

Crystal growth, magnetic and thermal properties of quasi two-dimensional quantum magnets

विद्या वाचस्पति की
उपाधि की अपेक्षाओं की आंशिक पूर्ति में प्रस्तुत शोध प्रबंध

A thesis submitted in partial fulfillment of the requirements of the
degree of Doctor of Philosophy

द्वारा / By
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भारतीय विज्ञान शिक्षा एवं अनुसंधान संस्थान पुणे
INDIAN INSTITUTE OF SCIENCE EDUCATION AND RESEARCH PUNE

2024

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Title of Thesis:

Crystal growth, magnetic and thermal properties of quasi two-dimensional quantum magnets

I declare that this written submission represents my idea in my own words and where others ideas have been included; I have adequately cited and referenced the original sources. I declare that I have acknowledged collaborative work and discussions wherever such work has been included. I also declare that I have adhered to all principles of academic honesty and integrity and have not misrepresented or fabricated or falsified any idea/data/fact/source in my submission. I understand that violation of the above will be cause for disciplinary action by the Institute and can also evoke penal action from the sources which have thus not been properly cited or from whom proper permission has not been taken when needed.

The work reported in this thesis is the original work done by me under the guidance of

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Acknowledgments

The PhD journey is an intense adventure, filled with evolving experiments, endless questions, and unexpected twists at every stage of research. It's a true test of patience, resilience, and determination to push through failed trials and elusive results. But, in all honesty, none of it would have been possible without the support and encouragement of those who stood by me through every high and low.

I am grateful to my supervisor, Prof. Surjeet Singh, whose analytical skills, creativity and curiosity to understand the tiny details of the experiments and deep understanding of fundamental concepts helped me to overcome the complex problems which were difficult to understand in my systems and have been a constant support throughout my PhD. His genuine belief in me, kept me going, especially during times when experiments seemed impossible and my confidence wavered. He always knew just how to help me see things in a new light and encouraged me to keep trying. His patience, kindness, and encouragement have made all the difference in this journey, and I am truly thankful to have had him as a mentor.

I would like to express my sincere gratitude to my RAC members, Prof. Zakir Hussain and Prof. Mukul Kabir, for their valuable suggestions and guidance during the annual RAC meetings.

I am grateful to Dr. Surajit Saha and his student, Devesh Negi, for their collaboration and support in conducting low-temperature Raman measurements in their laboratory. I extend my appreciation to Dr. Rajeev Rawat at the UGC-DAE Consortium for Scientific Research in Indore, Madhya Pradesh, where I performed low-temperature heat capacity and magnetic measurements. A special thanks to Priyanshi Tiwari, a second-year PhD student in Dr. Rawat's lab, for her assistance during late-night measurements to ensure completion within the allotted time. I am also thankful to Prof. G. V. Pavan Kumar and his student, Ashutosh Shukla, for the opportunity to carry out room-temperature Raman measurements. My thanks go to Prof. Nirmalya Ballav for allowing me to perform Raman measurements in his lab's setup. I am thankful to Prof. Abhay Shukla for his collaboration on Raman and PL

measurements performed on single crystals grown in our lab. I am also grateful for his approval for me to work in his lab for three months under the Erasmus Exchange Programme, though unfortunately, I could not visit due to the COVID-19 pandemic. I am grateful to Prof. Avinash Mahajan and his student, Dr. Sanjay Bachhar, for their collaboration on multiple systems. I deeply appreciate Prof. Mahajan's participation in my RAC meetings and his valuable guidance and suggestions, which helped me advance in my research. Lastly, I thank Dr. Sitaram Ramakrishna for his collaboration in solving the single crystal x-ray diffraction data.

None of this would have been possible without the research-driven environment and outstanding infrastructure provided by IISER Pune. I am particularly grateful to the technical staff for their support in maintaining the research instruments. Special thanks to Mr. Nilesh Dumbre and Mr. Karthikeyan for their help in repairing the PPMS. I also extend my sincere appreciation to Mr. Anil Prathamshetti, Mr. Sudhir Lone, Mr. Yatish, for their invaluable technical assistance throughout my PhD journey. Thanks to Mr. Parveen Nasa and Mr. Ravinder for arranging SCXRD slots. Additionally, I am deeply thankful to the non-academic staff, especially Mr. Prabhakar Anagare, Mrs. Dhanashree, Mr. Prabhas, Mrs. Sayalee, Mr. Tushar, and Mr. Ranjan for their unwavering support.

I would like to express my heartfelt gratitude to the Council for Scientific and Industrial Research (CSIR) for providing me with the Ph.D. fellowship STARS funding (sanction order no. STARS/APR2019/PS/358/FS) which has been instrumental in supporting my research journey. I am also deeply thankful to the Science and Engineering Research Board (SERB) for granting international travel support, which enabled me to attend an international conference SCES 2023 held in South Korea. Furthermore, I extend my sincere appreciation to Infosys for their generous funding that covered my accommodation during the conference. My gratitude also goes to the Department of Physics at IISER Pune for their financial assistance in covering additional travel expenses and food costs during my stay. These contributions were pivotal in making my participation in the conference a fruitful and enriching experience.

I owe the knowledge and insights I have gained during my Ph.D. to the invaluable guidance and mentorship of Luminita Maam. She has been an extraordinary presence in my life. Starting with her academic contributions to my PhD journey, she is an exceptionally skilled and knowledgeable materials scientist. Her expertise in crystal growth allowed me to grasp the fundamentals of designing a crystal growth experiment and understanding the thermodynamics of the process. Her practical tips and techniques saved me countless hours of work, making the challenges far more manageable. Every discussion with her about a chemical reactions left me with valuable insights and ideas for my experiments. When experiments seemed hopeless and nothing seemed to work, she would always remind me to "take a pulse" and keep moving forward, a small but powerful nudge that helped me overcome some of my toughest moments. Beyond her tremendous support in my academic life, she has also been an incredible friend, someone anyone would be lucky to have in their life. Our long conversations not only helped relieve stress but also provided clarity and solutions to many of my problems. And as an exceptional baker, she made a memorable impression on my family; my daughter still fondly remembers the delicious strawberry cake she offered us. I will always cherish the memorable times spent with her, both in the lab and beyond.

I would like to thank my seniors, Saurabh, Dibyata, and Navita, who were always willing to help with anything, big or small, no matter what time of day I asked. Many thanks to Dibyata who trained me for PPMS measurement and analyzing the data and various other long discussions where she always tries to give her full input. Thanks to Navita and Saurabh for thier help in operation of TGDSC instrument. I am also grateful to all my lab members, including my batchmates Ankit and Sagar, and my juniors Dinesh, Pankaj, and Prabhu, who were always there to lend a hand and helped create a supportive atmosphere in the lab.

Last but certainly not least, this PhD journey would not have been possible without the unwavering support of my family. My husband has been an extraordinary source of encouragement, always pushing me to recognize my true potential. Not only did he support me in fulfilling my dreams, but he actively helped me pursue them. My father has been a pillar of strength, standing by me through every challenge, no matter the circumstances. And then

there is the most beautiful creation on earth, my mother, whose support has been nothing short of extraordinary. She selflessly cared for both her daughter and granddaughter, ensuring that my daughter never felt my absence, whether I was away for weeks at conferences or conducting experiments. I dedicate this thesis to my mother, without whose love and support this journey would have been not just difficult, but truly impossible.

Dedicated to my Mother.....

**Our greatest weakness lies in giving up. The most certain way to succeed is always to
try just one more time**
- Thomas Edison

Abstract

Quantum materials is a broad and evolving term with no universally agreed-upon definition. Generally, materials are considered quantum in nature when their specific properties cannot be fully explained using classical paradigms and are intrinsically governed by quantum mechanical principles. Initially, the term "quantum materials" was associated with strongly correlated electron systems, such as heavy fermion systems and high-temperature superconductors. Over time, it has expanded to encompass a wide range of systems, including low-dimensional quantum magnets, two-dimensional van der Waals materials, frustrated spin systems (e.g., spin-1/2 or spin-1), semimetals (Dirac, Weyl, and nodal-line semimetals), two-dimensional and three-dimensional topological insulators, and more. On a microscopic scale, these materials involve the complex interplay of huge number of electrons interacting with each other or with ions in the materials in ways that give rise to exotic phases of matter. These phenomena often challenge conventional understanding and remain a frontier of exploration. Examples include quantum spin liquids with fractionalized excitations, quantum spin ices, the up-up-down (uud) field-induced 1/3 magnetization plateau in triangular lattice antiferromagnets, exotic multiband superconductivity in iron pnictides, large and non-saturating positive magnetoresistance in topological semimetals, the chiral anomaly in Weyl semimetals, and remarkable effects like the giant anomalous Nernst and Hall effects in topological materials. These discoveries illustrate the rich and diverse physics enabled by the quantum nature of these systems.

A notable special case within quantum materials is the realm of two-dimensional (2D) magnets. These materials consist of atomically thin layers, often just a few atoms thick, where quantum effects are significantly enhanced due to their reduced dimensionality. In traditional three-dimensional materials, magnetic order is typically governed by long-range interactions that diminish in lower dimensions. However, 2D magnets defy these classical rules and maintain magnetic order down to a single atomic layer in some systems which provides a unique opportunity to explore quantum magnetism in reduced dimensions. Moreover, 2D magnets are highly tunable, with their magnetic properties easily controlled by

external factors such as electric fields or strain, making them ideal for next-generation technologies. Their integration with other 2D materials, like graphene, makes them promising candidates for applications in spintronics, quantum information processing, and advanced magnetic memory devices. Hence exploring new 2D magnets or reinvestigating the huge pool of existing 2D magnets is essential for the discovery of new exotic quantum phases which not only deepen our understanding of fundamental physics but also pave the way for future technological applications in areas like quantum computing, spintronics, and low-power electronic devices.

This thesis focusses on the high-quality single crystal growth of novel low-dimensional honeycomb quantum magnets where the magnetic spins are decorated on the honeycomb or pseudo honeycomb lattice. By employing various crystal growth techniques and optimizing the thermodynamic conditions, We have grown defect/impurity free large high-quality single crystals of these materials. The absence of defects and impurities is essential for accurately probing the intrinsic physical properties of these materials, which can otherwise be obscured or altered. The structural quality of the grown single crystals is rigorously characterized using a range of X-ray diffraction methods to ensure the high-quality of the crystals. Following this, detailed investigations of magnetic and thermal properties are carried out in order to reveal the nature of their magnetic ground states, and the effect of external perturbations, such as, doping, and applied magnetic field

Chapter 1 of this thesis provides an introduction to the development and recent advances in the field of 2D materials, with a focus on the unique advantages of 2D magnets where the spin degrees of freedom are coupled with lattice and electronic degrees of freedom. It offers an overview of the exotic physics arising in low-dimensional magnets and explores how the properties of these materials can be tuned through various external perturbations. A detailed discussion is dedicated to the quantum spin liquid state, and in particular Kitaev quantum spin liquid. Additionally, other relevant phenomena, such as the negative charge transfer insulator and the magnetocaloric effect, both crucial for understanding the findings presented in later chapters, are briefly introduced.

Chapter 2 of this thesis provides a detailed discussion of the crystal growth methods used to produce high-quality single crystals of various low-dimensional magnets, with a particular emphasis on the vapor transport method. It explores key aspects of the vapor transport technique aimed at enhancing both the quality and size of the grown crystals. Additionally, the chapter covers the directional solidification of crystals from melt using the Bridgman-Stockbarger technique. The chapter also explains the basic principles and operation of various experimental techniques used to characterize the structure and homogeneity of the grown crystals, as well as to investigate their magnetic and thermal properties. Finally, practical tips and strategies are presented for utilizing these techniques effectively, with a special focus on handling highly hygroscopic samples without compromising the quality of the samples.

Chapter 3 summarizes first report on the crystal growth of YbI_3 , a quasi-two-dimensional van der Waals magnet with a structure similar to the low-temperature polymorphs of $\alpha\text{-RuCl}_3$, where the magnetic Yb^{3+} ions with $j_{\text{eff}} = 1/2$ are arranged on an ideal honeycomb lattice, making it an ideal template to realize Kitaev physics. Large single crystals, on the order of centimeters in size, were grown using a vapor transport reaction by carefully manipulating the growth parameters. Magnetization measurements reveal easy-plane-like anisotropy, and heat capacity measurements show distinct transitions below 1 K, indicative of both short-range and long-range antiferromagnetic ordering. Additionally, an unconventional ground state is observed with a critical exponent value of $\alpha = 2.5$ obtained by fitting the low-temperature upturn attributed to the nuclear Schottky anomaly.

Chapter 4 of this thesis focuses on optimizing the single-crystal growth of rare earth triiodides. These compounds crystallize in two distinct symmetries: the lighter rare earth iodides adopt an orthorhombic structure, while the heavier ones form a trigonal symmetry analogous to $\alpha\text{-RuCl}_3$. The crystallographic details and chemical homogeneity of the grown single crystals are thoroughly examined using various experimental techniques. Additionally, heat capacity and magnetization measurements are conducted down to 2 K to explore the magnetic and thermal properties of the rare earth tri-iodides.

Chapter 5 of this thesis, describes the growth of high-quality single crystals of CeCl_3

where the Magnetic Ce^{3+} ions with spin $1/2$ are arranged on the psuedo honeycomb lattice formig the hexagonal structure in 3D. The crystals were grown using an image furnace by employing the Bridgman method, where the homogeneous melt is slowly cooled from the hot zone of the image furnace to the cold zone to obtain single crystals of CeCl_3 . To prevent the crystals from cracking, we experimented with varying the speed of the growth ampoule's movement from the hot to cold zone, ultimately determining an optimized speed that yields crack-free single crystals. The crystals were then aligned, and preliminary magnetization and heat capacity measurements were performed. The preliminary measurements reveal significant anisotropy in the magnetization along the parallel and perpendicular orientations of the crystallographic c -axis. Small exchange coupling between the Ce moments leading to a very low long-range ordering temperature (0.01 K) and large out-of-plane anisotropy are indicative of potential magnetocaloric properties. The magnetocaloric effect was estimated indirectly using magnetization isotherms. CeCl_3 exhibits a magnetic entropy change of $-23 \text{ J/mol}\cdot\text{K}$ at 5T and 2K, suggesting its potential as a magnetocaloric material and a possible candidate for cryogenic magnetic cooling under favorable conditions.

Chapter 6 focuses on NiPS_3 , a van der Waals antiferromagnet in which the magnetic Ni ions with spin = 1 form a zigzag-type antiferromagnetic arrangement on the honeycomb lattice. NiPS_3 has previously been shown to exhibit spin-charge coupling and spin-phonon coupling below the ordering temperatures. In this study, we demonstrate for the first time, using an asymmetric Fano lineshape in Raman spectroscopy, that NiPS_3 shows charge-phonon coupling at room temperature. This evidence is further supported by studying Zn-doped NiPS_3 single crystals, which show an increasing charge-phonon coupling with increasing dilution of Zn at the Ni site. This is explained by the fact that NiPS_3 is a negative charge transfer insulator, meaning that Ni in NiPS_3 is not only in the d^8 state, but also in a linear combination of d^8 , d^9 , and d^{10} states. The additional charge carriers on Ni due to the NCT behavior eventually lead to electron-phonon coupling in both parent and diluted NiPS_3 .

In **Chapter 7** we summarize the new findings from the work conducted in this thesis and conclude by providing a broad outlook on the future potential of the investigated systems,

both in terms of fundamental research and practical applications.

The Appendix section of this thesis provides a detailed description of the crystal growth process of α -RuCl₃ using the vapor transport technique. Various factors influencing the growth of high-quality, large single crystals of α -RuCl₃, free from impurities and stacking faults, are discussed comprehensively. Additionally, efforts to introduce spin vacancies in α -RuCl₃ by substituting Ru ions with non-magnetic ions are described. To this end, doping experiments were conducted with Al, In, Sc, Ir, and Y at the Ru site. The challenges encountered during the doping process are addressed, and successful outcomes with some dopants, such as Sc, Ir, and Y, are summarized in this chapter. The experience gained in overcoming the challenges of achieving high-quality α -RuCl₃ crystals using the vapor transport method provided valuable insights into the crystal growth process. This knowledge was instrumental in successfully growing RX₃ compounds (where X = Cl or I, and R is a rare earth element in the +3 oxidation state), as detailed in Chapters 3 and 4 of this thesis.

List of publications

- *Anisotropic magnetic ground state of single-crystalline quasi-two-dimensional honeycomb antiferromagnet YbI_3* ; **Nashra Pistawala**, Luminita Harnagea, Sitaram Ramakrishnan, Priyanshi Tiwari, M. P. Saravanan, Rajeev Rawat and Surjeet Singh, Phys. Rev. B 110, 104421 (2024).
- *Crystal growth and magnetic properties of rare earth triiodides quasi two-dimensional quantum magnets*; **Nashra Pistawala**, Luminita Harnagea, Sitaram Ramakrishnan, Ashutosh Shukla, G. V. Pavan Kumar, Priyanshi Tiwari, Rajeev Rawat and Surjeet Singh,(to be submitted).
- *Crystal growth, magnetic and magnetocaloric properties of $J_{eff} = 1/2$ quantum antiferromagnet CeCl_3* ; **Nashra Pistawala**, Luminita Harnagea, Suman Karmakar, Rajeev Rawat, and Surjeet Singh, Phys. Rev. Materials 8, 076201 (2024).
- *Probing electron-phonon coupling in magnetic van der Waals material NiPS_3 : A non-magnetic site-dilution study*; **Nashra Pistawala**, Ankit Kumar, Devesh Negi, Dibyata Rout, Luminita Harnagea, Surajit Saha and Surjeet Singh, 2D Mater. 11, 025035 (2024).
- *Single Crystal Growth and Properties of 2D Antiferromagnet $\text{Ni}_{1-x}\text{Zn}_x\text{PS}_3$* ; **Nashra Pistawala**, Ankit Kumar, Dibyata Rout, Luminita Harnagea, and Surjeet Singh, New Phys.: Sae Mulli; 73: 1140-1144 (2023).
- *Crystal growth of quantum materials: a review of selective materials and techniques*; **Nashra Pistawala**, Dibyata Rout, Kumar Saurabh, Rabindranath Bag, Koushik Karmakar, Luminita Harnagea and Surjeet Singh, Bull Mater Sci, 45, 10 (2022).

Additional Publication

- *Tuning the robust magnetic properties in MPS_3 ($M = Mn, Fe, \text{ and } Ni$) by proximity-induced Dzyaloshinskii-Moriya interactions*; Suvodeep Paul, Devesh Negi, Saswata Talukdar, Saheb Karak, Shalini Badola, Bommareddy Poojitha, Manasi Mandal, Sourav Marik, R. P. Singh, **Nashra Pistawala**, Luminita Harnagea, Aksa Thomas, Ajay Soni, Subhro Bhattacharjee, and Surajit Saha, Phys. Rev. B 109, 085136 (2024).
- *Gate and Temperature Driven Phase Transitions in Few-Layer $MoTe_2$* ; Hugo Kowalczyk, Johan Biscaras, **Nashra Pistawala**, Luminita Harnagea, Surjeet Singh, Abhay Shukla, ACS Nano, 17, 7, 6708 (2023).

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Chapter 1

Introduction

1.1 Two-dimensional materials

The field of two-dimensional (2D) materials began with the groundbreaking discovery of graphene in 2004 by Novoselov and Geim [22]. Graphene is a single layer of carbon atoms arranged in a honeycomb-like hexagonal structure. This atomic arrangement leads to remarkable properties, such as extraordinarily high electrical conductivity, mechanical strength, flexibility, and thermal conductivity. The zero bandgap and massless Dirac fermions in graphene give rise to its exceptional electronic properties, including ultra-high electron mobility, which is essential for nanoelectronics and next-generation transistors [23]. This discovery won Novoselov and Geim the Nobel Prize in Physics in 2010 [24], setting off a global research boom focused on exploring other atomically thin materials. However, despite its numerous advantages, graphene's lack of an intrinsic bandgap limits its applications in semiconductor and optoelectronic devices. Researchers thus began looking beyond graphene to other 2D materials that could offer tunable electronic properties. This exploration led to the emergence of several other classes of 2D materials, each with unique characteristics and potential applications [25].

After graphene, transition metal dichalcogenides (TMDs) like MoS_2 , WS_2 , and WSe_2 garnered substantial interest [26]. TMDs consist of a transition metal atom (e.g., Mo, W)

sandwiched between two layers of chalcogen atoms (S, Se, Te). Unlike graphene, which is a semi-metal, TMDs can exhibit semiconducting behavior, with a bandgap that changes from indirect in the bulk form to direct in the monolayer form. This tunable bandgap is a crucial property for optoelectronic devices, photodetectors, and transistors. MoS₂, for example, is one of the most widely studied TMDs for its potential use in field-effect transistors (FETs). Its monolayer form exhibits a direct bandgap of 1.8 eV, making it suitable for light-emitting devices and phototransistors [27]. WS₂ and WSe₂ are also significant for their strong spin-orbit coupling and potential applications in spintronics and valleytronics [28], where the control of electron valleys in momentum space is used to encode information. TMDs have also shown promise in flexible electronics due to their mechanical resilience, making them suitable for wearable devices and foldable technologies. Additionally, the ability to create atomically thin heterostructures by stacking different TMD layers leads to fascinating new phenomena, including tunneling devices and novel quantum states [29]

Hexagonal boron nitride (h-BN), sometimes referred to as white graphene, is another significant 2D material [30]. Unlike graphene and TMDs, h-BN is an insulator with a wide bandgap of around 5.9 eV. It is known for its chemical and thermal stability, making it an excellent substrate and dielectric material in electronic devices [31]. One of the key roles of h-BN is in van der Waals heterostructures, where it is used as a smooth, defect-free substrate for other 2D materials like graphene. This helps improve the electronic properties of the overlying materials by reducing charge impurities and enhancing mobility. The insulating nature of h-BN has made it crucial for the development of high-performance 2D transistors, where it acts as an ideal dielectric spacer, reducing electronic noise and improving overall device performance. Phosphorene, the monolayer form of black phosphorus (BP), emerged as an exciting new 2D material in 2014 due to its tunable direct bandgap and high charge carrier mobility. The bandgap of phosphorene can be tuned by varying the number of layers, making it useful for electronic and optoelectronic applications like transistors, sensors, and solar cells [32]. Its higher mobility compared to TMDs makes phosphorene a promising material for applications that require fast charge transport. However, phosphorene's susceptibility

to degradation in ambient conditions (due to its reactivity with oxygen and water) presents challenges, leading researchers to explore protective encapsulation techniques to stabilize it for practical applications. MXenes, a relatively new class of 2D transition metal carbides and nitrides, have gained attention for their unique electronic, magnetic, and electrochemical properties. MXenes are synthesized from layered MAX phases, which are ceramics composed of transition metals, aluminum, and carbon or nitrogen [33].

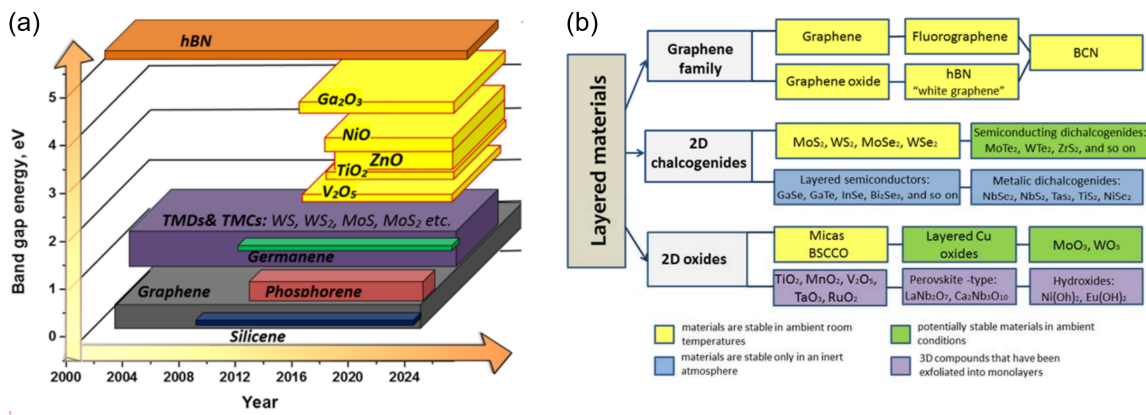


Figure 1.1: Progress in 2d materials. (a) A visual representation showing the progression of 2D material families over time (horizontal axis) along with their corresponding band gap values (vertical axis). (b) A diagram depicting the organized collection of various 2D materials. The images are adapted from ref [1].

While 2D materials like graphene, TMDs, and MXenes summarized in Fig. 1.1 have shown immense potential in electronics and optoelectronics, the inclusion of magnetism can significantly broaden their scope of applications. Magnetism in 2D materials would enable spin-based technologies, such as spintronics, which utilizes the electron's spin in addition to its charge, leading to faster and more energy-efficient devices. This could revolutionize data storage by enabling non-volatile memory that requires less power and offers greater storage density. Moreover, integrating magnetism into 2D systems could unlock new possibilities in quantum technologies, allowing for the control of quantum states and spin dynamics at the atomic level, which is essential for quantum computing and advanced sensing technologies. However, the lack of intrinsic magnetism in most existing 2D materials has driven the search for magnetic counterparts, as adding this functionality could greatly enhance the versatility

and performance of these systems across various fields.

1.2 Emergence of two-dimensional magnets

The study of magnetic materials has long been a cornerstone of condensed matter physics, traditionally focusing on three-dimensional bulk systems where magnetic order is well understood. However, the discovery of two-dimensional (2D) materials has revolutionized this field by demonstrating that intriguing and novel properties can emerge in reduced dimensions. Among these properties, magnetism in 2D materials has garnered significant attention due to its potential implications for fundamental science and technological applications.

Efforts to isolate magnetic 2D materials commenced in 2016 with the exfoliation of monolayer and few-layer structures of NiPS_3 [34], FePS_3 [35, 36], and CrSiTe_3 [37]. These compounds exhibited intrinsic magnetic order in their bulk states, with Raman spectroscopy providing indirect evidence of magnetic retention in their reduced dimensions. A significant milestone was achieved in 2017 with the first unambiguous experimental observation of magnetism in atomically thin CrI_3 [38] and CrGeTe_3 [39], extending down to the monolayer and bilayer limits, respectively, both being magnetic insulators. Alternatively, recent findings have confirmed that 2D Fe_3GeTe_2 functions as a magnetic conductor [40]. These pioneering experiments have triggered widespread research into atomically thin magnetic crystals [3] summarized in Fig. 1.2, opening up vast opportunities with the advent of magnetic van der Waals (vdW) material [2].

These opportunities extend to the detailed investigation of several fundamental theoretical models. One such model is the Ising transition [41], which describes a critical phase transition in a system with discrete spin orientations. Another important phenomenon is the Berezinskii-Kosterlitz-Thouless (BKT) transition in the XY model, observed in two-dimensional systems. This transition involves the unbinding of skyrmions which are topological defects resembling vortex-antivortex pairs. Below the BKT transition temperature, skyrmions remain bound, leading to quasi-long-range order with algebraic decay of correlations. Above the transition temperature, skyrmions unbind, resulting in a disordered phase

Chalcogenides	$\text{Cr}_2\text{Ge}_2\text{Te}_6$, $\text{Cr}_2\text{Si}_2\text{Te}_6$, Fe_3GeTe_2 , VSe_2 , MnSe_x	FePS_3 , FePSe_3 , MnPS_3 , NiPS_3 , NiPSe_3 , CuCrP_2S_6 , AgVP_2S_6 , AgCrP_2S_6 , CrSe_2 , CrTe_3 , $\text{Ni}_3\text{Cr}_2\text{P}_2\text{S}_9$, MnBi_2Te_4 , MnBi_2Se_4	CuCrP_2S_6
Halides	CrI_3 , CrBr_3 , GdI_2	CrCl_3 , FeCl_2 , FeBr_2 , FeI_2 , MnBr_2 , CoCl_2 , CoBr_2 , NiCl_2 , VCl_2 , VBr_2 , VI_2 , FeCl_3 , FeBr_3 , CrOCl , CrOBr , CrSBr , MnCl_2 , VCl_3 , VBr_3	CuCl_2 , CuBr_2 , NiBr_2 , NiI_2 , CoI_2 , MnI_2
			$\alpha - \text{RuCl}_3$
			RX_3 (R = Rare earth element), (X = Cl , Br , I)
Others	VS_2 , InP_3 , GaSe , GaS	MnX_3 (X = F , Cl , Br , I), FeX_2 (X = Cl , Br , I), MnSSe , TiCl_3 , VCl_3	SnO , GeS , GeSe , SnS , SnSe , SnTe , GaTeCl , CrN , CrB_2

Figure 1.2: Library of some Van der Waals magnets. The color code in the Figure indicates the magnetic ground state of the system. The cyan color indicates the bulk ferromagnet, Magenta color indicates bulk antiferromagnetic, Yellow indicates bulk multiferroics, light blue color is a well kitaev quantum spin liquid candidate, Red color indicates the the antiferromagnetic with some of the materials has been experimentally shown to have layered nature and the one in purple color indicates theoretically predicted 2D materials. To know more details about these materials refer to ref [2].

with exponential decay of correlations. Understanding this transition is crucial for exploring how topological defects like skyrmions affect the collective behavior of two-dimensional systems, particularly those with broken inversion symmetry [42,43]. Additionally, the Mermin-Wagner theorem [44] states that in two-dimensional systems with continuous symmetries, spontaneous long-range order cannot exist at finite temperatures due to strong thermal fluctuations, which cause correlations to decay exponentially rather than algebraically. The development of new 2D materials provides an opportunity to explore the interplay between lattice and spin dimensionality. For instance, in the Ising model, spins can point either up or down ($n = 1$), while in the XY model, spins are confined to a plane ($n = 2$), and in the Heisenberg model, spins can orient in three dimensions ($n = 3$). This interplay is crucial for investigating magnetic states and can be influenced by external factors such as strain, light, electric gating, proximity effects, and moire patterns, as summarized in Fig. 1.3.

Furthermore, a wide range of intriguing quantum phases is anticipated to emerge, including phenomena such as the quantum Hall effect, quantum spin Hall effect, and quantum spin liquids. Among these, the Kitaev quantum spin liquid stands out due to its unique characteristics, most notably the presence of fractionalized excitations, like Majorana fermions,

which are predicted to arise from the highly frustrated interactions in the system. The discovery of such fractionalized particles in a condensed matter system presents an exciting avenue for future research, as it could potentially lead to breakthroughs in quantum computing and topological quantum matter. In light of this, we explore in detail some of the recent experimental and theoretical evidence of exotic physics within 2D magnetic systems. These materials, with their low-dimensionality and strong spin-orbit coupling, provide a fertile ground for observing novel quantum states, including those governed by unconventional magnetic interactions and topological excitations.

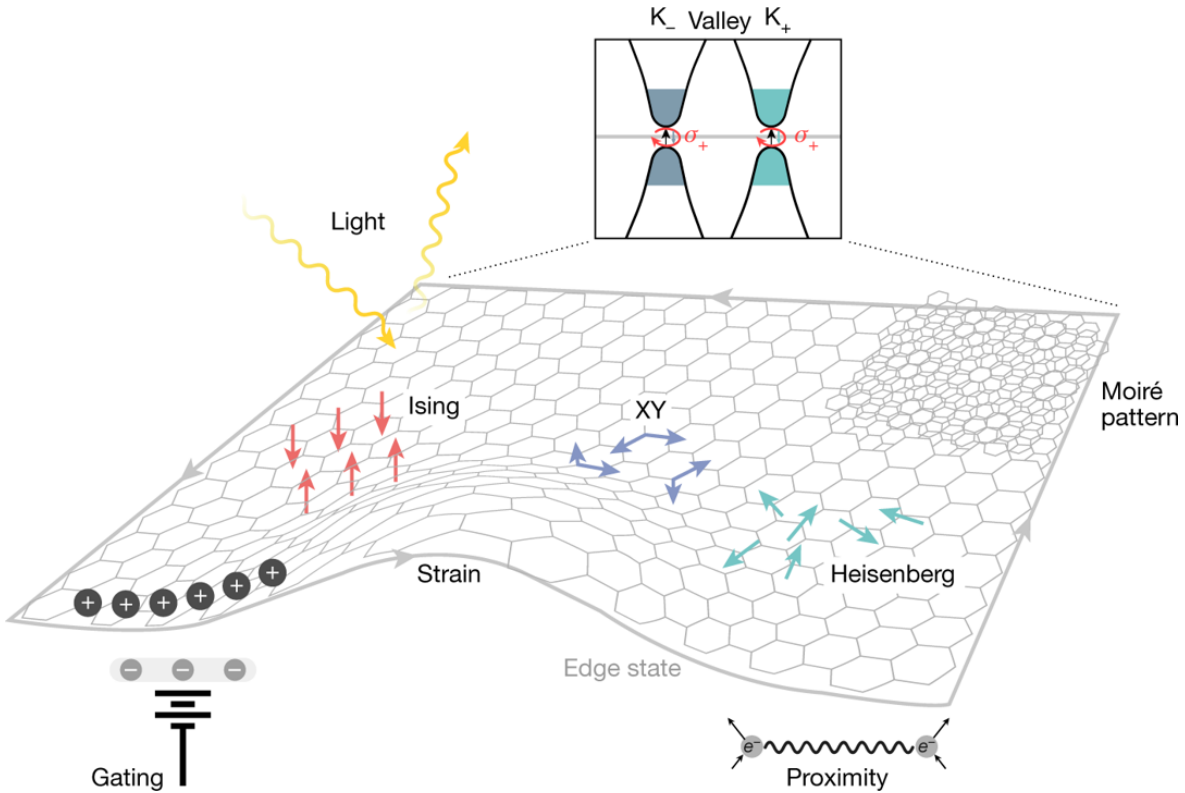


Figure 1.3: Two-dimensional magnetic van der Waals (vdW) materials offer a unique platform to study how the Hamiltonians of key magnetism models such as the Ising, XY, and Heisenberg models operate in the 2D regime shown by red purple and cyan arrows. Additionally, the magnetic ground states in these systems can be influenced by external stimuli like gating, strain, proximity effects, or moiré patterns. The honeycomb lattice structure of these materials also presents opportunities for light matter interactions through valley coupling at the K^+ and K^- points in momentum space, as well as via edge states. The image is adopted from the ref [3].

1.3 Quantum spin liquid

A quantum spin liquid (QSL) is an exotic phase of matter that remains disordered even at absolute zero temperature with no spontaneous symmetry breaking. Unlike traditional magnetic phases, such as ferromagnets, where a system transitions from a high-symmetry disordered state to a lower-symmetry ordered state as the temperature decreases, breaking rotational symmetry. Similarly, in antiferromagnets, spins align in an alternating pattern, breaking translational symmetry. The absence of long-range order despite having magnetic ions in the system with no symmetry breaking, even in the presence of strong interactions and long range entanglement, is a hallmark of quantum spin liquids and distinguishes them from other magnetic phases. But what is more interesting about QSL is the evidence of fractionalized quasi particle excitations and topological order [45,46]. Note that a QSL is fundamentally distinct from a classical spin liquid. The latter is because the thermal fluctuation energy $k_B T$ dominates over J , and the magnetic order is not established at high temperatures. The defining features, long-range entanglement and fractional spin excitations for a QSL are absent in such a classical state.

Quantum spin liquids (QSLs) typically arise in systems with geometrically frustrated lattices, where the geometry of the lattice prevents the antiferromagnetic arrangement of spins leading to frustration. Three key lattice structures that promote this frustration are the triangular, kagome, and pyrochlore lattices [47,48]. In a triangular lattice with antiferromagnetically interacting spins, the first two spins align antiferromagnetically. However, the third spin struggles to align in a way that satisfies the antiferromagnetic interactions with both of its neighbors. This frustration leads to a sixfold degenerate ground state, making it challenging to achieve a configuration that minimizes the energy of all neighboring spins simultaneously. This geometric frustration leading to strong quantum fluctuations, can stabilize a QSL phase, as seen in materials like YbMgGaO_4 [49] with no long range magnetic ordering down to lowest temperature measured. In contrast, the kagome lattice, composed of corner-sharing triangles, creates an even higher level of frustration. Here, spins cannot easily align,

resulting in a highly degenerate ground state. Herbertsmithite ($\text{ZnCu}_3(\text{OH})_6\text{Cl}_2$) is a notable example, showing no magnetic order down to very low temperatures, providing strong evidence for quantum spin liquid behavior [50]. In the pyrochlore lattice, a three-dimensional network of corner-sharing tetrahedra, frustration arises from the complex interactions between spins in this structure, particularly in systems with small spins. This frustration can prevent conventional magnetic order, allowing quantum spin liquids to form. Examples such as $\text{Tb}_2\text{Ti}_2\text{O}_7$ [51] and $\text{Pr}_2\text{Zr}_2\text{O}_7$ [52] exhibit this behavior, where the lack of long-range order suggests the existence of a QSL phase. In all of these cases triangular, kagome, and pyrochlore lattices geometric frustration plays a critical role in generating a QSL state. An important parameter that quantifies the degree of frustration is the frustration index denoted as f given by Arthur Ramirez [53]. The frustration index f can be expressed as:

$$f = \frac{|\Theta_{\text{CW}}|}{T_N} \quad \text{or} \quad f = \frac{|\Theta_{\text{CW}}|}{T_f} \quad (1.1)$$

Where:

- Θ_{CW} is the Curie-Weiss temperature, which is a measure of the strength of magnetic interaction between the nearest-neighbour spins within the mean-field framework, and represents the temperature at which spins should order in the absence of frustration. The sign of Θ_{CW} is negative for antiferromagnetic compounds and positive for ferromagnets.
- T_N is the actual ordering temperature (such as the Neel temperature in an antiferromagnet) where long-range order appears and T_f is the freezing temperature.

Interpretation:

- If $f = 1$, the system is unfrustrated.
- If $f > 1$, the system is frustrated and the actual ordering temperature T_N is much lower than $|\Theta_{\text{CW}}|$.

Values of $f > 10$ suggest a highly frustrated system, where frustration strongly inhibits the development of long-range magnetic order. In such systems, the frustration can give rise to exotic quantum states of matter, including spin liquids [54], spin ices [55], and spin glasses [56]. Different lattice geometries are summarized in Fig. 1.4. The concept of a quantum spin liquid in these systems is closely related to the resonating valence bond (RVB) model introduced by P. W. Anderson, which describes a superposition of various spin-pairing configurations that lead to a disordered but highly entangled ground state [57]. Although the RVB model provides valuable insights, an exact solvable model for QSLs in most systems remains elusive.

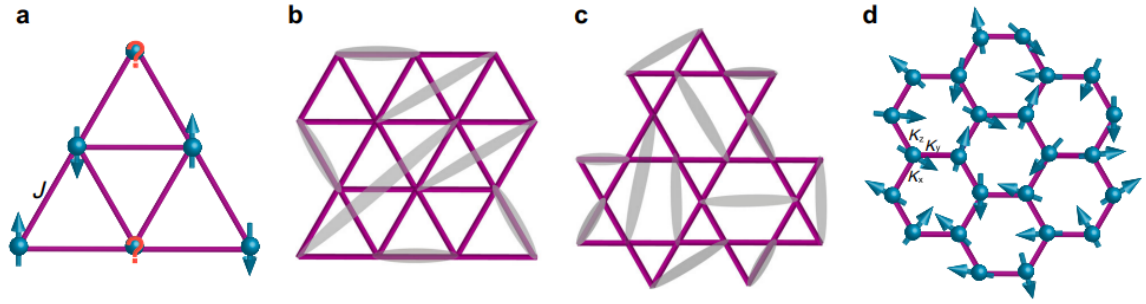


Figure 1.4: Schematics of some typical two-dimensional crystal structures on which quantum spin liquids may be realized. (a, b) Triangular, (c) Kagome, and (d) Honeycomb structures. Arrows and question marks represent spins and undetermined spin configurations due to geometrical frustration, respectively. J is the Heisenberg exchange interaction, and K_x , K_y , K_z are Kitaev interactions along three bonds. The shades illustrate spin singlets with a total spin $S = 0$, each formed by two spins antiparallel to each other. This figure is taken from ref [4].

1.4 Kitaev quantum spin liquid

A major breakthrough in the field of quantum spin liquids came in 2006 when Alexei Kitaev introduced an exactly solvable model in two dimensions, where spins are arranged on a honeycomb lattice [58]. In this model, the ground state of the system is a quantum spin liquid, with quasi-particle excitations described as Majorana fermions. Unlike quantum spin liquids that arise due to geometric frustration, the Kitaev model realizes the quantum spin liquid state through exchange frustration [59]. This distinction is crucial because, although

the honeycomb lattice is bipartite and typically allows for conventional magnetic ordering (such as antiferromagnetism or ferromagnetism), the special interactions defined by the Kitaev model prevent such ordering and stabilize the quantum spin liquid state under specific conditions, as will be discussed in the following section.

1.4.1 Kitaev model

The Kitaev model is a theoretical framework that describes spins $S = 1/2$ located on a honeycomb lattice, interacting through nearest-neighbor Ising interactions with bond-dependent easy axes aligned along the x , y , or z directions. The Hamiltonian for the Kitaev model is given by

$$H = - \sum_{\langle i,j \rangle_\gamma} K_\gamma S_i^\gamma S_j^\gamma \quad (1.2)$$

where $\langle i, j \rangle_\gamma = x$ - type, y - type and z - type bond and the summation is taken over all the honeycomb bonds. K_γ indicates the strength of interactions on three different bonds which may vary depending on the type of the bond giving rise to gapped or gapless quantum spin liquid discussed below.

The Kitaev model is one of the rare models in two dimensions which is exactly solvable. Kitaev derived the full ground-state phase diagram as shown in Fig. 1.5, which displays four distinct ground states governed by the strength of coupling co-efficients K_x , K_y , and K_z , and plotted on a plane where $K_x + K_y + K_z = 1$. When one of the couplings co-efficient dominates, indicated by the three light blue triangles, the system forms a gapped topological spin liquid ground state. On the other hand, when the couplings co-efficient are isotropic, meaning $K_x = K_y = K_z$, the system transitions into a gapless spin liquid phase around an isotropic point shown by a gray triangle. The analytical method used in the Kitaev model is notable because it effectively breaks down the fundamental spin degrees of freedom. Each spin-1/2 is fractionalized into four flavours of Majorana fermions as shown in Fig. 1.6. These fermions are combined by pairing two adjacent ones on each bond into a single $\mathbb{Z}_2$ variable (shown as ellipses in Fig. 1.6). This variable acts as the $\mathbb{Z}_2$ gauge field, while the remaining Majorana fermion serves as an additional degree of freedom. This approach allows Kitaev

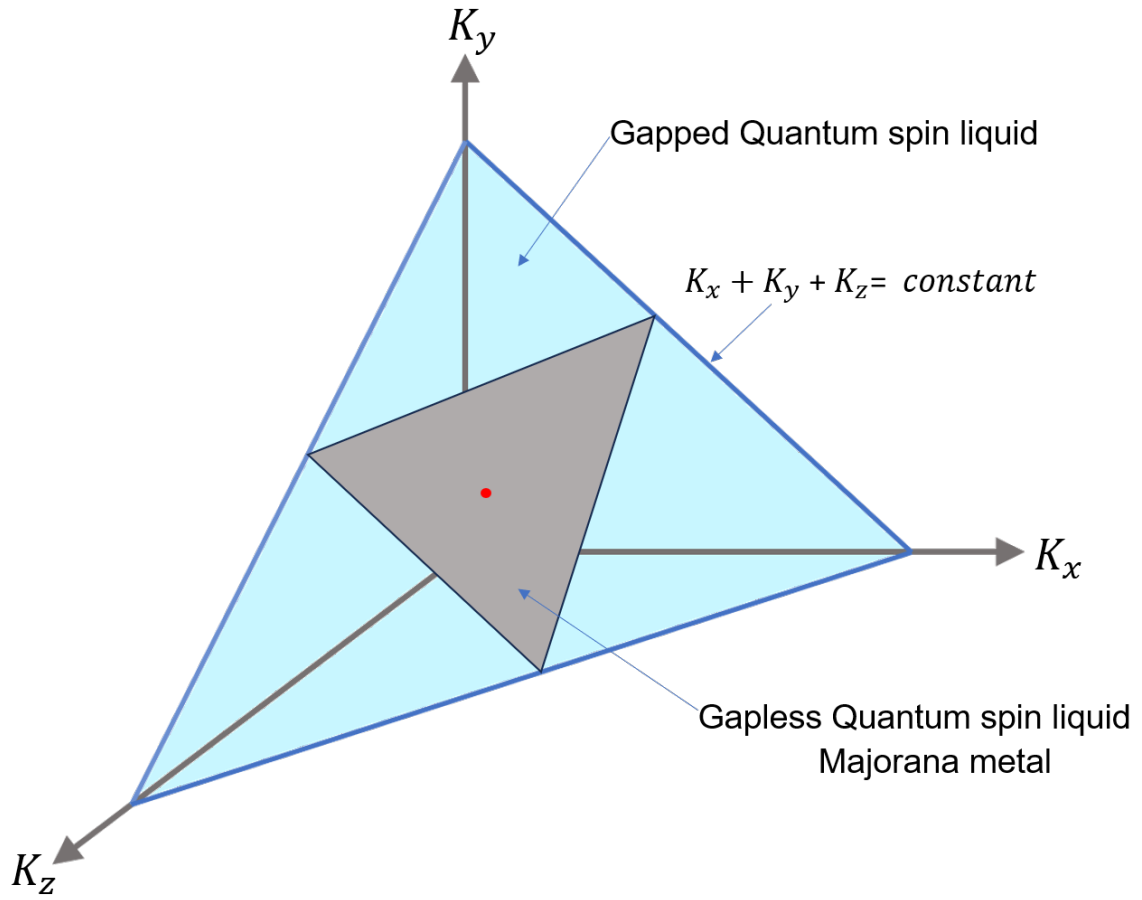


Figure 1.5: Phase diagram for Kitaev quantum spin liquid ground state showing two distinct ground states which stabilize depending on the strength of Kitaev coupling co-efficient K_x , K_y , and K_z [5].

to introduce these new fractionalized components through an exact operator decomposition. Importantly, the two types of degrees of freedom behave quite differently. Majorana fermions can move freely across the lattice, similar to free particles, while the $\mathbb{Z}_2$ gauge field remains fixed and does not fluctuate. Gauge excitations, called visons, are also static. This setup simplifies the lattice gauge theory in the Kitaev model, making it easier to solve. Looking at the phase diagram of the Kitaev model, we see that the picture of Majorana fermions moving within a static $\mathbb{Z}_2$ gauge field helps us understand the gapless quantum spin liquid phase at the center. This phase can be described as a "Majorana metal" or, more precisely, a semi-metal with a point-like Fermi surface arising from the Dirac cone in the Majorana band structure [5].

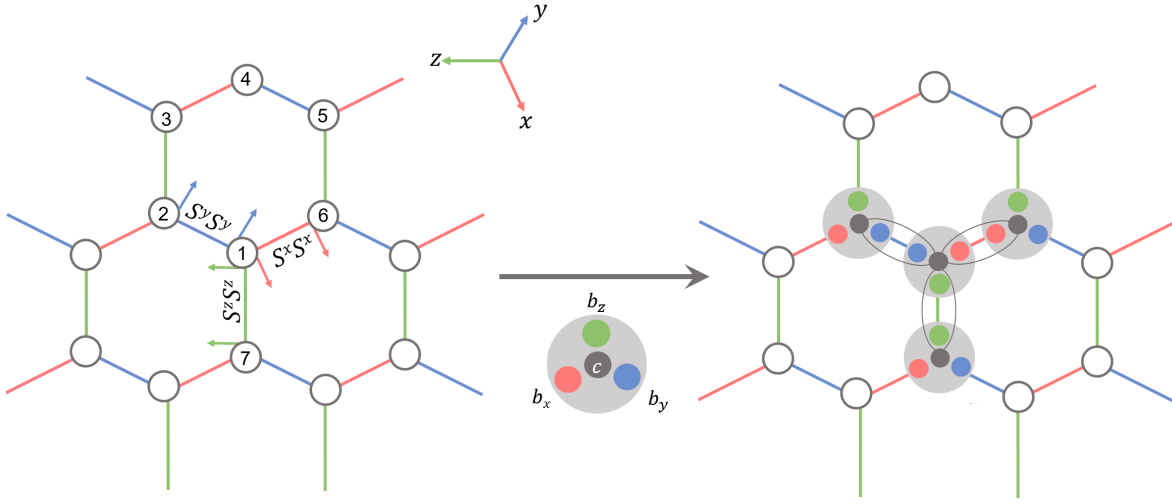


Figure 1.6: The Kitaev model can be transformed into a fermionic model, demonstrating the fractionalization of spin degrees of freedom into Majorana fermions. (Left) The schematic of the Kitaev model features spin- $\frac{1}{2}$ particles arranged on a honeycomb lattice, with bond-dependent interactions. These interactions are represented by red, blue, and green bonds, corresponding to three anisotropic interactions, each aligned with the x , y , and z axes, respectively. (Right) The fractionalization of the spin- $\frac{1}{2}$ is depicted as four flavors of Majorana fermions, represented by differently colored circles at each vertex of the honeycomb. The b_γ fermions are static Majorana fermions, while the one labeled c is itinerant.

1.4.2 Realization of Kitaev model

Initially, the Kitaev model was considered a theoretical construct, as there were no known materials where spin $1/2$ particles on a honeycomb lattice exhibited bond-dependent anisotropic Ising-like interactions. This changed with the groundbreaking work by G. Jackeli and G. Khaliullin in 2009 [6], which provided a practical approach to realize the Kitaev model in real materials. They identified two key conditions for achieving the Kitaev model in practice. The first condition involves the formation of a doublet with effective angular momentum $J_{eff} = 1/2$. This arises from the interplay of crystal field splitting, spin-orbit coupling, and electronic correlations. Specifically, this condition is met in Mott insulators containing transition metal ions with $4d^5$ or $5d^5$ electronic configurations. These configurations, when coupled with strong spin-orbit coupling and an octahedral crystal electric field, lead to $J_{eff} = 1/2$ states in the presence of a finite onsite Coulomb repulsion. The second condi-

tion addresses the suppression of conventional Heisenberg interactions. This suppression is achieved through quantum interference between different exchange processes mediated by ligand ions. For this condition to be satisfied, the transition metal ions must be in an edge-sharing octahedral environment with the ligand ions which leads to a 90° bond geometry as shown in Fig. 1.7(b). In this configuration, destructive interference between exchange paths cancels out the isotropic Heisenberg interactions, making the anisotropic Kitaev interactions dominant. These two conditions are summarized in Fig. 1.7(a, b).

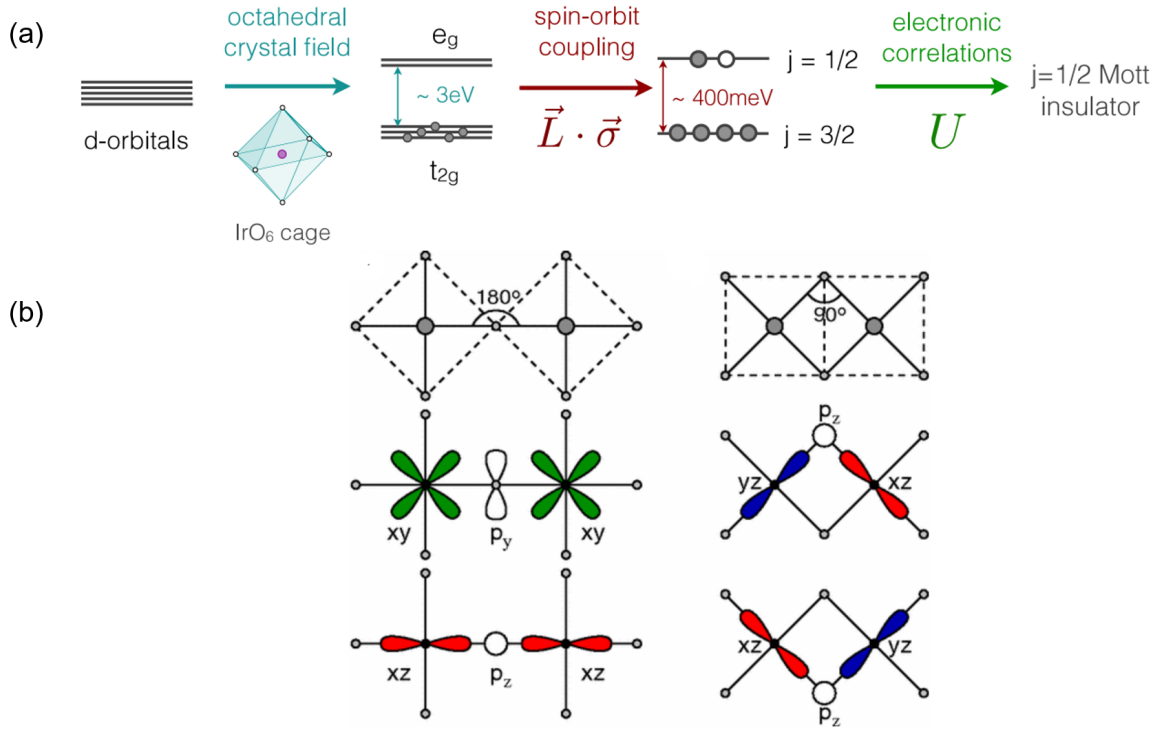


Figure 1.7: (a) Realization of $J_{\text{eff}} = \frac{1}{2}$ states due to octahedral crystal electric field splitting, spin-orbit coupling, and electronic correlations in 4d and 5d based compounds. The figure is taken from Ref. [6]. (b) Comparison of 90° and 180° bond geometry. In 180° bond geometry (left), there exists a single exchange path between the metal ion, ligand, and metal ion, whereas in the 90° bond geometry, there are two paths between the metal ion, ligand, and metal ion, leading to the suppression of Heisenberg interactions. The figure is taken from Ref. [5].

In Appendix A of this thesis, We present a detailed study on the crystal growth and dilution of the well-known Kitaev candidate material, $\alpha\text{-RuCl}_3$. The unique and exotic properties exhibited by $\alpha\text{-RuCl}_3$ have driven the search for new materials with analogous structures that

could potentially realize similar Kitaev physics. Chapters 3 and 4 provide a comprehensive exploration of newly discovered potential Kitaev materials, offering valuable insights into their crystal growth and physical properties, further contributing to the ongoing quest for novel quantum magnetic phases

1.5 Negative charge transfer insulator

Here, we focus on transition metal compounds to explain the concept of negative charge transfer insulators, with a particular emphasis on transition metal oxides, although the same principles apply to other compounds containing anions in the -2 oxidation state, such as sulfides.

In transition metal oxides, the properties of the material are primarily determined by two groups of electrons: the partially filled d-electrons of the transition metal ion (in a d^n configuration), and the fully filled 2p-electrons of oxygen (p^6). Due to the small and localized nature of the d-orbitals, there exists a significant Coulomb interaction between the d-electrons on the same site, referred to as the Hubbard interaction. When this interaction is strong enough, it splits the partially filled d-band into two separate bands: the lower Hubbard band (LHB) and the upper Hubbard band (UHB), with an energy gap corresponding to the Hubbard U parameter (U). This concept was formalized in the 1960s by John Hubbard, leading to the development of the Hubbard model, which describes the electronic structure of transition metal compounds where strong electron correlations are crucial [60].

In 1985, Jan Zaanen, George Sawatzky, and James Allen proposed a more sophisticated model to differentiate between two types of insulators: Mott-Hubbard insulators and charge transfer insulators [61]. The key parameter in this distinction is the relative position of the transition metal d-levels (E_d) and the oxygen p-levels (E_p). The type of insulator, whether Mott-Hubbard or charge transfer, depends on the ratio between the Hubbard U (which describes the strength of the Coulomb repulsion) and the energy difference between the transition metal d-orbitals and the oxygen p-orbitals ($E_d - E_p$).

The distinction can be described through two cases:

Case 1: Mott-Hubbard Insulator ($\Delta = (E_d - U) - E_p > U$)

In this case, the lowest energy excitations involve transferring an electron between two transition metal ions, resulting in a configuration where one ion gains an extra electron (d^{n+1}) and another ion loses one (d^{n-1}). This transition occurs across a charge gap $E_g = U$, and the material is classified as a Mott-Hubbard insulator. Here, the electron-electron interactions within the d-orbitals are the primary cause of the insulating behavior.

Case 2: Charge Transfer Insulator ($\Delta < U$)

When the oxygen p-levels are not deep enough, the lowest energy excitations involve transferring an electron from the oxygen's p-orbitals to the transition metal's d-orbitals, creating a configuration where the oxygen p-shell loses an electron (p^5) and the transition metal gains one (d^{n+1}). In this scenario, the energy gap E_g is determined by Δ , the charge transfer gap. Materials in this category are classified as charge transfer insulators, where the insulating behavior arises due to electron transfer between the oxygen p-levels and the metal d-levels.

Most transition metal oxides fall into one of these two categories and exhibit insulating behavior. The magnetic properties of these materials are primarily governed by the partially filled d-shells of the transition metals, where the exchange interaction often occurs through an oxygen ion (a mechanism known as superexchange). The specifics of the magnetic structure depend on factors such as the type of d-orbitals involved and the geometrical arrangement of ions, following the Goodenough-Kanamori-Anderson rules [62, 63].

In certain cases, where the oxygen p-band lies above or very close to the initially empty d-band (UHB), and the charge transfer gap Δ is small or even negative, the material becomes a **negative charge transfer insulator**. In such a scenario, some of the electrons from the oxygen p-band transfer to the transition metal d-orbitals, leaving behind holes in the oxygen p-band. This process occurs naturally due to the specific positioning of the energy levels and is referred to as **self-doping** [7]. The appearance of these holes in the oxygen p-band is not due to external impurities but rather an intrinsic property of the electronic structure of the material.

