

Emergent Critical Phases in Strongly Correlated Low-Dimensional Magnetic Systems



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I dedicate this thesis to my beloved parents, who have granted me the freedom and unconditional support to venture into a world of physics they are not familiar with.

Declaration

I hereby declare that this thesis is the result of my own work and contains nothing which is the outcome of work done in collaboration with others, except as specified in the text. I further state that no substantial part of my thesis has already been submitted, or, is being concurrently submitted for any such degree, diploma or other qualification at the University of Cambridge or any other University or similar institution except as declared in the Preface and specified in the text. This thesis does not exceed 60,000 words, including summary/abstract, tables, footnotes and appendices, but excluding table of contents, photographs, diagrams, figure captions, list of figures/diagrams, list of abbreviations/acronyms, bibliography and acknowledgements for the Physics and Chemistry Degree Committee.

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Abstract

This thesis delves into the realm of condensed matter physics, where the discovery of novel quantum states, from unconventional superconductors to non-trivial metallic behaviours, has led to promising applications and intriguing questions regarding the underlying physics. Understanding these non-trivial phenomena demands a combined theoretical and experimental effort. While the exact mechanisms remain under ongoing investigations, it is widely acknowledged that emergent phenomena often arise in the presence of strongly correlated electrons with reduced dimensions, in many cases in proximity to quantum critical points.

This thesis contributes to the exploration of a relatively unexploited and highly fertile collection of van der Waals magnetic insulators known as transition metal phosphorous trichalcogenides, denoted as $TMPX_3$ ($TM = \text{Mn, Fe, Ni}$, $X = \text{S, Se}$). These compounds have proven to be ideal examples where structural, magnetic and electronic properties evolve into novel states when their dimensionality is tuned with a clean and controllable parameter, pressure. At ambient pressure, they are two-dimensional van-der-Waals antiferromagnets with strongly correlated physics. Recent experimental findings have unveiled pressure-induced dimensionality crossover, crystalline structure change, insulator-to-metal transitions and the emergence of novel magnetic phases and superconductivity.

Solving high-pressure structure models, particularly in terms of interplanar stacking geometry, has posed challenges due to the nature of van der Waals materials, which often exhibit mosaicity in single crystals or strong preferred orientation in powder samples. To elucidate the relationships between structural transitions, magnetism and electronic properties, this thesis employs a random structure search using first-principles calculations at high pressures and Density Functional Theory (DFT) + Hubbard U studies. FePS_3 has been chosen as the stereotype compound within the family and has been investigated thoroughly. The coexistence of the low- and intermediate-pressure phases has been carefully examined and explained with theoretical models. Additionally, novel high-pressure phases with distinctive

dimensionality and possible alternative options for interpreting the origins of metallicity have been predicted. The validity of the methodology can be extended to other compounds within the family.

The thesis also presents a comprehensive high-pressure synchrotron X-ray study of FePSe_3 using both single crystal and powder samples at the Diamond Light Source. Although FePSe_3 shares a similar intraplanar configuration with FePS_3 , it exhibits differences in interplanar stacking at both ambient and elevated pressures. Pressure-induced superconductivity has only been reported in the FePSe_3 so far, occurring at 2.5 K and 9.0 GPa. Despite challenges in defining the crystalline structure models at high pressure, this work provides definitive crystallographic insights into the phases that emerge under pressure. Additionally, magnetic phases have been explored using powder samples within a specially designed pressure cell, with results obtained at the Institut Laue Langevin.

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Chapter 1

Introduction and Background

In recent years, there has been accumulating evidence, revealing novel quantum states in condensed matter physics. These states encompass phenomena such as strange metallic behaviour in certain materials and the emergence of unconventional superconductivity. It has become increasingly clear that these non-trivial states cannot be explained within the framework of the conventional theory of matter at low temperature. New theoretical models, along with the continuous experimental discoveries, are necessary.

One of the most established example is the discovery of "high-temperature superconductivity" in the layered cuprates by G. Bednorz and K.A. Müller in 1986 [1]. Since then, the study of high-temperature superconductivity and more generally that of strongly correlated systems has presented a host of complex challenges and intriguing phenomena. This landmark discovery opens a major and formidable chapter in condensed matter physics, which continues to be a fruitful resource for research projects to this day.

Beyond the fundamental significance, the unconventional electronic and magnetic properties possess essential potential for groundbreaking applications. They can lead to innovative applications such as spintronics with faster and more energy-efficient computing capabilities, high-speed train constructed on superconducting magnets and so on. Intensive research efforts are required to address the associated challenges of these materials in order to realize their full capabilities for practical applications.

This thesis is organized into several chapters, each addressing specific aspects of the research. Chapter 1 begins by elucidating examples of deviations from the conventional theory of metals, focusing on the behaviour of strongly correlated electrons within the system and the role of dimensionality in shaping these phenomena. Then it goes on to explore the emergent

phenomenon on the border of quantum phase transitions. In Chapter 2, the focus shifts to the subject matter of this thesis, the $TMPX_3$ compounds. Here, I will introduce the compounds and provide the necessary context for understanding subsequent discussions. Chapters 3 and 4 introduce the methodologies employed in this research, which are instrumental in deriving the results presented in Chapters 5-8. In the last chapter, I will summarise the key results and discussions, and provide insights into the prospects for further exploration within this research domain.

1.1 Strongly Correlated Electron Systems

1.1.1 From Fermi Liquid to Strongly Correlated Electrons

Correlation effects among electrons in solids are indicated, though not formally recognised as such at the time, by early experimental observations. These observations include the persistence of magnetisation in ferrous materials, the phenomenon of superconductivity in mercury (Hg) at low temperatures [2] and the curious case of NiO, being an insulator despite having partially filled $3d$ bands [3]. The field was particularly excited by the 1986 discovery of unconventional superconductivity in cuprates, observed in a narrow regime on the border of magnetism [1]. These solid experimental observations cannot be explained within the context of the conventional Fermi-liquid theory, which describes most metals at low temperatures [4], or the traditional Bardeen-Cooper-Schrieffer (BCS) theory, which is formulated under the weak electron pairing assumption [5].

These collective behaviours, in sharp contrast to the collective behaviour of individual non-interacting electrons, necessitate a deviation from the conventional models based on the one-electron (or one-quasiparticle) approximation for instance in silver and gold. A new theory different from the previous models based on free electrons is required. This is encapsulated by the phrase "more is different", as Nobel laureate Philip Anderson titled his 1972 Science paper [6]. Since then, strongly correlated electronic materials have evolved into one of the most intensively explored research areas in condensed matter physics.

Materials characterised by strongly correlated electrons exhibit a broad range of interesting phenomena, including high-temperature superconductivity and colossal magnetoresistance. These novel properties hint at evolutionary applications in quantum electronics, superconducting spintronics and more efficient energy harvesting and conversion.

1.1.2 Insulators with Half-filled d Bands

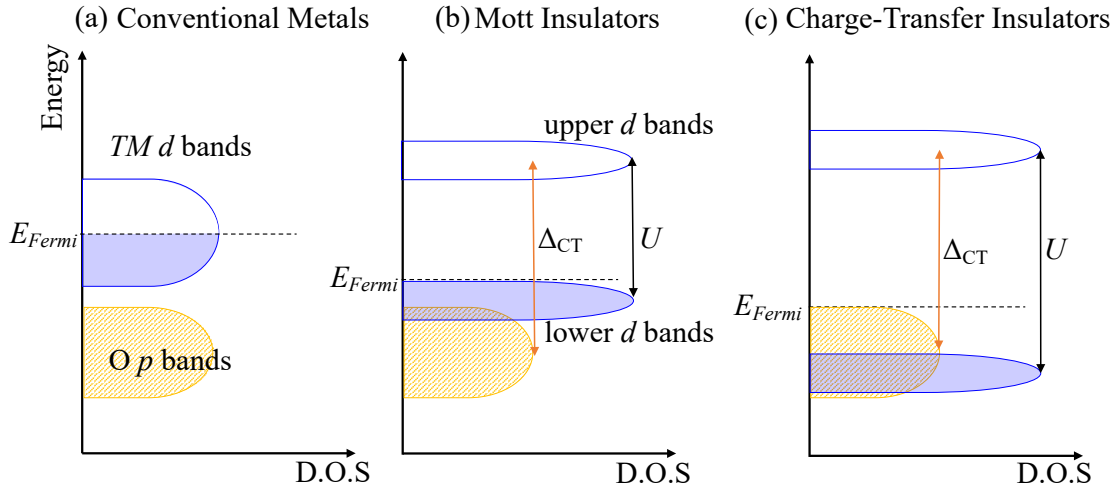


Fig. 1.1 The energy bands density of states (D.O.S.) for (a) conventional metals, (b) Mott insulators and (c) Charge-Transfer insulators. The shaded orange area represents the fully occupied ligand p bands, for instance, oxygen (O). The blue region represents the d bands of the TM atoms, shaded being occupied while white being empty states. The Hubbard U and charge-transfer energy cost Δ_{CT} terms are indicated with black and orange double arrows, respectively.

Mott insulator is an instructive example for demonstrating the fundamental principles underlying strongly correlated electrons. According to the conventional Fermi Liquid theory, systems with half-filled d orbitals would be anticipated to exhibit metallic behaviour characterised by the free movement of electrons within the material. However, intriguing deviations from this anticipated metallic behaviour have been observed in multiple systems, with the case of NiO serving as a prominent example [3].

In 1968, Sir Nevill Francis Mott addressed this phenomenon systematically in his paper titled "Metal-Insulator Transition" [7]. He explained that the Coulomb repulsion between electrons hinders free motion and ultimately leads to the localisation of charge carriers within the d orbitals. Such localisation in the d -electrons is usually associated with transition metal (TM) atoms, and effectively turns a predicted metal into an insulator.

Take transition-metal oxides as the illustrating example. A schematic representation of the metal-to-insulator transition is depicted in Fig. 1.1. It is essential to recognise that the systems subject to investigation are typically composed not only of TM atoms but also of ligand atoms such as oxygen (O) or sulphur (S). In transition-metal oxides, for instance, the energy of the oxygen p -band is close to that of the TM d -bands. Consequently, the

p -bands effectively play a significant role in the system's physical properties. Typically, the oxygens exist in the O^{2-} state, possessing fully occupied p bands. Meanwhile, the d bands accommodate a certain number of d -electrons in the d^n configuration. There are two essential terms regarding transition-metal oxides with half-filled d -electrons being insulators [8], seen from the schemes in Fig. 1.1:

- One is the Hubbard term U , which accounts for the Coulomb repulsion between electrons occupying the same orbital. That is, it quantifies the energy cost associated with placing two electrons with opposite spins into the same orbital within the d -bands. It is a critical term to describe the transition from the conventional picture of metals to Mott insulators.
- In addition to the standard Hubbard repulsion term, there exists another type of excitation in transition metal oxides. Electrons from the occupied oxygen p -bands can be transferred to the d -bands of the TM ions at an energy cost of Δ_{CT} . During the process, the charge state for the TM and O will change coherently. The corresponding compounds are known as charge-transfer insulators.

1.1.3 Unconventional Superconductors

Another pivotal example demonstrating the strongly correlated electrons is the high- T_c superconductors, from the first discovery of cuprates [1, 10] to the second generation of Fe-pnictides [11].

The Barden-Cooper-Schrieffer (BCS) theory, formulated in the late 1950s, predicted that the critical transition temperature T_c of conventional superconductors (SC) could not exceed 30 K [5]. In BCS's framework, electrons form Cooper pairs and simultaneously undergo condensation into a superconducting state. The fundamental fact is that despite the strong direct Coulomb repulsion, the relatively weak attractions between electrons mediated by lattice vibrations (phonons) can bind electrons into pairs at energies lower than the typical phonon energy.

In 1986, Bednorz and Müller [1], for the first time, observed superconductivity at approximately 30 K in the bulk $La_{2-x}Sr_xCuO_2$ compounds. Two years later, Sheng *et. al* identified another compound featuring similar copper oxide planes, exhibiting a T_c as high as 120 K [10]. Further studies pushed the T_c to a remarkably elevated value of approximately 165 K under pressures of up to about 30 GPa in mercury-based triple layer cuprates [12]. Fig. 1.2

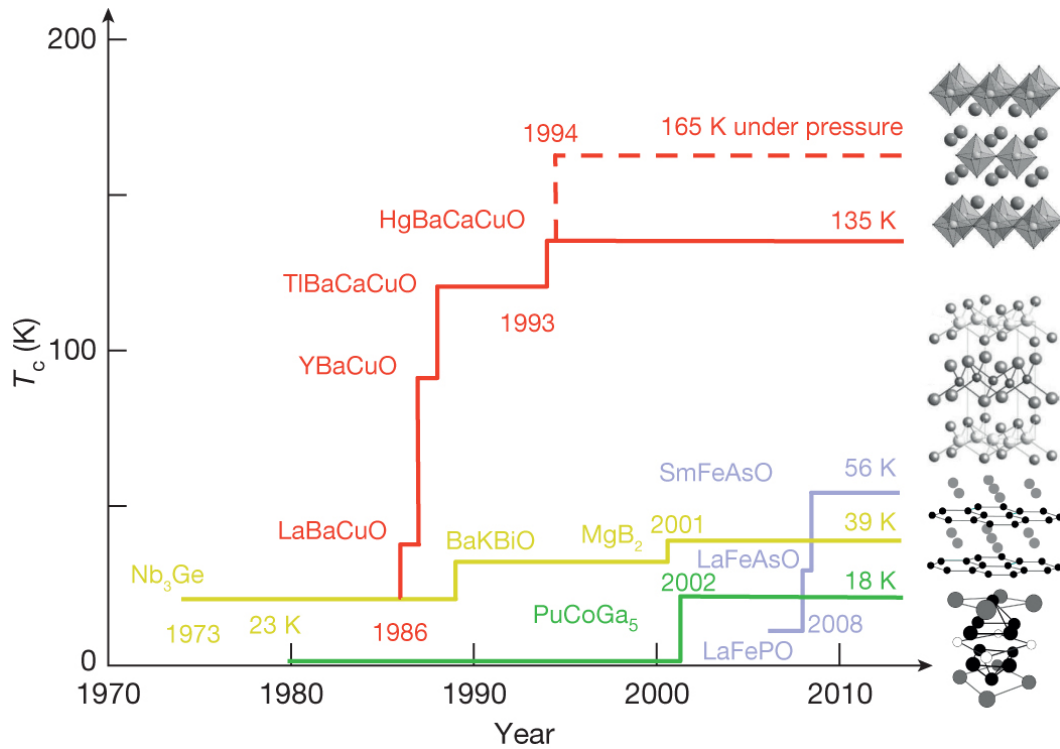


Fig. 1.2 The superconducting transition temperatures T_c versus years of discovery for conventional electron-phonon superconductors (yellow), heavy fermion superconductors (green, purple) and the record holders of the cuprates family (red). The insert on the right are the crystal structures of representative compounds. This figure is cited from Ref. [9].

highlights in red the development of elevated critical temperatures (T_c) over recent decades in these compounds, known as high T_c cuprates, in contrast to conventional superconductors or heavy fermion superconductors.

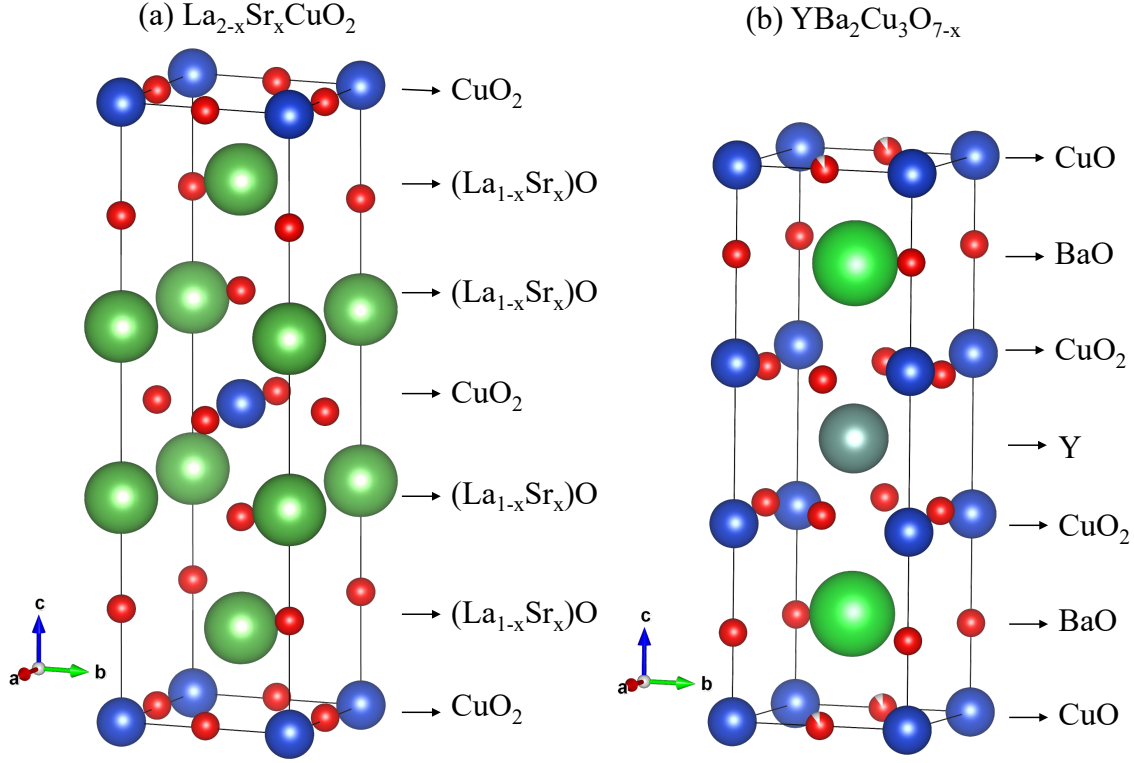


Fig. 1.3 The crystalline structures of two prototypical cuprate high- T_c superconductors, (a) $\text{La}_{2-x}\text{Sr}_x\text{CuO}_2$ [13] and (b) $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ [14]. These structures have been visualised using VESTA, and the crystallographic planes are indicated on the right side of each diagram.

Various studies have attempted to address the mechanism of the unconventional superconductivity in cuprates [9]. The superconducting state is usually obtained by doping the antiferromagnetic Mott insulator precursors. The dominant microscopic interactions have been understood as arising from the interplay of strongly correlated electrons, amplified by Coulomb repulsion, in both the undoped Mott insulator precursor state and the doped superconducting phase. The intricacies of Mott physics and the antiferromagnetic correlations inherited from the undoped precursor compound combine to allow for the emergence of various forms of order.

It is worth emphasising that all these distinctive physical properties find their origins in the underlying crystal structures, as shown in Fig. 1.3. It can be seen that cuprates feature two-dimensional planes of the Cu-O. As suggested by elementary analysis, dimensionality is a critical parameter for achieving an elevated superconducting transition temperature

[15, 16]. Previous cases have supported this analytical result. For instance, the maximum superconducting transition temperature increases and the superconducting dome expands by stretching the simple cubic CeIn_3 into quasi-two-dimensional GeMIn_5 ($M = \text{Co, Rh or Ir}$) [17].

This exploration naturally leads to another significant concept, namely, the manifestation of long-range-order magnetism within two-dimensional crystal planes. Further elaboration on two-dimensional magnetism will be provided in the subsequent section.

1.2 Two-dimensional Magnets

Two-dimensional (2D) materials possess many intriguing properties compared to their 3D counterparts, as the number of atomic layers introduced a new degree of freedom in the 2D layered structure. A typical example is the van der Waals (vdW) compound graphene, which is rich in physics via simple mechanical exfoliation using Scotch tape. The relatively small band gap of graphene ($\sim 8.6 \text{ e}^{-7} \text{ eV}$) hindered broader applications and intrigued extended explorations into other 2D vdW systems, such as MoS_2 , transition-metal dichalcogenides and so on.

For several decades, however, the study of magnetism in low-dimensional systems has been inhibited due to an emphasis on looking at dimensionality largely through the length of the well-known Hohenberg-Mermin-Wagner theorem [18, 19]. This area did not get much attention until the recent observation of intrinsic long-range magnetic order in 2D materials, including the ferromagnetic (FM) conductor Fe_3GeTe_2 [20], magnetic insulator $\text{Cr}_2\text{Ge}_2\text{Te}_6$ [21] and antiferromagnetic (AFM) insulators $T\text{MPX}_3$ ($TM = \text{Mn, Fe, Ni, V, etc.}$, and $X = \text{S, Se}$) [22–24], which are the focus of this thesis. It has been found that magnetic anisotropy could open up an excitation energy gap to counteract the enhanced thermal fluctuations in low dimensional materials [25]. Different from conventional thin films [26], 2D materials bound only by van der Waals (vdW) interactions offer more precise manufacturing control and reproducibility [27–29]. They can be more easily decoupled from the substrate and thus free from the problems arising as a result of inter-facial hybridisation, atomic diffusion, strain, crystalline reconstruction, finite-size islands and irregular shapes.

In the following section, I will recap the conceptual principles of intrinsic long-range-order magnetism in two dimensions and discuss the recent discoveries of exotic phenomena in 2D magnets.

1.2.1 Breakdown of Hohenberg-Mermin-Wagner (HMW) theorem

Macroscopically, magnetism is the phenomenon of many-body electron interaction involving both short- and long-range orderings. For a long time, 2D systems have been excluded from hosting long-range magnetic order at finite temperature due to excited thermal fluctuations and the absence of spontaneous symmetry breaking by the Hohenberg-Mermin-Wagner theorem [18, 19]. In 1988, M. Bander and D. L. Mills argued that small anisotropy could enable ferromagnetism in thin films [30]. Latter efforts have clarified that the exclusion of long-range order in itinerant electron systems is only constrained within isotropic Heisenberg systems. Magnetic anisotropy is one of the key factors that can remove the constraint [25].

Magnetic anisotropy describes the directional dependence of a material's magnetic moment. The magnetic moments on hosting atoms are in essence not uniform in all directions but have preferred orientations, known as easy magnetisation axes or planes. Deviation from the easy axes or plane will impose an additional energy penalty on the system, anisotropy energy. Under such circumstances, an excitation energy gap opens up, and, thus stabilises the long-range magnetic order in 2D compounds.

Magnetic anisotropy can arise from spin-orbit coupling, crystal symmetry, the presence of external fields, or structural defects within the material. In this thesis, I will focus mainly on magneto-crystalline anisotropy, which is an intrinsic property originating from the spin-orbit interaction of the electrons. The spatial arrangement of the electron orbitals is strongly coupled to the crystallographic structure. Consequently, the spins are forced by the electrons interaction to align along the well-defined crystallographic axes. The crystal symmetry of the lattice structure (crystal anisotropy) is thus responsible for the magnetic anisotropy.

1.2.2 Magnetic Exchange Interaction

In this section, I would like to brief on another important concept in the area of magnetism, that is, the exchange interaction between individual atoms. In general cases of magnets in the absence of an external magnetic field, the spin Hamiltonian can be written as Eq. 1.1.

$$\hat{\mathcal{H}} = - \sum_{\langle ij \rangle} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j - \Delta \sum_i (S_i^z)^2 \quad (1.1)$$

When there exists strong anisotropy, that is $\Delta \gtrsim \max(|J_{ij}|)$, it can be simplified as Ising Hamiltonian as below,

$$\hat{\mathcal{H}}_{Ising} = - \sum_{\langle ij \rangle} J_{ij} S_i^z \cdot S_j^z - H^z \sum_i S_i^z \quad (1.2)$$

The exchange interaction in the system's spin Hamiltonian itself can be complicated depending on to which extent the neighbouring coupling is considered. If only the nearest-neighbour coupling (J_1) affects, the system would be antiferromagnetic on bipartite lattices when $J_1 > 0$. If the next-nearest-neighbour coupling (J_2) is turned on, frustration would be introduced into the system if J_2 is of the same sign as J_1 [31, 32].

1.2.3 van der Waals Magnets

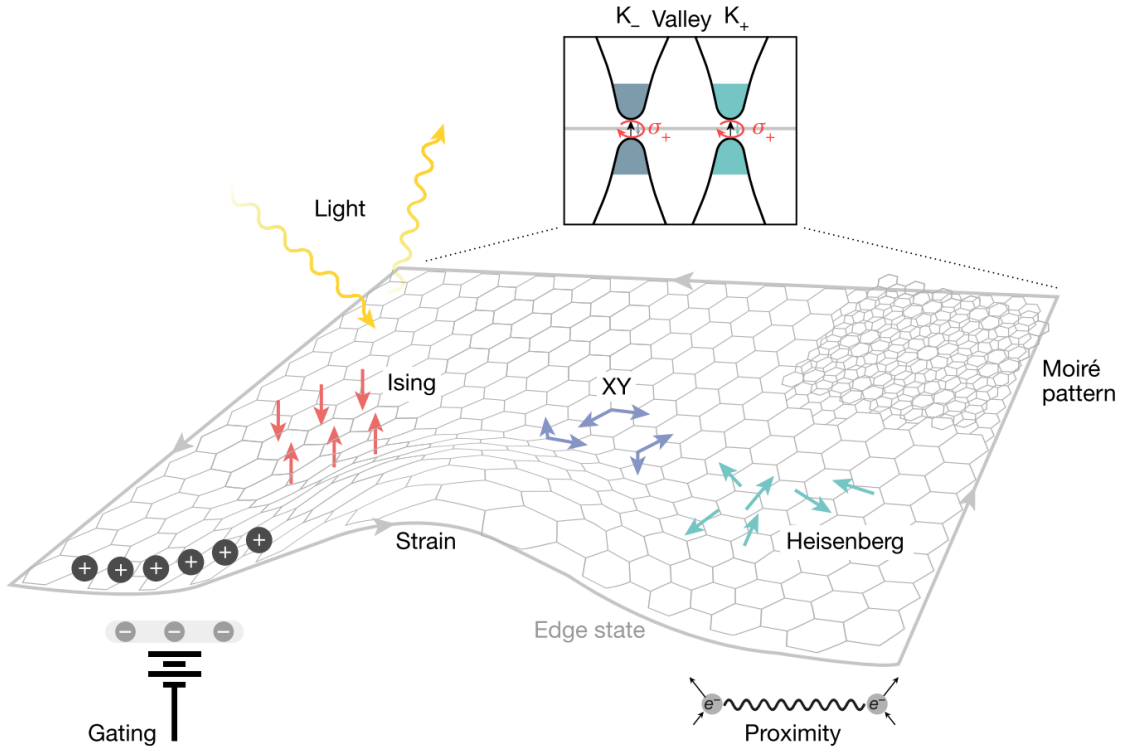


Fig. 1.4 The various phenomena in magnetic van der Waals materials and different Hamiltonian models in the 2D limit. This figure is cited from [33].

Though the theory has been revised, intrinsic 2D magnets are still rare in practice. Among them, the van der Waals magnets present a promising branch and open a brand-new chapter for fundamental exploration and applications, removing the limitation of quantum size effects on the traditional Moore's law. Fig. 1.4 summarises a collection of various phenomena and

the corresponding Hamiltonian models in magnetic van der Waals compounds. The magnetic moments in different Hamiltonian systems (Ising, XY and Heisenberg models) are indicated by arrows (red, purple and cyan, respectively) in the 2D limit. The magnetic ground states of these materials could be controlled by external perturbations, including gating and strain, or via proximity effects and moire patterns. The honeycomb lattice also allows the possibility of light-matter interactions through valley coupling of K_- and K_+ points in the momentum space and the edge states (grey arrows).

The well-established chemical vapour transport flux zone control method is an effective and reliable technique that can synthesise high-quality crystalline layered magnets, including $TMPX_3$ [34]. The choice of flux and precise temperature zone control are critical factors in successfully growing crystals.

More recently, there have been numerous demonstrations of synthesising van der Waals magnets using methods such as chemical vapour deposition or molecular beam epitaxy. These advancements in synthesis feasibility open the door to broader applications of these materials.

However, it's worth noting that achieving a fundamental understanding of emergent phenomena in the 2D limit of magnetism and strongly correlated electrons still requires a substantial research effort.

1.2.4 Emergent Phenomena and Quantum Criticality

Systems exhibiting two-dimensional intrinsic long-range magnetic ordering, combined with strongly correlated electrons, provide an ideal platform for exploring emergent novel states in response to external tuning parameters such as pressure, strain, and chemical doping. In the following discussion, I will use cuprates as an illustrative example. In the phase diagram shown in Fig. 1.5, nontrivial states emerge at the boundaries of antiferromagnetic ordering. These states are primarily studied as emergent phenomena in close proximity to the antiferromagnetic ordering and are closely related to quantum fluctuations. To understand how the states are identified as nontrivial, it is essential to revisit the concept of phase transitions.

