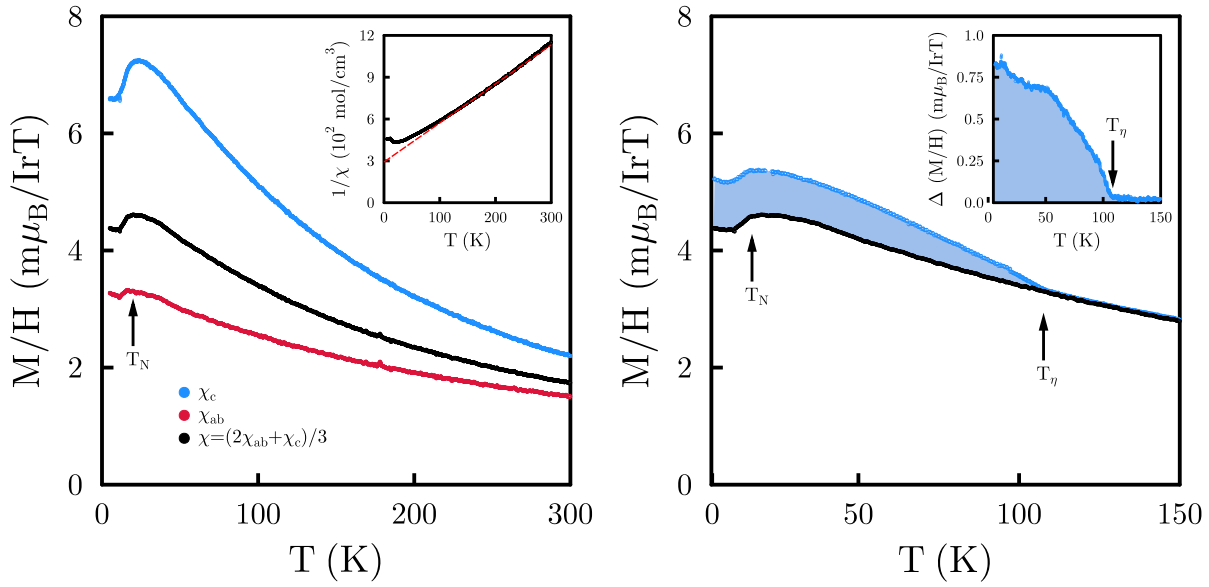


Figure 3.6: (a) Anisotropic magnetic susceptibility of Na_2IrO_3 in a 1 T magnetic field. The arrow indicates the onset of the long-ranged zig-zag ordering at $T_N = 15$ K. The inset shows the inverse of the powder average susceptibility $\chi = (2\chi_{ab} + \chi_c)/3$, yielding effective moment $\mu_{eff} \sim 1.8\mu_B/\text{Ir}$ and Weiss constant $\Theta_{CW} \sim T_\eta \sim 110$ K. (b) Polycrystalline measurements were carried out using 0.01 T. This data coincides with the powder average data (1 T) above T_η . However, a kink is observed at this temperature followed by a gradual increase. The inset accentuates this behavior by taking the difference between both curves in the main panel.

3.4 Na_2IrO_3

I would like to close this chapter with a brief discussion on Na_2IrO_3 . This 2D honeycomb¹ system has been a prototype for the study of Kitaev physics [46, 76], and it has provided direct the first experimental observation of bond-directional Kitaev exchange using diffuse magnetic X-ray scattering [77].

Anisotropic magnetic susceptibility measurements taken with a 1 T field show a transition at $T_N = 15$ K, which corresponds to the onset of a collinear zig-zag ordering with propagation vector $q = (0, 1, 1/2)$ [78, 43, 79], and confirm the $\mathcal{J} = 1/2$ nature of the local isospin with $\mu_{eff} \sim 1.8\mu_B/\text{Ir}$ and $\Theta_{CW} \sim 110$ K (Figure 3.6(a)). The magnetic anisotropy ratio is $\chi_\perp/\chi_\parallel = 2$ which can be contrasted with our finding for $\beta, \gamma\text{-Li}_2\text{IrO}_3$ (see chapter 2 section 2.3). On the other hand, the frustration parameter $f = |\Theta_{CW}|/T_N \sim 7$, is unusually high for a quantum spin in a bipartite lattice, and has been attributed to either exchange or geometric frustration [80, 76].

¹monoclinic, space group $2C/m$

Most recently, I have measured a polycrystalline sample of Na_2IrO_3 using 0.01 T magnetic field and observed a transition at $T_\eta = 110$ K as seen in Figure 3.6(b). The figure inset shows the difference between the average susceptibility ($\chi = (2\chi_{ab} + \chi_c)/3$) and the polycrystalline data to accentuate the behavior below T_η . Interestingly, $T_\eta \sim \Theta_{CW}$ which means that $|\Theta_{CW}|/T_\eta \sim 1$. These measurements were repeated on various single crystals with no success. Therefore, follow up experiments must be conducted.

Chapter 4

Resonance X-ray Scattering Technique

In this chapter I will describe the basic aspects of Resonant X-ray Scattering. This technique emerged in the 1970's when Bergevin and Brunel [81] demonstrated that x-rays are also sensitive to the distribution of electronic spins in magnetic materials by detecting anti-ferromagnetic Bragg reflections in NiO, thus confirming theoretical predictions by Platzman and Tzoar [82].

Resonant X-ray Scattering is a "photon in–photon out" technique that combines x-ray diffraction with x-ray spectroscopy in a single experiment [83]. Diffraction provides information about the spatial order, while spectroscopy offers sensitivity to the electronic state involved in the ordering. This second order process consists of two steps:

- **Absorption:** An incoming photon with energy $\hbar\omega_i$ and momentum $\mathbf{k}_i$ is absorbed by the sample, causing a transition of a core electron up to some unoccupied state close to the Fermi level.
- **Emission:** This intermediate state is short-lived ($\sim 10^{-15}$ s) so that the electron immediately decays back to its initial core state, emitting a photon of energy $\hbar\omega_f$ and momentum $\mathbf{k}_f$.

The total energy and momentum of the system (photons + electrons) are conserved such that:

$$\begin{aligned}\hbar\omega_f - \hbar\omega_i &= \hbar\omega \\ \hbar\mathbf{k}_f - \hbar\mathbf{k}_i &= \mathbf{Q}\end{aligned}\tag{4.1}$$

Generally, excitations are created with energy $\hbar\omega$ and momentum $\mathbf{Q}$. The study of the energy/momentum dependence of these excitations is called Resonant Inelastic X-ray Scattering (RIXS). When incoming and outgoing photons have the same energy ($\hbar\omega_i = \hbar\omega_f$), the scattering is purely elastic and only momentum is transferred to the system. This Resonant Elastic X-ray Scattering (REXS) gives access to the ground state of the system

and permits the study of lattice, charge, orbital and magnetic ordering phenomena, complementing more traditional methods such as non-resonant x-ray diffraction and neutron scattering.

Neutron scattering has been the prevailing technique in the study of magnetic structures for many decades. However, it has several limitations that the x-ray counterpart helps to address. For example, due to the low neutron fluxes available, big sample size is usually a requirement. Furthermore, the strong neutron absorption of some isotopes has to be taken into account. Since iridium has a strong neutron absorption cross-section and only small single crystals of Li_2IrO_3 are available, neutron scattering is very challenging technique to study these iridates.

4.1 Classical description

x-ray diffraction

Single crystals form a periodic pattern of atoms in three dimensions which can be characterized by an array of (h, k, l) planes. Electromagnetic radiation is scattered by the electrons in these planes, producing spherical waves which mostly cancel one another except when a specific condition is met. W.L. Bragg and W.H. Bragg showed that when the wavelength of the incoming x-ray (λ) equals the periodicity of the (h, k, l) planes (d), the outgoing rays constructively interfere to give rise to Bragg reflections:

$$2d \sin \theta = n\lambda \quad (4.2)$$

where θ is the incident angle, and n is an integer value. These diffraction peaks reflect the underlying symmetry of the crystal and it is regularly used to determine crystal's structure by measuring the angle and intensity of the diffracted beam.

Light-Matter interactions

All interaction effects of polarized photons with matter can be expressed in terms of a complex atomic scattering length:

$$f_n(\mathbf{Q}, \omega, \epsilon, \epsilon') = f^o(\mathbf{Q}) + f^m(\mathbf{Q}) + f'(\omega, \epsilon, \epsilon') - i f''(\omega, \epsilon, \epsilon') \quad (4.3)$$

where $f^o(\mathbf{Q})$ and $f^m(\mathbf{Q})$ are the non-resonant charge and magnetic scattering form factors. The Thomson scattering term is proportional to the atomic number, $f^o(\mathbf{Q}) \sim Z$, where all core and valence electrons interact with the radiation field. The dispersion correction term or resonant contribution, $f^{RXS}(\omega, \epsilon, \epsilon') = f'(\omega) - i f''(\omega)$, is a function of the photon energy and polarization of the incoming and scattered x-ray beams. Away from an absorption edge, Thomson scattering ($f^o(\mathbf{Q})$) becomes the only important and detectable contribution. As we approach an absorption edge, the dispersion correction ($f^{RXS}(\omega, \epsilon, \epsilon')$) becomes very important.

Physically, the scattering length describes the change in amplitude and phase suffered by the incident plane wave ($\sim e^{ik \cdot r}$) during the scattering process ($\sim f_n e^{ik \cdot r}/r$). In a periodic arrangement, each atom's contribution is discretely summed to yield the crystal structural factor:

$$\begin{aligned} F(\mathbf{Q}, \omega) &= \sum_{m,n} f(\mathbf{Q}, \omega, \epsilon, \epsilon') e^{i\mathbf{Q} \cdot (\mathbf{R}_m + \mathbf{r}_n)} \\ &= \left(\sum_m f(\mathbf{Q}, \omega, \epsilon, \epsilon') e^{i\mathbf{Q} \cdot \mathbf{r}_m} \right) \cdot \left(\sum_n e^{i\mathbf{Q} \cdot \mathbf{R}_n} \right) \end{aligned}$$

where $\mathbf{R}_m = n_1 \hat{a}_1 + n_2 \hat{a}_2 + n_3 \hat{a}_3$ represents the vector pointing to the origin of a unit cell m and r_n is the position of the scattering atom from that origin. The first sum describe the interference of waves scattered from different sites within a unit cell, while the second sum is due to the interference from different unit cells. The scattered intensity, $I = |F(\mathbf{Q}, \omega)|^2$, is related to the correlation length of the studied order, and it show interference maxima when the Laue condition, $\mathbf{Q} \cdot \mathbf{R} = 2m\pi$ for integer m , is met. This allows to measure reciprocal lattice positions, with a reciprocal vector $\mathbf{G} = h\hat{b}_1 + k\hat{b}_2 + l\hat{b}_3$, using diffraction techniques. The diffraction maxima will repeat when $\mathbf{Q} = \mathbf{G}$ (h, k, l integers) so that different crystal's symmetry will give rise to different selection rules. If other orders are present (spin, charge or orbital), they can change the crystal symmetry and give rise to new periodicity, which are labeled as $(\frac{h}{n_1}, \frac{k}{n_2}, \frac{l}{n_3})$. Integer values of n_i refer to a manifold multiplication of the unit cell and are referred to as *commensurate* orders. When n_i takes non-integer values, the order is known as *incommensurate*, an example of which will be studied in the next few chapters.

4.2 REXS Cross-section

Let us calculate the REXS/RIXS scattering cross-section by considering the time dependent perturbation of an ensemble of electrons by a quantized electromagnetic field. The incident EM field is described by the vector potential $\mathbf{A}(\mathbf{r}, t)$, which can be expanded in plane waves as:

$$\mathbf{A}(\mathbf{r}, t) = \sqrt{\frac{2\pi\hbar c^2}{V_q}} \sum_{q,\lambda} (\epsilon_\lambda a_q e^{i(q \cdot r - \omega t)} + \epsilon_\lambda^* a_q^\dagger e^{-i(q \cdot r - \omega t)}) \quad (4.4)$$

where ϵ_λ is the polarization unit vector associated with a mode $\lambda = 1, 2$ and, $a_q^\dagger(a_q)$ is the operator that creates (annihilates) a photon with wave vector $\mathbf{q}$ and polarization state λ . This EM field induces transitions between an initial state $|i\rangle$ ($\hbar\mathbf{k}_i, \hbar\omega_i, \epsilon_i$) and a final state $|f\rangle$ ($\hbar\mathbf{k}_f, \hbar\omega_f, \epsilon_f$), where both states contain an electronic and a photon part [84]. A first order process occurs when the system evolves directly from $|i\rangle$ to $|f\rangle$, while in a second order process, an intermediate state $|n\rangle$ is involved. In these processes, the photon

transfers energy ($\hbar\omega_f - \hbar\omega_i = \hbar\omega$) and momentum ($\hbar\mathbf{k}_f - \hbar\mathbf{k}_i = \hbar\mathbf{Q}$) to the sample, and the transition probability between the initial and final quantum states can be calculated using "Fermi Golden Rule":

$$\omega_{i \rightarrow f} = \frac{2\pi}{\hbar} \left| \langle f | H_{ext} | i \rangle + \sum_n \frac{\langle f | H_{ext} | n \rangle \langle n | H_{ext} | i \rangle}{E_i - E_n} \right|^2 \delta(E_f - E_i) \quad (4.5)$$

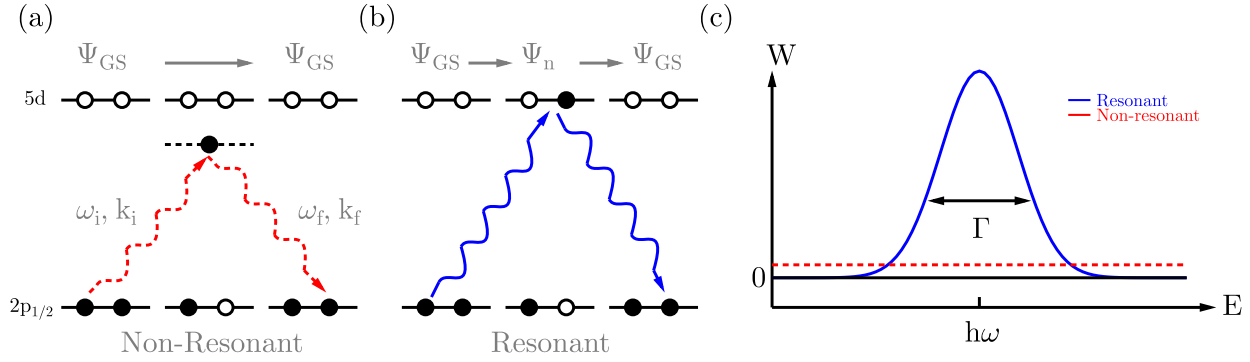


Figure 4.1: Resonant and non-resonant scattering processes. (a) The H_2 and H_4 terms in the light-matter interaction Hamiltonian give rise to non-resonant scattering amplitudes. This first order process consist in the excitation of a core electron into a virtual state, followed by instantaneous decay to the ground state. (b) The H_1 and H_3 terms contribute to second order processes where the incident photon energy is tuned to an electronic absorption edge, promoting an excitation from the ground state (Ψ_{GS}) to a real excited state (Ψ_n) and subsequent decay back to Ψ_{GS} . In the iridates systems we study, the transition corresponds to $2p^{1/2} \leftarrow 5d (L_2)$ and $2p^{3/2} \leftarrow 5d (L_3)$. (c) First order processes are nearly energy independent, whereas second order processes resonate around the electronic transition energy of an absorption edge [85].

The sum is over all possible n states and the dimension of $\omega_{i \rightarrow f}$ is inverse time. This transition probability can be calculated using a time-dependent Hamiltonian of the form $H = H_o + H_{ext}$, where the initial $|i\rangle$ and final $|f\rangle$ states are eigenstates of the unperturbed Hamiltonian H_o , and H_{ext} is the perturbation Hamiltonian describing the light-matter interaction. The total Hamiltonian of the system in the non-relativistic limit can be written

as:

$$\begin{aligned}
H &= \sum_j \left\{ \frac{1}{2m_e} \left(p_j - \frac{e}{c} A(r_j) \right)^2 + V(r_j) \right\} + \sum_{j \neq k} \frac{e^2}{|r_j - r_k|^2} + \sum_q \hbar\omega (a_q^\dagger a_q + 1/2) \\
&\quad - \frac{e\hbar}{m_e c} \sum_j s_j \cdot (\nabla \times A(r_j)) - \frac{e\hbar}{2m_e^2 c^4} \sum_j s_j \cdot (\partial_t A \times A) \\
&= H_o + \underbrace{\sum_j \left[\frac{e}{m_e c} A \cdot p_j \right]}_{H_1} + \underbrace{\sum_j \left[\frac{e^2}{2m_e c^2} A^2 \right]}_{H_2} - \underbrace{\sum_j \left[\frac{e\hbar}{m_e c} s_j \cdot (\nabla \times A(r_j)) \right]}_{H_3} - \underbrace{\sum_j \left[\frac{e\hbar}{2m_e^2 c^4} s_j \cdot (\partial_t A \times A) \right]}_{H_4}
\end{aligned}$$

where the gauge was fixed by choosing $\nabla \cdot A$ and all terms independent of A are included in H_o . The perturbation Hamiltonian H_{ext} , therefore, has four terms:

- H_2 and H_4 are quadratic in the vector potential A and contribute to first order amplitude since the scattering process conserves the number of photons. These terms describe the Thomson scattering and the non-resonant magnetic scattering, respectively.

$$\begin{aligned}
f^o(Q) &= \epsilon \cdot \epsilon^* \langle i | e^{iQ \cdot r} | i \rangle = \epsilon \cdot \epsilon^* \int \rho(r) e^{iQ \cdot r} d^3r \\
f^m(Q) &= \frac{\hbar\omega}{mc^2} \left(\frac{1}{2} L(Q) \cdot P_L(k, k', \epsilon, \epsilon^*) + S(Q) \cdot P_S(k, k', \epsilon, \epsilon^*) \right)
\end{aligned}$$

where $\rho(r)$ is the electronic density, $\mathbf{P}_L$ and $\mathbf{P}_S$ are vectors depending on the wave-vector and polarization of the incoming and outgoing light, and $L(Q)$, $S(Q)$ are Fourier transform of the orbital and spin momenta. For photons at the Ir $L_{2,3}$ edges (11 – 13 keV) and given $mc^2 \sim 0.511$ MeV, then $\hbar\omega/mc^2$ is about 0.02, and therefore, $f^m(Q)$ is very difficult to detect.

- H_1 and H_3 are linear in A and only contribute to second order amplitude. Thus they give rise to resonant processes. The relevant transition probability becomes:

$$f^{RXS}(Q, \omega) = -\frac{1}{m} \sum_n \frac{\langle i | \tilde{O}^* | n \rangle \langle n | \tilde{O} | i \rangle}{E_i - E_n + \hbar\omega + i\Gamma/2} \quad (4.6)$$

where the intermediate state is characterized by energy E_n and lifetime $2\pi\hbar/\Gamma$. This lifetime accounts for the many non-radiative interaction terms that are not included in H_{ext} which make the intermediate states very short lived.

The imaginary part $f''(Q, \omega)$ of the forward scattering amplitude at a site j is proportional to the absorption cross-section at the same site. In order to obtain absorption/emission cross-sections or the resonant scattering amplitude, the matrix elements $\langle n | \tilde{O} | i \rangle$ have to be evaluated. The operator is given by [86]:

$$\tilde{O} = (\epsilon \cdot \mathbf{p} + i\mathbf{S} \cdot (\mathbf{k} \times \epsilon)) e^{i\mathbf{k} \cdot \mathbf{r}} \quad (4.7)$$

where Taylor expansion of the exponential $e^{i\mathbf{k}\cdot\mathbf{r}} \sim 1 + \mathbf{k} \cdot \mathbf{r} + \dots$ allows us to obtain a multiple expansion for the transition matrix, with contributions from the electric dipole, quadrupole, octupole (E1, E2, E3), and the magnetic dipole, quadrupole (M1, M2) [87]:

$$\begin{aligned}\tilde{O} &= \tilde{O}_{E1} + \tilde{O}_{E2} + \tilde{O}_{E3} + \tilde{O}_{M1} + \tilde{O}_{M2} \\ \tilde{O}_{E1} &= \epsilon \cdot \mathbf{r} \\ \tilde{O}_{E2} &= \frac{i}{2}(\epsilon \cdot \mathbf{r})(\mathbf{k} \cdot \mathbf{r}) \\ \tilde{O}_{E3} &= \frac{1}{6}(\epsilon \cdot \mathbf{r})(\mathbf{k} \cdot \mathbf{r})^2 \\ \tilde{O}_{M1} &= \frac{\hbar}{2m(E_n - E_i)}(\mathbf{k} \times \epsilon) \cdot (\mathbf{L} + 2\mathbf{S}) \\ \tilde{O}_{M2} &= i\frac{\hbar}{2m(E_n - E_i)}(\mathbf{k} \times \epsilon) \cdot \left(\frac{2}{3}\mathbf{L} + 2\mathbf{S}\right)(\mathbf{k} \cdot \mathbf{r})\end{aligned}$$

Dipole Approximation

The 5d orbitals involved in the magnetic and electronic interactions of iridates, can be access by electric dipole transitions [84]. The relevant matrix elements can be found by expressing the momentum operator $\mathbf{P} = \frac{im}{\hbar}[H, \mathbf{r}]$ such that,

$$\begin{aligned}\langle n|\tilde{O}|i\rangle &= \langle n|\epsilon \cdot \mathbf{P}|i\rangle \\ &= \frac{im}{\hbar} \langle n|\epsilon \cdot [H, \mathbf{r}]|i\rangle \\ &= \frac{im}{\hbar}(E_n - E_i) \langle n|\epsilon \cdot \mathbf{r}|i\rangle\end{aligned}$$

The dipole approximation assumes that the size of the absorbing atomic state is small compared to the x-ray wavelength such that the electric field driving the transition is constant over the atomic volume. The polarization dependent x-ray resonant intensity in the dipole approximation becomes:

$$I^{RXS} = 4\pi^2\alpha_f(E_n - E_i) |\langle n|\epsilon \cdot \mathbf{r}|i\rangle|^2 \quad (4.8)$$

where α_f is the fine structure constant and the intensity has dimension of $[\text{length}^2 \times \text{energy}]$. This expression doesn't have an explicit dependence on scattering from magnetic moments such that one may wonder where the sensitivity to magnetic degrees of freedom comes from. This is mainly due to the joint effect of (1) the Pauli exclusion and, (2) the Spin-Orbit coupling. Since the scattering amplitude depends on the availability of intermediate states and the spin is conserved in optical transitions, ground state electrons with the same spin as the unoccupied intermediate states will be promoted from a core level

to the valence band. In case of core levels with $l \neq 0$, the SOC acts to polarize the orbital state as it is the case of the L_2 and L_3 edge of Ir. Because of the selection rules to the intermediate state, this orbital polarization translates into an imbalance in the different matrix elements which lead to a non-vanishing magnetic scattering amplitude.

To interpret REXS results, it is not necessary to evaluate equation 4.8. However, we still need to understand the relation between the polarization of the photons and the direction of the magnetic moments. This can be achieved by expanding the matrix elements in terms of spherical harmonics¹ such that the moment and the photon's energy/polarization can be treated separately $F^{REXS} = F_1(\omega, \epsilon)F_2(\hat{m})$ [88]. The final expression for the resonant magnetic form factor in terms of the experimental parameters (ϵ^* , ϵ), was derived by Hannon et. al. [89] and becomes:

$$F^{mag} = F^{(0)}(\epsilon^* \cdot \epsilon) + F^{(1)}(\epsilon \times \epsilon^*) \cdot \hat{m} + F^{(2)}(\epsilon^* \cdot \hat{m})(\epsilon \cdot \hat{m}) \quad (4.9)$$

where $\hat{m}$ is the direction of the local moment, and $(0, 1, 2)$ denote the order of the term with respect to $\hat{m}$. $F^{(0,1,2)}$ are functions of the spherical harmonic of degree l and order m , such that:

$$\begin{aligned} F^{(0)} &= \frac{3}{4k}(F_{11} + F_{1\bar{1}}) \\ F^{(1)} &= \frac{3}{4k}(F_{11} - F_{1\bar{1}}) \\ F^{(2)} &= \frac{3}{4k}(2F_{10} - F_{11} - F_{1\bar{1}}) \end{aligned}$$

$F^{(0)}$ is not proportional to $\hat{m}$ so that is ignored in resonant magnetic scattering. $F^{(1)} \sim \hat{m}$ is related to magnetic circular dichroism in x-ray absorption and gives rise to first harmonic satellite peaks of antiferromagnets. Finally, $F^{(2)} \sim \hat{m}^2$ is related to linear dichroism and it is not sensitive to antiferromagnetism but gives rise to second harmonic in spiral systems.

Polarization effect

The polarization vector ϵ is defined by a linear combination of two orthogonal basis vectors, either parallel (π) or perpendicular (σ) to the scattering plane. The scattering amplitude during the resonance process can be described by a second rank tensor in the (σ, π) basis [85]:

$$(\epsilon^* \cdot F \cdot \epsilon) = \begin{pmatrix} \sigma^* \cdot F \cdot \sigma & \sigma^* \cdot F \cdot \pi \\ \pi^* \cdot F \cdot \sigma & \pi^* \cdot F \cdot \pi \end{pmatrix} = \begin{pmatrix} F_{\sigma\sigma} & F_{\sigma\pi} \\ F_{\pi\sigma} & F_{\pi\pi} \end{pmatrix}$$

¹ $\epsilon \cdot \mathbf{r} = \epsilon_x \sin \theta \cos \phi + \epsilon_y \sin \theta \sin \phi + \epsilon_z \cos \theta = \sqrt{\frac{4\pi}{3}} \sum_q Y_{1,q} P_{\epsilon,q}$ where $q = 0, 1, -1$ for linear, right-circular or left-circular polarized light respectively, $Y_{1,q}$ are the spherical harmonics and $P_{1,q}$ are the polarization factors. The scattering geometry and the polarization of the radiation enter in the calculation of the cross section by means of these polarization factors.