The transition from a positive charge transfer insulator to a negative charge transfer insu-

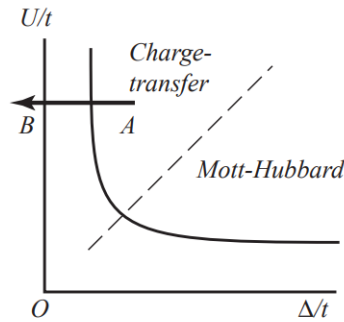


Figure 1.8: Schematic of the phase diagram for transition metal compounds [7] .

lator is marked by a small or negative value of Δ . This transition is represented by an arrow from point A to point B (decreasing Δ value from A to B) in Fig. 1.8. The complete scheme that differentiates Mott-Hubbard insulators from charge transfer insulators, highlighting the emergence of negative charge transfer insulators in comparison is illustrated in Fig. 1.9. This distinction helps explain the unique electronic and magnetic properties observed in these materials.

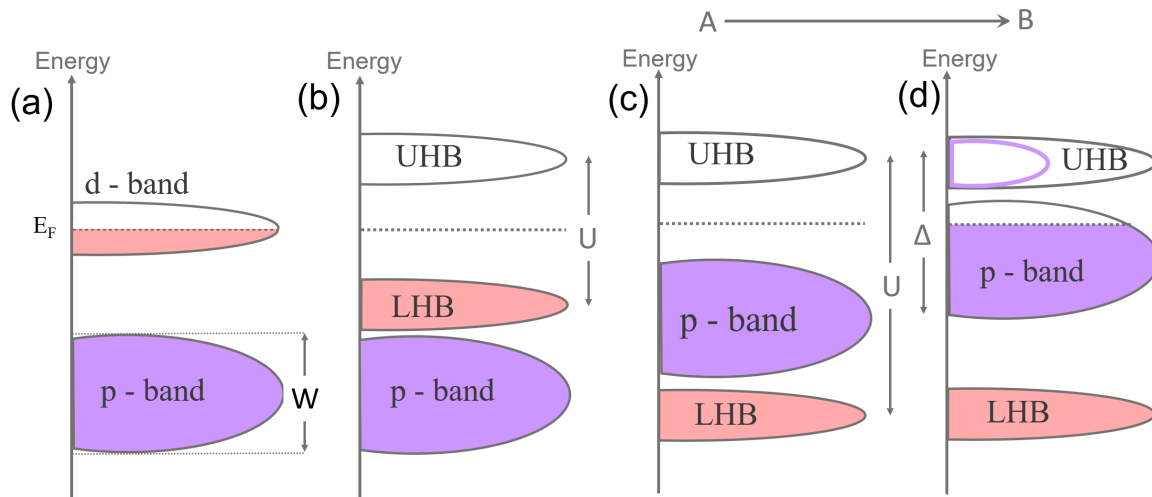


Figure 1.9: Schematic of the phase diagram for transition metal compounds distinguishing between different type of insulator. (a) Metallic (b) Mott - Hubbard Insulator. (c) Charge transfer Insulator. (d) The negative charge transfer insulator showing a self-doped effect. The purple color band shows the p-band of oxygen, and the red color band shows the d-band of transition metal. W, U, and Δ indicate the bandwidth of the p band, Hubbard gap, and the charge transfer gap, respectively. The arrow marked from A to B is the change of band position going from positive charge transfer to negative charge transfer insulator.

The concept of negative charge-transfer energy (often called "negative Δ ") was introduced by Fujimori et al [64]. In their study of NaCuO_2 , where Cu^{3+} tends to resemble Cu^{2+} due to oxygen being in a p^5 configuration. Other compounds within this category, such as LaCuO_3 , RNiO_3 [65], and $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$ [66], display a broad spectrum of properties, ranging from insulating to metallic. For example, NaCuO_2 is a diamagnetic insulator, LaNiO_3 is a paramagnetic metal, and LaCoO_3 exhibits magnetic behavior that changes with temperature. These materials showcase the diverse electronic and magnetic characteristics associated with negative charge-transfer systems.

The chapter 6. of this thesis focuses on NiPS_3 , the first known magnetic two-dimensional negative charge-transfer insulator. In this material, the self-doping effect occurs due to the transfer of electrons from the sulfur p-orbitals to the nickel d-orbitals.

1.6 Magnetocaloric effect

The magnetocaloric effect (MCE) describes the temperature change in a magnetic material when exposed to an external magnetic field. This phenomenon has been historically referred to as adiabatic demagnetization, which remains a practical application of the MCE in magnetic materials [8, 67].

The MCE was first observed in 1881 by Warburg, who detected it in iron [68]. Later, Debye [69] and Giauque [70] independently explained the phenomenon and proposed adiabatic demagnetization as the first practical application. This method facilitate to achieve temperatures lower than that of liquid helium, which had previously been the coldest achievable experimental temperature.

Thermodynamics is essential for understanding the MCE as it relates magnetic properties like magnetization and external magnetic fields to temperature and entropy. Although all magnetic materials exhibit the MCE, the magnitude of the effect depends on each material properties.

The MCE originates from the coupling between the magnetic sublattice and the applied magnetic field H , which alters the magnetic contribution to the material entropy. This pro-

cess can be compared to the thermodynamics of a gas. For example, isothermal gas compression (applying pressure to reduce entropy) is analogous to isothermal magnetization (applying a magnetic field to reduce magnetic entropy in a paramagnet or soft ferromagnet). Conversely, adiabatic gas expansion (reducing pressure while keeping entropy constant, causing the temperature to drop) is similar to adiabatic demagnetization, where reducing the magnetic field H keeps total entropy constant but lowers the temperature as magnetic entropy increases. These two processes are summarised in Fig. 1.10.

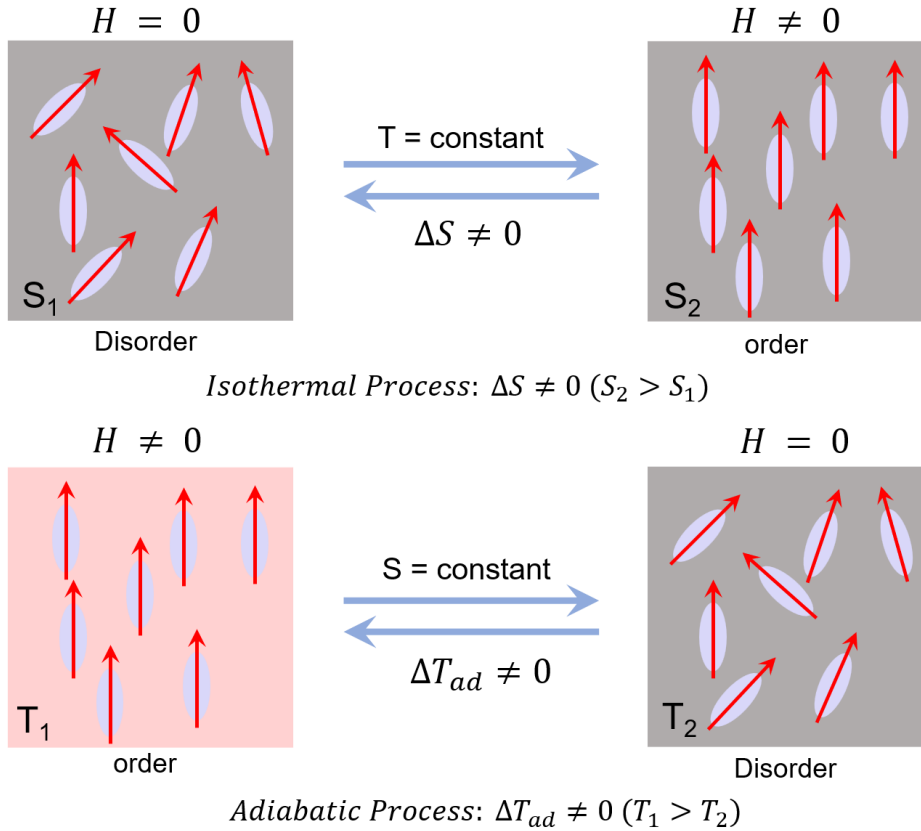


Figure 1.10: The schematic illustrates the basic magnetocaloric effect through two distinct processes. At the top, the isothermal process is depicted, where the temperature of the system remains constant while the entropy changes due to the application of a magnetic field. Conversely, the bottom section presents the adiabatic process, in which the system's entropy remains constant, and the temperature changes in response to the application or removal of the magnetic field.

For ferromagnets (FM) at constant pressure, the total entropy depends on both the temperature T and the magnetic field H . It includes contributions from the lattice S_{lat} , the

electronic S_{el} , and the magnetic S_m components:

$$S(T, H) = S_m(T, H) + S_{lat}(T) + S_{el}(T) \quad (1.3)$$

Figure 1.2 shows how the entropy of a ferromagnet changes near its Curie temperature T_C as a function of temperature, with an applied magnetic field H_1 and zero field H_0 . The magnetic entropy is shown for both field conditions [8].

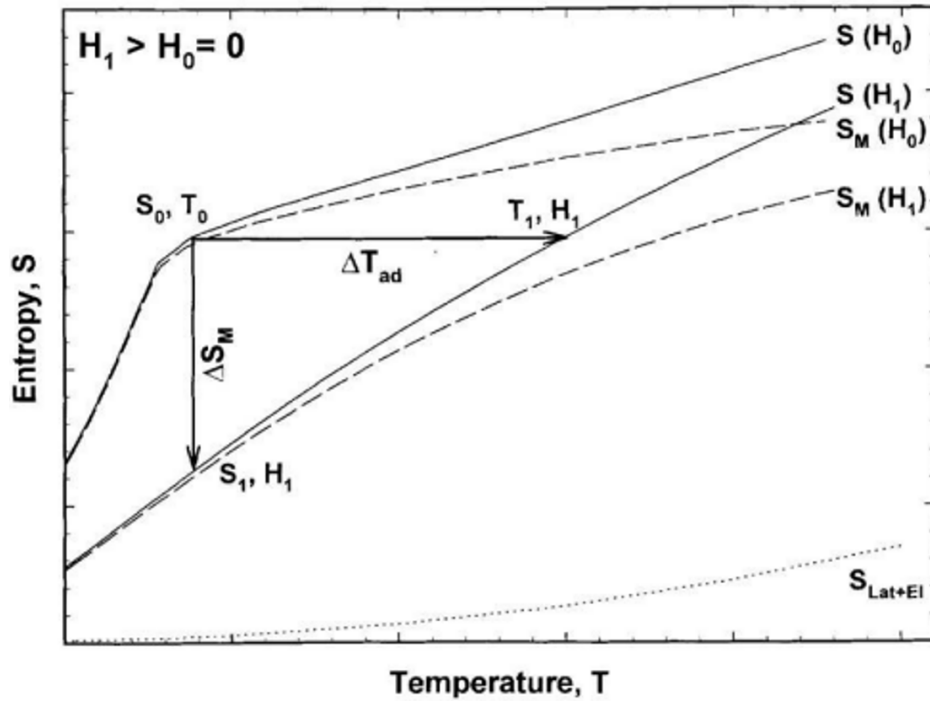


Figure 1.11: The S-T diagram illustrating the magnetocaloric effect (MCE) features solid lines that represent the total entropy at two different magnetic fields ($H_0 = 0$ and $H_1 > 0$). The dotted line indicates the contributions to the entropy from electronic and lattice sources (non-magnetic), while the dashed lines depict the magnetic entropy for both fields. A horizontal arrow denotes ΔT_{ad} , and a vertical arrow represents ΔS_m as the magnetic field transitions from H_0 to H_1 . This diagram is adapted from Ref. [8].

Two key processes explain the thermodynamics of the MCE:

1. **Adiabatic process:** When the magnetic field is applied adiabatically (i.e., without changing the total entropy), the magnetic entropy decreases, but the total entropy remains constant:

$$S(T_0, H_0) = S(T_1, H_1) \quad (1.4)$$

As a result, the temperature increases. The adiabatic temperature change ΔT_{ad} is given by:

$$\Delta T_{\text{ad}} = T_1 - T_0 \quad (1.5)$$

This temperature rise is a measure of the MCE and can be visualized as the isentropic difference between the entropy curves $S(T, H)$.

2. Isothermal process: When the magnetic field is applied isothermally (i.e., at a constant temperature), the total entropy decreases because the magnetic entropy decreases. The isothermal magnetic entropy change ΔS_{m} is expressed as:

$$\Delta S_{\text{m}} = S(T_0, H_0) - S(T_0, H_1) \quad (1.6)$$

Both ΔT_{ad} and ΔS_{m} are key indicators of the MCE. These values depend on the initial temperature T_0 and the change in the magnetic field $\Delta H = H_1 - H_0$.

In situations where the magnetic order decreases, applying a negative change in the magnetic field $-\Delta H$ has the opposite effect: the adiabatic temperature change $\Delta T_{\text{ad}}(T, -\Delta H)$ becomes negative, leading to cooling. Simultaneously, $\Delta S_{\text{m}}(T, -\Delta H)$ becomes positive, indicating an increase in magnetic entropy.

The relationship between the magnetic field H , magnetization M , and temperature T for $\Delta T_{\text{ad}}(T, \Delta H)$ and $\Delta S_{\text{m}}(T, \Delta H)$ is derived from one of the Maxwell relations:

$$\left(\frac{\partial S(T, H)}{\partial H} \right)_T = \left(\frac{\partial M(T, H)}{\partial T} \right)_H \quad (1.7)$$

For an isothermal (and isobaric) process, this can be integrated to give the magnetic entropy change:

$$\Delta S_m(T, \Delta H) = \int_{H_1}^{H_2} \left(\frac{\partial M(T, H)}{\partial T} \right)_H dH \quad (1.8)$$

This equation shows that the magnetic entropy change ΔS_m is directly proportional to both the rate of change of magnetization with respect to temperature at a constant magnetic field and the variation in the applied magnetic field.

Direct and Indirect Measurement of MCE

Direct methods for measuring the MCE involve determining the sample's initial temperature T_0 and final temperature T_F after the external magnetic field changes from an initial value H_0 to a final value H_F . The adiabatic temperature change ΔT_{ad} can be calculated as:

$$\Delta T_{ad}(T_0, H_F - H_0) = T_F - T_0 \quad (1.9)$$

These measurements can be performed using either contact or non-contact techniques, depending on whether the temperature sensor is physically attached to the sample.

In contrast to direct measurements, which typically yield only the adiabatic temperature change, indirect experiments can calculate both $\Delta T_{ad}(T, \Delta H)$ and $\Delta S_m(T, \Delta H)$ through heat capacity measurements. For magnetization measurements, however, only $\Delta S_m(T, \Delta H)$ can be obtained. In this case, magnetization must be measured as a function of temperature T and magnetic field H . This approach allows for the numerical integration of Eq. (6) to derive $\Delta S_m(T, \Delta H)$, making it a valuable method for rapidly screening potential magnetic refrigerant materials [71].

The accuracy of the calculated $\Delta S_m(T, \Delta H)$ depends on the precision of the measurements of the magnetic moment, temperature T , and magnetic field H . Additionally, errors arise because the exact differentials in Eq. (1.6) (i.e., dM , dH , and dT) are substituted with measured variations (i.e., ΔM , ΔT , and ΔH). Considering all these factors, the error in the value of $\Delta S_m(T, \Delta H)$ typically falls within a range of 3-10% [8, 71].

In Chapter 5 of this thesis, we summarize the crystal growth of the quantum magnet CeCl_3 , where Ce^{3+} ions with a spin of 1.2 occupy a pseudo-honeycomb lattice in the ab

plane. Using indirect measurements, we demonstrate that CeCl_3 exhibits a significant magnetocaloric effect. This effect is estimated by calculating the change in magnetic entropy from the magnetization isotherm, suggesting its potential as a coolant.

1.7 Candidate materials

There exists a vast family of two-dimensional (2D) magnets, many of which have been known for decades, while others remain largely unexplored. According to a recent study published in *Nature Nanotechnology* by Nicolas Mounet *et al.* [72], high-throughput computational exfoliation of 108,423 unique experimentally known three-dimensional (3D) compounds identified 5,619 layered materials. Of these, 1,825 are readily exfoliable, with 1,036 exhibiting novel structure types. This study highlights that despite extensive efforts devoted to exploring the chemical space of bulk 3D compounds, the domain of 2D materials is still relatively underexplored. The limited number of known 2D material prototypes further emphasizes the potential for significant discoveries in this field.

In this thesis, we aim to investigate certain existing quasi-2D quantum magnets and also explore new novel 2D magnetic systems. Motivated by the promise of uncovering new physics and materials, we explored various classes of 2D magnets. These systems span a diverse range of structural, magnetic and thermal properties, each offering unique opportunities to study low-dimensional quantum magnetism.

One such class includes the Kitaev Quantum Spin Liquid (KQSL) candidates, with $\alpha\text{-RuCl}_3$ as a prominent example. Following the theoretical prediction of Kitaev physics in Na_2IrO_3 , numerous iridium- and ruthenium-based compounds have been examined for their potential to host Kitaev interactions. These compounds share structural motifs, such as honeycomb or hyperhoneycomb arrangements of magnetic Ru and Ir ions. Key systems include $\alpha\text{-A}_2\text{IrO}_3$ ($A = \text{Li, Na}$), $\text{A}_3\text{LiIr}_2\text{O}_6$ ($A = \text{H, Cu, Ag}$), $\alpha\text{-RuCl}_3$, and $\beta\text{-Li}_2\text{IrO}_3$ [9]. The structure of these compounds are summarized in Fig. 1.12

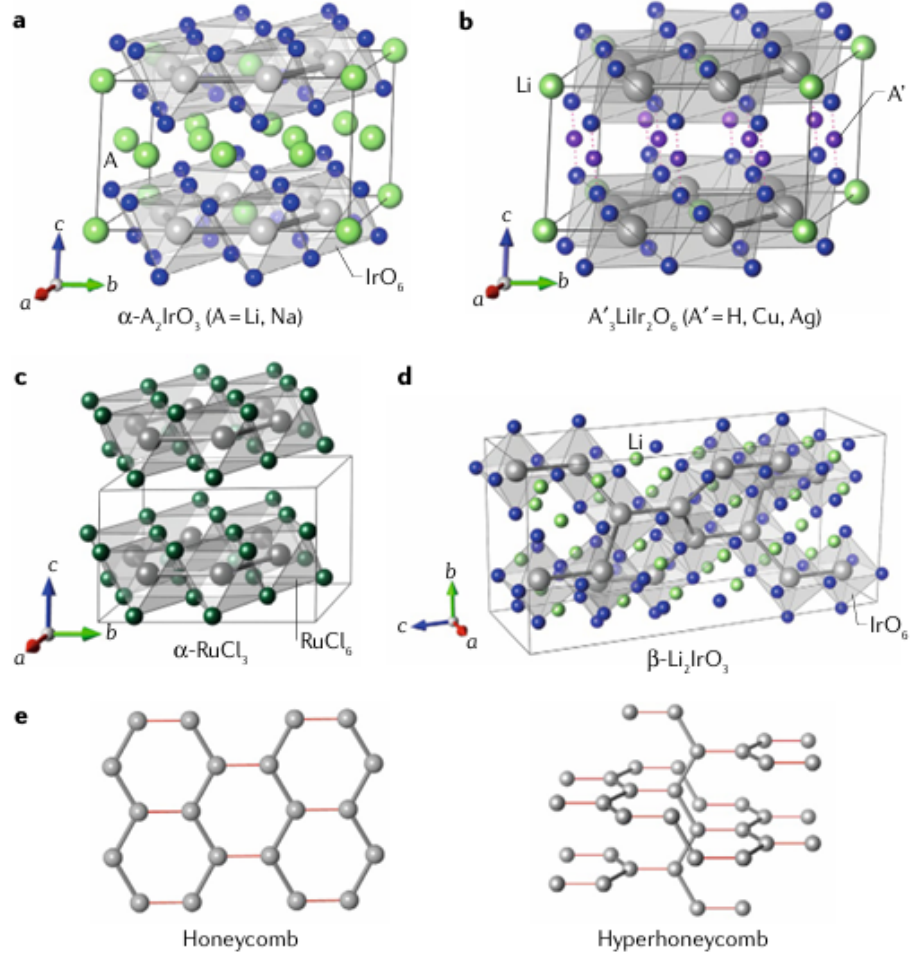


Figure 1.12: Kitaev candidate materials. (a) Crystal structure of Na_2IrO_3 and $\alpha\text{-Li}_2\text{IrO}_3$. (b) Crystal structure of $A'_3\text{LiIr}_2\text{O}_6$ ($A' = \text{H, Cu, Ag}$). (c) Crystal structure of $\alpha\text{-RuCl}_3$. (d) Crystal structure of $\beta\text{-Li}_2\text{IrO}_3$ showing the hyperhoneycomb Ir sublattice. (e) Relationship between the 2D honeycomb and 3D hyperhoneycomb lattices, with honeycomb bonds decomposed into zigzag chains (grey) and bridges (red). This figure is adapted from ref [9].

With this initial focus on Kitaev QSL candidates, our attention turned to systems involving $4f$ electrons. We investigated the compound YbI_3 , a rare-earth triiodide known for its quasi-2D nature which is iso structural to the well known KQSL candidate $\alpha\text{-RuCl}_3$. Building on insights from YbI_3 , we expanded our study to a broader series of rare-earth tri-iodides, including LaI_3 , CeI_3 , GdI_3 , DyI_3 , HoI_3 , and ErI_3 .

Another intriguing system we examined is CeCl_3 , inspired by theoretical predictions of optically driven chiral phonon modes capable of generating magnetic fields as high as 100 T,

acting on the paramagnetic $4f$ spins [73]. This work was motivated by recent experimental investigations in related materials, such as CeF_3 [74], and seeks to elucidate the underlying mechanisms driving such phenomena.

Lastly, we studied NiPS_3 , a member of the transition metal thiophosphates (MPS_3) family. This material is notable for its spin-phonon coupling below the magnetic ordering temperature and evidence of two-magnon scattering [75]. These characteristics make NiPS_3 a compelling platform for studying magnetoelastic interactions in low-dimensional systems.

In summary, our motivation stems from the desire to understand and uncover novel magnetic phenomena in low-dimensional systems. By systematically investigating these diverse material classes, we aim to contribute to the growing field of 2D quantum magnetism and provide insights into their underlying physics, which may have implications for future technological applications. .

Chapter 2

Experimental Methods

The most challenging task to progress in the field of Quantum Materials is to obtain a desired material with high purity, precise stoichiometry, and the desired crystal structure, which serves as the foundation for studying the rich physics governed by these systems. Before exploring the magnetic and physical properties of a synthesized sample, it is essential to confirm its phase purity, homogeneity, stoichiometry, and crystal structure. To ensure the sample's high quality, a range of experimental tools is used to thoroughly examine its chemistry and crystallography. Once a high-quality sample of the desired compound is obtained, its magnetic and physical properties are investigated. Initial characterization is typically performed using basic measurement techniques, such as the physical property measurement system (PPMS). Following this, more advanced techniques, which are beyond the scope of present work, including muon spin rotation (μ SR) and elastic and Inelastic neutron scattering, are employed to gain deeper insights about the magnetic structure and dynamics of spin at low temperatures.

The aim of this section is to describe in detail the methods used for synthesizing high-quality single crystals and characterizing them through techniques such as powder X-ray diffraction (PXRD), single-crystal X-ray diffraction, SEM-EDX, HRTEM and Raman spectroscopy. These techniques confirm the homogeneity and crystal structure of the sample under investigation. The high-quality single crystals are then further studied using the phys-

ical property measurement system over a wide temperature range, from room temperature down to 2 K or even lower, to explore detailed knowledge of their magnetic and physical properties.

2.1 Crystal growth

Crystals, characterized by their regular atomic arrangement, are the most common form of solid materials in nature. In the Earth's crust, they grow under extremely high pressure and temperature, where slow cooling of magma over thousands to millions of years allows large, well-ordered crystals to form. On the Earth's surface, various processes such as evaporation, supersaturation, rapid cooling of lava, and organic activity contribute to the growth of different types of crystals. Evaporation leads to minerals crystallizing from solutions, while rapid cooling of lava forms smaller crystals. Organic processes, like those in mollusks and corals, also result in crystalline structures. Depending on the conditions, crystallization can take anywhere from days to thousands of years.

Crystals of scientific significance, which serve as crucial platforms for both technological applications and the exploration of fundamental physics, can also be synthesized in the laboratory using methods that mimic natural crystal formation processes. Various techniques are employed to grow crystals in controlled environments, depending on the material and desired crystal properties. One major category is vapor phase growth, which includes chemical vapor transport (CVT) and physical vapor transport (PVT) methods, both of which involve crystallization from a vaporized material. Crystals can also be grown from a melt, with techniques such as the Bridgman-Stockbarger and Czochralski methods, which require a crucible to contain the molten material. In contrast, crucible-free methods like the Verneuil process, floating zone technique, and zone movement method allow for crystal growth without contamination from container walls, leading to purer crystals. Additionally, growth from solution is another important approach, including techniques such as flux growth, gel growth, and hydrothermal growth. These methods are particularly useful for materials that are difficult to melt or vaporize. The various crystal growth processes are summarized in Fig. 2.1,

providing an overview of the diverse techniques employed to synthesize high-quality crystals in the laboratory. Here we focus two important crystal growth methods: Vapour transport (vapor phase growth) and the Bridgman method (growth from the melt)

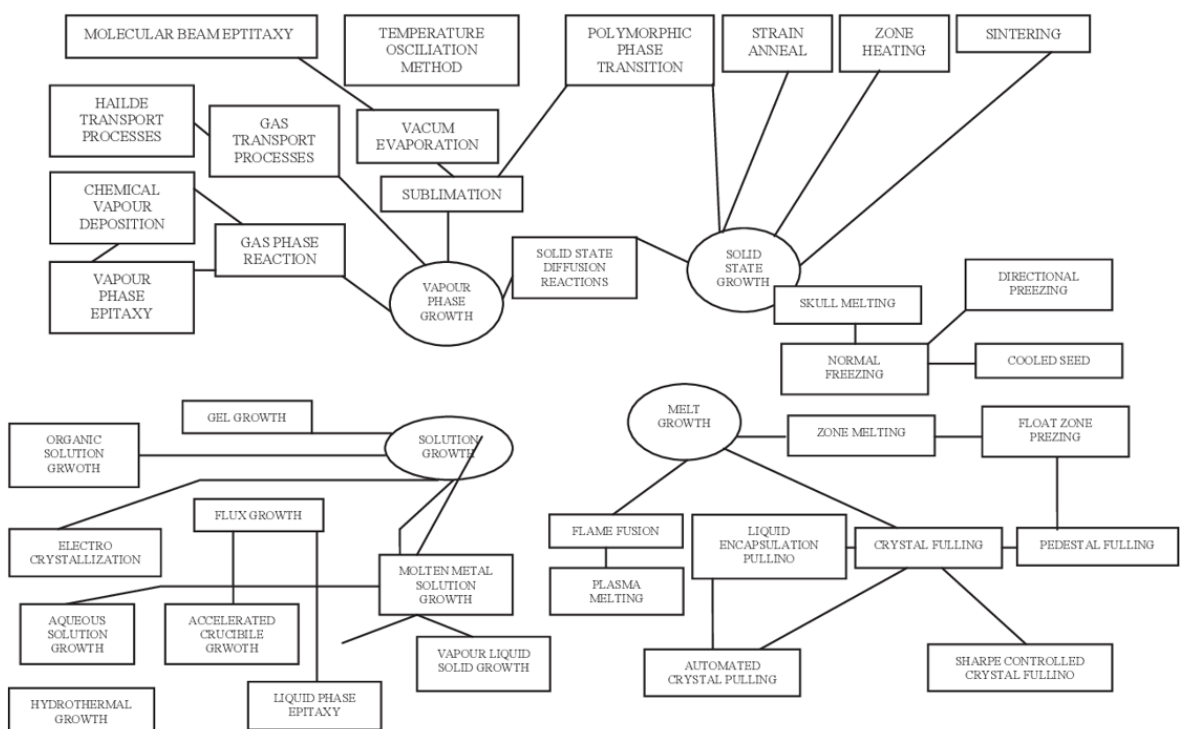


Figure 2.1: Main categories with sub-Family of crystal growth techniques. The figure is adapted from ref. [10]

2.1.1 Vapor transport growth

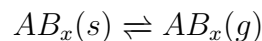
Vapor transport is an extensively used technique, particularly in the growth of layered or 2D Van der Waals materials from various families, including halides, oxides, sulfides, selenides, tellurides, chalcogenide-halides, pnictides, thiophosphates [76, 77]. Here, we shall discuss the closed tube variant of the vapor transport technique, typically used for bulk crystal growth. The material whose crystals are to be grown is generally taken in a powdered form and placed at one end of an evacuated sealed quartz ampoule. The ampoule is then placed in a tubular furnace with a predefined temperature gradient along the length of the ampoule. When the furnace is heated to a sufficiently high temperature, the powder starts to

vapourize and, under the temperature gradient, migrates to the colder end where nucleation (typically at multiple sites) and growth occur for several days or even weeks. That end of the ampoule where the material is kept is called the source, and the colder end where the crystallization occurs is called the sink. The reaction mechanism can be inferred from the thermodynamic considerations of heterogeneous solid-gas equilibria. It should be pointed out that for an exothermic reaction at the source, the migration direction can reverse. Depending on the kinematic and the thermodynamics of the reaction, an external transporting agent may be needed to facilitate the vapor transport growth which classifies the process into PVT and CVT described below. The schematic of the reaction is shown in Fig. 2.2

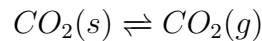
Physical Vapor Transport (PVT)

The vapor transport reaction, which does not require any external transporting agent for crystal growth, is known as a Physical Vapor Transport (PVT) process. In this reaction, a condensed substance experiences a temperature gradient, allowing it to move from the place of dissolution to the place of deposition via various heterogeneous reactions. The schematic of a PVT process is shown in Fig. 2.2(Top). PVT process include three different processes sublimation, decomposition sublimation and auto transport described below [76]:

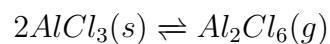
1. Sublimation: In sublimation, a solid substance is directly converted into a gas. The general reaction is:



For example, carbon dioxide (dry ice) sublimates as follows:

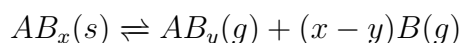
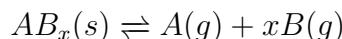


Similarly, an ionic compound like aluminum chloride ($AlCl_3$) exists in the gaseous phase as a dimer, Al_2Cl_6 :



2. Decomposition Sublimation: In this process, the solid decomposes into various gaseous

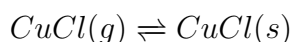
products upon heating. These gaseous products are transported due to the temperature gradient, and the solid phase recrystallizes. The general process is:



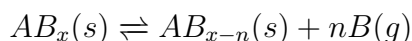
This reaction can be congruent or incongruent. In a congruent reaction, the composition of the recrystallized solid remains the same as the initial compound, while in an incongruent reaction, the final solid differs in composition. For example, ammonium chloride undergoes congruent decomposition:



An example of an incongruent reaction is the decomposition of copper(II) chloride:

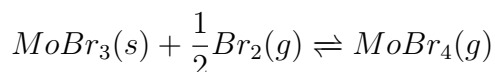
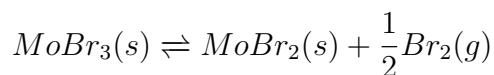


3. Auto Transport: This process combines both sublimation and decomposition sublimation. The initial solid in the absence of any transporting agent decomposes at high temperatures to form gaseous species. These gaseous species act as a transporting agent, enabling the solid to convert into the gas phase. The general reaction is:



Auto transport occurs when the solid alone cannot generate enough vapor pressure for transport, and decomposition creates a species that reacts with the solid to facilitate transport. It is generally an endothermic process. An example of auto transport is the transport of

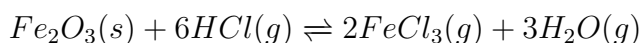
molybdenum tribromide:



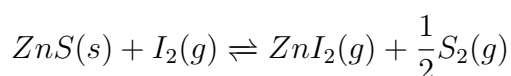
Chemical Vapour Transport (CVT)

When the starting materials lack sufficient vapor pressure, or the decomposition reactions do not generate transport-effective species capable of facilitating the movement of the initial condensed solid, an external agent with a high vapor pressure is introduced. This external transporting agent aids in the efficient transport of the initial compound under suitable thermodynamic conditions.

Chemical vapor transport is not really an invention but an observation by Bunsen in 1852 when he noticed the formation of crystalline iron oxide in the presence of volcanic gasses that contained gaseous hydrogen chloride and we now understand that volatilization and separation of iron oxide is based on the following reaction:



Due to the forward reaction, Fe_2O_3 reacts with HCl gas and transforms into the gas phase, and the reverse reaction deposits the pure Fe_2O_3 and releases HCl gas. HCl gas here act as a transporting agent to facilitate the growth of Fe_2O_3 . In the laboratory, the reactions can be performed in an open as well as in a closed tube. A closed tube is a sealed ampoule made up of glass or quartz, and a very small amount of transporting gas suffices the reaction conditions to form transport-effective gas species. An example of a typical reaction performed in the laboratory is the transport of ZnS shown below:



Here, I_2 is used as a transporting agent, and ZnI_2 and S_2 are called the transport-effective

species.

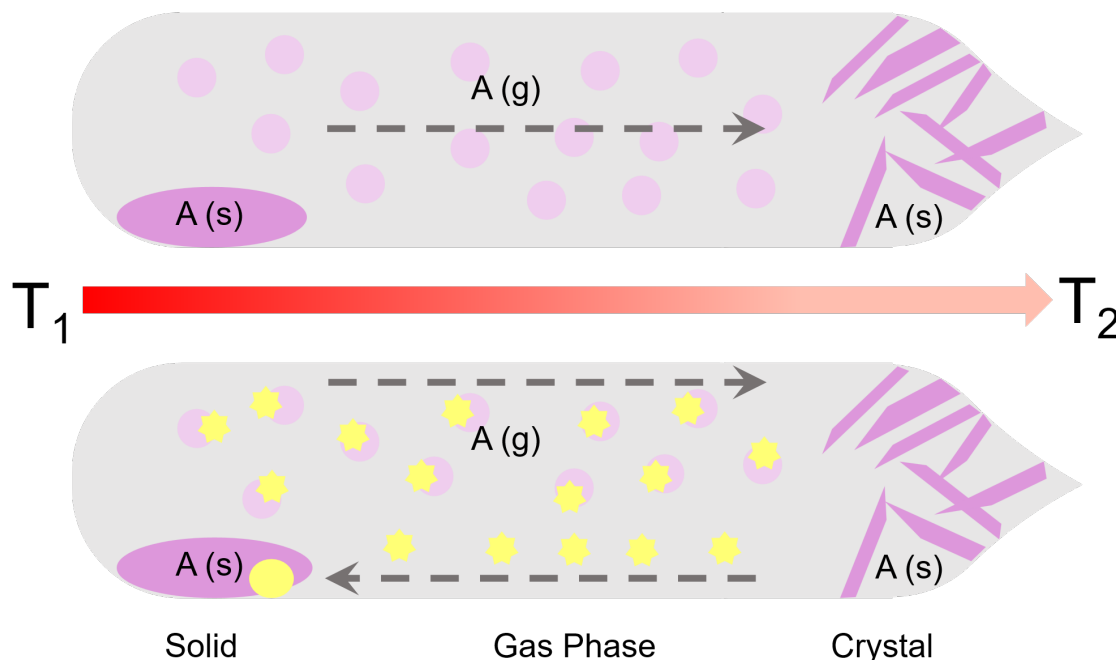


Figure 2.2: The schematics of Physical Vapour Transport (top) and Chemical Vapor Transport (bottom). The initial precursor is shown in a purple color oval at the source side, the yellow stars depict the transporting agent, and the single crystals are shown using a purple needle-shaped figure.

Self-Selecting Vapor transport Growth (SSVG)

Unlike Physical Vapor Transport (PVT) and Chemical Vapor Transport (CVT) reactions, where the starting material and grown crystals are spatially separated, the initial powder is placed in the source zone, and crystals grow in the sink zone, Self-Selective Vapor Growth (SSVG) involves crystal growth on top of polycrystalline starting material placed in the source zone. In SSVG, a very small temperature gradient, is maintained between the bottom and top of the polycrystalline powder to prevent spatial transport of the material to the opposite end of the ampoule [11, 78].

In vapor transport reactions like CVT or PVT, a large temperature gradient, often exceeding 20°C , is used to drive the process, whereas in SSVG, only a small gradient of $1 - 2^{\circ}\text{C}$ is necessary. The term self-selecting refers to the nature and dynamics of the crystal growth

process. Under suitable thermodynamic conditions, the fastest-growing crystal orientation is naturally selected, initiating growth and increasing in size. In a typical SSVG experiment, the entire polycrystalline powder can transform into either one large crystal or a few large crystals, free from defects and impurities.

A schematic of the SSVG process is shown in Fig. 2.3. In cases where the initial compound does not possess sufficient vapor pressure, a suitable transporting agent can be introduced to facilitate the crystal growth process. Several important parameters need to be carefully considered when designing an SSVG experiment. First, the purity of the starting material plays a crucial role in determining the size of the grown single crystals. Impurities can act as seed crystals, increasing the number of nucleation points and leading to the formation of many small crystals rather than one large single crystal.

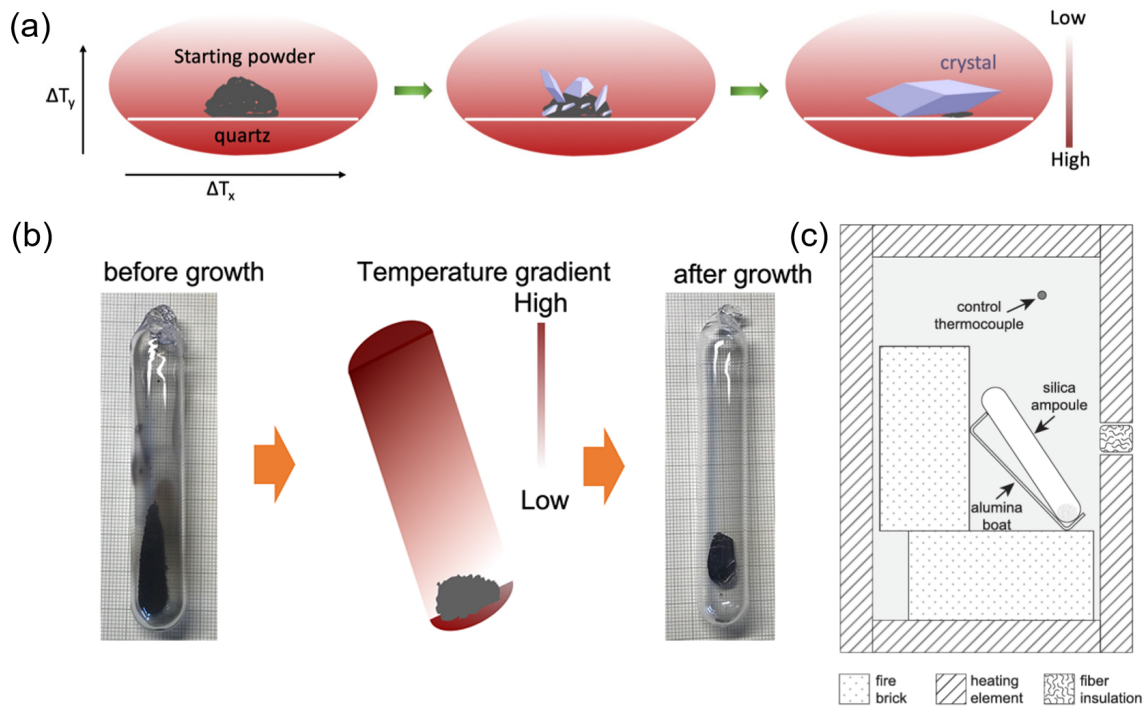


Figure 2.3: The schematic of self-selecting vapor transport growth (SSVG). (a) Schematic of crystal growth in the in horizontal configuration in the tube furnace showing both the horizontal and vertical temperature gradient and increase in the size of crystal with time. (b) Schematic of the crystal growth in the box furnace in vertical configuration. (c) schematic of the furnace turned on the side in order to obtain a small temperature gradient as shown in (b). The images are adapted from the ref [11]

Another critical factor is the position of the ampoule within the furnace. The ampoule must be positioned so that both ends are exposed to high temperatures, with only a minimal temperature gradient applied above the polycrystalline powder. Typically, a box furnace in the configuration shown in Fig. 2.3(c) is used to create the small vertical temperature gradient necessary for SSVG. However, the experiment can also be conducted in a tube furnace with a horizontal configuration, where both horizontal and vertical temperature gradients are present, as shown in Fig. 2.3(a). The horizontal gradient aids in selecting the most suitable grain for nucleation, while the vertical gradient promotes the growth of larger single crystals. A similar method is used to grow large single crystal of α -RuCl₃ which is summarized in chapter 3 of this thesis

2.1.2 Growth from melt

As shown in the Fig. 2.1, different crystal growth methods can be employed by melting the material. One such method is the Bridgman method described below.

Bridgman method

The traditional Bridgman Stockbarger method involves a very slow translation of a crucible holding the homogenized melt of the compound whose crystals are desired into a region of negative temperature gradient. The required gradient can, for instance, be achieved in a suitably wound tubular furnace or by using a two-zone furnace. The crucible typically has a sharp conical bottom which facilitates nucleation. In an ideal process, as the crucible is lowered, the crystal first nucleates at the tip of the crucible and grows in size as the crucible is made to slowly traverse through the temperature gradient as shown in Fig. 2.2(a). This method is very handy when it comes to growing large single crystals of congruently melting compounds. However, the choice of crucible material is often an important consideration; this is particularly important when the material to be grown has a high melting temperature. Also, the highest temperature one can practically use in this technique is often limited to 1600 or 1700°C.

Instead of moving the crucible, in some cases one can place the crucible under a small

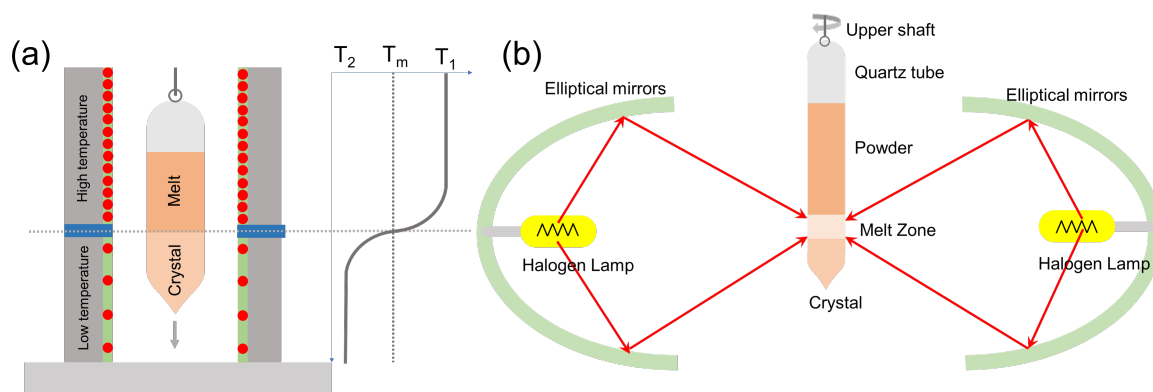


Figure 2.4: (a) The schematics of traditional Bridgman method. (b) Schematic of Image furnace used as Bridgman furnace

horizontal temperature gradient near the compound which can be manipulated by using multiple jackets around the crucible. Now slowly cooling the ampoule lead to nucleation at the tip followed by a directional solidification leading to the crystal growth. This is often known as the modified Bridgman technique.

The directional solidification can also be done in the optical image furnace by sealing the initial compound in a quartz tube and suspending it from the upper shaft of the furnace as shown in Fig. 2.2(b). An example of one such optimized growth is summarized in Chapter 6 of this thesis.

2.2 Structural and chemical homogeneity characterization techniques

2.2.1 Powder x-ray diffraction

Powder X-ray Diffraction (PXRD) is a fundamental technique used in material science to analyze the phase purity and crystallographic structure of materials. One of its primary applications is phase identification, as each crystal structure produces a unique diffraction pattern that allows for the precise identification of different phases present in a sample. The technique is also used to determine lattice parameters, as the positions of diffraction peaks correspond to the spacing between atomic planes, providing information about the unit cell

dimensions of the material. Additionally, PXRD is also used to analyze crystallite size and strain by examining the broadening (FWHM) of diffraction peaks. Furthermore, PXRD enables quantitative phase analysis, where the intensity of the diffraction peaks is used to determine the relative amounts of different crystalline phases in a material, making it a versatile tool in material science.

When X-rays are scattered from periodic arrangements of atoms (the crystal lattice), they can interfere constructively or destructively depending on the geometry. Constructive interference produces distinct diffraction peaks, while destructive interference leads to no observed intensity.

The condition for constructive interference is given by Bragg's Law, which is:

$$n\lambda = 2d \sin \theta$$

Here, n is the order of diffraction (usually taken as 1 for first-order diffraction), λ is the wavelength of the incident X-rays, d is the spacing between atomic planes in the crystal (interplanar spacing), θ is the angle at which the X-rays are incident on the planes. The schematic illustration of the Bragg's law is shown in Fig. 2.5(b). When the path difference between X-rays scattered from successive crystal planes is an integer multiple of the wavelength, the waves interfere constructively, producing a diffraction peak.

X-rays used in diffraction are produced through a process known as X-ray fluorescence. In a typical setup, a high-energy beam of electrons is directed at a metal target, such as copper, commonly used for producing Cu $K\alpha$ X-rays with a wavelength of 1.5406 Å. When these electrons strike the metal atoms, they eject inner-shell electrons from the target atoms. To stabilize, outer-shell electrons drop down to fill these vacancies, releasing energy in the form of X-rays. This process produces both continuous radiation, known as Bremsstrahlung, and characteristic X-rays. The characteristic X-rays consist of several components: $K\alpha_1$ (with a shorter wavelength and higher intensity) and $K\alpha_2$ (with a longer wavelength and lesser intensity) being the most common one. The emitted X-rays have a specific wavelength determined by the metal used as the target. This X-ray beam is then directed onto

the powdered sample, where it interacts with the crystal lattice and produces a diffraction pattern, which is characteristic of the material's structure.

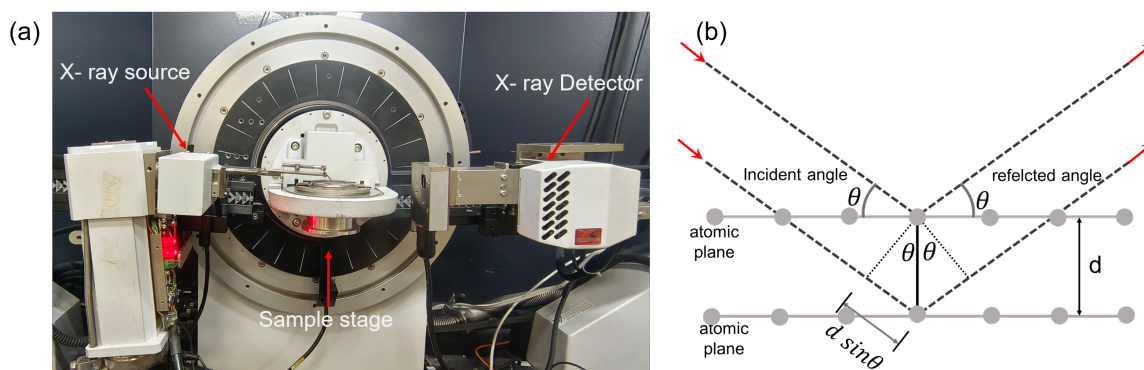


Figure 2.5: (a) The Bruker D8 advance diffractometer used for the analysis. (b) Schematic of the Bragg's law.

The powder X-ray diffraction (PXRD) data collected for the samples in this thesis was obtained using a Bruker D8 Advance diffractometer with a Cu-K α source ($\lambda_1 = 1.54060$ Å, $\lambda_2 = 1.54442$ Å) equipped with a Lynxeye detector as shown in Fig. 2.5(a). The instrument operates using Bragg-Brentano geometry, also known as θ - 2θ geometry (as shown in Fig. 2.5(b)), a widely adopted configuration in PXRD. In this setup, the incident X-ray beam strikes the sample at an angle θ , while the detector moves at an angle 2θ to capture the diffracted X-rays. This geometry optimizes constructive interference according to Bragg's Law, resulting in distinct diffraction peaks. The diffraction data is typically plotted as intensity versus the diffraction angle (2θ), providing essential information about the crystallographic structure of the material. The Bragg-Brentano setup offers high angular resolution and peak intensity, making it particularly suitable for phase identification and lattice parameter determination in powdered or polycrystalline materials. Additionally, it can be used to assess the quality and orientation of single crystals by analyzing diffraction peaks from specific crystallographic planes (hkl) when a single crystal facet is placed on the sample holder, enabling precise determination of crystal orientation.

The compounds investigated in this thesis using the PXRD technique either in single crystals or polycrystalline forms are generally extremely hygroscopic and hence conven-

tional sample holders or a normal glass slide in which the samples are exposed to ambient atmosphere, cannot be used for data collection. The polycrystalline samples are loaded inside the glove box in the air tight sample holder as shown in Fig. 2.6(a, b). The single crystalline samples are placed on a preheated glass slide inside the glove box and secured with a kapton tape in order to prevent it from getting exposed to the ambient atmosphere.

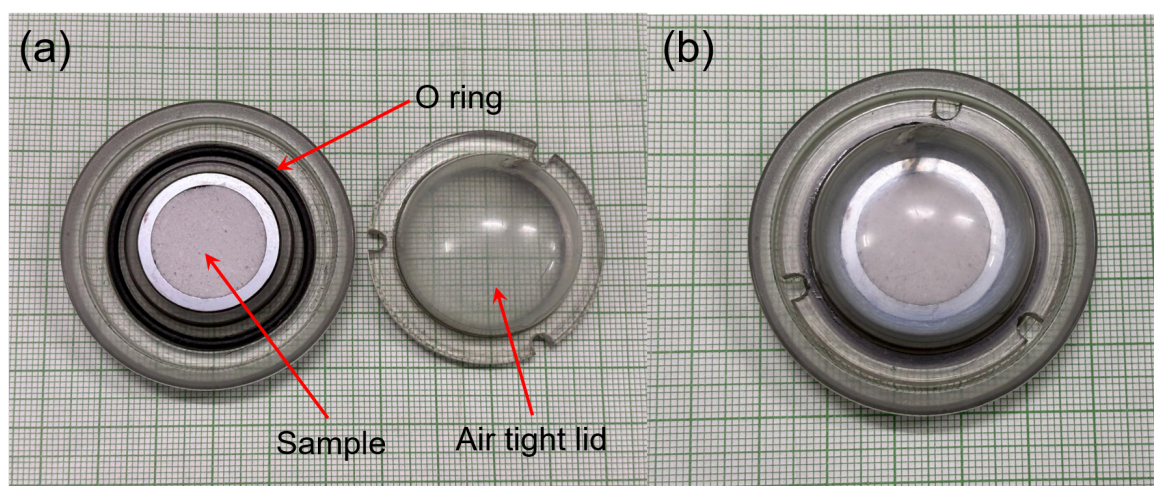


Figure 2.6: Air tight sample holder used for XRD of polycrystalline samples (a) the base and the lid of the air tight sample holder (b) Closed holder used for XRD measurement.

2.2.2 Single crystal x-ray diffraction

SCXRD is an essential technique to precisely determine the crystal structure of the grown single crystal without using any external standard for structure solution and refinement. The Single crystals X-ray diffraction data shown in this thesis is collected on Bruker smart apex duo diffractometer shown in Fig. 2.7(b). It's a sophisticated instrument with a four-circle diffractometer equipped with a Mo $K\alpha$ X-ray source. The name "four-circle" refers to the four degrees of rotational freedom, each corresponding to a specific angular motion, enabling the crystal and detector to be rotated independently which helps to precisely orient the crystal with respect to the incident X-ray beam, allowing for the collection of diffraction data from various angles. The Schematic of a four-circle diffractometer is shown in Fig. 2.7(a). Omega (ω) represents the rotation of the crystal around an axis perpendicular to the X-ray beam,

adjusting the angle between the incident beam and the crystal planes. Chi (χ) refers to the tilt angle of the crystal relative to the rotation axis, allowing the exploration of different atomic planes. Phi (ϕ) is the rotation of the crystal around the vertical axis, facilitating various orientations to capture more reflections. Finally, Theta (2θ) denotes the angle of the detector relative to the incident beam, moving to capture X-rays diffracted at various angles. These are electronically controlled in a diffractometer.

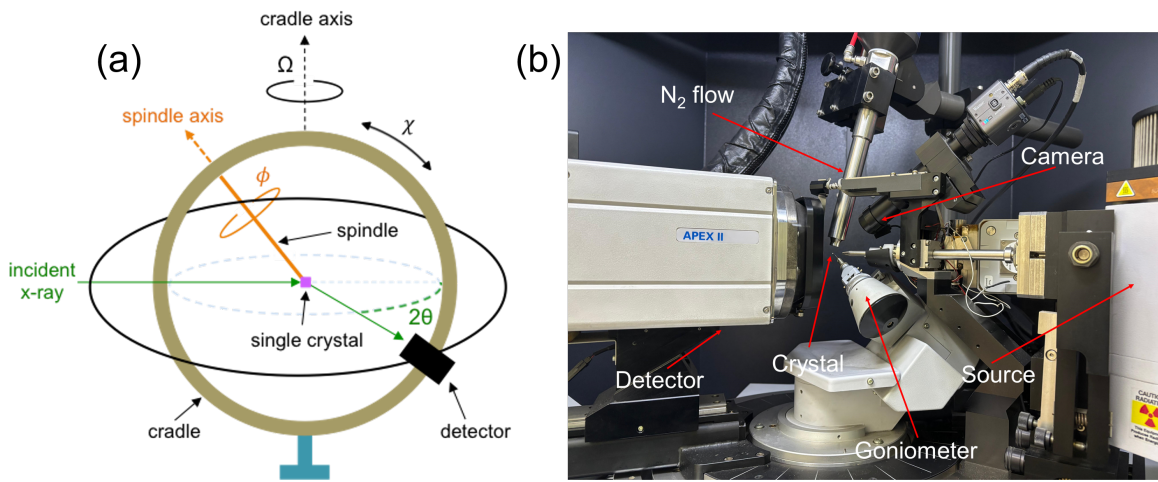


Figure 2.7: (a) Schematic of the four circle diffractometer (b) Bruker Apex Duo instrument used for data collection.

A tiny single crystal specimen typically 0.1 - 0.2 mm lateral dimension is carefully selected using an optical microscope which helps to pick a homogenous defect free single crystal specimen. The single crystal is mounted on a goniometer head, which is then attached to the diffractometer. The goniometer can rotate in multiple directions (tilt and rotation), giving the crystal different orientations relative to the incident X-ray beam. The X-ray source generates a monochromatic X-ray beam, which is directed toward the crystal. The X-rays are aimed at the crystal in various orientations by adjusting the four rotational angles. The four rotational movements (ω , χ , ϕ , 2θ) allow precise alignment of the crystal and measurement of diffracted X-rays. By rotating the crystal and the detector through different angles, a complete dataset of diffraction spots is recorded. By systematically varying ω , χ , and ϕ , and measuring the diffracted intensity at different 2θ angles, a full three-dimensional set of

diffraction data is collected.

The collected diffraction data (intensities and positions of spots) undergoes a data integration and reduction process, which converts these raw frames into a .hkl file, which tabulates the hkl index of all the recorded spots along with their intensities. The structure solution process will then reconstruct the atomic structure of the crystal using techniques like Fourier transformation, yielding the positions of the atoms within the crystal by determining the electron density map. Accurate information about the position of the atoms, the lattice parameters, the bond distances, the bond angles and the anisotropic atomic displacement parameters can be obtained by refining the model obtained after structure solution.

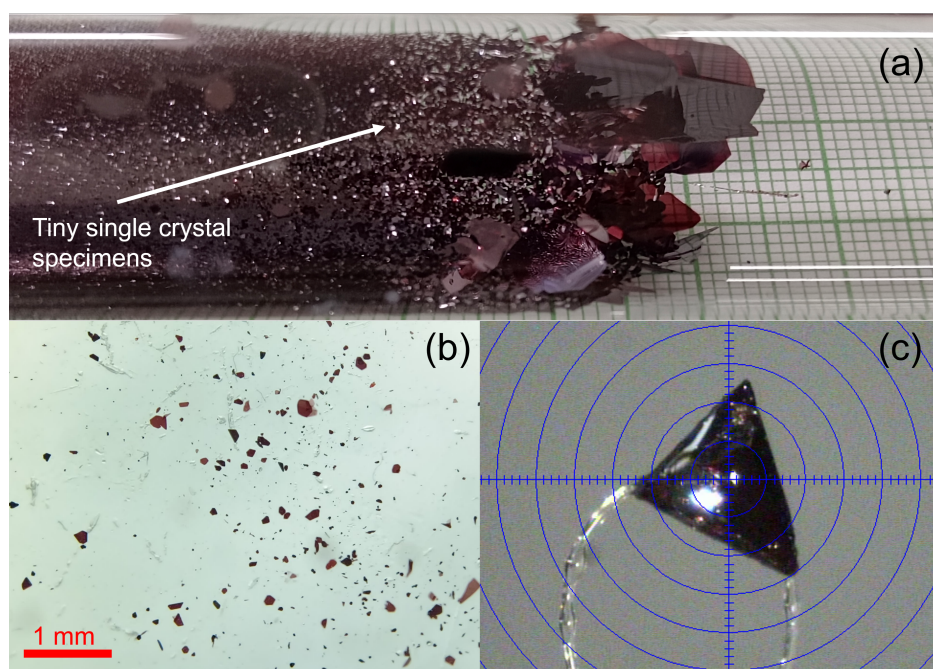


Figure 2.8: (a) A crystal growth ampoule of YbI_3 marked with an arrow showing tiny crystals of 0.1 - 0.2 mm dimensions. (b) An optical microscope image of the crystals in the petri dish covered in oil. (c) A single crystal specimen mounted on the goniometer loop for data collection.