The process in which a system changes from one state to another is commonly referred to as a phase transition. The Landau theory, initially proposed by Lev Landau in 1937 and later extended [4, 35], provides a phenomenological approach to describe phase transitions in general. The description is based on the mean-field approximation assumption near a phase

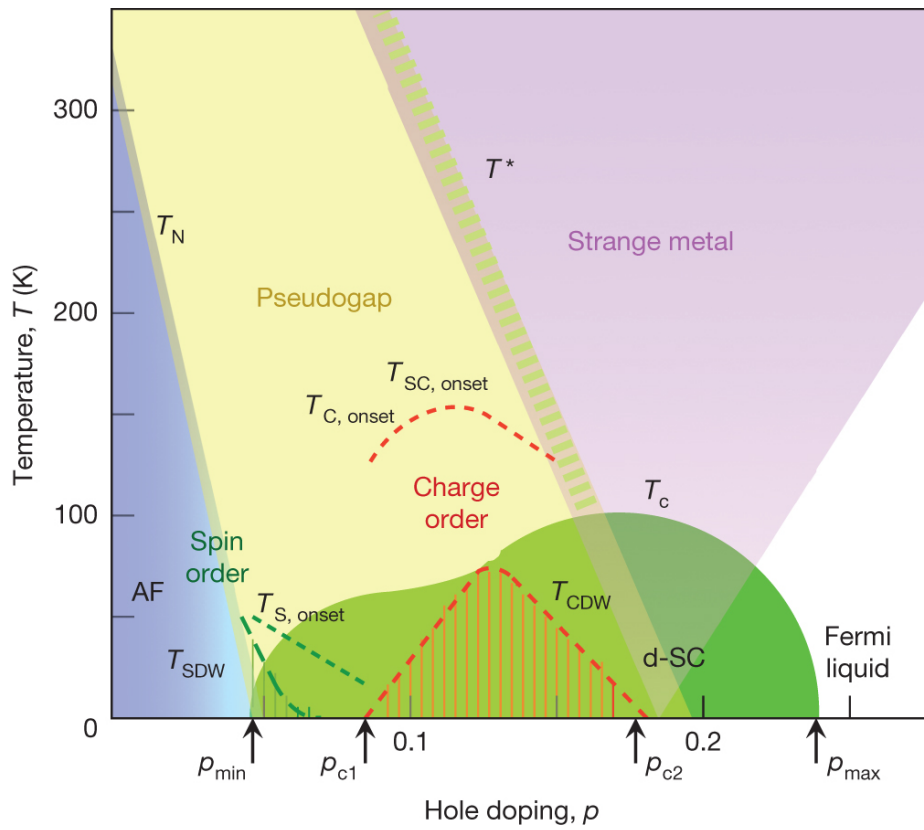


Fig. 1.5 The phase diagram of cuprate compound with various phases. The blue represents the antiferromagnetic ordered states while the green indicates the superconducting region. The arrows point out the quantum critical points. This figure is cited from Ref [9].

transition. In the absence of a conjugate external field, the free energy F can be expressed analytically as a Taylor expansion of the order parameter ϕ . A detailed description of Landau theory and its extensions, from classic to quantum mechanics, can be found in numerous textbooks. Here, I would like to highlight one of its key outcomes, the critical exponents.

In a continuous phase transition, often referred to as "second-order", fluctuations of ϕ become critical near the critical transition temperature T_c . The critical and divergent behaviour of thermodynamic physical properties can be expressed as power laws with respect to the reduced temperature t , where t is defined as $(T_c - T)/T_c$. These power laws are listed in Eq. 1.3 for specific heat C_P , order parameter ϕ , susceptibility χ and correlation length ξ .

$$C_P \sim |t|^\alpha \quad (1.3a)$$

$$\phi \sim t^\beta \quad (1.3b)$$

$$\chi \sim |t|^{-\gamma} \quad (1.3c)$$

$$\xi \sim |t|^{-\nu} \quad (1.3d)$$

The corresponding critical exponents (α, β, γ and ν) are dimensionless and possess qualitative significance in describing continuous phase transitions [36]. Notably, these critical exponents remain the same for systems of the same class, regardless of factors like the alignment of spins in itinerant systems, the emergence of superconductivity, or even the formation of the Universe [37]. This concept is known as the "Universality Hypothesis". However, recent observations challenge this hypothesis, particularly in the low-temperature regime where critical exponents deviate from known classes. In most cases, these deviations occur in systems with strongly correlated electrons or reduced dimensionality.

Moreover, as physical properties can be experimentally measured using various techniques, the corresponding critical exponents can be obtained through experimental means and compared with theoretical predictions. Previous studies of systems with strongly correlated electrons have indeed shown deviation from the behaviour exhibited by conventional Fermi-liquid compounds. More recently, further deviations have been observed in materials like FePS₃ and SrTiO₃ at sufficiently low temperatures using high-precision measurement setups. None of the existing theoretical models are able to provide a comprehensive explanation for these observations. Quantum fluctuations are suspected to be the driving force behind these novel quantum orderings, which become enhanced in the vicinity of a quantum critical point [38]. For instance, there has been a growing interest in exploring quantum criticality in two-dimensional magnets due to the naturally enhanced spin fluctuations [39]. A prominent emergent phenomenon is the appearance of a superconducting dome on the border of the

magnetic ordering, as exemplified in Fig. 1.6 for antiferromagnetic and ferromagnetic cases, respectively.

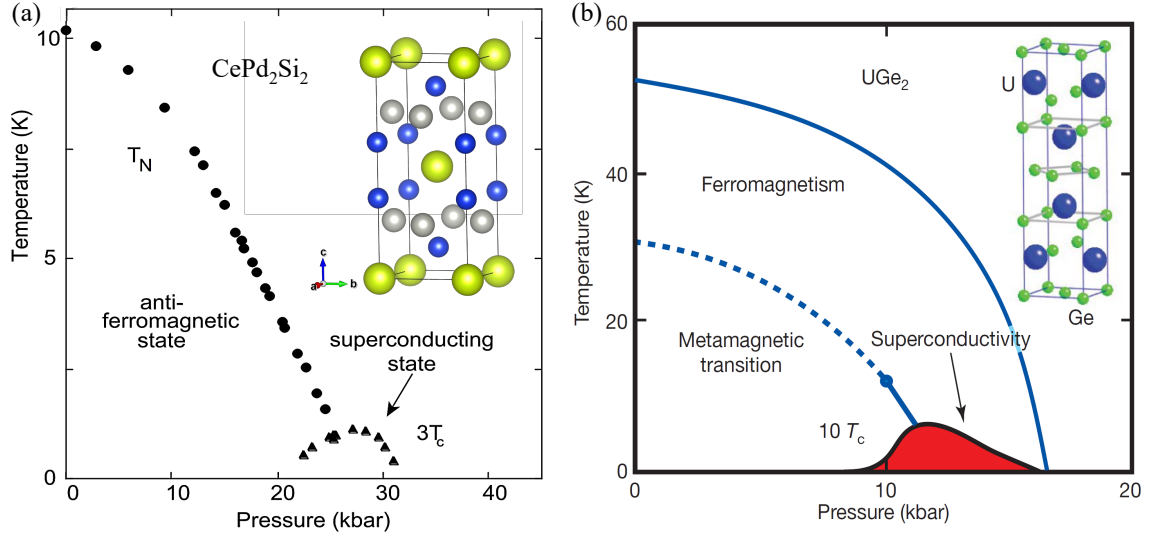


Fig. 1.6 The temperature-pressure phase diagram of (a) CePd_2Si_2 [40] and (b) the ferromagnetic superconductor UGe_2 [41, 42]. There is only one superconducting dome in both cases on the border of magnetic ordering.

1.3 Promising Research Scheme and Aims of the Thesis

The quest to understand the enigma of emergent novel phenomena, distinct from conventional descriptions, continues to motivate scientific exploration in the realm of systems with strongly correlated electrons and reduced dimensionality. Recent investigations have revealed that the pairing mechanisms for unconventional high-temperature superconductors are notably enhanced in two-dimensional compounds, particularly within the realm of intrinsic 2D magnets, a domain that was overlooked for a long time [43, 33]. While it has been widely acknowledged that strongly correlated electrons and magnetism in the 2D limit are the underlying playground for the emergent phenomena, the complex interactions and proximity to the quantum criticality point present formidable challenges that demand collaborative efforts.

This thesis is motivated by the desire to explore the complex underlying mechanism in simpler compounds, utilising a clean and controllable tuning parameter (here, pressure). This approach allows us to minimise uncertainties and avoid extra complexities such as dislocations introduced by chemical dopings. In cuprates, for instance, the unconventional

superconducting phase is obtained from doping the antiferromagnetic Mott insulator precursors. In addition, cuprates, being ionic compounds, are more difficult to compress compared to other covalent compounds.

This thesis focuses on a novel compound family, the transition metal chalcogenophosphates ($TMPX_3$). These van der Waals compounds possess intrinsic long-range-order antiferromagnetism and exhibit strongly correlated physics at ambient pressure. Recent studies have reported various pressure-induced transitions in crystalline structures, transport and magnetic properties in these compounds, including emergent superconductivity. We aim to establish a fundamental and comprehensive understanding of the phase transitions in the $TMPX_3$ compounds. A careful understanding of these simpler model compounds could provide insights into more complex systems.

In the forthcoming chapter, I will provide an overview of the structural, electronic and magnetic properties inherent to the $TMPX_3$ compounds, both at ambient and high pressures.

Chapter 2

TMPX₃ Family

The $TMPX_3$ compounds were first discovered by C. Friedel in 1894 [C. Friedel, Compt. Rend. 119, 240 (1894)]. Initially, they gathered significant attention regarding their promising applications as new anode materials for Lithium-ion batteries [44, 45], including recent extensions as layered active materials for rechargeable Mg-batteries and other energy storage applications [46]. They are non-toxic and air-insensitive materials. The appeal to study these compounds is not limited to battery technology.

They are two-dimensional (2D) materials with tunable electrical and magnetic properties, and have substantial potential in the design of atomically thin devices for data storage, quantum computing [27], clean energy generation related to photo-catalytic water splitting applications [47] and the very recent application in cancer therapy as magnetic resonance imaging (MRI) and photoacoustic imaging (PAI) agents [48, 49].

For several decades, however, the study of 2D phenomena in magnets has been inhibited due to particular interpretations of the well-known Hohenberg-Mermin-Wagner theorem [18, 19]. However, this is beginning to change given the recent observation of intrinsic long-range magnetic order in 2D materials, including the ferromagnetic (FM) conductor Fe_3GeTe_2 [20], magnetic insulator $Cr_2Ge_2Te_6$ [21] and antiferromagnetic (AFM) insulators $TMPX_3$ ($TM = Mn, Fe, Ni, V$, etc., and $X = S, Se$) [22–24], which are the focus of this thesis. It has been found that magnetic anisotropy could open up an excitation energy gap to counteract the enhanced thermal fluctuations in low dimensional materials [25]. Different from conventional thin films [26], 2D materials bound only by van der Waals (vdW) interactions offer more precise manufacturing control and reproducibility [28, 29]. They can be more easily decoupled from the substrate and thus free from the problems arising

as a result of inter-facial hybridisation, atomic diffusion, strain, crystalline reconstruction, finite-size islands and irregular shapes.

A recently realised advantage of 2D magnets is that they are often materials where the ground state is dominated by the physics of strong correlations. These materials thus become fertile ground for exploring novel phases and emergent phenomena. For instance, the well-known high- T_c cuprates are obtained via doping the 2D AFM precursors [1, 10]. Most recently, the pressure-induced superconductivity (SC) in the vicinity of AFM order has attracted much interest, with prominent examples being the iron-based layered compound LaFeAsO [50], FeSe [51, 52], and other transition-metal compounds e.g. MnSe [53], CrAs [54] and AuTe₂Br [55]. The phenomena of emergent unconventional superconductivity from a 2D AFM precursor have been studied extensively for decades. In such systems, reduced dimensionality is believed to enhance SC [15, 56]. However, understanding the fundamental physics of these emergent phenomena is still hindering proper theoretical formulation. One of the most prominent difficulties is that the chemical composition is challenging to be identified explicitly due to the nature of chemical doping.

In this regard, transition metal phosphorous trichalcogenides $TMPX_3$ family represents a promising new avenue of research [43, 33]. Being Mott or charge-transfer insulators at ambient pressure, the band gap of $TMPX_3$ could be tuned systematically via the application of pressure. Recent high-pressure studies have revealed spin-crossover transitions, insulator-to-metal transitions (IMT) and the emergence of novel metallic state and superconductivity in these compounds [57–62].

This thesis focuses on the pressure-induced phenomena within the $TMPX_3$ compounds family. To establish the context, I start with the ambient-pressure crystalline structures and the magnetic configurations below the transition temperature. We will also introduce the electronic properties and discuss the strongly correlated electrons at ambient pressure, followed by the recent discoveries of the pressure-induced phenomena.

2.1 Phases at Ambient Pressure

In this section, I will discuss the crystalline structures, magnetic configurations below the transition temperature and the electronic properties of the $TMPX_3$ compounds.

2.1.1 Crystalline Structures

Table 2.1 The space group symmetry, cation configuration, volume per formation unit (f.u.), lattice parameters and the Fe-Fe distances in the hexagon for $TMPX_3$ ($TM = Mn, Fe, Ni, X = S, Se$) at ambient pressure [63, 64].

	Space Group	Volume ($\text{\AA}^3/\text{f.u.}$)	Lattice Parameters, Fe-Fe distances ($\text{\AA}, ^\circ$)					
			a	b	c	β	d_1	d_2
MnPS ₃	$C2/m$	103.7	6.077	10.524	6.796	107.35	3.524	3.500
FePS ₃		98.3	5.947	10.300	6.722	107.16	3.448	3.426
NiPS ₃		92.8	5.812	10.070	6.632	106.98	3.365	3.358
NiPSe ₃		106.7	6.137	10.611	6.870	107.46	3.544	3.538
			$a = b$		c	γ	$d_1 = d_2$	
MnPSe ₃	$R\bar{3}$	117.7	6.387		19.996	120	3.687	
FePSe ₃		112.1	6.262		19.805	120	3.615	

The $TMPX_3$ compounds constitute layered lattices with the building blocks of double-layer chalcogen atoms ($X = S, Se$) sandwiching the Fe atom and P_2 pairs. The chalcogen atoms form a nearly hexagonal close-packed skeleton in the sequence of $ababab.....$ or a cubic close-packing in the sequence of $abcabc.....$. The TM atoms and P_2 pairs with axes perpendicular to the plane are accommodated in the octahedral gaps of the chalcogen sublattice. Each TM is enclosed by six S/Se in an almost perfect octahedral coordination. In the context of this coordination, one would expect the spin state of the TM^{2+} ion to be in a nearly isotropic Heisenberg state. However, subtle deviations from the characteristics of transition metals can result in the spin state being Ising in the case of Fe compounds, for example. The complex magnetic interactions will be discussed in detail in a later section. Each P is surrounded by three S/Se and one additional P in approximately tetrahedral coordination.

FePS₃ and FePSe₃ have been subjected to a full X-ray structural characterisation since 1973 [65], being the first compounds among the $TMPX_3$ family. A complete structure determination for the first-row transition metal phosphorous trisulfide was accomplished in 1985 [64]. Table 2.1 summarises the space group symmetry and the lattice information for the representative compounds within the family. MnPS₃, FePS₃, NiPS₃ and NiPSe₃ crystallise in the centrosymmetric monoclinic space group $C2/m$, while MnPSe₃ and FePSe₃

host the $R\bar{3}$ space group symmetry [63]. The crystalline structure falls into two categories, FePS₃-type and FePSe₃-type stacking, which will be discussed in the following details.

The FePS₃-type Stacking

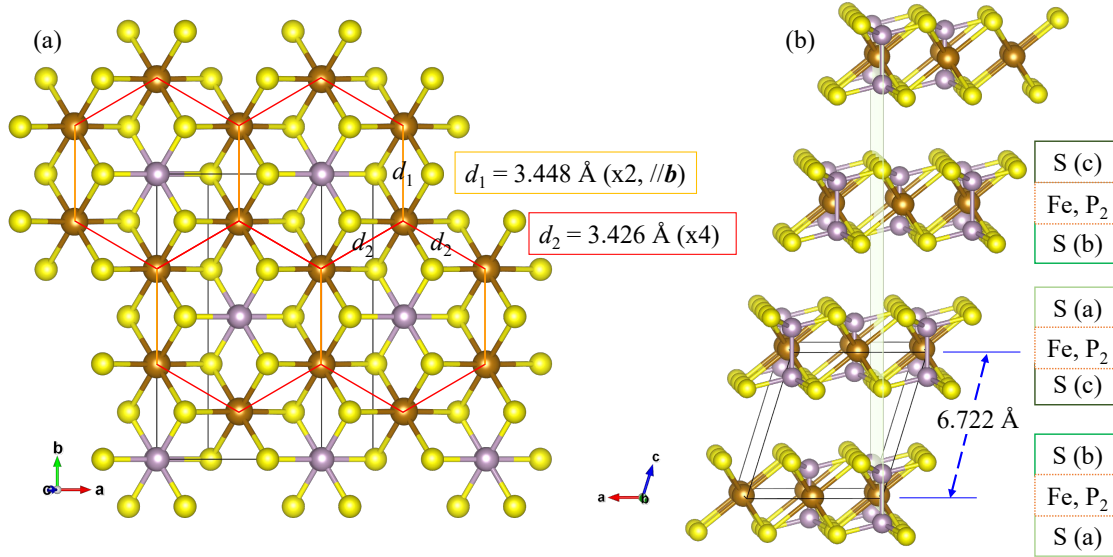


Fig. 2.1 The crystalline structure of FePS₃ with $C2/m$ space group at ambient pressure and room temperature 293 K. (a) The single-layer *ab* plane with the rigid rods indicating the Fe-honeycomb pattern. Two types of Fe-Fe nearest-neighbour distances are shown in red and orange, respectively. (b) The layered van der Waals bulk structure. The S anions are closely stacked in the *abcabc* sequence. The structures are plotted using VESTA. Brown: Fe; Yellow: S; Grey: P.

Fig. 2.1 displays the crystalline structure of FePS₃ at ambient pressure (LP phase), with the Fe²⁺ honeycomb being illustrated by rigid rods. Within each *ab* plane, consistent with the conventional cell description, the Fe²⁺ form a honeycomb skeleton with slightly elongated Fe hexagons, as displayed in Fig. 2.1 (a). The inter-site exchange within and in-between the planes is mediated through the surrounding P₂S₆ clusters, with P₂ centred within the distorted Fe hexagons. When examining each *ab* plane, one might anticipate that the Fe-hexagons would maintain the trigonal $C3$ rotational symmetry, given that each Fe site has equivalent coordination. However, the observed elongation of the Fe-hexagons in the bulk may be connected to the monoclinic stacking of these planes. The orange rods corresponding to the Fe-Fe distances along *b* axis (d_1) are 3.448 Å in length, while the red ones representing the shearing direction (d_2) are 3.426 Å. The symmetry breaking distorts the Fe hexagons by a ratio of $\frac{|d_1-d_2|}{d_1} = 0.65\%$ at ambient pressure. The *b/a* ratio is, however, only very slightly

affected, staying very close to the ideal $b/a = \sqrt{3}$. The S atoms follow a cubic close-packing in the sequence of $(ab)(ca)(ab)$, with the bracket indicating each stacking unit containing only a double layer of S atoms. Taking the Fe and P_2 layers into consideration, the effective stacking is $ABCABC.....$ for $FePS_3$ and other isostructural compounds crystallising in the monoclinic space group $C2/m$.

To be noted, $NiPS_3$ is identified to have $\sim 3\%$ disorder at the cation octahedral sites, that is, a certain amount of TM^{2+} being substituted by P_2 , and vice versa. Such substitution has also been evidenced in $V_{0.78}PS_3$ [66].

The $FePSe_3$ -type Stacking

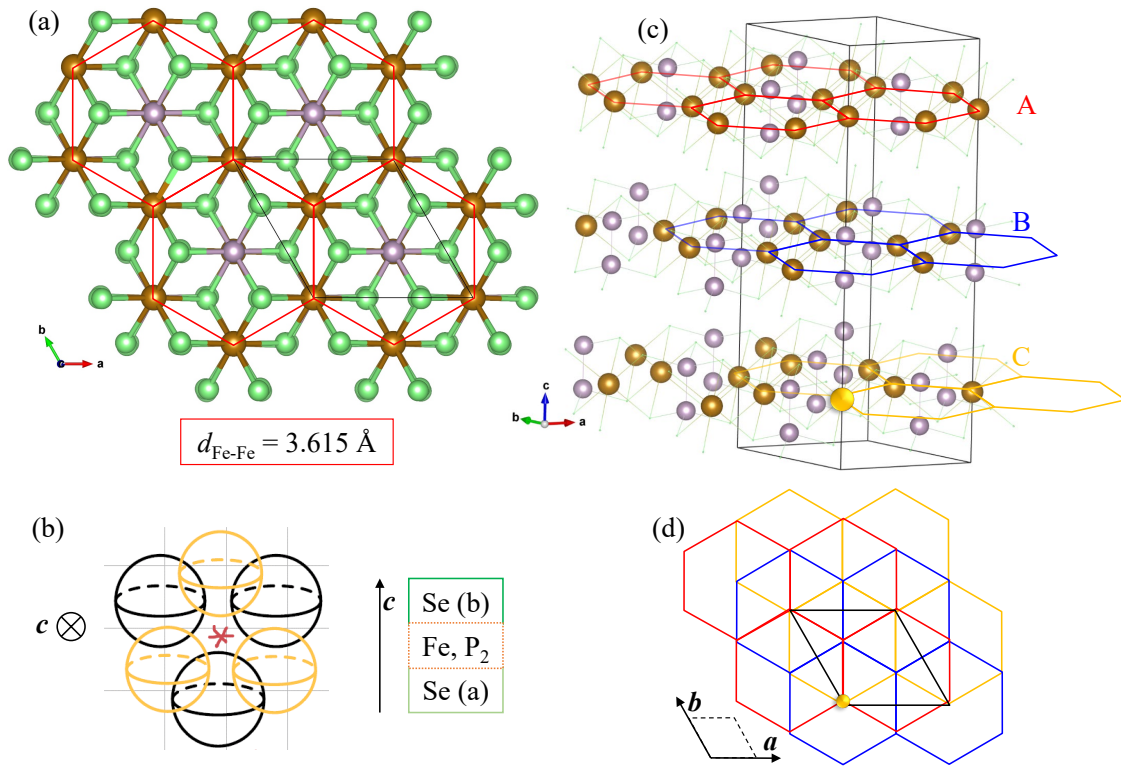


Fig. 2.2 The crystalline structure of $FePSe_3$ with $R\bar{3}$ space group. (a) The single layer ab plane with the rigid rods presents the Fe ideal hexagon. (b) The Se close packing and the illustration of the Se octahedral coordination for Fe or P_2 , are shown as the brown star. (c, d) The stacking of ABC layers viewing from the side and perpendicular directions. The structures are plotted using VESTA. Brown: Fe; Green: Se; Grey: P.

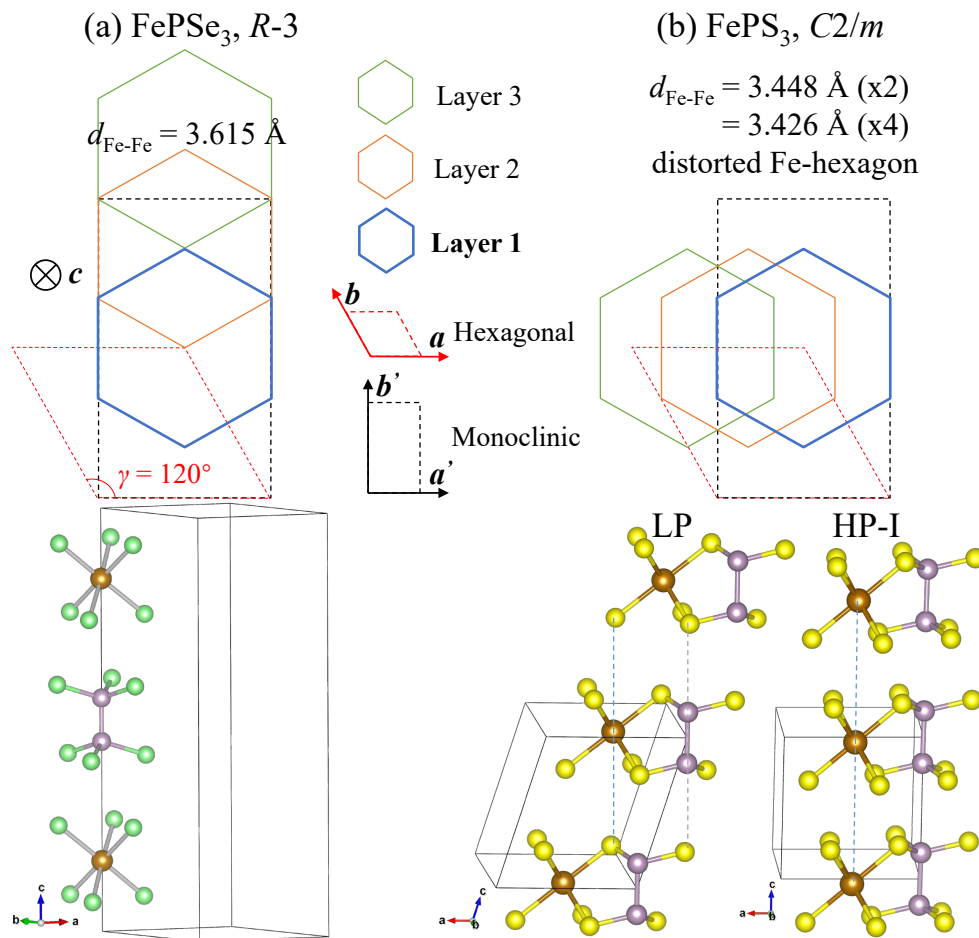
MnPSe₃ and FePSe₃ are isostructural and crystallise in the rhombohedral space group of $R\bar{3}$. Below I will use FePSe₃ as the example to discuss the structural details of the ambient pressure rhombohedral phase.

Like FePS₃ and other compounds within the family, FePSe₃ is a van der Waals layered compound. Fig. 2.3 (a) displays the stacking layer, here *ab* planes, viewing from the perpendicular stacking direction. It can be seen that the Fe atoms form an ideal honeycomb skeleton, exhibited by rigid red rods. The edge of each Fe-hexagon is measured to be around 3.615 Å. In the centre of each Fe-hexagon sits the P₂ dimer. The Fe layer is sandwiched by the chalcogen double-layer, here Se. The Se atoms form a nearly hexagonal close-packed skeleton in the sequence of *ababab*. The Fe atoms and P₂ pairs with axes parallel to the *c*-axis are accommodated in the octahedral gaps of the Se sublattice, as is illustrated in Fig. 2.3 (b). Each Fe is enclosed by six Se in octahedral coordination, while each P is surrounded by three Se and one additional P in approximately tetrahedral coordination. , forming the [FeSe₆] and [P₂Se₆] clusters, respectively.

The layers stack together in accordance with the rhombohedral stacking sequence of *ABCABC*, as shown in Fig. 2.2 (c) and (d). For clarity, I only plot the Fe and P₂ sites and use the Fe honeycomb pattern as the representative of each individual stacking layer. In contrast to the monoclinic stacking observed in FePS₃-type compounds, there is no monoclinic distortion in this case, and all Fe-hexagons remain undistorted.

Comparative Stacking Patterns

I summarise the stacking pattern's difference in Fig. 2.3 between the two distinct types of stacking in FePSe₃ and FePS₃. Both ambient pressure (LP) and intermediate pressure (HP-I) phases before the dimensionality collapse crystallise in the centrosymmetric monoclinic space group of *C2/m* [59, 67, 68]. At ambient pressure (LP), FePS₃ differs from FePSe₃ in the arrangement of the double-layer chalcogen atoms. The S atoms form a cubic close packing instead, in the sequence of *(ab)(ca)(bc).....* with the bracket indicating the layers. The cartoon in Fig. 2.4 displays the close packing of the S atoms (blue, yellow and orange solid circles representing different layers) and the octahedral sites which would host Fe atoms or P₂ dimers. The Fe-hexagon is slightly elongated in FePS₃ by a ~ 0.6% difference in the Fe-Fe distances, thus breaking the *C3* rotation symmetry. Despite the slight distortion, the Fe-honeycomb sublattice and the P₂ dimer pairs are also accommodated in the octahedral gaps in the chalcogen sublattice. And the coordination situation for Fe and P is the same.

Fig. 2.3 The stacking of FePSe_3 versus FePS_3 at ambient pressure.

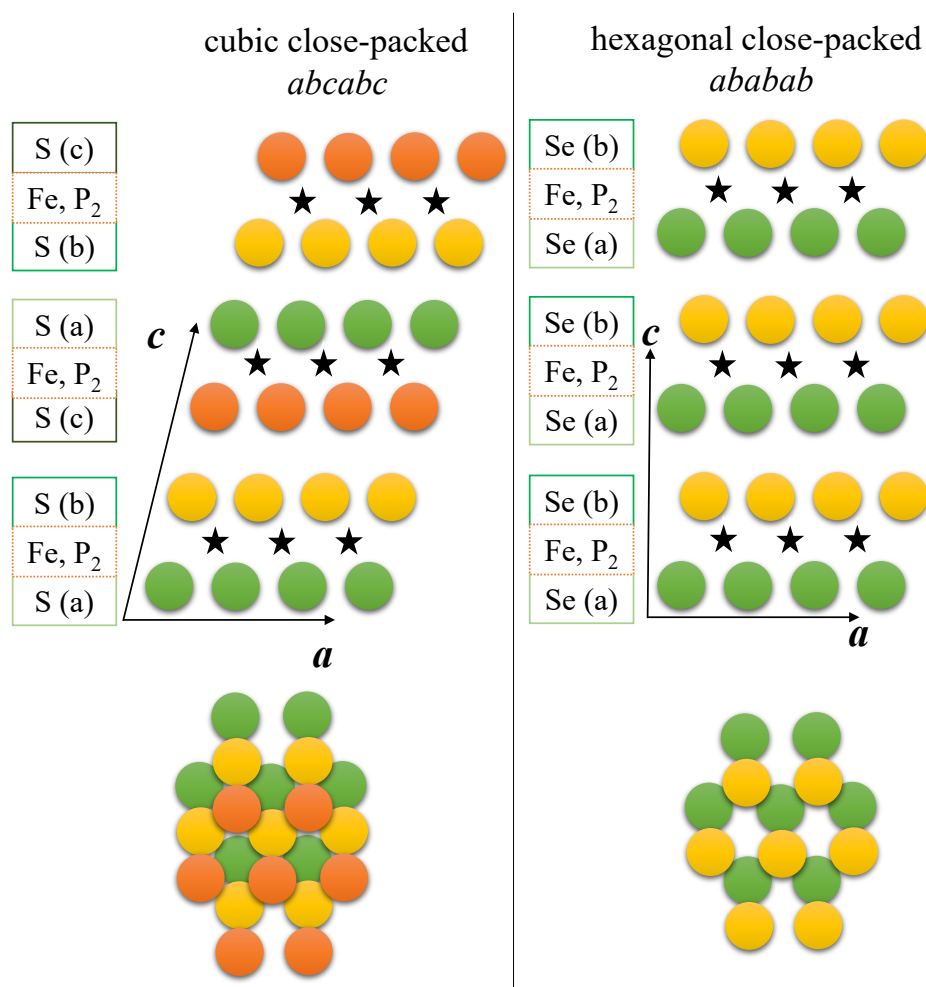


Fig. 2.4 The cubic versus the hexagonal close packing for chalcogen (S, or Se) atoms in FePS₃- and FePSe₃-type structures. The solid circles with green, yellow and orange colours represent the S or Se atoms. The black star indicates the octahedral gaps, which would host the transition metal ions or P₂ dimers.

