Electronic and Magnetic Properties of Pyrochlore

$(Eu_{(1-x)}Dy_x)_2Ir_2O_7$

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Abstract

The pyrochlore \((Eu_{(1-x)}Dy_x)_2Ir_2O_7\) for \(x = 0, 0.25, 0.50, 0.75,\) and 1.0 were prepared using solid-state reaction method. As the \(Dy\) concentration increases, the X-ray results indicate a systematic decrease of the cubic lattice parameter of \((Eu_{(1-x)}Dy_x)_2Ir_2O_7\). We observed metal insulator transition in all compounds in addition two new anomalies at high temperatures in specific heat and resistivity results. The origin of these anomalies have not yet been identified. The metal insulator transition temperature \(T_{MI}\) of \((Eu_{(1-x)}Dy_x)_2Ir_2O_7\) increases with the reduction in the lattice parameter. In the magnetic susceptibility results, the effective magnetic moment increases with the increment of the \(Dy\) substitution for \(Eu\) ions. The magnetic field dependence of resistivity was investigated for all samples, negative and positive magnetoresistance effects are discussed.
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Chapter 1

Introduction - Overview of Oxide Pyrochlore

1.1 Material Background

The pyrochlore transition-metal oxides possess unique specifications of geometric frustration, small magnetic moment, and the interplay between a strong spin-orbit coupling [1]. The general formula of the oxide pyrochlores $A_2B_2O_7$ (A and B are metals), produce a family of phases isostructural to the mineral pyrochlore, $(Na, Ca)_2(Nb, Ta)_2O_6(F/O)$ [2]. The pyrochlore oxides are all cubic structures classified under the space group $Fd\bar{3}m$ [2]. $A_2B_2O_7$ compounds possess a wide diversity of interesting physical properties such as the B element can be a transition metal with variable oxidation states and the A element is a rare-earth lanthanide. Consequently, the electrical properties of the pyrochlores change from highly insulating to semiconducting to a metallic behavior with some compounds presenting a semiconductor-to-metal transition [2]. A very good cationic conductivity can be found in many defects, that is vacancy-containing, pyrochlores which can be used as solid electrolytes and some of the defect phases containing 4d or 5d elements at the B site render them useful as oxygen electrodes by virtue of their excellent ionic ($O^{2-}$) conductivity [2]. In recent years, 4d and 5d transition-metal pyrochlore oxides have attracted interest because of their unusual transport properties such as the anomalous Hall effect in $Nd_2Mo_2O_7$, superconductivity in $Cd_2Re_2O_7$ and $AOs_2O_6$ (A = K, Rb, and Cs), the metal insulator transition (MIT) in $Cd_2Os_2O_7$, and the under-screened Kondo
The pyrochlore iridates $R_2Ir_2O_7$ (R is a rare-earth element) reveal a systematic dependence of their properties on R. For instance, Pr is a paramagnetic metal in which resistivity decreases as the temperature decreases down to the lowest measured temperature. Other R Pyrochlores exhibit metal-insulator transitions (MIT). The MIT are accompanied by magnetic phase transitions however, the reasons for this transition are still under debate [4]. This might be due to the R ion which is trivalent causing the $5d^5$ electrons of $Ir^{4+}$ to have an unfilled $t_{2g}$ band [3]. The $4f$ electrons are generally well localized, consequently, only the $5d$ electrons contribute to the electrical conductivity [3]. For $R = Pr, Nd, Sm,$ and Eu in $R_2Ir_2O_7$ the conductivity exhibits metallic behavior at high temperatures, while for $R = Gd, Tb, Dy, Ho, Er, Yb,$ and Y it exhibits semiconducting behavior. This diversity in conductivity behavior was ascribed to the reduction of the structural band of the ($Ir^{4+}$) derived from a decrease in the ionic radius of the R atom across the rare-earth series [5]. In other words, as the ionic radius of R decreases (see Figure 1.1), the Ir-O-Ir bond angle decreases, as a result, the $t_{2g}$ band width becomes narrower [2]. The Iridium-based oxides are associated with a wider electronic band width ($W$) and with a relatively weaker electron correlation potential ($U$). Also, these iridates are expected to be metallic in nature because of the extended nature of the $5d$ orbitals of Ir as observed in the layered $Sr_2IrO_4$ oxide [6]. The spin orbit coupling ($SOC$) is playing an important role due to the large atomic number of Ir. As a result, $SOC$ splits the $t_{2g}$ level into two bands with the doublet $J_{eff} = \frac{1}{2}$ and the quadruplet $J_{eff} = \frac{3}{2}$. Because of that, the band width is effectively reduced (see Figure 1.2(a)), and because of the half filled $J_{eff} = \frac{1}{2}$ and a Mott gap occurs through the electron correlations [6]. However, if the band width of the $t_{2g}$ level is large, the system can have a metallic ground state (see Figure 1.2(b)) [6].
Figure 1.1: Replacing the R site in $R_2Ir_2O_7$ changes the Ir-O-Ir bond angle [7].

Figure 1.2: (a) Schematic description of Ir 5d splitting of the $t_{2g}$ band under SOC and U, which is leading to an insulator state. The lower Hubbard band (LHB), which is completely filled, is separated from the empty upper Hubbard band (UHB) by an energy gap. (b) The bandwidth when ($W \geq SOC$, U), overlapping bands can lead to a metallic state [6].
<table>
<thead>
<tr>
<th>Atom</th>
<th>Position</th>
<th>Coordinates</th>
</tr>
</thead>
<tbody>
<tr>
<td>R</td>
<td>16d</td>
<td>$\frac{1}{2} \frac{1}{2} \frac{1}{2}$</td>
</tr>
<tr>
<td>Ir</td>
<td>16c</td>
<td>0,0,0,</td>
</tr>
<tr>
<td>O</td>
<td>48f</td>
<td>x, y, z</td>
</tr>
<tr>
<td>O'</td>
<td>8b</td>
<td>$\frac{1}{2} \frac{1}{2} \frac{1}{2}$</td>
</tr>
</tbody>
</table>

Table 1.1: Atomic positions in space group $Fd\overline{3}m$ for $R_2Ir_2O_7$ pyrochlores [1, 8].

1.2 Crystallography

The oxide pyrochlores, $A_2B_2O_6O'$, possess eight molecules per unit cell ($Z = 8$) and are classified under the $Fd\overline{3}m$ space group. The crystal structure consists of two types of cation coordination polyhedron. The A cations are 8 coordinated, which contain six equally spaced anionic oxygen atoms ($O$) at a slightly shorter distance from the location of the central cation, and the other two anions ($O'$) are on the poles (distorted cube) [2]. The B site cations are smaller than the A site and are six coordinated by six anions at equal distances from the location of the central cation (trigonal antiprisms) [2]. Since A and B are both cations and thus can be at inversion centers, consequently, either of these cation sites can be used as the origin [8]. In the case of $R_2Ir_2O_6O'$, the preferred description has the Ir cation at the origin, and this characterization is given in (Table 1.1). The lattice constant $a$ and the $x$ coordinate associated with the $O$ site are only the two free parameters in this structure. All pyrochlore iridates have an $x$ value larger compared to an ideal $IrO_6$ octahedra ($x = \frac{5}{16}$), pointing out that a compressive trigonal destination is presented [1, 8].

1.2.1 Description of the Pyrochlore Structure

Due to the polyhedra coordination around the R and Ir cations, the pyrochlore structure has been described in several different ways [2].
Figure 1.3: The crystal structure of pyrochlore iridates. (a) The Ir sublattice forming corner-shared tetrahedra. (b) The local characteristic at the Ir atom site. The position of each Ir atom is at the center of a trigonally compressed $IrO_6$ octahedra, which surrounded by a hexagonal ring of R atoms [1].

