Magnetism in doped Honeycomb Iridates $Na_2Ir_{1-x}Ru_xO_3$

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

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Certificate of Examination

This is to certify that the dissertation titled “Magnetism in doped Honeycomb Iridate $Na_2Ir_{1-x}Ru_xO_3$ ” submitted by Mr. Narendra Pal Singh (Reg. No. MS09087) for the fulfilment 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.Yogesh Singh Dr.Sanjeev Kumar Dr. Goutam Sheet
(Supervisor)

Dated: 25 April 2014

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.

Narendra Pal Singh
(Candidate)
Dated:25 April 2014

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)

Acknowledgement

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Abstract

A_2IrO_3 materials (A=Na,Li) have recently been shown to harbor novel magnetism and the possibilty of spin liquids. The novel magnetism is thought to stem in part from the spin-orbit coupling present in these Iridates which leads to anisotropic exchange interactions which in turn lead to magnetic frustration as evident from large Weiss temperature compared to a relatively low ordering temperature. The aim of this project is to synthesize single crystals of $Na_2Ir_{1-x}Ru_xO_3$ (x=0.02, 0.05, 0.1, 0.2, 0.3) to study the effect of disorder, reduced spin-orbit coupling, and local moment impurities in the magnetic properties of the parent compound. There are also theoretical predictions that unconventional superconductivity might emerge in these systems if they can be turned metallic.

Chapter 1

Introduction

The study of cooperative phenomena in magnetism has provided a fertile playground for testing theories of interacting systems that possess different spatial dimensions, ranges and sign of interactions, and that exhibit local anisotropy of the basic interacting unit, the magnetic spin. Among the known classes of magnets, spin glasses are among the most fascinating, displaying in their bulk properties simultaneous sharp ordering features in their magnetic response while exhibiting no such anomalies in their thermal response. The microscopic parameters empirically associated with spin glass behavior are site disorder and frustration. Ferromagnets, antiferromagnets and ferrimagnets correspond to both weak frustration and low disorder. High frustration and high disorder are exhibited by spin glass while geometrical frustrated magnets possess a high degree of frustration, while having little or no disorder. In this thesis we study materials which combine geometrical frustration and glassy behavior.

1.1 Spin Glass

In majority of spin glasses, the microscopic conditions of site disorder and frustration go hand-in-hand, namely the process of disordering the lattice leads to frustrated interactions. This can be illustrated in a simpler fashion in figure 1.1 where a plaquette of a host lattice with a two dimensional-

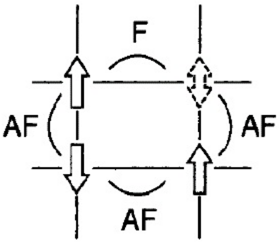


Figure 1.1: Spin Glass Frustration

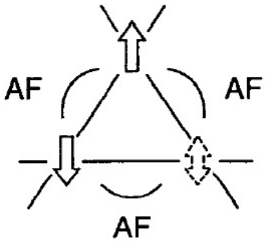


Figure 1.2: Frustrated Glass Magnets

grid of spins with only antiferromagnetic (AF) bonds between the spins is shown. Introduction of randomly spaced ferromagnetic (FM) bonds (like by modifying the exchange interaction by hole doping) leads to frustration that results from competing interaction; the local field at one spin on the plaquette is much smaller than its neighbors.

1.2 Geometrical frustrated Magnets

In the case of Geometrically frustrated Magnets, frustration arises from the structure. Here the lattice itself, represented by the triangular plaquette, possesses a fundamentally different symmetry than the square lattice case (fig 1.2). Because of the spatial symmetry, it is possible to have the same qualitative local condition of frustration for one of the spins on the plaquette, but without having to introduce disorder. In these examples, the ground state is not uniquely defined. For example, there are six lowest energy states for a single triangle.

1.3 Identifying Frustration experimentally

Before we move to how one can identify the frustration, we need to look how spins align as we change the temperature of the material.

1.3.1 Ferromagnetism

Ferromagnetism is the phenomenon of spontaneous magnetization. The best known examples of ferromagnets are the transition metals Fe, Co, and Ni, but other elements and alloys involving transition or rare earth elements also show ferromagnetism.
Ferromagnetism involves the alignment of an appreciable fraction of the molecular magnetic moments in some favorable direction in the crystal. The fact that the phenomenon is restricted to transition and rare earth elements indicates that it is related to the unfilled 3d and 4f shells in these substances. Ferromagnetism appears only below a certain temperature which is known as the ferromagnetic transition temperature or simply the Curie temperature. Above the Curie temperature, the moments are oriented randomly, resulting in a zero net magnetization. In this region the substance is paramagnetic and its susceptibility is given by $\chi = \dfrac{C}{T - T_f}$ which is known as the Curie Weiss law. The constant **C** is called the Curie constant and temperature T_f the Curie temperature. This temperature depends on the substance but its order of magnitude is about 1000K for elemental ferromagnets.