Therefore, equation 4.9, can be expressed in this matrix form as:

$$\begin{aligned} F^{mag} &= F^{(0)} \begin{pmatrix} 1 & 0 \\ 0 & \hat{k}' \cdot \hat{k} \end{pmatrix} + F^{(1)} \begin{pmatrix} 0 & \hat{k} \\ -\hat{k}' & \hat{k}' \times \hat{k} \end{pmatrix} \cdot \hat{m} \\ &= F^{(0)} \begin{pmatrix} 1 & 0 \\ 0 & \cos 2\theta \end{pmatrix} + F^{(1)} \begin{pmatrix} 0 & x \cos \theta + z \sin \theta \\ z \sin \theta - x \cos \theta & -y \sin 2\theta \end{pmatrix} \end{aligned}$$

where θ is the scattering angle, and the spin direction (x, y, z) are defined with respect to the diffraction plane. The first term is related to charge scattering where the polarization remains unchanged. The second is the first harmonic resonant magnetic scattering term which allows for mixing between different channels except for $F_{\sigma\sigma}$. It is therefore possible to determine which component of the magnetic moment contributes to the resonant scattering intensity $I^{REXS} \sim |(\epsilon^* \times \epsilon) \cdot \hat{m}|^2$ by performing polarization analysis ($I_\pi = I_{\pi\sigma} + I_{\pi\pi}$ and $I_\sigma = I_{\pi\sigma}$) and 'azimuthal scans' (ϕ):

$$\begin{aligned} I_{\pi\pi} &\sim (k' \cdot \hat{m})^2 \sim (\cos \phi \cos \theta)^2 \\ I_{\pi\sigma} &\sim ((k' \times k) \cdot \hat{m})^2 \sim (\sin \phi \sin 2\theta)^2 \end{aligned}$$

The azimuth angle ϕ defines rotation of the sample around the scattering wave vector, $\mathbf{Q} = \mathbf{k}' - \mathbf{k}$ while meeting this Laue scattering condition. For σ polarized incident x-ray, the projection of the structure factor onto the (fixed) direction k' varies depending on the azimuth angle, with maximum magnetic intensity when the magnetic moments that give rise to the scattering make the smallest angle with k' and zero intensity when they are perpendicular.

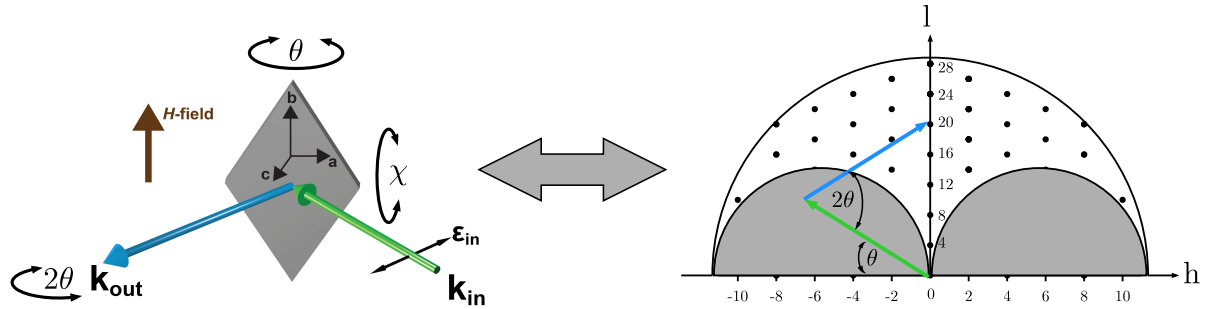


Figure 4.2: **Definition of the angles and vectors used in the main text to describe the scattering process.** The real space (left) shows the crystal orientation with respect to the applied magnetic field used in next chapter. The momentum and polarization of the incident and scattered beams are shown. The angles 2θ , θ , χ allows us to access any (h, k, l) reciprocal lattice position (right). The large semicircle defines the Ewald sphere while the shaded areas denote the inaccessible region on the sample horizon.

4.3 Experimental Set-up

Resonant elastic and inelastic x-ray scattering measurements were carried out at the Advanced Photon Source, Argonne National Lab:

- **Beamline 6 ID-B:** REXS on $\beta\text{-Li}_2\text{IrO}_3$ and $\text{Li}_2\text{Ru}_x\text{Ir}_{1-x}\text{O}_3$ to determine the magnetic ground state.
- **Beamline 6 ID-C:** REXS on $\beta\text{-Li}_2\text{IrO}_3$ under a $H = 5\text{ T}$ variable magnetic field to understand the suppression of incommensurate order and the behavior above the critical field H^* .
- **Beamline 4 ID-D:** REXS on $\gamma\text{-Li}_2\text{IrO}_3$ under a $P = 2\text{ GPa}$ variable hydrostatic pressure to study the effect of pressure on the ground state.
- **Beamline 27 ID-B:** RIXS on $\beta\text{-Li}_2\text{IrO}_3$ to study the excitation spectrum (dispersion) of the coexisting magnetic states.

These techniques require high photon flux, energy tunability, well-defined incident polarization, analysis of the scattered beam polarization, and high momentum resolution.

In a typical resonant x-ray scattering experiment, an incident photon with momentum and polarization (k, ϵ) is scattered as a photon with momentum and polarization (k', ϵ^*) as shown in Figure 4.2. Any position in reciprocal space (h, k, l) can be accessed by adjusting a set of real space angles $(2\theta, \theta, \chi, \phi)$, where 2θ is the angle between the incoming and scattered x-rays (corresponding to the Bragg condition) which can be changed by rotating the detector, θ denotes sample's rotations in the scattering plane, while χ corresponds to sample's rotations with respect to the scattering plane (in and out), and ϕ rotates the sample around an (h, k, l) position while meeting the scattering condition. The gray shaded areas represent the sample horizon-blocked areas and the large semi-circle represents the Ewald's sphere defined by the Ir L_3 edge absorption $E_{L3} = 11.215\text{ keV}$. Each of these experiments has further restrictions defined by the required geometry, e.g. split coil magnets, diamond anvil cells, etc.

Chapter 5

REXS Under Applied Field on $\beta\text{-Li}_2\text{IrO}_3$

The work described in this chapter has been published as Ref. [42].

The Mott-Kitaev honeycomb iridates crystallize in 2D and 3D structures (the harmonic honeycombs [32]), and all known compounds are found to magnetically order at low temperature in one of two ways: a commensurate ‘zig-zag’ phase (found in $\alpha\text{-Na}_2\text{IrO}_3$ and $\alpha\text{-RuCl}_3$ [43, 44, 45]), and an incommensurate order (found in $\alpha, \beta, \gamma\text{-Li}_2\text{IrO}_3$ [32, 33, 47]). This suggests that there are non-Kitaev terms in the Hamiltonian, relieving the frustration and obscuring any low-energy signature of the Kitaev physics [38, 23, 39]. As a result, the presence of Kitaev interactions is often inferred from scattering studies [90, 77] or from evidence of anomalous dissipative processes in spectroscopic measurements [91, 92]. A central question in these materials is how these different ordered states are connected, and how their strongly correlated nature is evident in their low energy response functions.

In this chapter, we find evidence for nearly degenerate broken symmetry states in $\beta\text{-Li}_2\text{IrO}_3$, a signature of the underlying magnetic frustration. This compound is the simplest of the 3D harmonic honeycomb structures, composed of interwoven networks of hexagonal chains propagating in the $\mathbf{a} \pm \mathbf{b}$ directions. Importantly, Kitaev exchange along the $\mathbf{c}$ -axis bonds should couple spins pointing in the $\mathbf{b}$ -axis, making the $\mathbf{b}$ -axis magnetically special, and thus I focus on the response of the system to an applied field in this direction. We find that in this configuration, (1) the incommensurate order (INC) is very fragile against a magnetic field and it disappears at the characteristic field H^* , (2) a relatively small field can induce a strongly correlated state with uniform ‘zig-zag’ component along the $\hat{a}$ -axis, (3) This commensurate ‘zig-zag’ component (COM) grows linearly with field but it is otherwise undetectable at zero field, (4) the sum of the intensities of the Bragg reflections associated with the INC and COM components remains constant up to a field slightly larger than H^* . These observations are signatures of the smallness of the Heisenberg term J compared to the Kitaev K and off-diagonal Γ terms.

This work provides evidence for strong correlations and a possible familial connection between the low energy Hamiltonian of different Kitaev systems.

5.1 Hyperhoneycomb lattice symmetries

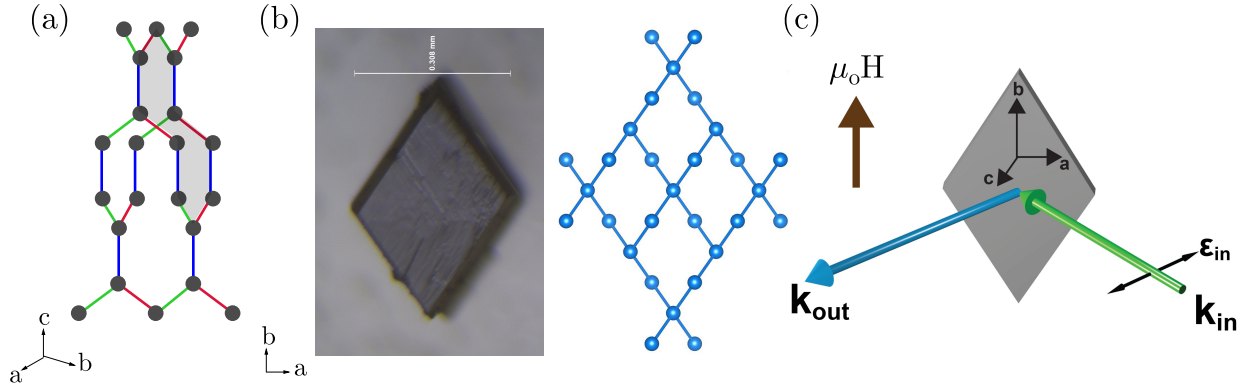


Figure 5.1: (a) Crystal structure of the three dimensional hyperhoneycomb $\beta\text{-Li}_2\text{IrO}_3$ (b) Photo of a single crystal of $\beta\text{-Li}_2\text{IrO}_3$ and projection of the crystal lattice in the ab -plane. The Ir atoms (blue dots) form zigzag chains stacked along the c and alternating along the directions $a \pm b$. (c) The scattering geometry used during this experiment showing the polarization of the incoming x-ray beam (π -polarized) and the direction of the applied magnetic field (along the b -axis).

As previously discussed in Chapter 2, the hyperhoneycomb lattice's space group is $Fddd$, number 70. Together with the primitive translation vectors of the face-centered Bravais lattice, there are two-fold rotations through c -bonds, and inversion centers and glide planes through d -bonds, as follows:

- There are two-fold rotations R , of three types, corresponding to each of the three orthorhombic axes a, b, c . Each is a rotation by π around one of the orthorhombic axes. The rotation axis passes through a midpoint of a c -bond.
- There are inversion centers I , at the midpoint of d -bonds. (The d -bonds are the remaining "diagonal" bonds, which form the zigzag chains; they carry Kitaev labels x or y .)
- There are glide operations G , again of three types corresponding to the three orthorhombic axes a, b, c . The c -type glide plane involves reflection across the (a, b) plane normal to c , together with translation by half the primitive lattice vector normal to c , i.e. translation by $(1/4, 1/4, 0)$ in orthorhombic coordinates. The a and b glide planes are similarly defined. For all of the glide operations, the reflection plane passes through a midpoint of a d -bond.

The midpoint of a c-bond is related to the midpoint of a d-bond through a translation by vectors such as $(1/8, 1/8, 1/8)$, up to component-wise $\pm$ signs. Note that the standard setting of Fddd (origin choice 2) places the origin at the midpoint of a d-bond.

The primitive unit cell of the lattice contains 4 sites. Taking the origin to be at a c-bond midpoint, we can write the coordinates of the first two sites, across this c-bond, as $(0, 0, \pm 1/12)$. The other two sites have coordinates $(1/4, 1/4, 1/4 \pm 1/12)$. We can shift the origin to a d-bond midpoint by shifting the sites by $-(1/8, 1/8, 1/8)$.

Finally, we note the relations among the symmetry operations. Each glide operation is related to the respective (a, b, c) rotation, through a product with the inversion symmetry. Moreover, each pair of rotations generates the third. Thus the full lattice symmetries can be generated from the translations, an inversion center and two rotations.

5.2 Zero-Field Incommensurate order Ψ_I

The zero field magnetic order of β - Li_2IrO_3 , studied by Biffin et. al.[49], was reported to be a complex, incommensurate state with non-coplanar and counter-rotating Ir moments. Figure 5.2(a) shows a projection of the magnetic structure on the ac plane. This magnetic structure is very similar to the structure found in the related compound γ - Li_2IrO_3 [48], both with propagation vector $q = (0.57, 0, 0)$. The curly arrows indicate the counter-rotation of the moments between consecutive c-axis sites, where the plane of rotation alternates between two directions tilted away from the ac plane. The tilt angle is smaller in β - Li_2IrO_3 but apart from this difference, both magnetic structures can be regarded as equivalent. This suggests that the defining features of the magnetic structure (non-coplanarity, counter-rotation, incommensurate wavevector) are determined by the same type of short-range magnetic interactions in both polytypes, and that those features are robust against changes in the global lattice connectivity. Nonetheless, this complex order can be obtained by considering the microscopic $K - J - \Gamma$ Hamiltonian introduced by Lee et. al. [39].

In previous chapters, we showed the thermodynamic response of a single crystal of β - Li_2IrO_3 . The anomaly at $T_I = 38$ K corresponds to the onset of the incommensurate magnetic state with order parameter Ψ_I . REXS experiments showed that upon cooling below T_I , new satellite peaks appeared at reciprocal lattice points $(h, k, l) + q$, with h, k, l integers and $q = (0.57, 0, 0)$. Scans through this peaks are shown in Figure 5.2(b). These INC peaks are very sharp in all three orthogonal directions, with a full-width-half-maximum (FWHM) ~ 350 Å (20 unit cells), indicating that the magnetic order is well developed and as long-range as the structure itself.

The magnetic origin of the observed INC peaks can be tested by studying its temperature and energy dependence. In Figure 5.2(c), we illustrate that the integrated intensity of $\mathbf{Q} = (-0.574, 0, 16)$, evolves like an order parameter Ψ_I as a function of temperature. A power-law fit gives an onset temperature $T_{fit} = T_I$ which agrees with the thermodynamics data. Furthermore, below T_I the INC intensity shows a maximum at the resonance

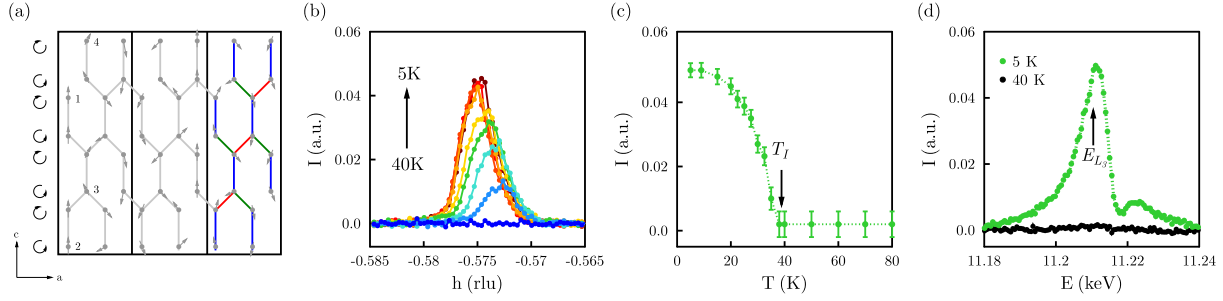


Figure 5.2: Temperature and energy dependence of the zero-field incommensurate magnetic ground state. (a) Projection of the magnetic structure in the ac plane. The curly arrows indicate the counter-rotation of the moments between consecutive sites along the c -axis. The four Ir sites in the primitive unit cell are labeled 1-4. In unit cell 3, the bonds have been colored red/green/blue to indicate the different ferromagnetic Ising axis for each bond in the Kitaev Model. This figure has been adapted from reference [49] (b) Magnetic Bragg peak at $(-0.57, 0, 16)$ taken at different temperatures. (c) Temperature dependence of the integrated intensity showing an order parameter behavior with an onset at $T_I = 38$ K. A Gaussian fit to the integrated intensity in (b) gives the χ^2 uncertainty shown by the error bars. (d) Energy scans through the magnetic peak for temperatures above (40 K) and below (5 K) the ordering temperature T_I .

energy below T_I as expected from magnetic scattering at an absorption edge, while no enhancement is observed to the changing x-ray energy above T_I (see Figure 5.2 (d)).

$\beta\text{-Li}_2\text{IrO}_3$ Magnetic basis vectors and Selection rules

As discussed in previous work [48], the Ir^{4+} moments occupy a single crystallographic site with ions located at $(1/8, 1/8, z)$ with $z = 0.70845(7)$. The four Ir ions in the primitive unit cell are labeled 1-4 in Figure 5.2 (a). To describe the structure formed by these four moments, we consider the symmetry-allowed basis vectors for a magnetic structure with propagation vector $q = (0.57, 0, 0)$ which yields:

$$F = \begin{bmatrix} 1 \\ 1 \\ \delta \\ \delta \end{bmatrix}, C = \begin{bmatrix} 1 \\ 1 \\ -\delta \\ -\delta \end{bmatrix}, A = \begin{bmatrix} 1 \\ -1 \\ -\delta \\ \delta \end{bmatrix}, G = \begin{bmatrix} 1 \\ -1 \\ \delta \\ -\delta \end{bmatrix} \quad (5.1)$$

where for each vector the four values are relative phase factors between the Fourier components at the four magnetic sites in the primitive cell, and $\delta = e^{-i\pi q/2}$. Each magnetic basis vector contains a strict, symmetry-imposed phase relation between the magnetic moments at the various sites in the primitive unit cell. It follows that simply the presence

or absence of magnetic Bragg peaks at certain positions can already identify which basis vectors are present.

Using these basis vectors, we can derive selection rules for the magnetic scattering with the following form for the structural factor:

$$\mathcal{F}(\mathbf{Q}) = f_S \sum_i \mathbf{M}_i e^{i\mathbf{Q} \cdot \mathbf{r}_i} \quad (5.2)$$

where $\mathbf{Q}$ is the reciprocal lattice vector, $\mathbf{M}_i$ is the ordered moment on the Ir ion at position $\mathbf{r}_i$ and the prefactor $f_S = e^{i\pi(h+k)} + e^{i\pi(h+l)} + e^{i\pi(k+l)}$ is the structure factor for the face-centered orthorhombic lattice. Direct calculation of the structural factor gives the following selection rules:

- F, A basis: h, k, l are all odd, or all even with $h + k + l = 4n$, n integer, with no contribution from A if $l = 6m$ and no contribution from F if $l = 3 + 6m$, m integer. In the limit $q \rightarrow 0$, F basis vector recovers ferromagnetic order.
- C, G basis: h, k, l are all odd, or all even with $h + k + l = 4n + 2$, n integer, with no contribution from G if $l = 6m$ and no contribution from C if $l = 3 + 6m$, m integer.

Using these selection rules and performing azimuth scans (ϕ) at the allowed magnetic Bragg peaks positions, we can determine the relative phase between two basis vectors. Biffin et.al. concluded that the magnetic structure of β - Li_2IrO_3 is described by a single irreducible representation $\Gamma_4 = (iA_x, iC_y, F_z)$, where x, y, z refer to spin directions along the orthorhombic axes a, b, c respectively. Here F is uniform, and is $\pi/2$ out of phase with the non-uniform basis vectors A and C which are present. The magnitude of the resulting ordered moment was found to be $0.47(1)\mu_B$ when aligned along the c -axis [49].

5.3 In-Field Incommensurate order Ψ_I

Let us now focused on the field dependence of INC order parameter Ψ_I . For this, we performed resonant x-ray scattering experiments at the Ir- L_3 edge ($E = 11.215$ keV) using a Huber Ψ -diffractometer located in beamline 6ID-C at the Advanced Photon Source - Argonne National Laboratory. The sample used was a clearly faceted single crystal of β - Li_2IrO_3 about $100 \times 150 \times 150 \mu\text{m}^3$ which was glued onto a copper mount using very low quantities of Stycast 1266 epoxy and, its quality and alignment were checked using the x-ray micro-diffraction facility at the Advanced Light Source - Lawrence Berkeley National Laboratory (beamline 12.3.2). The diffraction experiments were carried out in a reflection geometry, using a π -polarized incident beam $\sim 150 \times 150 \mu\text{m}^2$, with the crystal mounted so that the $\mathbf{b}$ -axis was parallel to the applied magnetic field. A split-coil magnet, mounted on the cold finger of a closed-cycle He cryostat with three 60° Be windows, provided up to 4 T of continuous magnetic field and sample temperature as low as that of liquid He. A horizontal scattering geometry allowed us to measure both π - π and π - σ

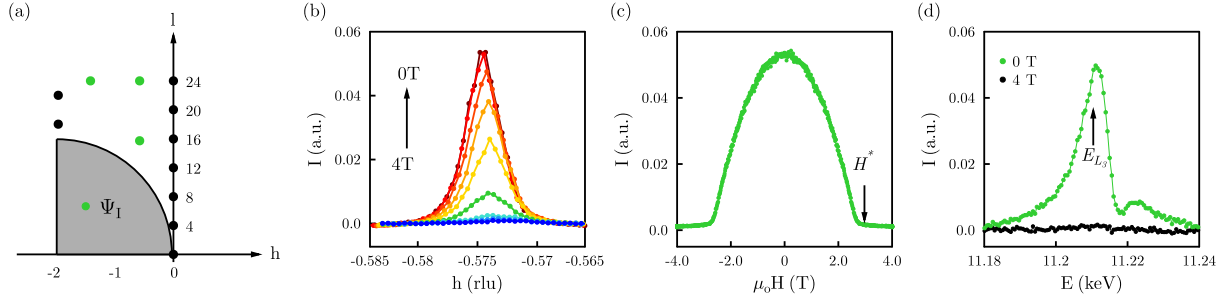


Figure 5.3: **Fate of the incommensurate order $\mathbf{q} = (0.574, 0, 0)$ under an applied field H_b .** (a) The panel displays all the surveyed positions in our restricted reciprocal space. (b) Integrated intensity of the $(-0.57, 0, 16)$ peak taken at different values of applied magnetic field. It can be seen that the $\mathbf{q}$ -vector remains constant while the intensity decreases. (c) Field dependence of the scattering intensity at $T = 5$ K showing complete suppression at $\mu_0 H^* = 2.8$ T. (d) Energy dependence of the scattering intensity at $T = 5$ K for $\mu_0 H = 0$ T and 4 T.

channels and the scattering data was collected using a photodiode point detector. Due to the size of the split gap, we were only able to access $\pm 3.4^\circ$ in the vertical direction while keeping the magnetic field parallel to the $\mathbf{b}$ -axis. Therefore, we were only allowed to survey the $(h, 0, l)$ plane. The allowed INC peaks in our restricted reciprocal space are shown in Figure 5.3(a): $(0, 0, 16) - \mathbf{q}$, $(0, 0, 24) - \mathbf{q}$ and $(-2, 0, 24) + \mathbf{q}$ with $\mathbf{q} = (0.57(4), 0, 0)$.

The response to an applied field at 5 K is shown in Figure 5.3(b). The peak intensity is reduced with increasing field, without changing its wavevector $\mathbf{q}$. In other words, although Ψ_I is strongly suppressed in magnitude, its translational symmetry remains rigid. This is different from the behavior observed as a function of temperature, where the incommensurability changes. Figure 5.3(c) shows that the integrated intensity follows a quadratic dependence as a function of applied magnetic field from $-H^*$ to $+H^*$, with a complete suppression at this critical field. The energy dependence of the INC order in Figure 5.3(d), shows a strong resonance enhancement at zero field but no response at $H = 4$ T, indicating that at H^* the INC magnetic state completely vanishes.