**Description Based on $Ir_2O_6$ and $R_2O'$ Interpenetrating Networks**

The crystal structure of pyrochlore iridates (Figure 1.3) is formed of two interpenetrating $Ir_2O_6$ and $R_2O'$ sublattices. In the $Ir_2O_6$ sublattice, each of the oxygen atoms of $IrO_6$ octahedra are corner-shared and can be viewed to form regular $Ir_4$ tetrahedra. Each $O'$ in the $R_2O'$ sublattice is coordinated with four R cations to form a second tetrahedral network. In the $R_2Ir_2O_6O'$ each R cation is surrounded by six O and two $O'$ atoms, and each O is surrounded with two Ir and two R cations in a distorted tetrahedron with local symmetry [1, 9].

**Structure Based on Fluorite Type Cell**

A fluorite structure can be used to describe the structure of the pyrochlores with $x$ value in the proximity of 0.375 [2, 8, 10]. Most values of $x$ lie well below this value, where the limiting values of $x$ are 0.3125 and 0.375. As an example to possess such structure, is $Zr^{4+}$ for $B$ site in pyrochlores. In other words, this description is useful with large ionic radius for $B$ site and higher $x$. Compared to the fluorite structure type ($A_4O_8$), the cations $A$ and $B$ are alternated ordered on fluorite cation sites and possess oxygen vacancies (see Figure 1.4). The position of the atoms are shown in Table 1.1, and
Figure 1.4: The crystal structure of pyrochlores based on the fluorite type cell [11].

the vacancy is at 8a site. The shape of polyhedra coordinate changes with the oxygen parameter $x$, as mentioned earlier. When $x = 0.3125$ (see Figure 1.5), $B$ ion possess a perfect octahedral coordination while $A$ ion are eight coordinated. In this case, the $A$ ion forms a distorted hexagon of six oxygens (48f) and the $A−O$ distance is longer than the $A−O'$. For $x = 0.375$, $A$ ion will be located in a regular cubic 8-fold coordination. The $B$ cation will be at the center of a regular cube of oxygen anions with missed two diagonal oxygens.
Figure 1.5: The change of the shape in $A_2B_2O_6O'$ is based on changing the coordination polyhedra of $A$ and $B$ ions with $48f$ oxygen parameter $x$. It is regular octahedron for $x = 0.3125$ and regular cube for $x = 0.375$ [2].
Chapter 2

Background

2.1 Magnetic properties

2.1.1 Magnetic Moments and Exchange Interactions in Rare Earth elements

Rare earth elements are similar in chemical properties due to the identity of the outermost electron shells in the $5s^25p^6$ configuration. Lanthanum, which is at the beginning in the rare earth group, its $4f$ shell is empty and cerium has one (1) electron in $4f$ shell. Throughout the group, the number of electrons in $4f$ shell will increase steadily until the Lutetium with $4f^{14}$ filled shell. The radii of the trivalent ions decrease as the Lanthanide go through the series from 1.11Å at cerium to 0.94Å at ytterbium, which is known as the "lanthanide contraction". The number of $4f$ electrons that are compacted in the inner shell with a radius of about 0.3Å are responsible for distinguishing the magnetic behavior from one ion to another [12].

In rare earth metals, the magnetic electrons in the $4f$ shells are covered by the $5s$ and $5p$ electrons. Consequently, the $4f$ electrons are localized and wave functions overlapping comparatively small. Thus, the direct interaction between the magnetic moments is difficult. The magnetic moments of the electrons interact over relatively large distances through the conduction electrons, known as indirect exchange interaction RKKY. Based on the separation between a pair of ions, the indirect interaction can be ferromagnetic or antiferromagnetic [13].
The magnitude of the moment can be derived from the paramagnetic susceptibility using the Brillouin function $B_J(x)$ [12]:

$$M(H,T) = \frac{N_A}{V} g_J \mu_B J B_J(x)$$  (2.1)

where the Landé g-factor $g_J$ is:

$$g_J = \frac{3}{2} + \frac{S(S+1)I(I+1)}{2J(J+1)}.$$  (2.2)

and where $B_J(x)$ is the Brillouin function:

$$B_J(x) = \frac{2J+1}{2J} \coth\left(\frac{2J+1}{2J} x\right) - \frac{1}{2J} \coth\left(\frac{1}{2J} x\right)$$  (2.3)

and $x$ is:

$$x = \frac{g_J \mu_B H}{K_B T}$$  (2.4)

here $K_B$ is the Boltzmann constant and $\mu_B$ is the Bohr magneton.

For large values, $g_J \mu_B H \gg K_B T$:

$$B_J(x) \rightarrow 1$$  (2.5)

therefore, the magnetization saturation is given by

$$M_{\text{saturation}} = \frac{N_A}{V} g_J \mu_B J$$  (2.6)

and for small $x$, $g_J \mu_B H \ll K_B T$:

$$M(H,T) = \frac{N_A}{V} \frac{g_J^2 \mu_B^2 2J(J+1)}{3K_B T} H$$  (2.7)

In that limit, the magnetic susceptibility $\chi$ is equal to $\chi = \frac{\partial M}{\partial H}$, thus:
\[
\chi(T) = \frac{N_A g_J^2 \mu_B^2 J(J+1)}{3K_B T} = \frac{C}{T}
\]
\[
\frac{1}{\chi(T)} = C T
\]

The equation 2.9 is known as Curie’s Law.

Therefore, it has become customary to define an effective magnetic moment \( \mu_{\text{eff}} \):

\[
\mu_{\text{eff}} = g_J \sqrt{J(J+1)}
\]

In Table 2.1, shows the experimentally measured \( \mu_{\text{eff}} \) corresponds to the equation 2.10 for Europium and Dysprosium ions. There is an additional Van Vleck contribution to the magnetic susceptibility for \( Eu^{3+} \) [14].

2.1.2 Van Vleck Paramagnetism

The Van Vleck susceptibility is approximately temperature-independent paramagnetism, and it becomes important when an ion has low-lying excited states. The contribution into the susceptibility could be in two ways: they might be as a result of the Zeeman splitting, or the application of magnetic field causes the mixing of the exited state with the ground state, which produces Van Vleck paramagnetism. The Van Vleck paramagnetism contribution to \( Eu^{3+} \) is high, causing it to become paramagnetic rather than nonmagnetic (see Figure 2.1) [14]. The Europium atomic number is 63 with the electron configuration of \( 4f^76s^2 \). In pyrochlore iridates, \( Eu \) possess the oxidation state

<table>
<thead>
<tr>
<th>Ion</th>
<th>S</th>
<th>L</th>
<th>J</th>
<th>( g_J )</th>
<th>( M_{\text{sat.}} = g_J J )</th>
<th>( \mu_{\text{eff}} = g_J \sqrt{J(J+1)} )</th>
<th>( \mu_{\text{eff}}^{\exp.} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Eu^{3+} )</td>
<td>6</td>
<td>3</td>
<td>3</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>3.4</td>
</tr>
<tr>
<td>( Dy^{3+} )</td>
<td>9</td>
<td>( \frac{5}{2} )</td>
<td>5</td>
<td>( \frac{15}{2} )</td>
<td>10.0</td>
<td>10.65</td>
<td>10.6</td>
</tr>
</tbody>
</table>

Table 2.1: The saturation moment \( M_{\text{sat.}} \) and the paramagnetic moment \( \mu_{\text{eff}} \), in units of \( \mu_B \) [14].