1.3.2 Antiferromagnetism

In antiferromagnetic substances, adjacent magnetic moments point in opposite directions. Thus the moments cancel each other, resulting in zero net magnetization.
As in ferromagnetism, antiferromagnetism also disappears above a certain temperature which is called *Néel temperature* T_N. Above this point the substance is paramagnetic, and the susceptibility is well represented by the

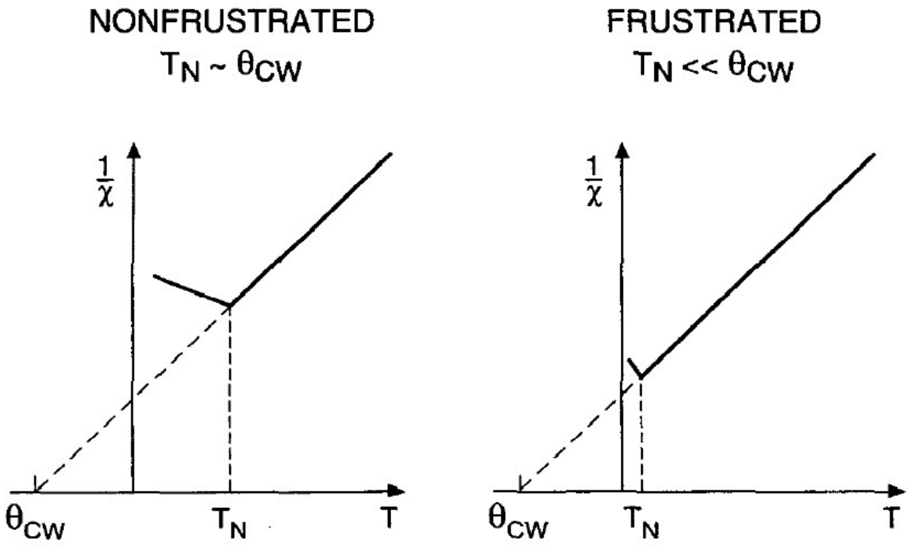


Figure 1.3: Frustration in antiferromagnet

formula $\chi = \dfrac{C}{T + T_N'}$ where C and T_N' are constants depending on the substance. In this case, susceptibility does not diverge at the transition point, unlike the ferromagnetic case.

1.3.3 Experimental method

By fitting $\chi(T)$ in the paramagnetic state to the Curie Weiss law $\chi(T) = \dfrac{C}{T - \theta}$, we can determine the temperature θ at which an antiferromagnet would order if it was not frustrated .

If the material is frustrated then the ordering temperature will be suppressed compared to θ (figure 1.3).The degree of frustration can then be given by the ratio $f = \dfrac{|\theta|}{T_N}$ called the frustration index. Clearly f>1 corresponds to a frustrated systems. For example, for Na_2IrO_3 $f \approx 8$.

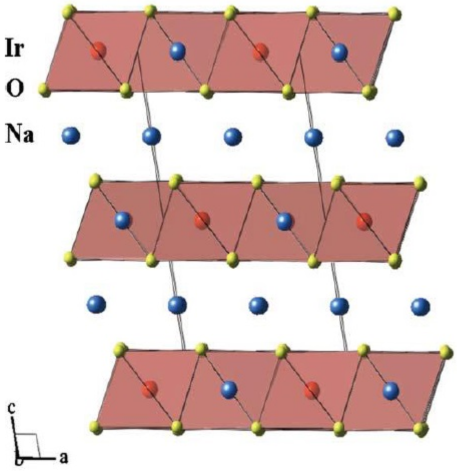


Figure 1.4: The Crystallographic Structure of Na_2IrO_3(view perpendicular to c axis)[Yogesh Singh and P. Gegenwart, Phys. Rev. B **82**, 064412, (2010)]

1.4 Sodium Iridate

1.4.1 Crystal Structure

This structure is made up of layers containing only the Na atoms alternating with $NaIr_2O_6$ layers stacked along the c axis as shown in fig 1.4. Within the $NaIr_2O_6$ layers edge sharing IrO_6 octahedra form a honeycomb lattice as shown in fig 1.5. The Na atoms occupy voids between the IrO_6 octahedra. Within the $NaIr_2O_6$ layers the Ir^{4+} moments sit on the haneycomb lattice.

