

Exploring structure-property relationships in layered perovskite iridates

A thesis

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Doctor of Philosophy

by:

Charu Garg

Registration ID: 20132016



Department of Physics

INDIAN INSTITUTE OF SCIENCE EDUCATION AND RESEARCH

PUNE - 411008, India

Certificate

Certified that the work incorporated in the thesis entitled “**Exploring structure-property relationships in layered perovskite iridates**” submitted by **Charu Garg** was carried out by the candidate, under my supervision. The work presented here or any part of it has not been included in any other thesis submitted previously for the award of any degree or diploma from any other university or institution.



Date: December 28, 2020

(Supervisor)

Declaration

I hereby certify that the work which is being presented in the thesis entitled “**Exploring structure-property relationships in layered perovskite iridates**” in partial fulfillment of the requirements for the award of the Degree of **Doctor of Philosophy** and submitted in the Department of Physics of the Indian Institute of Science Education and Research, Pune is an authentic record of my own work carried out during a period from August, 2013 to December, 2020 under the supervision of Dr. Sunil Nair, Associate Professor, Department of Physics, Indian Institute of Science Education and Research, Pune. The matter presented in the thesis has not been submitted by me for the award of any other degree of this or any other institute.

A handwritten signature in black ink, appearing to read 'Charu', followed by a horizontal line and a period.

Date: December 28, 2020

(Charu Garg)

Abstract

Thesis title: *Exploring structure property relationships in layered perovskite iridates*

Geometrically frustrated perovskites- where the symmetry of the underlying crystal structure inhibits long range magnetic ordering- is the most prominent structural class, where the search for non-trivial spin structures appears to bear fruit. The physics of these systems is especially rich, when they comprise of $4d$ and $5d$ transition metals, where the large spin-orbit coupling is known to be responsible for the stabilization of a number of novel magnetic and electronic ground states. During the course of this thesis, we have investigated a number of Iridium based systems crystallizing in the triple perovskite structure of the form $\text{Ba}_3\text{M}\text{Ir}_2\text{O}_9$ ($\text{M}=\text{Co}, \text{Ni}$ or Na) with the aim of understanding their structure-property relationships. Our results show that the ground state of these systems are remarkably diverse, with factors like multiple valence states of M and Ir , Jahn-Teller distortion, anti-symmetric Dzyaloshinskii-Moriya interaction, multiple super-exchange pathways, crystal field splitting, spin-orbit coupling, and hybridization being the driving forces. For instance, $\text{Ba}_3\text{CoIr}_2\text{O}_9$ and $\text{Ba}_3\text{NiIr}_2\text{O}_9$, both stabilize in a hexagonal symmetry at room temperature with Ir in the +5 oxidation state. $\text{Ba}_3\text{CoIr}_2\text{O}_9$ exhibits a magneto-structural transition to a monoclinic phase at 107K - the highest known amongst all the triple perovskite iridates - and transforms to a monoclinic phase with even lower symmetry at 70K, with both these phases coexisting down to the lowest measured temperatures. Interestingly, $\text{Ba}_3\text{NiIr}_2\text{O}_9$ retains the hexagonal symmetry down to the lowest measured temperature and exhibits two magnetic transitions at 106K and 6K that are attributed to antiferromagnetic ordering. $\text{Ba}_3\text{NaIr}_2\text{O}_9$, with a mixed valent state of Ir^{+5} and Ir^{+6} , is a geometrically frustrated antiferromagnet exhibiting a co-operative paramagnetism starting at around 200K. On reducing the temperature, one

observes a strain induced structural transition to an orthorhombic phase nucleating at 40K. Below 6K, it exhibits glassy dynamics, originating as a consequence of mixed interactions and phase coexistence. The results obtained would add significantly to our current understanding of the structure-property relationships in this class of materials with strong spin-orbit coupling. We have also explored a hitherto unreported family of Sr based triple perovskites where we have successfully found many new potential quantum spin liquid candidates.

In addition, we have also investigated the possible existence of a multiglass state- where both the magnetic and polar orders are frozen- in the doped quantum paraelectric SrTiO_3 and KTaO_3 . The feasibility of multiglass state in doped quantum paraelectrics has been under debate for a long time. By doping of magnetic transition metals (Mn, Fe, Co, or Ni), we observe that the doped quantum paraelectric appear to remain intrinsically paramagnetic down to the lowest measured temperatures, settling the conflict and thus providing a concrete proof on the absence of multiglass state in these doped quantum paraelectrics.

Synopsis

A relatively recent addition to the area of strongly correlated oxides pertains to the influence of spin orbit coupling on the low temperature magnetic and electronic ground states of these materials. Given the inherently extended nature of the orbits, these $4d$ or $5d$ systems were expected to be relatively simple metals, devoid of strong correlation effects. Contrary to this, it is now known that the competing crystal field splitting, spin-orbit coupling, on-site Coulomb interaction, and Hund's coupling lead to many novel electronic and magnetic states ranging from Mott insulators to conventional long range magnetic order to quantum spin and orbital liquids in the iridates. Not surprisingly, the $5d$ Iridates are proving to be an extremely fertile playground for uncovering spin-orbital driven phenomena. The possible utility of a different structural class has recently come to the fore - the triple perovskite iridates of the form $A_3M\text{Ir}_2\text{O}_9$ which exhibits a remarkable diversity in their structural and magnetic ground states. In the quest for finding new functionalities driven by large spin-orbit coupling, we have investigated in detail the structure-property relationships of hitherto new triple perovskite iridates where interesting ground state are observed as a convolution of exotic crystallographic phases and spin-phonon dynamics. The thesis explores a range of empirical trends in $\text{Ba}_3M\text{Ir}_2\text{O}_9$ ($M=\text{Co}, \text{Ni}, \text{Na}$) series of compounds and we demonstrate that observed unique crystallographic and magnetic phases is the resultant of the complex coupling between various competing interactions - crystal field splitting energy (CFE), spin-orbit coupling (SO), Hubbard interaction (U), electron's kinetic energy (t) and Hund's coupling (J_H), unique to this class of materials.

The thesis is divided into the following sections:

Chapter 1: This chapter provides an introduction to the crystal structure of triple

perovskite oxides. We also introduce various interaction energies that dictate the ground state dynamics of these systems. The motivation of the thesis is discussed and a concise review of the current understanding of these family of compounds is present with a focus on a few celebrated examples, demonstrating the rich physics of these systems with novel magnetic and electronic ground states.

Chapter 2: A brief introduction to the various characterization tools is presented in this chapter with details on method used for synthesis, measurement tools and techniques, and software/programs employed for data evaluation and processing.

Chapter 3: This chapter presents a comprehensive investigation of the triple perovskite iridate $\text{Ba}_3\text{CoIr}_2\text{O}_9$. Stabilizing in the hexagonal $P6_3/mmc$ symmetry at room temperature, this system transforms to a monoclinic $C2/c$ symmetry at the magnetic phase transition. On further reduction in temperature, the system partially distorts to an even lower symmetry ($P2/c$), with both these structurally disparate phases coexisting down to the lowest measured temperatures. The magnetic structure as determined from neutron diffraction data indicates a weakly canted antiferromagnetic structure, which is also supported by first-principles calculations. Theory indicates that the Ir^{5+} carries a finite magnetic moment, which is also consistent with the neutron data. This suggests that the putative $J = 0$ state is avoided. Measurements of heat capacity, electrical resistance noise and dielectric susceptibility all point towards the stabilization of a highly correlated ground state in the $\text{Ba}_3\text{CoIr}_2\text{O}_9$ system.

Chapter 4: The strongly coupled spin-phonon dynamics brings about an anomalous thermal expansion in the layered $3d$ - $5d$ based triple perovskite iridate $\text{Ba}_3\text{CoIr}_2\text{O}_9$ and this is investigated using high resolution synchrotron diffraction. We observe negative thermal expansion in the phase co-existence regime below 70K, which appears to be intimately connected to the temperature driven relative fractions of these monoclinic phases. The significant NTE observed in this system could be driven by magnetic ex-

change striction, and is of relevance to a number of systems with pronounced spin orbit interactions.

Chapter 5: After a rigorous investigation of $3d-5d$ based triple perovskite $\text{Ba}_3\text{CoIr}_2\text{O}_9$, an analogous $3d$ based iridate $\text{Ba}_3\text{NiIr}_2\text{O}_9$ is studied with the aim to understand the affect of site manipulation. Unlike $\text{Ba}_3\text{CoIr}_2\text{O}_9$, $\text{Ba}_3\text{NiIr}_2\text{O}_9$ retains its overall hexagonal symmetry down to the lowest measured temperature. The two magnetic transitions at 106K and 6K are attributed to antiferromagnetic ordering. Both the compounds belong to the same structural class, yet, the filled and partially filled t_{2g} shells in Nickel and Cobalt respectively drives different ground state in these compounds. Our study demonstrate that the choice of M site cation plays a crucial role in understanding the structural trends and magnetic ordering as it affects one of the physically significant parameters, the bond distances and bond linkages in these compounds tampering the resultant orbital overlap, energy splitting and exchange mechanisms.

Chapter 6: In this chapter we present the study of structure-property relationship in the mixed valent geometrically frustrated triple perovskite iridate $\text{Ba}_3\text{NaIr}_2\text{O}_9$. In contrast to what is expected from purely structural considerations, this system stabilizes in a high symmetry hexagonal symmetry at room temperatures. On reducing the temperature, the lattice prefers to be strained rather than distort to a low symmetry phase, as is the norm in this family of materials. Though a low symmetry orthorhombic phase is finally nucleated below 50 K, this conversion is only partial and the high symmetry hexagonal structure remains the dominant one down to the lowest measured temperatures. Magnetic measurements indicate an extended co-operative paramagnetic regime, which finally freezes to a cluster glass-like phase at very low temperatures, as is also evidenced from specific heat measurement. This makes an interesting addition to the family of triple perovskite iridates which exhibit material sensitive physical properties arising as a consequence of a number of competing energy scales.

Chapter 7 (Appendix 1): In addition to the Barium based triple perovskites, we also synthesized a number of new Sr based triple perovskites in order to study their structure-property relationships and examine the possibility of the purported $J=0$ state in them. A number of new compounds of the form $\text{Sr}_3\text{MM}'_2\text{O}_9$ ($\text{M}=\text{Cu,Na,Bi,Zn,Co,Na,Ni}$; $\text{M}'=\text{Ir,Sb}$) were synthesized for the first time. All these compounds exhibit diverse structural and magnetic ground states where we were able to stabilise crystal structures ranging from monoclinic to tetragonal to orthorhombic to hexagonal symmetry. Interestingly, we were able to find many new potential candidates that did not order down to the lowest measured temperatures, manifested in our magnetization, neutron diffraction and heat capacity results. We are currently in the process of analysing the obtained results.

Chapter 8 (Appendix 2): We critically investigate the purported existence of a multi-glass state in the most celebrated quantum paraelectrics hosts SrTiO_3 and KTaO_3 doped with magnetic 3d transition metals. We observe that the transition metals have limited solubility in these hosts, and that traces of impurity magnetic oxides persist even in the most well processed specimens. Our dielectric measurements indicate that the polar nano-regions formed as a consequence of doping appear to lack co-operativity, and the associated relaxation process exhibits a thermally activated Arrhenius form. All these doped quantum paraelectrics exhibit a crossover from the high temperature Curie-Weiss regime to one dominated by quantum fluctuations, as evidenced by a T^2 dependence of the temperature dependent dielectric susceptibility. At lower temperatures, the dielectric susceptibility could be fit using the Barrett's formalism, indicating that the quantum-paraelectric nature of the host lattices are unaltered by the doping of magnetic transition metal oxides. The temperature dependence of the magnetic susceptibility indicate that magnetic signatures observed in few of the specimens and those features could be solely ascribed to the presence of impurity oxides corresponding to

the magnetic dopants used. Hence, the doped quantum paraelectrics appear to remain intrinsically paramagnetic down to the lowest measured temperatures, ruling out the presence of a multiglass state.

Chapter 9: This chapter presents a brief summary of the results present in the thesis.

Dedicated to
my mother
and
Ramesh Sir

Publications from the thesis work

- Evolution of the structural, magnetic and electronic properties of the triple perovskite $\text{Ba}_3\text{CoIr}_2\text{O}_9$; **Charu Garg**, Deepak Roy, Martin Lonsky, Pascal Manuel, Antonio Cervellino, Jens Müller, Mukul Kabir and Sunil Nair, *arXiv:2009.13822*, (2020), in print in the Physical Review B.
- Phase coexistence and negative thermal expansion in the triple perovskite iridate $\text{Ba}_3\text{CoIr}_2\text{O}_9$; **Charu Garg**, Antonio Cervellino, and Sunil Nair, *arXiv:2010.03940*, (2020), submitted to Physical Review Research.
- Absence of a multiglass state in some transition metal doped quantum paraelectrics; **Charu Garg**, Jitender Kumar, and Sunil Nair. *Physical Review Materials*, **2:094409**, (2018)

List of other publications

- Enhanced magnetism and time-stable remanence at the interface of hematite and carbon nanotubes; Aakanksha Kapoor, Arka Bikash Dey, **Charu Garg** and Ashna Bajpai. *Nanotechnology*, **30**, 385706 (2019)

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Chapter 1

Introduction

In this chapter, the structure property relationships of perovskites, in particular, the triple perovskites are discussed in detail. Special focus is on the iridate family and a brief introduction to the various interacting energy scales is presented, the competition between which leads to many novel structural and magnetic ground states in the family of triple perovskite iridates.

1.1 The Perovskite oxides

The perovskite structure was named after the Russian mineralogist Lev Aleksevich von Perovski [11] and has the general chemical formula ABX_3 , where X is an anion (e.g. oxygen) bonded to both the cations A and B. It is composed of a three dimensional network of regular corner-shared BX_6 octahedra. In the ideal case, the B-site cations are at the center of the octahedra with the 12-fold co-ordinated A cation located in the body center of the cube formed by eight corner-shared octahedra as shown in Fig. 1.1. Due to the extensive chemical flexibility this structure offers, one can almost span the entire periodic table just by replacing elements at A and B site. This is evident by the wide range of structural and magnetic ground states that are now known for this family

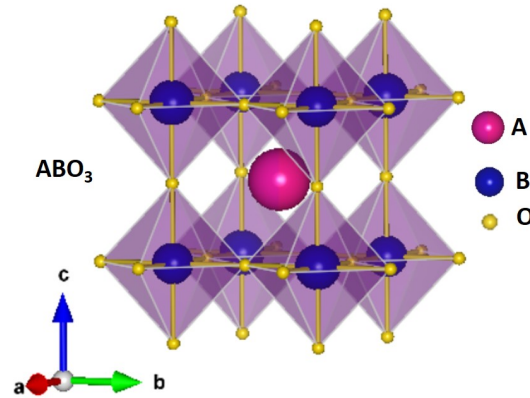


Figure 1.1: A schematic of an ideal cubic perovskite structure ABO_3 . The 12-fold coordinated A cation sits at the centre of the cube and the BX_6 octahedra sits at the corners forming a 3-dimensional network of corner-shared octahedra. The structure was drawn using Vesta [1].

of compounds [12].

The perovskite shown in Fig. 1.1 represents an ideal cubic structure. However, in real systems, slight deviations might be present in the lattice framework due to mismatch in ionic radii and that can result in distortions in the lattice. In order to account for such deformations and possibly predict the influence of A and B site ionic radii on the structure, Victor Moritz Goldschmidt introduced the concept of a tolerance limit (t_f) [13]. It is given by

$$t_f = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)}$$

where r_A, r_B and r_O are the ionic radii of A, B and O ions respectively. Relative change in the ionic radii of A and B lead to tilting and distortions of the BO_6 octahedra and the symmetry moves away from ideal cubic symmetry ($t_f=1$) to orthorhombic and hexagonal (t_f) as shown in Fig. 1.13. This additional flexibility of chemical tunability they offer makes these perovskites quite interesting, both for physicists and chemists alike. Another advantage they offer is the possibility of layering ABO_3 sheets, giving rise to double $A_2BB'O_6$ and triple perovskites $A_3BB'_2O_9$ as shown in Fig. 1.3. The layered arrangement, and the addition of one more element (B') provides a playground to explore

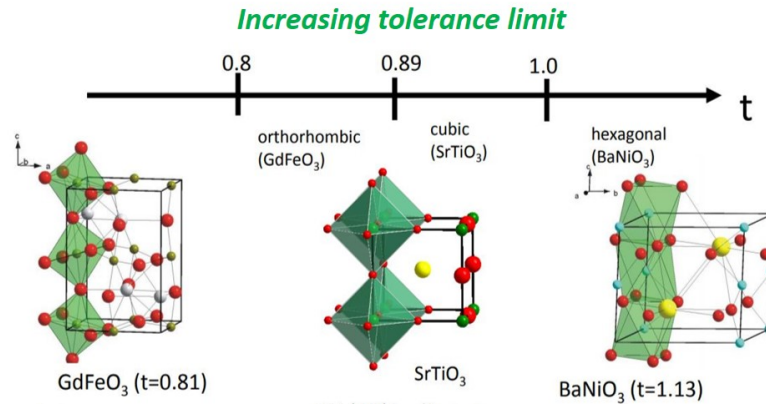


Figure 1.2: A schematic of changes in crystal structure symmetry with the variation of tolerance limit governed by ionic radii of elements A and B in ABO_3 perovskite.

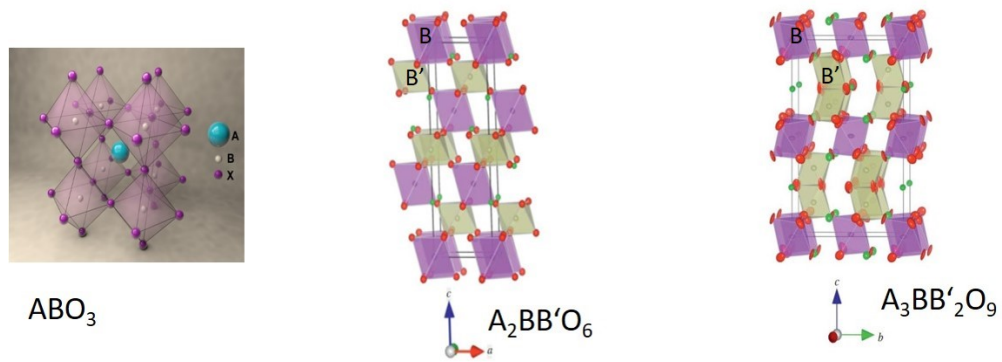


Figure 1.3: The stacking of ABO_3 (left) sheets leads to formation of double $A_2BB'O_6$ (center) and triple perovskites $A_3BB'_2O_9$ (right).

many new structural and magnetic ground states and also opens up more opportunities to study structure-property relationships. A wide range of double, triple perovskites and other layered oxides have been reported with different stacking arrangements as shown in Fig. 1.4. These perovskites can be represented by using a standard nomenclature consisting of a number and an alphabet for example, 6H, 21R etc. The number represents the count of structural layers within the unit cell and the alphabet denotes the type of stacking arrangement where R, H and C represents rhombohedral, hexagonal and cubic layers. Therefore, 6H represents a hexagonal layered stacking with 6 different layers within the unit cell. From the symmetry point of view, the building blocks of the struc-

ture are the octahedra, which although considered as rigid units, can tilt, distort or rotate in order to accommodate varying A site ions. The overall symmetry is a joint convolution of the choice of A, B, B' ions, external factors including pressure, temperature, synthesis conditions etc. The tilting of the octahedra, from the chemical and quantum perspective, alters the degree of overlap between the oxygen p and metal d orbitals at the connections between the corner and face sharing MO_6 ($\text{M}=\text{B}, \text{B}'$) octahedra in the respective perovskite framework, which brings about a significant impact on the electronic and magnetic properties of the material.

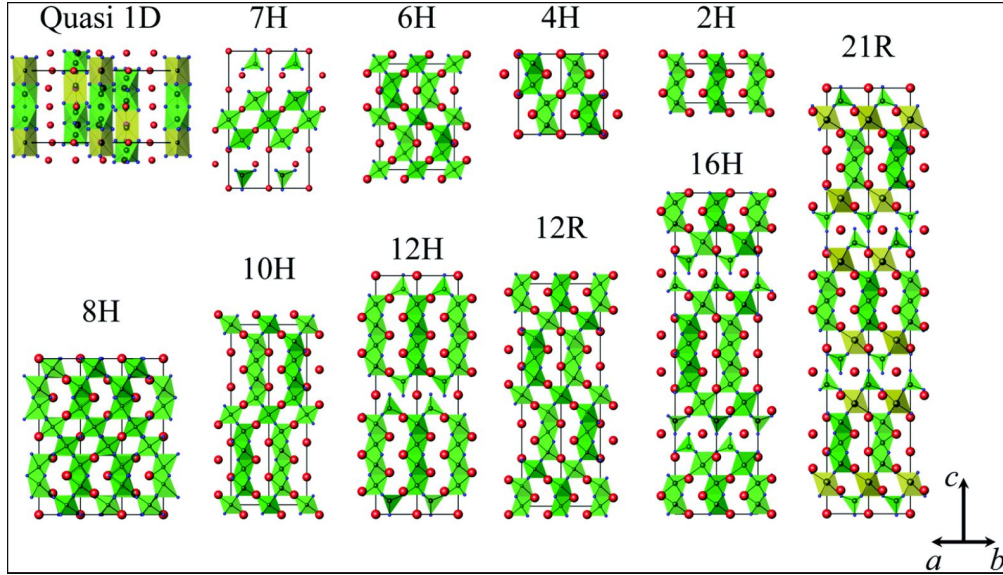


Figure 1.4: A schematic of different polytypes of layered perovskites structures is shown for various stacking arrangements. The blue and red spheres indicate oxygen and A site cation respectively. The green polyhedra are occupied by B and B' cations. [2].

1.2 $5d$ transition metal oxides

Transition metal oxides (TMO) have fascinated both the applied and basic science communities, underpinned by the enormous activity in this area [14]. Due to the extensive

chemical flexibility they offer, transition metal based perovskites and their variants have provided a fertile playground for exploring the complex interplay between the lattice, spin and orbital degrees of freedom. However, an inordinate attention has been devoted to the 3d transition metal based elements for decades. The other heavier elements 4d-5d and their respective oxides were believed to be uninteresting. As we move down the periodic table from 3d to 5d, the orbitals become more extended in space thereby increasing the electronic bandwidth. Thus, one would expect metallic and less magnetic behaviour compared to 3d counterparts. In this context, the notability of the 5d transition metal based oxides - especially the iridates - have come to the fore very recently. Two distinctive families of the 5d iridates, namely, Ruddlesden-Popper series $\text{Sr}_{n+1}\text{Ir}_n\text{O}_{3n+1}$ (n represents the number of Ir-O layers in a unit cell and can take values 1, 2 etc.) and hexagonal BaIrO_3 presented the initial evidences of magnetic ordering at high temperatures, low ordering moment values, "exotic" insulating states, all in conflict to the prior understanding [15, 16]. Marked by the discovery of Mott insulator state in anti-ferromagnetic Sr_2IrO_4 [17], an appreciable interest was ignited in these heavier elements series. The empirical trends, far from the conventional wisdom obtained from 3d counterparts, led to an upsurge for the quest in understanding the unique behaviours observed. The spin orbit interaction along with competing crystal field splitting, spin-orbit coupling, on-site Coulomb interaction, and Hund's coupling lead to many novel electronic and magnetic states ranging from Mott insulators to conventional long range magnetic order to quantum spin and orbital liquids in the iridates [18]. Most of the current work in condensed matter physics caters to the study of these interactions and understanding the various ground states as a consequence of their interplay. Various factors influence the relative magnitude of each of these energy scales like the crystal geometry, nature of elements present, ligand environment, valence state, external factors like magnetic field, temperature, pressure etc. In the next section, a brief introduction

to these interactions that governs the ground state dynamics of $5d$ TMOs studied in this thesis work is presented.

1.3 Hubbard interactions

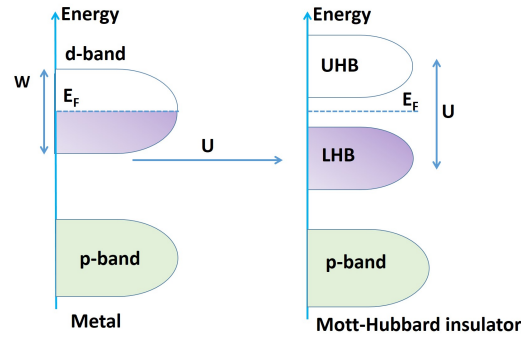


Figure 1.5: A representation for the Hubbard model for the case of half filled d band. The figure represents the d -band splitting without (left) and with (right) the consideration of electron Coulomb interaction (U). W , E_F denotes the bandwidth and Fermi energy respectively. The d band splits into lower and upper Hubbard band (LHB and UHB respectively) with the introduction of U .

N.F. Mott and R. Peierls presented an unique example, NiO, where as per band theory, the presence of partially filled d orbital should have resulted in a metallic state but contrary to this, an insulating behaviour was observed [19]. This was the first example of the failure of band theory and a possible indication of the role electron-electron correlations could play. This led Hubbard to formulate a many body Hamiltonian to describe the behaviour of such transition metal monoxides (like FeO, NiO, CoO). These systems were observed to be antiferromagnetic insulators, though they had been predicted to be metallic by band theory and tight binding model which does not take strong electron correlations into consideration [20]. The Hubbard model was a modification of the tight

binding model and is given by,

$$H_{Hubbard} = - \sum_{(i,j);\alpha} t_{ij} (c_{i\alpha}^\dagger c_{j\alpha} + c_{j\alpha}^\dagger c_{i\alpha}) + U \sum_i^n n_{i,up} n_{i,down} \quad (1.1)$$

The first term represents the kinetic term (a part of tight binding model), the hopping energy (t) associated with transfer of electrons between lattice sites i and j ; therefore favouring delocalization and the second term is the on site Coulomb interaction (U) that promotes localization. The ratio of Coulomb interaction (U) to the hopping energy (t) drives the system from metallic to insulating states. The left panel of Fig. 1.5 shows the case of a material with $U=0$ exhibiting a metallic state as per band theory. With the introduction of U , the electrons become localized and the d band splits into lower and upper Hubbard band (LHB, HUB) driving the Mott insulating state. The energy difference between U and W is referred to as the Hubbard gap. Despite its simplicity, the Hubbard model has proven to be very useful in the understanding of systems with strong correlations and to understand Mott insulators, magnetic or even superconducting behaviours.

1.4 Exchange mechanisms

The dipole-dipole interaction could not explain the magnetically ordered states at high temperatures observed in many materials [21]. It was realized by Heisenberg in 1928 that the responsible interaction is Coulomb repulsion between electrons that follows Pauli's principle, which states that no two electrons with the same spin can appear at the same location simultaneously [22]. This direct exchange mechanism requires substantial orbital overlap. In most transition metal oxides, the d orbitals are localized and the transition metal cations are separated by oxygen ions. In such cases, direct hopping between d orbitals is rare. Therefore, the magnetism of these transition metal oxides

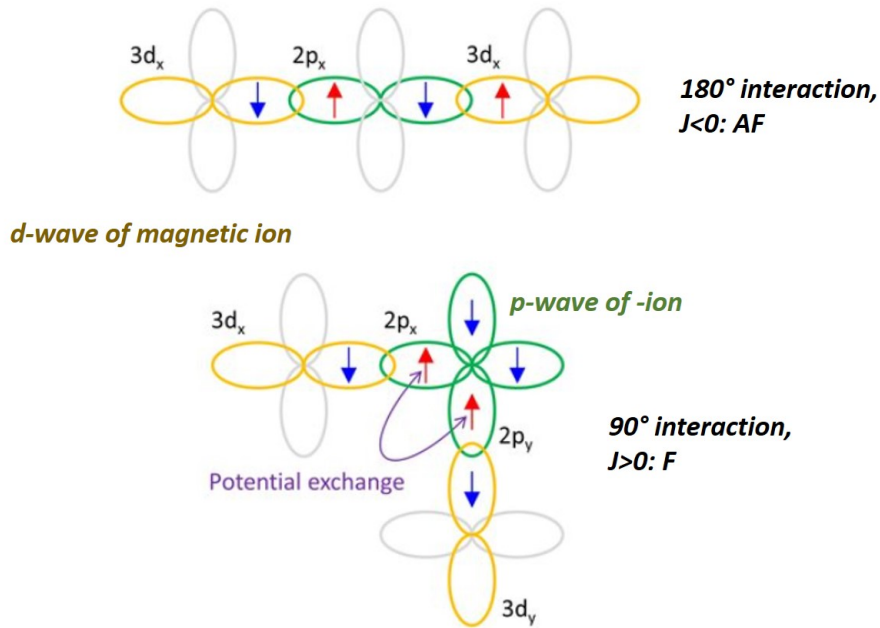


Figure 1.6: Superexchange interaction between d orbital spin of transition metal ion and p orbital of oxygen. The two possible magnetic exchanges, antiferromagnetic and ferromagnetic are shown for 180° and 90° metal ion-ligand- metal ion arrangement.

is dictated by the exchange interaction between the corner and face sharing octahedra. The exchange interaction is mediated via the intermediate p orbital of oxygen ion and is termed as double exchange or super exchange depending upon state of the cations. Superexchange interaction was first proposed by Kramer in 1934 [23] and later the details were provided by Anderson, Goodenough and Kanamori [24–26]. They proposed a set of semi-empirical rules which predict the magnitude and type of magnetic interaction based on metal ion- ligand- metal ion ($\angle MOM$) bond angle and the filling of d orbitals known as Goodenough Kanamori Anderson (GKA) rules [27]. According to these rules, a strong antiferromagnetic state is predicted for partially filled d orbitals when the $\angle MOM$ is close to 180° and a weak ferromagnetism is expected for an angle close to 90° as shown in Fig. 1.6. In case the interacting metal ions are in different valence state, the nature of magnetic interaction changes. First proposed by C. Zener [28], this phenomena known as double exchange, is similar to superexchange as described

above where both ferro and anti ferro alignment is possible between atoms of same valence states. In contrast, in double exchange, the interaction only occurs when one atom has an extra electron compared to other and always results in ferromagnetic coupling.

1.5 Crystal field splitting

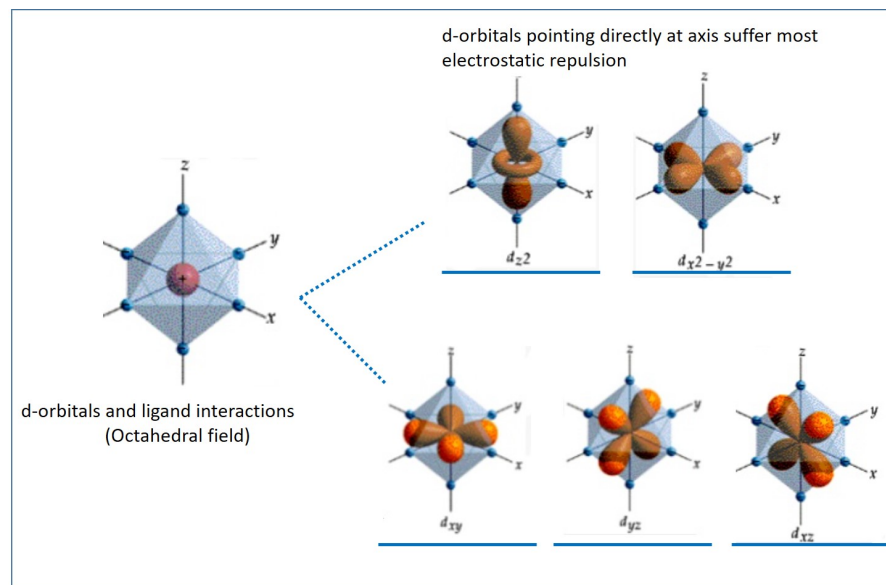


Figure 1.7: A $5d$ transition metal ion (orange) present in an octahedral environment where it is surrounded by 6 oxygen ions (blue). The right side shows the angular distribution of the d orbitals as a consequence of crystal field splitting.

An isolated ion has a spherical symmetry which gets broken when it is surrounded by a set of ligands [29]. In transition metal oxides (TMOs), this ligand is Oxygen, which act as a point charge surrounding the transition metal ion. Many TMOs are formed by corner or face sharing octahedral or tetrahedral units as shown in Fig. 1.4. The repulsion between orbital electrons of the central ion with the surrounding ion leads to splitting of the degenerate d levels. This effect is called crystal field effect and is a special case of ligand field theory developed by H. Bethe and J. H. Van Vleck [30]. The splitting of the d orbitals depends on the angular distribution of their wave function as well as the

arrangement of the surrounding oxygen ions. Fig. 1.7 shows the octahedral arrangement of oxygen around the transition metal ion (left) and the d orbital wave function (d_{xy} , d_{yz} , d_{xz} , d_{z^2} , $d_{x^2-y^2}$) on the right side. Clearly, the maximum charge density for d_{xy} , d_{yz} and d_{xz} lies in the region between the Cartesian axis while for the d_{z^2} and $d_{x^2-y^2}$ it lies along z , x and y axis. All the five orbitals are degenerate but in the presence of surrounding ion (oxygen in this case), it splits into t_{2g} (d_{xy} , d_{yz} , d_{xz}) and e_g (d_{z^2} , $d_{x^2-y^2}$) levels, opening up a gap Δ_{CFE} .

In an octahedral environment as shown in Fig. 1.7, the maximum electron repulsion between electrons will be along the Cartesian axis, therefore, the energy to put electrons in the e_g level will be higher. As a result, the electrons get confined to the t_{2g} levels. On the other hand, in the case of tetrahedral ligand arrangement, the orbitals in the t_{2g} level are closer to the oxygen environment and therefore, it lies higher in energy. If the magnitude of the crystal field splitting energy Δ is much higher (lower) compared to the Hund's exchange energy, a low (high) spin configuration is established. Therefore, not only the on-site Coulomb interactions, the surrounding environment also contributes substantially to the resultant ground state of the compound. An additional complexity arises when the splitting of these d orbitals gets tampered. This leads to interesting energy scales distribution and will be discussed in the next section.

1.6 Jahn Teller distortion

The previous case described an ideal scenario where symmetric octahedral environment split the degenerate t_{2g} levels. In most systems, due to structural transformations to lower symmetry, distortions/tilting of the polyhedra, a non-cubic crystal environment can persist. A special form of distortion, known as Jahn Teller distortion (JT) results in octahedral complexes where the two axial bonds can be shorter or longer than those of the equatorial bonds [31]. Such deformations break the degeneracy of the d orbitals.

These geometric distortions depends on the transition metal ion, its valence state, underlying crystal geometry, temperature etc. The Fig. 1.8 shows various possible scenarios of distortions in the octahedra. Depending on the axis of compression, expansion or deformation, the corresponding orbitals experience non-uniform electrostatic repulsions and as a result split into non-degenerate levels.

Although, the Jahn Teller distortions results from electron-phonon coupling and is not a spin-dependent phenomenon, it can indirectly affect the spin-dependent parameters via spin-orbit interaction. The changes in JT distortions can also result from the spin orbit coupling as a consequence of the transformation of the wavefunctions [32]

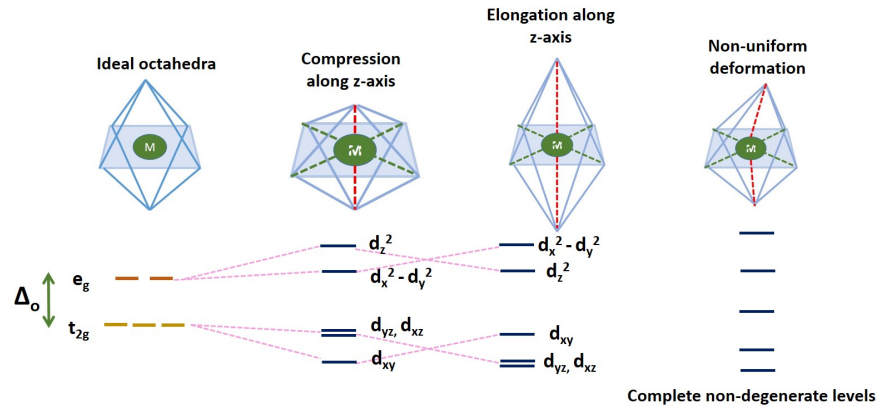


Figure 1.8: A symmetric octahedral environment splits the d orbitals into t_{2g} (d_{xy} , d_{yz} , d_{xz}) and e_g (d_{z^2} , $d_{x^2-y^2}$) orbitals. In the presence of various distortions (compression, elongation or non-uniform), there is a further loss of degeneracy called Jahn Teller distortion and almost a complete removal of degeneracy in the presence of extremely distorted octahedral environment around the transition metal ion.

1.7 Spin-orbit coupling

Spin-orbit interaction (SOI) refers to the coupling between the spin and orbital degrees of freedom, and is a relativistic effect proportional to Z^2 (Z is the atomic number). It is to be noted that many reports claim the dependence to be Z^4 [33], though this is only true

Table 1.1: Comparison between $3d$, $4d$ and $5d$ electrons

Electron type	$U(\text{eV})$	$\lambda(\text{eV})$	Spin state	Interactions	Ground state
$3d$	5-7	0.01-0.1	High	$U > CF > \lambda$	Magnetism/HTSC
$4d$	0.5-3	0.1-0.3	Low/intermediate	$U \sim CF > \lambda$	p-wave SC
$5d$	0.4-2	0.1-1	Low	$U \sim CF \sim \lambda$	$J_{eff}=1/2$ Mott state, QSL

for unscreened hydrogenic wave functions. In case of elements with large Z , the core electrons screen the nuclear charge rendering an effective Z^2 dependence [34]. The spin orbit coupling increases as we move down the periodic table from the approximate value of SOI of 0.4eV in $5d$, compared to only $\sim 20\text{meV}$ in $3d$ transition materials [35, 36]. With increase in Z , the d orbitals become more extended and, therefore, the electronic repulsion U decreases as we get closer to $4d$ and $5d$ rows in the periodic table. The Table. 1.1 lists the comparison and evolution of different energy scales as we go from $3d$ to $5d$ with a brief note of many possible ground states exhibited. In such a scenario, unlike in $3d$ materials, many energy scales like on-site Hubbard interaction (U), Hund's coupling (J_H), spin orbit coupling (λ), crystal field energy (δ) and electron's kinetic energy or hopping (t) have comparable energy scales.

As a result of the relative interaction of these competing energy scales, a plethora of interesting observations have been reported and can be represented as function of changing U/t and λ/t using a phase diagram as shown in Fig. 1.9 [3, 37]. The phase diagram is divided in 4 regions marked by the two black lines moving horizontally and vertically. These four areas represent relative weak and strong regimes for both SOI and Hubbard correlations. Simple metal or band insulator state is found for weak SOC $\frac{\lambda}{t} \ll 1$. As SOC increases, with $\frac{U}{t} \ll 1$, the conductivity decreases and a semi metal or topological insulator state can be achieved. Interesting physics occurs when SOC and U have comparable energies giving rise to exotic ground states like Axion insulator [38], spin orbit coupled Mott insulator [39], Quantum spin liquids [40, 41] etc.

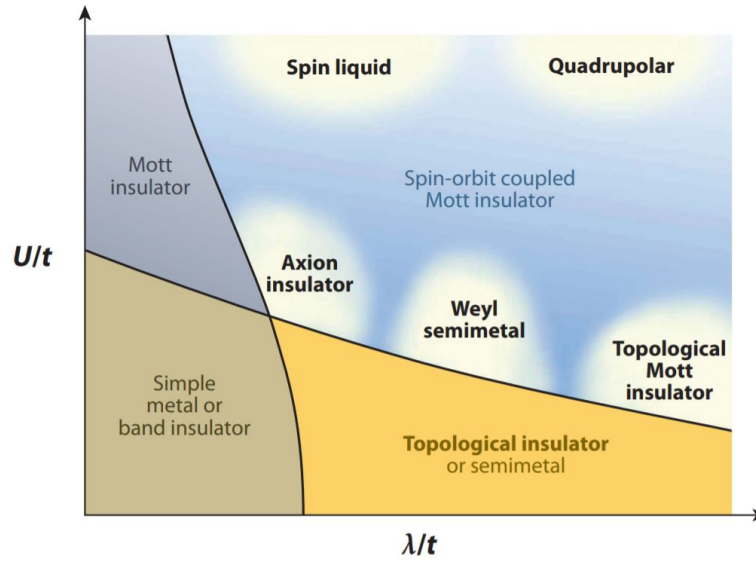


Figure 1.9: A phase diagram representing the evolution of various exotic states as a function of U/t and λ/t where U , λ and t represents onsite Coulomb interaction, spin orbit coupling and hopping energy respectively. [3]

The Hamiltonian based on above discussion can be summarized as,

$$H = \sum_{i,j;\alpha\beta} t_{ij;\alpha\beta} c_{i\alpha}^\dagger c_{j\beta} + h.c. + \lambda \sum_i L_i \cdot S_i + U \sum_{i,\alpha} n_{i,\alpha} (n_{i,\alpha} - 1) \quad (1.2)$$

where $c_{i\alpha}$ is the annihilation operator for an electron in orbit α at site i and $n_{i\alpha} = c_{i\alpha}^\dagger c_{i\alpha}$ is the corresponding occupation number, t is the hopping integral, λ is the spin orbit entanglement, U is the Hubbard interaction. A major consequence of this relativistic spin orbit interaction is the shift in the electron's energy levels as a result of interaction between electron's magnetic dipole, it's orbital motion and the electrostatic field of positively charged nucleus. The presence of spin orbit coupling, therefore, splits the degenerate t_{2g} levels into $J_{eff}=1/2$ and $J_{eff}=3/2$, the latter having lower energy. Consider the case of Ir^{4+} ($5d^5$) sitting in an octahedral environment. Due to crystal field splitting the degenerate $5d$ level splits into t_{2g} and e_g as shown in Fig. 1.10. Under the octahedral crystal field stronger than the Hund's on-site repulsion, the system prefers to stabilize in

a low spin t_{2g}^5 configuration and the e_g level lies way higher in energy and can be ignored for the time being. This should result in a metallic ground state, in stark contrast to what was observed for iridate materials. Kim et al., reported the observation of an insulating state in iridate, otherwise predicted to be metal using spin orbit coupling [15, 17]. They proposed that under the influence of spin orbit coupling, five electrons in t_{2g} are rearranged in the new J_{eff} bands due to t_{2g} splitting. The resultant spin orbit entangled state can be written as,

$$\left| \frac{1}{2}, \pm \frac{1}{2} \right\rangle = \sqrt{\frac{1}{3}} (|d_{yz}, \mp\rangle \pm i |d_{xz}, \mp\rangle \pm |d_{xy}, \pm\rangle) \quad (1.3)$$

$$\left| \frac{3}{2}, \pm \frac{3}{2} \right\rangle = \sqrt{\frac{1}{2}} (|d_{yz}, \pm\rangle \pm i |d_{xz}, \pm\rangle) \quad (1.4)$$

$$\left| \frac{3}{2}, \pm \frac{1}{2} \right\rangle = \sqrt{\frac{1}{6}} (|d_{yz}, \mp\rangle \pm i |d_{xz}, \mp\rangle - 2 |d_{xy}, \pm\rangle) \quad (1.5)$$

where $|d_{yz}, \pm\rangle$, $|d_{xy}, \pm\rangle$ and $|d_{xz}, \pm\rangle$ are the t_{2g} states and $\pm$ represent spin in up and down state respectively.

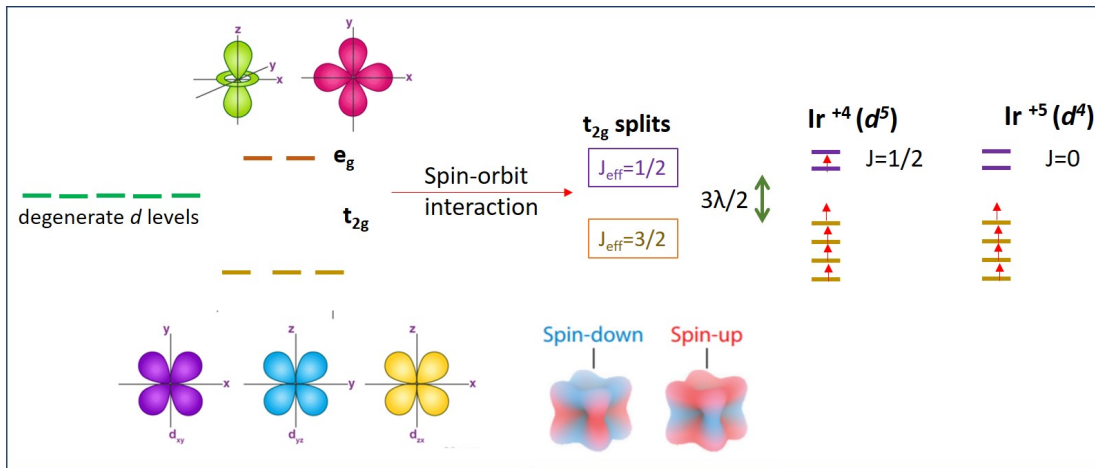


Figure 1.10: A schematic representation of splitting of d orbitals in the presence of first crystal field and spin orbit coupling. The final obtained J_{eff} states are a convolution of the the d orbitals as evident in the angular distribution of the wave function for the new J_{eff} shown in blue and red. The case study of Iridium in +5 and +4 valence state shows resultant $J=1/2$ and $J=0$ states respectively, as a consequence of spin orbit coupling.

The 4 electrons are occupied by the lower energy $J_{eff}=3/2$ band, making it completely filled and 1 electron sits in the $J_{eff}=1/2$, where the Fermi level E_F resides, making it partially filled. SOI and U together leads to opening of an energy gap δ of the Mott type in the $J_{eff}=1/2$ band substantiating the observation of the insulating state in iridates. The $J_{eff}=1/2$ Mott state served as an early manifestation of combined effect of SOC, U and CFE. Therefore, instead of spin (s) and orbital angular momentum (l) as for $3d$ transition metals, the total angular momentum (j) becomes the new quantum number for $4d$ and $5d$ series. An impressive amount of experimental and theoretical work has appeared in the recent years focusing on this correlated spin orbit coupled regime [3, 18, 36]. The most promising candidates are iridates and an increasing number of systems are now being studied to understand the interplay of SOC with various other interactions. Few famous examples includes Ruddlesden-Popper series $[Sr_{n+1}Ir_nO_{3n+1}]$ ($n=1,2,\infty$) [15, 17, 42], hexagonal insulators $[(Na/Li)_2IrO_3]$ [43–46], the family of pyrochlores ($R_2Ir_2O_7$) [47, 48] and few spinel related structures [49, 50]. Most of these systems do not fall under either a LS coupling regime or a strong spin orbit coupled jj regime but present an intermediate correlated regime between weak to strong spin-orbit coupling.

1.8 Triple perovskites oxides

After a brief introduction to the various interactions that drive novel exotic states in iridates, we can move to the main focus of the thesis: triple perovskite iridates. In this section, we introduce the crystal structure and then give a brief overview of the various interesting structural and magnetic ground states observed in this family of compounds.

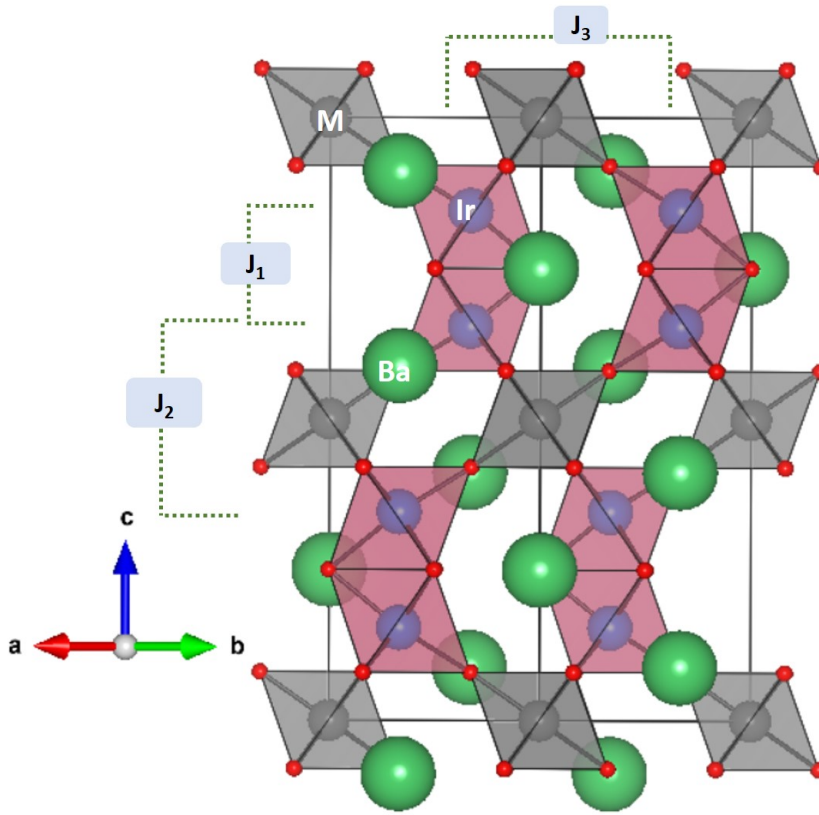


Figure 1.11: A schematic of the crystal structure of the $\text{Ba}_3\text{M Ir}_2\text{O}_9$ triple perovskite. Here, pink and grey octahedra represent iridium and cobalt sites respectively, with the Barium atoms being represented by green circles. The structure comprises of a single MO_6 octahedron sharing corners with Ir_2O_9 dimers, which in turn are formed by two face-sharing IrO_6 octahedra.

1.8.1 Crystal structure

The triple perovskite iridates of the form $\text{Ba}_3\text{M Ir}_2\text{O}_9$ (with M being an alkali, alkaline earth, or transition metal) offers significant chemical flexibility and have proven to be an extremely useful structural motif in the study of many interesting pentavalent Ir^{5+} complexes. Most of these triple perovskites are known to stabilize in the 6H-type BaTiO_3 hexagonal structure (or its distorted variants), as is depicted in Fig. 1.11 [51]. The structure consists of MO_6 octahedra (grey) connected via corners to face sharing Ir_2O_9 dimers (pink) along the crystallographic c axis. This is a layered perovskite structure with the famous 6H stacking arrangement based on the six-layer cchcch sequence.

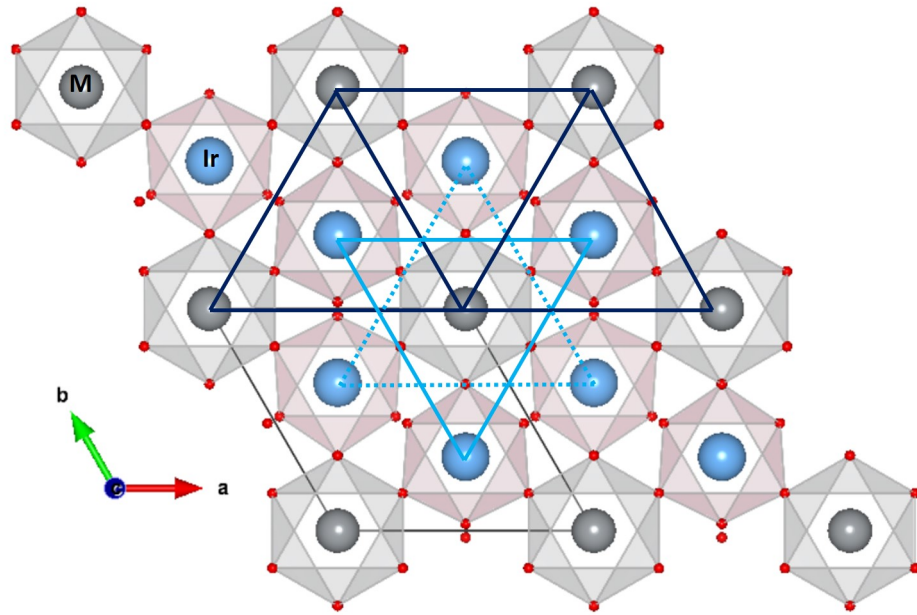


Figure 1.12: A schematic of the crystal structure of the $\text{Ba}_3M\text{Ir}_2\text{O}_9$ triple perovskite along the c -axis. The structure comprises of triangular units of MO_6 octahedron and Ir_2O_9 dimers indicate by black and blue lines respectively, stacked along the c -axis.

The Ba ion (green) sits in a 12 fold coordination site, as is the norm for the perovskites. The choice of the M site cation strongly influences the geometry of the compound leading to different chemical stabilities and magnetic ground states. A vast range of literature based on many $4d$ and a few $5d$ based triple perovskites is present where exotic ground states like charge order, spin gap, structural and magnetic phase transitions, etc. are now known [10, 52–59]. The properties of this class of materials sensitively depend on the relative strengths of competing spin-orbit coupling (SOC), electronic correlation (U), and a hybridization interaction controlled by the $M\text{-O-Ir}$ and Ir-O-Ir bond angles. The possible source of magnetic coupling are $J_{1,2,3}$ coming from the intradimer and interdimer exchange interactions as shown in Fig. 1.11. Thus, small perturbations can easily tip the balance between the competing energies and lead to different ground states. There are many possible ways to visualize the hexagonal structure, and Fig. 1.12 shows the projection of the structure along the c -axis. This structure can also be understood as

a layered arrangement of three different triangular lattices stacked on top of each other along the c -axis. The first triangular layer is formed by MO_6 octahedra as denoted by the solid black lines. The other two layers are formed by Ir_2O_9 dimers with their respective triangular motifs rotated such that they form a hexagonal arrangement as shown by blue dotted and solid lines.

A careful choice of the M site ion, magnetic and non-magnetic, appears to enable the stabilisation of these systems in a number of different Ir oxidation states and structural modifications. These systems typically stabilise in the hexagonal symmetry, or in closely related structures with varying degrees of orthorhombic or monoclinic distortions [55]. A non magnetic ion would be expected to induce 2D magnetism coming from the Ir_2O_9 dimers where dimer correlations might be observed. On the other hand, a magnetic ion would introduce a 3D connection between the layers, inducing inter dimer interactions and possible extended super exchange pathways. Needless to say, the associated changes in both the extent of crystal field splitting, the valence of the (magnetic) Ir ion, as well as the superexchange paths dramatically change their magnetostructural properties.

1.8.1.1 Geometric Frustration

In addition, these triangular motifs coupled with antiferromagnetic ordered spins are a recipe for the phenomenon of Geometric frustration. The term frustration with respect to magnetic systems was first introduced by Gerald Toulouse [60]. On a triangular lattice, antiferromagnetic arrangement of spins always leaves one spin uncompensated/ confused and hence frustrated. Geometric frustration occurs when the interaction between the magnetic degrees of freedom in the lattice are not compatible with the underlying crystal geometry. The frustration in a lattice can be quantified by using a parameter

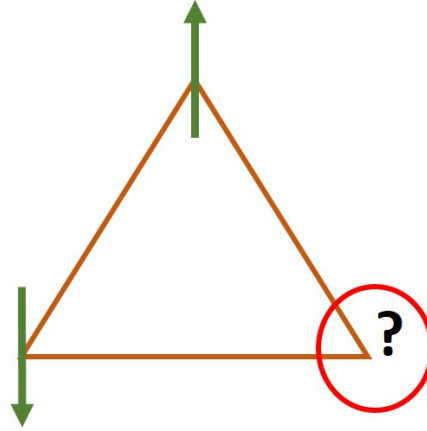


Figure 1.13: A schematic of geometrical frustration in a triangular lattice with antiferromagnetic interactions among all the Ising spins. Clearly all the spins cannot be satisfied simultaneously and leads to a frustration.

frustration index (f_c) = $\frac{|\theta_{CW}|}{T_C}$ where θ_{CW} is Curie Weiss temperature and T_C is the magnetic transition temperature. Frustration index gives the extent of suppression of the magnetic order, and $f_c > 10$ indicates a highly frustrated system. In such a scenario, the lattice geometry inhibits the formation of an ordered arrangement of spins. Therefore, this gives rise to degenerate manifold of ground states, leading to analogous of liquid and ice phases called spin liquid and spin ice states respectively [61, 62].