The single-crystal compounds investigated in this thesis are highly hygroscopic, as mentioned earlier. Therefore, it is crucial to prevent decomposition of the samples during its transfer from the glove box to the SCXRD instrument. The small single crystals, which adhere to the inner walls of the reaction ampoule as shown in Fig. 2.8(a), are carefully dis-

lodged by gently tapping them into a petri dish. This process scatters numerous tiny crystals, typically around 0.1 mm in size, across the petri dish. The crystals are then covered with Paratone oil. After a few minutes, once the crystals are evenly coated with the oil, the petri dish is sealed in an airtight container and removed from the glove box. The petri dish is then placed under an optical microscope to select a suitable single-crystal specimen for the experiment. An image of a petri dish under microscope is shown in Fig. 2.8(b). the selected crystal is then glued on th tip of the goniometer as shown in Fig. 2.8(c) which is mounted on the instruemnt for the data collection. Throughout this process, the crystals remain in an inert atmosphere, maintained by a continuous stream of N_2 gas around the petri dish. Since the SCXRD instrument is equipped with a cryostat, the single-crystal sample remains in an inert environment for the entire duration of data collection.

2.2.3 Laue diffraction

The Laue technique is an invaluable tool for determining the structure, symmetry, orientation, and imperfections of grown single crystals. Named after Max von Laue, who first demonstrated X-ray diffraction by crystals in 1912, the method relies on the interaction between a stationary crystal and a polychromatic (white) X-ray beam. Unlike diffraction techniques that use monochromatic X-rays, the Laue method uses a broad spectrum of X-ray wavelengths. This allows various atomic planes in the crystal to simultaneously satisfy the Bragg condition at different angles and wavelengths, producing a series of diffraction spots, as illustrated in Fig. 2.9(a)

In the Laue method, the crystal remains fixed in a specific orientation while the polychromatic X-ray beam is directed at it. The resulting diffraction pattern is captured on a detector, such as photographic film or an electronic detector, positioned either behind the crystal (transmission geometry) or in front of it (reflection geometry).

For the single crystals reported in the present work, a Laue Camera from Photonic Science, UK, operating in backscattering geometry, was used for characterization. Tungsten is used as a target material with an X-ray wavelength ranging from 0.35 to 2.5 Å with sample to

screen distance of 4.5 cm, and the representative image of the Laue diffractometer is shown in Fig. 2.9(b).

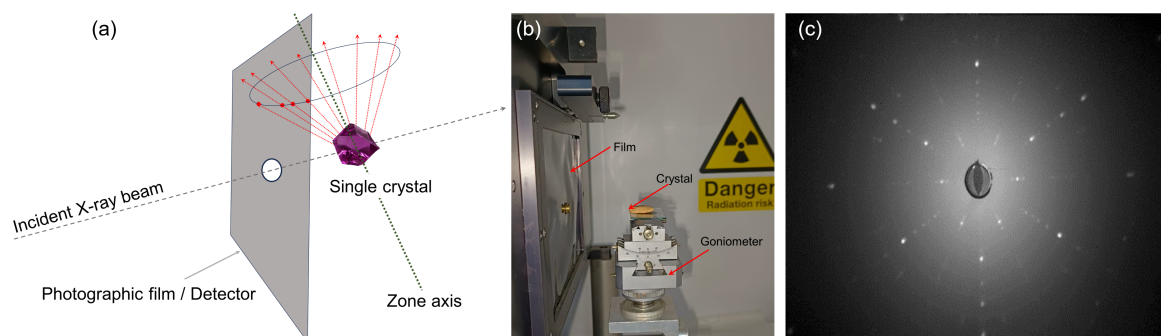


Figure 2.9: (a) Schematic of the Laue diffraction (b) Laue diffractometer used for the sample analysis. (c) A typical Laue image collected on CeCl_3 crystal specimen

The Laue diffraction patterns obtained were analyzed using OrientExpress software, which has a simple and user-friendly interface. The software compares the experimental data with theoretical Laue patterns generated for known crystallographic structures and computes the orientation matrix of the crystal. This allows for accurate determination of the crystal's orientation relative to the incoming X-ray beam. Moreover, OrientExpress automates the indexing of Laue spots, using algorithms to identify the Miller indices (hkl) of the observed diffraction spots, making the analysis process efficient and precise.

The single-crystalline samples investigated in this thesis are extremely hygroscopic, so special precautions were necessary to protect the crystals from exposure to ambient atmosphere during Laue measurements. This was in particular important for CeCl_3 single crystals, which are not quasi two-dimensional but rather three-dimensional in structure. Determining the precise c-axis and the orientation of the ab-plane was particularly challenging. A small piece of the crystal was mounted on a low-speed saw cutting machine using mounting wax, and the cutting was performed inside the glove box as shown in Fig. 2.10 (a, b). After cutting a small piece of the crystal specimen, it was uniformly coated with mounting wax for protection. Once the crystal was secured in wax, it was removed from the glove box for the Laue measurement. Using the OrientExpress software, the direction of the c-axis was determined. The wax coated crystal as shown in Fig. 2.10 (c) was then inserted in the

glove box, where it was cut along the desired orientation. The crystal was subsequently submerged in dichloromethane, a water-repellent solvent, to dissolve the mounting wax. Once precisely oriented, the crystal could be used for magnetic and heat capacity measurements. The two-dimensional crystals on the other hand are easier to align where the direction of c -axis is investigated using the X-ray diffraction on the plane of the crystal specimen in the bragg-brentano geometry. These details are further discussed in chapter 6. of this thesis.

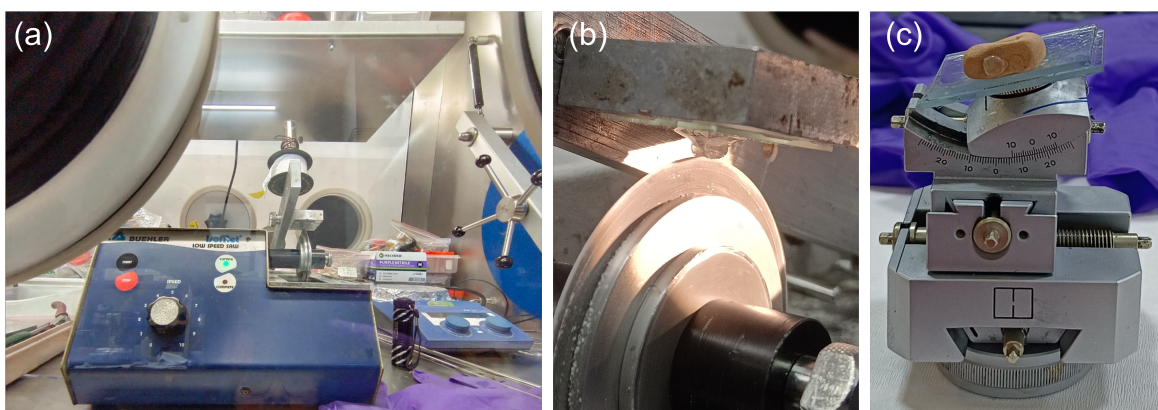


Figure 2.10: (a) Cutting of CeCl_3 single crystal performed inside the glove box (b) Zoomed in image of the cutting of the crystal specimen (c) A typical crystal coated in the wax mounted on the goniometer.

2.2.4 Scanning Electron Microscopy (SEM) and Energy Dispersive x-ray Spectroscopy (EDS).

Field Emission Scanning Electron Microscopy (FESEM) is a sophisticated imaging technique that utilizes a focused beam of electrons to generate high-resolution images of a sample's surface topography. This technique employs a field emission gun, which produces electrons by applying a strong electric field to a sharp metallic tip, typically made of tungsten. This method allows for the emission of electrons from the tip at relatively low temperatures, resulting in a highly focused and intense electron beam. Once emitted, the electrons are accelerated and concentrated into a fine beam using electromagnetic lenses, as shown in Fig. 2.11(a). The focused electron beam is then raster-scanned across the sample surface. As the beam interacts with the sample, various signals are emitted, including secondary elec-

trons, backscattered electrons, and characteristic X-rays, as illustrated in Fig. 2.11(b).

Secondary electrons, which are low-energy electrons emitted from the sample surface due to the interaction with the primary electron beam, play a crucial role in producing surface topography images. Conversely, backscattered electrons are high-energy electrons scattered back from the sample, providing insights into the chemical homogeneity of the material. Additionally, when the high-energy electron beam from FESEM interacts with the sample, it excites the atoms within the material. This excitation leads to the ejection of inner-shell electrons, creating vacancies. Electrons from higher energy levels transition to fill these vacancies, releasing energy in the form of X-rays characteristic of the specific elements present in the sample.

In FESEM analysis, the secondary and backscattered electrons are detected by detectors, allowing for the creation of high-resolution images that provide detailed information about the morphology and chemical homogeneity of the sample. In parallel, Energy Dispersive X-ray Spectroscopy (EDS) detects the emitted X-rays, converting their energy into an electrical signal. This process produces an energy spectrum that displays peaks corresponding to different elements present in the sample.

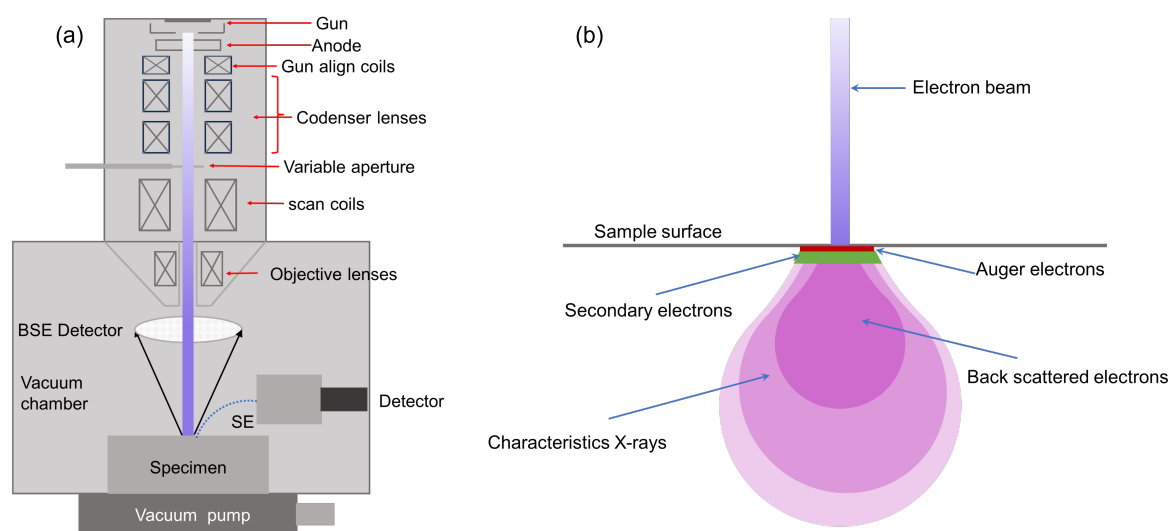


Figure 2.11: (a) Schematic of FESEM instrument (b) Schematic of the interaction of incident electron beam with the sample

The samples synthesized in this thesis are analyzed using a field emission secondary electron microscope (FESEM) from Zeiss Ultra Plus, Germany equipped with EDS analysis probe that had a 20 mm^2 detector from Oxford Inca. A freshly cleaved single crystal specimen of 2D material is glued on the FESEM stub using double-sided carbon tape. In case of extremely hygroscopic samples, the crystal specimen was mounted on the SEM stub and packed in a air tight box before taking it out of the glove box. A suitable energy of incident electron beam is selected to have a precise compositional analysis. Generally an incident energy twice that of energy of the highest excitation line for the elements present in the sample is selected to avoid any error in the analysis.

2.2.5 Transmission Electron Microscopy (TEM)

High-resolution transmission Electron Microscopy (HRTEM) is a powerful technique based on the wave properties of electrons and can provide information on the atomic arrangement, crystal structure, crystallinity, strain, voids, defects, and grain boundary effects in the sample. Since the de-Broglie wavelength of the electron is much smaller than that of visible light, it provides a high-resolution image (up to atomic scales) of the sample compared to light microscopy. Basically, in a transmission electron microscope, a thin specimen (typically less than 100 nm thick) is bombarded with a beam of electrons. The electrons pass through the sample (hence the name transmission), and their interactions with the material create a high-resolution image of the sample where one can observe the atomic arrangement of atoms.

In a typical High-Resolution Transmission Electron Microscope, the process begins with an electron gun, typically a field emission gun (FEG) or a thermionic source, which generates a coherent beam of high-energy electrons. These electrons are then accelerated through a potential difference, usually in the range of 80-300 kV, which increases their energy and reduces their wavelength, enabling high-resolution imaging. A series of condenser lenses focuses the electron beam onto the specimen, carefully manipulating the electron paths to form a coherent and well-collimated beam. As the electron beam interacts with the thin

specimen, some electrons pass through, while others are scattered depending on the atomic structure, density, and thickness of the material. The transmitted electrons are collected by an objective lens, which magnifies the image of the sample. The resulting image is captured on a detector, typically a charge-coupled device (CCD) or photographic film, where variations in electron density within the sample create contrast. After the image is obtained, it can undergo several post-processing techniques, such as Fourier filtering, phase retrieval, and image averaging, to further enhance the resolution and extract detailed information from the sample.

High-Resolution Transmission Electron Microscopy (HRTEM) can operate in different modes, including bright field (BF) and dark field (DF) imaging. In the Bright field mode, the image is formed by collecting transmitted electrons. The electron beam is focused onto the specimen, with most electrons passing through the material. The objective lens then directs the transmitted electrons onto the imaging detector. The intensity of the resulting image is based on electron transmission, where denser regions scatter more electrons and appear darker, while less dense areas appear lighter. In the Dark field mode the scattered electrons are collected to form the image, rather than directly transmitted. A small aperture (the dark field aperture) is placed in the back focal plane of the objective lens. This aperture is aligned with the diffracted beams (i.e., scattered electrons) coming from specific crystallographic planes in the specimen. The image is formed by the scattered electrons that pass through the dark field aperture, creating a bright image on a dark background. The schematic for the working of two different configurations is illustrated in Fig. 2.12(a,b)

The sample preparation plays a crucial role in acquiring high resolution image from HRTEM instrument. The samples investigated in this thesis are analyzed using JEOL JEM 2200FS from Japan equipped with a 200KeV field emission gun (FEG) and an in-column energy filter (Omega filter), that allows for a zero-loss image. The sample is prepared by liquid exfoliation technique, for which a thin single crystal specimen is sonicated using ethanol. The dispersed solution is drop cast on the TEM carbon coated copper grid as shown in Fig. 2.13(a) and allowed to dry under vacuum for at least 2-3 hours. The sample is

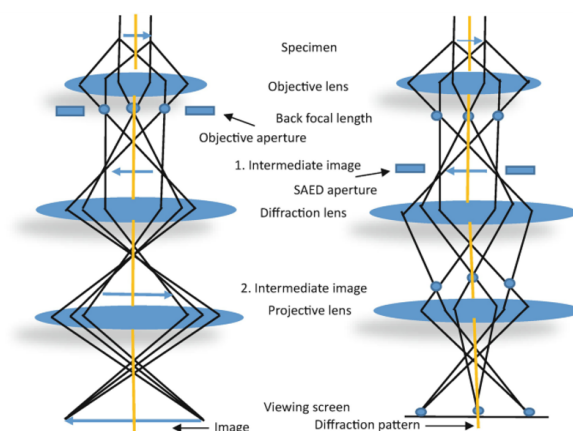


Figure 2.12: Schematic of image formation from the HRTEM instrument in two different mode, image mode and diffraction mode. The image is taken from ref. [12]

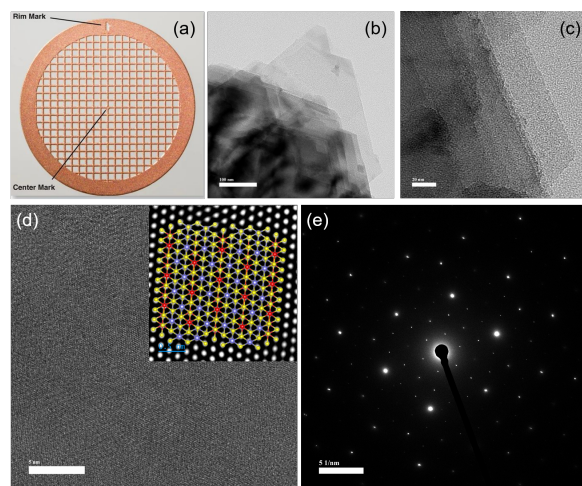


Figure 2.13: (a) A carbon coated copper grid on which the sample is drop cast for HRTEM analysis. (b) a low resolution image of a layered material NiPS_3 . (c) A high resolution image collected at a specific area of image (b). the inset shows the IFFT pattern overlapped with the actual crystal structure in the ab - plane of the sample. (d) The selected area diffraction pattern of the image in (c). (e) The selected area electron diffraction (SAED) pattern of the image in (c).

then mounted on the TEM sample holder, and high-resolution images along with the SAED patterns are collected. The images are analysed using GATAM GMS-3 software package. Fig. 2.13(b-e) shows how a high-resolution image and a Selected Area Electron Diffraction (SAED) pattern are obtained by increasing the resolution.

2.2.6 Raman spectroscopy

Raman spectroscopy is a non - destructive spectroscopic technique based on the principle of inelastic scattering of light which was first studied by Adolf Smekal in 1923 and the first experimental evidence was seen by C.V. Raman in 1928, known as Raman effect. The Raman scattering works by directing a monochromatic electromagnetic source, typically a laser, onto a sample, where the light interacts with the molecules of the material. Most of the light is scattered elastically in a process called Rayleigh scattering, meaning the scattered photons have the same energy (wavelength) as the incident photons, which does not provide molecular information. However, a small fraction of the scattered light (1 in 10 million photons) experiences an energy shift due to interactions with the vibrational or rotational energy levels of the molecules, a process known as Raman scattering. In this case, the scattered photons either lose energy (Stokes shift) if the molecule absorbs energy or gain energy (Anti-Stokes shift) if the molecule loses energy. These energy shifts are measured by the Raman spectrometer and correspond to specific vibrational modes of the molecules, creating a unique molecular fingerprint for the sample. The magnitude of the raman shift is dependent on the change in the polarizability of the bond which is a key difference between the the phonon mode to be Raman or IR active, the later need the change in the dipole moment. The schematic illustrating the basics of Raman scattering processes is shown in Fig. 2.14

Apart from providing a characteristic fingerprint of a sample, various parameters in a Raman spectrometer can be tuned to extract specific and detailed information about the material. The polarization of the incident light and the scattered light can be controlled, and detailed investigation about the symmetry of vibrational modes can be studied. Since molecular vibrations and phonon modes in crystalline materials interact differently with light depending on their symmetry and orientation, varying the polarization allows to selectively enhance or suppress certain vibrational modes. Temperature-dependent Raman spectroscopy, on the other hand, provides detailed information about structural and magnetic phase transitions. Changes in the peak position and linewidth of Raman-active phonon modes as a function of

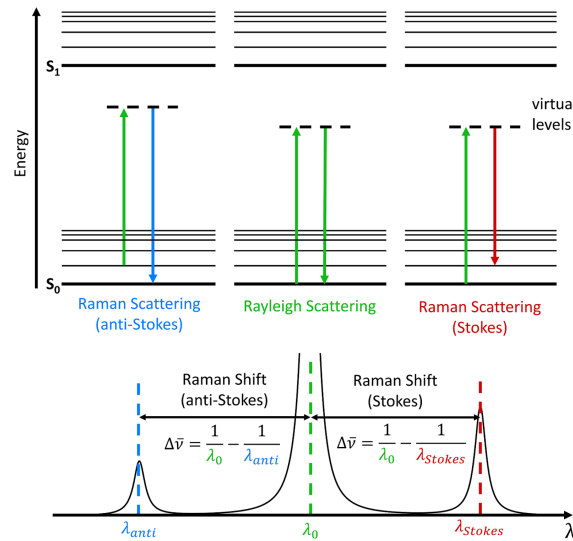


Figure 2.14: Schematic of the processes in the Raman scattering. The image was taken from the Edinburg Instruments website.

temperature allow for the study of deviations from expected anharmonicity in the phonon modes. The appearance of a broad continuum in the Raman spectrum, in addition to the discrete phonon modes, can indicate strong correlations between the lattice, spin, and electronic degrees of freedom, revealing complex interactions within the material. Magnetic field-dependent Raman spectroscopy complements these techniques by providing detailed information about magnetic excitations in the material. This approach helps explore magnetic phenomena such as spin interactions and magnon excitations, offering valuable insights into the magnetic properties of the material.

The Raman spectra on the samples in this thesis is collected in the back scattering geometry using the Horiba Jobin-Yvon LabRAM HR spectrometer equipped with a liquid nitrogen cooled charge-coupled detector (CCD) and laser of 633 nm as a source of excitation was used. The laser excitation power, the acquisition time, and the number of iterations were optimized to obtain high-quality Raman spectra for the analysis. The hygroscopic samples were either coated a small amount of N grease or secured with a kapton on a glass slide inside the glove box. The Raman spectra for the N -grease is separately taken without the crystal specimen to exclude the background.

2.3 Physical properties measurement techniques

The magnetic and thermal properties of the single crystals reported in this thesis are measured using a Physical Properties Measurement System (PPMS) from Quantum Design, Model 6000, USA. The system can measure different electronic, magnetic and thermal properties of the materials in the range of 1.9 - 400 K with applied magnetic field upto 9 T. The magnetic measurement are conducted in Vibrating sample magnetometer attachment option in PPMS at UGC - DAE Indore. The measurements were conducted from 300 K down to 2 K and under a magnetic field upto 16 T. The samples in this thesis were analyzed using heat capacity and magnetization measurements, and the details of these techniques are summarized in the sections below.

2.3.1 Heat capacity

Heat capacity is the amount of heat needed to raise the temperature of material by 1-degree Celsius. The heat capacity option provided with PPMS measures the heat capacity of a sample by adding and removing the heat from the sample and monitoring the change in the temperature at constant pressure given by the equation.

$$C_p = \left(\frac{dQ}{dT} \right)_p$$

where dQ is the differential heat added to the system, and dT is the differential change in temperature. The heat capacity measurement provides detailed information about the electronic, magnetic, and structural properties of the materials and hence it is a crucial and extremely sensitive tool to investigate the magnetic transitions, structural transitions, charge density, and spin density waves and Schottky anomaly due to crystalline electric field splitting or the Nuclear Schottky. All these physical phenomena, when investigated gives detailed knowledge about the interaction of charge, spin and lattice degrees of freedom in the material.

The sample for the heat capacity measurement is mounted on a puck, which acts as

the heat capacity sample holder. This puck consists of a sample stage, connecting wires, a thermometer, and a heater. The sample stage is supported by four connecting wires that provide both electrical connections to the heater and thermometer and structural support for the platform. A schematic is shown in Fig. 2.15(a).

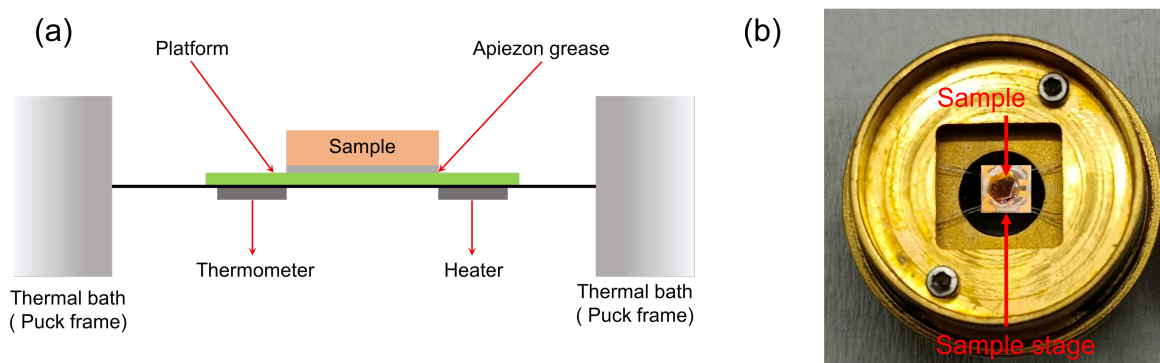


Figure 2.15: (a) Schematic of heat capacity puck used in the PPMS. (b) The actual image of the puck with the sample mounted on it

Typically, the sample mass ranges from 2 to 200 mg, with dimensions smaller than $3 \times 3 \text{ cm}^2$. The sample is mounted on the stage using a small amount of N grease, which ensures good thermal contact between the sample and the platform. Initially, the heat capacity of the N grease, known as the addenda, is measured. The sample is then placed on top of the grease without disturbing the addenda, and the heat capacity of both the sample and addenda is measured together. The software subsequently subtracts the heat capacity of the addenda, providing the heat capacity of the sample alone. The entire measurement is conducted in a high-vacuum environment, created using a turbo pump, to ensure that the thermal conductance between the sample platform and the thermal bath is primarily governed by the conductance of the wires. An image of the puck along is shown in Fig. 2.15(b). For the hygroscopic samples the crystals were coated with a thin layer of N grease inside the glove box and hence for such samples the exact contribution of the addenda heat capacity cannot be subtracted. However, for all practical purposes the the addenda heat capacity is very small in the low temperature regime and hence can be neglected.

2.3.2 Vibrating Sample Magnetometer (VSM)

The VSM (Vibrating Sample Magnetometer) option in the PPMS allows for the measurement of DC magnetization as a function of temperature and magnetic field. This system includes several components to accurately measure the sample's magnetization: a VSM linear motor transport (head) for vibrating the sample, a coilset puck for detection, and electronics for driving the motor and detecting signals from the pickup coils. The hardware and data collection are controlled automatically via the MultiVu software. The technique involves oscillating the sample near a pickup coil while detecting the induced voltage. A compact gradiometer pickup coil is used to achieve a large oscillation amplitude (1-3 mm peak) at a frequency of 40 Hz, which allows for the detection of magnetization changes as small as 10^{-6} emu at a data rate of 1 Hz. The schematic of the working of VSM is shown in Fig. 2.16.

The fundamental principle behind the operation of the VSM is that the changing magnetic flux will induce a voltage in a pickup coil. The time-dependent induced voltage is given by the following equation:

$$V_{\text{coil}} = \frac{d\Phi}{dt} = \left(\frac{d\Phi}{dz} \right) \left(\frac{dz}{dt} \right)$$

Φ represents the magnetic flux enclosed by the pickup coil, z is the vertical position of the sample relative to the coil, and t is time. For a sample oscillating sinusoidally, the induced voltage is expressed as:

$$V_{\text{coil}} = 2\pi f C m A \sin(2\pi f t)$$

Here, C is a coupling constant, m is the DC magnetic moment of the sample, A is the oscillation amplitude, and f is the frequency of oscillation. The working principle is demonstrated in Fig. 2.16.

The magnetic measurement for the extremely hygroscopic samples discussed in this thesis are mounted on the sample holders of VSM using different techniques in order to prevent them from exposing to the atmosphere. The crystals for field applied parallel to the ab plane were mounted on the quartz sample holder inside the glove box using a Kapton tape as shown in Fig. 2.17(a) and for the field applied perpendicular to the ab plane, the specimen

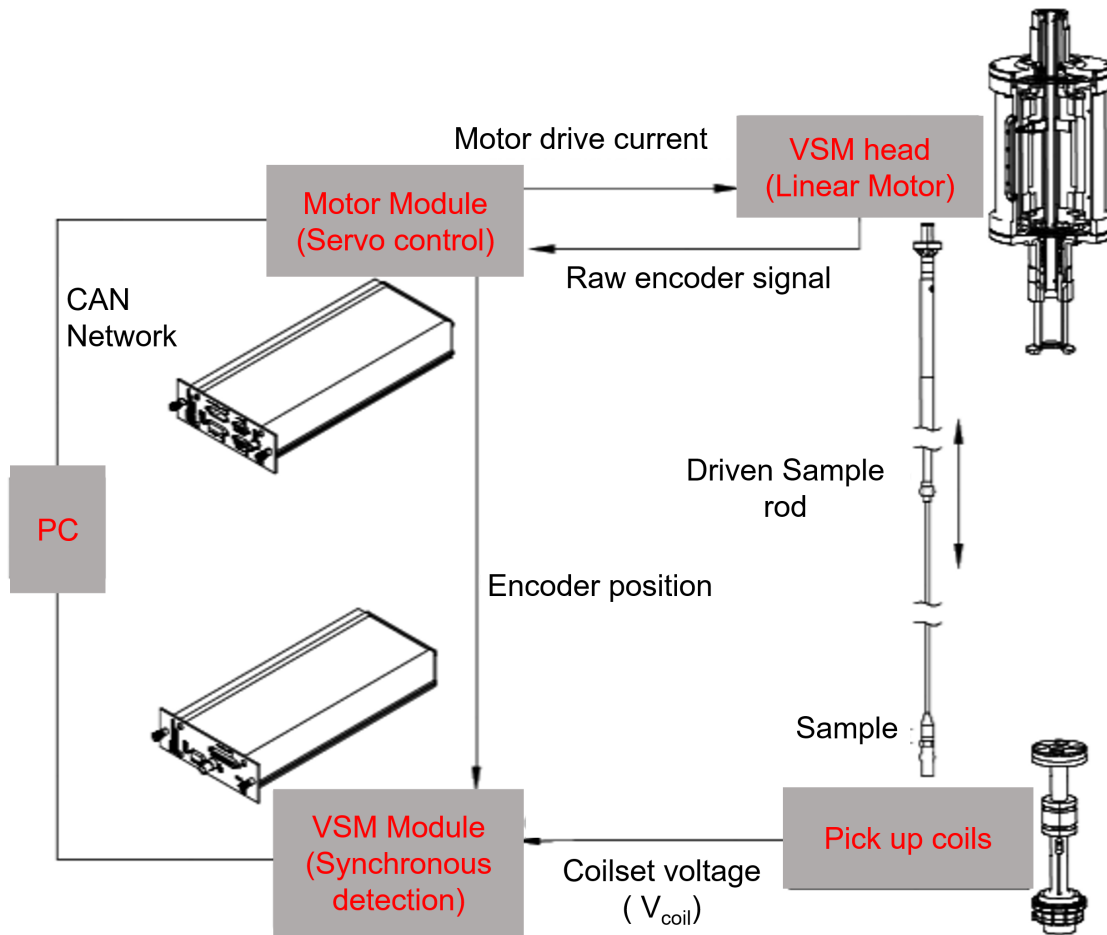


Figure 2.16: Operating principle for the PPMS VSM option. The image is adapted from the PPMS VSM options manual.

was mounted on the brass sample holder in between two quartz rod as shown in Fig. 2.17(b).

A kapton tape or N grease was use to prevent the crystal from degradation.

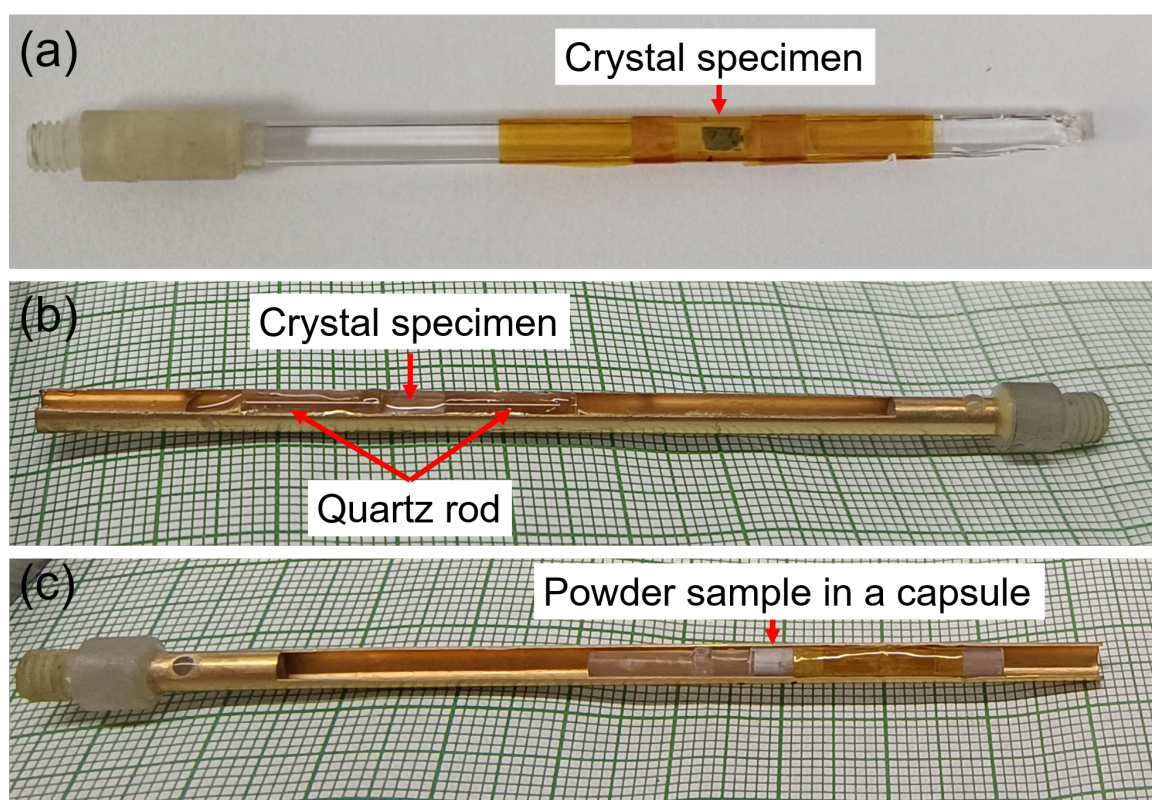


Figure 2.17: Hygrscopic samples mounted inside the glove box for different orientations on different sample holders of the VSM. (a) Magnetic field applied parallel to the ab-plane of YbI_3 specimen, mounted on a quartz sample holder. (b) Magnetic field applied perpendicular to the ab-plane of CeCl_3 specimen, mounted on a brass sample holder. (c) Polycrystalline CeCl_3 samples filled in a capsule and mounted on a brass sample holder.

Chapter 3

Crystal growth, magnetic and thermal properties of quasi two-dimensional honeycomb magnet YbI_3

The work described in this chapter is published in Physical Review B. with the title of ”Anisotropic magnetic ground state of single-crystalline quasi-2D honeycomb antiferromagnet YbI_3 ”

- *The Magnetic and heat capacity measurements discussed in this chapter were performed by me at UGC-DAE Consortium for Scientific Research, University Campus, Khandwa Road, Indore 452001, Madhya Pradesh, India in the group of Dr. Rajeev Rawat.*

3.1 Introduction

Quantum magnetism is one of the frontier areas in condensed matter physics, showcasing unusual ground states, such as, spin liquids with emergent quasiparticles, and exotic spin textures driven by competing interactions [47, 79]. magnetic interactions in these systems are generally frustrated, which prevents simple, ordered spin arrangements, leading to complex or unconventional ground states. The spin systems based on triangular, Kagome, or pyrochlore lattices are model geometrically frustrated systems, where the competing interactions result from the lattice geometry which does not allow all the nearest-neighbor couplings to be simultaneously satisfied. .

The Kitaev model, introduced by Alexei Kitaev in the year 2006 [80], opened-up a new frontier for exploring magnetic frustration. This groundbreaking theoretical framework describes a spin-1/2 system on a two-dimensional honeycomb lattice, where the bond-dependent nearest-neighbor couplings give rise to a strong frustration. The ground state of Kitaev model is a novel quantum spin liquid with Majorana fermions as quasiparticle excitations.

The quest for experimental realization of Kitaev model gained momentum following the seminal work by Jackeli and Khaliullin [81], who laid out a roadmap for uncovering potential Kitaev candidates among the spin-orbit-assisted Mott insulators, specifically the $4d^5$ ruthenates and $5d^5$ iridates. In these compounds, the complex interplay between the strong spin-orbit coupling, octahedral crystal electric field splitting, and electronic correlations give rise to a $J_{\text{eff}} = 1/2$ Kramers doublet ground state with highly anisotropic bond-dependent interactions, which serves as a prerequisite for realizing the Kitaev model.

The electronic and magnetic properties of candidate materials, including, Na_2IrO_3 [82–84], α - Li_2IrO_3 [85, 86], β - Li_2IrO_3 [87, 88], γ - Li_2IrO_3 [89], $\text{H}_3\text{LiIr}_2\text{O}_6$ [90], Cu_2IrO_3 [91], $\text{Cu}_3\text{LiIr}_2\text{O}_6$ [92], $\text{Ag}_3\text{LiIr}_2\text{O}_6$ [93], α - RuCl_3 [94–100] has been extensively studied in recent years to explore the manifestations of Kitaev physics.

The f -electron systems, based on the rare-earths with $J_{\text{eff}} = 1/2$ Kramer’s doublet

ground state and edge-shared octahedra have also been theoretically predicted to host Kitaev physics [101–104]. However, suitable materials embodying this concept remain sparse. Xing *et al.* recently investigated the crystal growth and magnetic properties of YbCl_3 , aiming to explore its potential for Kitaev physics [105]. YbCl_3 is a two-dimensional van der Waals material, where the Yb atoms form a slightly distorted honeycomb net, where each Yb atom has nearest-neighbors at 3.886 Å and 3.864 Å [13]. The previous studies reveal short-range ordering of Yb^{3+} moments ($J_{\text{eff}} = 1/2$) around 1.2 K and a Neel-type antiferromagnetic long-range order at 0.6 K, with Yb spins antiferromagnetically aligned within each honeycomb plane, pointing primarily along the a -axis with a small tilt of $\sim 5^\circ$ along the c -axis [105–107].

A recent study by Matsumoto *et al.* provides evidence for Bose-Einstein condensation in YbCl_3 . When the magnetic field is aligned parallel to the a -axis, YbCl_3 has been argued to undergo a transition from Heisenberg to XY-like state, ultimately achieving a field-polarized state at $H_s = 5.93$ T, marked as the quantum critical point. Upon reducing the field slightly below H_s , YbCl_3 allegedly behaves as a two-dimensional gas of bosons, showing signatures of Bose-Einstein condensation possibly stabilized by a small but non zero interlayer interaction ($\Lambda_\perp \approx 0.1$ mK and $\Lambda_\parallel \approx 5$ K, where $\Lambda_\perp$ and $\Lambda_\parallel$ are interlayer and intralayer nearest neighbor interactions) [14]. Hence, YbCl_3 is posited as an exemplary two-dimensional system for studying quantum magnetism on a honeycomb lattice.

Conversely, YbBr_3 , also comprising $J_{\text{eff}} = 1/2$ Heisenberg spins on a honeycomb lattice, demonstrates no long-range ordering down to 100 mK. Based on their inelastic neutron scattering data, Wessler *et al.* argued that despite lacking Kitaev-type anisotropic interactions, YbBr_3 exhibits pronounced quantum fluctuations, perhaps signature of a quantum spin liquid ground state [108]. Considering the novel magnetic behavior associated with the YbCl_3 and YbBr_3 , we set out to investigate the previously unexplored member YbI_3 of this family.

Here, we report the crystal growth of a new two-dimensional van der Waals material, YbI_3 , using the vapor transport technique. YbI_3 crystallizes in $R\bar{3}$ symmetry, determined using the single crystal x-ray diffraction. In this structure, the Yb^{3+} ions form an ideal honey-

comb network, with equidistant nearest neighbors with the honeycomb plane. This structure is analogous to the low-temperature ($T < 150$ K) phase of α -RuCl₃, suggesting that YbI₃ is a possible candidate material for studying Kitaev physics. The ground state of Yb³⁺ in YbI₃ is shown to be a well-isolated Kramers doublet with an effective moment, $J_{\text{eff}} = 1/2$. The magnetic behavior is found to be slightly anisotropic. While the in-plane saturation moment at 2 K is $\approx 1.5 \mu_B/\text{Yb}^{3+}$, it is $\approx 1 \mu_B/\text{Yb}^{3+}$ for the out-of-plane orientation, suggesting an easy-plane behavior analogous to YbCl₃ (here in-plane and out-of-plane refers to the orientation of the applied field with respect to the *ab*-plane). The low-temperature heat capacity shows a broad peak at $T_1 = 0.95$ K due to short-range ordering of the Yb moments, and a sharp peak at $T_2 = 0.6$ K that marks the onset of long-range antiferromagnetic ordering. The value of critical exponent α obtained from fitting the low-temperature heat capacity using the power-law is 2.5, different from $\alpha = 3$ for a 3D Heisenberg antiferromagnets or $\alpha = 2$ for the Heisenberg spins on a 2D lattices, suggesting a possible unconventional quantum ground state for this system.

3.2 Experimental methods

Single crystals of YbI₃ are grown using the vapor transport technique in a two-zone furnace. The details of the crystal growth are given in sec. 3.3.1. The x-ray diffraction patterns are recorded using a Bruker D8 advance diffractometer in the Bragg Brentano geometry employing Cu K_α ($\lambda = 1.5406$ Å) radiation, as described in 2.2.1. The 2Θ values ranged from 5° to 90° with a step size 0.02°. For this purpose, a thin plate-like single crystal was placed over a oven-dried glass-slide and completely covered by a layer of Kapton tape to avoid degradation due to moisture.

Single crystal x-ray diffraction (SCXRD) was carried out using a Bruker Smart Apex Duo diffractometer employing Mo-K_α radiation ($\lambda = 0.70173$ Å) at 250 K and 150 K using an open-flow nitrogen cryostat. The details of the single crystal x-ray diffraction experiment is elaborated in 2.2.2. A tiny crystal of approximately 1-2 μm lateral dimensions was covered in paratone oil to avoid exposure to the atmosphere and mounted on a goniometer loop. The

intensities were integrated using the Crystalis Pro [109]. The refinement was performed using Jana 2006 [110].

The layered morphology of the single crystals was confirmed using a scanning electron microscope (SEM) (FEI Make), and the Chemical composition was verified using an Energy Dispersive x-ray (EDX) (Quanta 2003D) detector attached to the SEM instrument in the Secondary Electron (SE) mode as described in 2.2.4. The EDX spectra was collected at 15 – 20 different points, spread across the platelet-shaped single crystal specimen, to obtain the averaged elemental composition. The elemental mapping was also performed over a micron size area of the single crystal to check the compositional homogeneity of the grown crystal.

Raman spectra were collected at room temperature in the back scattering configuration using a Horiba Jobin-Yvon LabRAM HR spectrometer equipped with liquid nitrogen cooled Charge-Coupled Detector (CCD) and a laser of 532 nm as the source of excitation. The instrumentation is described in 2.2.6 The excitation was maintained at 75% of the maximum power, and the accumulation time for each spectrum was 10 s with 30 iterations each time to improve the resolution and intensity of the Raman modes. For the purpose of obtaining Raman spectrum, the YbI_3 crystal was coated with a thin-layer of Apiezon N grease to prevent degradation due the measurement.

Magnetic measurement between 2 – 300 K are performed at the UGC-DAE CSR, Indore using the VSM probe in a Physics Property Measurement System (PPMS), Quantum design, USA. The heat capacity was measured 0.11 K to 4 K using a dilution insert in the PPMS at UGC-DAE-CSR, Indore. Due to highly hygroscopic nature of YbI_3 , the crystal was covered with an unknown amount of Apiezon N grease, hence the addenda could not be measured accurately. However, in the temperature range of our measurement, the magnetic specific heat of YbI_3 is 3 – 4 orders of magnitude higher than that of the Apiezon N grease, and can therefore be safely ignored while analyzing the measured data.

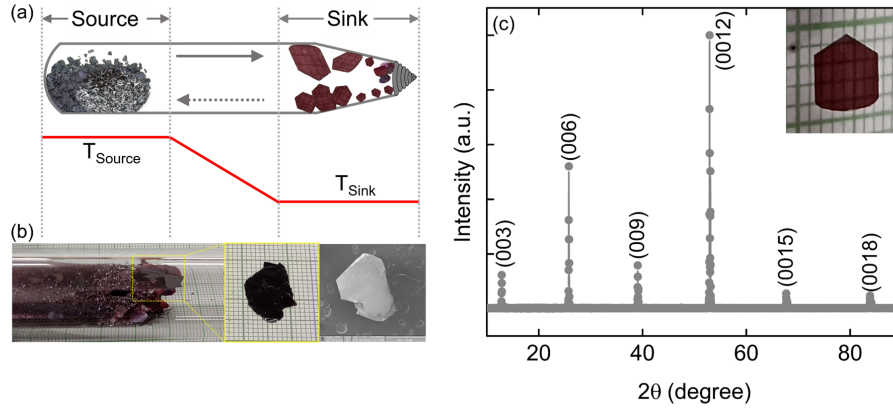


Figure 3.1: (a) Schematic of the vapor transport reaction in a sealed quartz ampoule kept in a temperature gradient furnace. The source end of the ampoule contains a mixture of Yb powder and I_2 flakes. At the sink end the crystals of YbI_3 nucleates and grow as explained in the text. $T_{\text{source}} = 750^\circ\text{C}$ and $T_{\text{sink}} = 650^\circ\text{C}$. The arrows indicates the direction of transport of the Yb-I complexes (solid), and I_2 vapors (dashed); (b) Actual growth ampoule (left), containing several small crystals, and a large cm-sized single crystal (middle). A scanning electron microscope image of a small crystal specimen used for chemical analysis (right). (c) x-ray diffraction was conducted in Bragg-Brentano geometry, displaying the (0 0 l) reflections which confirms the ab - plane of the single crystal specimen shown in the inset.

3.3 Results and discussion

3.3.1 Crystal growth of YbI_3

High-quality single crystals of YbI_3 are grown using the physical vapor transport (self-transport) technique. Ytterbium powder (99.9% REO, Alfa Aesar) and Iodine flakes (ACS reagent, $\geq 99.8\%$, Sigma Aldrich) are used in their elemental form as starting precursors. The stoichiometric quantities of the starting materials are loaded in a quartz ampoule, measuring approximately 15 cm in length, with an inner diameter of about 2 cm and wall-thickness of 2 mm, resulting in a volume of around $40 - 50 \text{ cm}^3$. To compensate for iodine sublimation losses during the evacuation process, an additional 10% excess of iodine is included. The entire procedure of handling and storing the precursors is carried in an argon-filled glove box with oxygen and moisture content $< 0.1 \text{ ppm}$. Before loading the precursors into the ampule, thorough cleaning steps are undertaken. The ampule undergoes sonication

in acetone, followed by rinsing with deionized water. Subsequently, it is preheated to 1000°C to eliminate residual moisture and organic impurities sticking to its inner walls. The filled ampule is evacuated down to 10^{-5} torr, and thereafter flame-sealed under dynamic vacuum. Given iodine's high vapor pressure at room temperature (approximately 100 Pa at 309 K), the ampule was kept under an ice bath during evacuation and sealing to minimize iodine losses. The sealed ampoule is then kept in a two-zone furnace under a temperature gradient $\Delta T = 100^\circ\text{C}$, with the source temperature set at 750°C (T_{source}), and the sink temperature (T_{sink}) at 650°C. The schematic of vapor transporter reaction is shown in Fig. 3.1(a). Optimal growth conditions for producing the largest and highest quality single crystals involve simultaneous cooling of both the zones at a rate of 0.3°C h^{-1} down to $T_{\text{source}} = 600^\circ\text{C}$ and $T_{\text{sink}} = 500^\circ\text{C}$. Subsequently, both zones of the furnace are cooled simultaneously to room temperature. The experiments performed using different growth conditions are summarized in Table 3.1. Shiny, plate-like single crystals, with typical lateral dimensions of $1\text{ cm} \times 1\text{ cm}$, and dark-brown/transparent appearance, as shown in Fig. 3.1(b), are obtained. The plate-like morphology of the grown crystals is a reflection of the underlying layered or quasi-two-dimensional structure of YbI_3 .

Table 3.1: Summary of various parameters used during the crystal growth attempts: Source temperature (T_{source}), sink temperature (T_{sink}), Dwell time, Rate of cooling, and total duration of the crystal growth experiment needed to obtain high-quality single crystals.

Growth attempt	T_{source}	T_{sink}	Dwell time	Rate of cooling	Duration	Conclusion
1	750 Å°C	650 Å°C	20 days	100 Å°C/hr below 650 Å°C	30 days	Many small crystals of typical Size ranging from 3 - 4 mm lateral dimension
2*	750 Å°C	650 Å°C	24 hours	0.3 Å°C/hr ($T_{\text{source}} = 750\text{ Å°C}$ to 600 Å°C)	30 days	large crystals of Size nearly 10 mm lateral dimension
3	1050 Å°C	1000 Å°C	24 hours	0.3 Å°C/hr ($T_{\text{source}} = 1050\text{ Å°C}$ to 900 Å°C)	30 days	very few small crystals of size 1 mm lateral dimension

*The optimal thermodynamic conditions for obtaining centimeter-sized crystals have been identified, and crystals from this batch are being used for further analysis in this study.

The Chemical composition was checked on a crystal specimen shown in the Fig. 3.2(a). The EDX spectra were collected at 15 - 20 different areas marked with yellow rectangles on the specimen in order to confirm the homogeneity. The atomic % for Yb and I and

their corresponding composition is shown in Table 3.2. The data was corrected using ZAF method. The error bar in the measurement is estimated to be 4 - 5 atomic %. The sample begins to crack once it is exposed to the ambient atmosphere. During loading into the sample chamber, the specimen was exposed to the atmosphere for a few seconds, resulting in slight cracking in the few parts of the sample as seen in the SEM image.

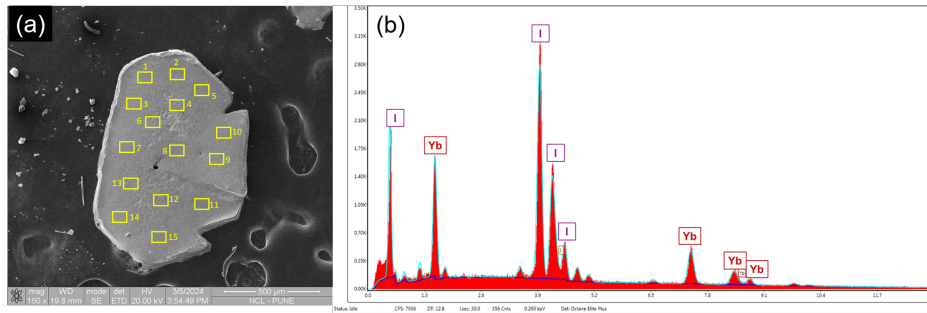


Figure 3.2: EDX spectra taken at 15 different areas to show the homogeneity of the single crystal. (a) The scanning electron microscope image of YbI_3 crystal specimen taken using Secondary electron (SE) mode. The yellow rectangles marked on the images are different areas on which EDX spectra were collected. One such spectrum is shown in (b).

Table 3.2: The composition of Yb and I at 15 different areas of the single crystal, showing the homogeneity of the crystal specimen.

Area	Yb (atomic %)	I (atomic %)	Yb (composition)	I (composition)
1	23.52	76.48	0.9408	3.0592
2	24.76	75.24	0.9904	3.0096
3	23.34	76.66	0.9336	3.0664
4	23.40	76.60	0.9360	3.0640
5	23.33	76.67	0.9332	3.0668
6	23.40	76.60	0.9360	3.0640
7	21.85	78.15	0.8740	3.1260
8	23.36	76.64	0.9344	3.0656
9	22.88	77.12	0.9152	3.0848
10	23.46	76.54	0.9384	3.0616
11	24.40	75.60	0.9760	3.0240
12	24.11	75.89	0.9644	3.0356
13	23.25	76.75	0.9300	3.0700
14	22.51	77.49	0.9004	3.0996
15	23.62	76.38	0.9448	3.0552

The x-ray diffraction pattern collected from a plate-like single crystalline specimen is shown in Fig. 3.1(c). An image of the specimen used for the experiment is shown in the inset. The pattern is collected in the Bragg-Brentano geometry, revealed diffraction peaks with miller indices $(00l)$, where $l = 3, 6, \dots$, suggesting that the large lateral surface of the measured specimen is oriented perpendicular to the c -axis. The crystals are found to be extremely hygroscopic, decomposing into white powder and eventually into a liquid droplet when exposed to the ambient atmosphere. Therefore, the specimen is covered with a kapton tape while taking the XRD on the ab - plane of the sample as described in Sec. 3.2.

3.3.2 Crystal structure

The symmetry of YbI_3 was found to be trigonal $R\bar{3}$ (# 148) from single crystal x-ray diffraction, which is in agreement with the L Asprey et al. [16]. Temperature-dependent single crystal x-ray diffraction measurements at 250 K and 150 K show an absence of structural transition and that the symmetry remains trigonal as shown in Fig. 3.3, unlike $\alpha - \text{RuCl}_3$, which exhibits a change of symmetry from room-temperature monoclinic ($C2/m$) to low-temperature trigonal ($R\bar{3}$) symmetry below a temperature of 150 K [111]. The symmetry of the lattice is further substantiated by the reciprocal space cuts shown in Fig. 3.3

Crystal structure of YbI_3 in the ab -plane is shown in Fig. 3.4(a), illustrating the honeycomb network of Yb atoms similar to $\alpha\text{-RuCl}_3$ [112] and YbBr_3 [108]. Each Yb atom is coordinated to six neighboring I atoms in an almost ideal edge-sharing octahedral arrangement. In the honeycomb layer, the Yb-Yb bond distance is $4.226(1) \text{ \AA}$, while the distance along the c -axis is $6.803(4) \text{ \AA}$ as shown in Fig. 3.4(c), where the stacking of the honeycomb layers perpendicular to the c -axis can be seen. The Yb-I-Yb bond angle in the honeycomb layer is $91.76(3)^\circ$ (see panel (e) in Fig. 3.4). The octaheron of ligands I atoms around the central Yb atom is shown in Fig. 3.4(g). The details of the data collection strategy, crystallographic information and refinement parameters are summarized in Table 3.3. The atomic positions with their corresponding isotropic displacement parameters (ADPs) are listed in Table 3.4.

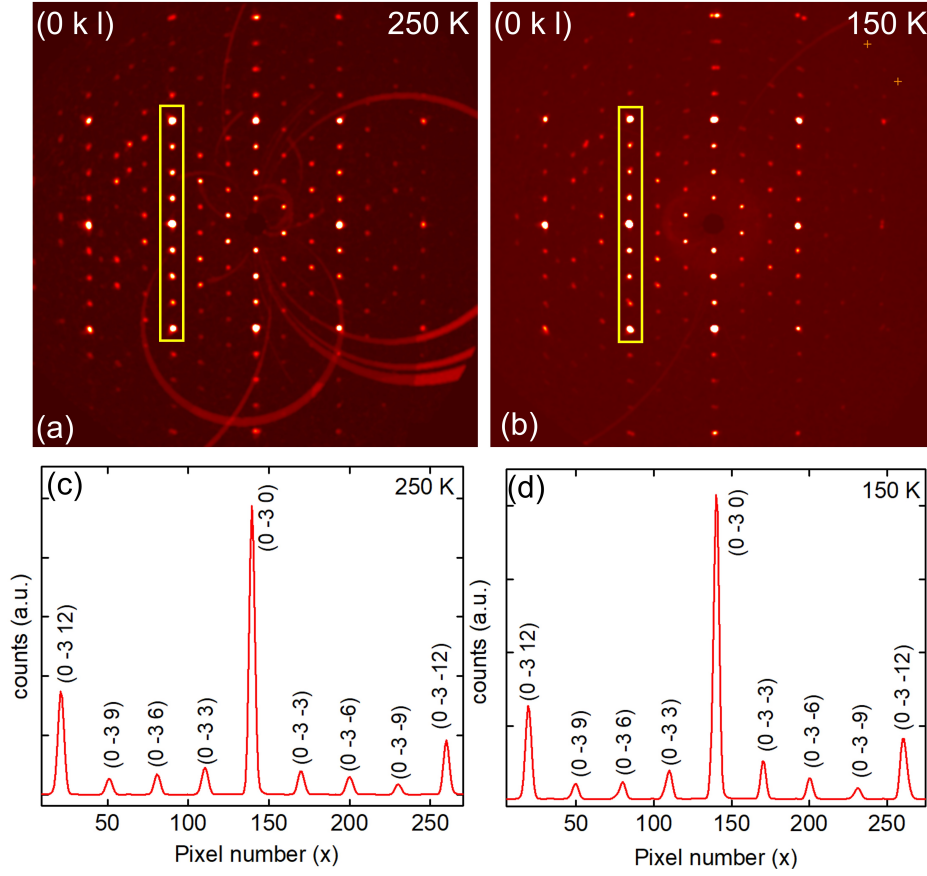


Figure 3.3: Reconstructed plot of reciprocal space along (0 k l) direction.(a) 250 K. (b) 150 K. Two-dimensional plot of (0 k l) reflections marked as a rectangle in (c) and (d). The x-axis indicates the x-coordinate (position) of the spots in units of detector pixel, and y-axis indicates the intensity of the spots.