1.4.2 Magnetic Susceptibility measurement of Na_2IrO_3

The magnetic properties of Na_2IrO_3 have been reported recently[1]. The inverse magnetic susceptibility $\frac{1}{\chi_{pol}} = \frac{H}{M}$ versus T data between 1.8 K to 400 K in an applied magnetic field $H = 2T$ for a collectiion of randomly oriented single crystal of Na_2IrO_3 are shown in fig 1.6. The data between 200K to 400K were fit by the Curie-Weiss expression $\chi = \chi_0 + \frac{C}{T-\theta}$ with χ_0 , C and θ as fitting parameters. This fit is extrapolated to T=0K which

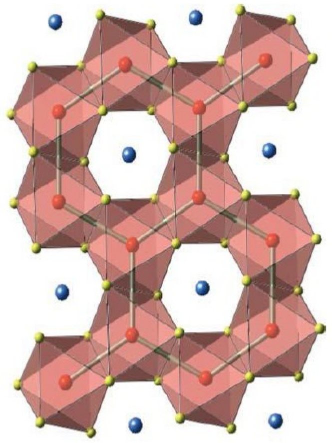


Figure 1.5: The Crystallographic Structure of Na_2IrO_3(view down the c axis to highlight the honeycomb lattice of Ir atoms within the layer)[Yogesh Singh and P. Gegenwart, Phys. Rev. B **82**, 064412, (2010)]

gives $\chi_0 = 3 \times 10^{-5} cm^3/mol$, $C = 0.41 cm^3 K/mol$ and $\theta = -116K$ respectively.This value of C correspond to an effective moment of $\mu_{eff} = 1.81\mu_B$ assuming a g-factor of 2 by the expression $\chi = \dfrac{\mu_0 N \mu_{eff}^2}{3K_B T}$

This value of μ_{eff} is close to the value 1.74 μ_B expected for spin $\dfrac{1}{2}$ moment.

$\chi_{eff} = p\mu_B = g\sqrt{j(j+1)}\mu_B = 2 \times \frac{\sqrt{3}}{2} = \sqrt{3}\mu_B = 1.73\mu_B$

This indicates that the Ir^{+4} moments are in an effective spin $S_{eff} = \dfrac{1}{2}$ state.

The large and negative $\theta = -116K$ further indicates that the strong antiferromagnetic interactions exist between these $S_{eff} = \dfrac{1}{2}$ moments.

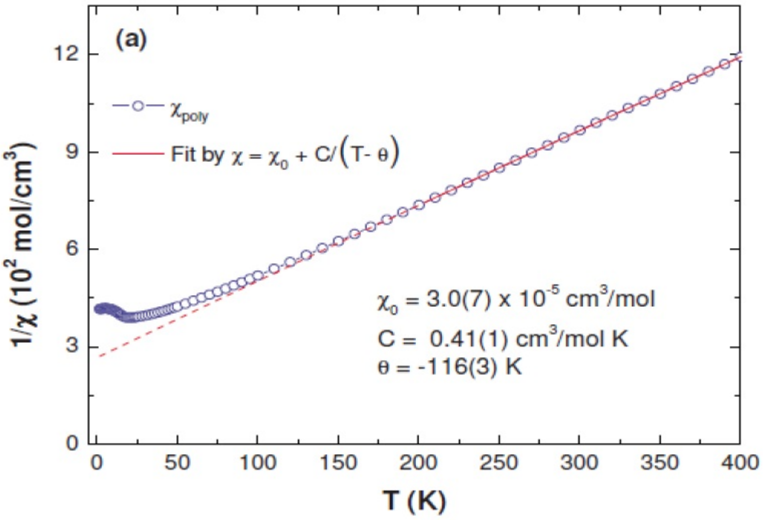


Figure 1.6: Inverse magnetic susceptibility $\frac{1}{\chi_{pol}} = \frac{H}{M}$ versus Temperature T for collection of randomly oriented single crystals of Na_2IrO_3 in a magnetic field of $H = 2T$. The solid curve through the data is fit by the expression $\chi = \chi_0 + \frac{C}{T-\theta}$ and the dashed curve is an extrapolation to $T = 0K$.[Yogesh Singh and P. Gegenwart, Phys. Rev. B **82**, 064412, (2010)]

Chapter 2

Synthesis and Analysis

Single crystals of $Na_2Ir_{1-x}Ru_xO_3$ [x=0.02, 0.05, 0.1, 0.2, 0.3, 1] were attempted. We were able to successfully synthesize single crystals of $Na_2Ir_{1-x}Ru_xO_3$ for x= 0.2, 0.3 and 0.05.

2.1 Synthesis of $Na_2Ir_{0.8}Ru_{0.2}O_3$ and $Na_2Ir_{0.7}Ru_{0.3}O_3$

The detailed synthesis procedure which worked for synthesis of x=0.2 and 0.3 samples was the same and is described below.