In 1973, Phil Anderson proposed a ground state for a system with antiferromagnetic interactions on a triangular lattice and named it Quantum spin liquids (QSLs) [63]. The QSL is obtained by a superposition of many valence bond states (VBS), a state where 2 electron spins form a spin single state due to antiferromagnetic interactions. Quantum spin liquids represent an enigmatic state of matter, where zero-point quantum fluctuations ensure that a lattice of highly interacting spins fail to exhibit any magnetic order, and continue to fluctuate (coherently) down to the lowest measured temperatures [64]. Though experimental realisations have been scarce, such quantum spin liquids are the focus of extensive investigations, both as a potential test-bed for exotic theories, as well as in the quest for futuristic applications like quantum computing using highly entan-

gled spins. Not surprisingly, geometrically frustrated systems where the symmetry of the underlying crystal structure inhibits long range magnetic ordering, is the single most prominent structural class, where the search for elusive quantum spin liquids appears to bear fruit. A celebrated example is the case of the Kagome lattice antiferromagnet $\text{ZnCu}_3(\text{OD})_6\text{C}_{12}$ [65], which does not order down to low temperatures and was also seen to exhibit signatures of fractionalised spin excitations. This physics of these systems is especially rich when they comprise of $4d$ and $5d$ transition metals, with the large spin-orbit coupling being known to be responsible for the stabilisation of novel magnetic and electronic ground states. Examples include the quasi- 2 dimensional RuCl_3 [66] and the hyperKagome $\text{Na}_4\text{Ir}_3\text{O}_8$ [50]. The family of triple perovskites, $\text{Ba}_3\text{M}\text{Ir}_2\text{O}_9$ have recently been identified as a geometrically frustrated systems and have shown potential to host a quantum spin liquid state. Recent addition to this class from the iridate family is the spin orbit liquid state in $\text{Ba}_3\text{ZnIr}_2\text{O}_9$ [67] and $\text{Sr}_3\text{CuSb}_2\text{O}_9$ [68].

1.8.1.2 RUM- Rigid Unit Modes

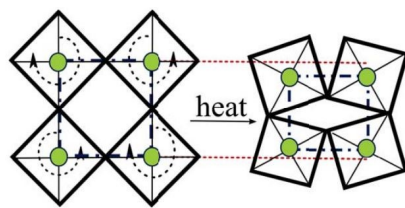


Figure 1.14: A schematic representation where the presence of transverse thermal vibrations or rigid unit modes can lead to negative thermal expansion in a material.

Further, the geometry of this compound allows for interesting modes of transverse vibrations, underpinned by the open framework network due to corner and face sharing octahedra. Consider a structure that can be described as a 3-D network of polyhedral units. The Rigid Unit Modes or RUMs, are defined as the set of lattice vibrations which

allows the polyhedra to move, translate or rotate without distorting the polyhedral units. Since they involve negligible stretching of bonds, they are associated with very low energies and frequencies. A major contribution of RUMs was in the understanding of displacive phase transition [69]. In many of these materials, negative thermal expansion (NTE) has been explained using the theory of rigid unit modes RUMs whereby the contraction of the material is driven by soft vibrations of approximately rigid polyhedral units [70]. With increasing temperature, the amplitudes of these vibrations increase and all units are drawn closer together through an effect known as the tension mechanism [71]. Active modes that drive NTE have negative Grüneisen parameters [72], which quantify how mode frequencies change with cell volume and, thereby, the contribution of each mode to the overall thermal expansion or contraction.

1.8.2 Negative thermal expansion (NTE)

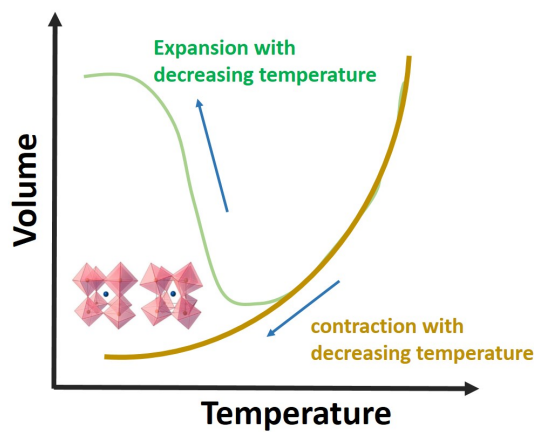


Figure 1.15: The yellow line represents the thermal expansion curve in a material where the volume decreases with lowering temperature. The green curve represents negative thermal expansion where the upturn in volume on lowering temperature indicates expansion in material on cooling as shown by the octahedral schematic in the inset.

Negative thermal expansion (NTE) refers to the non generic behaviour where the solid expands on cooling, rather than contract as observed for many materials. The well

known example of NTE is water at 0~4C [73]. The most important physical processes that cause NTE can be broadly labelled under RUMs and phase transitions [74]. As shown in Fig. 1.15, for a compound it is expected that the volume reduces as a function of decreasing temperature (yellow curve), on the contrary, many materials are now known where increase in volume is seen with lowering temperature (green). The most celebrated material exhibiting NTE is zirconium tungstate ZrW_2O_8 [75]. The Zr-O-W bridging oxygen groups are the source of the negative thermal expansion in this material. A systematic change in these bond angles, corresponding to a coupled twisting of polyhedra could give rise to the volume NTE observable by X-ray diffraction. For a more sophisticated understanding of this mechanism, a rigid unit mode (RUM) can be expressed as following: The WO_4 tetrahedra and ZrO_6 octahedra are considered to be rigid on the relative energy scale of all other deformations of the ZrW_2O_8 structure. Then in a dynamic situation the tetrahedra/octahedra will undergo continuous rotary oscillation backwards and forwards due to the propagating RUM phonons, with no distortions of the tetrahedra/octahedra themselves, thereby resulting in NTE. This compound contracts continuously over the entire temperature range of 0.3 to 1050 K and degrades beyond this temperature. The study of oxide NTE materials has focused mainly on materials that fall into the following five major families: AM_2O_7 (A= Si, Ti, Ge, Zr, Nb, Mo, Sn, Hf, W, Re, Pb, Ce, Th, U or Pu; M= P, V, As), AM_2O_8 (A= Zr; M= W, Mo), $\text{A}_2\text{M}_3\text{O}_{12}$ (A= most cations that can accept octahedral coordination; M= W, Mo), AO_2 networks or framework silicates/zeolite (A= Si, Al, P) and the AMO_5 networks (A= V, Nb, Mo, Sb, Ta and W; M= P, V, As and Mo) [74, 76–82]. There are some general structural features that can be associated with these compounds, which include

- 1) strongly bonded polyhedra/octahedra linked in three dimensions,
- 2) open and flexible structures, and
- 3) ferromagnetic or ferroelectric microdomains.

Thus the linkages and rotations of the polyhedral/octahedral network is likely to accommodate transverse vibrational modes, which can lead to a significant negative contribution to the thermal expansion if the Grüneisen parameters are large enough [72]. Therefore, the key ingredient to observe NTE can be summarized as:

1. The presence of soft phonon modes that drive contraction (have negative Grüneisen parameters [72])
2. Anisotropic elastic compliance that predisposes the material to the deformations required for NTE along a specific axis.

1.8.3 Magnetism in triple perovskites iridates

It is now known that the spin orbit interaction along with competing energy scales, like the electronic Coulomb repulsion, can drive novel ground states in iridates. Further, the physics dramatically depends on the electronic configurations of the partially filled t_{2g} orbital that leads to different magnetic ground states. Due to the effect of strong spin orbit coupling, the threefold degenerate t_{2g} levels split up into $j_{\text{eff}} = 3/2$ quartet and the $j_{\text{eff}} = 1/2$ doublet leading to non-trivial magnetic ground states. The most common configurations d^1 and d^5 in transition metal compounds are very well studied within this picture and leads to the $j_{\text{eff}} = 3/2$ and $1/2$ states, respectively [15, 17, 83–86]. The other configuration with d^2 filling leads to non-Kramers $j_{\text{eff}} = 2$ ground state [87, 88], however, a trivial spin-only $S = 3/2$ state emerges for d^3 filling in a cubic environment as spin-orbit coupling gets quenched [89]. Within the same description a special case arises for d^4 configuration. When the spin orbit coupling dominates over the Hund's coupling, the d^4 configuration with 4 electrons completely fills the $j_{\text{eff}} = 3/2$ quadruplets and as a consequence of this, there is no local moment description for this particular state. The effective spin-orbit coupling lifts this degeneracy, ultimately favouring a trivial $j_{\text{eff}} = 0$ state. Moreover, in the limit when the Hund's coupling dominates over the spin-orbit

coupling, the d^4 electrons are distributed over the three-fold degenerate t_{2g} states leading to a spin $S=1$ solution. Though this may seem like the only possible ground state, novel magnetism is often observed in the compounds with d^4 electrons in both 4d and 5d transition metals like tetravalent Ru^{4+} and pentavalent Ir^{5+} ions [67,90–94].

Investigation on the microscopic origin of this deviation has lead to many possible explanations, some of which remain contested:

1. the gapped singlet-triplet excitonic magnetism, which can be further stabilized by the reduction in excitation energy in non-cubic crystal field [90,95]
2. mixing of $t_{2g} - e_g$ orbitals [96]
3. disorder [97,98]
4. mixing of the $j_{\text{eff}} = 3/2$ and $1/2$ states [99]

In addition, a rich phase diagram for the quantum phase transition from the expected nonmagnetic insulator to novel magnetic state as a function of spin-orbit coupling, Hund's coupling and on-site Coulomb interaction was predicted [100].

Few triple perovskites are now known, where Ir being the only magnetic ion, the primary contribution to magnetization comes from the multiple superexchange paths available to the Ir ions, with octahedral distortions and direct Ir-Ir exchange adding to its complexity. For example, $\text{Ba}_3\text{ZnIr}_2\text{O}_9$ was reported to exhibit a spin-orbital liquid state, with an effective moment of about $0.26 \mu_B/\text{Ir site}$ [67]. The closely related $\text{Ba}_3\text{CdIr}_2\text{O}_9$ [101] and $\text{Ba}_3\text{MgIr}_2\text{O}_9$ [9] were also seen to exhibit no long range magnetic order down to the lowest measured temperatures. On the other hand, $\text{Ba}_3\text{CaIr}_2\text{O}_9$ and $\text{Ba}_3\text{SrIr}_2\text{O}_9$ systems were observed to exhibit weak-dimer-like, and ferromagnetic-like features in magnetic susceptibility respectively, though these transitions could not be identified in heat capacity measurements [9]. The $\text{Ba}_3\text{BiIr}_2\text{O}_9$ system crystallises in a monoclinic distorted structure and exhibits a giant magnetoelastic transition which is the largest reported amongst all 5d oxides [102]. Therefore, as a consequence of change of M site

Table 1.2: Literature survey of triple perovskite iridates of the form $\text{Ba}_3\text{M}\text{Ir}_2\text{O}_9$

Compound name	Crystal symmetry	Ionic radii of M ($\text{\AA}$)	Ir valence state	Magnetic ground state
$\text{Ba}_3\text{ZnIr}_2\text{O}_9$	$P6_3/\text{mmc}$	0.74	+5	close realization of $J_{eff}=0$ state [67]
$\text{Ba}_3\text{MgIr}_2\text{O}_9$	$P6_3/\text{mmc}$	0.72	+5	antiferromagnetic exchange [9]
$\text{Ba}_3\text{CaIr}_2\text{O}_9$	$C2/c$	1.00	+5	weak dimer interaction [9]
$\text{Ba}_3\text{SrIr}_2\text{O}_9$	$C2/c$	1.18	+5	ferromagnetic interactions [9]
$\text{Ba}_3\text{LiIr}_2\text{O}_9$	$P6_3/\text{mmc}$	0.76	+5.5	AFM ordering with $T_N=75\text{K}$ [52]
$\text{Ba}_3\text{BiIr}_2\text{O}_9$	$C2/c$	0.895	+4.5	Spin gap opening at 75K [53]
$\text{Ba}_3\text{NdIr}_2\text{O}_9$	$C2/c$	0.983	+4.5	Ferromagnet, $T_C=17.6\text{K}$ [58]
$\text{Ba}_3\text{YIr}_2\text{O}_9$	$AP:P6_3/\text{mmc}$	0.9	+4.5	anti-ferromagnet, $T_N=4.0\text{K}$ [57, 106]
$\text{Ba}_3\text{CaIr}_2\text{O}_9$	$C2/c$	0.9	+5	non magnetic state, Kotani theory [10]
$\text{Ba}_3\text{CdIr}_2\text{O}_9$	$C2/c$	0.95	+5	no ordering down to 2K [101]

ion, such wide range of ground states are possible, yet, it is to be noted that in all these systems, Ir_2O_9 dimers are connected via a magnetically inert MO_6 octahedra. The other end of the spectra is where the M site is magnetic and Ir is replaced by a non magnetic ion. For instance, it has been reported that the $\text{Ba}_3\text{CuSb}_2\text{O}_9$ system exhibits short range spin-orbital order, with the honeycomb lattice of Cu^{2+} ions exhibiting a broad spectrum of spin-dimer like excitations within a new quantum state in which spins and orbitals are entangled [103–105]. Hence, insertion of a magnetically active ion at this site would add to the complexity of these triple perovskites, providing additional superexchange paths which would be expected to modify the magnetic ground state and possibly promote long range magnetic order. The Table. 1.2 presents a brief summary of the various reports on iridium based triple perovskites, presenting a glimpse of the plethora of novel states exhibited by these systems and therefore continue to captivate many researchers.

1.9 Motivation of the thesis

The primary focus of this thesis is to study the structure-property relation of the triple perovskite iridates. These systems have gained considerable attention after the report of putative $J=0$ state in $\text{Ba}_3\text{ZnIr}_2\text{O}_9$. Interestingly, many complex scenarios happens when

presence of non-cubic crystal field leads to mixing of $J_{eff}=3/2$ and $J_{eff}=1/2$ states and results in a qualitatively different picture. This thesis explores various ground states that are a convolution of interesting spin-phonon dynamics. The resultant unique crystallographic and magnetic phases reveal the complex coupling between various competing interactions (crystal field splitting, spin-orbit coupling, on-site Coulomb interaction, and Hund's coupling), which under a small perturbation, lead to many novel electronic and magnetic states ranging from Mott insulators to conventional long range magnetic order to quantum spin and orbital liquids in the iridates. Therefore, this lattice geometry, in addition to the various coexisting energy scales with comparable spin orbit coupling offers many complex and interesting ground state scenarios. We have explored these triple perovskite structures by varying the element at the M site with various magnetic ions and alkali metal with the hope to bring an important addition to the investigation of these classes of strongly correlated materials which are characterised by large spin-orbit coupling.

Chapter 2

Experimental techniques and methodology

This chapter presents a brief introduction to the methods used for synthesis, characterization tools and techniques, and the software employed for the detailed analysis.

2.1 Structural and compositional characterization

2.1.1 Synthesis of materials

Solid state synthesis has been used to make polycrystalline compounds mentioned in this thesis. High purity oxides typically (99.99%) in the form of carbonates and oxides were used for the synthesis. Few reagents which were extremely sensitive to air and moisture, were preheated before weighing. Preheating was performed at $\sim 250^{\circ}\text{C}$ after which the re-agents were immediately transferred to the anti-chamber of the glove box and stoichiometric amounts were then mixed. All the precursors were ground thoroughly for hours in acetone before providing the first heat treatment. The sample in the powder or pellet form was transferred to an alumina crucible and placed in the furnace.

The compounds were subjected to the following sintering profile.

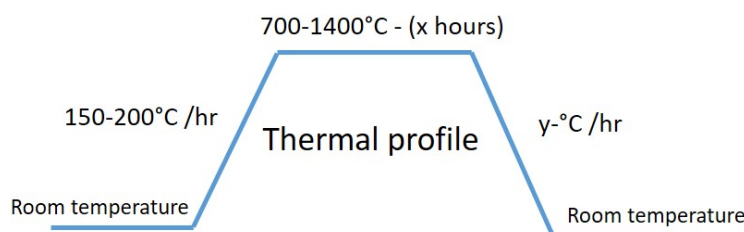


Figure 2.1: A schematic of the thermal profile used to synthesize the iridates described in this thesis. The starting material is ground well in mortar and pestle and transferred to a crucible. The sample is then subjected to heat treatment in high temperature furnaces (x hours). The heating and cooling rates (y) are predefined. Different environments are used as per sample requirement.

Various profiles with different ramp rates, temperatures, environments (oxygen, air flow), and waiting times were used, based on the requirement of the reaction. This process was repeated till the desired phase was formed and no further changes in the X-ray diffraction pattern were observed. Details of temperature profile, environmental conditions and specific reagents will be mentioned in the corresponding chapters.

2.1.2 Powder X-ray diffraction

Powder X-ray diffraction is one of the most powerful tools to decipher the crystal structure of a system. In addition to the information regarding the crystal structure (lattice parameters, atomic positions, particle size etc.), one can extract information about strain, disorder, thermal expansion, phase dynamics, anti-site disorder etc. from the diffraction data. Therefore, although being a macroscopic measurement, it provides a microscopic view of the crystal structure. It is based on the principle of Bragg's law [107, 108].

$$2d_{hkl}\sin\theta = n\lambda$$

where d_{hkl} denotes the interplanar spacing, h, k, l represents Miller indices unique to each lattice plane, λ is the wavelength of the incident X-ray radiation, θ is the angle of

the incident beam and n is the order of reflection. Consider a crystal as a periodic arrangement of atoms as shown in Fig 2.2. If the X-ray radiation is incident on the atomic planes such that the wavelength of the incident beam is of the order of the atomic spacing between planes, each crystal plane scatters radiations and as a result of constructive interference, we get the Bragg diffraction pattern. X-rays are generated in a cathode

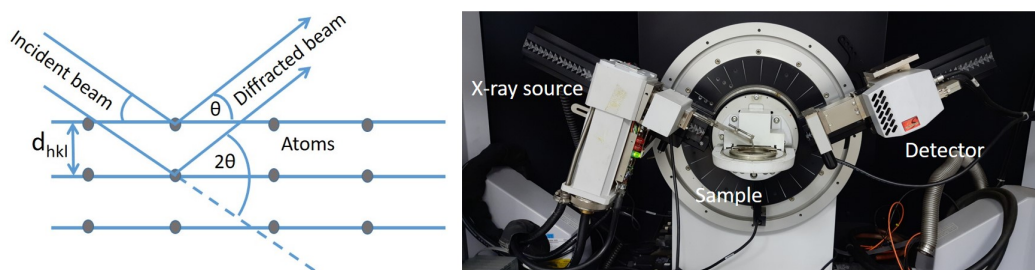


Figure 2.2: Left: A schematic diagram showing the Bragg diffraction condition. Right: The experimental setup from Bruker AXS: D8 Advance X-ray diffractometer showing the XRD diffraction measurement in a Bragg-Brentano focussing geometry.

tube where a heated filament emits electrons by thermionic emission. These electrons are accelerated with the help of high voltage generator and the X-rays are produced when these high speed electrons hit the metal target. The most commonly used anode is a copper target with two characteristic spectrum K_{α} and K_{β} with wavelengths $1.5406\text{\AA}$ and $1.5444\text{\AA}$ respectively. These wavelengths corresponds to the transition of electron from the second (L) and third (M) shell to the innermost (K) shell. However, in this process, 99% of the energy of the electron gets converted into heat and therefore, close to only 1% is converted into X-rays. In addition, materials situated close to Copper in the periodic table shows low signal to noise ratio due to absorption. This can be avoided by using different target sources (Molybdenum etc.) or high-intensity synchrotron radiation.

Room temperature XRD pattern for the present study was collected using a Bruker D8 Advance diffractometer with a Cu K_{α} source ($\lambda = 1.5406\text{\AA}$) and a solid state linear detector. In addition, synchrotron XRD scans were collected at the Indian beamline at

Photon Factory, KEK, Japan [109]. All the samples were ground for hours (5-6 hours) before performing synchrotron measurements to avoid preferred orientation in the polycrystalline sample. The prepared fine powder was mounted on a copper plate and data was collected in the temperature range 15-300K. Further, the temperature dependent synchrotron XRD measurements were also performed using the Materials Science (MS) X04SA beam line (wavelength=0.5653Å) at the Swiss Light Source (SLS, PSI Switzerland) [110]. The powder sample was filled in a 0.3mm capillary and the experiments were carried out in the temperature range 4.2-300K. The synchrotron measurements provide large beam flux, variable wavelengths, large temperature scanning range and fast data acquisition.

2.1.3 Neutron Diffraction

Neutrons were discovered by J.Chadwick in 1932 [111] followed by many possible measurement techniques developed to study neutron diffraction of liquids, thin films, single crystals, powder sample, high pressure measurements, etc. There are two ways of generating neutrons. First, by using spallation source in which high energy protons are bombarded on lead nuclei releasing spallation neutrons. The time of flight technique is used to select energies/wavelengths of incoming neutrons. The neutrons reach the sample over a wide range of flight path and the time taken by them gives the estimate of their wavelengths. This relation can be expressed using the wave particle duality expression [112],

$$t = \frac{h}{mv} = \frac{ht}{mL} = 2d\sin\theta$$

The obtained t (TOF) gives information about d, the inter planer spacing of the lattice. An advantage of using high- resolution T.O.F measurement is that one can probe a wide range of d values given the multiple detectors available. The other way is use a of fission reactor where ^{235}U nuclei breaks into lighter elements liberating 2-3 neutrons

per fissioned element. On the basis of the incoming energy (wavelength), the neutrons can be characterized as hot (small wavelength) or cold neutrons (large wavelength). The sample is placed in a beam of cold or thermal neutrons and the diffraction pattern is collected as a function of 2θ , energy or time of flight (T.O.F.). Neutron diffraction provides information about the crystal and magnetic structure of a material and acts as a complementary measurement due to the following reasons: 1. X-rays interact with electrons of the material and neutron being chargeless, shows no interaction and hence has more penetration depth. 2. Neutrons are sensitive to lighter elements. Elements like O_2 can be detected much more precisely by using neutrons as the scattering function is not proportional to the atomic number. 3. Most importantly, neutrons have spins and therefore interact with unpaired electrons spins in the material and are used to determine the magnetic spin structure.

In this work, neutron powder diffraction was performed at various sources: 1. Neutron Spallation source ISIS (Rutherford Appleton laboratory) [113], 2. The Swiss Spallation Neutron Source (PSI) at DMC (Cold Neutron Powder Diffractometer, $\lambda = 2.4576 \text{ \AA}$) and HRPT (High-Resolution Powder Diffractometer for Thermal Neutrons, $\lambda = 1.4940 \text{ \AA}$). A detailed description of these diffractometers can be found at [114, 115]. The cold neutron powder diffraction at PSI (DMC) is designed for high intensity performance for efficient neutron powder diffraction studies. This instrument is particularly useful for large crystal structures with big unit cells. It provides an accessible wavelength range of $2.3\text{-}5 \text{ \AA}$. It is used as a complementary measurement with respect to HRPT. High resolution ($\frac{\delta d}{d} < 0.001$) can be achieved by thermal neutrons in addition to the large scattering angles of monochromator and the sample (165°) in the wavelength range $1.04\text{-}2.96 \text{ \AA}$. One of the disadvantages of Neutron diffraction is that it requires large amounts of sample compared to X-rays. This is a major issue when using sample with expensive elements like Iridium. Also, due to the high absorption coefficient of

Iridium, long waiting times were employed in order to get better statistics.

2.1.4 Rietveld refinement

Rietveld refinement [116] named after Hugo Rietveld [117], is one of the most powerful refinement techniques, widely used to characterise and study a wide range of compounds. The computational fitting software is based on the least square refinement of the experimentally observed pattern with the stimulated pattern based on the user defined structural model. The least square residual ϕ , to be minimised, is given by,

$$\phi = \sum_i^n w_i (y_{io} - y_{ic})^2$$

where y_{io} and y_{ic} are the observed and calculated intensities at the i^{th} step of diffraction pattern and $w_i = 1/y_{io}$. The calculated intensity y_{ic} is based on this model and is defined as

$$y_{ic} = s \sum_k L_K |F_K|^2 \phi(2\theta_i - 2\theta_K) P_K A + y_{ib}$$

where s is the scale factor, K denotes a given Bragg reflection, L_K is the Lorentz polarisation and multiplicity factors, ϕ is the reflection profile function, P_K is the preferential orientation function, A is an absorption factor, F_K is the structure factor of the K^{th} Bragg reflection and y_{ib} is the background intensity at the i^{th} step.

This method is used for the refinement of both neutron and synchrotron diffraction and helps in the identification of both crystal and magnetic structure. Each peak in the spectra contains useful information about crystal structure, the diffraction optics and the instrumental factors etc., as shown in the Fig.2.3. A prior knowledge of the structure under consideration helps in building up the user defined model. This model is based on parameters like the background, peak profile variables, space group, lattice parameters, atomic positions etc. The reported crystal structure information can be obtained

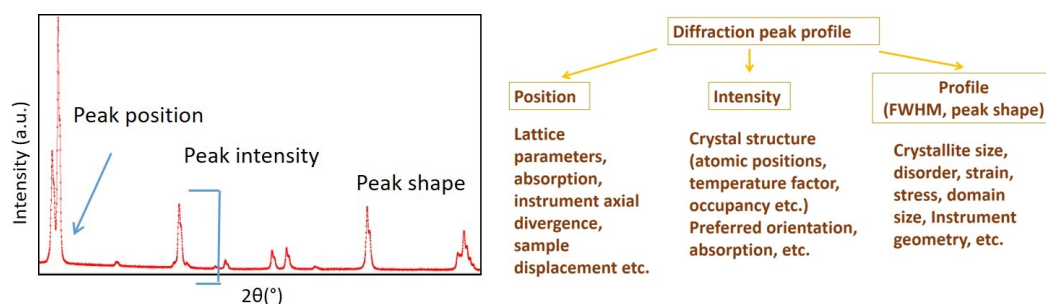


Figure 2.3: Left: A schematic for the X-ray diffraction pattern where each peak shape, position and intensity contains information about crystal structure and its variation with temperature, distortions etc. Right: A detailed list of various parameters that can be extracted from Rietveld analysis.

via various sources (websites and databases). Few of them are mentioned below:

1. Inorganic Crystal Structure Database (ICSD) <https://icsd.products.fiz-karlsruhe.de/>
2. Crystallography Open Database (<http://www.crystallography.net/>)
3. Minicryst (<http://database.iem.ac.ru/minicryst/index.php>)
4. WebMineral (<http://www.webmineral.com/>)
5. PDF4 from the ICDD (<https://www.icdd.com/pdf-4/>)
6. Cambridge Structure Database

(<https://www.ccdc.cam.ac.uk/solutions/csd-system/components/csd/>)

All the information received in the above section could be used to fit the obtained diffraction profile with the reported literature values. All the synchrotron and neutron diffraction profiles in this thesis were analyzed by the Rietveld method using the FullProf refinement program [116]. FullProf is a program designed for Rietveld Refinement and Pattern Matching Analysis. In the case of an unknown symmetry, FullProf [118] provides options like Dicvol [119] where indexing of the diffraction peaks can be done provided sufficient reflections are observed. This is the first stage towards finding a new structural model. A previous knowledge of crystal symmetry and a thorough literature survey helps substantially in formulating a base model to begin with. This initial guess may then be improved with the help of the least square algorithm used in Rietveld. In

addition to the crystal structure parameters, information about the instrument geometry, absorption coefficients and structure factors of elements also play a key role in order to reach a good fit. A detailed layout of sequence of refinement of a crystal structure is described in the FullProf manual [118]. In the present work, many structural phase transitions have been studied using the aforementioned procedure. As phase transitions lead to a subtle distortions and many peculiar changes in crystal symmetry, it is indeed necessary to test many different models and evaluate the best refinement of data based on the quality of fit. There are few parameters to indicate quality of fit called crystallographic figures of merit for powder diffraction given by,

$$R_p = 100 \frac{\sum_{i=1}^n |y_{io} - y_{ic}|}{\sum_{i=1}^n y_{io}}$$

$$R_{wp} = 100 \sqrt{\frac{\sum_{i=1}^n w_i |y_{io} - y_{ic}|^2}{\sum_{i=1}^n w_i y_{io}^2}}$$

$$R_{exp} = 100 \sqrt{\frac{n - p}{\sum_{i=1}^n w_i y_{io}^2}}$$

$$R_B = 100 \frac{\sum_{i=1}^k |I_{io} - I_{ic}|}{\sum_{i=1}^k I_{io}}$$

where k is the number of independent Bragg reflections,

I_{io} and I_{ic} are the observed and calculated profile intensities according to the user defined model,

n is the total number of variables measured in the experimental powder diffraction measurement,

p is the number of free least squares parameters.

GOF evaluates how well the model fits the experimental data and is given by,.

$$GOF = \chi_r^2 = \left[\frac{R_{wp}}{R_e} \right]^2$$

The value of GOF is unity for the most appropriate model. A value greater than 1 indicates systematic errors in the model and a value less than 1 might indicate the model is incorrect. Slight deviations may occur due to various systematic errors arising from background anomaly, impurity peaks, sample absorption, etc.

Once the structure is refined, the obtained list of structural parameters needs to be scrutinized to ascertain a physical meaning. FullProf also provides an option to work with various models to tune strain and stress effects, peak profiles, backgrounds, asymmetry and even multiple phases and patterns for compounds with phase coexistence, impurity phases etc. A deeper investigation/inspection involves calculating bond lengths, bond angles, polyhedral volume, distortion index etc. This can be done using software which allows to reconstruct a schematic layout of the lattice using the refined parameters obtained from Rietveld refinement. The structures shown in this work has been constructed using the software Vesta [1].

2.1.5 Scanning electron microscope

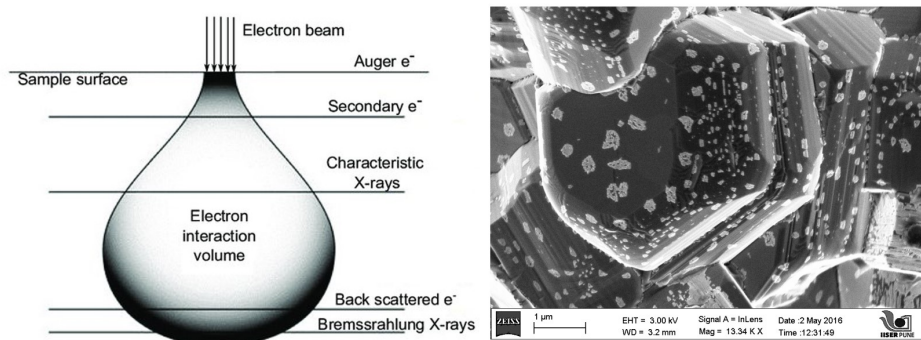


Figure 2.4: Left: A schematic of different emissions that occur when a high energy electron beam hits the sample. Image source [4]. Right: SEM image of a triple perovskite iridate exhibiting hexagonal symmetry. Clean facets can be seen of this layered structure.

The composition and morphology of all the compounds mentioned in this work has been studied using SEM (Scanning electron Microscope) and EDX/EDAX (Energy dis-

persive X-ray analysis) [120]. These measurements provides a microscopic picture of the sample surface with the help of a focused beam of electrons. The sample is exposed to a high energy beam of electrons. As a result, secondary electrons, backscattered electrons and characteristic x-rays are emitted. These signals are collected by multiple detectors. Each peak in the obtained EDAX spectrum contains characteristic information about every element present in the sample. The image of the surface topography is a resultant of the interaction of electron beam with the atoms at various depths within the sample surface. Fig.2.4 shows the schematic of different emissions that occur when high energy electrons are incident on the sample surface. An example where clean layered facets can be seen from the EDAX imaging is shown on the right. Another useful function is the provision to have high contrast resolution imaging. Proportional to the atomic density, some of the incident electrons gets backscattered by the atomic cloud of the sample. These BSE (backscattered electrons) provides a contrast imaging where different phases shows varied grey scale. This method is particularly useful in finding trace impurities ($< 2\%$) in compounds where even long waiting times x-ray diffraction scans fail to quantify the presence of small percentage of secondary phases. The measurements were performed on both pellet and powder forms of the compound to identify the type of elements, their weight or atomic percentage ratio, impurity phases etc. All the compositions mentioned in this thesis are studied by using an Energy dispersive X-Ray spectrometer from Zeiss Ultra Plus (409).

2.1.6 X-ray photoelectron spectroscopy

XPS (X-ray Photo-electron Spectroscopy), also known as electron spectroscopy for chemical analysis (ESCA), is a surface-sensitive spectroscopic technique used to investigate the elemental composition and chemical state of a material [121, 122]. It is based on the photoelectric effect and requires ultra-high vacuum ($< 10^{-7}$ Pa). A schematic

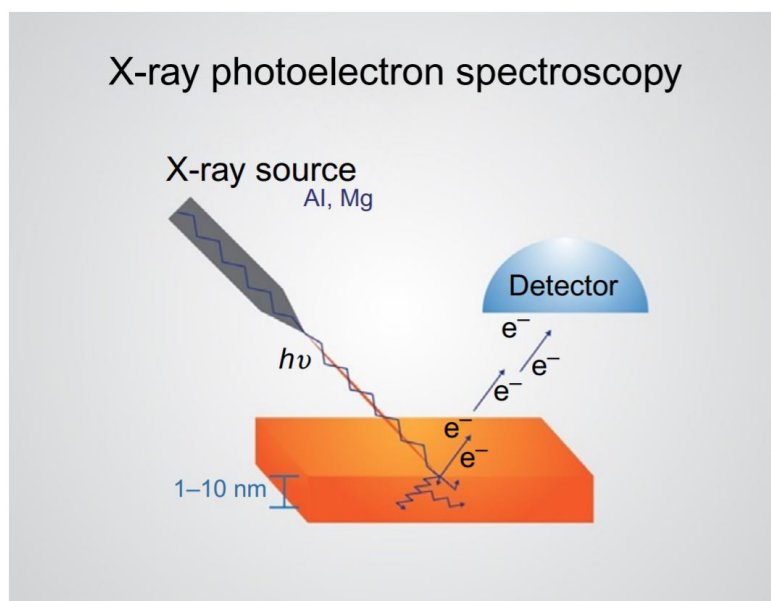


Figure 2.5: A schematic of the X-ray photoelectron spectroscopy measurement. Image source [5].

representation of measurement geometry has been shown in Fig.1.5. First, the surface is flushed with Argon to avoid any contamination. The sample surface is then irradiated with a beam of x-ray of a particular wavelength with enough energy to eject an electron from the atom. The spectrum of these emitted electrons, known as photoelectrons, is measured by counting ejected electrons over a range of kinetic energies. The relation between the energy of the incident X-ray and the emitted electrons' kinetic energy can be summarised using the photoelectric effect equation:

$$E_{\text{binding}} = E_{\text{photon}} - (E_{\text{kinetic}} + \Phi)$$

where E_{binding} is the Binding energy of the electron measured, E_{photon} is the energy of the incident X-rays, E_{kinetic} is the Kinetic energy of the emitted electron and Φ is the work function. Each peak in the spectra corresponds to a particular characteristic energy of the element from which the photoelectron originated. The obtained values of energy and intensity of photoelectron peaks enable the identification of the desired chemical state and provides additional quantitative information about the surface elements (ex-

cept hydrogen). The X-ray photoelectron spectroscopy (XPS) measurements were carried out on a laboratory setup (K Alpha+ model, ThermoFisher Scientific Instruments) on pellets of the compounds. The X-ray source used was Al K α with 6mA beam current(12KV) with a spot size of 400 μ m. The instrument was calibrated with Ag 3d with binding energy of 352eV and the reference used for binding energy was C1s (284.8 eV). The obtained XPS spectrum was analysed using the software CasaXPS [123].

2.2 Physical property measurements

2.2.1 DC Magnetization studies

The Superconducting QUantum Interference Device (SQUID) combines the phenomena of Josephson junction and flux quantization in superconducting rings. The working of SQUID is based on the principle of Faraday's Law. It states that the rate of change of magnetic flux in a circuit is proportional to the induced voltage. It is given by

$$\varepsilon_{emf} = -N \frac{d\phi}{dt}, \quad (2.1)$$

where N is the number of turns, $\phi=BA$ is the magnetic flux, B is the external magnetic field and A is the area of the coil. The "-" sign denotes the Lenz's law. ε_{emf} denotes the generated or induced voltage. A SQUID consists of a superconducting ring having one or two Josephson junctions (JJ) as shown in Fig.2.6 [124]. The electrical current density through a weak electric contact between two superconductors depends on the phase difference δ of the two superconducting wave functions. Moreover, the time derivative of δ is correlated with the voltage across this weak contact and is additionally influenced by the magnetic flux ϕ through this ring. Such a structure can be used to convert magnetic flux into an electrical voltage [125].

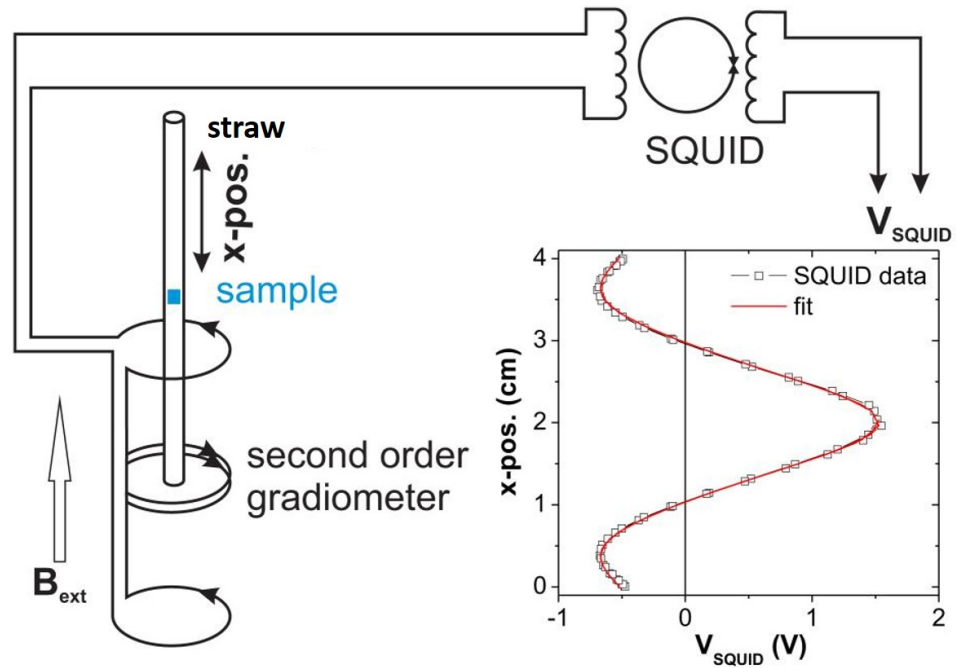


Figure 2.6: When the sample is moved up and down it produces an alternating magnetic flux in the pick-up coil. The magnetic signal of the sample is picked by a Superconducting pick-up coil with 4 windings. This voltage is then amplified and read out by the magnetometer's electronics. Image source [6].

The sample in powder or pellet form was loaded in a gelatine capsule and placed at the center of a plastic straw. This assembly has been carefully designed so that the sample sits close to the center of detection coils. The straw was attached to a transfer rod with an inbuilt stepper motor that helps in fine tuning the position of the sample inbetween the coils. During the course of measurement, the sample is moved up and down that causes a change in magnetic flux in the pick up coils. This signal is sent to SQUID antenna where this is converted into voltage and further SQUID electronics amplify and convert it to magnetic moment [126]. This system can detect low magnetic moment with very high resolution. A SQUID acts as a magnetic flux to voltage converter with extremely high sensitivity. The high resolution of SQUID allows for detection of a change by a single flux i.e. 10^{-15} Tesla.

Magnetic measurements were performed using various protocols based on the sample

specifics. The standard protocol included performing ZFC (Zero field cooled) and FC (Field cooled) measurements in order to establish the presence of a phase transition. In ZFC, the sample is cooled to the lowest temperature in the absence of field and magnetic field is applied on warming while simultaneously measuring magnetization. In FC, the sample is cooled in the presence of magnetic field and the measurement is done in the presence of the same field while warming (FCW) or during cooling (FCC). Isotherm magnetization $M(H)$ were performed where the sample is cooled in the presence or absence of field to a certain temperature and the magnetization is measured as a function of applied field (0 to $\pm 7T$). In addition, TRM (Thermo-Remnant Magnetization) and IRM (Isothermal Remanent Magnetization) were also performed. In both these protocols, the measurement involves cooling the sample to a certain temperature in the presence of a magnetic field. In TRM, the field is switched off and magnetization is measured as a function of increasing temperature where as in IRM, the field is switched off and the magnetization is measured as function of time.

Magnetization measurements were performed using a commercial Quantum Design MPMS(Magnetic property measurement system)-XL SQUID Superconducting Quantum Interference Device) from Quantum Design, USA) magnetometer. The maximum available magnetic field was 7T and the lowest temperature of 2K could be reached.

2.2.2 Noise spectroscopy

Noise, often considered as an unwanted disturbance limiting the accuracy of measurements, can provide valuable information about the systems that have characteristic fluctuations. For example, in the fluctuations of the conductivity (ρ) or resistivity (R) measurements (variation is ρ and R across a constant value), there is hidden information about the dynamics and correlation of charge carriers, which is not present in the measurements of the mean quantity i.e. the conductivity or resistivity itself. Electronic

noise refers to random fluctuations in the current flowing through a material or in the voltage across the sample. Electrical noise can have many different origins for example, defect motions, magnetic domains, structural excitations, spin fluctuations, energy barriers, percolation effects etc. All these sources can be regarded as fluctuators. The fluctuations in resistance or conductance is caused when these fluctuations couple to the current carrying electrons. Depending on the frequency dependence of their PSD (power spectral density), they can be categorized in three broad noise forms as shown in Fig.1.6. The first in the list is thermal noise or Johnson noise, the noise familiar to all systems. As the name suggests, this noise occurs as a result of random motion of charge carriers. The second noise, random walk, is derived from the Brownian motion of particles in a fluid. Both these cases represent extreme ends of noise spectra and usually most physical systems are an "intermediate case". This is give by $(\frac{1}{f})^\alpha$ where both rapid fluctuations and slow general trend seem to occur on all time scales making it the most interesting noise form [7].

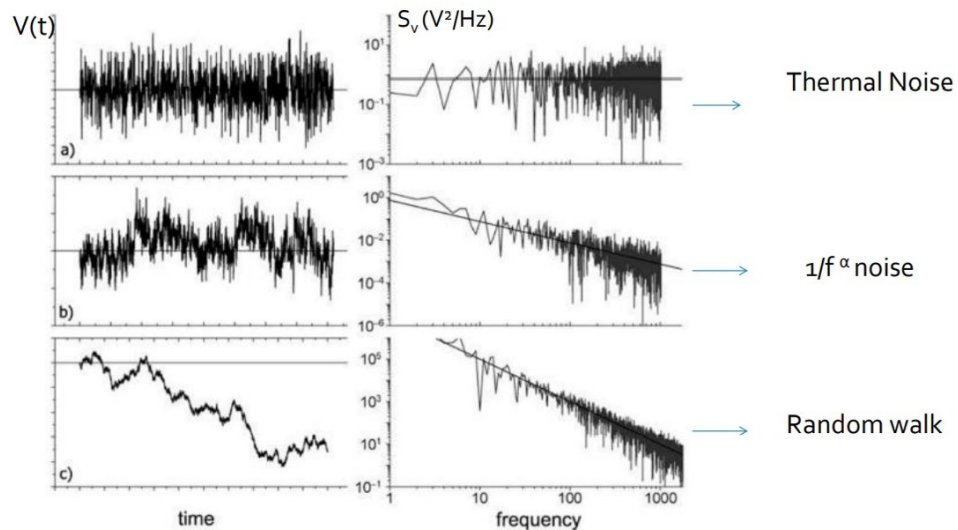


Figure 2.7: Left: Time profiles of different noise signals. (a) Random noise or white noise. (b) Flicker noise or $1/f$ noise and (c) Random walk noise. Right: The corresponding power spectra of the all noise signals. Image source [7]

1/f noise is universally observed in many wide range of systems including thin films, spin glasses, semiconductors, magnetoresistance materials etc [127–130]. To understand this further, consider a time dependent physical quantity like the voltage drop $V(t)$ across a sample, which fluctuates around a mean value

$$\langle V \rangle = \lim_{T \rightarrow \infty} \frac{1}{T} \int_{-T/2}^{T/2} V(t) dt, \quad (2.2)$$

The next step is to know how much power is associated with different parts of the frequency spectrum. During the measurements, the fluctuating voltage signal is preamplified and processed by a spectrum analyzer yielding the voltage noise power spectral density (PSD) $S_V(\omega)$ defined by:

$$S_V(\omega) = 2 \lim_{T \rightarrow \infty} \frac{1}{T} \left| \int_{-T/2}^{T/2} e^{i\omega t} \delta V(t) dt \right|^2, \quad (2.3)$$

where $\delta V(t)$ represents the fluctuating voltage drop across the sample and $\omega = 2\pi f$ the angular frequency. In an attempt to find a common origin of 1/f fluctuations, F.N. Hooge in 1969 gave an empirical formula given by [131, 132],

$$S_V(f) = \frac{\gamma_H \cdot V^2}{n\Omega f^\alpha}, \quad (2.4)$$

the magnitude of the voltage noise scales as $S_V \propto V^2 \propto I^2$, where I represents the current flowing through the sample. Here, n is the charge carrier density and Ω the 'noisy' sample volume, i.e. $n\Omega = N_c$ gives the total number of charge carriers in the material causing the observed 1/f noise. The Hooge parameter γ_H is widely used to compare the noise level of different systems and covers a range of $\gamma_H = 10^{-6}$ – 10^7 for different materials [133]. For bulk semiconductors, γ_H usually is of order 10^{-2} – 10^{-3} . α describes the frequency exponent which is commonly in the range $0.8 \leq \alpha \leq 1.4$ for

$1/f$ -type fluctuations. However, it is useful to normalize the noise magnitude with respect to the applied current, $S_R = S_V/I^2$, and to the resistance of the sample, resulting in S_R/R^2 . Further details about the fluctuation spectroscopy technique can be found elsewhere [7, 133].

In this study, noise spectroscopy was conducted in a five-terminal ac setup, where the sample is placed in a bridge circuit in order to suppress the constant dc voltage offset and is designed to avoid the influence of fluctuations in external sources, such as the voltage source, the bath temperature etc [134, 135]. Low-frequency fluctuation spectroscopy measurements were carried out in a continuous-flow cryostat with a variable temperature insert. The measurements were performed in the temperature range 50-180K in the presence of magnetic field 0-5T.

2.2.3 Resistivity

The resistivity measurements in this thesis were performed using the conventional four probe method in PPMS (Physical Property Measurement System) as shown in Fig.1.7. This technique was developed by F. Wenner in 1915 [136] to exclude the presence of contact resistance of intermediate wirings, unavoidable in a two probe measurement. The measurements were performed on a rectangular pellet piece of the sample. The

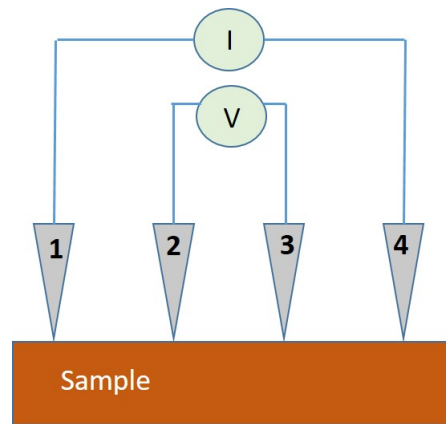


Figure 2.8: Four probe contact arrangement for measuring resistivity.

PPMS puck platform was covered with cigarette paper to avoid electrical contact between them. With the help of GE varnish, the sample was glued on top of the cigarette paper. Four Cu/Al wires were used to make four probe contact. The wires were soldered on specified notch present on the puck with labels (I^+ V^+ V^- I^-) for driving the current and measuring voltage simultaneously. The other end of the wires were connected to the sample using silver paste. The contacts were made under the microscope to avoid any unwanted contact during soldering or applying silver paste. The resistivity of the specimen was measured by applying constant current and measuring the corresponding voltage. The resistivity is given by

$$\rho = 2\pi a \frac{V}{I}$$

where ρ is the resistivity of the sample, a is the distance between the two silver contacts, V and I are the measured voltage and current applied. All the measurements were performed in PPMS by Quantum Design in the presence and absence of magnetic field from 2-300K. Most of the oxides mentioned in the thesis have extremely high resistances (of the order of $G\Omega$) at low temperatures. Limited by the compliance of the constant current source available in PPMS, low temperature resistivity data of some compounds could not be collected.

2.2.4 Heat Capacity

Heat capacity is defined as the heat required to raise the temperature of the specimen by one Kelvin per unit mass. The measurement of heat capacity gives information about the lattice, electronic and magnetic properties of a solid. It also helps in identifying whether a feature observed in other physical or magnetic measurement is indeed a true phase transition. The heat capacity measurements were done at constant pressure

$$C_P = \left(\frac{dQ}{dT} \right)_P$$

The measurement configuration is shown in Fig.1.8. The geometry consists of a sam-

ple platform with inbuilt temperature sensor and heater. The basic puck configuration allows for a maximum value of $3 \times 3 \text{ mm}^2$ dimension of the sample and the sample mass can range from 2 mg to 200 mg. The platform is suspended by 8 connecting wires which provide electrical connection to both the heater and the sensor. Apiezon grease provides the thermal coupling between the sample and the platform. The measurement assembly requires a high vacuum so that the thermal contact between the puck (thermal bath) and sample platform is not disturbed. Before measuring the samples, an empty run

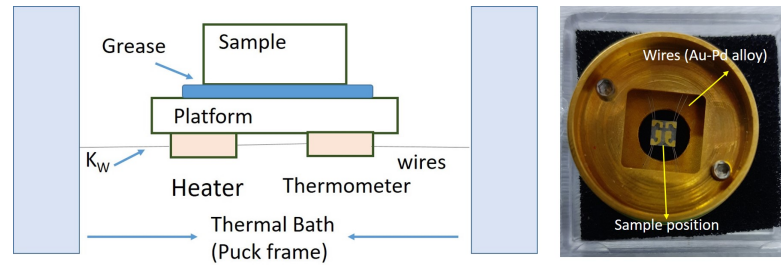


Figure 2.9: Left: A schematic of the of heat capacity measurement geometry. Right: Specific heat puck from the heat capacity setup in PPMS. The sample sits in the centre suspended by 8 Au-Pd wires.

is done using a small amount of Apiezon N grease. The grease is carefully placed on the heat capacity platform which is suspended by four thin wires. The heat capacity of only grease is measured in this particular arrangement for the entire temperature range of interest (C_{grease}). This first run acts as a background from the platform and grease. Then, a small pellet piece of compound (7-9mg) is mounted on top of the same grease and the measurement is done in cooling or heating mode in the presence/ absence of magnetic field ($C_{total} = C_{grease} + C_{sample}$). The contribution of heat capacity from the sample is obtained by subtracting (C_{grease}) from the C_{total} .

For measuring heat capacity, the bath and sample are ensured to be in thermal equilibrium at temperature T . A well defined constant heat pulse (P) is sent to the sample for a duration of time (t). As soon as the steady state is reached, power is switched off. The temperature slowly decays back to T with a time constant τ ,

$$\tau = (C_{sample} + C_{plat})$$

where C_{sample} and C_{plat} are the heat capacity contributions from the sample and the platform respectively. Considering good thermal contact between sample and platform, the relation between the temperature of the platform as a function of time can be written as,

$$(C_{sample} + C_{plat}) \frac{dT}{dt} = -K_w(T - T_B) + P(t)$$

where K_w is the thermal conductance of the supporting wires, T_B is the temperature of the puck frame and $P(t)$ is the power of the heat pulse. The solution of this equation gives the value of heat capacity C_{total}/K . [137, 138]. The low temperature region (2-15K) was used to evaluate the contribution from phonons, electrons and magnons using the Dulong and Petit law [8]. The heat capacity on the samples mentioned in this thesis was measured using a PPMS (Physical Property Measurement System) from Quantum Design.

2.2.5 Dielectric Spectroscopy

Dielectric spectroscopy measures impedance of a sample as a function of frequency or time with temperature. The measurement is based on the response of electric dipole moments on the application of electric field. Electric dipole can be formed in a structure in various ways. For example, in a perfect perovskite lattice (ABO_3), doping at the A site leads to off centre displacement at 12 fold coordination site and leads to the formation of electric dipoles which can potentially form polar or spin clusters. In such cases, having a measurement that directly caters to the electric dipole dynamics proves advantageous. Further, many interesting phenomena like glassy dynamics, potential ferroelectricity, multiferroicity, multiglass state etc. could be studied well using dielectric spectroscopy.

Temperature dependent dielectric measurements were performed in the standard paral-

parallel plate geometry, using a NOVOCONTROL (Alpha-A) High Performance Frequency Analyzer. Measurements were typically done using an excitation ac signal of 1V at frequencies varying from 1 kHz to 0.5 MHz.

Chapter 3

Structural, magnetic and electronic properties of $\text{Ba}_3\text{CoIr}_2\text{O}_9$

The contents of this chapter are in print in the Physical Review B under the title *”Evolution of the structural, magnetic and electronic properties of the triple perovskite $\text{Ba}_3\text{CoIr}_2\text{O}_9$ ”* (arXiv:2009.13822) [139].

3.1 Introduction

A relatively recent addition to the area of strongly correlated oxides are the iridates. They are currently in vogue due to a number of unusual phases they exhibit, given the multiple oxidation states adopted by them in different crystallographic environments coupled with its inherently large spin orbit coupling [18]. In Chapter 1, we presented a brief overview of spin orbit interaction, where SOC with comparable energy scales like electron correlation (U), hopping energy (t), crystal field splitting (CFE) results in a rich phase diagram of interesting properties. As a consequence, it has proven to be a fertile ground for uncovering exotic states of matter like QSL, Weyl semi-metals, superconduc-

tivity etc. [36]. The significant interest in iridates led to many interesting discoveries in various class of materials ranging from the most celebrated Ruddlesden-Popper series ($\text{Sr}_{n+1}\text{Ir}_n\text{O}_{3n+1}$, $n=1,2,\infty$), to studies in geometrically frustrated systems like the honeycomb lattices Na_2IrO_3 , Li_2IrO_3 , $\beta\text{Li}_2\text{IrO}_3$, $\gamma\text{Li}_2\text{IrO}_3$, hyperkagome $\text{Na}_4\text{Ir}_3\text{O}_8$ and an array of pyrochlore based iridates [36]. However, a recent addition to this family are the triple perovskite iridates. As we know, perovskites and its variants continue to be desirable hosts in order to study structure property relationships, due to their remarkable flexibility to chemical substitution and the staggering array of emergent properties they exhibit. In this context, the possible utility of this relatively new structural class has recently come to the fore- triple perovskites iridates of the form $\text{A}_3\text{M}\text{Ir}_2\text{O}_9$ (with A is alkaline earth metal, M being an alkali, alkaline earth, or transition metal), where careful synthesis appears to enable the stabilization of these systems in a number of different Ir oxidation states and structural motifs as briefly discussed in Chapter 1. Most of these

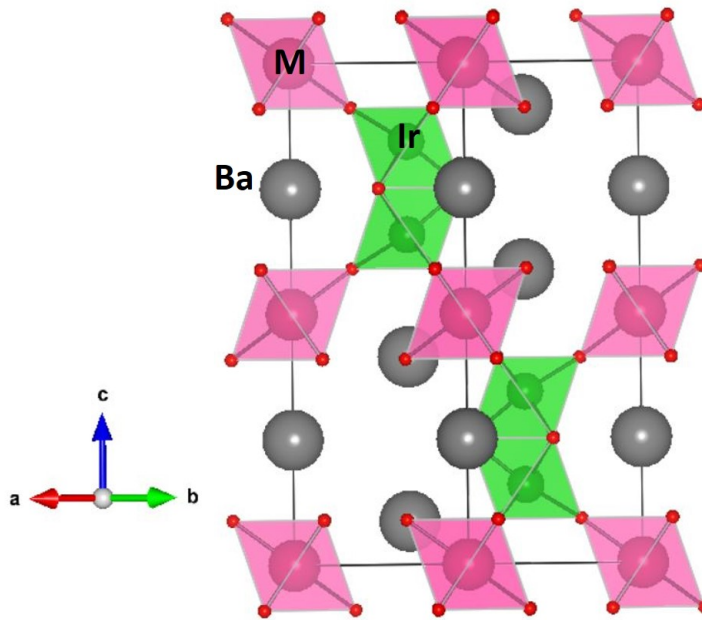


Figure 3.1: A schematic of the crystal structure of the $\text{Ba}_3\text{M}\text{Ir}_2\text{O}_9$ triple perovskite. Here, pink and green octahedra represent cobalt and iridium sites respectively, with the Barium atoms being represented by grey circles. The structure comprises of a single MO_6 octahedron sharing corners with Ir_2O_9 dimers, which in turn are formed by two face-sharing IrO_6 octahedra.

are known to stabilize in an aristotype hexagonal structure as shown in Fig 3.1 where face sharing Ir_2O_9 dimers (green) are connected via corners to M octahedra (pink) and A sits at a 12-fold co-ordination site (grey). Along the crystallographic c axis, the structure can be viewed as alternate layers which exclusively comprise of Ir_2O_9 dimers and MO_6 octahedra.