\( 4f^n \) Ion  S  L  J  \( g_J \)  \( M_{\text{sat.}} = g_J J \)  \( \mu_{\text{eff}} = g_J \sqrt{J(J+1)} \)  \( \mu_{\text{eff}}^{\exp.} \)
Figure 2.1: The energy levels of Eu$^{3+}$ in the absence of an external magnetic field [15].

of 3+ with the 4$f^6$ electron configuration. The ground state level for Eu$^{3+}$ is $^7F_0$, which indicates the zero total quantum number ($J = |L - S| = 3 - \frac{6}{2} = 0$). Consequently, the ground state is nonmagnetic and the Curie-Weiss susceptibility of Eu ion should be zero [13]. The non-zero effective magnetic moment for the Eu$^{3+}$ (see Table 2.1) arises from the overlapping between the ground state and the first excited state, because the energy interval is not large compared to the $K_B T$ [13]. Since there is no paramagnetic effect in the ground state $|0>$ if $J = 0$ [16] then,

$$<0 | g_J \mu_B J | 0 > = 0. \quad (2.11)$$

This indicates that there is no paramagnetic susceptibility and the ground state of the system does not change the magnetic field, which is only accurate in the first order perturbation theory. However, the second-order perturbation theory anticipates a change in the ground state energy $E_0$ because it considers the excited states are being mixed in
with $J = 0$. Therefore, for an ion with $J = 0$ the change of the ground state energy $E_0$ can be [16]:

$$\Delta E_{VV} = \mu_B^2 \sum |< 0 | (L + g_0S)H | n >|^2 \left( \frac{E_n - E_0}{E_n - E_0} \right)$$ (2.12)

where,

$$g_J J = L + g_0 S.$$ (2.13)

Then, the Van Vleck contribution to the magnetic susceptibility is:

$$\chi_{VV} = N_A \frac{2\mu_B^2}{V} \left( \sum |< 0 | (L + g_0S)H | n >|^2 \left( \frac{E_n - E_0}{E_n - E_0} \right) \right)$$ (2.14)

where $E_n > E_0$.

### 2.1.3 Antiferromagnetism

When ions have a non-zero spin quantum number, below a specific temperature known as Néel temperature $T_N$, a long-range antiparallel alignment of the spins can occur [17]. The case of a long-range parallel alignment of spins is known as a ferromagnetic order. This antiparallel alignment of the spins can be described as two equal and oppositely directed sublattices of ferromagnetic order and results in no net magnetization. In some compounds, the magnetic moments of the two sublattices are not equivalent, which causes a net magnetization. This type of magnetization is known as ferrimagnetism. In a range of temperatures above Néel temperature, the thermal energy is enough to destroy the interatomic spin-coupling which produces the antiferromagnetic state, thus giving rise to the metal-oxide to behave as a paramagnet. In this paramagnet range, the effective magnetic moments can be calculated using the Curie-Weiss law [17].
2.1.4 Magnetic Frustration in Crystalline Samples

Magnetic frustration in a system occurs when it is not possible to satisfy all of its magnetic exchange interactions to find the ground state [16]. This leads to a variety of similar low energy states of the system [16]. To clarify this phenomenon, we consider a triangular lattice shown in Figure (2.2). If two neighbouring spins are antiparallel, the third spin is in a difficult situation as it cannot be antiparallel to both spins simultaneously. Any choice by orienting up or down one of the two adjacent spins will not minimize the energy. As a result, the system cannot achieve a state that entirely settles its microscopic constraints, but possess multiple equal unsettled states, thus the system is frustrated [16].”The magnetic frustrated systems usually do not exhibit the long-range magnetic order due to the magnetic ground state degeneracy” [13].

In pyrochlores, the geometric frustration contributes to the magnetic properties. The B cations in the pyrochlores might be viewed as clustered into tetrahedral units sharing corners to form infinite, intersecting chains. Antiferromagnetic interactions $B - B$ is expected to control through the $B - O - B$ super-exchange, but these interactions are
frustrated by the tetrahedral arrangement [8].

2.2 Electrical Resistivity

Electrical resistivity measurements can help to characterize electronic phase transitions such as a metal-insulator transition or superconductivity [17]. The temperature dependence of the resistivity can provide information about the activation energy $E_a$ of a semiconductor, using the equation [17]:

$$\rho = \rho_0 e^{(E_a/k_B T)}$$  \hspace{1cm} (2.15)

2.3 Magnetoresistance

Magnetoresistance ($MR$) can be defined as changing the resistance of a material under an applied magnetic field $H$ [16],

$$MR = \frac{\Delta \rho}{\rho_0} = \frac{\rho(H) - \rho(0)}{\rho(0)}.$$ \hspace{1cm} (2.16)

$MR$ materials are extensively used in applications for magnetoresistance sensors such as measuring the magnetic field from the magnetic strip on a credit card [16]. $MR$ effect can be negative or positive. If the electrons are forced to take a different path in the sample by applying a magnetic field, the scattering will increase resulting a positive MR [16]. A negative $MR$ effect might be observed at low temperatures due to scattering reduction [16].

2.4 Heat Capacity

Specific heat or heat capacity is defined by the quantity of heat that is required to
raise the temperature of a unit of mass of the material by a unit degree of temperature [19]. When a heat input \( dQ \) raises the temperature of a unit mass of the material, while the properties \( x, y, \ldots \) are fixed, then

\[
C_{x,y,\ldots} = \lim_{\frac{dT}{dt} \to 0} \left( \frac{dQ}{dt} \right)_{x,y,\ldots}
\]

(2.17)

Some properties of specific heat follow the fundamental laws of thermodynamics. The first law states that if a quantity of heat \( dQ \) is supplied to a material, a part of it goes to increase the internal energy \( E \) of the system and the other is used to do external work \( W \),

\[
dQ = dE + dW.
\]

(2.18)

The entropy \( S \) can be calculated by using the second law of the thermodynamics from the relation

\[
dQ = TdS.
\]

(2.19)

The pressure \( P \) can be expressed in terms of volume and temperature. Hence, during the change of temperature, \( P \) can be kept constant, and the heat capacity will be

\[
C_p = \left( \frac{dQ}{dT} \right)_p = T \left( \frac{\partial S}{\partial T} \right)_p
\]

(2.20)

In solids, the heat capacity at low temperature is as a result of the electronic contribution \( C_e \) and the lattice contribution \( C_{\text{latt}} \). \( C_e \) increases linearly with \( T \), and \( C_{\text{latt}} \) is proportional to \( T^3 \), which \[19, 20\]

\[
C = C_{\text{latt}} + C_e = \beta T^3 + \gamma T.
\]

(2.21)

The measurements of the heat capacity of solids can provide the necessary information
about the lattice, electronic, and the magnetic properties of substances with the temperature. The Debye model has been used successfully to explain the lattice contribution to the specific heat of solids, at low temperatures with the temperature variation of $C_p$ can be given by the relation,

$$C_p = \frac{12}{5} NR\pi^4 \left(\frac{T}{\theta_d}\right)^3$$

(2.22)

where $N$ number of atoms, $R$ the universal gas constant 8.314 J/mole·K [19, 20].
Chapter 3

Experimental Methods

3.1 Synthesis of Samples

The polycrystalline samples \((\text{Eu}_ {(1-x)}\text{Dy}_x)\text{Ir}_2\text{O}_7\) \((x=0, 0.25, 0.50, 0.75, \text{and } 1)\) were synthesized by a standard solid state reaction method [3, 9]. Mixtures of \(R_2\text{O}_3\) (99.99%, rare-earth oxides for \(R = \text{Eu, Dy}\)) and \(\text{IrO}_2\) (99.99%) in stoichiometric ratios were pressed into pellets. The pellets were inserted into Pt cylinders and placed in evacuated quartz ampoules (see Figure 3.1). Then, these objects were heated at 900°C for about three days. After this reaction, the pellets were ground and additional 3% of \(\text{IrO}_2\) was added. The pellets of this mixtures were inserted into a Pt cylinder and placed in evacuated quartz ampoules again and heated at 1200°C for about ten days. In this process, a number of intermediate grindings are needed to fully react the samples [21].