2.1.1 Reaction followed

$$Na_2CO_3 + (1-x)Ir + (x)Ru \xrightarrow{in\ air} Na_2Ir_{1-x}Ru_xO_3 + CO_2(gas)$$

2.1.2 Procedure

Starting material Na_2CO_3, Ru and Ir metal powder were mixed and placed in an Al_2O_3 crucible with a lid and heated to $725^{\circ}C$ in 5 h and held there for 24 h after which it was furnace cooled to room temperature. The resulting mixture was ground and placed again in crucible and heated to 1100 degree celcius(in case of $Na_2Ir_{0.8}Ru_{0.2}O_3$) and 1000 degree celcius(in case of $Na_2Ir_{0.7}Ru_{0.3}O_3$) and held there for 72 h before cooling to room tempera-

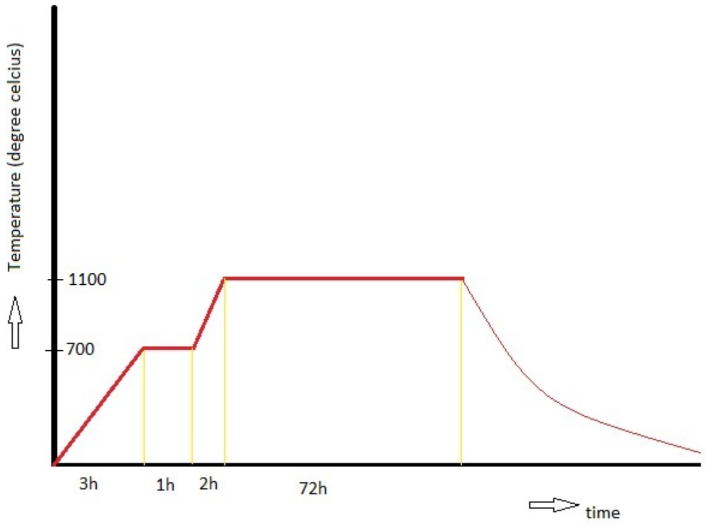


Figure 2.1: Temperature Profile

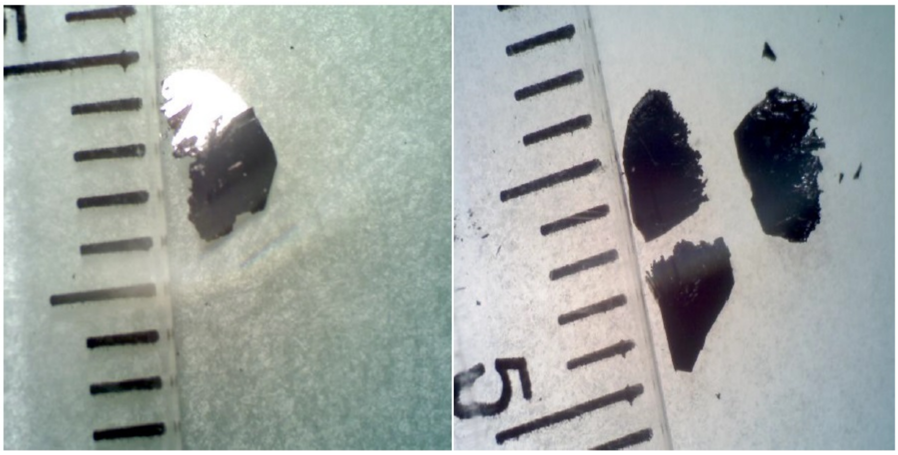
ture. The furnace was programmed to temperature profile as given in fig 2.1. Crystals of about 3-4 mm were obtained for $Na_2Ir_{0.8}Ru_{0.2}O_3$ and 2-3 mm for $Na_2Ir_{0.7}Ru_{0.3}O_3$) as shown in fig 2.2.

2.2 Synthesis of $Na_2Ir_{0.95}Ru_{0.05}O_3$

To grow crytals of $Na_2Ir_{0.95}Ru_{0.05}O_3$, first powder of Na_2IrO_3 was made. In the next step 5% Ru (relative to Ir in Na_2IrO_3) was added and crystals were grown using the tempeture profile given in fig 2.3 .Crystals of about 1-2 mm length were obtained by this procedure (figure 2.4).

2.3 Chemical Analysis

To estimate the chemical composition of grown crystals, the relative atomic fraction of Na, Ir and Ru in the crystals was measured using energy dispersive



$Na_2Ir_{0.8}Ru_{0.2}O_3$ $Na_2Ir_{0.7}Ru_{0.3}O_3$

Figure 2.2: Single Crystals of $Na_2Ir_{0.8}Ru_{0.2}O_3$ and $Na_2Ir_{0.7}Ru_{0.3}O_3$