Recent work in triple perovskite iridates has been mostly concentrated on $\text{Ba}_3\text{M}\text{Ir}_2\text{O}_9$ compounds wherein this MO_6 layer is inherently non-magnetic. Such systems offer a fertile playground for investigating the physics of the $\text{Ir}^{+5}(5d^4)$ ions in varying crystallographic environments. Interestingly, even within this sub-class, the magnetic ground states are seen to be varied and many interesting observations have now been reported. A recent example is the possible spin liquid candidate $\text{Ba}_3\text{ZnIr}_2\text{O}_9$, where it was suggested that the $\text{Ir}^{+5}(5d^4)$ sublattice provides a very close realization of the elusive $\text{Jeff}=0$ state [67]. The M site substituted with other non-magnetic ions like $\text{M} = \text{Zn}, \text{Mg}, \text{Sr}, \text{Cd}, \text{Ca}$ resulted different in structural magnetic and structural ground states as tabulated in Table. 1.2. Therefore, not only this lattice framework is susceptible to small perturbations, the unique exchange network mediated by corner and face sharing octahedra opens up window for exploring the complex interplay between the lattice, spin and orbital degrees of freedom. Given the perovskite lattice, this structures offers structural flexibility in terms of element choice for the M site and the high symmetry hexagonal lattice allows for various low symmetry structural modifications. Hence, in addition to many comparable energy scales like crystal field splitting, spin-orbit coupling, on-site Coulomb interaction, and Hund's coupling, this lattice geometry offers unconventional interplay of spin-phonon dynamics leading to many interesting ground state scenarios. Although research on triple perovskite Iridates has generated much interest in the last few years, reports of compounds containing magnetic ion, apart from Ir is still scarce. However, the 4d analogue of the triple perovskites have been scrutinized to quite an

extent [56, 140–143]. For instance, the $\text{Ba}_3\text{CoRu}_2\text{O}_9$ is reported to exhibit an antiferromagnetic transition at $\sim 93\text{K}$ accompanied by a semiconductor-semiconductor electronic transition where orbital ordering [143] and hybridization [144] were suggested to be the possible explanations for the observed properties.

In this chapter, we present an iridate analogue of this compound, $\text{Ba}_3\text{CoIr}_2\text{O}_9$. It is the first study of a hitherto unreported triple perovskite $\text{Ba}_3\text{CoIr}_2\text{O}_9$, where Ir^{5+} ions interact with each other and magnetic $M = \text{Co}$ ion within the framework of the triple perovskite structure. Insertion of a magnetically active ion at M site added to the complexity of this triple perovskite, providing additional superexchange paths which modified magnetic and structural ground state promoting long range magnetic order. We discuss in detail the unique the structural, magnetic and electronic properties of this compound using XPS, EDAX, synchrotron and neutron diffraction, first principle calculations, resistivity, specific heat, dielectric susceptibility, and electronic noise spectroscopy. All the measurements together point towards the stabilization of a highly correlated ground state in this $3d\text{-}5d$ based triple perovskite with unconventional magnetism, spin-orbit coupling and structural and electronic phase co-existence being critical ingredients.

3.2 Experimental Methods

Polycrystalline specimens of $\text{Ba}_3\text{CoIr}_2\text{O}_9$ were synthesized by the standard solid state reaction technique. Stoichiometric amounts of high purity BaCO_3 , Co_3O_4 and IrO_2 were thoroughly ground using a mortar and pestle to get homogeneous mixtures, which were then fired in air at 950°C for 24 hrs, followed by a heat treatment at 1200°C for 48 hrs. These powders were then cold pressed and heat treated in air repeatedly at 1200°C till no change in the powder X-Ray Diffraction (XRD) peak shape was observed. The details of the experimental techniques used has been discussed in Chapter 2.

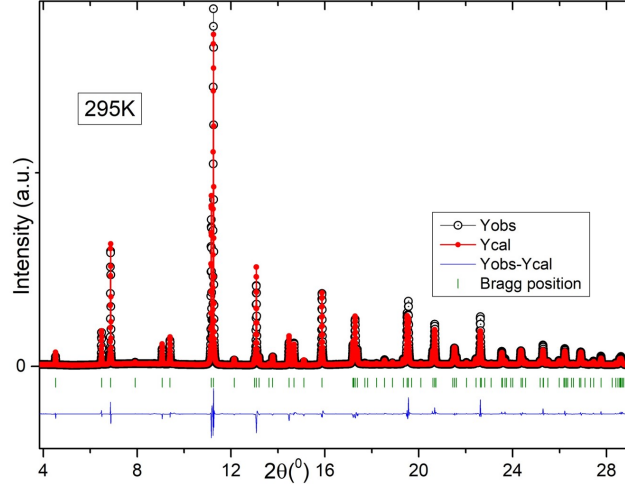


Figure 3.2: Rietveld refinement of synchrotron powder diffraction pattern of $\text{Ba}_3\text{CoIr}_2\text{O}_9$ at 295 K. The compound crystallizes in a 6H-hexagonal perovskite with space group (P6₃/mmc). The calculated and observed diffraction profiles are shown as red and black markers respectively. The vertical green lines indicates the calculated Bragg positions. The blue line at the bottom is the difference between observed and calculated intensities.

To get additional insight into the electronic and magnetic ground states, our collaborators performed first-principles density functional theory calculations [145, 146], as realized in the VASP code [147–150]. The wavefunctions are described within projector augmented wave formalism with 550 eV cutoff for the kinetic energy [151]. The exchange-correlation energy was described within the Perdew-Burke-Ernzerhof functional form of generalized gradient approximation [152], and the spin-orbit coupling was considered. The reciprocal space integration was carried with a $7 \times 4 \times 3$ Monkhorst-Pack k -mesh. The correlation effect was corrected using the Hubbard like on-site Coulomb interaction U parameter, which was set to 3 and 2.4 eV for Co-3d and Ir-5d electrons, respectively, within the rotationally invariant Dudarev’s approach [153]. The experimental lattice parameters derived from the synchrotron data at 80 K were used in the theoretical calculations, and various initial magnetic configurations were considered and optimized.

Table 3.1: Structural parameters of $\text{Ba}_3\text{CoIr}_2\text{O}_9$ at 295 K.

Space group $P6_3/mmc$ (No. 194)				
$a = b = 5.7639(1) \text{ \AA}$, $c = 14.2949(3) \text{ \AA}$, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$				
Atom	x	y	z	occupancy
Ba1	0.3333	0.6666	0.9120(1)	1
Ba2	0.0000	0.0000	0.2500	1
Co	0.0000	0.0000	0.0000	1
Ir	0.3333	0.6666	0.1540(1)	1
O1	0.5004(14)	1.0007(28)	0.2500	1
O2	0.1619(9)	0.3238(18)	0.4196(2)	1

3.3 Results and Discussion

3.3.1 Sample characterization

3.3.1.1 Powder Diffraction

The room temperature synchrotron XRD data for $\text{Ba}_3\text{CoIr}_2\text{O}_9$ and its Rietveld refinement is shown in Fig 3.2. $\text{Ba}_3\text{CoIr}_2\text{O}_9$ is seen to crystallize in the aristotype 6H-type BaTiO_3 hexagonal layered structure $P6_3/mmc$ (space group (#194)), consistent with the previously reported triple perovskites [55, 143]. This structure, as shown in Fig 5.14 constitutes of IrO_6 octahedra sharing a face along the crystallographic c axis, with the Ir_2O_9 dimers connected by corner sharing CoO_6 octahedra, and Ba occupying the 12 fold c-ordination site. The lattice parameters obtained from the fit are $a = b = 5.7596 \text{ \AA}$, $c = 14.2801 \text{ \AA}$ and $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$. The resultant structural parameters for 295K from the Rietveld refinement of synchrotron data are listed in Table 5.1.

3.3.1.2 EDAX

After the confirmation of the crystal structure, the morphology and chemical composition was confirmed with the help of EDX analysis. The Ba:Co:Ir ratio was inferred to be 3.02:1:1.95 which is close to the expected stoichiometric value of 3:1:2. The

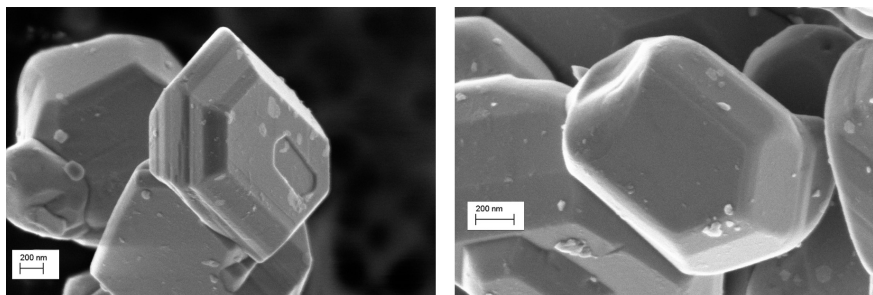


Figure 3.3: Scanning electron microscope images of $\text{Ba}_3\text{CoIr}_2\text{O}_9$ where clear hexagonal facets can be seen.

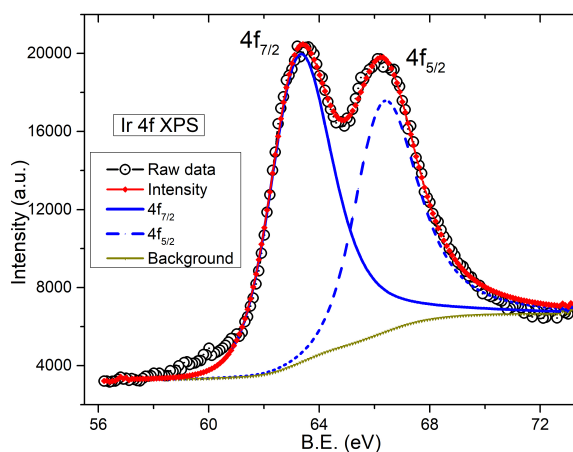


Figure 3.4: The XPS fit for the Ir $4f$ core level is depicted on the left. Black circles are the data points and the red line is the fit. The solid and dashed blue lines depicts the deconvolution of the $4f_{7/2}$ and $4f_{5/2}$ contributions respectively.

inset of Fig. 3.3 shows the scanning electron images of the compound exhibiting clear hexagonal facets.

3.3.1.3 X-ray photoelectron spectroscopy

Since both cobalt and iridium can stabilize in multiple valence states, it is imperative to ascertain the valence of these ions, which in turn would critically influence the electronic and magnetic properties. Our XPS measurements of the Ir $4f$ core level is shown in the inset of Fig 3.4. The best result was obtained by using only a single orbit spin doublet, and the binding energy position and gap thus obtained confirms the presence of only

Ir^{5+} (and by corollary Co^{2+}) in this system. Another way to validate the charge state of Ir in hexagonal lattices can be done by the Ir-Ir bond distance calculation [154]. The bond length is reported to increase with the valence state of iridium as a function of electrostatic repulsion, resulting in the bond distances of the order of 2.55, 2.65 and 2.75 Å for Ir^{4+} , $\text{Ir}^{4.5+}$ and Ir^{5+} respectively. The obtained value of the Ir-Ir distance (≈ 2.75 Å) from our room temperature Rietveld refinement fit is in good agreement with the +5 state in iridium.

3.3.2 Magnetic Properties

3.3.2.1 dc magnetization

The temperature dependence of the dc magnetic susceptibility as measured in $\text{Ba}_3\text{CoIr}_2\text{O}_9$ is shown in Fig. 3.5, where a pronounced irreversibility between ZFC-FC curves indicates the presence of a magnetic transition at 107 K. This is in agreement with a solitary prior report of this system [56] where the magnetization was reported, although the nature of the transition remained unclear. Also, the ruthenate analogue of this compound, $\text{Ba}_3\text{CoRu}_2\text{O}_9$ has been reported to exhibit an antiferromagnetic transition at 93K, in close proximity to our observations. A Curie Weiss fit to our magnetization data (Fig. 3.5(b)) gives a Curie-Weiss temperature (θ_{CW}) of 6.35 K, and an effective magnetic moment of $4.72 \mu_B/\text{f.u.}$ respectively. The small positive value of θ_{CW} is clearly suggestive of mixed ferro-antiferromagnetic interactions. This is also confirmed by the MH isotherm at 5K [Fig. 3.5(c)], where a non-saturating magnetization, along with a small loop opening is observed - typical of ferri-, or weak ferromagnetic systems. The effective magnetic moment of $4.72 \mu_B/\text{f.u.}$ obtained by the Curie-Weiss fit can be accounted for by considering $\text{Co}^{2+}(d^7)$ in the high spin state ($S = 3/2$) and iridium in the $\text{Ir}^{5+}(d^4)$ state. The spin only contribution from Co^{2+} is $3.88 \mu_B$, implying that the contribution from the $\text{Ir}^{5+}(d^4)$ is $0.41 \mu_B$. Though Ir^{5+} , by virtue of its electronic con-

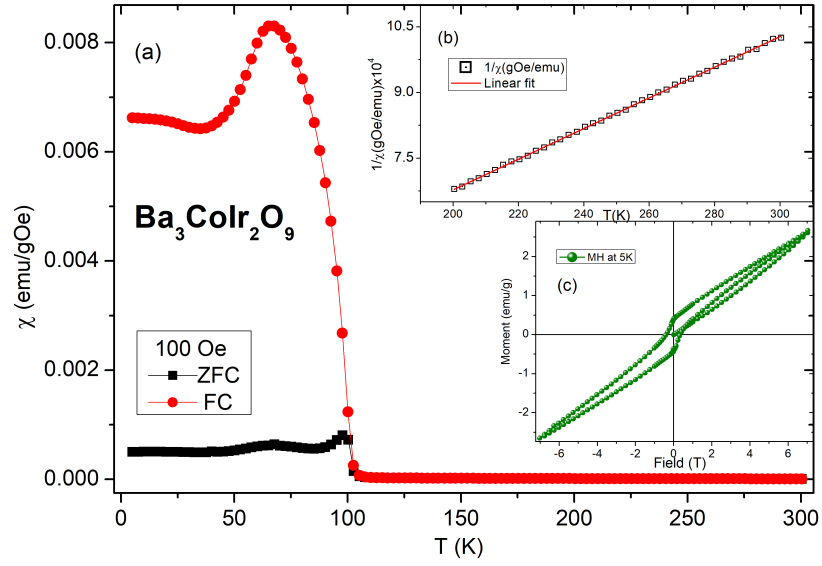


Figure 3.5: (a) Temperature dependent magnetization of $\text{Ba}_3\text{CoIr}_2\text{O}_9$ as measured in the zero field cooled (ZFC) and field cooled (FC) protocols with an applied magnetic field of 100 Oe. (b) A Curie Weiss fit to the high temperature magnetization data. The black squares are the experimental data points and red line is the corresponding fit. (c) depicts the MH isotherm as measured at 5 K, with a finite opening of the loop indicating a finite ferromagnetic contribution to the otherwise antiferromagnetic system.

figuration ($5d^4$) and under the influence of strong spin orbit coupling ($t_{2g}^4 e_g^0$) is expected to exhibit a $J = 0$ non-magnetic state, our data indicates a contribution from both the magnetic entities. This breakdown of the $J = 0$ state has been observed previously in systems like $\text{Ba}_3\text{ZnIr}_2\text{O}_9$ [67] and $\text{Ba}_3\text{MgIr}_2\text{O}_9$ [9] where the Ir moment was reported to be $0.2 \mu_B$ and $0.5\text{-}0.6 \mu_B$ respectively. A defining feature of these triple perovskites is the presence of Ir_2O_9 dimers in the backdrop of strong spin orbit coupling. It has been suggested that inter and intra dimer interactions are strongly influenced by the local distortions creating complex Ir-O-Ir pathways leading to the breaking of degenerate t_{2g} levels. Under the influence of strong SO coupling, these states reform into mixed J states, which in turn facilitate hopping induced superexchange interactions that result in a finite magnetic moment at the Ir site.

3.3.2.2 Magneto-structural transition

In addition to the magnetic transition, this class of triple perovskites, specially ruthenates, are known to exhibit magneto-structural coupling at low temperature. $\text{Ba}_3\text{CoRu}_2\text{O}_9$, has been proven to exhibit a hexagonal to orthorhombic structural phase transition with an antiferromagnetic ordering at 93K [143]. For the iridates, it is known that the monoclinically distorted $\text{Ba}_3\text{BiIr}_2\text{O}_9$ system exhibits a giant magnetoelastic transition - the largest reported amongst all $5d$ oxides - at ~ 75 K. Interestingly, this transition was not accompanied by a change in space group symmetry, but was characterized by a 4% increase in the Ir-Ir bond distance and 1% negative thermal volume expansion. It was proposed that the transition occurred due to the existence of an electronically unstable (nominal) Bi^{4+} valence state, which then correspondingly influences the valency of Ir [53, 54, 102]. However, the Bi based system is an exception, and most triple perovskite iridates -especially where Ir stabilizes in the $5d^4$ configuration - do not exhibit long range magnetic order, or at best exhibit weak dimer-like magnetism. In other triple perovskite iridates with mixed valent Ir ions, low magnetic ordering temperatures have been reported, though there are no reports of magneto-structural transitions in any of them [9, 52, 67, 154].

Interestingly, the onset of magnetic order in $\text{Ba}_3\text{CoIr}_2\text{O}_9$ is accompanied by a structural transition, and the system is observed to distort from a 6H hexagonal structure ($P6_3/mmc$) to a monoclinic phase ($C2/c$). This was confirmed by our low temperature synchrotron diffraction studies where lowering the temperature lead to splitting of diffraction peaks as shown in Fig. 3.6, a notable feature of structural transformation. This leads to a doubling of the crystallographic unit cell, and the new lattice parameters are $a = 5.7368 \text{ \AA}$, $b = 9.9833 \text{ \AA}$, $c = 14.2686 \text{ \AA}$, with $\alpha=\gamma=90^\circ$ and $\beta= 90.0663^\circ$. As a consequence, both the Ir and Co octahedra are now highly distorted. Fig. 3.7 shows the comparison of the octahedra on either side of this magneto-structural transition. The

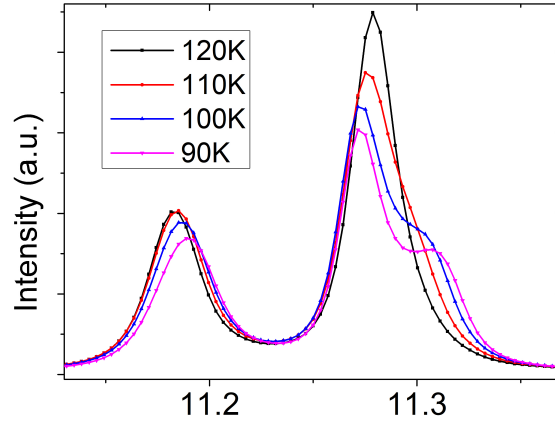


Figure 3.6: Temperature evolution of the highest intensity diffraction peak at 120K, 110K, 100K and 90K. Clearly, the peak splitting occurs between 110K and 120K, indicating the onset of structural transition.

bond-lengths with equal magnitudes are assigned same colors for the sake of clarity. In the case of cobalt, a highly symmetric octahedron with only one Co-O bond length in the high T phase transforms into 3 pairs of Co-O bonds, with a maximum of 3.87% change in the bond length below the transition. On the other hand, the iridium octahedron distorts from three Ir-O1 and Ir-O2 bonds above T_N to six different pairs of Ir-O bonds below the transition. it is to be noted that this kind of a magneto-structural transition has not been previously observed in any Ir-based triple perovskite till date, and the $\text{Ba}_3\text{CoIr}_2\text{O}_9$ system exhibits the highest magneto-structural transition temperature reported for any Ir based triple perovskite.

3.3.2.3 Neutron Diffraction

The multiple Ir-O-Ir and Co-O-Ir bond angles (and bond lengths) formed as a consequence of this monoclinic distortion creates multiple exchange paths that influence the magnetic and electronic structure. Since the Co-Co distance is very large (7.14 Å), the two primary magnetic interactions are between the Ir and Co edge sharing octahedra and amongst the Ir_2O_9 dimers. To ascertain the contribution from both these magnetic ions

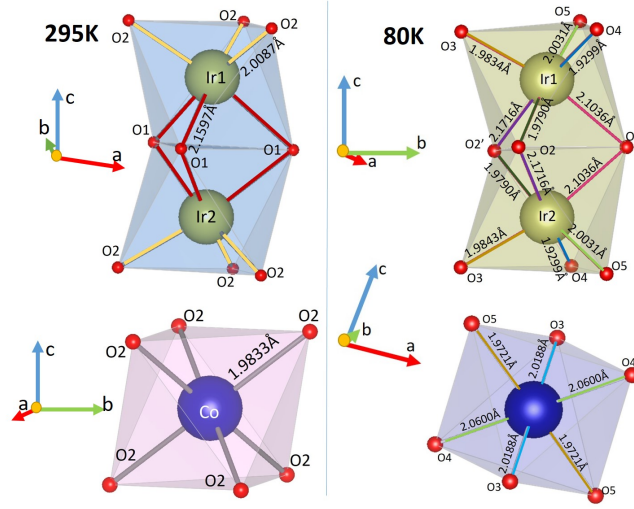


Figure 3.7: Schematic representation of Ir dimers and Cobalt octahedra at 295 K (left) and 80 K (right). The cobalt octahedra has only one Co-O bond at high temperatures, which splits into 3 pairs of Co-O bonds at 80 K. Similarly, Ir has 2 different bonds associated with Ir face sharing and corner sharing O atoms in the high symmetry structure, which transforms into 6 different pairs of Ir-O bonds below the magnetostructural transition. The bond lengths with equal magnitudes are represented with the same color for the sake of clarity.

and get an insight into the magnetic structure, we performed powder neutron diffraction measurements at 80K. The parent structure used for the symmetry analysis was $C2/c$ (Space group: 15). Our neutron diffraction measurements indicate that the nuclear and magnetic peaks appear at the same Bragg position, suggesting that the propagation vector of the magnetic structure is $\mathbf{K}=(0,0,0)$ which was also confirmed by using the K search program in FullProf [118]. We performed the symmetry analysis using BasIreps to find the possible magnetic structure based on this propagation vector. Out of the multiple solutions, the two indicating zero moment on Cobalt were naturally ruled out, and we converged to two different magnetic representations Γ_1 and Γ_3 , with almost similar goodness of fit ($R_{wp}/R_e \approx 3.3$ and 3.5 respectively). Both the magnetic models showed antiferromagnetically coupled Ir dimers, although they suggest FM and AFM Co/Ir interactions along different crystallographic directions. With the help of first principle calculations, as will be discussed in the next section, the magnetic representation using

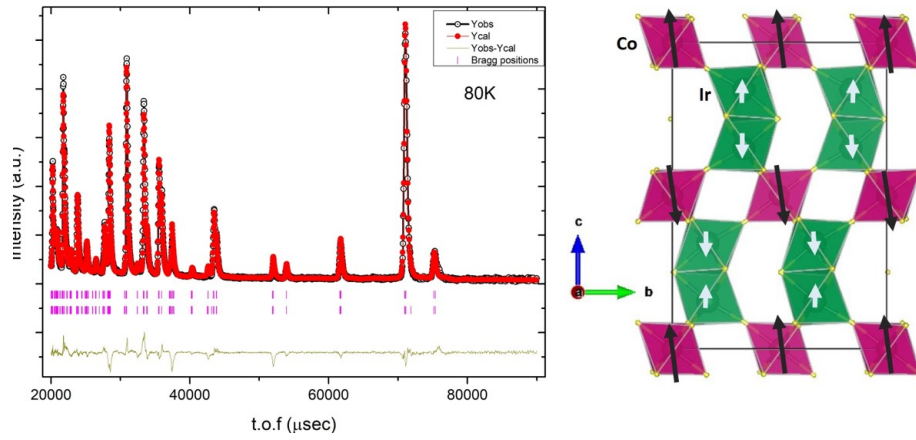


Figure 3.8: Left panel: Neutron powder diffraction pattern of $\text{Ba}_3\text{CoIr}_2\text{O}_9$ measured at 80K using the WISH diffractometer. The calculated and observed diffraction profiles are shown in red and black respectively. The upper and lower vertical pink marks represent the positions of nuclear and magnetic reflections respectively, and the green line at the bottom is the difference between observed and calculated intensities. The fit was for Ireps Γ_1 , and the symmetry operators and magnetic basis vectors are (1) x, y, z $[u, v, w]$, (2) $-x, y, -z + 1/2$ $[-u, v, -w]$, x, y, z $[u, v, w]$, (3) $-x, -y, -z$ $[u, v, w]$, and (4) $x, -y, z + 1/2$ $[-u, v, -w]$ for Iridium at 8(f) and (1) and (2) for more symmetric site 4(a) for Cobalt. Here, u , v , and w indicate the components of the magnetic moment. Right panel: A schematic of magnetic spin structure as determined from the neutron diffraction results. Cobalt spins (black) are ferromagnetically coupled to the antiferromagnetic coupled Iridium spins (white).

Γ_1 was considered correct for the magnetic structure refinement.

The Rietveld fit to the neutron diffraction data at 80K is shown in the left panel of Fig. 3.8. A schematic of the obtained magnetic spin structure is shown on the right where the black and white arrows indicate the direction of magnetic spins for Cobalt and Iridium respectively. We observed a weakly canted antiferromagnetic spin arrangement with Cobalt magnetic spins inclined at an angle ($\sim 11^\circ$) with respect to c -axis. It is imperative to point out that due to small ordered moment of Iridium, the magnetic spin directions were restricted to the c -axis, therefore, the canting in the Iridium spins is not observed. The intra-dimer Ir–Ir interaction is antiferromagnetic, which is similar to other iridates and ruthenates [9, 67, 91, 143], while the in-plane Co spins interact ferromagnetically. The antiferromagnetic alignment between the Co-planes is observed where the Ir–Co interaction is found to be ferromagnetic, in turn leading to the

inter-dimer Ir–Ir coupling to be ferromagnetic. In the non-collinear magnetic ground state, the net moment along the c -axis is zero due to completely compensated AFM coupling, while the (small) spin components along the b -direction align parallelly giving rise to weak ferromagnetism. This picture agrees well with the current experimental observation that the magnetic structure is predominantly AFM with superimposed weak ferromagnetism supported by our observation of a weak loop opening in MH isotherms (Fig. 3.5(c)). The obtained magnetic moment from neutron diffraction for cobalt is $2.45 \pm 0.19 \mu_B$, which is close to the moment obtained ($2.84 \mu_B$) for the ruthenate analogue $\text{Ba}_3\text{CoRu}_2\text{O}_9$ [143].

The obtained value of moment for Co^{2+} is lower than the spin only value for high spin state of cobalt ($3.88 \mu_B$). This could be due to hybridization effects and covalency effects as has been speculated earlier for the ruthenate analogue and the cobalt based double perovskite Sr_2CoWO_6 [144, 155]. An unrestrained fit of the neutron diffraction data suggests that Ir^{5+} has a finite moment value ($0.57 \pm 0.12 \mu_B$) which is close to the moment value of $0.421 \mu_B$ obtained from our Curie-Weiss fit. With Iridium being a strong absorber of neutrons, it is difficult to unambiguously resolve the details of the magnetic structure using the neutron data alone, and hence we rely on our first principles density functional theory calculations to substantiate our key inferences, as described below.

3.3.2.4 First principle calculations

In order to further probe the moment at Iridium site, first-principles density functional theory calculations as realized in the VASP code was used by our collaborators. Four different magnetic structures (all noncollinear) based on our refinement of neutron powder diffraction data at 80K were used, as shown in Fig. 3.9. The second magnetic representation in Fig. 3.9 belongs to irreducible representation Γ_3 . The first-principles calculations did not presume any magnetic structure but was guided by

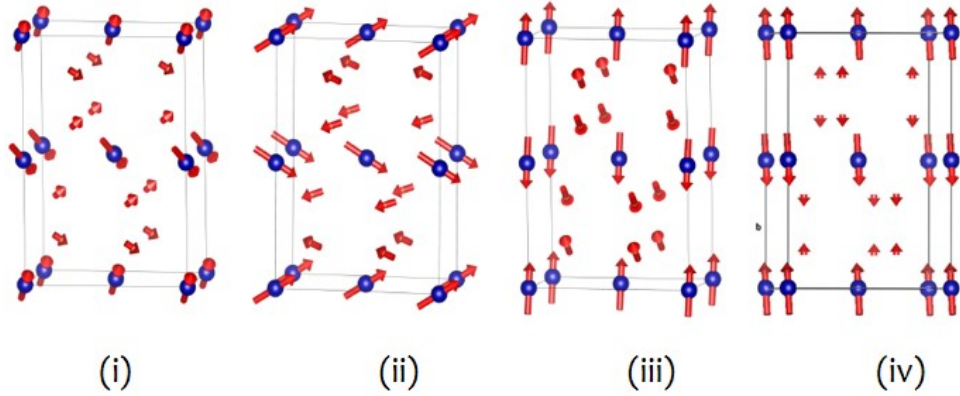


Figure 3.9: Schematic of the possible four different magnetic spin structure representations for the monoclinic (C2/c) phase at 80 K for $\text{Ba}_3\text{CoIr}_2\text{O}_9$

the experimental possibilities. The first-principles calculations, including the spin-orbit coupling within the GGA + U + SOC formalism, predicts a weakly $a - b$ -canted AFM structure as the ground state that agrees well with the magnetic structure derived from the neutron diffraction at 80 K (Fig. 3.10). The spin canting is relatively more prominent in Ir sites than the Co moments. In our calculations, even after considering several other magnetic structures, all configurations converged back to the ground state discussed above, thus reinforcing our choice to use the magnetic representation $\text{Ireps } \Gamma_1$. This picture agrees well with the current experimental observation from our neutron diffraction and magnetization results. The XPS data reveals $\text{Ir}^{5+}-d^4$ and $\text{Co}^{2+}-d^7$ electronic configurations, and the first-principles GGA + U + SOC calculations predict 0.86 and $2.76 \mu_B$ local moments at the Ir and Co sites, respectively. The results are consistent with the present experimental results and previous reports on iridates [9, 67, 91].

The curiosity to know how much energetically favourable is the constrained spin structure- all spins pointing along c -axis) in comparison to the canted one, constrained collinear calculations were also performed. As a result, it is observed that the non-collinearity is rather weak as the commensurate collinear spin configuration lies only 1.75 meV/f.u. higher, where all the spins align along the c -direction, and resembles

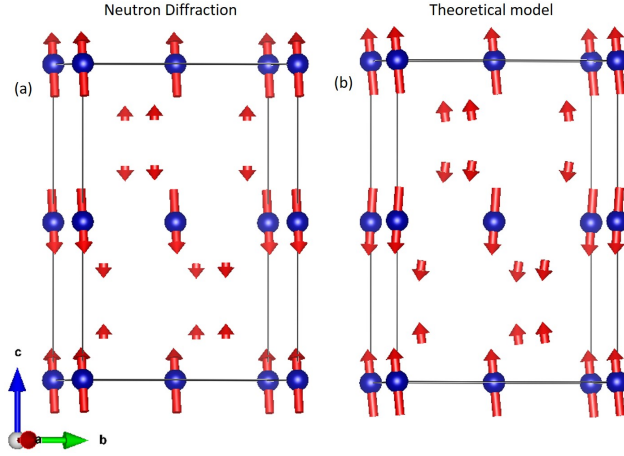


Figure 3.10: Schematic of the magnetic structure of the monoclinic ($C2/c$) phase at 80 K from (a) the Rietveld analysis of neutron diffraction data, and (b) using first-principles GGA + U + SOC calculations. Here, the blue solid circles and the small red arrows represent cobalt and iridium atoms respectively.

with that of a previously reported ruthenate, $\text{Ba}_3\text{NiRu}_2\text{O}_9$ [140]. In the present case, both electron correlation and SOC play important roles in determining the correct magnetic structure as the GGA + U calculations indicate unphysical FM ground state, and this will be discussed ahead. Within the GGA + U + SOC calculations, the constrained collinear moments along the c -direction are very similar ($\mu_{\text{Ir}} = 0.85$ and $\mu_{\text{Co}} = 2.76 \mu_B$) to the noncollinear moments, further indicating weak noncollinearity. This is consistent in the low value of ferromagnetic component ($0.47 \pm 0.21 \mu_B$) obtained by our neutron diffraction results. The Co^{2+} - d^7 ions stabilize in a high-spin $S = 3/2$, $t_{2g}^5 e_g^2$ state due to the low crystal field splitting $\Delta_{\text{Co}} \sim 1$ eV and high spin pairing energy of 2.3 eV in such compounds [140, 144, 156, 157]. In the contrary, the GGA + U calculations indicate a ferromagnetic metal with FM Ir–Ir coupling within the $\text{Ir}_2^{5+}\text{O}_9$ dimer, which is expected [67] and that is 16.5 meV/f.u. lower than the AFM coupling. This demonstrates the importance of the SOC in describing the magnetic and electronic structure correctly.

However, the generation of a local moment at the Ir^{5+} - d^4 site is complex. Ideally and

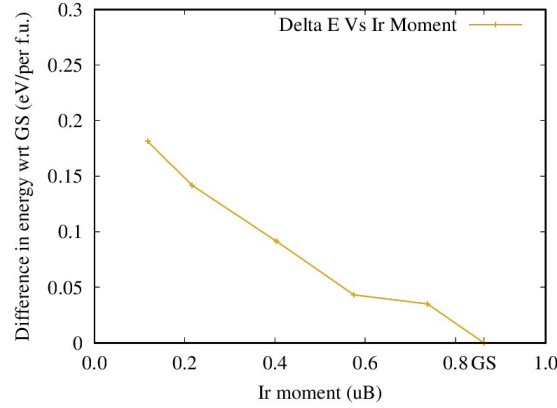


Figure 3.11: The variation in energy of $\text{Ba}_3\text{CoIr}_2\text{O}_9$ system with respect to the ground state versus the constrained moment on Iridium atoms. The energy of the system monotonically increases as a function of reducing moment at Ir sites.

owing to the large crystal field splitting of 3-4 eV, high SOC, and low pairing energy, the $\text{Ir}^{5+}-d^4$ should be hosting a $j_{\text{eff}}=0$ state [9, 67, 91, 158]. In contrast, the local moments are spontaneously generated at the $\text{Ir}^{5+}-d^4$ site within the GGA + U + SOC calculations that are in agreement with the present experimental results. The results are similar to $\text{Ba}_3\text{ZnIr}_2\text{O}_9$ iridate, including the proposed mechanism for the $\text{Ir}^{5+}-d^4$ moment formation [67, 100]. Calculations show that forcing the iridium moment to zero increases the energy by 200meV/f.u., indicating that the ground state must have non-zero iridium moment as shown in Fig. 3.11. In the ground state, Iridium has a moment of about 0.86 μ_B but as this moment was forcibly reduced, the energy of the system monotonically increases. While it was not possible to directly calculate the unphysical zero Ir moment case, it is clear from the plot that the system with Ir moment approximately zero will have a much higher energy. The corresponding orbital moments of 0.29 and 0.04 μ_B at the Ir and Co sites indicate strong spin-orbit coupling.

The Ir^{5+} moment is spontaneously generated due to the superexchange between the occupied $j_{\text{eff}} = 3/2$ and empty $j_{\text{eff}} = 1/2$ states within the $\text{Ir}_2^{5+}\text{O}_9$ dimer. However, in the absence of SOC, a ferromagnetic ground state emerges within the GGA + U calculations, due to spin conserved hopping of electrons between the $\text{Ir}^{5+}-t_{2g}$ orbitals. The

hopping between the half-filled $\text{Co}^{2+}-e_g^2$ and empty $\text{Ir}^{5+}-e_g^0$ states triggers the ferromagnetic superexchange according to the Goodenough-Kanamori-Anderson rule, consistent with the experimental magnetic structure obtained here.

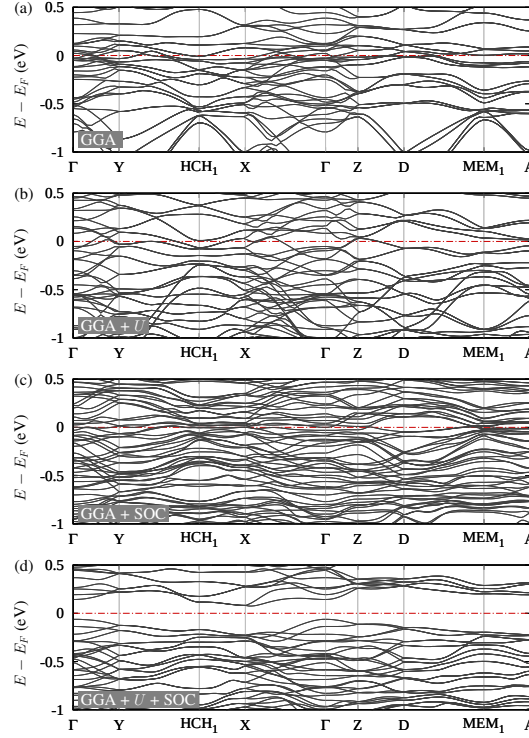


Figure 3.12: The calculated band structure at various theoretical hierarchy, (a) GGA, (b) GGA + U ($U_{\text{Co}} = 3$ and $U_{\text{Ir}} = 2.4$ eV), (c) GGA + SOC, and (d) GGA + U + SOC for $\text{Ba}_3\text{CoIr}_2\text{O}_9$. While the GGA + U + SOC ($U_{\text{Co}} = 3$ and $U_{\text{Ir}} = 2.4$ eV) results correctly predicts a Mott insulating electronic structure along with the correct magnetic solution, all other calculations predict metallic band structure. These calculations together indicate the interplay between the Coulomb interaction U and spin-orbit coupling.

Though an insulating electronic state is expected due to the antiferromagnetic intradimer $\text{Ir}^{5+}-\text{Ir}^{5+}$ superexchange coupling, all the calculations excluding the GGA + U + SOC predicts a metallic structure indicating the important interplay of Coulomb interaction and SO coupling (Fig. 3.12). For example, the GGA + U calculation predict a ferromagnetic metal [Fig. 3.12(b)]. In contrast, the GGA + U + SOC calculation with $U_{\text{Co}} =$

3 and $U_{\text{Ir}} = 2.4$ eV on-site Coulomb interactions correctly predicts an insulating state with 189 meV electronic gap [Fig. 3.12(d)] that is consistent with the resistivity data. The valence and conduction bands are composed with the hybridized Ir- d –O- p states, and thus the Coulomb interaction at the Ir-site is important for the insulating state. The calculated gap in Fig. 3.12(d) depends on U_{Ir} and decreases to 136 and 60 meV for $U_{\text{Ir}} = 2$ and 1.5 eV, respectively, below which the system becomes metallic. Therefore, spin orbit coupling and Coulomb interaction plays a crucial role in determining the ground state of $\text{Ba}_3\text{CoIr}_2\text{O}_9$.

3.3.3 Low temperature dynamics

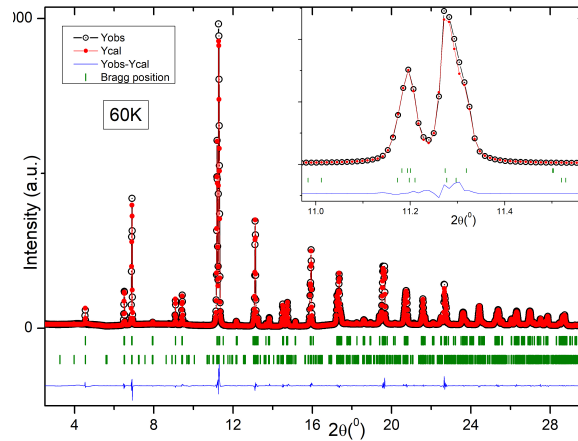


Figure 3.13: Main Panel: Rietveld refinement of synchrotron powder diffraction pattern of $\text{Ba}_3\text{CoIr}_2\text{O}_9$ at 60 K. The calculated and observed diffraction profiles are shown as red and black markers respectively. The vertical green lines indicate the calculated Bragg positions for the monoclinic $C2/c$ (top) and $P2/c$ (bottom) phases. The blue line at the bottom depicts the difference between observed and calculated intensities. The inset shows an expanded view of the main peak fitted using this two-phase model.

Below 80K, the synchrotron diffraction peaks further started splitting up signalling the emergence of another structural transformation. The fitting of the low temperature XRD data reveals a gradual distortion of the structure to an even lower monoclinic symmetry ($P2/c$) below 70K, which coexists with the monoclinic $C2/c$ phase down to the

Table 3.2: Structural parameters of Ba₃CoIr₂O₉ at 60 K.

Space group $C2/c$ (No. 15)				
$a = 5.7340(1) \text{ \AA}, b = 9.9841(1) \text{ \AA}, c = 14.2652(2) \text{ \AA}$				
$\alpha = \gamma = 90^\circ, \beta = 90.0385(10)^\circ$				
Atom	x	y	z	occupancy
Ba1	0.0004(13)	0.3312(05)	0.0877(03)	1.00
Ba2	0.0000	-0.0006(07)	0.2500	1.00
Co	0.0000	0.0000	0.0000	1.00
Ir	-0.0060(08)	0.3337(04)	0.8462(05)	1.00
O1	0.0000	0.5030(29)	0.2500	1.00
O2	0.2662(62)	0.2414(30)	0.2381(18)	1.00
O3	0.0296(70)	0.8401(29)	0.0805(33)	1.00
O4	0.2567(51)	0.1003(24)	0.0814(19)	1.00
O5	0.7709(83)	0.0744(56)	0.0784(50)	1.00

Space group $P2/c$ (No. 13)				
$a = 5.7550(1) \text{ \AA}, b = 9.9452(1) \text{ \AA}, c = 14.2634(2) \text{ \AA}$				
$\alpha = \gamma = 90^\circ, \beta = 90.2291(19)^\circ$				
Atom	x	y	z	occupancy
Ba1	0.5049(22)	0.1660(19)	0.9156(08)	1.00
Ba2	0.0000	0.0017(22)	0.2500	1.00
Ba3	0.5000	0.4986(27)	0.2500	1.00
Ba4	-0.0018(23)	0.6676(18)	0.9092(07)	1.00
Co1	0.0000	0.0000	0.0000	1.00
Co2	0.5000	0.5000	0.0000	1.00
Ir1	0.4989(17)	0.1671(13)	0.1554(06)	1.00
Ir2	-0.0015(18)	0.6654(13)	0.1532(07)	1.00
O1	0.729(19)	0.241(11)	0.263(44)	1.00
O2	0.180(15)	0.748(10)	0.247(53)	1.00
O3	0.0000	0.521(09)	0.7500	1.00
O4	0.5000	-0.008(21)	0.7500	1.00
O5	0.277(19)	0.089(14)	0.4142(55)	1.00
O6	0.799(20)	0.5636(79)	0.4209(58)	1.00
O7	0.019(18)	0.165(13)	0.9162(75)	1.00
O8	0.482(23)	0.674(12)	0.919(10)	1.00
O9	0.728(16)	0.071(11)	0.4618(43)	1.00
O10	0.267(16)	0.562(14)	0.4077(39)	1.00

lowest measured temperature. The Rietveld refinement of the diffraction pattern measured at 60 K, which has been fit using coexisting $C2/c$ and $P2/c$ monoclinic phases

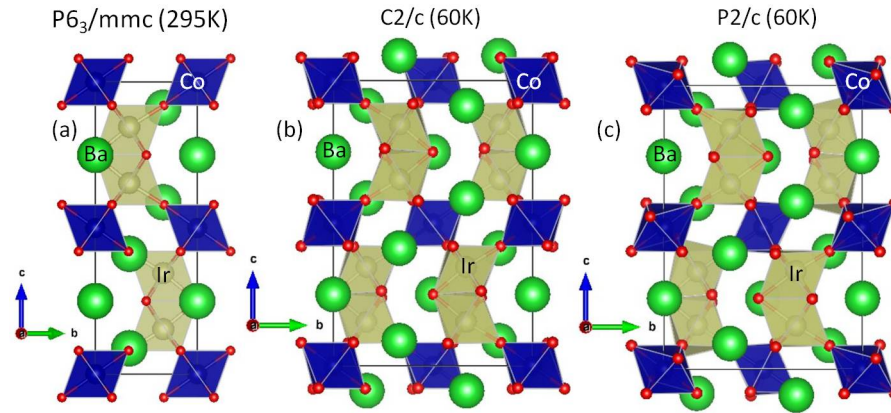


Figure 3.14: Main Panel: Schematic crystal structures exhibited by $\text{Ba}_3\text{CoIr}_2\text{O}_9$ across the temperature range of our investigations. Here, the blue and yellow octahedra represent the cobalt and iridium sites respectively. The high symmetry $P6_3/mmc$ structure (a) transforms to a monoclinically distorted $C2/c$ structure (b) at the magnetostructural transition. On further reduction in temperature, a part of the system transforms to an even lower symmetry $P2/c$ (c), with both these monoclinic phases coexisting down to the lowest measured temperatures.

is shown in Fig.3.13. The inset shows an expanded view of the fit of the major Bragg peak where the incorporation of both the phases can be seen explicitly. The refinement parameters R_p , R_{wp} and R_e obtained for this fit was 6.4, 9.9 and 1.2 respectively, and all our low temperature fits yielded similar values. The crystal structure of $\text{Ba}_3\text{CoIr}_2\text{O}_9$ at room temperature, as well as the two monoclinic phases at 60 K is depicted in Fig.3.14, and the structural parameters for these phases (at 60 K), as deduced from the refinement procedure, are summarized in Table 3.2.

The temperature dependence of the lattice parameters as determined in $\text{Ba}_3\text{CoIr}_2\text{O}_9$ is depicted in Fig. 3.15. The graph has been divided in three regions. Region I is associated with the hexagonal phase $P6_3/mmc$ where the lattice parameters a , b and c reduce as a function of decreasing temperature. At the magnetostructural transition temperature 107K, advent of region II, all the parameters exhibits a slope change, where the lattice parameter b increases sharply across the transition as a consequence of lattice doubling. The ensuing distortion in the lattice is also evidenced in the form of octahedral tilting and distortion, as is also corroborated by considerable changes in the Co-O and Ir-O

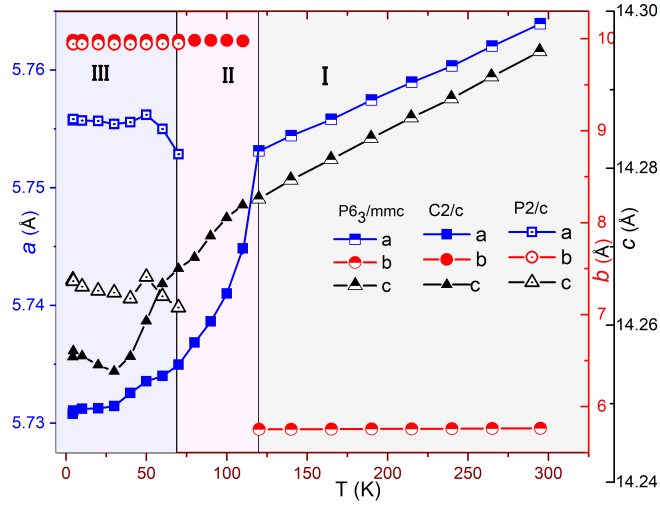


Figure 3.15: Variation of the lattice parameters of $\text{Ba}_3\text{CoIr}_2\text{O}_9$ as a function of temperature. The three regions correspond to 3 different structural phases. Region I - $P6_3/mmc$, II - $C2/c$ and III - $C2/c + P2/c$.

bond lengths and angles.

Region III corresponds to the phase co-existence regime where both the monoclinic phases $P2/c$ and $C2/c$ are present. The phase evolution of $P2/c$ symmetry was studied and resulted in an interesting observation. The phase fractions of the $P2/c$ and $C2/c$ phase as a function of temperature is depicted in the Fig. 3.16, the black and red curves denote $C2/c$ and $P2/c$ monoclinic symmetry respectively. As the temperature is lowered, the percentage fraction of $C2/c$ slowly reduces, concurrent with the increase in $P2/c$ phase with decreasing temperatures. However, at around 30K, this trend is seen to reverse and $P2/c$ slowly starts to transform back to the high symmetry phase $C2/c$. We note that a similar co-existence (and competition) between these two phases is been reported earlier in the vanadate perovskites of the form $R\text{VO}_3$ (with $R = \text{Sm}, \text{Ho}, \text{Yb}, \text{Pr}$ or Y) [159]. We believe that this is the first report of such phase coexistence in the triple perovskite iridates, and it remains to be seen whether other members of this extended family also exhibit similar features.

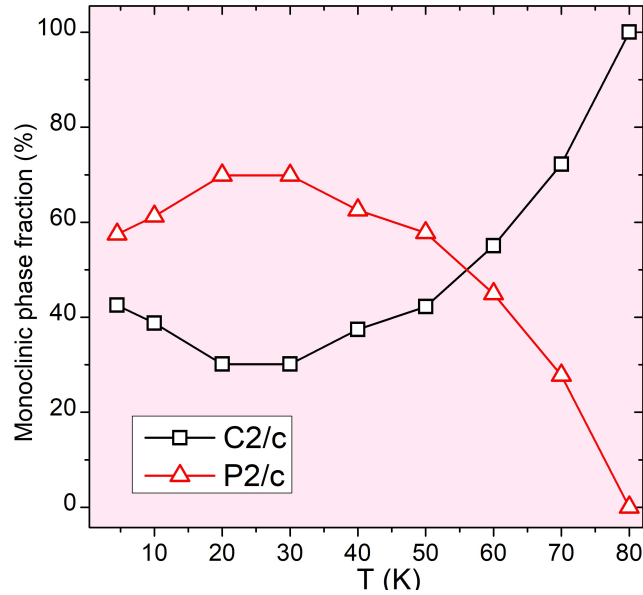


Figure 3.16: Variation of the phase fraction of the two monoclinic phases- $C2/c$ and $P2/c$, as a function of temperature, determined from the analysis of structural data.

3.3.4 Physical Properties

3.3.4.1 Specific Heat

Both the transitions- magnetostructural and the phase co-existence regime, could be observed in the specific heat measurement. The magnetostructural transformation manifests in the form of a peak at 107K (main panel Fig. 3.17), reflecting a large change in entropy associated with it. In the absence of the non-magnetic analogue, it is difficult to quantify the change in entropy for this triple perovskite near the magneto-structural transition. Additionally, it is also difficult to determine the contribution of C_M (magnetic contribution to specific heat) to the total specific heat. Interestingly, there is no appreciable shift in the antiferromagnetic transition to lower temperatures as a function of the applied field as shown in Fig. 3.17(a). This is possibly a consequence of the fact that the applied field (of 5T) is rather small. However, the entropy release in the paramagnetic side of the phase transition clearly increases as a function of the applied magnetic field, with all the data merging together at around 115 K. It appears that what

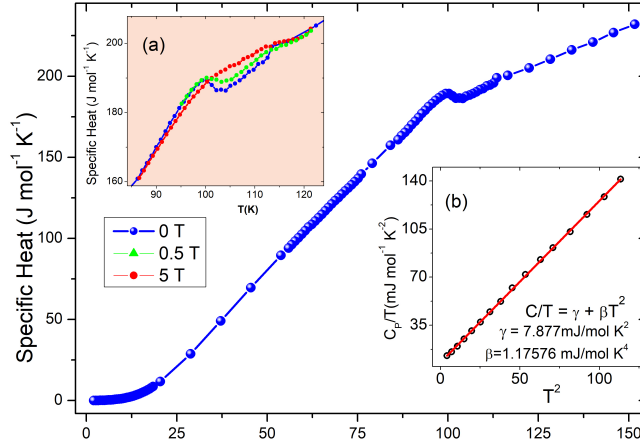


Figure 3.17: Main panel: The heat capacity measured as a function of temperature, with a peak characterizing the magnetic transition. (a) Specific heat in the presence of various magnetic fields (0, 0.5 and 5 T). (b) The black circles are the experimentally observed specific heat at low temperature and the red line is the fit to the Dulong and Petit's law [8].

we are observing is an intricate interplay between the applied field, short range magnetic correlations, and the frustration incipient to the hexagonal $\text{P6}_3/\text{mmc}$ lattice. We speculate that application of the magnetic field might be contributing to a release of the frustration by the formation of low symmetry clusters within the paramagnetic matrix. This is reflected in the form of a larger entropy release in the $T > T_N$ regime. A magnetic field dependent high resolution x-ray diffraction would be useful in unambiguously explaining this observation.

Fig. 3.17(b) shows the low temperature specific heat data fit to the expression $C_p = \gamma T + \beta T^3$, where γ and β are related to the electronic and vibrational degrees of freedom respectively. The density of states at the Fermi surface (N_{ϵ_F}) was deduced using the expression $\gamma = \gamma_0(1 + \lambda_{e-ph})$, where $\gamma_0 = \frac{\pi^2 k_B^2}{3} N_{\epsilon_F}$, where k_B is the Boltzmann constant, and λ_{e-ph} is the electron phonon coupling which can be ignored here as the system is insulating at low temperatures. The obtained density of states is $3.3 \text{ eV}^{-1} \text{ f.u.}^{-1}$, which is consistent with the semi-conducting nature of $\text{Ba}_3\text{CoIr}_2\text{O}_9$. The co-existence of two structurally disparate phases in $\text{Ba}_3\text{CoIr}_2\text{O}_9$ also manifests itself in the form of a

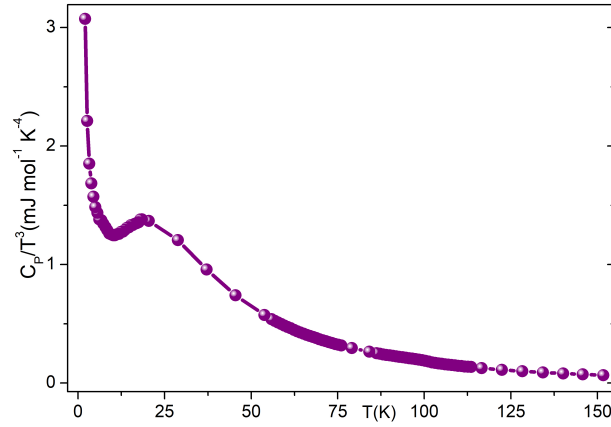


Figure 3.18: The low temperature specific heat C_p/T^3 as a function of temperature as measured in $\text{Ba}_3\text{CoIr}_2\text{O}_9$.

pronounced deviation of the measured specific heat from the standard Debye T^3 dependence at low temperatures. This is seen in the main panel of Fig. 3.18, where C_p/T^3 is plotted as a function of temperature. This excess entropy is a signature of a glassy phase [160] and is similar to what is seen in structural glasses, as well as in systems like the mixed valent manganites, where the electronic phase separation results in the formation of magnetically (and structurally) dissimilar phases which co-exist with each other. In most of the manganites, these competing phases are ferromagnetic and antiferromagnetic [161–163], whereas in this case, both the phases appear to be predominantly antiferromagnetic, albeit with varying amounts of monoclinic distortion.

