Investigation Of Magnetic Ground State of Cu_2IrO_3

Piyush Sakrikar

A dissertation submitted for the partial fulfilment of BS-MS dual degree in Science

Supervised by

Dr. Yogesh Singh

May 2020

Certificate of Examination

This is to certify that the dissertation titled "Investigation Of Magnetic Ground State of Cu_2IrO_3 " submitted by Piyush Sakrikar (Reg.No. MS15096) for the partial fulfillment of BS-MS dual degree programme of the Institute, has been examined by the thesis committee duly appointed by the Institute. The committee finds the work done by the candidate satisfactory and recommends that the report be accepted.

Dr. Goutam Sheet Dr. Sanjeev Kumar Dr. Yogesh Singh

(Supervisor)

Dated:

Declaration

The work presented in this dissertation has been carried out by me under the guidance of Dr. Yogesh Singh at the Indian Institute of Science Education and Research Mohali.

This work has not been submitted in part or in full for a degree, a diploma, or a fellowship to any other university or institute. Whenever contributions of others are involved, every effort is made to indicate this clearly, with due acknowledgement of collaborative research and discussions. This thesis is a bonafide record of original work done by me and all sources listed within have been detailed in the bibliography.

Piyush Sakrikar

(Candidate)

Dated: May 4, 2020

In my capacity as the supervisor of the candidate's project work, I certify that the above statements by the candidate are true to the best of my knowledge.

Dr. Yogesh Singh

(Supervisor)

Acknowledgements

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I would like to acknowledge the XRD facility and the SEM facility of IISER Mohali.

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Last but not the least, I must express my very profound gratitude to my parents and to my sister for providing me with unfailing support and continuous encouragement throughout my years of study and writing this thesis. This accomplishment would not have been possible without them. Thank you.

Piyush Sakrikar

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Abstract

There are conflicting reports in the literature regarding the magnetic ground state of the frustrated Kitaev material Cu_2IrO_3. While one group reported spin-glass (SG) features in susceptibility measurements[1], another group showed an absence of SG and only spin liquid behavior[2]. In this thesis we aim to understand the influence of synthesis conditions on the magnetic ground state of Cu_2IrO_3 with the eventual aim to be able to establish a recipe for synthesizing Cu_2IrO_3 hosting the quantum spin liquid state. Towards this goal, we have synthesized polycrystalline samples of Cu_2IrO_3 with different synthesis conditions and studied their structural and magnetic properties. We also synthesized the non-magnetic isostructural material $Cu[Li_{1/3}Sn_{1/3}]O_2$ with an aim to extract the magnetic contribution to the heat capacity of Cu_2IrO_3 and to check for it's proximity to Kitaev's QSL.

Contents

1 General Introduction

Quantum spin liquid (QSL) is an elusive state of matter formed by an ensemble of interacting spins[3]. It can be intuitively pictured as fluctuating sea of spins, which does not order even at zero temperature. The peculiar thing about this state is that it has non-magnetic ground state even though the system is made up of strongly interacting local magnetic moments.
The possibility of QSL material has been greatly sought after in Condensed matter community. The resonant valence bond theory by Phil Anderson led to exploration of QSLs in more than one dimension and prediction of an exotic form of superconductivity[4]. A new direction in search of QSLs came with Kitaev's exactly solved model of spins S = 1/2 on a honeycomb lattice interacting with bond-directional exchange[5]. The exact ground state of the Kitaev model was shown to be a QSL.
Researchers are now seeking QSL state in honeycomb lattice showing mott insulating behaviour. Search for an experimental realization has led to the discovery of several candidate materials like $\mathrm{Li_2IrO_3}$, $\mathrm{Na_2IrO_3}$, and recently Cu_2IrO_3.

1.1 Kitaev Model

Alexei Kitaev[5] wrote down and exactly solved the following Hamiltonian for spins S = 1/2 on a honeycomb lattice, interacting with a bond dependent Ising exchange interaction K_γ,

$$H_{ij} = \sum_{\gamma} K_\gamma S_i^\gamma S_j^\gamma \tag{1}$$

Here index γ = x-type, y-type, or z-type bond that are at 120° on the honeycomb lattice, as shown in figure 1.1. The Hamiltonian is of the form of a 2-spin nearest-neighbor interaction. This model exhibits strong exchange frustration arising from bond directional interactions. The exact solution of Kitaev model has QSL ground state and predicts exotic Majorana fermions as the excitation particle.

Jackeli and Khaliullin[6] gave the recipe of realizing dominant Kitaev interaction in the actual material. They showed that in certain transition metal compounds, where the ions are in a d^5 electronic configuration and have strong Spin

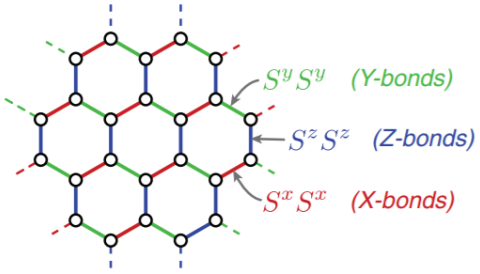


Figure 1.1: (from [7])The X-, Y-, and Z- bonds in Kitaev Model.