5.4 In-field Commensurate order Ψ_V

We now turn our attention to the properties of this material beyond the phase boundary delimited by H^* . Our thermodynamic data indicate a smooth evolution of the entropy-carrying degrees of freedom across H^* . While no field-induced changes are observed by REXS at high symmetry (e.g. $h, l = 1/4, 1/3, 1/2$ etc.) nor any other incommensurate positions, we found intensity changes at certain reciprocal *lattice* vectors (blue dots in Figure 5.4(a)). In Figure 5.4(b, c) we plot the field response of the scattering intensity at two kinds of reciprocal space points, one belonging to structurally allowed $(2m, 0, 4n + 2m)$

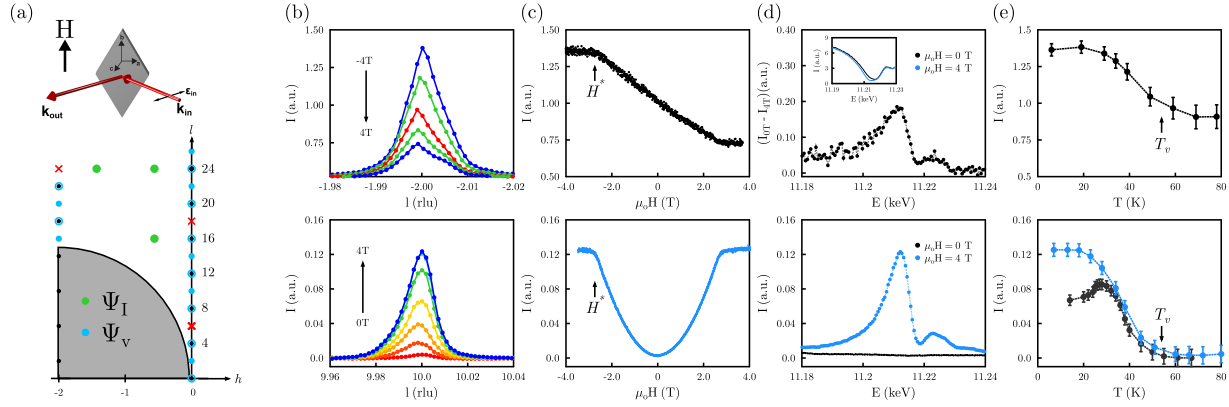


Figure 5.4: **Field, energy and temperature dependence of the commensurate order $q = (0,0,0)$.** Field dependence of the scattering intensity taken at $T = 5$ K and $E = 11.215$ keV around: (a) the structurally allowed $(2m, 0, 14n + 2m)$ peaks (e.g. $(0, 0, 20)$) which show a linear dependence and, (b) the symmetry disallowed peaks $(2m, 0, 12n \pm 2 + 6m)$ (e.g. $(0, 0, 10)$) which show a quadratic dependence to the applied field. A kink was again observed at $\mu_0 H^* = 2.8$ T. The energy dependence for the allowed peaks is shown in the inset (c) with a dip at the absorption edge $E = 11.215$ keV. The main panel (c) shows the difference between the intensity at $\mu_0 H = 0, 4$ T which can be attributed to a magnetic contribution. (d) Energy dependence of the magnetic peak $(2m, 0, 12n \pm 2 + 6m)$ taken at $\mu_0 H = 0, 4$ T. (e) $(0, 0, 10)$ and $(0, 0, 20)$ peaks widths (a lower bound on the correlation length) remain constant under the applied field, suggesting there is no macroscopic phase separation. (f) Temperature dependence of the integrated intensities for the $(0, 0, 10)$ at applied fields above and below H^* . Above H^* the onset of the FIZZ state is continuous, while below H^* this onset is cut off by the incommensurate order. The Gaussian fit to the integrated RMXS intensity gives the χ^2 uncertainty shown by the error bars in e) and f).

peaks and the other to structurally forbidden $(2m, 0, 12n \pm 2 + 6m)$ peaks, where n, m are two arbitrary integers. In the former, the response is linear with a negative slope, and shows a kink at H^* . In the latter case, we find that the peaks have a quadratic dependence on H , again with a kink at H^* . This indicates that in the coexistence region of Ψ_I and Ψ_V , the coupling of the observed ordered states to magnetic field is *linear*. The intensity of a diffraction peak goes as the square of the structure factor so that $I \propto |f_o + \sum_i f_i g(H)|^2$, where f_o is the charge contribution, $g(H)$ is some function describing the response to the magnetic field and f_i is the magnetic structure factor associated with either magnetic order parameter Ψ_I or Ψ_V . For simplicity, let's concentrate on the $(0, 0, l)$ direction. For structurally forbidden peaks, $l = 12n \pm 2$, $f_o = 0$ so that $I_{12n \pm 2} \propto |g(H) f_c|^2$. Given $I_{12n \pm 2}$ peaks grow quadratically in applied field, this immediately suggests that their response must be linear, $|g(H)| = |H|$. For the structurally allowed peaks, $l = 4n$, $f_o \neq 0$, therefore $I_{4n} \propto f_o^2 + 2f_o f_V \cdot g(H) + f_V^2 g(H)^2$. The linear dependence of the I_{4n} peaks therefore

implies that $g(H) = -H$. By the Landau theory, this would immediately suggest that Ψ_V transforms as the magnetic field H . The appearance of structurally forbidden peaks immediately suggests that there is an additional $\mathbf{q} = 0$ broken symmetry induced by the applied field.

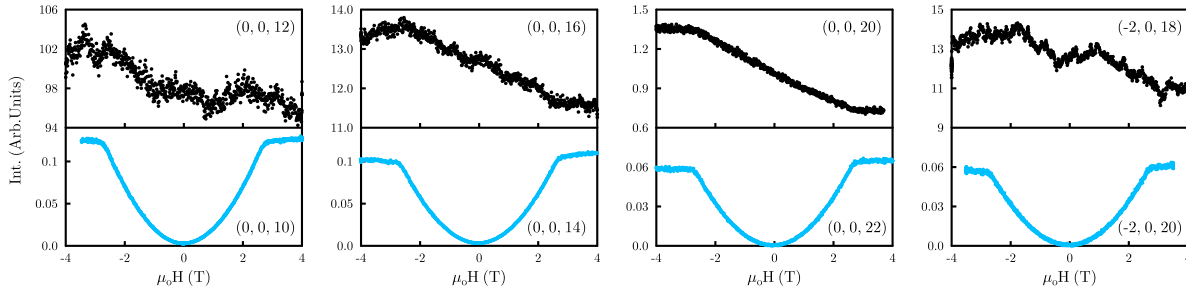


Figure 5.5: Field sweeps at the structurally-allowed and field-induced peaks. The $(2m, 0, 4n + 2m)$ peaks show a linear dependence to an applied field while the $(2m, 0, 4n \pm 2 + 6m)$ respond quadratically, which indicates that the order parameter is linearly coupled to the magnetic field.

The energy dependence of these peaks highlights an important contrast in behavior between structurally allowed and forbidden peaks. The former, as shown in Figure 5.4 (d), have a dip at the Ir L_3 -edge due to the resonant absorption of the Ir lattice, while the field-induced change of intensity occurs only near the Ir resonance, suggesting a change in the spin population. Moreover, the structurally forbidden peaks are enhanced at the L_3 -edge in an applied magnetic field, suggesting that the $\mathbf{q} = 0$ field-induced state is electronic in origin and, as we argue below, most likely magnetic.

In Figure 5.4 (d) we illustrate the temperature dependence of the intensity for the field-induced peak with H above and below H^* . The evolution of the 4 T curve is closely reminiscent of the temperature dependence of a symmetry-breaking order parameter, turning on at ~ 50 K. The 2.3 T curve continuously increases up to T_I , where the incommensurate order turns on. Below T_I , the integrated intensity is reduced, indicating a competition between two coexisting, low temperature states. We assign Ψ_V as the parameter describing this field induced broken symmetry which, given that the field dependence of the intensity $I_{12n \pm 2 + 6m}$ is quadratic (Figure 5.4 (c)), suggests Ψ_V is linearly proportional to the scattering form factor.

To understand why Ψ_V grows with rising field or decreasing temperature, we note that the cross section for resonant x-ray magnetic scattering at a given $\mathbf{q}$ -vector is proportional to $\sum_i e^{i\mathbf{q} \cdot \mathbf{r}_i} (\boldsymbol{\epsilon}_{out} \times \boldsymbol{\epsilon}_{in}) \cdot \mathbf{m}_i \boldsymbol{\sigma}_i$, where $\boldsymbol{\epsilon}_{out(in)}$ denotes the polarization state of the scattered (incident) beam, $\mathbf{m}_i$ is a unit vector along the magnetic moment at site i , and the sum in i runs over the magnetic unit cell. $\boldsymbol{\sigma}_i$ is a quantity proportional to the local imbalance of magnetic up-down states, and thus proportional to the magnetic moment at site i . Therefore, the height of a magnetic Bragg peak can grow by virtue of three things:

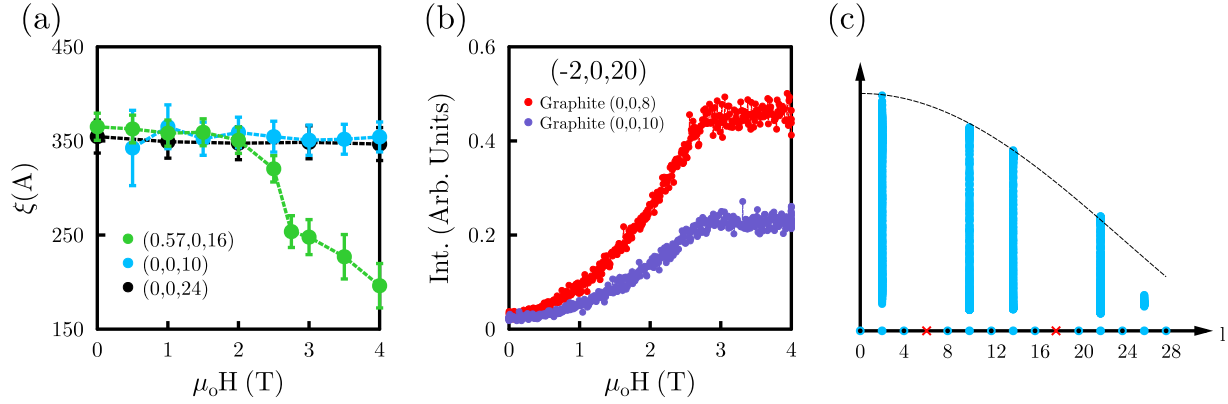


Figure 5.6: (a) Calculated correlation length for both commensurate and incommensurate peaks. This data shows that along the $(0,0,l)$ direction the correlation length is ~ 350 Å, indicating long-range magnetic correlations. (b) Polarization study of a $h + l = 12n \pm 2$ peak using the $(0,0,8)$ and $(0,0,10)$ directions of a graphite analyzer. (c) q -dependent of the commensurate peaks intensity along the $(0,0,l)$ direction showing a $\sim \cos \theta$ dependence.

- **An increase in correlation length:** In the present case, the intensity of magnetic peaks increases dramatically with H , and the peak width remains constant (Figure 5.6 (a)). This width is a measure of correlation length¹ and is resolution limited down to the lowest field measured (0.1 T), implying that macroscopic phase separation is highly unlikely.
- **A canting of the moment that enhances scattering cross-section:** A field-enhanced cross-section would imply the existence of a zero-field magnetic order. To enhance the cross section, we require a field-induced canting of ordered moments parallel to the term $(\epsilon_{out} \times \epsilon_{in})$, and this can only be achieved for one polarization state at a given incidence angle. Considering we are measuring both the $\pi - \sigma$ and $\pi - \pi$ channels, and see no intensity for all $(2m, 0, 12n \pm 2 + 6m)$ peaks at $\mu_0 H = 0$ T, we can rule out a zero-field phase with continuous canting of the moments by the field.
- **An increase in the ordered local moment:** This implies that our observations are most likely explained by an increasing moment size, with long-range quantum correlations turning on ~ 50 K, which cannot develop a sizable ordered moment at zero field, presumably due to the system's intrinsic magnetic frustration.

This behavior differs from archetypical examples of phase transitions in magnetic field such as spin-flops or incommensurate to commensurate transitions [93, 94, 95, 96, 97, 98,

¹The correlation length along the c -axis can be obtained from the FWHM from l -scans since $\xi_c = \frac{1}{2\pi FWHM}$

99]. These are usually first order transitions; the former is between an antiferromagnetic state and a spin-polarized state, while the latter will often cause the incommensurate order to soften, shifting toward a commensurate $\mathbf{q}$ as it is suppressed by the field. In the present case, far from there being a phase transition between one kind of order and another [54], all broken symmetry states coexist, retaining their intrinsic periodicity as a function of field. The ordered moment is somehow shared between different states, indicating their near degeneracy.

$\epsilon_{in} \times \epsilon_{out}$	$\mathbf{m} = \mathbf{a}$	$\mathbf{m} = \mathbf{b}$
$\pi \times \sigma = \mathbf{k}_{in}$	$\mathbf{k}_{in} \cdot \mathbf{a} \sim \cos \theta$	$\mathbf{k}_{in} \cdot \mathbf{b} = 0$
$\pi \times \pi = \sigma$	$\sigma \cdot \mathbf{a} = 0$	$\sigma \cdot \mathbf{b} \sim 1$

Table 5.1: The incident beam is π -polarized. The magnetic field is along the $\mathbf{b}$ -axis, in this geometry, parallel to the σ direction.

Polarization dependence of Ψ_V

For a π -polarized incoming beam, magnetic resonant scattering occurs in both the π - π and π - σ channels. The product $\epsilon_\pi \times \epsilon_\sigma = \mathbf{k}_{in}$ and $\epsilon_\pi \times \epsilon_\pi = \epsilon_\sigma$ so that the only contribution of the moment to the scattering intensities comes from the parallel projection along the incoming beam, $\mathbf{k}_{in}$, and/or along the normal polarization direction of the beam, ϵ_σ . Typically, azimuthal scans are performed to infer the moment's direction by keeping the set-up in the scattering condition and rotating the sample around the scattering wavevector, $\mathbf{Q} = k_{out} - k_{in}$. The projection of the moment onto the fixed directions, ϵ_σ and/or $\mathbf{k}_{in}$, varies depending on the azimuthal angle ϕ , with maximum scattering for small angle between $\mathbf{m}$ and the fixed directions, and minimum scattering when they are perpendicular. Unfortunately, we were not able to perform azimuthal scans to determine the moment's direction and the relative phase between the possible basis vector because of restriction of the magnet. However, by probing the polarization of the outgoing beam and by studying the $\mathbf{q}$ -dependence along the $(0, 0, l)$ direction, we can infer information about their orientation.

Figure 5.6 (c) shows the $\mathbf{q}$ -dependence along the $(0, 0, l)$ direction at 4 T. This data can be directly compared with the expected intensity behavior of the π - π and π - σ channels with moments along the $\mathbf{a}$ and $\mathbf{b}$ -axis listed on Table 5.1. Since the scattered intensity decreases as the $\mathbf{q}$ -vector is increased, we conclude that the moments are mostly along $\mathbf{a}$ and that the major contribution to the intensity is in the π - σ channel.

Furthermore, polarization analysis were performed using the $(0, 0, 8)$ and $(0, 0, 10)$ directions of a graphite crystal with structural factor $F_{(0,0,8)} \sim 4.40$ and $F_{(0,0,10)} \sim 3.24$ and

intensity ratio:

$$\frac{|F_{(0,0,8)}|^2}{|F_{(0,0,10)}|^2} \sim 2 \quad (5.3)$$

which is very similar to that observed on the data (Figure 5.6 (b)). Since $I = I_{\pi\sigma} + \cos \phi \cdot I_{\pi\pi}$, where ϕ is the polarization angle, and we observed no ϕ dependence in the polarization data (except for what's expected from the intensity ratio), we conclude that most of the intensity comes from the $\pi - \sigma$ channel which agrees with the $\mathbf{q}$ -dependence and the energy arguments presented below.

5.5 Possible Basis Vector for Ψ_V

We now consider the possible symmetry-allowed states for Ψ_V . As previously mentioned, there is one magnetic Ir^{4+} site, and four such ions in the β - Li_2IrO_3 primitive unit cell, connected by the symmetry of the $Fddd$ space group. Any commensurate magnetic order can be represented by a four dimensional vector of the relative phases of the Fourier components at the four magnetic sites in the primitive unit cell. Assuming a propagation vector $\mathbf{q} = (0, 0, 0)$, the possible basis vectors obtained using the *BasIReps* tool in FULLPROF are:

$$F = \begin{bmatrix} 1 \\ 1 \\ 1 \\ 1 \end{bmatrix}, C = \begin{bmatrix} 1 \\ 1 \\ -1 \\ -1 \end{bmatrix}, A = \begin{bmatrix} 1 \\ -1 \\ -1 \\ 1 \end{bmatrix}, G = \begin{bmatrix} 1 \\ -1 \\ 1 \\ -1 \end{bmatrix} \quad (5.4)$$

According to the language of Ref. [38], F corresponds to ferromagnetic order, A corresponds to Néel order, C to stripy order and G to zig-zag order. Using these basis vectors, we can derive selection rules for the magnetic scattering which are independent of the spin orientation and can be used to distinguish the possible magnetic orders. In the $(h, 0, l)$ plane, the Bragg peaks can be parametrized by two arbitrary integers m, n as follows:

- **F-type, FM peaks:** $(2m, 0, 4n + 2m)$, with strong peaks at $(2m, 0, 12n + 6m)$.
- **C-type, Stripy peaks:** $(2m, 0, 4n + 2m + 2)$, with strong peaks at $(2m, 0, 12n + 6m + 6)$.
- **A-type, Néel peaks:** $(2m, 0, 12n + 6m \pm 4)$.
- **G-type, Zigzag peaks:** $(2m, 0, 12n + 6m \pm 2)$.

The real space configuration of magnetic ions and their relative phases are shown in figure 5.7, where red (blue) dots represents spin up (down) and the symmetry-allowed peaks for each basis vector are also shown. If we compare these selection rules to what is experimentally observed at 4 T (Figure 5.6 (c)), we conclude that a combination of G and F basis vectors is needed to explain our data.

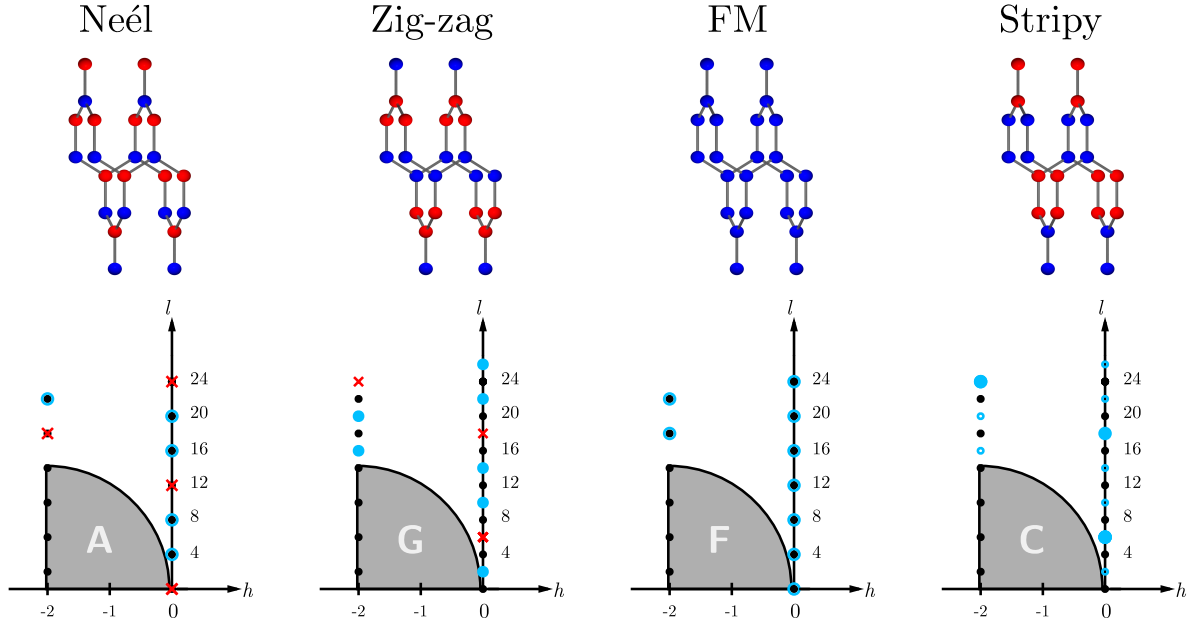


Figure 5.7: Possible basis vectors describing the magnetic order of $\beta\text{-Li}_2\text{IrO}_3$, where F corresponds to ferromagnetic order, A to Néel order, C to stripy order and G to zig-zag order.

Linear coupling of Ψ_V to a uniform magnetic field.

To look for possible coupling between a spatial spin pattern and an external field, such as a spatial modulation of g -factor anisotropy, we perform a full analysis of the lattice symmetries. Table 5.5 show the symmetry transformations of various magnetic configurations under the symmetries of the hyperhoneycomb lattice of $\beta\text{-Li}_2\text{IrO}_3$, together with time reversal. We find that an external field couples only to a particular configuration, denoted as zig-zag order. The zig-zag order of S^a (S^b) spins couples linearly to a uniform magnetic field along the $\hat{b}$ ($\hat{a}$) axis.

To see this, let us consider the environment of an iridium moment. As we showed, the local environment of the oxygen octahedra sets the g -factor anisotropy. The symmetry analysis above shows that it is possible for the material to have a spatially modulated g -factor with off-diagonal terms, akin to that of Sr_2IrO_4 . However, here the iridium-oxygen octahedra do not exhibit significant rotations. We therefore expect the magnitude of the site-modulated off-diagonal g^{ab} term to be quite small, less than a few percent. In fact, Rousochatzakis and Perkins [100] recently showed that although the zigzag component couples linearly to the applied field along $\hat{b}$ via g^{ab} , its significant growth is not related to g^{ab} , and it even occurs in the absence of the off-diagonal element g^{ab} . This zig-zag

component is already present at zero field, albeit with an amplitude too weak to detect so that the zigzag component does not originate in its linear coupling to the field, but rather in an intrinsic coupling with the INC order [101].

Once magnetic correlations sample the environment beyond a single Ir site, however, the lattice symmetries immediately come into play. In particular, the local orientation of a zig-zag chain produces a preferred local coordinate system for the renormalized magnetic susceptibility. This local coordinate system alternates among sites, in precisely the zig-zag pattern. One can model this effect as a spatial modulation in a local magnetic susceptibility tensor. The tensor is diagonal in the $\hat{a}, \hat{b}, \hat{c}$ axis, but has an additional off-diagonal component,

$$\chi^{ab} = -\chi^{ba} = (-1)^{\text{zigzag chain}} \quad (5.5)$$

The sign of this component alternates upon crossing a $\hat{c}$ -axis bond, i.e. it alternates between successive zigzag chains. The effect of this coupling is to produce a zigzag-a (zigzag-b) configuration, together with net $\hat{b}$ ($\hat{a}$) alignment, when a magnetic field is applied along the $\hat{b}$ ($\hat{a}$) axis.

The zigzag component is strongly intertwined with both the INC counter-rotating spiral and the longitudinal magnetization, which is the one most likely driven by the applied field. This field effectively acts as a FM Heisenberg coupling that counteracts the effect of the AFM Heisenberg coupling (J), and the state reached above H^* is qualitatively the same as the state stabilized by a negative J at zero field. In fact, the characteristic field H^* depends on the coupling parameters. H^* tends to decrease with increasing $|K|$ and $|\Gamma|$. However, H^* has a much stronger dependence on J compared to K, Γ , and it grows at a constant rate with increasing J . The experimental value $H^* = 2.8$ T corresponds to a value $J \sim 4$ K assuming $g^{ab} = 0.1$ and $g^{bb} = 2$ [100].

Symmetries of Ψ_I on hyperhoneycomb lattice.

Let us consider the incommensurate spiral order observed in β - Li_2IrO_3 with propagation vector along a . Its basis vectors all belong to a single irreducible representation $\Gamma_4 = (iA_x, iC_y, F_z)$ where F is uniform, and is $\pi/2$ out of phase with the nonuniform basis vectors A and C which are present. Now consider its lattice symmetries. As seen in Table 5.5, the operations $I, G_a, G_b, G_c, R_b, R_c$ are completely broken, in that they each take the spin configuration into a completely different configuration, which remains different even up to an overall spin flip. Thus, the product of each of these symmetry operations with time reversal T also remains broken. However, the remaining operation R_a takes each magnetic moment precisely to its opposite. So its product with time reversal, TR_a , is preserved as a symmetry of the spiral.

This symmetry analysis assumes that translations are fully broken along the spiral wavevector. A commensurate spiral can have a few additional symmetry operations, associated with its very large commensurate unit cell. However, these symmetry operations require fine-tuning of the overall phase of a commensurate order. Lacking any experimen-

		R_a	R_b	R_c	I	T
FM	S^a	+	−	−	+	−
	S^b	−	+	−	+	−
	S^c	−	−	+	+	−
Stripy	S^a	+	−	−	−	−
	S^b	−	+	−	−	−
	S^c	−	−	+	−	−
Zigzag	S^a	−	+	−	+	−
	S^b	+	−	−	+	−
	S^c	+	+	+	+	−
Néel	S^a	−	+	−	−	−
	S^b	+	−	−	−	−
	S^c	+	+	+	−	−
Non-coplanar spiral		−	0	0	0	−

Table 5.2: Transformation rules for g -factor anisotropies and various magnetic orders under all β - Li_2IrO_3 lattice symmetries. The symmetry generators are: π rotations R around the orthorhombic axes a, b, c , centered at a c -bond midpoint; inversion centers I at the midpoint of d -bonds; and time-reversal T . The space group Fddd also contains glide reflections, which are generated by $R \times I$. The symbols $+$, $-$, 0 denote that a configuration with a given spin orientation $S^{a,b,c}$ is respectively even, odd, or fully-breaking under the symmetry. The zigzag order of S^a (S^b) spins couples linearly to a uniform magnetic field along the $\hat{b}$ ($\hat{a}$) axis.

tal evidence for such phase-locked commensurate ordering, we here focus on the generic case, where the wavevector is incommensurate or, if commensurate, with generic overall phase.

From the analysis above, we see that aside from the lattice translations along b and c direction, the spiral INC ordering preserves only a single space-group symmetry operation: TR_a , the product of time reversal and a rotation by π around the crystallographic a -axis passing through a c -bond midpoint. It is therefore possible for the system to simultaneously develop an order parameter for any order which preserves these symmetries, namely TR_a as well as b, c translations. Together with the a -axis spiral, the following $q = 0$

orders are therefore symmetry allowed:

1. Ferromagnetic alignment along S^b or S^c (FM-b,c).
2. C-Stripy order (spins aligned across z -type i.e. c -type bonds and antialigned elsewhere), with spins again along S^b or S^c (Stripy-b,c).
3. Néel order with spins along S^a (Néel-a).
4. C-Zigzag order (spins anti-aligned across z -type i.e. c -type bonds and aligned elsewhere), with spins again along S^a (Zigzag-a).

Energetic of possible vestigial orders Ψ_V

Based on the known information on the Hamiltonian of the zero-field spiral order, which has dominant FM Kitaev exchange K , we can estimate the relative energies of these competing vestigial orders. The Néel state is disfavored due to the strong FM exchange along all nearest neighbor bonds. For the stripy pattern, where spins are aligned only along c -bonds, the FM b -axis Kitaev coupling on these c -bonds would favor *Stripy-b*. For the zigzag pattern, where spins are aligned only along x, y -bonds, the FM a, c -axis Kitaev coupling on these bonds would favor *Zigzag-a*.

Finally by observing the known magnetic susceptibility, which is much stronger along b than along a , we note that for the FM patterns, the FM-b is observed to be more easily stabilized than FM-c. The candidate phases with likely lower energy are thus as follows:

1. FM-b;
2. Stripy-b;
3. Zigzag-a.

The Zigzag-a configuration is linearly coupled to FM-b. Applying an external b -field would then be expected to disfavor Stripy-b as well as the more energetically-costly vestigial possibilities, while favoring FM-b together with Zigzag-a.