In order to prepare the samples, a stoichiometry calculation was done to obtain the correct amount of each material. The chemical equation used, is

\[(1 - x)\text{Eu}_2\text{O}_3 + (x)\text{Dy}_2\text{O}_3 + 2\text{IrO}_2 \rightarrow \text{Eu}_{2(1-x)}\text{Dy}_x\text{Ir}_2\text{O}_7.\]

The evacuated ampoules method was selected because the samples prepared by solid state reaction in air possess impurity phases due to the volatility of \(\text{IrO}_2\). Moreover, the reflection peaks in the XRD patterns were much broader, which were noticed on the Matsuhira et al. studies [3].

3.2 X-Ray diffraction

X-Ray diffraction measurements were carried out using a Rigaku Smartlab diffrac-
Figure 3.1: The sample wrapped with Pt foil in an evacuated ampoule.
tometer with a Ge monochromator. The incident X-ray waves on the sample are diffracted by the electrons, and some of the waves are passing through it. These waves are reflected from many planes within the sample, not only from the compound surface. Bragg’s law (see Figure 3.2) derived by using a condition for constructive interference, which occurs when the path-length difference $d$ between the waves diffracted by two planes of atoms needs to be equal to the wavelength $\lambda$ [17]. The Bragg’s law equation is:

$$n\lambda = 2d\sin\theta.$$  \hspace{1cm} (3.1)

![Figure 3.2: Bragg’s law [17].](image)

### 3.3 Magnetic Susceptibility

DC magnetization was measured using the Quantum Design Magnetic Properties Measurement System (MPMS) used to study the magnetic properties of a material. The most important component of this measurement system is as follow (see Figure 3.3)
1. A temperature control system for controlling the sample temperature between 2 K and 400 K.

2. A magnetic control system, which provides magnetic fields from zero to $\pm 5.5$ T by current from a power supply.

3. A superconducting Quantum Interference Device (SQUID) amplifier system, which is the heart of the magnetic moment detection system.

4. A sample handling system for moving the sample smoothly through the detector coils.

5. A computer operating system for automatically control all operating features on the MPMS.

The SQUID is responsible for detecting the magnetization of the sample, which has to move through the detection coil (pick-up coil) that consists of a set of three coils (Figure 3.4). The center coil is a two-turn wound counter clockwise and the upper and the bottom coils are a single turn wound clockwise. Superconducting wires connect the pick-up coil with the input coil, which are inducing current proportional to the sample magnetization.
into the SQUID. The voltage is produced by the SQUID output and then amplified and read out by the magnetometer’s electronics. The output voltage is measured as a function of the sample temperature and gives the changes in the sample magnetization with the temperature [13].

![Diagram](image_url)

Figure 3.4: Schematic description of (a) the SQUID detector system, (b) The sample holder part [13].

### 3.4 Resistivity

Physical Property Measurement System (PPMS) was used to investigate the AC electrical resistivity and magnetoresistance (MR), in frequency of 17 Hz, by using the resistivity option. The samples were mounted on standard PPMS sample pucks (see Figure 3.5) using four 0.05 mm thick gold wires, where two wires served as current contacts and others were attached to the samples to serve as voltage contacts. All wires were attached to the sample using 16031 Colloidal Silver paint. This work was done under the microscope.
Figure 3.5: The samples were mounted on a tape and attached into four gold wires on the resistivity puck.

3.5 Heat Capacity

The Quantum Design Physical Property Measurement System (PPMS) was used to investigate the specific heat properties for the samples $Eu_2Ir_2O_7$ and $Dy_2Ir_2O_7$ at constant pressure. The Quantum Design Heat Capacity option controls the heat that was added to the sample and was removed from it. Within the measurement, there are two periods: the heating one, which occurred by applying a known quantity of heat at constant power for a fixed time, and the cooling period that is followed the heating of the same duration. Figure 3.6 presents the attachment between the platform heater and platform thermometer to the bottom side of the sample platform. The electrical connection to the platform heater and platform thermometer is provided by small wires as shown in the schematic graph. A thin layer of grease is used to mount the sample to the platform, which provides the required thermal contact to the platform [20].
Figure 3.6: A schematic view of the connection between the platform heater and platform thermometer at the bottom side of the sample [20].
Chapter 4

Experimental Observations

4.1 X-Ray Diffraction Results

The X-ray diffraction (XRD) patterns of the samples, $Eu_{2(1-x)}Dy_{2x}Ir_2O_7$ where $x = 0, 0.25, 0.50, 0.75,$ and $1$, are shown in Figure 4.2. All samples’ patterns indicate a cubic pyrochlore structure with the space group $Fd\bar{3}m$ (No 227). The structure parameters for all the samples are indicated in Table 4.1 with $x = 0.339$ (see Table 1.1). The $R$ factors of the refinements $R_{wp}$ (weighted profile residual), $R_e$ (expected value of $R_{wp}$), and $S = R_{wp}/R_e$ (analytical accuracy) are presented in Table 4.1, pointing out that the qualities of the fits are good. For the refined data of all the samples, please refer to the Appendix A.

The $Dy_2Ir_2O_7$ sample possesses small amount of secondary phases of $Dy_2O_3$ and $Eu_2O_3$, which might accrue because of using the same Pt foil to wrapped the sample throughout the synthesises, (see Figure 4.1). However, it does not affect much on the physical properties that expected.

The peaks shift to a higher angle with increasing $x$, which is shown in the inset in

<table>
<thead>
<tr>
<th>Sample</th>
<th>$R_{wp}$</th>
<th>$R_e$</th>
<th>$S$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Eu_2Ir_2O_7$</td>
<td>10.26</td>
<td>11.05</td>
<td>0.9283</td>
</tr>
<tr>
<td>$Eu_{1.5}Dy_{0.5}Ir_2O_7$</td>
<td>9.09</td>
<td>9.59</td>
<td>0.9475</td>
</tr>
<tr>
<td>$EuDyIr_2O_7$</td>
<td>9.65</td>
<td>10.08</td>
<td>0.9564</td>
</tr>
<tr>
<td>$Eu_{0.5}Dy_{1.5}Ir_2O_7$</td>
<td>8.48</td>
<td>9.29</td>
<td>0.9128</td>
</tr>
<tr>
<td>$Dy_2Ir_2O_7$</td>
<td>8.36</td>
<td>9.02</td>
<td>0.9258</td>
</tr>
</tbody>
</table>

Table 4.1: The final $R$ factors for $Eu_{2(1-x)}Dy_{2x}Ir_2O_7$ ($x = 0, 0.25, 0.50, 0.75,$ and $1$) and $S$ values of the refinements.
Figure 4.1: The x-ray diffraction pattern of $Dy_2Ir_2O_7$ sample. The secondary phases of $Eu_2O_3$ and $Dy_2O_3$ are labeled with the colors black and blue, respectively.