Orbit Coupling (SOC), the model is applicable. The materials should contain Ir^{4+} ($5d^5$) and Ru^{3+} ($4d^5$) and be honeycomb layered mott insulator.

1.1.1 Identification of Kitaev QSL

The definition or at least a negative one for QSL is an absence of ordering even at T = 0 K. The Kitaev candidates like $\mathrm{Li_2IrO_3}$, $\mathrm{Na_2IrO_3}$ ..etc are magnetically ordered or freeze into a spin-glass state at low temperature scale, and hence we call them candidate material. Identification of QSL is challenging so multiple tools are used in reaching a conclusion.

- Magnetic Measurement: At high temperature the magnetic susceptibility follows Curies-Weiss form $\chi = \frac{C}{T-\theta_{CW}}$, where C is the Curie constant. The Curie-Weiss temperature θ_{CW} gives an estimate of the strength of magnetic ordering. Let T_c denote the temperature at which the material freezes or order then Frustration parameter is given by

$$f = \frac{|\theta_{CW}|}{T_c} \tag{2}$$

  the larger the parameter f the stronger the suppression of ordering.

- Thermodynamic Measurement: From the specific heat data at low temperature information regarding the nature of excitation (localized or itinerant) and power law dependence of density of state thus, the dispersion law can be obtained.

- Spectroscopic Tools: To show absence of static moments in the materials, nuclear magnetic resonance (NMR) and/or muon spin resonance probes may be used. Inelastic neutron scattering experiment have advantage of probing excited state beyond low-temperature regime of thermodynamic measurement.

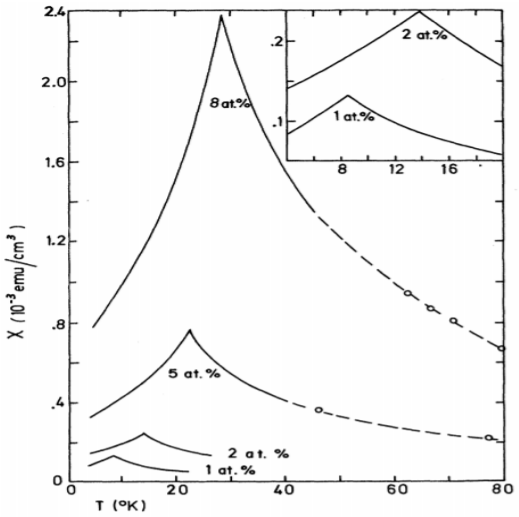
1.2 Spin Glass

Spin Glass represents the class of materials exhibiting the frozen state transition. Below a certain freezing temperature T_f the system orients such that $< S_i >$ = 0 and is neither ferro- nor anti-ferromagnetic. Physically this can be pictured as: for T$\longrightarrow T_f$ random anisotropy takes hold and preferred orientations are established throughout the crystal. Below T_f many randomly small cluster of rigidly frozen spins are generated with random freezing direction.
For this to happen in a system there must be randomness in either position of the spins, or the signs of the neighbouring couplings[8]. This ensures that the magnetic transition is not the standard long-ranged ordering ferromagnetic or anti ferromagnetic type. The combination of the randomness with the competing or mixed interactions causes frustration.
Interesting experimental manifestations of conventional spin glasses include:

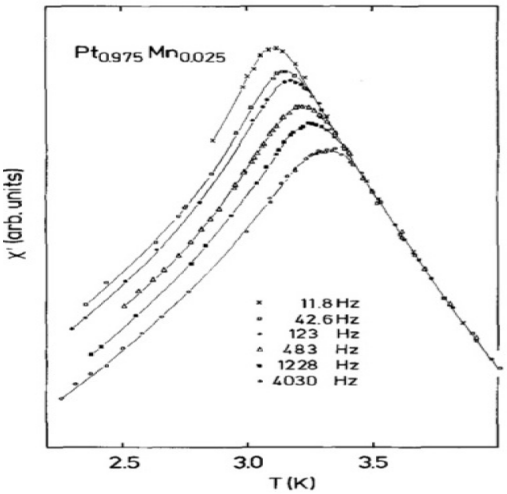
1. A peak in the static zero-field-cooled susceptibility in the small-field limit at a critical temperature T_f (1.2a).

2. The temperature-shifts in the positions of peaks in the a.c. susceptibility, higher frequencies showing peaking at higher temperatures(1.2b).

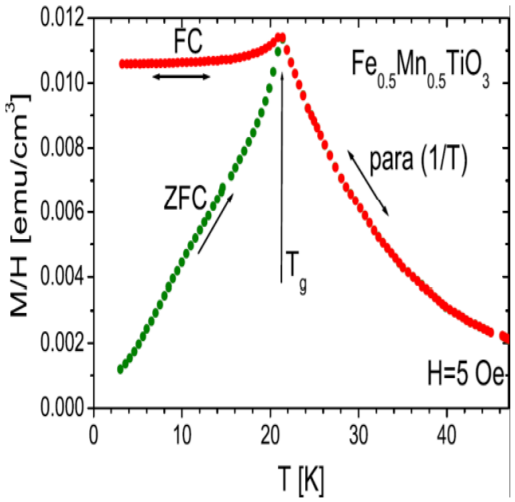
3. A non-ergodic behavior beneath T_f this is shown by the onset of differences between field-cooled (FC) and zero-field-cooled (ZFC) susceptibilities(1.2c).