The stacking sequence of ABCABC....., coupled with the broken $C3$ symmetry, leads to the monoclinic symmetry in FePS_3 .

Consistent with previous literature, the monoclinic cell (the black coordinates) of FePS_3 has the lattice constants $a' = 5.934(6) \text{ \AA}$, $b' = 10.28(1) \text{ \AA}$, $c' = 6.772(7) \text{ \AA}$ and the monoclinic angle $\beta' = 107.2(1)^\circ$. If we convert it into the hexagonal cell description, the two types of cells are connected as follows, $a = a'$, $b = b' / \sqrt{3}$ and $c = 3 * c' * \sin\beta$.

Looking at the stacking along the perpendicular direction of ab planes, the atoms in FePS_3 follow $[\text{Fe}(1) - \text{P}_2(2) - \text{Fe}(3)] - [\text{Fe}(1) - \text{P}_2(2) - \text{Fe}(3)]$ stacking mode. The numbers in the brackets indicate the relative layer ordering. Though the environment around P_2 dimer pairs is relatively symmetrical, the Fe atoms are in an unsymmetrical distribution. The upper and lower neighbours of each Fe atom within one layer are not identical in the Fe - Fe - P order. Meanwhile, the stacking in the LP of FePS_3 follows $[\text{S}(1) - \text{Fe}(2) - \text{S}(3)] - [\text{S}(1) - \text{Fe}(2) - \text{S}(3)]$ or $[\text{P}_2(1) - \text{S}(2) - \text{S}(3)] - [\text{P}_2(1) - \text{S}(2) - \text{S}(3)]$. The transition from LP to HP-I occurs along with a sliding of the neighbouring layers, ending with Fe from different layers lying on each other. In any case, the Fe remains in a symmetrical situation.

If we adopt the monoclinic cell description to track the stacking of the Fe-hexagon skeleton across different layers, they shift by $1/3$ along the translation direction of b' axis in FePS_3 . In FePS_3 , by contrast, the stacking shifts along the a' axis and the absolute value of translation is determined by the size of the monoclinic angle. From LP to HP-I, the absolute shifting shrinks to zero as the β approaches 90° . And the S atoms change from cubic to hexagonal close packing.

2.1.2 Temperature-induced Phase Transitions

Lattice Parameters: First VS Second-Order Transitions

In 1984, Jernberg, *et al.* investigated the temperature-dependent phase transition in FePS_3 using Mössbauer spectroscopy observation [69]. The upper part of Fig. 2.5 showed the lattice parameter change with the temperature of FePS_3 , in comparison with that of NiPS_3 . The abrupt change in a and b suggested a strong first-order crystalline structure transition. By contrast, the phase transition of NiPS_3 is second-order. The conclusion was enhanced by a subsequent differential scanning calorimetry measurement [70]. In the two heat transition plots within Fig. 2.5, an endothermic peak can be clearly observed for FePS_3 , while it is almost smoothed out for NiPS_3 . The strong first-order nature of FePS_3 with temperature, in

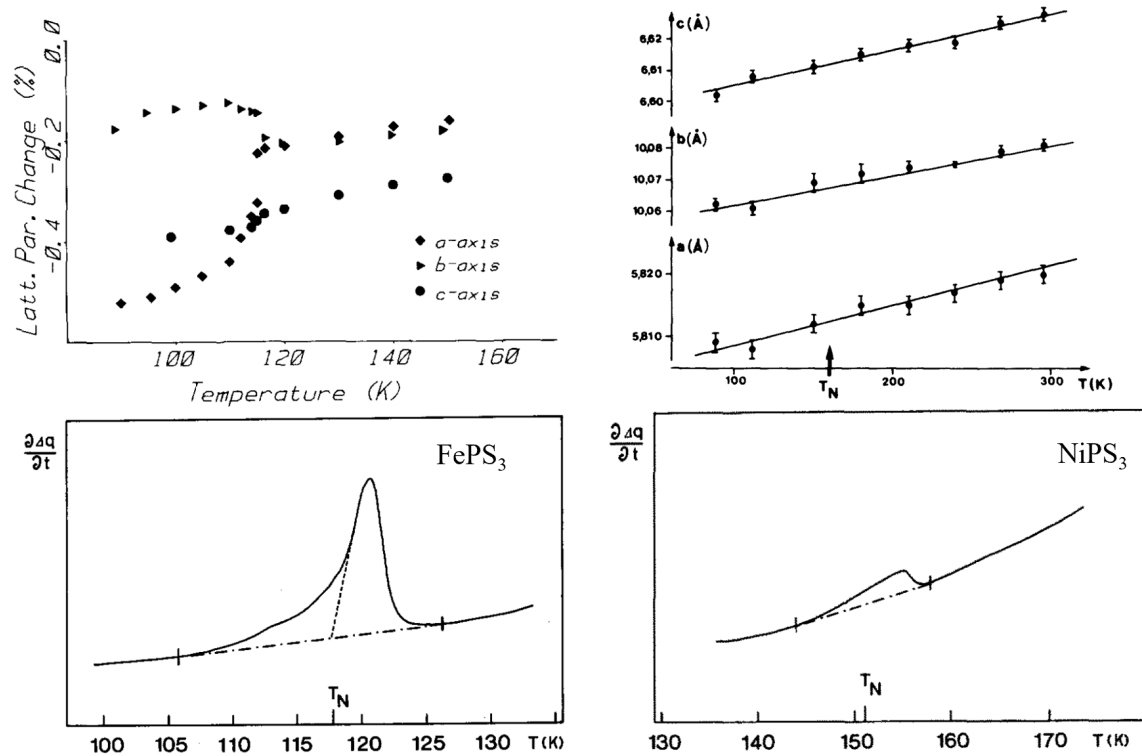


Fig. 2.5 The thermal evolution of lattice parameters [69] and heat transition [70] for FePS₃ (left), in comparison with those for NiPS₃ [70] (right). To be noted, the y-scale of heating transition in NiPS₃ is 2.5 times to that in FePS₃.

combination with the magnetic transition to be discussed in the following section, suggests large magnetoelastic coupling and strong dependence on the interatomic distances. In other words, FePS_3 would be more sensitive to external tuning parameters, e.g. pressure.

Magnetic Susceptibility and Anisotropy

The $T\text{MPX}_3$ compounds are known to exhibit antiferromagnetism below their respective Néel temperature, which is the temperature at which the slope of the magnetic susceptibility (χ) versus temperature (T) curve is maximum. Fig. 2.6 displays the measured magnetic susceptibility (χ) for MnPS/Se_3 (a, b), FePS/Se_3 (c, d) and NiPS/Se_3 (e, f) as a function of temperature (T).

1. MnPS_3 and MnPSe_3

In the case of MnPS_3 , as shown in Fig. 2.6 (a), the $\chi_{\parallel}$ (open circles) decreases rapidly with decreasing temperature, while $\chi_{\perp}$ (solid circles) remains relatively constant after reaching its maximum value. This behaviour indicates that the magnetic moments of Mn^{2+} in MnPS_3 prefer an orientation perpendicular to the ab plane.

In contrast, in selenide MnPSe_3 , $\chi_{\parallel}$ is always smaller than $\chi_{\perp}$, suggesting that the spin moments lie within the ab plane instead [72]. The substantial difference in the magnetic susceptibilities anisotropy between MnPS_3 and MnPSe_3 is quite interesting. The significant difference in magnetic susceptibility anisotropy between MnPS_3 and MnPSe_3 is intriguing and is attributed to the change in ligand field spin-orbit contributions from S to the heavier Se atom.

Last but not least, both compounds have a broad temperature range when χ approaches the maximum value. Such behaviours are argued to arise from typical spin-spin correlations in low-dimensional systems.

2. FePS_3 and FePSe_3

On the other hand, the susceptibility of FePX_3 compounds falls rapidly as T approaches T_N . Notably, $\chi_{\parallel}$ is significantly larger than $\chi_{\perp}$, and there is a clear decrease indicating T_N at ~ 120 K for FePS_3 and ~ 108 K for FePSe_3 . This behaviour is consistent with the Ising nature of the magnetic moments in FePX_3 compounds, where the moments are oriented perpendicular to the ab planes.

Recent Raman spectroscopy experiments examined the existence of Insing-type antiferromagnetic ordering down to the monolayer limit. The T_N remained almost

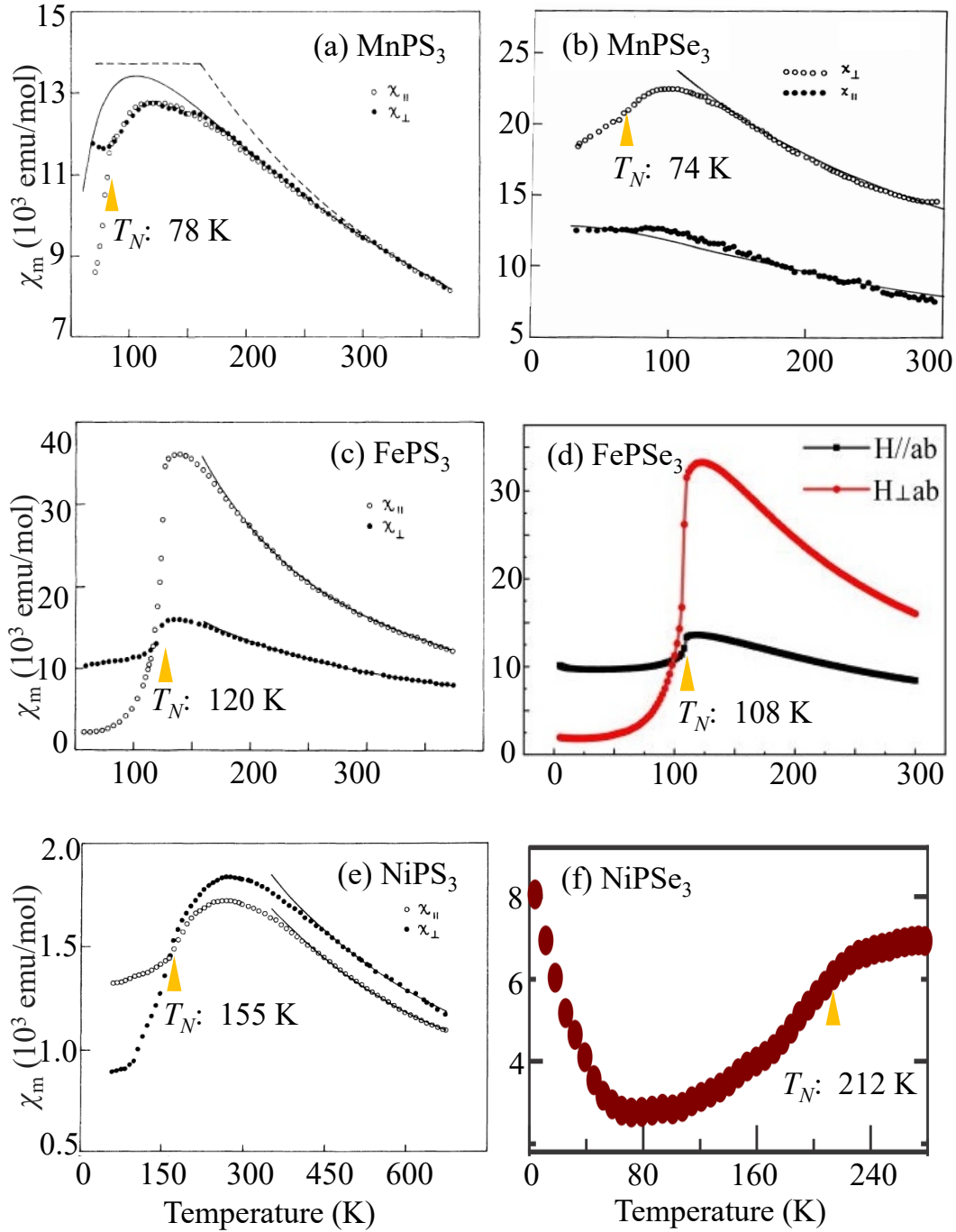


Fig. 2.6 The temperature dependence of magnetic susceptibility for (a) MnPS_3 [71], (b) MnPSe_3 [72], (c) FePS_3 [71], (d) FePSe_3 [73], (e) NiPS_3 [74] and (f) NiPSe_3 [75]. The arrow indicates the antiferromagnetic transition temperature T_N in each figure.

independent of the thickness of the samples, being measured to be ~ 118 K in the monolayer limit [24].

3. NiPS_3 and NiPSe_3

Both NiPS_3 and NiPSe_3 crystallise in the $C2/m$ space group and their T_N values increase from the sulphide (155 K) to the selenide (212 K) compound [22]. This trend differs from that observed for Mn and Fe compounds.

The paramagnetic susceptibility above T_N is isotropic, suggesting that the magnetic Hamiltonian is Heisenberg-like [74, 76]. The fact that NiPS_3 has the highest T_N in the thiophosphate family indicates more significant interplanar magnetic interactions than its sister compounds. This is also supported by recent Raman spectroscopy measurements of NiPS_3 which revealed that the long-range magnetic ordering in the compound retains only till two layers thick.

It is evident that magnetic anisotropy plays a significant role in these compounds, ensuring the stability of long-range magnetic ordering in two dimensions. Notably, the Fe compounds exhibit the most substantial anisotropy, which is consistent with the Ising nature of the spin moments on Fe sites. However, resolving the magnetic configurations in these compounds has proven to be challenging. The following section will provide an overview of the magnetic phases discussed in the latest literature.

2.1.3 Magnetic Structures

Despite their significant potential in applications such as spintronics and other fields, experimental examples of ordered 2D magnets have remained extremely rare. $TMPX_3$ compounds have been under investigation in recent decades as nearly ideal intrinsic 2D magnets, offering an alternative platform to atomically thin magnets obtained through defect engineering in materials like graphene and MoS_2 . The fundamental discoveries and studies of van der Waals (vdW) crystals with long-range magnetic order have ignited a renaissance in the field.

The following section offers a review and discussion of the current state of knowledge regarding magnetic ordering in vdW $TMPX_3$ compounds.

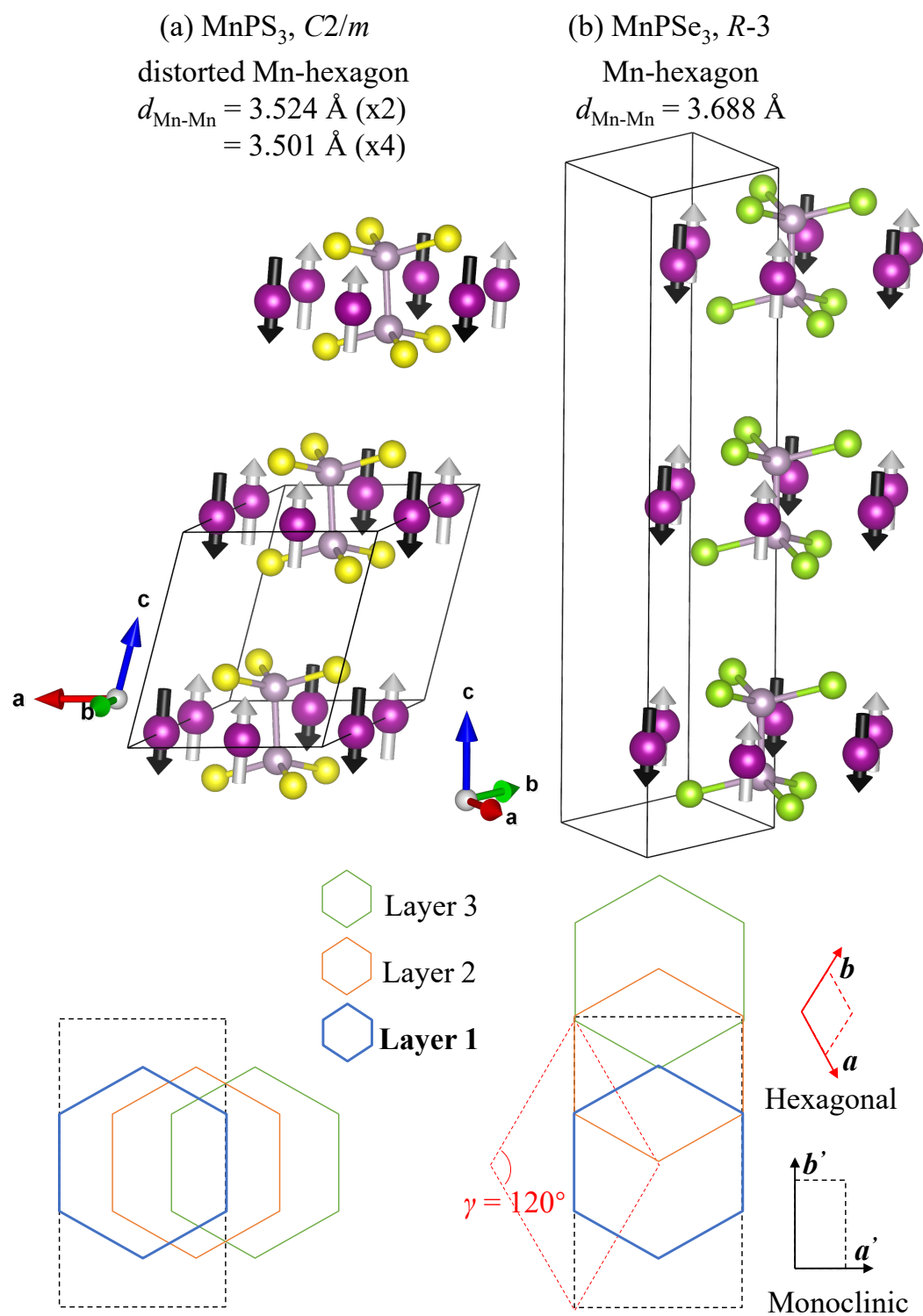


Fig. 2.7 The magnetic configuration of MnPS₃ and MnPSe₃. The structures are visualised using VESTA referring to the reported magnetic structures [77–79, 23, 63].

MnPX₃: Néel-type AFM, interplanar FM

In MnPS₃ and MnPSe₃, the magnetic moments come from the half-filled $3d^5$ of Mn²⁺ with a total spin of $S = 5/2$. This was confirmed through neutron diffraction analyses by Kurosawa in 1983 [80] and Wiedenmann in 1981 [63]. Subsequent studies by Wildes and Rule [77–79, 23] further clarified that the spin moments in these compounds exhibit antiferromagnetic ordering within the plane in a Néel-type antiferromagnetic configuration, while they are ferromagnetically coupled between the planes. The magnetic cell is the same as the crystalline nuclear one. As a reminder, though MnPS₃ and MnPSe₃ share the same in-plane configurations except for the bonding length when S is replaced by Se, their interplanar stacking in the bulk is different. MnPS₃ has a $C2/m$ monoclinic space group, while MnPSe₃ has a $P\bar{3}1m$ structure.

In 2010, Ressouche *et al.* revisited the spin polarisations of MnPS₃ using spherical-neutron-polarimetry experiments and found that the magnetic moments on Mn²⁺ ions are canted by approximately 8° away from the c axis.

Fig 2.7 exhibits the magnetic configurations of MnPS₃ and MnPSe₃ according to the latest literature, respectively. The breaking of both time reversal and space inversion symmetries in the magnetic point group allows for linear magneto-electric (ME) coupling in these compounds [81]. In 2019, Dinh *et al.* successfully demonstrated the electrical control of magnetic properties in MnPS₃, providing experimental validation of the existence of ME coupling in MnPS₃ [82].

FePX₃: Zigzag AFM, interplanar AFM

In FePS₃ the magnetic moments come from the $3d^6$ of Fe²⁺, resulting in a total spin of $S = 2$. Determining the magnetic structure of FePS₃ has been a challenging task due to the complex interplay among exchange coupling, magnetic anisotropy, crystal ligand field effects, and spin-orbit coupling.

Early theoretical work by Flem *et al.* proposed a magnetic structure for FePS₃ in which the spin moments formed ferromagnetic chains elongating in the [110] direction, with antiferromagnetic coupling between the chains within the plane [22]. This model was experimentally supported by Kurosawa *et al.* using neutron scattering experiments in the early 1980s [80].

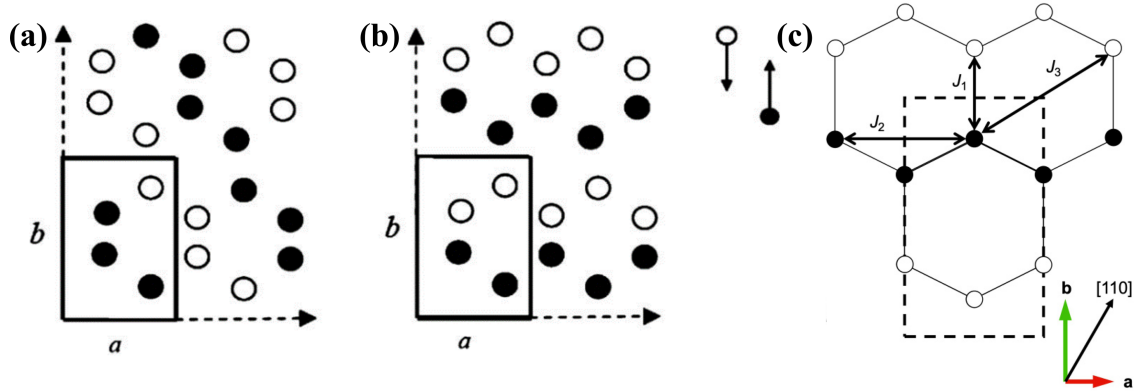


Fig. 2.8 The two different proposed magnetic structures of FePS₃ within the *ab* plane. (a) was proposed by Flem *et al.* [22] while (b) initially by Kurosawa *et al.* [80] and later confirmed by Rule *et al.* [83] and Wildes *et al.* [84]. (c) displays the nearest, second- and third nearest neighbour exchange J_i ($i = 1, 2, 3$) in FePS₃.

At that time, there was limited discussion about long-range order along the *c* axis, possibly due to challenges in obtaining large single-crystal samples suitable for neutron scattering. To satisfy the sample size requirement for neutron-diffraction experiments, samples were assembled by piling up a hundred single crystals of FePS₃. This pseudo-crystal with substantial mosaicity resulted in the observation of a relatively broad and asymmetric peak at the corresponding position of the propagation vector. Nevertheless, this model successfully described the Ising feature of FePS₃ with regard to in-plane propagation vectors.

Over subsequent decades, this magnetic structure model faced challenges and revisions. Rule *et al.* in 2007 [83] and Wildes *et al.* in 2012 [84] proposed a different in-plane magnetic configuration for FePS₃, suggesting that ferromagnetic chains elongate along the [100] direction (the *a* axis) instead. Fig. 2.8 exhibits the two models in (a) and (b) for contrast. They also argued that the magnetic structures observed in Kurosawa *et al.*'s experiments were not consistent with the theoretical model proposed by Flem *et al.*, but were in line with the ferromagnetic chains along the *a* axis description. The distorted Fe-hexagon geometry results in different energy states for the two elongation directions.

The interplanar magnetic coupling in FePS₃ was explored in detail in recent decades. In 2002, Rule and her collaborators found several missing peaks in the neutron powder pattern and suggested the presence of long-range antiferromagnetic order perpendicular to the *ab* planes [79]. This was further confirmed by Lançon *et al.* [85], leading to the magnetic configuration shown in Fig. 2.9 (a).

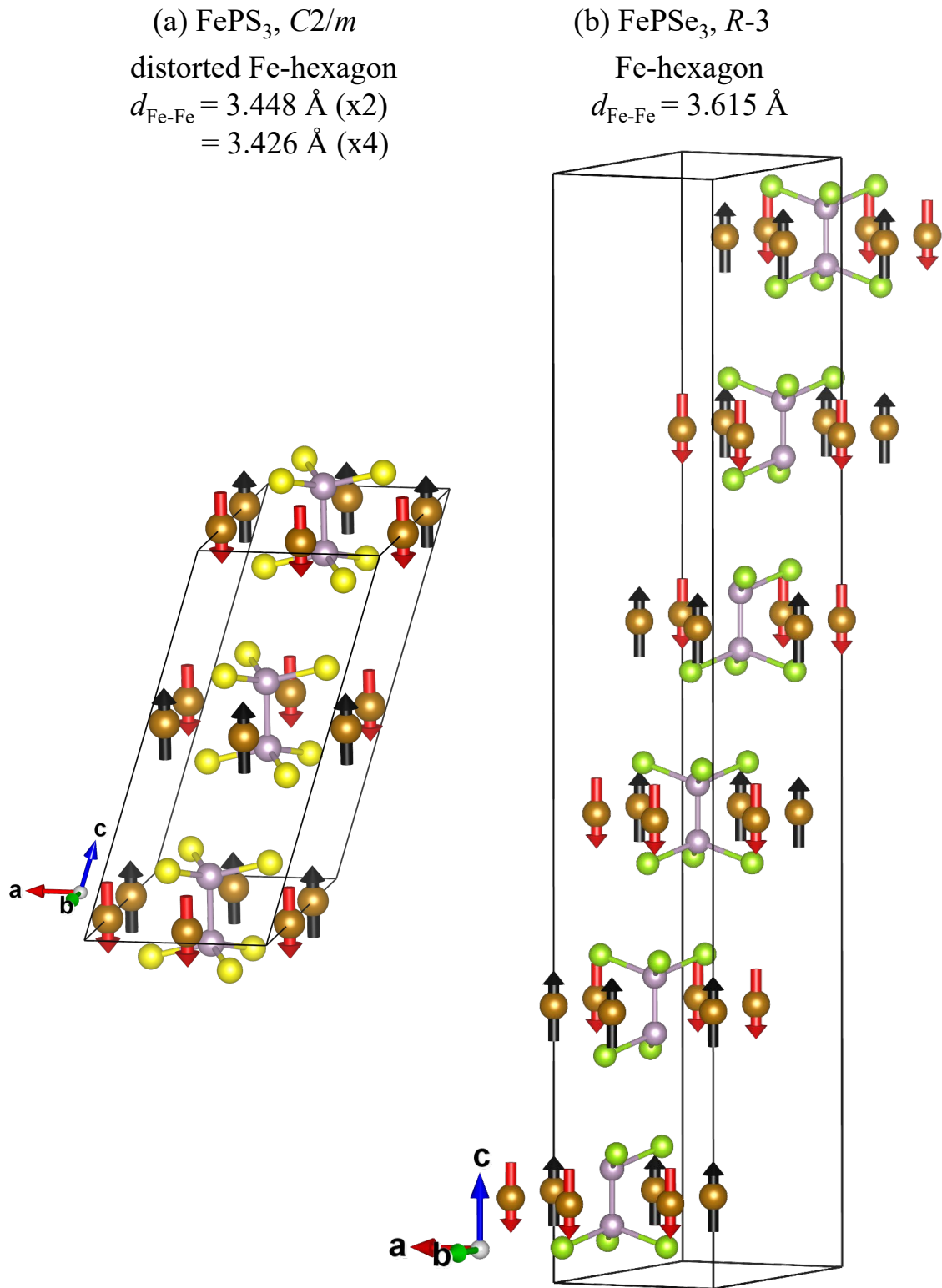


Fig. 2.9 The magnetic configuration for (a) FePS_3 and (b) FePSe_3 . These figures are plotted referring to the magnetic structure in [63] using VESTA.