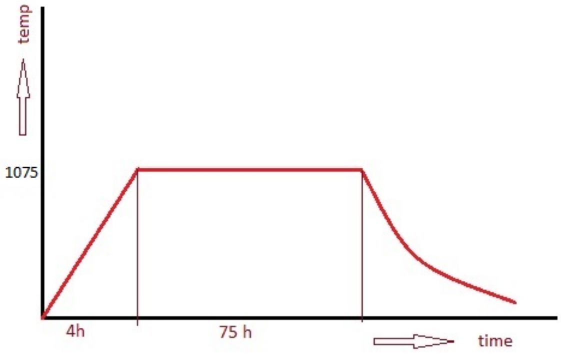


Figure 2.3: Temperature profile for $Na_2Ir_{0.95}Ru_{0.05}O_3$

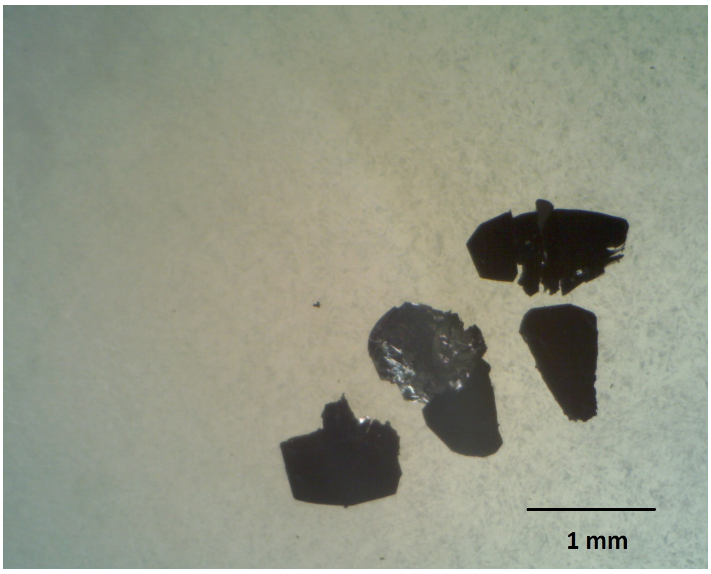


Figure 2.4: Single Crystals of $Na_2Ir_{0.95}Ru_{0.05}O_3$

spectroscopy (EDS) using a JEOL SEM.

2.3.1 SEM

A scanning electron microscope (SEM) is a type of electron microscope that produces images of a sample by scanning it with a focused beam of electrons. The electrons interact with atoms in the sample, producing various signals that can be detected and that contain information about the sample's surface topography and composition.

Spectrums and tables received from SEM have been attached showing individual components in the sample of $Na_2Ir_{0.7}Ru_{0.3}O_3$, $Na_2Ir_{0.8}Ru_{0.2}O_3$ and $Na_2Ir_{0.95}Ru_{0.05}O_3$(table 2.1, 2.2 and 2.3). The chemical formula for the three samples from these measurements come out to be $Na_{1.6}Ir_{0.72}Ru_{0.28}O_3$, $Na_{1.7}Ir_{0.8}Ru_{0.2}O_3$, $Na_{1.62}Ir_{0.91}Ru_{0.09}O_3$ respectively. Therefore for the first two samples, the measured chemical compositions match well with what was expected from starting compositions. However for $x = 5\%$ Ru sample the grown crystal has $x = 9\%$ Ru doped into it.