(a) (from [9]) Low field susceptibility of AuFe alloy at different dilutions.



(b) (from [10])Frequency-dependent a.c susceptibilities of PtMn.



(c) (from [11])Magnetization divided by the applied field, as a function of temperature, measured along the usual ZFC-FC procedures for $Fe_{0.5}Mn_{0.5}TiO_3$.

Figure 1.2: Experimental signatures of spin glass.

2 Material And Method

The solid-state reaction method was used to synthesize all the polycrystalline samples. Ions in solids are not mobile at low temperatures. For diffusion of the components, the mixture requires was heated to high temperature scale. We took the following precautions and steps for the reactions:

- To ensure proper mixing reactants were thoroughly mixed in agate mortar and pestle for approximately 30 min. Depending on reactivity of materials, this was done either in argon-filled glovebox or in air.
- To make a hard pellet of the mixture 5 bar pressure was used. This was done in 25-ton hydraulic press by Kimaya engineers.

For the synthesis of all materials, high-purity (99.99 %) starting materials (Alfa Aesar) was used. And for the heat treatment of different samples, high-temperature box furnace, manufactured by Nabertherm, Germany was used.

2.1 Preparation

2.1.1 Synthesis of Na_2IrO_3

To make Na_2IrO_3 polycrystalline sample we take Na_2CO_3 and Ir / IrO_2 in 1.05:1 mole ratio, mix thoroughly. We put the mixture in alumina crucible with lid and heat to 750C in 4 hrs and leave for 16 hrs to remove CO_2. After which we grind the powder and pelletize the mixture. Then put it in a crucible with lid and heat to 900 in 6 hrs and leave for 16hrs. This annealing step was repeated at 950°C, and 1000°C.

2.1.2 Synthesis of SG Na_2IrO_3

To get a structurally disordered state that gives a spin-glass magnetic ground state. We give the heat treatment at 750° to remove CO_2 from Na_2CO_3 same as above. But then we take the pellet straight to 1050C in 6 hrs and stay for 24 hrs.

2.1.3 Synthesis of Cu_2IrO_3

The ion exchange was performed by mixing $\mathrm{Na_2IrO_3}$ and CuCl in the mole ratio 1:2.05[1]. The mixture with total mass 350 mg was pelletized, place in alumina crucible and sealed under vacuum in quartz tube. The tube was heated at 1° C/min to 350° C , kept at that temperature for 16 h and then cooled to room temperature at same rate. Then the sample was grounded into fine powder and washed five times with ammonium hydroxide (NH_4OH) and twice with distilled water. After being washed, all samples were dried at room temperature under vacuum for 2 h.

2.2 Powder X-Ray Diffraction (XRD)

The structural information of the prepared polycrystalline samples were inferred by XRD data. This was performed on the Rigaku Ultima IV fully automatic high-resolution X-ray diffractometer system at the X-ray Facility of IISER Mohali. Copper was the target material with Cu-Kα wavelength of 1.5418$\mathring{A}$.
The XRD spectral data was recorded as peaks intensity as a function of 2θ from 5° to 90° in steps of 0.02°. Then Rietvield refinement was carried out using FullProf Suite software. Using which lattice cell parameter, atomic coordinates , space group geometry etc were calculated for the sample.

2.3 Energy-dispersive X-ray spectroscopy (EDX)

EDX is an analytical technique used to determine which chemical elements are present in a sample and to estimate their relative abundance. A high energy beam of electrons focused on the sample, strikes electrons in the inner shell of the atoms and creates a hole. An electron from outer shell fills this hole and in this process releases energy in form of X-rays.
The Cliff-Lorime sensitivity factor between elements A and B is denoted by k_{AB} and this factor signifies the relative efficiency of production and detection of the X-rays. This factor is experimentally calibrated with a standard containing a known ratio of the two elements. The quality of EDS analyses depends significantly on the accuracy of the k_{AB} values. For lighter elements k_{AB} values are less accurate

and this one of the drawbacks of EDX. Also, oxygen's abundance is not accurately computed as a complete vacuum environment is not possible for the sample.