A quantitative estimate of the energetics of the field-induced vestigial order can shed light on the Kitaev-based model for $\beta\text{-Li}_2\text{IrO}_3$ at zero field. Consider the vestigial order parameter Ψ_V , defined as the magnitude (in units of $\hbar/2$) of the local spin whose magnetic moment orientation is locked to the lattice $b \pm a$ directions. Its energy per site E is given by an expectation value of the $\beta\text{-Li}_2\text{IrO}_3$ Hamiltonian supplemented by a Zeeman term for the applied field H . Using the K - J - I_c model Hamiltonian for $\beta\text{-Li}_2\text{IrO}_3$ given in Ref.[38],

one finds that the pseudo-dipolar I_c parameter drops out, resulting in the expression:

$$\begin{aligned} E &= -\frac{g\mu_B}{2}(\mathbf{H} \cdot \mathbf{b}) \cos \theta \Psi_V \\ &\quad + \frac{J}{8}(3\cos^2\theta + \sin^2\theta)(\Psi_V)^2 \\ &\quad + \frac{K}{8}(\cos^2\theta + \sin^2\theta)(\Psi_V)^2 \\ E_V &= -0.047H(T)\Psi_V + (0.292J + 0.125K)(\Psi_V)^2 \end{aligned}$$

with $g = 2$ and $\theta = \tan^{-1} 1/\sqrt{2} \approx 0.2\pi$ corresponding to the $b \pm a$ lattice locking of Ψ_V . Constraints on the magnitude of the ferromagnetic Kitaev ($K < 0$) and antiferromagnetic Heisenberg ($J > 0$) interactions can be derived by comparing E_V to the energy per site of the incommensurate spiral order, estimated via mean-field from $T_I = 38$ K to be about $E_I \approx -1.6$ meV.

Our measurement, showing that a small field $H = 2.8$ T is sufficient for destroying the incommensurate order in favor of a saturated vestigial order Ψ_V , implies a high degree of fine tuning between E_V and E_I : taking $\Psi_V = 1$ at $H = 2.8$ T, we find that the Kitaev and Heisenberg interactions must obey the following constraint,

$$K(\text{meV}) \approx -(11.8 + 2.3 J)(\text{meV}) \quad (5.6)$$

The few-Tesla instability of the incommensurate spiral in favor of the vestigial order thus directly implies that the Kitaev interaction must be significantly larger than the Heisenberg exchange, and indeed must dominate the physical response of the material at both zero and finite applied fields. In facts, using the result from the previous section $J \sim 4$ K ~ 0.34 meV, we can estimated $K \sim -12.6$ meV.

5.6 $H - T$ Phase diagram

In figure 5.4 we show the $\mathbf{q}=0$ broken symmetry states that could describe Ψ_V , denoted using the conventional nomenclature [49]. The symmetries of the state consistent with the primary features of the data above H^* are two-fold: G -type (zig-zag) broken symmetry, explaining the appearance of the $(2m, 0, 12n \pm 2 + 6m)$ peaks and, F -type order, explaining the linear dependence of the the allowed structural peaks $(2m, 0, 4n + 2m)$. Importantly, these symmetries are broken by the applied magnetic field itself. First, an induced moment along the applied magnetic field on each ion would transform as an F -type object with moments along $\mathbf{b}$ (denoted F_b). Second, the effective local susceptibility tensor χ_{ij} is anisotropic (including orbital g_{ij} -factor as well as correlation effects, see reference [32] for a discussion of $\gamma\text{-Li}_2\text{IrO}_3$). By symmetry, χ_{ij} can be decomposed into components parallel and perpendicular to the two honeycomb chain directions along $\mathbf{a} \pm \mathbf{b}$. This implies that the moments will in general cant along the chains, leading to G -type configuration,

with moments staggered along **a** (denoted G_a). The symmetry analysis above showed that F_b and G_a not only belong to the same irreducible representation as Ψ_I (allowing Ψ_V to coexist on symmetry grounds), but are in fact energetically favored over other broken symmetry states. Our observations are completely consistent with the Landau theory of second order phase transitions - the combined effect of magnetic field and crystal symmetry is to act as a ‘field’ on Ψ_V , so that the observed zig-zag pattern is linearly coupled to magnetic field (leading to an intensity I_V that is quadratic in field, as seen in Figure 5.5).

This scenario explains why there is no sharp thermodynamic anomaly on cooling in the heat capacity at $H > H^*$ (See chapter 2 figure 2.6 (e) for more details): the symmetry breaking associated with Ψ_V is already imposed by the applied field. However, the temperature dependence is very similar to that of an order parameter with an onset temperature of ~ 50 K, even showing signs of competition with the incommensurate state at intermediate fields (Figure 5.4 (e)). Moreover, the spin degrees of freedom are clearly frozen out in temperature (at $H > H^*$), appearing as a cusp in the heat capacity, and as a broad peak in field. Plotting the location of this peak on a phase diagram (Figure 5.8), we observe immediately that it maps directly onto a constant contour line of the I_I and I_V amplitude, the experimental measure of Ψ_I and Ψ_V themselves.

The field-induced ‘zig-zag’ (FIZZ) state may help explain why the magnitude of the induced moment at $H^* \sim 0.31\mu_B$ per Ir. If we assume that the moment associated with Ψ_V is canted entirely along the diagonal bond axes $\mathbf{a} \pm \mathbf{b}$ (which would be equivalent to the zig-zag order seen in α - Na_2IrO_3 and α - RuCl_3) we find a quantitative agreement with the known ordered moment of Ψ_I . To see this, note the induced magnetic moment at H^* implies that the moment along the chains is $0.31/\cos(0.2\pi)$, where 0.2π is around half the angle between the diagonal chains. This yields $\sim 0.40\mu_B$ per Ir, accounting for most of the moment in Ψ_I , measured independently to be $\sim 0.47\mu_B$ per Ir at zero field [49]. The view that only the ordered moment is transferred between the states Ψ_I and Ψ_V is also consistent with the simple sum rule satisfied by their respective intensities as a function of field (Figure 5.8 (a)).

Intensity Sum Rule

To understand why the sum of intensities corresponding to Ψ_I and Ψ_V peaks remains constant, we will make use of the formalism used in reference [100], where the Bragg peak intensities can be written as:

$$\begin{aligned} I_I &= |M_a|^2 + |M_b|^2 + |M_c|^2 \\ I_V &= |M'_a|^2 + |M'_b|^2 \\ I_{tot} &= (I_I + \alpha I_V)/I_I(0) \end{aligned}$$

where $M_I = (iM_aA, iM_bC, M_cF)$, $M_V = (M'_aG, M'_bF, 0)$ and the constant $\alpha = I_I(0)/I_V(H^*)$ fixes $I_{tot}(H^*) = 1$. We showed that the total intensity (I_{tot}) remains constant up to the maximum field measured 4 T.

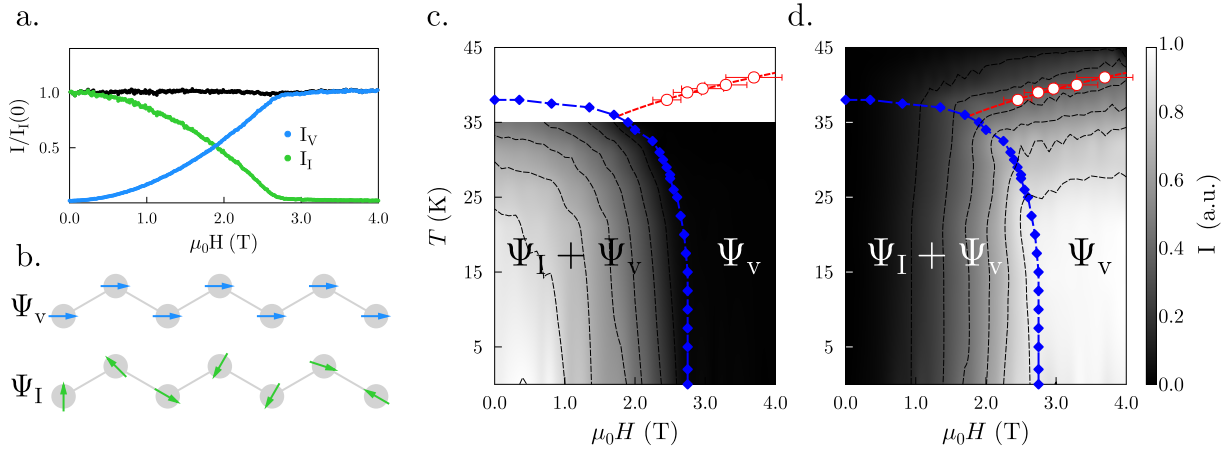


Figure 5.8: **Coexistence of incommensurate spiral and commensurate zig-zag states.** (a) Integrated intensity of two representatives peaks for the INC spiral and COM Zig-zag orders. The INC order intensity is suppressed with field and completely destroyed for $H > H^*$. The zig-zag state is not present at zero field but it starts to form as the field is increased. (c-d) Phase diagram constructed from the thermodynamic measurements superimposed on contour maps of the integrated intensity. Light color indicates a maximum in the intensity while dark means absence of intensity. Notice that crossover found in the heat capacity, directly maps into a constant contour line of the intensity of the zig-zag order.

Reference [100] argues that the observed INC order can be thought of as a long wavelength twisting of a nearby commensurate state, called the "K state", where J is much smaller than both K and Γ . They showed that in this state, the sum rule is obeyed by all I_I and I_V magnetic peak intensities, as observed experimentally. We can therefore conclude that the experimental observation of the sum rule is an independent signature of the smallness of the Heisenberg coupling J . More importantly, the study revealed that the INC counter-rotating component, the 'zig-zag' component and the magnetization along $\hat{b}$ are intertwined components of the same order.

Conclusions

At a fixed field $H > H^*$, our data suggest that there is a crossover from a trivial paramagnet at high temperature to a low temperature quantum-correlated state. At fixed temperatures $T < T_I$, adding a small magnetic field ($\mu_0 H^* \sim T_I/10 \text{ } k_B/\mu_B$) is sufficient to drive the magnetic state of $\beta\text{-Li}_2\text{IrO}_3$ from the zero-field incommensurate spiral order Ψ_I into the FIZZ state Ψ_V . Since a small magnetic field drives a transition into the FIZZ spin configuration, it may be natural to interpret this correlated paramagnet as a vestige of a zero-field, zig-zag ground state that is proximate in the thermodynamic phase

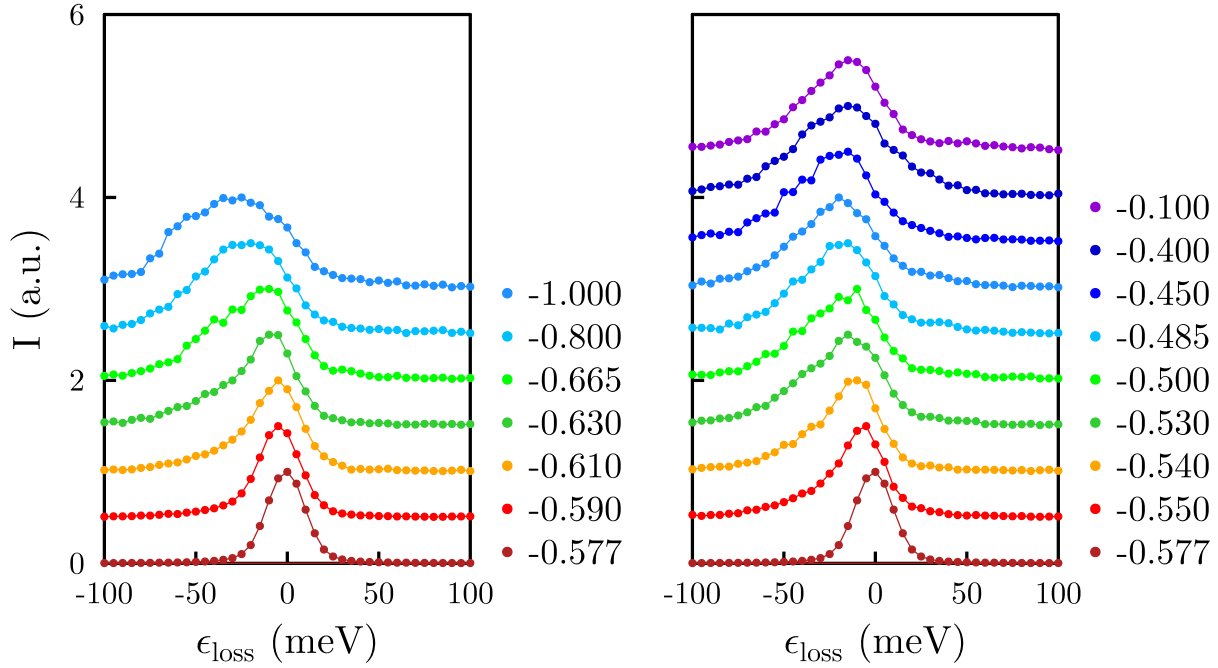


Figure 5.9: **Zero-field RIXS spectra of incommensurate order Ψ_I .** Momentum dependence of the RIXS spectra taken at 5 K near the $(0.574, 0, 22)$ position.

diagram. This would establish a familial link between the lithium based iridates and $\alpha\text{-RuCl}_3/\text{Na}_2\text{IrO}_3$ [44, 43, 45] by connecting these ground states through a field-tuned quantum phase transition at H^* [102, 103]. In this case, the system's response at finite field should be understood much like a ferromagnet in an applied field, where the field breaks the same symmetry as the order parameter. As the system is cooled in field, the spins are strongly correlated but they collectively break no new symmetries. We should mention that there is another, yet more exotic interpretation, in which there exists a field-induced 'spin liquid' state, similar to what has been recently suggested as the high-field state of $\alpha\text{-RuCl}_3$ [104] and $\gamma\text{-Li}_2\text{IrO}_3$ [55] (note that in $\alpha\text{-RuCl}_3$, $\mu_0 H^* \sim T_I k_B / \mu_B$). In this scenario, it is only the applied field that directly breaks zig-zag symmetries, and the response of the system is then determined by the temperature/field dependence of the correlations themselves. The onset of spin-correlations will have no thermodynamic discontinuity, as observed in the heat capacity, but may evolve with increasing rigidity in a manner that mimics the appearance of an underlying order parameter, as seen in the $I_{12n+6m\pm 2}$ intensity. In either case, the ease with which the system can be transitioned from incommensurate to FIZZ states is a striking signature of the delicate balance of interactions in these materials. All that remains is to learn how to tune that balance to achieve a true Kitaev spin liquid.

5.7 RIXS on $\beta\text{-Li}_2\text{IrO}_3$

I will like to finalize this chapter by presenting some preliminary zero-field resonant inelastic x-ray scattering (RIXS) data on $\beta\text{-Li}_2\text{IrO}_3$. RIXS is a powerful tool use to probe the excitation spectrum of materials. This technique is complementary to neutron scattering and photo-emission spectroscopy, but unlike these other techniques, it is ideal to study small insulating samples with high neutron absorption cross-section.

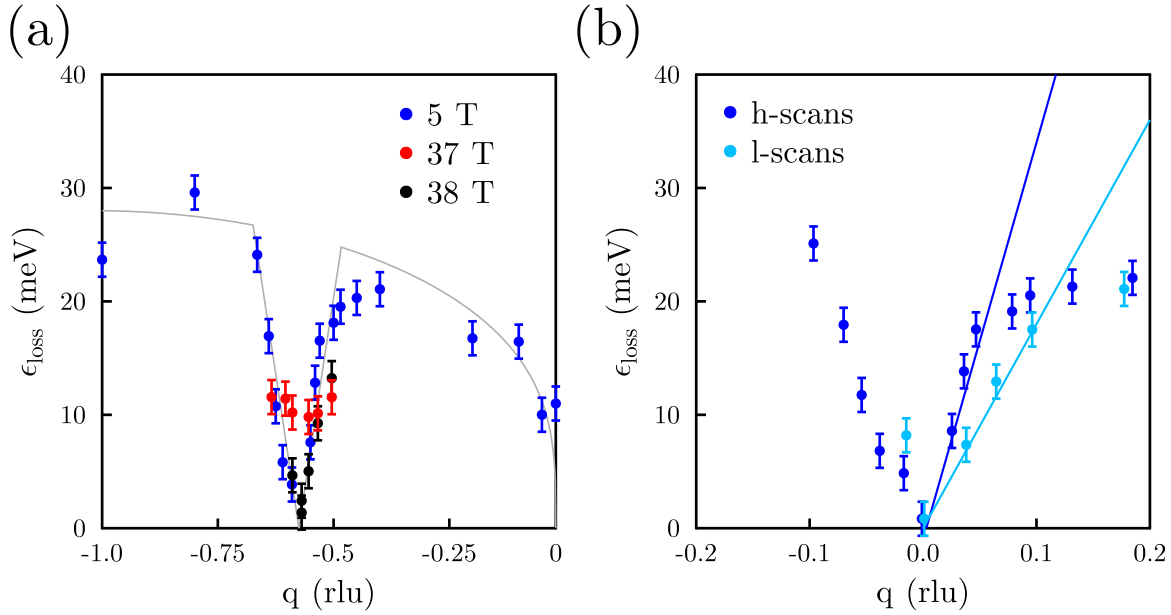


Figure 5.10: **Zero-field RIXS spectra of incommensurate order Ψ_I .** (a) The peak position versus momentum shows the dispersion of the incommensurate order excitations at three different temperatures. The black and blue curves were taken within the order state ($T < 38$ K), while the red curves were taken at the transition temperature 38 K. (b) Base temperature dispersion relation of the incommensurate order taken along two orthogonal directions $q = h, l$.

These measurements were carried out at the MERIX beamline (sector 27) at the Advanced Photon Source, Argonne National Lab. In order to study collective spin excitations, the photon energy was tuned to the Ir L_3 -edge ($E = 11.215$ keV). The spherical 2 m radius diced Si(844) analyzer yields a resolution of FWHM ~ 30 meV, which can be used to measure the low energy spin dynamics. They also offer a variable temperature cryostat which allowed us to access the desired temperature range (5 – 300 K).

Our measurements were performed at the $(-0.57, 0, 22)$ and $(0, 0, 22)$ peaks due to their close-to-normal scattering geometry that reduces charge scattering. We have identified a clear acoustic magnon branch near $q = (0.57, 0, 0)$ (Figure 5.10(a)) reaching energies

of $>20\text{meV}$ at the top of the branch. Despite the resolution limitations of the state-of-the-art RIXS setup, we can easily track the excitation energy as function of momentum - overcoming the medium resolution of the RIXS setup.

Surprisingly, the magnon velocity ² has a very steep slope near the spiral q -vector (Figure 5.10(b)). The slope of this acoustic branch differs between in- and out-of plane directions with dispersion velocities $v_g(h) = 16\text{ km/s}$ and $v_g(l) = 24\text{ km/s}$, which is much higher than the expected $\sin(qa/2)$ behavior. The origin of these features may be linked to the Hamiltonian's anisotropy and exotic exchange mechanisms, both of which lead to magnetic frustration.

In addition, we have seen that the magnon dispersion develop a gapped structure for sample temperatures slightly above the spiral ordering temperature $T_I = 38\text{ K}$ (red curve in Figure 5.9(c)). We also noticed a softening at $q = (0, 0, 22)$, a position which is not allowed by the lattice symmetry but that corresponds to the Ψ_V commensurate state. In fact, recent theoretical calculations [101] showed that spin soft modes should be expected at both of these locations. Moreover, the measured RIXS spectra is very closed to the measured dispersion of the zig-zag order in Na_2IrO_3 [105]

In the future, we propose to investigate the nature of these spin excitations of both the incommensurate Ψ_i and commensurate Ψ_V phases by tracking low-energy excitations near their respective q -vectors in an applied magnetic field. Near $q = 0.57$, we will address whether the magnetic field opens a gap in the excitation spectrum, or whether it broadens the spectrum like in RuCl_3 . Similarly, near $q = 0$ we will look for the reverse effect: does the magnetic field induce a conventional magnon behavior or does the coexistence region host more exotic excitations? These results would provide crucial information about the nature of frustrated/competing magnetic ordered phases in the 3D honeycomb iridates. Further, they will broaden the scope of RIXS experiments by demonstrating the feasibility of scattering with a locally applied magnetic field.

²The group velocity $v_g = \frac{\partial\omega}{\partial q} = \frac{1}{\hbar} \frac{\partial\epsilon}{\partial q} = \frac{1}{\pi\hbar} \frac{a\Delta\epsilon}{\Delta h}$ can be found from the slope of the curves in Figure 5.9(d).

Chapter 6

REXS Under Applied Hydrostatic Pressure on γ -Li₂IrO₃

The work described in this chapter has been published as Ref. [54].

As we have previously demonstrated, the spin coupling terms in the minimal Hamiltonian describing the Kitaev honeycomb iridates, are delicately balanced. Minor changes in its parameters may result in a drastic alteration of the magnetic ground state. These changes may tune away from long-range magnetic order and perhaps towards unexplored phases such as a quantum spin liquid or correlated spin glasses. One experimental approach to achieve this goal is to apply an external perturbation and study the evolution of the magnetic ground state. For example, a magnetic field applied to β -Li₂IrO₃ suppresses the spiral order and stabilizes a canted zigzag spin texture, as described in the previous chapter [42].

Hydrostatic pressure can also be a useful control parameter. X-ray magnetic circular dichroism (XMCD) experiments on β -Li₂IrO₃ suggest the disappearance of the material's ferromagnetic response in $\mu_0 H = 4$ T near 2 GPa, which has been put forth as evidence of a new magnetic ground state [33]. However, the lack of momentum space (Q) resolution of XMCD leaves open the question of which of the nearby magnetic phases responds to hydrostatic pressure. High-pressure setups pose broad experimental challenges for techniques (such as magnetic x-ray scattering) that track individual magnetic orders; to date there have been no such studies under pressure in the honeycomb iridates.

Recent developments in high-brightness synchrotron x-ray sources have allowed for a high-pressure apparatus to be integrated in a resonant elastic x-ray scattering (REXS) experiment. REXS directly probes electronic and magnetic orders resolved in Q space by tuning the energy of incident x-rays to be on resonance with an element's absorption edge. The resulting scattering process is sensitive to both charge and magnetic order of the valence electrons. At the Ir $L_{2,3}$ -edge, for example, the intermediate states in the scattering process are sensitive to both the spin and orbital character of the 5d hole states [89]. REXS is particularly useful when neutron scattering is rendered unfeasible by small sam-

ple sizes or elements with large neutron absorption cross sections like iridium. Thus, the enhanced cross section at the Ir L_3 resonance along with the large Ewald sphere afforded by 11.215 KeV x-rays has made REXS the best-suited scattering technique to investigate the ambient-pressure magnetic order in the honeycomb iridates. REXS studies under applied pressure, however, are strongly constrained by the apparatus geometry and resulting limitations on the sample dimensions and available reciprocal space. As a result, the precise influence of hydrostatic pressure on the ground state of Kitaev honeycomb iridates remains unknown.

In this work we use REXS to track the evolution of the γ -Li₂IrO₃ incommensurate spiral order with applied hydrostatic pressure and observe the suppression of this magnetic phase. While we find no discontinuity in the lattice structure or an associated change in symmetry to the highest pressures measured, we observe an abrupt disappearance of the spiral Bragg peak at a critical pressure $P_c = 1.4$ GPa. This disappearance signals the transition to a distinct electronic ground state.

6.1 Stripy honeycomb lattice symmetries

The stripy honeycomb lattice's space group is Cccm, number 66. Beyond the primary translations of the base-centered orthorhombic Bravais lattice, it features:

- Rotation (R) by π around the c-axis, along a line passing through intra-hexagon c-bonds.
- Inversion (I) with inversion center at the midpoint of intra-hexagon c-bonds.
- A glide plane (G) which can be taken to be a mirror reflection perpendicular to b, whose mirror plane passes through inter-hexagon c-bonds, followed by translation $c/2$.

This complete operation interchanges the two orientation of hexagon strips. By multiplying it by the rotation generator, it can also be seen to be a mirror reflection perpendicular to a followed by translation $c=2$. Multiplying it with the inversion gives a b-axis rotation by π around the mid-point of an intra-hexagon c-axis bond, followed by a translation by $c/2$. Finally note that the inversion and π c-rotation combine to form a mirror symmetry normal to c. Connecting the bond midpoints, on a given hexagon stripe, forms its mirror plane.

γ -Li₂IrO₃ Magnetic basis vectors and Selection rules

The magnetic moments occupy two inequivalent sublattices in the primitive unit cell (Ir and Ir') each of which contain four sites labeled 1-4 and 1'-4'. For a propagation vector $(0.571, 0, 0)$, four types of magnetic basis vectors are allowed for each sublattice, such that the magnetic structure can be described by the basis vector combination $i(A, -A)_x$,

$-i(F, -F)_y, (F, F)_z$, which corresponds to a mixture of two irreducible representations Γ_3 and Γ_4 . Each of the four types of basis vectors has its own selection rules for the magnetic scattering with the following form for the structural factor:

$$\mathcal{F}(\mathbf{Q}) = f_S \sum_i \mathbf{M}_i e^{i\mathbf{Q} \cdot \mathbf{r}_i} \quad (6.1)$$

where $\mathbf{Q}$ is the reciprocal lattice vector, $\mathbf{M}_i$ is the ordered moment on the Ir ion at position $\mathbf{r}_i$, the prefactor $f_S = 1 + e^{i\pi(h+k)}$ is the structure factor for the base-centered (C) orthorhombic lattice, and the sum runs over $i = 1 - 4, 1' - 4'$. Direct calculation of the structural factor gives the following selection rules [48]:

- In the $(h, 0, l)$ plane, for all $l = 6n$ with n integer, only F basis contribute. This satellite peaks can be further split into those corresponding to F and $-F$ (For example, $(0, 0, 24) + q$ comes from (F, F) while $(2, 0, 24) + q$ comes from $(F, -F)$). In this plane, satellites occur only for h even with further selection l odd for both c, G basis, and l even for both F, A basis.
- In the $(\text{odd}, \text{odd}, l)$ plane with $l = 3 + 6n$ and n integer, only A, G basis contribute.