The crystal structure of YbI_3 is different from YbCl_3 , where the later crystallizes with a monoclinic $C2/m$ crystal structure [13, 105], analogous to the room-temperature phase of $\alpha\text{-RuCl}_3$. However, unlike $\alpha\text{-RuCl}_3$, which undergoes a structural phase transition to $R\bar{3}$ symmetry below 150 K, YbCl_3 remains in the $C2/m$ symmetry over the whole temperature range. In $C2/m$ symmetry, the hexagonal ring of the Yb atoms is not perfect with two different Yb-Yb bond distances of 3.886 Å and 3.864 Å. The Yb-Cl-Yb bond angles also take two different values, namely 96.12° and 96.73°, thus lacking the C_3 symmetry [13]. The effect of symmetry breaking has been discussed in the recent study by Kim et. al [113]. The C_3 symmetry with 90° bond angles and larger inter-layer separation along the c -axis are ideal

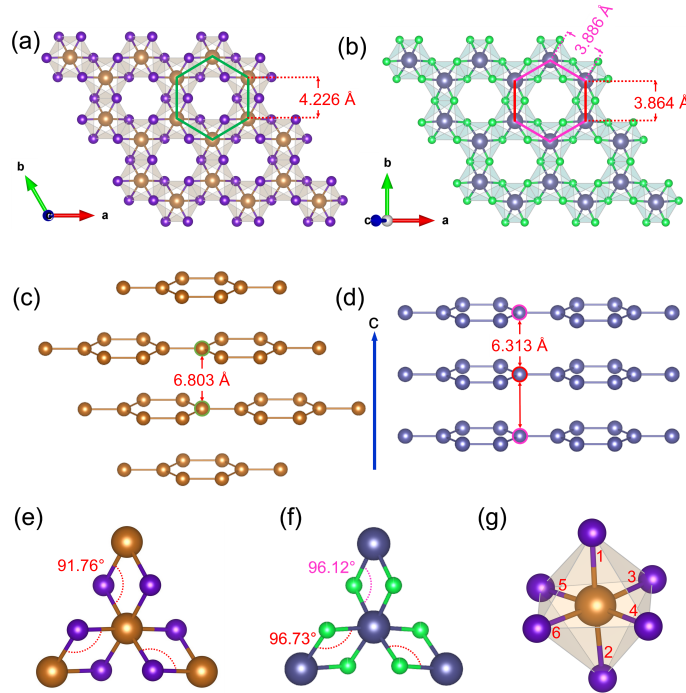


Figure 3.4: Crystal structure of YbI_3 . (a) Projection of the ab -plane showing the arrangement of Yb ions on a honeycomb lattice. The hexagonal rings formed by the Yb atoms, exemplified using green solid lines, is regular with each side $4.226(1)$ Å. (b) Analogous image for YbCl_3 is shown for comparison. In this case the hexagonal ring is slightly distorted with Yb-Yb distances 3.886 Å and 3.864 Å [13]. (c) Stacking of the honeycomb layers of YbI_3 perpendicular to the c -axis. The nearest neighbor Yb-Yb distance along the c -axis is $6.803(4)$ Å. (d) Analogous image for YbCl_3 is shown for comparison, where the nearest neighbor Yb-Yb separation is 6.313 Å [13]. (e) and (f) comparison of Yb-I-Yb bond angles along the three nearest neighbors in the ab -plane. These angles are uniformly $91.76(3)^\circ$ in YbI_3 , and 96.12° and 96.73° in YbCl_3 [13]. (g) A regular octahedron of I atoms around the Yb atom. Each Yb-I bond distance is close to $2.942(3)$ Å.

criteria for realizing the Kitaev model [114], which minimizes the Heisenberg interaction, allowing Kitaev interactions to dominate, as shown in the case of $\alpha\text{-RuCl}_3$ [112, 115]. As mentioned above, YbCl_3 has a slightly distorted honeycomb net with different bond angles and with more number of nearest neighbors along the c -axis [13]. YbBr_3 , on the other hand, has a similar structure as that of YbI_3 and low-temperature phase of $\alpha\text{-RuCl}_3$ but with small site-disorder on the Yb site [108]. To summarize, between the three Yb based halides compared here, YbI_3 appears to have the closest resemblance to the low-temperature phase of $\alpha\text{-RuCl}_3$.

Table 3.3: Crystallographic data and refinement parameters for SCXRD of YbI₃ single crystal at 250 K.

Temperature (K)	250
Crystal system	Trigonal
Lattice system/Setting	Hexagonal
Space group	$R\bar{3}$
No.	148
a (Å)	7.3201(8)
c (Å)	20.4545(27)
Volume (Å ³)	949.2(3)
Z	6
Wavelength (Å)	0.71073
Detector distance (mm)	40
Scan type	Full sphere (ϕ , ω scans)
Rotation per image (deg)	0.8
Exposure time (sec)	10
$(\sin(\Theta)/\lambda)_{max}$ (Å ⁻¹)	0.743374
Absorption, μ (mm ⁻¹)	29.261
T_{min} , T_{max}	0.84, 1.08
Criterion of observability	$I > 3\sigma(I)$
No. of reflections measured	10072
Unique reflections (obs/all)	561/728
R_{int} (obs/all)	0.1022/0.1054
No. of parameters	14
R_F (obs)	0.0556
wR_F (all)	0.0720
GoF (obs/all)	3.98/3.50
$\Delta\rho_{min}$, $\Delta\rho_{max}$ (e Å ⁻³)	-3.59, 3.77

Table 3.4: Atomic coordinates x , y , z and atomic displacement parameters (ADPs) of YbI₃ single crystal at 250 K in Å². Unique reflections (obs/all) = 561/728, criterion of observability: $I > 3\sigma(I)$, $R_F = 0.0556$, No. of refined parameters = 14, refinement method: least-squares on F, Space group: $R\bar{3}$.

Atoms	Wyck	x	y	z	Occ.	U_{iso}^{eqi}
Yb	6c	0	0	0.3337(4)	1	0.0182(3)
I	18f	0.3229(1)	0.3341(1)	0.4165(1)	1	0.0228(4)

3.3.3 Raman spectroscopy

As discussed above, YbI_3 has a Trigonal symmetry with the point group symmetry C_{3i} . According to the group theory, the irreducible representation of the zone-center Raman active phonon modes in YbI_3 are $\Gamma(C_{3i}) = 4A_g + 4^1E_g + 4^2E_g$. However, if the inter-layer coupling is treated as a small correction, the single-layer of YbI_3 has the D_{3d} point group symmetry, rendering six Raman active modes, $\Gamma(D_{3d}) = 4E_g + 2A_{1g}$. Fig. 3.5 shows the observed Raman spectrum for YbI_3 single crystal. The whole spectrum could be nicely fitted using a total of six Lorentzian lineshapes corresponding the six expected Raman active phonon modes. The modes are labeled from P_1 to P_6 in the increasing order of frequency as $\Delta\omega = 38.4$ (P_1), 56.4 (P_2), 69.4 (P_3), 94.0 (P_4), 118.5 (P_5), and 142.5 (P_6) cm^{-1} . The modes P_1 , P_3 , P_4 , and P_6 have the E_g symmetry, whereas symmetry of P_2 and P_5 is A_{1g} .

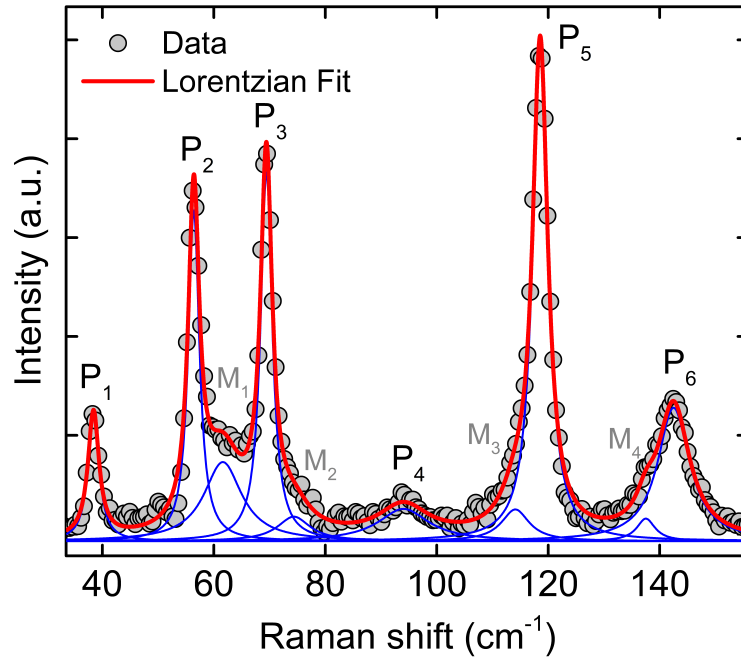


Figure 3.5: Raman spectrum of YbI_3 single crystal. The six Raman active phonon modes are labelled from P_1 to P_6 .

Additionally, four weak modes at 61.6 (M_1), 74.3 (M_2), 114.1 (M_3), and 137.5 (M_4) are also observed. The presence of weak extra modes in the Raman spectrum are not unusual.

These are often assigned as infrared active modes rendered Raman active due to lowering of the local symmetry at some sites [116]. In some cases, the extra modes are assigned to second-order Raman scattering [117]. The observed spectrum (including some of the weak extra modes) agrees well with that reported for the isostructural compound DyI₃ [118]. The observed phonon modes for YbI₃ and DyI₃, and their corresponding symmetries in the D_{3d} representation, are listed in Table 3.5.

Table 3.5: Experimental Peak positions for YbI₃ and DyI₃ at room temperature

Label	Positions (cm ⁻¹) YbI ₃ (This work)	Positions (cm ⁻¹) DyI ₃ [118]	Mode (D_{3d})
P_1	38.41	39	E_g
P_2	56.42	55	A_{1g}
P_3	69.43	71	E_g
P_4	94.04	94	E_g
P_5	118.56	120	A_{1g}
P_6	142.51	146	E_g
M_1	61.63	-	-
M_2	74.35	-	-
M_3	114.10	-	-
M_4	137.53	139	-

3.3.4 Heat capacity

Fig. 3.6(a) shows the heat capacity C_p , plotted as C_p/T , as a function of temperature from $0.1 \text{ K} \leq T \leq 1.5 \text{ K}$. The heat capacity is an additive quantity comprising various contributions and can be expressed as: $C_p(T) = C_{\text{mag}} + C_{\text{latt}} + C_{\text{nuc}}$, where C_{mag} is contribution of the $4f$ electrons of Yb^{3+} , C_{nuc} is the nuclear Zeeman contribution, and C_{latt} is the lattice contribution. In the temperature range of measurement, the lattice contribution becomes extremely small and can therefore be neglected. As shown in Fig. 3.6(a), the C_p/T exhibits three distinct features at temperatures T_1 , T_2 , and T^* . The broad anomaly around 0.95 K, labeled as T_1 , is attributed to the short-range ordering of the Yb^{3+} moments, whereas the sharp λ -type anomaly at 0.6 K, labeled as T_2 , has been tentatively attributed to the long-range ordering of the Yb^{3+} moments. The upturn below T^* is due to nuclear Zeeman splitting caused

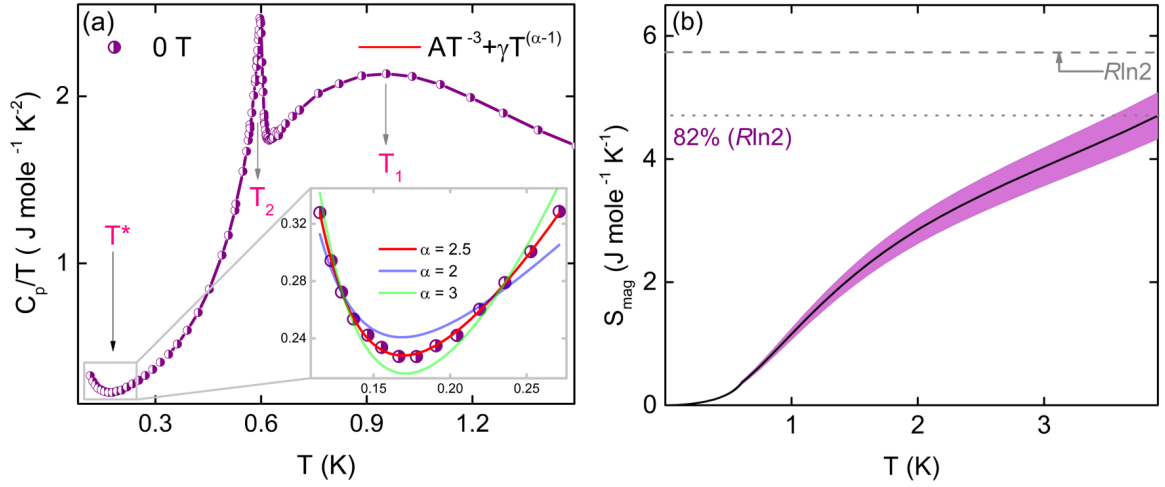


Figure 3.6: The temperature variation of heat capacity (C_p) and magnetic entropy released (S_{mag}): (a) C_p/T is shown as a function of temperature. Inset: solid red line is a fit to the low temperature experimental data for $\alpha = 2.5$. The fit using $\alpha = 2, 3$ is also shown for reference (see text for details). (b) S_{mag} is shown as a function of temperature. The purple shaded region indicates the error bars.

by the internal field generated by ordered Yb moments [119].

Here, it will be instructive to bring a comparison with much more extensively studied YbCl_3 . In the case of YbCl_3 , a similar broad peak attributed to short-range ordering appears at 1.2 K, followed by weaker anomalies at 0.6 K and 0.4 K upon further cooling [105]. While the 0.6 K anomaly is linked to the long-range ordering of the Yb moments, the the 0.4 K anomaly is sample-dependent and has been attributed to the presence of defects/imperfections or impurities. In contrast, in YbI_3 , the peak corresponding to the long-range ordering at $T_2 = 0.6$ K is sharp and much more robust, while no other feature analogous to the 0.4 K anomaly in YbCl_3 could be detected.

We fitted the heat capacity data of YbI_3 below 0.3 K using the expression: $C_p = AT^{-2} + \gamma T^\alpha$, where the first term in the equation is the high-temperature approximation of the two-level Schottky equation [120], and the second term is written based on the assumption that C_{mag} follows a certain power-law behavior in the ordered state. The data fits well as shown with a red solid curve in the inset of Fig. 3.6(a). The values obtained for the parameters A , γ and α from the fitting are: $A = 3.67 \times 10^{-4} \text{ J mole}^{-1} \text{ K}$, $\gamma = 2.2 \text{ J mole}^{-1} \text{ K}^{-3.5}$, and $\alpha = 2.5$. For YbCl_3 , the exponent α is 1.5 [14]. The fits using $\alpha = 2$, and 3 are

also shown in the inset of Fig. 3.6(a) using blue and green solid curves, respectively. The fittings clearly suggest that $\alpha = 2.5$ gives the best fit. In the magnetically ordered state of traditional antiferromagnets, the exponent α is expected to be 3, but in layered antiferromagnets the expected value of α should be 2. On the other hand, $\alpha \approx 1$, corresponding to a linear temperature dependence of low-temperature heat capacity, conventionally holds for the spinons in gapless quantum spin liquids; whereas a more unconventional quadratic temperature dependence ($\alpha \approx 2$) is expected for a gapless Dirac fermions [121]. The value of $\alpha \approx 2.5$ lies between 2 and 3, and it possibly indicates of an intermediate behavior between 3D ($\alpha = 3$) and 2D ($\alpha = 2$), justified by the presence of a finite inter-layer coupling. However, it is reminded that the temperature range over which the data are analyzed is rather small, not enough to draw a concrete conclusion concerning the value of α and hence the nature of the ground state. Also, we note that even for YbCl₃, the coefficient α becomes 2.5 under a moderate applied magnetic field of < 0.5 kOe and retains this value at higher fields (See Supplementary Information in Ref. [14] where the magnetic field variation of α is discussed). Further, experiments in the presence of applied magnetic field, currently not accessible to us, will be illuminating in understanding the ground state of YbI₃ accurately.

Fig. 3.6(b) shows the magnetic entropy released as a function of temperature calculated using $S_{\text{mag}} = \int_0^{T_0} C_{\text{mag}}(T)/T dT$. We extracted C_{mag} by subtracting the nuclear contribution from the total heat capacity. As mentioned in the beginning (Sec. 3.2), the addenda accounting for the contribution from the Apiezon N grease used for thermal contact and for covering the same to prevent it from decomposing in the process of loading for low-temperature measurements has not been subtracted. However, at low-temperatures, where C_{mag} is overwhelmingly large, we do not expect the Apiezon N contribution to be of much significance. The temperature variation of S_{mag} is shown in Fig. 3.6(b). Above 0.5 K, S_{mag} rises sharply, tapers a bit around 2 K, but do not show any signs of saturation up to 4 K. At 4 K, the value approaches 82% of $R \ln 2$. Since the measurements were only conducted up to 4 K, the exact temperature at which the magnetic entropy plateaus at $R \ln 2$ is not known. However, a comparison with previous reports on YbCl₃ [105] suggests that S_{4f} should plateau

near 10 K. A value of $S_{\text{mag}} \approx R \ln 2$, shows that the crystal field split ground state of Yb^{3+} in YbI_3 is a Kramer's doublet. To establish this further, we investigated the magnetic behavior of our YbI_3 crystals, discussed next.

3.3.5 Magnetization

Magnetic susceptibility (χ) is measured by applying a magnetic field of 10 kOe, in the parallel ($\chi_{\parallel}$) (in-plane) and perpendicular ($\chi_{\perp}(T)$) (out-of-plane) orientations. The temperatures variation of in-plane and out-of-plane susceptibilities are shown in Fig. 3.7(a). For the out-of-plane orientation, the zero-field-cooled (ZFC) and field-cooled (FC) curves overlap over the whole temperature range, but in the in-plane susceptibility, a very weak splitting is observed below approximately 150 K (not shown). The high temperature $1/\chi$ data ($150 \leq T \leq 300$) are fitted using a modified Curie-Weiss (CW) expression: $\chi = \chi_0 + C/(T - \Theta_{\text{CW}})$, where C is the Curie-constant from which the value of the effective magnetic moment (μ_{eff}) can be derived using $\mu_{\text{eff}} = \sqrt{8C}$; Θ_{CW} is the Weiss temperature, and χ_0 is a small temperature independent term that usually arise due to core diamagnetism and/or van Vleck type paramagnetism.

The values of the fitting parameters for the in-plane and out-of-plane orientation are as follows: $\chi_0^{\perp} = 3.8 \times 10^{-4} \text{ emu mole}^{-1} \text{ Oe}^{-1}$, $\Theta_{\text{cw}}^{\perp} = -55 \text{ K}$, and $\mu_{\text{eff}}^{\perp} = 4.53 \mu_{\text{B}}/\text{Yb}^{3+}$; the corresponding values in the in-plane orientation are: $\chi_0^{\parallel} = 1.9 \times 10^{-4} \text{ emu mole}^{-1} \text{ Oe}^{-1}$, $\Theta_{\text{cw}}^{\parallel} = -24 \text{ K}$, and $\mu_{\text{eff}}^{\parallel} = 4.53 \mu_{\text{B}}/\text{Yb}^{3+}$. In both cases, the value of μ_{eff} agrees well with the calculated value of $\mu_{\text{eff}} = g_J \sqrt{J(J+1)} = 4.53 \mu_{\text{B}}$ for Yb^{3+} ($4f^{13}$: $L = 3, S = 1/2$, and $J = 7/2$). The large values of Θ_{CW} for both the orientations are unrealistic, which may be due to the large crystal field splitting of the $J = 7/2$ manifold. In the presence of an octahedral crystal field environment of surrounding I^- ions, the eight-fold degenerate, $J = 7/2$ manifold in a free Yb^{3+} ion will split into four Kramers doublet. As a reference, we note that in YbCl_3 , the four Kramer's doublets are located at energies, 0, 243, 371, and 456 K. Clearly, in the range over which the fitting is performed, the van Vleck contribution from the higher-lying levels will be small but not insignificant.

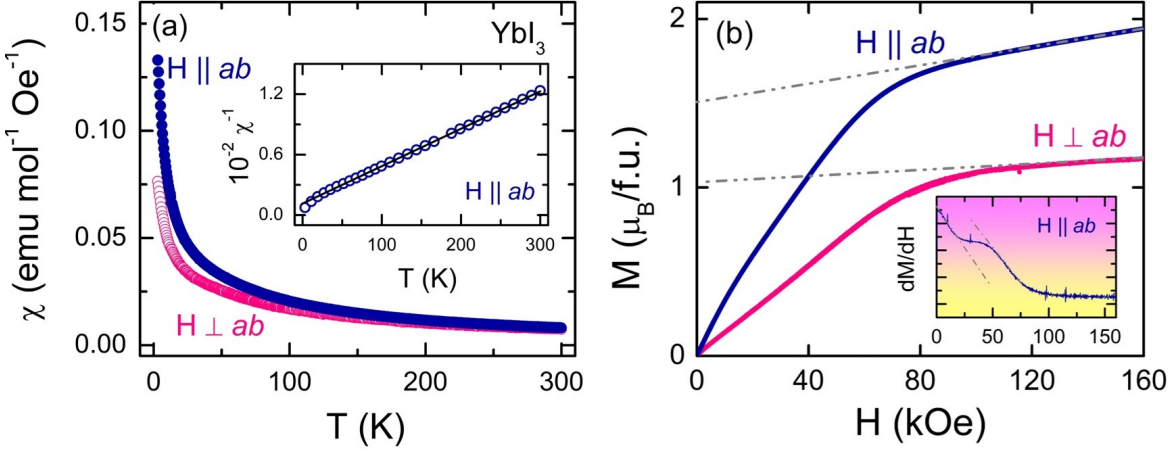


Figure 3.7: The magnetic susceptibility (χ) and isothermal magnetization $M(H)$ of YbI_3 : (a) Temperature variation of $\chi_{\parallel}$ and $\chi_{\perp}$ measured under an applied field magnetic field of 10 kOe. Inset: $\chi^{-1}(T)$ plotted as a function of temperature for $H \parallel ab$. The solid line through the data points in the inset is the modified Curie-Weiss fit (see text for details). (b) $M(H)$ at 2 K for $H \perp ab$ and $H \parallel ab$. The dashed lines represent linear extrapolation of the high-field data to $H = 0$. Inset: derivative dM/dH plot.

Table 3.6: Summary of fitting parameters χ_0 (emu mole $^{-1}$ Oe $^{-1}$), C (emu mole $^{-1}$ Oe $^{-1}$ K), μ_{eff} (μ_B), anisotropic Lande g-factor and Θ_{CW} (K) obtained by fitting the magnetic susceptibility data for in-plane ($H \parallel ab$) and out-of-plane ($H \perp ab$) orientations.

Orientation	Temperature range (K)	χ_0	C	μ_{eff}	g-factor	Θ_{CW}	Ref.
$H \perp ab$	150 – 300	3.82×10^{-4}	2.57	4.53	—	−55	
	4 – 12	0 ^a	0.98	2.80	3.2	−10	This work
	4 – 12	5.5×10^{-3} ^b	0.82	2.56	3.0	−8	
	^c 3 – 15	0	1.12	3.0(1)	3.5(1)	−9	[105]
$H \parallel ab$	150 – 300	1.95×10^{-4}	2.57	4.53	—	−24	
	4 – 12	~ 0 ^a	1.32	3.24	3.8	−7	This work
	4 – 12	16×10^{-3} ^b	0.93	2.73	3.2	−5	
	^c 3 – 15	0	1.20	3.1(1)	3.6(1)	−6	[105]

^a When χ_0 is fixed as 0; ^b When χ_0 is fixed to the value obtained from the slope of the linear section of the high field isothermal magnetization plots. ^c YbCl_3 .

In such scenarios where the crystal field splitting is large, it is more instructive to fit the low-temperature data to estimate the magnetic moment in the lowest Kramers doublet. We fitted the data in the temperature range from 4 K to 12 K using the modified Curie-Weiss expression. The values of the fitting parameters thus obtained are listed in Table. 3.6. For both

the orientations, if we fix $\chi_0 = 0$, we get $\mu_{\text{eff}}^{\perp} = 2.8 \mu_B/\text{Yb}^{3+}$, $\mu_{\text{eff}}^{\parallel} = 3.24 \mu_B/\text{Yb}^{3+}$; and, $\Theta_{\text{CW}}^{\perp} = -10$ K, $\Theta_{\text{CW}}^{\parallel} = -7$ K. In YbCl_3 , the corresponding values are [105]: $\mu_{\text{eff}}^{\perp} = 3.0 \mu_B/\text{Yb}^{3+}$, $\mu_{\text{eff}}^{\parallel} = 3.1 \mu_B/\text{Yb}^{3+}$; and, $\Theta_{\text{CW}}^{\perp} = -9$ K, $\Theta_{\text{CW}}^{\parallel} = -6$ K. The two sets of values are in good agreement with each other, suggesting some degree of similarity between the two systems. In both cases, the value of Θ_{CW} is somewhat higher than expected as we do not expect the exchange interaction to be of the order of 10 K for the reason that the $4f$ -electrons in rare-earths are highly sequestered, shielded by $5d$ and $6s$ electrons, which prevents them from making an appreciable overlap with the ligand p orbitals. For example, in the Yb-based pyrochlore oxides, the exchange interaction is of the order of 1 K. The other problem with these values is that the estimated Weiss temperature is comparable from the two orientations, which appears improbable given the layered nature of these materials, which suggests that the interaction within the plane should be much stronger than out-of-plane. In YbCl_3 , the in-plane nearest-neighbor coupling strength is $\Lambda_{\parallel} \approx 5$ K and $\Lambda_{\perp}/\Lambda_{\parallel} \approx 10^{-5}$ [107]. The exact reason for the high Weiss temperature in the low-temperature Curie-Weiss fits is not yet clear. Fixing χ_0 to some high value ($\sim 10^{-4} - 10^{-3}$ emu mole $^{-1}$ Oe $^{-1}$) did not decrease the Weiss temperature significantly either. We believe that the short-range magnetic correlations, that persists up to very high temperatures, may have contributed to the high value of Θ_{CW} . Strong spin fluctuations or short-range correlations are intrinsic to the layered (or quasi-2D) magnets, which is reflected in the broad peak in the heat capacity and a nearly linearly increasing S_{mag} up to temperatures as high as $\sim 7T_N$ (here $T_N = T_2$ corresponds to the sharp anomaly in C_p). The value of anisotropic g -factor in YbI_3 is estimated to be $g_J^{\perp} = 3.2$ and $g_J^{\parallel} = 3.8$, assuming $J_{\text{eff}} = 1/2$. In comparison, from a similar analysis the anisotropic g -factor in YbCl_3 is $g_J^{\perp} = 3.5$ and $g_J^{\parallel} = 3.6$ [105]. Slightly smaller values for the g -factors are obtained by taking χ_0 values from the isothermal magnetization, as discussed below. However, the values obtained using the electron spin resonance (ESR) probe, $g_J^{\perp} \approx 1.5$ and $g_J^{\parallel} \approx 3$ [122], differ considerably from those obtained using $\chi(T)$ or $M(H)$ data. The exact reason for this discrepancy is not clear. Investigating YbI_3 using ESR probe may throw light on this issue.

Isothermal magnetization, $M(H)$, for out-of-plane ($H \perp ab$) and in-plane ($H \parallel ab$) orientations, is shown in Fig. 3.7 (b). In the out-of-plane orientation, the magnetization nearly saturates above a field of $H \approx 120$ kOe. The small slope that still persists can be attributed to the van Vleck term (χ_0), which can be calculated by fitting the high-field data to an expression of the $M = M_s^\perp + \chi_0^\perp H$, where $M_s^\perp$ is the saturation magnetization in the out-plane orientation. The fit, which is shown in the Fig. 3.7(b) using a dashed line (shown extrapolated to $H = 0$), gives $M_s^\perp \approx 1 \mu_B/\text{Yb}^{3+}$ and $\chi_0^\perp = 5.5 \times 10^{-3} \text{ emu mol}^{-1} \text{ Oe}^{-1}$; and $M_s^\parallel \approx 1.5 \mu_B/\text{Yb}^{3+}$ and $\chi_0^\parallel = 1.6 \times 10^{-4} \text{ emu mol}^{-1} \text{ Oe}^{-1}$. Using these values of χ_0 for two orientations (instead of fixing them to zero, as done in the previous paragraph), we get $g_J^\perp = 3.0$ and $g_J^\parallel = 3.2$ (see Table. 3.6). Combining the two results, we can conclude that the approximate g_J values for the two orientations are: $g_J^\perp \approx 3.0 \pm 0.2$ (out-of-plane), and $g_J^\parallel \approx 3.4 \pm 0.3$ (in-plane). For the in-plane $M(H)$ a more intriguing field variation is observed, as depicted using the derivative (dM/dH) plot in the inset of Fig. ??(b). With increasing field, dM/dH exhibits a plateau in the field ranging from 20 kOe to 40 kOe, suggesting a field induced transition. In the high-field region dM/dH becomes almost flat and very small. The field-induced transition in the in-plane data suggests the presence of a weak in-plane anisotropy. Since our in-plane data is collected by applying the field in an arbitrary orientation with respect to the crystal axes, the direction of easy-axis within the plane remains uncertain. In future, torque magnetometry (or any other equivalent magnetization measurement where the sample plane can be rotated) as a function of θ , where θ is the angle that the applied field makes with crystallographic a - or b -axis, will be useful in characterizing the in-plane anisotropy more accurately. Using, the g -factor obtained for the two orientations from the susceptibility data, a back calculation of the saturation moment suggests $J_{\text{eff}} \leq 1/2$.

3.3.6 YbI₃ versus YbCl₃

To begin with, the crystal structures of YbI₃ and YbCl₃ are somewhat distinct from one another. While YbI₃ exhibits a trigonal symmetry, YbCl₃ displays monoclinic symmetry [13]. This primary difference is due to the variation in the stacking sequence of YbX₃ layers along

the c -axis. In YbI_3 , three layers form a repeating unit, resulting in nearest neighbor Yb-Yb distance of $6.803(4)$ Å along the c -axis, as shown in Fig. 3.4(c). In contrast, YbCl_3 consists of a single layer repeated along the c -axis, leading to nearest neighbors at 6.313 Å in the layers above and below the middle layer, as shown in Fig. 3.4(d). Beyond the global symmetry, the local symmetry within a single YbX_3 layer in the ab -plane also differs slightly for the two compound, which may be crucial for understanding the differences in their magnetic behaviors. In YbCl_3 , the Yb-Yb honeycomb bond distances are 3.886 Å and 3.864 Å; accordingly, the bond angles are 96.12° and 96.73° , respectively [13]. Conversely, YbI_3 features a uniform bond distance of $4.226(1)$ Å and a bond angle of $91.76(3)^\circ$, resulting in an isotropic honeycomb lattice. Although the distortion in YbCl_3 is very small, it nevertheless breaks the C_3 symmetry, which is preserved in the case of YbI_3 . The temperature variation of heat capacity reveals two distinct transitions in both the compounds. Using data from Ref. [14], we plotted their heat capacities on the same scale in the Fig. 3.8. In YbI_3 , short-range ordering (SRO) occurs at $T_1 = 0.95$ K (broad peak), followed by long-range ordering (LRO) at $T_2 = 0.6$ K (sharp peak). Similarly, in YbCl_3 , short-range ordering occurs at $T_1 = 1.2$ K, followed by long-range ordering at $T_2 = 0.65$ K. The entropy release for both compounds approaches $R \ln 2$ towards, indicating a $J_{\text{eff}} = 1/2$ Kramers doublet ground state. Regarding differences, the T_2 transition, attributed to the long-range ordering of Yb moments, is more robust and sharp in YbI_3 compared to YbCl_3 . We note that the broad peak associated with short-range ordering (T_1 -peak)) has nearly the same height and width for the two compounds. It however appears at a lower temperature by about 0.26 K in YbI_3 as compared to YbCl_3 . The combined effect of sharper T_2 -peak (LRO) and downshifting (in temperature) of the T_1 -peak (SRO) is that in the low temperature range ($T \lesssim 1.5$ K), S_{4f} for YbI_3 exceeds that for YbCl_3 , but as the temperature increases the S_{4f} plot for YbCl_3 increases rapidly to match with that for YbI_3 . Note that S_{4f} shows a small step across T_2 in YbI_3 , but in YbCl_3 the variation across T_2 is smooth due to the difference in the robustness of T_2 -peak associated with the long-range ordering. Another notable difference in the heat capacities of two compounds is that in YbCl_3 , a weak sample dependent anomaly is reported at 0.4 K, which is absent in

YbI₃.

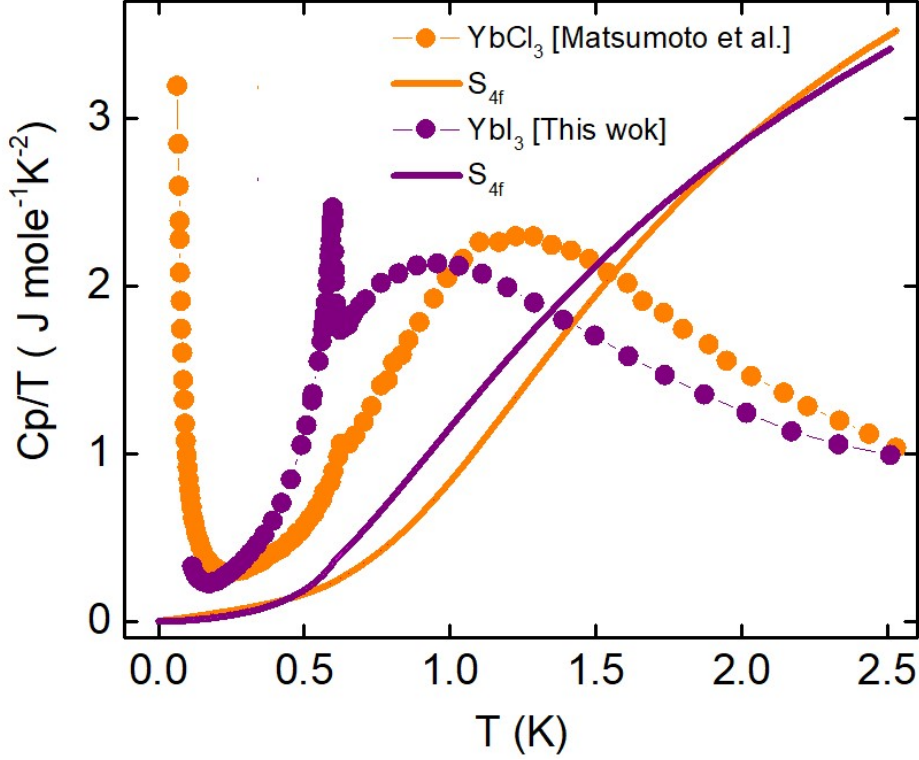


Figure 3.8: Low-temperature heat capacity and magnetic entropy of YbI₃ (this work) and YbCl₃ [14].

Magnetic behavior of the two compounds above 2 K is qualitatively similar. Further low temperature measurements on YbI₃ might prove useful in this context. The saturation moments $M_s^{\parallel} \approx 1.5 \mu_B/\text{Yb}^{3+}$ and $M_s^{\perp} \approx 1 \mu_B/\text{Yb}^{3+}$ is nearly the same for both the compounds. The differences may crop-up at lower temperatures, hence, magnetic measurements below 2 K would be interesting. In conclusion, YbI₃ possesses a more symmetric structure compared to YbCl₃, with C_3 symmetry preserved, similar to $\alpha\text{-RuCl}_3$, whereas YbCl₃ exhibits broken C_3 symmetry. The nearest neighbor Yb–Yb separation along the c -axis is found to be larger in YbI₃ compared to YbCl₃. Heat capacity measurements show a similar two-step ordering for both compounds: initial short-range ordering followed by long-range antiferromagnetic ordering. Any further additional anomaly due to poor quality of the sample is absent in YbI₃. In the paramagnetic state ($T > 2$ K), the magnetic behavior of YbI₃ resembles that of YbCl₃.

3.4 Summary & conclusions

To conclude, we have successfully grown high-quality single crystals of YbI_3 using a vapor transport reaction, taking elemental Yb and I as the starting precursors. The crystal field split ground state of Yb^{3+} in YbI_3 is a well-isolated Kramer's doublet with $g_J^\perp \approx 3.0 \pm 0.2$ (out-of-plane), and $g_J^\parallel \approx 3.4 \pm 0.3$ (in-plane). The in-plane isothermal magnetization shows a weak field induced transition, indicating the presence of slight anisotropy even within the *ab*-plane.

Heat capacity show a two-step magnetic transition with a broad peak $T_1 = 0.95$ K due to short-range correlations between the Yb moments, followed by a sharp peak at 0.6 K, signaling transition into a long-range magnetically ordered state. No additional anomaly, except an upturn below about 0.25 K due to nuclear Schottky effect, could be seen. The magnetic entropy, reaches almost 80% of $R \ln 2$ near 4 K (highest temperature in our experiment), consistent with the Kramer's doublet ground state. The value of critical exponent α of 2.5 from the heat capacity data suggests a possible unconventional ground state for YbI_3 . To conclude, YbI_3 appears to harbor very interesting physics associated with $J_{\text{eff}} = 1/2$ on an ideal 2D honeycomb lattice. We believe that our preliminary study will trigger further experimental investigation to explore the spin Hamiltonian and exact ground state of this compound.

Chapter 4

Crystal growth, magnetic and thermal properties of quasi two-dimensional honeycomb magnet RI_3

The work described in this chapter will be submitted in Physical Review B. with the title of "Crystal growth and magnetic properties of rare earth tri-iodides: Quasi-2D Van der Waals antiferromagnets"

- *The Magnetic and heat capacity measurements discussed in this chapter were performed at UGC-DAE Consortium for Scientific Research, University Campus, Khandwa Road, Indore 452001, Madhya Pradesh, India under the supervision of Dr. Rajeev Rawat.*

4.1 Introduction

Two-dimensional (2D) magnetic van der Waals (vdW) materials are an intriguing class of systems, often displaying novel magnetic ground states and exotic phases, not generally found in traditional three-dimensional (3D) magnetic systems [123, 124]. Some well studied examples of 2D magnetic materials from recent literature include CrI_3 [38], spiral spin-liquid candidate FeCl_3 [125], ferromagnetic semiconductors $\text{Cr}_2(\text{Si,Ge})_2\text{Te}_6$ [126, 127], itinerant ferromagnets such as Fe_3GeTe_2 [40], negative charge transfer antiferromagnetic insulator NiPS_3 [128, 129], topological magnonic candidate CrCl_3 [130], and CrBr_3 hosting chiral phonon modes [131]. Comprising weakly bonded layers, these materials can be stacked in various configurations, offering remarkable control over their magnetic properties. The ability to manipulate these properties using external factors such as electric fields, mechanical strain, or heterostructure engineering has made 2D magnetic vdW materials a fertile ground for uncovering novel physical phenomena, and for advancing technologies in spintronics and quantum devices. The identification and characterizations of new 2D materials with correlated lattice, spin, charge, and orbital degrees of freedom is therefore at the forefront of this rapidly evolving field.

Among many exotic phases these materials can host, quantum spin liquids (QSLs) are particularly significant. In a QSL, due to strong quantum fluctuations, the conventional long-range or short-range magnetic order does not set-in even at absolute zero despite strong spin-spin correlations. Instead, the spins remain in a disordered but highly entangled state, resulting in unique characteristics including fractionalized excitations and topological order [47, 79]. The exploration of quantum spin liquids (QSLs) has historically centered on geometrically frustrated lattices, such as triangular, kagome, or pyrochlore structures, inspired by Anderson's 1973 resonating valence bond (RVB) model [132]. These lattices prevent spins from simultaneously satisfying all magnetic interactions, leading to a disordered but entangled ground state. In 2006, Alexei Kitaev introduced a breakthrough model that expanded the understanding of QSLs beyond geometrical frustration. The Kitaev

model describes a spin-1/2 system on a two-dimensional honeycomb lattice, characterized by highly anisotropic, bond-dependent interactions between nearest neighbors. Remarkably, this model is exactly solvable with a ground state characterized as a QSL where spins fractionalize into four types of emergent quasiparticles known as Majorana fermions [80].

The pursuit of real materials embodying Kitaev physics accelerated after the seminal work of Jackeli and Khaliullin, which identified a promising pathway among spin-orbit-assisted Mott insulators, particularly within $4d^5$ ruthenates and $5d^5$ iridates [81]. In these systems, the combination of strong spin-orbit coupling, octahedral crystal field splitting, and electronic correlations results in a $J_{\text{eff}} = 1/2$ Kramers doublet ground state. This state exhibits the highly anisotropic bond-dependent interactions necessary for realizing the Kitaev model, marking a significant step towards. The electronic and magnetic properties of candidate materials, including, Na_2IrO_3 [82–84], $\alpha\text{-Li}_2\text{IrO}_3$ [85, 86], $\beta\text{-Li}_2\text{IrO}_3$ [87, 88], $\gamma\text{-Li}_2\text{IrO}_3$ [89], $\text{H}_3\text{LiIr}_2\text{O}_6$ [90], Cu_2IrO_3 [91], $\text{Cu}_3\text{LiIr}_2\text{O}_6$ [92], $\text{Ag}_3\text{LiIr}_2\text{O}_6$ [93], $\alpha\text{-RuCl}_3$ [94, 95] have been extensively studied in recent years to explore the possibility of realizing the Kitaev QSL.

The 2D f -electrons systems with similar honeycomb structure are also predicted to host interesting magnetic ground states including the Kitaev QSL phase due to strong spin-orbit coupling and localized f -orbitals [101–104]. In this regard, YbCl_3 , where Yb^{3+} ($J_{\text{eff}} = 1/2$) ions form a honeycomb lattice has been extensively studied [13, 105–107, 122, 133]. While at first it was thought to be a potential Kitaev material, a recent study clarified the ground state of YbCl_3 . It is shown that YbCl_3 exhibits a Bose-Einstein condensation (BEC) in an in-plane magnetic field near a quantum critical point (QCP) [14]. Thus, YbCl_3 is a unique example of a quantum magnet showing BEC-QCP in the 2D limit. Recently, we reported the crystal growth of YbI_3 and showed that barring some subtle differences in the structure, the magnetic and thermodynamic properties of YbI_3 are analogous to that of YbCl_3 [134]. More precisely, we showed that the stacking sequence of honeycomb layers in YbI_3 is of A–B–C type [exactly similar to the low-temperature phase of $\alpha\text{-RuCl}_3$], while in YbCl_3 the layers are stacked exactly one of top of another in an A–A–A type stacking. Further, while

the Yb-honeycomb net is slightly distorted in YbCl_3 with two type of Yb-Yb distances, in YbI_3 the honeycomb net is perfect. Analogous to YbCl_3 , the crystal-field in YbI_3 results in a $J_{\text{eff}} = 1/2$ ground state and a magnetic behavior characterized by weak anisotropy with $\chi^{\parallel}$ (in-plane) $>$ $\chi^{\perp}$ (out-of-plane), and low-temperature heat capacity showing two-step ordering: a broad peak at high-temperatures (0.95 K) due to short-range spin correlations followed by a sharp peak at 0.6 K due to long-range ordering, analogous to YbCl_3 .

Motivated by these developments, we investigate other members of the RI_3 series (R: rare-earth) to explore possible novel magnetic phases associated with rare-earth magnetism in the 2D limit. In this work, we have grown high-quality single crystals of LaI_3 , CeI_3 , GdI_3 , DyI_3 , HoI_3 , and ErI_3 . Their structural properties are thoroughly investigated using single-crystal x-ray diffraction and Raman spectroscopy. Heat capacity (C_p) measurements down to 1.8 K indicate the possibility of realizing different types of magnetic ground states for these compounds influenced by the crystal field splitting. The magnetic susceptibility and isothermal magnetization shows anisotropic behavior with antiferromagnetic interaction between the rare-earth moments in all cases.

4.2 Experimental methods

Single crystals of RI_3 (R = La, Ce, Gd, Dy, Ho, and Er) are grown using the vapor transport technique in a two-zone furnace. The details of the crystal growth are given in sec. 4.3.1. The x-ray diffraction patterns are recorded using a Bruker D8 advance diffractometer in the Bragg Brentano geometry employing Cu-K_{α} ($\lambda = 1.5406 \text{ \AA}$) radiation, as described in 2.2.1. The 2θ values ranged from 5° to 90° with a step size 0.02° . For this purpose, a thin plate-like single crystal was placed over a oven-dried glass-slide and completely covered by a layer of Kapton tape to avoid degradation of the crystal due to moisture.

Single crystal x-ray diffraction (SCXRD) was carried out using a Bruker Smart Apex Duo diffractometer employing Mo-K_{α} radiation ($\lambda = 0.70173 \text{ \AA}$) at $T = 150 \text{ K}$ using an open-flow nitrogen cryostat. The details of the single crystal x-ray diffraction experiment is elaborated in 2.2.2. A tiny crystal, typically of a few hundreds of microns lateral dimensions, was

covered in paratone oil to avoid exposure to the atmosphere and mounted on a goniometer loop. The intensities were integrated using the CrysAlisPro [109] and the refinement was performed using Jana 2006 [110].

The layered morphology of the single crystals was confirmed using a scanning electron microscope (SEM) (FEI Make), and the chemical composition was verified using an Energy Dispersive X-ray (EDX) (Quanta 2003D) detector attached to the SEM instrument in the Secondary Electron (SE) mode as described in 2.2.4. The EDX spectra was collected at 10-15 different points, spread across the single crystal specimen to obtain the averaged elemental composition. The elemental mapping was also performed over a micron sized area of the single crystal to check the compositional homogeneity of the grown crystal.

Raman spectra were collected at room temperature in the back scattering configuration using a Horiba Jobin-Yvon LabRAM HR spectrometer equipped with liquid nitrogen cooled Charge-Coupled Detector (CCD) and a laser of 532 nm as the source of excitation as described in 2.2.6. The excitation was maintained at 75% of the maximum power, and the accumulation time, along with the number of iterations, was varied for each sample to improve the resolution and intensity of the Raman modes. To obtain Raman spectrum, the RI_3 crystal was coated with a thin-layer of Apiezon N grease to prevent degradation during the measurement.

Magnetic measurement between 2 – 300 K are performed at the UGC-DAE CSR, Indore using the VSM probe in a Physics Property Measurement System (PPMS), Quantum design, USA. The heat capacity was measured between 2 K to 300 K in the PPMS at UGC-DAE-CSR, Indore. Due to the highly hygroscopic nature of RI_3 , the crystal was covered with an unknown amount of Apiezon N grease. Hence, the addenda could not be subtracted from the raw data. For this reason, in the main text, we have shown heat capacity at low temperatures, where the addenda contribution, except in the case of LaI_3 , is negligible compared to the magnetic heat capacity associated with the $4f$ electrons of the magnetic rare-earth ions.

4.3 Results and discussion

4.3.1 Crystal growth of RI_3

High-quality single crystals of RI_3 are grown using the physical vapor transport or self-transport technique. For this purpose, rare-earth precursory powders (99.9% REO, Alfa Aesar) and Iodine flakes (ACS reagent, $\geq 99.8\%$, Sigma Aldrich) are used. The stoichiometric quantities of starting materials are loaded in a quartz ampoule, measuring approximately 15 cm in length, with an inner diameter of about 2 cm and wall-thickness of 2 mm, resulting in a volume of around 40 – 50 cm^3 . To compensate for iodine sublimation losses during the evacuation process, an additional 10% excess of iodine is included. The entire procedure of handling and storing the precursors is carried out in an argon-filled glove box with oxygen and moisture content < 0.1 ppm. Before loading the precursors into the ampoule, several precautionary steps are undertaken to avoid contamination. The ampoule undergoes sonication in acetone, followed by rinsing with deionized water. Subsequently, it is pre-heated at 1000°C to eliminate residual moisture and organic impurities sticking to its inner walls. The ampoule is then transferred immediately into the glovebox for filling the precursors (rare-earth metal and iodine). After filling, it is evacuated down to 10^{-5} torr outside the glove-box, and thereafter flame-sealed under dynamic vacuum. Given iodine's high vapor pressure at room temperature (approximately 100 Pa near 300 K), the ampoule was kept under an ice bath during evacuation and sealing to minimize iodine losses. The sealed ampoule is then kept in a two-zone furnace under a temperature gradient $\Delta T = 40 - 100^\circ\text{C}$ (where, $\Delta T = T_{\text{source}} - T_{\text{sink}}$), the source temperature (T_{source}) is set at 750°C , and the sink temperature (T_{sink}) is decided according to the selected temperature gradient between the T_{source} and T_{sink} .

The experiments were performed using different growth conditions to obtain the largest and highest quality single crystals. The optimal thermodynamic condition for each compound is summarized in Table 4.1. The LaI_3 and CeI_3 were grown under a temperature gradient of 50°C , maintaining source and sink temperatures at 750°C and 700°C , respec-

Table 4.1: Summary of various parameters used during the crystal growth experiments leading to the best results: Source temperature (T_{source}), sink temperature (T_{sink}), Dwell time [time for which the ampoule is kept at specified source and sink temperatures], rate of cooling, and total duration of the crystal growth experiment.

Compound	T_{source}	T_{sink}	Dwell time	Cooling rate	Duration	Conclusion
LaI_3	750°C	700°C	20 days	100 °C h ⁻¹	30 days	Needle-like ~ 20 mm × 3 mm × 3 mm
CeI_3	750°C	700°C	20 days	100 °C h ⁻¹ till room temperature	30 days	Needle-like ~ up to 20 mm × 3 × 3 mm
GdI_3	750°C	650°C	24 h	0.3 °C h ⁻¹ ($T_{\text{source}} = 750\text{ °C}$ to 600°C)	30 days	large crystals of Size ~ 10 mm × 10 mm lateral dimensions
DyI_3	750°C	650°C	24 hours	0.3 °C h ⁻¹ ($T_{\text{source}} = 750\text{ °C}$ to 600°C)	30 days	Plate-like ~ 20 mm × 20 mm lateral dimensions
HoI_3	750°C	710°C	20 days	0.3 °C h ⁻¹ ($T_{\text{source}} = 750\text{ °C}$ to 600°C)	30 days	Plate-like ~ 20 mm × 20 mm lateral dimensions
ErI_3	750°C	650°C	24 hours	0.3 °C h ⁻¹ ($T_{\text{source}} = 750\text{ °C}$ to 600°C)	30 days	Plate-like ~ 15 mm × 15 mm lateral dimensions

tively, for 20 days. This duration was sufficient to obtain *cm*-sized single crystals. Extending this time further or applying a slow cooling did not affect the size or the quality of the grown crystals. On the other hand, Gd, Dy, Ho, and Er iodides required slow cooling in addition to the temperature gradient to achieve larger crystals. For these compounds, the ampoule was initially subjected to a temperature gradient of 100°C (or 40°C in case of HoI_3) for 24 hours with the source and sink temperatures set at 750°C and 650°C, respectively. Subsequently, the temperature of both ends was simultaneously reduced at a rate of 0.3 °C h⁻¹ until they reached 600°C at the source and 500° at the sink.

Shiny, needle-like single crystals of lateral dimension 2 cm × 0.2 cm are obtained for LaI_3 , and CeI_3 . On the other hand, plate-like single crystals, with typical lateral dimensions of 1 cm × 1 cm, are obtained for GdI_3 , DyI_3 , HoI_3 , and ErI_3 as shown in Fig. 4.1(a - f). The needle and the plate-like morphology of the grown crystals reflect the underlying layered or quasi-two-dimensional structure of rare earth iodide single crystals. A scanning electron microscope image of a small crystal specimen for CeI_3 and HoI_3 is shown in Fig. 4.1(g) and Fig. 4.1(h) respectively. The chemical composition, obtained using EDX, confirms the 1:3 ratio of R:I (see Table 4.2. to Table 4.7).

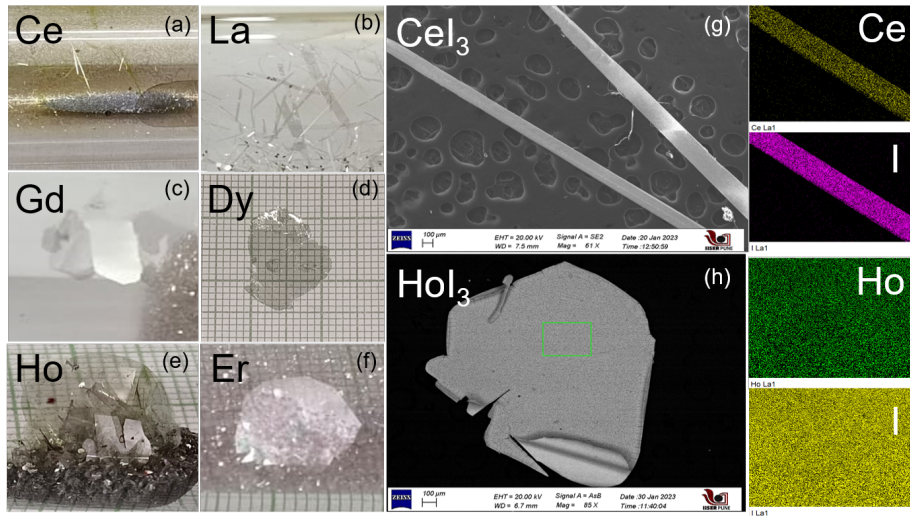


Figure 4.1: (a - f) Images of the grown crystals. (g) A scanning electron microscope image of a small crystal specimen of CeI_3 in the secondary electron modes exhibiting needle-like morphology (left). Elemental mapping for Cerium and Iodine showing the homogeneity of the grown single crystal (right) (h) A scanning electron microscope image of a small crystal specimen of HoI_3 in the backscattering mode exhibiting Plate-like morphology (left). Elemental mapping for Holmium and Iodine showing the homogeneity of the grown single crystal (right).

Table 4.2: The composition of La and Iodine at 12 different areas of the single crystal shows the homogeneity of the crystal specimen.

Area	La (atomic %)	I (atomic %)	La (composition)	I (composition)
1	26.33	73.67	1.0532	2.9466
2	26.55	73.45	1.062	2.938
3	27.26	72.74	1.0904	2.9096
4	26.90	73.10	1.076	2.924
5	25.27	74.63	1.0108	2.9852
6	27.26	73.49	1.0904	2.9396
7	27.84	73.94	1.1136	2.9576
8	25.83	74.17	1.0332	2.988
9	25.68	74.32	1.0272	2.9728
10	26.06	73.94	1.0424	2.9576
11	27.26	72.74	1.0904	2.9096
12	24.83	75.17	0.9932	3.0068

Table 4.3: The composition of Ce and Iodine at 11 different areas of the single crystal shows the homogeneity of the crystal specimen.

Area	Ce (atomic %)	I (atomic %)	Ce (composition)	I (composition)
1	23.27	76.73	0.9308	3.0692
2	24.42	75.58	0.9768	3.0232
3	24.37	75.63	0.9748	3.0252
4	25.46	75.54	1.0184	3.0216
5	25.54	74.46	1.0216	2.9784
6	26.01	73.99	1.0404	2.9596
7	25.03	74.97	1.0012	2.9988
8	25.27	74.73	1.0108	2.9892
9	25.07	74.93	1.0028	2.9972
10	24.12	75.88	0.9648	3.0352
11	25.60	74.40	1.024	2.976

Table 4.4: The composition of Gd and Iodine at 11 different areas of the single crystal shows the homogeneity of the crystal specimen.

Area	Gd (atomic %)	I (atomic %)	Gd (composition)	I (composition)
1	26.14	73.86	1.0564	2.9512
2	26.05	73.95	1.042	2.958
3	26.97	73.03	1.0788	2.9212
4	26.79	73.21	1.0716	2.9284
5	28.42	71.58	1.1368	2.8632
6	27.68	72.32	1.1072	2.9328
7	25.59	74.41	1.0236	2.9764
8	26.08	73.64	1.0432	2.9456
9	27.78	72.22	1.1112	2.8888
10	27.04	72.96	1.0816	2.9184
11	26.64	73.36	1.0656	2.9344

Table 4.5: The composition of Dy and Iodine at 15 different areas of the single crystal shows the homogeneity of the crystal specimen.

Area	Dy (atomic %)	I (atomic %)	Dy (composition)	I (composition)
1	24.33	75.67	0.9732	3.0268
2	24.64	75.36	0.9856	3.0144
3	25.73	74.27	1.0292	2.9708
4	24.24	75.76	0.9696	3.0304
5	24.94	75.06	0.9976	3.0024
6	25.49	74.51	1.0196	2.9804
7	24.19	75.81	0.9676	3.0324
8	26.62	73.38	1.0648	2.9352
9	25.47	74.53	1.0188	2.9812
10	24.43	75.57	0.9772	3.0228
11	25.76	74.24	1.0304	2.9696
12	25.67	74.33	1.0268	2.9732
13	25.78	74.22	1.0312	2.9688
14	25.41	74.59	1.0164	2.9836
15	25.95	74.05	1.0380	2.9620

Table 4.6: The composition of Ho and Iodine at 11 different areas of the single crystal shows the homogeneity of the crystal specimen.

Area	Ho (atomic %)	I (atomic %)	Ho (composition)	I (composition)
1	23.58	76.42	0.9432	3.0568
2	25.49	74.51	1.0196	2.9804
3	25.2	74.8	1.008	2.9920
4	23.77	76.23	0.9508	3.0492
5	26.25	73.75	1.000	2.9500
6	23.23	76.77	0.9292	3.0708
7	24.78	75.22	0.9912	3.0088
8	24.64	75.36	0.9856	3.0144
9	23.19	76.81	0.9276	3.0724
10	25.21	74.79	1.0084	2.9916
11	24.08	75.92	0.9632	3.0368

Table 4.7: The composition of Er and Iodine at 15 different areas of the single crystal shows the homogeneity of the crystal specimen.