Figure 4.2. From the Bragg equation 3.1, if the peaks shift to higher angle, that indicates a change in the lattice parameters (see Table 4.2). As a result, a smaller unit cell occurs with increasing $x$, which is viewed in Figure 4.3.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Lattice parameter ($\bar{A}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Eu_2Ir_2O_7$</td>
<td>10.28</td>
</tr>
<tr>
<td>$Eu_{1.5}Dy_{0.5}Ir_2O_7$</td>
<td>10.27</td>
</tr>
<tr>
<td>$EuDyIr_2O_7$</td>
<td>10.24</td>
</tr>
<tr>
<td>$Eu_{0.5}Dy_{1.5}Ir_2O_7$</td>
<td>10.22</td>
</tr>
<tr>
<td>$Dy_2Ir_2O_7$</td>
<td>10.20</td>
</tr>
</tbody>
</table>

Table 4.2: The cubic lattice parameters for $Eu_{2(1-x)}Dy_{2x}Ir_2O_7$ ($x = 0, 0.25, 0.50, 0.75,$ and 1).
Figure 4.2: The x-ray diffraction pattern of $Eu_{2(x-1)}Dy_2Ir_2O_7$ ($x = 0, 0.25, 0.50, 0.75, \text{ and } 1$) samples. The inset indicates the shift of the (1240) reflection with substitution.

Figure 4.3: The changes of the cubic lattice parameter as a function of $x$ concentration.
4.2 Magnetization Results

The temperature dependence of the magnetization for $Eu_2Ir_2O_7$ was measured under zero field-cooled (ZFC) and field-cooled (FC) conditions in a magnetic field of 1000 Oe. The magnetic susceptibility ($\chi$) in Figure 4.4 (a) above $T_{MI}$ shows a weak temperature dependence, which is generated by the $Eu$ ions. The ZFC and FC magnetic susceptibility split from each other at the metal-insulator transition temperature ($T_1$) 119 K. The reason of this splitting is because in ZFC magnetization measurement, there is no applied magnetic field during cooling, so the amount of magnetization is lower comparing with the FC magnetization measurement [23].

In order to calculate the effective magnetic moment for $Eu^{3+}$ ions, a fitting was done in a range above the $T_{MI}$ for $\chi^{-1}$ (mol/emu) versus T (K). From this fitting, we obtained the Curie constant $C = 7.95$ emu K/mol $\pm 0.02$ giving an effective moment $\mu_{\text{eff}} = 5.6 \mu_B \pm 0.01$, which is much larger than expected for $Eu^{3+}$ ($\mu_{Eu^{3+}} = 3.4 \mu_B$). Also we obtained a negative Curie-Weiss temperature $\theta_{cw} = -287 K \pm 0.9$ indicating an antiferromagnetic spin exchange interaction. All plots and fitting were performed in Origin 2018 software.

An alternative method, which takes into consideration Van Vleck paramagnetic susceptibility, was used by taking the Van Vleck contribution from Ishikawa et al. calculations [24]. At a certain range of temperature between 125 K to 240 K and after subtracting the Van Vleck contribution ($\chi_{vv}$) from the observed susceptibility ($\chi_{obs}$), the magnetic susceptibility is following the Curie-Weiss (CW) law (see Figure 4.4 (b) and the inset in the Figure 4.5). This temperature dependence is due to the low energy excited states, which leads the $Eu^{3+}$ to be non-zero. From this fitting, we obtained $C = 2.93$ emu K/mol $\pm 0.09$ and $\mu_{\text{eff}} = 3.41 \mu_B \pm 0.16$, which is in good agreement with studies having been done in [14] and [25]. The range from 240 K up to room temperature are strongly suggesting that this contribution comes from $\frac{2}{3}$ Pauli paramagnetism, which consider the contribution from $t_{2g}$ band from the spin $\frac{1}{2}$ in $Ir^{4+}$ ions (see Figure 4.5) [3] [24]. There is a slight upturn below 10 K, which has been reported also by Matsuhira et
Figure 4.4: (a) Magnetic susceptibility $\chi$ of $Eu_2Ir_2O_7$ in a magnetic field of 1000 Oe. The black and red lines represent the ZFC and FC, respectively. The blue line indicates the Van Vleck contribution estimated by Ishikawa et al. [24] calculation, the green line indicates the susceptibility without Van Vleck contribution. (b) Reciprocal magnetic susceptibility $\chi^{-1}$ of $Eu_2Ir_2O_7$.

al. [3] and in a single crystal in Ishikawa et al. studies [24], might be attributed to a magnetic impurity.

Figure 4.6 shows the magnetic susceptibility $\chi$ of $Eu_{1.5}Dy_{0.5}Ir_2O_7$ in a magnetic field of 1000 Oe. It is clear that the compound exhibit paramagnetic behavior, as the inset indicates a magnetic transition at 121 K. Due to the presence of $Eu^{3+}$ ions, the Van Vleck paramagnetic susceptibility should be considered as well. The calculation data for Van Vleck magnetization was fitted to my data results and subtracted from the total magnetic susceptibility in order to calculate the effective magnetic moment contributed from $Eu^{3+}$ and $Dy^{3+}$ ions. Above the transition temperature $T_{MI}$, the $\chi^{-1}$ of $Eu_{1.5}Dy_{0.5}Ir_2O_7$ is well followed by the CW law (see Figure 4.7). Note that in this case magnetization is contributed from 75% $Eu^{3+}$ and 25% $Dy^{3+}$, so 75% form $\chi_{VV}$ was
Figure 4.5: The contribution obtained after subtracting Van Vleck contribution from the observed susceptibility of $Eu_2Ir_2O_7$ in a magnetic field of 1000 Oe at range above $T_{MI}$. The inset shows the fitting for the Curie-Weiss law.
Figure 4.6: Magnetic susceptibility $\chi$ of $Eu_{1.5}Dy_{0.5}Ir_2O_7$ in a magnetic field of 1000 Oe. The inset shows a magnetization obtained after subtracting Van Vleck contribution from the observed susceptibility at range above the transition temperature.

Calculated and subtracted from $\chi_{obs}$. Curie constant in this case is $C = 9.27$ emu K/mol $\pm 0.01$, $\theta_{cw} = -22K \pm 0.4$, and $\mu_{eff} = 6.07\mu_B \pm 0.01$.

Next, the $\chi$ of $EuDyIr_2O_7$ exhibits a magnetic transition temperature at 123 K from antiferromagnetic to paramagnetic state. Figure 4.8 shows the paramagnetic behavior of this sample under ZFC and FC measurement with an applied magnetic field of 1000 Oe. Same procedure as in $x = 0.25$ sample was done in order to calculate the effective magnetic moment. Figure 4.9 shows the reciprocal magnetic susceptibility $\chi^{-1}$ of $EuDyIr_2O_7$, the inset indicates the fitting of CW law. In this case the $\mu_{eff}$ contributed from 50% from $Eu^{3+}$ and $Dy^{3+}$ as well. In this sample $C = 16.89$ emu K/mol $\pm 0.03$, $\theta_{cw} = -27K \pm 0.5$, and $\mu_{eff} = 8.19\mu_B \pm 0.01$. 
Figure 4.7: Reciprocal magnetic susceptibility $\chi^{-1}$ of $Eu_{1.5}Dy_{0.5}Ir_2O_7$. The inset shows the CW law fitting.

Figure 4.8: Magnetic susceptibility $\chi$ of $EuDyIr_2O_7$ in a magnetic field of 1000 Oe. The inset represents a magnetization obtained after subtracting Van Vleck contribution from the observed susceptibility at range above the transition temperature $T_{MI}$. 
Figure 4.9: Reciprocal magnetic susceptibility $\chi^{-1}$ of $EuDyIr_2O_7$. The inset shows the CW law fitting.