3.3.4.2 Resistivity

Measurements of the temperature dependent resistivity indicate that the transport properties are governed by Variable Range Hopping (VRH) dynamics in the entire temperature range, and a change in the slope demarcates this semiconductor to semiconductor transition as shown by the blue line in Fig. 3.19(a). The figure shows a plot of $\ln \rho$ vs $T^{1/4}$, where the red line is the linear fit in the high temperature region. The magneto-structural transition is seen more clearly in the derivative plot, which shows a peak at $\sim$

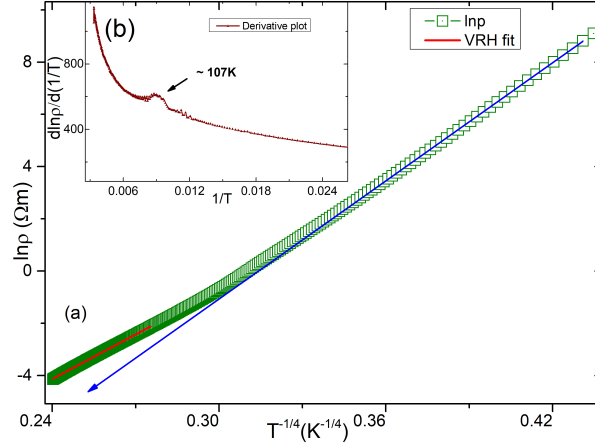


Figure 3.19: (a) Resistivity ($\ln \rho$) plotted as a function of temperature ($T^{-1/4}$). The red line is the linear fit to the high temperature region using the Variable Range Hopping formalism (b) Derivative of $\ln \rho$ exhibits a peak close to 107 K marking the onset of the magneto-structural transition.

107 K as shown in the inset Fig. 3.19(b).

Noise Spectroscopy

We have also investigated the $\text{Ba}_3\text{CoIr}_2\text{O}_9$ using resistance noise spectroscopy, which provides an interesting perspective - especially near phase transitions - in strongly correlated oxides. Fig. 3.20 shows the normalized resistance noise PSD evaluated at $f = 1$ Hz. Noise measurements were performed at temperatures between 50 K and 180 K and for various external magnetic fields between 0 T to 10 T. In order to verify that the measured $1/f$ -type noise spectra originate from the investigated sample, we checked the scaling of the voltage noise magnitude S_V with the applied current I . After Hooge's empirical law [131, 132],

$$S_V(f) = \frac{\gamma_H V^2}{n \Omega f^\alpha}, \quad (3.1)$$

the magnitude of the voltage noise is expected to scale as $S_V \propto V^2 \propto I^2$. Here, V represents the applied voltage, γ_H the material-dependent Hooge parameter, α the frequency exponent, n the charge carrier density, and Ω the "noisy" sample volume, i.e. $n\Omega = N_c$

gives the total number of charge carriers in the material causing the observed $1/f$ noise. The inset of Fig. 3.20 demonstrates the expected scaling behavior of the acquired noise spectra at a selected temperature of 50 K. Note that for zero applied current, only the frequency-independent background noise of the experimental setup is observed.

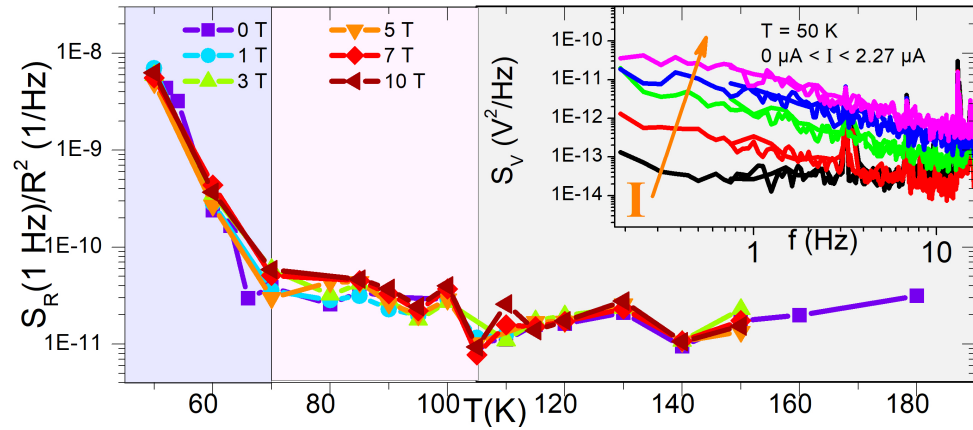


Figure 3.20: The main panel depicts the temperature-dependent normalized resistance noise evaluated at 1 Hz for $\text{Ba}_3\text{CoIr}_2\text{O}_9$ at different magnetic fields. The inset depicts the scaling of the voltage noise magnitude S_V with the applied current I at a fixed temperature of 50 K.

As depicted in the main panel of Fig. 3.20, the normalized noise magnitude exhibits only a weak temperature dependence at high temperatures. At the onset of the magnetostructural transition, the noise is observed to increase by almost an order of magnitude. Moreover, on further reduction in temperature, a drastic increase of about two orders of magnitude is observed between 70 K and 50 K, where our structural data infers on the co-existence of the two structurally disparate monoclinic phases. There is no pronounced and systematic dependence of the normalized noise magnitude on the applied magnetic field. Even though there is no additional signature in the resistivity below the phase transition, the resistance noise is clearly far more sensitive to the onset of phase coexistence than to the magnetostructural transition at 107 K.

It is known that noise spectroscopy provides a more microscopic picture and is more sensitive to electronic inhomogeneity and the microgeometry of a sample, in marked

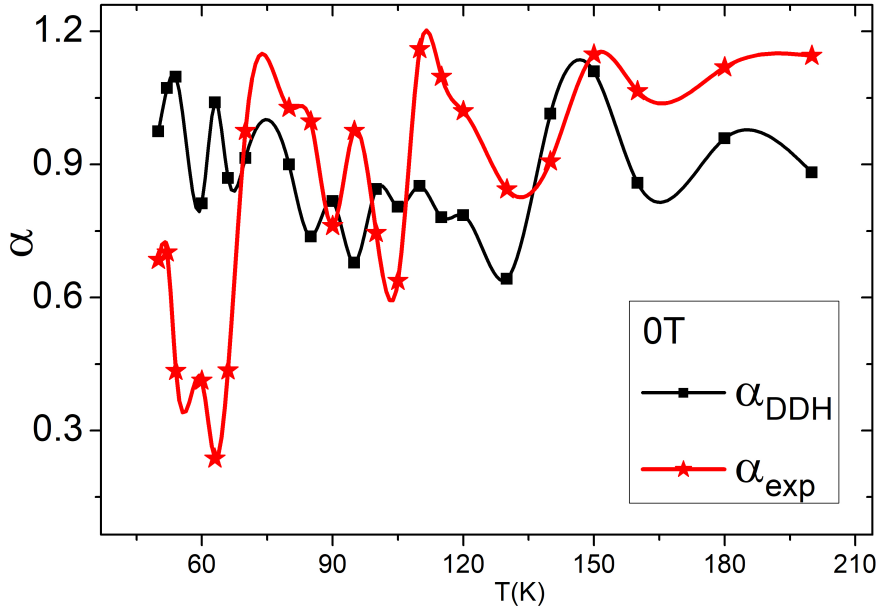


Figure 3.21: DDH model

contrast to routine resistivity measurements. Since we did not observe any significant features in the resistivity around 70 K, our study of the low-frequency $1/f$ -noise reaffirms our observation of the coexistence of different phases and its impact on the electronic transport. A possible explanation for the strongly enhanced $1/f$ -type fluctuations below 70 K is the presence of inhomogeneous current paths due to the occurrence of different structural phases. These coexisting phases can be assumed to differ in their individual electronic properties. It is well known for other materials with coexisting electronic phases that an inhomogeneous conduction can lead to strong modifications of the measured noise magnitude [164, 165]. This is a useful addition to the overall picture obtained from the powder diffraction and specific heat measurements - and it is also complemented by the dielectric susceptibility results as will be shown ahead. Therefore, the noise data serve as a good complement to the resistivity measurements, in which no signatures of an electronic phase separation can be seen. In the entire temperature range, we also studied the relation of frequency exponent (α), defined as the slope of the $1/f$ -type spectrum in a log-log plot of S_V and frequency, as a function

of varying temperature. We used the approach formulated by Dutta, Dimon, and Horn to infer on the strongly correlated nature of this system. The Fig3.21 shows the DDH (Dutta, Dimon, and Horn) model applied for the $B=0T$ data set. DDH formulated an approach to study noise in metals and ascribe the obtained dynamics to random fluctuations with thermally activated characteristic times [166]. The model assumes that a large number of random and independent fluctuators or switching entities present in a system are spread over a broad distribution of activation energies and leads to an approximate $1/f$ spectra which can be characterized by using thermally activated time constants. The strong disagreement between the theoretically predicted and the experimentally determined α is pronounced in the entire temperature range, implying that the assumption of independent fluctuators does not seem to be valid anymore.

3.3.5 Dielectric Spectroscopy

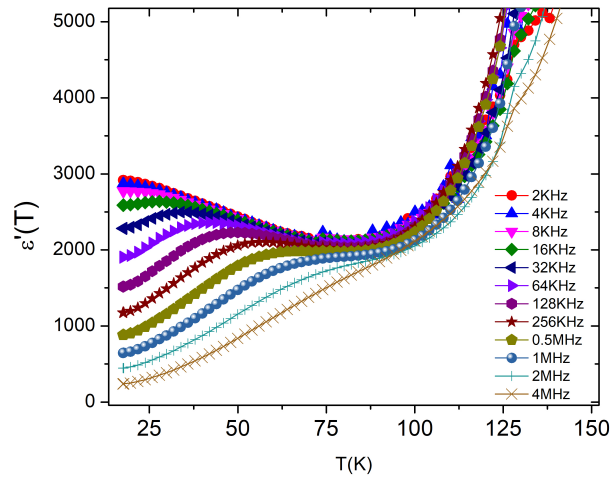


Figure 3.22: depicts the temperature dependence of the real part of the dielectric susceptibility as measured in frequencies ranging from 2 KHz to 4 MHz.

The inferences drawn from the noise measurements are also reinforced by our dielectric data, with the real part of the dielectric susceptibility exhibiting a substantial

frequency dependence in the magnetically ordered state, with this dispersion being even more pronounced below 70 K where we have coexisting monoclinic phases (Fig. 3.22). The fact that we observe this frequency dependence only below the magnetic transition temperature clearly indicates a coupling of electric and magnetic order parameters. We note that such a frequency dependent feature in dielectric susceptibility is characteristic of charge relaxation processes, and has been observed in a number of phase separated systems [167]. However, our attempts to fit the frequency dependent peaks to both the Arrhenius and Vogel-Fulcher-Tammann (VFT) formulations were unsuccessful, indicating that the dynamics of these charge relaxations and also their magnetic field dependence would need additional investigations. One possible origin of the deviation from these standard models could be the presence of phase co-existence regime. The measured dielectric response is a resultant of the two co-existing monoclinic phases and therefore, most probably multiple parameters are at play here. The contribution for both the phases would add to the dielectric response and a single fitting function will thus be insufficient to fit the experimentally obtained dynamics.

3.3.6 Magnetization in external environments

The open framework network of this triple perovskite in the form of corner and face sharing linkages offer opportunities to tune magnetic exchange interactions using external perturbations like pressure and electric fields.

3.3.6.1 Pressure dependent magnetization

High pressure magnetization measurement was performed on $\text{Ba}_3\text{CoIr}_2\text{O}_9$ and the influence of the pressure on the magnetic transition was studied. The model LPC-15 from Quantum Design, Japan which is a traditional beryllium copper (BeCu) cylindrical high pressure cell for performing magnetization measurements was used. The different com-

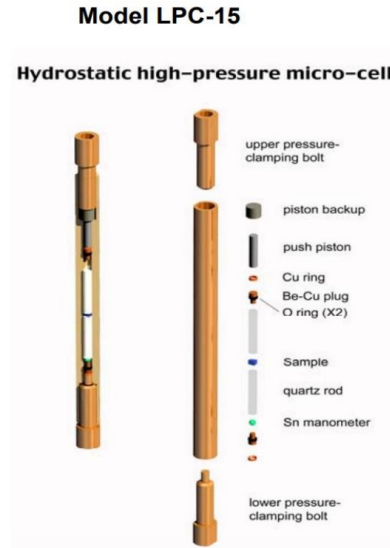


Figure 3.23: Hydrostatic pressure cell assembly from Quantum Design, Japan.

ponents and the sample configuration of the set-up is shown in Fig.3.23. For the following measurement, lead (Pb) was used for the calibration as it has a robust pressure dependent magnetization shift which can be used to calculate the pressure inside the cell. The relation between change in transition temperature (T_P) to the corresponding pressure inside the cell (P) is given by,

$$\frac{dT_c}{dP}(K/GPa) = -0.379(K/GPa)$$

Fig.3.24 shows the influence of pressure on the magnetic transition temperature. A relatively small pressure of 0.527 GPa shifted the transition by 1.82K as shown in the inset of Fig.3.24. The obtained relative change in transition temperature (T_P) to the corresponding pressure inside the cell (P) is $\frac{dT_c}{dP}(K/GPa) = 3.453(K/GPa)$ which is in line with many $4d$ and $5d$ based oxides as tabulated in Table. 3.3.

The application of pressure could modify the strength of the hybridization between Iridium and Cobalt octahedra without causing any change in the compound's inherent chemical environment. This can modify inter and intra layer interactions dictated by bond distances and angles, altered in the presence of pressure. These pressure induced

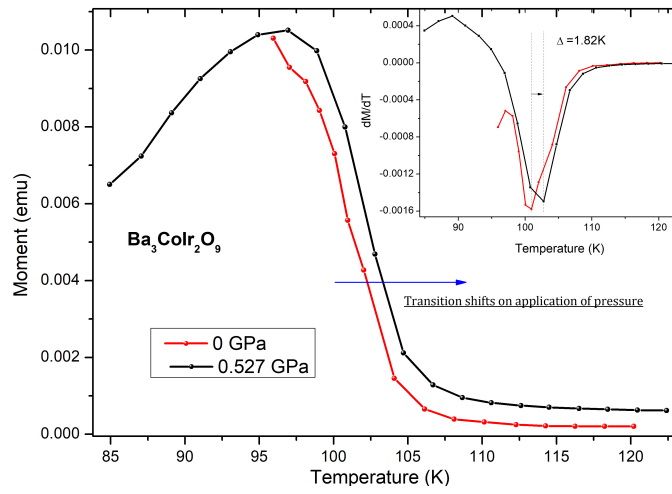


Figure 3.24: Zero field cooled magnetization at 1000 Oe in the presence of external pressure.

Compound Name	$\frac{dT_c}{dP}$ (K/GPa) [ref.]
$\beta\text{Li}_2\text{IrO}_3$	+0.9 [168]
BaIrO_3	-16 [169]
$\text{Ba}_{0.96}\text{Eu}_{0.04}\text{IrO}_3$	-15 [170]
SrRuO_3	-5.7 [171]

Table 3.3: The values of the relative change in magnetic transition temperature with the application of pressure.

interaction in frustrated lattices can provide a path to attain quantum spin liquid state thus proving to be a promising direction to look at [172]. Some pressure dependent studies on the family of double/triple perovskites resulted in many interesting results. Few notable results where effect of pressure has been studied are:

1. On charge state- A first-order transition is realized on application of 5 GPa, by the internal transfer of valence electrons between Bismuth and Iridium/ Ruthenium in three different hexagonal perovskites- $\text{Ba}_3\text{BiIr}_2\text{O}_9$, $\text{Ba}_3\text{BiRu}_2\text{O}_9$ and $\text{Ba}_4\text{BiIr}_3\text{O}_{12}$ [102].
2. Theoretical calculations- The band gap of $\text{Ba}_2\text{CrTaO}_6$ and $\text{Ba}_2\text{MnTaO}_6$ varied from 2.63 to 2.56 eV and 2.24 to 1.95 eV respectively on application of pressure ranging 0 to 25 GPa. The magnetization showed reduced magnetic moment as a function of increasing pressure. [173].

3. Change in magnetic structure- $\text{Sr}_2\text{FeOsO}_6$ exhibits an antiferromagnetic ordering below 140K and a spin structure transformation from AF1 to AF2 near 70K at ambient pressure. A transition from antiferromagnetic to the ferrimagnetic state is observed under the influence of pressure using Raman spectra and Os $L_{2,3}$ x-ray magnetic circular dichroism (XMCD) spectra. [174, 175]

However, studies where pressure dependence on spin and phonon coupling are focused, are still lacking. Therefore, high pressure synchrotron and neutron diffraction studies of $\text{Ba}_3\text{CoIr}_2\text{O}_9$ are imperative to decipher the structural modifications and the subsequent changes in magnetic spin structure due to pressure. Hence, more detailed high pressure magnetization studies could offer a new perspective to understand spin-phonon dynamics.

3.3.6.2 Electric field dependent magnetization

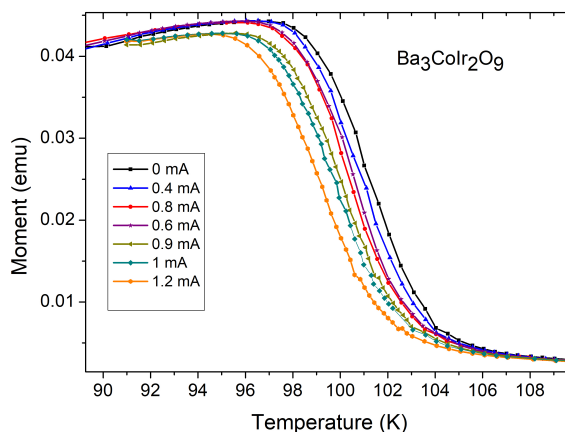


Figure 3.25: The shift in the magnetic transition temperature of $\text{Ba}_3\text{CoIr}_2\text{O}_9$ as a function of applied external electric current.

Given the small amount of pressure required to shift the magnetic transition temperature, we also attempted to study the effect of electric field on magnetization. The measurements were performed using a Manual Insertion Utility Probe (MIUP) available in the MPMS-XL (Quantum Design) as an additional probe option. MIUP or multifunc-

tional probe, as the name suggests, provides utility to do measurements under various external environments. The MIUP probe contains a 10 point panel for electrical wire connection with a copper plate at the bottom for sample placement. These 10 contacts are available on the other end of the probe, that is, the user end, to make electrical connections using current or voltage source. The copper plate was removed and a rectangular shaped pellet of $\text{Ba}_3\text{CoIr}_2\text{O}_9$ sample was mounted on a straw attached at the end of the probe. Two electrical contacts were made using thin copper wires between the sample (using silver paste) and MIUP probe (soldered). The probe was loaded inside SQUID and the magnetization was measured as a function of temperature in various applied electric currents. Using MIUP, it was possible to measure magnetization in MPMS XL while an electrical bias was applied to the sample. Since MPMS-XL is very sensitive to measure magnetization, it is advantageous to study the change in magnetization with the applied electric field and study the electromagnetic susceptibility.

$4d$ and $5d$ based oxides are potential candidates to study the effect of electric current on magnetisation given the strong spin orbit interaction and extended d orbitals leading to comparable on-site Coulomb interactions. The triple perovskite discussed in this chapter, $\text{Ba}_3\text{CoIr}_2\text{O}_9$, with a delicate balance of comparable energy scales is extremely susceptible to even small external stimuli leading to intriguing spin-phonon dynamics. The external stimuli discussed in this section is electric current. Previously, it has been reported for the popular iridate Sr_2IrO_4 , the application of electric current can relax or expand the lattice, presenting a promising avenue to study a new horizon- current controlled quantum states, which can bear great significance both for fundamental research and technological applications. The obtained response of magnetization for $\text{Ba}_3\text{CoIr}_2\text{O}_9$ as a function of electric current is summarized in Fig.3.25. As the electric current is increased from 0mA to 1.2mA, the transition shifts towards lower temperature, contrary to what was observed on application of pressure. This is indeed an interesting observa-

tion where application of pressure and electric field leads to opposite response from the system.

Similar to the triple perovskite discussed in this chapter, Sr_2IrO_4 has a canted spin arrangement for Iridium which leads to rigid rotations of the IrO_6 octahedra [176]. The coupling between the canted spin and the applied electric current leads to reduction in Néel temperature. This also results in a large spin-lattice coupling where a large non-linear lattice expansion increases the Ir canting angle, thereby, favouring electron hopping which is reflected in the magnetization too. We believe a similar mechanism is at play here. The bond linkages between Ir and Co, Ir-O-Ir and Co-O-Ir drives the ground states in these oxides, whereby, their movement affects the extent of hybridization and inturn the orbital overlap, spin and orbit coupling. We speculate that the application of electric current leads to changes in these bond angles, ultimately promoting weakening of the antiferromagnetic order, as evident by the reduction in T_N in Fig.3.25. The same mechanism has been demonstrated for Sr_2IrO_4 , where even small changes in lattice geometry can give rise to drastic affect in the physical properties as a consequence of the inherently stronger spin-orbit coupling in these iridium based oxides [177, 178].

A synchrotron diffraction studied in the present of electric field could offer a clear picture where even the small changes in bond angles and lengths can be easily captured. In addition, a crystal of $\text{Ba}_3\text{CoIr}_2\text{O}_9$ would help perform a directional dependent study and would help shed more light on the inherent dynamics. Therefore, more measurements with electric field as a probe and high quality crystals would be required to do thorough study on this system.

3.4 Summary

In summary, we report on a comprehensive experimental and theoretical investigation of the triple perovskite iridate $\text{Ba}_3\text{CoIr}_2\text{O}_9$. Stabilizing in the hexagonal $P6_3/mmc$ sym-

metry at room temperature, it exhibits a magneto-structural transition to a monoclinic $C2/c$ phase at 107 K- the highest known amongst all the triple perovskite iridates. Below 70 K, a part of the system transforms to a monoclinic phase with even lower symmetry ($P2/c$), and both these phases coexist down to the lowest measured temperatures. First-principles calculations, including the spin-orbit coupling within the GGA + U + SOC formalism, predicts a weakly $a - b$ -canted AFM structure as the magnetic ground state for the $C2/c$ phase that agrees well with the magnetic structure derived from the neutron diffraction data. The observation of excess entropy in the low temperature specific heat, a pronounced increase in the resistance noise and the frequency dependent dispersion in the dielectric susceptibility, all point towards a highly correlated ground state in $\text{Ba}_3\text{CoIr}_2\text{O}_9$. In addition, we also studied the affect of various perturbations like electric field and pressure in modifying the magnetic exchange pathways, further providing more probes to tune spin-phonon dynamics in this layered triple perovskite iridate.

Chapter 4

Negative thermal expansion in $\text{Ba}_3\text{CoIr}_2\text{O}_9$

The contents of this chapter are under review in Physical Review Research under the title-

”Phase coexistence and negative thermal expansion in the triple perovskite iridate $\text{Ba}_3\text{CoIr}_2\text{O}_9$ ”
(arXiv:2010.03940) [179].

4.1 Introduction

Negative Thermal Expansion (NTE) - the counter intuitive contraction of solids on heating - has been the focus of extensive experimental and theoretical investigations for many years [74, 79, 81, 82]. By virtue of their structural diversity and chemical flexibility, the transition metal oxides have proven to be a fertile playground for uncovering new candidates which exhibit this phenomena [180–184]. From the structural perspective, this phenomena is feasible in systems where the crystallographic framework consists of strongly bonded polyhedra units (also called rigid unit modes) [185], and here the

NTE occurs as a consequence of the transverse vibrations of these units. NTE can also arise due to underlying electronic and magnetic phenomena [186–188]. A significant advance in this field was the observation of giant NTE in ZrW_2O_8 [189,190], which then paved the way for this phenomena to be discovered in a number of other transition metal oxides. A variety of structural classes like the zeolites, perovskites and its variants, as well as spinels are now known to exhibit NTE [187, 191–194].

In the previous chapter, a detailed structural and magnetic investigations of $\text{Ba}_3\text{CoIr}_2\text{O}_9$, where this $3d-5d$ based member of the triple perovskite family exhibits a structural transition at 107 K, accompanied by the onset of canted antiferromagnetic order was presented. Unlike any other reported triple perovskite, this system shows two structural transitions with clear evidence of phase co-existence below 70 K. In addition to this, we also observed strongly coupled spin-phonon dynamics leading to anomalous thermal expansion in this iridate. Signatures of magnetic stress driven negative thermal expansion at low temperatures in both the coexisting monoclinic phases was observed. Such a correlation between the stress and the crystallographic structure is possible due to the open framework structure and flexible network intrinsic to this system, where open spaces facilitate lattice deformations and octahedral rotations. This stress, which has a magnetic origin, could be important in several related systems with large spin-orbit interactions.

4.2 Results and Discussion

4.2.1 Phase coexistence and phase reversal

$\text{Ba}_3\text{CoIr}_2\text{O}_9$ crystallizes in an aristotype 6H-type BaTiO_3 hexagonal ($P6_3/mmc$) structure at room temperature, consistent with the previously reported triple perovskites [55, 143] as discussed previously. As the size of the A cation increases, the BO_6 and

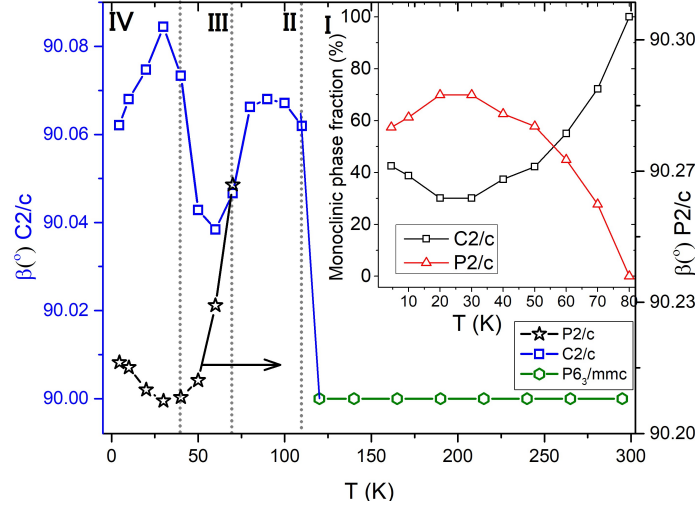


Figure 4.1: Main panel: Temperature dependence of the monoclinic angle β for the $P6_3/mmc$ (○), $C2/c$ (□) and $P2/c$ (★) phases of $Ba_3CoIr_2O_9$. The variation of phase fraction of the monoclinic $P2/c$ and $C2/c$ phases with temperature is depicted in the inset.

$B'O_6$ octahedra rotate in order to minimize the lattice energy. This tilting of octahedra then modifies bond lengths and bond angles, as a consequence of which the effective crystallographic symmetry is reduced.

The crystal structure details have been discussed in Chapter 1, where below 70 K, co-existing monoclinic phases ($P2/c$ and $C2/c$) are present down to the lowest measured temperatures. The evolution of relative ratios of both the monoclinic phases with temperature is shown here again for reference in the inset of Fig.4.1. For all the crystallographic parameters deduced from analysis of diffraction data, the error bars are of the same order (or smaller) than the symbol size used. As the temperature is reduced, the $C2/c$ phase gradually converts to the lower $P2/c$ symmetry. Interestingly, close to 40 K (T_p), this phase ratio is reversed and a part of the system slowly transforms back to the higher $C2/c$ monoclinic symmetry. The evolution of these phases can be clearly observed in β which is the angle between the crystallographic a and c axes, as depicted in the main panel of Fig.4.1. The plot can be divided into 4 regions. Region I corresponds to the (paramagnetic) hexagonal phase where β remains constant based on

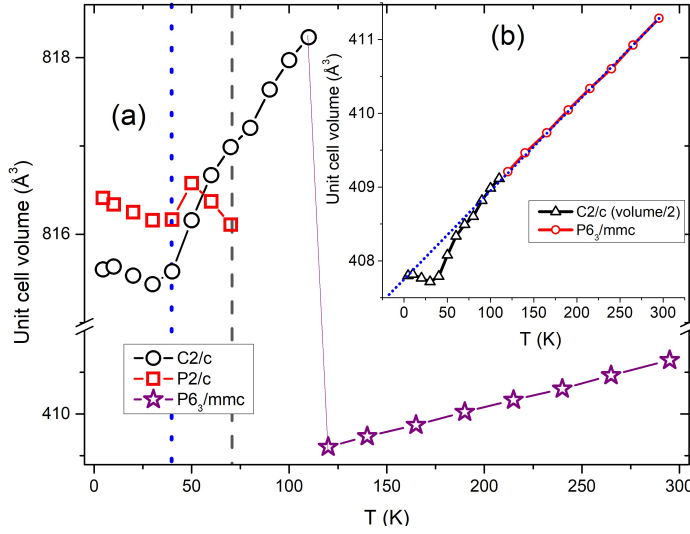


Figure 4.2: (a) Temperature dependence of volume as determined for $P6_3/mmc$ ($\star$), $C2/c$ ($\circ$) and $P2/c$ ($\square$). The vertical bar at 70K and 40K indicate the onset of phase co-existence and the phase cross over temperature T_P respectively. (b) The reduced volume for $C2/c$ is plotted for comparison and a strong upturn is observed close to 40 K. (c) Variation of the coefficient of volume thermal expansion α_V for the $C2/c$ and $P2/c$ phases.

symmetry constraints. In region II, there is a sharp increase in β because of the change in symmetry at the magnetostructural transition. Region III corresponds to the phase coexistence regime, and as the $C2/c$ phase transforms to $P2/c$, the β value sharply increases till the phase cross over temperature (T_p) is reached. As soon as a maximum tilt angle of 90.084° is achieved, the phase reversal is triggered. This corresponds to region IV, where β decreases with a concomitant increase in the relative fraction of the $C2/c$ phase. A similar trend is also observed for the lower symmetry $P2/c$ phase, with temperature dependence of β and the phase fraction being inversely correlated to each other.

4.2.2 Negative thermal expansion

On careful observation, these regions are also clearly demarcated in the temperature dependence of the volume, as is shown in Fig.4.2(a). A steep rise in the volume at

107 K marks the onset of AFM order and a magnetostructural transition as confirmed by synchrotron and neutron diffraction. A dashed vertical bar at 70 K indicates the onset of second phase transition concomitant with the onset of a phase co-existence region. Interestingly, the monoclinic $P2/c$ phase shows an anomalous behaviour where the volume increases as the temperature is lowered. This negative thermal expansion is observed right from the phase transformation at 70 K with a discontinuity at the phase crossover temperature T_p of 40 K. Since the magnetostructural transition from the hexagonal $P6_3/mmc$ to the monoclinic $C2/c$ phase at 107 K is accompanied by unit cell doubling, the reduced volume of the $P6_3/mmc$ phase and the volume of the $C2/c$ phase are plotted against temperature in Fig.4.2(b) for an easy comparison. A subtle change in the slope the structural transition at 107 K is followed by an marked upturn in the volume at 40 K as is also depicted in the main panel. This clearly indicates the presence of negative thermal expansion in the $C2/c$ phase as well below the phase crossover temperature T_p .

The crossover from positive to negative thermal expansion results from the balance between two competitive factors: anharmonic phonon vibration and magnetic exchange-striction, with each contributing to positive and negative thermal expansion respectively. The typical value of the coefficient of volume thermal expansion α_V [$= (1/V)dV/dT$] for the prototypical NTE system ZrW_2O_8 is $-2.7 \times 10^{-5} \text{ K}^{-1}$. The highest values of α_V for the $P2/c$ and $C2/c$ phases of $Ba_3CoIr_2O_9$ are -1.21×10^{-5} and $-0.8 \times 10^{-5} \text{ K}^{-1}$ respectively, which is of the same order as that reported in many prototypical NTE materials [195, 196].

4.2.3 Magnetic exchange striction

The temperature dependence of the c/a ratio for all the structural phases is depicted in Fig.4.3, and significant change is observed just below the magnetostructural transition.

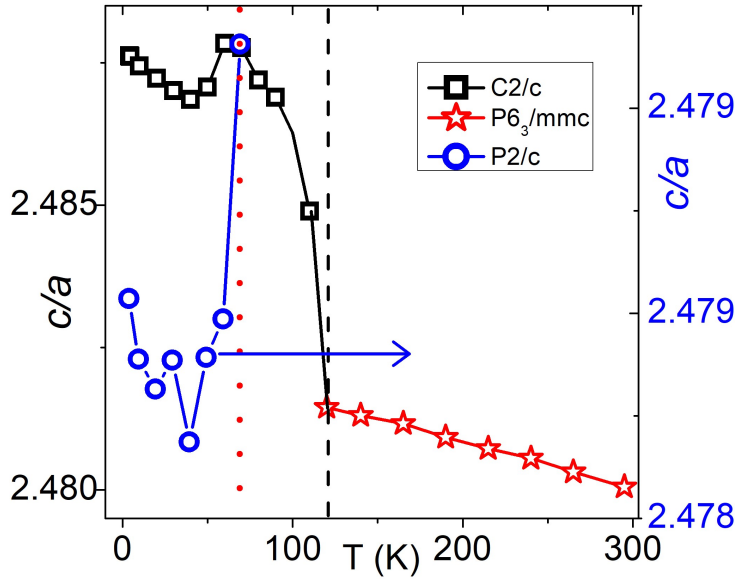


Figure 4.3: Temperature dependence of the c/a ratio for all the structural phases encountered in $\text{Ba}_3\text{CoIr}_2\text{O}_9$. The dashed bar indicates the onset of magneto-structural transition and the dotted line represents the start of phase co-existence regime.

This is indicative of a structural distortion arising due to magnetic exchange striction - which in antiferromagnetic transition metal oxides results in the generation of a strain field aimed at increasing the magnetic exchange energy [197]. The lattice parameter c for both the monoclinic phases is depicted in Fig4.4(a). For the $P2/c$ phase, it increases as a function of decreasing temperature for the entire temperature range, with a discontinuity at T_p . On the other hand, in the $C2/c$ phase, a negative slope is attained only at T_p . Interestingly, the lattice parameter a shows a NTE in the $P2/c$ phase and a Positive Thermal Expansion (PTE) in the $C2/c$ phase throughout the temperature range as shown in Fig4.4(b). The contrasting temperature dependence of the lattice parameters is indicative of anisotropic thermal expansion and also reinforces the critical influence which the lattice parameter c has on the NTE in this material. The fact that none of the other triple perovskites reported till date are known to exhibit NTE suggests that this phenomena is driven by the phase coexistence and phase reversal which is unique to the $\text{Ba}_3\text{CoIr}_2\text{O}_9$ system. There are broadly two types of NTE [74]: one which arises solely

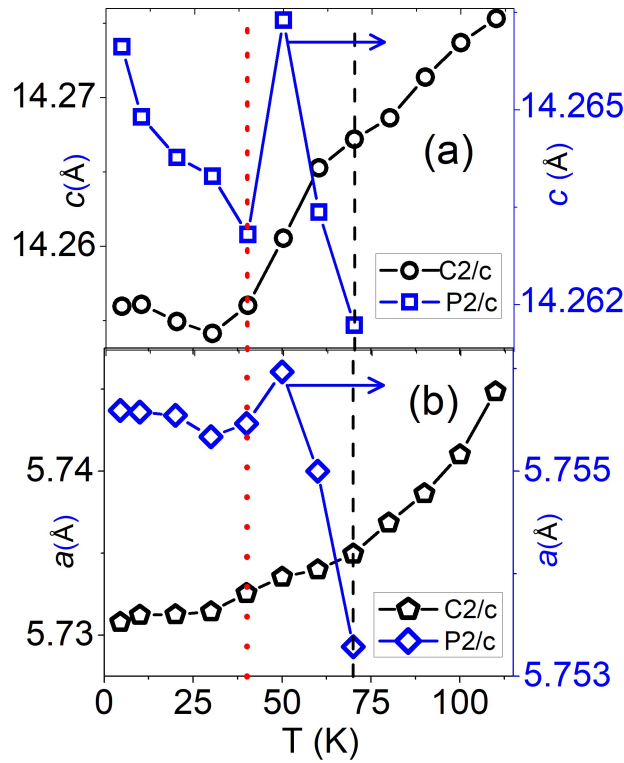


Figure 4.4: Variation of lattice parameters c and a with temperature is depicted in (a) and (b) respective. The dashed and dotted line indicates onset of phase co-existence and the phase cross-over temperature respectively.

due to a structural origin - often termed as conventional NTE. In these systems, the structural framework consists of strongly bonded polyhedra units called RUMs (rigid unit modes) [185] and NTE occurs as a consequence of the transverse vibrations of these units. Due to its structural origin, they are generally present over a broad temperature range. The other type of NTE is driven by phase transitions, with underlying phenomena like charge transfer [198], ferroelectric order [199], magnetic and orbital ordering [200], giant magnetocaloric effect [201] being responsible. Interestingly, many oxides like LaMnO_3 [182, 183], SrRuO_3 [184], AlFeO_3 [187] exhibit this type of NTE. Prerequisites for observing negative thermal expansion by the transverse thermal motion of oxygen include: (i) an open framework structure with oxygen in a two-fold coordination, (ii) strong metal-oxygen bonds to avoid significant thermal expansion of the bond

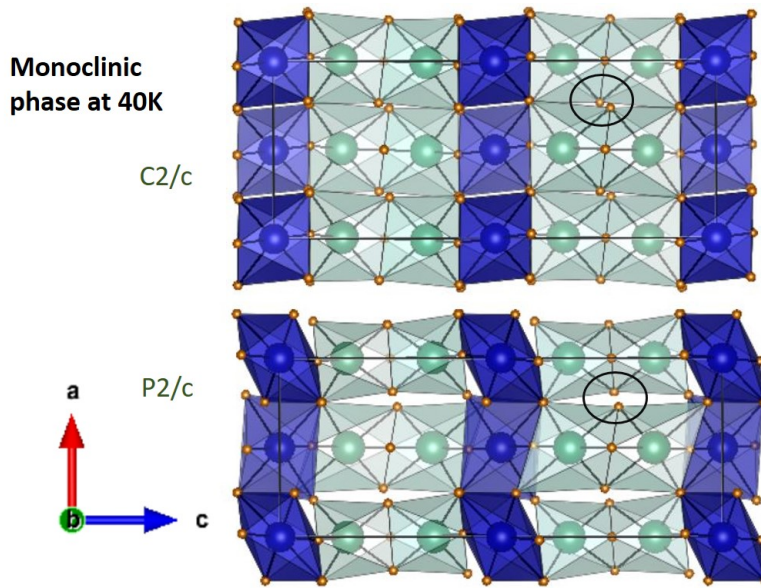


Figure 4.5: A schematic crystal structure representation for the two coexisting monoclinic phases, $C2/c$ (top) and $P2/c$ (bottom) at 40K along b -axis. The encircled region denotes the change in open area network with structural transformation, that eventually leads to excitation of rigid unit modes.

length, and (iii) rigid polyhedra which are free to tilt back and forth with little or no change in shape. The monoclinically distorted triple perovskite structure of $\text{Ba}_3\text{CoIr}_2\text{O}_9$ appears to be susceptible to distortions allowed by the RUM model due to the flexible network and open framework structure intrinsic to this symmetry as shown in Fig.4.5. Interestingly, these rotations of the IrO_6 and CoO_6 octahedra also allows for the overall monoclinic symmetry to be preserved while transforming to a lower space group. Fig.4.6(a) displays the change in the Ir-O-Ir bond angles in the face sharing dimer for the $C2/c$ phase. Although the Ir-O2-Ir angle remains relatively rigid below the magnetostructural transition, the Ir-O1-Ir angle has a strong temperature dependence. As soon as it reaches the maxima of octahedral tilting at the phase cross over temperature (T_P), the octahedra are buckled, as is reflected in the sharp decrease in the Ir-O1-Ir angle. A similar trend is seen in Co-O-Ir for the $P2/c$ monoclinic phases as shown in the Fig.4.6(b), where a distinct change of slope corresponding to the buckling of the

octahedra is observed.

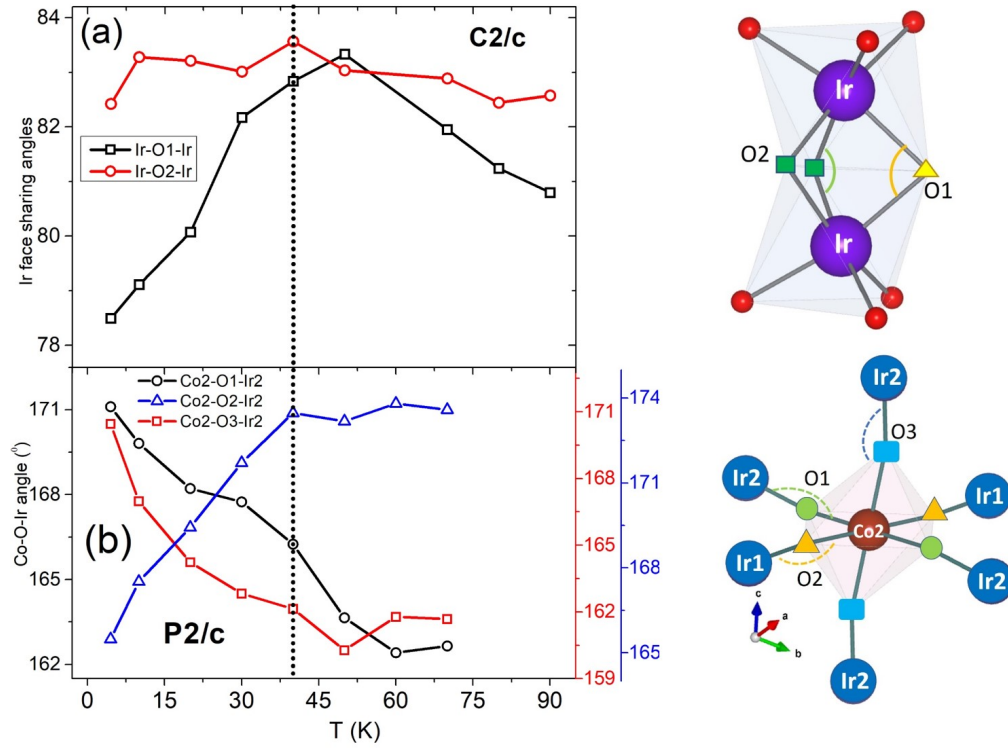


Figure 4.6: (a) Main panel: Thermal evolution of face sharing Ir-O-Ir angles within the Ir dimer depicted pictorially in the inset. O1(▲) and O2(■) represents the face sharing oxygen. (b) Main panel: Temperature variation of the 3 unique Co-O-Ir angles made by cobalt and Iridium in the $C2/c$ and $P2/c$ phases. Inset: A schematic representation of the cobalt octahedra connected via corner to Iridium. The vertical dotted line represents the phase crossover temperature T_P .

This correlation between the NTE and the octahedral distortions is seen even more clearly in the temperature dependence of the tilt angle of the CoO_6 octahedra which sits at the corners of the unit cells in both the $C2/c$ and the $P2/c$ phases, as is depicted in Fig.4.7(b). In the monoclinic $C2/c$ phase, this angle is initially invariant, and increases on approaching the phase co-existence regime as shown in Fig.4.7(a). The stabilization of the monoclinic $P2/c$ phase partially relieves this rotation, and this quantity is seen to be inversely correlated in both the phases. This is an indicator of how the lattice strain in one of the phases is relieved by the stabilization of the other. Moreover, signatures

of this phase coexistence is also seen as a hump in the dc magnetization, which is also plotted in the same graph for clarity. Though there is no evidence of a low temperature magnetic transition in this system, it is evident that the magnetization is modulated by the crystallographic structure, indicating the intimate connection between the two. Our prior neutron diffraction and first principles calculations indicate that the spins are

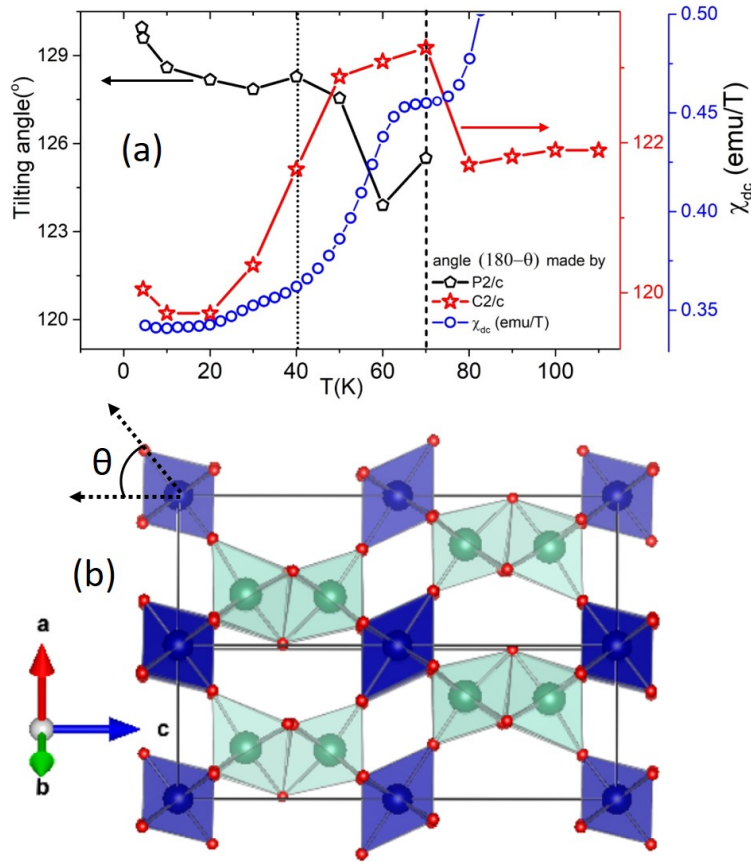


Figure 4.7: Top panel: Temperature-dependent dc magnetization data measured in a magnetic field of 100 Oe for $\text{Ba}_3\text{CoIr}_2\text{O}_9$. Red and black curves indicates the tilt angle of CO_6 octahedra for C2/c and P2/c respectively, as shown in the schematic below. The CO_6 octahedra sits at the corner and θ is the angle formed by the apical oxygen with the c -axis.

predominantly aligned along the crystallographic c -axis in this system [139]. With the structural distortions and magnetization appearing to be intimately coupled, it is not surprising that the major lattice change is observed along this direction. Fig.4.8 depicts the hysteresis in the magnetization as measured in the Field Cooled Cooling (FCC)

and the Field Cooled Warming (FCW) protocols in the phase coexistence regime. This indicates the first order nature of this transition, which is associated with formation of a new $P2/c$ phase inside the monoclinic $C2/c$ phase which is stabilized below the magnetostructural transition at 107 K.

4.2.4 Mechanism for NTE in $\text{Ba}_3\text{CoIr}_2\text{O}_9$

This intimate coupling between the magnetism and NTE is reminiscent of the large magnetostriction and NTE observed in the frustrated spinel ZnCrSe_4 [191]. It was suggested that the NTE in that system arose as a consequence of a highly frustrated lattice, with exchange-striction being the driving mechanism. We note that in $\text{Ba}_3\text{CoIr}_2\text{O}_9$ which orders magnetically at 107 K, a fit to the high temperature magnetization data gave a Curie-Weiss temperature (θ_{CW}) of 6.35 K, which is clearly suggestive of mixed ferro-antiferromagnetic interactions. This was also confirmed by measurements of MH isotherm, where a small loop opening -typical of ferri-, or weak ferromagnetic systems- was observed. The magnetic structure in the $C2/c$ phase was deduced to be a canted antiferromagnet, with the main antiferromagnetic component along the c axis. Though the antiferromagnetic magnetic structure in the $P2/c$ phase remains to be ascertained, it is likely that it only differs in the extent of the canting angle. An interesting aspect of $\text{Ba}_3\text{CoIr}_2\text{O}_9$ pertains to the temperature regime in which NTE is observed. For instance, in systems like Ca_2RuO_4 [188], $\text{Pb}(\text{Ti},\text{V})\text{O}_3$ [202], Mn_3ZnN [80], the NTE is driven by an electronic or magnetic phase transition, and is observed (or has its onset) in the transition region. Conversely, in the ZnCrSe_4 system, NTE was observed predominantly in the paramagnetic regime (starting from $T > 3 \times T_N$) down to the magnetic transition temperature, owing to short range spin fluctuations characteristic to geometrically frustrated magnets. In contrast to these cases, the NTE in $\text{Ba}_3\text{CoIr}_2\text{O}_9$ is observed deep within the AFM state, and is intimately related to a phase coexistence between the two

disparate monoclinic phases.

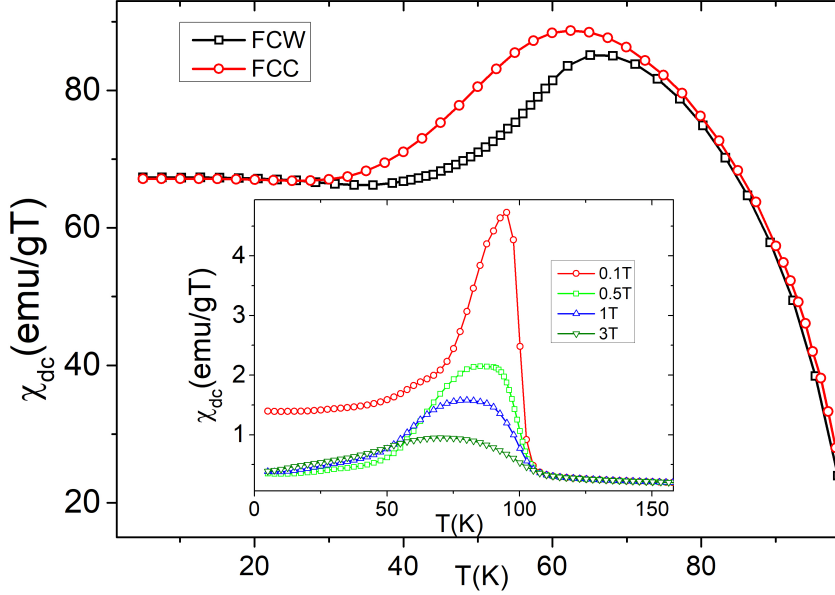


Figure 4.8: Main panel:) Temperature-dependent dc magnetization data measured under a magnetic field of 100Oe under field-cooled warming (FCW) and field-cooled cooling (FCC) protocols. Inset: Temperature dependence of zero field-cooled (ZFC) dc magnetization data of $\text{Ba}_3\text{CoIr}_2\text{O}_9$ at different magnetic fields.

This situation is similar to that reported earlier in the rare earth vanadates of the form $R\text{VO}_3$ (with $R = \text{Sm}, \text{Ho}, \text{Yb}, \text{Pr}$ or Y) [159, 203], where competing orbitally ordered phases coexist as a consequence of the competition between the lattice strain arising out of octahedral tilting and that due to exchange-striction. We speculate that a similar mechanism is at play here, and that the temperature evolution of the structurally disparate monoclinic phases in $\text{Ba}_3\text{CoIr}_2\text{O}_9$ arises as a consequence of the interplay between exchange striction, relative energy difference between the $C2/c$ and $P2/c$ phases, as well as octahedral rotations in each phase. On traversing the magnetostructural transition from the high temperature paramagnetic ($P6_3/mmc$) state, we first encounter the $C2/c$ phase which appears to be energetically most favorable. However, increasing exchange striction as a function of reducing temperature strains the lattice, which in turn

is partially relieved by a conversion of a part of the $C2/c$ phase to the lower symmetry $P2/c$ phase starting from 70 K. The relative energy difference between these monoclinic phases appear to be dynamic, and below the crossover temperature, a part of the $P2/c$ phase converts back to the higher symmetry $C2/c$ phase. However, this alone does not compensate for the exchange striction induced strain, and a part of it is accommodated by the octahedral rotations in both these disparate phases which then manifests itself in the form of NTE in *both* of them.

4.2.5 Why both the monoclinic phases exhibit NTE

Although the symmetry of the both the crystal structure is different, the connectivity and topology on a local scale does not alter much for both the phases. It can therefore be appreciated that the RUM distribution need not alter significantly as we move from one phase to the other and the negative thermal expansion continues in much the same fashion for both the phases. In addition, the phonon excitations which have been proposed to facilitate the negative thermal expansion are very low energy modes and are a result of the topology of the structure. Since this topology is preserved at least locally, the mechanism is also retained.

This interplay between competing phases is also likely to make the ground state amenable to external perturbations. A pronounced magnetic field dependence of the NTE has been previously observed in ZnCrSe_4 [191] where the balance between the AFM and FM states in the frustrated magnetic spinels can be easily tuned with the application of a magnetic field [191,204]. Though both the co-existing phases in the case of $\text{Ba}_3\text{CoIr}_2\text{O}_9$ are AFM, it is quite likely that perturbations like pressure, or magnetic fields can tilt the balance between them. Our Zero field cooled measurements at different applied magnetic fields as shown in the inset of Fig.4.8 indicates that the broad hump-signifying the

region of phase co-existence gets suppressed and shifts to even low temperature values as a function of increasing magnetic fields. Magnetic field dependent measurements of x-ray diffraction and magnetostriction are likely to throw more light on the evolution and dynamics of these co-existing phases.

4.3 Conclusions

In summary, we report on the existence of a low temperature regime of negative thermal expansion in a new $3d$ - $5d$ based triple perovskite iridate $\text{Ba}_3\text{CoIr}_2\text{O}_9$. This unusual temperature dependence of the volume is intimately related to the co-existence of two closely related monoclinic phases, and the temperature dependence of their relative phase fractions. The underlying driving mechanism appears to be the antiferromagnetic exchange striction, which precipitates a phase conversion from a monoclinic $C2/c$ phase to a more distorted $P2/c$ phase as a function of decreasing temperatures. Below a phase crossover temperature of 40 K, the phase ratios of these monoclinic phases inverts, with remainder of the strain being accommodated by octahedral distortions which manifests itself in the form of a negative thermal expansion in both these phases. This work opens up opportunities in exploring NTE in intrinsically layered systems which are characterized by strong spin orbit interactions.

Chapter 5

Structural, magnetic and electronic properties of $\text{Ba}_3\text{NiIr}_2\text{O}_9$

5.1 Introduction

The study of correlated phases in 5d transition metal oxides (TMO), specially double ($A_3B\text{IrO}_6$) and triple perovskites ($A_3B\text{Ir}_2\text{O}_9$) have gained considerable theoretical and experimental attention and many possible exotic states like Quantum spin liquids (QSL), Weyl semimetal, axion insulator, topological Mott insulator etc. have been reported [3, 18]. As a consequence of competing energy scales of lattice disorder, Coulomb repulsion, SOC, crystal field splitting, in addition to spin, charge, lattice degrees of freedom, a plethora of ground states are now known [36]. Small perturbations like doping, pressure, etc., can tip the balance between the comparable energy scales and lead to different structural and magnetic ground states. The choice of the A or B site cation strongly influences the geometry of the compound leading to different chemical stabilities and magnetic ground states.

For example, a comparative study of isoelectronic and isovalent compounds, $\text{Ba}_2\text{CeIrO}_6$ and $\text{Sr}_2\text{CeIrO}_6$, revealed that both crystal deformations and SOC go hand in hand in de-

termining a particular ground state. Due to the presence of strong Jahn-Teller distortion and comparable SOC, $\text{Sr}_2\text{CeIrO}_6$ exhibits a weak orbital ordering and lies in the intermediate region between complete L-S coupling and j-j coupling regime whereas in $\text{Ba}_2\text{CeIrO}_6$, due to large ionic radii of Ba^{+2} , the tolerance limit of the structure is close to 1 and does not exhibit any distortion and is a candidate for strong antiferromagnetic Kitaev interactions [205–207].

Similarly in triple perovskites, $\text{Ba}_3\text{ZnIr}_2\text{O}_9$ is a close realization of $J=0$ QSL state [67], whereas, substitution of B site ion by Mg, Sr and Ca, dramatically influences the ground state. $\text{Ba}_3\text{MgIr}_2\text{O}_9$ exhibits deviation from the non-magnetic $J=0$ state and strong antiferromagnetic interactions and higher magnetic moment compared to $\text{Ba}_3\text{ZnIr}_2\text{O}_9$ [9]. A monoclinic distortion of the hexagonal structure with weak dimer and ferromagnetic like features has been observed for $\text{Ba}_3\text{M}\text{Ir}_2\text{O}_9$ ($\text{M}=\text{Ca}$ and Sr) respectively. Replacing the M site ion by a 3d transition metal can further add to the complexity of the system. This is observed in the newly reported $\text{Ba}_3\text{CoIr}_2\text{O}_9$, as discussed in previous chapter where Cobalt, being a magnetic ion strongly influences exchange paths leading to weak ferromagnetism at low temperature and the highest magneto structural transition at 107K reported for a triple perovskite iridate [139].