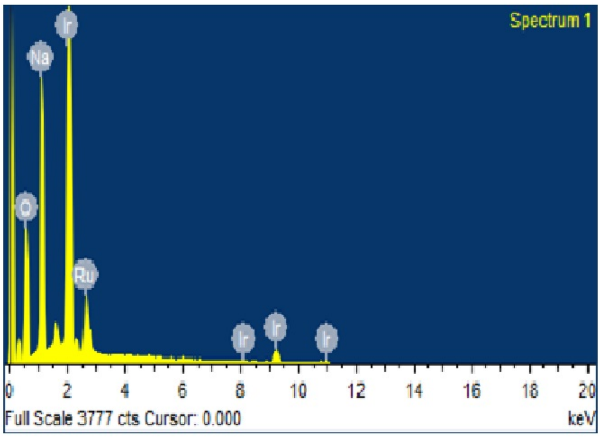


Figure 2.5: SEM of $Na_2Ir_{0.7}Ru_{0.3}O_3$

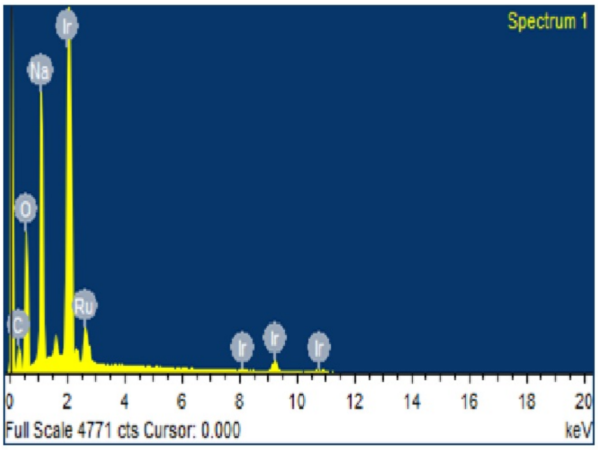


Figure 2.6: SEM of $Na_2Ir_{0.8}Ru_{0.2}O_3$

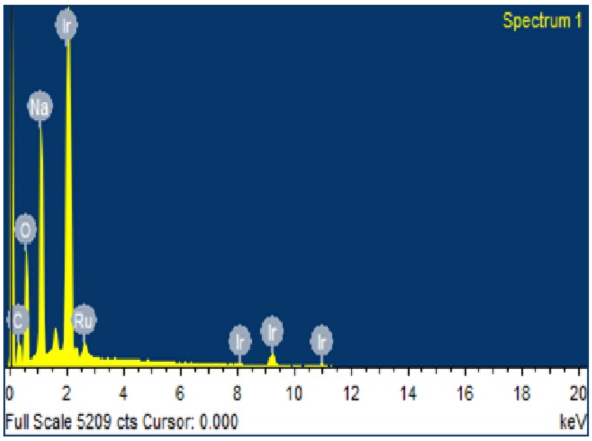


Figure 2.7: SEM of $Na_2Ir_{0.95}Ru_{0.05}O_3$

Table 2.1: SEM data of $Na_2Ir_{0.7}Ru_{0.3}O_3$

Element	**weight %**	**atomic %**
O	20.80	56.25
Na	14.31	26.93
Ru	10.91	4.67
Ir	53.98	12.15

Table 2.2: SEM data of $Na_2Ir_{0.8}Ru_{0.2}O_3$

Element	**weight %**	**atomic %**
C	4.91	15.54
O	20.59	48.87
Na	13.46	22.24
Ru	7.27	2.73
Ir	53.77	10.63

Table 2.3: SEM data of $Na_2Ir_{0.95}Ru_{0.05}O_3$

Element	**weight %**	**atomic %**
C	5.58	18.30
O	18.87	46.43
Na	12.73	21.80
Ru	3.21	1.25
Ir	59.6	12.21

2.4 Magnetic Properties

Plots of inverse magnetic susceptibility versus temperature and their variations with different magnetic fields (H=0.05, 0.1, 0.5, 1, 2 T) were analyzed and given in the next section.

2.4.1 Susceptibility versus Temperature

Plots for susceptibility vs temperature for 5% and 20% concentration of Ru in Sodium Iridate were obtained using PPMS (Fig2.8 and Fig2.9 respectively) and were fitted by the following expression called Curie Weiss law between 100 to 300K. The expression is as follow $\chi = \chi_0 + \frac{C}{T - \theta}$. Curie constants 0.665694 and 0.636914 were obtained after fitting which suggest that Ru has been mixed in the mixture as it is spin 1 magnetic moment(for Na_2IrO_3 it was 0.41 cm^3/mol). The Weiss temperature $\theta = -190K$ and $\theta = -160K$ are obtained for 5% and 20% samples respectively ($\theta = -116K$ for Na_2IrO_3) . The large negative values indicate strong antiferromagnetic interactions. However, no long ranged order was found down to 2 K although a broad anomaly is observed around $T \approx 5K$ as shown in the insets of figures 2.8 and 2.9. The low temperature data is shown next.

2.4.2 Field dependence of the magnetic anomaly

The low temperature susceptibility for both materials shows a cusp at about 5K at low magnetic fields (Fig 2.10 and 2.11). Moreover, the data measured while warming up in a field after it has been cooled in zero field (ZFC) and data measured while cooling in a field(FC) shows a bifurcation below the cusp temperature. The degree of bifurcation gets smaller when larger fields are applied and the cusp become less sharp and more rounded for larger fields. These observations suggest that these materials undergo a transition into some frozen spin-glassy state at low temperatures.

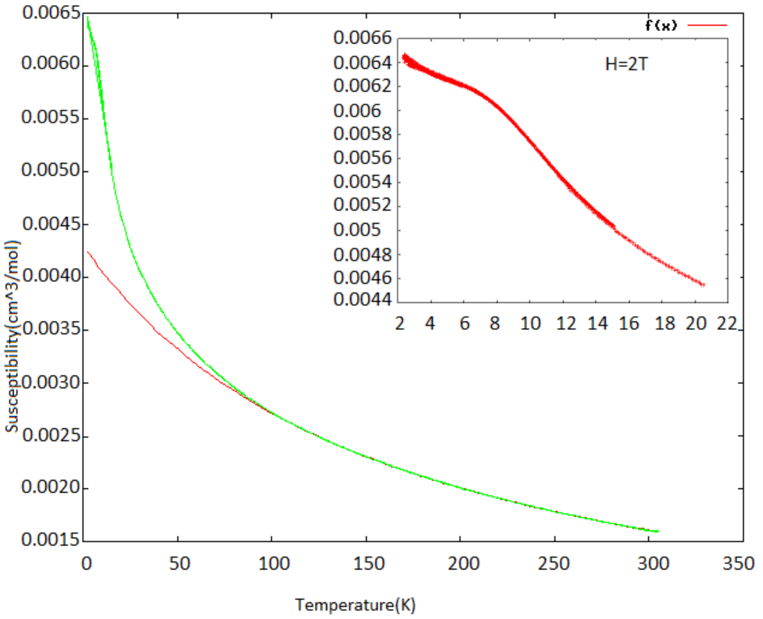


Figure 2.8: Plot for Susceptibility(cm^3/mol) versus temperature(K) for $Na_2Ir_{0.95}Ru_{0.5}O_3$