Next, the $\chi$ of $Eu_{0.5}Dy_{1.5}Ir_2O_7$ under ZFC and FC measurement with an applied magnetic field of 1000 Oe, indicates a magnetic transition temperature at $T_{MI} = 125$ K, which indicates a transition from antiferromagnetic to paramagnetic states (see Figure 4.10). Note that the Van Vleck contribution in this case is much smaller comparable with the previous samples, which yield to $\frac{1}{4}$ Van Vleck susceptibility due to the 25% $Eu^{3+}$ ions. A linear fit is applied on $\chi^{-1}$ versus temperature at range above $T_{MI}$, (see the inset in Figure 4.11), yielding $C = 24.59$ emu K/mol $\pm 0.03$, $\theta_{cw} = -16K \pm 0.3$, and $\mu_{\text{eff}} = 9.88 \mu_B \pm 0.01$. 
Figure 4.10: Magnetic susceptibility $\chi$ of $Eu_{0.5}Dy_{1.5}Ir_2O_7$ sample in a magnetic field of 1000 Oe. The inset shows a magnetization obtained after subtracting Van Vleck contribution from the observed susceptibility at range above the transition temperature.
In Figure 4.12 the behavior of the magnetization for $Dy_2Ir_2O_7$ sample is paramagnetic and exhibits a magnetic transition from antiferromagnetic to paramagnetic state at $T_{MI} = 133$ K. The enlarged Figure 4.13 presents the transition temperature, which agrees well with previously reported $T_{MI}$ transition measurement at 134 K [3]. Also a broad peak was observed at low temperature around 4.5 K, which also has been reported by Matsuhira et al. [26]. However their peak is much broader than this result. The reason might be related to the impurity or the synthesis technique for preparing the sample. In Matsuhira et al. [26], the percentage added $IrO_2$, as described in chapter 3, was 10% rather than 3% in this work. The effective magnetic moment was calculated by fitting the data above $T_{MI}$ to CW law (see Figure 4.14, the value of the constant C and $\mu_{\text{eff}}$ respectively are 25.36 emu K/mol $\pm 0.3$ and 10.04 $\mu_B$ $\pm 0.1$, and the CW temperature $\theta_{cw} = -20K \pm 3$. 

Figure 4.11: Reciprocal magnetic susceptibility $\chi^{-1}$ of $Eu_{0.5}Dy_{1.5}Ir_2O_7$. The inset shows the CW law fitting.
Figure 4.12: Magnetic susceptibility $\chi$ of $Dy_2Ir_2O_7$ in an applied magnetic field of 50 Oe. The inset shows the magnetic susceptibility behavior at low temperature around 4.5 K.
Figure 4.13: An enlarged view of the metallic-insulator transition temperature $T_{MI}$ for $Dy_2Ir_2O_7$ sample.
Table 4.3: The transition temperature $T_{MI}$, the effective magnetic moment $\mu_{\text{eff}}$, the Curie constant $C$, and the Curie-Weiss temperature $\theta_{\text{CW}}$ for samples $Eu_{2(1-x)}Dy_xIr_2O_7$ ($x = 0, 0.25, 0.50, 0.75, \text{and} 1$).

<table>
<thead>
<tr>
<th>Sample</th>
<th>$T_{MI} (K)$</th>
<th>$\mu_{\text{eff}}(\mu_B)$</th>
<th>$C$ (emu K/mol)</th>
<th>$\theta_{\text{CW}}$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Eu_2Ir_2O_7$</td>
<td>119</td>
<td>3.41</td>
<td>2.93</td>
<td>-287</td>
</tr>
<tr>
<td>$Eu_{1.5}Dy_{0.5}Ir_2O_7$</td>
<td>121</td>
<td>6.07</td>
<td>9.27</td>
<td>-22</td>
</tr>
<tr>
<td>$EuDyIr_2O_7$</td>
<td>123</td>
<td>8.19</td>
<td>16.89</td>
<td>-27</td>
</tr>
<tr>
<td>$Eu_{0.5}Dy_{1.5}Ir_2O_7$</td>
<td>125</td>
<td>9.88</td>
<td>24.59</td>
<td>-16</td>
</tr>
<tr>
<td>$Dy_2Ir_2O_7$</td>
<td>133</td>
<td>10.04</td>
<td>25.36</td>
<td>-20</td>
</tr>
</tbody>
</table>

Figure 4.14: Reciprocal magnetic susceptibility $\chi^{-1}$ of $Dy_2Ir_2O_7$. The inset shows the CW law fitting.

The transition temperature, the effective magnetic moment, the Curie constant, and the Curie-Weiss temperature for all samples are recorded in Table 4.3.

### 4.3 Electrical Resistivity Results

Figure 4.15 (a)-(e) show the temperature dependence of the electrical resistivity for
all the samples \((Eu_{(1-x)}Dy_x)_{2}Ir_{2}O_7\), where \(x = 0, 0.25, 0.50, 0.75, \text{ and } 1\). The resistivity \(\rho(T)\) at 298 K for the parents \(Eu_{2}Ir_{2}O_7\), \(Dy_{2}Ir_{2}O_7\) are \(3.98 \times 10^{-2}\) and \(1.25 \times 10^{-1}\) Ω·cm respectively, which are in good agreements with the results found in Subramanian and Sleight reports [8]. The parents and doped samples exhibit metallic-insulator transitions (MIT) at 119 K, 121 K, 123 K, 125 K, and 133 K for \(x = 0, 0.25, 0.50, 0.75, \text{ and } 1\), respectively (see Figure 4.16 (a)). The derivative of the resistivity, which has been done by using Origin 2018 software, indicates systematic increasing of the MIT. As the temperature increases to room temperature the slope decrease from \(x = 0\) to \(x = 1\) samples, see Figure 4.16 (b).

However, the \(x = 0\) sample exhibits more than one transition as seen in Figure 4.17. It has been also observed in specific heat measurements, this will be discussed later. DC resistivity was measured by standard four-probe method in order to assist our result obtained from AC resistivity represented in Figure 4.17 (a). Figure 4.17 (b) shows the first MIT temperature at 119 K, which indicates a transition from insulator to semiconductor state. The second transition at 143 K indicates a transition from semiconductor to semimetallic state as shown in (c). Additional scattering appear in the resistivity result above 200 K, which cause the resistivity reach its maximum at about 250 K. It might be another transition to a semiconductor state.