Symmetries of Ψ_I on the stripy honeycomb lattice

Let us consider the incommensurate spiral order present in γ -Li₂IrO₃ with propagation vector along a . Its basis vector belong to *two* irreducible representation (irreps): the A_x and F_z in $\Gamma_3 = (A_x, C_y, F_z)$ and the F_y in $\Gamma_4 = (G_x, F_y, C_z)$. The $\hat{a}$ and $\hat{c}$ components of spins ($\langle S_a \rangle$ and $\langle S_c \rangle$), which form the coplanar spiral mode, preserve the lattice c-mirror symmetry. The $\hat{b}$ component of spins ($\langle S_b \rangle$), which tilts the spiral, breaks the c-mirror symmetry. Hence the full non-coplanar spiral, which is the sum of these two modes, is composed of these two separate irreducible representations.¹ There is also a glide symmetry which is preserved by the a, c coplanar mode but broken by the b tilt mode. In particular, the glide operations map the spiral ordering to itself but with the a and c components of each spin reversed.

Therefore, the a, c coplanar mode preserves the π c-rotation (R_c), the π the b-rotation (R_b), and the inversion across the bond midpoint of c-aligned spins (I) as well as the c-mirror ($I \times R_c$), but not the glide (G_c). In contrast, the b tilt mode preserves the π c-rotation (R_c), π b-rotation (R_b), and the inversion across the bond midpoint of c-perpendicular spins (I) as well as the glide (G_c), but not the c-mirror ($I \times R_c$).

¹Let us keep in mind that spins are invariant under inversion (I), and they transform under mirror reflections by decomposing the mirror into an inversion times a rotation ($I \times R$).

6.2 Experimental Procedure

We begin by reviewing the details of our experimental procedure before presenting the experimental results and analysis. Figure 6.1 (b) shows the intersecting Ir honeycomb layers in one unit cell of the orthorhombic $Cccm$ crystal structure. To track the evolution of the spiral magnetic order in γ - Li_2IrO_3 , REXS experiments were conducted using single crystals in a transmission (Laue) scattering geometry. Polished samples were 20 – 30 μm thick, chosen to match the absorption length of x-rays near the Ir $L_{2,3}$ -edge of $\sim 10 \mu\text{m}$. The transmission scattering scheme is shown in Figure 6.1 (c). Samples were prealigned for scattering within the crystal $a - c$ plane in a vertical geometry. The specular $(H, 0, 0)$ direction was verified with several peaks, as described below. The polarization of the incoming x-rays was horizontal (σ), with no polarization analysis of the scattered (π) beam. The magnetic scattering intensity, proportional [89] to $|\sum_i e^{i\mathbf{Q}\cdot\mathbf{r}_i} (\boldsymbol{\sigma} \times \boldsymbol{\pi}_{\text{out}}) \cdot \mathbf{m}_i|^2$, where $\mathbf{m}_i$ is the magnetic moment at site $\mathbf{r}_i$, projects the component of $\mathbf{m}_i$ parallel to the outgoing wavevector $\mathbf{k}'$ (in the $a - c$ scattering plane).

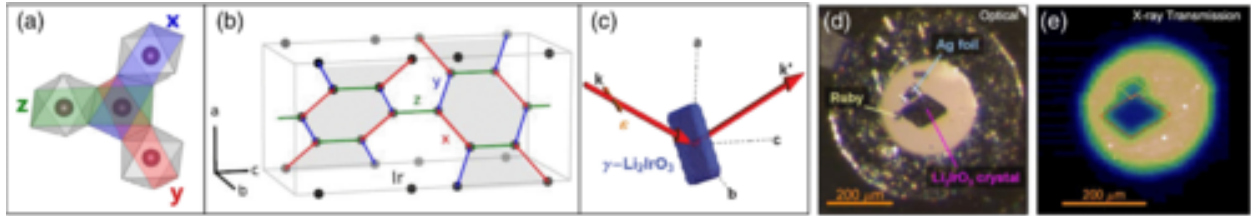


Figure 6.1: (a) Local geometry of edge-sharing IrO_6 octahedra and (b) 3D network of Ir atoms composed of intersecting honeycomb layers (gray) in the orthorhombic crystal structure of γ - Li_2IrO_3 ; x , y , z Kitaev bonds are highlighted in both panels. (c) Laue (transmission) scattering geometry; x rays with initial wave vector k and polarization ϵ scatter into k' within the γ - Li_2IrO_3 crystallographic $a - c$ plane. (d) Micrograph of the loaded diamond-anvil cell with a polished single crystal and Ag foil and ruby spheres for pressure calibration and *in-situ* monitoring. (e) X-ray transmission image of the sample *in-situ*; both γ - Li_2IrO_3 crystal and Ag foil are outlined.

X-ray scattering studies under pressure (up to 3 GPa) and at temperatures between 5 and 300 K were performed at beamline 4-ID-D of the Advanced Photon Source at Argonne National Laboratory. Merrill-Bassett-type diamond anvil cells (DACs) with 800 μm culets were used with stainless-steel gaskets of 250 (150) μm initial (preindented) thicknesses, with 400 μm sample chamber holes [106]. The gaskets were loaded with γ - Li_2IrO_3 single crystals (cross-sectional area $150 \times 100 \mu\text{m}^2$), along with several ruby balls and $40 \times 40 \mu\text{m}^2$ pieces of 12 μm thick Ag foil for ambient and low-temperature pressure calibration [107]. The pressure medium was a 4:1 methanol:ethanol mixture. After preparing the DAC, the cell pressure at ambient temperature was monitored using a custom-built optical spectrometer and a Raman system to measure the ruby R1 fluorescence peak. The

target pressure on loading was ~ 0.1 GPa. The pressure at low temperature was determined *in-situ* using Ag powder peaks and the isothermal bulk modulus of Ag at 5 K ($K_{\text{Ag}} = 110.85$ GPa, $K'_{\text{Ag}} = 6.0$ GPa) [107]. We estimate a systematic uncertainty of ± 0.1 GPa in the pressures quoted below by comparing the estimated pressure from (1, 1, 1), (2, 0, 0), and (2, 2, 0) Ag powder peaks and from repeated pressure measurements before and after scans.

All measurements reported were performed on two samples at the cryostat base temperature of 4.7 ± 0.5 K. Pressure was changed *in-situ* using a helium membrane. Cell layout and sample status were checked after loading (see optical image in Figure 6.1(d), showing diamond-shaped γ - Li_2IrO_3 crystal, Ag foil, and ruby spheres in the DAC gas-ket hole) and monitored using x-ray transmission maps (Figure 6.1(e), obtained using a slit-defined $30 \times 30 \mu\text{m}^2$ beam). To track the absolute magnetic Bragg peak intensities with pressure, peak areas were normalized to the integrated (4, 0, 0) rocking curve intensities. The mosaic FWHM values are 0.05° – 0.10° for sample 1 between 0 and 3.0 GPa and 0.01° for sample 2 at 2.0 GPa.

Suppression of Ψ_I under hydrostatic pressure

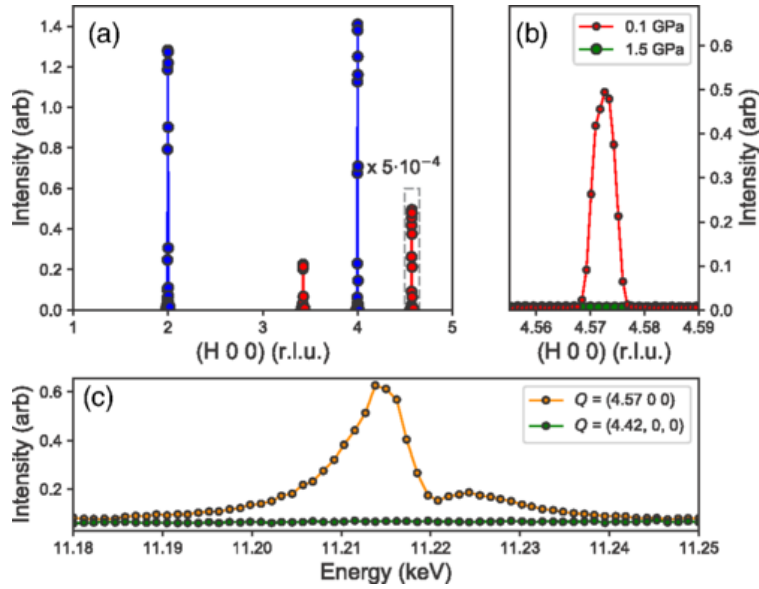


Figure 6.2: (a) Magnetic (red) and structural (blue) Bragg peaks along the $(H, 0, 0)$ direction measured at 4.7 K; the (4, 0, 0) peak has been scaled by a factor of 5×10^4 . (b) Close-up of the dashed region in (a) showing scans near $(4, 0, 0) + q_I = (4.57, 0, 0)$. The magnetic Bragg peak visible at 0.1 GPa (red) disappears abruptly above 1.4 GPa (green). (c) Energy scans at fixed $Q = (4.57, 0, 0)$ and away from the magnetic peak $Q = (4.42, 0, 0)$ showing a featureless background.

Based on the restricted scattering geometry imposed by the DAC, we focused our study on (h 0 0) peaks in reciprocal space. In γ - Li_2IrO_3 , the structural selection rules listed on table 2.3 forbid the (1 0 0) and (3 0 0) lattice peaks, while the structure factor for the (2 0 0) order is strongly suppressed. Figure 6.2 (a) shows a reciprocal space map of the (h 0 0) axis, where an intense structural (4 0 0) Bragg peak and weaker (2 0 0) peak are both observed (In the β - Li_2IrO_3 polytype the (2 0 0) peak is forbidden). Nonstructural peaks located at $(4 \pm 0.57 \ 0 \ 0)$ correspond to the incommensurate spiral magnetic order, which at ambient pressure appears below $T_I = 38$ K. The main finding of this work is the disappearance of this peak at $P_c = 1.4$ GPa, shown in Figure 6.2 (b) at 4.7 K. The electronic nature of these peaks is confirmed by fixed- Q energy scans (Figure 6.2 (c)) showing a strong enhancement of the diffracted intensity near the 11.215 keV Ir L_3 resonance, in contrast to the weak background observed away from the spiral order peak at (4.42 0 0) that shows an increase of $\sim 10\%$ above the Ir edge due to fluorescence.

Under applied hydrostatic pressure we observe a continuous reduction in the unit-cell volume with a large bulk modulus typical of iridates. Figure 6.3 (a) shows the pressure dependence of the (4 0 0) Bragg peak (normalized), and the spiral order peak is shown in Figure 6.3 (b). The curves are vertically offset for clarity and labeled with the corresponding pressure; because of the fine incremental changes we quote the most precise estimate for each pressure, suppressing the ± 0.1 GPa systematic uncertainty. The shift in the 3.3 GPa (4 0 0) scan is a consequence of a large pressure increment; the a-axis lattice parameter evolves linearly with pressure over the entire range studied, shown in Figure 6.3 (c). Also shown in Figure 6.3 (c) is a linear fit yielding $\frac{da}{dP} = 0.015 \text{ \AA/GPa}$. Assuming an isotropic fractional change in the unit-cell dimensions, the $T = 4.7$ K bulk modulus $K_0 = \frac{1}{3}a(\frac{da}{dP})^{-1} = 130 \pm 20$ GPa. Electronic structure calculations for β - Li_2IrO_3 indicate anisotropic compressibility of lattice parameters [108]. Recent diffraction experiments [109] report anisotropic compression and $K_0 = 100(8)$ GPa, significantly lower than 150-250 GPa values typical of other iridates [110].

Neither the (4 0 0) Bragg peak amplitude nor width changes appreciably with increasing pressure, indicating that the crystal quality remains constant. Aside from contraction of the unit cell (shown in Figure 6.3 (c)), no structural changes were observed; the symmetry of the lattice appears intact throughout this pressure range.

Figure 6.3 (b) shows the pressure evolution of the spiral order peak, tracking its position along the (h 0 0) axis as the pressure increases. The incommensurate wave vector q_I , normalized to the change in lattice constant, decreases with increasing pressure, as shown in Figure 6.3 (d) (top panel); q_I decreases by 0.3% before the spiral order disappears at P_c . The linear and continuous decrease observed in q_I , ending at an apparently irrational fraction, precludes an incommensurate to commensurate transition. Furthermore, we monitored the peak position along directions orthogonal to (h 0 0) by performing angular motions (θ and χ scans). The magnetic peak position does not shift with respect to the Bragg reflection (4 0 0) over the corresponding reciprocal space ranges shown in Figure

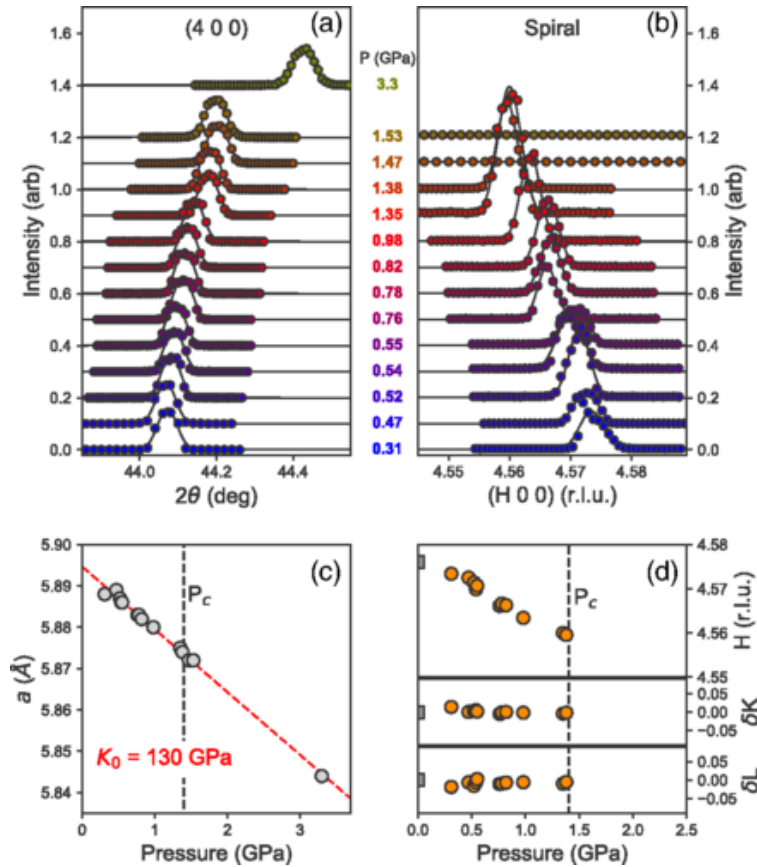


Figure 6.3: Evolution under applied pressures from 0.3 to 3 GPa, as labeled, for (a) the (4 0 0) Bragg peak intensity versus 2θ and (b) the spiral order peak. Solid lines are guides to the eye. (c) Decrease in lattice constant a with applied hydrostatic pressure, extracted from the (4 0 0) structural Bragg peak; assuming a relative change in volume that is isotropic, the bulk modulus $K_0 = 130$ GPa. (d) Top: Decrease in the spiral order wave vector q_I with applied pressure. The wave vector is not close to a commensurate value at P_c . Bottom: dependence of the magnetic peak's component along (0 K 0) and (0 0 L), relative to the position of the (4 0 0) Bragg reflection. The gray squares were obtained from companion experiments at ambient pressure.

6.3(d) (bottom panels). As the peak width is also pressure independent, we conclude that q_I is not continuously developing a component along k or l . Above an applied pressure of $P_c = 1.4$ GPa, the spiral order peak is abruptly extinguished, as shown in Figure 6.3(b). We scanned the entire accessible range of $2 < h < 6$ reciprocal lattice units as well as within the orthogonal ranges of Figure 6.3(d) (bottom panels) and found no evidence for the incommensurate peaks anywhere in this reciprocal space volume.

6.3 $P - T$ Phase Diagram

To further consider the evolution of the spiral magnetic order, we integrate the q_I peak intensity as a function of applied pressure, as shown in Figure 6.4 (a). To within the uncertainty associated with consistent realignment of the sample after changing pressure, the peak intensities gradually increase with pressure until abruptly disappearing at P_c . The otherwise identical sample 2 also showed no sign of the spiral order at 2.0 GPa, the only pressure studied. (The apparatus allows the pressure to be increased only after loading and cooling. For this sample, this initial pressure was 2.0 GPa.)

We present a schematic pressure-temperature phase diagram for γ - Li_2IrO_3 in Figure 6.4 (b); the dark region indicates the observed extent of the spiral magnetic order, and the light shaded region represents the simplest associated phase boundary. Ongoing studies of this material indicate paramagnetic behavior with rapidly emerging magnetic anisotropy favoring the b (easy)-axis direction at ambient pressure [32, 42]. As T approaches 0 K, P_c likely continues to represent a sharp phase boundary between the spiral magnetic order and the as-yet undetermined high-pressure electronic phase; the sharp disappearance could signal a first-order quantum phase transition. As there is no change in the lattice symmetry and no symmetry-breaking field being used to perturb the material, it is unclear what ordered state may exist beyond P_c , if any.

Under an applied magnetic field, a correlated state which admixes the broken symmetry of zigzag order [42, 55] appears to be the next competitive magnetic ground state at ambient pressure. However, the transition observed under applied magnetic field appears to be continuous, in contrast to the pressure-tuned transition at P_c ; a different ground state may emerge in this case.

The effect of pressure on the crystal structure and associated Kitaev, Heisenberg, and other exchange couplings was recently studied theoretically for β - Li_2IrO_3 [108]. In this closely related polytype, the Kitaev exchange coupling was predicted to decrease with increasing pressure above ambient conditions, disappearing at 5–10 GPa. If a similar evolution of the magnetic interactions appears in γ - Li_2IrO_3 , our results firmly demonstrate that the spiral magnetic order is stabilized by Kitaev exchange and is suppressed as this mechanism weakens. This could also answer why the intensity of the spiral order peak grows with pressure. For example, relieving the Kitaev frustration may allow a greater share of the $\mathcal{J} = 1/2$ moment to appear in the incommensurate order before this state is suppressed at P_c . Finally, experimental studies of pressure evolution of the local Ir environment in Li_2IrO_3 will also allow for a quantitative analysis of how the change in structure serves to push this material closer to or farther from the pure Kitaev limit.

Recent experimental work used x-ray circular dichroism (XMCD) to study the effect of pressure on the lattice structure, local moment and exchange couplings in β - Li_2IrO_3 [109]. This work revealed an electronic reconstruction below 2 GPa, which although preserves the lattice symmetry, it manifest manifests as a reduction of SOC and pushes β - Li_2IrO_3 further away from the the pure $\mathcal{J} = 1/2$ limit. A most recent study demonstrated that its incommensurate spiral order also disappears upon a first order transition

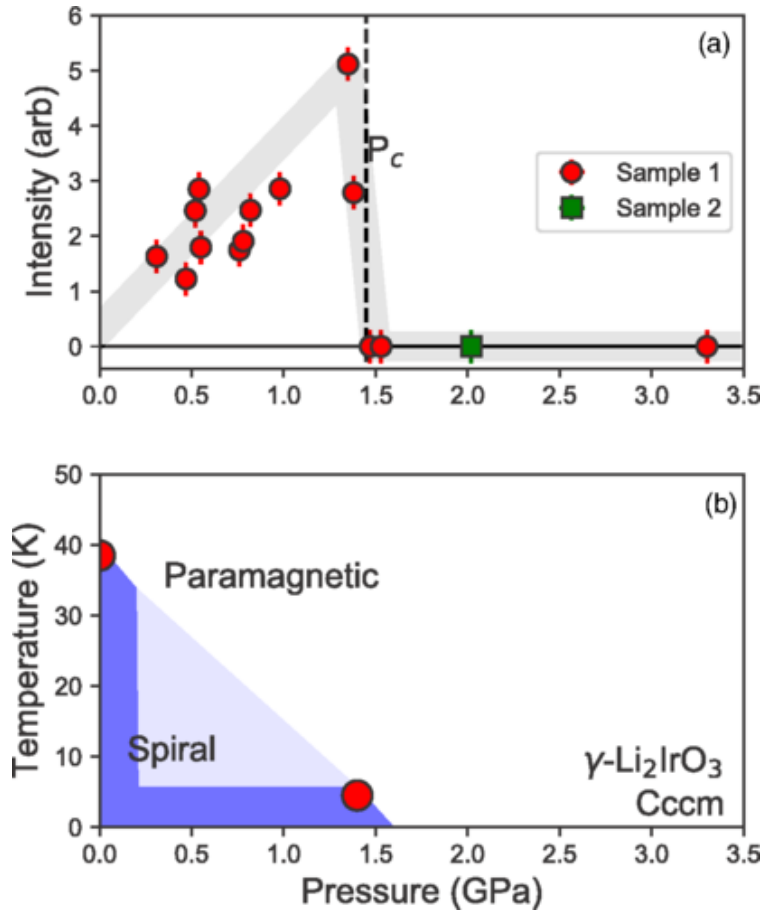


Figure 6.4: (a) Magnetic Bragg peak intensity versus applied pressure for two samples. The intensity for sample 1 disappears abruptly at $P_c = 1.4$ GPa; no magnetic peak is observed at 2.0 GPa for sample 2. (b) Schematic pressure-temperature magnetic phase diagram for γ - Li_2IrO_3 ; the dark region indicates the extent of direct studies of the spiral-order phase to date. No discontinuous change in the lattice (space group Cccm) is observed to 3.0 GPa.

at 1.4 GPa [111]. Above this critical pressure, a fraction of the spin freeze and form a spin glass while the rest forms a dynamic state identified as a classical spin liquid. Therefore, the high pressure ground state is phase separated and it represents a mixture of two correlated disorder phases: spin glass and spin liquid. This work also showed that T_I increases with pressure, while the critical field H^* , decreases which could be an indication that the Heisenberg coupling term J decreases, while μSR data and *ab initio* calculations showed that pressure increases the ratio of $|\Gamma/K|$ as P_c is approached [100].

The scale of P_c is modest compared to the 17 GPa required to suppress weak ferromagnetism in Sr_2IrO_4 [112]. The pressure roughly corresponds to an energy density of 9 meV/ $\text{\AA}^3$, or 0.08 eV/Ir; while less than both the spin-orbital energy $\lambda_{SO} \sim 0.2$ –0.5 eV and

electronic interaction $U \sim 0.5$ eV that have been reported in 5d iridate materials [112, 113, 114], it is beyond the ~ 1 meV scale that was proposed to separate β - Li_2IrO_3 from a 3D spin-liquid state [115]. Mixing of the (nominally filled) $\mathcal{J} = 3/2$ manifold of states could serve to disrupt the $\mathcal{J} = 1/2$ doublet that stabilizes the unconventional magnetic orders in these materials. Such a picture could be investigated quantitatively with high-pressure studies of x-ray absorption and XMCD spectroscopies that provide a quantitative probe of the spin and orbital components of the local magnetic moments.

In summary, we are able to observe the disappearance of the spiral magnetic order in γ - Li_2IrO_3 at an applied pressure of 1.4 GPa upon a first order transition by conducting resonant x-ray scattering studies at the Ir L_3 -edge. This observation provides strong evidence for tunability of the Kitaev, Heisenberg, and other magnetic exchange couplings with applied pressure. Future resonant diffraction studies will be able to incisively address the possibility of complete disappearance of long-range magnetic order in the high-pressure ground state of this Kitaev candidate material.

Chapter 7

Doping Effect on β -Li₂IrO₃

So far I have shown that the 3D Kitaev-candidate materials β, γ -Li₂IrO₃ have very unusual magnetic properties that can be attributed to the presence of strong bond directional Ising-like interactions. The low temperature magnetically ordered incommensurate state is very fragile to external perturbations such as a magnetic field applied along the special $\hat{b}$ -axis or hydrostatic pressure. The first effect was presented in chapter 5, where I showed that Ψ_I is completely suppressed at a critical field $H^*(\hat{b}) = 2.8$ T, which at the same time gives rise to a commensurate zig-zag component Ψ_V . On the other hand, in chapter 6 I showed that applied hydrostatic pressure also destroys the incommensurate state at a critical pressure $P_c = 1.4$ GPa, while stabilizing a state that admixes frozen (spin-glass) and dynamical (spin-liquid) spins [111]. Both of this studies concluded that the incommensurate ground state was extremely fragile to external perturbations.

In this chapter, we will further explore the fragility of Ψ_I by showing that the systematic substitution of *Ir* by magnetic *Ru* ions with a different spin state in the frustrated magnet β -Li₂IrO₃ rapidly induces a spin-glass state ($x \sim 2\%$), indicating strong frustration. I will emphasize the influence of moment depletion on the magnetic properties of these materials and their relevance in the *JKT* model. This study provides new insights into the nature of the magnetic exchange interactions, and will show that, upon doping, the magnetic state is replaced by a spin-glass state with short-ranged correlations.

The effect of *Ru* substitution in powder α -Li₂IrO₃ and Na₂IrO₃ has previously been studied in the context of electro-chemical properties [116], and structural, magnetic and electrical properties [117, 118, 117]. However, to the best of our knowledge, this is the first doping study of β -Li₂Ru_{*x*}Ir_{1-*x*}O₃ single crystals, which allows us to answer opened questions about the evolution of the anisotropic magnetic properties of these iridates. I would like to note that although I will only discussed the effect of *Ru* doping in this chapter, I have also tried *Pt*, *Os* and *Pd* doping with various success.

7.1 Experimental Procedures

Crystal Synthesis and Structural Characterization

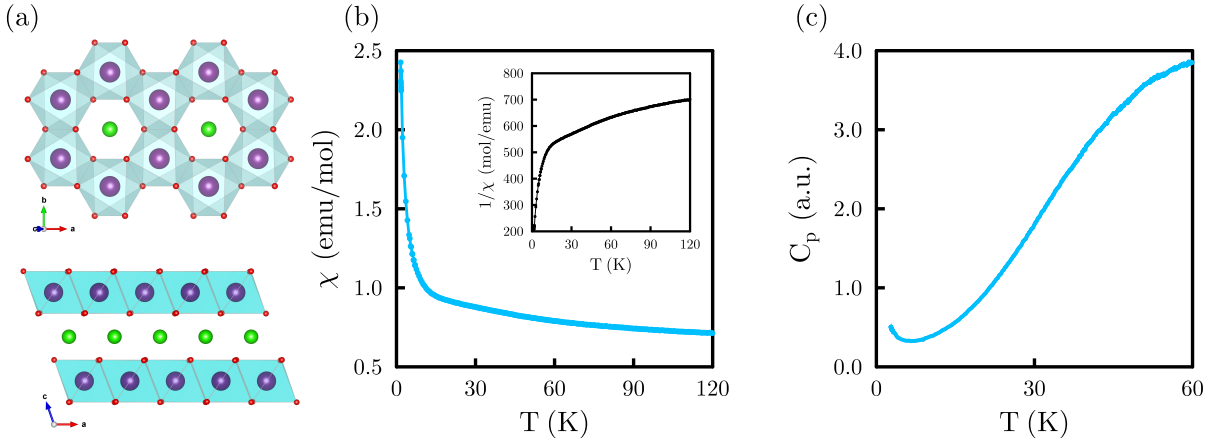


Figure 7.1: (a) Crystal structure of the layered honeycomb Li_2RuO_3 . (b-c) Magnetic susceptibility and heat capacity measurements show paramagnetic response down to base temperature.