Area	Er (atomic %)	I (atomic %)	Er (composition)	I (composition)
1	24.21	75.79	0.9684	3.0316
2	24.67	75.33	0.9868	3.0132
3	25.46	74.54	1.0184	2.9816
4	24.67	75.33	0.9868	3.0132
5	24.73	75.27	0.9892	3.0108
6	25.55	74.45	1.022	2.9780
7	24.24	75.76	0.9696	3.0304
8	23.99	76.01	0.9596	3.0404
9	25.77	74.23	1.0308	2.9692
10	23.94	76.06	0.9576	3.0424
11	23.83	76.17	0.9532	3.0468
12	24.38	75.62	0.9752	3.0248
13	24.09	75.91	0.9636	3.0364
14	25.2	74.77	1.0092	2.9908
15	25.34	74.66	1.0136	2.9864

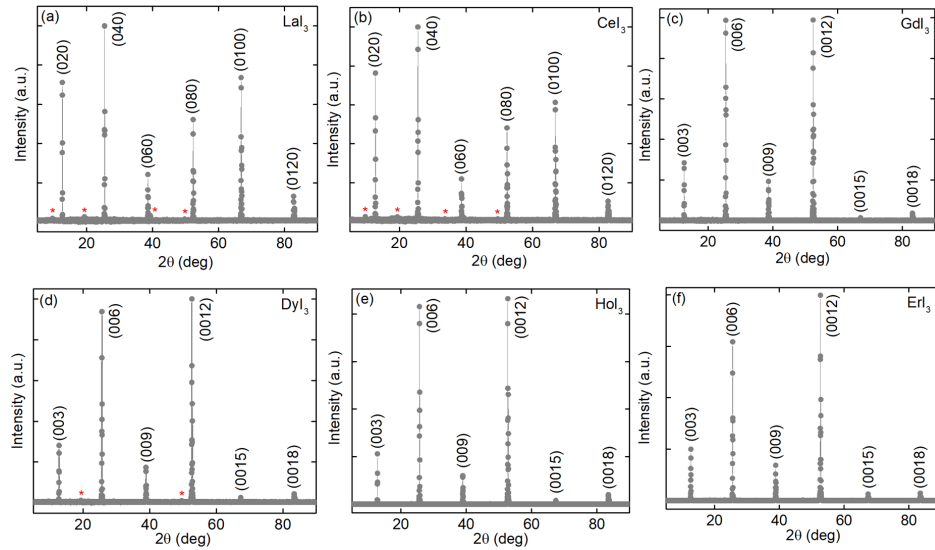


Figure 4.2: The powder x-ray diffraction patterns in the Bragg-Brentano geometry for single-crystal specimens of RI_3 are shown. Panel (a, b) displays the $(0\ k\ 0)$ reflections for CeI_3 and LaI_3 indicative of orthorhombic symmetry, while panel (c - f) shows the $(0\ 0\ l)$ reflections indexed according to trigonal symmetry for GdI_3 , DyI_3 , HoI_3 and ErI_3 . Both $K\alpha$ components ($K\alpha_1$ and $K\alpha_2$) appear in the diffraction patterns, with additional unindexed peaks marked by red asterisks. These extra peaks might result from slight decomposition of the sample surface during data collection due to larger surface required compared to size required in single crystal diffraction.

The x-ray diffraction pattern collected on the plane of the single crystal specimen is shown in Fig. 4.2 (a - f). The pattern is collected in the Bragg Brentano geometry, revealing diffraction peaks with miller indices $(0k0)$, where $k = 2, 4, 6, \dots$, for LaI_3 and CeI_3 suggest that the lateral surface of the measured specimen is oriented perpendicular to the b -axis. Whereas in the case of GdI_3 , DyI_3 , HoI_3 , and ErI_3 , the $(00l)$ reflections with $l = 3, 6, \dots$ indicates that the large lateral surface is oriented perpendicular to c -axis.

The crystals are found to be extremely hygroscopic, decomposing into white powder and eventually into a liquid droplet when exposed to the ambient atmosphere. Therefore, due care is required during sample preparation and while loading the sample for measurements in a cryostat as described in Sec. 4.2.

4.3.2 Crystal structure

Rare earth tri-iodides crystallize with two distinct symmetries. The lighter rare earth tri-iodides from La to Nd form an orthorhombic structure with space group $Cmcm$ (No. 63) while the heavier rare earth tri-iodides from Sm to Lu crystallize in a trigonal symmetry with space group $R\bar{3}$ (No. 148) [16]. The single crystal x-ray diffraction performed at 150 K on LaI_3 and CeI_3 single crystal specimens confirms its orthorhombic symmetry with the $Cmcm$ space group. The crystallographic information along with the refinement parameters are summarized in Table 4.8, and the atomic coordinates along with the anisotropic atomic displacement parameters are summarized in Table 4.9 and Table 4.10. The schematic of the crystal structure is shown in Fig. 4.3 (a, b). The ac -plane as seen along the b -axis is illustrated in Fig. 4.3(a). The Ce atoms (depicted as yellow balls) are arranged on a distorted hexagonal lattice with hexagonal edges measuring 5.422 Å and 4.348 Å. Fig. 4.3(b) shows the stacking of layers along the b -axis. Single crystal x-ray diffraction of compounds belonging to the heavier rare earth iodide, GdI_3 , DyI_3 , HoI_3 , and ErI_3 confirms their trigonal structure. The crystallographic information and the refinement parameters are shown in Table 4.11. The atomic coordinates and the anisotropic atomic displacement parameters are shown in Table 4.13. to Table 4.15. The schematic of the crystal structure is shown in Fig. 4.3(c, d). The

honeycomb arrangement of atoms in the ab -plane forming regular hexagons of side 4.293 Å is shown in Fig. 4.3(c), and the stacking of layers along the c -axis is shown in Fig. 4.3(d). The structure of the heavier rare-earth iodides is similar to the low-temperature structure of α -RuCl₃ [113]. YbI₃, a member of this series, has also been shown to exhibit a similar structure [134]. The trend in the normalized volume (volume/formula unit) as a function of ionic radii for the entire series of rare earth tri-iodides is shown in Fig. 4.4.

Table 4.8: Crystallographic data and refinement parameters in the single-crystal X-ray diffraction (SCXRD) refinement of lighter RI₃ samples at T = 150 K.

Property	LaI ₃	CeI ₃
Ionic Radii of R ³⁺ (Å)	1.160	1.143
Temperature (K)	150	150
Crystal system	Orthorhombic	Orthorhombic
Space group	Cmcm	Cmcm
Space group No.	63	63
a (Å)	4.4095(3)	4.3482(5)
b (Å)	13.9299(10)	13.9422(11)
c (Å)	9.9898(7)	9.9243(9)
Volume (Å ³)	613.61(7)	601.6(10)
Z	4	4
Wavelength (Å)	0.71073	0.71073
Detector distance (mm)	40	40
Scan type (ϕ , ω scans)	Full Sphere	Half Sphere
Rotation per image (deg)	1	0.5
Exposure time (sec)	10	10
$(\sin(\Theta)/\lambda)_{\max}$ (Å ⁻¹)	0.738662	0.737961
Absorption, μ (mm ⁻¹)	21.897	22.797
T _{min} , T _{max}	0.98, 1.13	0.83, 1.23
Criterion of observability	$I > 3\sigma(I)$	$I > 3\sigma(I)$
No. of reflections measured	3660	1167
Unique reflections (obs/all)	536/589	500/529
R_{int} (obs/all)	7.22/7.30	2.65/2.66
No. of parameters	16	16
R_F (obs)	3.57	3.45
wR_F (all)	3.91	5.62
GoF (obs/all)	2.39/2.38	3.82/3.72
$\Delta\rho_{\min}$, $\Delta\rho_{\max}$ (e Å ⁻³)	-3.33, 3.87	-3.1, 2.8

Table 4.9: Atomic Coordinates x, y, z and anisotropic displacement parameters(ADPs) of LaI_3 single crystal at 150 K in $\text{\AA}^2$. Unique reflections (obs/all) = 536/589, criterion of observability: $I > 3\sigma(I)$, $R_F = 0.0357$, No. of refined parameters = 16, Refinement method used: least-squares on F, Space group: $Cmcm$.

Atoms	Wyck	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	U_{iso}^{eq}
La	4d	0.5	0.2426(6)	0.75	0.0031(3)	0.0113(4)	0.0058(4)	0	0	0	0.0068(2)
I	4d	0	0.0781(6)	0.75	0.0064(4)	0.0097(4)	0.0102(4)	0	0	0	0.0087(2)
I	8d	0	0.3560(4)	0.5643(6)	0.0063(3)	0.0111(3)	0.0058(3)	0	0	0.0003(2)	0.0078(18)

Table 4.10: Atomic Coordinates x, y, z and anisotropic displacement parameters(ADPs) of CeI_3 single crystal at 150 K in $\text{\AA}^2$. Unique reflections (obs/all) = 500/529, criterion of observability: $I > 3\sigma(I)$, $R_F = 0.0345$, No. of refined parameters = 16, Refinement method used: least-squares on F, Space group: $Cmcm$.

Atoms	Wyck	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	U_{iso}^{eq}
Ce	4d	0.5	0.2422(7)	0.75	0.0033(5)	0.0125(5)	0.0032(5)	0	0	0	0.0064(3)
I	4d	0	0.0789(8)	0.75	0.0057(6)	0.0109(5)	0.0067(5)	0	0	0	0.0078(3)
I	8d	0	0.35541(6)	0.5649(8)	0.0061(5)	0.0119(4)	0.0035(4)	0	0	0.0004(2)	0.0072(3)

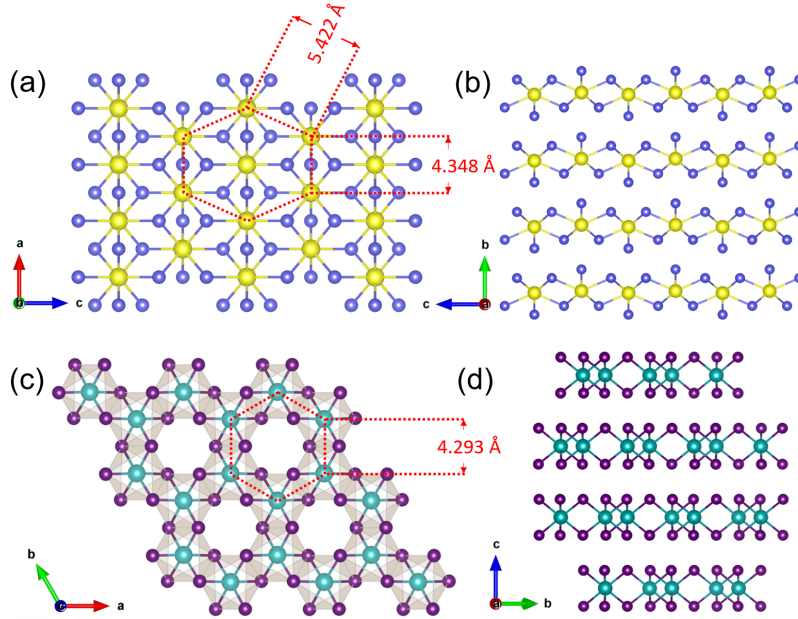


Figure 4.3: The schematic of the crystal structure of CeI_3 (a, b) and DyI_3 (c, d) created using Vesta [15]. Here Ce and Dy, respectively, are chosen to represent the lighter and heavier members of RI_3 series. (a) The view along the b -axis shows the arrangement of Ce atoms (yellow balls) forming a distorted hexagonal ring with bond distances of 5.422 Å and 4.348 Å. The iodine atoms are shown in blue color (b) The stacking of layers of CeI_3 along b -axis. (c) The view along the c -axis exhibiting the arrangement of Dy atoms in the regular hexagonal lattice with side 4.293 Å in the ab plane. (d) The stacking of layers along the c -axis.

Table 4.11: Crystallographic data and refinement parameters in the single-crystal X-ray diffraction (SCXRD) refinement of heavier RI_3 samples at $T = 150$ K.

Property	GdI_3	DyI_3	HoI_3	ErI_3
Ionic Radii of R^{3+} (Å)	0.938	0.912	0.901	0.890
Temperature (K)	150	150	150	150
Crystal system	Trigonal	Trigonal	Trigonal	Trigonal
Space group	$R\bar{3}$	$R\bar{3}$	$R\bar{3}$	$R\bar{3}$
Space group No.	148	148	148	148
a (Å)	7.4745(5)	7.4358(3)	7.4049(7)	7.3915(8)
c (Å)	20.5730(17)	20.5950(11)	20.5854(2)	20.639(3)
Volume (Å ³)	995.39(13)	986.16(8)	977.53(17)	976.52(19)
Z	6	6	6	6
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Detector distance (mm)	40	40	40	40
Scan type (ϕ , ω scans)	Full sphere	Full sphere	Half sphere	Full sphere
Rotation per image (deg)	1	1	1	1
Exposure time (sec)	10	10	10	10
$(\sin(\Theta)/\lambda)_{\text{max}}$ (Å ⁻¹)	0.745584	0.745399	0.742722	0.743647
Absorption, μ (mm ⁻¹)	23.804	25.304	26.203	26.967
T_{min} , T_{max}	0.80, 1.03	0.77, 1.24	0.95, 1.03	0.93, 1.05
Criterion of observability	$I > 3\sigma(I)$	$I > 3\sigma(I)$	$I > 3\sigma(I)$	$I > 3\sigma(I)$
No. of reflections measured	4361	4603	2204	3695
Unique reflections (obs/all)	637/745	652/730	611/694	583/710
R_{int} (obs/all)	10.85/10.94	8.75/8.8	4.85/4.92	6.79/6.98
No. of parameters	14	14	14	14
R_F (obs)	7.98	5.37	4.51	3.49
wR_F (all)	8.63	6.54	5.16	3.93
GoF (obs/all)	5.93/5.49	4.33/4.11	2.72/2.61	2.30/2.13
$\Delta\rho_{\text{min}}$, $\Delta\rho_{\text{max}}$ (e Å ⁻³)	7.47, -7.01	-3.62, 8.98	2.96, -5.32	-3.64, 2.1

Table 4.12: Atomic Coordinates x , y , z and anisotropic displacement parameters (ADPs) of GdI_3 single crystal at 150 K in Å². Unique reflections (obs/all) = 637/745, criterion of observability: $I > 3\sigma(I)$, $R_F = 0.0809$, No. of refined parameters = 14, Refinement method used: least-squares on F, Space group: $R\bar{3}$.

Atoms	Wyck	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	U^{eqi}_{iso}
Gd	6c	0	0	0.3337	0.0084	0.0114	0.0114	0.0057	0	0	0.0135
I	18f	0.32557	0.3343	0.4177	0.0148	0.0109	0.0163	0.0054	-0.0037	0	0.0145

Table 4.13: Atomic Coordinates x, y, z and anisotropic displacement parameters(ADPs) of DyI_3 single crystal at 150 K in $\text{\AA}^2$. Unique reflections (obs/all) = 652/730, criterion of observability: $I > 3\sigma(I)$, $R_F = 0.053$, No. of refined parameters = 14, Refinement method used: least-squares on F, Space group: $R\bar{3}$.

Atoms	Wyck	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	U_{iso}^{eqi}
Dy	6c	0	0	0.3337(2)	0.0089(3)	0.0089(3)	0.0208(5)	0.00443(15)	0	0	0.0128(3)
I	18f	0.3249(9)	0.3344(8)	0.4177(4)	0.0140(3)	0.0103(3)	0.0216(4)	0.0050(2)	-0.0035(2)	-0.0001(2)	0.0158(3)

Table 4.14: Atomic Coordinates x, y, z and anisotropic displacement parameters(ADPs) of HoI_3 single crystal at 150 K in $\text{\AA}^2$. Unique reflections (obs/all) = 611/694, criterion of observability: $I > 3\sigma(I)$, $R_F = 0.0451$, No. of refined parameters = 14, Refinement method used: least-squares on F, Space group: $R\bar{3}$.

Atoms	Wyck	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	U_{iso}^{eqi}
Ho	6c	0	0	0.3337	0.0105	0.0105	0.0105	0.0053	0	0	0.0121
I	18f	0.3248	0.3342	0.4175	0.0151	0.0114	0.0153	0.0057	-0.0032	0.0002	0.0143

Table 4.15: Atomic Coordinates x, y, z and anisotropic displacement parameters(ADPs) of ErI_3 single crystal at 150 K in $\text{\AA}^2$. Unique reflections (obs/all) = 583/710, criterion of observability: $I > 3\sigma(I)$, $R_F = 0.034$, No. of refined parameters = 14, Refinement method used: least-squares on F, Space group: $R\bar{3}$.

Atoms	Wyck	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	U_{iso}^{eqi}
Er	6c	0	0	0.3337(2)	0.0098(2)	0.0098(2)	0.0137(3)	0.0049(10)	0	0	0.0111(17)
I	18f	0.3246(7)	0.3343(6)	0.4173(3)	0.0144(3)	0.0106(3)	0.0145(3)	0.0052(2)	-0.0033(16)	0.0001(16)	0.0136(2)

4.3.3 Raman spectroscopy

As mentioned above, the rare earth tri-iodides crystallize in two distinct symmetries depending on the choice of the rare earth element. The lighter rare earth tri-iodides ($R = \text{La}$ to Nd) adopt an orthorhombic structure, isostructural to the PuBr_3 -type structure (space group $Cmcm$), while the heavier rare earths ($R = \text{Gd}$ to Lu) crystallize in a trigonal structure, isostructural with the BiI_3 -type structure (space group $R\bar{3}$). Here, we examine the Raman spectra of two representative compounds from each group: CeI_3 from the lighter rare earth tri-iodides, and HoI_3 from the heavier group.

For CeI_3 , the factor group theory analysis predicts the zone-center phonon modes as follows: $\Gamma(D_{2h}) = 4A_g + 3B_{1g} + B_{2g} + 4B_{3g}$, resulting in twelve Raman-active phonon modes. On the other hand, for HoI_3 , the irreducible representation is given by $\Gamma(C_{3i}) = 4A_{1g} + 4E_g$, predicting eight Raman-active phonon modes [135].

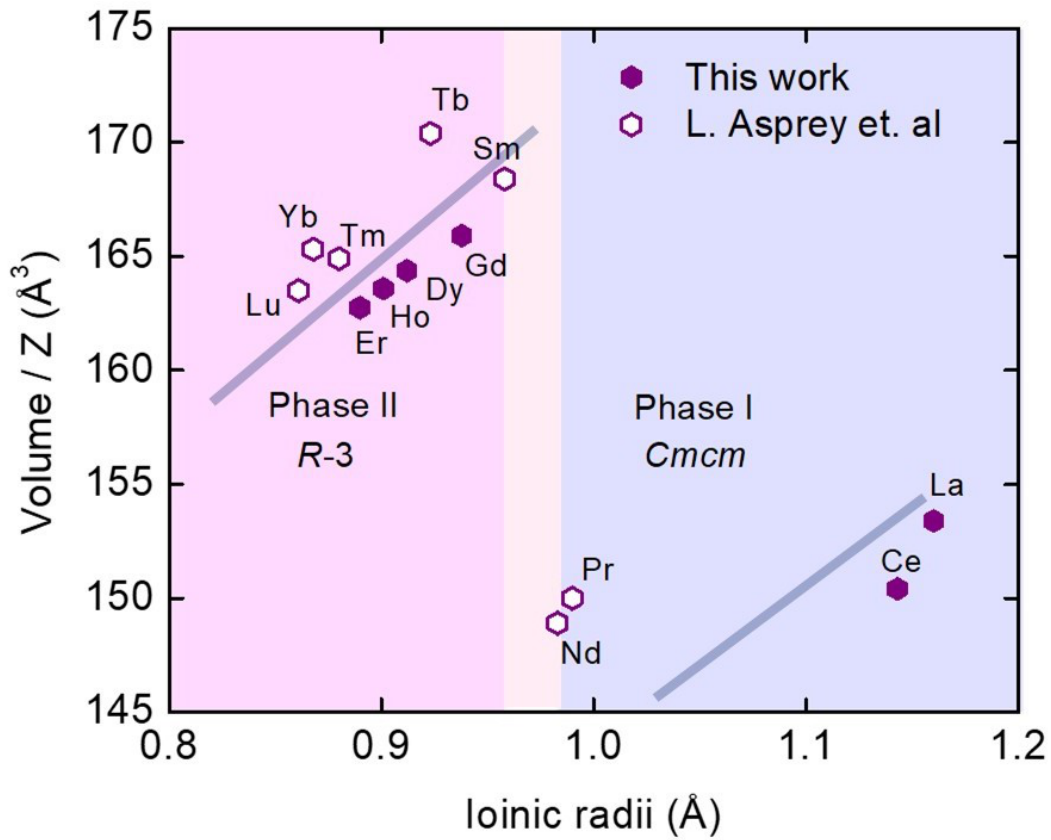


Figure 4.4: Normalized Volume (in $\text{\AA}^3$) (i.e., volume per formula unit) plotted as a function of ionic radii of R^{3+} (in $\text{\AA}$) for a series of rare earth (R) tri-iodides. The lattice parameters for LaI_3 , CeI_3 , GdI_3 , DyI_3 , HoI_3 , and ErI_3 are obtained from the single-crystal refinement in this work. The lattice parameter for PrI_3 , NdI_3 , SmI_3 , TbI_3 , TmI_3 , YbI_3 and LuI_3 are taken from Ref. [16]. The phase diagram illustrates the crystallization of rare earth iodides into two distinct crystallographic structures: the lighter rare earth iodides crystallize in the $Cmcm$ space group (indicated by the light blue section), while the heavier rare earth iodides adopt the $R\bar{3}$ space group (represented by the light purple section). The lines are drawn as a guide to eye to indicate the expected lanthanide contraction. The data reported by L. Asprey *et al.* show a systematic positive shift which could be due to different methods used in the two studies. Note that the lattice parameter in Ref. [16] are obtained using the powder diffraction method on polycrystalline samples.

Figures 4.5(a, b) present the experimentally measured room-temperature Raman spectra of CeI_3 and HoI_3 , respectively. In CeI_3 , five Raman-active phonon modes, labeled R_1 , R_2 , ..., R_5 , are observed at $44.3 (A_g)$, $83.6 (B_{2g})$, $100.9 (A_g)$, $111.0 (A_g)$, $137.1 (A_g) \text{ cm}^{-1}$. The observed spectrum is in good agreement with the previous report on polycrystalline CeI_3 [135], based on which the mode assignment has been done. The experimentally observed phonon

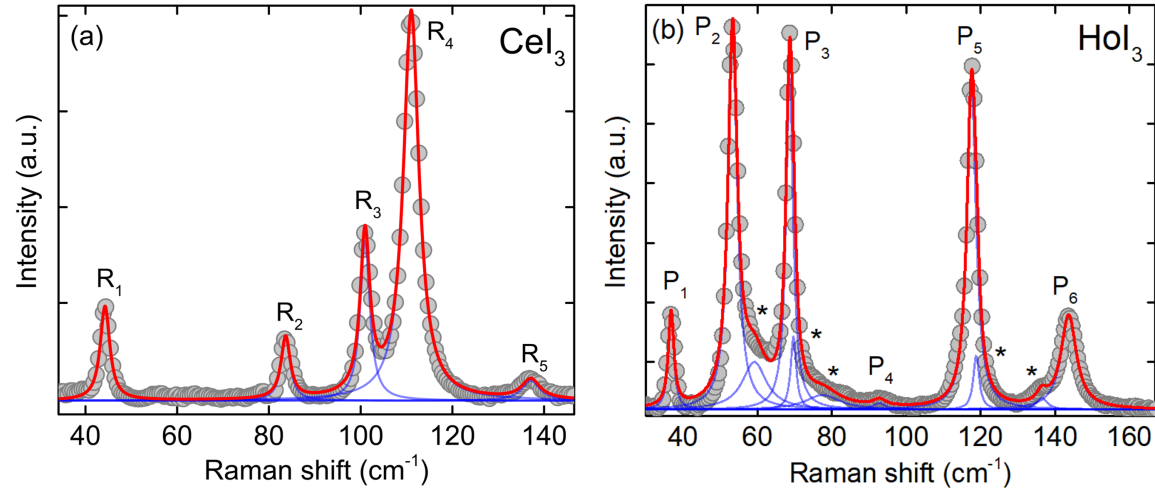


Figure 4.5: Representative Raman spectra of RI_3 compounds at $T = 300$ K. (a) CeI_3 . (b) HoI_3 . The grey circles denote the experimental data points, the blue lines are the Lorentzian fits of the individual Raman mode, and the red solid line indicates the cumulative fitting of the entire spectrum. The weak extra modes are marked with black asterisk (see text for more details).

modes are fewer than the theoretical prediction. A similar discrepancy has been previously reported in other isostructural compounds, such as orthorhombic PmI_3 , where only five Raman modes were observed up to 200 cm^{-1} [136]. The observation of fewer modes than expected is possibly related to the presence of preferred orientation arising due to a needle-like morphology of these materials. This is supported by the fact that in a polycrystalline sample, which is also expected to suffer from the presence of preferred orientation albeit to a somewhat lesser extent, two additional *weak* modes at $73 (\text{B}_{1g})$ and $79 (\text{B}_{2g}) \text{ cm}^{-1}$ are also reported [135]. More careful polarization dependent measurements, preferably at low temperatures that will help resolve the weaker modes, are needed to fully understand the Raman spectra of these materials.

We now turn to HoI_3 , where six Raman-active phonon modes, labeled $P_1, P_2, \dots, P_6$, at $36.8, 53.4, 68.7, 92.8, 117.6, 136.4$, and 143.7 cm^{-1} respectively, are observed. A few weak *extra* modes (marked with black asterisk) near $59, 69.7, 79, 118.9$ and 136.4 cm^{-1} are also observed. Overall, a good agreement, *including the weak extra modes*, has been seen with the isostructural compounds YbI_3 [134] and DyI_3 [135]. The fewer modes observed

experimentally may have the same origin as discussed above in the case of CeI_3 . As for the weak extra modes, they can arise for a variety of reasons. For example, infrared active phonon modes rendered Raman active due to lowering of the local symmetry at some sites with decreasing ionic radius of the rare-earths [116]. In some cases, the extra modes may also arise due to the second-order Raman scattering [117]. Further careful temperature and polarization dependent Raman experiments are needed to understand the Raman spectra of these materials.

4.3.4 Heat capacity

Before proceeding any further, it is worth reminding the reader that the heat capacity data in this study were collected using an unknown quantity of Apiezon N grease, which was employed not only for thermally anchoring the crystal on the sample platform, but also for protecting the crystal from decomposing. This is done by covering the crystal with a thick layer of grease, preventing it from coming in contact with the atmosphere. The heat capacity data recorded, therefore, has contributions not only from the sample but also from an unknown quantity of N grease. Since the crystals used in these measurements are thin, weighing < 1 mg, the N grease contribution cannot be neglected except at very low temperatures, i.e., the temperature range where the magnetic contribution of $4f$ electrons of R^{3+} overwhelms the diminishing lattice heat capacity of the N grease. Since C_p/T for N grease shows a monotonic increase over the whole temperature range [137, 138], any non-monotonicity in our measured C_p/T can be attributed to the sample as elaborated further.

Typically, in an electrically insulating crystal one expects C_p at low temperatures to follow the Debye T^3 law ($C_p/T = \beta T^2$), but the presence of magnetic degrees of freedom due to incompletely filled $4f$ -shell also contribute to the heat capacity of these samples at low temperatures, causing it to deviate from the T^3 behavior. For example, due to the exchange interaction between the neighboring rare-earth moments, short-range ordering is expected above the actual ordering temperature, which is manifested in the temperature variation of heat capacity as a deviation from T^3 behavior. Even if the interaction strength is weaker than

the available thermal energy in the temperature range under consideration, the single-ion effects due to the crystal field splitting may give rise to a Schottky-type contribution that will also cause the heat capacity to deviate from the T^3 law. Further, due to the layered nature of RI_3 compounds, the two-dimensional (2D) magnetic correlations persist up to high temperatures, which is manifested in the form of a broad peak in the heat capacity, as reported for YbX_3 ($X = \text{Cl}, \text{I}$) [105, 134] and ErX_3 [139] ($X = \text{Cl}, \text{I}, \text{or Br}$) compounds. Due to a finite interlayer coupling, at very low temperatures a second anomaly due to three-dimensional (3D) magnetic order may set-in as seen in the case of Yb and Er trihalides mentioned above.

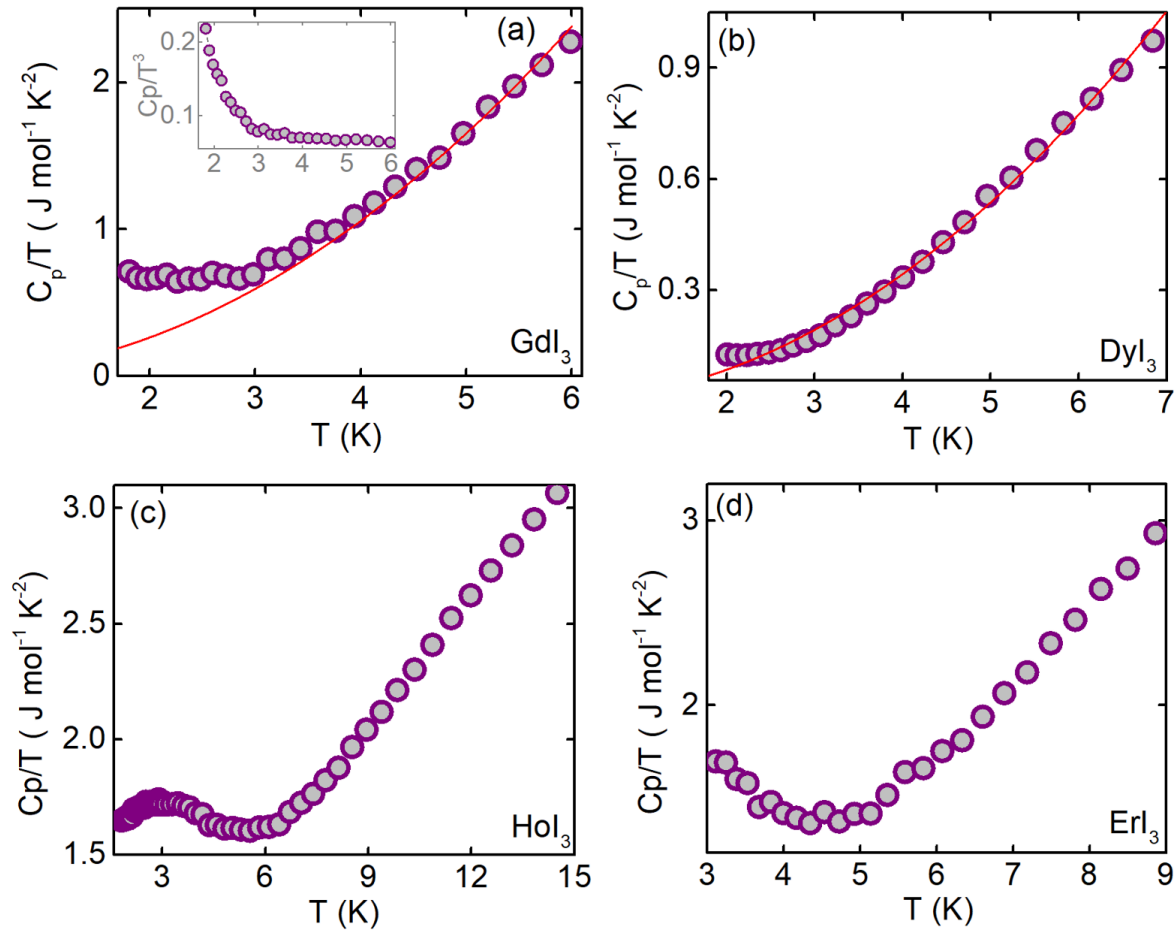


Figure 4.6: The heat capacity C_p is plotted as C_p/T against temperature T for different rare earth triiodides. The solid red line is the T^2 fitting to the experimental data to estimate the lattice contribution. (a) GdI_3 , (b) DyI_3 , (c) HoI_3 , (d) ErI_3 .

Fig. 4.6(a - d) shows C_p/T versus T plots of GdI_3 , DyI_3 , HoI_3 , and ErI_3 in the low temper-

ature range. We start by discussing the heat capacity of GdI_3 where the crystal field effect is expected to be negligible since the half-filled $4f$ shell has no net orbital angular momentum ($L = 0 \Rightarrow J = S$, where S , L , and J are spin, orbital, and total angular momenta), leading to a spin-only moment ($S = 7/2$). This makes the interpretation of heat capacity data relatively simpler as the crystal field-assisted Schottky contribution is not expected in this case. As shown in Fig. 4.6 (a), C_p/T data follows the expected T^2 behavior between 4 K and 7 K, which represents the combined lattice contributions of sample and N grease. However, a clear deviation from the T^2 dependence can be seen below ~ 3 K, which we attribute to the presence of short-range 2D correlations between the Gd spins.

In DyI_3 , C_p/T roughly follows a T^2 dependence between 7 K and 3 K but deviates from this behavior at lower temperatures. The deviation of C_p/T from T^2 is weaker in this case compared to GdI_3 , which either suggests weaker exchange interaction between the Dy moments or it is related to the fact that in the Gd compound the magnetic entropy buried below 3 K is $R \ln 8$, whereas for Dy it will be simply be $R \ln 2$ (assuming the crystal field split ground state is a doublet, but even if it is a quartet the argument remains valid).

The heat capacity of HoI_3 has a different temperature dependence than the previous two compounds. In this case, C_p/T shows a distinct hump around 3 K. The behavior of C_p/T at higher temperatures (above the hump) also does not conform to the conventional T^2 behavior, suggesting that the magnetic heat capacity of Ho dominates in the entire investigated temperature range. The presence of the hump in the heat capacity may be either due to the presence of a low-lying crystal field level (i.e., the first excited state to lie a few $k_B T$ above the ground state) or due to 2D magnetic correlations. Further clarity on this requires accurate determination of C_p , down to much lower temperatures.

The heat capacity of ErI_3 is unfortunately measured only down to 3 K. The observed behavior in this case is somewhat similar to that of HoI_3 , displaying a prominent upturn in C_p/T below 4.5 K. This may be a precursory rise leading eventually to a hump (as in the case of HoI_3) if the data are extended below 3 K. In a previous report, it was shown that ErI_3 displays prominent short-range 2D magnetic correlations in this temperature range due

to dominant dipolar interactions [140].

4.3.5 Magnetization

Magnetic susceptibility (χ) for samples RI_3 ($\text{R} = \text{Gd}, \text{Dy}, \text{Ho}, \text{and Er}$) is shown in Fig. 4.7. The plotted data are collected as a function of temperature under an applied field of 10 kOe, in both in-plane, $\text{H} \parallel ab$ ($\chi_{\parallel}$) and out-of-plane, $\text{H} \perp ab$ ($\chi_{\perp}$) configurations. The high- and low-temperature data for each compound are fitted using the modified Curie-Weiss (CW) expression: $\chi = \chi_0 + C/(T - \Theta_{\text{CW}})$, where C is the Curie-constant, from which the effective magnetic moment (μ_{eff}) is derived using the formula $\mu_{\text{eff}} = \sqrt{8C}$, Θ_{CW} is the Weiss temperature. Here χ_0 is included to account for the curvature in $1/\chi$. This can arise from core diamagnetism and/or van Vleck paramagnetism, and in some cases even from the crystal field splitting, whose contribution to the susceptibility is roughly accounted for by a temperature independent term [141].

Isothermal magnetization measurements were conducted as a function of applied field (0 - 160 kOe) at 2 K for both the orientations. The saturation magnetization (M_s) is obtained as the asymptotic limit of the magnetization curve as the applied field approaches its upper limit of 160 kOe, the highest applied field in our experiments.

As the single-crystal specimens used in this study were thin flakes with small masses (~ 1 mg), the main source of error in our magnetization data arises from the measurement of sample mass. The samples were weighed inside a glovebox using an analytical balance. Though the resolution of the balance is 0.1 mg, due to various practical reasons, the *maximum* weighing error in recording the sample masses can be taken as $\pm 15\%$. This can affect the value of the magnetic moment estimated from the Curie-Weiss fit, as explained further. parameters from the Curie-Weiss fit for samples RI_3 ($\text{R} = \text{Gd}, \text{Dy}, \text{Ho}, \text{and Er}$), are summarized in Table 4.16.

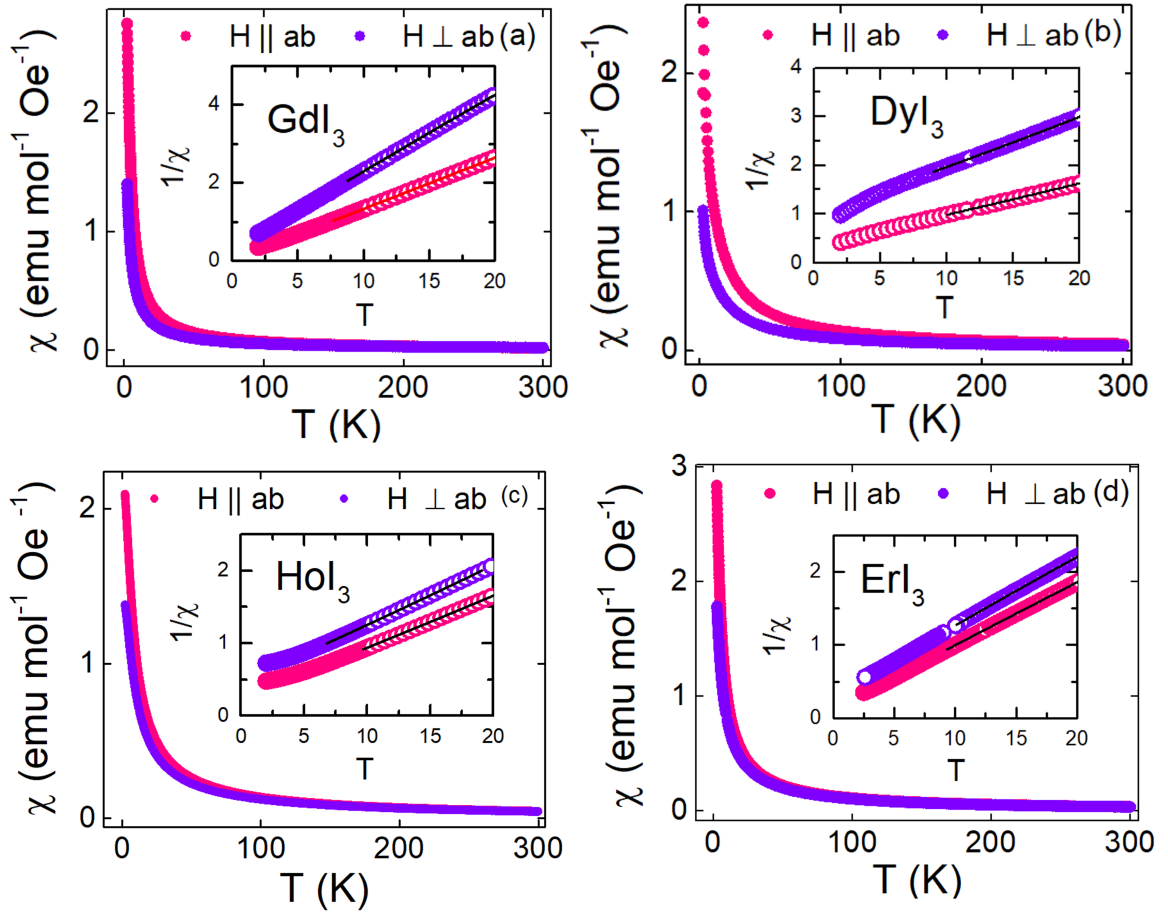


Figure 4.7: Magnetic susceptibility (χ) as a function of temperature measured on rare earth triiodides single crystal specimen for two anisotropic orientations $H \parallel ab$ and $H \perp ab$. (a) GdI_3 (b) DyI_3 (c) HoI_3 (d) ErI_3 . The inset shows the variation of inverse magnetic susceptibility ($1/\chi$) as a function of temperature with solid black line representing the Curie-Weiss fit (see text for details).

We first discuss the results for GdI_3 shown in Fig. 4.7(a). In GdI_3 , the Gd^{3+} ions ($L = 0$, $S = 7/2$, $J = 7/2$) are expected to have an effective magnetic moment of $\mu_{\text{eff}} = g_J \sqrt{J(J+1)} = 7.94 \mu_B$ per Gd-mol, and a saturation magnetization $M_s = g_J J = 7 \mu_B$ per Gd-mol, where g_J is the g -factor. An effective moment of 7.9 and 7.8 μ_B per Gd-mol from the high- and low-temperature fits are in good agreement with the expected value. However, in the perpendicular orientation, the μ_{eff} value has reduced to about 6.5 μ_B per Gd-mol, which lies outside the lower margin of the 15% error band. The anisotropy between the two orientations is evident from the χ versus T plots, where a difference between the two orientations can be

seen below about 100 K [As a matter of fact, this difference persists up to further higher temperatures but gets increasingly smaller as the temperature increases]. For example, at 2 K, $\chi_{\perp}$ is about 3/5 of $\chi_{\parallel}$. In fact, the $M(H)$ data at 2 K (see Fig. 4.8) show this anisotropy even more strikingly with $M_s = 7.8 \mu_B$ for $H \parallel ab$ but only $4.4 \mu_B$ for $H \perp ab$. For GdI_3 , the magnetization saturates in both directions above a field of 60 kOe. While the saturation value in the parallel orientation is in good agreement with the expected value well within the 15% error band, the value in the perpendicular orientation is too small, suggesting the unexpected presence of a very strong magnetic anisotropy in GdI_3 .

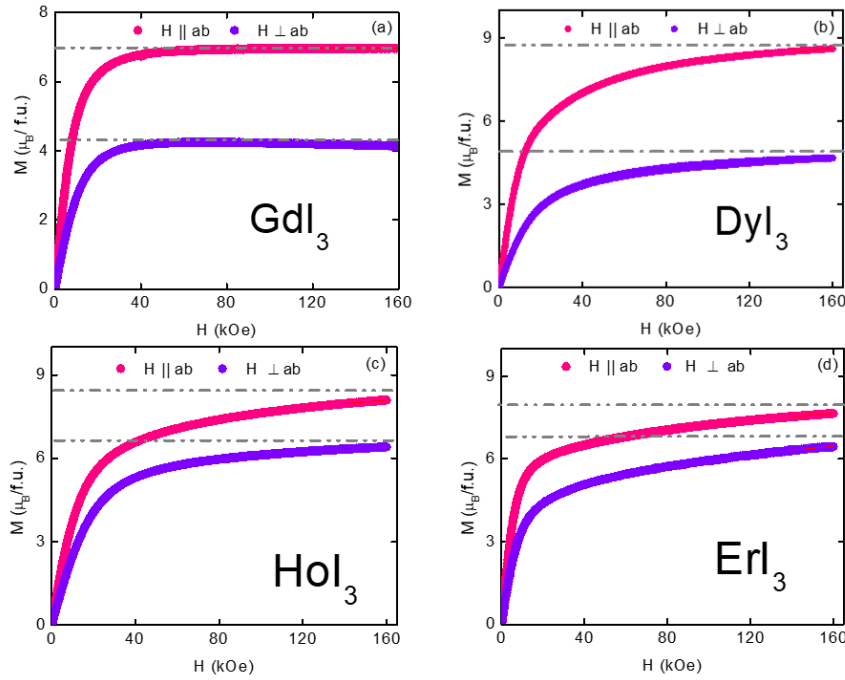


Figure 4.8: Isothermal magnetization of RI_3 compounds at $T = 2$ K for $H \parallel ab$ and $H \perp ab$. The grey colored, dashed horizontal lines are drawn as a guide to eye indicating approximate asymptotic limit.

The magnetic anisotropy in rare-earth compounds typically arises from single-ion, dipolar, and exchange terms. As explained above, in Gd^{3+} , the single-ion anisotropy is not expected due to cancellation of orbital angular momentum. However, a sizable anisotropy in such cases may arise from either the anisotropic dipolar interactions or due to the presence of biquadratic terms in the exchange [142]. But the anisotropy from such sources is typically

weak and should only be seen at low temperatures, and is therefore not sufficient to explain the observed behavior. The possibility of a large *surface* anisotropy pinning the large Gd moments parallel to the *ab*-plane can be a viable possibility due to the thin-flakey shape of the crystals examined here. It should be stressed that we measured a second, slightly heavier, GdI₃ specimen formed by stacking two crystal flakes, in the perpendicular orientation, and found a similarly smaller value of the saturation magnetization, ruling out the possibility of an experimental artifact in giving rise to the observed magnetization reduction (see Fig. 4.9).

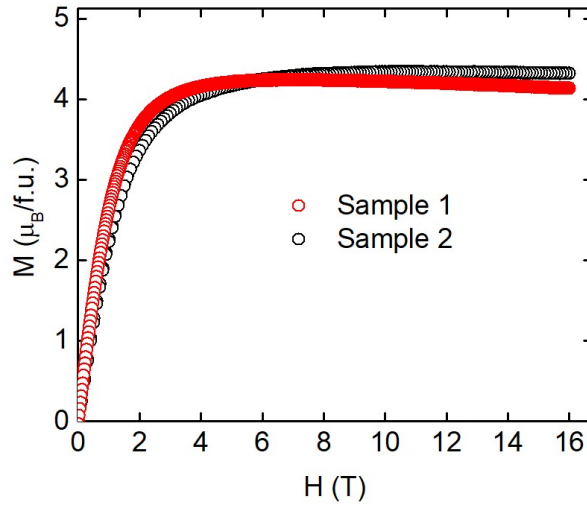


Figure 4.9: $M(H)$ data for GdI₃ sample for field applied perpendicular to the *ab*-plane at $T = 2$ K. The measurements were performed on two different specimens weighing 0.8 mg (red open circles), and 1.2 mg (black open circles). The 1.2 mg specimen was obtained by stacking two flakes of nearly equal masses.

The magnetization data for DyI₃ is shown in Fig. 4.7(b). For Dy³⁺ ion ($L = 5, S = 5/2, J = 15/2$), the calculated effective magnetic moment and saturation magnetization are, respectively, $10.63 \mu_B$, and $10 \mu_B$. The experimentally obtained effective magnetic moment from the high-temperature and low temperature fits is in good accord with the calculated value for the parallel orientation, as shown in Table 4.16. The effective moment in the perpendicular orientation is less than expected, 8.6 and $9.7 \mu_B$ per Dy-mol from high and low temperature fits, as in the case of GdI₃. The isothermal magnetization at 2 K (see Fig. 4.8)

similarly saturates at 8.8 ($H \parallel ab$) and 4.9 ($H \perp ab$) μ_B per Dy-mol. The anisotropy in DyI_3 seems to be even more pronounced than in the case of GdI_3 . However, this is not surprising given that Dy^{3+} may have a significant single-ion anisotropy, which is perhaps complements the surface anisotropy (i.e., the single-ion anisotropy also favors in-plane alignment more than out-of-plane, thereby augmenting the overall anisotropic behavior. Before proceeding further, it is worth looking at the low-temperature behavior more carefully. We see that there is a small but clearly perceptible downturn in $1/\chi$ for both the orientations below about 5 K. The large value of effective magnetic moment from the low-temperature Curie-Weiss fit (almost close to the full moment), suggests that the crystal field split ground state wave-function has a significant contribution of the $\pm 15/2$ Kramers doublet as in the pyrochlore $\text{Dy}_2\text{Ti}_2\text{O}_7$, where the crystal field split Kramers doublet ground state of Dy is nearly pure $\pm 15/2$ [143]. The magnetic susceptibilities of HoI_3 and ErI_3 are shown in Figs. 4.7(c) and 4.7(d), respectively. In both cases, $\chi_\perp < \chi_\parallel$ similar to the previous two cases. However, the anisotropy for either of them is not as strong as in DyI_3 . This is also reflected in the value of M_{16} shown the last column of Table. 4.16. The Curie-Weiss fits derived μ_{eff} values are also in agreement with the calculated value of 10.6 μ_B and 9.5 μ_B for Ho^{3+} and Er^{3+} , respectively. The low-temperature effective moment values are also high suggesting that the ground states in these case is also pure, corresponding to the $M_J = \pm 8$ (Ho) or $\pm 15/2$ (Er). We also note that while in ErI_3 , both $1/\chi_\parallel$ and $1/\chi_\perp$ remain nearly linearly linear down to the lowest temperature, a clear upward deviation can be seen for HoI_3 . The case of ErI_3 is similar to that GdI_3 which also shows a linear $1/\chi$ down to the lowest temperature. Since short-range two-dimensional spin correlations are expected to develop in all cases below 4-5 K, the deviation from linearity seen for Dy and Ho compounds can be attributed to the crystal field—at least in the HoI_3 sample the crystal-field is manifested as a broad peak in the heat capacity centered around 3 K. The effect of low-lying crystal field levels in DyI_3 might be more subtle. We now come to the observation concerning the relatively weaker anisotropic magnetic behavior of Ho and Er samples. While the exact reason for this is not clear, it maybe that the single-ion anisotropy in these cases favors an out-of-plane orientation, which tends to

weaken the surface anisotropy.

Table 4.16: Summary of fitting parameters χ_0 (emu mol⁻¹ Oe⁻¹), C (emu mol⁻¹ Oe⁻¹ K), μ_{eff} (μ_B), Θ_{CW} (K), and M_{sat} (μ_B) obtained from the Curie-Weiss analysis for parallel and perpendicular directions. M_{16} is the isothermal magnetization (in μ_B per R-mol) at 16 T. The sample mass (in mg) and the temperature range (in K) over which the Curie-Weiss fit is performed are also shown. Note that measurements for parallel and perpendicular orientations were done on different crystals from the same batch.

Sample	Sample Mass (mg)	Orientation	Fitting Range (K)	χ_0	C	μ_{eff} (μ_B)	Θ_{CW} (K)	M_{16} (μ_B)
GdI ₃	0.9	H $\parallel$ ab	100–250	-8.2×10^{-4}	7.9	7.9	-2.7	7.8
			10–20	-8.1×10^{-4}	7.6	7.8	-0.19	–
	0.8	H $\perp$ ab	150–300	0.01	5.24	6.5	-7.9	4.4
			10–20	0.006	4.88	6.3	-1.4	–
DyI ₃	1.6	H $\parallel$ ab	150–300	-0.003	15.6	11.2	-9.2	8.8
			10–20	-0.002	17.7	11.8	-6.8	–
	1.4	H $\perp$ ab	150–300	0.004	9.3	8.6	-11.8	4.9
			10–20	-0.042	11.8	9.7	-11.5	–
HoI ₃	0.8	H $\parallel$ ab	150–300	-0.003	15.3	11.1	-8.2	8.5
			10–20	-0.021	14.7	10.8	-3.5	–
	1.2	H $\perp$ ab	150–300	-2.1×10^{-4}	14.1	10.6	-14.5	6.6
			10–20	-0.032	13.5	10.4	-6.2	–
ErI ₃	1.9	H $\parallel$ ab	150–300	-0.001	11.9	9.7	-2.7	7.6
			10–20	0.008	11.4	9.5	-1.4	–
	1.2	H $\perp$ ab	150–300	5.7×10^{-4}	11.1	9.4	-5.2	6.9
			10–20	0.019	9.9	8.9	-2.9	–

^a and ^b refer to different crystal specimens from the same batch.

4.4 Summary & conclusions

High-quality single crystals of rare earth tri-iodides are grown using a vapour transport technique. This report details the crystal growth method, which yields centimeter-sized single crystals of various rare earth tri-iodides including LaI₃, CeI₃, GdI₃, DyI₃, HoI₃, and ErI₃. The crystals are thoroughly characterized using single-crystal x-ray diffraction to precisely determine their crystal structure, which was further characterized using Raman spectroscopy. The homogeneity of the crystal is verified using the EDX probe and chemical mapping on a micron size area of the single crystal,

confirming their 1:3 stoichiometry. The heat capacity and magnetization probes reveal distinct magnetic ground states for different tri-iodides dominated by crystal electric field splitting and strong surface anisotropy. Further exploration of their exact magnetic ground states through neutron scattering, muon spin resonance, or electron spin resonance experiments, and low-temperature specific heat and bulk magnetization is essential for a comprehensive understanding of their magnetic behavior. The heavier rare earth tri-iodides are iso-structural to the low-temperature phase of $\alpha\text{-RuCl}_3$, and are therefore potential kitaev materials. In contrast, the lighter RI_3 can be further explored to search for chiral phonons that generate a high magnetic field using the inverse Faraday effect similar to CeCl_3 and CeF_3 .

Chapter 5

Crystal growth and magnetic behavior of $J_{eff} = 1/2$ quantum antiferromagnet CeCl_3

The work described in this chapter is published in Physical Review B. with the title of ” Crystal growth, magnetic and magnetocaloric properties of $J_{eff} = 1/2$ quantum antiferromagnet CeCl_3 ”

- *The Magnetic measurements discussed in this chapter were performed by me at UGC-DAE Consortium for Scientific Research, University Campus, Khandwa Road, Indore 452001, Madhya Pradesh, India in the group of Dr. Rajeev Rawat.*

5.1 Introduction

Quantum antiferromagnets have garnered enormous attention in the past few years. They exhibit exotic phases at low temperatures including Quantum Spin Liquids (QSLs) with fractional excitations and long-range entanglement [144]. The triangular and Kagome lattice antiferromagnets are ideal platforms to realize the QSL phase. In 2006, Kitaev proposed an exactly solvable model for anisotropic spin $1/2$ on a honeycomb lattice. The ground state of this model is QSL whose excitations are Majorana fermions [145]. Unlike geometric frustration, where the frustration arises due to the geometry of the underlying lattice, in the Kitaev model it is the bond-dependent Ising-like interactions that give rise to a strong frustration, resulting in the QSL behavior [146]. The iridates (e.g., Na_2IrO_3) and the ruthenates (e.g., $\alpha\text{-RuCl}_3$) have been extensively studied to realize the Kitaev model [147]. Search for a half-quantization plateau in the thermal Hall effect, which would confirm the existence of Majoranas, is currently one of the burning topics in quantum condensed matter [148, 149]. Recently, YbCl_3 has also attracted attention as a quantum antiferromagnet with a honeycomb lattice of the Yb^{3+} ions in their Kramer's doublet ground state ($J_{eff} = \frac{1}{2}$) [150–152]. YbCl_3 belongs to the rare-earth trichloride family with the general formula RCl_3 (R = Rare earth element). While the heavier rare-earth members ($\text{R} = \text{Tb}$ to Lu) of this series crystallize with a monoclinic structure analogous to $\alpha\text{-RuCl}_3$, the lighter members ($\text{R} = \text{La}$ to Gd) crystallize with a hexagonal structure where the R^{3+} ions arrange on triangular plaquettes, stacked to form chains of R^{3+} ions running parallel to the c -axis [153–155]. Here, we focus on the member CeCl_3 of this series, an antiferromagnetic insulator with an electronic band gap of 4.3 eV [156]. Both Yb^{3+} and Ce^{3+} are Kramer's ions, but while Yb^{3+} is just one short of a completely filled f -shell, Ce^{3+} has only one electron in the f -shell. The previous reports on CeCl_3 concentrated only on the low-temperature behavior ranging from 0.1 K to 4.2 K, and in magnetic fields up to 12 kOe [18]. The Cl Nuclear Quadrupole Resonance (NQR) on some rare-earth trichlorides and tribromides was reported previously over the same temperature range [157]. According to this report, in CeCl_3 , Ce^{3+} ions carry an effective spin $1/2$, which undergoes long-range antiferromagnetic ordering around 0.11 K. The physical properties of CeCl_3 show strong sample dependence, which has been attributed to the presence of impurities in the grown crystals [18, 158]. Our study is motivated by the recent interest in quantum materials (e.g., $\alpha\text{-RuCl}_3$) showing unusual ground states. While CeCl_3 is not isostructural with the $\alpha\text{-RuCl}_3$, the heavier members of the RCl_3

series are, and their growth optimization and properties are therefore of significant interest. The recent theoretical studies on CeCl_3 , in particular, have shown the emergence of optically driven chiral phonon modes in this material which should generate giant effective magnetic fields ($\sim 10^2$ T) acting on the paramagnetic $4f$ spins [73]. This requires high-quality crystals where the induced magnetization can be probed experimentally via the inverse Faraday effect. Despite these interests, the magnetic and thermodynamic properties of CeCl_3 remain unexplored above 4.2 K, where the crystal electric field levels of Ce are expected to dominate the magnetic and thermodynamic properties.

In this study, we report the crystal growth, structural, magnetic, and thermodynamic characterizations of high-quality single crystals of CeCl_3 . It should be pointed out that while the older studies furnish adequate details of the precursor purification, the details of the crystal growth method or the structural characterization of CeCl_3 are not well documented. In our work, the mm-size, transparent, high-quality crystals are grown by the modified Bridgman-Stockbarger method in an infrared image furnace. The grown crystals are thoroughly characterized using powder and single-crystal X-ray diffraction, and Laue diffraction. The magnetic susceptibility and specific heat are measured from 2 K to 300 K.