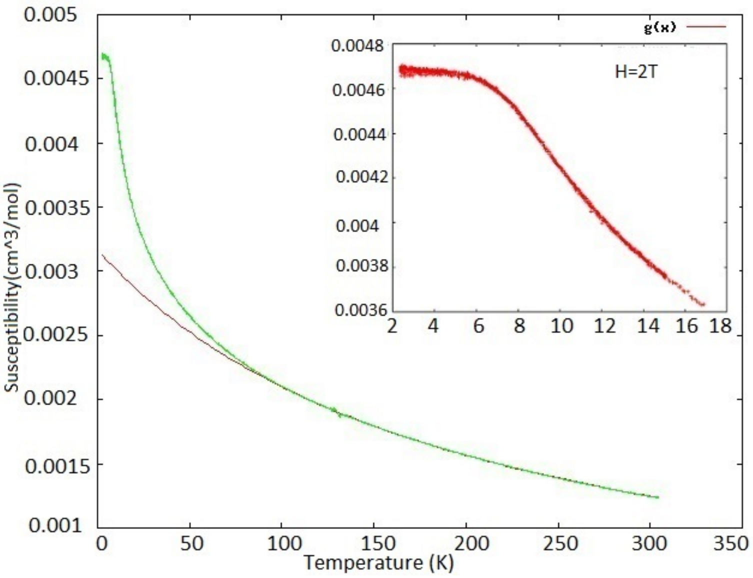


Figure 2.9: Plot for Susceptibility(cm^3/mol) versus temperature(K) for $Na_2Ir_{0.8}Ru_{0.02}O_3$

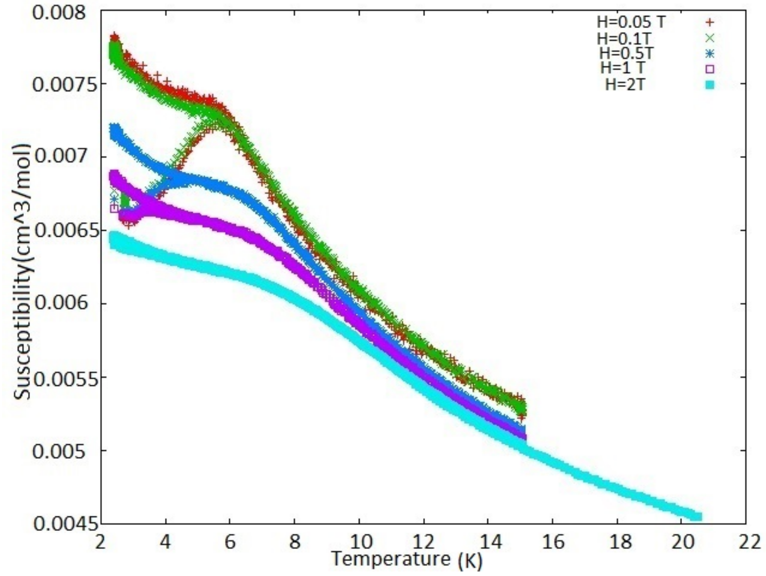


Figure 2.10: Plot for Susceptibility(cm^3/mol) versus temperature(K) for $Na_2Ir_{0.95}Ru_{0.5}O_3$ in low temp range for different magnetic fields