Li_2RuO_3 features $\text{Ru}^{4+}(4d^4)$ ions with intermediate strength spin-orbit coupling $\lambda_{SO} \sim 0.16 \text{ eV}$ [119], much weaker than the 0.4 eV of Ir ions. Nonetheless, this Mott insulator is very similar to the honeycomb iridates Li_2IrO_3 and Na_2IrO_3 but with one more hole in the t_{2g} band [120] such that $\mathcal{J} = 1$ ¹. This material adopts a low spin configuration because the crystal field overpowers the Hund's coupling. Single crystals of Li_2RuO_3 were grown by a calcination reaction of elemental Ru and Li_2CO_3 at 1010°C , dwelling for 84 hrs and cooling-down at a rate of 6 K/hr . Structural analysis revealed a single phase powder and crystals with a space group $C2/m$ and lattice constants $a = 5.091\text{\AA}$, $b = 8.759\text{\AA}$, $c = 5.941\text{\AA}$, $\alpha = \gamma = 90^\circ$ and $\beta = 100.92^\circ$. On the other hand, powder magnetization and heat capacity measurements showed a paramagnetic response all the way down to base temperature (Figure 7.1) with an effective moment $\mu_{eff} = 2.79\mu_B/\text{Ru}$ close to the expected value $2.83\mu_B/\text{Ru}$ for spin $S = 1$ moment, and $\theta_{CW} \sim -116 \text{ K}$, very similar to what has been reported elsewhere [121, 122].

To grow single crystals of $\beta\text{-Li}_2\text{Ru}_x\text{Ir}_{1-x}\text{O}_3$, we react grounded crystals of the layered honeycomb system Li_2RuO_3 with elemental Ir powder and Li_2CO_3 following identical steps as described in chapter 2. Although single crystals were obtained for all doping levels, the size of the crystals decreases with doping. Phase purity and structural ordering were verified using powder and single crystal x-ray diffraction, while the elemental

¹This is still debated, with some groups reporting $\mathcal{J} = 0$ or $1/2$ from spin quenching [120, 121].

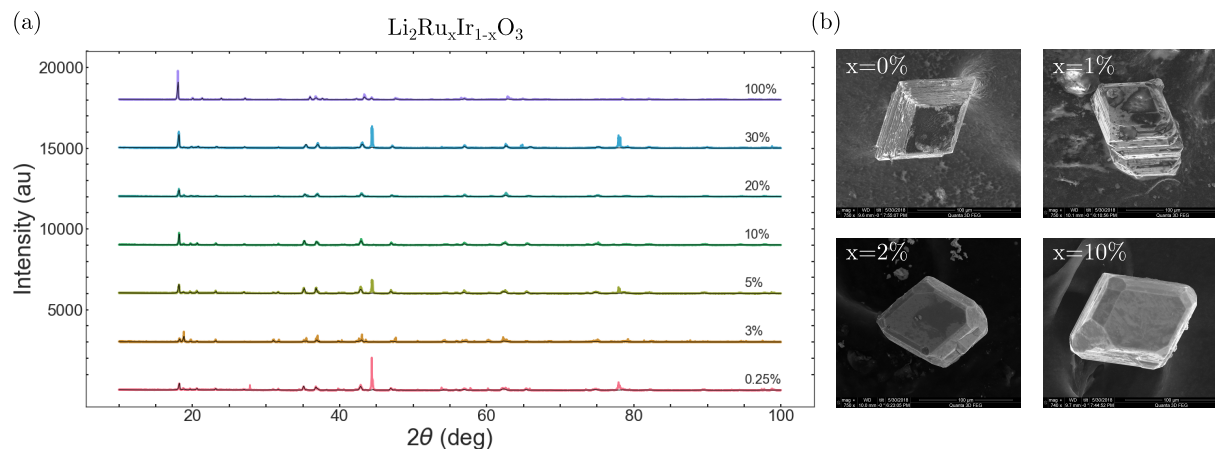


Figure 7.2: (a) Powder x-ray diffraction for a selection of doping levels. (b) Scanning electron microscopy (SEM) images for a few selected $\text{Li}_2\text{Ru}_x\text{Ir}_{1-x}\text{O}_3$ single crystals. An Energy Dispersive x-ray Spectrometer attached to the SEM was used to confirm the doping level listed on table 7.1.

quantification of the Ir and Ru content was studied using an energy dispersive x-ray spectrometer (EDS described below). Powder x-ray diffraction was collected with a Rigaku SmartLab SE diffractometer for the scattering angle range $10^\circ < 2\theta < 100^\circ$ with a $\text{Cu } K_\alpha$ radiation to estimate the change in the lattice parameters. Single crystals were collected from the powder for doping level $x = 0\%$ to $x = 60\%$, and the properties discussed below correspond to single crystal measurements.

Since Ru ions have one less d shell electron than Ir , the Ru substitution is considered as hole doping. It is important to notice that the ionic radius of Ru^{4+} and Ir^{4+} are $0.62 \text{ \AA}$ and $0.63 \text{ \AA}$ respectively and that their local connectivity is the same, which assures a good statistical mixing of Ir and Ru ions in the diluted systems. Therefore, their compatibility allows for easy substitution, even though their structures (2D honeycomb and 3D hyperhoneycomb) are different [123, 116]. The $\text{Ir} - \text{Ir}$ bond lengths in $\beta\text{-Li}_2\text{IrO}_3$ are mostly the same, whereas a third of the $\text{Ru} - \text{Ru}$ bonds in Li_2RuO_3 are significantly shorter below a metal-insulator transition at 540 K , where ordered dimers are formed, attributed to the formation of molecular orbitals [124, 125, 120] or spin singlets [126]. Away from the end members, the bond length alternation in Li_2RuO_3 and the incommensurate order in Li_2IrO_3 are suppressed in favor of a correlated spin glass [117]. Surprisingly, $\text{Li}_2\text{Ru}_x\text{Ir}_{1-x}\text{O}_3$ remains insulating for all doping levels, in contrast to $(\text{Sr,Ba})_2\text{IrO}_4$ where Ru and K , La substitution drives the system into a robust metallic state [127, 128, 129].

Nominal x	1%		2%		10%	
$T(\text{K})$	300 K	4 K	300 K	4 K	300 K	4 K
a (Å)	5.952(8)	5.917(0)	5.890(3)	5.952(8)	5.899(8)	5.899(8)
b (Å)	8.605(5)	8.623(6)	8.421(5)	8.405(9)	8.297(9)	8.325(5)
c (Å)	17.788(6)	17.788(2)	17.795(5)	17.776(6)	17.722(4)	17.713(5)
EDS x	0%		2.5%		12%	

Table 7.1: Lattice constants of selected β - $\text{Li}_2\text{Ru}_x\text{Ir}_{1-x}\text{O}_3$ measured at 4 K and 300 K. The last row has the calculated ruthenium content from our EDS measurements.

Energy Dispersive x-ray Spectroscopy (EDS)

In the energy dispersive x-ray spectrometry (EDS) method, elemental quantification is done from the characteristic x-rays spectrum emitted due to bombardment of a solid sample with a high energy focused electron beam ($E = 30 \text{ meV}$). Most equipment can detect elements with $Z < 10$ while more sophisticated instruments are required for light elements. Characteristic X-rays lines ($K_\alpha, L_\alpha, M_\alpha, K_\beta$) from electronic transitions between inner orbits are fingerprints for different elements having different electronic configurations. Rarely, some spectral lines of different elements overlap such that the quantification must be done from the intensity of the lines compared with the calibration. This technique is a very local probe so homogeneity of the composition within a crystal can be determined with an accuracy $\sim \pm 2\%$. An scanning electron microscope is also included to image the sample's surface [130].

Muon Spin Relaxation/Rotation/Resonance (μSR)

Later in this chapter, I will present some crucial data taken using μSR technique. This technique is one of the most sensitive probe of internal magnetic fields and, in contrast to the REXS technique described in chapter 4, scattering is not involved. In a typical experiment, a beam of 100% spin polarized muons (with its polarization antiparallel to its momentum) is implanted on the sample, where the muon spin precesses around the local magnetic field until it decays into a positron and two neutrinos after a lifetime $\tau = 2.2 \mu\text{s}$ and it directly yield oscillating signals whose frequency is proportional to the internal magnetic field. [131].

$$\mu^+ \rightarrow e^+ + \nu_e + \bar{\nu}_\mu$$

The positive muon (μ^+) is the one used in magnetism experiments since this small, positive charged particle would be attracted to areas of large electron density. The muon stops in the sample and the resulting positron is emitted along the direction of the muon

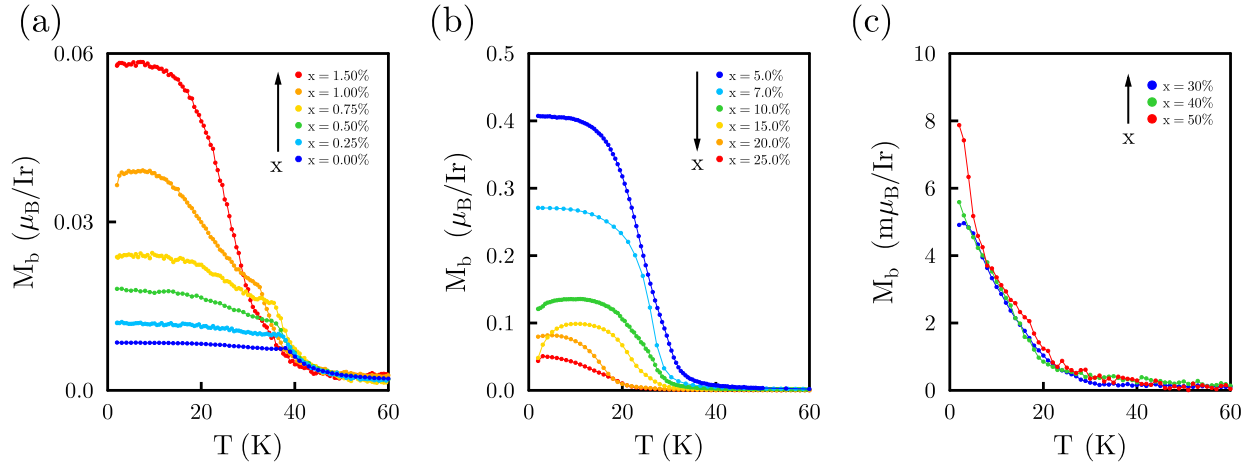


Figure 7.3: **Temperature dependent magnetization of $\text{Li}_2\text{Ru}_x\text{Ir}_{1-x}\text{O}_3$ under a 0.1 T magnetic field.** (a) For $x > 1.5\%$ we observed the continuous suppression of T_I from 38 K to 30 K. (b) For $2 < x < 20\%$ the magnetic substitution rapidly changes the the magnetically ordered state into a spin glass. (c) For $x < 30\%$ no magnetic transition was observed down to base temperature. (d) $T - x$ phase diagram with the Ψ_I denoted in red and spin glass state shown in gray.

spin at the time of decay. Positron detectors are placed around the sample to track the time evolution of the positrons in the forward (N_F) and backwards (N_B) directions. The asymmetry function ($A(t)$) can then be obtained as:

$$A(t) = \frac{N_B(t) - N_F(t)}{N_B(t) + N_F(t)} \quad (7.1)$$

where $N = N_0 e^{-t/\tau_\mu}$. This dimensionless quantity removes the natural exponential decay of the radioactive process, and the way it evolves gives information about the local magnetism. The asymmetry is defined as $A(t) = A_{max} G_z(t)$ where $A_{max} \sim 1/3$ is the initial asymmetry value and $G_z(t)$ is the projection of the muon spin along the z axis, given by [132]:

$$G_z(t) = \cos^2 \theta + \sin^2 \theta \cos(\gamma_\mu B t) \quad (7.2)$$

where B is the internal field and θ is the angle between the local field and the initial muon spin direction. If the direction of the local magnetic field is totally random, then:

$$G_z(t) = 1/3 + 2/3 \cos(\gamma_\mu B t) \quad (7.3)$$

If there is a distribution of internal field B , each muon would precess at a different frequency such that the second term would exhibit additional relaxations. μSR experiments are typically conducted in zero applied magnetic field (ZF), in a longitudinal field (TF)

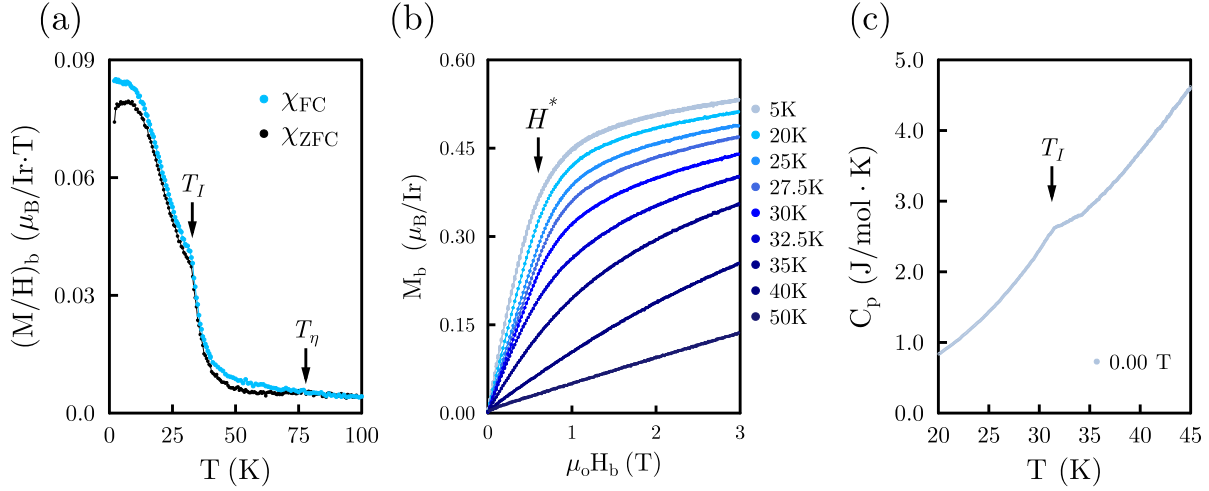


Figure 7.4: **Thermodynamic response of $\text{Li}_2\text{Ru}_x\text{Ir}_{1-x}\text{O}_3$ with $x = 1\%$.** (a) The magnetic susceptibility shows a transition at $T_I = 32 \text{ K}$ followed by continuous increase. (b) The field dependent magnetization shows that the critical field H^* has shifted to less than 1 T at base temperature. (c) Heat capacity shows a broad transition around T_I which extends over 2 K.

along the initial muon spin direction or in a weak transverse field (wTF) perpendicular to the muon spin, depending on the requirements. In ZF measurements, paramagnetic spins will show no relaxation, whereas magnetically ordered spins will oscillate for dynamical internal fields or rapidly damp for static internal fields. The last two scenarios can be distinguished in a LF, where the initial asymmetry will be recovered for static spins, whereas relaxation will persist for dynamical spins [133].

Finally, in a powder sample with coexisting paramagnetic and magnetically ordered regions (like what we will study), the asymmetry spectrum will result on two distinct signals proportional to the volume fraction f of the magnetically ordered phase, and $(1 - f)$ for the paramagnetic phase. In a weak transverse field (wTF) it can be approximated as

$$G_z(t) = f[1/3 + 2/3 \cos(\gamma_\mu B_{\text{int}} t)] + (1 - f) \cos(\gamma_\mu B_{\text{ext}} t) \quad (7.4)$$

where B_{int} and B_{ext} are the internal and external magnetic field.

7.2 Magnetic Characterization

The measured $\hat{b}$ -axis magnetic susceptibility of $\text{Li}_2\text{Ru}_x\text{Ir}_{1-x}\text{O}_3$ is shown in figure 7.3 for $x = 0, 0.25, 0.50, 0.75, 1, 1.5, 2, 5, 7, 10, 15, 20, 25, 30, 40, 50\%$. All samples show the behavior of local-moment magnetism indicating that Ru substitution does not lead to charge-carrier doping. Panel (a) shows the suppression of the incommensurate transi-

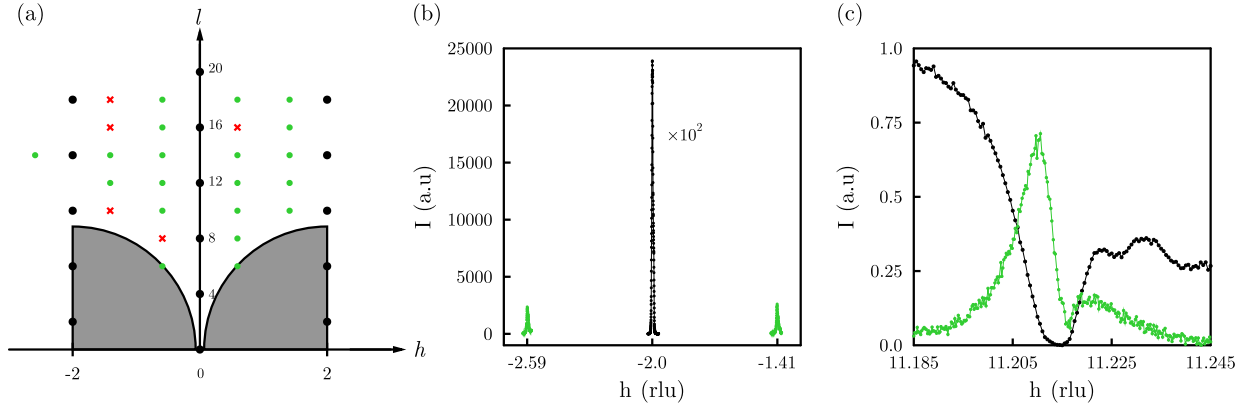


Figure 7.5: **REXS results for a single crystal of $\text{Li}_2\text{Ru}_x\text{Ir}_{1-x}\text{O}_3$ with $x = 1\%$** (a) $(h, 0, l)$ plane showing the 20 magnetic peaks (green) observed during this experiment. Other magnetic peaks were also observed in other planes not shown. (b) An 'H-scan' around the $(-2, 0, 14)$ shows both satellite magnetic peaks (green) at either side of the structural peak. (c) Energy scans around the $(0, 0, 14)$ structural (black) and the $(-1.41, 0, 14)$ magnetic peak (green).

tion temperature T_I with increasing doping from 38 K to 30 K. On the other hand, the magnitude of the magnetic moment per Ir site increases, which could be an indication of the release in magnetic frustration. However, this could also be due to the fact that we are substituting Ir^{4+} moments ($S = 1/2$) with Ru^{4+} moments ($S = 1$). Figure 7.3 (b) shows the region of doping from 2% to 20%, where the incommensurate transition T_I is no longer visible and a spin glass state is observed (more details to follow) to set in around $T_C = 30$ K. At the same time, we observed that the magnitude of the magnetic moment per site decreases with further increase in doping. Finally, Figure 7.3 (c) shows the magnetization for crystals with $x > 20\%$ where no magnetic transition was observed down to base temperature. This results immediately suggest that disturbing the short-ranged magnetic exchange pathways lead to drastic modification of the magnetic ground state and it reinforces the notion that the ground state is extremely fragile against external perturbations, since less than 2% magnetic impurity is enough to induce a frozen spin state. It also suggests that the magnetic behavior and ground state are driven by nearest neighbor exchanges since small disturbances of the sublattice leads to disorder driven freezing of spins [118, 134].

Spin Glass State

A spin glass is a random magnetic system with mixed interactions characterized by a random, yet cooperative, freezing of spin at a well-defined temperature T_f below which a highly irreversible, metastable frozen state appears without the usual magnetic long-

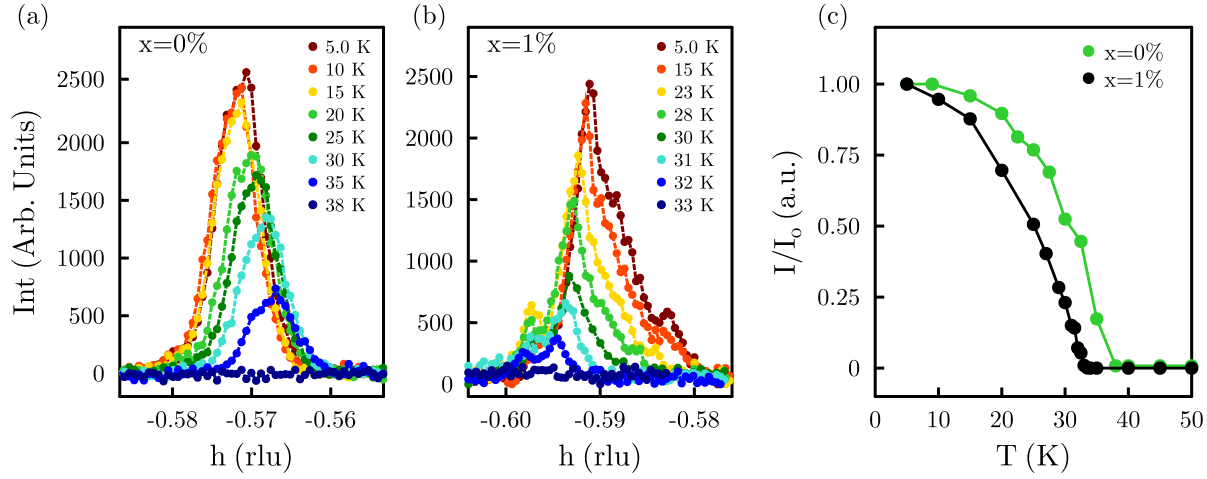


Figure 7.6: **Comparing the REXS data of $\text{Li}_2\text{Ru}_x\text{Ir}_{1-x}\text{O}_3$ for $x = 0\%$ and $x = 1\%$.** The temperature dependence of the integrated intensity behaves like an order parameter, and power-law fit to the data gives onset temperatures that coincide thermodynamics results. The transition temperature is suppressed from $T_I(0\%) = 38$ K to $T_I(1\%) = 32$ K.

range spatial magnetic ordering [131, 135]. The two most important requirements for a spin glass are:

- **Randomness:** Either random position of the spins in the lattice (site randomness), or random signs of the neighboring ferromagnetic and antiferromagnetic couplings (bond randomness). Site randomness refers to a distribution of distances between the spin sites, whereas bond randomness account for variations between parallel and antiparallel nearest neighbor couplings.
- **Competing or mixed interactions:** RKKY, Superexchange, dipolar, Dzyaloshinskii-Moriya (DM), or other types of magnetic interaction are necessary.

The combination of the randomness with the competing or mixed interactions causes frustration, which in terms gives rise to many interesting macroscopic properties unique to a disorder, yet cooperative spin glass, such as macroscopic anisotropy and metastabilities (time and aging dependences).

The concept of magnetic frustration has been a central part in this work, and it arises when a system cannot achieve a single state that simultaneously satisfies all the microscopic interaction present, inhibiting the formation of a simple, ordered, low-temperature spin configuration. Frustration (geometric or exchange) leads to a large ground states degeneracy, and as a result, frustrated systems exhibit metastability, hysteretic effects, and time dependent relaxation toward equilibrium [136]. Spin glasses not only show all these interesting properties, but they also display a new effect, a cooperative freezing transition T_f , where the system finds one of its many ground states and freezes. As $T \rightarrow T_f$,

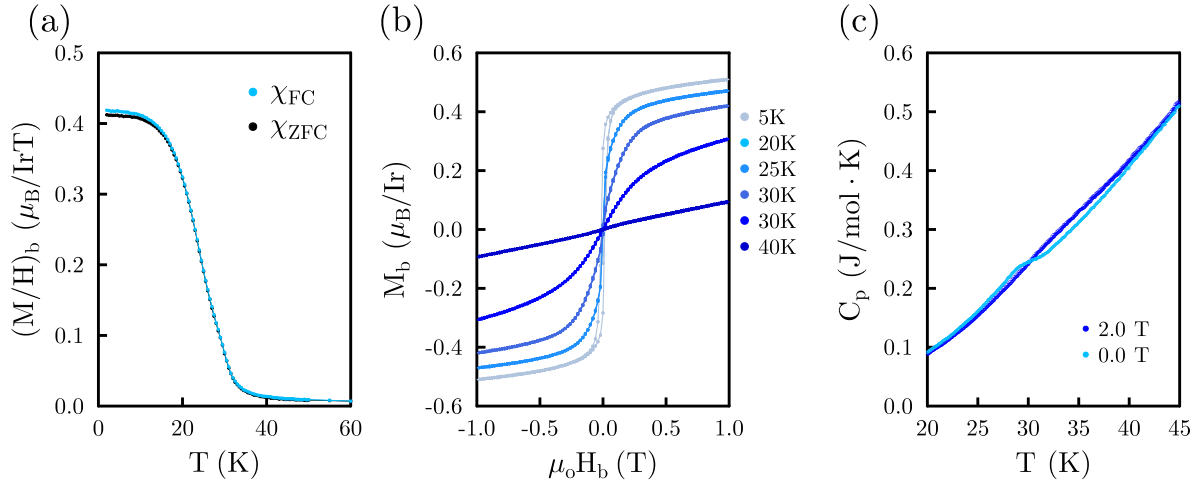


Figure 7.7: **Thermodynamic response of $\text{Li}_2\text{Ru}_x\text{Ir}_{1-x}\text{O}_3$ with $x = 2\%$.** (a) Magnetic susceptibility shows an onset at $T_C = 30$ K which is confirmed by heat capacity measurements in (C). (b) Field dependent magnetization shows hysteresis at base temperature with a very small coercive field.

independent spins slow down and build up into locally correlated clusters. Below T_f , the ground state appears glassy, with metastability and slow relaxation behaviors. This phase transition does not give rise to magnetic diffraction peaks (since there is no true long-range order) and it is still not well-understood.