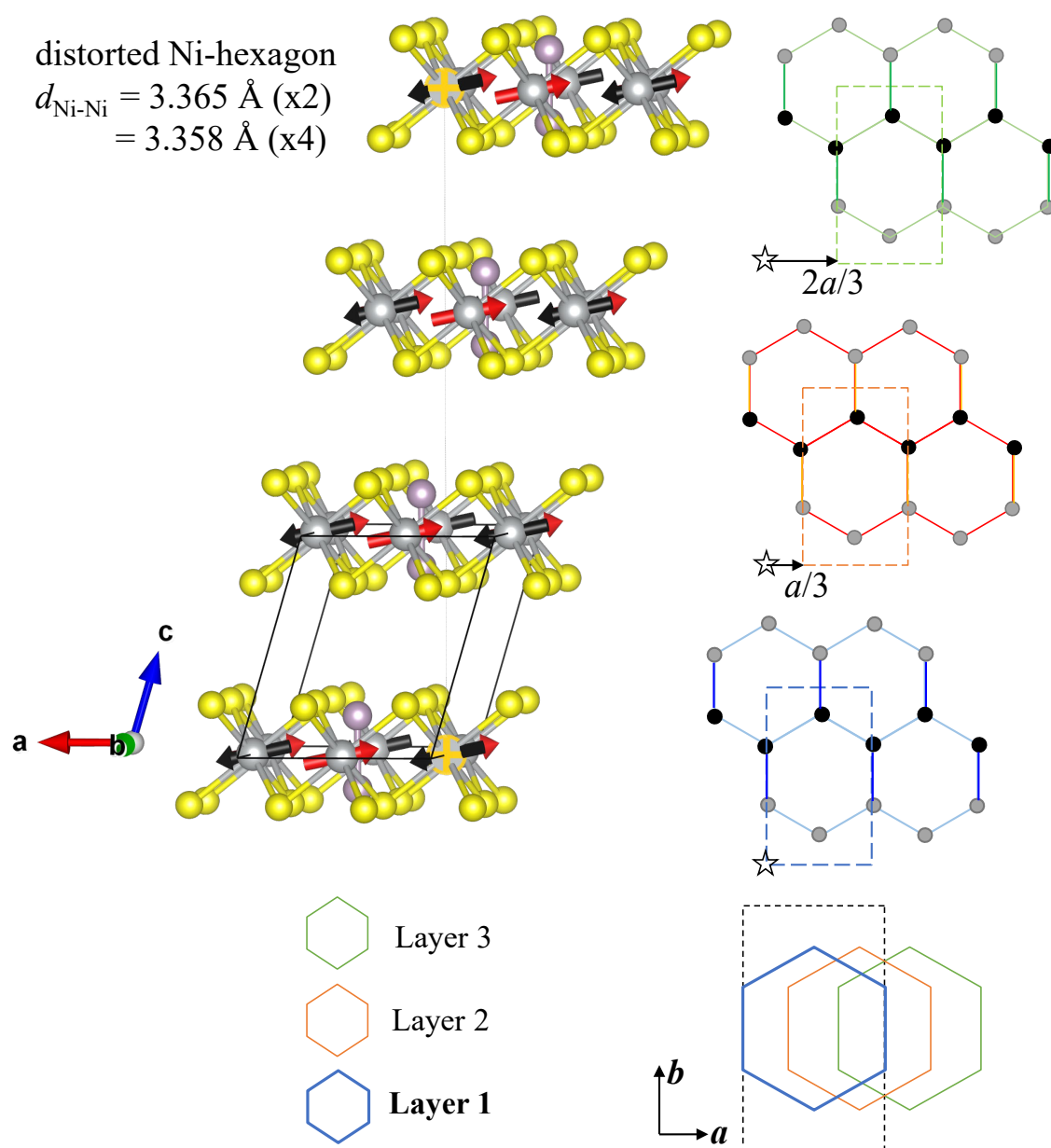
Additionally, Lee *et al.* [24] and Wang *et al.* [86] explored the AFM order in FePS₃ from bulk to monolayer. They found that the intralayer magnetic configuration remained consistent with the nearly thickness-independent transition temperature ($T_N = 118 \sim 123$ K), indicating a minimal influence of interlayer interactions on the antiferromagnetic order. Consequently, FePS₃ is considered a prime example of an Ising antiferromagnet.

In FePS₃, the strong *c*-axis anisotropy makes the system favour spin moments perpendicular to the *ab* plane. Hence, it can be described with a simplified Ising Hamiltonian. Within each layer, each Fe²⁺ ion has three first (J_1), six second (J_2) and three third (J_3) nearest neighbours on the honeycomb lattice, as shown in Fig. 2.8 (c). As for FePS₃, J_1 is FM while J_2 and J_3 are AFM, leaving a collinear antiferromagnetic order in the system. The interlayer J' has also been determined to be negative, consistent with the previous observation of antiferromagnetic interlayer long-range order.

However, in previous modelling and fitting efforts, the anisotropy in the exchange parameters J_i was not considered. At ambient pressure, the distorted Fe-hexagon naturally leads to different nearest J_1 values in [100] and [110] directions. Recent work by Wildes *et al.* used high-field magnetisation measurements to re-examine the magnetic ground state in FePS₃ and attempted to incorporate anisotropic exchange parameters into the spin Hamiltonian [87]. They found that different fitting methodologies could yield divergent ground-state magnetic configurations and J values. These subtle differences may not be readily discernible under current experimental conditions, and metastable magnetic phases are challenging to access. Consequently, there is motivation to simulate various magnetic phases, including anisotropic exchange parameters, within the framework of density functional theory (DFT) calculations.

As for FePSe₃, early Mossbauer effect measurements by Taylor *et al.* in 1974 suggested that the dominant axis of magnetisation is perpendicular to the *ab* plane [88]. Subsequent neutron diffraction experiments by Wiedenmann *et al.* in 1981 provided detailed insights into the magnetic structure and phase transitions [63]. The magnetic cell of FePSe₃ doubles in size along both *a* and *c* axes, resulting in a lowering of symmetry from rhombohedral to triclinic.

Fig. 2.9 (b) displays the magnetic structure of FePSe₃ with the unit cell adapted from the hexagon to monoclinic description. Within each *ab* plane, the Fe²⁺ atoms form FM chains that are anti-ferromagnetically coupled with one another. Notably, the interlayer stacking in FePSe₃ differs from that in FePS₃, as the Fe-hexagon skeletons are translated along the *b* axis in the monoclinic cell description. This difference in interlayer stacking contributes to the distinct magnetic properties observed in FePSe₃ compared to FePS₃.

Fig. 2.10 The magnetic configuration of NiPS₃ at ambient pressure.

NiPX₃: Zigzag AFM, interplanar FM

In the case of NiPS₃ and NiPSe₃, the magnetic moments arise from the $3d^8$ electronic configuration of Ni²⁺, resulting in a total spin of $S = 1$. While NiPSe₃ shares the same magnetic configuration as NiPS₃, determining the exchange strengths in these materials has proven to be challenging. Therefore, I will focus on NiPS₃ for the discussion of the magnetic structure.

In NiPS₃, the magnetic pattern within the plane is similar to that of FePS₃, with the formation of zigzag ferromagnetic chains along the a axis that are antiferromagnetically coupled with their neighbouring chains. However, in NiPS₃, the magnetic moments have been reported to lie almost parallel to the ab plane, with neighbouring planes being ferromagnetically coupled. This collinear spin arrangement in NiPS₃ is best described using an anisotropic Heisenberg Hamiltonian [22, 71, 74, 89]. The specific magnetic properties of NiPS₃ make it an interesting material for further investigation in the context of two-dimensional magnetism.

Summary

Table 2.2 The cation electronic configuration, antiferromagnetic transition temperature T_N , the direction of the spin moments on the TM sites and the magnetic configuration within and in-between the planes of $TMPX_3$ ($TM = \text{Mn, Fe, Ni}$, $X = \text{S, Se}$) at ambient pressure.

	TM^{2+}	T_N (K)	Spin Direction	Magnetic Configuration	
				Within the Plane	Interplane
MnPS ₃	$3d^5 (t_{2g}^3 e_g^2)$	78	canted	Neel AFM	FM
FePS ₃	$3d^6 (t_{2g}^4 e_g^2)$	120	out-of-plane	Zigzag Chain	AFM
NiPS ₃	$3d^8 (t_{2g}^6 e_g^2)$	154	almost in-plane	Zigzag Chain	FM
NiPSe ₃	$3d^8 (t_{2g}^6 e_g^2)$	206	almost in-plane	Zigzag Chain	FM
MnPSe ₃	$3d^5 (t_{2g}^3 e_g^2)$	74	canted	Neel AFM	FM
FePSe ₃	$3d^6 (t_{2g}^4 e_g^2)$	108	out-of-plane	Zigzag Chain	AFM

Altering the choice of the transition metal ion gives rise to the Ising-type, XY or Heisenberg antiferromagnetic magnetic order, different spin states, and subtly differing exchange interac-

tion strengths. These naturally lead to a wide selection of magnetic structures and interactions, as summarised in Table 2.2. The different antiferromagnetic ordering patterns observed at low temperatures are governed intrinsically by the complex competition among direct $TM-TM$ exchange and indirect $TM-S-TM$ super-exchange interactions within each layer, together with the interlayer exchange ones. This compound family thus forms an ideal platform for investigating a broad range of phenomena fundamentally in low-dimensional magnets and how the phases and physical properties evolve as we tune that system towards 3D with pressure or conversely reduce the thickness to a single atomic layer limit.

2.1.4 Electronic Properties

Table 2.3 The experimentally observed band gap from optical measurement and room-temperature resistivity of $TMPX_3$ ($TM = \text{Mn, Fe, Ni}$; $X = \text{S, Se}$) at ambient pressure [90, 91], except for NiPSe_3 that only calculated value using HSE06 functional of 2.2 eV is available.

	Band Gap (eV)	Resistivity ($\Omega \text{ cm}$)
MnPS_3	3.0	1.0×10^{12}
FePS_3	1.5	4.0×10^8
NiPS_3	1.6	5.0×10^9
MnPSe_3	2.5	$\sim 10^9$
FePSe_3	1.3	-
NiPSe_3	-	-

Following the classic Fermi liquid theory, the half-filled $3d$ states of the TM^{2+} ions would typically suggest that these compounds should exhibit metallic properties. Contrastingly, these materials behave as insulators or semiconductors with varying band gaps ranging from 0.2 to 3.0 eV, as confirmed by previous optical [90, 91] and ultraviolet photoemission spectroscopy (UPS) [92] measurements. The presence of a band gap opens up potential applications in optoelectronics across a wide wavelength range.

Table 2.3 provides a summary of the band gap sizes and room temperature resistivity values obtained through four-probe Van der Pauw measurements [90, 93]. Among the listed

compounds, the Fe-based materials exhibit the lowest values in comparison to their Mn and Ni counterparts.

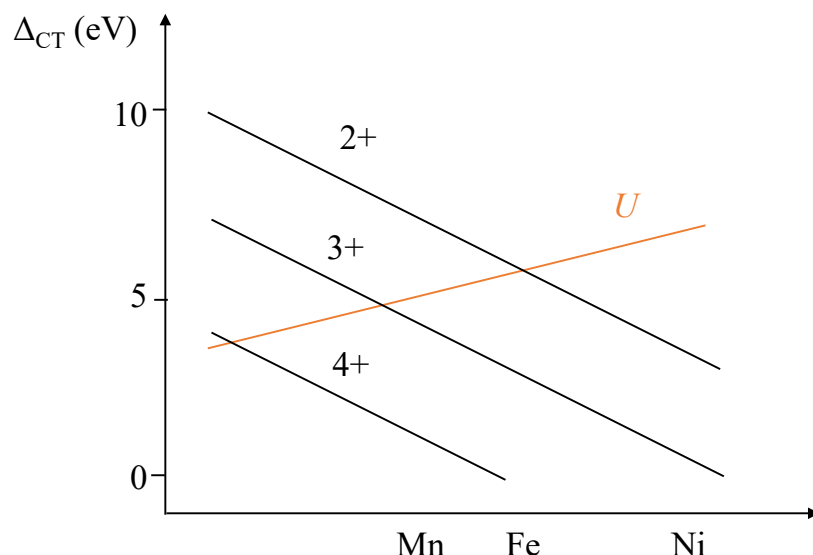


Fig. 2.11 Characteristic values of the Hubbard U and the charge-transfer energy and Δ_{CT} for the 3d series compounds. The values are taken from Ref. [94].

$TMPX_3$ being insulators at ambient pressure is attributed to the strongly correlated electrons of the 3d orbitals in TM . The principles have been introduced in Chapter 1, and more details can be found in various textbooks [96]. Here, I will provide further details on the relative scale of the Hubbard U and the charge-transfer energy Δ_{CT} in the context of Mn, Fe and Ni.

In Fig. 2.11, a trend is observed that the Hubbard U increases while Δ_{CT} decreases from left to right in the 3d series of periodic table along with the increase in nuclear charge Z . This can be explained by the energy level of d -bands moving lower as Z increases. The binding energy of d -electrons increases due to the small radius and incomplete electron screening. Meanwhile, the energy of p -electrons, which are further away from the TM nuclei, remain nearly unchanged. Consequently, the energy of $p-d$ electron transfer decreases with increasing Z .

This energy level scheme (Fig. 2.12) provides a qualitative explanation for the electronic properties and trends observed in $TMPX_3$ compounds. $MnPS_3$ and $FePS_3$ are considered as Mott-insulators while $NiPS_3$ is classified as a charge-transfer insulator. These 2D AFM insulators, whether Mott or charge transfer, are of great interest for the study of strongly correlated electron systems. One of their most notable features is their tunability towards phase transitions through various means, such as pressure, chemical doping, or other pa-

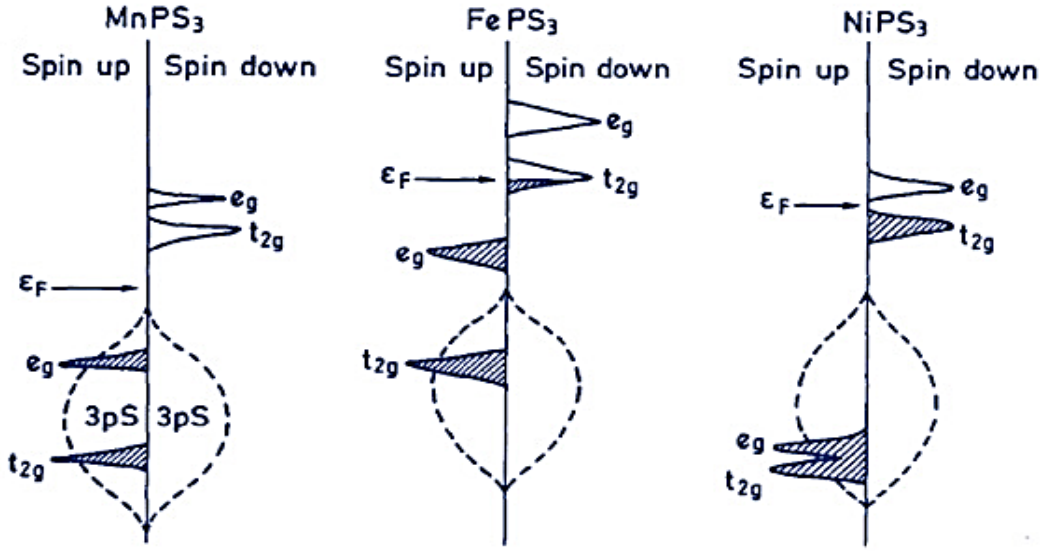


Fig. 2.12 The diagram illustrates the energy levels for TMPs_3 compounds and presents characteristic values of U and Δ for various transition metals. This figure is sourced from Ref. [95].

rameters, which can lead to the emergence of novel phenomena, including unconventional superconductivity and other exotic states.

2.2 Pressure-induced Transitions

One major advantage of the van der Waals (vdW) nature of the TMPX_3 compounds is that the dimensionality of these materials can be tuned in a clean and controllable way, either by exfoliation with the "Scotch tape" method [97] into the 2D limit or by applying hydrostatic pressure towards 3D. In this thesis, I focus on the pressure-induced transitions as pressure stands as a cleaner and more controllable tuning parameter than thickness control or chemical doping. The way how pressure is continuously and controllably varied will be discussed in the experimental method chapter. In the following sections, I will outline and discuss the recent results of the pressure-induced changes in the structure, electrical transport and magnetic ordering.

2.2.1 Evolution of Crystalline Structures

Under pressure, the weaker van der Waals (vdW) interactions between stacking planes in $TMPX_3$ compounds become more vulnerable compared to the interactions within the plane. As a result, the dominant effect is the reduction of the vdW gap between adjacent planes, which promotes the formation of bonds between neighbouring planes. This is an important aspect in the pressure-induced structural evolution of these compounds.

Previous powder diffraction measurements of crystal structures upon the application of pressure for the isostructural $C2/m$ $FePS_3$, $MnPS_3$, $NiPS_3$ and $NiPSe_3$ at room temperature have suggested common trends, particularly the collapse of the inter-plane spacing. These observations provide valuable insights into the high-pressure behaviour of these compounds.

However, the exact transition model for $FePSe_3$ and $MnPSe_3$ under pressure is still a subject of investigation, and there is insufficient evidence to establish a definitive model at this time. In the following discussion, I will focus on the reported pressure-induced transition models for the isostructural phases with the space group $C2/m$ at ambient pressure, which shed light on the structural changes occurring in these materials as pressure is applied.

Shown Example: $FePS_3$

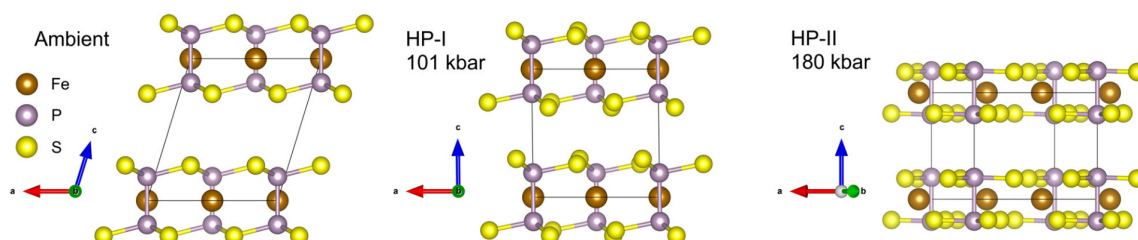


Fig. 2.13 The structure evolution of $FePS_3$ with pressure. The high-pressure structure models are established from the synchrotron powder x-ray diffraction on $FePS_3$ powder sample in DAC with helium medium. The figure is cited from Ref [59].

Using $FePS_3$ as an example, I will discuss structural changes under pressure. $FePS_3$ is the first among these compounds to have its high-pressure structures resolved [59]. In 2018, Haines *et al.* [59] and Wang *et al.* [60] performed independent high pressure experiments on $FePS_3$ powder samples. Both groups observed the insulator-to-metal transition (IMT) and volume collapse in response to the external pressure but proposed incompatible models for the high-pressure (HP) phase.

Wang *et al.* [60] claimed that the low-pressure (LP) monoclinic symmetry remains until the HP region and the in-plane lattice collapse contributed the most to the volume collapse during the iso-structural phase transition at ~ 13 GPa. They also reported that when the HP phase turns into a metallic phase in the case of FePSe_3 , which is a related compound with similar structural and magnetic properties, superconductivity (SC) was observed at 2.5 K and 9.0 GPa [60].

Meanwhile, Haines *et al.* [59] claimed that there are two transitions. The first happens around 4 GPa via inter-planar sliding. The LP phase evolves into HP-I without symmetry and dimensionality change and remains insulating. This transition is seen to evolve over a wide pressure range from 2 to 6 GPa with a phase coexistence of the LP and HP-I phases. The next occurs around 14 GPa with an interlayer lattice collapse and a sharp reduction of unit cell volume by up to 20%. The bulk symmetry changed to $P\bar{3}1m$ from HP-I to HP-II. The HP-II phase was determined to be metallic and more 3D-like.

Subsequently, two computational studies by Zheng *et al.* [98] and Evarestov *et al.* [99] did not come up with consistent conclusions regarding the origins of IMT or the impact of magnetic configurations on the crystal structure. A later Raman spectroscopy work by Das *et al.* has detected two phase transitions at 4.6 GPa and 12.0 GPa, complementing the previous experimental observations and models [100].

Our recent study [67] compares the different experiments utilising powder samples with and without the helium pressure medium, and includes the single crystal diffraction results in the discussions. The experimental environment plays an essential role in the high-pressure behaviour, in particular the inter-plane change.

Other compounds crystallisation in $C2/m$ symmetry

Alongside the investigations into the high-pressure crystal structure of FePS_3 , similar efforts have been applied to explore the closely related compounds. The key questions to identify the high-pressure structure model come along with experimental difficulties in reaching stable and hydrostatic pressures and interpreting the diffraction pattern correctly with careful consideration of the preferred orientation.

As for MnPS_3 and MnPSe_3 , in 2016 Wang *et al.* employed a pre-compressed pellet with a diamond anvil cell using silicon oil as the pressure-transmitting medium [57]. They observed dramatic cell volume collapse (-19.8%) in MnPS_3 around 30 GPa and that (-20.7%) in MnPSe_3 around 25 GPa, indicating first-order transition with major changes in the

atomic arrangement. However, they proposed the high-pressure structure model with abrupt shrinkage of the in-plane lattice rather than the interplane changes, bringing the formation of metallic Mn-Mn bonds of 2.75 Å and elongated Mn-Mn of 3.69 Å. A similar model had been proposed for FePS₃ and FePSe₃ in 2018 by Wang *et al* [60]. In 2019, Kim *et al.* [58] reported the isosymmetric structural transition within a monoclinic space group around 63 GPa, applying density-functional-theory-based first-principles calculations with Hubbard *U* correction to explore the cell evolution. They found that the lattice collapse happened both within the plane relating to the formation of Mn-Mn dimers and in between the planes. The other theoretical study by Zhang *et al.* [101] employing hybrid functional and predicted a monoclinic-to-rhombohedral ($C2/m$ to $R\bar{3}$) stacking-order transition around 35 GPa.

Our recent independent measurement of MnPS₃ and NiPS₃ using diamond anvil cells with helium as the pressure-transmitting medium evidenced the inter-plane collapse, in contrast to the previous model proposed by Wang *et al.* Similar to the case of FePS₃, two transition pressures were determined around 2 and 28 GPa for MnPS₃, while being around 10 and 26 for NiPS₃. In addition to PXRD, single crystal samples were employed subject to synchrotron XRD measurements under pressure, giving more information on the atomic positions. The high-pressure phases were identified with substantial clarity. Due to experimental constraints, however, the transition points were not able to be determined but the pressure region before and after the transition was consistent with the PXRD results.

Subsequently, Ma *et al.* [102] reported the same two-stage phase transitions in NiPS₃ in the year 2021. The first structural transition from LP to HP-I ($C2/m$) is around 15 GPa and the second one to the HP-II ($P\bar{3}1m$) is around 27 GPa, exhibiting 3D behaviour. They initially constructed the high-pressure structure model manually via the layer-by-layer slip mechanism and then relaxed the structure with first-principles calculations. The calculated structures were confirmed by high-pressure powder XRD measurements with silicone oil as the pressure-transmitting medium. Recent high-pressure powder XRD studies on NiPSe₃ reported similar transitions at pressures of ~4.0 and ~15.0 GPa [103].

Summary

To summarise, FePS₃, MnPS₃, NiPS₃ and NiPSe₃ have the same crystal structure of the space group $C2/m$ and $ABC\ ABC$ stacking with the β angle close to the ideal monoclinic phase angle at ambient pressure. The first transition from LP to HP-I, regardless of the exact values of transition pressure, preserves the same monoclinic space group symmetry with the layer sliding and the β angle approaching 90 degrees. The $ABC\ ABC$ stacking changes to

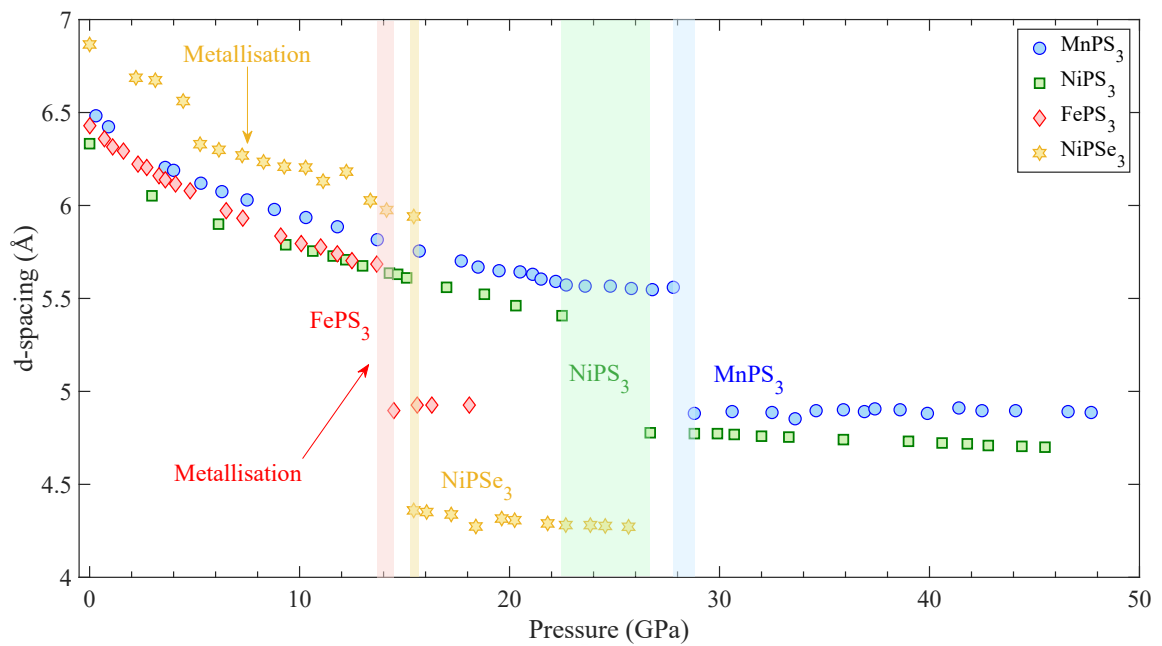


Fig. 2.14 The interplanar distance, independent of the symmetry or unit cell model used, is plotted against pressure at room temperature for FePS₃, MnPS₃, NiPS₃ and NiPSe₃ [59, 61, 104, 103]. They are isostructural compounds at ambient pressure with the $C2/m$ space group and show a common trend of sliding and then inter-plane collapse upon pressure. The colour block indicates the transition region during which the d-spacing experiences a drastic collapse for each compound, serving as a visual guide. The width of the region depends on data availability, not representing the actual transition process. Arrows on the plot signify the insulator-to-metal transition.

almost AAA during the transition. The transition metal and the exchange ligands sit on top of the corresponding sites from the neighbouring planes, viewing from the stacking direction. The second transition, from HP-I to HP-II, occurs with a drastic change in the inter-planar spacing, as exhibited in Fig. 2.14. Notably, FePS₃ exhibits the most sensitivity to external pressure, as reported so far.

Table 2.4 The pressure values of the first transition from LP to HP-I via sliding (P_1) and the second transition from HP-I to HP-II involving symmetry and dimensionality change (P_2) in FePS₃, MnPS₃, NiPS₃ and NiPSe₃.

	P_1 (GPa) LP → HP-I	P_2 (GPa) HP-I → HP-II	Synchrotron XRD sample pressure-transmitting medium	References
FePS ₃	4	14	powder, helium	[59]
	n.a.	14.4~17.9	single crystal, helium	[104, 67]
	-	14	powder, silicon oil	[60]
MnPS ₃	2	28	powder, helium	[104]
	0.9~2.1	n.a.	single crystal, helium	[104]
	-	30	powder, silicon oil	[57]
NiPS ₃	10	26	powder, helium	[104]
	5.7~10.4	24.9~26.9	single crystal, helium	[104]
	15	27	powder, silicon oil	[102]
NiPSe ₃	3.2 - 4.5	14.3 - 15.5	powder, silicon oil	[103]

The summary of reported transition pressures for FePS₃ based on the two-step transition model is given in Table 2.4. This model distinguishes between two critical pressures, P_1 and P_2 , which represent key structural changes as pressure is applied [59].

- P_1 marks the transition pressure when the ideal monoclinic angle in the low-pressure phase (LP) becomes close to 90 degrees, while the $C2/m$ symmetry is still preserved.
- P_2 corresponds to the pressure at which interlayer collapse occurs. It also refers to the pressure at which a drastic volume collapse takes place in another proposed model based on major intraplanar lattice changes [57, 60].

Determining these transition pressures precisely has been challenging due to limitations in experimental data, particularly in obtaining accurate atomic positions. Powder samples in diamond anvil cells using helium or silicon oil as pressure-transmitting media have been employed in experiments. Extracting precise crystal structure details from powder

patterns is complicated, given the pronounced orientation preference in layered compounds. Without accurately determining characteristics of, for example the main (0 0 1) peak, it is almost impossible to create a reliable structural model under different pressures. The correct interpretation of this peak is essential for understanding the spacing between planes, which is the most essential parameter for controlling dimensionality. Getting accurate crystal structure information and its changes is crucial for understanding the physics of these compounds and guiding further theoretical calculations.

2.2.2 Insulator-to-metal Transitions and Emergent Superconductivity

$TMPX_3$ compounds exhibit strongly correlated electron physics being Mott or Charge transfer insulators at ambient pressure. Insulator-to-metal transitions (IMT) [105] and the occurrence of superconductivity have been observed and reported in this family. Fascinating phenomena suggesting new physics related to strongly correlated electrons or quantum fluctuations are also reported and still under investigation. In this section, I will discuss the evolution of the electrical transport properties with elevated pressure with regard to different transition metals and ligands.

Insulator-to-metal Transition versus Dimensional Collapse

Most compounds show a coincident IMT with the dimensionality collapse from HP-I to HP-II structural phase transition, except for $NiPSe_3$ and $V_{0.9}PS_3$. The drastic collapse of the interplanar separation brings, for instance, the P atoms down to a length where electron overlap and bond formation can be expected. Taking $FePS_3$ as a shown example, Haines *et al.* [59] performed transport measurement under pressure for bulk $FePS_3$ and quantitatively described the insulator-to-metal transition, as is shown in Fig. 2.15. With increased pressure, $FePS_3$ became metallic with the resistivity dropping down. An additional interesting behaviour of a nontrivial upturn of resistivity at low temperatures in the high-pressure metallic state was observed. The deviation from conventional Fermi-liquid description at low temperature in (c, d) suggested strong correlations in $FePS_3$.

In $NiPS_3$ and $NiPSe_3$, by contrast, there is no observed structural change with the IMT pressure within the monoclinic symmetry $C2/m$. The active e_g orbitals make them rare candidates of electronic-controlled IMTs [58].