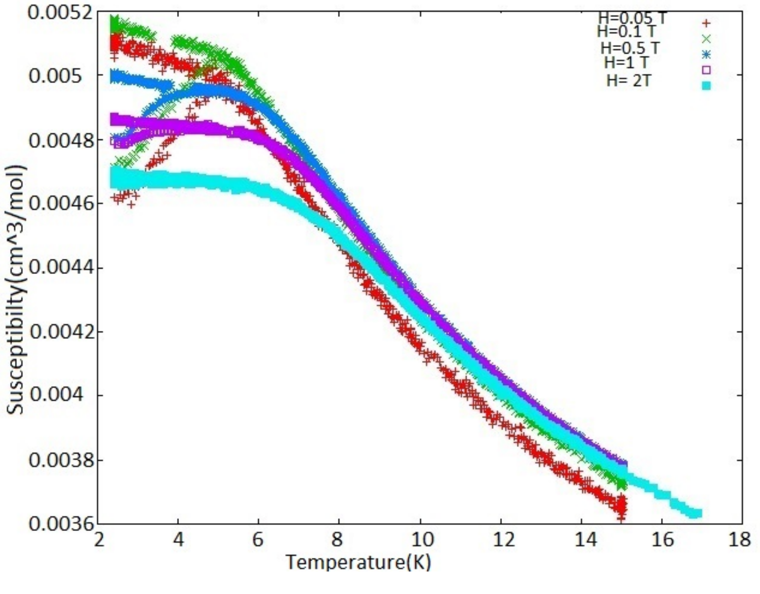


Figure 2.11: Plot for Susceptibility(cm^3/mol) versus temperature(K) for $Na_2Ir_{0.8}Ru_{0.02}O_3$ in low temp range for different magnetic fields

2.5 Attempt to synthesize $Na_2Ir_{0.98}Ru_{0.02}O_3$

Sodium Carbonate and Iridium were mixed according to the equation

$$Na_2CO_3 + Ir \longrightarrow Na_2IrO_3 + CO_2 \tag{2.1}$$

and heated to $700^{\circ}C$ in 3 h and held there for 16 h(HT-1). After that mixture was furnace cooled and 2% Ru of Iridium weight was mixed and it was ground and put back in the furnace for another heat treatment(HT-2) as given in fig 2.12

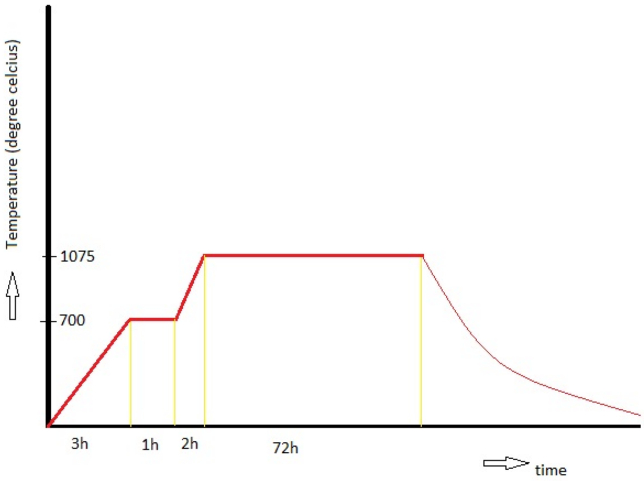


Figure 2.12: Heat treatment-2

No crystals were obtained after heat treatment-2

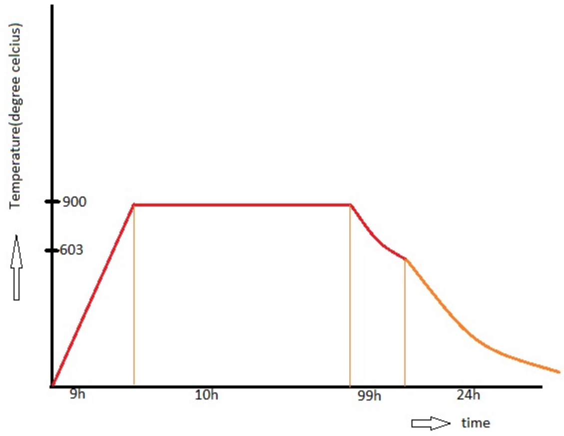


Figure 2.13: Heat Treatment-3

2.6 Attempt to synthesize Sodium Ruthenate Na_2RuO_3

Initially we took Ru and placed it in tube furnace filled with oxygen gas and heated it to $800^{\circ}C$ in 5 h and held there for 24 h(HT-1). Mixture was taken out after cooling and ground and placed back into oxygen filled tube furnace for another heat treatment. This time also it was heated to $800^{\circ}C$ in 5 h and held there for 24 h(HT-2). After HT-2 we got RuO_2. We then mixed it with Na_2CO_3 and NaCl according to the reaction

$$Na_2CO_3 + RuO_2 + 5NaCl \longrightarrow \tag{2.2}$$

and heated to $900^{\circ}C$ as given in HT-3(fig2.13)

No crystals were obtained after heat treatment.

Chapter 3

Conclusion

Single Crystals of $Na_2Ir_{1-x}Ru_xO_3$(x=.09,0.20,0.28) have been successfully grown in the lab. The magnetic measurement on these materials suggest that the magnetic order previously seen in the parent compound Na_2IrO_3 gives way to a glassy magnetic state in the doped materials although the freezing temperature does not seem to change with x which points to the fragility of the magnetic order in Na_2IrO_3. Since Ru is 4d transition metal atom compared to Ir which is 5d transition metal atom, therefore by replacing Ir partially by Ru, we are reducing the effective spin orbit coupling. Also Ru is a smaller atom than Ir and hence Ru substitution amounts to application of chemical pressure. The Ru doped samples could thus be expected turn the system metallic. However, evidence for this was not found .

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