After presenting a diverse range of properties and phenomena in $\text{Ba}_3\text{CoIr}_2\text{O}_9$, a promising avenue to look for is the next element to Cobalt in the periodic table, Nickel. Interestingly, $\text{Ba}_3\text{NiIr}_2\text{O}_9$, stabilizes in the same hexagonal framework discussed previously and the magnetic transition also lies close to the Cobalt analogue, though it exhibits different magnetic and structural ground state, reinforcing our claims of the influence of small perturbation to the ground states. An earlier report on $\text{Ba}_3\text{NiIr}_2\text{O}_9$ describes only the structural aspects with no magnetic anomaly, which needs to be looked into carefully [208].

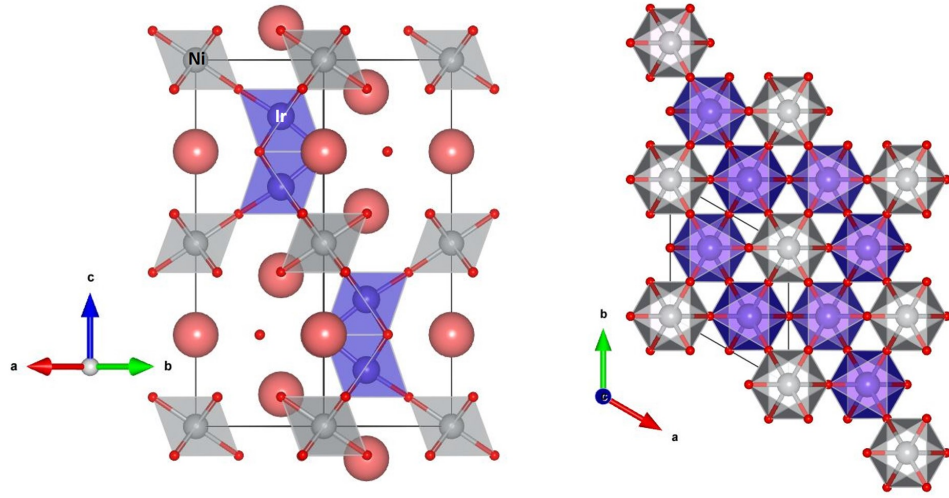


Figure 5.1: Left panel: A schematic of the crystal structure of the $\text{Ba}_3\text{NiIr}_2\text{O}_9$ triple perovskite. Here, grey and purple octahedra represent Nickel and Iridium sites respectively, with the Barium atoms being represented by red circles. The structure comprises of a single NiO_6 octahedron sharing corners with Ir_2O_9 dimers, which in turn are formed by two face-sharing IrO_6 octahedra. Right panel: The projection of the structure along the c -axis is shown where Ir octahedra can be seen sitting in a hexagonal ring.

Nickel based triple perovskites gained considerable attention as potential candidate with high spin $S=1$ Quantum spin liquid state. In $\text{Ba}_3\text{NiSb}_2\text{O}_9$, the ground state evades any kind of ordering as a consequence of strong quantum fluctuations, frustration and topological effects [209]. Other members of the family include $\text{Ba}_3\text{NiOs}_2\text{O}_9$, $\text{Ba}_3\text{NiNb}_2\text{O}_9$ and $\text{Ba}_3\text{NiTa}_2\text{O}_9$ where antiferromagnetism to high T_C weak ferromagnetism, multiferrocity and a 120° spin arrangement in the frustrated triangular lattice is observed respectively [210–212]. These compounds belong to the family of Heisenberg like triangular lattice antiferromagnet (TLAF) where sheets of triangular array of Nickel ions are stacked along the c -axis, decoupled by various non magnetic ions. The magnetic frustration in the a - b plane containing the triangular lattice of magnetic ions would make long range ordering difficult. In such systems, antiferromagnetic interaction between nearest neighbour ions creates frustration as is not possible to satisfy all pairs of nearest neighbours at the same time. Furthermore, the difference in linkage of

such triangles (edge, corner, and face-sharing) makes the ground state properties very complicated. All the members shows diverse ground state in terms of crystal symmetry evolutions and magnetic spin dynamics. Though, a wide variety of examples have been reported with frustrated lattice based on a triangular or tetrahedral array of magnetic ions, very few examples with 2 magnetic ions in the lattice have been reported. Introduction of magnetic ion can affect the frustration and make the interaction 3D and introduce inter-planar interactions and possibly lead to exciting ground states .

In this chapter, a study of $\text{Ba}_3\text{NiIr}_2\text{O}_9$, focusing on the structural and magnetic aspects of it is presented. The aim of this work is to investigate the peculiar structure dynamics in a hexagonal perovskite using synchrotron diffraction, magnetization, resistivity and specific heat studies.

5.2 Experimental Details

Polycrystalline specimens of $\text{Ba}_3\text{NiIr}_2\text{O}_9$ were synthesized by the standard solid state reaction technique. Stoichiometric amounts of high purity BaCO_3 , NiO and IrO_2 were thoroughly ground using a mortar and pestle to get homogeneous mixtures, which were then fired in air at 950°C for 24 hrs, followed by a heat treatment at 1100°C for 48 hrs. These powders were then cold pressed and heat treated in air repeatedly at 1100°C till no change in the powder X-Ray Diffraction (XRD) peak shape was observed . The details of the experimental techniques used has been discussed in Chapter 2.

5.3 Crystal structure

Most of the derivatives of $\text{Ba}_3MM'_2\text{O}_9$ (with M being an alkali, alkaline earth, or transition metal; $M' = \text{Ir, Ru}$) family of triple perovskites crystallize in the 6H hexagonal lattice framework with $P6_3/mmc$ symmetry [9, 67, 101, 143, 154]. This is an aristotype

structural symmetry constituting of $M'O_6$ octahedra sharing a face along the crystallographic c axis, with the M'_2O_9 dimers connected by corner sharing MO_6 octahedra, and Ba occupying the 12 fold c-ordination site, usually represented by (cch)2 layered arrangement. As shown in Fig. 5.1 for $Ba_3NiIr_2O_9$, each Ir is surrounded by one Ir (sharing face) on one side and 3 Ni ions via corner shared links on the other side. On the other hand, each Ni ion is connected to 6 different Ir ions, 3 above and below the a - b plane respectively.

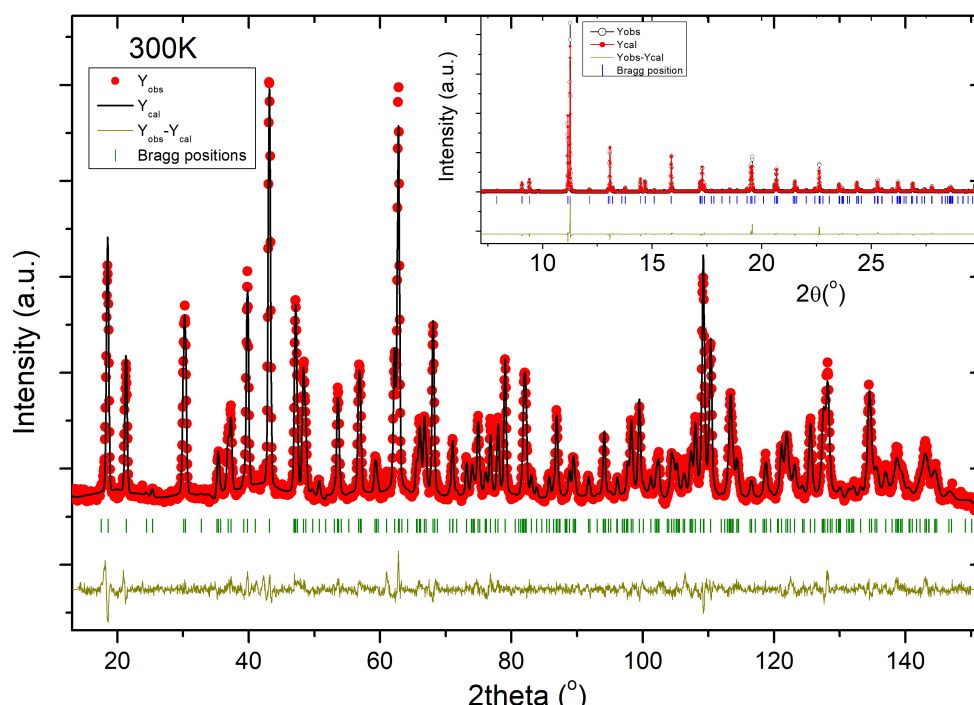


Figure 5.2: Rietveld refinement of neutron (main panel) and synchrotron powder diffraction pattern (inset) for $Ba_3NiIr_2O_9$ at 295 K, obtained at HRPT and SLS (PSI, Switzerland) respectively. The compound crystallizes in a 6H-hexagonal perovskite with space group ($P6_3/mmc$). The calculated and observed diffraction profiles are shown as black and red markers respectively. The vertical green lines indicates the calculated Bragg positions. The brown line at the bottom is the difference between observed and calculated intensities.

The room temperature neutron and synchrotron XRD data for $Ba_3NiIr_2O_9$ and its Rietveld refinement is shown in Fig 5.2. The inset shows an enlarged view of a selected 2θ region. The lattice parameters obtained from the fit are $a = b = 5.76008 \text{ \AA}$, $c = 14.2942$

Table 5.1: Structural parameters of $\text{Ba}_3\text{NiIr}_2\text{O}_9$ at 295 K.

Space group $P6_3/mmc$ (No. 194)				
$a = b = 5.76007(4) \text{ \AA}$, $c = 14.2942(1) \text{ \AA}$, $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$				
Atom	x	y	z	occupancy
Ba1	0.3333	0.6666	0.9123(1)	1
Ba2	0.0000	0.0000	0.2500	1
Ni	0.0000	0.0000	0.0000	1
Ir	0.3333	0.6666	0.15364(6)	1
O1	0.4844(29)	0.9684(28)	0.2500	1
O2	0.1686(20)	0.3341(18)	0.4180(6)	1

$\text{\AA}$ and $\alpha=\beta=90^\circ$, $\gamma=120^\circ$. The resultant structural parameters at 295K from the Rietveld refinement of synchrotron data are listed in Table 5.1. Many thorough studies for Ni based triple perovskites have been conducted to confirm the presence or absence of any possible local cationic disorder with different arrangement of $\text{M}'(=\text{Sb}, \text{Os})$ and Ni over face and corner sharing octahedra [209,210,213]. These studies are essential in the understanding of ground of these systems and identify the possible origin of deviation from $J=0$ state expected for the $\text{Ir}^{+5} (\text{d}^4)$ or the possibility of $S=1$ quantum spin liquid state. Small manipulations in the structure in the form of antisite disorder, pressure etc., lead to different structural and magnetic ground states. For a correct interpretation of physical properties of this compound, it was therefore mandatory to clarify on the nature of disorder (if present) and confirm (discard) the existence of triangular Ni planes and antisite disorder between Ni and Ir. We performed a thorough investigation using XPS, EDAX and synchrotron studies to ascertain the true crystal structure nature of this compound.

The first step was to look for the presence of mixed valent state as both Nickel and Iridium can stabilize in multiple valence states. This could critically influence the electronic and magnetic properties. Our XPS measurements of the Ni 2p and Ir 4f core level are shown in the Fig 5.3 (a) and (b). The spectrum could be resolved using peaks associated

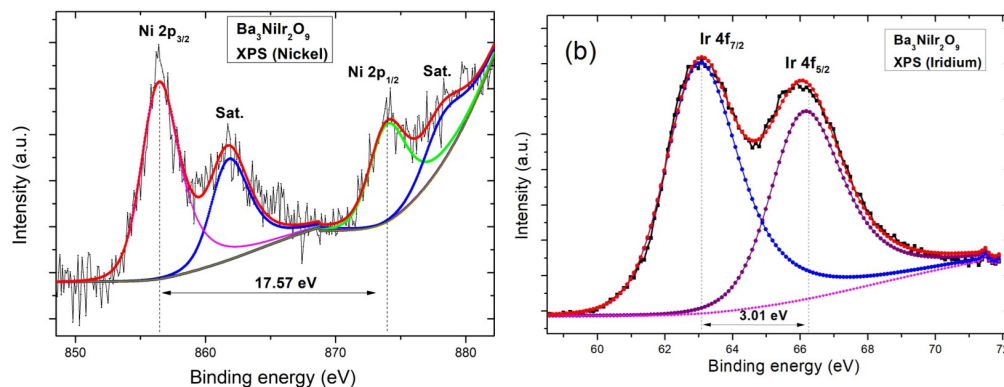


Figure 5.3: The XPS fit for the Ir $4f$ and Ni $2p$ core level is depicted on the left. Black circles are the data points and the red line is the envelope of the fit. The deconvolution of the $2p_{3/2}$ and $2p_{1/2}$ for Nickel, $4f_{7/2}$ and $4f_{5/2}$ for Iridium contributions respectively are labelled. The satellite peaks are labelled as Sat.

with a single valence state for both Ir^{5+} and Ni^{2+} . The corresponding binding energy peaks for Ir^{5+} $4f$ level are 66.00 eV and 62.91 eV, for Ni^{2+} $2p$ level are 856.27 eV and 873.84 eV with corresponding satellite peaks at 861.64 eV and 878.12 eV. The obtained spin energy gap of 17.57 eV and 3.01 eV is characteristic for Nickel and Iridium and is consistent with the reported literature values [214, 215].

Also, another way to validate the valence state of Ir in hexagonal lattices is by using the Ir-Ir bond distance calculation [154]. The bond length is reported to increase with the valence state of iridium as a function of electrostatic repulsion, resulting in the bond distances of the order of 2.55, 2.65 and 2.75 Å for Ir^{4+} , $\text{Ir}^{4.5+}$ and Ir^{5+} respectively. The obtained value of the Ir-Ir distance (≈ 2.75 Å) from our room temperature Rietveld refinement fit is in good agreement with the +5 state in iridium.

After confirming the valence state, we checked for the possible mixing of Ni at Ir sites. A careful analysis revealed no antisite disorder between Ni/Ir sites due to appreciable mismatch between their ionic radii and valence states. A forced placement of Ni at Ir site and vice versa led to negative value of occupancies for both the magnetic ions.

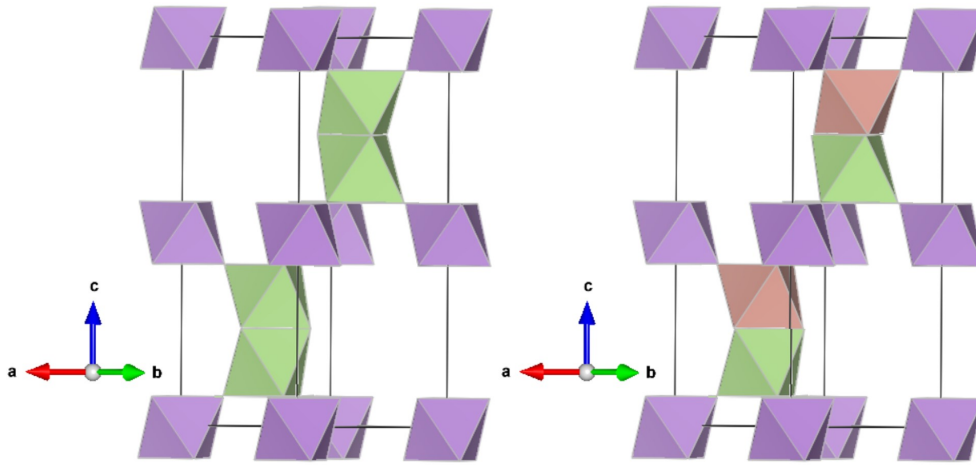


Figure 5.4: A schematic representation of two possible hexagonal lattice frameworks for $P6_3/mmc$ (space group=194) and $P6_3mc$ (space group= 186) for $\text{Ba}_3\text{NiIr}_2\text{O}_9$. The left panel shows $P6_3/mmc$, the dimers are occupied by Iridium (green) and Cobalt sits at the corners (purple). In contrast, $P6_3$, as shown in the right panel, allows for a shared occupancy for Cobalt at dimer and corner site (purple and brown). Barium atoms in both the structures have not been shown for clarity.

Another way to check for possible mixing of Ni and Ir sites is to attempt fitting with a lower space group symmetry $P6_3mc$ which allows for sharing of lattice sites between these ions. We used the structural details of $\text{Ba}_3\text{NiSb}_2\text{O}_9$ reported in [213] where finite mixing for Ni and Sb sites was confirmed. A schematic structural representation for both the hexagonal phases ($P6_3/mmc$ and $P6_3mc$) has been shown in Fig. 5.4(a) and (b). The essential difference between the two models is that in $P6_3/mmc$, the sites in the dimer are occupied only by Iridium (green) whereas in $P6_3mc$, Nickel gets the freedom to form an ordered, or partially ordered (red) distribution over the corner sharing and face sharing sites. The Rietveld refinement fit for the synchrotron data at 295K using the $P6_3mc$ symmetry model led to unsatisfactory fit to the experimentally obtained results, as shown in Fig. 5.5.

From the symmetry point of view, a clear deviation from $P6_3mc$ indicates absence of any possible disorder between Ir and Ni sites. In addition, we also attempted fitting to the low symmetry monoclinic phase $C2/c$ (Space group=15), exhibited by many

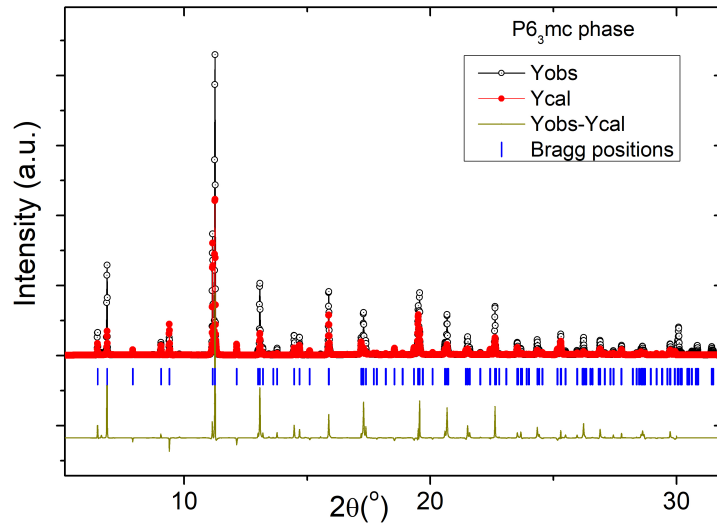


Figure 5.5: Attempt to perform Rietveld refinement of synchrotron powder diffraction pattern of $\text{Ba}_3\text{NiIr}_2\text{O}_9$ at 295 K using the hexagonal perovskite model with space group $P6_3mc$ (S.G.=186). The calculated and observed diffraction profiles are shown as red and black markers respectively. The vertical blue lines indicates the calculated Bragg positions. The green line at the bottom is the difference between observed and calculated intensities. Clearly, the substantial mismatch with the experimental data precludes the presence of $P6_3mc$ phase. The reliability factors obtained from refinement parameters are: $R_{wp}=56.9$, $R_p=47.5$, $R_e=1.27$, $R_{Bragg}=42.9$.

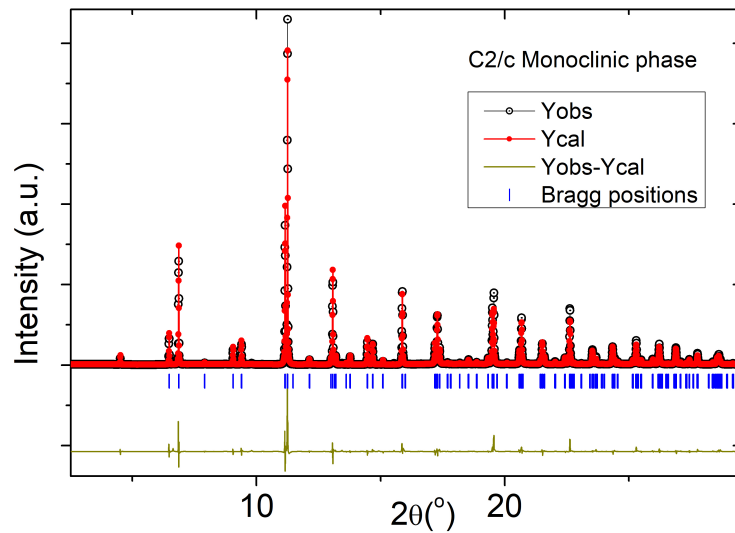


Figure 5.6: Rietveld refinement test for $\text{Ba}_3\text{NiIr}_2\text{O}_9$ at 295 K using the monoclinic phase model with with space group $C2/c$ (15). The calculated and observed diffraction profiles are shown as red and black markers respectively. The vertical blue lines indicates the calculated Bragg positions. The green line at the bottom is the difference between observed and calculated intensities. This model fits comparatively better than the $P6_3mc$ model, though the obtained goodness of fit is higher than for $P6_3/mmc$ phase fitting.

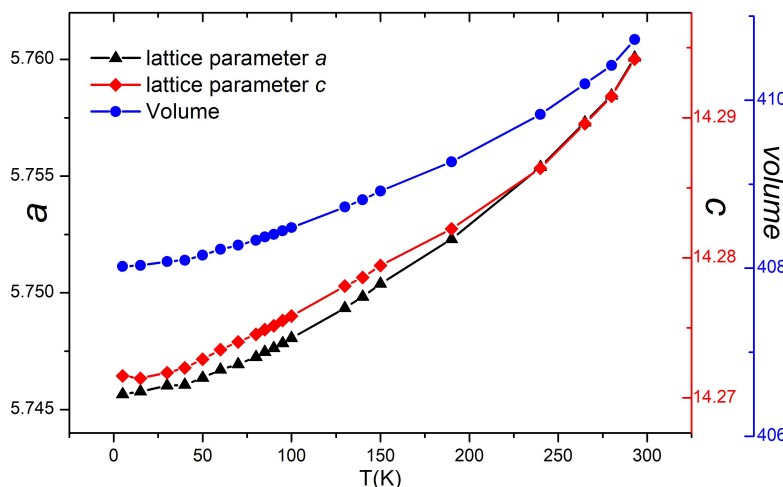


Figure 5.7: Variation of the lattice parameters a , c and volume for $\text{Ba}_3\text{NiIr}_2\text{O}_9$ as a function of temperature.

triple perovskites [9, 53, 55, 101, 154] and the resultant Rietveld fit at 295K is shown in Fig. 5.6. Although, the fit was marginally worse compared to the hexagonal symmetry $\text{P6}_3/\text{mmc}$ as revealed by the obtained structural refinement parameters R_{wp}/R_e , Bragg R factor (R_{Bragg}) and crystallographic R_F factor for the monoclinic ($\text{C2}/c$) (17.2, 8.5 and 4.11) and hexagonal structure ($\text{P6}_3/\text{mmc}$) (15.2, 6.4 and 3.21) respectively. $\text{C2}/c$ is a lower symmetry and allows for large number of parameters to fit in terms of multiple Ni and Oxygen positions, which in turn influences the refinement in Rietveld and might lead to increased quality of the fit. Therefore, after a thorough investigation, we confirm that $\text{Ba}_3\text{NiIr}_2\text{O}_9$ stabilizes in a 6H hexagonal symmetry at room temperature and further analysis was performed considering this particular structural symmetry.

Our low temperature synchrotron studies revealed a shift of diffraction peaks towards higher θ angles as a function of decreasing temperature and no discernible peak splitting till the lowest temperature measured (4.3K). This suggests no structural transformation is present for the current compound, unlike what was observed for the Cobalt analogue. The temperature evolution of lattice parameters obtained from the Rietveld refinement is shown in Fig. 5.7, where a gradual decrease in volume with temperature is seen.

5.4 Resistivity

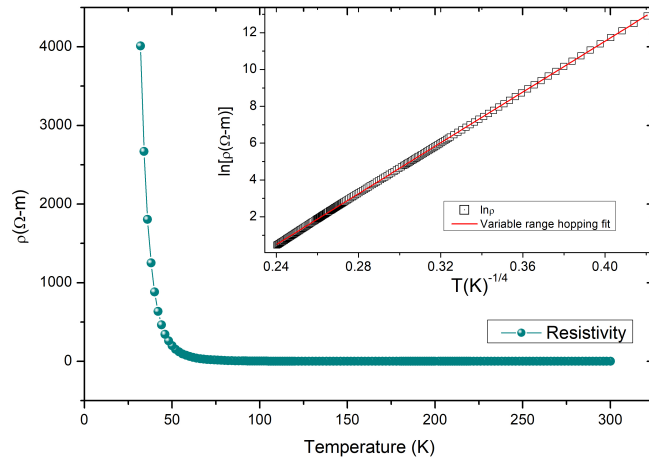


Figure 5.8: Main panel: Temperature evolution of resistivity of $\text{Ba}_3\text{NiIr}_2\text{O}_9$. The resistance increases sharply as a function of decreasing temperature. Inset: Resistivity ($\ln\rho$) plotted as a function of temperature ($T^{-1/4}$). The red line is the linear fit using the Variable Range Hopping formalism .

Resistivity shows a monotonic increase with decrease in temperature with a change in resistance value by 5 orders from magnitude from the room temperature value of 3Ω , confirming the insulating nature of the compound as shown in the main panel of Fig. 5.8 . A plot of $\ln\rho$ vs $T^{1/4}$ of the temperature dependent resistivity indicate that the transport properties in the entire temperature range are governed by Variable Range Hopping (VRH) dynamics [216] given by

$$\rho = \rho_o \exp\left(\frac{T_o}{T}\right)^{1/4}$$

where ρ_o and T_o are constants. The inset of Fig. 5.8 shows the fit to the VRH dynamics, where the red line is the linear fit to VRH and the obtained value T_o of is 22.71×10^6 , in lines with reported values for many oxides [217].

5.5 Magnetization

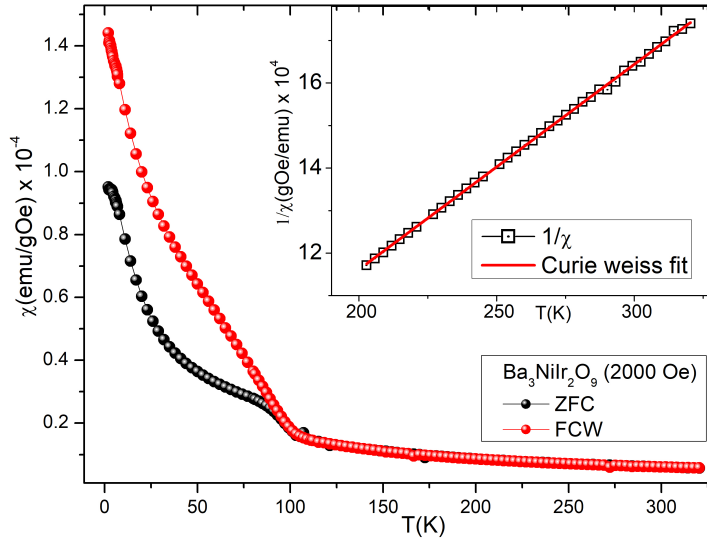


Figure 5.9: Main panel: Temperature dependence of the dc magnetic susceptibility of $\text{Ba}_3\text{NiIr}_2\text{O}_9$ as measured in the zero field cooled and field cooled protocols at 2000 Oe. Inset: A Curie Weiss fit to the high temperature magnetization data. The black squares are the experimental data points and red line is the corresponding fit.

The temperature dependence of magnetic susceptibility of $\text{Ba}_3\text{NiIr}_2\text{O}_9$ revealed two anomalies as shown in Fig. 5.9. The ZFC-FC bifurcation starts close to 106K (T_{N1}), indicating a magnetic phase transition and an additional features at low temperature is observed around 6K (T_{N2}). The Curie Weiss fit to the temperature range 200-320K, shown in the inset of Fig. 5.9, gives a negative Weiss temperature (θ_W) of -40.984K, indicating predominant antiferromagnetic exchange interactions and an effective magnetic moment of $4.069 \mu_B/\text{f.u.}$. Considering the spin only value, the theoretical values of magnetic moment for Ni^{+2} (d^8 : t_{2g}^6, e_g^2) and Ir^{+5} (d^4 : t_{2g}^4) is $2.83\mu_B$. Therefore, the expected moment for $\text{Ba}_3\text{NiIr}_2\text{O}_9$ is $8.49\mu_B/\text{f.u.}$. Clearly, this calculated moment is much larger than the experimentally obtained value of $4.069 \mu_B/\text{f.u.}$. This can be attributed to the over estimation of moment at Ir site, where the influence of strong spin orbit coupling, t_{2g} - e_g mixing, hopping, excitonic magnetism splits degenerate t_{2g} levels

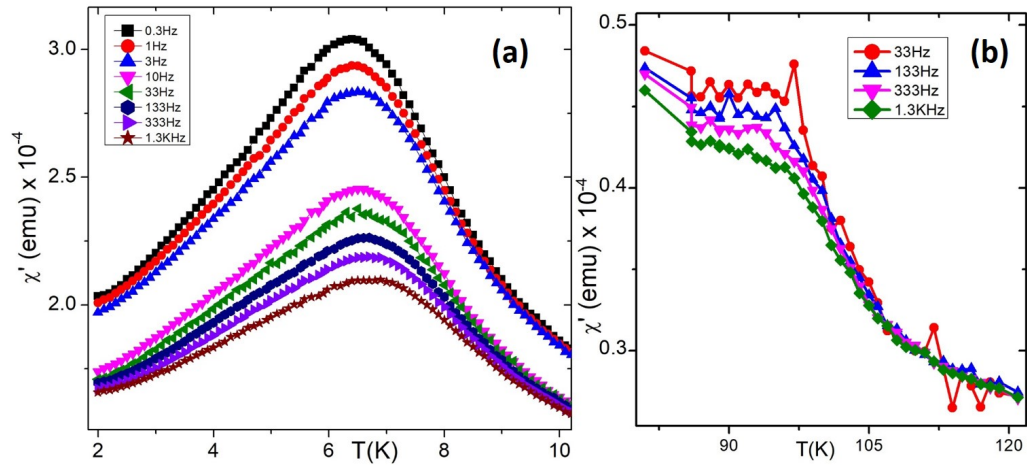


Figure 5.10: Temperature dependence of the real part $\chi'(T)$ of ac magnetic susceptibility as function of frequency ranging from 0.3Hz-1.3KHz. for low (a) and high temperature (b) transitions.

and has been suggested to be responsible for reduction in moment for Ir^{+5} (d^4), leading to a close approximant to the $J=0$ states [18, 67, 90, 91, 95, 96]. Although, so far, none of the experimental reports confirms a successfully implementation of a system where a complete suppression in magnetic moment at Ir site, though many close realizations have been reached [9, 67, 218]. Therefore, the average moment for Ir^{+5} (d^4), in the case strong spin orbit coupling but effective $J \neq 0$ can be considered to be $0.5\mu_B$ based on many experimental reports on Ir based triple perovskites of the same structural class [9, 90, 219, 220]. This value is close to the experimentally observed value of $0.62\mu_B$ at Ir site for $\text{Ba}_3\text{NiIr}_2\text{O}_9$ in the present study. Neutron diffraction measurements were performed at DMC and HRPT, PSI, Switzerland. But due to high absorption cross-section of Iridium, only a weak magnetic intensity was observed at low temperatures and it was not sufficient to determine the magnetic structure unambiguously.

In order to investigate the nature of low temperature transition, we performed ac susceptibility measurements as shown in Fig. 5.10. Two transitions were observed in the phase $\chi'(t)$ component of the ac susceptibility in accordance with the dc susceptibility results. There is no discernible frequency dependence in the low and high tempera-

Temperature (K)	Coercivity (Oe)
2K	237.5
3K	84.15
5K	37.9

Table 5.2: The values of coercivity deduced from the magnetic isotherms at various temperatures.

ture region as shown in Fig. 5.10(a,b). The low temperature ac magnetic susceptibility, Fig. 5.10(a), shows broadening in peak position as function of frequency. In addition, various low temperature magnetic isotherms were measured below T_{N2} . The MH for 2K is shown in Fig. 5.11. The magnetization isotherms shows a sharp increase in coercivity as shown in Table. 5.2.

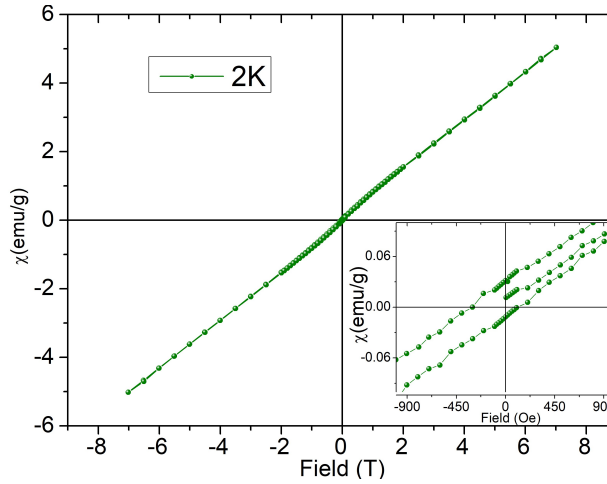


Figure 5.11: The figure depicts the MH isotherm as measured at 2 K, with a finite opening of the loop indicating a finite coercivity in $\text{Ba}_3\text{NiIr}_2\text{O}_9$.

5.6 Specific heat

Both the magnetic transitions could be observed in the specific heat measurement. The low temperature manifests in the form of a sharp peak at 6K (main panel) Fig. 5.12),

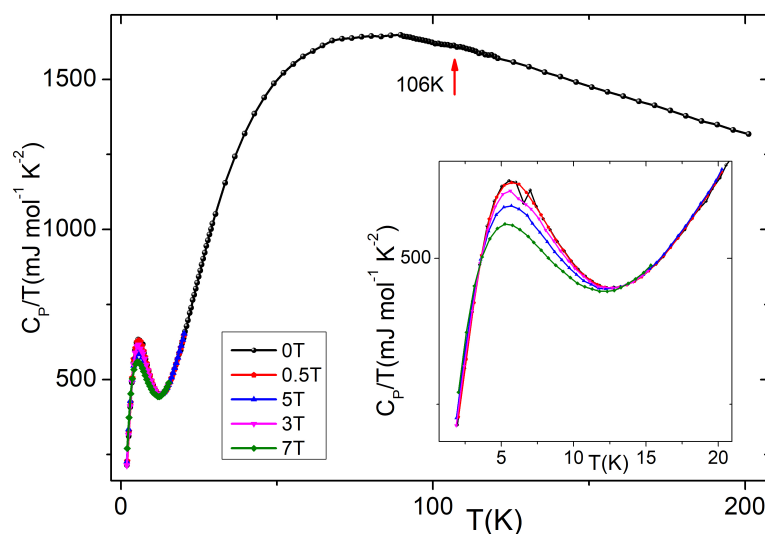


Figure 5.12: Main panel: The heat capacity measured as a function of temperature where a pronounced peak and a weak feature (marked by red arrow) is observed for the low and high temperature transitions respectively. Inset: The magnetic field dependence of the peak corresponding to the low temperature magnetic transition is shown for various fields (0, 0.5T, 3T, 5T and 7T). The peak is suppressed and moves slightly towards low temperatures on application magnetic field.

reflecting a large change in entropy associated with it. The inset of Fig. 5.12 shows that the application of a magnetic field slightly shifts the peak towards low temperature and suppresses it as a function of increasing magnetic field. This is a robust antiferromagnetic transition. However, the high temperature transition only reflects as a weak hump possibly because of the low entropy release.

We speculate that the high temperature transition (T_{N1}) corresponds to ordering of Ir_2O_9 dimers and the low temperature (T_{N2}) is the antiferromagnetic ordering of Ni^{+2} spins. As discussed, the ground state of these family of compounds sensitively depends on the relative strength of many competing energy scales controlled by exchange mechanisms mediated by corner and face sharing octahedra. The bond linkages Ir-O-Ir and Ir-O-M are strongly influenced by small perturbations which can result into different ground states.

5.7 Discussion

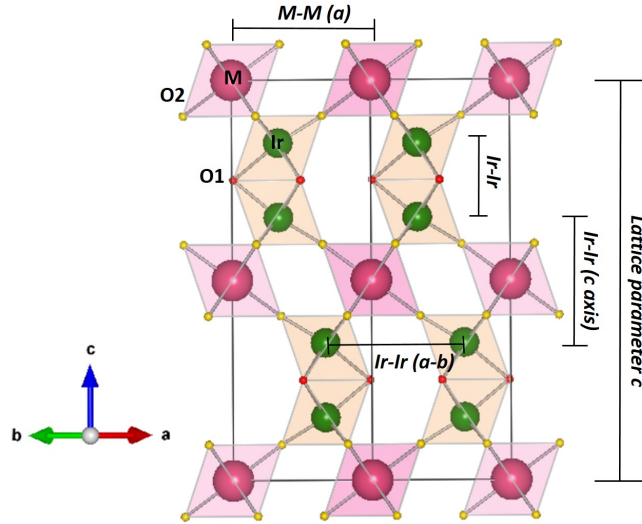


Figure 5.13: A schematic of the crystal structure with a hexagonal lattice framework for the $\text{Ba}_3M\text{Ir}_2\text{O}_9$ triple perovskites. Here, pink and green atoms represent M and iridium sites respectively. The structure comprises of a single MO_6 octahedron sharing corners with Ir_2O_9 dimers, which in turn are formed by two face-sharing IrO_6 octahedra. Various bond distances are mentioned which are tabulated in Table 5.3. Barium atoms are not shown for clarity.

A representative schematic of the hexagonal symmetry $\text{P6}_3/\text{mmc}$ is shown in Fig. 5.13. For a conclusive study, a range of M^{+2} Ir based triple perovskites stabilizing in the same framework with their corresponding structural parameters, bond angles and bond lengths are listed in the Table 5.3 in the increasing order of their ionic radii. As shown in Fig. 5.13, relative changes in bond lengths for Iridium is observed as a function of increasing ionic radii of M site ion. Above an ionic radii for $M > 1.0\text{\AA}$, impeded by the tolerance limit, the structure favours to stabilize in a lower monoclinic symmetry, Na being an exception here and it will be discussed in detail in the next chapter. As discussed for $\text{Ba}_3\text{CoIr}_2\text{O}_9$, many competing energy scales are at play here and the ground state of the material sensitively depends on the relative energy strengths of competing spin orbit coupling (SOC), electron correlations (U) and hybridization. The magnetic properties are believed to be dominated by the superexchange interactions by the 3d transition

Ionic radii (Å)	Ion (Ir valence state)	Ir-O1	Ir-O2	Ir-Ir	Ir-Ir (c)	Ir-Ir (a-b)	Ir-O1-Ir	M-O2-Ir	lattice parameter a	lattice parameter c	Nature of transition
0.69	Ni(5)	2.04196	1.94894	2.75935	5.50562	5.76008	85.0111	176.5951	5.76008	14.2942	AF
0.72	Mg(5)	2.05777	2.01292	2.74459	5.5239	5.7645	83.654	-	5.7645	14.3066	AF
0.74	Zn(5)	2.02116	1.94806	2.75475	5.54466	5.7833	85.918	-	5.77034	14.3441	QSL
0.745	Co(5)	2.15965	2.00869	2.74548	5.51828	5.76387	78.9337	176.1576	5.76387	14.2949	AF canted
1.0	Ca(5)	2.01008	2.07885	2.73524	5.56351	5.9091	85.7468	-	5.9091	14.7624	weak dimer
1.02	Na(5.5)	2.02135	1.85063	2.73262	5.69366	5.86282	83.5264	176.1739	5.86282	14.6192	AF
1.18	Sr(5)	2.04131	2.02658	2.69319	5.85665	5.9699	82.5501	-	5.9978	15.1681	Ferro

Table 5.3: Structural parameters obtained after refinement of various $\text{Ba}_3M\text{Ir}_2\text{O}_9$ [9, 10]

metal in these triple perovskite oxides, because the Ir_2O_9 units tend to exhibit a weak temperature dependent behaviour in magnetization [9, 67, 90, 101]. These interactions are drastically influenced by the choice of M site ion that further dictates Ir-O-M and Ir-O-Ir bond linkages resulting in different microscopic behaviours. For instance, the monoclinically distorted $\text{Ba}_3\text{BiIr}_2\text{O}_9$ is seen to exhibit a pronounced magnetostructural transition which is seen to be associated with a giant magnetoelastic effect - the largest observed for any 5d oxide till date [53, 54]. However, the closely related hexagonal $\text{Ba}_3\text{ZnIr}_2\text{O}_9$ exhibits dramatically different properties, since this system does not order down to the lowest measured temperatures and is now thought to harbour a spin-orbital liquid state [67] whereas $\text{Ba}_3\text{CoIr}_2\text{O}_9$ stabilises in the hexagonal ($P6_3/mmc$) symmetry and exhibits a magneto-structural transition at around 107K. Needless to say, the associated changes in both the extent of crystal field splitting, as well as the superexchange paths dramatically change the magneto-structural properties of these systems.

In stark contrast to the other members of the family where clear structural phase transitions were observed denoting release of frustration, $\text{Ba}_3\text{NiIr}_2\text{O}_9$ resembles the $\text{Ba}_3M\text{Ir}_2\text{O}_9$ ($M = \text{Mg}, \text{Sr}, \text{Ca}$) family, as evident in the Table 5.3. $\text{Ba}_3M\text{Ir}_2\text{O}_9$ exhibits antiferro-

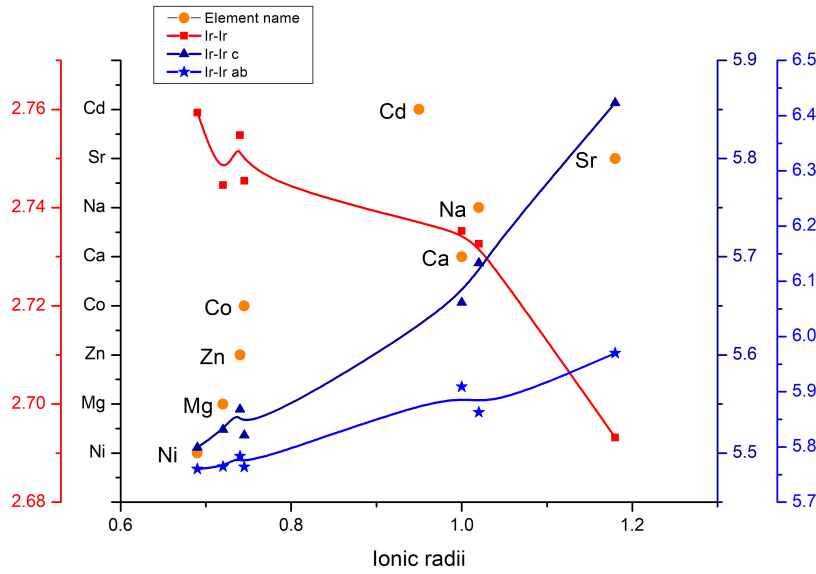


Figure 5.14: A comparative study for the change in Ir-Ir distances along various axis as a function of changing M site cation in $\text{Ba}_3M\text{Ir}_2\text{O}_9$.

magnetic exchange interactions, weak dimer and ferromagnet like features in magnetization for $M = \text{Mg}, \text{Ca}, \text{Sr}$ respectively and yet no structural transformation were observed down to the lowest temperatures. Although, it is worth mentioning that in all these compounds, the M site cation is non-magnetic.

One obvious question that arises is the presence of such different structural behaviour in Ni as compared to Co despite having the same structure, valence state and proximity in the periodic table. The contrasting ground states could stem from the different ionic radii ($\text{Co}=0.745\text{\AA}$, $\text{Ni}=0.690\text{\AA}$) and electronic configuration for both Nickel and Cobalt ($\text{Co}^{+2} = t_{2g}^5 e_g^2$, $\text{Ni}^{+2} = t_{2g}^6 e_g^2$). The antiferro super exchange paths $M\text{-O-O-}M$, within the ab plane are strengthened by the partially filled t_{2g} levels in the case of Cobalt. In comparison, the filled t_{2g} shells of Ni do not participate in such an interaction leading to reduced Ni-Ni distance (lattice parameter a), lowest in the series as shown in table. The significant difference in bond lengths and angles for these systems, results in creation of different local environments in these lattices and may result in different mi-

croscopic behaviours. In order to compare the interaction dynamics when two magnetic ions are at play, a close analogue that could be considered are the double perovskites of the form $\text{Sr}_2\text{MM}'\text{O}_6$ ($\text{M}=\text{Fe}, \text{Cr}, \text{Co}$; $\text{M}'=\text{Os}, \text{W}, \text{Re}, \text{Mo}$) [205, 221–223]. Theoretically expected to be a ferrimagnet semiconductor [224], $\text{Sr}_2\text{FeOsO}_6$, was reported to exhibit antiferromagnetism with two magnetic phase transitions at 140K and 67K [225]. The investigations of the magnetic spin structure revealed the presence of two different antiferromagnetic spin arrangements (AF_1 and AF_2) with phase co-existence of both the antiferromagnetic phases below 67K, where lattice instability fine tunes the competing exchange interactions [221]. Similarly, $\text{Sr}_2\text{CoOsO}_6$ exhibits two antiferromagnetic transitions at 108K and 70K corresponding to ordering of Os^{+6} ions and Co^{+2} ions respectively [226]. Density functional theory revealed that the long range super-exchange interactions between Co and Os are transformed by weak energetic overlap between the $3d$ Co orbitals and $5d$ Osmium orbitals leading to different magnetic ordering temperatures. We speculate, a similar mechanism is at play in $\text{Ba}_3\text{NiIr}_2\text{O}_9$.

5.8 Summary

In summary, we report a hitherto new compound, $\text{Ba}_3\text{NiIr}_2\text{O}_9$, that contrary to $\text{Ba}_3\text{CoIr}_2\text{O}_9$, retains overall hexagonal symmetry down to the lowest temperature measured. The magnetization studies revealed two transitions 106K and 6K, speculated to be due to the antiferromagnetic ordering of Ir_2O_9 dimers and Ni_{+2} spins respectively. Although belonging to the same structural class, the diverse phonon dynamics in $\text{Ba}_3\text{M}\text{Ir}_2\text{O}_9$ ($\text{M}=\text{Co}, \text{Ni}$) and magnetic ground state is driven by distinct magnetic anisotropies in these oxides as a consequence of filled and partially filled t_{2g} shells in Nickel and Cobalt respectively. Due to isoelectronic substitution, the spin orbit interaction is unlikely to be modified, although changes in crystal field splitting and bandwidths can be expected as evident in different structural and magnetic modifications in this structural class. There-

fore, these family of compounds provide a unique platform to study the interplay of coupled and competing order parameters as the choice of M site cation plays a crucial role as it mediates the frustration in the lattice via the corner shared arrangement with iridium and extended super-exchange in the a-b plane. We emphasize on the importance of a single crystal in this material for a more coherent directional dependent study.

Chapter 6

Cooperative paramagnetism to cluster glass in a $\text{Ba}_3\text{NaIr}_2\text{O}_9$

6.1 Introduction

Geometrically frustrated magnets- where triangular lattice antiferromagnets (TLAFs) are considered to be an archetype- remain at the forefront of contemporary condensed matter [3]. Of particular interest in the recent years have been a number of Ruthenium and Iridium based perovskite variants which stabilize in an inherently frustrated environment. In general, the stabilization of a particular structural ground state depends on the tolerance limit of the corresponding symmetry which in turn is related to the relative ionic radii of the constituent elements. For instance, in the perovskite ABO_3 , introducing a bigger element at the A and B sites can progressively tune the lattice from a high symmetry hexagonal to a lower symmetry orthorhombic, or even a monoclinic one [227]. The same is true for the double ($\text{A}_2\text{BB}'\text{O}_6$) and triple layered perovskites ($\text{A}_3\text{BB}'_2\text{O}_9$) as well, where it has been shown that B site cations with higher atomic radii stabilizes in a lower symmetry [9, 10].

A relatively recent addition to this family of geometrically frustrated magnets are

the Barium based triple perovskite iridates of the form $\text{Ba}_3\text{M}\text{Ir}_2\text{O}_9$ (M =alkali metal, alkaline earth metal, $3d$ transition metal or lanthanides) as discussed in the previous chapters. The structure-property relationships in these systems are clearly driven by a complex interplay between the relative strengths of competing spin-orbit coupling (SOC), electronic correlation (U), and a hybridization interaction controlled by the Ir-O-Ir bond angle. Thus small perturbations, such as changes in lattice parameters caused by variations of different M ions, can tip the balance between the competing energies and ground states.

In all the reported 6H hexagonal triple perovskite iridates, the ionic radii of the M site cation lies in the range of $0.605\text{\AA}$ - $0.947\text{\AA}$, beyond which the internal pressure forces the lattice to stabilize in a lower symmetry. For example, the $\text{Ba}_3\text{CaIr}_2\text{O}_9$ system has been reported to stabilize in $C2/c$ monoclinic symmetry [10] which is line with the expected structural ground state based on the tolerance limit. Interestingly, an exception appears to be the $\text{Ba}_3\text{NaIr}_2\text{O}_9$ system, which - in spite of the similar ionic radii of Na ($1.02\text{\AA}$) and Ca ($1.00\text{\AA}$) - has been reported to stabilize in the high symmetry hexagonal structure at room temperatures. In this chapter, we discuss this relatively un-investigated Na based triple perovskite iridate, where iridium is forced to be in the unconventionally high charge state of 5.5. We investigate polycrystalline specimens of this system using a combination of high resolution synchrotron diffraction, magnetization, resistivity and specific heat measurements. We observed that the lattice appears to accommodate strain as the temperature is reduced, which in turn precludes the stabilization of a lower symmetry structural phase. This is in contrast to what is typically observed in this class of materials. On the other hand, a very gradual and incomplete transformation to a low symmetry orthorhombic phase is observed, and the high symmetry hexagonal phase survives till the lowest measured temperatures. Measurements of the magnetization and specific heat point towards the existence of a extended cooperative paramagnetic regime

characterized by short range magnetic correlations, which condenses into a cluster glass like state at low temperatures.

6.2 Experimental Details

Polycrystalline specimens of $\text{Ba}_3\text{NaIr}_2\text{O}_9$ were synthesized by using the standard solid state reaction route. Stoichiometric amounts of high purity BaCO_3 , Na_2O_3 and IrO_2 were thoroughly ground and then sintered at 1100°C under oxygen atmosphere to maintain the high oxidation state of Iridium. The details of the experimental techniques used has been discussed in Chapter 2.

6.3 Results and Discussion

A Rietveld fit to the synchrotron diffraction data obtained at 300 K is shown in Fig. 6.1 $\text{Ba}_3\text{NaIr}_2\text{O}_9$ is seen to stabilize in the high symmetry hexagonal ($P6_3/mmc$) symmetry, and the lattice parameters are deduced to be $a = b = 5.8629\text{\AA}$, $c = 14.6192\text{\AA}$ and $\alpha = \beta = 90^\circ$; $\gamma = 120^\circ$. This is in good agreement with previous reports [140–142,228]. The room temperature structure is illustrated in Fig. 6.2(a) where face sharing octahedra (in pink) forms a Ir_2O_9 dimer and are connected via corners to NaO_6 octahedra (in green). Fig. 6.2(b) represents the projection along the crystallographic c -axis where IrO_6 octahedra forms a hexagonal ring around the NaO_6 octahedra. Since Na is in the +1 oxidation state, Ir is forced to stabilize in an atypical high oxidation state of +5.5. EDAX measurements were also used to confirm the stoichiometry. Since it is difficult to quantify the lighter elements (Na and O) using this technique, the atomic percentage ratio between heavy elements Ba and Ir was compared. The Ba:Ir ratio obtained from EDAX was observed to be 1.54 which is very close to the stoichiometric ratio of $3:2=1.5$ expected from the chemical formula. A scanning electron micrograph image is shown

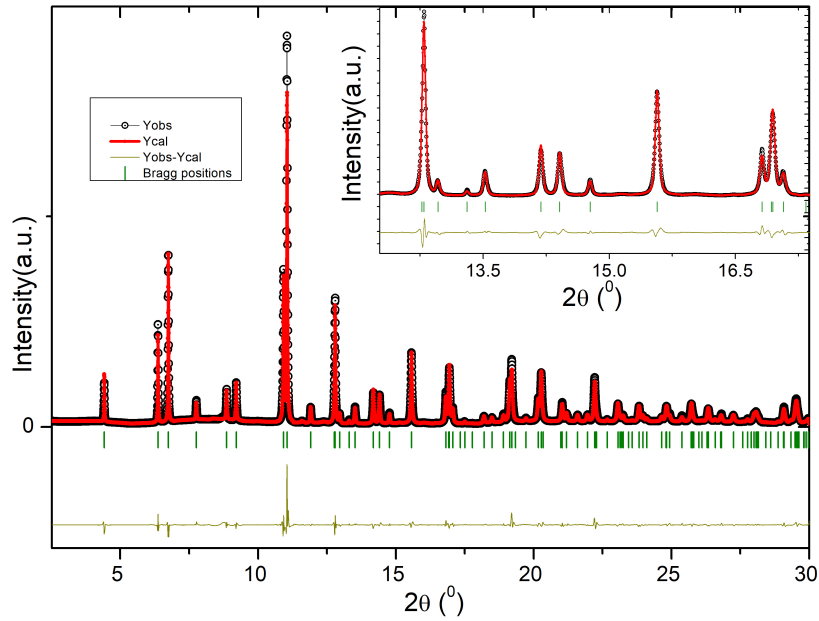


Figure 6.1: Main panel: Fit to the Rietveld refinement of the synchrotron data at 295 K for $\text{Ba}_3\text{NaIr}_2\text{O}_9$. The compound crystallizes in a 6H-hexagonal perovskite with space group (194). The calculated and the observed diffraction profiles are shown in red and black respectively. The vertical green lines indicates the Bragg positions and the brown line at the bottom is the difference between observed and calculated intensities. Inset: Enlarged view of the higher angle peaks and the corresponding fit.

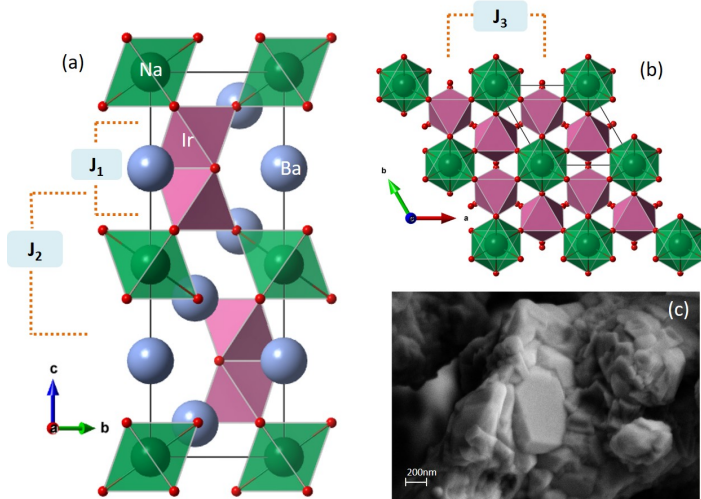


Figure 6.2: (a) A schematic representation of the crystal structure of $\text{Ba}_3\text{NaIr}_2\text{O}_9$ using Vesta. Here pink and green octahedra represents Iridium and Sodium respectively. The Barium atoms are represented in Blue. (b) The projection of the structure along the c-axis is shown. The Iridium octahedra form a hexagonal ring surrounded by Sodium. (c) SEM image of the compound showing hexagonal facets.

in Fig. 6.2(c) where hexagonal facets - a reflection of the crystallographic symmetry - can be clearly seen.

A comparison of the temperature dependence of a few representative x-ray diffraction peaks as measured at the extreme temperatures of 5 K and 300 K is shown in Fig. 6.3(a). As the temperature is lowered, the diffraction peaks shift to higher angles and also become anisotropic. The modification of the peak profile could either signal the presence of strain in the lattice or a transformation to a lower symmetry phase. The former could be a consequence of the large ionic radii which Na possesses, whereas the latter has been reported in a number of triple perovskite iridates earlier. Since there were no additional peaks visible in the low temperature scan, the data was initially fit using a hexagonal model alone. These attempts were not successful, as is shown in the Fig. 6.3(b). Addition of strain using the broadening model available in FullProf made the fit better as can be seen in Fig. 6.3(c). This method is based on Stephens model [229] of anisotropic broadening, where the refinement of microstrain covariance parameters S_{400} , S_{004} and S_{112} corresponds to strain along the 100, 001 and 101 hkl planes. Though strain does appear to have an impact on the low temperature phase, the fitting was still not satisfactory enough, which hints at the possible presence of an additional low symmetry phase at low temperatures.