$x < 2\%$ doping

In figure 7.3(a) we showed the continuous suppression of T_I with increasing doping. In figure 7.4 we focus on a 1% crystals and show that the incommensurate transition has been shifted down to $T_I = 32$ K which is accompanied by a broadening of the heat capacity response around this temperature (figure 7.4(c)). Field-cool versus zero field-cool measurements show that the high temperature transition (discussed in chapter 3) is also shifted from 100 K to $T_\eta = 80$ K with 1% substitution. The field dependent magnetization is presented in figure 7.4(b). We can immediately see a few differences when compared to the pristine β - Li_2IrO_3 (see figure 2.6). The critical field H^* is not as sharp and it has shifted down from 2.8 T to ~ 1 T. We previously mentioned that H^* depends on the coupling parameters and it becomes smaller with a decreasing Heisenberg term J .

To understand the effect of Ru doping on the magnetic ground state of β - Li_2IrO_3 , we performed REXS measurements at the Ir L_3 edge. Figure 7.5(a) shows the 20 magnetic peaks (green) observed in the $(h, 0, l)$ plane of a single crystal of 1% $\text{Li}_2\text{Ru}_x\text{Ir}_{1-x}\text{O}_3$, and the calculated structural peaks (black). Panel (b) shows scans along the $(h, 0, 14)$ direction where we can observe the structural peak at $h = -2$ and the satellite magnetic peaks

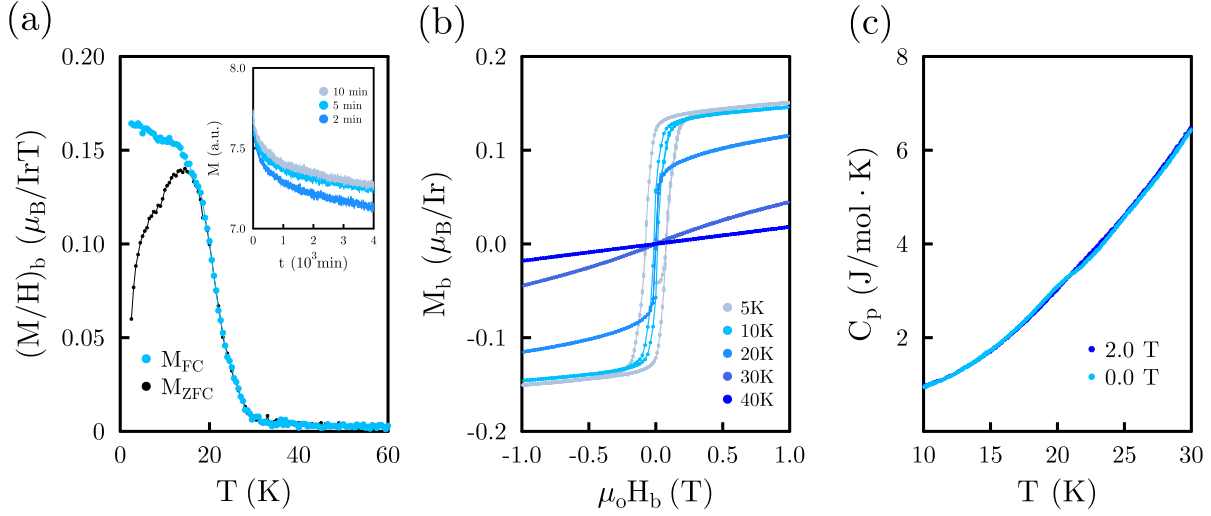


Figure 7.8: **Thermodynamic response of $\text{Li}_2\text{Ru}_x\text{Ir}_{1-x}\text{O}_3$ with $x = 10\%$.** (a) Field cooled versus zero-field cooled measurement show an onset of correlations at $T_C = 30$ K and spin freezing at $T_f = 15$ K. The inset shows spin relaxation, a characteristic property of spin glasses. (b) Field dependent magnetization shows linear behavior above T_c and non-linearity below T_c , while hysteretic behavior is observed below T_f . (c) Heat capacity measurements show a very broad transition around 20 K.

at $h = -2.59, -1.41$, respectively. Finally, figure 7.5 (c) shows energy scans through the $(-1.41, 0, 14)$ magnetic peak (green) and the $(0, 0, 14)$ structural peak (black). This energy dependence shows a large enhancement of the scattering intensity close to the absorption edge which corroborates the magnetic character of the satellite reflections.

Surprisingly, the incommensurate wave vector shifted from $q(0\%) = (0.57, 0, 0)$ to $q(1\%) = (0.59, 0, 0)$ with no trace of any new zero field order found (see figure 7.6 (a,b)). The structural parameter were carefully studied to make sure this observed shift was not related to changes in the structure itself. The normalized integrated intensity shown in figure 7.6 (c) has a typical order parameter behavior and it is suppressed at $T_I = 32$ K, in agreement with the thermodynamic data.

$2 \leq x \leq 20\%$ doping

For doping level $x > 2\%$, the incommensurate transition is no longer observed in thermodynamic measurements, and its complete suppression was confirmed using REXS (no peaks magnetic were found). The magnetic susceptibility of a 2% sample is shown in figure 7.7 (a) with an onset at $T_c = 30$ K. Field dependent measurements show linear behavior above T_c and non-linearity below it, with a very small hysteresis observed at base temperature. Heat capacity, on the other hand, shows a very broad transition around

T_c (as compared to the sharp triangular transition observed for the pristine samples in figure 2.6). A 2 T magnetic field flattens the transition.

To contrast this behavior, let us also look at the 10% doping data presented in figure 7.8. The magnetic susceptibility shows an onset at $T_c = 30$ K, however, splitting between FC and ZFC measurements is observed at a lower temperature $T_f = 14$ K. Figure 7.8(a) inset shows time dependent spin relaxation, a hallmark of a frustrated spin glass. Field dependent magnetization show hysteretic behavior below T_f , while heat capacity measurements only show a broad crossover around T_c , but no signatures around T_f .

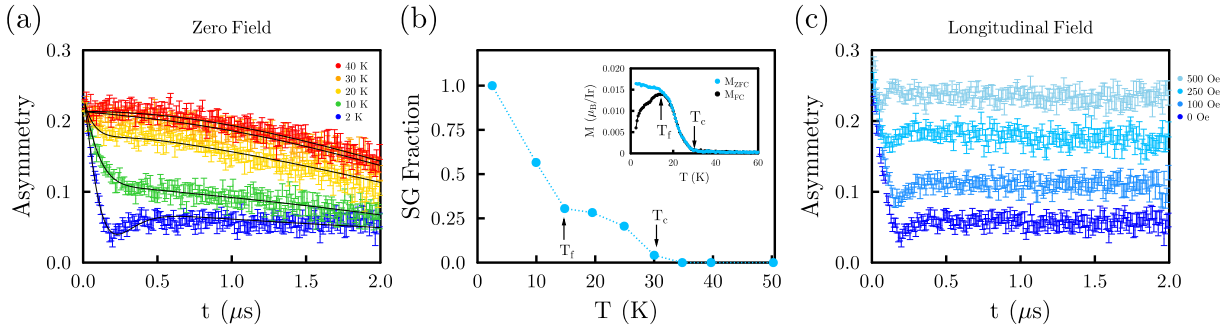


Figure 7.9: **Muon Spin Resonance (μSR) measurements on $\text{Li}_2\text{Ru}_x\text{Ir}_{1-x}\text{O}_3$ with $x = 10\%$.** (a) Rapid spin relaxation followed by a slight recovery of asymmetry is observed at low temperature. (b) Spin glass fraction shows that onset of correlations at $T_C = 30$ K and the spin freezing at $T_f = 15$ K in perfect agreement with the magnetization measurements. (c) The initial asymmetry ($t = 0$ s), is recovered under a 500 Oe longitudinal field which proves that the spins are frozen.

To study the dynamics of this spin glass, we performed muon spin resonance (μSR) experiments (described above). The onset of rapid relaxation at early times in Figure 7.9(a) indicates the development of magnetic correlations. The minimum in the 2 K spectrum around $0.2 \mu\text{s}$ followed by a slight recovery of the asymmetry is characteristic of a random distribution of static spins (spin glass). The weight of the fast relaxing component can be used to determine the fraction of the sample in the frozen state. Figure 7.9(b) shows that this spin glass fraction perfectly agrees with the SQUID measurements, where correlations develop below $T_C = 30$ K and the spin glass freezing happens at below $T_f = 15$ K. Figure 7.9(c) shows the 2 K spectra for various longitudinal fields. These data proves that the spins are in a frozen state since a 500 Oe field recovers the asymmetry to the value observed at 0 s. This complete recovery of the asymmetry occurs when the LF is about 10 times the internal field at the muon stopping site, suggesting that the magnetic field at the muon stopping site in this material is fairly weak field about 50 Oe.

7.3 Conclusions

Theoretical work predicted that depletion moments in the two dimensional honeycomb iridates would inevitably stabilize a spin-orbit glassy state with short-range zig-zag order [134]. It has also been predicted that hole doping in the $HK\Gamma$ model would stabilize a superconducting ground state [137, 138]. Experimentally, it was shown that replacing Ir with non-magnetic Ti ($S = 0$) rapidly changes the ground state of both Na_2IrO_3 and α - Li_2IrO_3 [139]. It has also been shown that Ru ($S = 1$) substitution in Na_2IrO_3 stabilizes a spin glass state for less than 5% doping [118]. In the case of the non-magnetic impurity (Ti), there is an obvious interruption of the magnetic exchange pathways which weakens the average exchange. However, a magnetic impurity (Ru) should leave the exchange pathway intact. The observed spin glassy behavior, therefore, reinforces that the honeycomb iridates are frustrated magnets, where frustration is not due to geometric factors but to the nature of the exchange itself.

In this work, we used a combination of magnetometry, heat capacity, resonant scattering and muon spin relaxation techniques to study the behavior of $\text{Li}_2\text{Ru}_x\text{Ir}_{1-x}\text{O}_3$. We concluded that a correlated spin glass state is observed, emphasizing the fine balance of the interaction terms in the underlying microscopic Hamiltonian.

Chapter 8

Conclusions and Outlook

Frustration is an undeniable part of life. In physical systems, it arises from the combined influence of competing interactions that cannot be simultaneously satisfied, and it often leads to exotic emergent properties. One of the most intriguing examples is the quantum spin-liquid (QSL), first proposed in 1973 by P.W. Anderson as the ground state of frustrated magnetic system [140]. Unfortunately, the experimental realization of such a state has remained elusive with only few known candidates. In recent years, a considerable boost in the field was triggered by (1) the formulation in 2006 by Alexei Kitaev [26] of an exactly solvable model on the honeycomb lattice with a QSL ground state and fractionalized excitations, and (2) by the microscopic description in 2009 by George Jackeli and Giniyat Khaliullin of a mechanism for designing Kitaev-type interactions in the two-dimensional layered honeycomb iridates $A_2\text{IrO}_3$ with $A = \text{Li}, \text{Na}$ [23]. In the search for single crystals of the 2D $\alpha\text{-Li}_2\text{IrO}_3$, other 3D polytypes were discovered ($\beta, \gamma\text{-Li}_2\text{IrO}_3$) with the same local environment but with different connectivity along the c -axis, offering an exciting venue to explore Kitaev physics in 3D [32, 33].

This was precisely the aim of this dissertation; to understand the ground state and the excitation spectrum of the 3D $\beta, \gamma\text{-Li}_2\text{IrO}_3$ and to drive these systems into either a QSL or an adjacent exotic states. A fruitful approach taken by this author was the use of external perturbations to tune the magnetic response in these materials. From previous work, it was known that the low temperature magnetic order was an incommensurate spiral, featuring non-coplanar and counter-rotating moments [48, 49]. However, the nature of this complex order and its response to external magnetic field, hydrostatic pressure or doping was not understood.

In this work we explored the anisotropic properties of $\beta, \gamma\text{-Li}_2\text{IrO}_3$ in three different regions: the high temperature paramagnetic regime, the intermediate correlated region and the low temperature ordered state. Our study showed that at high temperatures, the magnetic anisotropy is dictated by the local geometry of the iridium moments. However, at $T_\eta = 100$ K the magnetically special $\hat{b}$ -axis softens and strongly deviates from g -factor anisotropy. Moreover, we observed a true phase transition at T_η , the origin of which still needs to be understood. At low temperature, however, an applied magnetic field estab-

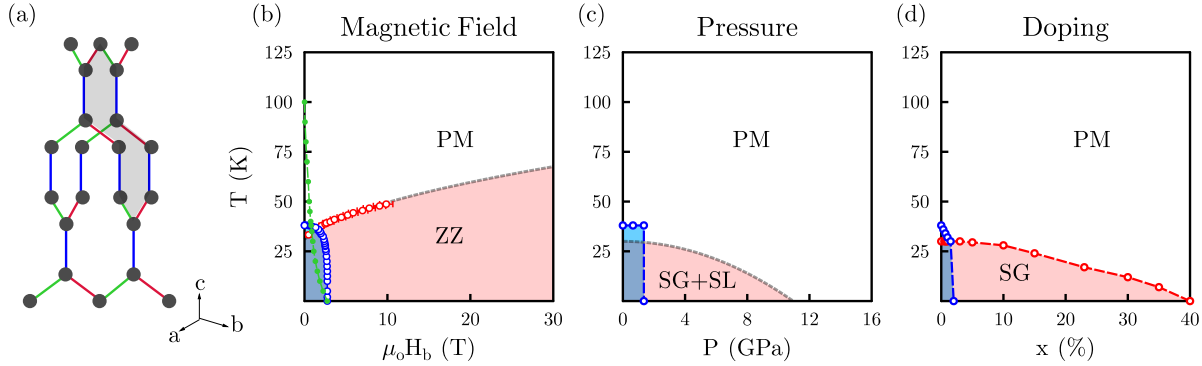


Figure 8.1: **Summary of the main results presented in this dissertation for the three dimensional Kitaev materials $\beta, \gamma\text{-Li}_2\text{IrO}_3$.** (b) Chapter 2,3,5 studied the effect of an applied magnetic field using magnetometry, heat capacity and resonant scattering techniques. (c) Chapter 6 explored the consequences of applied hydrostatic pressure. (d) Chapter 7 was devoted to understanding the effect of non-magnetic chemical substitution.

lishes a clear connection between the zig-zag order Ψ_V observed in $\text{Na}_2\text{IrO}_3/\text{RuCl}_3$ and the incommensurate order Ψ_I stabilized in the Li_2IrO_3 family. Under an applied field, a zig-zag component is induced while the incommensurate spiral is linearly suppressed. As the field increases, these states coexist up to a critical field $H^* \sim 2.8$ T where the incommensurate spiral completely disappears and the zig-zag state becomes the sole spin texture. This work demonstrated that these materials have nearly degenerate states, which is a hallmark of a QSL, and further corroborated the tunability of these systems and the delicate balance of the underlying interactions, with dominant Kitaev interactions and a small Heisenberg contribution. On the other hand, hydrostatic pressure suppresses Ψ_I upon a first order transition at a critical pressure $P_c = 1.4$ GPa while stabilizing an admixture of frozen and dynamical spins [111]. Finally, we showed that non-magnetic chemical substitution destroys the incommensurate state around 2% and a correlated spin glass emerges instead.

Although this work answered a lot of opened questions, it also created new ones to be addressed by future work.

- Chapter 2: how is the structural connectivity of $\beta, \gamma\text{-Li}_2\text{IrO}_3$ giving rise to the different thermodynamics response even when the critical values are the same (T_I, H^*, P_c)?
- Chapter 3: what is the exact nature to the T_η transition; is it a signature of the spin fractionalization, a kiral spin liquid, or a correlated spin glass emerging from intrinsic vacancies and disorder? What's the order parameter and what symmetry is being broken? How is it connected to the low temperature ordered states, or the torque signatures previously reported?

- Chapter 5: are Ψ_I and Ψ_v truly coexisting orders, or intertwined components of the same ground state (K state)? How does the RIXS spectra change under an applied field?
- Chapter 6: are the dynamical spin above P_c in a truly spin liquid state? Is it a classical or quantum spin liquid? How is this state related to the microscopic HKT model?
- Chapter 7: What happens to the field induced state Ψ_V as a function of doping? What does this tell us about the balance of interaction energies? What is the percolation threshold? Is this an ordinary spin glass or does Kitaev physics affects its behavior?

Appendix A

Ionic Environment

A.1 Single Ion Physics

Octahedral Crystal Field

In an isolated atom, the potential experienced by a single electron is spherically symmetric. However, when the atom is on a crystal or molecule, its electrons experience a crystal electric field potential of lower symmetry and, as a result, degeneracy of electric states is lifted. The electron many-body Hamiltonian is defined as:

$$\begin{aligned}
 H &= \sum_{i \neq i'} \left(\frac{p_i^2}{2m} + \frac{e^2}{|r_i - r_{i'}|} \right) + \sum_{i, \alpha} \left(\frac{Z_\alpha e^2}{|R_\alpha - r_i|} + \frac{Z_\alpha Z'_\alpha}{|R_\alpha - R'_\alpha|} \right) \\
 &= T_e + V_{ee} + V_{en} + V_{nn}
 \end{aligned} \tag{A.1}$$

where the first sum accounts for the kinetic and potential energy of the interacting electrons, while the second sum account for electron-nucleus and nucleus-nucleus interactions. V_{en} is the potential energy term that causes crystal field splitting.

In the IrO_6 octahedral cage example, we consider a hydrogen-like Ir atom surrounded by 6 point charges, with charge $-Ze$ at a distance a from the central Ir atom. A test charge at a position $\mathbf{r}$ will experience a potential energy generated by the 6 oxygens at positions $\mathbf{R}_i$ given by:

$$\begin{aligned}
V_{en}(r) &= \sum_{i=1}^6 \frac{Ze^2}{|R_i - r|} \\
&= Ze^2 \left[\frac{1}{\sqrt{(x-a)^2 + y^2 + z^2}} + \frac{1}{\sqrt{(x+a)^2 + y^2 + z^2}} \right. \\
&\quad \left. \frac{1}{\sqrt{x^2 + (y-a)^2 + z^2}} + \frac{1}{\sqrt{x^2 + (y+a)^2 + z^2}} \right. \\
&\quad \left. \frac{1}{\sqrt{x^2 + y^2 + (z-a)^2}} + \frac{1}{\sqrt{x^2 + y^2 + (z+a)^2}} \right]
\end{aligned} \tag{A.2}$$

Expanding $V_{en}(r)$ around the origin yields:

$$V_{en}(r) = V_o + D(x^4 + y^4 + z^4 - \frac{3}{5}r^4)$$

where $V_o = \frac{6Ze^2}{a}$ shifts all the atomic energies by the same amount, and $D = \frac{35Ze^2}{4a^5}$ is responsible for splitting the degeneracy of the atomic states.

To determine the energy splitting, let's calculate the matrix elements of this cubic potential in the d -orbital basis: $\langle \Psi | V_{en}(r) - V_o | \Psi \rangle$. Since atomic d -wave functions can be written as the product of a radial wave $R_{nd}(r)$ that depends on principle quantum number n , and a spherical harmonics $Y_m^l(\theta, \phi)$ representing the angular component of the wave functions: $\Psi_{nlm}(r) = R_{nd}(r) \cdot Y_m^l(\theta, \phi)$, then it is convenient to expand $V_{en}(r)$ in terms of spherical harmonics:

$$V_{en}(r) - V_o = D \frac{2}{5} \sqrt{\frac{4\pi}{9}} r^4 \left[Y_0^4(\theta, \phi) + \sqrt{\frac{5}{14}} (Y_{-4}^4(\theta, \phi) + Y_{-4}^4(\theta, \phi)) \right] \tag{A.3}$$

where:

$$\begin{aligned}
Y_0^4(\theta, \phi) &= \frac{3}{16\sqrt{\pi}} (3 - 30 \cos^2 \theta + 35 \cos^4 \theta) \\
Y_{\pm 4}^4(\theta, \phi) &= \frac{3}{16} e^{\pm 4i\phi} \sqrt{\frac{35}{2\pi}} \sin^4 \theta
\end{aligned}$$

Therefore, the matrix elements become:

$$\begin{aligned}
\langle \Psi_{nlm} | V_{en}(r) - V_o | \Psi_{nlm'} \rangle &= \int \Psi_{nlm}^* (V_{en}(r) - V_o) \Psi_{nlm'} dr \\
&= \int_0^\pi \int_0^{2\pi} Y_m^2(\theta, \phi)^* Y_k^4(\theta, \phi) Y_{m'}^2(\theta, \phi) \sin \theta d\phi d\theta
\end{aligned}$$

And the non-vanishing matrix elements will be:

$$\begin{aligned}\langle \Psi_{n20} | V_{en}(r) - V_o | \Psi_{n20} \rangle &= 6Dq \\ \langle \Psi_{n2\pm 1} | V_{en}(r) - V_o | \Psi_{n2\pm 1} \rangle &= -4Dq \\ \langle \Psi_{n2\pm 2} | V_{en}(r) - V_o | \Psi_{n2\pm 2} \rangle &= Dq \\ \langle \Psi_{n2\pm 2} | V_{en}(r) - V_o | \Psi_{n2\mp 2} \rangle &= 5Dq\end{aligned}$$

where $q = \frac{2}{105} \langle r^4 \rangle_{nd}$ and $\langle r^4 \rangle_{nd} = \int r^4 |r R_{nd}|^2 dr$. This leads to the following cubic crystal-field Hamiltonian:

$$H_{\Delta} = \begin{pmatrix} Dq & 0 & 0 & 0 & 5Dq \\ 0 & -4Dq & 0 & 0 & 0 \\ 0 & 0 & 6Dq & 0 & 0 \\ 0 & 0 & 0 & -4Dq & 0 \\ 5Dq & 0 & 0 & 0 & Dq \end{pmatrix} \quad (\text{A.4})$$

The energy splitting can be obtained by diagonalizing this Hamiltonian, and determining the eigenvalues and eigenvectors:

$$\det H_{\Delta} = \begin{vmatrix} 6Dq & 0 & 0 & 0 & 0 \\ 0 & 6Dq & 0 & 0 & 0 \\ 0 & 0 & -4Dq & 0 & 0 \\ 0 & 0 & 0 & -4Dq & 0 \\ 0 & 0 & 0 & 0 & -4Dq \end{vmatrix}$$

We find that the eigenvectors are:

A. The double degenerate e_g states with energy $\Delta_{CEF} = 6Dq$

$$\begin{aligned}|\Psi_{n20}\rangle &= |3z^2 - r^2\rangle \\ \frac{1}{\sqrt{2}}(|\Psi_{n22}\rangle + |\Psi_{n2-2}\rangle) &= |x^2 - y^2\rangle\end{aligned} \quad (\text{A.5})$$

B. The triple degenerate t_{2g} states with energy $\Delta_{CEF} = -4Dq$

$$\begin{aligned}\frac{i}{\sqrt{2}}(|\Psi_{n2-2}\rangle - |\Psi_{n22}\rangle) &= |xy\rangle \\ \frac{1}{\sqrt{2}}(|\Psi_{n2-1}\rangle - |\Psi_{n21}\rangle) &= |xz\rangle \\ \frac{i}{\sqrt{2}}(|\Psi_{n2-1}\rangle + |\Psi_{n21}\rangle) &= |yz\rangle\end{aligned} \quad (\text{A.6})$$

Therefore, a cubic CEF results on an energy splitting between the e_g and t_{2g} orbitals equal to:

$$\begin{aligned}\Delta_{CEF} &= E(e_g) - E(t_{2g}) = 10Dq = 10 \left(\frac{35Ze^2}{4a^5} \right) \left(\frac{2}{105} \langle r^4 \rangle_{nd} \right) \\ &= \frac{5}{3} \frac{Ze^2}{a^5} \langle r^4 \rangle_{nd}\end{aligned}\tag{A.7}$$

To understand what this implies, let's compare the CEF effect in cobalt and iridium ions. For Co, $\langle r^4 \rangle_{3d} = 1.28527 a_o^4$ which means $\Delta_{CEF} \sim 151$ meV. On the other hand, Ir has $\langle r^4 \rangle_{5d} = 20.2859 a_o^4$ which yields $\Delta_{CEF} \sim 2.34$ eV. This purely ionic model, where the covalency of the bonds has been neglected, provides a good estimate for the change in strength of crystal field interactions when going from $3d$ to $5d$ TMO.

A.2 Spin-Orbit Coupling

The spin-orbit interaction is a relativistic effect that leads to splitting of the electron's atomic energy levels, due to the electromagnetic interaction between the electron's magnetic dipole, its orbital motion and the electrostatic field of the positively charged nucleus. The energy splitting of the magnetic moment (μ) in a magnetic field ($\mathbf{B}$) can be described by:

$$H = -\mu \cdot \mathbf{B}\tag{A.8}$$

To derive in a semiclassical way the spin-orbit coupling, we consider a hydrogen-like system with an electron orbiting around a positively charged nucleus of charge Ze . This problem can be most easily calculated if we find the magnetic field the electron experiences in its rest frame due to the orbiting nucleus,

$$\mathbf{B} = \frac{\mu_o I}{2r} = \frac{\mu_o Ze}{2rT}$$

where $I = Ze/T$ is the effective current due to the charge orbiting with a period T . If we now consider the electron's orbital angular momentum in the nucleus reference frame, $\hbar L = m_e (\mathbf{r} \times \mathbf{v}) = 2\pi m_e r^2/T$, and the fact that the speed of light $c = 1/\sqrt{\epsilon_o \mu_o}$, the field experienced by the electron becomes:

$$\mathbf{B} = \frac{\hbar}{4\pi\epsilon_o} \frac{Ze}{m_e c^2 r^3} \mathbf{L}$$

Let us now recall that for a given $|n, l\rangle$ state, the expectation value of $1/r^3$ equals:

$$\left\langle \frac{1}{r^3} \right\rangle_{n,l} = \frac{Z^3}{a_o^3} \frac{2}{n^3 l(l+1)(2l+1)}$$

where a_o is the Bohr radius, n is the principle quantum number, l is the orbital quantum number and Z is the atomic number. Therefore, an electron orbiting around a nucleus experiences a magnetic field:

$$\mathbf{B} = \frac{\hbar}{2\pi\epsilon_o} \frac{Z^4 e}{m_e c^2} \frac{1}{a_o^3 n^3 l(l+1)(2l+1)} \mathbf{L} \quad (\text{A.9})$$

Finally, let's make use of the fact that the magnetic moment of the electron is proportional to its spin angular momentum $\mathbf{S}$, as given by:

$$\mu = -\frac{e\hbar g}{2m_e} \mathbf{S} = -\frac{e}{m_e} \hbar \mathbf{S} \quad (\text{A.10})$$

where e is the electron's charge, m_e is the electron's mass, $\hbar$ is Planck's constant, and a spin g -factor $g = 2$ have been assumed.