2.4 Magnetization Measurement

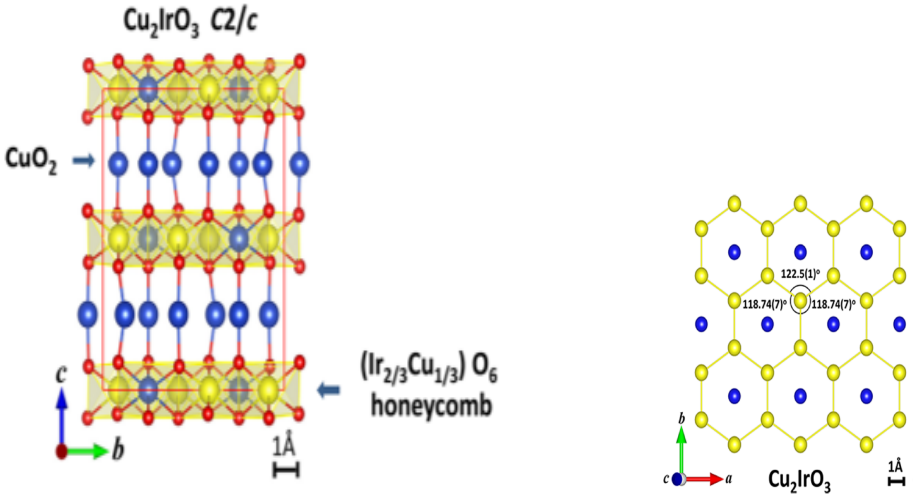
The bulk measurements were carried out using commercial Quantum Design physical property measurement system (QD-PPMS). This PPMS is equipped with a 9 T magnet and can measure magnetization with a temperature range between 1.8 and 400 K. It is an Evercool II system, which features an integrated cryocooler-Dewar system that re-condenses and liquefies gaseous helium directly within the EverCool II Dewar. The PPMS probes can be changed to take different physical property measurements like AC susceptibility, DC susceptibility, heat capacity etc .

3 Effect of Stoichiometry and Temperature Profile On Cu_2IrO_3

3.1 Introduction

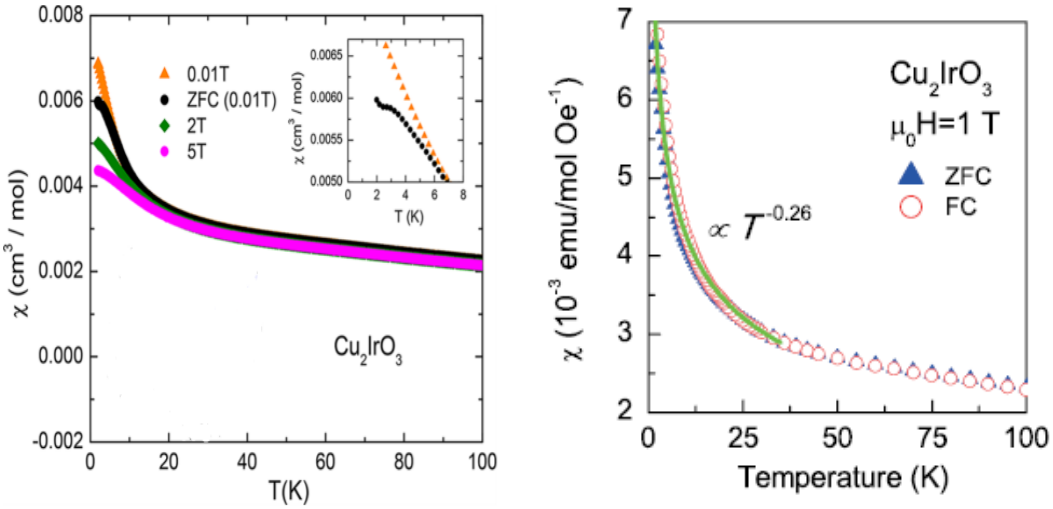
Alkali honeycomb iridate Li_2IrO_3 and Na_2IrO_3 [12, 13] that have been intensely studied in last decade. Both materials, however show antiferromagnetic order at low temperatures and hence are not Kitaev QSLs. This AFM order was explained as a result of two competing interactions on the honeycomb lattice Kitaev FM interaction and the conventional Heisenberg AFM interaction[14]. The relative magnitude of the two terms tunes magnetism from quantum spin liquid state to an AFM order.

Due to the large ionic radii of K, Rb, and Cs, another alkali honeycomb iridate was not produced. But a breakthrough came few year ago when honeycomb iridate was made with a transition metal Cu by David and Fazel[1]. The magnetic ordering was replaced by a spin-glass state below 3 K. This suggests proximity to the Kitaev limit.



(a) **(b)**

Figure 3.1: (from [1]) (a) The structure of Cu_2IrO_3 consists of edge-sharing $(Ir_{2/3}Cu_{1/3})O_6$ octahedra in honeycomb layers and copper dumbbells between the layers. (b) The honeycomb lattice of edge sharing octahedra viewed from top.



(a) (from [1])Spin Glassy behavior **(b)** (from [2])AFM behavior

Figure 3.2: Contrasting magnetic behavior for Cu_2IrO_3

Figure 3.1a presents the crystal structure of $\mathrm{Cu_2IrO_3}$ (C2/ c space group), in which the honeycomb layers are stacked by CuO_2 dumbbells, distinct from CuO_6 octahedra within the honeycomb layers. The interlayer dumbbell structure arises from the eclipsed stacking of adjacent layers that align the oxygen and interlayer copper atoms in a line.

This structural alteration leads to an elongation of the c axis and closeness of the Ir-Ir-Ir bond angles to the ideal 120°, as shown in Figure 3.1b . The elongation of c axis with little difference in the monoclinic angles means Cu_2IrO_3 has larger interlayer spacing ($d = \frac{c}{2} \sin \beta$) compared to its predecessor Na_2IrO_3.