To identify the possible symmetry of the additional low temperature phase, existing literature in the ruthenate triple perovskite family was referred to, where multiple scenarios ranging from monoclinic (Space group = $P2_1/c$, $C2/c$) to orthorhombic (S.G.= $Cmcm$), or even different structural models for the same compounds [230, 231] have been reported. After exploring all these possible options, the orthorhombic phase [231] resulted in the best fit, with R_{wp} and R_p values of 3.24 and 2.47 respectively. The generated pattern was seen to match well with the high resolution synchrotron data as

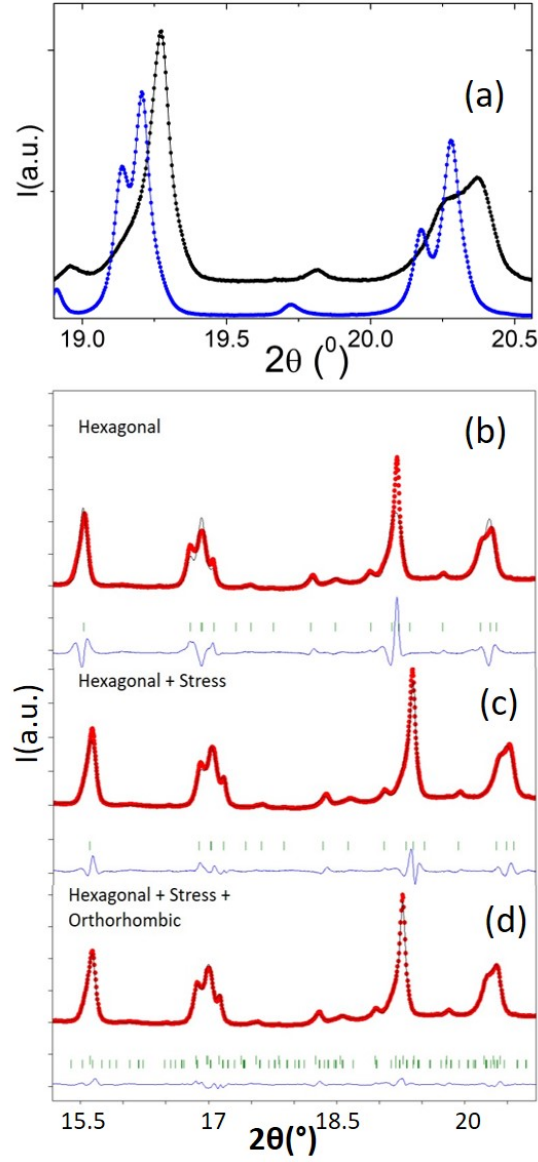


Figure 6.3: (a) Temperature evolution of synchrotron peaks at 5K and 300K. The lattice strain manifests in the form of broadening of diffraction peaks.(b,c,d) Attempts to fit the synchrotron diffraction data at 5K using various model as indicated.

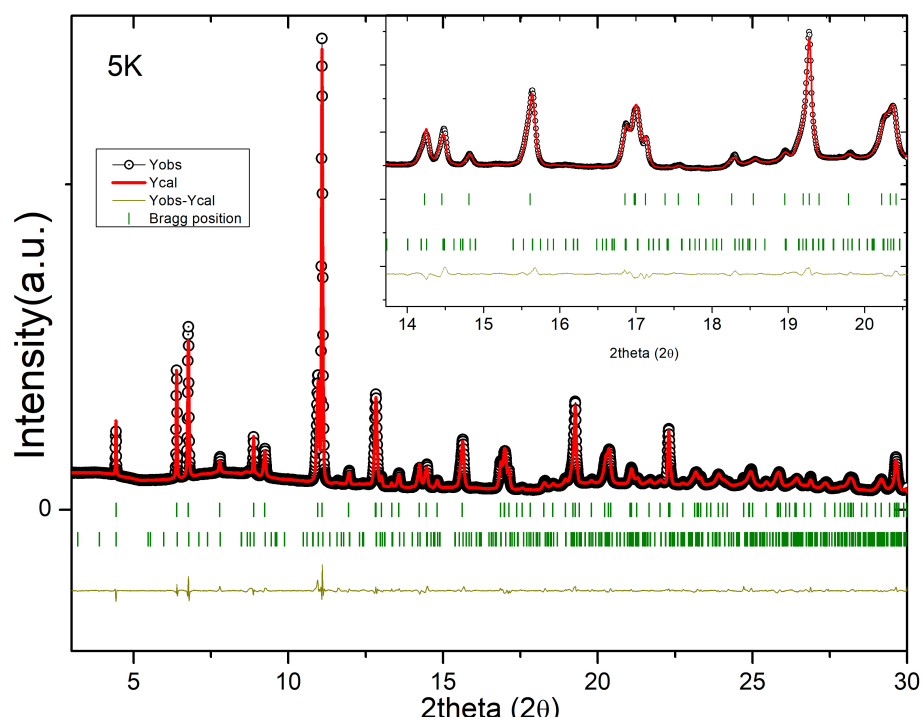


Figure 6.4: Main panel: Fit to the Rietveld refinement of the synchrotron data at 5K for $\text{Ba}_3\text{NaIr}_2\text{O}_9$. The calculated and the observed diffraction profiles are shown in red and black respectively. The vertical green lines at top and bottom indicates the Bragg positions for hexagonal and orthorhombic symmetry respectively. The brown line at the bottom is the difference between observed and calculated intensities. Inset: Enlarged view of the Rietveld refinement of the synchrotron data at higher theta values.

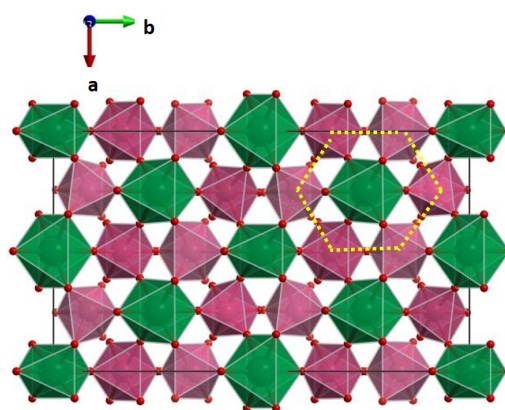


Figure 6.5: A schematic representation of the crystal structure of $\text{Ba}_3\text{NaIr}_2\text{O}_9$ using Vesta for the orthorhombic phase. Here pink and green octahedra represents Iridium and Sodium respectively. The Barium atoms are not shown for clarity. The yellow dotted line shows the hexagonal arrangement for Iridium octahedra.

shown in Fig. 6.3(d). Fig. 6.4 shows the Rietveld fit to the synchrotron diffraction data obtained at 5 K for the entire temperature range with selected 2θ range zoomed in the inset. The lattice parameters obtained from the fit for the additional orthorhombic phase at 5K are $a=11.6574\text{\AA}$, $b=20.1975\text{\AA}$, $c=14.5773\text{\AA}$ and $\alpha = \beta = \gamma = 90^\circ$. Fig. 6.5 depicts this orthorhombic phase as viewed along the crystallographic c -axis. The yellow dotted line indicates the hexagonal arrangement formed by Ir octahedra. The high temperature hexagonal structural symmetry allows for only one crystallographic position (4f) for Iridium. Therefore, given the presence of mixed valent state $\text{Ir}^{5.5}$, this position is highly disordered. This fact becomes crucial when we consider the orthorhombic phase. The resulting low temperature C-centred orthorhombic symmetry is in fact a $2a \times 2b$ primitive hexagonal pseudo-cell called orthohexagonal cell and allows for three different crystallographic sites for Ir (8f,8f,16h) making it possible for the charge to be redistributed at these distinct cation sites. In addition, Na also now has 3 unique Wyckoff positions (4a, 4b 8d) allowing for the movement of Iridium while still maintaining the orthorhombic crystal framework. This is a complex low symmetry where each element has multiple unique positions, and the structural details are given [230]. There have been prior reports of orthorhombic phases with only one crystallographic position for Ir, but attempts to fit the current compound's low temperature profile using this symmetry were not successful. Interestingly, in the ruthenium analogue, this need for multiple Ru positions was attributed to the presence of a charge ordered state.

It was observed that down to 50 K, a single structural model (hexagonal) with strain parameters was sufficient for the fitting. As a function of reducing temperatures, the phase fraction of hexagonal symmetry is invariant till 50 K, below which the orthorhombic symmetry is seen to stabilize, reaching 20% of the total volume fraction at 5 K (Fig. 6.6(d)). The temperature dependence of volume and c/a ratio for the primary

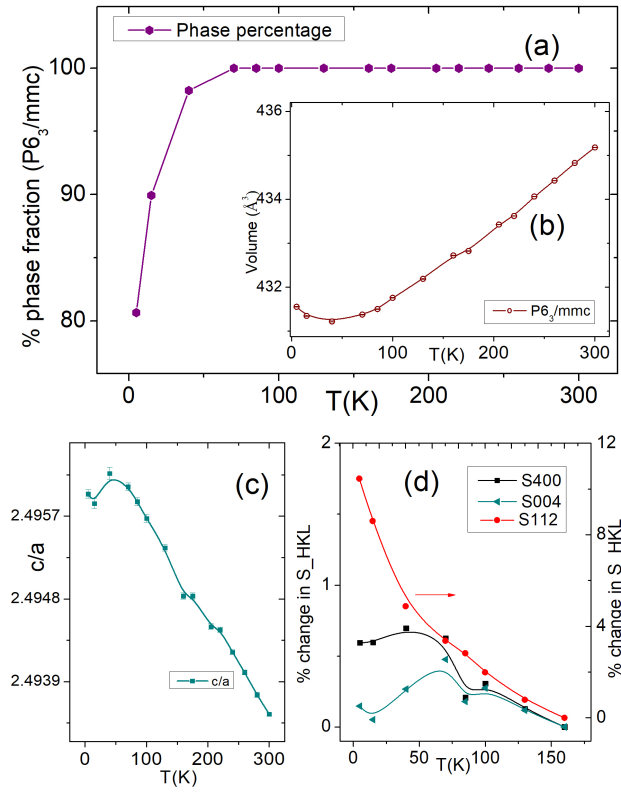


Figure 6.6: (a) Temperature evolution of the phase fraction, (b) volume, (c) ratio of lattice parameters c/a for of $P6_3/mmc$, (d) The temperature dependence of the microstrain parameters S_{HKL} .

hexagonal phase are depicted in in Fig. 6.6(b) and Fig. 6.6(c) respectively. Clearly, below 50 K, the c/a ratio shows a change in slope associated with onset of the partial structural phase transformation. The evolution of the secondary orthorhombic phase is also evident in the temperature dependence of the microstrain covariance parameters as in depicted in Fig. 6.6(a). The strain parameters S_{400} and S_{004} show a sharp change close to the structural transformation temperature and remains almost constant below it, whereas the parameter S_{112} increases dramatically. These changes in the microstrain parameters are an indicative of deviations in the α and β angles of the hexagonal lattice framework, and consistent with a distortion towards an orthorhombic symmetry. It is interesting to note that the emergence of the secondary orthorhombic phase at low tem-

peratures is not associated with the observation of a splitting of the hexagonal peaks, as was observed in [232]. We believe that this is due to the excess broadening of the diffraction peaks due to strain. This incipient strain not only masks the peak splitting expected due to the orthorhombic distortion, but also results in an incomplete conversion of the high temperature hexagonal phase to the lower symmetry orthorhombic one.

Fig. 6.7(a) shows the temperature dependence of the magnetic susceptibility of $\text{Ba}_3\text{NaIr}_2\text{O}_9$ as measured at an applied field of 500 Oe. The susceptibility increases with decrease in temperature with the zero field cooled (zfc) and field cooled (fc) curves diverging close to 6 K as shown in Fig. 6.7(b). This is at variance with what has been reported in early single crystalline specimens of this system, where features in the magnetization was observed at 75 K and 50 K [52, 232]. The temperature dependence of the heat capacity as measured from 2-250 K is depicted in Fig. 6.7(c). Clearly, the low temperature anomaly observed in magnetization is absent here which implies that the change in entropy is rather small. Fig. 6.7(d) shows the temperature dependence of reciprocal magnetic susceptibility ($1/\chi$). Interestingly, a linear region was observed well in excess of 200 K, and hence only the temperature range 260- 300 K was chosen to fit the inverse magnetic susceptibility using the Curie-Weiss law. An effective magnetic moment value $3.428\mu_B$ per formula unit and a Weiss temperature (θ_c) of -285.36 K were obtained, with the former being indicative of the extent of frustration in this system, since we only observe a feature in magnetization at 6 K.

Since Iridium is the only magnetic ion in this system, the magnetic moment arises from the charge balance between Ir(V) ($5d^4$) and Ir(VI) ($5d^3$). Based on these oxidation states and the octahedral coordination environments, the theoretical spin-only moment for non-interacting mixed valent Ir^{5+} ($S=1$, $2.83 \mu_B$) and Ir^{6+} ($S=3/2$, 3.87

μ_B) is $6.7\mu_B$ per formula unit for the high spin state. Considering the case of strong spin-orbit coupling, the low spin state Ir^{5+} ($S=0$, $J=0 \mu_B$) and Ir^{6+} ($S=1/2$, $1.73 \mu_B$) leads to a moment of $1.73 \mu_B$ for the compound. These calculated moments are significantly larger (smaller) for the high (low) spin states than the experimentally determined value $3.428\mu_B$ per formula unit. However, the experimentally obtained value is close to the reported magnetic moments $3.6\mu_B$ per formula unit for $\text{Ba}_3\text{NaIr}_2\text{O}_9$ and $3.93\mu_B$ per formula unit for $\text{Ba}_3\text{LiIr}_2\text{O}_9$, both having Ir in a similar 5.5 charge state [52]. Such reduction in moment is a peculiar feature seen in iridates and has been reported for a wide range of iridium based oxides [9, 18, 233, 234].

The strong suppression of the magnetic moment here is ascribed to the joint effect of spin orbit interaction and strong covalency, resulting in the formation of metal-metal bonds. They act against the intraatomic Hund's rule exchange interaction to reduce the total magnetic moment on the Iridium dimer. This was further confirmed by our synchrotron measurements where anomalous shortening of Ir-Ir bond distance in +5.5 valence state ($2.73\text{\AA}$) as compared to the +5 state ($2.75\text{\AA}$) corroborate the formation of the metal-metal bonds. Na being non-magnetic, the inter and intra dimer interactions between Ir ions drives the magnetic ground state of the system. In the absence of super exchange path for inter dimer interactions (J_2 and J_3), the extended superexchange pathways Ir-O-O-Ir could possibly influence the magnetic exchange interactions. The Ir dimers are separated from each other via non magnetic Na octahedra (green) as shown in Fig. 6.8. The next nearest neighbour inter dimer Ir ($5.86106(4)$ and $5.69368(4)$) are connected via 2 oxygens from the Na octahedra as shown by the dotted lines. Thus, in addition to metal-metal bonds, the presence of super exchange and extended super exchange interactions pathways lead to complex magnetic exchange interactions.

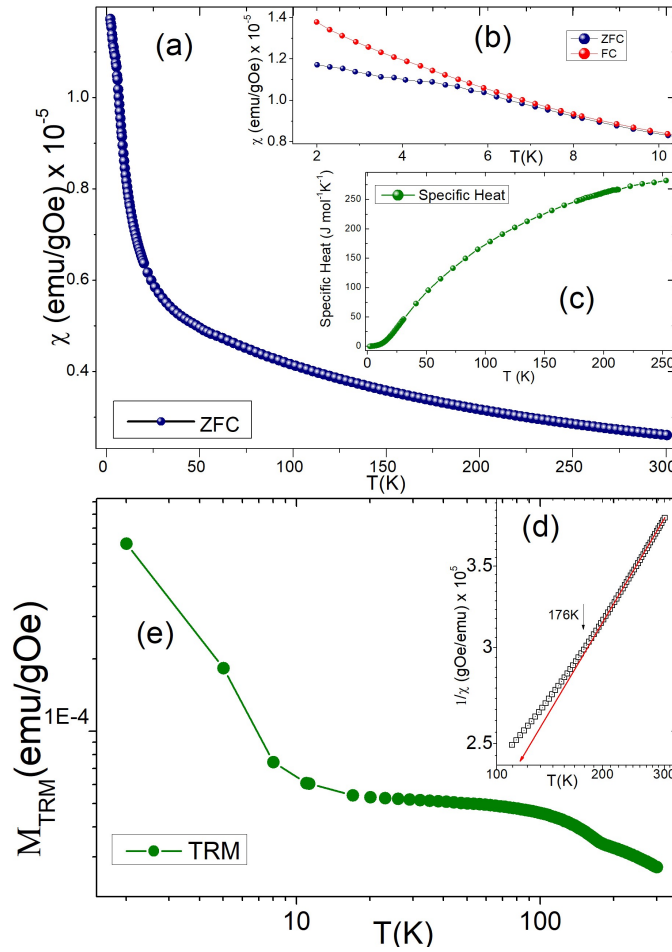


Figure 6.7: (a) Temperature dependent magnetization in zero field cooled at 500 Oe for $\text{Ba}_3\text{NaIr}_2\text{O}_9$. (b) ZFC-FC bifurcation at low temperatures (c) Specific heat vs T for $\text{Ba}_3\text{NaIr}_2\text{O}_9$ with no discernible anomaly at 200K, (d) log-log plot of inverse plot of magnetic susceptibility data at 500Oe. The solid red line is guide to the eyes to show the deviation from Curie Weiss law starts close to 175K. (e) TRM at 1000Oe with two systematic jumps corresponding to both the magnetic transitions.

Though heat capacity measurement did not show evidence of any long range ordered state, a Curie Weiss fit of the inverse magnetic susceptibility was valid only in temperatures in excess of 260 K, indicating the presence of extended regime of short range magnetic correlations. To gain further insight in to the extent of this regime, we performed temperature dependent measurements of the Thermo-remnant magnetization (TRM), which have proven to be an effective tool in the investigation of magnetically

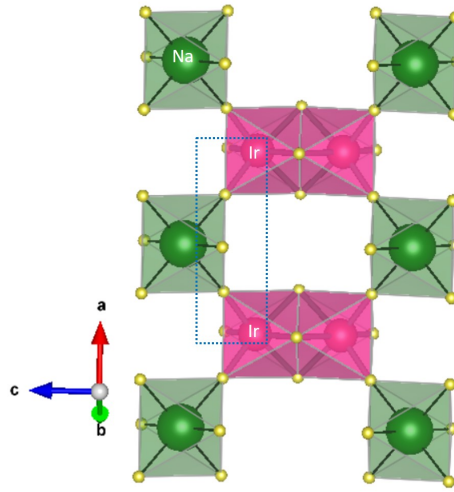


Figure 6.8: A schematic representation of the crystal structure of $\text{Ba}_3\text{NaIr}_2\text{O}_9$ using Vesta. The projection of the structure perpendicular to the c-axis is shown. Here pink and green octahedra represents Iridium and Sodium respectively. The Barium atoms are not shown for clarity. The Ir dimers are separated by Na octahedra along the c-axis where the extended super exchange between Ir dimers is mediated by oxygens in Na octahedra as shown by dotted line.

frustrated systems. A TRM measurement as performed on the $\text{Ba}_3\text{NaIr}_2\text{O}_9$ system in a cooling field of 1 kOe is depicted in Fig. 6.7(e). Two precipitous jumps are clearly observed - one below 10 K, which corresponds to the low temperature magnetic transition observed in the ZFC-FC measurements, and one just below 175 K, which roughly corresponds to the region where the inverse magnetic susceptibility deviates from the linear Curie-Weiss fit. In the absence of long range order, this feature at high temperature could be ascribed to the onset of a cooperative paramagnetic regime. First coined by Villain [235], cooperative paramagnetism was used to describe the low temperature dynamics of a classical Heisenberg spins on a corner sharing tetrahedral framework, and is a defining feature of systems with high geometric frustration. Cooperative paramagnetism is seen in many transition metal oxides which crystallizes in magnetic spin configurations that are geometrically or topologically prone to frustration due to underlying lattices based upon corner, edge or face sharing triangles or tetrahedra. A wide range of systems including pyrochlore, spinels, and jarosites are now known to exhibit

this phenomena [236–238]. This state can also be looked upon as being analogous to the Griffiths phase, with the notable difference that the low temperature magnetic ground state instead of being magnetically ordered, now undergoes a glass-like dynamical phase transition. We believe that the nucleation of finite size correlated regions within the antiferromagnetic matrix starts to develop close to 175 K. As the temperature reduces, magnetic frustration develops due to competing intra dimer (nearest neighbour J_1) and inter dimer (next- nearest neighbour J_2 and J_3) interactions. The absence of conventional long range antiferromagnetic order is due to the interplay between frustration and quenched disorder. As proposed by Imry and Ma [239], a random quenched disorder inhibits the transition to a long range magnetically ordered state but instead favors the nucleation of correlated magnetic clusters [240].

Interestingly, the high temperature magnetic feature (~ 175 K) which we observe in the TRM measurements is not easily discernible in other measurements, and hence has gone unreported in prior single crystal measurements of $\text{Ba}_3\text{NaIr}_2\text{O}_9$ as well [52]. This is a consequence of the fact that the magnetic susceptibility of the paramagnetic matrix (χ_{PM}) would be of the same order (or even larger) than that of the antiferromagnetic clusters (χ_{AFM}), making it difficult to unambiguously determine the contribution of the antiferromagnetic clusters in traditional in-field magnetic measurements. On the other hand, since TRM is a zero-field measurement, the contribution of the paramagnetic magnetic susceptibility is likely to be suppressed, allowing for one to identify more clearly the temperature regime at which the antiferromagnetic clusters begin to nucleate. Interestingly, the ruthenate analogue of this triple perovskite was reported to exhibit the opening of a charge gap at 210 K [230], though we do not observe any evidence of a similar phenomena in its Iridium counterpart investigated here. The magnetic transition in these family of oxides is typically associated with a symmetry breaking lattice

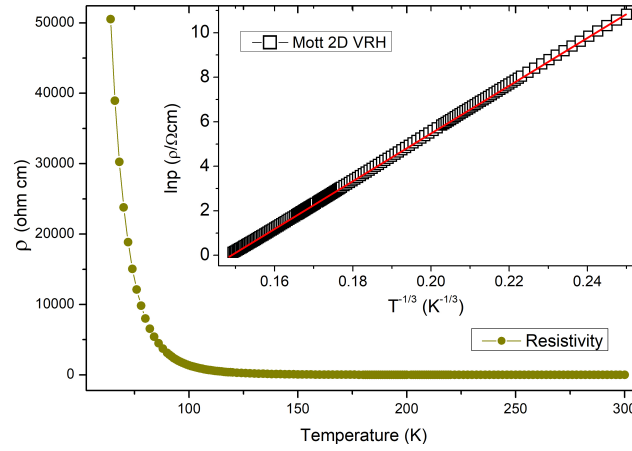


Figure 6.9: Main panel: Resistivity (ρ) plotted as a function of temperature. Inset: Resistivity ($\ln \rho$) plotted as a function of temperature ($T^{-0.33}$). The red line is the fit to the Mott variable range hopping (VRH) model.

distortion which alters the exchange parameters, thereby neutralizing the frustration. In the case of $\text{Ba}_3\text{NaIr}_2\text{O}_9$, the interesting capacity of the system to hold strain impedes a traditional structural transformation. Therefore, rather than observing a first order transition from hexagonal symmetry to an orthorhombic one, we observe a slowly evolving strained lattice gradually transforming to a lower symmetry where the major phase still retains the original high temperature symmetry. A strained lattice of this nature is probably closer to the reports of the triple perovskite family when subjected to external pressure [10, 241]. For instance on application of pressure, the $\text{Ba}_3\text{NaRu}_2\text{O}_9$ transforms to a new phase, $3\text{C}_{1:2}\text{-Ba}_3\text{NaRu}_2\text{O}_9$, where the charge gap completely disappears and Pauli paramagnetism emerges, possibly as a consequence of strong electron-electron correlations. The $\text{Ba}_3\text{CaRu}_2\text{O}_9$ system has also been reported to exhibit excess strain in the lattice, in the form of peak broadening as the temperature was lowered. Therefore, the ground state in $\text{Ba}_3\text{NaIr}_2\text{O}_9$ is clearly influenced by the complex interplay of a mixed valent Ir, frustration, phase coexistence and strain.

The temperature dependence of the electrical resistivity is shown in the inset of

Fig. 6.9. The system is semiconducting in nature, with the magnitude of resistivity changing by 4 orders of magnitude from its room temperature value. Attempts to fit using the Arrhenius model and Efros-Shklovskii variable range hopping (ES-VRH) model were unsuccessful. A better fit was obtained by using the Mott variable-range hopping (VRH) model which is given by,

$$\rho \propto \exp((T_0/T)^\nu) \quad (6.1)$$

where the best fits were obtained for $\nu=1/3$ indicating variable range hopping in two dimensions [242]. The magnetic Ir dimers are connected via non-magnetic Na octahedra, generating a pseudo 2D structure. Thus, the crystal structure of this triple perovskite can be expressed by alternate stacking of two kinds of 2-D layers which consist of the NaO_6 octahedra and the Ir_2O_9 polyhedra. This structure feature may account for the observed 2-D resistivity behavior. The resistivity of $\text{Ba}_3\text{NaIr}_2\text{O}_9$ as a function of $\ln\rho$ vs $T^{-0.33}$ is shown in the inset of Fig. 6.9. The localization of states due to strong Coulomb interactions and slight structural disorder would be consistent with variable range hopping behaviour. The resistivity of the ruthenate analogues of the triple perovskites $\text{Ba}_3\text{MRu}_2\text{O}_9$ ($\text{R}=\text{Fe}, \text{Co}, \text{Ni}, \text{Cu}, \text{In}, \text{Ln}$), all follows the same characteristics [156, 243].

In addition to frustration, the presence of mixed valent states of Iridium and phase co-existence sets the stage for inhomogeneous magnetic exchange interactions. The observation of an anomaly below 6 K in the $M(T)$ curves indicates the emergence of glassy dynamics owing to this frustration. The presence of the spin frustration was investigated using ac susceptibility measurement but the signal was too small to identify a frequency dependent peak in this temperature region was observed. Another method to probe glassy dynamics is to use the time evolution of Isothermal Remanent Magnetization (IRM). This involves cooling the sample from 300 K to 2 K in the presence of a

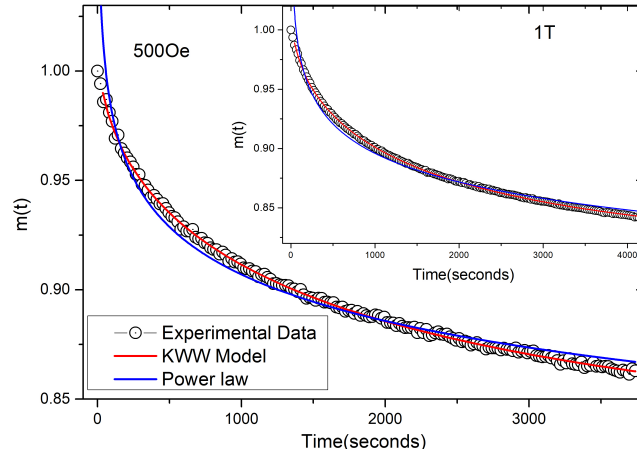


Figure 6.10: Normalised Isothermal Remanent Magnetization (IRM) at 2K in cooling fields 500Oe and (inset) 1T fitted using KWW (Kohlrausch Williams Watt) stretched exponential (red) and power law (blue).

magnetic field, after which the magnetic field is switched off and the decay of magnetization is measured as function of time. A special formulation of power law is known to study the time dynamics of magnetization for glasses under stress known as Kohlrausch Williams Watt (KWW) stretched exponential equation [244]. It is given by [245, 246]

$$m(t) = m_0 - m_g \exp\{-(t/\tau)^\beta\}$$

where m_0 is related to initial remanent magnetization, m_g is magnetization of glassy component, τ and β are the characteristic relaxation time constant and stretching exponent respectively. Here $m(t)$ is representative of the sum of many exponential decays weighted by a distribution of individual relaxation times, with the magnitude of β indicating the breadth of that distribution [247]. The value of β has been reported to lie between 0 and 1 for a wide range of disordered systems. The normalized magnetization $m(t) = (M_t/M_{t=0})$ as measured in $\text{Ba}_3\text{NaIr}_2\text{O}_9$ at 2 K with cooling fields of 500 Oe (main panel) and 1T (inset) at 2K is plotted in Fig. 6.10. As depicted by the blue curve, the fit to a simple power law was not satisfactory. However, a good fit was obtained for the KWW model and the resultant values of β are 0.518(14) and 0.5464(68) for 500Oe and 1T respectively. These values are in lines with the reported values for cluster glass

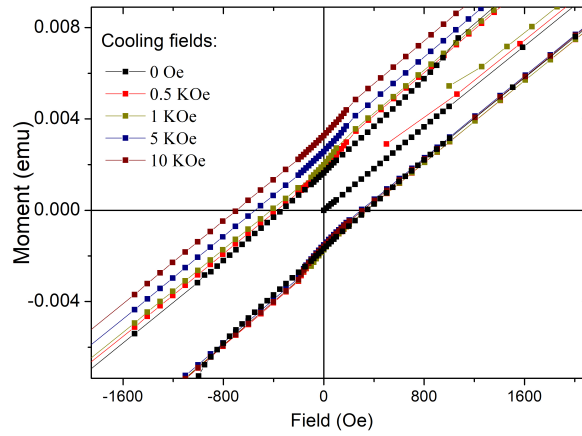


Figure 6.11: Field cooled M-H isotherms showing exchange bias

phase in many double perovskites [240,248], and reinforces our contention that the low temperature magnetic ground state is one which has magnetically frozen clusters.

The magnetic interactions in $\text{Ba}_3\text{NaIr}_2\text{O}_9$ are predominantly antiferromagnetic, though, signatures of the presence of mixed magnetic interactions are suggested by a weak loop opening in magnetization isotherms at 2 K as shown in Fig. 6.11. As revealed by our synchrotron studies, the low temperature structure comprises of a highly strained lattice with two unique structural motifs coexisting. This coupled with the existence of finite size antiferromagnetic clusters allow for exchange bias, with the antiferro and ferro-magnetic contributions arising from the magnetic order within ordered clusters and uncompensated spins at the surface of these clusters respectively (Fig. 6.11). The presence of a low temperature glass-like magnetic ground state is also evidenced in a strong upturn in C/T^3 vs T Fig. 6.12, with a clear deviation from what is expected from Debye's law. This excess entropy arises as a consequence of the glassy dynamics [160], and appears to be a signature common to structural and magnetic glasses. This is also evident on plotting C/T vs T^2 curve, indicating the presence of an excess entropy that releases as a consequence of short range ordering. The inset of Fig. 6.12 shows the

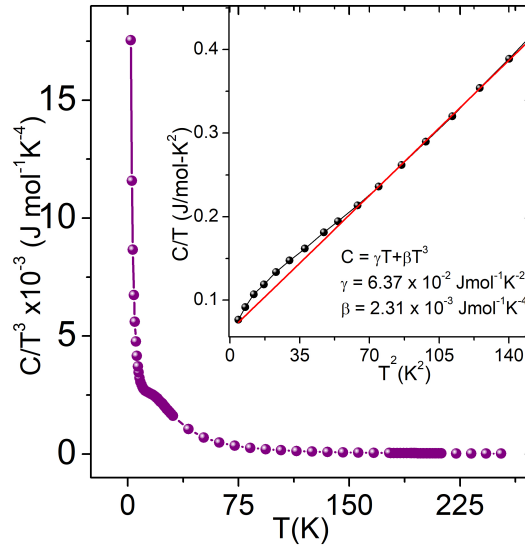


Figure 6.12: Main panel: The low temperature specific heat C_P/T^3 as a function of temperature. The slight upturn in the very low T range is a strong indication of disorder in the system. Inset: Low temperature fit using Debye and Petit law.

fit to the low temperature C/T vs T^2 curve. The data is fitted using the expression $C_p = \gamma T + \beta T^3$ where γ and β are related to the electronic and vibrational degrees of freedom respectively. We also calculated the Debye temperature θ_D , which is derived from the expression, $\theta_D = (12\pi^4 p R / 5\beta)^{1/3}$, where R is the ideal gas constant and p is the number of atoms per formula unit. The calculated value of θ_D is 236.84K. The obtained values of γ and β are 77mJ/molK² and 2.19mJ/molK⁴T respectively. The high value of γ , unusual for insulating systems, can be attributed to the inherent disorder which affects the spin, charge and orbital degrees of freedom. This has been previously observed in insulating tripe perovskite iridate ($\text{Ba}_3\text{ZnIr}_2\text{O}_9$ -25.9mJ/molK²), and manganites [67, 249]. The high value observed here signifies the excess entropy imparted by the frustration and disorder in this oxide owing to the mixed valence state and stress. Interestingly, on the application of a moderate magnetic field (0.5T), no change in the heat capacity was observed (not shown here), which suggests against the presence of paramagnetic impurity centers [250, 251].

6.4 Summary

In summary, we report on the structure-property relationship in the mixed valent geometrically frustrated triple perovskite iridate $\text{Ba}_3\text{NaIr}_2\text{O}_9$. In contrast to what is expected from purely structural considerations, this system stabilizes in a high symmetry hexagonal symmetry at room temperatures. On reducing the temperature, the lattice prefers to be strained rather than distort to a low symmetry phase, as is the norm in this family of materials. Though a low symmetry orthorhombic phase is finally nucleated below 50 K, this conversion is only partial and the high symmetry hexagonal structure remains the dominant one down to the lowest measured temperatures. Magnetic measurements indicate an extended co-operative paramagnetic regime, which finally freezes to a cluster glass-like phase at very low temperatures, as is also evidenced from magnetization decay and specific heat data. This makes an interesting addition to the family of triple perovskite iridates which exhibit material sensitive physical properties arising as a consequence of a number of competing energy scales.

Chapter 7

Appendix1: Potential Quantum Spin Liquid candidates

Sometimes a little frustration can make life interesting - Leon Balents [252].

7.1 Introduction

In the chapters discussed so far, we have presented a thorough investigation of the structure-property relationships in the geometrically frustrated triple perovskites of the form $\text{Ba}_3\text{M}\text{Ir}_2\text{O}_9$ ($\text{M} = \text{Co}, \text{Ni}, \text{Na}$). A wide range of ground states have resulted from the comparable energy scales of the spin orbit coupling (SOC), Hubbard interaction (U), hopping energy (t), Hund's coupling (J_H), which are tuned by the choice of M site ion. In addition, the physics of these iridates dramatically evolves into various forms depending on the configuration of the t_{2g} shell for Ir and M ion, the ionic radii and valence state of M site cation. We aimed at providing a broad spectra where various magnetic and non-magnetic elements were used to tune the ground state dynamics, exhibited by

Table 7.1: New Sr based triple perovskite iridates of the form $\text{Sr}_3\text{M}\text{Ir}_2\text{O}_9$

Compound name	Crystal symmetry	Space group	a	b	c	α	β	γ	Transition temperature
$\text{Sr}_3\text{CuSb}_2\text{O}_9$	Tetragonal	P4/mmm (123)	5.5313	5.5313	8.0832	90	90	90	Possible QSL
$\text{Sr}_3\text{ZnIr}_2\text{O}_9$	Hexagonal	P6 ₃ /mmc (194)	5.64	5.64	6.90	90	90	120	Possible QSL
$\text{Sr}_3\text{CuIr}_2\text{O}_9$	Orthorhombic	Pmmm (47)	19.401	8.0143	5.5855	90	90	90	Possible QSL
$\text{Sr}_3\text{CoIr}_2\text{O}_9$	Monoclinic	C ₁₂ /m1 (12)	5.5134	5.5302	7.8241	90	90.35	90	225K
$\text{Sr}_3\text{NiIr}_2\text{O}_9$	Monoclinic	P2/m (10)	4.8688	12.848	4.1474	90	90.15	90	265K

the diverse outcomes as discussed in the preceding chapters.

The motivation of the work reported in this chapter was led by the search to find a highly spin orbit entangled state where a complete suppression of magnetic moment at Ir site results in the $J_{eff}=0$ state, giving rise to the anticipated Quantum Spin Liquid state. This is one of the most sought-after phase where even though the spins are highly correlated, they lack long range order and strongly fluctuate down to the lowest temperatures as discussed in Chapter 1. So far, few close realizations have been reported, namely, $\text{Ba}_3\text{ZnIr}_2\text{O}_9$ [67], $\text{Ba}_3\text{CuSb}_2\text{O}_9$ [253] and a very recent addition, $\text{Sr}_3\text{CuSb}_2\text{O}_9$ [68]. Although, the ambiguity still remains and a complete vanishing moment is yet to be reported.

In this context, it is interesting to note that Ba has been the element of choice as far as the A site ion in these triple perovskites, $\text{A}_3\text{MM}'_2\text{O}_9$, are concerned. We have been recently investigating a number of Sr based triple perovskites, in an attempt to uncover their magnetic and electronic ground states as listed in Table. 7.1. Like the earlier known Barium based systems, we observe that different members of the Strontium based triple perovskite Iridates also exhibit a marked diversity - both in terms of their room temperature crystallographic structures as well as their magnetic properties. A wide range of systems ranging from magnetic (Co, Cu, Ni, Ir) and non-magnetic (Sb, Zn) M and M' site ion to spanning the entire crystal structure symmetry ranging from monoclinic

to orthorhombic to tetragonal to hexagonal are displayed. In addition to these, we also synthesized $\text{Sr}_3\text{BiIr}_2\text{O}_9$ and $\text{Sr}_3\text{NaIr}_2\text{O}_9$, but they were found to be extremely unstable at room temperature leading to degradation and non-reproducibility amongst different batches prepared.

We are currently in the process of investigating these family of compounds and a brief overview of the crystal and magnetic structure results are described ahead.

7.2 $\text{Sr}_3\text{CoIr}_2\text{O}_9$

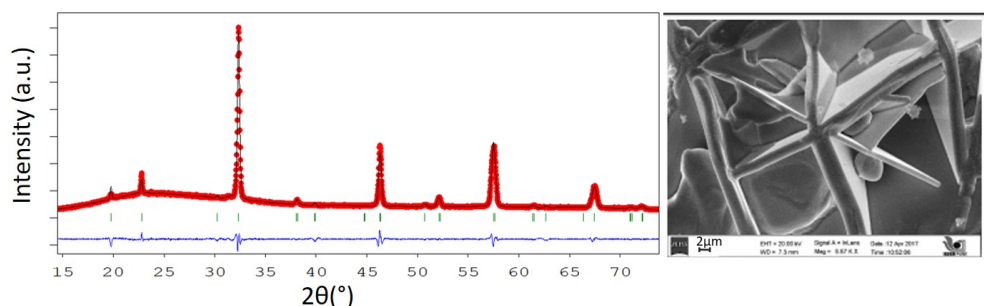


Figure 7.1: Left panel: Rietveld refinement of the powder diffraction pattern of $\text{Sr}_3\text{CoIr}_2\text{O}_9$ at 295 K. The compound crystallizes in a monoclinic perovskite with space group ($C2/m$). The calculated and observed diffraction profiles are shown as black and red markers respectively. The vertical green lines indicates the calculated Bragg positions. The blue line at the bottom is the difference between observed and calculated intensities. Right panel: The scanning electron images of the compound exhibiting sheet formation.

Replacing Ba with Sr in $\text{Ba}_3\text{CoIr}_2\text{O}_9$ leads to a drastic change in not only crystal structure but also in the magnetic ground state. This is the first study of this new compound, $\text{Sr}_3\text{CoIr}_2\text{O}_9$, which stabilizes in the monoclinically distorted ($C2/m$) in comparison to a hexagonal symmetry for the Ba analogue. The evolution of the peak profile from the synchrotron diffraction measurement reveals no sign of structural transformation as shown in Fig. 7.2, a stark contrast to the multiple phase transitions observed for

$\text{Ba}_3\text{CoIr}_2\text{O}_9$.

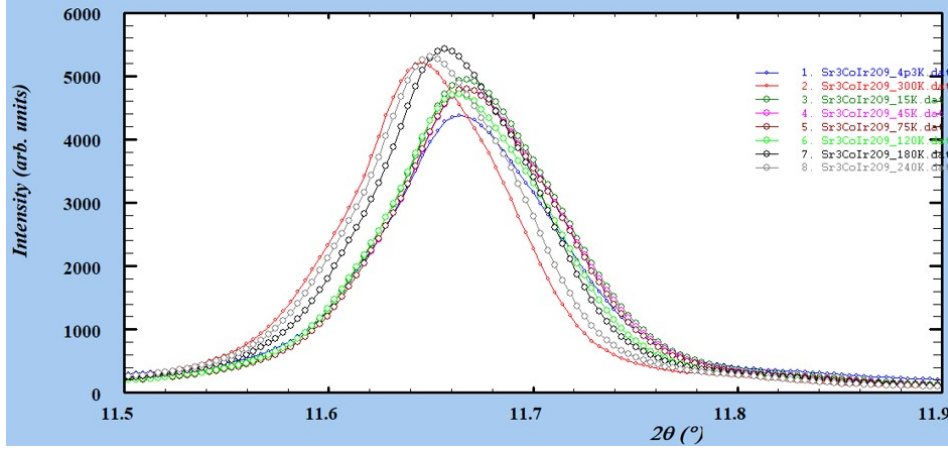


Figure 7.2: Temperature dependence of the peak profile obtained from the synchrotron diffraction for $\text{Sr}_3\text{CoIr}_2\text{O}_9$. Clearly, the compound seems to exhibit the room temperature symmetry down to the lowest measured temperature 4.2K with no indications of peak splitting.

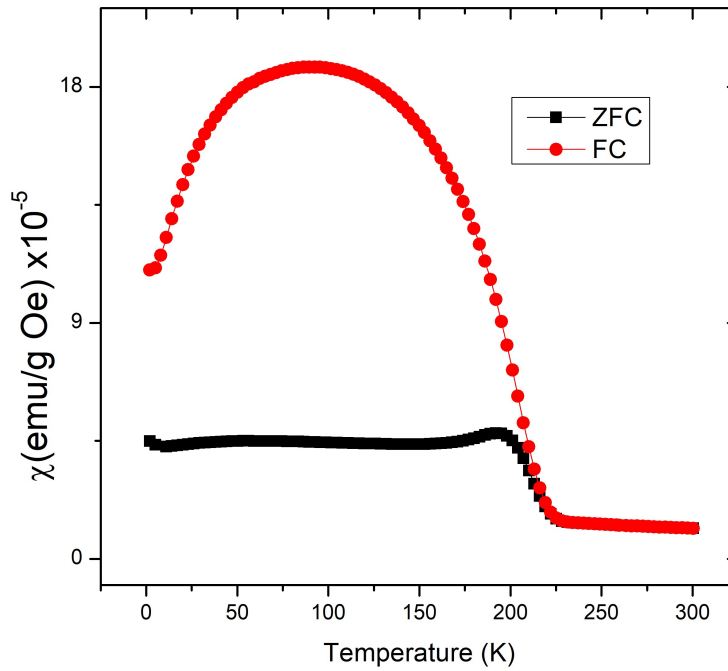


Figure 7.3: Temperature dependent magnetization of $\text{Sr}_3\text{CoIr}_2\text{O}_9$ as measured in the zero field cooled (ZFC) and field cooled (FC) protocols with an applied magnetic field of 20 Oe.

In addition, $\text{Sr}_3\text{CoIr}_2\text{O}_9$ pushes up the temperature of the magnetic transition to 200K which appears to be the largest amongst all the triple perovskite Iridates with the

obtained magnetic moment at Ir site equal to $1.058\mu_B/\text{f.u.}$, twice that of the Ba analogue.

7.3 $\text{Sr}_3\text{NiIr}_2\text{O}_9$

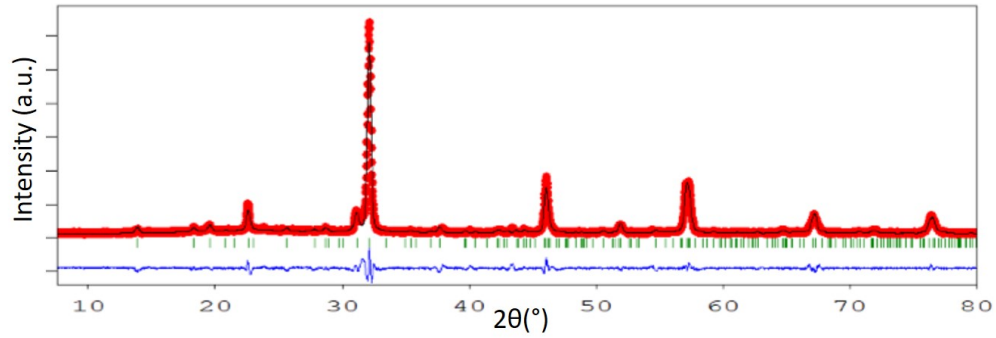


Figure 7.4: Rietveld refinement of the powder diffraction pattern of $\text{Sr}_3\text{NiIr}_2\text{O}_9$ at 295 K. The compound crystallizes in a monoclinic perovskite with space group (P2/m). The calculated and observed diffraction profiles are shown as black and red markers respectively. The vertical green lines indicates the calculated Bragg positions. The blue line at the bottom is the difference between observed and calculated intensities.

For the first time, we have succeeded in synthesising the closely related Sr analogue for Nickel, $\text{Sr}_3\text{NiIr}_2\text{O}_9$. We observe that this system crystallises in a monoclinic (P2/m) crystallographic symmetry, in contrast to the hexagonal symmetry observed for the Ba analogue $\text{Ba}_3\text{NiIr}_2\text{O}_9$. Interestingly, the magnetic behaviour of this system appears to be completely different, and we only see the hint of a magnetic transition in the form of a bifurcation between the ZFC and FC measurements at around 120K as shown in Fig. 7.5(a). There is no discernible transition in specific heat, clearly seen in Fig. 7.5(b). Although, the resistivity showed a prominent loop opening at $\sim 265\text{K}$ in the heating and cooling runs. As thermo-remnant measurements (TRM) are more effective in identifying the magnetic ordering temperatures, we performed a TRM at 1000Oe and three magnetic anomalies marked by pink dotted lines at 20K, 50K and $\sim 225\text{K}$ are clearly

visible as shown in Fig. 7.6.

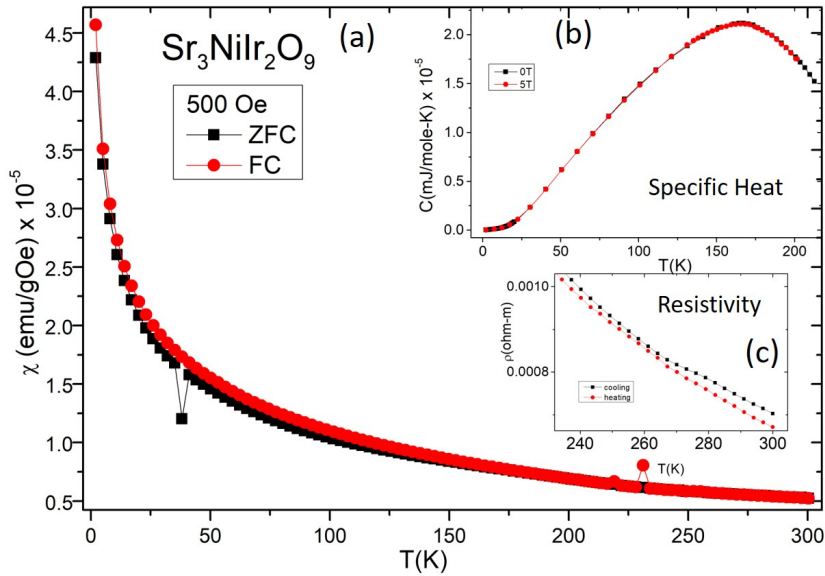


Figure 7.5: (a) Temperature dependent magnetization of $\text{Sr}_3\text{NiIr}_2\text{O}_9$ as measured in the zero field cooled (ZFC) and field cooled (FC) protocols with an applied magnetic field of 500 Oe. (b) The heat capacity measured as a function of temperature at zero (black) and 5 T (red) (c) Resistivity (ρ) plotted as a function of temperature where a loop opening at 265K in the heating and cooling run is discernible.

Moreover, the Curie Weiss fit indicates that Ir has an effectively same moment as that in its Ba analogue, $0.67\mu_B/\text{f.u.}$ The low temperature MH isotherms as shown in the inset of Fig. 7.6, also indicate the presence of a small ferromagnetic component as evidenced by a finite opening of the MH loop (of the order of 60 Oe), in addition to the robust antiferromagnetic character and signatures of meta stable states close to 75K. The weak ferromagnetic contribution could originate from the anti-symmetric Dzyaloshinskii-Moriya interaction, which is now known to be responsible for a host of interesting ground states in transition metal oxides with large spin orbit coupling. Needless to say, the change in A site ion leads to different structure property relationships in these Ni based triple perovskite systems.

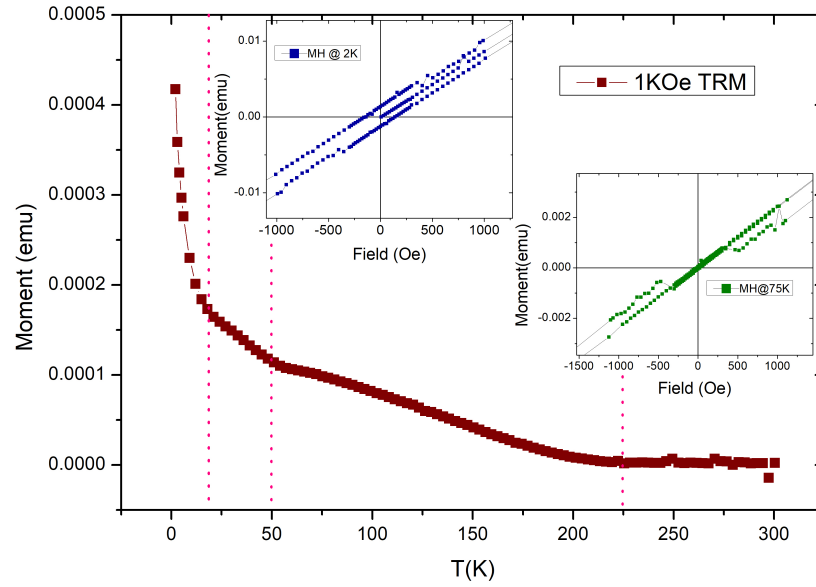


Figure 7.6: TRM at 1000Oe with two systematic jumps corresponding to two magnetic transitions. The insets shows magnetic isotherms measured at 2K and 75K.

7.4 $\text{Sr}_3\text{MM}'_2\text{O}_9$ (M=Cu,Zn; M'=Sb,Ir)

In all the above mentioned compounds, there is a hint of possible long range magnetic order. We went further and played with the M and M' site to tune the spin-lattice coupling in order to achieve a completely spin-entangled state with no freezing or ordering of spins. In this context, we synthesised the $\text{Sr}_3\text{CuSb}_2\text{O}_9$, hitherto unreported $\text{Sr}_3\text{CuIr}_2\text{O}_9$ and the $\text{Sr}_3\text{ZnIr}_2\text{O}_9$ systems, and observe that all of them do not exhibit any magnetic order down to the lowest measured temperatures. Moreover, the inverse of the magnetic susceptibility does not exhibit a linear high temperature paramagnetic regime -presumably due to persistence of short range magnetic correlations up to higher temperatures.

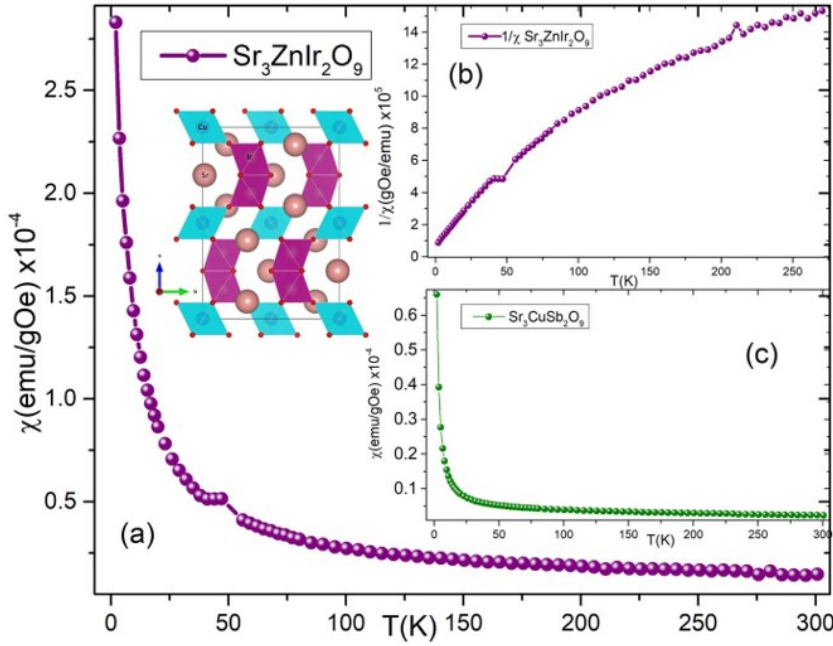


Figure 7.7: The inset depicts the structure of the triple perovskite Iridates $\text{Sr}_3\text{ZnIr}_2\text{O}_9$ (a) and (c) depicts the absence of a magnetic transition in $\text{Sr}_3\text{ZnIr}_2\text{O}_9$ and $\text{Sr}_3\text{CuSb}_2\text{O}_9$ respectively. (the feature near 50K in the former is due to an oxygen impurity in the magnetometer). (b) depicts the inverse of the magnetic susceptibility as measured in the $\text{Sr}_3\text{ZnIr}_2\text{O}_9$ system, indicating short range magnetic correlations until high temperatures.

Even more interesting is the case of the $\text{Sr}_3\text{CuIr}_2\text{O}_9$ system - where both Cu and Ir are magnetic (Cu^{2+} and Ir^{5+} as determined from XPS measurements). We note that when M site ion is magnetic (like Co, Ni, etc) and the Ir also hosts a magnetic moment, the enhanced connectivity offered by the magnetic MO_6 layer typically manifests itself in the form of pronounced magnetic (and structural) transitions. For instance, our investigations on the $\text{A}_3\text{M Ir}_2\text{O}_9$ systems with $\text{A} = \text{Ba}$ or Sr and $\text{M} = \text{Co}$ or Ni have revealed robust long range magnetic order in all of them.