A previous study [24], focused on the strong sensitivity to the off-stoichiometry on \(Eu_{2}Ir_{2}O_7\) single crystals, was compared to our sample. It is found that the \(Eu_{2}Ir_{2}O_7\) sample chemical formula can be written as \(Eu_{2(1-x)}Ir_{2(1+x)}O_{(7+\delta)}\), where \(x = 0.026\) in our case. The charge gap, using the equation 2.15, was calculated in a range from 40 to 60 K for all samples presents in Table 4.4, the fitted data for all samples are shown in Figure 4.15 (f). \(Eu_{2}Ir_{2}O_7\) sample possess a narrow gap semiconductor, which increasing through out the substitution until the \(Dy_{2}Ir_{2}O_7\) sample. In a range above 250 K for the \(Eu_{2}Ir_{2}O_7\) sample, the value of the energy gap is 7.7 meV. Thereby, the energy gap changes with increasing the temperature and the material is less conductor at this
Figure 4.15: (a)-(e) Electrical resistivity of $Eu_{2(1-x)}Dy_{2x}Ir_2O_7$ samples for $x=0$, 0.25, 0.50, 0.75, and 1 Dysprosium, respectively. (f) Linear fitting for the activation energy calculation of all samples.
Figure 4.16: (a) The derivative of electrical resistivity for all the samples starts from the top with $x = 0$ and end with $x = 1$. (b) Enlarged view of electrical resistivity in range 100 K to room temperature for all the samples.
Figure 4.17: (a) Temperature dependence of the DC resistivity for $Eu_2Ir_2O_7$ sample. (b)-(d) Enlarged view to show the transitions at 119, 143, and 200 K, respectively.
Table 4.4: The activation energy in the insulator state for $Eu_{2(1-x)}Dy_xIr_2O_7$, $(x = 0, 0.25, 0.50, 0.75,$ and $1)$ samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_a$(meV)</th>
<th>Error(±)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Eu_2Ir_2O_7$</td>
<td>4.9</td>
<td>0.6</td>
</tr>
<tr>
<td>$Eu_{1.5}Dy_{0.5}Ir_2O_7$</td>
<td>7.6</td>
<td>1.2</td>
</tr>
<tr>
<td>$EuDyIr_2O_7$</td>
<td>10.5</td>
<td>1.4</td>
</tr>
<tr>
<td>$Eu_{0.5}Dy_{1.5}Ir_2O_7$</td>
<td>9.3</td>
<td>1.3</td>
</tr>
<tr>
<td>$Dy_2Ir_2O_7$</td>
<td>11.1</td>
<td>1.6</td>
</tr>
</tbody>
</table>

4.4 Magnetoresistance Results

The network of corner shared tetrahedron in pyrochlore iridates is occupied by $Ir^{4+}$ spins, which give rise to strong geometric frustration and unusual fluctuations. The 5$d$ electrons can produce novel electronic properties such as Giant Magnetoresistance (GMR) as a function of a magnetic field [27]. Figure 4.18 shows the magnetic field dependence of the magnetoresistance ($\Delta \rho/\rho_0$) for the $Eu_2Ir_2O_7$ sample, which indicates a small negative MR effect up to 9 T at 5 K that may be related to a transition. And shows small positive MR effects at 20 K, 50 K, 140 K, and 300 K.

In Figure 4.19 the change in the magnetoresistance for data at 5 K, 20 K, 50 K, and 300 K is more obvious. The positive MR effect, by using the equation 2.16, at 20 K, 50 K, and 300 K reaches 0.22, 0.12, and 1.4 %, respectively. The small negative MR also reaches 1.4 % at 5 K, this negative effect might be due to the magnetic impurity that observed earlier in the magnetic susceptibility.

Figure 4.20 shows the magnetoresistance $\Delta \rho/\rho_0$ for $Eu_{1.5}Dy_{0.5}Ir_2O_7$ sample, and how the behavior of MR changes with different set of temperatures. At 5 K, 20 K, 140 K and 50 K negative MR effects were observed that reach 17, 3.5, 0.17 %, respectively. This effect might due to the suppression of carrier scattering because of the spin-flip configuration with increasing field. At room temperature the MR posses a small positive effect for the
Figure 4.18: The magnetic field dependence of the magnetoresistance $\frac{\Delta \rho}{\rho_0}$ for $Eu_2Ir_2O_7$ at 5 K, 20 K, 50 K, 140 K, and 300 K.

Figure 4.19: The field dependence of magnetoresistance for $Eu_2Ir_2O_7$ at 5 K, 20 K, 50 K, 140 K, and 300 K.
metallic state, which indicates more carrier scattering due to the spin fluctuation with increasing field.

Figures 4.21, 4.22 and 4.23 show the field dependence of the magnetoresistance for the $Eu_{1.5}Dy_{0.5}Ir_2O_7$, $Eu_{0.5}Dy_{1.5}Ir_2O_7$, and $Dy_2Ir_2O_7$ samples, respectively. The same systematic changes on the MR effects were observed as in the $Eu_{1.5}Dy_{0.5}Ir_2O_7$ sample. MR effect was observed at 5 K for the $Dy_2Ir_2O_7$ sample reaches 62 %, and the MR effect at 20 K reaches 14 %. For $R_2Ir_2O_7$ the negative MR effect is related to the magnetic moment that contributed from the R site. Based on Matsuhira et al. [27] study, the negative MR effect is might related into the $d - f$ interaction. This interaction arises from the $5d^5$ electrons from the $Ir$ with the $4f$ electrons from the $Eu$ and $Dy$.

If the magnetic structure of the $R$ moments reach to finite moments with applying magnetic field, the moments begin to align in the magnetic field direction against the internal field produced by $d - f$ interaction. Thus, the disorder in the magnetic structure
Figure 4.21: \( \frac{\Delta \rho}{\rho_0} \) for \( EuDyIr_2O_7 \) at 5 K, 20 K, 50 K, 140 K and, 300 K.

of the \( R \) moments is suppressed by applying the magnetic field. As a result, and because of this fluctuation on the internal field at the \( Ir \) sites, the MR effect might be negative.

The following Table 4.5 shows the MR effects for all the samples at low temperatures, at 5 and 20 K.

<table>
<thead>
<tr>
<th>Sample</th>
<th>MR effect at 5 K(%)</th>
<th>Error (±)</th>
<th>MR effect at 20 K(%)</th>
<th>Error (±)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Eu_2Ir_2O_7 )</td>
<td>1.4</td>
<td>0.0002</td>
<td>0.22</td>
<td>0.002</td>
</tr>
<tr>
<td>( Eu_{1.5}D_{y0.5}Ir_2O_7 )</td>
<td>17</td>
<td>0.08</td>
<td>3.5</td>
<td>0.003</td>
</tr>
<tr>
<td>( EuDyIr_2O_7 )</td>
<td>23</td>
<td>0.02</td>
<td>2.6</td>
<td>0.0004</td>
</tr>
<tr>
<td>( Eu_{0.5}D_{y1.5}Ir_2O_7 )</td>
<td>58</td>
<td>0.2</td>
<td>9.2</td>
<td>0.003</td>
</tr>
<tr>
<td>( Dy_2Ir_2O_7 )</td>
<td>62</td>
<td>0.01</td>
<td>14</td>
<td>0.0003</td>
</tr>
</tbody>
</table>

Table 4.5: The magnetoresistance effect for \( Eu_{2(1-x)}D_{y2x}Ir_2O_7 \) \( (x = 0, 0.25, 0.50, 0.75, \) and 1) samples at low temperatures, 5 K and 20 K.
Figure 4.22: $\frac{\Delta \rho}{\rho_0}$ for $Eu_{0.5}Dy_{1.5}Ir_2O_7$ at 5 K, 20 K, 50 K, and 300 K.

Figure 4.23: $\frac{\Delta \rho}{\rho_0}$ for $Dy_2Ir_2O_7$ at 5 K, 20 K, 50 K, 140 K, and 300 K.
4.5 Heat Capacity Results

Figure 4.24 shows the temperature dependence of the specific heat divided by temperature $C_p/T$ for the sample $Eu_2Ir_2O_7$. Three anomalies are observed at $T_1 = 119$ K, $T_2 = 143$ K, and $T_3 = 200$ K, which confirm the transitions on the electrical resistivity measurements. The anomaly at $T_1$ is caused by the transition from insulator to semiconductor state, and the anomalies at $T_2$ and $T_3$ providing evidence of semiconductor-semimetallic and semimetallic-semiconductor transitions, respectively. To estimate the electronic specific heat coefficient $\gamma$, a linear fit $C_p/T = \gamma + \beta T^2$ is applied at low temperatures for $C_p/T$ vs $T^2$ this yielding $\gamma = 24.7$ mJ/mol·K$^2$ $\pm 2 \times 10^{-4}$. Also, from the slope and by using $\Theta_D = (12\pi^4 R_g n/5\beta)^{1/3}$ (see equation 2.22), we obtained the Debye temperature $\Theta_D = 451$ K $\pm 2$, where $R_g$ is the gas constant 8.314 J/mol·K and $n = 11$. These results are in good agreement with a previous study on a single crystal by Ishikawa et al. [24] ($\gamma = 24.9$ mJ/mol·K$^2$ and $\Theta_D = 472$ K). The $\gamma$ value of the $Eu_2Ir_2O_7$ is much larger than the $\gamma$ value of the copper Cu ($\gamma = 0.69$ mJ/mol·K$^2$ [28]), which means $Eu_2Ir_2O_7$ sample does absorb more heat per mole than Cu.