Although magnetically frustrated Cu_2IrO_3 has been studied extensively over the years, but the nature of its ground state is still ambiguous. David and Fazel[1] reported a spin glass transition with short-range correlations below 3k as shown in Figure 3.2a. While our group[1] reported absence of such glassy behavior as apparent in 3.2b.

3.2 Sample Preparation

We hypothesize that occurrence of this glassy behavior is due to disorder in the material and can in principle, be decreased or tuned by optimizing the synthesis process. So we have synthesized the compound with different temperature treatments to study the effect on the structure and magnetic properties of $\mathrm{Cu_2IrO_3}$.

3.2.1 Stoichiometric Sample

We prepared **Sample 1** with the same procedure as 2.1.3, only took $\mathrm{Na_2IrO_3}$ and CuCl in the nearly Stoichiometric mole ratio 1:2.2 and annealed at a temperature of 320° C.

3.2.2 Off-Stoichiometric Sample

For off-stiochiometric samples the mole ratio of $\mathrm{Na_2IrO_3}$ and CuCl was taken to be 1:3. The two materials made using this Stoichiometric are **Sample 2** and **Sample 3** which were annealed at a temperature of 350° C and 320° C respectively.

3.3 Results

3.3.1 Powder XRD

Refined parameter	Sample 1	Sample 2	Sample 3
a	5.379364	5.383019	5.392732
b	9.345991	9.334531	9.331887
c	11.521887	11.504005	11.510029
β	99.0962	98.588501	98.573891

Table 1: A table with the cell parameter for the three samples.

We performed Rietveld refinement on PXRD pattern using FullProf suite software. Peak shapes were modeled using Pseudo-Voight profile, B_{iso} and occupation number were not refined. The CIF file of $\mathrm{Cu_2IrO_3}$ was taken from Ref[1].
There are some secondary phase peaks for sample 2, as apparent from Figure 3.3.

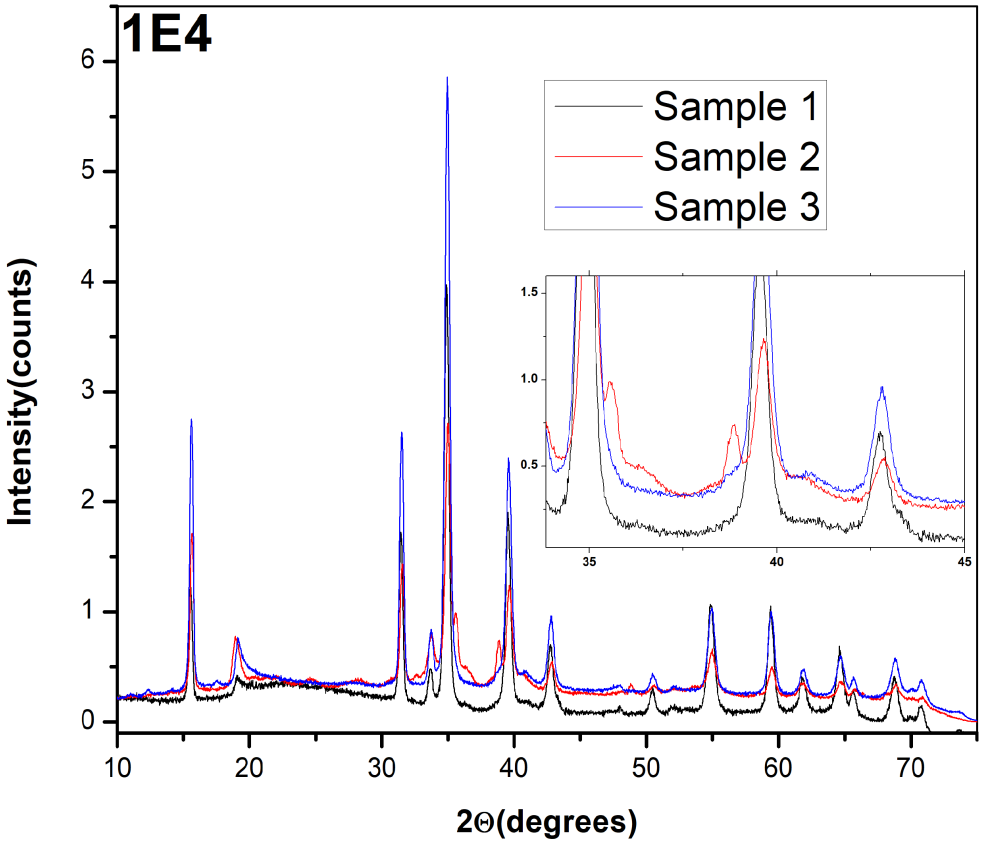


Figure 3.3: Room temperature powder X-ray pattern for the three Cu_2IrO_3.Inset shows magnified peaks in the range of 35-45 degree.

The results of the refined parameter are shown in Table 1. From which we infer that the structure change from our synthesis profile is minimum.