Therefore, the spin-orbit coupling Hamiltonian can be found by substituting eqn. A.9 and A.10 into eqn. A.8, to obtain:

$$H_{SO} = \frac{e^2 \hbar^2}{4\pi\epsilon_o} \frac{Z^4}{m_e^2 c^2} \frac{1}{a_o^3 n^3 l(l+1)(2l+1)} \mathbf{S} \cdot \mathbf{L} = \lambda_{SO} \mathbf{S} \cdot \mathbf{L} \quad (\text{A.11})$$

where a factor $1/2$ have been included as a relativistic kinematic correction. This Thomas precession term takes care of the fact that the rest frame of the electron where we started this analysis is not an inertial frame.

Appendix B

Bond-directional Interactions

The spin-orbit entangled isopins can be represented in the d-orbital basis as follows:

$$\begin{pmatrix} \left| \frac{3}{2}, \frac{3}{2} \right\rangle \\ \left| \frac{3}{2}, \frac{1}{2} \right\rangle \\ \left| \frac{3}{2}, -\frac{1}{2} \right\rangle \\ \left| \frac{3}{2}, -\frac{3}{2} \right\rangle \\ \left| \frac{1}{2}, \frac{1}{2} \right\rangle \\ \left| \frac{1}{2}, -\frac{1}{2} \right\rangle \end{pmatrix} = \begin{pmatrix} \frac{1}{\sqrt{2}} & 0 & \frac{i}{\sqrt{2}} & 0 & 0 & 0 \\ 0 & \frac{1}{\sqrt{6}} & 0 & \frac{i}{\sqrt{6}} & \frac{2}{\sqrt{6}} & 0 \\ \frac{1}{\sqrt{6}} & 0 & -\frac{i}{\sqrt{6}} & 0 & 0 & \frac{2}{\sqrt{6}} \\ 0 & \frac{1}{\sqrt{2}} & 0 & -\frac{i}{\sqrt{2}} & 0 & 0 \\ 0 & \frac{1}{\sqrt{3}} & 0 & \frac{i}{\sqrt{3}} & -\frac{1}{\sqrt{3}} & 0 \\ -\frac{1}{\sqrt{3}} & 0 & \frac{i}{\sqrt{3}} & 0 & 0 & \frac{1}{\sqrt{3}} \end{pmatrix} \begin{pmatrix} |d_{yz}, \uparrow\rangle \\ |d_{yz}, \downarrow\rangle \\ |d_{zx}, \uparrow\rangle \\ |d_{zx}, \downarrow\rangle \\ |d_{xy}, \uparrow\rangle \\ |d_{xy}, \downarrow\rangle \end{pmatrix} \quad (\text{B.1})$$

This can then be used to find the nearest neighbor hopping elements through the oxygen p -orbitals. Therefore, the O-Ir hopping elements for the spin-up ($\uparrow$) become:

$$\begin{aligned}
\left\langle p_{\uparrow}^z \left| \hat{T}_{yz} \right| \frac{3}{2}, \frac{3}{2} \right\rangle &= \frac{1}{\sqrt{2}} t & \left\langle p_{\uparrow}^z \left| \hat{T}_{xz} \right| \frac{3}{2}, \frac{3}{2} \right\rangle &= \frac{i}{\sqrt{2}} t \\
\left\langle p_{\uparrow}^z \left| \hat{T}_{yz} \right| \frac{3}{2}, -\frac{3}{2} \right\rangle &= 0 & \left\langle p_{\uparrow}^z \left| \hat{T}_{xz} \right| \frac{3}{2}, -\frac{3}{2} \right\rangle &= 0 \\
\left\langle p_{\uparrow}^z \left| \hat{T}_{yz} \right| \frac{3}{2}, \frac{1}{2} \right\rangle &= 0 & \left\langle p_{\uparrow}^z \left| \hat{T}_{xz} \right| \frac{3}{2}, \frac{1}{2} \right\rangle &= 0 \\
\left\langle p_{\uparrow}^z \left| \hat{T}_{yz} \right| \frac{3}{2}, -\frac{1}{2} \right\rangle &= \frac{1}{\sqrt{6}} t & \left\langle p_{\uparrow}^z \left| \hat{T}_{xz} \right| \frac{3}{2}, -\frac{1}{2} \right\rangle &= -\frac{i}{\sqrt{6}} t \\
\left\langle p_{\uparrow}^z \left| \hat{T}_{yz} \right| \frac{1}{2}, \frac{1}{2} \right\rangle &= 0 & \left\langle p_{\uparrow}^z \left| \hat{T}_{xz} \right| \frac{1}{2}, \frac{1}{2} \right\rangle &= 0 \\
\left\langle p_{\uparrow}^z \left| \hat{T}_{yz} \right| \frac{1}{2}, -\frac{1}{2} \right\rangle &= -\frac{1}{\sqrt{3}} t & \left\langle p_{\uparrow}^z \left| \hat{T}_{xz} \right| \frac{1}{2}, -\frac{1}{2} \right\rangle &= -\frac{i}{\sqrt{3}} t
\end{aligned}$$

Only two orbitals are active on a given bond (e.g. $|d_{xz}\rangle$ & $|d_{yz}\rangle$ in the z-direction). The hopping matrix has now only nondiagonal elements, and there are two possible paths for a charge transfer (via upper or lower oxygen). The transfer amplitudes destructively interfere so that the isotropic interaction vanishes while the finite, anisotropic term is due to the J_H -multiplet structure of the excited levels ($|3/2, 3/2\rangle$).

$$\begin{aligned}
&\mathcal{J}_{1/2} - \mathcal{J}_{1/2} : \text{Upper path} + \text{Lower path} \\
&\left\langle \frac{1}{2}, -\frac{1}{2} \left| \hat{T}_{yz} \right| p_{\uparrow}^z \right\rangle \left\langle p_{\uparrow}^z \left| \hat{T}_{zx} \right| \frac{1}{2}, -\frac{1}{2} \right\rangle + \left\langle \frac{1}{2}, -\frac{1}{2} \left| \hat{T}_{xz} \right| p_{\uparrow}^z \right\rangle \left\langle p_{\uparrow}^z \left| \hat{T}_{zy} \right| \frac{1}{2}, -\frac{1}{2} \right\rangle \\
&\quad -\frac{i}{3} t^2 + \frac{i}{3} t^2 \\
&\quad = 0
\end{aligned}$$

$$\begin{aligned}
&\mathcal{J}_{1/2} - \mathcal{J}_{3/2} : \text{Upper path} + \text{Lower path} \\
&\left\langle \frac{1}{2}, -\frac{1}{2} \left| \hat{T}_{yz} \right| p_{\uparrow}^z \right\rangle \left\langle p_{\uparrow}^z \left| \hat{T}_{zx} \right| \frac{3}{2}, \frac{3}{2} \right\rangle + \left\langle \frac{1}{2}, -\frac{1}{2} \left| \hat{T}_{xz} \right| p_{\uparrow}^z \right\rangle \left\langle p_{\uparrow}^z \left| \hat{T}_{zy} \right| \frac{3}{2}, \frac{3}{2} \right\rangle \\
&\quad (-\frac{1}{\sqrt{3}} t)(\frac{i}{\sqrt{2}} t) + (\frac{i}{\sqrt{2}} t)(-\frac{1}{\sqrt{3}} t) \\
&\quad -\frac{i}{\sqrt{6}} t^2 - \frac{i}{\sqrt{6}} t^2 \\
&\quad = -\frac{2i}{\sqrt{6}} t^2
\end{aligned}$$

Appendix C

Magnetometry

C.1 Introduction

Magnetization is defined as the magnetic moment per unit volume,

$$\vec{M} = \frac{\vec{\mu}}{V} \quad (\text{C.1})$$

where the magnetic moment of an orbiting electron always lies along the direction of the electron's angular momentum and it's scaled by the gyromagnetic ratio, $\vec{\mu} = \gamma \vec{L}$. In a magnetic field, the magnetic moment's energy and torque are given by:

$$\begin{aligned} E &= -\vec{\mu} \cdot \vec{B} \\ \vec{\tau} &= \vec{\mu} \times \vec{B} \end{aligned} \quad (\text{C.2})$$

Since the magnetic moment is associated with the angular momentum and because torque is equal to the rate of change of angular momentum, the magnetic field causes the direction of $\vec{\mu}$ to precess around $\vec{B}$.

A magnetic solid consists of a large number of atoms with magnetic moments. In the special case of linear materials, the magnetization is linearly related to the applied field $\vec{H}$,

$$\vec{M} = \chi \vec{H} \quad (\text{C.3})$$

where χ is the magnetic susceptibility, a dimensionless quantity that indicates the degree of magnetization of a material in response to an applied magnetic field. For low magnetic fields, the susceptibility is given by:

$$\begin{aligned} \chi &= \frac{M}{H} \approx \frac{\mu_o M}{B} \\ &= \frac{C}{T - \Theta} = \frac{\mu_o N_A \mu_B^2 \mu_{eff}^2}{3k_B(T - \Theta)} \end{aligned} \quad (\text{C.4})$$

C.2 SQUID

A Superconducting Quantum Interference Device (SQUID) magnetometer is used to study the magnetic properties of materials as a function of temperature and applied magnetic field. To detect the magnetic moment of a sample in a DC magnetic field, the sample is moved through a superconducting pickup coil which detects a signal proportional to the trapped magnetic flux inside a superconducting loop of two Josephson junctions.

Appendix D

Calorimetry

D.1 Introduction

Heat capacity is defined as the amount of heat, dQ , needed to be supplied to an object to raise its temperature by a small amount dT .

$$C_x = \left(\frac{dQ}{dT} \right)_x \quad (\text{D.1})$$

where x denotes any of several constant variables, like pressure, volume, magnetic field, magnetization etc. Heat capacity gives information about lattice, electronic, and magnetic properties of materials, as well as the nature of phase transitions. As many other physical properties, it can be defined in terms of other thermodynamic state variables.

1st Law of Thermodynamics

According to the first law of thermodynamics, the heat added or removed from a system is $dQ = dU + PdV$, where dU is the internal energy of the system, and the external work PdV consists only of work done by the system in increasing its volume V against an external pressure P , which yields,

$$\begin{aligned} C_V &= \left(\frac{dQ}{dT} \right)_V = \left(\frac{dU}{dT} \right)_V \\ C_P &= \left(\frac{dQ}{dT} \right)_P = \left(\frac{dU}{dT} \right)_P + P \left(\frac{dV}{dT} \right)_P \end{aligned} \quad (\text{D.2})$$

Experimental data usually gives heat capacity at constant pressure because of the practical difficulty of keeping the volume constant. In systems with relevant magnetic properties, C_H or C_M may be used to designate the heat capacity at a constant applied magnetic field or magnetization, respectively. To determine these relationships, we must add an energy term to the first law, $dQ = dU + PdV + MdH$, coming from the influence of a

magnetic field. All magnetic behavior of materials influence the specific heat, except diamagnetism and Pauli paramagnetism which are independent of temperature, therefore, it can be used to determine the magnetic entropy.

2nd Law of Thermodynamics

According to the second law of thermodynamics, the entropy of a reversible process is $dQ = TdS$, where dS , a measure of the number of microscopic configurations that a thermodynamic system can be in. Thus the heat capacity can be expressed as a function of the entropy,

$$C_x = T \left(\frac{dS}{dT} \right)_x \quad (\text{D.3})$$

which can be used to compute the entropy and compared to the theoretically expected values. For example, the total magnetic entropy is $S_M = R \ln(2J + 1)$, where R is the gas constant and J is the ground state total angular momentum.

Free Energy

Combining the equations for the first and second law of thermodynamics yields $dU = TdS - PdV$ which is a very useful quantity. The internal energy is a state function, which means the system undergoes the same change when we move it from one equilibrium state to another, irrespective of which route we take through parameter space. Other useful thermodynamic potentials can be defined by adding various combinations of P, V, T , and S to the internal energy:

$$\begin{aligned} dH &= dU + PdV + VdP = TdS + VdP \\ dF &= dU - SdT - TdS = -SdT - PdV \\ dG &= dU + PdV + VdP - TdS - SdT = -SdT + VdP \end{aligned} \quad (\text{D.4})$$

Using these equations, we can redefine the heat capacity as a function of the Helmholtz (F) or Gibbs (G) free energy:

$$\begin{aligned} C_V &= T \left(\frac{\partial^2 F}{\partial T^2} \right)_V \\ C_P &= T \left(\frac{\partial^2 G}{\partial T^2} \right)_P \end{aligned} \quad (\text{D.5})$$

These relationships will come in handy in the framework of Landau phase transitions, in which, the free energy is expanded in terms of an order parameter, and the heat capacity response is calculated using the equations above.

D.2 Heat Capacity of Solids

Let's first understand the heat capacity response of a solid in the absence of a phase transition. At high temperatures, the heat capacity approaches a classical value dictated by all modes of lattice vibrations, while at low temperatures, the heat capacity depends on lattice, electronic, and magnetic contributions.

High Temperature

In solids, the atoms are held rigidly in the lattice. There is no translational motion but atoms can vibrate about their mean position. Considering a cubic solid in which each atom is connected by springs to its six neighbours, we find that at high temperatures ($T > 100K$), the mean energy of a solid is $U = 3Nk_B T$ and the heat capacity is:

$$C_s = 3Nk_B = 3nR \sim 25n \frac{J}{mol \cdot K} \quad (D.6)$$

where n is the number of atoms per formula unit. This result is known as the Dulong–Petit rule.

Low Temperature

The low temperature heat capacity of solids has three contributions: an electronic, a phonon and a magnetic contribution. Detail derivations of the temperature dependence of these terms can be found in most solid state and thermodynamic books. The result for a 3D solid is:

$$\begin{aligned} C_s &= \gamma T + \beta T^3 + AT^\alpha \\ &= \frac{\pi^2}{2} \frac{Nk_B}{T_F} T + \frac{12\pi^4}{5} \frac{Nk_B}{\Theta^3} T^3 + AT^\alpha \end{aligned} \quad (D.7)$$

where the 1st term comes from electronic interactions ($\sim T$), the 2nd term is the phonon contribution ($\sim T^3$) and the 3rd term is a spin component which could be a Schottky anomaly ($\sim T^{-2}$), a ferromagnetic ($\sim T^{3/2}$) or anti-ferromagnetic ($\sim T^3$) order.

Assuming no magnetic contribution, a fit of C_p/T vs T^2 would yield a straight line with an intercept equal to the Sommerfeld constant (γ) which gives information about the density of states at the Fermi surface, and a slope equal to the Debye constant (β) which gives information about the temperature above which all modes of the atoms are excited.

For an insulator, the electronic heat capacity is zero and the total heat capacity is described by the 2nd and 3rd term in equation D.7 while metals are described by all terms. If a phase transition occurs as a function of temperature, the heat capacity will show an irregularity as a result of either a first-order, second-order, or λ -type transitions. Let's see the characteristic behavior for the different types of phase transitions.

D.3 Landau Theory of Phase Transition

A phase transition occurs when an equilibrium state of a system changes qualitatively as a function of an externally imposed constraints, like temperature, pressure, magnetic field, etc. Phase transitions often involve the development of some type of order with an associated symmetry breaking. The broken symmetry is described by an order parameter which is zero in the disordered phase and increases on moving deeper into the ordered phase, and which measures the degree of order as the phase transition proceeds. The order parameter is a physical observable, like magnetisation M for a ferromagnet, electrical polarisation P for a ferroelectric, or the degree of alignment of the molecules in a liquid crystal.

An i -order transition is characterized by a discontinuity in the i^{th} order derivative of the Gibbs free energy. According to the Landau–Ginsberg theory of phase transitions, the free energy can be expanded as a power series of the order parameter with the condition $G(-Q) = G(Q)$ requiring only even powers of Q so that:

$$\begin{aligned}\Delta G &= \frac{1}{2}a(T - T_0)Q^2 + \frac{1}{4}bQ^4 + \frac{1}{6}cQ^6 \\ \Delta G &= \Delta H - T\Delta S\end{aligned}\tag{D.8}$$

The sign of the coefficient b determines the order of the transition: $b < 0$ first-order, $b > 0$ second-order, $b \sim 0$ tricritical. Minimizing equation D.8 gives insight into the behavior of the order parameter, the latent heat, the system's entropy and heat capacity. Let's take a closer look.

1st Order

A first-order phase transition is characterized by a discontinuity in the first derivative of the Gibbs free energy while the second derivative goes to infinity. The specific heat is finite in both phases until the transition is reached, that is, there is no anticipation of the transition. Therefore, first-order transition have:

- a jump in the order parameter $Q^2 = \frac{3b}{4c}$,
- a latent heat $\Delta H = -\frac{3ab}{8c}T_c$,
- a divergent heat capacity $C_p(T_c) \rightarrow \infty$,
- a finite change in volume $V = \left(\frac{\partial G}{\partial P}\right)_T$ and entropy $S = \left(\frac{\partial G}{\partial T}\right)_P$,
- and thermal hysteresis.

2nd Order

A second-order transition is a continuous transition characterized by a discontinuity in the second derivative of the free energy. Like in the case of a first-order transition, there is no anticipation of the transition. Unlike a first-order transition, it involves neither latent heat nor hysteresis. The defining characteristic are:

- a continuous increase in the order parameter $Q = \sqrt{\frac{a}{b}(T_c - T)}$,
- absence of latent heat or thermal hysteresis,
- a triangular discontinuity of the heat capacity around T_C ,

$$C_P = T \left(\frac{\partial^2 G}{\partial T^2} \right)_P = \begin{cases} 0 & \text{if } T > T_c \\ \frac{a^2}{2b} T & \text{if } T < T_c \end{cases} \quad (\text{D.9})$$

λ transition

Another type of phase transition frequently observed experimentally is the so-called λ transition. Entropy, volume and free energy remain constant (like in a second-order transition); however, λ transition produce infinite change in the second derivatives, C_P (like in a first-order transition). There is, in this case, a transition anticipation which leads to the λ shape observed. It is therefore difficult to distinguish between a first order transition and a λ -shaped continuous phase transition. In such cases, hysteresis is a useful tool to help distinguish a first and continuous phase transition.

D.4 Calorimetry

This section is devoted to the description of calorimetric techniques used to measure heat capacity of solids: AC calorimetry & DC relaxation calorimetry. Using the thermal conductance of the thermal link, K , we can express the thermal power $P(t)$ as the heat transferred from the thermal bath:

$$\begin{aligned} P(t) &= \frac{dQ}{dt} = T_s \frac{dS}{dt} = K(T_b - T_s) + P_{app} \\ T_s \left(\frac{dS}{dT} \right)_H \frac{dT_s}{dt} + T_s \left(\frac{dS}{dH} \right)_T \frac{dH}{dt} &= K(T_b - T_s) + P_{app} \\ C_s \frac{dT_s}{dt} + T_s \left(\frac{dS}{dH} \right)_T \frac{dH}{dt} &= K(T_b - T_s) + P_{app} \end{aligned} \quad (\text{D.10})$$

where T_s is the sample temperature, T_b is the bath temperature, K is the thermal conductance of the bath, and P_{app} is the applied AC or DC power. This equation can be solved to describe the temperature dependence of the sample's heat capacity.

DC Calorimetry

As with other techniques for measuring heat capacity, the Quantum Design Heat Capacity option controls the heat added to and removed from a sample, $P(t)dt$, while monitoring the resulting change in temperature ΔT . During the heating period, a known amount of heat is applied at constant power for a fixed time, t , which is followed by a cooling period of the same duration with relaxation time τ . Assuming constant field, the power equation D.10 becomes:

$$\begin{aligned}
 C_s \frac{dT_s}{dt} &= -K(T_s - T_b) + P_{dc} \\
 \frac{dT_s}{dt} &= -\frac{K}{C_s}(T_s - T_b - \frac{P_{dc}}{K}) \\
 \frac{d\left(T_s - T_b - \frac{P_{dc}}{K}\right)}{T_s - T_b - \frac{P_{dc}}{K}} &= -\frac{K}{C_s}dt \\
 \ln\left(T_s - T_b - \frac{P_{dc}}{K}\right) &= -\frac{K}{C_s}t + A \\
 T_s(t) - T_b &= \Delta T e^{-t/\tau}
 \end{aligned} \tag{D.11}$$

Therefore, the sample heat capacity can be calculated by measuring the relaxation time constant and the thermal link to the bath:

$$C_s(T) = K\tau = \frac{P(t)}{\Delta T} \tau \tag{D.12}$$

To experimentally measure C_P , a heater and thermometer are attached to the bottom side of the sample platform. Small wires provide the electrical connection to the heater and thermometer and also provide the thermal connection and structural support for the platform. The sample is mounted to the platform by using a thin layer of grease, which provides the required thermal contact to the platform.

The relaxation technique is performed at a low, constant pressure of less than 1 mTorr. A turbo pump provides a sufficient vacuum so that the thermal conductance between the sample platform and the thermal bath (puck) is totally dominated by the conductance of the wires. This gives a reproducible heat link to the bath with a corresponding time constant that is large enough to allow both the platform and sample to achieve sufficient thermal equilibrium during the measurement.

This option accomodate samples approximately 1 to 200 mg. Given the thermal characteristics of the calorimeter, this range of masses produces, for most solids, varying relaxation time constants that may be a fraction of a second at 1.9 K or many minutes at 300 K. A single heat capacity measurement can require nearly 10-time constants for the settling time that occurs between measurements. Measuring very large samples can thus be

prohibitively time consuming. The addenda heat capacity, however, limits the size of the smallest samples. Measurement accuracy, which is generally a percentage of the total heat capacity, is sacrificed when the sample heat capacity is small compared to the addenda heat capacity. However, relaxation techniques are traditionally used at temperatures that are below approximately 100 K, because relaxation times are relatively short below 100 K.

AC Calorimetry

AC calorimetry consists of generating an oscillating power $P_{app}(t)$ with frequency 2ω that heats the sample of heat capacity C_s . The measured temperature oscillates with the same frequency but develops a phase shift ϕ with respect to the power due to the finite thermal resistance between sample and thermal bath. The equation describing the applied power:

$$\begin{aligned} P_{app}(t) &= RI^2(t) = RI_0^2 \sin^2(\omega t) \\ &= \frac{RI_0^2}{2} (1 - \cos(2\omega t)) \\ &= P_{ac} (1 - \cos(2\omega t)) \end{aligned} \tag{D.13}$$

can be inserted into [D.10](#) and the differential equation can be solved to yield a complex temperature $T_s = T_b + T_{dc} + T_{ac}$ with:

$$\begin{aligned} T_{dc} &= \frac{P_{ac} - T_b \left(\frac{\partial S}{\partial H} \right)_T \frac{dH}{dt}}{K + \left(\frac{\partial S}{\partial H} \right)_T \frac{dH}{dt}} \\ T_{ac} &= \frac{P_{ac}}{K + \left(\frac{\partial S}{\partial H} \right)_T \frac{dH}{dt} + i2\omega C_s} \\ \tan \phi &= -2\omega \frac{C_s}{K} + \left(\frac{\partial S}{\partial H} \right)_T \frac{dH}{dt} \\ |T_{ac}| &= \frac{P_{ac}}{\sqrt{\left[K + \left(\frac{\partial S}{\partial H} \right)_T \frac{dH}{dt} \right]^2 + (2\omega C_s)^2}} \end{aligned} \tag{D.14}$$

Under a constant applied field, the sweeping rate $dH/dt = 0$, and equation D.14 simplifies to:

$$\begin{aligned}
 T_{dc} &= \frac{P_{ac}}{K} = \frac{RI_o^2}{2K} \\
 T_{ac} &= \frac{P_{ac}}{K + i2\omega C_s} \\
 \tan \phi &= -\frac{2\omega C_s}{K} \\
 |T_{ac}| &= \frac{P_{ac}}{2\omega C_s} \left[1 + \left(\frac{K}{2\omega C_s} \right)^2 \right]^{-1/2} \\
 &= \frac{P_{ac}}{2\omega C_s} |\sin \phi|
 \end{aligned} \tag{D.15}$$

The modulation method requires either a heat loss by conduction to the thermal bath or by radiative cooling toward the shield. As a consequence, AC calorimetry can never operate under adiabatic conditions and there always exists a heat flow from the sample to the thermal bath. If the frequency is chosen such that $K \ll \omega C_s$, the heat loss to the surroundings can be neglected in the calculation of heat capacity:

$$\begin{aligned}
 C_s &\simeq \frac{RI_o^2}{4\omega |T_{ac}|} \\
 \phi &\simeq -\pi/2
 \end{aligned} \tag{D.16}$$

These are the usual working conditions of a traditional AC calorimeter and in this case, the system works under quasiadiabatic conditions. For all other cases, heat losses and phase shifts between input power and sample temperature must be taken into account using the full formula.

These AC temperature oscillations T_{ac} are superimposed on an DC temperature increase T_{dc} which is used when plotting $C_s(T)$. The overall temperature is measured using six thermocouples connected in series which have negligible heat capacity and follow the instantaneous temperature of the sample. The signal from the thermocouples is measured by a lock-in amplifier, therefore the amplitude and phase are detected simultaneously. These values, together with an independently measured heater power, are used to calculate the heat capacity.

This option requires samples with a flat face $\sim 100 \times 100 \times 50 \text{ m}\mu$. Using bigger samples may cause systematic errors due to inhomogeneous temperature distribution in the sample. In order to provide good thermal contact with the micron-thick, free-standing silicon nitride membrane, it is recommended to use small amount of Apiezon N grease. This method is both fast and capable of resolving details that would be very difficult if not impossible to see using other methods such as relaxation calorimetry.

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