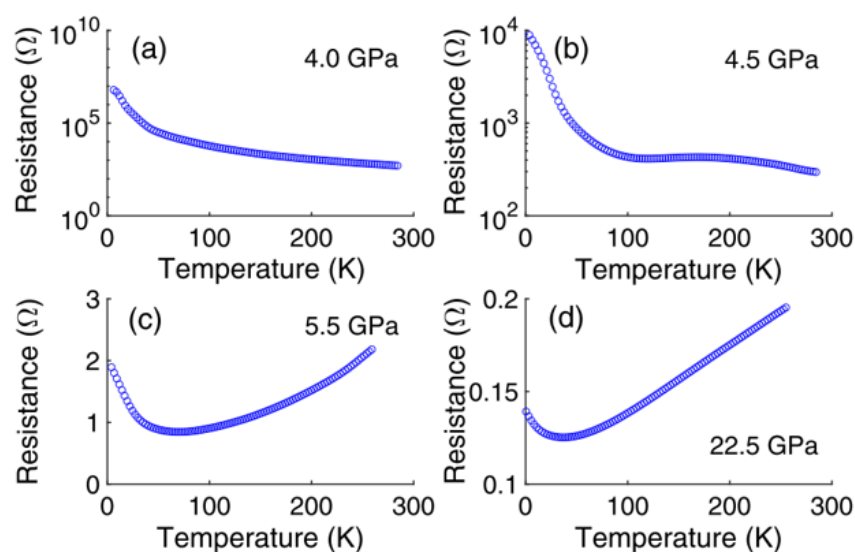


Fig. 2.15 The resistance of FePS₃ versus temperature estimated as (a) 4.0 GPa, (b) 4.5 GPa, (c) 5.5 GPa, and (d) 22.5 GPa. A transition from insulating to a metallic state can be seen with increased pressure. Also, there exists an upturn in the resistivity at low temperatures in the high-pressure measurements. The figure is cited from Ref [59].

Emergent Superconductivity

In the neighbouring compound FePSe₃, superconductivity (SC) has been reported at high pressures [60]. The SC state starts around 9 GPa with the critical transition temperature T_c starting ~ 2.5 K and approaching the maximum of ~ 5.5 K at approximately 30 GPa. Though SC has not been reported in FePS₃ by far, the complexity and experimental settings and high-resolution requirement cannot rule out its existence. The existence of SC dome in particular attracts our interest as this might be a sign of quantum criticality in the Fe phosphorous compounds.

NiPSe₃ is recently reported to become completely metallic at ~ 8.0 GPa, which is between the first and second phase transitions. In conjunction with this IMT, a significant drop in resistance below 4.9 K was also observed, indicating the emergence of superconductivity. The SC transition temperature reaches a maximum of 5.9 K around 27.6 GPa and remains constant to the highest pressure being measured. A similar phenomenon has been reported in FePSe₃, as is displayed in Fig. 2.16.

The observation of superconductivity in FePSe₃ and NiPSe₃, but not yet in other compounds, for instance, FePS₃, presents interesting questions for further investigation. This is a difficult and challenging project regarding the quality of selected samples and the sophisticated setup

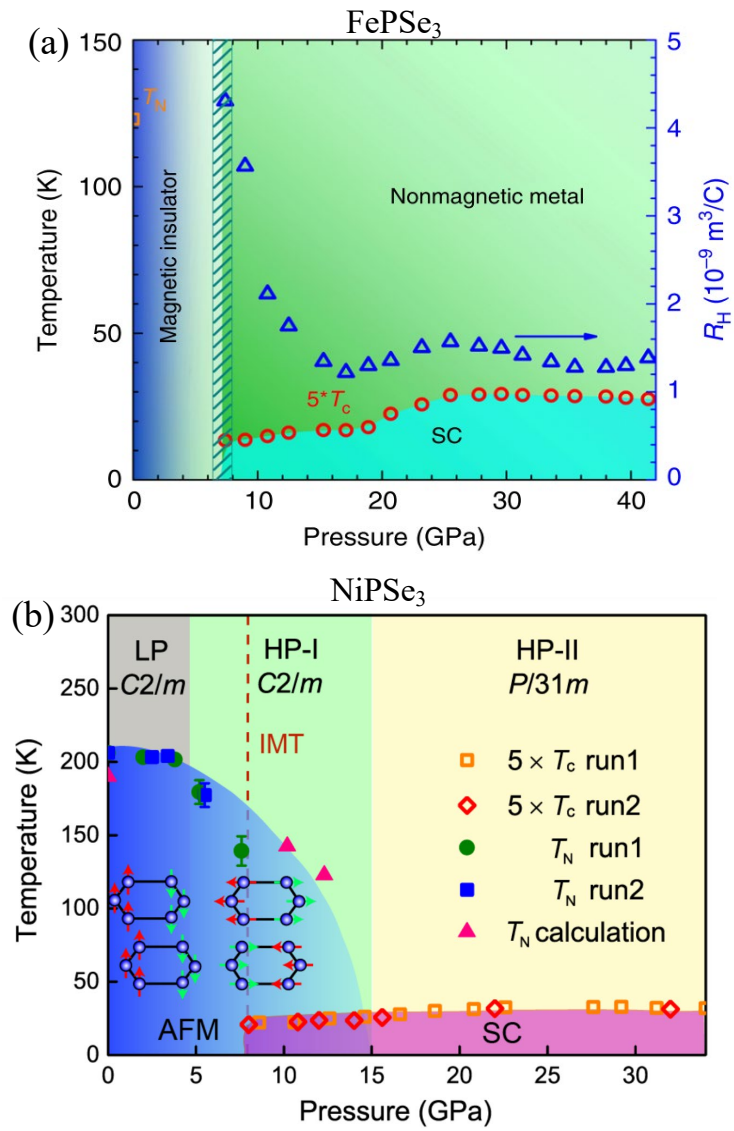


Fig. 2.16 The pressure-induced superconductivity reported in (a) FePSe₃ [60] and (b) NiPSe₃ [103].

of the high-pressure resistivity measurements. Meanwhile, the calculation of high-pressure crystal structures and the band structures could aid the search for superconductivity.

2.2.3 Emergence of Novel Magnetic Phases

While the fundamental discoveries and studies of the vdW magnetic TMPX₃ have stimulated the field of atomically thin magnets, the observed phenomena of magnetic phase transitions in these compounds present some interesting questions.

The detailed magnetic structure of FePS₃ is challenging to resolve even at ambient pressure [79, 83, 106, 107] and affects the high-pressure phases as well. A recent study by Coak and Jarvis *et al.* [62, 104] further characterised the LP, HP-I and HP-II phases of FePS₃ up to about 18.3 GPa, as is shown in Fig. 2.17. They first examined the evolution of magnetic phases with pressure using powder neutron diffraction and proposed that from LP to HP-I the interlayer interaction transforms from antiferromagnetic to ferromagnetic. In the metallic HP-II phase, the long-range magnetic order is suppressed while a form of short-range order emerges. The inherent experimental difficulties and the viability of the use of double-toroidal diamond anvil cells for this type of experiment will be introduced in the later chapter.

This is a rather different result from the spin crossover (SCO) transition model proposed by Wang *et al.* [60], where the final state is claimed to be non-polarised. The SCO model was proposed based on the in-situ X-ray emission spectroscopy (XES) measurements under high pressure and the quantitative analysis using the integrals of the absolute values of the difference spectra (IAD) method, as presented in Fig. 2.18.

In MnPS₃ and MnPSe₃, the magnetic moment on Mn²⁺ dropped from $S = 5/2$ to $S = 1/2$ with increased pressure accompanying the structural and electronic transitions [57] at around 28 GPa and 23 GPa, respectively. As for FePS₃, this reported SCO remains to be explored directly via techniques like neutron scattering.

2.3 Scheme and Aims

In this family, FePS₃ is an ideal prototype to start with, considering the Ising nature of the magnetic moments of Fe ions [79, 85], the small band gap of about 1.5 eV, lowest resistivity of $1.0 \times 10^{12} \Omega \text{ cm}$ [90] at ambient pressure and experimental evidence for the evolution of the structural, electronic and magnetic properties at high pressures [59–61].

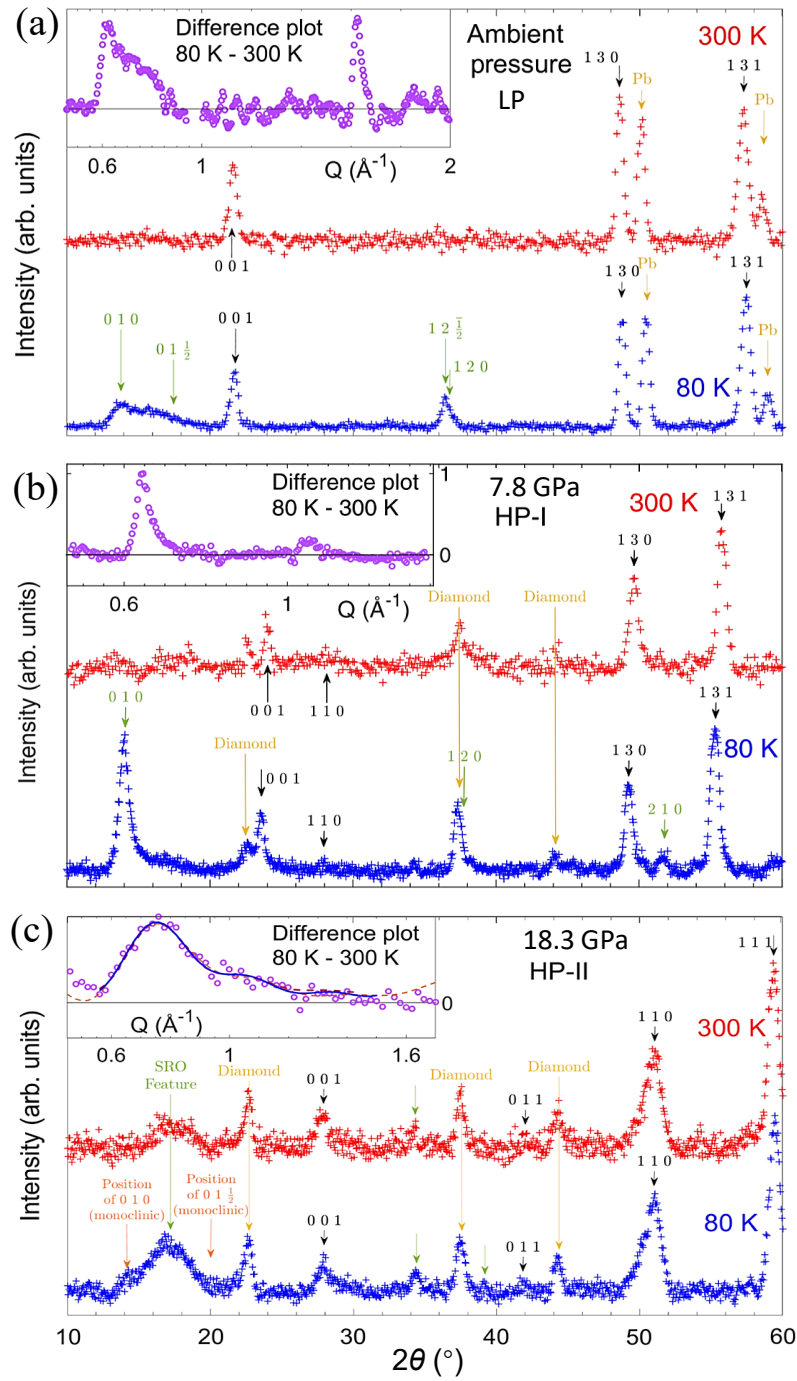


Fig. 2.17 Powder neutron diffraction patterns of FePS_3 at 300 K (red) and 80 K (blue), before and after the antiferromagnetic transition, for (a) LP at ambient pressure, (b) HP-I at 7.8 GPa, and (c) HP-II at 18.3 GPa, taken on D20, ILL. The difference plots are inserted in each subplot [62].

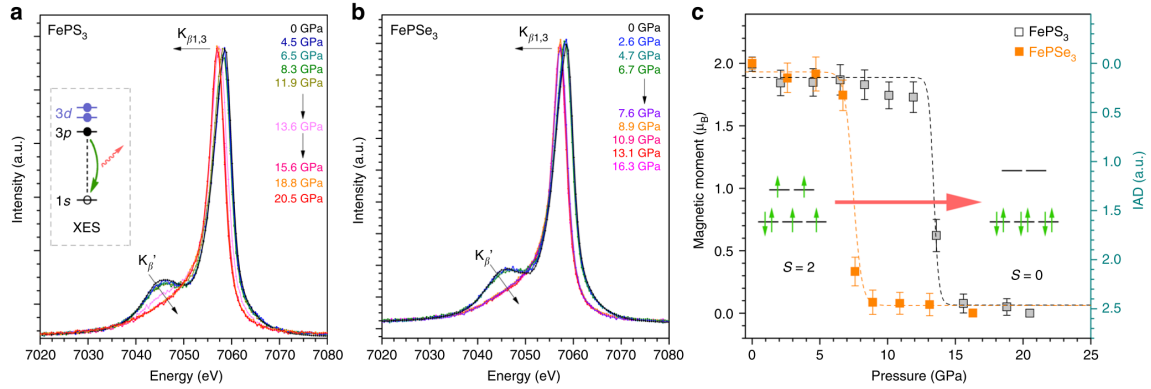


Fig. 2.18 In situ X-ray emission spectroscopy (XES) data of FePX₃ under high pressures. The figures are cited from Ref. [60].

To understand how external pressure tunes the dimensionality, structural, electronic and magnetic properties in FePS₃, it is essential to grasp the systematic evolution of the crystalline phase with applied pressure. Given the fact that different experimental environments and setups affect the high-pressure behaviour, we re-examine the high-pressure structures via a random structure search method using density functional theory. The advantage of this method is that it does not require empirical knowledge of the experimental findings and thus allows us to search for the most stable and metastable structures from the energy considerations. We are able to reproduce the proposed phases and predict a novel one in the high-pressure region. Moreover, we look into the interlayer sliding and dimensionality change in FePS₃ as it undergoes the phase transitions in detail, together with the evolution of electronic and magnetic properties.

On the other hand, the FePSe₃ compound under pressure also presents interesting phenomena including pressure-induced superconductivity. However, there is no available experimental and theoretical model for the crystalline and magnetic structure at high pressures. It is the ground, for further exploration of any other physical properties, and the intrinsic understanding of the structures. Hence, this thesis will also aim to resolve the structures at the atomic level. Last but not least, a comparison between FePS₃ and FePSe₃ could be constructed and discussed under a more general scheme of pressure-tuning in low dimensional intrinsic magnets with strongly correlated electrons.

Chapter 3

Theoretical Simulation with Density Functional Theory

Theoretical simulations within the framework of Density Functional Theory (DFT) offer insights into the physical properties microscopically. I will introduce the working principle of the DFT-based first-principles calculations in this chapter, and the random structure search methodology as well. I will also discuss the validity of these approaches in the subject compounds of this thesis.

3.1 First-principles Calculations

3.1.1 Overview of Density Functional Theory

Density Functional Theory (DFT) is an effective quantum mechanical computational method to simulate materials' crystal structures and structure-related electronic properties [108]. It starts by solving the time-independent Schrödinger equation of given systems with interacting electrons and nuclei (Eq. 3.1). The position vectors are referred to as $\mathbf{r}$ and $\mathbf{R}$, respectively. The first two terms of the Hamiltonian describe the kinetic energies of electrons and nuclei, followed by the Coulomb potentials of electron-nuclei, electron-electron and nuclei-nuclei interactions. The pre-factor of 1/2 accounts for double-counting in the later two. In principle, a "real" picture can be obtained by solving the many-body equation exactly. However, it is computationally impossible to solve such an "accurate" function in solid-state systems. To save calculation time while maintaining the key features of a given system, a set of

approximations is utilised to describe the exchange and correlation interactions in the system.

$$\hat{H}\Psi(\mathbf{r}_i, \mathbf{R}_j) = E\Psi(\mathbf{r}_i, \mathbf{R}_j), \text{ where} \quad (3.1a)$$

$$\begin{aligned} \hat{H} = & -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 - \frac{\hbar^2}{2M_n} \sum_j \nabla_j^2 \\ & - \frac{1}{4\pi\epsilon_0} \left(\sum_i \sum_j \frac{eZ_j}{|\mathbf{r}_i - \mathbf{R}_j|} + \frac{1}{2} \sum_i \sum_{j \neq i} \frac{e^2}{|\mathbf{r}_i - \mathbf{r}_j|} + \frac{1}{2} \sum_i \sum_{j \neq i} \frac{Z_i Z_j}{|\mathbf{R}_i - \mathbf{R}_j|} \right) \end{aligned} \quad (3.1b)$$

The Born-Oppenheimer approximation [109] is introduced as the very first approximation in DFT, where the motion of nuclei and electrons are treated separately. The kinetic energy of nuclei can thus be neglected and the Coulomb repulsion between electrons and nuclei can be treated as a constant. The wave function $\Psi(\mathbf{r}_i, \mathbf{R}_j)$ can also be decoupled into $\psi(\mathbf{r}_i)\phi(\mathbf{R}_j)$. This approximation lies in the fact that the mass of nuclei is substantially large compared to that of electrons.

Then came the Kohn-Sham simplification [110], which was developed from the Hohenberg-Kohn theorem [111]. It has been argued that a system of N interacting particles can be replaced by N non-interacting particles in an effective external potential. The single-particle K-S equation is displayed in Eq. 3.2. The four terms on the left in order are non-interacting kinetic energy, potential from ion, Hartree term describing Coulomb interactions and the exchange-correlation (XC) term.

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + V_{\text{ion}}(\mathbf{r}) + V_{\text{Hartree}}(\mathbf{r}) + V_{\text{XC}}(\mathbf{r}) \right) \psi_i(\mathbf{r}) = \epsilon_i \psi_i(\mathbf{r}) \quad (3.2)$$

Summing up the amplitudes of all K-S orbitals for both spin up and down states, the electron density is given. For simplicity, orbitals with different spin states are not differentiated here:

$$n(\mathbf{r}) = \sum_i |\psi_i(\mathbf{r})|^2 \quad (3.3)$$

Revisiting Eq. 3.2, the problems now shrink down to solving the exchange-correlation potential V_{XC} . By definition, $V_{\text{XC}}(\mathbf{r}) = \partial E_{\text{XC}}[n]/\partial n(\mathbf{r})$. The DFT thus transforms the complex many-body interaction problems into finding the proper functionals to describe the density. Many approaches have been adopted to approximate the XC energy. Among them, the simplest one is the local density approximation (LDA) [112] derived from a homogeneous electron gas model for non-polarised systems. Adding spins, the approximation will be

generalised into local spin density (LSD). LDA ignores the local inhomogeneity. A more generalized approximation is thus developed involving the density gradient to improve calculation accuracy [113]. This is referred to as the generalised gradient approximation (GGA) [114]. Within the framework of GGA, the most overwhelming description is proposed by Perdew, J. P. and Burke, K. and Ernzerhof, M. (PBE) [115, 116]. In general, GGA-PBE works better to describe the bonding than LDA whereas it might underestimate the band gap due to gradient discontinuities at the band gap.

3.1.2 DFT + Hubbard U Method for Strong Correlated Electrons

Though LDA and GGA can successfully predict the crystalline structures, structure-related properties including phonon spectrum, and corresponding electronic properties, they fail to work in strongly correlated systems, such as Mott insulators. The $V_{XC}(\mathbf{r}) = \partial E_{XC}[n]/\partial n(\mathbf{r})$, where $n(\mathbf{r})$ denotes the density, is a mean-field solution, indicating no correlation among electrons. The given potentials remain identical for both occupied and unoccupied states and the on-site repulsion is not properly counted. The band gap would thus be underestimated in a Mott insulator. Mott and Peierls addressed this physical idea in 1937 [105] and Hubbard proposed a canonical model for it in 1963 [117]. In computational feasibility, the DFT+ U method has been developed in 1991 [118]. It has been accepted that the multi-band Hubbard model predicts the strongly correlated systems quite well [119]. There, the localised d or f electrons are subject to on-site Coulomb interactions U , as shown in Eq. 3.4. The modified functional, Eq. 3.5, includes E^{dc} to account for the "double counting" so as to remove the orbital energy which has already been counted in LDA/GGA functional.

$$\hat{H}_{Hubbard} = -t \sum_{\langle ij \rangle} a_{i\sigma}^\dagger a_{j\sigma} + U \sum_i \hat{n}_{i\uparrow} \hat{n}_{i\downarrow} \quad (3.4)$$

$$E^{DFT+U}[n] = E^{DFT}[n] + E^U[n_i^\sigma] - E^{dc}[n_i^\sigma] \quad (3.5)$$

The "double counting" (DC) problem arises because the electron-electron interactions are already partially considered in the exchange-correlation at standard DFT level (V_{XC}). When the U term is added for on-site interactions, some electron-electron interactions would end up with being double-counted, leading to an inaccurate overestimation. To address this problem, various correction schemes have been proposed. In 1998, Dudarev *et al.* demonstrated a correction for electron correlations in nickel oxide [120]. This correction subtracts the self-interaction term which is already included in the DFT functional from the U term. The

"Dudarev correction" approach is now commonly used in *ab initio* studies of transition-metal oxides, aligning with the methodology applied in our studies. A practical implementation of this correction will be introduced in the following section when discussing the software employed in this research.

The exact expression of E^{dc} remains as an open problem. Apart from adding correction terms, another way to predict a strongly correlated system is using the dynamical mean-field theory (DMFT) [121, 122]. DMFT, a many-body theory focusing on the local behavior of electrons within a material, provides more accurate results at the expense of substantial calculation time. Recently, a combination of DFT and DMFT has been explored as a more comprehensive treatment [123–126]. Such methods are computationally more demanding. Since DMFT is not used in our work, I will skip this part.

3.1.3 DFT + Dispersion Corrections

It is important to note that standard LDA and GGA functionals cannot correctly describe long-range dispersion interactions, usually referred to as the attractive part of the van der Waals (vdW) interactions. Since vdW interactions play a significant role in the subject of this thesis, the $TMPX_3$ compounds, it is necessary to apply corrections to standard DFT to improve the accuracy of describing the system's physical properties. Here I provide a brief overview of dispersion corrections to standard DFT functionals.

It has been an active research field to understand the limitation of standard DFT-based methods in describing dispersion or vdW interactions [127, 128]. After decades of investigations, it has become clear that the semi-local functionals (LDA/GGA) cannot provide the correct $-C_6/R^6$ dependence of the dispersion interaction energy as the function of the interatomic distance R , especially in the long-range asymptotic regions. LDA/GGA functionals perform well at short electron-electron distances, where bonding behaviours are closely related to electron density changes. At intermediate and long-range scales, however, these standard functionals fail to describe the electron correlations.

Over the past few decades, various approaches allowing for dispersion corrections have been developed, such as adopting nonlocal vdW density functionals (vdW-DF) or adding atom pairwise sum over the $-C_6/R^6$ potentials to the Kohn-Sham DFT energy (DFT+D). The vdW-DF is non-empirical but numerically more complex, and how "double-counting" effects are treated in vdW-DFs remains unclear. Meanwhile, the DFT+D is semiclassical with reduced numerical complexity, providing a good-quality analysis of physical properties.

The "double-counting" in DFT+D is typically addressed by introducing damping functions. Further details can be found in the literature hence I will not elaborate on it here.

The dispersion energy is generally expressed as follows:

$$E_{\text{disp}}^{\text{DFT+D}} = - \sum_{\text{AB}} \sum_{n=6,8,10,\dots} s_n \frac{C_n^{\text{AB}}}{R_{\text{AB}}^n} f_{\text{damp}}(R_{\text{AB}}) \quad (3.6)$$

In this equation, C_n^{AB} refers to the averaged n^{th} -order dispersion coefficient ($n = 6, 8, 10, \dots$) for atomic pair AB at the distance of R_{AB} . It is still an open question how many higher-order terms are necessary for a more accurate description of the physical system. Since the focus of this thesis is not on numerical methodology regarding dispersion corrections, I adopt the most commonly developed and used DFT+D corrections considering the vdW nature of the compound family. The practical application of DFT+D approach will be covered in the subsequent software section.

In summary, the many-body time-independent Schrödinger equations can be computationally tackled given the Born-Oppenheimer, and Kohn-Sham approximations and the electron density functionals. DFT can predict the solid-state system without any empirical knowledge, thus giving the name "first-principles" or "*ab initio*" calculations. For systems featuring strongly correlated electrons or dispersion (vdW) interactions, Hubbard U terms and dispersion corrections (D) can be applied for improved accuracy. The continuous exploration of fundamental theories, together with the rapid development of highly efficient computational algorithms, have turned DFT into one of the most popular calculation tools to investigate materials structure and structure-related properties [129, 130]. Now we will move on to the specific software packages used in this thesis.

3.1.4 Software Package: CASTEP

CASTEP is a first-principles quantum mechanical code for performing electronic structure calculations. It was originally developed by Payne M. C. and his co-workers in the early 1990s [131] and has been updated continuously [132, 133]. It follows the general approach within the DFT framework and is able to simulate the geometry optimisation, total energy, electronic structure, exchange and correlation, *etc.* It uses plane waves to model the electron density in periodic cells based on the fact that bulk materials in a condensed matter state are constituted of infinitely repeated identical cells. Usually, the primitive cell (the smallest repeating unit) is preferred to minimise computational time. Within each cell, the wave

functions at position $\mathbf{r}$ can be constructed of series of plane-waves following completeness and orthogonality,

$$\psi(\mathbf{r}) = \sum_{\mathbf{G}_{\max}} c_{\mathbf{G}} e^{i(\mathbf{G} \cdot \mathbf{r})} \quad (3.7)$$

The $\mathbf{G}$ is a reciprocal space lattice vector and $c_{\mathbf{G}}$ is the coefficient constant for each plane wave. For accurate simulations, a large number of plane waves are needed which will be computationally demanding. This is amended by introducing pseudopotential approximation [134]. Since the core electrons are tightly bonded with the nuclear region and barely contribute to the physical properties, it requires quite high kinetic energy to oscillate. Hence, they can be replaced, together with the original cores, as pseudo-cores. A smoother potential is thus established.

Pseudopotentials

CASTEP supports both ultra-soft [135] and norm-conserving pseudo-potentials [136, 137], together with a specially "built-in" pseudopotential generator "on-the-fly" [138].

- Norm-Conserving Pseudopotentials (NCP) were initially proposed by Hamann *et al.* in 1979 [136]. It is crucial that the integrals from 0 to r of the real and pseudo charge densities agree for $r > r_c$ for each valence state (norm conservation). Additionally, the logarithmic derivatives of the real and pseudo wave function and their first energy derivatives agree for $r > r_c$. NCPs provide accurate self-consistent calculations of the electronic structure near the nucleus.
- Ultrasoft Pseudopotentials (USP) were introduced by Vanderbilt in 1990 [135] to facilitate calculations to be performed with as small as possible a cutoff energy for the plane-wave basis set. The core potential near the nucleus gets softened in a way that the potential smoothly goes to zero within a specified cutoff radius. The potentials can thus be constructed more compatibly and efficiently with the plane-wave expansion of wavefunctions without requiring an excessively large basis set. Consequently, USP facilitates more rapid convergence of the calculations.

CASTEP's "on-the-fly" (OTF) pseudopotential generator [138] provides a dynamic and adaptive approach to generate pseudopotentials during simulations. It means that the pseudopotentials are generated in real-time as needed, optimising the trade-off relation between

calculation accuracy and computational cost. During the calculation, I performed a test run with the OTF option to generate pseudopotentials for geometry optimisation. The pseudopotentials were written in the output file and had been carefully checked. I then kept the same pseudopotentials for a systematic exploration and comparison across various phases of the compound.

The ultra-soft ones require fewer plane waves than norm-conserving ones. Here we will not go further into the details as they are beyond the main focus of our work. Considering the computational efficiency, we chose the ultra-soft pseudopotential for geometry optimisations and the non-conserving ones for more accurate electronic property simulations.

Plane-wave energy cutoff E_c^{PW}

In addition, the cut-off energy is required to fix the number of plane waves. The larger the cut-off energy is, the larger the basis set will be, increasing the computational time dramatically. As long as the fundamental features can be captured, there is no need to use extremely large cut-off energy.

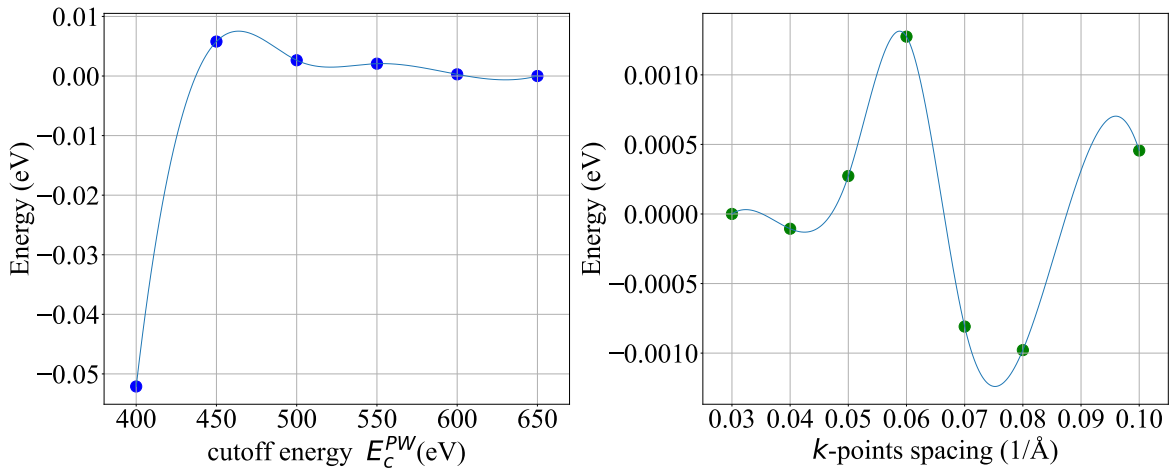


Fig. 3.1 Convergence with plane-wave energy cutoff E_c^{PW} of the total energy of the LP phase of FePS₃ at ambient pressure (left), and with k -point spacing (right). The vertical axis of energy has been rescaled so that the energies calculated with the highest energy cutoff ($E_c^{PW} = 650$ eV) and the highest k -point density (spacing = 0.03 1/Å) corresponds to 0.