3.3.2 EDS

Electron dispersive X-ray(EDX) measurements were performed at 30keV energy The atomic ratio's of samples measured are presented in Table 2. Sample 1 is either Ir deficient or small amounts of CuCl are left unwashed, and thus the ratio is larger than the ideal. The sample 3 value shows only small divergence. While the atomic value for sample 2 shows a huge deviation from ideal ratio. This along with the secondary phase peaks in X-ray patterns in Figure 3.3, shows that 350° C is not a suitable temperature to synthesize Cu_2IrO_3. This temperature leads to

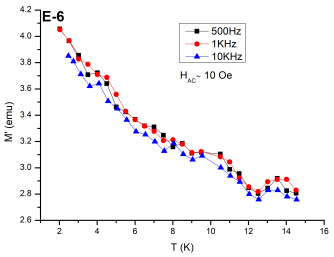
impurity phases as seen from x-ray, and leads to loss of CuCl as seen in EDS.

	Ideal	Sample 1	Sample 2	Sample 3
Copper	2	2.47	1.62	2.04
Iridium	1	1	1	1

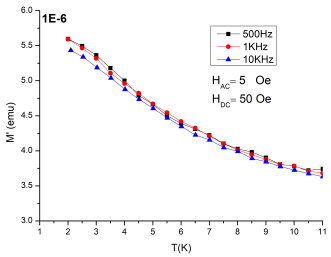
Table 2: The atomic ratio of elements from EDS of the samples.

3.3.3 Magnetization Measurement

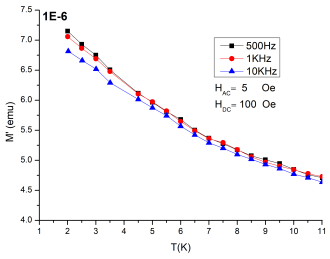
Temperature dependent AC magnetization results are plotted in Figure 3.4. None of the three samples show a sharp cusp that varies with frequency. This indicates an absence of the spin glass state, so we conclude that the spin glass behavior is not originating from stoichiometry of CuCl or the temperature of synthesis.



(a) Sample 1



(b) Sample 2



(c) Sample 3

Figure 3.4: AC Magnetization measurement plotted as a function of Temperature for the three Cu_2IrO_3 samples.

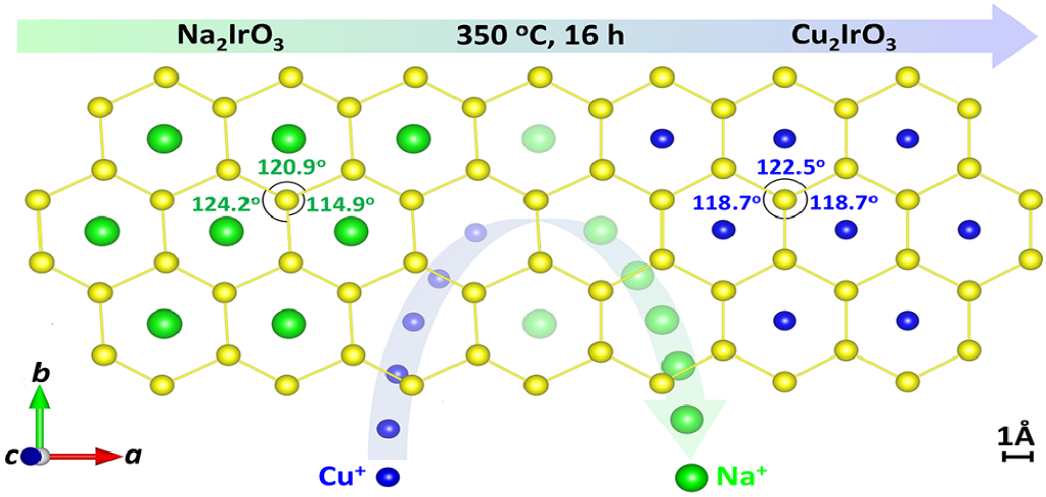


Figure 3.5: Topotaction reaction where sodium is replaced by copper under mild conditions.

3.4 Future Work

Our hypothesis that stoichiometry of CuCl or the temperature of synthesis play an important role in spin glass transition of Cu_2IrO_3 turns out to be wrong. Thus the question: When does Cu_2IrO_3 show SG behavior? Remains open at the moment.

Since this synthesis process is an ion exchange method between the Na and Cu ions, as shown in figure 3.5. It would be natural to now hypothesize that the SG behavior is originating from parent compound Na_2IrO_3 and passing onto Cu_2IrO_3.

To test this hypothesis, we need to prepare a Na_2IrO_3 showing spin glass ground state. To get structurally disorder Na_2IrO_3 state we use procedure mentioned in Section 2.1.2. The magnetization for this structurally disordered Na_2IrO_3 is shown in Figure 3.6 and shows an anomaly around 5 K, and a small bifurcation below the peak temperature. This demonstrates that we have succeeded in producing Na_2IrO_3 having a SG ground state. The next step is to synthesize Cu_2IrO_3 using this Na_2IrO_3 and check for the SG state in Cu_2IrO_3.