We show that the magnetic susceptibility of CeCl_3 crystals shows a huge anisotropy that originates from the crystal electric field splitting of the lowest J-multiplet of Ce^{3+} . The susceptibility along the two orientations is fitted using the crystal electric field analysis. The Ce-Ce exchange coupling is estimated to be weak (~ 0.1 K). The low-temperature specific heat changes substantially in the presence of an applied magnetic field, showcasing a peak at 2.5 K under an applied magnetic field of 30 kOe. The zero-field magnetic specific heat (C_{4f}) is fitted using the crystal field splitting inferred from the magnetic susceptibility data. Given the large magnetic anisotropy and a sizeable ground state magnetic moment, the magnetocaloric assessment was done, which gave a high maximum-magnetic-entropy-change of $-\Delta S_{4f} = 23 \pm 1 \text{ J K}^{-1} \text{ K}^{-1}$ near 2 K for $\Delta H = 6 \text{ T}$.

5.2 Experimental methods

Single crystals of anhydrous CeCl_3 are grown from a stoichiometric melt using two different methods: the static Bridgman method and the traditional Bridgman-Stockbarger method in an image furnace. The details of the crystal growth methods and experiments are given in Sec. III.A. The single crystal specimens for various experiments were cut inside an Ar-filled glove box to prevent decomposition

upon exposure to atmospheric air. For this purpose, the crystals were embedded in a thin layer of mounting wax (used for sample cutting or polishing) before taking them out of the glove box. At the end of the experiment, the wax layer was dissolved inside the glove box using dichloromethane (CH_2Cl_2), which is both water-repellent and anhydrous. Single crystal X-ray diffraction was carried out using a Bruker Smart Apex Duo diffractometer at 100 K using MoK_α radiation ($\lambda = 0.71073$ Å). The details of the single crystal x-ray diffraction experiment is elaborated in 2.2.2. The total exposure time was 2.01 h. The frames were integrated using the Bruker SAINT software package with a narrow frame algorithm. Data were corrected for absorption effects using the multiscan method (SADABS). The structure was solved and refined using the Bruker SHELXTL software package. The grown crystals were oriented using a Laue camera (Photonic Science, UK) in backscattering geometry with Tungsten as a source material ($\lambda = 0.35 - 2.5$ Å), accelerating voltage 30 kV, tube current 0.3 mA) as described in 2.2.3. The Laue pattern was analyzed using Orient Express 3.4 (V 3.3) software package.

Raman spectra were collected at room temperature in backscattering configuration using a Horiba Jobin-Yvon LabRAM HR spectrometer equipped with a liquid nitrogen-cooled Charge-Coupled Detector (CCD) and a laser of 532 nm as a source of excitation as described in 2.2.6. The excitation was maintained at 25% of the maximum power, and the accumulation time for each spectrum was 30 s with 25 iterations each time to improve the resolution and intensity of the Raman modes. The $CeCl_3$ crystal was coated with a thin layer of Apiezon N grease to prevent degradation due to its extremely hygroscopic nature. The Raman signal from the Apiezon N was measured separately and subtracted from the total signal to eliminate the background.

The specific heat measurements were done using the relaxation method in a Physical Property Measurement System (PPMS), Quantum Design, USA. A small piece of crystal was cut into a 2 mm by 2 mm piece, weighing around 10 mg, and mounted on the heat capacity sample holder using low-temperature Apiezon N grease. The addenda (heat capacity of the sample holder and Apiezon N grease) was measured before loading the sample. Sample degradation from moisture effects was minimized by handling, weighing, and cutting the $CeCl_3$ crystal inside the glove box. The magnetic susceptibility was measured at the UGC-DAE CSR, Indore center, Indore, using a VSM probe option in a Physics Property Measurement System (PPMS), Quantum Design, USA.

5.3 Results and discussion

5.3.1 Specific difficulties in the crystal growth of CeCl_3

The anhydrous rare-earth trichlorides (RCl_3) in general and CeCl_3 in particular are highly sensitive to the presence of moisture in the air, reacting readily to form $\text{RCl}_3 \cdot x\text{H}_2\text{O}$ ($x = 6$), especially during a humid day when this reaction happens over a time scale of few minutes. It is therefore difficult to grow large single crystals of rare-earth trichlorides from a melt as the adsorbed moisture, when not carefully removed, reacts with RCl_3 at elevated temperatures leading to a formation of various oxychlorides (for example: ROCl) and oxides which makes the melt hazy. The grown crystal in such cases also has a hazy appearance with large number of cracks. It is, therefore, necessary to remove the absorbed moisture by dehydrating the hexahydrated $\text{RCl}_3 \cdot x\text{H}_2\text{O}$ under vacuum in the presence of ammonium chloride or halides of carbon or sulphur. These methods have their own drawback as they tend to introduce undesirable impurities (rare-earth carbides or sulfides) [159].

The crystals of rare-earth trichlorides can be grown using the chemical vapor transport method employing AlCl_3 as the transporting agent [160]. In this reaction, the rare-earth (R) oxides are first reacted with AlCl_3 to form corresponding anhydrous rare-earth trichlorides. These are then further reacted with an excess AlCl_3 through a reversible reaction to form gaseous complexes, including $\text{RAI}_3\text{Cl}_{12}$ and $\text{RAI}_4\text{Cl}_{15}$. These gaseous complexes, having a significantly high vapor pressure, are transported to the colder end of the tube, where mm-sized transparent crystals of RCl_3 can be extracted. This method is, however, complex and the resulting crystals are small and not of very high quality. Mroczkowski et al. reported crystal growth of EuCl_3 using the vertical Bridgman method in the presence of Cl_2 gas under high pressure [161]. They purified hydrated precursor by placing it in a stream of HCl gas, before subjecting it to crystal growth. A similar method has been cited for the crystal growth of CeCl_3 in Ref. [155]. However, as noted above, Ref. [161] uses Cl_2 gas under high-pressure to prevent Eu^{2+} from stabilizing. It is therefore not evident if the complex approaches described in previous studies are necessary presently due to the availability of high-quality precursor materials. We, therefore, used a relatively simpler approach to grow high-quality single crystals of anhydrous CeCl_3 . Our method involves a simple purifying step followed by crystal growth from a stoichiometric melt. We explored two slightly different methods of crystal growth: the static Bridgman

method and traditional Bridgman-Stockbarger method in an image furnace.

The anhydrous CeCl_3 powder (Alfa Aesar 99.9%) was stored and handled in an argon filled glove box where O_2 and H_2O level is maintained at less than 0.1 ppm at all times. The as-purchased CeCl_3 powder was heat-treated under a dynamic vacuum. For this, the CeCl_3 powder is loaded in a quartz ampoule that was preheated overnight at 1000°C to remove any adsorbed moisture on the walls of the ampoule. This ampoule was then transferred into the glove-box at 200°C . The mouth of the ampoule was temporarily sealed using a bottle-cork to prevent any moisture from entering it. Inside the glove-box, the as purchased CeCl_3 powder was poured into the ampoule. The loaded ampoule was then removed from the glove-box and connected to a turbomolecular pump, while its other end, where the CeCl_3 powder is located, is gradually heated in a furnace at 230°C . After heating at this temperature for 24 h under the dynamic vacuum, the ampoule was allowed to cool down to room temperature before flame-sealing under dynamic vacuum (10^{-5} mbar). Up to here the procedure is common for both methods.

Static Bridgman

In the case of static Bridgman method, the sealed ampoule was placed in a vertical tubular furnace under a temperature gradient. The furnace was heated to 870°C , which is higher than the melting point of anhydrous CeCl_3 (817°C), at a rate of 50°C/h and allowed to dwell at this temperature for 12 h. After this, the furnace was slowly cooled to 750°C at a rate of 0.3°C/h , and finally cooled down to room temperature at a rate of 50°C/h . Shiny transparent crystals measuring up to a few mm in size were extracted from the ampoule.

Bridgman-Stockbarger

In this case, the size of the quartz ampoule used was chosen to be around 4-5 mm ID and 8 mm OD. In the first step, the ampoule was placed in a muffle furnace and heated up to 850°C to obtain a premelted, highly dense ingot about 15-20 mm long, which is subsequently subjected to the crystal growth in an infrared image furnace. For this, the quartz ampoule containing the premelted ingot was loaded in a four-mirror image furnace by suspending it from the upper shaft of the furnace (see, Fig. 5.1(a)). The shaft was then lowered until the lower end of the ampoule reached the center of the furnace (the common foci of the four ellipsoidal reflectors), where the light rays converge to form the molten-zone during the floating zone experiment [162]. The lamp power was then gradually raised

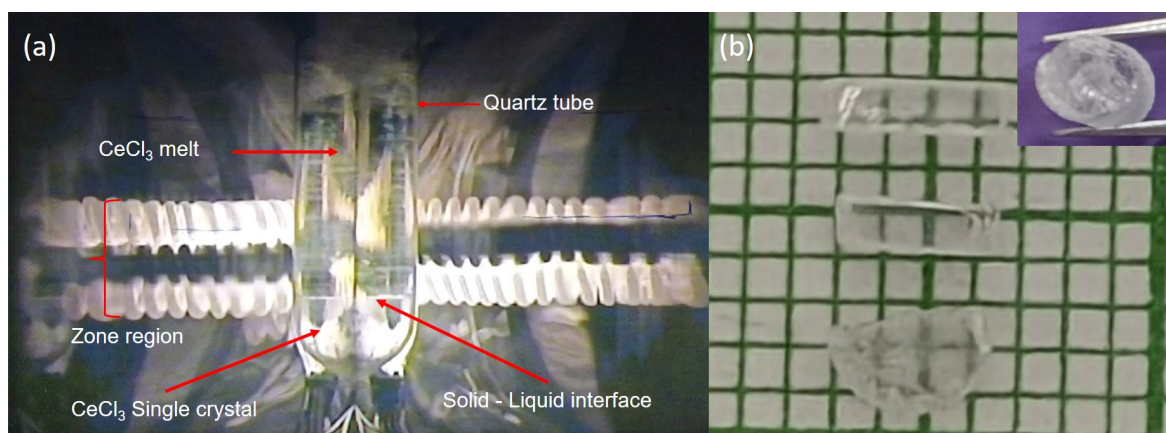


Figure 5.1: (a) Crystal growth of CeCl_3 using a four-mirror image furnace equipped with 1 kW halogen lamps. The lower part below the solid-liquid interface is the CeCl_3 crystal being grown. (b) Images of the crystals pieces obtained after cutting the crystal boule shown in the inset.

until CeCl_3 started melting. After achieving a homogenous melt, the ampoule was allowed to travel downwards into the region of steep vertical temperature gradient. The lamps used were 1 KW each with the zone-region of about 8-10 mm length. In a mirror furnace with 1 KW lamps, the vertical temperature gradient outside the molten zone is typically several hundred $^{\circ}\text{C}/\text{cm}$. In order to optimize the growth parameters for obtaining crack-free, high-quality crystals, several growth experiments were conducted at various traveling speeds, varying from 1 mm h^{-1} to 0.2 mm h^{-1} . At 1 mm h^{-1} , the crystal boule developed numerous cracks yielding very small, irregular shaped, crystal pieces. At slower growth speeds the results improved, but even at the slowest growth speed of 0.2 mm h^{-1} the cracks could not be avoided completely. In this case, however, the cracks were fewer, and hence large crystal pieces, several mm long by several mm across, could be obtained. The crystals were cut using a low-speed saw inside the glove box. While cutting, small rectangular crystal pieces cleaved-off the crystal boule. These crystal pieces are fully transparent with atomically flat facets as shown in Fig. 5.1(b). The flat surfaces of the semicircular piece were dry polished using a silicon-carbide paper of grit-size 1200. The slight haziness seen is due to imperfect surface polishing and not because the crystal piece is hazy inside.

Between the two growth methods, the crystals obtained using the image furnace are of higher quality. They are fully transparent and hence one can say are essentially defect-free. The presence of defects or impurities (typically oxychlorides and oxides mentioned above) in the crystal leads to hazy or milky appearance. Analysis of impurities in the crystals is summarized in Fig. 5.2(a-c).

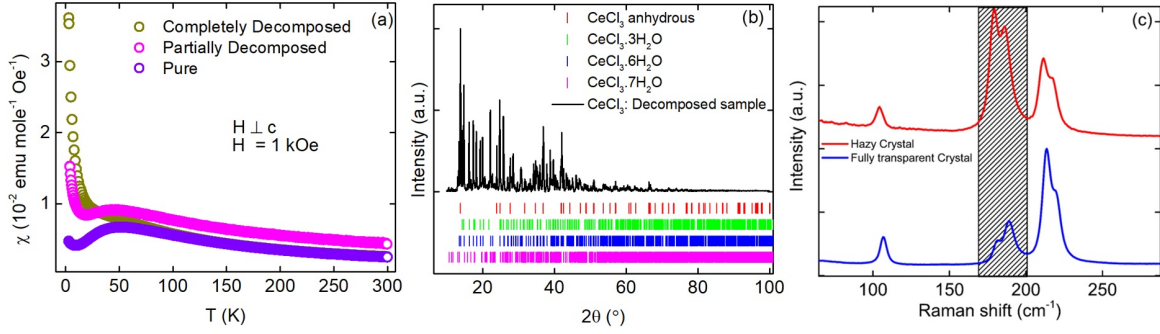


Figure 5.2: (a) Magnetic susceptibility for the perpendicular orientation ($H \perp c$) for: (i) a fully transparent crystal (labelled as 'Pure' and shown using the purple colour), (ii) a hazy specimen, which is partially decomposed (shown using the magenta colour), (iii) a fully decomposed sample (shown using the dark yellow colour). Note that the decomposition was allowed after the specimen was mounted on the sample holder. Though the decomposed crystal turns into a powder, the orientation of the particles in the powder is expected to remain the same. Note the increase in the Curie-tail upon decomposition. (b) Powder X-ray diffraction of a decomposed specimen showing diffraction peaks due to the formation of $\text{CeCl}_3 \cdot x\text{H}_2\text{O}$ species. (c) Raman spectra of a transparent crystal specimen shown in blue color and a hazy crystal specimen shown in red color.

The X-ray diffraction pattern, recorded in the Bragg-Brentano geometry is shown in Fig. 5.3(a) top, on a flat crystal specimen, such as one shown in the inset. The only reflections seen are those corresponding to the bc -plane either in the trigonal or hexagonal symmetries. This shows that the specimen being investigated is an oriented single crystal of high-quality. The orientation of the surface was further confirmed using the X-ray Laue diffraction (see Fig. 5.3(b)), where sharp Laue spots were observed, which suggest that the grown crystals are of high quality.

5.3.2 Single crystal x-ray diffraction

A small crystal specimen was selected for single crystal X-ray diffraction (SCXRD). A detailed examination of the collected diffraction data was carried out to establish the crystal structure of CeCl_3 . The data was collected at $T = 100$ K. The SCXRD data refinement was done using two different structural models, namely, hexagonal and trigonal. As far as diffraction is concerned, the essential difference between these structures lies in the presence or absence of $(00l)$ reflections, where $l = (2n + 1)$. In the trigonal symmetry, these reflections are allowed, whereas in the hexagonal symmetry, they are forbidden.

In the raw frames, weak $(00l)$ reflections could be identified, as shown in Fig. 5.3(c). These

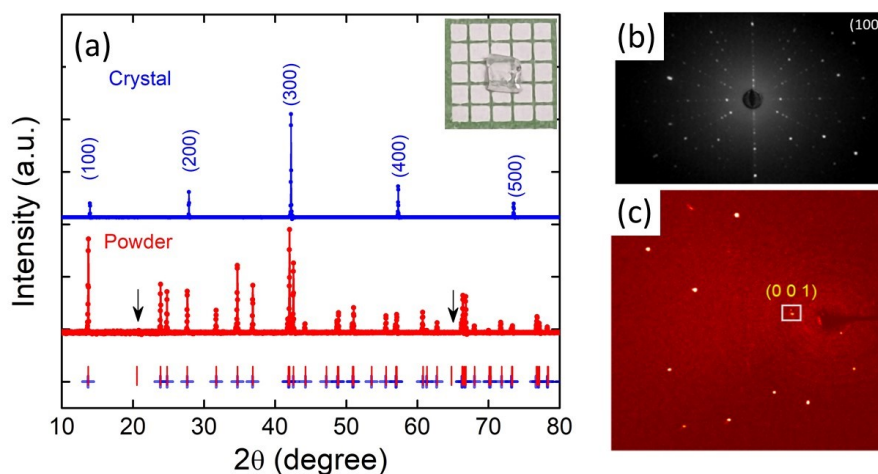


Figure 5.3: (a) The x-ray diffraction pattern of a single crystal specimen of CeCl_3 in the Bragg-Brentano geometry (blue); The powder x-ray diffraction pattern of CeCl_3 obtained by crushing a small crystal piece (red); The calculated Bragg positions for hexagonal (blue plus sign) and trigonal (red vertical line) symmetries. The arrows indicate the positions of (001) and (003) peaks in the trigonal symmetry. (b) The x-ray Laue diffraction pattern, and (c) A raw frame during the single crystal x-ray diffraction data, where the (001) spot is marked. Inset in (a) shows a representative crystal specimen used in the x-ray diffraction experiments.

reflections are better depicted in Fig. 5.4(a-c), where the reconstructed $h0l$ reciprocal space planes and three-dimensional plots for the (001) reflections are presented. Here, the weak (001) and (003) reflections can be seen unambiguously. This is further corroborated by the structural refinement data. In the trigonal case, all the diffraction spots can be successfully indexed, with no systematic absences observed. Conversely, in the hexagonal model, the (001) reflections remain unindexed.

In both cases, we used the observability criterion $I > 3\sigma(I)$, where $\sigma(I)$ is the standard deviation in the intensity distribution. The intensity (I) and the corresponding $\sigma(I)$ values for the unindexed reflections under the hexagonal space group are listed in Table 5.1. A comparison of structural refinement parameters for the two models is outlined in Table 5.2 below. The goodness of fit and R_{int} values favor the trigonal structure, but the difference in their values is not overwhelming. This is also reflected in the structural parameters obtained in the two cases. For example, in the trigonal model, the space group turned out to be $P\bar{3}(147)$ and the corresponding Wyckoff sites as: Ce(2d) with fractional coordinate $(\frac{2}{3}, \frac{1}{3}, z_{\text{Ce}})$ and Cl(6g) with fractional coordinates $(x_{\text{Cl}}, y_{\text{Cl}}, z_{\text{Cl}})$. The best-fit values obtained for these coordinates are: $z_{\text{Ce}} = 0.25004(8)$ and

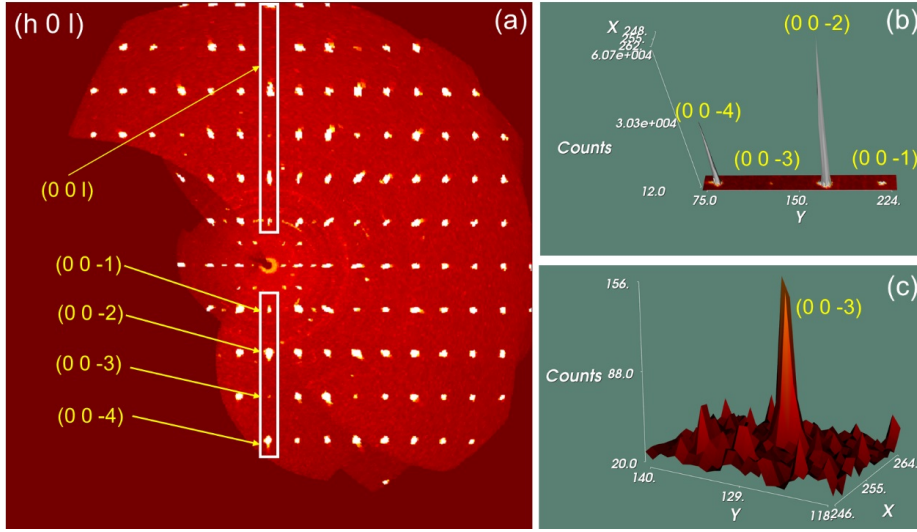


Figure 5.4: (a) Reconstructed plots of reciprocal space along $(h0l)$ direction. The X and Y scale are position of spot measured in the units of detector pixel (b) Three-dimensional view of $(00l)$ reflections marked with a rectangle in the lower part of (a). (c) Three-dimensional view of $(00-3)$ reflection.

$x_{\text{Cl}} = 0.91350(14)$, $y_{\text{Cl}} = 0.61249(15)$, $z_{\text{Cl}} = 0.7500(3)$. On the other hand, in the hexagonal case, space group $P6_3/m$ (176), the Wyckoff sites came out to be: Ce(2c) with fixed fractional coordinate $(\frac{2}{3}, \frac{1}{3}, \frac{3}{4})$ and Cl(6h) with fractional coordinates $(x_{\text{Cl}}, y_{\text{Cl}}, \frac{1}{4})$, where $x_{\text{Cl}} = 0.91348(15)$, $y_{\text{Cl}} = 0.61256(16)$. The coordinates z_{Ce} and z_{Cl} in the trigonal symmetry relate to the hexagonal case by $1 - z$. On the other hand, the x - and y -coordinates of Cl in the two cases differ, if at all, by a very small amount. Besides this difference, and the minute differences in the bond lengths and bond angles, the two structures nearly overlap.

Table 5.1: Intensity and systematic absent reflections in hexagonal space group

hkl	I	$\sigma(I)$	Why rejected
0 0 1	21.60	2.20	
0 0 1	17.10	1.90	
0 0 1	21.90	2.20	Systematically absent but $I > 3\sigma(I)$
0 0 1	20.50	2.80	
0 0 3	22.50	6.80	

To conclude, though the crystal structure of CeCl_3 is trigonal in the true sense, in practical terms, it deviates from the hexagonal symmetry only marginally. The summary of crystallographic data using the trigonal model is shown in Table 5.3, and the atomic coordinates for Ce and Cl along with

Table 5.2: Summary of refinement parameters for two different models

Model	Trigonal	Hexagonal
Crystal system	P $\bar{3}$ (147)	P6 $\bar{3}/m$ (176)
Goodness of fit	1.292	1.372
R_{int} (%)	4.45	4.85
Final R indices (%) R_1	2.50	2.47
wR_2	6.54	6.04
Number of refined Parameters	14	10

their isotropic displacement parameters are listed in Table 5.4.

The calculated powder X-ray diffraction profile shows zero-intensity for the (0 0 1) and (0 0 3) lines. The non-zero intensity of these peaks requires the z -coordinate of Ce in the trigonal structure to differ sufficiently from the value in the hexagonal case; or for the Cl atoms at 6g (trigonal) or 6h (hexagonal) to have substantially different coordinates in the two structures. Since the differences in the variable coordinates in the two structures are too small, it will be practically impossible to detect the (0 0 1) or (0 0 3) lines in the powder pattern. The measured powder X-ray diffraction pattern shown in Fig. 5.3(a) confirms this assertion, as the superstructure lines could not be detected beyond uncertainty. The (0 0 1) line may possibly be picked in a longer run, but keeping the sample undecomposed over a longer duration, even in an airtight sample holder, is a challenge. Using synchrotron-based experiments, one can try to overcome this challenge. In previous studies, the structure of CeCl_3 was reported to be hexagonal [153–155]. However, as we found, the deviation from the ideal hexagonal structure is so minor that for all practical purposes, one can consider the structure of CeCl_3 to be hexagonal.

In both the structures, each Ce^{3+} ion is nine-fold coordinated by Cl^- ions, as shown in Fig. 5.5(c). Of these, three Cl^- are coplanar with the central Ce^{3+} ion. These are labelled 1, 2, and 3 in Fig. 5.5(c). The other six Cl^- ions are located above and below the central Ce^{3+} ion. These are labelled from 4, 5, and 6 (above), and 7, 8, and 9 (below) in Fig. 5.5(c). In the ac -plane, shown in Fig. 5.5(a), the Ce^{3+} ions form a zig-zag chain running parallel to the c -axis. The bond distances for the trigonal case are also shown in Fig. 5.5(a). The Ce-ions marked with a yellow border are located at a distance of 4.319 Å from the central Ce ion (blue) along the c -axis. This is the nearest-neighbor (nn) Ce-Ce distance. The three second-nearest neighbors (nnn) are at a distance of 4.799 Å. They are shown with a pink border for easy identification. The third nearest neighbor (nnnn) distance is 7.424 Å. The

Table 5.3: Summary of the crystallographic data, Data collection strategy and structural refinement parameter in the trigonal model

Chemical formula	CeCl_3
Formula weight	246.47 g/mol
Temperature	100 K
Wavelength	0.71073 Å
Crystal system	trigonal
Space group	P -3
Unit cell dimensions	$a = 7.4242(15) \text{ Å}, \alpha = 90^\circ$ $b = 7.4242(15) \text{ Å}, \beta = 90^\circ$ $c = 4.3189(13) \text{ Å}, \gamma = 120^\circ$
Volume	$206.16(10) \text{ Å}^3$
Z	2
Density (calculated)	3.970 g/cm^3
Absorption coefficient	12.742 mm^{-1}
F(000)	218
Theta range for data collection	3.17 to 29.06°
Index ranges	$-8 \leq h \leq 10, -9 \leq k \leq 10, -5 \leq l \leq 5$
Reflections collected	2441
Independent reflections	374 [R(int) = 0.0445]
Structure solution technique	direct methods
Structure solution program	XT, VERSION 2018/2
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-2019/1 (Sheldrick, 2019)
Function minimized	$\sum w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	374 / 0 / 14
Goodness-of-fit on F^2	1.292
Final R indices	369 data; $I > 2\sigma(I)$ $R_1 = 0.0250, wR_2 = 0.0654$ all data $R_1 = 0.0257, wR_2 = 0.0658$
Weighting scheme	$w = \frac{1}{[\sigma^2(F_o^2) + (0.0317P)^2 + 0.8350P]}$ where $P = \frac{(F_o^2 + 2F_c^2)}{3}$
Extinction coefficient	0.0590(60)
Largest diff. peak and hole	1.722 and -1.448 eÅ^{-3}
Root mean square (RMS) deviation from mean	0.380 eÅ^{-3}

Table 5.4: Atomic coordinates and equivalent isotropic atomic displacement parameters (Å^2)

Atoms	x/a	y/b	z/c	U(eq)
Ce	0.666667	0.333333	0.25004(8)	0.0037(2)
Cl	0.91350(14)	0.61249(15)	0.7500(3)	0.0048(3)

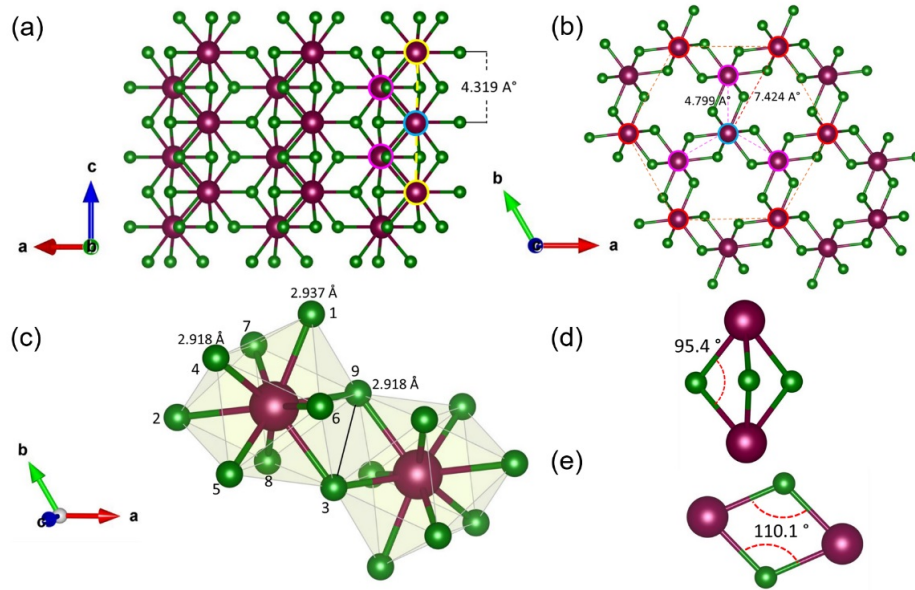


Figure 5.5: Crystal structure of CeCl_3 obtained using VESTA [17]. The brown spheres represent Ce and green spheres (smaller in size) represent Cl. (a) Structure as viewed along the b -axis. The nearest neighbors around the central Ce (blue border) are shown with yellow borders ($d_{nn} = 4.319 \text{ \AA}$); (b) View along the c -axis showing the second nearest neighbor (magenta border) and the third nearest neighbor Ce (red border) around the central Ce (yellow border). $d_{nnn} = 4.799 \text{ \AA}$, and $d_{nnnn} = 7.424 \text{ \AA}$ (c) 9-fold coordination of Ce^{3+} ions where Cl^- ions.

third neighbors are shown with a red border, as in Fig. 5.5(b). The polyhedra around the Ce^{3+} are edge-shared, forming a ring in the ab -plane as shown in Fig. 5.5(b). The magnetic exchange path between any two nearest neighbor Ce ions is via three Ce-Cl-Ce pathways along the c -axis, where the Ce-Cl-Ce bond angle is 95.4° , as shown in Fig. 5.5(d). The nnn interaction is mediated via two Ce-Cl-Ce pathways with bond angle Ce-Cl-Ce of 110.1° , as shown in Fig. 5.5(e).

5.3.3 Raman spectroscopy

Fig. 5.6(a) shows the Raman spectra of a high-quality single crystal of CeCl_3 . The observed spectrum is satisfactorily fitted using five Lorentzian line shapes. For simplicity, the modes are labelled from R_1 to R_5 and their positions are: 106.8 cm^{-1} , 181.2 cm^{-1} , 189 cm^{-1} , 213 cm^{-1} , and 219.7 cm^{-1} . In an older study, CeCl_3 is reported to show six Raman modes at E_{2g} (106 cm^{-1}), A_g (176 cm^{-1}), E_{2g} (180 cm^{-1}), E_{1g} (193 cm^{-1}), A_g (216 cm^{-1}), and E_{2g} (218 cm^{-1}) [163]. The comparison with our data suggests the presence of an extra peak at 176 cm^{-1} in the spectra reported in Ref. [164]. Incidentally, in the isostructural LaCl_3 , only five Raman modes are reported at 108 cm^{-1} , 179 cm^{-1} ,

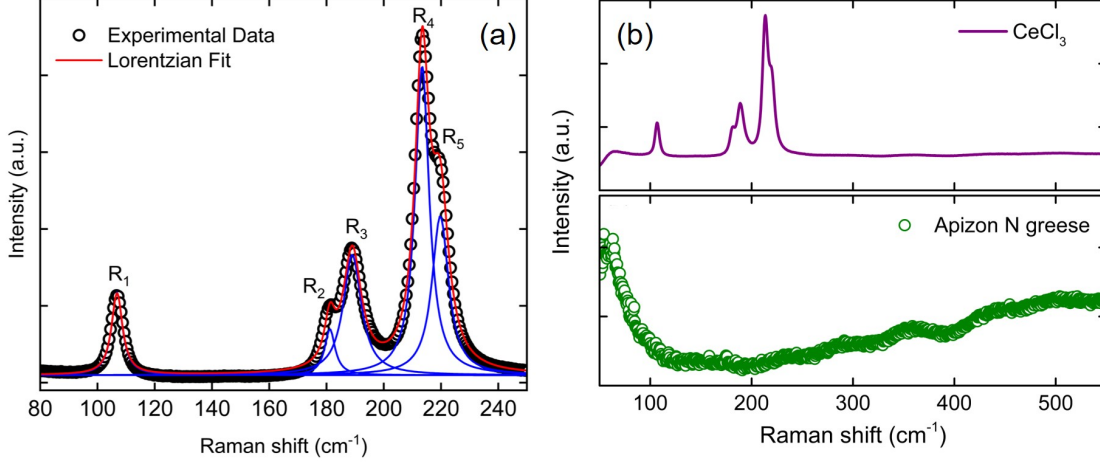


Figure 5.6: (a) The Raman spectra of CeCl_3 . The five Raman modes are labelled R_1 to R_5 . The blue curves are individual Lorentzian fits for each mode. The red line through the data point is a total fitted spectrum obtained by adding up the individual Lorentzian. (b) The raw data up to 550 cm^{-1} and the Raman spectra of the N grease used for protecting the crystal from ambient atmosphere.

186 cm^{-1} , 210 cm^{-1} , and 217 cm^{-1} [164]. The extra mode in CeCl_3 , can be due to the presence of local defects or impurities.

Although the polarization dependence of the Raman active mode centered at 179 cm^{-1} was previously reported [163], a more careful polarization-dependent study of the entire spectrum is lacking to understand the symmetry (A_g or E_g) of all the modes present in CeCl_3 . Also, a temperature and magnetic field dependent study on high-quality crystals is needed to understand the evolution of Raman modes with temperature and magnetic field. Previously, it was reported that the degenerate E_{1g} and E_{2g} Raman modes split under a magnetic field into left- and right-handed circular polarization, leading to chiral behavior [165]. With the availability of high-quality single crystals of CeCl_3 , such experiments involving temperature and field dependence will be carried out in the future.

5.3.4 Magnetic susceptibility

Curie-Weiss analysis

The magnetic susceptibility of CeCl_3 is measured under a magnetic field of 1 kOe for two different orientations, namely $H \parallel c$ and $H \perp c$ axis. Additionally, measurements are also done on a powder

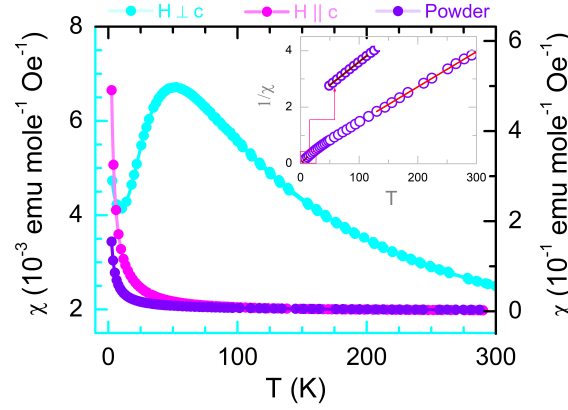


Figure 5.7: The magnetic susceptibility χ is plotted as a function of temperature for $H \parallel c$, $H \perp c$, and powder specimens of CeCl_3 . The inset shows the reduced inverse magnetic susceptibility as a function of temperature. The solid lines in the inset represent the Curie-Weiss fit (see text for details). In the main panel, the lines are guides to the eye.

specimen of CeCl_3 , obtained by crushing a small crystal piece. The magnetic susceptibility plots are shown in Fig. 5.7. The susceptibility measurements are performed in both Zero Field Cooling (ZFC) and Field Cooling (FC) modes. The two runs exactly overlap, and hence only the ZFC run is shown in Fig. 5.7. Upon cooling, $\chi^\perp(T)$ (i.e., $\chi(T)$ for $H \perp c$) exhibits a broad peak at 50 K, followed by a sharp increase below 9 K, as shown in Fig. 5.7. This broad peak is due to the crystalline electric field (CEF) splitting of the $J = 5/2$ ground state of Ce^{3+} . The CEF splitting scheme for Ce^{3+} is discussed in the next section. The Curie-Weiss analysis was performed in the low and high-temperature ranges for both orientations and the powder sample. Due to the presence of a small curvature in χ^{-1} , we used the modified Curie-Weiss expression, $\chi = \chi_0 + \frac{C}{T - \Theta_{CW}}$, where χ_0 , C , and Θ_{CW} represent the temperature-independent van Vleck contribution, Curie constant, and Curie-Weiss temperature, respectively. The symbols $\chi_0^\parallel$, $\chi_0^\perp$; $C^\parallel$, $C^\perp$; and $\Theta_{CW}^\parallel$, $\Theta_{CW}^\perp$ are used to replace χ_0 , C , and Θ_{CW} in the Curie-Weiss expression for $H \parallel c$ and $H \perp c$ orientations, respectively. The value of μ_{eff} can be obtained from the Curie constant using the expression $\mu_{\text{eff}} = \sqrt{8C}$. The results are summarized in Table 5.5. The fitting for the powder specimen is shown in the inset of Fig. 5.7, as a representative case.

The analysis of $H \parallel c$ data yielded the following values of the fitting parameters: $\chi_0^\parallel \sim -5.1 \times 10^{-4} \text{ emu mol}^{-1} \text{ Oe}^{-1}$, and $C^\parallel = 0.81 \text{ emu mol}^{-1} \text{ Oe}^{-1} \text{ K}$, giving $\mu_{\text{eff}}^\parallel = 2.53(1) \mu_B/\text{Ce}$. This value of μ_{eff} matches closely with the theoretical value of $2.54 \mu_B/\text{Ce}$ calculated using $J = 5/2$

and $g_J = 6/7$, where J is the total angular momentum and g_J is the Lande-g factor. The value of $\Theta_{CW}^{\parallel} = 18.7$ K is positive, indicating that the Ce-Ce interaction along the c-axis is ferromagnetic. The large value of $\Theta_{CW}^{\parallel}$ compared to the long-range antiferromagnetic ordering temperature ($T_N \sim 0.1$ K [18]) is simply an artifact arising due to the large crystal field splitting.

The low temperature fitting is performed in the range $3 \text{ K} < T < 10 \text{ K}$, yielding $C^{\parallel} = 1.47 \text{ emu mol}^{-1} \text{ Oe}^{-1} \text{ K}$ or an effective magnetic moment of $\mu_{eff}^{\parallel} = 3.42 \mu_B/\text{Ce}$. As we show below, at low temperatures, only the lowest Kramer's doublet $|\frac{5}{2}, \pm\frac{5}{2}\rangle$ contributes to the magnetic moment. We can therefore estimate $g^{\parallel}$ using the expression: $\mu_{eff}^{\parallel} = g_J^{\parallel} \sqrt{J(J+1)}$ by taking $J = 1/2$ and the experimentally obtained value of $3.43 \mu_B/\text{Ce}$ for $\mu_{eff}^{\parallel}$. This gives a value of $g^{\parallel} \sim 4$, which agrees fairly nicely with the value reported previously using the electron spin resonance (ESR) study [166]. The value of $\Theta_{CW}^{\parallel} = 0.017$ K obtained from the low temperature fit is rather small but still positive.

Similar analysis for $\chi^{\perp}(T)$ yields $\chi_0^{\perp} \sim 2.7 \times 10^{-4} \text{ emu mol}^{-1} \text{ Oe}^{-1}$; $C^{\perp} = 0.75 \text{ emu mol}^{-1} \text{ Oe}^{-1}$, giving $\mu_{eff}^{\perp} = 2.46 \mu_B/\text{Ce}$. This value of the effective moment is slightly reduced compared to the theoretical value. The value of $\Theta_{CW}^{\perp}$ turned out to be -32.7 K. The negative sign of $\Theta_{CW}^{\perp}$ indicates the interaction between the Ce moments is antiferromagnetic in the ab-plane. As above, the enhanced magnitude of $\Theta_{CW}^{\perp}$ is due to the crystal field splitting. From a similar low-temperature fit (see Table 5.5), we estimate $g^{\perp} \sim 0.17$, in good agreement with the ESR value of 0.17. In samples with large magnetic anisotropy, it is often more insightful to analyze the powder averaged data. The powder susceptibility shown in Fig. 5.7 agrees well with the calculated values obtained using the equation: $\chi_{avg} = \frac{2}{3}\chi^{\perp} + \frac{1}{3}\chi^{\parallel}$. The Curie-Weiss analysis, similar to the one above, yielded the values of fitting parameters consistent with the single crystal values, as shown in Table 5.5. The negative sign of the Weiss temperature for the powder sample indicates that the average Ce-Ce interaction in CeCl_3 is antiferromagnetic in nature. The low-temperature fit gives a value of $\Theta_{CW} = -0.12$ K, which is negative and small as expected, and is closer to the actual ordering temperature.

Crystal field analysis

The degeneracy of the lowest J -multiplet in an isolated Ce^{3+} ion ($S = \frac{1}{2}$, $L = 3$, and $J = \frac{5}{2}$) is given by $2J + 1 = 6$. In a trigonal crystalline electric field (CEF), this degeneracy is lifted by splitting the ground state into three Kramer's doublets. The CEF Hamiltonian is given by:

Table 5.5: Fitting parameters in the Curie-Weiss fit of the susceptibility data for single crystal and powder samples

	Fitting range (K)	χ_0 (emu mole ⁻¹ Oe ⁻¹)	C (emu mol ⁻¹ Oe ⁻¹ K)	μ_{eff} (μ_B)	Θ_{CW} (K)
H $\parallel$ c	150 - 300	-5.1×10^{-4}	0.81	2.54	18.7
	3 - 10	-2.3×10^{-3}	1.47	3.42	0.017
H $\perp$ c	200 - 300	2.7×10^{-4}	0.75	2.46	-32.7
	3 - 7	3.8×10^{-3}	0.003	0.15	-0.39
Powder	130 - 300	8.8×10^{-4}	0.81	2.54	-18.2
	3 - 10	1.8×10^{-3}	0.47	1.95	-0.12

$$H_{\text{CEF}} = \sum_{m,n} B_m^n O_m^n, \quad (1)$$

where B_m^n are the CEF parameters, and O_m^n are the Stevens operators. Since the trigonal distortion in CeCl₃ is at best marginal, for the purpose of CEF analysis we can assume the point group symmetry to be hexagonal. With this simplification, the only non-zero parameters in equation (1) are B_2^0 and B_4^0 [167, 168]. Hence, we rewrite equation (1) as:

$$H_{\text{CEF}} = B_2^0 O_2^0 + B_4^0 O_4^0. \quad (2)$$

Now, the magnetic susceptibility can be calculated from the van Vleck formula [169]:

$$\chi_i = \frac{2N_A g_J^2 \mu_B^2}{Z} \left[\sum_n \beta \langle J_{i,n} \rangle^2 e^{-\beta E_n} + 2 \sum_{m \neq n} \frac{|\langle m | J_{i,n} | n \rangle|^2 (e^{-\beta E_m} - e^{-\beta E_n})}{E_n - E_m} \right], \quad (3)$$

where $N_A = 6.023 \times 10^{23}$ is the Avogadro's number of Ce³⁺ ions, $g_J = \frac{6}{7} \sim 0.857$, $\mu_B = 0.927 \times 10^{-20}$ erg Oe⁻¹, $\beta = \frac{1}{k_B T}$, $k_B = 1.38 \times 10^{-16}$ erg K⁻¹, $Z = \sum_n e^{-\beta E_n}$, and $n, m = 0, 1, 2$. Here, index i corresponds to orientation: $i = x$ for $H \perp c$, and $i = z$ for $H \parallel c$. As shown in Ref. [169], for the hexagonal symmetry, the eigenstates of Hamiltonian (2) are simply the unmixed or pure states of the form $|\frac{5}{2}, \pm\frac{5}{2}\rangle$, $|\frac{5}{2}, \pm\frac{3}{2}\rangle$, and $|\frac{5}{2}, \pm\frac{1}{2}\rangle$. We know from the low-temperature magnetic susceptibility analysis that the crystal field split ground state is $|\frac{5}{2}, \pm\frac{5}{2}\rangle$, which implies that the first excited state is either $|\frac{5}{2}, \pm\frac{3}{2}\rangle$ or $|\frac{5}{2}, \pm\frac{1}{2}\rangle$. We tried both these combinations and found that only in the

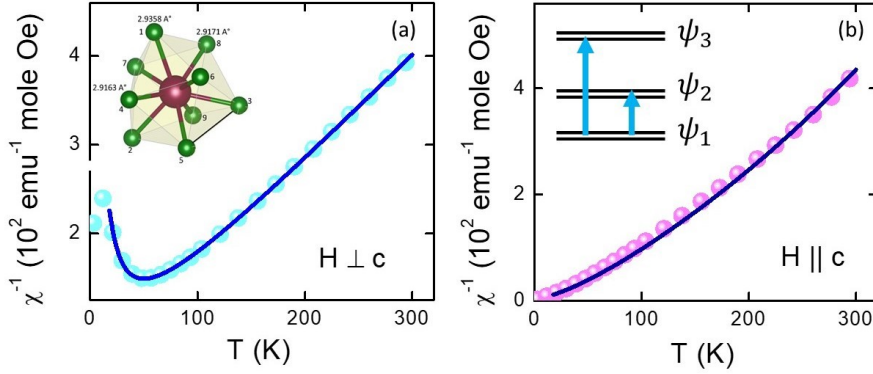


Figure 5.8: $\chi^{-1}(T)$ is plotted as a function of temperature for the orientations (a) $H \perp c$ and (b) $H \parallel c$. The lines through the data points are best fit curves obtained using the crystal electric field analysis (see text for details). The inset in (a) shows the arrangement of ligand ions around the Ce^{3+} ion at the center. The inset in (b) shows the crystal field splitting of the lowest $J = 5/2$ multiplet of Ce^{3+} in a hexagonal crystal electric field (CEF), where $\psi_1 = |\pm \frac{5}{2}\rangle$, $\psi_2 = |\pm \frac{1}{2}\rangle$, and $\psi_3 = |\pm \frac{3}{2}\rangle$ are the three Kramer's doublets.

case where $|\frac{5}{2}, \pm \frac{1}{2}\rangle$ is taken as the first excited state gives a satisfactory result. The expressions for $\chi^\perp$ and $\chi^\parallel$ using $|\frac{5}{2}, \pm \frac{1}{2}\rangle$ as the first-excited state and $|\frac{5}{2}, \pm \frac{3}{2}\rangle$ as the highest state are as follows:

$$\chi^\perp = \frac{N_A g_J^2 \mu_B^2}{Z k_B} \left[\frac{9}{2} \frac{e^{-\beta E_1}}{T} + 5 \left(\frac{1 - e^{-\beta E_2}}{E_2} \right) + 8 \frac{(e^{-\beta E_2} - e^{-\beta E_1})}{(E_1 - E_2)} \right], \quad (4)$$

$$\chi^\parallel = \frac{N_A g_J^2 \mu_B^2}{2Z k_B} \left[\frac{25 + e^{-\beta E_1} + 9e^{-\beta E_2}}{T} \right]. \quad (5)$$

where $Z = 2(1 + e^{-\beta E_1} + e^{-\beta E_2})$, and E_1 and E_2 are the energy eigenvalues measured with respect to the ground state doublet. The inverse of expressions (4) and (5) are fitted to the experimental $\chi^{-1}(T)$. Fig. 5.8(a) and Fig. 5.8(b) show the fitting results for $E_1 = 61$ K and $E_2 = 218$ K. The CEF splitting scheme is shown in the inset of Fig. 5.8(b), where $\Psi_1 = |5/2, \pm 5/2\rangle$, $\Psi_2 = |5/2, \pm 1/2\rangle$, and $\Psi_3 = |5/2, \pm 3/2\rangle$. These values are in good agreement with Schaack et al., who predicted these splittings to be 47 cm^{-1} (~ 68 K) and 116 cm^{-1} (~ 167 K) using magneto-Raman spectroscopy [165].

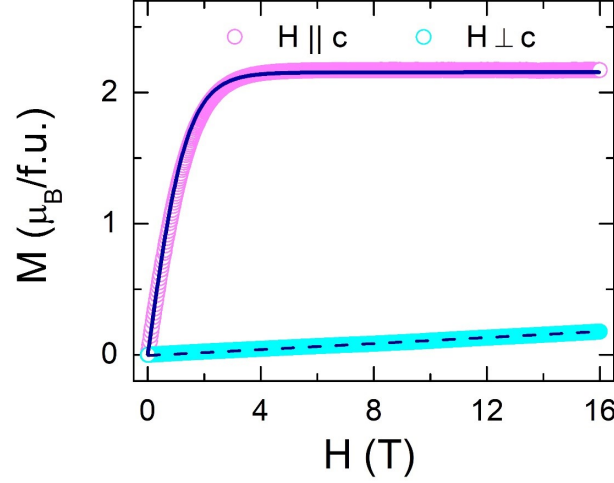


Figure 5.9: The isothermal magnetization $M(H)$ at 2 K for the orientations $H \perp c$ and $H \parallel c$. The solid line is a fit to the data. The dashed line is a guide to the eye (see text for details).

5.3.5 Isothermal magnetization

Isothermal magnetization, $M(H)$, plots at 2 K for both orientations ($H \perp c$ and $H \parallel c$) are shown in Fig. 5.9. A large anisotropy is observed between the orientations. Along the perpendicular orientation, the magnetization is small and linear up to 160 kOe. On the other hand, when the field is applied parallel to the c -axis, $M(H)$ tends to saturate above a relatively small field of 20 kOe. A saturation magnetization value of $M_s = 2.17 \mu_B/\text{f.u.}$ is close to the saturation moment calculated theoretically, using $M_s = Jg_{\parallel}\mu_B \approx 2\mu_B$, with $J = \frac{1}{2}$ and $g_{\parallel} \approx 4$. The entire range of $M(H)$ data could be nicely fitted using the Brillouin function, as shown in Fig. 5.9.

5.3.6 Specific heat

The specific heat of CeCl_3 and LaCl_3 , the latter being the non-magnetic analogue of CeCl_3 , was measured between 250 K and 2 K, as shown in Fig. 5.10(a). The low-temperature data for LaCl_3 can be fitted using the equation: $C_p = \gamma T + \beta T^3$, where γ and β correspond to the electronic and lattice contributions, respectively. Since LaCl_3 is an insulator with an electronic band gap of 5.1 eV [156], the electronic term can be ignored. The data are replotted as C_p/T vs T^2 . The variation appears linear (inset in Fig. 5.10(a)). Performing a linear fit yields $\beta = \text{slope} = 5.68 \times 10^{-4} \text{ J mol}^{-1} \text{ K}^{-4}$. From this, we calculate the Debye temperature $\Theta_D = 239 \text{ K}$ using the formula: $\beta = \frac{12\pi^4 NR}{5\Theta_D^3}$, where R is

the universal gas constant. Note that this value of Θ_D is not the same as the one reported by Landau et al. ($\Theta_D = 155$ K) [?]. Upon examining their data, we found that the value of Θ_D obtained by them ignores the factor N (number of atoms per formula unit = 4). At high temperatures, the specific heat rises toward the Dulong-Petit value of $3NR \approx 100 \text{ J mol}^{-1} \text{ K}^{-1}$.

To extract the $4f$ contribution to the specific heat, we subtracted the lattice part, assuming LaCl_3 as the lattice template. Being isostructural to CeCl_3 and having a comparable molecular weight, LaCl_3 is the closest material to model the lattice specific heat of CeCl_3 . Fig. 5.10(c) shows the $4f$ electron contribution (C_{4f}) in zero-field above 2 K. The C_{4f} rises sharply above 2 K, showcasing a broad peak centered around 30 K. This is attributed to the Schottky anomaly associated with the crystal field-split Kramer's doublets. The C_{4f} is fitted using the three-level Schottky expression:

$$C_{\text{Schottky}} = R \frac{1}{T^2} \left\{ \frac{g_1 g_0 E_1^2 e^{-\beta E_1} + g_2 g_0 E_2^2 e^{-\beta E_2} + g_1 g_2 e^{-\beta(E_1+E_2)} [E_1(E_1 - E_2) + E_2(E_2 - E_1)]}{g_0 + g_1 e^{-\beta E_1} + g_2 e^{-\beta E_2}} \right\},$$

where E_1 and E_2 are the energies of the first and second excited doublets above the ground state, and $g_0 = g_1 = g_2 = 2$ is the degeneracy of the states [170]. The best fit to the experimental data is obtained for $E_1 = 67$ K and $E_2 = 200$ K. These values are in close agreement with those obtained from the susceptibility analysis. While the position of the first excited state is in good agreement with previous reports, the energy of the higher-lying excited state is somewhat higher than the value of 167 K reported using magneto-Raman spectroscopy [18, 165].

Next, we discuss the field dependence of the low-temperature specific heat of our CeCl_3 crystal. The magnetic field-dependent measurements are summarized in Fig. 5.10(b). The in-field measurements ($H \parallel a$) are superimposed with the data from the previous study [18], where specific heat is reported only below 4.2 K and up to a maximum applied magnetic field of 14 kOe. Our zero-field data overlap nicely with the zero-field data in Ref. [18]. In zero-field, C_p shows an upturn below 1 K, which is precursory to the long-range ordering of the Ce moments at still lower temperatures, at $T_N \sim 0.11$ K [18]. The magnetic entropy below 2 K ($\approx R \ln 2$) corroborates the long-range ordering (vide infra). Due to the weak exchange coupling between the Ce moments, even a weak applied magnetic field has a strong effect on the specific heat peak, which broadens and shifts toward higher temperatures as the field strength increases, occurring near 2.5 K in an applied magnetic field of 30

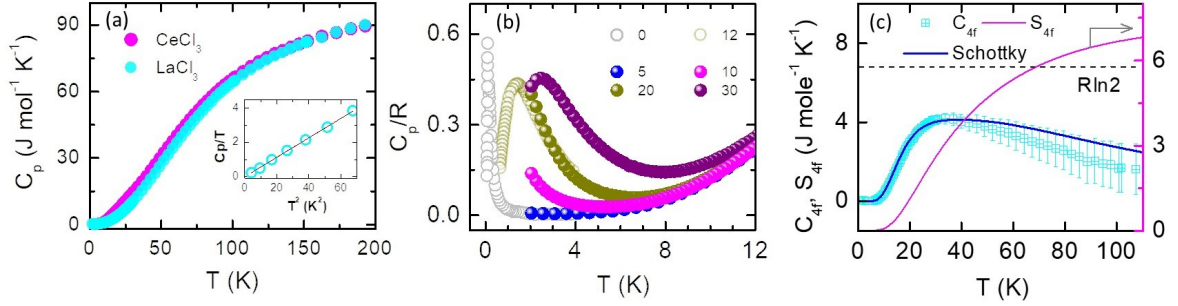


Figure 5.10: (a) The specific heat (C_p) of CeCl₃ and its non-magnetic analogue LaCl₃ plotted as a function of temperature. Inset shows C_p/T of LaCl₃ plotted against T^2 . The line through the data points is a linear fit to extract the Debye temperature (see text for details). (b) C_p/R , where R is the gas constant, plotted as a function of temperature for applied magnetic fields of $H = 5, 10, 20$, and 30 kOe. Low-temperature zero-field and 12 kOe plots are recreated using data from Landau et al. [18], where C_p is given in the range $T < 4.2$ K and $H < 14$ kOe. (c) C_{4f} and S_{4f} are plotted as a function of temperature. The solid line through the data points (C_{4f}) is a three-level Schottky fit using the crystal field splitting estimated from the magnetic susceptibility data (see text for details).

kOe.

Unfortunately, our attempts to measure the specific heat at higher fields were unsuccessful, as the crystal dislodged from the sample platform and shattered into pieces upon cooling below 4.5 K under a field of 50 kOe. This is due to the strong magnetic torque that acts on the specimen due to the huge anisotropy and large, but weakly interacting, magnetic moment ($\pm 5/2$) in the crystal field-split ground state. A slight discrepancy between the in-field data in our study and that taken from Ref. [18] (12 kOe data from Ref. [18] is close to our 20 kOe, indicating a small field offset) may arise from the actual value of the field and the crystal orientation.

We estimated the entropy associated with the $4f$ electrons, S_{4f} , above $T_0 = 2$ K, using the formula: $S_{4f} = \int_{T_0}^{T_1} \frac{C_{4f}}{T} dT$. As shown in Fig. 5.10(c), the recovered entropy exceeds the $R \ln 2$ value near 70 K and continues to rise up to the highest temperature in our measurements. This behavior requires a comment: First, we have not considered a large chunk of S_{4f} buried below 2 K, the range over which the Ce moments order magnetically. If we include the low-temperature specific heat data from previous literature [18], where data are reported between 0.05 K and 4 K, the resulting S_{4f} plot plateaus at $R \ln 2$ around 2 K, and this plateau stretches up to 10 K. Thus, the first excited state starts contributing to S_{4f} only around 10 K, the temperature above which C_{4f} in Fig. 5.10(c) rises sharply. As shown in the Fig. 5.11, the total S_{4f} (i.e., including the low-temperature contribution)

overshoots the value $R \ln 4$ near 70 K. Thus, S_{4f} crossing $R \ln 2$ near 70 K in Fig. 5.10(c) reflects the contribution from the excited states, excluding the $R \ln 2$ contribution from the ground state doublet.

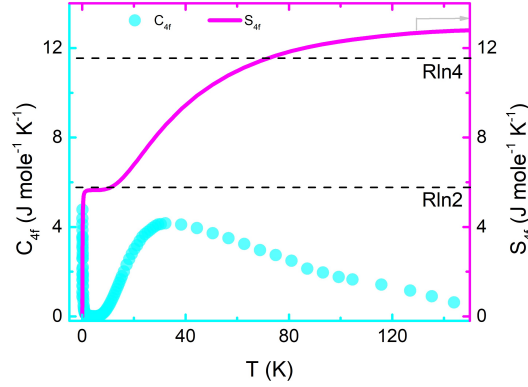


Figure 5.11: Contribution to specific heat and entropy due to $4f$ electrons. The C_{4f} clearly shows a two-peak feature; the low-temperature feature is attributed to the ordering of Ce^{3+} ions, and the broad peak centered around 30 K is due to the CEF splitting of the $J = \frac{5}{2}$ multiplet into three doublets. This is reflected in the entropy data (see main text for details). The data below 2 K is taken from P. Landau et al. [18].