***k*-point spacing**

In reciprocal space, the cell's information is described by sampling the Brillouin zone (BZ). All points can be mapped periodically, therefore the entire bulk system is captured by sampling the BZ. The concept can be described with the "kspacing" variable in CASTEP, which is the smallest spacing between K-points in the unit of $\text{\AA}^{-1}$.

We have performed the convergence tests for the plane-wave cutoff energy (E_c^{PW}) and *k*-points sampling within the framework of static single-point calculations using CASTEP. The LP phase of FePS₃ at ambient pressure has been chosen to perform the tests. The total energy dispersions as a function of E_c^{PW} and the maximum spacing between each *k*-point are displayed in Fig. 3.1. Based on the convergence tests, the $E_c^{PW} = 550$ eV and *k*-points sampling of $0.03 \text{ \AA}^{-1}$ along each axis has been set for the rest of all calculations, including the high-pressure phases.

DFT + *U*

CASTEP implements DFT + *U* using a simplified, rotationally invariant approach [120, 139]. The only external parameter required is the effective value of the on-site Coulomb parameter, *U*, for each targeted orbital. In this work, I considered the on-site Coulomb repulsion for the 3*d* orbital of Fe atom. While, in principle, the *U* parameter could be calculated theoretically [139], its value might vary depending on the specific physical property of interest. Therefore, with CASTEP, I did not calculate the value of *U* but used it as an input parameter instead. The effect of varying *U* is explored and discussed in Chapter 6.

DFT + *D*

CASTEP incorporates several computational schemes within the "DFT+D" framework to facilitate vdW dispersion corrections. Two notable options are the Tkatchenko-Scheffler (TS) scheme, relying on C_6 values derived from atomic volumes [140], and the Grimme scheme, employing damped $C_6 R^{-6}$ terms [141]. The TS scheme extends its applicability to many-body dispersion effects, going beyond the pairwise interatomic interactions covered by the Grimme scheme. Despite the increased computational cost, simulation with TS scheme has been evaluated to remain within manageable limits. For most of the work involving DFT+D in this thesis, the TS correction scheme was utilised. A comparison of utilising different vdW correction schemes is given in Chapter 6.

3.2 Random Structure Search Methodology

3.2.1 Working Principles

The arrangement of atoms in compounds determines the structure and structure-related physical properties. How to search for stable structures of materials theoretically is a rapidly growing field as it would help researchers to search for promising new materials or metastable phases. Computational search can benefit experimental studies as it provides structure details from the energy point of view. The accuracy and efficiency of the search methodology are thus important in this case. Here we describe one simple yet powerful approach to search for structures with the framework of DFT, the *ab initio* random structure searching (AIRSS), developed by Pickard, C. J. and his co-workers [142].

In a given system, the number of local minima in the potential energy surface (PES) will increase exponentially with the number of atoms [143]. It suggests that determining the global minimum of a PES will be very difficult to solve in large systems. AIRSS focused on the energy functions representing the PES of assemblies of atoms. Structures in which the atoms are much closer to their neighbours than the equilibrium bond length will naturally be high in energy. They will thus be disregarded. Though we would like to exert an unbiased sampling among the PES, reasonable limits must be imposed on the initial structures to improve the calculation efficiency, e.g. setting the minimum bond length between atoms. In our work, since we already know the ambient pressure phase and also have the experimental indexed high-pressure structure, we can set an initial volume and minimum bond length (relatively smaller than those in known phases) for better calculation performance. Then a random cell will be generated with a normalised volume within $\pm 50\%$ of the chosen mean volume. For period solids, the lattice parameters and angles will be generated with a certain degree of symmetry being imposed on them. To be noted, the cell size can be specified or randomly chosen as well, allowing for more configurations which might be overlooked in smaller cells with boundary conditions. Once the structure is generated, the energy will be calculated with implemented DFT code, here CASTEP, until reaching the stopping criterion specified in the input parameters.

AIRSS is designed in a way that various randomly generated structures can be calculated at once. Ultimately, all structures can be listed in ascending enthalpy reduced to a given formation unit. During the random search step, the geometry optimisation with CASTEP can be set with lower convergence criteria for prediction efficiency. When we filter out the

"good" candidates, finer optimisations can be performed with higher energy convergence criteria.

3.2.2 Implementation of AIRSS in $TMPX_3$

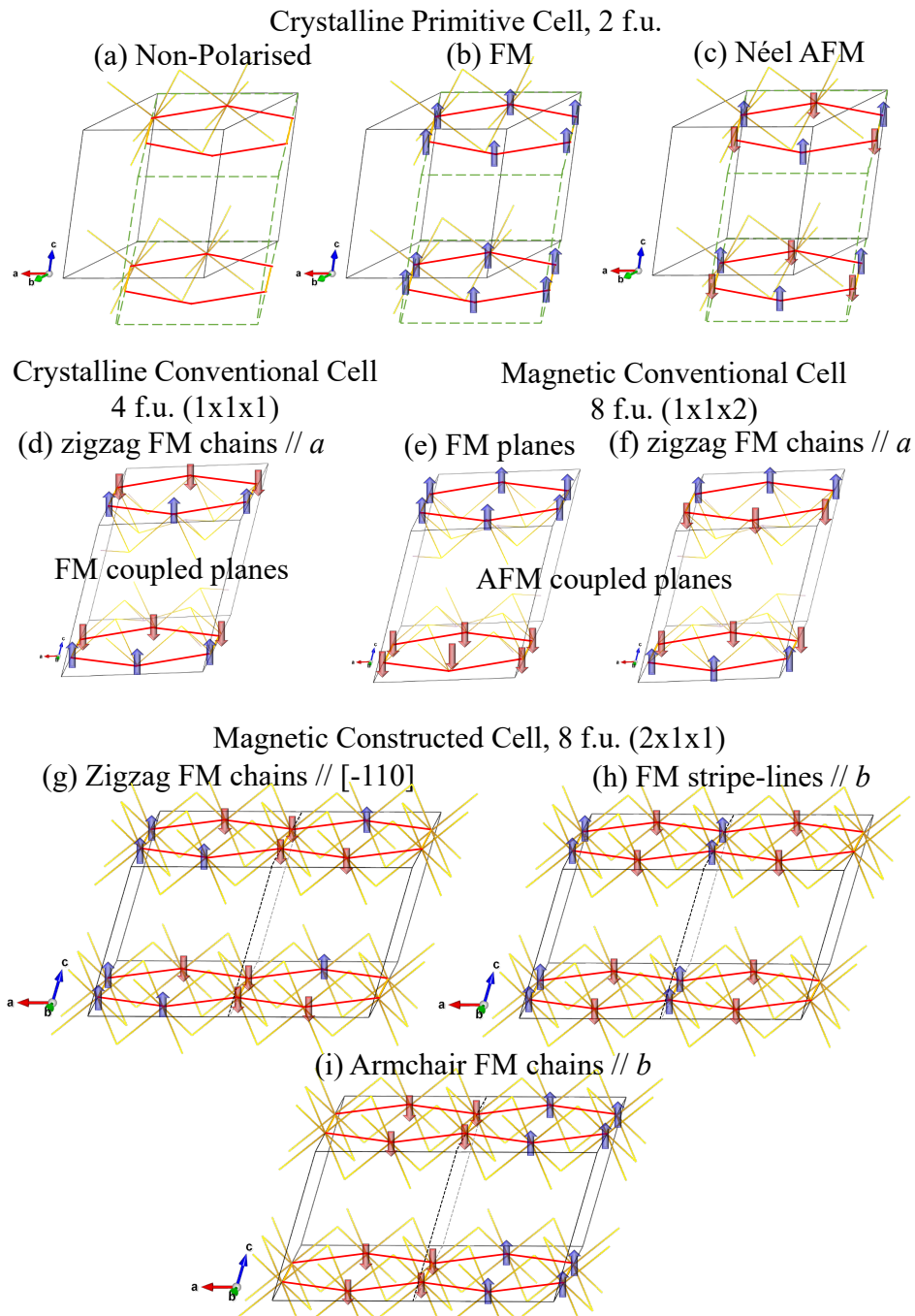
We implemented AIRSS for structure search and CASTEP for geometry relaxation for the $TMPX_3$ compounds family. We started with $FePS_3$ to test the feasibility of such a methodology in the compound system. It has been rather computationally demanding to perform the structure search together with geometry optimisation. At each pressure point, we used 4, 6 and 8 chemical formation units [$FePS_3$] inside the simulation cell to allow for the generation of as many random structures as possible. Detailed discussions about the results will be covered in Chapter 5.

3.3 Exploring the Simulation Setup for $FePS_3$

3.3.1 Magnetic Configurations

If we denote [$FePS_3$] as the formation unit (f.u.), the primitive cell of $C2/m$ contains 2 f.u. Leveraging the symmetry of the known experimental ambient pressure phase, we constructed several crystalline supercells based on the primitive one to accommodate various magnetic configurations while minimizing supercell size. For consistency with previous literature and to provide a clear presentation of the crystallographic planes, we opted for the conventional cell with 4 f.u., defining it as a $1 \times 1 \times 1$ supercell. Fig. 3.2 presents a simplified demonstration of the diverse magnetic configurations in $FePS_3$. To facilitate a more straightforward comparison, we have omitted the display of P atoms. And the [FeS_6] clusters are plotted using the wireframe option in VESTA instead. The Fe-honeycomb networks are denoted by solid frames (red and orange). The blue and red arrows signify the spin-up and spin-down magnetic moments on Fe.

The primitive cell allows for three fundamental configurations: (a) non-polarised, (b) ferromagnetic (FM), and (c) in-plane Néel antiferromagnetic (AFM) configurations. The transition from the primitive cell (2 f.u.) to the crystalline conventional cell (4 f.u., $1 \times 1 \times 1$) is indicated by dotted green lines in (a-c) as well. Within a crystalline conventional cell ($1 \times 1 \times 1$), all three of these magnetic configurations can be generated through symmetry operations. Consequently, we exclusively illustrate a distinct magnetic configuration characterised by zigzag

Fig. 3.2 Various magnetic phases for FePS₃ at ambient pressure.

FM chains along a axis. These FM chains are antiferromagnetically coupled within each ab plane, while the interplanar coupling is ferromagnetic, in alignment with the repeating unit of the cell.

Upon doubling the cell along the c axis, antiferromagnetic coupling between adjacent planes becomes possible, leading to two additional distinctive configurations shown in (e) and (f). One configuration consists of FM planes stacked together through AFM interplanar interactions. The other corresponds to the known experimental ground-state magnetic configuration of FePS₃. In this configuration, zigzag FM chains form and elongate along the a axis, with all neighbouring chains being antiferromagnetically coupled, either within or in between the planes.

Additionally, we constructed an alternative magnetic cell with a doubled a lattice (2x1x1). This cell enables the elongation of zigzag FM chains along the $[-110]$ vector in (g), FM stripe lines along the b axis in (h), and armchair-shaped FM chains elongating along the b axis in (i). The 2x1x1 supercell prohibits AFM coupling across the planes.

3.3.2 Strongly Correlated Electrons

In this section, we initiated an investigation into the impact of the on-site Coulomb repulsion parameter, denoted as U , during geometry optimisations for different phases. Fig. 3.3 (upper panel) clearly shows that without considering the U parameter (DFT+D), the most energetically stable phase will fall into the one without any spin polarisation, contradicting with the known zigzag chains one. However, when we performed the DFT+D+ U calculations, the non-polarised phases became energetically unfavourable (lower panel). Those with zigzag ferromagnetic chains along the a axis become energetically more favourable, consistent with the experimental observations.

It's worth noting that the 4 f.u. configuration, initially displaying lower energy than the experimental configuration in 8 f.u., differs due to variations in interlayer coupling, which is known to be weak and sensitive to van der Waals (vdW) forces. To unravel this enigma, we performed geometry optimisation for Fig.3.2 (d) within the 8 f.u. 1x1x2 supercell to minimise different parameters' influence. Consequently, the formation energy increased by 0.021 meV/atom, surpassing the optimised experimental configurations. This subtle disparity emphasises the need for precision in geometry optimisations across distinct magnetic configurations. It implies that denser k -point sampling or adjustments to other parameters,

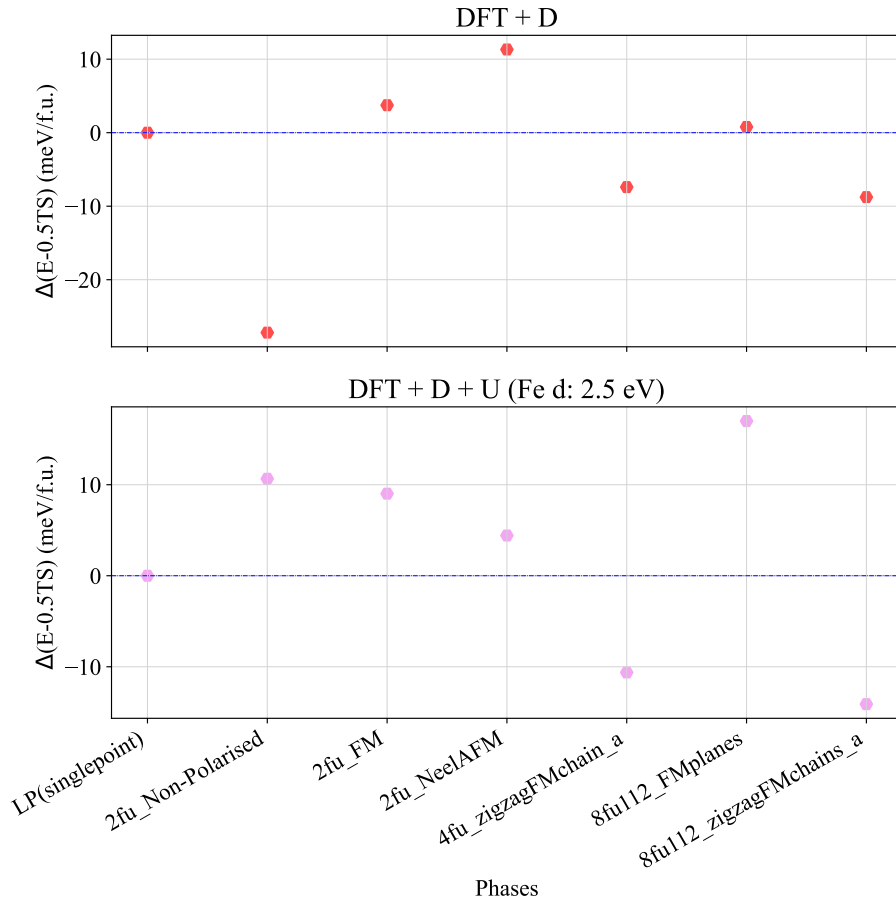


Fig. 3.3 The energy of various optimised magnetic phases of FePS₃ at ambient pressure, without and with considering the Hubbard U parameter for electrons on the Fe d orbitals. The reference zero point is chosen to be the static energy obtained from the single-point calculation using FePS₃ magnetic cell with known experimentally determined configuration, denoted by a dotted blue line.

such as vdW correction methodologies or functionals, may be required to meet more stringent convergence criteria.

Here, I provide a summary of post-optimisation lattice parameters and formation energy in Table 3.1. The optimised structure with an experimentally known magnetic configuration has been set as the reference phase, of which the energy is regulated to be zero. Remarkably, the armchair configuration exhibits an energy level that is -1.198 meV/atom lower than the experimentally agreed configuration. Further exploration regarding vdW interactions, k -point sampling, and related aspects may still be warranted.

Table 3.1 The lattice parameters and interatomic Fe-Fe distances of $C2/m$ FePS₃ involving the known experimental [64] phase and the fully optimised magnetic ones at ambient pressure with PBE+D+U (Fe d : 2.5 eV) calculations. d_1 denote the Fe-Fe in $[\pm 1/2, \pm 1/6, 0]$ while d_2 are that along b axis. Here, we set it to be the reference energy of the optimised phase with a zigzag FM chain along a direction AFM coupled for neighbouring chains and layers.

	Configurations	Lattice Parameters (Å)			Fe-Fe (Å)		Energy (meV/atom)
		a	b	c	d_1	d_2	
exp.	zigzag_AFM	5.947	10.345	6.722	3.426	3.448	-
8f.u. 1x1x2	FM	5.960	10.402	6.870	3.382	3.600	2.085
	zigzag_interlayerAFM	5.935	10.466	6.880	3.333	3.715	0
	zigzag_interlayerFM	5.935	10.468	6.877	3.333	3.716	0.021
	FM_plane	5.954	10.419	6.875	3.385	3.598	7.891
8f.u. 2x1x1	zigzag rotated by 60°	5.980	10.390	6.888	3.420	3.540	1.166
	stripeline_ b	5.961	10.433	6.878	3.382	3.617	6.619
	armchair_ b	5.984	10.376	6.887	3.526 3.385	3.515	-1.198

Chapter 4

Experimental Techniques

To get the full structural information, the work presented in this thesis also relied on X-ray and neutron diffraction measurements. Since the focus was to determine the high-pressure crystallographic structure of $TMPX_3$ compounds, pressure cells were used to reach the target pressure range and to satisfy the requirements of the diffraction experiments, here, being transparent to x-rays or neutrons. In this chapter, I will first describe the advanced approach of using Diamond Anvil Cells (DAC) with synchrotron X-ray beams to probe the crystallographic structure information from powder and single-crystal samples. The experiments on $FePSe_3$ were carried out on the beamlines I15, "Extreme Conditions", and I19-2, "Small Molecule Single Crystal Diffraction", at the Diamond Light Source (DLS), Didcot, UK. The samples were loaded into DACs by Dr Dominik Daisenberger, instrument scientist on I15 at DLS. I will also describe the technique of using Paris-Edinburgh pressure cell with inelastic neutron scatterings to explore the evolution of magnetic properties under pressure in $FePSe_3$. The experiments were performed at Institut Laue-Langevin, Grenoble, France.

4.1 Synchrotron X-ray Diffractions at Extreme Conditions

X-rays are electromagnetic waves with the wavelength in the same order as the atomic distances, $0.1 \sim 10.0 \text{ \AA}$. The atomic potential can alter them without being affected. Consequently, X-rays are useful to probe atomic information [144]. The fundamental principle underlying X-ray diffraction is Bragg's law, which describes the conditions for X-rays being scattered by the crystal lattice. For a given crystal plane hkl with spacing d , the incident

angle θ and the diffraction angle 2θ are related to the wavelength of the X-ray λ following Eq.4.1:

$$2 * d_{hkl} * \sin(\theta) = n * \lambda_{hkl} \quad (4.1)$$

, where n is an integer corresponding to the order of diffraction.

For the reliability and quality of the data, X-ray experiments must be prepared and performed in alignment with the needs of the experiments. Synchrotron X-ray sources offer higher intensity (flux) and better spatial resolution over traditional lab-level X-ray sources, enabling a more comprehensive analysis of the material's crystallographic properties. Below I will describe the principles, experimental setups and data analysis for the synchrotron X-ray diffraction experiments on single crystal and powder samples with monochromatic beams.

4.1.1 Single Crystal X-ray Diffraction

Theory and Principles

In an ideal single crystal, the atoms repeat themselves in an ordered and periodic pattern in three dimensions. When subjected to X-ray diffraction, single crystals generate sharp and intense diffraction peaks corresponding to the lattice structure. Define the repeated unit with translation vectors $\mathbf{a}_1$, $\mathbf{a}_2$ and $\mathbf{a}_3$, and the position of an atom in the unit cell by the basis vector $\mathbf{r}_n$. Then the position of any atom in unit cell $m_1m_2m_3$ can be written as

$$\mathbf{R}_{n,m_1m_2m_3} = m_1\mathbf{a}_1 + m_2\mathbf{a}_2 + m_3\mathbf{a}_3 + \mathbf{r}_n \quad (4.2)$$

The intensity of the X-ray beams scattered by a single atom at 2θ is given by

$$I_n = f_n^2 \frac{I_0 e^4}{m^2 c^4 R^2} \left(\frac{1 + \cos^2 2\theta}{2} \right) \quad (4.3)$$

, where f_n is the atomic scattering factor.

When a monochromatic X-ray beam with wavelength λ and incident wavevector $\mathbf{s}_0$ interferes with a single crystal of $(N_1\mathbf{a}_1, N_2\mathbf{a}_2, N_3\mathbf{a}_3)$, the intensity of the scattered x-rays in the direction $\mathbf{s}$ is given by

$$\begin{aligned}
I &= \frac{I_0 e^4}{m^2 c^4 R^2} \left(\frac{1 + \cos^2 2\theta}{2} \right) \sum_{nm} f_n \exp \left[\frac{2\pi i}{\lambda} (\mathbf{s} - \mathbf{s}_0) \cdot \mathbf{R}_{n,m} \right] \sum_{nm} f_n \exp \left[\frac{-2\pi i}{\lambda} (\mathbf{s} - \mathbf{s}_0) \cdot \mathbf{R}_{n,m} \right] \\
&= \frac{I_0 e^4}{m^2 c^4 R^2} \left(\frac{1 + \cos^2 2\theta}{2} \right) F^2 \frac{\sin^2 \frac{\pi}{\lambda} (\mathbf{s} - \mathbf{s}_0) \cdot N_1 \mathbf{a}_1}{\sin^2 \frac{\pi}{\lambda} (\mathbf{s} - \mathbf{s}_0) \cdot \mathbf{a}_1} \frac{\sin^2 \frac{\pi}{\lambda} (\mathbf{s} - \mathbf{s}_0) \cdot N_2 \mathbf{a}_2}{\sin^2 \frac{\pi}{\lambda} (\mathbf{s} - \mathbf{s}_0) \cdot \mathbf{a}_2} \frac{\sin^2 \frac{\pi}{\lambda} (\mathbf{s} - \mathbf{s}_0) \cdot N_3 \mathbf{a}_3}{\sin^2 \frac{\pi}{\lambda} (\mathbf{s} - \mathbf{s}_0) \cdot \mathbf{a}_3}
\end{aligned} \tag{4.4}$$

with the structure factor F expressed in terms of the fractional coordinates of an atom in the position (x, y, z) by

$$F = \sum_n f_n e^{2\pi i(hx+ky+lz)} \tag{4.5}$$

The intensity in Eq. 4.4 reaches a sharp maximum when the divisors in the three sine divisions approach zero. That leads to the following conditions,

$$\begin{aligned}
(\mathbf{s} - \mathbf{s}_0) \cdot \mathbf{a}_1 &= h\lambda \\
(\mathbf{s} - \mathbf{s}_0) \cdot \mathbf{a}_2 &= k\lambda \\
(\mathbf{s} - \mathbf{s}_0) \cdot \mathbf{a}_3 &= l\lambda
\end{aligned} \tag{4.6}$$

When these conditions are simultaneously satisfied, there will be high-intensity peaks in the X-ray diffraction pattern. From the geometry, the translation axes $\mathbf{a}_i$ ($i = 1, 2, 3$) can be determined. However, the atomic positions within the unit cell depend on the intensity of various diffracted X-ray beams.

Experiment Setup: Rotating Crystal Method

One standard technique to collect the diffraction data from a single crystal is to systematically rotate the crystal along two orthogonal axes, usually labelled as ϕ and ω . Diffraction data are collected at each orientation. This method allows for the characterisation of crystal structures with complete information on unit cell parameters, lattice symmetry and atomic positions.

The single crystal is mounted on a sample stage capable of accurate angular rotations. It is required that one of the axes, e.g. $\mathbf{a}_3$, of the crystal should be approximately parallel to the

incident beam. Under such configuration, the crystal can be rotated around $\mathbf{a}_3$ and $\mathbf{s}_0 \cdot \mathbf{a}_3 = 0$. Follow Eq. 4.6, it can be derived that

$$|a_3| = l\lambda / \sin\beta_l \quad (4.7)$$

I19-2 at DLS

Single crystals of FePSe_3 were grown by chemical vapour transport method, provided by the group of Je-Guen Park at Seoul National University. Samples were manually reduced to a thickness of about $10\ \mu\text{m}$ and squares of side length $80\ \mu\text{m}$. Single-crystal x-ray diffraction data were collected on the I19-2 beamline at DLS at room temperature. The samples were mounted in a way that the $\mathbf{c}^*$ axis was as parallel to the direction of the incident beam as possible. Diffraction data were collected as the crystal was rotating in a standard configuration and analysed using the software CrysAlis Pro [145]. An incident beam of wavelength $0.4859\ \text{\AA}$ was utilised to collect the diffraction patterns using a Dectric Pilatus 300 K detector. The details of data analysis and the corresponding results will be thoroughly discussed in Chapter 8.

4.1.2 Powder X-ray Diffraction (PXRD)

Theory and Principles

The powder sample consists of a vast amount of arbitrarily oriented small single crystals. The Bragg condition allows freedom in sample orientation as the vectors of the incident beam, the exit beam, and the wave vector transfer, which in the Bragg case, are identical to the reciprocal lattice vectors within a two-dimensional plane and an undefined third dimension. When X-rays with a given wavelength interfere with the powder sample, each small crystal generates a diffraction pattern fulfilling the different Bragg conditions. The scattered X-rays are then collected by a two-dimensional detector, which records the diffraction pattern. Since the scattering comes from all possible orientations, power rings are observed in PXRD. The feature of the ring depends strongly on the number of small crystals and whether there is a preferred orientation or not.

To analyze the data, the centre of the powder rings should be determined carefully. The intensity of all the rings is integrated over the diameter $\varnothing$ at a constant offset r from the

determined centre. The resulting $I(r)$ can also be converted to $I(q)$ in the 2θ space. Specialised software (for instance, DAWN – II [146] in our experiments) can be used to determine the positions and intensities of the diffraction peaks. The intensity of powder rings must be corrected by the multiplicity of the Bragg peaks to match the structural factor. The peak positions give information about the interplanar spacing of the crystal lattice, while the peak intensities indicate the abundance of different crystallographic planes.

The Rietveld refinement method is used to determine the crystal structure from the PXRD data. The strategy is to fit the experimental data to a given structural model while adjusting lattice parameters, atomic positions, and/or thermal vibrations to minimise the difference between the observed and calculated diffraction patterns. Several software, for example, GSAS – II [147] or TOPAS, are designed for performing the refinement. Once the crystallographic information is extracted from the PXRD data, we can explore the sample's lattice parameters and crystal structures in response to the tuning parameter, here, pressure.

I15 at DLS

High-pressure powder x-ray diffraction data were collected at room temperature on the I15 Extreme Conditions beamline at the Diamond Light Source. As described previously, the pressure was applied via a gas-loading system. Measurements were performed for powder samples immersed in helium pressure-transmitting medium. To explore the effect of hydrostatic condition, another DAC without any medium, just being filled with the FePSe₃ samples, was prepared and explored. A MAR345 area detector was used to record the diffraction pattern with an exposure time of 120 seconds for each scan at a distinctive pressure value. The instrument parameters were calibrated with LaB₆. The data were initially processed using the data analysis software DAWN – II [146]. Further, Le Bail and Rietveld refinements were performed using GSAS – II [147].

4.1.3 Diamond Anvil Cell and Pressure Transmitting Medium

To achieve the high-pressure environment experimentally, there are various designs of pressure cells. The methods could be grouped into piston cylinder cells (PCC) and anvil cells. The former has a larger sample volume yet lower maximum pressure without increasing the cell apparatus excessively large, compared to the latter. Diamond Anvil Cells (DAC) were used for the work in this thesis. DAC can be designed to perform contactless measurements by X-ray or wired measurements of resistivity or AC susceptibility.

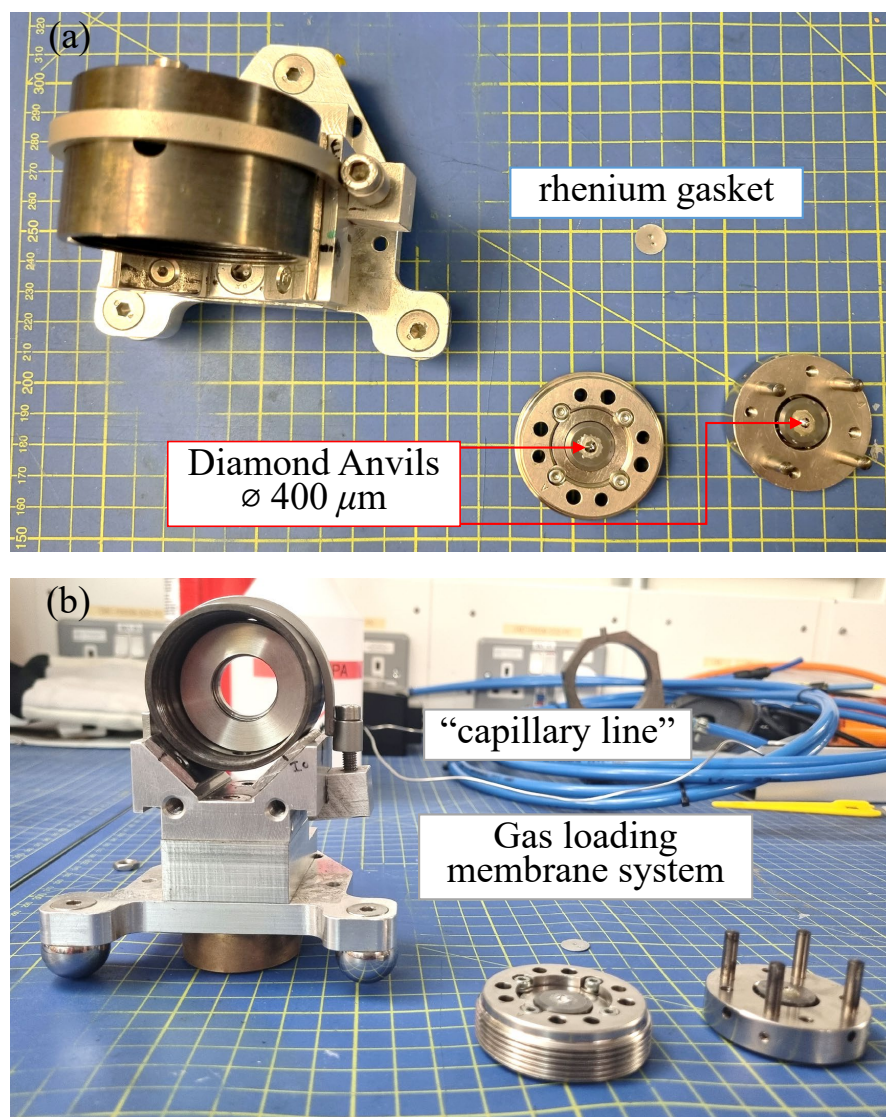


Fig. 4.1 The Diamond Anvil Cells used in the DLS experiments on I15.