Using this Cu_2IrO_3 was made with the standard procedure as in section 2.1.3. The measurement could not be carried out, and thus this is still work in progress!

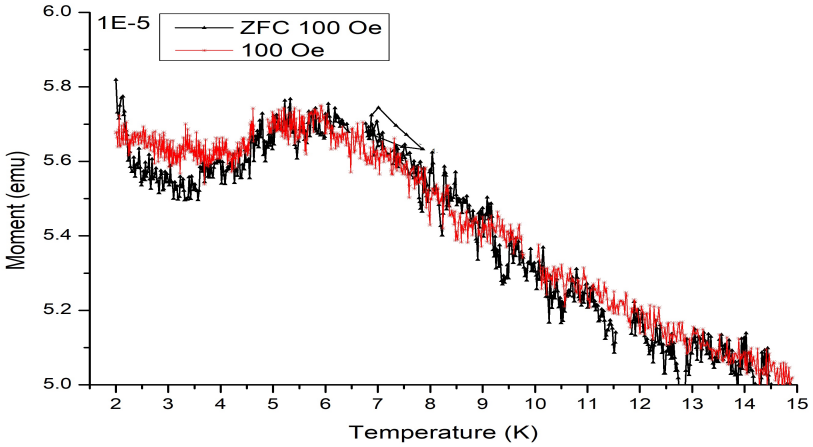


Figure 3.6: (from [1])Small spitting between Zero Field Cooling and Field Cooling magnetization below 5 K.

4 Magnetic Contribution To Heat Capacity In Quantum Spin Liquid Candidate Cu_2IrO_3

4.1 Introduction

The exact solution of the Kitaev model is provided by representing S = 1/2 spins by two types of Majorana fermions: localized and itinerant. Recently the thermal excitation from these two kinds of fermions was predicted to manifest as two peaks in graph of specific heat C dependence on temperature T[15]. A half of the entropy would be released successively in each peak. And so magnetic entropy S_{mag} would show half plateau between two peak and the value of S_{mag} at the plateau would be $\frac{1}{2}Rln(2)$.

The heat capacity $C = C_M + C_L + C_E$ where C_L is the lattice contribution and C_E is the electronic contribution, which for Mott insulator is zero, while C_M is the magnetic term that we are interested in. To isolate the contribution to heat capacity from magnetic excitations, namely, magnons or spinons, we need to subtract the lattice (phonons) contribution from the total heat capacity.
For this we synthesis a nonmagnetic honeycomb delafossites $\mathrm{Cu[Li_{1/3}Sn_{1/3}]O_2}$ in the following manner[16]:

4.2 Sample Preparation

4.2.1 Synthesis of $\mathrm{Li[Li_{1/3}Sn_{1/3}]O_2}$

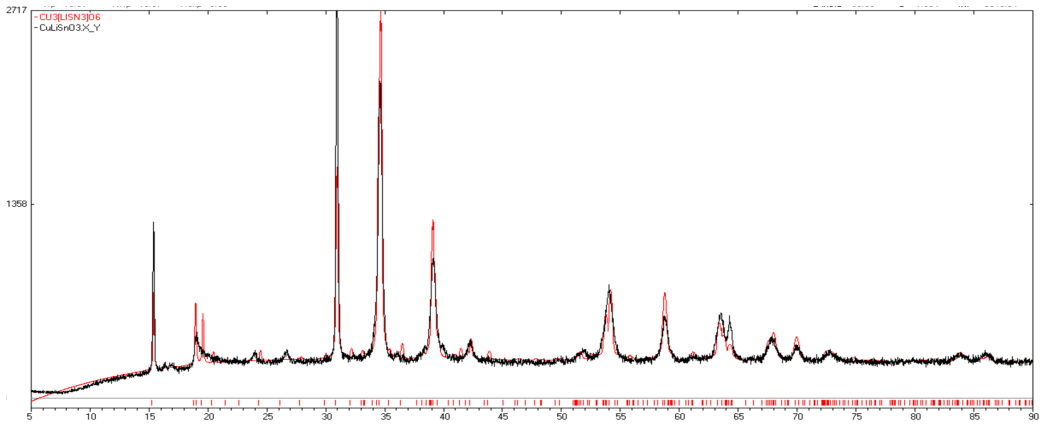
A stoichiometric mixture of Li_2CO_3 and SnO_2 was mixed in mortar and pestle in glovebox and placed into a covered alumina crucible. The crucible was then heated at 5° C/min to 740° C, kept at 740° C for 20 h, then cooled at 10° C/min to 300° C, and quenched into the antechamber of the argon glovebox. Successively annealing steps were performed for 20 h in 50° C steps up to 1000° C to reduce the amount of stacking disorder in the crystal structure. At each step 5% Li_2CO_3 was added to compensate for the volatility of lithium at high temperatures.