To estimate the magnitude and the shape of the specific heat anomalies, a smooth polynomial was fitted to the data outside the region of the anomalies (see the line fitted in Figure 4.24). A range of temperature $78K < T < 124K$ was taken to integrate $\Delta C_p/T$ with respect to $T$. The integration was done for both, the anomaly and the polynomial fitting. After subtracting the polynomial fitting integration from the anomaly integration, this yields the entropy $\Delta S = 1.51$ J/mol·K at 119 K. This result is in good agreement with $\Delta S = 1.4$ J/mol·K which is obtained from a previous study by Matsuhiroa et al. [3]. For the second anomaly at 143 K, the range of temperature 131 K to 144 K was taken to calculate the change in entropy. For the transitions at 143 K and 200 K and at ranges $131K < T < 144K$ and $195K < T < 206K$, respectively, the integrations were done and subtracted. The entropy at these anomalies are $\Delta S = 0.35$ J/mol·K and 0.06 J/mol·K, respectively.
Figure 4.24: $C_p/T$ versus temperature for $Eu_2Ir_2O_7$ sample indicating the transitions at 119 K, 143 K, and 200 K. The solid black line is the fitted polynomial. 
Inset: Linear fit at low temperatures in order to calculate the electronic specific heat coefficient $\gamma$ and the Debye temperature $\Theta_D$.

The $Ir$ ions in $Eu_2Ir_2O_7$ possess an oxidation state 4+, which has one electron in $t_{2g}$ band. By using the Hund’s rule, the spin $s$ is equal to 1. If the transition is accompanied by magnetic ordering, then the entropy of Ir ions are expected to result $2R \ln(2s + 1) = 11.5$ J/mol·K. This is clearly much larger than the value obtained of 1.5 J/mol·K and this gives a suggestion that the transition does not involve long-range magnetic ordering, at least at the localized moments, might be due to the frustration.

Figure 4.25 shows the temperature dependence of the specific heat divided by temperature $C_p/T$ versus $T$ for the sample $Dy_2Ir_2O_7$. An upturn observed below 25 K, which is attributed to the tail of a Schottky anomaly due to the crystal electric field (CEF) ground state doublet that is almost degenerate. The Schottky anomaly is an effect observed in solids where the specific heat has an anomaly at low temperatures [16]. If the temperature approaches the difference between the energy levels, it is possible to
thermally excite transitions between two states of the system [16]. This upturn from the specific heat measurement at low temperatures was also observed in the $Sm_2Ir_2O_7$ sample by Matsuhira et al. [3]. Previous studies focused on specific heat of $Dy_2Ir_2O_7$ sample at low temperature from 20 K down to 1 K, while in this study the temperature was down to 2.7 K. There is a slightly different behaviour around 4 K, see the inset Figure 4.25, which is recorded on magnetic susceptibility earlier in this chapter. Matsuhira et al. [26] have observed a broad peak at 2.5 K and no sharp anomaly was found at 4.5 K. Furthermore, Yanagishima et al. [29] have observed a sharp peak at 1.2 K. However, the origins of these anomalies have not yet been found.

At higher temperatures, a sharp anomaly is observed at 133 K, which confirms the metal-insulator transition. In order to estimate the entropy of this anomaly, a polynomial fitting was done on the data from 25 K up to room temperature and without the peak range. Then an integration was done on both peak ranges from 86 K to 138 K as well as the same range for the polynomial fitting. After removing the background integration, it yields for the entropy at 133 K, $\Delta S = 0.95 \text{ J/mol-K}$. The expected entropy is $2R \ln(2s+1) = 11.5 \text{ J/mol-K}$ as mentioned above, which is much larger than 0.95 J/mol-K. A short range ordering might occur in this sample as well because of the frustration.
Figure 4.25: $C_p/T$ versus temperature for $Dy_2Ir_2O_7$ sample indicating the transition at 133 K. The solid black line is the fitted polynomial, and the inset shows change the behavior at low temperature.
Chapter 5

Conclusions

Five samples were synthesized, two parents $Eu_2Ir_2O_7$, $Dy_2Ir_2O_7$ from pyrochlore iradates and the substituting $Eu^{3+}$ for $Dy^{3+}$. The polycrystalline samples $Eu_{2(1-x)}Dy_xIr_2O_7$ ($x = 0, 0.25, 0.50, 0.75, \text{ and } 1$) were prepared through the solid state reaction method. The reflection peaks in XRD patterns indicate a systematic decreasing in the cubic lattice parameter with the space group $Fd3m$ (No 227). The results from the magnetic susceptibility indicate a systematic increasing at the splitting temperature point with the substitution. It shows that with increasing the substituting $Eu^{3+}$ by $Dy^{3+}$ the transition temperature at 119 K increases. The effective magnetic moments for all the samples are increasing while increasing the value of $x$, starting with $3.4 \mu_B$ and ending with $10.04 \mu_B$ values. Furthermore, theses transitions 119 K, 121 K, 123 K, 125K, and 133 K are observed in the AC resistivity providing metal-insulator transitions. The $T_{MI}$ transitions comes from 5d electrons. The magnetoresistance effect MR of the samples was investigated at different temperatures. For $x = 0.25, 0.50, 0.75, \text{ and } 1$ sample negative MR effect presents before the $T_{MI}$ and continues up to 215 K. A positive MR effect is observed at room temperature. In $x = 0$ sample, all the MR exhibit positive effects except at 5 K, which is negative being caused by a small amount of magnetic impurity. Specific heat measurement was used to investigate the transitions at the parents’ samples, which confirm the three transitions in $Eu_2Ir_2O_7$ sample and the transition on $Dy_2Ir_2O_7$ sample.

In the future, it is recommendable to work on the X-ray diffraction measurement as a function of temperature in $Eu_{2(1-x)}Dy_xIr_2O_7$ pyrochlore. This will provide more
information about the MIT and the crystal-structure phase transition.
Appendix A

X-Ray Diffraction patterns

Figures A.1, A.2, A.3, A.4, and A.5 show the XRD patterns for the $Eu_{2(1-x)}Dy_xIr_2O_7$ samples ($x = 0, 0.25, 0.50, 0.75,$ and 1), respectively. The residual data indicates that the fitting for all the samples converges well.
Figure A.1: X-ray diffraction refined data for $\text{Eu}_2\text{Ir}_2\text{O}_7$ sample.

Figure A.2: X-ray diffraction refined data for $\text{Eu}_{1.5}\text{Dy}_{0.5}\text{Ir}_2\text{O}_7$ sample.
Figure A.3: X-ray diffraction refined data for $EuDYIr_2O_7$.

Figure A.4: X-ray diffraction refined data for $Eu_{0.5}Dy_{1.5}Ir_2O_7$. 
Figure A.5: X-ray diffraction refined data for $Dy_2Ir_2O_7$. 
Bibliography