Working Principles

The DAC consists of two opposing anvils, typically made of industrial-grade diamonds, each with a culet (flat and polished surface). The pressure chamber in the DAC is enclosed by the culets of the diamonds and a thin metal gasket between the two anvils. The hole in the gasket was made with a pre-dent and then drilled into the size of less than half the diameter of the culets. The space between the two anvils and the gasket is thus the sample chamber, where the samples are loaded. The gasket functions as a cell that prohibits the loaded sample from escaping in the application of pressure. Fig. 4.1 shows the DAC and the gas-loading membrane system we used for experiments at DLS.

To determine the pressure inside the DAC, a pressure gauge must also be put into the sample chamber, as close to the sample as possible. One method, used in this thesis's work, is to insert spheres of ruby with approximately 10 μm diameter into the sample chamber. The fluorescence spectrum of the ruby was measured using an exciting optical laser and a spectrometer. The wavelength of the *R1* fluorescence line shifts to higher values, indicating the increased pressure P according to Eq. 4.8 [148]:

$$P = \frac{A}{B} \left\{ \left[\frac{\lambda}{\lambda_0} \right]^B - 1 \right\} \quad (4.8)$$

where $A = 248.4 \text{ GPa}$, $B = 7.665 \text{ GPa}$ for hydrostatic pressures. λ_0 is the *R1* wavelength measured at ambient pressure. The value was measured and calibrated for each experiment before the sample loading. λ was measured at each pressure point before and after the sample data collection.

The pressure inside the DAC is generated by compressing the anvils together. The direct contact of anvils with the loaded sample can generate pressure. A non-reactive pressure-transmitting medium is usually used to generate more hydrostatic conditions for the samples. Hydrostatic pressure is a thermodynamic parameter, and the results obtained under such conditions are materials' intrinsic properties which can be compared with the results from theory. There are multiple choices of pressure transmitting medium, including methanol–ethanol mixtures, silicone oil, daphne 7474, argon, nitrogen, helium and so on [149]. When the sample is immersed in the pressure transmitting medium, the pressure is expected to evenly distribute the pressure across the whole sample chamber. However, the melting line of any pressure-transmitting medium will eventually increase with increased pressure. Solidification of the medium inevitably occurs at a particular pressure value. Beyond that point,

the pressure across the sample chamber is generally inhomogeneous. Consequently, the quality and accuracy of the data obtained from sophisticated high-pressure techniques must be scrutinised, ascribing to observed physical phenomena.

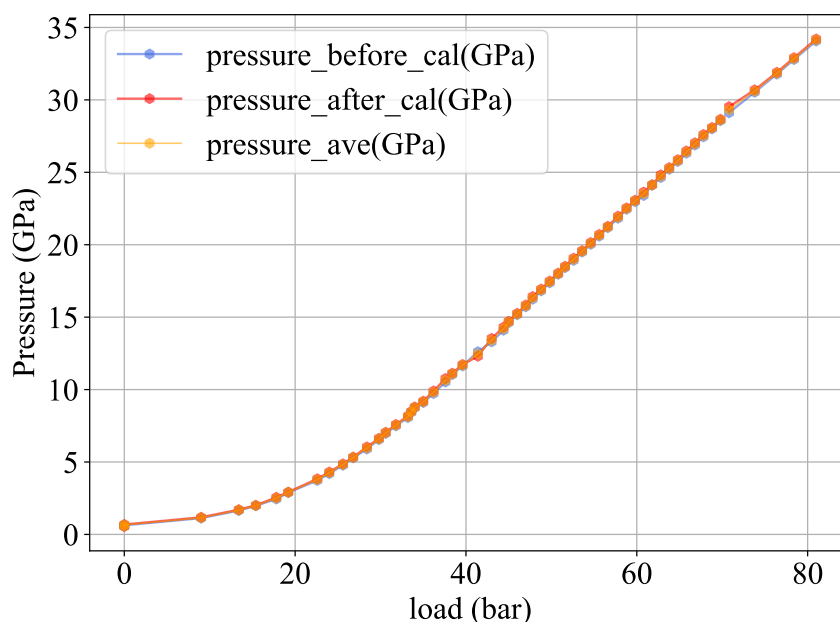


Fig. 4.2 The load versus pressure relationship obtained from the experiments on I15 at DLS using the DAC with helium medium.

A gas-loading membrane system is used together with the DAC to compress the anvils. The gas reservoir controls the load on the DAC through a capillary line. A DAC's load versus pressure relationship depends on multiple factors and differs in each experiment. We track the relationship during measurements to avoid exceeding the pressure limits of the DAC or causing damage to the sample during the experiment. As shown in Fig. 4.2, the relationship remains linear up to the highest pressure points. No "plateau" was observed in our experiments.

DAC used in I19-2 and I15 experiments

The presented work realised the pressure environment using DACs with rhenium gaskets. The culet size of DAC was $400\ \mu\text{m}$. The sample chamber in each DAC is enclosed by the culets of the diamonds and the metallic gasket through which a hole, with a diameter less than half that of the culets, has been drilled. As the culets are approximately circular, the diameter is an average and may shrink during pressurisation.

An incidence X-ray beam with the size of $30\ \mu\text{m}$ and the wavelength of $0.4246\ \text{\AA}$ (equivalently with the energy of $E = 29.2\ \text{keV}$) was used to collect the diffraction patterns. The use of a small-sized X-ray beam allows for enhanced spatial resolution and precision of the diffraction data with reduced background. In the meantime, the energy is sufficiently high to pass through the diamond anvils.

Helium gas was loaded as the pressure-transmitting medium for single crystal and powder experiments. Another DAC without helium gas was also prepared for the powder sample experiment to explore the effect of the pressure medium. The difference will be discussed in detail in the subsequent section. The load inside the sample chamber was applied through a gas-loading membrane system. And the generated pressure was determined by optical measurement of the fluorescence of the ruby sample nearby the FePSe_3 sample. We measured the Ruby optical peak before and after the data collection at the FePSe_3 sample position and took the average value of the pressure. The uncertainties of the pressure values were estimated to be approximately $\pm 0.1\ \text{GPa}$, based on the pressure change during the FePSe_3 data collection. Diffraction peaks from the DAC were identified by fitting the known diamond unit cell and removed for subsequent treatment. Regions of detector images containing powder-like rings from the rhenium gasket were also identified and excluded from refinements.

4.2 Neutron Scattering at Extreme Conditions

Since the first discovery back in the year 1932 [150], neutrons have been demonstrated as a robust probe for exploring crystal and magnetic structures. Neutron scattering provides extra information beyond the capability of X-rays scattering, which is related to the fundamental physical properties of the scattering beam, here, neutrons. Recent development of high-pressure cells transparent to neutrons or with a uniform background opens up the possibility to explore the magnetic structures directly at the atomic level. This advanced technique and delicate experimental setup has been used to study the TMPX_3 compounds and I will give an introduction to the involved scattering theory and techniques.

4.2.1 Powder Neutron Diffraction for Magnetic Phases

First, the large mass of neutrons gives the de Broglie wavelength in the order of interatomic distances. Hence, the interference of neutrons with the sample can yield information about the

crystalline structure. Secondly, the uncharged nature ensures that neutrons can penetrate the targeted sample without being screened by the electronic charge cloud. The incident neutrons can approach sufficiently close to the nuclei and interact directly, and they can also easily transmit through bulky devices that control the sample environment, such as low-temperature cryostats and pressure cells. Thirdly, the neutron has a magnetic dipole moment and can scatter from the magnetic moment of an atom via the dipole-dipole interaction. Last but not least, neutrons coming from a moderator near room temperature, known as "thermal" neutrons, have energies in the $1 \sim 100$ meV range, which is of the same order as many excitations in condensed matter.

Theory and Principles

In a neutron scattering experiment, we are interested in the rate at which neutrons, with a final wave vector $\mathbf{k}_f$ and a final energy between E_f and $E_f + dE_f$, are scattered into a given solid angle $d\Omega_f$. When a monoenergetic beam of neutrons characterised by initial wave vector $\mathbf{k}_i$ and flux $\phi(k_i)$ is incident on the sample, the neutrons will get scattered at the rate of the product $\phi(k_i)\sigma$. The symbol σ represents the scattering cross-section. The subscript i refers to the incident neutron beam on the sample, and f is the diffracted one. The rate of the scattered neutrons is given by the product of $\phi(k_i)$ and the double-differential cross-section. The latter is defined by Eq. 4.9, summing up the coherent and incoherent contribution:

$$\frac{d^2\sigma}{d\Omega_f dE_f} = \left. \frac{d^2\sigma}{d\Omega_f dE_f} \right|_{\text{coherent}} + \left. \frac{d^2\sigma}{d\Omega_f dE_f} \right|_{\text{incoherent}} \quad (4.9)$$

The coherent part describes cooperative effects among different atoms, including elastic Bragg scattering by nuclear and magnetic structures, and inelastic scattering by excitations like phonons or magnons. The incoherent part is proportional to the time correlation of an atom, such as individual particle motion in a diffusion process. In our experiments, we are interested in the coherent elastic scattering from nuclear and, in particular, magnetic orderings.

Since neutrons act as a very weak perturbation to the scattering system, causing the sample to transit from one quantum state to another without changing the nature of the state itself, the differential scattering cross section can be obtained from Fermi's Golden Rule. Following Van Hove's method and just considering the coherent scattering [151],

$$\left. \frac{d^2\sigma}{d\Omega_f dE_f} \right|_{\text{coherent}} = N \frac{k_f}{k_i} \frac{\sigma_{coh}}{4\pi} S(\mathbf{Q}, \omega) \quad (4.10)$$

where

$$S(\mathbf{Q}, \omega) = \frac{1}{2\pi\hbar N} \sum_{ll'} \int_{-\infty}^{\infty} dt \langle e^{-i\mathbf{Q}\cdot\mathbf{r}_{l'}(0)} e^{i\mathbf{Q}\cdot\mathbf{r}_l(t)} \rangle e^{-i\omega t} \quad (4.11)$$

Using the definition of the atomic density operator:

$$\rho_{\mathbf{Q}}(t) = \sum_l e^{i\mathbf{Q}\cdot\mathbf{r}_l(t)} \quad (4.12)$$

We can rewrite

$$S(\mathbf{Q}, \omega) = \frac{1}{2\pi\hbar N} \int_{-\infty}^{\infty} dt e^{-i\omega t} \langle \rho_{\mathbf{Q}}(0) \rho_{-\mathbf{Q}}(t) \rangle \quad (4.13)$$

The primary goal of neutron scattering experiments is to measure the scattering function $S(\mathbf{Q}, \omega)$, which depends on the momentum ($\hbar\mathbf{Q}$) and energy ($\hbar\omega_0$) transferred from the incident neutron to the sample,

$$\begin{aligned} \hbar\mathbf{Q} &= \hbar(\mathbf{k}_f - \mathbf{k}_i) \quad (\text{momentum transfer}) \\ \hbar\omega &= E_f - E_i = \frac{\hbar^2}{2m}(\mathbf{k}_f^2 - \mathbf{k}_i^2) \quad (\text{energy transfer}) \end{aligned} \quad (4.14)$$

The experiments discussed in this thesis are all elastic scattering measurements, with the constraint of $E_i = E_f$.

Elastic Scattering

For coherent elastic scattering in a Bravais lattice, taking the time average of the density operator will lead to

$$S(\mathbf{Q}, \omega) = \delta(\hbar\omega) \frac{1}{N} \left\langle \sum_{ll'} e^{i\mathbf{Q}\cdot(\mathbf{r}_l - \mathbf{r}_{l'})} \right\rangle = \delta(\hbar\omega) \frac{(2\pi)^3}{v_0} \sum_{\mathbf{G}} \delta(\mathbf{Q} - \mathbf{G}) \quad (4.15)$$

, where v_0 is the volume of the unit cell and $\mathbf{G}$ are reciprocal lattice vectors.

From a Bravais lattice to a solid crystal with more than one atom per unit cell, the coherent elastic differential cross section will be generalised to

$$\left. \frac{d\sigma}{d\Omega} \right|_{\text{coh}}^{\text{el}} = N \frac{(2\pi)^3}{v_0} \sum_{\mathbf{G}} \delta(\mathbf{Q} - \mathbf{G}) |\mathbf{F}_N(\mathbf{G})|^2 \quad (4.16)$$

where the static nuclear structure factor $\mathbf{F}_N(\mathbf{G}) = \mathbf{F}(hkl)$ contains information on the j^{th} atom within the unit cell at position $\mathbf{d}_j$.

Magnetic Scattering

In this thesis, the magnetic structures are measured with unpolarised neutrons. The principle follows that of the coherent elastic scattering from nuclear structures, as is introduced above. Measurements above and below the expected magnetic transition temperature T_N are taken. New peaks below T_N can be attributed to magnetic ordering assuming there is no simultaneous temperature-dependent essential structural transition. The differential cross section can straightforwardly be seen as a sum of the nuclear and magnetic components. Below I will highlight a few key points dealing with the scattering from the magnetic structures.

To start with, assume the atomic moment is due purely to spin (without orbital effect). For unpolarised neutrons scattering from a system containing a single species of magnetic atom, the differential cross section from the atomic magnetic scattering can be written as

$$\frac{d^2\sigma}{d\Omega_f dE_f} = \frac{N k_f}{\hbar k_i} p^2 e^{-2W} \sum_{\alpha\beta} (\delta_{\alpha\beta} - \hat{Q}_\alpha \hat{Q}_\beta) S^{\alpha\beta}(\mathbf{Q}, \omega) \quad (4.17)$$

with

$$S^{\alpha\beta}(\mathbf{Q}, \omega) = \frac{1}{2\pi} \int_{-\infty}^{\infty} dt e^{-i\omega t} \sum_l e^{i\mathbf{Q} \cdot \mathbf{r}_l} \langle S_0^\alpha(0) S_l^\beta(t) \rangle \quad (4.18)$$

The angle brackets denote averaging over all configurations.

The coherent elastic differential cross section for magnetic scattering from a magnetically ordered crystal is given by

$$\left. \frac{d\sigma}{d\Omega_f} \right|_{\text{coh}}^{\text{el}} = N_M \frac{(2\pi)^3}{V_M} \sum_{\mathbf{G}_M} \delta(\mathbf{Q} - \mathbf{G}_M) |\mathbf{F}_M(\mathbf{G}_M)|^2 \quad (4.19)$$

In the above equation, the subscript M is introduced to describe the magnetic unit cell. F_M is the static magnetic structure factor and N_M , V_M represents the number of magnetic unit cells and the volume of each cell. Except for a ferromagnet, the magnetic unit cell is usually larger than the nuclear unit cell, leading to a new set of reciprocal lattice vectors $\mathbf{G}_M$. The magnetic elastic scattering data of powdered sample is similar to that of the nuclear structure powder X-ray data analysis. The key question is to find the magnetic sub-space group which could fit and explain the observed intensity data in 2θ space.

4.2.2 Paris-Edinburgh Pressure Cell

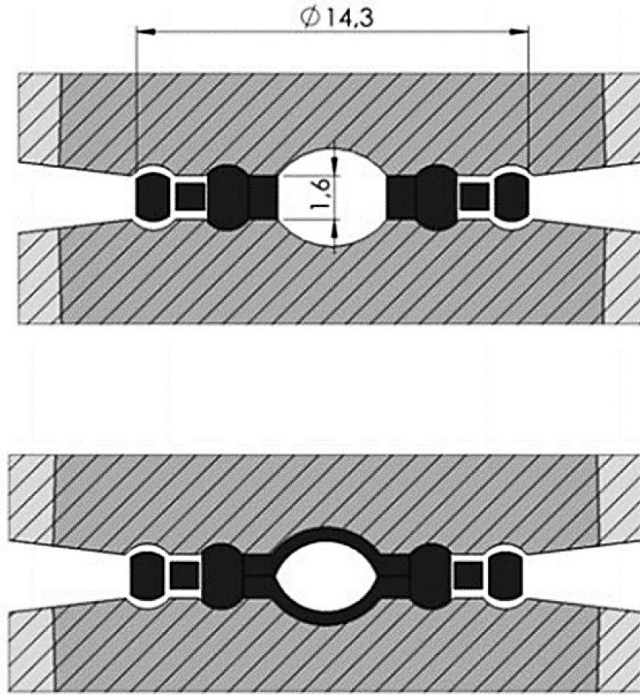


Fig. 4.3 The schematic design of the double-toroidal diamond anvils with Paris-Edinburgh cells utilized for the experiments on FePS_3 and FePSe_3 at D20, ILL. A standard (upper) and encapsulating (lower) gasket has been employed. This figure is taken from reference [152].

In this section, I will introduce the special setup to probe the magnetic structure under high pressures with neutron scattering technique.

For FePS_3 , data were collected during two separate experiments. The first attempt used a Paris-Edinburgh-type (PE) pressure cell with cubic boron nitride (cBN) anvils. The second one employed double-toroidal sintered diamond anvils to achieve higher pressure values while maximising the sample volume to get enough density for neutron diffraction experiments [152]. FePSe_3 used this setup only as the experiment came after the trials with FePS_3 . These cells were provided crediting to the collaboration of Prof. Stefan Klotz, Sorbonne University. The modified geometry of the anvils allows for a higher pressure range beyond the standard PE cell. Below I will further elaborate on the advantages and limitations of using the double-toroidal sintered diamond anvils with PE cells.

The major aim for using special double-toroidal sintered diamond anvils, instead of simpler standard ones, is to enable the exploration of the magnetic structure in the higher pressure region. As has been suggested by the synchrotron X-ray experiments, the transition pressure in FePS_3 , for instance, is as high as approximately 14 GPa. By modifying the geometry of the anvils, double-toroidal cells allow for achieving higher pressures beyond the capacity of a Paris-Edinburgh press with a single-toroidal or flat anvil shape. Meanwhile, the sample volume is reduced by half or more to a value of approximately 30 mm^3 . A detailed overview of the design and use of the double-toroidal cell may be found in the reference book by Prof. Stefan Klotz, *Techniques in High Pressure Neutron Scattering* (1st Edition, 2013, CRC Press) [152].

Another advantageous adaption is to use encapsulating gaskets, as shown in the lower of Fig. 4.3. Such setup in principle improves the hydrostatic condition over a standard setup where the sample touches the anvil directly [153]. This is important to reduce the risk of the failure of the pressure cell at high pressures, especially when there would be a substantial change of sample volume across the transition point from lower to higher pressures, as the case in TMPX_3 compounds.

4.2.3 D20 experiments at ILL

Powder neutron diffraction patterns were collected on D20 [154], High-Intensity Two-Axis Diffractometer, at ILL. Neutrons of wavelength $2.42 \text{ \AA}$ ($E = 13.97 \text{ meV}$) were selected through a graphite monochromator. During the experiment, the powdered sample was loaded in a tin-zirconium spherical encapsulating gasket. A deuterated methanol-ethanol

mixture (the hydrogen atom H is replaced with deuterium, heavy hydrogen isotope, ^2H or D) in the ratio of 4:1 by volume was utilised to wet the powder and to function as the pressure-transmitting medium.

Given that we can establish a solid solution of the crystalline structure at various pressures through synchrotron X-ray experiments, the calibration of pressure within the double-toroidal cell during neutron scattering experiments using the sample itself as the pressure gauge becomes feasible. Previous attempts to load both the FePS_3 sample and the pressure gauge encountered difficulties due to the limited sample size [104, 62]. As a result, the experimental approach was refined by exclusively loading the samples of interest into the sample chamber, on the premise that pressure could be accurately calibrated using the structural data obtained from synchrotron X-ray experiments. This adaptation led to an enhanced neutron signal.

Chapter 5

Predictive Construction of High-Pressure Phases

This chapter delves into the predictive results regarding high-pressure phases within the TMP_{x3} family. Two primary methods are employed to predict and construct these high-pressure phases.

The first approach involves using a random structure search coupled with first-principles structural relaxation at both ambient and high pressures. The predicted phases serve as a foundational basis for further theoretical investigations into their physical properties, facilitating comparisons with experimental observations.

The second approach entails substituting the TM element with a proposed high-pressure model. These models can be derived from experimental observations or predictions. Subsequently, atomic positions and lattice parameters are relaxed using first-principles calculations.

5.1 Random Structure Search in $FePS_3$

In the case of $FePS_3$, a structural search was conducted at pressures of 0.0, 10.0, and 20.0 GPa. Over a thousand structures were generated and relaxed at each pressure point. These structures were then ranked based on their enthalpy per formation unit, taking into account structural differences within a defined tolerance factor.

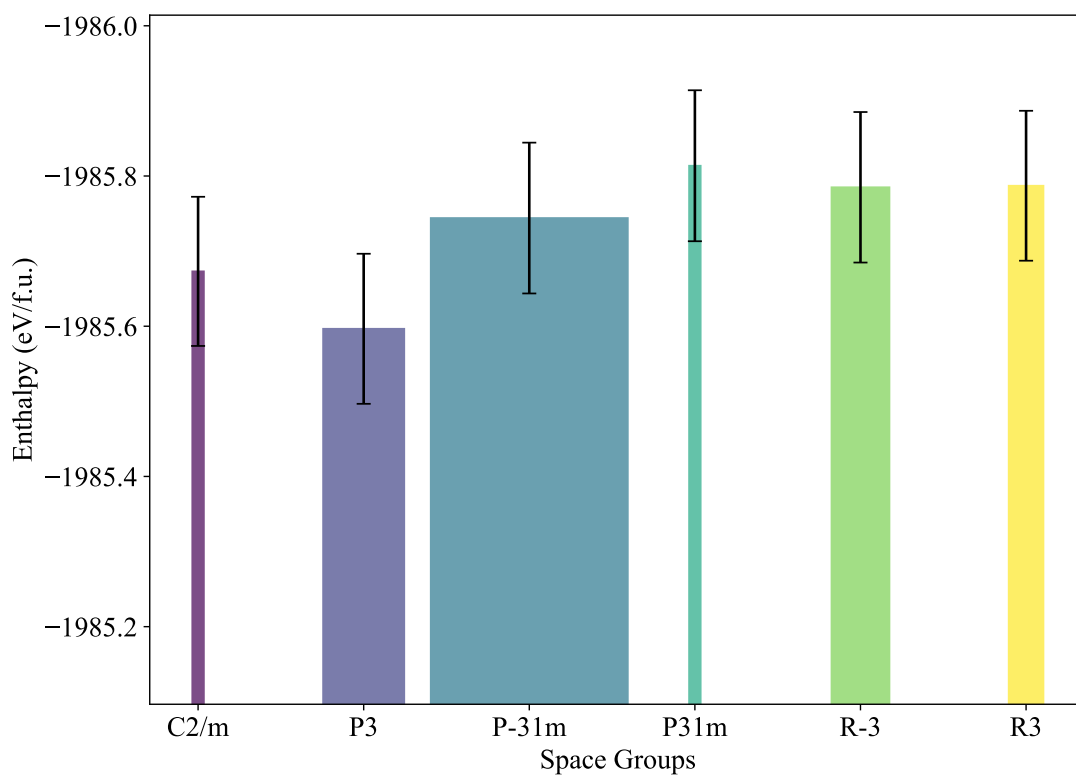


Fig. 5.1 The AIRSS predicted structures of FePS₃ at 10 GPa. The width of each bar indicates the frequency of occurrence of the crystalline structure with the same space group predicted by AIRSS. The width has been normalised to arbitrary units.

While the initial structure relaxation performed during the random structure search is coarse for the sake of efficiency, candidate structures worthwhile further examination were subjected to finer geometry optimisation criteria. The symmetry of the resultant phases was determined by analysing the Wyckoff positions and site symmetry groups of specific atomic positions, a procedure implemented using the Bilbao Crystallographic Server [155]. In some cases, the space group symmetry in the initially produced random structure was $P31m$ ($R3$), but the final optimised structure exhibited the $P\bar{3}1m$ ($R\bar{3}$) space group.

The phases obtained at ambient pressure (0.0 GPa) exhibit excellent agreement with known experimental structures, validating the effectiveness of the structural searching approach. Consequently, our focus here is on describing the novel phases predicted at higher pressures, complete with crystallographic details and symmetry relations.

At 10.0 GPa, four candidate structures are worthy of further investigation, and their enthalpy values are summarised in Fig. 5.1. The width of the bar in the figure represents the frequency with which each structure appeared in the AIRSS search.

At 20.0 GPa, the structure search predicted a novel phase crystallising in $P\bar{3}1m$, identified as the same phase as that predicted at 10.0 GPa, despite the difference in the precise bonding distance and lattice parameters.

Detailed discussions of the optimised novel structures will follow.

5.1.1 $P\bar{3}1m$ Phases with Distinct P₂ Dimer Chains

Among the candidate phases, those with the space group of $P\bar{3}1m$ and $P31m$ exhibit the lowest energy preferences. Further refinement of these phases, along with Wyckoff position analysis, led to the determination of the local minimum structure with the $P\bar{3}1m$ space group. This structure shares the same structural pattern within each individual ab plane as the HP-II phase proposed by Haines *et al.* in 2018 [59]. However, there are dimensionally different in the interlayer stacking configuration. Hereafter I will denote this phase as HP-II- β .

Fig. 5.2 summarises the two phases. The left side displays the ab planes, while the right side shows a view along the c axis. The Fe-hexagon remains within each ab plane for both HP-II and HP-II- β .

However, when viewing from the perpendicular direction, the P atoms in the HP-II phase form dimers within the double-sulphur layers at a distance of 1.932 Å. These P atoms are 2.738 Å away from the nearest P atoms in the neighbouring layer. In the HP-II- β phase,

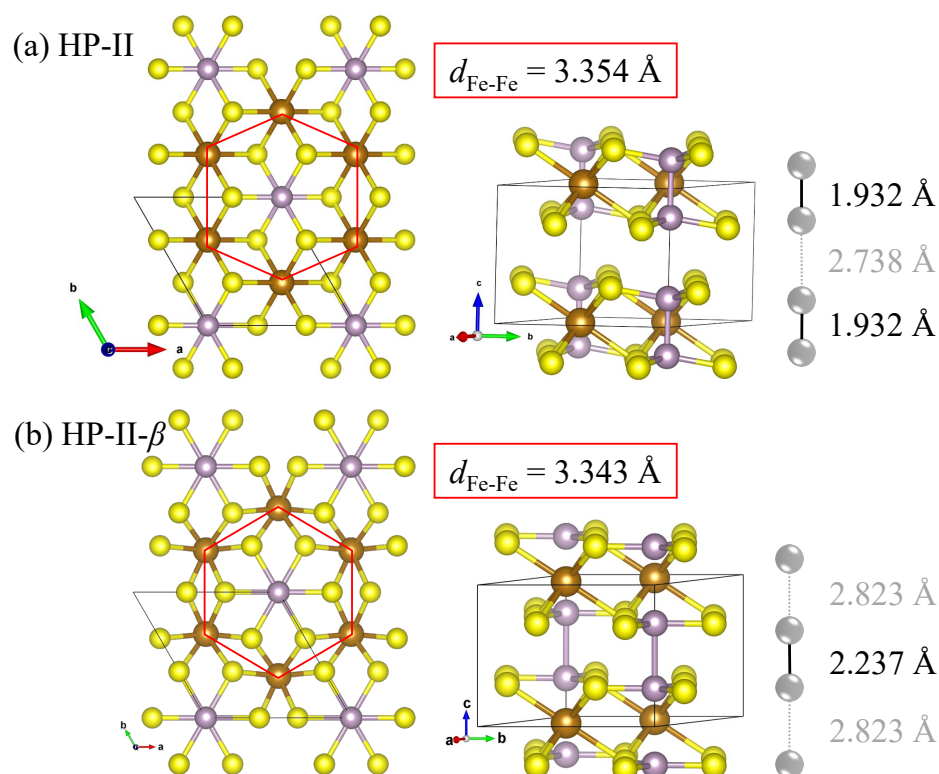


Fig. 5.2 Different $P\bar{3}1m$ structures of FePS_3 . (a) The HP-II phase proposed by Haines *et al* based on the powder X-ray diffraction pattern at 10.1 GPa [59], (b) HP-II- β , a novel predicted structure obtained after a more refined geometry optimisation at 10.0 GPa. Distinctive P_2 dimer chains characterize these two phases, as highlighted in the illustration, with solid sticks indicating stronger bonds and dotted sticks suggesting weaker bonds or van der Waals interactions.

in contrast, the P atoms establish strong chemical bonds with one another in between the double-sulphur layers at the distance of 2.237 Å. The P-P distance within each double-sulphur layer is 2.823 Å, longer than that of the interlayer P2 dimers. The HP-II- β is thus more three-dimensionally connected compared to the HP-II phase. In the subsequent chapter, I will explore the structure-related physical properties in more detail.