5.3.7 Magnetocaloric effect

A very small exchange coupling between the Ce moments and a large moment in the crystal field split ground state of Ce are good indicators that CeCl_3 may show promising magnetocaloric properties. In order to estimate the magnetocaloric effect from the indirect method, the isothermal magnetization is plotted as a function of magnetic field for different temperatures to obtain the change in the magnetic entropy of the system when the sample is magnetized up to a maximum applied field of 6 T. The measurements were done with the applied field acting along the crystallographic c-axis. Fig. 5.12(a) shows the $M(H)$ isotherms at different temperatures from 2 K to 10 K with a temperature interval $\Delta T = 1$ K. For $\Delta H = 6$ T, the change in the magnetic entropy is plotted as a function of average temperature, as shown in Fig. 5.12(b). The maximum value $-\Delta S_m = 23 \pm 1 \text{ J Kg}^{-1} \text{ K}^{-1}$ occurs at 2.5 K for $\Delta H = 50 - 60 \text{ kOe}$. This is a reasonably high value, making CeCl_3 a potential magnetocaloric material as a cryogenic magnetic coolant. However, the highly hygroscopic nature of this material must also be taken into consideration, which may require the coolant material to be permanently sealed in a non-magnetic but highly electrically conducting capsule.

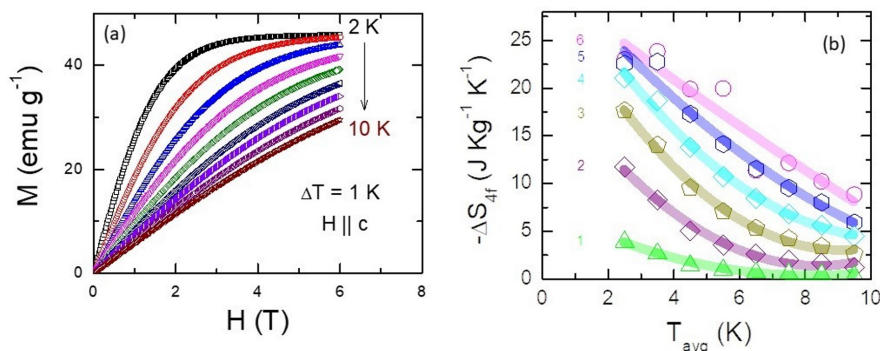


Figure 5.12: (a) Isothermal magnetization from $T = 2$ K to 10 K at $\Delta T = 1$ K interval. The field is applied parallel to the easy-axis (0 0 1) of magnetization. (b) The change in entropy as a measure of the magnetocaloric effect is plotted as a function of T_{avg} (see text for details).

In Table 5.6 below, we compare the $-\Delta S_m$ for a range of magnetocaloric materials with long-range ordering below 2 K. Among the known Ce-based compounds where magnetocaloric effects have been evaluated, CeCl_3 perhaps showcases the highest $-\Delta S_m$, which is in many cases comparable to the Gd-based compounds. This is not surprising given the high J value in the crystal field split ground state of CeCl_3 . Taking into consideration that the ordering temperature of CeCl_3 is an order of magnitude below our measurement temperature, an even higher level of $-\Delta S_m$ at lower fields is expected if the measurements are extended to lower temperatures.

5.4 Summary and conclusion

High-quality single crystals of CeCl_3 are grown using a modified Bridgman and Bridgman-Stockbarger method in an infrared image furnace. Using both methods, mm-sized single crystals were obtained. The crystals obtained using the Bridgman-Stockbarger method were bigger in size, fully transparent, and higher in yield compared to the crystals obtained using the static Bridgman technique.

The grown crystals were characterized using single-crystal X-ray diffraction, X-ray diffraction in Bragg-Brentano geometry, X-ray Laue diffraction, and powder X-ray diffraction techniques. While the overall structure is hexagonal, single-crystal X-ray diffraction shows very weak (0 0 1) superstructure reflections indicating a slight trigonal distortion. The crystals are highly sensitive to moisture and decompose within a few minutes to form white powder (hexahydrate).

The low-temperature thermal and magnetic properties of the grown crystals are studied between

Table 5.6: A comparison of $-\Delta S_m$ (maximum change in the magnetic entropy) for various previously studied potential cryogenic magnetic coolants at $T_{\min}$ (lowest temperature) and $H_{\max}$ (maximum magnetic fields).

Class of Material	Compound	$-\Delta S_{\max}$	T_N/T_C (K)	$T_{\min}$ (K)	$H_{\max}$ (kOe)	Ref.
RCl_3	CeCl_3	23.0	0.11	2.5	60	This work
Garnets	$\text{Gd}_3\text{Ga}_5\text{O}_{12}$ (GGG)	35.3	< 0.025	2	60	[171]
	$\text{Dy}_3\text{Ga}_5\text{O}_{12}$ (DGG)	14.5	0.37	2	60	[171]
	$\text{Tb}_3\text{Ga}_5\text{O}_{12}$ (TGG)	11.2	0.25	4	40	[171]
	$\text{Nd}_3\text{Ga}_5\text{O}_{12}$ (NGG)	16.0	0.52	1	50	[171]
R(OH)_3	Er(OH)_3	26.5	< 2	4	50	[172]
RF_3	GdF_3	67.1	< 2	2	50	[173]
	$\text{Cd}_{0.9}\text{Gd}_{0.1}\text{F}_{2.1}$	7.2	< 2	5	50	[174]
	$\text{Cd}_{0.9}\text{Tb}_{0.1}\text{F}_{2.1}$	2.7		5	50	[174]
	$\text{Cd}_{0.9}\text{Dy}_{0.1}\text{F}_{2.1}$	0.8		5	50	[174]
Pyrochlores	$\text{Gd}_2\text{Sn}_2\text{O}_7$	32.0	1	2	90	[175]
	$\text{Gd}_2\text{Ti}_2\text{O}_7$	17.9	< 2	2.5	50	[176]
Tripod Kagome	$\text{Gd}_3\text{Mg}_2\text{Sb}_3\text{O}_{14}$	33.0	1.7	2	90	[175]
Double Perovskite	$\text{Ba}_2\text{GdSbO}_6$	24.0	< 0.4	2	70	[177]

2 K and 300 K. The magnetic susceptibility is measured as a function of temperature for two different orientations: $H \parallel c$ and $H \perp c$, in addition to the polycrystalline sample. In $H \perp c$ measurements, a broad and prominent peak centered around 50 K is observed. The susceptibility in the $H \parallel c$ orientation, on the other hand, is not only two orders of magnitude larger but also shows a monotonic Curie-like increase upon cooling. We analyzed this behavior using the crystal field theory. The ground state J -manifold ($J = 5/2$) is shown to split into three Kramer's doublets. The eigenstates and energies of these doublets are found to be $|\psi_1\rangle = |5/2, \pm 5/2\rangle$ (the ground state), $|\psi_2\rangle = |5/2, \pm 1/2\rangle$ (the first excited state at $E_1 \approx 61$ K), and $|\psi_3\rangle = |5/2, \pm 1/2\rangle$ (the second excited doublet at $E_2 \approx 218$ K). Using these parameters, the susceptibility behavior along the two orientations is successfully described. The crystal field ground state of Ce^{3+} is nearly pure $|\pm 5/2\rangle$, wherein the large Ce moment is constrained to point along the c -axis, acting like an Ising system.

The specific heat is measured in the temperature range from 2 K to 300 K, with no anomalies seen at any temperature. The weak upturn at very low temperatures is attributed to short-range correlations between the Ce moments. The analysis of the 4f derived magnetic specific heat, showcasing a Schottky anomaly, is successfully done using the crystal field scheme obtained from the magnetic

susceptibility analysis.

With increasing applied magnetic field, the low-temperature upturn becomes more pronounced and shifts to higher temperatures, showcasing a peak above 2 K in fields as small as 25 kOe. The weak exchange between the Ce moments, the huge Ising-like anisotropy, and the large magnetic moment create ideal conditions for realizing a high magnetocaloric effect. Indeed, a maximum entropy change of $-\Delta S_m = 23 \pm 1 \text{ J kg}^{-1} \text{ K}^{-1}$ is found at 2.5 K in the field range 50-60 kOe, making CeCl_3 a potential magnetocaloric material for cryogenic applications as a magnetic coolant.

The Raman spectrum of CeCl_3 exhibits five Raman active modes at 106.8 cm^{-1} , 181.2 cm^{-1} , 189 cm^{-1} , 213 cm^{-1} , and 219.7 cm^{-1} . Future studies involving polarization, temperature, and magnetic field dependent Raman spectroscopy are needed to understand the evolution of Raman modes and the correlation between spin and lattice degrees of freedom.

Chapter 6

Evidence of charge-phonon coupling in the paramagnetic state of quasi two-dimensional van der Waals antiferromagnet $\text{Ni}_{1-x}\text{Zn}_x\text{PS}_3$

The work described in this chapter is published in the IOP journal, 2D Materials with the title of " Probing electron-phonon coupling in magnetic van der Waals material NiPS_3 : A non-magnetic site-dilution study"

A part of this work which describes in detail the crystal growth of the solid solution of $\text{Ni}_{1-x}\text{Zn}_x\text{PS}_3$ and the first evidence of Fano resonance in the parent NiPS_3 is published as a conference proceedings in New Physics: Sae Mulli under the title of "Single Crystal Growth and Properties of 2D antiferromagnet $\text{Ni}_{1-x}\text{Zn}_x\text{PS}_3$."

- *The low-temperature Raman measurement were done at IISER Bhopal by Devesh Negi under the supervision of Dr. Surajit Saha*

6.1 Introduction

Two-dimensional (2D) Van der Waals materials have attracted enormous attention in recent years. While most two-dimensional Van der Waals materials are non-magnetic, the inclusion of magnetic degrees of freedom gives rise to intriguing magnetic phases unique to the 2D world. Recent breakthroughs in detecting long-range magnetic ordering in 2D magnetic materials down to atomically thin limits, as demonstrated in the case of FePS_3 [35], CrI_3 [38] and $\text{Cr}_2\text{Ge}_2\text{Te}_6$ [39] have opened up new and remarkable possibilities for probing and manipulating the magnetic properties of these materials.

The transition metal chalcogen phosphates MPX_3 where $M = \text{Ni}, \text{Fe}, \text{Mn}, \text{Co}, \text{or Zn}$, and $X = \text{S or Se}$ are interesting magnetic Van der Waals materials with magnetic M atoms residing on a honeycomb lattice [178–181]. While all known MPX_3 compounds undergo some form of long-range antiferromagnetic ordering at low temperatures, the exact nature of the magnetic ground state depends on the choice of the transition metal ion, ranging from an Ising-type antiferromagnetic in FePS_3 [182], XY or XXZ-type antiferromagnetic in NiPS_3 [183], and nearly Heisenberg-type antiferromagnetic in MnPS_3 [184]. The Neel temperature (T_N) varies with the transition metal ion as: 78 K (MnPS_3) [185], 118 K (FePS_3) [186], 122 K (CoPS_3) [187], and 155 K (NiPS_3) [183]. The choice of transition metal ion also gives rise to a tunable electronic structure with widely ranging band gaps varying from 1.5 eV (FePS_3) to 3.5 eV (ZnPS_3) [188]. The recent studies unveiled emergence of interesting phenomena, including insulator-to-metal transition in CoPS_3 [189], MnPS_3 , NiPS_3 [190], FePS_3 [191], and $\text{V}_{0.9}\text{PS}_3$ [192], and superconductivity in FePSe_3 [193]. Recently, it has been shown that the intercalation of guest atoms between the layers can provide additional tunability parameter for the magnetic properties. For example, in NiPS_3 , Li-ion intercalation results in the emergence of ferrimagnetism at low temperature [194]. For a review of the progress on the synthesis and properties of MPX_3 -type materials under various perturbations, the readers are directed to the recent review paper by Dedkov et al. [195].

Here, we focus on NiPS_3 . Analogous to the other members of the MPX_3 family, NiPS_3 has a layered crystal structure with weak van der Waals bonding between the adjacent layers stacked along the c -direction, normal to the ab -plane, as shown in Fig. 6.1(a). In each layer, the Ni^{2+} ions form a honeycomb network. The P and S atoms bond covalently to form $[\text{P}_2\text{S}_6]^{4-}$ anionic units. These units sit at the center of the hexagon formed by Ni with their P-P bond aligned perpendicular to the

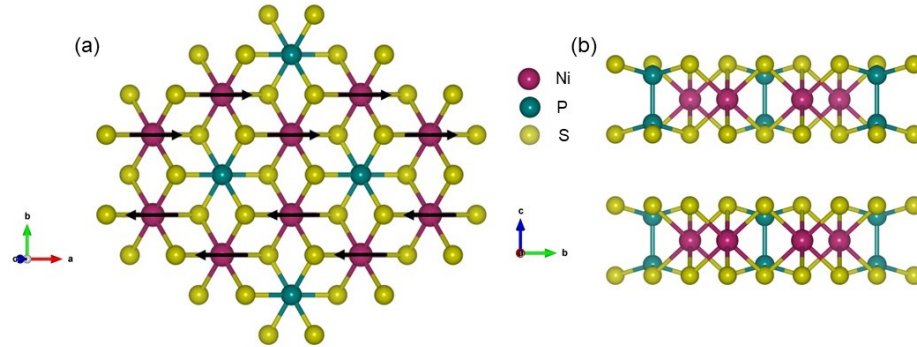


Figure 6.1: The schematic representation of the crystal structure is shown, where the pink, green, and yellow spheres represent Ni, P, and S atoms, respectively. In Fig. 6.1(a), the structure is viewed along the c^* -axis, perpendicular to the ab -plane, highlighting the van der Waals layers with Ni atoms forming a distorted honeycomb lattice. The black arrows indicate the alignment of Ni spins in this configuration. In Fig. 6.1(b), the structure is viewed along the a -axis, illustrating the layered nature of NiPS_3 . Within each layer, the P-P dimer bonds with six S atoms to form the $[\text{P}_2\text{S}_6]^{4-}$ anionic unit.

honeycomb plane of Ni, as shown in Fig. 6.1(b). This way, each Ni atom is surrounded by six S atoms in a trigonally distorted octahedral coordination (Fig. 6.1(b)). In the ordered phase below $T_N = 155$ K [183], the Ni spins, confined to the ab -plane with slight out-of-plane canting, form a zigzag anti-ferromagnetic pattern where ferromagnetic zigzag chains running parallel to the a -axis couple anti-ferromagnetically along the b -axis so that the spin direction rotates by 180° between the alternating chains [196], as shown in Fig. 6.1(a). Recently, it has been shown that NiPS_3 is a ‘self-doped’ negative charge transfer (NCT) insulator where the p orbitals of S display a strong hole-like character due to negative charge transfer energy. The Ni d orbitals accordingly form a linear combination of d^8 , $d^9\bar{L}$, and $d^{10}\bar{L}^2$ configurations, where $\bar{L}$ refers to a ligand (S) hole. The NCT state in NiPS_3 has been experimentally verified using x-ray absorption and photoemission experiments [197, 198].

Intriguingly, below T_N the photoluminescence (PL) spectra of NiPS_3 exhibits a sharp, spin-orbit entangled excitonic peak around 1.47 eV [199]. This peak becomes exceedingly sharp (FWFM = 0.4 meV) upon cooling below a temperature $T_{\text{coh}} = 50$ K [200]. Since the bandgap of NiPS_3 (=1.6 eV) [188] is larger than the energy of the PL peak, the resolution limited FWHM below T_{coh} is unusual and has been attributed to the coherent excitonic emission due to Zhang-Rice (ZR) triplet to singlet transition [200]. The NCT phenomenon or occurrence of S-defects are also used in the literature as alternative mechanisms to explain the ultra-sharp PL peak [199, 201]. This PL peak is also shown to disappear in the monolayer limit, which coincides with the vanishing of the long-

range antiferromagnetic ordering for a monolayer NiPS_3 . This observation has been used to suggest a correlation between the magnetic ordering and the appearance of the PL peak [199].

Recently, Raman spectroscopy has emerged as a powerful tool to investigate two-dimensional (2D) antiferromagnetic Van der Waals materials, particularly in the few-layers and monolayer limit where conventional techniques for bulk samples are not sensitive enough to detect the signature of magnetic long-range ordering due to the small sample mass [202–205]. In NiPS_3 , temperature and polarization-dependent Raman spectroscopy down to the monolayer limit revealed some intriguing features [75]. Firstly, a broad peak is observed in the Raman spectra centered around 550 cm^{-1} , attributed to two-magnon scattering. This peak is particularly pronounced in the ordered state at low temperatures ($T \lesssim T_N$). Secondly, one of the Raman-active modes at 561 cm^{-1} (P_9), which lies in the same energy range as the two-magnon peak, exhibits a prominent Breit-Wigner-Fano (BWF) line shape upon cooling below T_N , due to quantum interference between the P_9 phonon mode and the two-magnon continuum [75].

Equally intriguing, another Raman mode at 176 cm^{-1} (P_2) splits in the parallel- and cross-polarization geometries when the sample is cooled below T_N , whereas the splitting disappears above T_N . P_2 is a composite mode comprising two degenerate phonon modes of symmetry A_g and B_g . Both modes involve the vibration of Ni ions, but with a distinction: in the A_g mode, the displacement is perpendicular to the ordered moment, while in the B_g mode, it is parallel; this distinction disappears in the paramagnetic phase. Using these two features; the splitting of the P_2 phonon mode and the Fano resonance of the P_9 mode, both appearing below T_N , it was shown that antiferromagnetic ordering in NiPS_3 persists down to two layers with an almost unsuppressed T_N , before vanishing completely in the monolayer limit. However, persistent spin fluctuations were observed in monolayer NiPS_3 , as expected in the XY spin model. These observations, along with the optical conductivity study in Ref. [197], suggest the presence of strong spin-phonon and spin-charge coupling in NiPS_3 . Recently, using angle-resolved polarized Raman spectroscopy, Muhammad et al. [206] showed evidence of two anisotropic magnon modes below the ordering temperature: one centered at 179.03 cm^{-1} (M_1) and the other at 197.3 cm^{-1} (M_2). The magnon mode M_1 couples to the B_g phonon mode at 181.4 cm^{-1} and is observed in both parallel and cross-polarization (XY), whereas the second magnon mode M_2 is observed only in parallel (XX) polarization. The B_g phonon mode to which the magnon M_1 is coupled is the same as the P_2 phonon mode discussed above. In this work, we present a systematic study

of site-diluted $\text{Ni}_{1-x}\text{Zn}_x\text{PS}_3$ ($0 \leq x \leq 0.2$). The investigations are carried out on high-quality single crystals using temperature-dependent specific heat and Raman spectroscopy probes. More specifically, we carefully probe the behavior of the P_2 mode near 176 cm^{-1} as a function of temperature and Zn doping (x). We show that P_2 exhibits a Fano-like asymmetry in the paramagnetic phase above $T_N(x)$ due to its coupling with a broad electronic continuum. This continuum disappears in the magnetically ordered phase, making P_2 symmetric (Lorentzian) at low temperatures. We demonstrate that the value of the coupling coefficient increases with Zn doping. Therefore, we propose the existence of strong electron-phonon coupling in the paramagnetic phase of NiPS_3 .

6.2 Experimental methods

6.2.1 Crystal growth

High-quality single crystals of $\text{Ni}_{1-x}\text{Zn}_x\text{PS}_3$ were grown using the physical vapor transport technique. The starting materials were high purity elemental powders: Nickel (Sigma Aldrich 99.99% trace metal basis), Zinc (Sigma Aldrich 99%), Phosphorus (Sigma Aldrich 99.99%), and Sulfur (Sigma Aldrich 99.98% trace metal basis). The growth experiments were carried out in a sealed silica ampoule. All the room-temperature processes were conducted in an argon-filled glove box (O_2 and H_2O contents less than 0.1 ppm). More details concerning the crystal growth parameters can be seen in Ref. [19, 162]. The shiny black crystals thus obtained exhibit a hexagonal shape with lateral dimensions ranging up to 1 cm and thickness $\leq 0.5 \text{ mm}$, as shown in the insets of Fig. 6.2(a,b). The crystals showed a tendency to exfoliate rather easily.

6.2.2 Experimental techniques

The morphology and chemical composition of the crystals were verified using a field-emission scanning electron microscope (Zeiss Ultra Plus) equipped with Energy Dispersive X-ray (EDX) (Oxford Instruments) analysis, respectively as described in 2.2.4. The phase purity of the grown crystals was checked using powder X-ray diffraction (Bruker D8 Advance diffractometer)(see 2.2.1 for further details). For obtaining the powders, small crystal specimens were ground in an agate mortar-pestle. For an accurate determination of the lattice parameters, high-purity silicon was added as an internal standard.

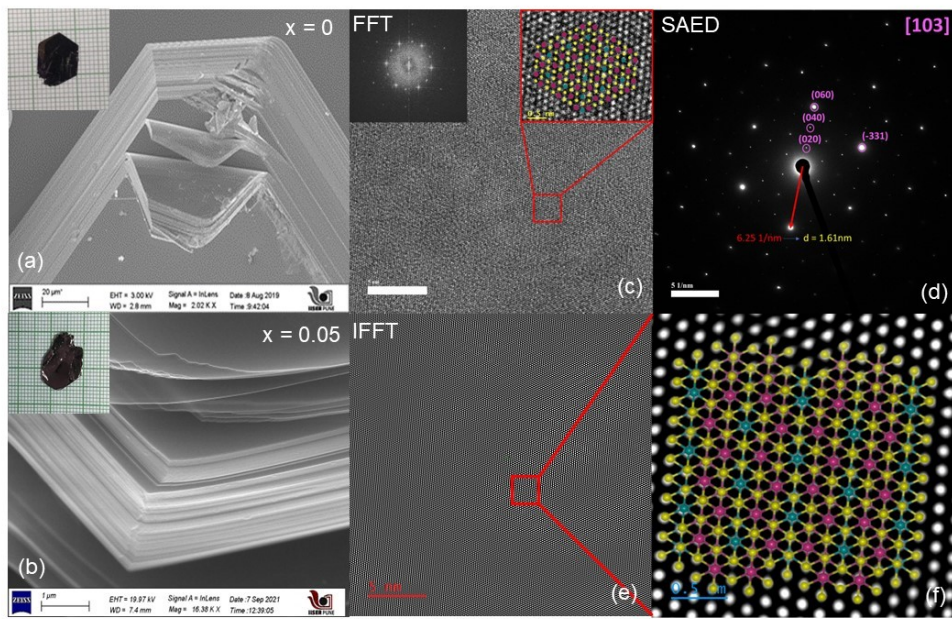


Figure 6.2: (a, b) A few representative FESEM images for $\text{Ni}_{1-x}\text{Zn}_x\text{PS}_3$. The EDX composition (x) of Zn is given at the top right corner. Inset shows representative images of the respective crystals. (c) High-Resolution TEM micrograph for NiPS_3 . Insets (left) show the corresponding FFT pattern; the arrangement of Ni (Pink), P (Green), and S (yellow) atoms (right) is also shown in the right inset where a magnified view is shown. (d) SAED pattern for NiPS_3 . (e) The IFFT pattern of the HRTEM image in (c). (f) IFFT pattern with Ni, P, and S atoms are also shown perpendicular to the [1 0 3] direction.

The quality of the grown crystals was assessed using high-resolution Transmission Electron Microscopy (HRTEM). The high-resolution TEM micrographs and corresponding Selected Area Electron Diffraction (SAED) patterns were collected using JEOL JEM 2200FS 200 keV TEM. For TEM sample preparation, the crystal specimens were sonicated in a cyclohexane bath and a small portion of the dispersed solution was drop-casted on a carbon-coated copper grid that was dried under vacuum for 3–4 h. The analysis of HRTEM images and SAED patterns was done using the GSM-3 package. Further details of TEM instrument is described in as described in 2.2.5

Raman spectra were collected on thin single crystal specimens in the backscattering configuration with incident laser light perpendicular to the crystalline ab-plane. The Horiba Jobin-Yvon LabRAM HR spectrometer, equipped with a liquid nitrogen cooled Charge-Coupled Device (CCD) and a 633 nm laser as a source of excitation, was used as described in 2.2.6. The excitation was maintained at 25% of the maximum power. The data acquisition time for each spectrum was 30 s with 15 iterations to get better resolution and intensity of the Raman modes. These parameters were kept constant across all samples for better comparison. The temperature-dependent Raman measurements between 80 K and 400 K were performed using a Linkam stage (Model No. HFS600EPB4) coupled with the LabRAM HR Evolution Raman spectrometer, attached to a Peltier-cooled CCD detector. The microscope was fitted with a 50X objective (Numerical Aperture = 0.5). The temperature-dependent measurements were carried out using laser excitation of 532 nm at 1 mW power. Raman spectra were acquired in both parallel and cross-polarization configurations at each temperature.

The specific heat was measured using a Physical Property Measurement System (PPMS), Quantum Design, USA. A crystal measuring 2 mm by 2 mm, cut from a larger crystal specimen, was mounted on the heat capacity sample holder using low-temperature Apiezon N grease. The heat capacity of the N grease was measured as an addenda correction prior to loading the crystal specimen.

6.3 Results and discussion

6.3.1 Structural analysis

The layered morphology of the grown crystals is clearly visible in the in-lens images shown in Fig. 6.2(a, b). The EDX composition was obtained by taking area scans at multiple regions on the crystal surface. The chemical homogeneity was verified using the elemental chemical mapping (see

Fig. 6.3).

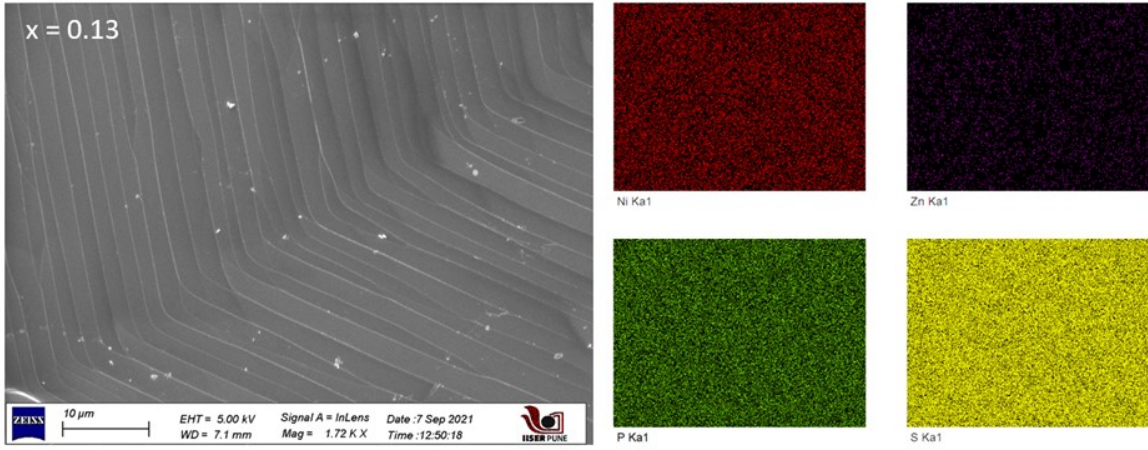


Figure 6.3: FESEM-images of single crystals of $\text{Ni}_{1-x}\text{Zn}_x\text{PS}_3$ ($x = 0.13$) investigated using in - Lense detector exhibiting layered structure.

Table 6.1: The Nominal and EDX composition of the grown $\text{Ni}_{1-x}\text{Zn}_x\text{PS}_3$ single crystals

Nominal composition	EDX composition	T_N (K)
NiPS_3	NiPS_3	154
$\text{Ni}_{0.99}\text{Zn}_{0.01}\text{PS}_3$	$\text{Ni}_{0.99}\text{Zn}_{0.01}\text{PS}_3$	-
$\text{Ni}_{0.98}\text{Zn}_{0.02}\text{PS}_3$	$\text{Ni}_{0.97}\text{Zn}_{0.03}\text{PS}_3$	
$\text{Ni}_{0.97}\text{Zn}_{0.03}\text{PS}_3$	$\text{Ni}_{0.95}\text{Zn}_{0.05}\text{PS}_3$	143
$\text{Ni}_{0.90}\text{Zn}_{0.10}\text{PS}_3$	$\text{Ni}_{0.92}\text{Zn}_{0.08}\text{PS}_3$	135
$\text{Ni}_{0.85}\text{Zn}_{0.15}\text{PS}_3$	$\text{Ni}_{0.87}\text{Zn}_{0.13}\text{PS}_3$	119
$\text{Ni}_{0.80}\text{Zn}_{0.20}\text{PS}_3$	$\text{Ni}_{0.86}\text{Zn}_{0.14}\text{PS}_3$	117

The nominal and EDX compositions for our crystals are shown in Table 6.1. The actual Zn composition is found to be somewhat less than the nominal composition. This is particularly evident in samples with higher Zn doping. All through the manuscript, the EDX composition has been used for both analysis and discussion. The presence of preferred orientation is clearly reflected in the powder pattern, where strong reflection due to preferred (00l) orientation can be seen in Fig. 6.4 (a). This is due to the platelet-like morphology of the grown crystals. The variation of lattice parameters with Zn doping concentration is shown in Fig. 6.4 (b).

The lattice parameters show a monotonic increase consistent with the larger ionic radius of Zn^{2+} (0.74 Å) compared to Ni^{2+} (0.69 Å). The details of crystal growth and structural analysis are recently

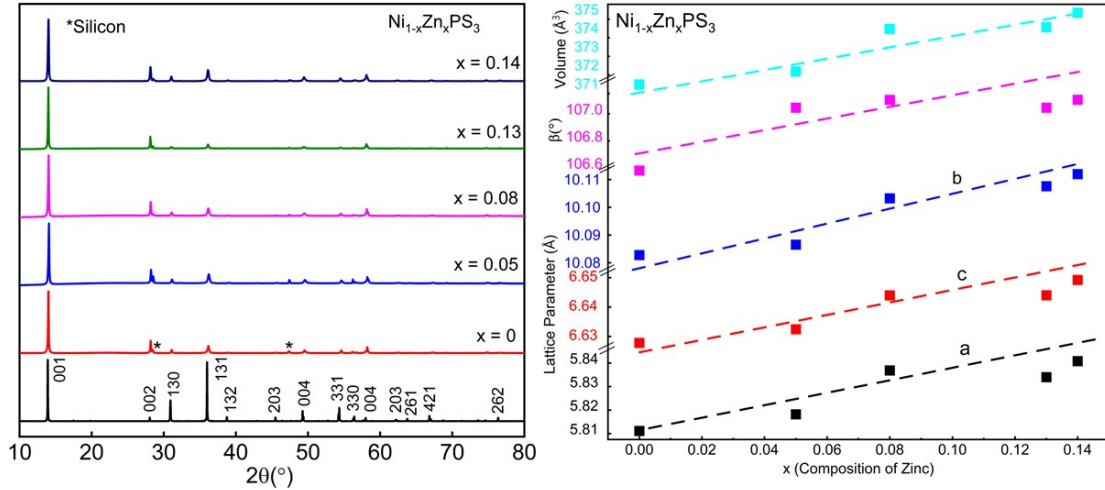


Figure 6.4: (a) Powder X-ray diffraction pattern for different Zn composition using Si as a standard to estimate accurate lattice parameter. (b) Trend in lattice parameter with x (Zn composition) [19].

published in [19]. Fig. 6.2(c) shows a representative high-resolution TEM image of a NiPS_3 crystal. The micrograph confirms the hexagonal arrangement of elements mapped in the inset, and in the corresponding FFT pattern. Fig. 6.2(d) shows the corresponding SAED pattern perpendicular to the ab -plane (along c^*). The sharp diffraction spots confirm the high quality of our single crystals. Fig. 6.2(e) shows the IFFT of the micrograph in Fig. 6.2(c). To index the SAED pattern, we used the general formula for the angle between the two $(h\ k\ l)$ indices in a monoclinic system. This is confirmed by measuring the angle (60°) between the diffraction spots $(0\ 6\ 0)$ and $(-3\ 3\ 1)$. As discussed in earlier reports on FePS_3 [207] and $\text{Fe}_{2-x}\text{Co}_x\text{P}_2\text{S}_6$ [208], these materials exhibit a pseudo threefold rotational symmetry by the formation of a rotational twin structure along the $[1\ 0\ 3]$ direction in the monoclinic system; a similar three-fold symmetry is evident from the SAED pattern in our crystal.

6.3.2 Specific heat

The specific heat (C_P) of our $\text{Ni}_{1-x}\text{Zn}_x\text{PS}_3$ crystals is shown in Fig. 6.5(a). In NiPS_3 , the specific heat exhibits a sharp anomaly near 155 K due to the onset of antiferromagnetic ordering of Ni spins, in agreement with the previous reports [209]. Due to non-magnetic Zn doping at the Ni site, the

antiferromagnetic ordering temperature (T_N) decreases, as shown in Fig. 6.5(b). The monotonic suppression of T_N with increasing Zn doping further confirms that Zn^{2+} is incorporated into the structure at the Ni^{2+} site. The decreasing behavior of T_N is consistent with the dilution effect, with the rate of decrease of T_N in very good agreement with the mean-field theory for spin 1 on a honeycomb lattice [20].

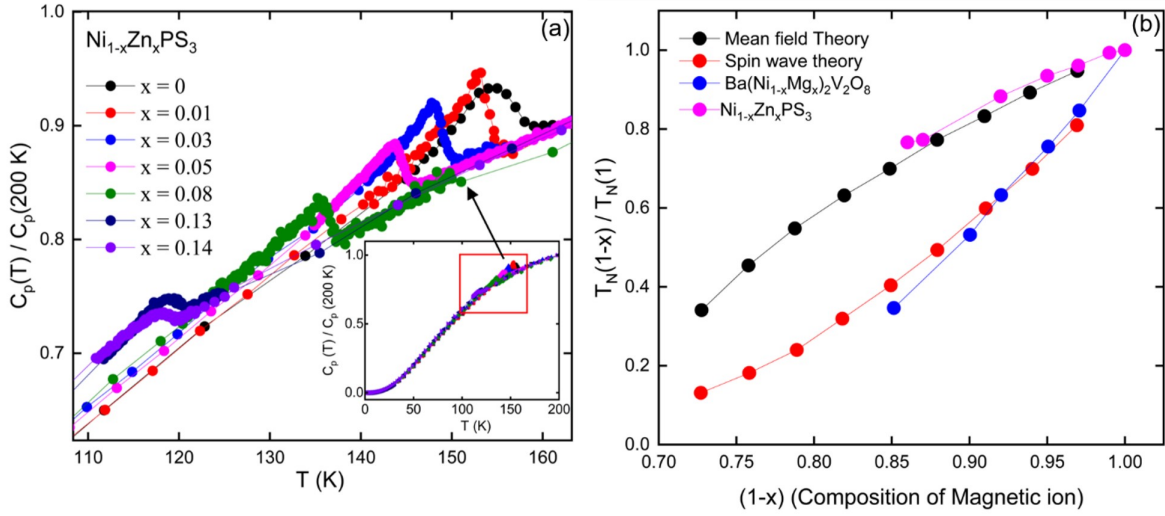


Figure 6.5: (a) The temperature variation of specific heat (C_p) of $\text{Ni}_{1-x}\text{Zn}_x\text{PS}_3$ crystals around $T_N(x)$. For each sample, the C_p normalized with respect to its value at 200 K is plotted. Inset shows the specific heat in the range 2 K to 200 K. (b) The plot of $T_N(1-x)/T_N(0)$ against $(1-x)$. The T_N suppression rate from the mean-field theory and spin-wave theory are also shown [20]. The variation of $T_N(1-x)/T_N(0)$ in the honeycomb lattice compound $\text{Ba}(\text{Ni}_{1-x}\text{Mg}_x)_2\text{V}_2\text{O}_8$ is also shown [21].

The departure from the quantum linear spin wave theory, which predicts a much steeper T_N suppression rate, is surprising and requires further attention. For comparison, the non-magnetic site-dilution due to Mg in the honeycomb lattice system $\text{Ba}(\text{Ni}_{1-x}\text{Mg}_x)_2\text{V}_2\text{O}_8$ from Ref. [21] is also shown. Interestingly, in this case, the T_N suppression follows the quantum linear spin wave theory. The departure in NiPS_3 can possibly arise from the fact that the Ni atoms form a distorted hexagonal lattice.

6.3.3 Raman spectroscopy

As shown by Kuo et al., the irreducible representations for zone-center phonon modes in NiPS_3 are $\Gamma = 8A_g + 7B_g + 6A_u + 9B_u$ [117]. Fig. 6.6(a) shows the room-temperature unpolarized Raman spectra of our NiPS_3 crystal. All the observed phonon modes are in good agreement with

those reported in previous studies [117, 210, 211]. We have labeled these modes as P_1 , P_2 , P_3 , etc., in order of increasing wavenumber in accordance with Ref. [75], and using the same peak labels as used there. The Raman modes at higher frequencies (above $\approx 200 \text{ cm}^{-1}$) are attributed to the intramolecular vibrations of the $(\text{P}_2\text{S}_6)^{4-}$ bipyramidal structure, whereas the low-frequency modes P_1 and P_2 are due to vibrations of Ni [75]. As shown in Ref. [210, 211], below T_N , the mode P_2 near 176 cm^{-1} appears at slightly different positions under different polarization configurations. This is related to the fact that P_2 is a composite mode, consisting of phonons with symmetries A_g and B_g . Both these modes involve vibration of Ni ions, but in the A_g mode the displacement of Ni is perpendicular to the direction of the ordered moment whereas in B_g it is parallel. This distinction, however, disappears in the paramagnetic phase, and the peak P_2 appears at the same position in either polarization configuration [75].

Unlike P_2 , which splits into two different modes below the ordering temperature, the mode near 133 cm^{-1} designated as P_1 remains almost degenerate in the entire investigated temperature range ($\Delta P_1 \approx 0.1346 \text{ cm}^{-1}$ at 80K and $\Delta P_1 \approx 0.3682 \text{ cm}^{-1}$ at 300 K), preserving the E_g symmetry even below the ordering temperature. On the other hand, the mode near 283 cm^{-1} designated as P_6 is non-degenerate within the examined temperature range, leading to a loss of E_g -like symmetry. The mode near 564 cm^{-1} (P_9), which exhibits Fano-like asymmetry, also remains degenerate in the investigated temperature range. The modes near 256 cm^{-1} (P_5) and 386 cm^{-1} (P_7) exhibit A_g symmetry. The experimentally observed modes and calculated phonon frequencies of different modes are shown in Ref. [75].

The splitting $\Delta P = P_2^{\parallel} - P_2^{\perp}$ has, therefore, been treated as an order-parameter which is non-zero only below T_N and grows analogously to the bulk magnetization for $T < T_N$. Hence, ΔP has been used as a probe to show that the magnetic ordering in NiPS_3 disappears in the monolayer limit [75]. Besides the point that $\Delta P \rightarrow 0$ for $T > T_N$, for the reasons discussed above, nothing else has been said or known about this mode in the paramagnetic phase in previous literature.

Upon careful examination of our 300 K Raman spectra, we found that P_2 exhibits a noticeable asymmetry. Attempts to fit P_2 using two Lorentzian line shapes did not yield satisfactory results (see, Fig. 6.7). This is further highlighted in Fig. 6.6(b, c, d, and e), where fittings with various lineshapes (Fano, Lorentzian, Gaussian, and Voigt) are shown. As is evident from these fits, the Breit-Wigner-Fano (BWF) lineshape gives the most satisfactory fit of all cases. The BWF lineshape is given by the

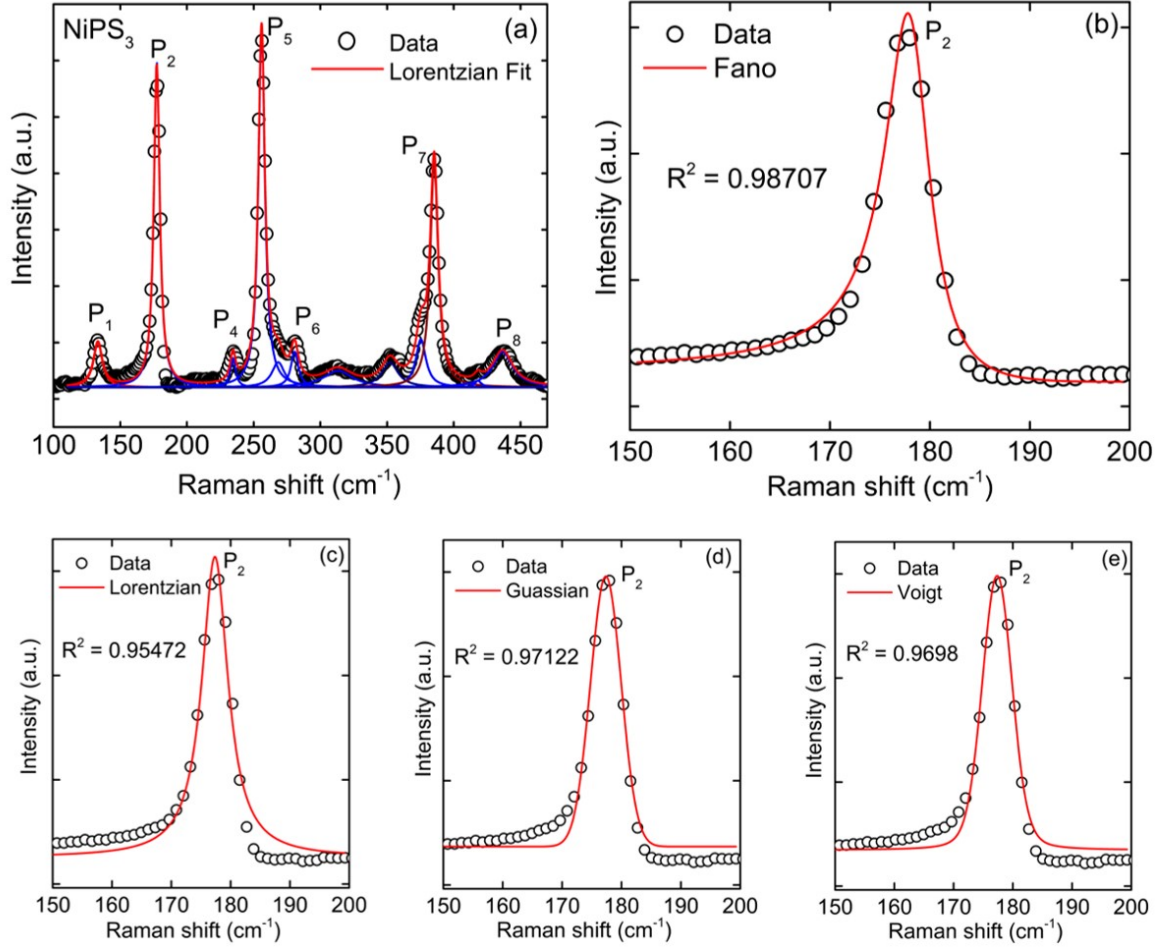


Figure 6.6: (a) Unpolarized room-temperature Raman spectra of NiPS_3 single crystal. The open circle represents the experimental data and the red solid line is the Lorentzian fit of the whole spectra. A zoomed-in view of the peak P_2 . (b) Fano (c) Lorentzian (d) Gaussian (e) Voigt. Fano shows the best fit with largest R-square value among all the line shapes.

expression [212,213]:

$$I(\omega) = I_0 \left[\frac{1 + 2(\omega - \omega_0)/(q\Gamma)}{1 + 4(\omega - \omega_0)^2/\Gamma^2} \right]^2 \quad (6.1)$$

where, I_0 is the peak intensity, $1/q$ is the coupling coefficient that describes the coupling of the discrete phonon mode in question with a continuum excitation, Γ is the linewidth, and ω_0 is the phonon frequency in the absence of the coupling.

The fit using the Fano lineshape is shown in Fig. 6.6(b). The dimensionless parameter q quantifies the degree of asymmetry in the line shape. As $1/q$ approaches zero, the Fano lineshape becomes Lorentzian, marking the disappearance of Fano resonance. In NiPS_3 , for the P_2 phonon in

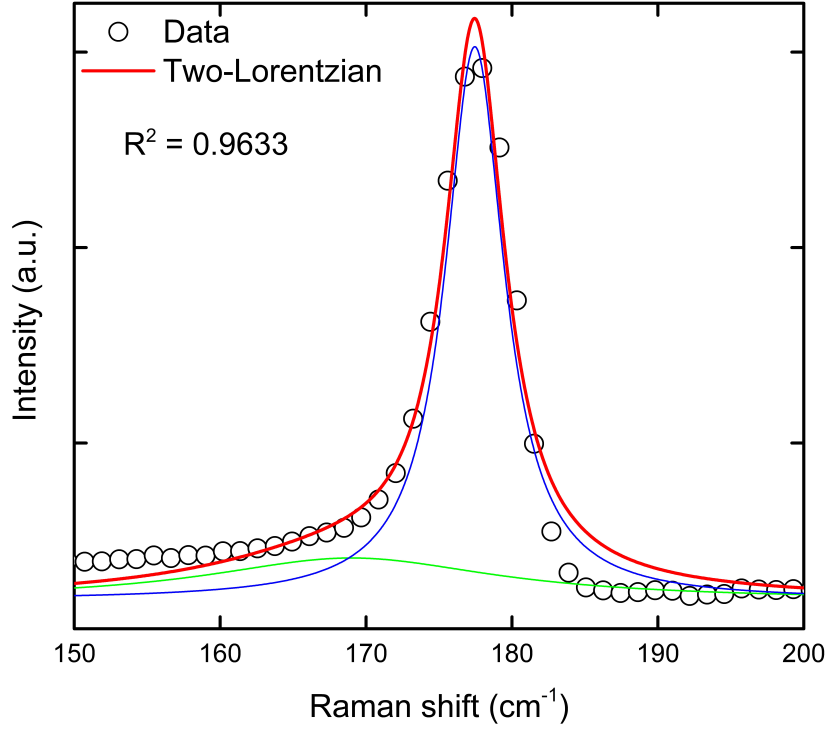


Figure 6.7: Fitting of Peak P_2 using two-lorentzian line shape

the unpolarized Raman spectra, the $|1/q|$ value at room temperature is 0.13, which is comparable to previously reported values for other well-investigated systems where Fano resonance has been reported, including (a) metallic carbon nanotubes ($|1/q|$: 0.04 to 0.10 depending on the diameter of the nanotube) [214], (b) $\text{LaMnO}_3 + \delta$ thin films ($|1/q|$: 0.2 to 0.4 depending on temperature and oxygen partial pressure during growth) [215], (c) Monolayer graphene ($|1/q|$: 0.07) [216], (d) $(\text{Ca/Sr})\text{Pd}_3\text{O}_4$ compounds ($|1/q|$: 0.07 to 0.2 depending on temperature) [217], and few-quintuple layers of topological insulator Bi_2Se_3 nanoplatelets ($|1/q|$: 0.047 to 0.084) [218].

In Fig. 6.8, we show a zoomed-in view of P_2 at 80 K and 300 K in the parallel ($\bar{z}xxz$) and cross ($\bar{z}xyz$) polarization. At 80 K, in both polarizations, the lineshape is symmetric and can be fitted satisfactorily using the Lorentzian lineshape. However, at 300 K, a clear characteristic Fano asymmetry, absent at 80 K, can be seen for both polarization configurations. Moreover, at 80 K, the positions $P_2^{\parallel} = 178.1 \text{ cm}^{-1}$ and $P_2^{\perp} = 180.2 \text{ cm}^{-1}$, giving $\Delta P = 2.1 \text{ cm}^{-1}$ in excellent agreement

with Ref. [75]. Not only are two peaks occurring at two distinct positions, their FWHMs also differ substantially with $FWHM^{\parallel} = 3.3 \text{ cm}^{-1}$, and $FWHM^{\perp} = 2.0 \text{ cm}^{-1}$, giving $\Delta FWHM = 1.3 \text{ cm}^{-1}$. On the other hand, at 300 K, the two configurations become degenerate with $P_2^{\parallel} = P_2^{\perp} = 176.0 \text{ cm}^{-1}$ and $FWHM^{\parallel} = FWHM^{\perp} \approx 3.4 \text{ cm}^{-1}$.

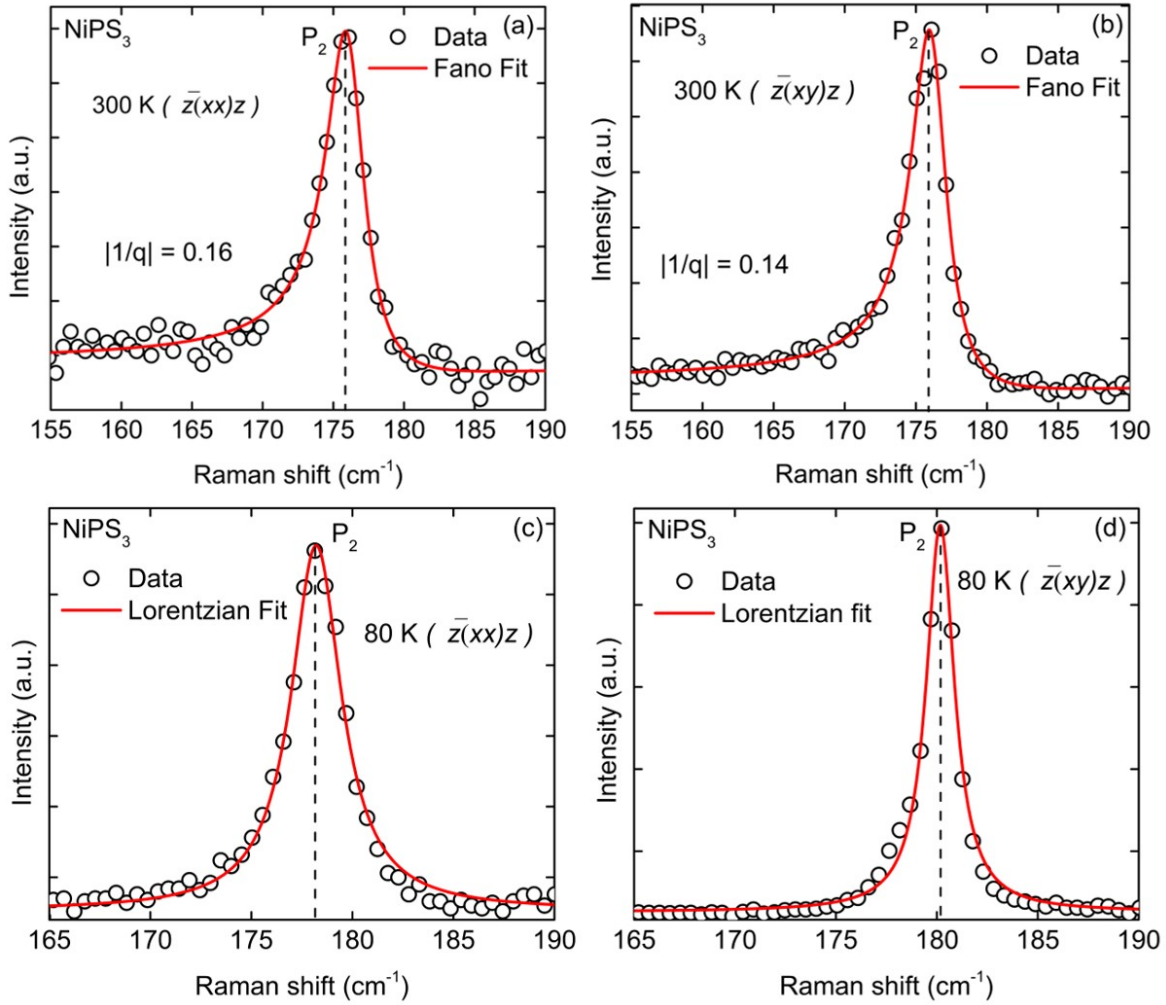


Figure 6.8: The Raman mode P_2 in a NiPS_3 single crystal was measured under two polarization configurations: parallel $[\bar{z}xx\bar{z}]$ and cross $[\bar{z}xy\bar{z}]$ at 80 K and 300 K. The measurements are presented as follows: (a) $[\bar{z}xx\bar{z}]$ at 300 K, (b) $[\bar{z}xy\bar{z}]$ at 300 K, (c) $[\bar{z}xx\bar{z}]$ at 80 K, and (d) $[\bar{z}xy\bar{z}]$ at 80 K.

In order to further probe the Fano asymmetry, Raman spectra were measured under cross-polarization $(\bar{z}xy\bar{z})$ configuration that suppresses the A_g type phonon modes and the quasi-elastic scattering (QES) contribution [75], as shown in Fig. 6.9(a). At 80 K, the most prominent feature is the presence of a

broad peak centered at $\sim 550 \text{ cm}^{-1}$. This peak is due to the two-magnon scattering. The phonon P_9 near 561 cm^{-1} exhibits a Fano lineshape below T_N in agreement with Ref. [75]. The Fano resonance of the P_9 phonon arises from its coupling with the two-magnon continuum, which has been established convincingly in the previous work [75]. Here, we focus on the mode P_2 , which we now know exhibits a Fano lineshape, but only at high temperatures. By fitting P_2 at various temperatures using the expression for the Fano lineshape in Eq. (7.1), we plot the temperature variation of parameter q in NiPS_3 in Fig. 6.9(b). The derivative dq/dT is also shown for clarity. We see that upon cooling the sample below T_N , q increases sharply, suggesting that the Fano resonance associated with P_2 vanishes at low temperatures in the magnetically ordered phase. The corresponding data for $\text{Ni}_{0.92}\text{Zn}_{0.08}\text{PS}_3$ ($x = 0.08$), for which T_N has reduced to 135 K (from 155 K for the pristine NiPS_3), is also shown in Fig. 6.9(b). In this case, a similar behavior is observed with Fano asymmetry disappearing below 135 K. The plot of q vs T for $\text{Ni}_{0.95}\text{Zn}_{0.05}\text{PS}_3$ and $\text{Ni}_{0.86}\text{Zn}_{0.14}\text{PS}_3$ is shown in Fig. 6.10(a,b). This supports the observation that the Fano resonance of P_2 in NiPS_3 disappears below T_N . This is contrary to the behavior of mode P_9 , where Fano resonance appears below T_N but weakens considerably at higher temperatures as the sample is warmed-up above T_N .

In order to understand the origin of the Fano resonance of P_2 in the paramagnetic phase, we notice that the broad continuum in the Raman spectra of NiPS_3 above T_N is best described by considering two broad peaks as shown in Fig. 6.9(a) using the orange and blue shades. The orange-shaded peak is the familiar two-magnon continuum, which is the only continuum that remains at low temperatures (for example, at 80 K it peaks around 550 cm^{-1} as shown previously in Ref. [75]). However, the spectra shown at 200 K and above necessarily require two broad peaks to be included in the fitting in order to get a satisfactory fit. As noted above, we reiterate that the quasi-elastic component is not significant in the cross-polarization at high temperatures for which the data is shown.

In fact, as shown in Fig. 6.9(a), at 80 K, a small QES signal can be seen in the form of a peak around 0 cm^{-1} ; however, the intensity of this signal suppresses rapidly and becomes insignificant upon warming. Thus, we can rule out QES as the origin of the second (blue shaded) continuum. We argue that the Fano lineshape of P_2 is a consequence of its destructive interference (antiresonance) with this continuum.

We now discuss the possible origin of the second continuum at high temperatures. From previous studies, we know that NiPS_3 is a 'self-doped' negative charge transfer (NCT) insulator [197].

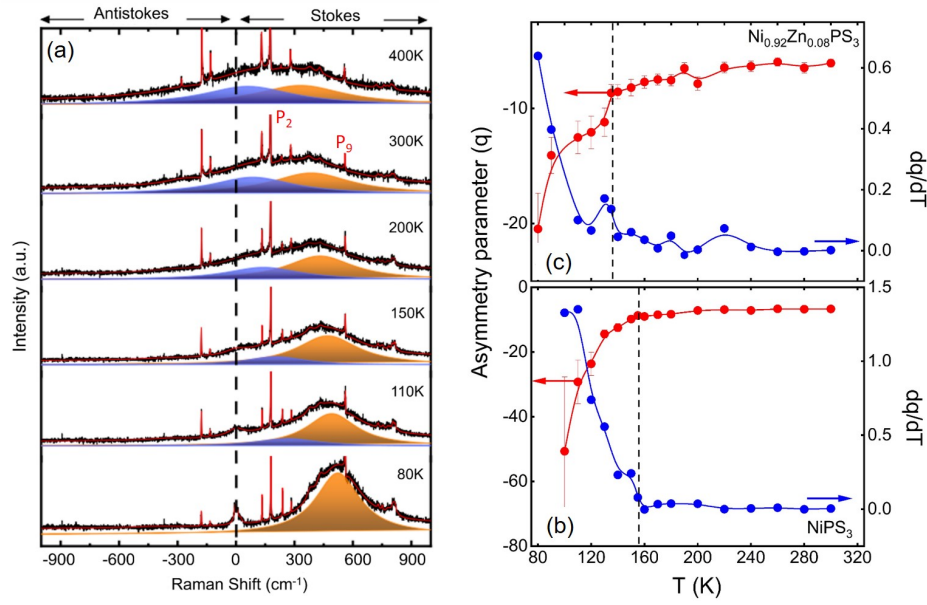


Figure 6.9: (a) Raman Spectra in the Stokes and Anti-Stokes region for NiPS_3 at various temperatures between 400 K and 80 K. The orange shaded region represents the two-magnon continuum and the blue shaded region represents the second continuum which appears at high temperatures. The red line through the data points is a fit to the data. The temperature variation of the asymmetry parameter (q) in (b) NiPS_3 and (c) $\text{Ni}_{0.92}\text{Zn}_{0.08}\text{PS}_3$. The derivative $\frac{dq}{dT}$ is also shown. The dashed line indicates the antiferromagnetic ordering temperature (T_N).