On the other hand, the $\text{Sr}_3\text{CuIr}_2\text{O}_9$ system appears to be dramatically different. Stabilising in the orthorhombic (Pmmm) symmetry, we observe that the system fails to order magnetically down to 1.8 K. We have also performed low temperature heat capacity measurements down to 0.4K, which confirm the absence of long range order. A small bump is observed at very low temperatures, which could either signify the crossover to

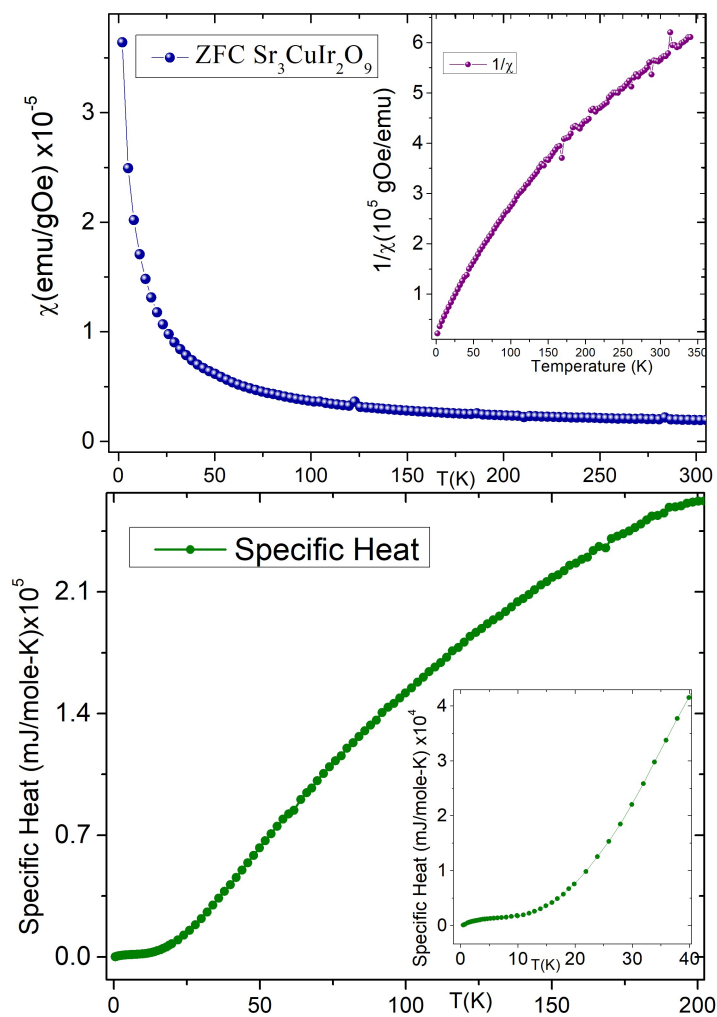


Figure 7.8: The absence of a magnetic transition in the $\text{Sr}_3\text{CuIr}_2\text{O}_9$ system, as inferred from magnetic susceptibility (top) and the presence of correlations can be seen right from the room temperature, evident by the non-linear $1/\chi$ variation with temperature. The heat capacity measurement (bottom) was performed down to 0.41K with no indications of magnetic ordering in the entire temperature range.

a quantum spin liquid state or a Schottky anomaly. In addition, our neutron diffraction data (performed at the DMC beamline of the Swiss Spallation Neutron Source) have ruled out a magnetic (or structural) transition down to 1.7K. Clearly, all these three systems could harbour potential spin liquid ground states. Moreover, the $\text{Sr}_3\text{CuIr}_2\text{O}_9$ system could also harbour a magnetic ground state where spontaneously generated local moments in Ir co-exist, and in all likelihood, strongly interact with the (spin $\frac{1}{2}$) Cu^{2+} spins, giving rise to a quantum spin liquid with a flavour different from that reported earlier in the $\text{Ba}_3\text{ZnIr}_2\text{O}_9$.

7.5 Conclusion

In summary, we have synthesized a number of new Sr based triple perovskites. We are in the process of performing a detailed analysis of the current system to help understand the nature of the interaction between the moments on the Ir and M sites. We reiterate that all these systems remains to be investigated till date and these compounds would make an important addition to the rather small number of experimental realisations of quantum spin liquids.

Chapter 8

Appendix2: Absence of a multiglass state in doped quantum paraelectrics

The contents of this chapter has been published as

"Absence of a multiglass state in some transition metal doped quantum paraelectrics".

Phys. Rev. Materials 2, 094409 (2018) [254].

8.1 Introduction

8.1.1 Multiglass

Multiferroics - materials with co-existing magnetic and polar orders - have been at the focus of extensive theoretical and experimental investigations. Initially thought to be phenomena which are inimical to each other, a variety of avenues are now known, by which a system can be tailored to exhibit both these orders [255]. Not surprisingly, advances in this area of research have been fuelled by the continuous availability of new materials, which exhibit coupling between electric and magnetic order parameters [256, 257]. Multiferroics can be broadly divided in two different classes: Type

-I multiferroics, where magnetic and polar orders arise from independent microscopic origins, and Type-II multiferroics, where a non-trivial magnetic order facilitates ferroelectricity [258,259]. An additional variant has also been reported - that in which both the magnetic and polar orders are frozen and these *multiglasses* are purported to be characterized by the co-existence of a magnetic spin/cluster glass with a polar cluster glass phase [260,261]. The cooperative random freezing of dipolar and magnetic spin

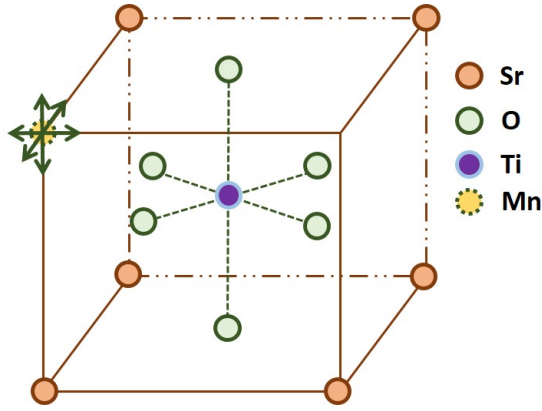


Figure 8.1: A schematic of the crystal structure of the Mn doped SrTiO_3 perovskite. Here orange, green and purple elements represents Strontium, oxygen and Titanium respectively. The green arrows represents the displacement vectors of an off-center Mn^{2+} ion doped at Sr-site.

degrees of freedom at low temperature leads to ferroelectric relaxor [262] and spin glass states [263]. The genesis of the area of multiglasses can be traced to the report of the simultaneous occurrence of a non-ergodic polar and magnetic glass state in the doped quantum paraelectric $\text{Sr}_{0.98}\text{Mn}_{0.02}\text{TiO}_3$ [264,265]. SrTiO_3 stabilizes in a cubic symmetry ($S.G=Pm-3m$) where Sr sits at the corners of the cube and Ti is placed at the centre surrounded 6 oxygen atoms forming an octahedra as shown in Fig8.1. It was suggested that the Mn^{2+} ions which replace the Sr^{2+} species in SrTiO_3 undergo off-centre displacements from their mean positions, creating a net electric dipole. Such polar clusters then undergo a low temperature transition to a frozen relaxor-like state at $T_G = 38\text{K}$ as was evidenced by a power law dependence of the frequency dependent dielectric susceptibility [264]. Since Mn^{2+} is also magnetic ($S = 5/2$), the generated electric dipoles couple

to each other via frustrated antiferromagnetic superexchange interactions, and below T_G the freezing of polar clusters also triggers the freezing of spin degrees of freedom. This effect is also augmented by the presence of a finite Magneto-electric coupling, which couples the polar and spin degrees of freedom, resulting in a *magnetoelectric multiglass* state in $\text{Sr}_{0.98}\text{Mn}_{0.02}\text{TiO}_3$. Though the closely related $\text{K}_{0.97}\text{Mn}_{0.03}\text{TaO}_3$ system was also reported to harbor such a state [266], it was later described as a spin cluster glass where the interacting polar clusters fail to condense into a glassy state [267]. The coexistence of a magnetic and polar glass like states was also reported in other family of compounds like the double perovskite $\text{La}_2\text{NiMnO}_6$ [268] and the delafossite $\text{CuCr}_{0.5}\text{V}_{0.5}\text{O}_2$ [269] systems, with the anti-site disorder (between the Ni-Mn and Cr-V species respectively) being responsible for the observed multiglass state.

8.1.2 Progress and challenges

There has been many reports where experimental signatures from magnetization, ac susceptibility and dielectric studies were used to characterize multiglass state in the celebrated Mn doped SrTiO_3 compound, $\text{Sr}_{0.98}\text{Mn}_{0.02}\text{TiO}_3$ [260, 261]. These included [264–266]

- (i) magnetic irreversibility in the zero field cooled and field cooled measuring protocols,
- (ii) the observation of a frequency dependent ac susceptibility which appears to coincide with the polar freezing temperature,
- (iii) a power law fit to the peak temperature of the real part of the dielectric permittivity $\epsilon'(T)$,
- (iv) memory effects in both the polar and magnetic sectors and
- (v) a peak in the non-linear dielectric susceptibility.

However, there have been a number of subsequent reports which have raised doubts about the validity of the multiglass scenario in this system [270], and in the transition

metal doped quantum paraelectrics in general. The significant observations which are not commensurate with the existence of a multiglass state included

- (i) The absence of magnetic freezing in specimens synthesized using different synthesis procedures like high energy ball milling [271], and the oxalate precipitate method [272]. This indicates the crucial role synthesis play in the observed ground state for such systems.
- (ii) Transmission Electron Micrographs indicating that the magnetic anomaly was only observed in those specimens where a network of structural defects were present [271]. Since the doping percentages are small, it is indeed necessary to make sure the dopants reach the specific site,
- (iii) Investigations with careful site specific Mn substitutions indicating that $\text{Sr}_{0.98}\text{Mn}_{0.02}\text{TiO}_3$ does not exhibit any magnetic ordering/anomalies, where as Mn co-doped in both the Sr and Ti sites exhibit glassy magnetic properties of extrinsic origin [270] , and
- (iv) the absence of a frequency dependence in the measured non linear dielectric susceptibility [266].

The main point of contention pertained to freezing in the magnetic sector, and the possibility that the observed glassy magnetic signatures arises from a small amount of the spinel Mn_3O_4 , which is reported to exhibit a ferrimagnetic transition at $\approx 43\text{K}$ [268, 271]. At the small doping percentages under consideration here, these trace impurities are not easily discernible from routine x-ray diffraction measurements. This problem is accentuated by the fact that Mn_3O_4 can dissolve small amounts of TiO_2 (which is typically used as a raw material in the synthesis of $\text{Sr}_{0.98}\text{Mn}_{0.02}\text{TiO}_3$) [271], and could also exhibit finite size effects when it exists in the form of small impurity clusters within the perovskite matrix, thus exhibiting a sample dependent variation of the observed (glass-like) magnetic transition temperature. In addition to this, the pristine Mn_3O_4 phase exhibits a phase transition in close vicinity to the energy scale of the

relaxor state and is also reported to be a magnetodielectric, which exhibits a number of closely spaced spin re-orientation transitions with clear dielectric anomalies corresponding to these different transitions [273, 274].

8.1.3 Possible solution and motivation for this work

All the above mentioned ambiguities should be unique to Mn and therefore other magnetic transition metal dopants (Co, Fe or Ni) could offer a means of evaluating the existence of a multiglass state in the doped quantum paraelectrics, with the apriori advantage that the transition temperatures associated with the possible trace impurities (CoO, Co₃O₄, Fe₂O₃, Fe₃O₄, NiO, or Ni₂O₃) are very different from the temperature range of interest here. This was the motivation for the current study, to do a thorough investigation of the role of doped transition metal oxides in quantum paraelectrics and shed some light on the possible existence of multiglass state in them. In the present study, we doped various transition metal oxides (M= Co, Fe, Mn, and Ni) in two quantum paraelectric lattices SrTiO₃ (SMT) and KTaO₃(KMT) by 2% and 3% respectively, using the solid state ceramic route. To the best of our knowledge there has been no attempt to evaluate the feasibility of a magnetically frozen state in quantum paraelectrics doped with different magnetic transition metal dopants. These samples are characterized using x-ray diffraction, energy dispersive x-ray analysis, and temperature dependent dielectric and magnetization measurements. Though, all the doped specimens exhibit frequency dependent features in the dielectric loss, our data does not indicate the presence of a frozen polar state in any of these systems. Moreover, all the observed magnetic signatures can be clearly attributed to arise from the presence of oxides of the magnetic dopants used. Thus, contrary to previous reports [266, 267], our observations suggests that transition metal doped quantum paraelectrics clearly do not harbor an intrinsic glassy state in either the polar or the magnetic sectors.

8.2 Experimental Details

Polycrystalline specimens of the $\text{Sr}_{0.98}\text{M}_{0.02}\text{TiO}_3$ and $\text{K}_{0.97}\text{M}_{0.03}\text{TaO}_3$ series were synthesized by the standard solid state reaction technique. For the SMT series, stoichiometric amounts of the preheated reagents were treated twice at 1150°C followed by pelletizing and a final treatment at 1500°C for 24 hours. For the KMT series, the protocol was slightly different, and stoichiometric amounts of the preheated reagents were mixed and ground thoroughly in a glove box for 3 hours, followed by a heat treatment at 1000°C . This mixture was then reground and pelletized before being subjected to a final heat treatment at 1000°C for 24 hours. All the pellets were made using PVA (polyvinyl alcohol) or binder to ensure that the pellets were highly dense. Multiple batches of samples were synthesized, and only the best ones were used for further investigations.

8.3 Results and Discussion

8.3.1 XRD Analysis

The SrTiO_3 and KTaO_3 specimens stabilize in the space group $Pm-3m$ with cubic symmetry, and doping them by these small percentages (2% and 3% in the SMT and KMT series respectively) only results in very small changes in the lattice parameters, with no discernible change in their crystallographic symmetry. All these doped transition metals, if left unreacted, can stabilize in various oxide forms (for example, Co_2O_3 , CoO , Co_3O_4 etc.) and with such low level of doping, their intensity (phase percentage) in XRD diffraction would be too low. Therefore, a critical evaluation of the XRD patterns is required to see if they can reveal the precipitation of any of the doped transition metal oxides in the form of impurity phases. Fig8.2 shows the normalized XRD patterns for all the doped SMT and KMT compounds. The 2θ range depicted here encompasses the

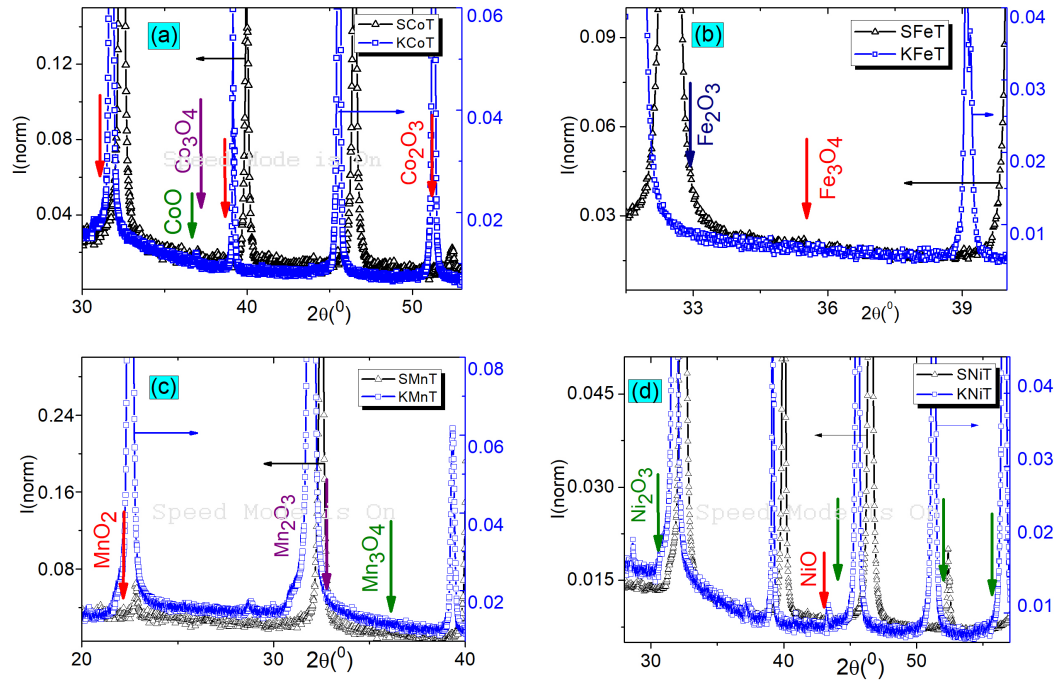


Figure 8.2: Room temperature x-ray diffraction data of the KTaO_3 and SrTiO_3 specimens doped with (a) Co, (b) Fe, (c) Mn and (d) Ni. The 2θ ranges have been selected such that it encompasses the region where the most intense peak of the possible magnetic impurities (if any) can be clearly seen.

values corresponding to the highest intensity peaks of all different stable forms of the transition metal oxides (Co_2O_3 , CoO , Co_3O_4 , Fe_2O_3 , Fe_3O_4 , MnO_2 , Mn_2O_3 , Mn_3O_4 , NiO or Ni_2O_3) possible as a result of Co, Fe, Mn or Ni doping. Though impurity phase detection with such small amounts of doping is typically difficult with the routine XRD measurements, we have tried to glean as much information as possible by using long counting times (of the order of 6-8 hours) in these selected 2θ ranges. In the case of the SMT series, all the doped specimens were seen to be phase pure, and no traces of any impurity oxides could be inferred from the same XRD measurement protocol. However, in the KMT series, the Co and the Ni doped specimens appear to show faint traces corresponding to the Co_3O_4 and NiO phases as shown in Fig8.2(a) and (d), with the Mn and Fe doped specimens being completely free from any spurious phases.

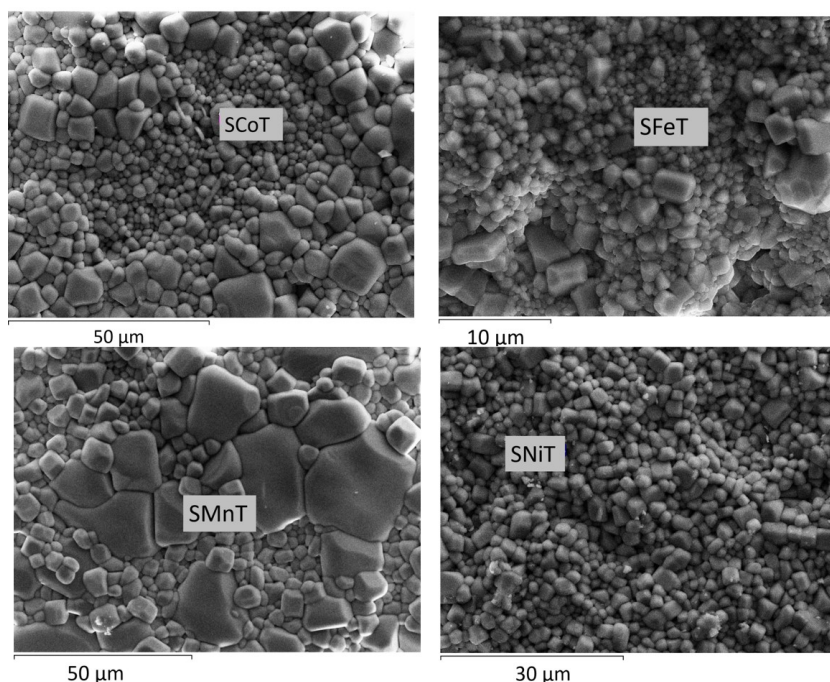


Figure 8.3: Scanning electron micrographs of the doped members of the SrTiO_3 series. Note that all the scans were performed on the piece of a pellet which gets manifested in the form of high density and homogeneity of grains. Scans were performed on various regions of the pellet and the obtained elemental contribution was consistent with the expected ratio.

8.3.2 Energy Dispersive X-ray Analysis

Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray Spectroscopy (EDS/EDAX) measurements were done on pellets of all the specimens of the SMT and KMT series (20KV) for micro structural analysis. EDAX not only helps in studying the sample topography but also can be used to probe region specific elemental composition. This helps in studying the morphology of the specimen, specially in cases where doping is involved. Fig8.3 depicts the micrographs for the SMT specimens, all of which show arbitrarily shaped grains with reasonably large size distribution. Since the dopant percentage was very low, EDS was performed at more than two dozen areas on the pellet of all the specimens. Though, the percentage of dopants deduced from the EDS measurements was consistent with the doping values, interestingly, we observed a lower

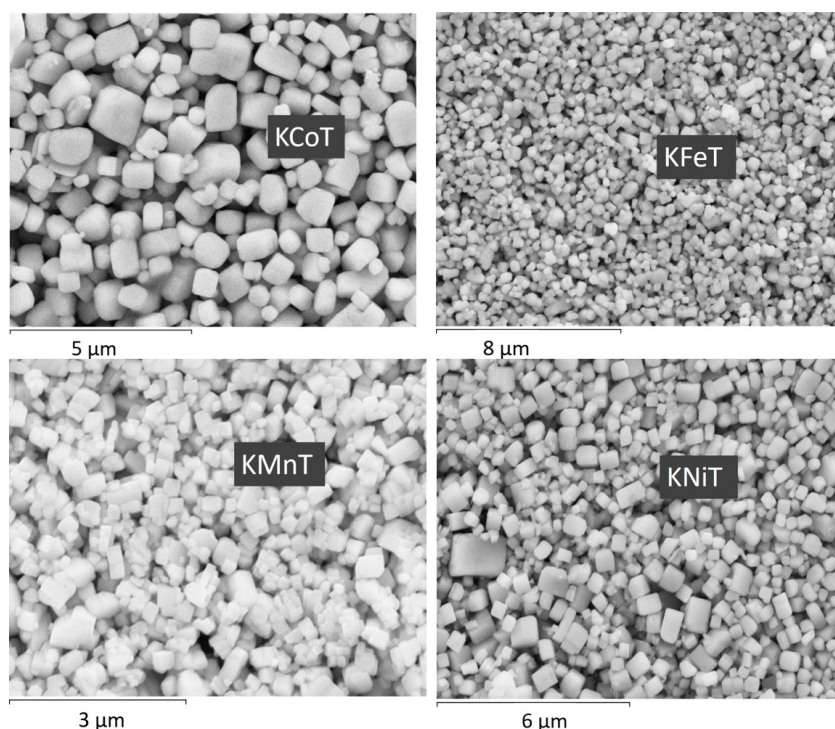


Figure 8.4: Scanning Electron Micrographs of the doped members of the KTaO_3 series. The sample is highly homogeneous and shows distinctly ordered cubic structure down to few μm . All the scans were performed on the pellet and showed great match with the expected stoichiometry of the elements.

percentage of Ti in some cases. This was observed specifically for the SMT series, possibly because A site substitution in SrTiO_3 is not completely site selective. It has been previously reported, at-least for the case of Mn substitution, that it continues to partially occupy the Ti site irrespective of the synthesis protocol used [275]. For this reason, the solid solubility limit of Mn in the Sr site of SrTiO_3 site could not be properly determined. Though conclusive similar studies are lacking for the other transition metals used in this study, our EDS investigations indicate that this problem appears to be generic to all the transition metals used in this investigation. In the case of the KMT series, Fig8.4, we observe uniform cube like microstructure, and the grains appear to have a much narrower size distribution densely packed together, with clean rectangular facets and no evidence of any kind of phase clustering. The results of EDS measurements in-

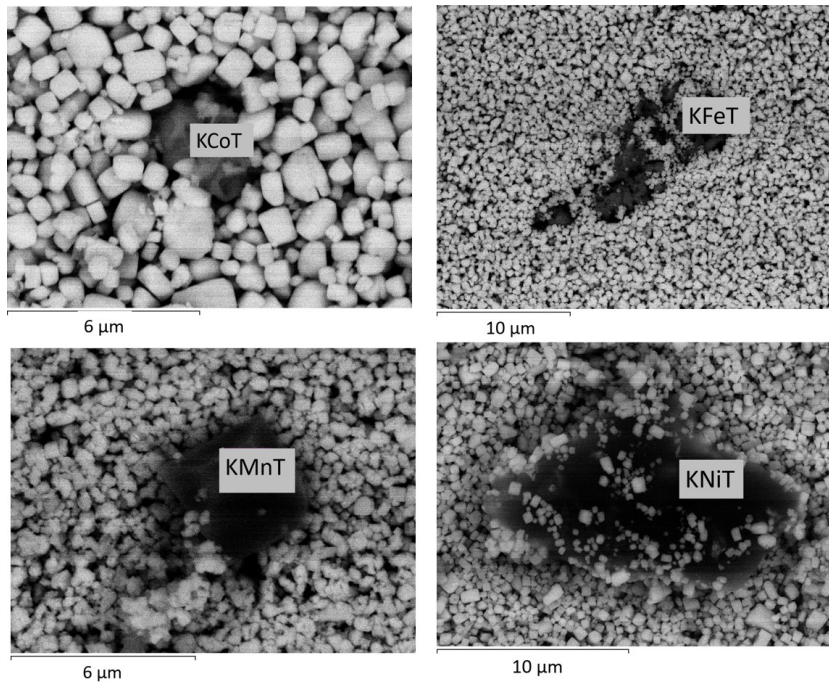


Figure 8.5: Backscattered images of the doped members of the KTaO_3 series. Selected regions (in the center) which exhibited an intensity contrast corresponding to possible chemical inhomogeneities are depicted. These dark regions depicts the segregation of the transition metal oxide by exhibiting high concentration values of the respective transition metal oxide when scanned within this region, implying segregation of dopant oxides.

dicating no observable deviation from the actual doping percentages, suggesting that the doped transition metals appear to be fully incorporated in the host lattice. However, considering the fact that long XRD scans suggested the possibility of spurious Co_3O_4 and NiO phases, and that the solubility limit of these dopants in the KTaO_3 lattice is questionable, we performed additional backscattered scans on all these specimens. The backscattered scans offer a contrast imaging tool, and since the backscattering coefficient is a function of the atomic number, it offers a means of identifying regions of compositional inhomogeneities more precisely [4]. After carefully sampling close to two dozen locations in the backscattering mode, we observed regions with varied grey scale where traces of the dopant oxides Mn_3O_4 , Co_3O_4 , Fe_2O_3 were found. Identifying traces of NiO was even more difficult, and such regions could only be identified after

extensive scanning. All the KMT images, where the trace impurities are evident in the form of an image contrast is depicted in Fig8.5.

In conclusion, our exhaustive EDS measurements indicates that the solubility limit of the transition metal dopants depends not only on the host lattice but also on the transition metal used. Considering the problem one is trying to address, a thorough structural study for these doped systems is crucial and our observations indicate that a combination of XRD, and normal and backscattering EDS measurements are imperative in evaluating the phase purity of these systems. Our observations also indicate that all these magnetic transition metal elements have limited solubility in the SrTiO_3 and KTaO_3 lattices, and use of x-ray diffraction alone is not adequate to comment the phase purity of such systems. In addition, high resolution synchrotron measurements could be more effective in identifying the presence of impurity phases as compared to long waiting times in lab based source. Also, additional information could also be obtained from RIXS (Resonant Inelastic X-ray Scattering) and synchrotron XPS.

8.3.3 Dielectric Spectroscopy

SrTiO_3 and KTaO_3 are both known to be polarizable soft ferroelectric hosts, and the off-centered shifts of the M^{2+} ions when doped at the 12-fold co-ordinated Sr or K sites is thought to induce electrical dipoles as discussed previously. These dipoles, then condense in the form of polar nano-clusters, the dynamics of which can be discerned using dielectric spectroscopy measurements. Fig8.6 summarizes the real part of the frequency dependent dielectric susceptibility ($\epsilon'(T)$) over a broad temperature range for both the SMT and KMT series. As is the norm for quantum paraelectrics, all the specimens exhibit a pronounced increase in $\epsilon'(T)$ as a function of decreasing temperature. A peak in the loss tangent and an anomaly in the real part of the permittivity has been previously reported for the pristine KTaO_3 [276, 277], possibly arising as a consequence of

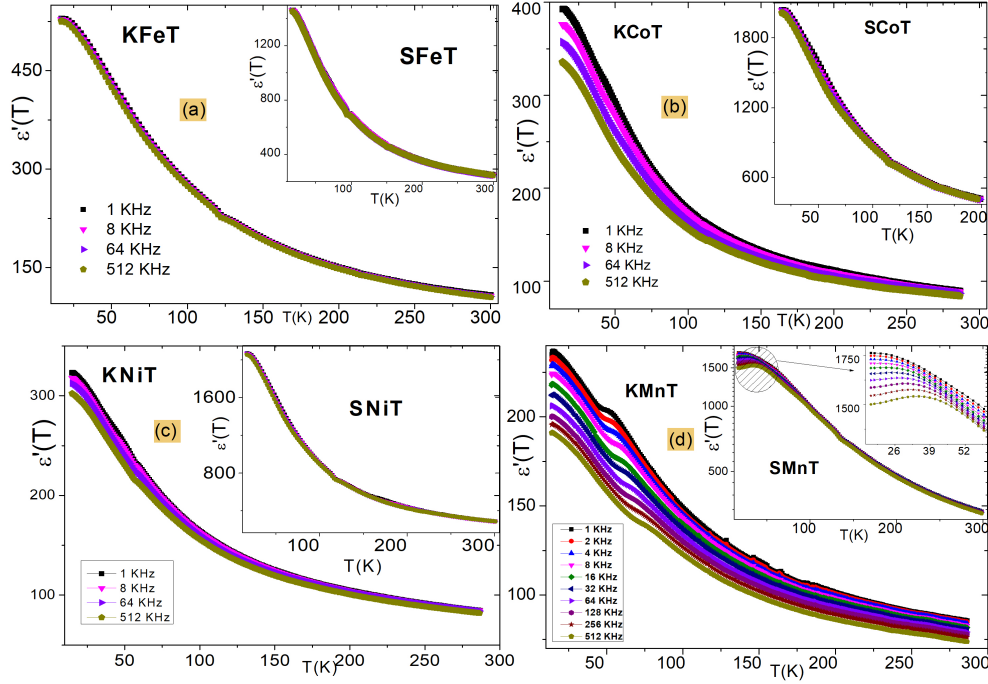


Figure 8.6: Temperature dependence of the real part of the dielectric susceptibility as measured at different probing frequencies for the doped SrTiO₃ (insets) and doped KTaO₃ (main panels) specimens. Only the Mn doped specimens appear to exhibit an appreciable frequency dependence.

defect dipoles. The influence of the polar regions formed as a consequence of transition metal doping was more clearly evident in the temperature dependent scans of the imaginary component of the dielectric susceptibility ($\epsilon''(T)$). The paraelectric lattices doped with (a) Co, (b) Fe, (c) Mn and (d) Ni is depicted in Fig8.7 for KTaO₃ and Fig8.8 for SrTiO₃. Here, a broad frequency dependent peak in $\epsilon''(T)$ was observed for all the specimens and the peak shifted to higher temperatures with increasing frequency. This is a signature of soft ferroelectric hosts, and reflects the dynamics of polar domains which form as a consequence of transition metal doping. The size/volume distribution of these domains is typically dependent on both the synthesis conditions as well as the nature of the dopant, as is reflected in subtle differences in both the peak position as well as its frequency dependence between the different specimens. The possible reason

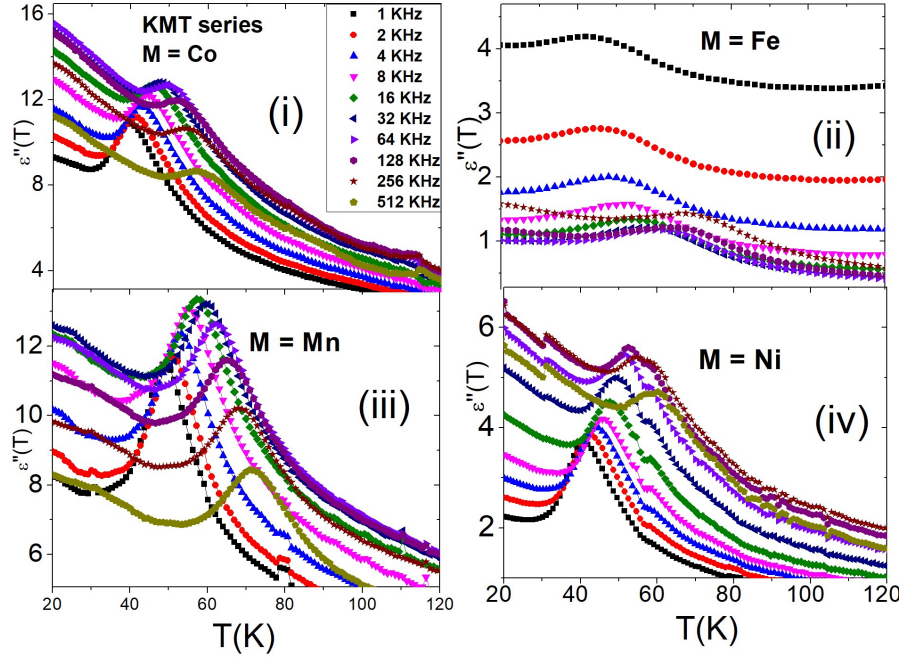


Figure 8.7: Temperature dependence of the imaginary part of the dielectric susceptibility as measured at different probing frequencies (1KHz to 0.5MHz) for the doped KTaO_3 specimens.

for not observing the dynamics associated with these polar regions in the real part of the dielectric susceptibility $\epsilon'(T)$ could be due to the dramatic increase of $\epsilon'(T)$ at low temperatures. This increase is 3 orders of magnitude larger than that observed for $\epsilon''(T)$ and is associated with the renormalization of the soft mode frequency. The thermodynamic fluctuations associated with the different dopants results in an effective softening (or hardening) of this mode and dictate the effective values of $\epsilon(T)$ attained at low temperatures. The frequency dependence of the relaxation process in the imaginary permittivity was studied to understand and evaluate the possible mechanism for the observed relaxation. The symmetry of the perovskite lattices, in our case SMT and KMT, allows it to hold several equivalent orientations for the dipoles formed due to disorder induced via doping. If these dipoles interact strongly and freezes into a glass-like state on lowering the temperature, one would expect to see signatures of a dynamical slowing down, which is described by a VFT formalism given as $f = f_0 \exp \frac{-E}{k_b [T - T_G]}$, where f_0 ,

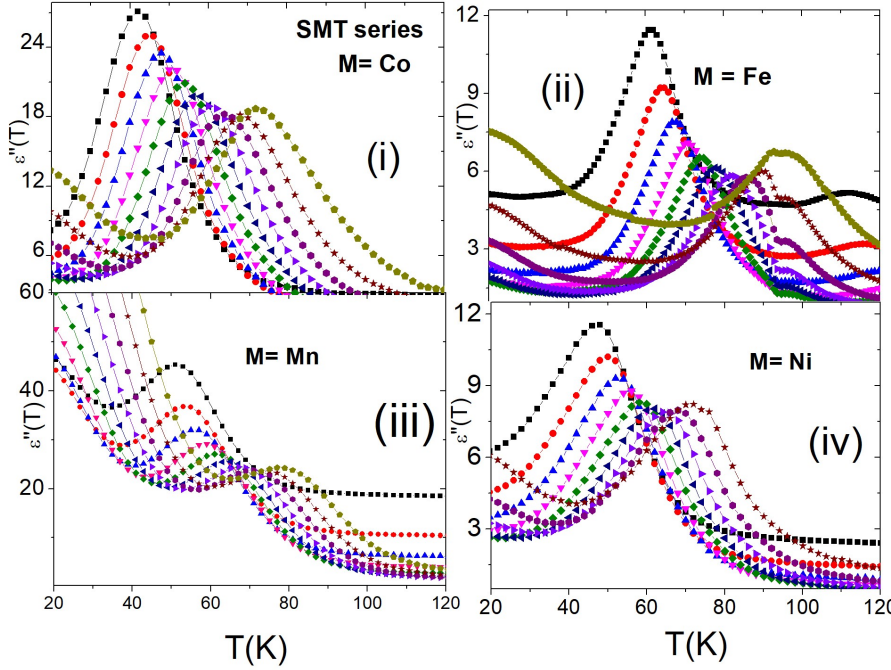


Figure 8.8: Temperature dependence of the imaginary part of the dielectric susceptibility as measured at different probing frequencies (1KHz to 0.5MHz) for the doped SrTiO₃ specimens.

E , and T_G correspond to the jump attempt frequency, the energy barrier associated with this process, and the temperature of the glass transition below which the dynamics are frozen in perspective with our measurement time scales. In contrast, if the dipoles lack co-operativity, the dipoles can hop amongst these equivalent orientations as a consequence of thermal activation. In this case, $T_G \rightarrow 0K$, and the VFT equation is modified to a thermally activated Arrhenius form given by $f = f_0 \exp \frac{-E}{k_b T}$. We attempted to fit the observed relaxation process to the VFT, power law, and Arrhenius forms, and observed that best fits in all cases are given by the Arrhenius equation. This is shown in Fig8.9, for all the members of the SMT and KMT series. This indicates that the density of dipoles formed by the doping of transition metal ions in the STO and KTO hosts are quite small for the doping percentages used in our investigations, and that the interaction between these dipoles are not strong enough to achieve collective freezing. There appears to be a trend in the deduced activation energies (Table I), as we see that $E_{Co} < E_{Ni} < E_{Mn}$

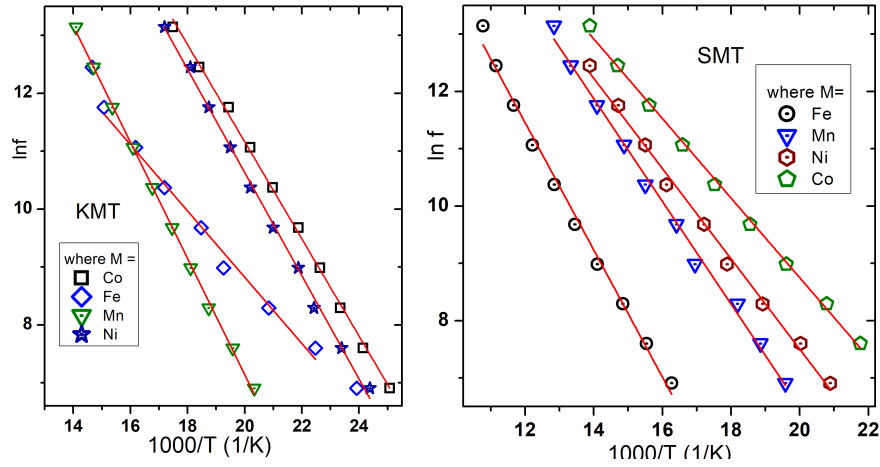


Figure 8.9: Arrhenius fits (solid lines) to the relaxation peak observed in the doped members of the KTaO_3 and SrTiO_3 series.

Dopant	SMT (meV)	KMT (meV)
Co	59.8 ± 1.0	72.2 ± 0.9
Ni	67.9 ± 1.6	76.8 ± 1.2
Mn	77.2 ± 1.8	86.4 ± 0.9
Fe	95.4 ± 2.6	49.3 ± 2.1

Table 8.1: The values of the activation energies deduced from the Arrhenius fit to the $\epsilon''(T)$ data

for both the families. Interestingly, Fe doping exhibits very different values for both the series, as the value of E_{Fe} is maximum in the SMT specimens and the lowest in the KMT ones. This could presumably arise due to a substantial difference in solubility limit of Fe in both the systems.

In doped quantum paraelectrics, the deviations from Curie-Weiss behavior is seen at low temperatures is typically ascribed to the influence of quantum fluctuations. The observed functional form has been described by the Barrett's equation

$$\epsilon'(T) = A + C / [(T_1/2) \text{Coth}(T_1/2T) - T_0], \quad (8.1)$$

where A is a fitting constant, C is the Curie constant, T_0 is equivalent to the classical Curie temperature, and T_1 represents the temperature below which quantum fluc-

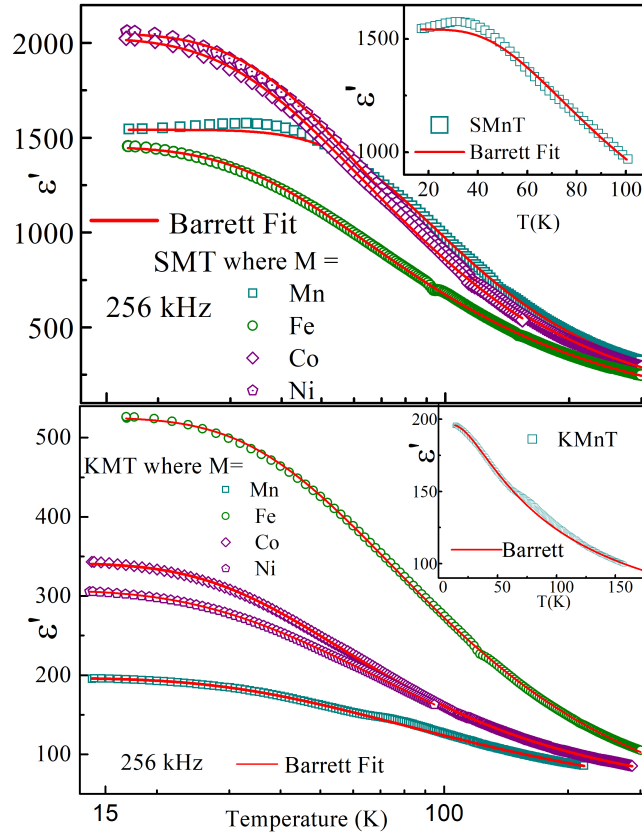


Figure 8.10: The measured $\epsilon''(T)$ for the doped SrTiO₃ and KTAO₃ specimens. The solid line corresponds to a fit using the Barrett's formalism. The insets depict deviations from the fit for the Mn doped specimens of both the series.

tuations overwhelm the thermal ones [278]. As is shown in Fig8.10, good fits to the Barret's equation were obtained for the $\epsilon''(T)$ data for the Ni, Co and Fe specimens of both the SMT and KMT series, reinforcing our observation regarding the absence of a relaxor state. The fits to the dielectric susceptibility data of the Mn doped specimens of both the series as is depicted in the insets of Fig8.10. This indicates that the dielectric behavior of the Mn doped specimens are distinct from those of the other transition metal doped members. This is also in broad agreement with an earlier report, where the dielectric properties of the Mn doped KTAO₃ was suggested to be different from its Fe doped analogue [279]. There, it was reported that whereas the Mn doped specimen depicted a peak like anomaly in $\epsilon''(T)$, the Fe doped analogue did not exhibit this feature

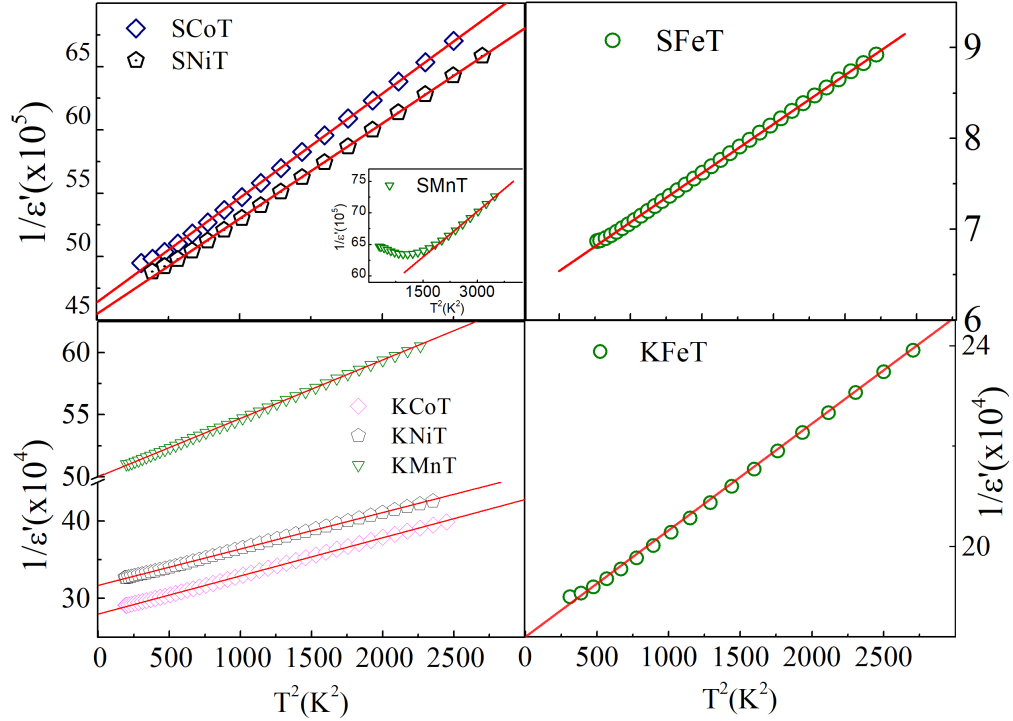


Figure 8.11: Inverse permittivity as the function of the square of the temperature of doped systems. The solid straight line fitting represents the quantum critical behavior.

and retained a quantum paraelectric like behavior down to the lowest measured temperatures. Pressure and temperature dependent dielectric measurements were also used to suggest that the Mn doping induced dipolar entities appear to couple more strongly to the soft mode of the host quantum paraelectric lattice.

The value of $(T_1 - 2T_0)$ deduced from our fitting is positive for all the doped specimens, implying the presence of a instability of the ferroelectric mode driven by quantum fluctuations, and conclusively rules out any possibility of ferroelectricity in these doped systems and further confirms that these doped systems retain their quantum paraelectric behavior down to the lowest measured temperatures. In the high temperature classical regime, the inverse of the dielectric susceptibility would exhibit a Curie Weiss (T^{-1}) dependence, and a defining feature of the quantum paraelectrics is the crossover to a low

Element	Possible Oxides	Magnetic Transition Temperature	Nature of Transition
Mn	MnO ₂	92K	AF
	Mn ₃ O ₄	41K-43K	Ferri
Ni	NiO	523K	AF
	Ni ₂ O ₃ .H ₂ O	525K	–
Fe	Fe ₃ O ₄	858K	Ferri
		120K	Verwey
	α Fe ₂ O ₃	260K	Morin
		950K	AF
Co	Co ₃ O ₄	40K	AF

Table 8.2: Magnetic transition temperatures corresponding to the different transition metal oxides which are likely to exist as possible impurities.

temperature regime where quantum fluctuations dominate. In this regime, the dielectric susceptibility is expected to vary as $1/\epsilon' \propto T^d + z - 2/2$, where d and z refer to the spatial and temporal dimensions respectively [280]. In the materials under consideration here, $d = 3$, and $z = 1$, resulting in the dielectric susceptibility varying as T^{-2} , as has been observed for both KTaO₃ and SrTiO₃ below $T \approx 50\text{K}$ [280]. Fig8.11 depicts the T^2 fit of $1/\epsilon$ for all our doped specimens below 50K, clearly indicating that doping of transition metal ions does not cause a significant change in the quantum paraelectric behavior of the host lattices [281], and further rules out the presence of any kind of polar order in these doped materials. The fact that Mn appears to behave little differently - at least as far as its dielectric properties are concerned - could possibly be due to the fact that Mn²⁺ has the largest number of unpaired electrons amongst all the doped magnetic transition metal ion configurations used in this investigation.

8.3.4 Magnetization

As discussed earlier, the presence (or the lack thereof) of a multiglass state in the doped quantum paraelectrics has been contentious due to the possibility that the magnetic spin glass like state observed in the Mn doped SrTiO_3 and KTaO_3 systems is extrinsic in origin. The lack of any conclusive understanding comes from the many ambivalent reports, thus, keeping the mystery on the presence of multiglass state in these systems still unresolved. A major contribution to this ambiguity comes from the fact that a possible impurity oxide (Mn_3O_4) has a magnetic transition in the temperature range of the potential multiglass temperature. Moreover, it was also reported that there is no observable scaling between the onset of the magnetic anomaly and the Mn doping level [282, 283]. Backed up from our observations in the structural characterization of our specimens, the solubility of magnetic ions in both SrTiO_3 and KTaO_3 hosts appears to be limited and kinetically hindered, making it imperative that the possibility of a magnetically frozen state is evaluated in these lattices doped with other magnetic transition metal ions. All these transition metal ions have many possible stable oxide forms with transition temperatures ranging from 40-860K. As a reference, Table 8.2 lists out the magnetic transition temperatures of these possible impurity oxides associated with the dopants being used in this study.

Fig 8.12 depicts the magnetic measurements performed on the SMT series in the zero field cooling mode. All the specimens (including the Mn doped one) are observed to be paramagnetic like, with no trace of any magnetic anomaly associated with long or short range magnetic order. Interestingly, this is in clear contradiction to the initial report in which Mn doped SrTiO_3 was suggested to be a magneto-electric multiglass. Our structural study suggests that most of the Mn have been successfully incorporated into the SrTiO_3 lattice and, as a result, the paramagnetic contribution effectively overwhelms

the magnetic contribution of the parasitic Mn_3O_4 phase. This scenario appears to be valid for all the doped members this series, as is evident from the fact that none of them exhibit magnetic anomalies in the temperature range of our measurements.

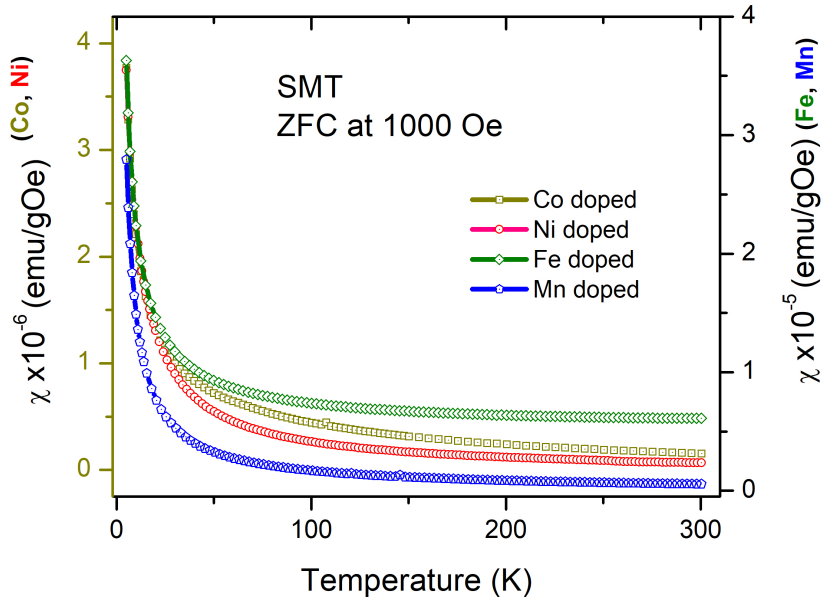


Figure 8.12: Temperature dependence of the dc magnetic susceptibility as measured in the doped SrTiO_3 systems using the zero field cooled protocol. All the specimens appear to be paramagnetic down to the lowest measured temperatures.

The magnetic measurements of the members of the KMT series as performed in the zero field cooled and field cooled protocols are shown in Fig8.13, and interestingly, all the members of this series exhibit features in the magnetization. Referring to Table 8.2, all the observed features could be ascribed to the corresponding antiferromagnetic transition of Co_3O_4 Fig8.13(a), the ferrimagnetic transition of Mn_3O_4 Fig8.13(b), and the Morin transition of $\alpha\text{-Fe}_2\text{O}_3$ Fig8.13(d) respectively. Although, the Ni doped specimen Fig8.13(c) does not exhibit any feature in the magnetization, it could probably be due to the fact that the magnetic transitions associated with the possible impurities (NiO and Ni_2O_3) lie well above the temperature ranges of our measurements. It should be

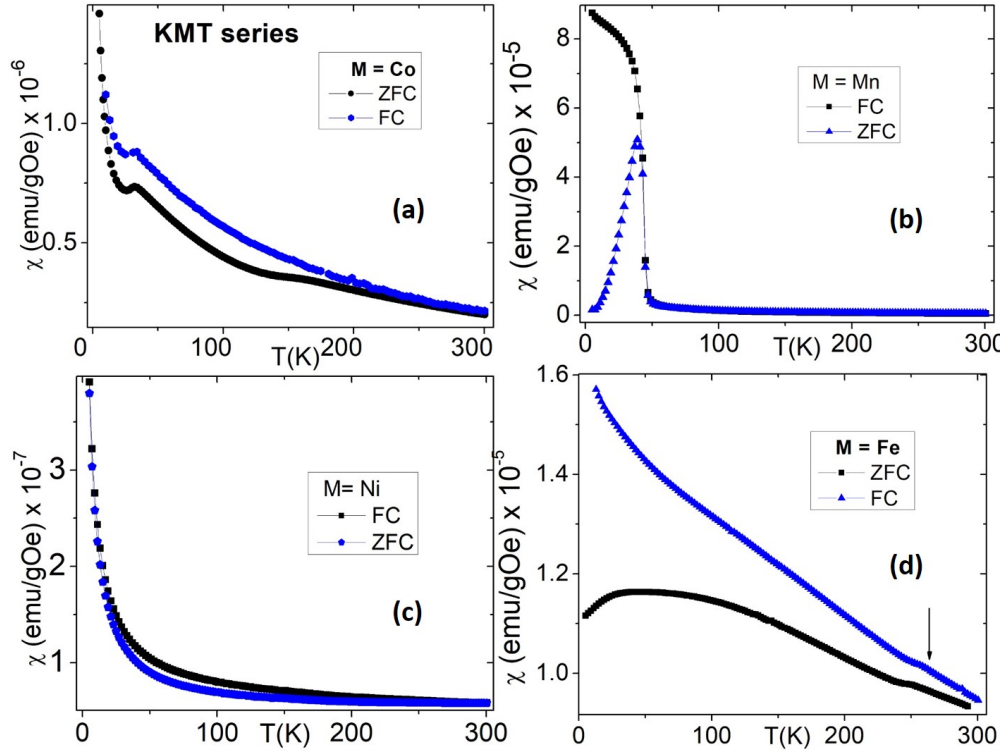


Figure 8.13: Temperature dependence of the dc magnetic susceptibility of the doped KTaO_3 specimens as measured in the zero field cooled and field cooled protocols. All these specimens exhibit signatures in the magnetization which corresponds to the magnetic transitions of one of the magnetic oxides listed in Table 2.

emphasized that these specimens were observed to be very homogenous, and traces of impurity phases could be observed only after collecting extensive backscattering images and long waiting X-ray scans. Though a significant amount of the magnetic dopants appear to have been incorporated into the host lattice, the doped KTaO_3 systems do not appear to exhibit any additional feature in the magnetization apart from the features from impurity oxides. Thus, our magnetic measurements rule out the possibility of any kind of intrinsic magnetic ordering in the doped members of both the KMT and SMT series. Our observations clearly indicate that the magnetization of these doped specimens could vary drastically as a function of the magnetic dopants incorporated in the host lattice. The measured bulk magnetization thus reflects the competition between

the intrinsic paramagnetic like susceptibility of the doped SrTiO_3 and KTaO_3 systems and contributions from remnant impurity oxides of the dopants. All the doped quantum paraelectrics clearly remains paramagnetic down to 5K and hence any report to the contrary is likely to originate from extrinsic effects alone.

8.4 Conclusion

In summary, we have investigated the doping of magnetic transition metals (Mn, Fe, Ni, or Co) in the quantum paraelectrics SrTiO_3 and KTaO_3 with the aim of verifying the existence (or lack thereof) of coupled magnetic and polar glass states in these systems. Extensive structural and scanning electron microscopy measurements clearly indicate that the magnetic dopants have limited solubility in these host lattices, and traces of spurious impurities are observed even in the most well processed specimens. Our dielectric measurements show that the doping induced electrical dipoles exhibit thermally activated hopping and appear to be too weakly coupled to exhibit a critical slowing down as is expected from a frozen polar state. Magnetic measurements indicate that all the observed magnetic signatures can be unambiguously attributed to the presence of oxides corresponding to the transition metal dopants, and that the doped SrTiO_3 and KTaO_3 specimens remain paramagnetic down to the lowest measured temperatures. Our results clearly show that the doped quantum para-electrics do not harbor a multiglass state, at least in the doping concentrations investigated here, and any report to the contrary arises from extrinsic considerations alone. Though the feasibility of concomitant glassy states in the polar and magnetic sectors is an intriguing one - especially due to the possibility of exploring cross-coupled aging and rejuvenation effects - doped quantum paraelectrics are unlikely to offer a testing ground for such an exploration.

Chapter 9

Conclusions and scope of future work

The study of spin orbit coupling, especially in the iridates, is in vogue in condensed matter physics, as its energy is comparable to the energy scales of crystal field splitting, on-site Coulomb interaction, and Hund's coupling, leading to a plethora of exotic ground states. Exhaustive theoretical and experimental studies, have led to a profusion of interesting outcomes in these iridium based oxides. The triple perovskite iridates of the form $\text{Ba}_3M\text{Ir}_2\text{O}_9$ (with M being an alkali, alkaline earth, or transition metal) attracted considerable attention as they seemed promising candidates with the potential to exhibit $J=0$ non magnetic state. The physics of these systems is especially rich, where the large spin-orbit coupling is known to be responsible for the stabilisation of a number of novel magnetic and electronic ground states.

We present a study of triple perovskite iridates with the objective to highlight the importance of these competing energy scales in this unique lattice framework. These samples were prepared using solid states route under ambient conditions and were studied using a wide range of characterization tools including synchrotron and neutron diffraction, specific heat, resistivity, x-ray photoelectron spectroscopy, magnetization, energy dispersive X-ray analysis and noise spectroscopy. A rigorous investigation of the physical properties were done for the first time on these compounds.

In the first chapter, we introduced the crystal structure of this family of compounds, various terminologies used in the thesis, in addition to a brief review of the current literature on iridates. The second chapter summarizes all the measurement techniques used and various software employed for data analysis.