4.2.2 Synthesis of $\mathrm{Cu[Li_{1/3}Sn_{1/3}]O_2}$

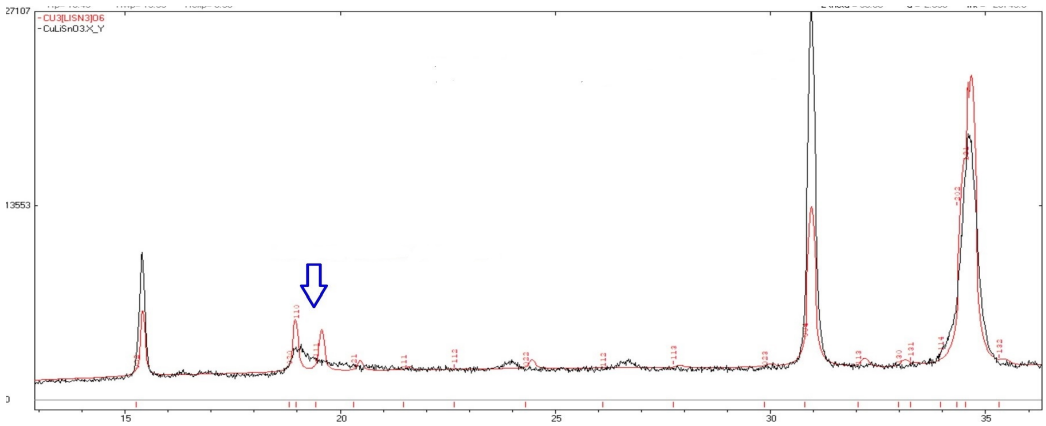
To synthesize this compound, the precursor Li[Li1/3Sn2/3]O2 and CuCl were mixed in the mole ratio 1:2. The mixture with total mass 350 mg was pelletized, place in an alumina crucible and sealed under vacuum in quartz tube. The tubes were heated at 1° C/min to 400° C for 24 h. It was then cooled to room temperature at the same rate. Then the samples was grounded into fine powder and washed five times with ammonium hydroxide (NH_4OH) and twice with distilled water. After being washed, all samples were dried at room temperature under vacuum for 2 h.

4.3 Results And Future Work

The Powder XRD data matches well with the theoretical pattern as shown in Figure 4.1. We plan to use $\mathrm{Cu[Li_{1/3}Sn_{1/3}]O_2}$ to calculate the phononic contribution to heat capacity for $\mathrm{Cu_2IrO_3}$.
For this the correction different molecular masses of $\mathrm{Cu_2IrO_3}$ and non-magnetic sample has to be taken into account. Accordingly, the ratio $r = \theta_D/\theta_D^{'}$ is determined where θ_D and $\theta_D^{'}$ are the Debye temperature for $\mathrm{Cu[Li_{1/3}Sn_{1/3}]O_2}$ and $\mathrm{Cu_2IrO_3}$ respectively. In a simple harmonic oscillator model debye temperature is inversely proportional to the square root of the mass, one can get a first estimate by using the molecular weights.
With this approximation of the Debye model, the lattice contribution of $\mathrm{Cu_2IrO_3}$ can be calculated by multiplying the temperature values of the total specific heat data C(T) of $\mathrm{Cu[Li_{1/3}Sn_{1/3}]O_2}$ by the factor r.
The heat capacity measurements of the materials as well as the estimation of the magnetic entropy will be carried out in the future.



(a)



(b)

Figure 4.1: Comparison of powder X-ray diffraction data for $\mathrm{Cu[Li_{1/3}Sn_{1/3}]O_2}$ sample (black) with the theoretical pattern(red). The blue arrow in the magnified image of the same marks the position of the stacking disorder common in all delafossites material.

5 Summary

In this thesis, we have investigated the magnetic ground state of Cu_2IrO_3. For this, the thesis is divided into two project- inducing spin glass transition and thermodynamic signature of quantum spin liquid in Cu_2IrO_3.

In the first we have attempted to find out what conditions lead to spin glass behavior in Cu_2IrO_3. We have concluded that neither the stoichiometry of CuCl nor the temperature of synthesis effect the ground state. We are thus able to give a recipe to synthesize Cu_2IrO_3 free of the SG state and confirm that it displays only QSL properties.

The glassy state in Cu_2IrO_3 may be passed by the parent compound Na_2IrO_3. This hypothesis is based on the fact that synthesis of Cu_2IrO_3 is an ion exchange method from Na_2IrO_3, the structure, and lattice essentially remains the same. To test the latter hypothesis, we have synthesized a structurally disordered Na_2IrO_3 and confirmed that it displays a SG below 5K. In the future, we will measure the magnetic properties of Cu_2IrO_3 synthesized from this structurally disordered Na_2IrO_3 to look for the SG state.

To measure the proximity of Cu_2IrO_3 to quantum spin liquid via specific heat measurement. Theoretically, there should be a distinct shoulder in magnetic entropy between two heat capacity peaks, and the value of this entropy should be $\frac{1}{2}Rln2$ between the peaks. This would provide thermodynamic evidence for proximity to Kitaev quantum spin liquid. We have successfully synthesized the nonmagnetic materials $Cu[Li_{1/3}Sn_{1/3}]O_2$. The heat capacity measurements and the estimation of the magnetic entropy will be carried out in the future.

Due to the lockdown imposed by the GOI to tackle the Covid-19 pandemic, the measurement could not be carried out and will be completed in the near future.

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