Therefore, the valence state of the Ni ion in NiPS_3 is a linear superposition of d^8 , $d^9\bar{L}$, and $d^{10}\bar{L}^2$ configurations, where $\bar{L}$ refers to a ligand hole [197]. We speculate that the second broad continuum at low wavenumbers is likely associated with the continuum of charge states formed by d^8 , $d^9\bar{L}$, and $d^{10}\bar{L}^2$ configurations. The discrete phonon mode P_2 , which lies in the same energy range, couples with the continuum of electronic states $\psi = \alpha d^8 + \beta d^9\bar{L} + \gamma d^{10}\bar{L}^2$, giving rise to the Fano resonance. To show this convincingly, one needs to establish the energy and symmetry equivalence of the continuum of electronic states ψ and phonon mode P_2 , which is beyond the scope of the present study. However, we indirectly corroborate this hypothesis using the experimental observations concerning the size of the coupling constant $|1/q|$ in the Zn-doped samples in the next paragraph.

The P_2 mode for all the different Zn-doped samples at 300 K is shown in Fig. 6.11. With increasing Zn, the mode P_2 undergoes a redshift; its intensity shows a monotonic decrease while the linewidth exhibits an increasing trend. The observed redshift is due to the higher ionic mass of Zn compared to Ni, and the increasing linewidth can be attributed to disorder caused by Zn doping.

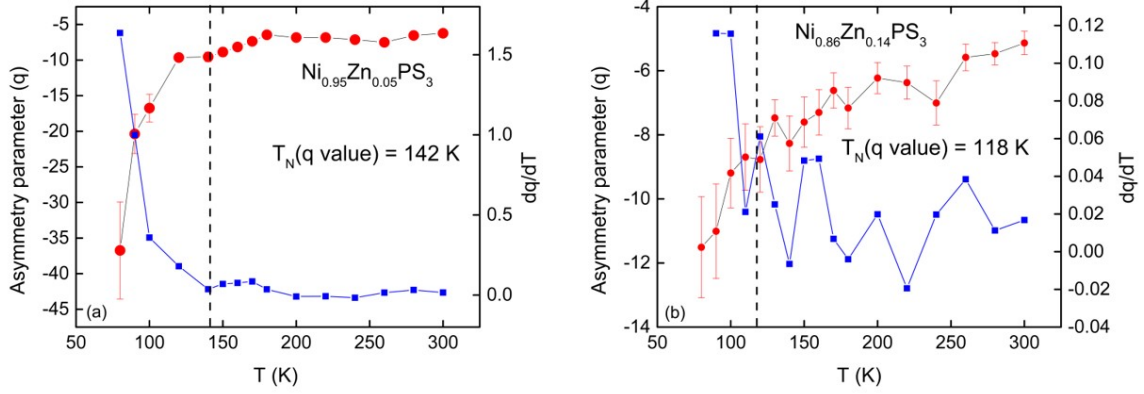


Figure 6.10: Temperature variation of asymmetry parameter for different Zn doping composition (a) $\text{Ni}_{0.95}\text{Zn}_{0.05}\text{PS}_3$ (b) $\text{Ni}_{0.86}\text{Zn}_{0.14}\text{PS}_3$.

The temperature variation of peak position ($\Delta\omega$) and linewidth (Γ) for mode P_2 is summarized in Fig. 6.12 for $\text{Ni}_{1-x}\text{Zn}_x\text{PS}_3$. The Fano line shape fits for different Zn concentrations are shown in Fig. 6.11. With the increase in Zn doping, the coefficient $|1/q|$, quantifying the peak asymmetry, increases monotonically with the doping concentration, as shown in the inset of Fig. 6.11. Since the laser wavelength in our experiments is fixed, the increase in the asymmetry cannot be attributed to the laser intensity [219].

To explain this increasing trend, we propose a mechanism, illustrated as a cartoon in Fig. 6.13. In the crystal structure of NiPS_3 , each sulfur is bonded to two neighboring Ni ions, as shown in Fig. 6.13(a). The negative charge transfer from S to Ni therefore occurs over two possible pathways indicated by the black arrows in Fig. 6.13(a). On the other hand, when Zn occupies one of the two Ni sites, the average number of Ni ions bonded to the central S will be less than 2. Since the d orbitals of Zn are fully occupied (d^{10}), the bridging S now has only one Ni site available to transfer the same quantity of electronic charge as before, as depicted in Fig. 6.13(b). Thus, in the presence of Zn doping, the average negative charge transferred to Ni should increase, resulting in enhanced weights of the $d^9\bar{L}$ and $d^{10}\bar{L}^2$ components, which in turn should enhance the electron-phonon coupling further.

To verify this scenario (that the weights of $d^9\bar{L}/d^{10}\bar{L}^2$ components increase), we carried out XPS on NiPS_3 and $\text{Ni}_{0.92}\text{Zn}_{0.08}\text{PS}_3$. The 2p core-level XPS spectra for the two samples are shown in Fig. 6.14. The XPS spectrum of NiPS_3 consists of three peaks positioned at binding energies (BE) 855 eV (M1), 860 eV (M2), and 865.6 eV (M3). The presence of these three peaks is a signature of

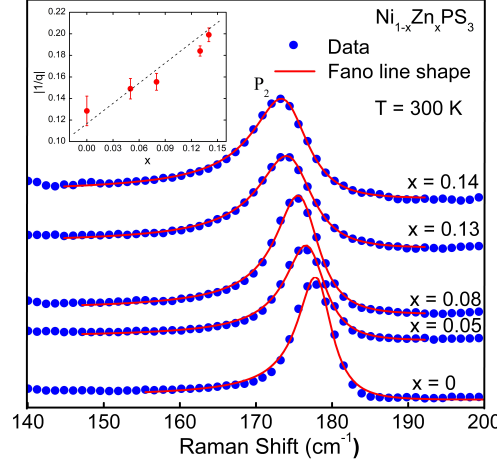


Figure 6.11: The Raman mode P_2 in $\text{Ni}_{1-x}\text{Zn}_x\text{PS}_3$ crystals at 300 K for $x = 0, 0.05, 0.08, 0.13$, and 0.14 . The inset shows the variation of the coupling coefficient $\left| \frac{1}{q} \right|$ as a function of x .

the NCT state with d^8 , $d^9\bar{L}$, and $d^{10}\bar{L}^2$ components, as shown theoretically as well as experimentally in the well-established NCT compound NiGa_2S_4 [198]. Our data are also in excellent agreement with previously reported XPS results for NiPS_3 [197]. Our main finding is that for $\text{Ni}_{0.92}\text{Zn}_{0.08}\text{PS}_3$, the spectrum shifts to lower binding energies, indicating that the weights of the $d^9\bar{L}$ and $d^{10}\bar{L}^2$ components have increased due to Zn doping. This suggests a strong electron-phonon coupling in the paramagnetic state of NiPS_3 . The 2p core level XPS spectra for the elements P and S in NiPS_3 and $\text{Ni}_{0.92}\text{Zn}_{0.08}\text{PS}_3$ is shown in Fig. 6.14(b,c,d e). As shown in Fig. 6.14(b,c), the 2p spin-orbit split doublet for P in NiPS_3 appear in the binding energy range 131 eV to 135 eV. In this range, besides the spin-orbit split doublet, no extra peak can be seen. On the other hand, in the Zn-doped sample the spectra could only be fitted satisfactorily when two doublets are considered. This difference can be attributed to the presence of two different chemical environments in the doped sample. Similarly, the S 2p spectra can be fitted to one doublet as expected in the pristine sample, and a second spin-orbit doublet had to be considered to account for the whole spectra in the presence of Zn-doping as shown on Fig. 6.14(d,e).

While the spin-phonon coupling in the magnetically ordered state is easy to understand, the reasons for the weakening of the electron-phonon coupling at low temperatures is not very clear. One can speculate that the antiferromagnetic ordering of the Ni spins results in a renormalization of

the electronic structure [220]. Another possibility is that at low temperatures, the charge density fluctuations, i.e., electron delocalization between d^8 , $d^9\bar{L}$, and $d^{10}\bar{L}^2$ components, freeze out. It may also be that our interpretation of the cause of the Fano resonance of phonon P_2 is simply the two-magnon continuum, which redshifts from 550 cm^{-1} at low temperatures to close to the location of mode P_2 at high temperatures; in this case, what we witness is nothing but the spin-phonon coupling manifested through P_2 at high temperatures. Of course, it is relevant to ask why the two-magnon continuum should survive up to very high temperatures relative to the antiferromagnetic ordering temperatures. The answer to this may lie in the fact that it is, after all, a two-dimensional magnet, and the short-range ordering may persist up to very high temperatures.

This interpretation (that P_2 shows Fano asymmetry due to its coupling with the two-magnon continuum) does not, however, explain why the value of the coupling coefficient ($|1/q|$) increases monotonically upon non-magnetic site dilution. Site dilution weakens the magnetism, and thus the spin-phonon coupling should diminish. These are intriguing questions that require further careful investigation, and we believe that the present study will stimulate additional experimental and theoretical studies to understand the plethora of coupled phenomena that NiPS₃ harbors. .

6.4 Summary and conclusions

We have grown high-quality single crystals of Ni_{1-x}Zn_xPS₃ ($x = 0, 0.01, 0.03, 0.05, 0.08, 0.13, 0.14$) using the physical vapor transport technique and characterized them using X-ray diffraction, FESEM, EDX, and HRTEM probes. The zigzag antiferromagnetic ordering temperature (T_N) is found to suppress with increasing Zn doping. The rate of suppression $\frac{dT_N}{dx}$ follows the mean-field prediction for spin 1 on a honeycomb lattice [20]. In previous Raman, photoluminescence, and XPS studies, NiPS₃ has been shown to exhibit several interesting features, indicative of the presence of spin-phonon and spin-charge coupling [75, 117, 210, 211, 221, 222].

Here, we show that the Raman mode due to the vibration of Ni near 176 cm^{-1} (called P_2) exhibits a Fano-type asymmetry at high temperatures, which is particularly pronounced above T_N . The measurements carried out, both below and above T_N , and under two different polarization configurations, confirm that P_2 exhibits a Fano resonance in the paramagnetic phase. We show that the non-magnetic site-dilution using Zn as a dopant weakens the magnetism but strengthens the Fano coupling ($|1/q|$), which increases monotonically (and almost linearly) with increasing Zn doping. We argue that these

unusual characteristics of mode P_2 are due to its coupling with a broad continuum of electronic excitation seen in the high-temperature Raman spectra. This electronic continuum suppresses rapidly below T_N and at the same time, the Fano-like asymmetry of P_2 also disappears, clearly indicating a correlation between the two. This correlation was further supported by a similar observation in the temperature-dependent experiments on a Zn-doped sample with reduced T_N .

As NiPS_3 is a negative charge transfer (NCT) insulator, with the electronic states of Ni described as $\psi = \alpha d^8 + \beta d^9 \underline{L} + \gamma d^{10} \underline{L}^2$, we argue that the Fano resonance arises due to the coupling of discrete phonon P_2 with the continuum of electronic states ψ . If we assume that upon small Zn doping the amount of charge transfer from S (p) to Ni (d) orbitals remains unaffected, then the amount of charge that was transferred to 1 Ni atom per formula unit in NiPS_3 is now transferred to $(1 - x)$ Ni atoms in $\text{Ni}_{1-x}\text{Zn}_x\text{PS}_3$, which implies that the weights of the $d^9 \underline{L}$ and $d^{10} \underline{L}^2$ components enhance, thereby enhancing the electron-phonon coupling. The peaks in the 2p core-level XPS of Ni in NiPS_3 are shown to redshift upon Zn doping, supporting the argument that the weights of $d^9 \underline{L}/d^{10} \underline{L}^2$ components increase upon Zn doping.

To summarize, we show that NiPS_3 is a unique 2D Van der Waals magnetic insulator that exhibits possible electron-phonon coupling in its paramagnetic state, in addition to the known spin-phonon coupling in the antiferromagnetically ordered phase.

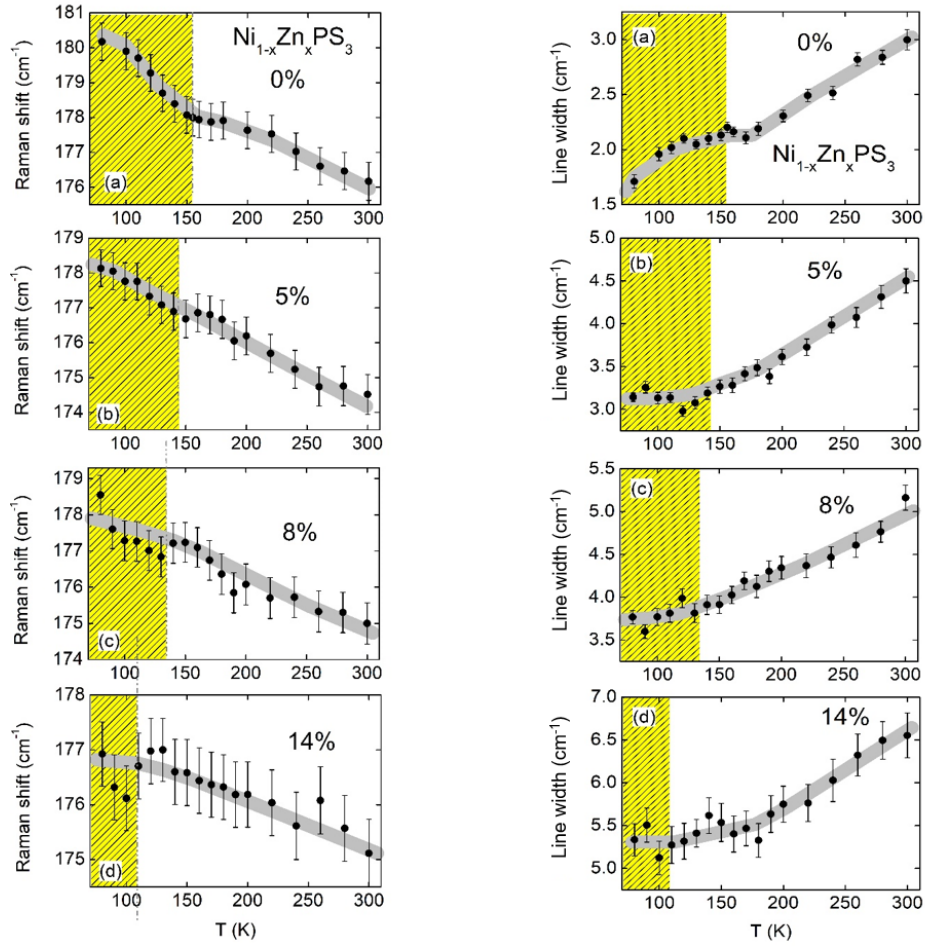


Figure 6.12: The temperature variation of Raman shift $\Delta\omega$ (left column) and line width Γ (right column) of mode P_2 for various $\text{Ni}_{1-x}\text{Zn}_x\text{PS}_3$ compositions. (a) pristine, (b) 5%, (c) 8%, and (d) 14%. The yellow hashed box represents the ordered state using the T_N obtained from the specific heat data. These T_N values are also shown in Table T2. The changes in $\Delta\omega$ and Γ at the para-to-antiferro phase boundary are not as clearly perceptible as in the pristine case, which is attributed to the presence of disorder and strain due to doping. The lines are drawn as a guide to the eye.

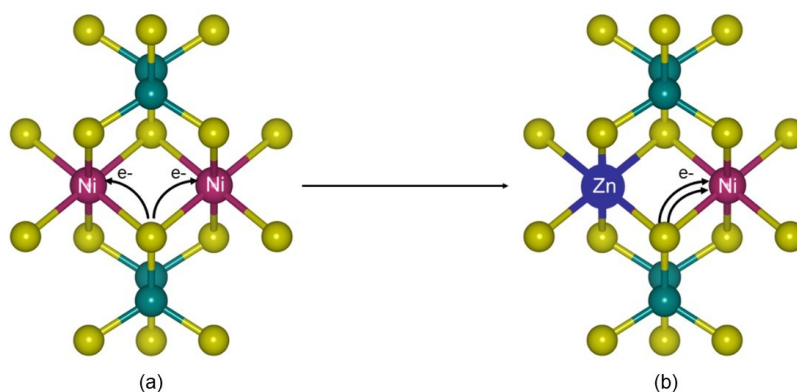


Figure 6.13: The Schematic depiction of charge transfer from Ni to S in the negative charge transfer insulator NiPS₃. In the left structure(a), each S atom is transferring electrons to two Ni atoms, upon Zn doping as shown in the right structure(b) each S atom is now transferring electrons to only one Ni atom and hence electron-phonon coupling is increased with Zn doping.

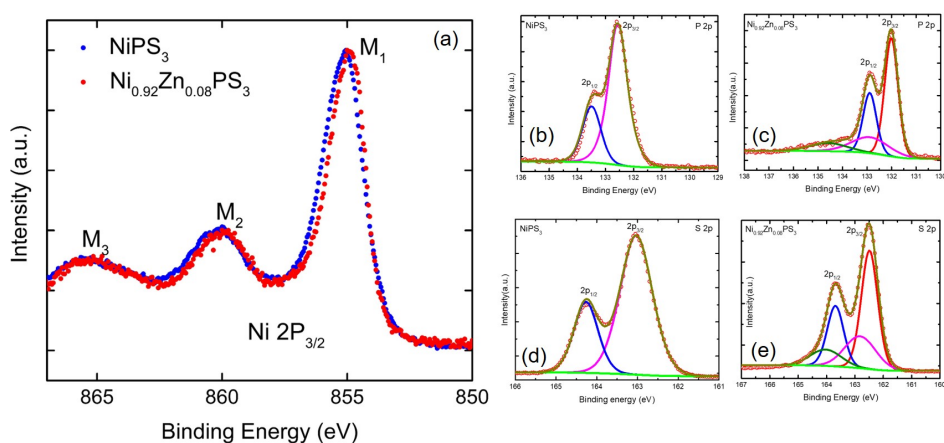


Figure 6.14: 2p core level XPS spectra of NiPS₃ (Blue circles) and Ni_{0.92}Zn_{0.02}PS₃ (Red circles).

Chapter 7

Summary and outlook

The primary motivation of the work described in this thesis was to advance the field of two-dimensional (2D) magnets, which host a variety of exotic physical phenomena, as outlined in the introduction. The central theme of this thesis is twofold: first, to perturb existing 2D magnets that already exhibit intriguing physics, using approaches such as chemical doping; and second, to grow high-quality single crystal of novel 2D magnetic compounds. These efforts aim to open new pathways for exploring fascinating physics and provide platforms to test theoretical models, such as the well known Kitaev model. This model beautifully demonstrates that a spin-1/2 system on a honeycomb lattice can realize a quantum spin liquid ground state with quasiparticle excitations in the form of Majorana fermions. In essence, the focus of this work was to investigate materials with magnetic spins on honeycomb lattices to discover new physical phenomena. The key findings from each of the studied compounds are summarized in the following paragraphs.

Chapter 3 of this thesis deals with the study of YbI_3 , a quasi-2D layered material with Yb atoms arranged on an ideal honeycomb network of edge-sharing YbI_6 octahedra, analogous to the low-temperature phase of $\alpha\text{-RuCl}_3$. High quality single crystals of YbI_3 are grown for the first time from Yb and I as starting precursors, using the vapor transport technique. The grown crystals are characterized by single crystal x-ray diffraction, Raman spectroscopy, magnetization, and heat capacity probes. The low-temperature heat capacity of YbI_3 reveals a broad peak at $T_1 = 0.95$ K due to short-range ordering of the Yb moments, followed by a sharp peak at $T_2 = T_N = 0.6$ K due to long-range ordering. The magnetic behavior is found to be weakly anisotropic with $\chi^{\parallel} > \chi^{\perp}$,

where $\chi^{\parallel}$ and $\chi^{\perp}$ refers to the in-plane ($H \parallel ab$) and out-of-plane ($H \perp ab$) susceptibilities. The 2 K isothermal magnetization saturates at $\approx 1.5 \mu_B/\text{Yb}^{3+}$ (in-plane) and $\approx 1 \mu_B/\text{Yb}^{3+}$ (out-of-plane), suggesting the anisotropy to be easy-plane type. The low-temperature heat capacity, well below T_N , is found to vary as T^{α} with $\alpha \approx 2.5$, indicating a possible unconventional magnetic ground state for YbI_3 . Hence, our preliminary characterization reveals that YbI_3 exhibits intriguing physics. The exotic nature of its ground state can be further explored through magnetic field-dependent heat capacity measurements and local probe techniques such as neutron scattering, muon spin relaxation/rotation (μSR), and nuclear magnetic resonance (NMR). These investigations will provide valuable insights into the precise ground state of this newly studied two-dimensional magnet.

Chapter 4 of this thesis discusses the Rare earth tri-iodides are intriguing series of two-dimensional quantum magnets with magnetic spins arranged on honeycomb or distorted hexagonal lattice. High-quality single crystals of rare earth tri-iodides were grown using vapor transport reactions, and a detailed synthesis protocol for producing large single crystals is presented in this work. The crystal structures of the grown samples were precisely determined through extensive characterization using single-crystal X-ray diffraction. Heat capacity measurements on well-characterized single crystals reveal evidence of exotic ground states in each rare earth tri-iodide. Specifically, GdI_3 exhibits a linear temperature dependence below 3 K, while DyI_3 shows no long-range order down to 1.8 K. HoI_3 displays a broad hump centered at 3 K, and ErI_3 provides evidence of onset of magnetic ordering below 4.5 K. The Curie-Weiss analysis indicates predominantly antiferromagnetic interactions among the magnetic rare earth ions. Notably, the heavier rare earth tri-iodides, which are isostructural to the well-studied Kitaev candidate material $\alpha\text{-RuCl}_3$, suggest the possibility of exotic magnetic ground states. The lighter rare earth tri-iodides, for example CeI_3 where it forms a chain of Ce ions along c-axis which are stacked along b-axis is another potential material to investigate for the existence of chiral phonons.

In **Chapter 5**, we have grown high-quality single crystals of CeCl_3 using a modified Bridgman Stockbarger method in an infrared image furnace. These crystals are characterized using single-crystal/powder X-ray diffraction, Laue X-ray diffraction, Raman spectroscopy, magnetization, and heat capacity probes. CeCl_3 crystallizes with a hexagonal structure ($P6_3/m$) with a very weak trigonal distortion ($P\bar{3}$). The Raman spectrum at 300 K showcases five clearly resolvable phonon modes at 106.8 cm^{-1} , 181.2 cm^{-1} , 189 cm^{-1} , 213 cm^{-1} , and 219.7 cm^{-1} . The magnetic susceptibility along

$H \parallel c$ ($\chi^{\parallel}$) and $H \perp c$ ($\chi^{\perp}$) axes is measured as a function of temperature and magnetic field. $\chi^{\perp}$ exhibits a broad peak in its temperature variation, with the peak centered around 50 K. In contrast, $\chi^{\parallel}$ is about two orders of magnitude larger and shows a monotonic Curie-like increase upon cooling. This behavior is explained using crystal field theory. The crystal field in CeCl_3 splits the $J = 5/2$ manifold of Ce^{3+} into three Kramers doublets, with $|\frac{5}{2}, \pm\frac{5}{2}\rangle$ as the ground state, $|\frac{5}{2}, \pm\frac{1}{2}\rangle$ at energy $E_1 = 61$ K, and $|\frac{5}{2}, \pm\frac{3}{2}\rangle$ at $E_2 = 218$ K as the first and second excited states. Accordingly, the magnetization $M(H)$ at 2 K along $H \perp c$ is small and shows a linear variation, whereas $M(H)$ along $H \parallel c$ saturates readily (easy-axis) to the expected value. In the specific heat, no magnetic ordering could be seen down to 2 K. However, in non-zero fields, the low-temperature specific heat changes dramatically, showcasing a peak at 2.5 K under a moderate field of 30 kOe. The weak Ce-Ce exchange, large Ce moment in the crystal field ground state, and huge anisotropy are all ingredients for realizing a high magnetocaloric effect. Indeed, measurements at low temperatures reveal a maximum entropy change of $-\Delta S_{4f} \approx 23 \pm 1 \text{ J Kg}^{-1} \text{ K}^{-1}$ near 2.5 K in the field range of 50 kOe to 60 kOe. These values are comparable to some of the best Gd-based magnetocaloric materials, signifying the potential of CeCl_3 as a magnetic coolant. Also with the availability of high quality single crystals, it will now be possible to perform terahertz measurement on CeCl_3 crystals and to test the theoretical prediction that optically driven chiral phonon modes in rare-earth trihalides generate giant effective magnetic fields upto 100 T acting on the paramagnetic 4f spins.

The last chapter **Chapter 6** deals with NiPS_3 , a Van der Waals antiferromagnet which has been shown to exhibit spin-phonon and spin-charge coupling in the antiferromagnetically ordered state below $T_N = 155$ K. It is also a rare Ni-based negative charge-transfer-type (NCT) insulator with Ni valence in a linear superposition state $\psi = \alpha d^8 + \beta d^9 \underline{L} + \gamma d^{10} \underline{L}^2$, where $\underline{L}$ is the ligand hole. Here, we study high-quality single-crystals of $\text{Ni}_{1-x}\text{Zn}_x\text{PS}_3$ ($0 < x < 0.2$) using temperature-dependent specific heat and Raman spectroscopy probes. We show that in pristine NiPS_3 , the phonon mode at 176 cm^{-1} (P2), associated with the vibrations of Ni, exhibits a distinct Fano asymmetry. The Fano resonance is found to be particularly pronounced in the paramagnetic phase above T_N , which was further confirmed by temperature-dependent Raman data on the Zn-doped crystals. In the Zn-doped crystals, while the magnetism weakens following the mean-field prediction for site-dilution in a honeycomb lattice, the Fano coupling $|1/q|$ strengthens, increasing monotonically with increasing Zn-doping. The X-ray photoemission spectra suggest an increase in the weight of the d^9

and d^{10} components in the Zn-doped crystals. These observations indicate the presence of strong electron-phonon coupling in $\text{Ni}_{1-x}\text{Zn}_x\text{PS}_3$, in addition to the spin-phonon and spin-charge coupling previously reported. Furthermore, XPS measurements conducted from room temperature down to the ordering temperature for each Zn-doped composition, combined with cluster model calculations to fit the XPS data, will provide robust evidence for electron-phonon coupling in these materials.

In the Appendix of this thesis, we report the detailed optimization of crystal growth process of $\alpha\text{-RuCl}_3$, a widely studied Kitaev candidate material, to produce large, high-quality single crystals free from stacking faults using the physical vapor transport technique. A significant achievement is the growth of a large single crystal weighing 650 mg, which was thoroughly characterized using various experimental probes to confirm its high quality. Additionally, efforts were made to dilute the honeycomb lattice of Ru^{3+} by introducing non-magnetic dopants, including Al^{3+} , In^{3+} , Ir^{3+} , Y^{3+} , and Sc^{3+} . Successful incorporation of Y^{3+} and Sc^{3+} at the Ru^{3+} site was achieved via solid-state synthesis, with the doped samples obtained in polycrystalline form. Here we also discuss the challenges and reasons behind the unsuccessful doping attempts with other elements through different synthesis routes. Finally, the effects of doping are examined using low-temperature heat capacity measurements. $\alpha\text{-RuCl}_3$ is the closest realization of the Kitaev model, where the spins on the honeycomb lattice experience highly anisotropic bond-dependent interactions, leading to frustration. This frustration results in evidence of exotic quasi-particle excitations, Majorana fermions, on each vertex of the honeycomb lattice. By doping a non-magnetic ion at the Ru site, spin vacancies are created, which eventually lead to dangling Majorana modes. These dangling Majorana modes simplify the detection and manipulation of Majorana fermions, which is a key ingredient in quantum computation. This study provides insights into the incorporation of different non-magnetic dopants at the Ru site to experimentally realize dangling Majorana modes in practical compounds.

Appendix A

Optimized crystal growth and dilution study of well-known Kiteav candidate material α - RuCl₃

The Crystal growth of α - RuCl₃ described in this chapter is published in Bulletin of Materials Science under the title of "Crystal growth of quantum materials: a review of selective materials and techniques" as a crystal growth study along with the review of other novel quantum materials grown and investigated in Crystal growth laboratory at IISER Pune under the supervision of Prof. Surjeet Singh.

A.1 Introduction

A.1.1 Crystal growth of α - RuCl_3

α - RuCl_3 is a well-established candidate for realizing the Kitaev quantum spin liquid (QSL), a state of matter that hosts fractionalized excitations and exotic magnetic properties [97]. The study of these properties, however, is highly sensitive to the quality of the single crystals used in experiments. In high-quality α - RuCl_3 crystals, a clear and sharp magnetic transition is observed around 7 K in both heat capacity and magnetic susceptibility measurements. This transition is attributed to the onset of magnetic ordering in the material [98]. Additionally, these high-quality crystals exhibit a well-defined three-layer periodicity of α - RuCl_3 planes stacked along the crystallographic c-axis, which is crucial for maintaining the integrity of the magnetic interactions that give rise to the Kitaev QSL behavior [223]. In contrast, poor-quality α - RuCl_3 crystals show a different set of characteristics, including multiple transitions in both heat capacity and magnetic measurements at temperatures above 7 K [98]. Specifically, additional anomalies around 10 K and 14 K have been reported. These transitions are believed to result from stacking faults or structural inhomogeneities in the crystal. Such faults disrupt the periodic arrangement of RuCl_3 layers, leading to variations in the local magnetic environment and causing the emergence of additional magnetic transitions. These stacking faults not only affect the magnetic transitions but also have a significant impact on the thermal conductivity of the material [224]. One of the most exciting observations in α - RuCl_3 is the half-quantized thermal Hall effect, which is considered a signature of the fractionalized Majorana fermion excitations predicted in the Kitaev QSL state [97]. However, the observation of this exotic behavior is highly dependent on the crystal quality. Any structural defects, including stacking faults, can obscure or even prevent the manifestation of such quantum effects.

As a result, it becomes essential to grow α - RuCl_3 single crystals of the highest possible quality, with minimal stacking faults, to probe the intrinsic magnetic and thermal properties of the material. To achieve this, we undertook an extensive effort to grow high-quality single crystals of α - RuCl_3 using different temperature profiles and synthesis techniques as described in the literature. By carefully controlling the growth conditions, we aimed to produce crystals free from stacking faults, ensuring that the magnetic and thermal properties observed in our experiments truly reflect the fundamental

physics of the material. The results of our crystal growth efforts and the corresponding analysis of the crystal quality are summarized in the first part of this chapter. By refining the growth techniques, we sought to minimize structural defects and stacking faults, which would allow us to investigate the intrinsic properties of α -RuCl₃ more accurately. These high-quality crystals are crucial for unraveling the complex physics associated with Kitaev interactions and the potential realization of a quantum spin liquid in α -RuCl₃.

A.1.2 Motivation for doping the Kitaev honeycomb model in α -RuCl₃

Another strong motivation to study the RuCl₃ system is to dilute the Kitaev Honeycomb Model. The Kitaev honeycomb model describes spin-1/2 particles on a two-dimensional honeycomb lattice, where bond-dependent anisotropic interactions lead to a quantum spin liquid (QSL) ground state with Majorana fermions as the emergent quasi-particle excitations [80]. In this model, each vertex of the honeycomb lattice hosts four flavors of Majorana fermions, with the interactions between them leading to fractionalized spin excitations. Diluting the honeycomb lattice implies introducing vacancies, which in turn creates dangling Majorana modes [225]. These modes are potentially easier to detect and manipulate due to the broken symmetry caused by the vacancies [59]. In real materials like α -RuCl₃, we can introduce such vacancies by replacing a fraction of Ru³⁺ ions with non-magnetic analogs. This substitution effectively recreates spin vacancies in the system, thus leading to the emergence of dangling Majorana modes [226]. Given this theoretical foundation, we propose doping α -RuCl₃ with Al³⁺, In³⁺, Ir³⁺, Y³⁺, and Sc³⁺ at the Ru³⁺ sites. This controlled doping process will allow us to study how the introduction of non-magnetic elements affects the magnetic and topological properties of the system. For example, doping with non-magnetic ions may reduce the long-range magnetic order, potentially driving the system closer to a QSL state where Majorana fermions could be more readily observed [5].

In addition, diluting the honeycomb lattice without disrupting the essence of Kitaev model might help suppress the magnetic ordering present in undoped α -RuCl₃, allowing the QSL phase to emerge at lower magnetic field. This could also enhance the visibility of the half-quantized thermal Hall effect, a key signature of Majorana fermion excitations in the Kitaev model [227]. Thus, by introducing vacancies through doping, we aim to explore new low-energy excitations and topological phenomena in the RuCl₃ system.

A.2 Experimental techniques

Single crystals of α - RuCl_3 were grown using the physical vapor transport (PVT) technique, which does not require any external transporting agent. Details of the crystal growth process aimed at improving the quality of the crystals are described in Section A.3.1. Non-magnetic doping at the Ru site in α - RuCl_3 was explored using four different synthesis routes. The first approach involved the growth of single crystals of dilute α - RuCl_3 using the PVT method, as described in Section A.3.2. Polycrystalline samples of $\text{Ru}_{1-x}\text{Al}_x\text{Cl}_3$ (with $x = 0, 0.1, 0.2$) were synthesized via three distinct routes to incorporate Al^{3+} at the Ru^{3+} site.

In **Method 1**, anhydrous powders of RuCl_3 and AlCl_3 were homogeneously mixed using an agate mortar and pestle, then sealed in a quartz ampoule. The ampoule was first heated to 150°C for 2 hours, allowing AlCl_3 to react with RuCl_3 , before gradually raising the temperature to 650°C for 24 hours. This step is essential since AlCl_3 sublimates at 180°C . It is important to note that this pre-reaction step is not necessary when synthesizing polycrystalline α - RuCl_3 itself. The starting RuCl_3 precursor contains impurities such as β - RuCl_3 , RuO_2 , and RuOCl_2 [228]. The β -phase of RuCl_3 converts to the α -phase at 450°C , while RuOCl_2 decomposes into RuO_2 and Cl_2 at 650°C [229]. Sintering at 650°C helps convert the β -phase to α -phase while reducing oxychloride impurities; however, a minor amount of RuO_2 impurity always persists in polycrystalline α - RuCl_3 and doped samples of $\text{Ru}_{1-x}\text{Al}_x\text{Cl}_3$.

In **Method 2**, anhydrous RuCl_3 powder and Al shots were combined with TeCl_4 and sealed in a quartz ampoule, then heated at 700°C for 48 hours. TeCl_4 , which sublimates around 200°C , acted as a chlorine source in this synthesis.

In **Method 3**, polycrystalline $\text{Ru}_{1-x}\text{Al}_x\text{Cl}_3$ was synthesized using a wet chemical approach. Stoichiometric amounts of $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (Sigma Aldrich) and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (Sigma Aldrich) were dissolved in water at room temperature. The resulting solution was heated to 150°C to evaporate the water. The remaining powder was transferred to a quartz ampoule, preheated under dynamic vacuum at 250°C for 24 hours, then sealed under vacuum and heated at 650°C for 24 hours. This final step converted the β -phase to α -phase and decomposed oxychlorides into oxides and chlorides.

Polycrystalline samples of α - $\text{Ru}_{1-x}\text{Ir}_x\text{Cl}_3$ ($x = 0.1$), α - $\text{Ru}_{1-x}\text{Y}_x\text{Cl}_3$ ($x = 0.1$), and α - $\text{Ru}_{1-x}\text{Sc}_x\text{Cl}_3$ ($x = 0.1$) were synthesized using **Method 1** using simple solid state synthesis, with stoichiometric

quantities of the precursors. The mixtures were sealed in evacuated quartz ampoules and heated at 650 °C for 24 hours for Ir, Y, and Sc doping.

The phase purity of the samples was analyzed using powder X-ray diffraction (PXRD) in Bragg-Brentano geometry with a Bruker D8 Advance diffractometer. The morphology and chemical composition of the single crystals and polycrystalline samples were studied using field-emission scanning electron microscopy (FE-SEM, Zeiss Ultra Plus) equipped with Energy Dispersive X-ray (EDX) analysis (Oxford Instruments). Raman spectra were collected in the backscattering configuration using a Horiba Jobin-Yvon LabRAM HR spectrometer equipped with a liquid nitrogen-cooled Charge-Coupled Device (CCD) and a 633 nm laser as the excitation source. Specific heat was measured using a Physical Property Measurement System (PPMS, Quantum Design, USA). The polycrystalline samples were pelletized using a 6 mm diameter die set inside a glove box due to their hygroscopic nature, and a small circular pellet was cut into a square piece of 2 mm × 2 mm. This small piece was then mounted on the heat capacity sample holder.

A.3 Results and discussion

A.3.1 Crystal growth of α - RuCl₃

The α -RuCl₃ crystals are grown using the vapour transport method with commercially procured RuCl₃ powders (sourced from Sigma Aldrich and Alfa Aesar). The as-purchased powders from both sources were found to contain a copious amount of β -RuCl₃ (a polymorph of α -RuCl₃, which transforms irreversibly into the α -phase upon heating above 395-450°C), and oxychlorides Ru₂OCl₆ and RuOCl₂ as impurities. In the first step, these powders were subjected to heat treatment in a vacuum-sealed silica ampoule at 650°C for 24 h, which resulted in almost phase-pure α -RuCl₃, along with some RuO₂ impurity as described for the synthesis of polycrystalline samples. The concentration of RuO₂ was found to be 4% for Alfa Aesar and 8% for Sigma Aldrich. After the heat treatment, the purified powder was stored in an Ar-filled glove box for subsequent crystal growth experiments.

Method 1: In method 1, the purified powder was transferred into a clean quartz ampoule and sealed under a high dynamic vacuum of 10⁻⁵ mbar. This ampoule was placed in a temperature gradient furnace with a gradient of about 40°C between the source and the sink. The temperature of the furnace was gradually increased to 700°C. After dwelling at 700°C for 24 h, slow cooling at a rate

of $-1.8^\circ\text{C h}^{-1}$ was initiated until the furnace temperature decreased to 500°C . After waiting at 500°C for 100 h, the furnace was further cooled down to room temperature at a rate of $-150^\circ\text{C h}^{-1}$ [230]. Thin, platelet-like, shiny black crystals of $\alpha\text{-RuCl}_3$ were obtained at the end of the ampoule. The typical lateral dimension of the crystals was approximately 1 cm by 1 cm, with a thickness of ~ 0.1 cm as shown in Fig. A.1(a).

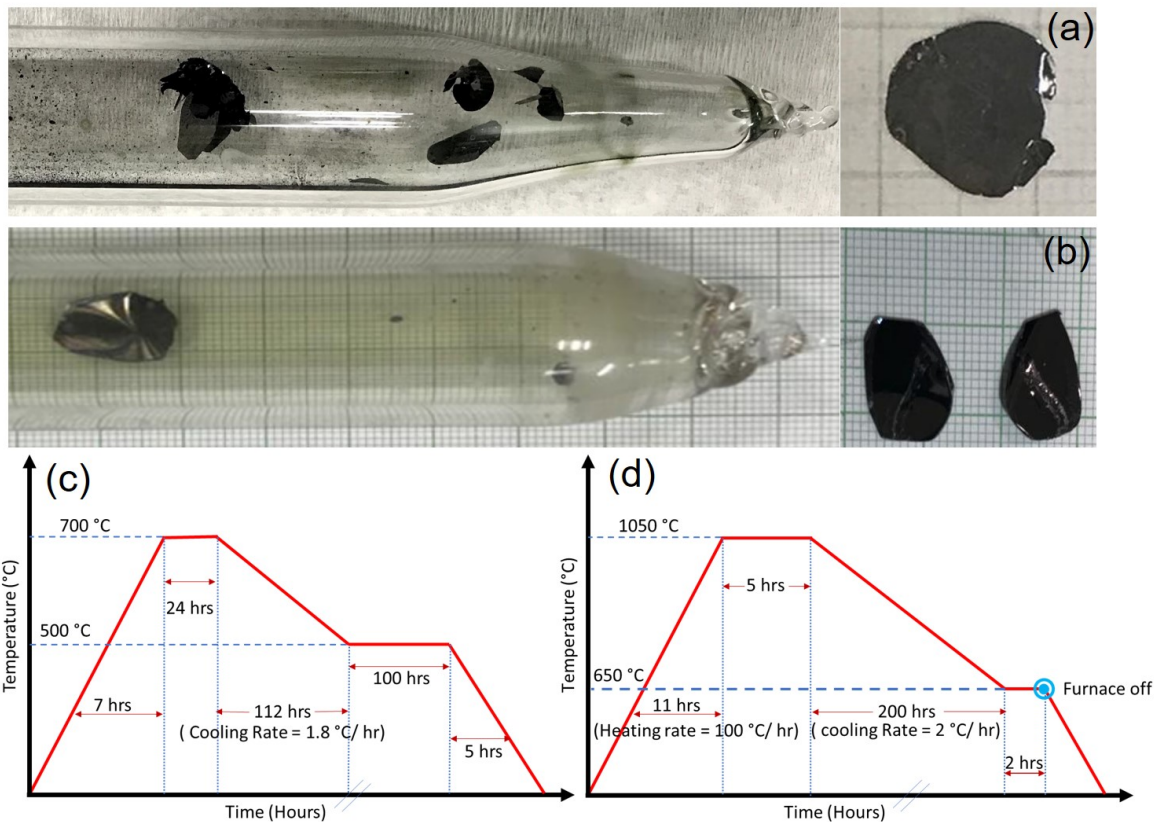


Figure A.1: Summary of crystal growth process obtained using two different temperature profiles labelled as Method 1 and Method 2 in the text. (a) Crystals obtained by employing Method 1. (b) Crystals obtained by employing Method 2. (c) Temperature Profile used on Method 1. (d) Temperature profile used in Method 2.

Method 2: In method 2, the purified powder was filled into a cleaned quartz ampoule and further dehydrated by heating at 250°C under dynamic vacuum for 7 h. The ampoule was then sealed and placed in a temperature gradient furnace as before. The temperature of the furnace was gradually raised to 1080°C . After dwelling at 1080°C for 5 h, the furnace was slow-cooled at a rate of -2°C h^{-1} down to 650°C . At this point, the furnace was switched off to let the ampoule cool down to

room temperature [231]. In this case, a single shiny black crystal with a mass of nearly 630 mg was obtained. The crystal dimensions were approximately 1.5 cm by 1.5 cm by 0.8 cm, as shown in Fig. A.1(b). The crystal cleaved easily, exhibiting large shiny facets. In the RuCl_3 crystals obtained using this method, the 12 K and 14 K transitions were significantly suppressed, as described in A.3.4

The growth of high-quality α - RuCl_3 single crystals depends on several factors, and simply employing a temperature profile shown in Method 2 does not guarantee large, defect-free crystals. One critical factor is the initial purity of the starting precursor. Using high-purity, anhydrous RuCl_3 ensures minimal amount of oxides and oxychlorides impurities, which could otherwise disrupt the crystal lattice and cause defects and stacking faults during the crystal growth process. Another important factor is the proper dehydration of the precursor to remove any adsorbed moisture. Moisture can lead to hydrolysis and the formation of oxides, hydroxides, and oxychlorides of Ruthenium upon reacting with RuCl_3 which interfere with the crystal growth process. To prevent this, the starting materials must be carefully dehydrated, often by heating at around 250°C under dynamic vacuum to remove any residual water as employed in Method 2. The positioning of the reaction ampoule in the furnace also plays a significant role, as it directly affects the temperature gradient within the ampoule. This gradient controls the rate of sublimation and deposition during vapor transport reaction, influencing the crystal size and quality. Precise placement of the reaction ampoule in the furnace ensures optimal conditions for growth. For RuCl_3 , in particular requires a very small temperature gradient nearly $2 - 3^\circ\text{C}$ between the sink and the source. This method is generally called as SSVG (Self Selecting Vapour transport Growth). Furthermore, optimizing the temperature profile in combination with these factors is crucial. Balancing the rate of transport and deposition is essential for growing large, high-quality crystals which is achieved by controlling the initial growth temperature and the cooling rate. When all these parameters - purity, dehydration, ampoule positioning, and temperature profile - are precisely controlled, the result can be a large, well-formed single crystal, as achieved in Method 2.

A.3.2 Crystal growth of dilute α - RuCl_3

Different non magnetic dopants were used which includes Al^{3+} , In^{3+} , Ir^{3+} , Sc^{3+} and Y^{3+} to dilute the honeycomb lattice of α - RuCl_3 . $\text{Ru}_{1-x}\text{Al}_x\text{Cl}_3$ ($x = 0.02, 0.1$), $\text{Ru}_{1-x}\text{In}_x\text{Cl}_3$ ($x = 0.02$), $\text{Ru}_{1-x}\text{Sc}_x\text{Cl}_3$ ($x = 0.10$), and $\text{Ru}_{1-x}\text{Y}_x\text{Cl}_3$ ($x = 0.10$) were different compositions of dopants tried to grow in the single crystalline form. For the crystals grown using PVT, the anhydrous powders of

RuCl_3 and BCl_3 ($\text{B} = \text{Al}, \text{In}, \text{Ir}, \text{Sc}, \text{Y}$) were mixed in stoichiometric amounts and loaded into a quartz ampoule which was then sealed under vacuum. The quartz tube was kept in a temperature gradient furnace at a similar temperature profile for the pristine α - RuCl_3 . The dwell time at 1080°C was increased from 5 hours to 12 hours to allow BCl_3 to react with RuCl_3 before sublimation. In most of the cases the initial chlorides of dopants tend to grow separately from the RuCl_3 single crystals. One possible reason is possibly the different vapour pressure of the two end members at growth temperatures. An optimized temperature profile is still under investigation to achieve the competing vapour pressure of two end members during the crystal growth process through vapour transport reaction.

A.3.3 Structural and compositional characterization

The grown single crystals and the polycrystalline samples were characterized using Powder X-ray diffraction technique to check the phase purity. Fig. A.2(a, b) shows the X-ray diffraction pattern on the ab-plane of the parent and doped single crystals. The diffraction pattern is similar to the parent α - RuCl_3 with a negligible shift in the peak positions. The ionic radii for each dopant are listed in Table A.1. since the ionic radii of Ru^{3+} is either smaller or larger than the respective dopant we expect to see a shift in the XRD peaks provide the fact that all the trichlorides of dopant crystallizes in the same monoclinic structure with space group C2/m as the parent RuCl_3 . However no shift in the XRD pattern is seen for any of the doped single crystals indicating that the doping of the non-magnetic dopant cannot be successfully completed via single crystal route. The doping of Al^{3+} is further verified using the X-ray powder diffraction of synthesized polycrystalline samples. Fig. A.2(c, d) shows very little or no change in the peak positions indicating that the doping of Al^{3+} at Ru^{3+} site is unsuccessful via single crystal and polycrystalline routes. On the other hand Fig. 3.4(e, f) shows the powder x-ray diffraction pattern of Sc^{3+} and Y^{3+} doped RuCl_3 polycrystalline samples. The shift in the (0 0 1) XRD peak clearly indicates the change in the lattice parameters indicating that the Sc^{3+} and Y^{3+} are doped at the Ru^{3+} site in RuCl_3 . These evidences are further supported by the heat capacity measurement shown in sec. A.3.4.

Table A.1: Ionic Radii of different non-magnetic dopant in +3 oxidation state

Non magnetic dopant	Ionic Radii ($\text{\AA}$)
Ru^{3+}	0.68
Ir^{3+}	0.68
Y^{3+}	0.90
Sc^{3+}	0.75
Al^{3+}	0.54
In^{3+}	0.8

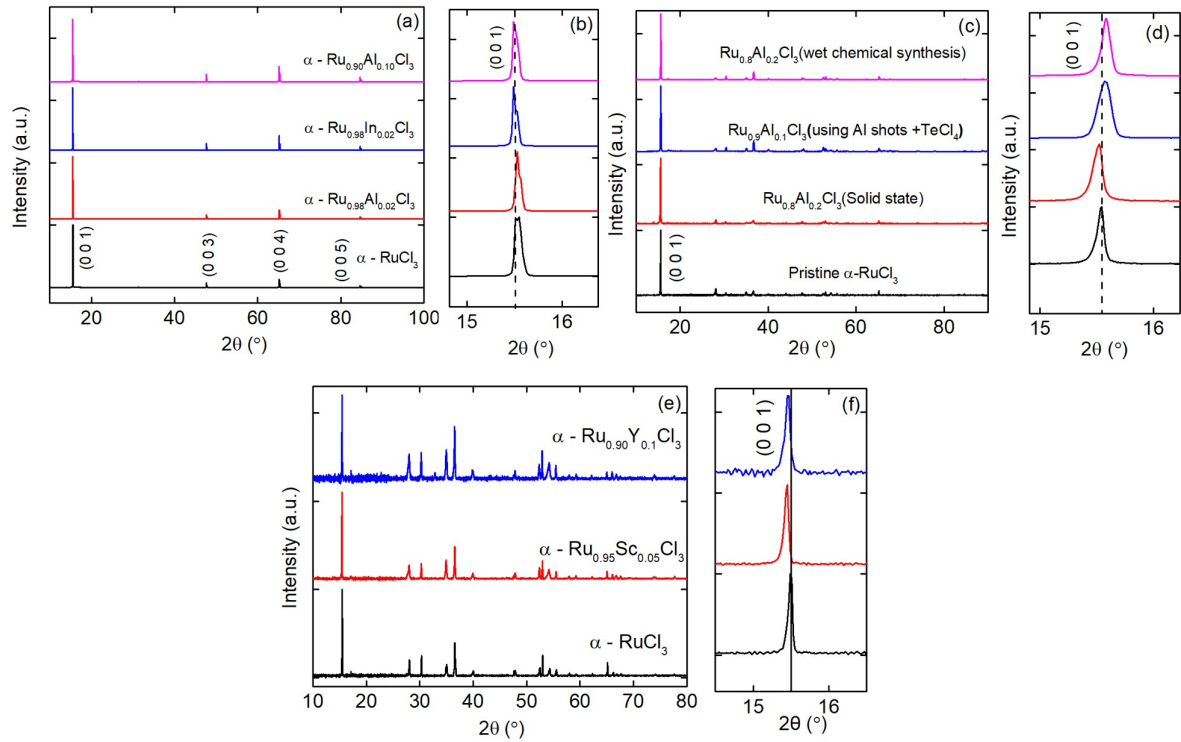


Figure A.2: (a, b) X-Ray diffraction on the ab - plane of the single crystals of Al^{3+} and In^{3+} doped at Ru^{3+} site. Powder X-Ray diffraction on the polycrystalline samples of doped RuCl_3 . (c, d) Al^{3+} as a dopant to test different synthesis route. (e, f) Sc^{3+} and Y^{3+} as a dopant for sample synthesized using solid state synthesis route.

A.3.4 Heat capacity

Fig. A.3 presents the heat capacity as a function of temperature for crystals grown using two different methods. Both crystals exhibit three transitions, located around 7 K, 10 K, and 14 K. However, the single crystals grown at higher temperatures show reduced intensities for the transitions at 10 K and

14 K, with the transition temperature lowered from 7.5 K (for crystals grown at 700°C) to 6.9 K (for crystals grown at 1080°C). The higher temperature transitions at 10 K and 14 K are attributed to stacking faults in the crystals. In contrast, high-quality single crystals without stacking faults, exhibiting a three-layer stacking sequence, show a single magnetic transition in heat capacity measurements. As previously discussed, these stacking faults can also be introduced by slight mechanical deformation of the crystal. Thus, in the heat capacity measurements, the single crystals grown at 1080°C exhibit reduced transition intensities at higher temperatures, with the slight humps likely introduced by mechanical pressure applied during the cutting and mounting of the sample on the heat capacity puck. Fig. A.4(a) shows the heat capacity of Al^{3+} doped single crystalline sample compared with the Parent RuCl_3 samples. Both the samples shows transition close to 14 K and hence no change in the transition temperature is observed on doping Al^{3+} at Ru^{3+} site via single crystal growth process. Fig. A.4(c) shows heat capacity of the Al^{3+} doped polycrystalline sample via different synthesis route but no change in the transition temperature is observed. Hence we conclude that doping of Al^{3+} at Ru^{3+} site in RuCl_3 is unsuccessful. Interestingly, Y^{3+} doped polycrystalline sample shows suppression of transition temperature similar to the Ir^{3+} doped sample as shown in Fig. A.4(c). The Sc^{3+} doped sample also shows signature of suppression of transition temperature as depicted in Fig. A.4(d).

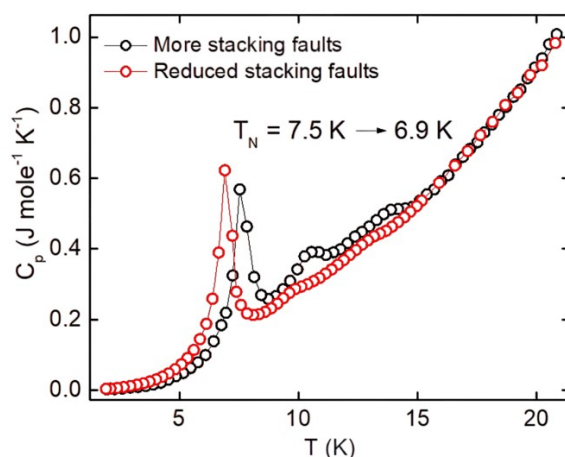


Figure A.3: Heat capacity as a function of temperature for crystals grown using two different temperature profiles. The black open circles indicates the crystals grown at 700°C and red open circles indicates the crystals grown at 1080°C. see text for more details.

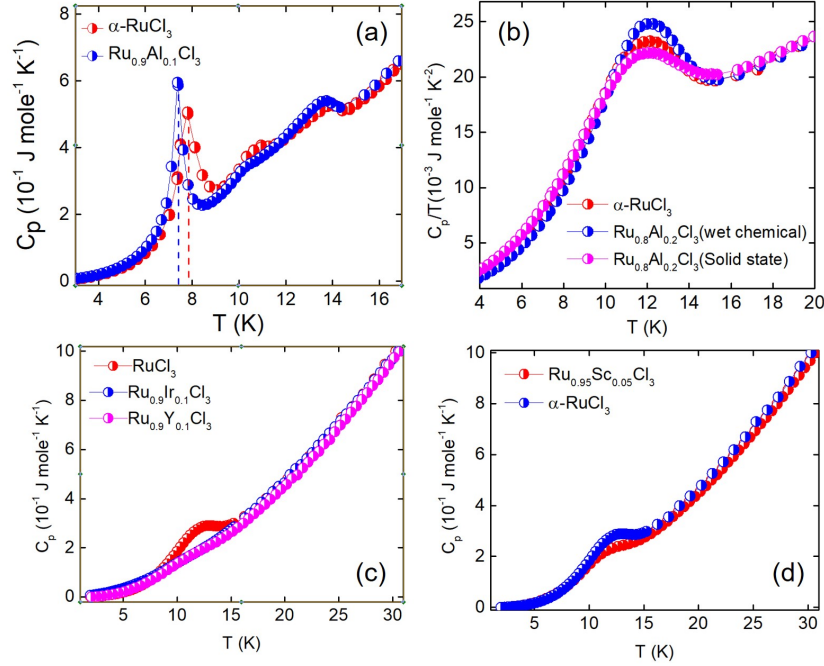


Figure A.4: (a) Heat capacity of Al^{3+} doped single crystals of RuCl_3 . (b) Heat capacity of Al^{3+} doped polycrystalline samples synthesized using different synthesis routes. (c) Heat capacity of Ir^{3+} and Y^{3+} doped RuCl_3 polycrystalline samples. (d) Heat capacity of Sc^{3+} doped RuCl_3 polycrystalline samples.

A.4 Summary and conclusion

In this chapter, we successfully grew high-quality single crystals of $\alpha\text{-RuCl}_3$ free from stacking faults using the vapor transport method. Achieving such high-quality crystals was critical for probing the magnetic and quantum phenomena in $\alpha\text{-RuCl}_3$, especially given the sensitivity of these properties to crystal quality. We then explored doping of $\alpha\text{-RuCl}_3$ with various non-magnetic elements, specifically Al^{3+} , In^{3+} , Y^{3+} , and Sc^{3+} , with the goal of investigating their effects on the magnetic behavior of the system. Our attempts to dope Al^{3+} and In^{3+} into the $\alpha\text{-RuCl}_3$ lattice were unsuccessful, both through single crystalline and polycrystalline routes. X-ray diffraction and heat capacity measurements confirmed the absence of successful doping in these cases. This failure can be attributed to the fundamental differences in bonding between Ru, a d-block transition metal, and Al^{3+} and In^{3+} , both p-block elements. On the other hand, Y^{3+} and Sc^{3+} doping proved successful, but only in polycrystalline form. The polycrystalline samples of $\text{Ru}_{1-x}\text{Y}_x\text{Cl}_3$ and $\text{Ru}_{1-x}\text{Sc}_x\text{Cl}_3$ exhibited suppression of magnetic ordering, as confirmed by heat capacity measurements. This suppression is similar to the

behavior seen in Ir-doped α -RuCl₃, indicating that Y³⁺ and Sc³⁺ successfully substituted Ru³⁺ in the lattice. The successful doping of Y and Sc, both d-block elements, is likely due to their more compatible bonding characteristics with Ru³⁺, as well as their more favorable vapor pressures compared to Al³⁺ and In³⁺. However, despite the success in polycrystalline samples, we were unable to incorporate Y³⁺ and Sc³⁺ dopants into single crystals of α -RuCl₃. The differing vapor pressures of YCl₃ and ScCl₃ during vapor transport growth likely contributed to this challenge, preventing uniform incorporation of the dopants. This underscores the complexities of doping in α -RuCl₃ and highlights the need for further refinement of synthesis techniques to achieve doped single crystals.

In summary, this work demonstrates the difficulty of doping p-block elements such as Al³⁺ and In³⁺ into α -RuCl₃, while showing that d-block elements like Y³⁺ and Sc³⁺ can be successfully incorporated in polycrystalline form. These findings pave the way for further studies to understand the magnetic and quantum phenomena in doped α -RuCl₃ systems.

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