In chapter 3, a comprehensive experimental and theoretical investigation of the triple perovskite iridate $\text{Ba}_3\text{CoIr}_2\text{O}_9$ is described in detail. Stabilizing in the hexagonal $P6_3/mmc$ symmetry at room temperature, it exhibits a magneto-structural transition to a monoclinic $C2/c$ phase at 107 K- the highest known amongst all the triple perovskite iridates. Below 70 K, a part of the system transforms to a monoclinic phase with even lower symmetry ($P2/c$), and both these phases coexist down to the lowest measured temperatures. First-principles calculations, including the spin-orbit coupling within the GGA + U + SOC formalism, predicts a weakly $a - b$ -canted AFM structure as the magnetic ground state for the $C2/c$ phase that agrees well with the magnetic structure derived from the neutron diffraction data. The observation of excess entropy in the low temperature specific heat, a pronounced increase in the resistance noise and the frequency dependent dispersion in the dielectric susceptibility, all point towards a highly correlated ground state in $\text{Ba}_3\text{CoIr}_2\text{O}_9$.

A close inspection of the phase co-existence regime revealed unusual temperature dependence of the volume. In chapter 4, we describe in detail the existence of a low temperature regime of negative thermal expansion (NTE) in $\text{Ba}_3\text{CoIr}_2\text{O}_9$. The NTE observed is intimately related to the co-existence of two closely related monoclinic phases, and the temperature dependence of their relative phase fractions. The underlying driving mechanism appears to be the antiferromagnetic exchange striction, which precipitates a phase conversion from a monoclinic $C2/c$ phase to a more distorted $P2/c$ phase as a function of decreasing temperatures. Below a phase crossover temperature of 40 K, the phase ratios of these monoclinic phases inverts, with remainder of the strain being

accommodated by octahedral distortions which manifests itself in the form of a negative thermal expansion in both these phases. We believe this work opens up opportunities in exploring NTE in intrinsically layered systems, which are characterized by strong spin orbit interactions.

We report in chapter 5 that replacement of 3d ion Cobalt with its neighbour in the periodic table, Nickel, drastically influenced the exchange mechanisms resulting in a complete transformation of structural and magnetic ground states. This hitherto new compound, $\text{Ba}_3\text{NiIr}_2\text{O}_9$, retains overall hexagonal symmetry down to the lowest temperature measured in sharp contrast to $\text{Ba}_3\text{CoIr}_2\text{O}_9$. The magnetization studies revealed two antiferromagnetic transitions at 106K and 6K. We speculate that the high and low magnetic transition temperatures correspond to the antiferromagnetic ordering of Ir dimers and Nickel respectively. In spite of the fact that $\text{Ba}_3\text{M}\text{Ir}_2\text{O}_9$ (M= Co, Ni) belongs to the same structural class, the diverse structural dynamics and magnetic ground state are driven by distinct magnetic anisotropies in these oxides as a consequence of filled and partially filled t_{2g} shells in Nickel and Cobalt respectively. The spin orbit interaction is not likely to alter with the isoelectronic substitution, though the significant structural and magnetic modifications implies changes in hybridization and therefore, exchange mechanisms resulting from different crystal field splitting. Clearly, the choice of the M site cation is a crucial parameter in determining the ground state as it provides an interlink between the Ir dimers and can easily influence the exchange pathways.

After exploring the magnetic M site in $\text{Ba}_3\text{M}\text{Ir}_2\text{O}_9$, we were curious to know the influence of non magnetic ion where we can stabilize iridium in a mixed valent state, adding further to the complexity of the problem. Chapter 6 presents a rare example of Ir in an unconventionally high valence state +5.5, where we show the structure-property relationship in the mixed valent geometrically frustrated triple perovskite iridate $\text{Ba}_3\text{NaIr}_2\text{O}_9$. Contrary to prior expectations from the tolerance limit, this com-

pound stabilizes in a hexagonal lattice framework rather than the monoclinic phase usually observed for elements with ionic radii similar to Na. With the reduction in temperature, the x-ray diffraction peaks show high anisotropy indicating the development of strain in the lattice. At low temperature, a structural transformation to orthorhombic phase is observed but the high symmetry hexagonal structure still remains the dominant one and only 20 percent of the total phase transforms into the lower symmetry at 5K. An extended co-operative paramagnetic regime is observed in magnetization which freezes to a cluster glass-like phase, confirmed by our specific heat and magnetization results.

In conclusion, we have examined various hexagonal lattice frameworks where the joint effects of spin orbit coupling, electron correlations and lattice geometry leads to different structural dynamics and associated magnetism. Unfortunately, the study of iridates is hindered by the large neutron absorption cross section of iridium but we believe alternate probes like muon spectroscopy, resonant x-ray scattering could enable a better evaluation of magnetic and electronic structure of the materials. In addition, doping this lattice with various magnetic and non-magnetic ions and thin film deposition or even exfoliation of hexagonal sheets could offer more playground in tuning the spin orbit coupling and lattice dynamics in this compound.

Given the frustrated hexagonal lattice geometry, these systems offer new prospects for investigation of quantum spin liquid in the iridates. In the quest for addressing the outstanding issue of the possibility of $J=0$ state, we have successfully discovered many new Ir based triple perovskites which seem to show no ordering down to the few millikelvin. We are currently in the process of analysing the obtained results summarised in Appendix 1.

In addition, we have also explored the possible existence of multiglass state, in which both magnetic and polar orders are frozen, in doped quantum paraelectrics. This has been a topic of constant debate where many reports raise doubts on the validity of such

scenario. In Appendix 2, we have investigated the doping of magnetic transition metals (Mn, Fe, Ni, or Co) in the quantum paraelectrics SrTiO_3 and KTaO_3 with the aim of verifying the existence (or lack thereof) of coupled magnetic and polar glass states in these systems. Extensive structural and scanning electron microscopy measurements clearly indicate that the magnetic dopants have limited solubility in these host lattices, and traces of spurious impurities are observed even in the most well processed specimens. Our dielectric measurements show that the doping induced electrical dipoles exhibit thermally activated hopping and appear to be too weakly coupled to exhibit a critical slowing down as is expected from a frozen polar state. Magnetic measurements indicate that all the observed magnetic signatures can be unambiguously attributed to the presence of oxides corresponding to the transition metal dopants, and that the doped SrTiO_3 and KTaO_3 specimens remain paramagnetic down to the lowest measured temperatures. Our results clearly show that the doped quantum para-electrics do not harbor a multiglass state, at least in the doping concentrations investigated here, and any report to the contrary arises from extrinsic considerations alone. Though the feasibility of concomitant glassy states in the polar and magnetic sectors is an intriguing one - especially due to the possibility of exploring cross-coupled aging and rejuvenation effects - doped quantum paraelectrics are unlikely to offer a testing ground for such an exploration.

Bibliography

- [1] Momma, K. and Izumi, F. *Journal of Applied Crystallography* **44**(6), 1272–1276 (2011).
- [2] Tarakina, N. V., Tyutyunnik, A. P., Bazuev, G. V., Vasilev, A. D., Gould, C., Nikolaenko, I. V., and Berger, I. F. *Dalton Trans.* **44**, 18527–18535 (2015).
- [3] Witczak-Krempa, W., Chen, G., Kim, Y. B., and Balents, L. *Annual Review of Condensed Matter Physics* **5**(1), 57–82 (2014).
- [4] Marturi, N. *Universite de Franche-Comte* (2013).
- [5] Yahia, L. and Mireles, L. In *Characterization of Polymeric Biomaterials*, 83 – 97. Woodhead Publishing (2017).
- [6] Buchner, M., Höfler, K., Henne, B., Ney, V., and Ney, A. *Journal of Applied Physics* **124**(16), 161101 (2018).
- [7] Müller, J. *ChemPhysChem* **12**(7), 1222–1245 (2011).
- [8] Lewis, G. N. *Journal of the American Chemical Society* **29**(8), 1165–1168 (1907).

- [9] Nag, A., Bhowal, S., Bert, F., Hillier, A. D., Itoh, M., Carlomagno, I., Meneghini, C., Sarkar, T., Mathieu, R., Dasgupta, I., and Ray, S. *Phys. Rev. B* **97**, 064408 (2018).
- [10] Zhao, J., Yang, L., Yu, Y., Li, F., Yu, R., and Jin, C. *Journal of Solid State Chemistry* **182**(2), 327 – 330 (2009).
- [11] De Graef, M. and McHenry, M. E. *Structure of materials: An introduction to crystallography, diffraction and symmetry*. Cambridge University Press, (2012).
- [12] Bhalla, A., Guo, R., and Roy, R. *Materials research innovations* **4**(1), 3–26 (2000).
- [13] Goldschmidt, V. M. *Naturwissenschaften* **14**(21), 477–485 (1926).
- [14] Rao, C. N. R. *Annual Review of Physical Chemistry* **40**(1), 291–326 (1989).
- [15] Kim, B. J., Ohsumi, H., Komesu, T., Sakai, S., Morita, T., Takagi, H., and Arima, T. *Science* **323**(5919), 1329–1332 (2009).
- [16] Cao, G., Crow, J., Guertin, R., Henning, P., Homes, C., Strongin, M., Basov, D., and Lochner, E. *Solid State Communications* **113**(11), 657 – 662 (2000).
- [17] Kim, B. J., Jin, H., Moon, S. J., Kim, J.-Y., Park, B.-G., Leem, C. S., Yu, J., Noh, T. W., Kim, C., Oh, S.-J., Park, J.-H., Durairaj, V., Cao, G., and Rotenberg, E. *Phys. Rev. Lett.* **101**, 076402 (2008).
- [18] Rau, J. G., Lee, E. K.-H., and Kee, H.-Y. *Annu. Rev. Condens. Matter Phys.* **7**, 195–221 (2016).
- [19] Mott, N. F. and Peierls, R. *Proceedings of the Physical Society* **49**(4S), 72–73 (1937).

-
- [20] Hubbard, J. *Proceedings of the Royal Society of London. Series A. Mathematical and Physical Sciences* **277**(1369), 237–259 (1964).
- [21] Dirac, P. A. M. *Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character* **112**(762), 661–677 (1926).
- [22] Heisenberg, W. *Zeitschrift für Physik* **38**(6-7), 411–426 (1926).
- [23] Kramers, H. *Physica* **1**(1-6), 182–192 (1934).
- [24] Anderson, P. W. *Phys. Rev.* **79**, 350–356 (1950).
- [25] Kanamori, J. *Journal of Physics and Chemistry of Solids* **10**(2), 87 – 98 (1959).
- [26] Goodenough, J. B. *Physical Review* **100**(2), 564 (1955).
- [27] Weiss, A. *Berichte der Bunsengesellschaft für physikalische Chemie* **68**(10), 996–996 (1964).
- [28] Zener, C. *Phys. Rev.* **82**, 403–405 (1951).
- [29] Ballhausen, C. J. and Weiner, M. A. *Journal of The Electrochemical Society* **110**(4), 97C (1963).
- [30] Van Vleck, J. H. *Phys. Rev.* **41**, 208–215 (1932).
- [31] Jahn, H. A., Teller, E., and Donnan, F. G. *Proceedings of the Royal Society of London. Series A - Mathematical and Physical Sciences* **161**(905), 220–235 (1937).
- [32] Streltsov, S. V. and Khomskii, D. I. *Phys. Rev. X* **10**, 031043 (2020).
- [33] Shanavas, K. V., Popović, Z. S., and Satpathy, S. *Phys. Rev. B* **90**, 165108 (2014).

- [34] Landau, L. D. and Lifshitz, E. M. *Quantum mechanics: non-relativistic theory*, volume 3. Elsevier, (2013).
- [35] Vijayakumar, M. and Gopinathan, M. *Journal of Molecular Structure: THEOCHEM* **361**(1), 15 – 19 (1996).
- [36] Cao, G. and Schlottmann, P. *Reports on Progress in Physics* **81**(4), 042502 (2018).
- [37] Pesin, D. and Balents, L. *Nature Physics* **6**(5), 376–381 (2010).
- [38] Varnava, N. and Vanderbilt, D. *Phys. Rev. B* **98**, 245117 (2018).
- [39] Zhang, J., Yan, D., Yesudhas, S., Deng, H., Xiao, H., Chen, B., Sereika, R., Yin, X., Yi, C., Shi, Y., Liu, Z., Pärschke, E. M., Chen, C.-C., Chang, J., Ding, Y., and Mao, H.-k. *npj Quantum Materials* **4**(1), 1–6 (2019).
- [40] Mehlawat, K. and Singh, Y. *arXiv:1908.08475* (2019).
- [41] Takagi, H., Takayama, T., Jackeli, G., Khaliullin, G., and Nagler, S. E. *Nature Reviews Physics* **1**(4), 264–280 (2019).
- [42] Kim, J., Casa, D., Upton, M. H., Gog, T., Kim, Y.-J., Mitchell, J. F., van Veenendaal, M., Daghofer, M., van den Brink, J., Khaliullin, G., and Kim, B. J. *Phys. Rev. Lett.* **108**, 177003 (2012).
- [43] Singh, Y. and Gegenwart, P. *Phys. Rev. B* **82**, 064412 (2010).
- [44] Singh, Y., Manni, S., Reuther, J., Berlijn, T., Thomale, R., Ku, W., Trebst, S., and Gegenwart, P. *Phys. Rev. Lett.* **108**, 127203 (2012).
- [45] Choi, S. K., Coldea, R., Kolmogorov, A. N., Lancaster, T., Mazin, I. I., Blundell, S. J., Radaelli, P. G., Singh, Y., Gegenwart, P., Choi, K. R., Cheong, S.-W., Baker, P. J., Stock, C., and Taylor, J. *Phys. Rev. Lett.* **108**, 127204 (2012).

- [46] Chun, S. H., Kim, J.-W., Kim, J., Zheng, H., Stoumpos, C. C., Malliakas, C., Mitchell, J., Mehlawat, K., Singh, Y., Choi, Y., et al. *Nature Physics* **11**(6), 462–466 (2015).
- [47] Fukazawa, H. and Maeno, Y. *Journal of the Physical Society of Japan* **71**(10), 2578–2579 (2002).
- [48] Qi, T. F., Korneta, O. B., Wan, X., DeLong, L. E., Schlottmann, P., and Cao, G. *Journal of Physics: Condensed Matter* **24**(34), 345601 (2012).
- [49] Okamoto, Y., Nohara, M., Aruga-Katori, H., and Takagi, H. *Phys. Rev. Lett.* **99**, 137207 (2007).
- [50] Singh, Y., Tokiwa, Y., Dong, J., and Gegenwart, P. *Phys. Rev. B* **88**, 220413 (2013).
- [51] Dickson, J. G., Katz, L., and Ward, R. *Journal of the American Chemical Society* **83**(14), 3026–3029 (1961).
- [52] Kim, S.-J., Smith, M. D., Darriet, J., and zur Loye, H.-C. *J. Solid State Chem.* **177**(4-5), 1493–1500 (2004).
- [53] Miiller, W., Avdeev, M., Zhou, Q., Kennedy, B. J., Sharma, N., Kuttah, R., Kearley, G. J., Schmid, S., Knight, K. S., Blanchard, P. E. R., and Ling, C. D. *J. Am. Chem. Soc.* **134**(6), 3265–3270 (2012).
- [54] Huang, Z., Avdeev, M., Kennedy, B. J., Knight, K. S., Zhou, Q., and Ling, C. D. *J. Phys.: Condens. Matter* **26**(27), 276003 (2014).
- [55] Treiber, U., Kemmler-Sack, S., and Ehmman, A. *Zeitschrift für anorganische und allgemeine Chemie* **487**(1), 189–198 (1982).

- [56] Battle, P., Gore, J., Hollyman, R., and Powell, A. *J. Alloys Compounds* **218**(1), 110 – 116 (1995).
- [57] Doi, Y. and Hinatsu, Y. *Journal of Physics: Condensed Matter* **16**(16), 2849–2860 (2004).
- [58] Takagi, Y., Doi, Y., Wakeshima, M., and Hinatsu, Y. *Journal of Solid State Chemistry* **286**, 121309 (2020).
- [59] Shlyk, L., Kryukov, S., Durairaj, V., Parkin, S., Cao, G., and Long, L. D. *Journal of Magnetism and Magnetic Materials* **319**(1), 64 – 68 (2007).
- [60] Vannimenus, J. and Toulouse, G. *Journal of Physics C: Solid State Physics* **10**(18), L537 (1977).
- [61] Ramirez, A. P. *Annual Review of Materials Science* **24**(1), 453–480 (1994).
- [62] Moessner, R. and Ramirez, A. P. *Phys. Today* **59**(2), 24 (2006).
- [63] Anderson, P. *Materials Research Bulletin* **8**(2), 153 – 160 (1973).
- [64] Balents, L. *Nature* **464**(7286), 199–208 (2010).
- [65] Han, T.-H., Helton, J. S., Chu, S., Nocera, D. G., Rodriguez-Rivera, J. A., Broholm, C., and Lee, Y. S. *Nature* **492**(7429), 406–410 (2012).
- [66] Banerjee, A., Bridges, C., Yan, J.-Q., Aczel, A., Li, L., Stone, M., Granroth, G., Lumsden, M., Yiu, Y., Knolle, J., et al. *Nature materials* **15**(7), 733–740 (2016).
- [67] Nag, A., Middey, S., Bhowal, S., Panda, S. K., Mathieu, R., Orain, J. C., Bert, F., Mendels, P., Freeman, P. G., Mansson, M., Ronnow, H. M., Telling, M., Biswas, P. K., Sheptyakov, D., Kaushik, S. D., Siruguri, V., Meneghini, C., Sarma, D. D., Dasgupta, I., and Ray, S. *Phys. Rev. Lett.* **116**, 097205 (2016).

- [68] Kundu, S., Shahee, A., Chakraborty, A., Ranjith, K., Koo, B., Sichel Schmidt, J., Telling, M. T., Biswas, P., Baenitz, M., Dasgupta, Pujari, I. S., and Mahajan, A. V. *arXiv:2012.01239* (2020).
- [69] Tao, J. and Sleight, A. *Journal of Solid State Chemistry* **173**(2), 442 – 448 (2003).
- [70] Hammonds, K. D., Dove, M. T., Giddy, A. P., Heine, V., and Winkler, B. *American Mineralogist* **81**(9-10), 1057–1079 (1996).
- [71] Dove, M. T., Trachenko, K. O., Tucker, M. G., and Keen, D. A. *Reviews in Mineralogy and Geochemistry* **39**(1), 1–33 (2000).
- [72] Grüneisen, E. *Annalen der Physik* **344**(12), 257–306 (1912).
- [73] Futamura, R., Iiyama, T., Hamasaki, A., and Ozeki, S. *Phys. Chem. Chem. Phys.* **14**, 981–986 (2012).
- [74] Takenaka, K. *Frontiers in Chemistry* **6**, 267 (2018).
- [75] Pryde, A. K., Hammonds, K. D., Dove, M. T., Heine, V., Gale, J. D., and Warren, M. C. *Phase Transitions* **61**(1-4), 141–153 (1997).
- [76] Mary, T. A. and Sleight, A. W. *Journal of Materials Research* **14**(3), 912–915 (1999).
- [77] Korthuis, V., Khosrovani, N., Sleight, A. W., Roberts, N., Dupree, R., and Warren, W. W. J. *Chemistry of Materials* **7**(2), 412–417 (1995).
- [78] Tschaufeser, P. and Parker, S. C. *The Journal of Physical Chemistry* **99**(26), 10609–10615 (1995).
- [79] Barrera, G. D., Bruno, J. A. O., Barron, T. H. K., and Allan, N. L. *Journal of Physics: Condensed Matter* **17**(4), R217–R252 (2005).

-
- [80] Hamada, T. and Takenaka, K. *Journal of Applied Physics* **109**(7), 07E309 (2011).
- [81] Takenaka, K. *Science and Technology of Advanced Materials* **13**(1), 013001 (2012).
- [82] Miller, W., Smith, C., Mackenzie, D., and Evans, K. *Journal of materials science* **44**(20), 5441–5451 (2009).
- [83] Jackeli, G. and Khaliullin, G. *Phys. Rev. Lett.* **103**, 067205 (2009).
- [84] Chen, G., Pereira, R., and Balents, L. *Phys. Rev. B* **82**, 174440 (2010).
- [85] Chen, G. and Balents, L. *Phys. Rev. B* **78**, 094403 (2008).
- [86] Shitade, A., Katsura, H., Kuneš, J., Qi, X.-L., Zhang, S.-C., and Nagaosa, N. *Phys. Rev. Lett.* **102**, 256403 (2009).
- [87] Chern, G.-W. and Perkins, N. *Phys. Rev. B* **80**, 180409 (2009).
- [88] Chen, G. and Balents, L. *Phys. Rev. B* **84**, 094420 (2011).
- [89] Meetei, O. N., Erten, O., Randeria, M., Trivedi, N., and Woodward, P. *Phys. Rev. Lett.* **110**, 087203 (2013).
- [90] Cao, G., Qi, T. F., Li, L., Terzic, J., Yuan, S. J., DeLong, L. E., Murthy, G., and Kaul, R. K. *Phys. Rev. Lett.* **112**, 056402 (2014).
- [91] Nag, A., Bhowal, S., Sala, M. M., Efimenko, A., Dasgupta, I., and Ray, S. *Phys. Rev. Lett.* **123**, 017201 (2019).
- [92] Jain, A., Krautloher, M., Porras, J., Ryu, G. H., Chen, D. P., Abernathy, D. L., Park, J. T., Ivanov, A., Chaloupka, J., Khaliullin, G., Keimer, B., and Kim, B. J. *Nat. Phys.* **13**, 633 (2017).

- [93] Souliou, S.-M., Chaloupka, Jiří and Khaliullin, G., Ryu, G., Jain, A., Kim, B. J., Le Tacon, M., and Keimer, B. *Phys. Rev. Lett.* **119**, 067201 (2017).
- [94] Riccò, S., Kim, M., Tamai, A., McKeown Walker, S., Bruno, F. Y., Cucchi, I., Cappelli, E., Besnard, C., Kim, T. K., Dudin, P., Hoesch, M., Gutmann, M. J., Georges, A., Perry, R. S., and Baumberger, F. *Nat. Commun.* **9**, 4535 (2018).
- [95] Khaliullin, G. *Phys. Rev. Lett.* **111**, 197201 (2013).
- [96] Stamokostas, G. L. and Fiete, G. A. *Phys. Rev. B* **97**, 085150 (2018).
- [97] Chen, Q., Svoboda, C., Zheng, Q., Sales, B. C., Mandrus, D. G., D., H., Zhou, J.-S., McComb, D., Randeria, M., Trivedi, N., and Yan, J.-Q. *Phys. Rev. B* **96**, 144423 (2017).
- [98] Hammerath, F., Sarkar, R., Kamusella, S., Baines, C., Klauss, H.-H., Dey, T., Maljuk, A., Gaß, S., Wolter, A. U. B., Grafe, H.-J., Wurmehl, S., and Büchner, B. *Phys. Rev. B* **96**, 165108 (2017).
- [99] Bhowal, S., Baidya, S., Dasgupta, I., and Saha-Dasgupta, T. *Phys. Rev. B* **92**, 121113 (2015).
- [100] Meetei, O. N., Cole, W. S., Randeria, M., and Trivedi, N. *Phys. Rev. B* **91**, 054412 (2015).
- [101] Khan, M. S., Bandyopadhyay, A., Nag, A., Kumar, V., Mahajan, A. V., and Ray, S. *Phys. Rev. B* **100**, 064423 (2019).
- [102] Blanchard, P. E., Chapman, K. W., Heald, S. M., Zbiri, M., Johnson, M. R., Kennedy, B. J., and Ling, C. D. *Inorg. Chem.* **55**(11), 5649–5654 (2016).
- [103] Smerald, A. and Mila, F. *Phys. Rev. B* **90**, 094422 (2014).

- [104] Man, H., Halim, M., Sawa, H., Hagiwara, M., Wakabayashi, Y., and Nakatsuji, S. *Journal of Physics: Condensed Matter* **30**(44), 443002 (2018).
- [105] Nakatsuji, S., Kuga, K., Kimura, K., Satake, R., Katayama, N., Nishibori, E., Sawa, H., Ishii, R., Hagiwara, M., Bridges, F., et al. *Science* **336**(6081), 559–563 (2012).
- [106] Dey, T., Mahajan, A. V., Kumar, R., Koteswararao, B., Chou, F. C., Omrani, A. A., and Ronnow, H. M. *Phys. Rev. B* **88**, 134425 (2013).
- [107] Bragg, W. H. and Bragg, W. L. *Proceedings of the Royal Society of London*. **88**(605), 428–438 (1913).
- [108] Cullity, B. D. *Elements of X-ray Diffraction*. Addison-Wesley Publishing, (1956).
- [109] Nagamiya, S. *AAPPS Bull.* **15**, 18–24 (2005).
- [110] Willmott, P. R., Meister, D., Leake, S. J., Lange, M., Bergamaschi, A., Böge, M., Calvi, M., Cancellieri, C., Casati, N., Cervellino, A., Chen, Q., David, C., Flechsig, U., Gozzo, F., Henrich, B., Jäggi-Spielmann, S., Jakob, B., Kalichava, I., Karvinen, P., Krempasky, J., Lüdeke, A., Lüscher, R., Maag, S., Quitmann, C., Reinle-Schmitt, M. L., Schmidt, T., Schmitt, B., Streun, A., Vartiainen, I., Vitins, M., Wang, X., and Wulschleger, R. *Journal of Synchrotron Radiation* **20**(5), 667–682 (2013).
- [111] Bacon, G. E. and Lonsdale, K. *Reports on Progress in Physics* **16**(1), 1–61 (1953).
- [112] Santisteban, J. R., Edwards, L., Steuwer, A., and Withers, P. J. *Journal of Applied Crystallography* **34**(3), 289–297 (2001).

- [113] Chapon, L. C., Manuel, P., Radaelli, P. G., Benson, C., Perrott, L., Ansell, S., Rhodes, N. J., Raspino, D., Duxbury, D., Spill, E., et al. *Neutron News* **22**(2), 22–25 (2011).
- [114] Fischer, P., Frey, G., Koch, M., Könnecke, M., Pomjakushin, V., Schefer, J., Thut, R., Schlumpf, N., Bürge, R., Greuter, U., et al. *Physica B: Condensed Matter* **276**, 146–147 (2000).
- [115] Blau, B., Clausen, K. N., Gvasaliya, S., Janoschek, M., Janssen, S., Keller, L., Roessli, B., Schefer, J., Tregenna-Piggott, P., Wagner, W., and Zaharko, O. *Neutron News* **20**(3), 5–8 (2009).
- [116] Young, R. *The Rietveld Method*. IUCr monographs on crystallography. Oxford University Press, (1995).
- [117] Rietveld, H. M. *Journal of Applied Crystallography* **2**(2), 65–71 (1969).
- [118] Rodríguez-Carvajal, J. *Laboratoire Leon Brillouin (CEA-CNRS)* (2001).
- [119] Boultif, A. and Louër, D. *Journal of Applied Crystallography* **37**(5), 724–731 (2004).
- [120] Kanda, K. (1991). US Patent 5,065,020.
- [121] Moulder, J., Chastain, J., and King, R. *Handbook of X-ray Photoelectron Spectroscopy: A Reference Book of Standard Spectra for Identification and Interpretation of XPS Data*. Physical Electronics, (1995).
- [122] Hüfner, S. *Photoelectron Spectroscopy: Principles and applications*. Springer Science & Business Media, (2013).
- [123] Fairley, N. *CasaXPS Manual 2.3. 15: CasaXPS Processing Software for XPS Spectra*. Casa Software Limited, (2009).

-
- [124] Jaklevic, R. C., Lambe, J., Silver, A. H., and Mercereau, J. E. *Phys. Rev. Lett.* **12**, 159–160 (1964).
- [125] Clarke, J. and Braginski, A. I. *The SQUID handbook: Applications of SQUIDS and SQUID systems*. John Wiley & Sons, (2006).
- [126] *Magnetic Property Measurement System- MPMS-XL Users Manual (Quantum Design)*.
- [127] Kogan, S. *Electronic noise and fluctuations in solids*. Cambridge University Press, (2008).
- [128] Dutta, P. and Horn, P. M. *Rev. Mod. Phys.* **53**, 497–516 (1981).
- [129] Hooge, F. N., Kleinpenning, T. G. M., and Vandamme, L. K. J. *Reports on Progress in Physics* **44**(5), 479–532 (1981).
- [130] Raquet, B., Coey, J. M. D., Wirth, S., and von Molnár, S. *Phys. Rev. B* **59**, 12435–12443 (1999).
- [131] Hooge, F. *Physics Letters A* **29**(3), 139–140 (1969).
- [132] Hooge, F. *Physica B* **83**(1), 14–23 (1976).
- [133] Raquet, B. In *Spin Electronics, Chapter: "Electronic Noise in Magnetic Materials and Devices"*, 232–273. Springer, Heidelberg (2001).
- [134] Scofield, J. H. *Rev. Sci. Inst.* **58**(6), 985–993 (1987).
- [135] Birol, T., Benedek, N. A., Das, H., Wysocki, A. L., Mulder, A. T., Abbett, B. M., Smith, E. H., Ghosh, S., and Fennie, C. J. *Current Opinion in Solid State and Materials Science* **16**(5), 227 – 242 (2012).

- [136] Schuetze, A. P., Lewis, W., Brown, C., and Geerts, W. J. *American Journal of Physics* **72**(2), 149–153 (2004).
- [137] Gopal, E. R. *Specific heats at low temperatures*. Springer Science & Business Media, (2012).
- [138] Tari, A. *The Specific Heat of Matter At Low Temperatures*. World Scientific, (2003).
- [139] Garg, C., Roy, D., Lonsky, M., Manuel, P., Cervellino, A., Müller, J., Kabir, M., and Nair, S. *arXiv:2009.13822* (2020).
- [140] Lightfoot, P. and Battle, P. *Journal of Solid State Chemistry* **89**(1), 174 – 183 (1990).
- [141] Lufaso, M. W. and zur Loye, H.-C. *Inorganic Chemistry* **44**(25), 9143–9153 (2005).
- [142] Doi, Y., Hinatsu, Y., Shimojo, Y., and Ishii, Y. *Journal of Solid State Chemistry* **161**(1), 113 – 120 (2001).
- [143] Zhou, H. D., Kiswandhi, A., Barlas, Y., Brooks, J. S., Siegrist, T., Li, G., Balicas, L., Cheng, J. G., and Rivadulla, F. *Phys. Rev. B* **85**, 041201 (2012).
- [144] Streltsov, S. V. *Phys. Rev. B* **88**, 024429 (2013).
- [145] Hohenberg, P. and Kohn, W. *Phys. Rev.* **136**, B864–B871 (1964).
- [146] Kohn, W. and Sham, L. J. *Phys. Rev.* **140**, A1133–A1138 (1965).
- [147] Kresse, G. and Hafner, J. *Phys. Rev. B* **48**, 13115–13118 (1993).
- [148] Kresse, G. and Furthmüller, J. *Phys. Rev. B* **54**, 11169–11186 (1996).

- [149] Kresse, G. and Joubert, D. *Phys. Rev. B* **59**, 1758–1775 (1999).
- [150] Paier, J., Marsman, M., Hummer, K., Kresse, G., Gerber, I. C., and Ángyán, J. G. *The Journal of Chemical Physics* **125**(24), 249901 (2006).
- [151] Blöchl, P. E. *Phys. Rev. B* **50**, 17953–17979 (1994).
- [152] Perdew, J. P., Burke, K., and Ernzerhof, M. *Phys. Rev. Lett.* **77**, 3865–3868 (1996).
- [153] Dudarev, S. L., Botton, G. A., Savrasov, S. Y., Humphreys, C. J., and Sutton, A. P. *Phys. Rev. B* **57**, 1505–1509 (1998).
- [154] Sakamoto, T., Doi, Y., and Hinatsu, Y. *J. Solid State Chem.* **179**(8), 2595–2601 (2006).
- [155] Viola, M., Martínez-Lope, M., Alonso, J., Martínez, J., De Paoli, J., Pagola, S., Pedregosa, J., Fernández-Díaz, M., and Carbonio, R. *Chemistry of materials* **15**(8), 1655–1663 (2003).
- [156] Rijssenbeek, J. T., Matl, P., Batlogg, B., Ong, N. P., and Cava, R. J. *Phys. Rev. B* **58**, 10315–10318 (1998).
- [157] Dunn, T. M., McClure, D. S., and Pearson, R. G. *Some aspects of crystal field theory*. Harper & Row, (1965).
- [158] Georges, A., Medici, L. d., and Mravlje, J. *Annu. Rev. Condens. Matter Phys.* **4**, 137–178 (2013).
- [159] Sage, M. H., Blake, G. R., Marquina, C., and Palstra, T. T. M. *Phys. Rev. B* **76**, 195102 (2007).

-
- [160] Banerjee, A., Rawat, R., Mukherjee, K., and Chaddah, P. *Phys. Rev. B* **79**, 212403 (2009).
- [161] Sharma, P. A., El-Khatib, S., Mihut, I., Betts, J. B., Migliori, A., Kim, S. B., Guha, S., and Cheong, S.-W. *Phys. Rev. B* **78**, 134205 (2008).
- [162] Kim, K. H., Uehara, M., Hess, C., Sharma, P. A., and Cheong, S.-W. *Phys. Rev. Lett.* **84**, 2961–2964 (2000).
- [163] Phan, M. H., Morales, M. B., Bingham, N. S., Srikanth, H., Zhang, C. L., and Cheong, S. W. *Phys. Rev. B* **81**, 094413 (2010).
- [164] Lonsky, M., Teschabai-Oglu, J., Pierz, K., Sievers, S., Schumacher, H. W., Yuan, Y., Böttger, R., Zhou, S., and Müller, J. *Phys. Rev. B* **97**, 054413 (2018).
- [165] Müller, J. and Thomas, T. *Crystals* **8**(4), 166 (2018).
- [166] Dutta, P., Dimon, P., and Horn, P. M. *Phys. Rev. Lett.* **43**, 646–649 (1979).
- [167] Freitas, R. S., Mitchell, J. F., and Schiffer, P. *Phys. Rev. B* **72**, 144429 (2005).
- [168] Majumder, M., Manna, R. S., Simutis, G., Orain, J. C., Dey, T., Freund, F., Jesche, A., Khasanov, R., Biswas, P. K., Bykova, E., Dubrovinskaia, N., Dubrovinsky, L. S., Yadav, R., Hozoi, L., Nishimoto, S., Tsirlin, A. A., and Gegenwart, P. *Phys. Rev. Lett.* **120**, 237202 (2018).
- [169] Laguna-Marco, M. A., Fabbri, G., Souza-Neto, N. M., Chikara, S., Schilling, J. S., Cao, G., and Haskel, D. *Phys. Rev. B* **90**, 014419 (2014).
- [170] Korneta, O. B. *Theses and Dissertations-Physics and Astronomy, University of Kentucky* (2012).

- [171] Neumeier, J., Cornelius, A., and Schilling, J. *Physica B: Condensed Matter* **198**(4), 324 – 328 (1994).
- [172] Biesner, T. and Uykur, E. *Crystals* **10**(1), 4 (2020).
- [173] Nabi, M., Bhat, T. M., and Gupta, D. C. *International Journal of Energy Research* **43**(9), 4229–4242 (2019).
- [174] Veiga, L. S. I., Fabbris, G., van Veenendaal, M., Souza-Neto, N. M., Feng, H. L., Yamaura, K., and Haskel, D. *Phys. Rev. B* **91**, 235135 (2015).
- [175] Adler, P., Medvedev, S. A., Naumov, P. G., Mohitkar, S., Rüffer, R., Jansen, M., and Felser, C. *Phys. Rev. B* **99**, 134443 (2019).
- [176] Cao, G., Terzic, J., Zhao, H. D., Zheng, H., De Long, L. E., and Riseborough, P. S. *Phys. Rev. Lett.* **120**, 017201 (2018).
- [177] Ye, F., Hoffmann, C., Tian, W., Zhao, H., and Cao, G. *Phys. Rev. B* **102**, 115120 (2020).
- [178] Cao, G. *Journal of Physics: Condensed Matter* **32**(42), 423001 (2020).
- [179] Garg, C., Cervellino, A., and Nair, S. *arXiv:2010.03940* (2020).
- [180] Chen, J., Hu, L., Deng, J., and Xing, X. *Chem. Soc. Rev.* **44**, 3522–3567 (2015).
- [181] Chatterji, T., Henry, P. F., Mittal, R., and Chaplot, S. L. *Phys. Rev. B* **78**, 134105 (2008).
- [182] García-Muñoz, J., Suaaidi, M., and Ritter, C. *Physica B: Condensed Matter* **234-236**, 854 – 855 (1997). Proceedings of the First European Conference on Neutron Scattering.

- [183] Huang, Q., Santoro, A., Lynn, J. W., Erwin, R. W., Borchers, J. A., Peng, J. L., and Greene, R. L. *Phys. Rev. B* **55**, 14987–14999 (1997).
- [184] Kiyama, T., Yoshimura, K., Kosuge, K., Ikeda, Y., and Bando, Y. *Phys. Rev. B* **54**, R756–R759 (1996).
- [185] Dove, M. T., Heine, V., and Hammonds, K. D. *Mineralogical Magazine* **59**(397), 629–639 (1995).
- [186] Takenaka, K., Ichigo, M., Hamada, T., Ozawa, A., Shibayama, T., Inagaki, T., and Asano, K. *Science and Technology of Advanced Materials* **15**(1), 015009 (2014).
- [187] Saha, R., Shireen, A., Bera, A., Shirodkar, S. N., Sundarayya, Y., Kalarikkal, N., Yusuf, S., Waghmare, U. V., Sundaresan, A., and Rao, C. *Journal of Solid State Chemistry* **184**(3), 494 – 501 (2011).
- [188] Takenaka, K., Okamoto, Y., Shinoda, T., Katayama, N., and Sakai, Y. *Nature communications* **8**(1), 1–7 (2017).
- [189] Mary, T. A., Evans, J. S. O., Vogt, T., and Sleight, A. W. *Science* **272**(5258), 90–92 (1996).
- [190] Ernst, G., Broholm, C., Kowach, G., and Ramirez, A. *Nature* **396**(6707), 147–149 (1998).
- [191] Hemberger, J., von Nidda, H.-A. K., Tsurkan, V., and Loidl, A. *Phys. Rev. Lett.* **98**, 147203 (2007).
- [192] Pokharel, G., May, A. F., Parker, D. S., Calder, S., Ehlers, G., Huq, A., Kimber, S. A. J., Arachchige, H. S., Poudel, L., McGuire, M. A., Mandrus, D., and Christianson, A. D. *Phys. Rev. B* **97**, 134117 (2018).

- [193] Villaescusa, L. A., Lightfoot, P., Teat, S. J., and Morris, R. E. *Journal of the American Chemical Society* **123**(23), 5453–5459 (2001).
- [194] Woodcock, D. A., Lightfoot, P., Villaescusa, L. A., Díaz-Cabañas, M.-J., Camblor, M. A., and Engberg, D. *Chemistry of materials* **11**(9), 2508–2514 (1999).
- [195] Takenaka, K. and Takagi, H. *Applied Physics Letters* **87**(26), 261902 (2005).
- [196] Yamada, I., Tsuchida, K., Ohgushi, K., Hayashi, N., Kim, J., Tsuji, N., Takahashi, R., Matsushita, M., Nishiyama, N., Inoue, T., Irifune, T., Kato, K., Takata, M., and Takano, M. *Angewandte Chemie International Edition* **50**(29), 6579–6582 (2011).
- [197] Filippetti, A. and Hill, N. A. *Phys. Rev. Lett.* **85**, 5166–5169 (2000).
- [198] Azuma, M., Chen, W.-t., Seki, H., Czapski, M., Olga, S., Oka, K., Mizumaki, M., Watanuki, T., Ishimatsu, N., Kawamura, N., et al. *Nature communications* **2**(1), 1–5 (2011).
- [199] Chen, J., Wang, F., Huang, Q., Hu, L., Song, X., Deng, J., Yu, R., and Xing, X. *Scientific reports* **3**, 2458 (2013).
- [200] Qi, T. F., Korneta, O. B., Parkin, S., Hu, J., and Cao, G. *Phys. Rev. B* **85**, 165143 (2012).
- [201] Hu, F., Shen, F., Hao, J., Liu, Y., Wang, J., Sun, J., and Shen, B. *Frontiers in Chemistry* **6**, 438 (2018).
- [202] Pan, Z., Chen, J., Jiang, X., Hu, L., Yu, R., Yamamoto, H., Ogata, T., Hattori, Y., Guo, F., Fan, X., et al. *Journal of the American Chemical Society* **139**(42), 14865–14868 (2017).

- [203] Saha, R., Fauth, F., Caignaert, V., and Sundaresan, A. *Phys. Rev. B* **95**, 184107 (2017).
- [204] Hemberger, J., Rudolf, T., Krug von Nidda, H.-A., Mayr, F., Pimenov, A., Tsurkan, V., and Loidl, A. *Phys. Rev. Lett.* **97**, 087204 (2006).
- [205] Kanungo, S., Mogare, K., Yan, B., Reehuis, M., Hoser, A., Felser, C., and Jansen, M. *Phys. Rev. B* **93**, 245148 (2016).
- [206] Revelli, A., Loo, C. C., Kiese, D., Becker, P., Fröhlich, T., Lorenz, T., Moretti Sala, M., Monaco, G., Buessen, F. L., Attig, J., Hermanns, M., Streltsov, S. V., Khomskii, D. I., van den Brink, J., Braden, M., van Loosdrecht, P. H. M., Trebst, S., Paramakanti, A., and Grüninger, M. *Phys. Rev. B* **100**, 085139 (2019).
- [207] Aczel, A. A., Clancy, J. P., Chen, Q., Zhou, H. D., Reig-i Plessis, D., MacDougall, G. J., Ruff, J. P. C., Upton, M. H., Islam, Z., Williams, T. J., Calder, S., and Yan, J.-Q. *Phys. Rev. B* **99**, 134417 (2019).
- [208] Ferreira, T., Carone, D., Huon, A., Herklotz, A., Stoian, S. A., Heald, S. M., Morrison, G., Smith, M. D., and Loye, H.-C. z. *Inorganic Chemistry* **57**(12), 7362–7371 (2018).
- [209] Fåk, B., Bieri, S., Canévet, E., Messio, L., Payen, C., Viaud, M., Guillot-Deudon, C., Darie, C., Ollivier, J., and Mendels, P. *Phys. Rev. B* **95**, 060402 (2017).
- [210] Feng, H. L., Chen, J., Hu, Z., Wang, X., Reehuis, M., Adler, P., Hoser, A., Wu, M.-X., Agrestini, S., Vasili, H. B., Herrero-Martin, J., Nataf, L., Baudelet, F., Chen, K., Matsushita, Y., Li, M.-R., Tjeng, L. H., Felser, C., Jansen, M., and Yamaura, K. *Phys. Rev. Materials* **4**, 064420 (2020).
- [211] Hwang, J., Choi, E. S., Ye, F., Dela Cruz, C. R., Xin, Y., Zhou, H. D., and Schlottmann, P. *Phys. Rev. Lett.* **109**, 257205 (2012).

- [212] Asai, S., Soda, M., Kasatani, K., Ono, T., Avdeev, M., and Masuda, T. *Phys. Rev. B* **93**, 024412 (2016).
- [213] Darie, C., Lepoittevin, C., Klein, H., Kodjikian, S., Bordet, P., Colin, C. V., Lebedev, O. I., Deudon, C., and Payen, C. *Journal of Solid State Chemistry* **237**, 166 – 173 (2016).
- [214] Liu, S.-Q., Wen, H.-R., Ying-Guo, Zhu, Y.-W., Fu, X.-Z., Sun, R., and Wong, C.-P. *Nano Energy* **44**, 7 – 14 (2018).
- [215] Dwivedi, V. K., Juyal, A., and Mukhopadhyay, S. *Materials Research Express* **3**(11), 115020 (2016).
- [216] Sun, Y., Xu, X., and Zhang, Y. *Journal of Physics: Condensed Matter* **12**(50), 10475–10480 (2000).
- [217] Aswathi, K., Palakkal, J. P., Lekshmi, P. N., and Varma, M. R. *New J. Chem.* **43**, 17351–17357 (2019).
- [218] Bremholm, M., Dutton, S., Stephens, P., and Cava, R. *Journal of Solid State Chemistry* **184**(3), 601 – 607 (2011).
- [219] Dey, T., Maljuk, A., Efremov, D. V., Kataeva, O., Gass, S., Blum, C. G. F., Steckel, F., Gruner, D., Ritschel, T., Wolter, A. U. B., Geck, J., Hess, C., Koepernik, K., van den Brink, J., Wurmehl, S., and Büchner, B. *Phys. Rev. B* **93**, 014434 (2016).
- [220] Terzic, J., Zheng, H., Ye, F., Zhao, H. D., Schlottmann, P., De Long, L. E., Yuan, S. J., and Cao, G. *Phys. Rev. B* **96**, 064436 (2017).

- [221] Paul, A. K., Reehuis, M., Ksenofontov, V., Yan, B., Hoser, A., Többens, D. M., Abdala, P. M., Adler, P., Jansen, M., and Felser, C. *Phys. Rev. Lett.* **111**, 167205 (2013).
- [222] Kobayashi, K.-I., Kimura, T., Tomioka, Y., Sawada, H., Terakura, K., and Tokura, Y. *Phys. Rev. B* **59**, 11159–11162 (1999).
- [223] Das, H., Sanyal, P., Saha-Dasgupta, T., and Sarma, D. D. *Phys. Rev. B* **83**, 104418 (2011).
- [224] Wang, J., Meng, J., and Wu, Z. *Chemical Physics Letters* **501**(4), 324 – 329 (2011).
- [225] Paul, A. K., Jansen, M., Yan, B., Felser, C., Reehuis, M., and Abdala, P. M. *Inorganic Chemistry* **52**(11), 6713–6719 (2013).
- [226] Morrow, R., Mishra, R., Restrepo, O. D., Ball, M. R., Windl, W., Wurmehl, S., Stockert, U., Büchner, B., and Woodward, P. M. *Journal of the American Chemical Society* **135**(50), 18824–18830 (2013).
- [227] Johnsson, M. and Lemmens, P. *Crystallography and Chemistry of Perovskites*. American Cancer Society (2007).
- [228] Rijssenbeek, J., Huang, Q., Erwin, R., Zandbergen, H., and Cava, R. *Journal of Solid State Chemistry* **146**(1), 65 – 72 (1999).
- [229] Stephens, P. W. *Journal of Applied Crystallography* **32**(2), 281–289 (1999).
- [230] Kimber, S. A. J., Senn, M. S., Fratini, S., Wu, H., Hill, A. H., Manuel, P., Attfield, J. P., Argyriou, D. N., and Henry, P. F. *Phys. Rev. Lett.* **108**, 217205 (2012).
- [231] Stitzer, K. E., Smith, M. D., Gemmill, W. R., and zur Loye, H.-C. *Journal of the American Chemical Society* **124**(46), 13877–13885 (2002).

- [232] zur Loye, H.-C., Kim, S.-J., Macquart, R., Smith, M. D., Lee, Y., and Vogt, T. *Solid State Sciences* **11**(3), 608 – 613 (2009).
- [233] Boseggia, S., Walker, H. C., Vale, J., Springell, R., Feng, Z., Perry, R. S., Sala, M. M., Rønnow, H. M., Collins, S. P., and McMorro, D. F. *Journal of Physics: Condensed Matter* **25**(42), 422202 (2013).
- [234] Ming, X., Wan, X., Autieri, C., Wen, J., and Zheng, X. *Phys. Rev. B* **98**, 245123 (2018).
- [235] Villain, J. *Zeitschrift für Physik B Condensed Matter* **33**(1), 31–42 (1979).
- [236] Lee, S.-H., Takagi, H., Louca, D., Matsuda, M., Ji, S., Ueda, H., Ueda, Y., Katsufuji, T., Chung, J.-H., Park, S., Cheong, S.-W., and Broholm, C. *Journal of the Physical Society of Japan* **79**(1), 011004 (2010).
- [237] Ueland, B. G., Gardner, J. S., Williams, A. J., Dahlberg, M. L., Kim, J. G., Qiu, Y., Copley, J. R. D., Schiffer, P., and Cava, R. J. *Phys. Rev. B* **81**, 060408 (2010).
- [238] van Duijn, J., Hur, N., Taylor, J. W., Qiu, Y., Huang, Q. Z., Cheong, S.-W., Broholm, C., and Perring, T. G. *Phys. Rev. B* **77**, 020405 (2008).
- [239] Imry, Y. and Ma, S.-k. *Phys. Rev. Lett.* **35**, 1399–1401 (1975).
- [240] Pal, A., Singh, P., Gangwar, V. K., Ghosh, S., Prakash, P., Saha, S. K., Das, A., Kumar, M., Ghosh, A. K., and Chatterjee, S. *Applied Physics Letters* **114**(25), 252403 (2019).
- [241] Senn, M. S., Arevalo-Lopez, A. M., Saito, T., Shimakawa, Y., and Attfield, J. P. *Journal of Physics: Condensed Matter* **25**(49), 496008 (2013).
- [242] Mott, N. F. and Davis, E. A. *Electronic processes in non-crystalline materials*. Oxford university press, (2012).

- [243] Hinatsu, Y. and Doi, Y. *Bulletin of the Chemical Society of Japan* **76**(6), 1093–1113 (2003).
- [244] Edwards, S. F. and Vilgis, T. *Physica Scripta* **T13**, 7–16 (1986).
- [245] Ito, A., Aruga, H., Torikai, E., Kikuchi, M., Syono, Y., and Takei, H. *Phys. Rev. Lett.* **57**, 483–486 (1986).
- [246] Ghara, S., Jeon, B.-G., Yoo, K., Kim, K. H., and Sundaresan, A. *Phys. Rev. B* **90**, 024413 (2014).
- [247] Sidebottom, D., Green, P., and Brow, R. *Journal of Non-Crystalline Solids* **183**(1), 151 – 160 (1995).
- [248] Anand, K., Pal, A., Singh, P., Alam, M., Joshi, A. G., Mohan, A., and Chatterjee, S. *arXiv:1910.13734* (2019).
- [249] Hardy, V., Maignan, A., Hébert, S., and Martin, C. *Phys. Rev. B* **67**, 024401 (2003).
- [250] Yamashita, S., Yamamoto, T., Nakazawa, Y., Tamura, M., and Kato, R. *Nature communications* **2**, 275 (2011).
- [251] Schliesser, J. M. and Woodfield, B. F. *Phys. Rev. B* **91**, 024109 (2015).
- [252] Balents, L. *Nature* **464**, 199–208 (2010).
- [253] Zhou, H. D., Choi, E. S., Li, G., Balicas, L., Wiebe, C. R., Qiu, Y., Copley, J. R. D., and Gardner, J. S. *Phys. Rev. Lett.* **106**, 147204 (2011).
- [254] Garg, C., Kumar, J., and Nair, S. *Phys. Rev. Materials* **2**, 094409 (2018).
- [255] Fiebig, M., Lottermoser, T., Meier, D., and Trassin, M. *Nature Reviews Materials* **1**, 16046 (2016).

- [256] Nan, C.-W. and Liu, J.-M. *National Science Review* **6**(4), 620–620 (2019).
- [257] Spaldin, N. A. and Ramesh, R. *Nature materials* **18**(3), 203 (2019).
- [258] Cheong, S.-W. and Mostovoy, M. *Nat Mater* **6**, 13–20 (2007).
- [259] Tokura, Y., Seki, S., and Nagaosa, N. *Reports on Progress in Physics* **77**(7), 076501 (2014).
- [260] Kleemann, W. and Binek, C. *Multiferroic and Magnetoelectric Materials*, 163–187. Springer Berlin Heidelberg, Berlin, Heidelberg (2013).
- [261] Kleemann, W., Borisov, P., Shvartsman, V. V., and Bedanta, S. *EPJ Web of Conferences* **29**, 00046 (2012).
- [262] Malibert, C., Dkhil, B., Kiat, J. M., Durand, D., Bérrar, J. F., and de Biré, A. S. *Journal of Physics: Condensed Matter* **9**(35), 7485–7500 (1997).
- [263] Binder, K. and Young, A. P. *Rev. Mod. Phys.* **58**, 801–976 (1986).
- [264] Shvartsman, V. V., Bedanta, S., Borisov, P., Kleemann, W., Tkach, A., and Vilarinho, P. M. *Phys. Rev. Lett.* **101**, 165704 (2008).
- [265] Kleemann, W., Shvartsman, V. V., Bedanta, S., Borisov, P., Tkach, A., and Vilarinho, P. M. *Journal of Physics: Condensed Matter* **20**(43), 434216 (2008).
- [266] Kleemann, W., Bedanta, S., Borisov, P., Shvartsman, V. V., Miga, S., Dec, J., Tkach, A., and Vilarinho, P. M. *The European Physical Journal B* **71**(3), 407 (2009).
- [267] Shvartsman, V. V., Bedanta, S., Borisov, P., Kleemann, W., Tkach, A., and Vilarinho, P. M. *Journal of Applied Physics* **107**(10), 103926 (2010).

- [268] Choudhury, D., Mandal, P., Mathieu, R., Hazarika, A., Rajan, S., Sundaresan, A., Waghmare, U. V., Knut, R., Karis, O., Nordblad, P., and Sarma, D. D. *Phys. Rev. Lett.* **108**, 127201 (2012).
- [269] Singh, K., Maignan, A., Simon, C., Kumar, S., Martin, C., Lebedev, O., Turner, S., and Tendeloo, G. V. *Journal of Physics: Condensed Matter* **24**(22), 226002 (2012).
- [270] Choudhury, D., Mukherjee, S., Mandal, P., Sundaresan, A., Waghmare, U. V., Bhattacharjee, S., Mathieu, R., Lazor, P., Eriksson, O., Sanyal, B., Nordblad, P., Sharma, A., Bhat, S. V., Karis, O., and Sarma, D. D. *Phys. Rev. B* **84**, 125124 (2011).
- [271] Valant, M., Kolodiazhnyi, T., Arčon, I., Aguesse, F., Axelsson, A.-K., and Alford, N. M. *Advanced Functional Materials* **22**(10), 2114–2122 (2012).
- [272] Meher, K. P., Bogicevic, C., Janolin, P.-E., and Varma, K. *Journal of Solid State Chemistry* **192**, 296 – 304 (2012).
- [273] Tackett, R., Lawes, G., Melot, B. C., Grossman, M., Toberer, E. S., and Seshadri, R. *Phys. Rev. B* **76**, 024409 (2007).
- [274] Suzuki, T. and Katsufuji, T. *Phys. Rev. B* **77**, 220402 (2008).
- [275] Lebedev, A., Sluchinskaya, I., Erko, A., and Kozlovskii, V. *JETP Letters* **89**(9), 457–460 (2009).
- [276] Trybuła, Z., Łoś, S., Miga, S., Kempański, W., Dec, J., and Trybuła, M. *Materials Chemistry and Physics* **219**, 278 – 282 (2018).
- [277] Fujishita, H., Kitazawa, S., Saito, M., Ishisaka, R., Okamoto, H., and Yamaguchi, T. *Journal of the Physical Society of Japan* **85**(7), 074703 (2016).

-
- [278] Barrett, J. H. *Phys. Rev.* **86**, 118–120 (1952).
- [279] Venturini, E., Samara, G., Laguta, V., Glinchuk, M., and Kondakova, I. *Physical Review B* **71**(9), 094111 (2005).
- [280] Rowley, S. E., Spalek, L. J., Smith, R. P., Dean, M. P. M., Itoh, M., Scott, J. F., Lonzarich, G. G., and Saxena, S. S. *Nature Physics* **10**, 367 (2014).
- [281] Pai, Y.-Y., Tylan-Tyler, A., Irvin, P., and Levy, J. *Reports on Progress in Physics* **81**(3), 036503 (2018).
- [282] Valant, M., Kolodiazny, T., Axelsson, A.-K., Babu, G. S., and Alford, N. M. *Chemistry of Materials* **22**(6), 1952–1954 (2010).
- [283] Kuzian, R. O., Laguta, V. V., Daré, A., Kondakova, I. V., Marysko, M., Raymond, L., Garmash, E. P., Pavlikov, V. N., Tkach, A., Vilarinho, P. M., and Hayn, R. *EPL (Europhysics Letters)* **92**(1), 17007 (2010).