5.1.2 Polymorphous $R\bar{3}$ Phase

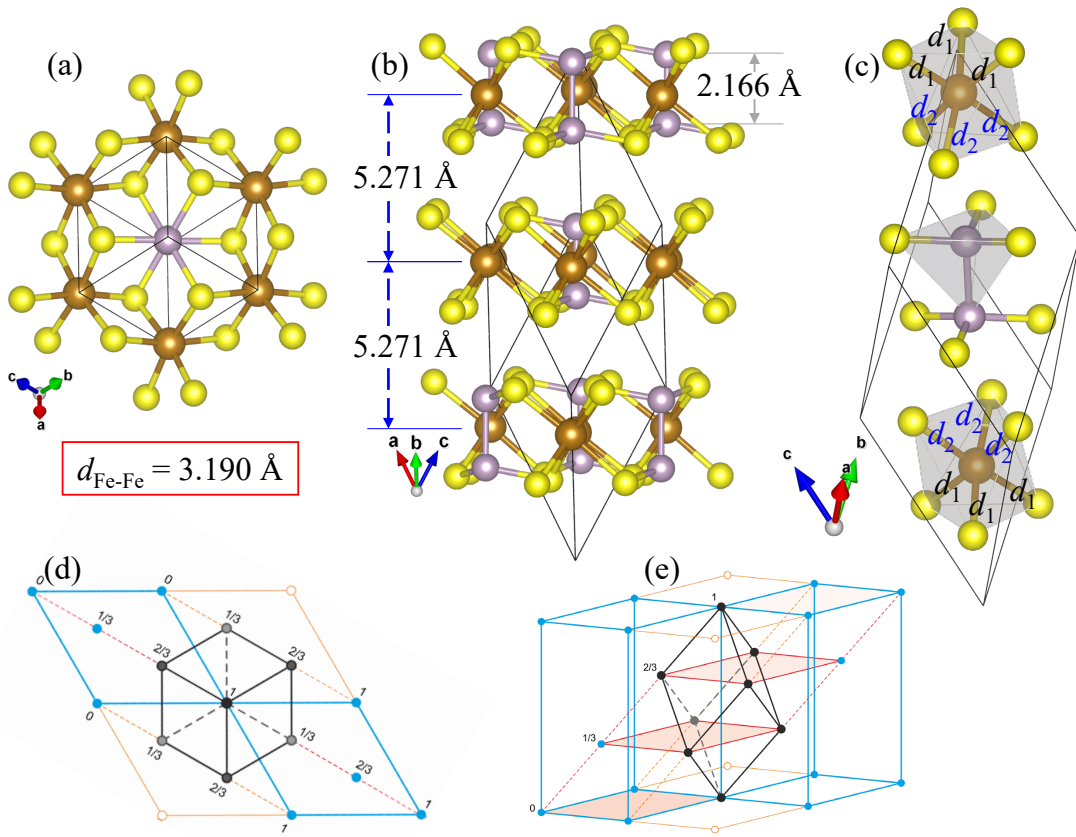


Fig. 5.3 The novel phase of FePS₃ with the space group symmetry of $R\bar{3}$, predicted by AIRSS and optimised by CASTEP at 10.0 GPa. (a) The layer building block viewed from the perpendicular direction, (b) the side view of the ABC stacking layers, (c) the demonstration of P₂S₆ and the FeS₆ clusters from neighbouring stacking layers.

The random structure search approach predicted a novel phase crystallising in the $R\bar{3}$ space group, featuring the ABC ABC stacking of double-sulphur layers. The S atoms follow *ababab* close-packing arrangement. Within each double-sulphur layer, the Fe atoms arrange themselves in hexagon patterns with the edge being 3.190 Å in length, as is displayed in Fig. 5.3 (a). When viewed from the stacking direction, Fig. 5.3 (b), the layers are separated by a

distance of 5.271 Å. The P_2 remains within each individual layer with the P-P distance being 2.166 Å. Fig. 5.3 (c, d) are illustrations of the unit cell symmetry, with the black solid lines indicating the primitive cell. This novel phase in $FePS_3$ at 10 GPa is similar to the ambient pressure phase of $FePSe_3$ (in conventional cell description).

The P_2S_6 cluster remains undisturbed, with all P-S bonds distributed evenly in an equal length of 2.068 Å. However, each FeS_6 cluster experiences local distortion. The stacking can be simplified as $[Fe_2S_6] - [P_2S_6] - [Fe_2S_6]$. Within each $[Fe_2S_6]$, the three Fe-S bonds closer to a different FeS_6 cluster from the neighbouring layer are 2.273 Å, denoted as d_1 . The rest three bonds pointing closer to the P_2S_6 from the neighbouring layer are measured to be 2.283 Å, referred to as d_2 . d_1 is measured to be 0.44% shorter than d_2 . That can be regarded as a local polarisation within each FeS_6 cluster. The polarization direction alternates among neighbouring Fe sites.

Such a transition from $C2/m$ to $R\bar{3}$ is quite common in other low dimensional materials, as seen in CrI_3 . And the neighbouring compound $FePSe_3$ crystallises in $R\bar{3}$ at ambient pressure. The fact that Se is larger than S could lead to chemical pressure inside the structure.

5.1.3 Triple-layer Sulphur Layered Phase

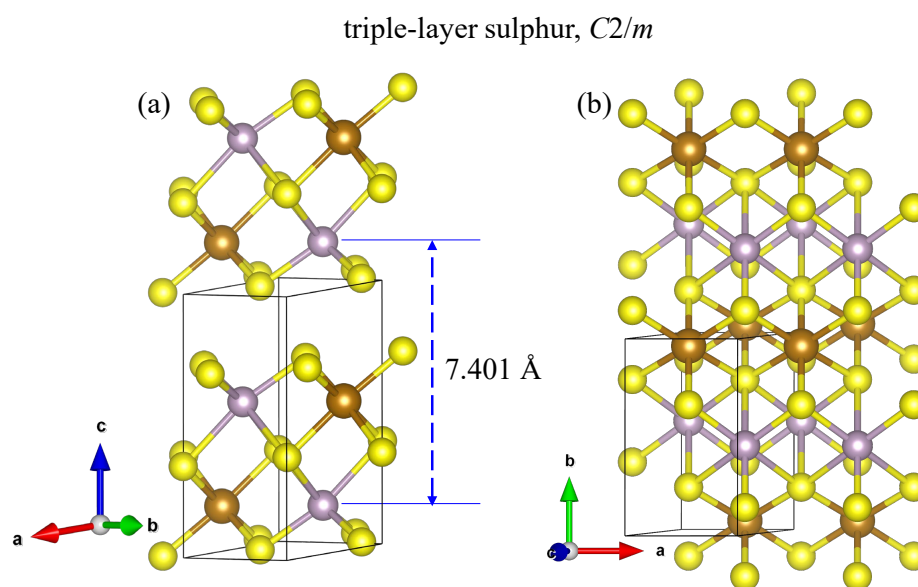


Fig. 5.4 The novel phase of $FePS_3$ with the space group symmetry of $C2/m$ but a different stacking unit of triple-layer sulphur, predicted by AIRSS and optimised by CASTEP at 10.0 GPa.

Other metastable phases, such as the double-Fe thick $C2/m$ phase shown in Fig. 5.4 and the cation-substituted $P3$ phase in Fig. 5.5, expand the structural diversity of the FePS₃ compounds. Despite being composed of distinct building blocks, these novel phases share commonalities in symmetry and the close packing of the S atoms.

In Fig. 5.4, the S atoms are closely packed in the sequence of $abc\ abc$. This novel structure differs from the known double-layer sulphur structure in that within each stacking layer, there are three layers of S atoms. The Fe and P alternates with one another to fill in the octahedral occupancy sites.

5.1.4 Cation substituted phase

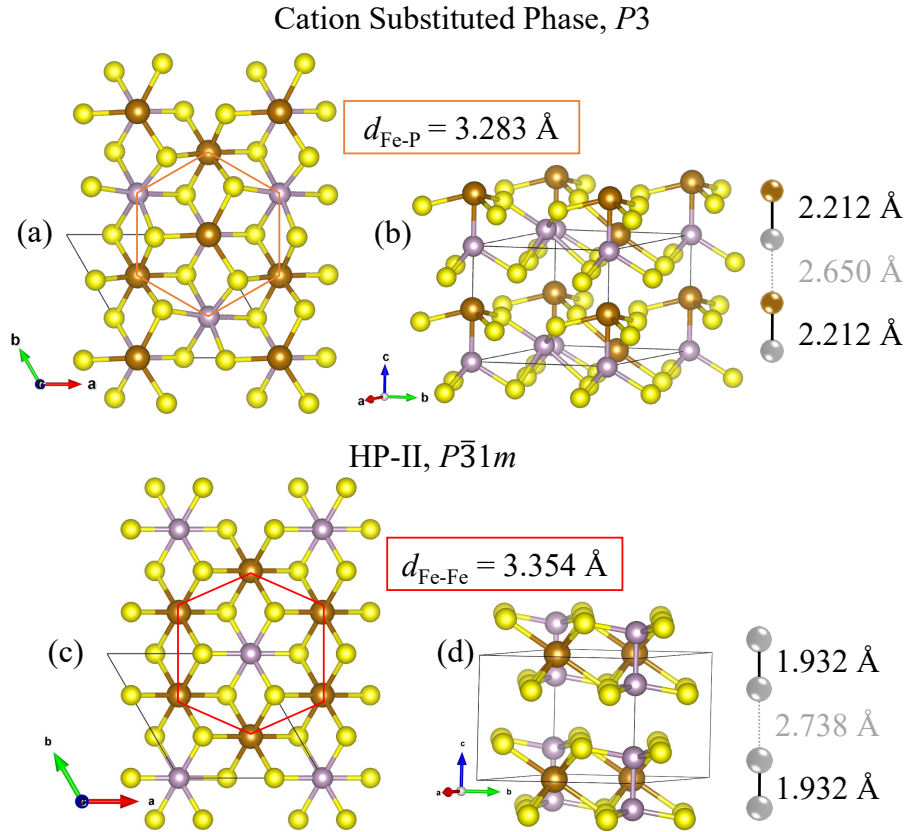


Fig. 5.5 The novel phase of FePS₃ with the space group symmetry of $P3$, predicted by AIRSS and optimised by CASTEP at 10.0 GPa. It can be seen as a modified structure from the $P\bar{3}1m$ HP-II phase with cation substitution.

With the AIRSS search, another novel FePS_3 structure has been predicted, as is displayed in 5.5. The S atoms are closely packed following the sequence of *ababab*. The stacking building block is also an individual double-sulphur layer sandwiching the Fe and P cations. In contrast to the previously discussed $C2/m$ low-pressure and $P\bar{3}1m$ high-pressure phases, this novel phase features the substitution of half of the Fe in the Fe-hexagon by P. The Fe-hexagon thus changes into a Fe-P hexagon, of which the edge is evenly distributed with a distance of 3.283 Å. As a result, the P_2 dimer in the centre of each hexagon is substituted by the P-Fe dimer. The distance between P and Fe within the S *ab* plane is 2.212 Å while the interlayer one is distanced at 2.738 Å. It can be seen as a 50% cation substituted crystal structure. The HP-II structure is displayed underneath the cation substituted phase for clearer structure comparison and understanding.

5.1.5 Summary and Predictive Results in Other $T\text{MPX}_3$

In summary, the random structure search methodology applied to FePS_3 has successfully replicated the ambient pressure phase and provided predictions for high-pressure structural models.

Among the candidate structures predicted at high pressure, the one with $P\bar{3}1m$ space group is particularly intriguing due to its structural resemblance to the previously proposed HP-II phase [59]. However, it differs in terms of the bonding of P atoms, leading to distinct dimensionalities.

Another candidate phase with the $R\bar{3}$ space group exhibits polymorphic characteristics and shares similarities with the ambient pressure phase of FePSe_3 . This suggests an alternative method for effectively tuning stacking geometry, that is, using chemical pressure.

Overall, the random structure search has expanded the structural diversity of FePS_3 . Considering that the random structure search is performed without spin-polarization, the imposition of magnetic configurations may alter the enthalpy of these metastable phases. Under specific conditions, these phases could become competitive.

The application of *ab initio* random structure search with first-principle calculations in the case of FePS_3 can be extended to other compounds within the family. As each comprehensive search is computationally demanding, and the primary objective is to resolve and predict high-pressure structure models, ambient pressure searches were not conducted for other compounds.

Furthermore, I have employed the AIRSS search for FePSe₃ at 10 GPa; MnPS₃ at 10, 20 GPa, and NiPS₃ at 15, 30 GPa. The same structure model of HP-II- β with the $P\bar{3}1m$ space group and P-P interlayer bonding has also been predicted in MnPS₃, NiPS₃ and FePSe₃ at high pressures. As this structure model closely resembles the HP-II phase, the subsequent chapter will focus on it.

5.2 Constructing High-Pressure Phases with Substitution

Another method to construct the high-pressure structure model is to utilise the proposed structure model of a known compound, for instance, FePS₃, and then substitute the Fe atoms with another transition metal (*TM*) atoms. Subsequently, a full geometry relaxation is performed at the desired pressure, allowing for complete relaxation of lattice parameters and atomic positions with respect to the different cation elements.

To illustrate this approach, consider NiPS₃ as an example. In this case, we create the HP-I and HP-II structural models by replacing Fe with Ni in the established HP-I and HP-II FePS₃ phases. This approach can provide useful guidelines in situations when experimental determination faces challenges, including issues related to the preferred orientations, difficulties in obtaining sufficiently small and unstained samples due to the material's cleavage nature, and technical complexities in setting up high-pressure cells and achieving the desired high pressures.

Fig. 5.6 displays the crystalline structures of NiPS₃ after geometry relaxation with first-principles calculations. The ambient-pressure (LP) phase is optimised from the reference structure [64]. The band structures, simulated using the DFT+*U* method and considering the spin polarisation (Fig. 5.6, b) are consistent with previous experimental observation that NiPS₃ is an insulator at ambient pressure.

The two high-pressure structure models, constructed from the FePS₃ HP-I and HP-II refined structures and relaxed at the desired pressure of 15 and 30 GPa respectively, exhibit the trend of insulator-to-metal transitions.

Constructing new high-pressure models in NiPS₃ based on the known FePS₃ is facilitated by their identical ambient pressure crystalline structure stacking modes. Additionally, both compounds share similar magnetic configurations, despite the direction of the spin moments on the *TM* sites and the exact interlayer interaction, which involve forming zigzag AFM chains along the *a* axis and the neighbouring chains being antiferromagnetically coupled.

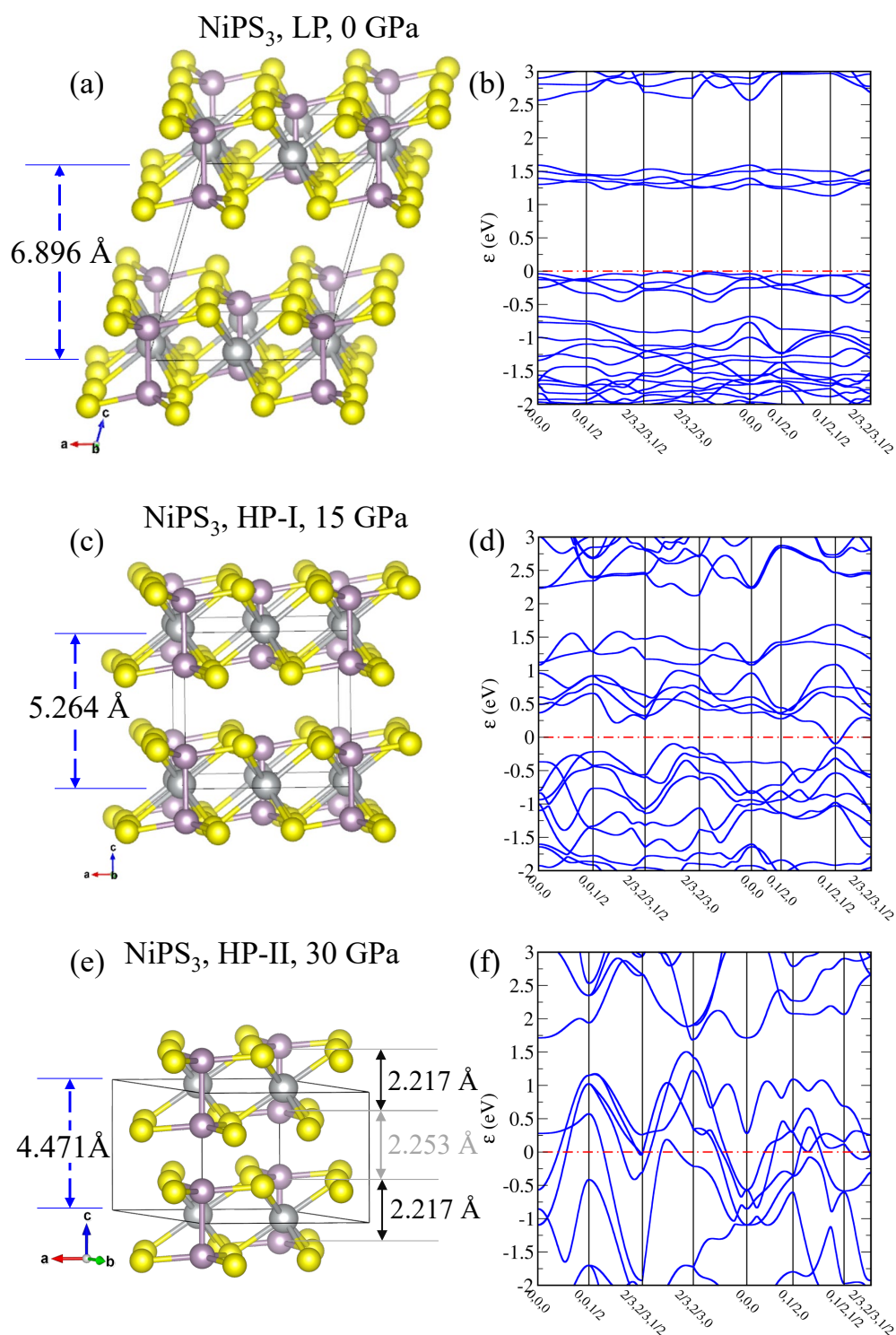


Fig. 5.6 The crystalline structure and calculated band structures for (a, b) the ambient pressure (LP), (c, d) HP-I and (e, f) HP-II phases of NiPS₃.

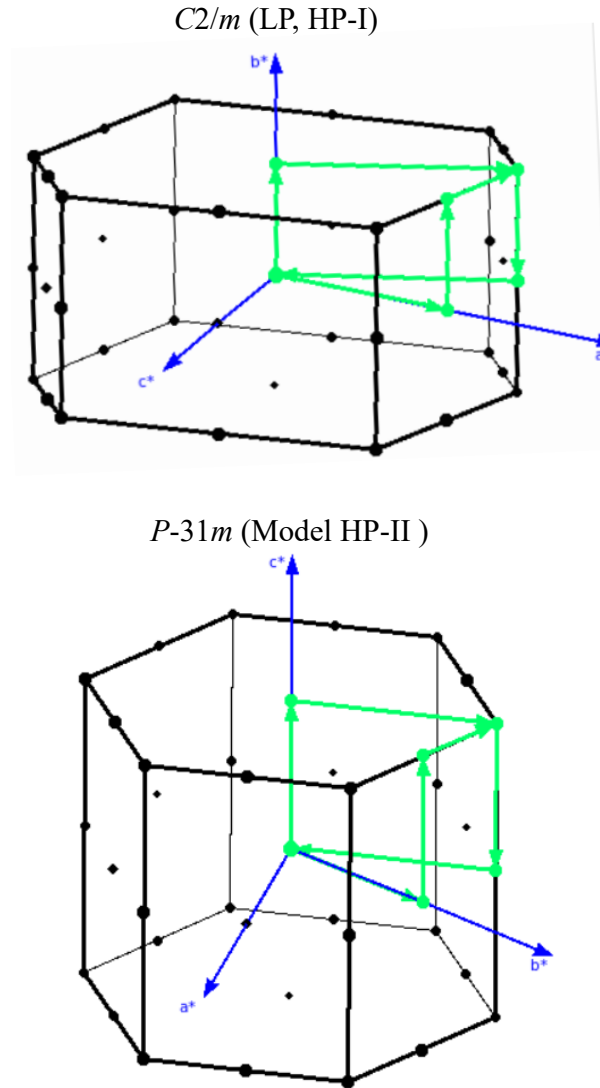


Fig. 5.7 The high-symmetry path employed in the calculation of band structures for NiPS_3 with $C2/m$ and $P\bar{3}1m$ space group respectively. The primitive Brillouin Zone is indicated in black solid lines with the vectors a^* , b^* and c^* in blue arrows. The K-path is highlighted in green solid lines.

This approach provides a starting point for exploring high-pressure structures and simulating related physical properties. However, it is important to note that actual high-pressure transitions may be more complex and could differ between compounds within the same family or even among those with the same initial stacking geometry. Therefore, further exploration and comprehensive investigations of the structures and related physical properties are necessary, both theoretically and experimentally. Subsequent chapters will illustrate our efforts in this regard.

Chapter 6

Pressure-induced transitions in FePS₃: Structural, magnetic and electronic properties

This chapter is published work in the journal SciPost Physics, 15, 020 (2023) [68].

With the AIRSS search we managed to reproduce the known phases and in addition predict a new one in the high-pressure region. The novel structure shares the same template of the honeycomb and space group symmetry as HP-II, though it distinguishes itself with the characteristic P₂ bonding. The P atoms form stronger chemical bonds between the neighbouring layers instead of the intralayer configuration of previously proposed structures. There are hints of a similar evolution in the related material NiPS₃ [102]. The now fully connected 3D structure therefore differs from the weakly bound two-dimensional layers found in the HP-II phase. We refer to this phase as HP-II- β going forward. Metastable phases with diverse building blocks are also predicted but in this work we focus on the phases in close proximity to the minimal enthalpy line, which happen to be close to experimental findings except for the mentioned HP-II- β phase. Fig.6.1 summarises the LP, HP-II, HP-I and HP-II- β phases and a detailed discussion of the evolution with pressure is given in the subsequent section.

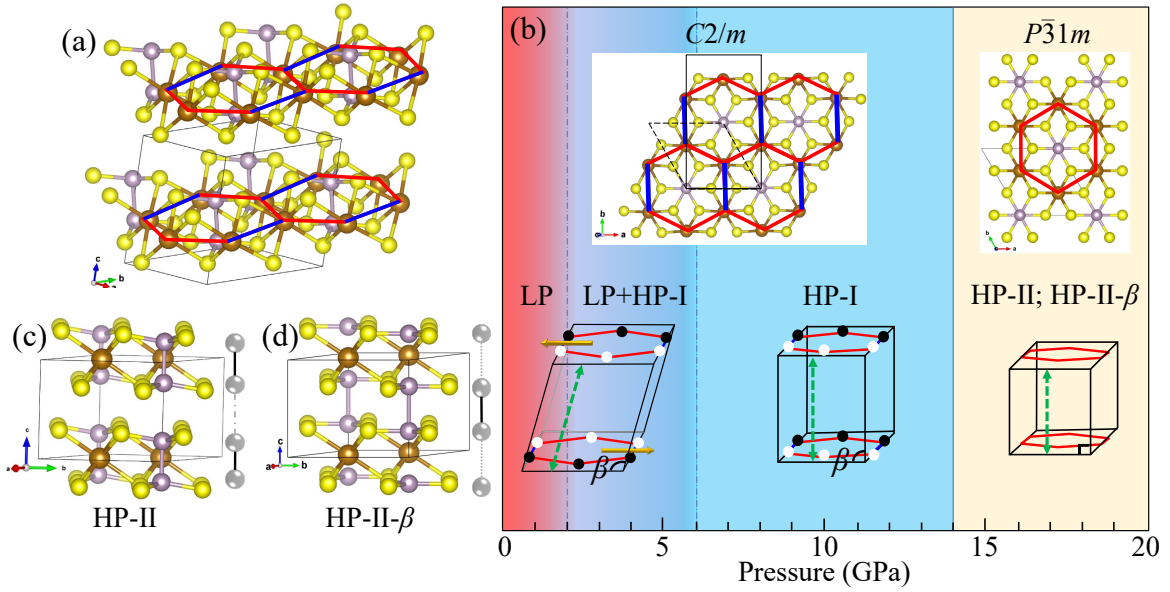


Fig. 6.1 Crystal structure of various FePS₃ phases and phase diagram vs pressure. (a), (c) and (d) show the LP, HP-II and HP-II- β structures. (b) Pressure phase diagram Ref.[62] and random structure search results in this thesis. The red and blue rods indicate the ferromagnetic (FM) and antiferromagnetic (AFM) coupling between the nearest neighbouring Fe ions, respectively. The black and white dots represent the magnetic moment on Fe²⁺ pointing up or down, normal to the ab plane. The LP and HP-I both host zigzag FM chains along a axis and the neighbouring chains within each plane are AFM coupled. From LP to HP-I, the interlayer AFM coupling changes into FM instead. Below we refer to them as (LP, AFM) and (HP-I, AFM) in contrast with the non-spin-polarised phases. The transition pressure value is sensitive to the magnitude of Hubbard U , for example, it is ~ 7.4 GPa for $U = 2.50$ eV (see Fig. 6.2), and ~ 11 GPa for $U = 3.75$ eV (see Fig. 6.5 in section 6.1.2).

6.1 Pressure-induced Crystalline Phase Transitions

To establish the context in which the crystalline structure evolves with pressure, we start with the LP phase. FePS_3 has been subjected to a full X-ray structural characterisation since 1973, being the first among the family [65]. The neighbouring layers stack together and the bulk crystallised in the monoclinic space group $C2/m$ with an ideal β angle, compared with the Mn and Ni counterparts [64], which suggest the least distortion within each layer. At ambient pressure, FePS_3 is a Mott insulator with a band gap of ~ 1.5 eV. Across the family, the complex competition among exchanges and anisotropy leads to different types of antiferromagnetic order with different directions for the collinear axes of the spin moments (Ising versus Heisenberg magnetic Hamiltonian). FePS_3 at ambient pressure has Ising-type AFM order with zigzag ferromagnetic (FM) chains along the a axis coupled antiferromagnetically along the b axis. The moments are normal to the ab planes [65]. Being a 2D AFM with correlated physics, FePS_3 has been studied extensively in recent years with pressure being the tuning parameter.

Fig. 6.1 (a) displays the crystalline structure of LP FePS_3 with the Fe^{2+} honeycomb being illustrated by a rigid rod. In the inset of Fig. 6.1 (b), the obtained spin up and down moments are indicated via black and white dots, respectively, defining ferromagnetically (FM) coupled lines of Fe atoms (red rods), which are antiferromagnetically ordered in respect to each other (blue rods). This is a striking result for a Fe essentially honeycomb arrangement, which being bipartite would not be expected to induce the kind of frustrations which give rise to the observed arrangement. It is, however, a known and expected result from the LP phase related to frustrations due to first vs longer range effective exchange couplings [106].

The magnetic configuration breaks the C_3 rotational symmetry and leads to slightly elongated Fe hexagons in the LP phase. The blue rods corresponding to the AFM coupling are $3.448 \text{ \AA}$ in length, while the red ones representing FM coupling are $3.426 \text{ \AA}$. The intersite exchange within and in-between the planes is mediated through the surrounding P_2S_6 clusters, with P atoms centred within the distorted Fe hexagons. The shear in the interlayer coupling can also be considered to be behind the C_3 symmetry breaking, but it is observed (see below) that the symmetry breaking remains when the shear is removed by pressure. Defining the formula unit (f.u.) as $[\text{FePS}_3]$, the primitive cell contains 2 f.u. in the cell, as indicated by the dotted line in the upper-left inset of Fig. 6.1 (b). The conventional cell consistent with previous literature involves 4 f.u. of $[\text{FePS}_3]$, shown in solid black lines. For consistency with previous works, we adopt the conventional description of the lattice parameters with $a = 5.947 \text{ \AA}$, $b = 10.300 \text{ \AA}$, $c = 6.722 \text{ \AA}$ and $\beta = 107.2^\circ$ for the LP. The symmetry breaking

distorts the Fe hexagons, showing sides along the zigzag spin chains that are shorter than the ones perpendicular to the chain, by a ratio of 0.65 % at ambient pressure. The b/a ratio is, however, only very slightly affected, staying very close to the ideal $b/a = \sqrt{3}$.

With increasing pressure, the crystalline structure of LP evolves into new phases but some features of the LP are retained. The HP-I phase shares the same crystalline building block as LP, but differs in the stacking angle β as neighbouring layers in LP slide towards each other. The β angle turns nearly 90° in HP-I. In addition, though the in-plane magnetic configuration has been preserved, the interlayer coupling has changed from AFM to FM [62]. Both phases crystallise in the space group of $C2/m$. Experimentally a coexistence region of both LP and HP-I is observed from 2 to 6 GPa, from the powder diffraction data without pressure medium [59, 62]. Nevertheless, no coexistence was seen in the single crystal, or in the powder data with He pressure medium [67]. We discuss the transition from LP to HP-I in Section 6.1.1.

At the higher pressure region, the long-range magnetic order is suppressed and the Fe²⁺ cations form perfect hexagons within the plane, as indicated in the upper-right inset of Fig. 6.1 (b). The recovery of the C_3 rotational symmetry at the centre of the Fe-hexagons leads to the symmetry crossover transition from $C2/m$ to $P\bar{3}1m$. The previously proposed HP-II and the predicted HP-II- β share the same intralayer S-Fe-S template. The side-view for these two phases is shown in Fig. 6.1 (c) and (d), respectively. The P₂ bonding behaviour alters the dimensionality in HP-II from that in HP-II- β . It offers an ideal platform to explore the effect of dimensionality on the electronic and magnetic properties, which will be discussed in detail in Section 6.2.

In order to understand how these phases evolve with pressure, we performed first-principles geometry optimisation at various pressure points. The enthalpy-pressure phase diagram is summarised in Fig. 6.2. The enthalpy for the non-polarised LP phase has been chosen as the reference line. The spin polarisation is shown to be essential in establishing the relative stability of the various phases, with a very significant energy scale of up to half an eV/f.u. stabilizing the LP and HP-I phases. However, given their full polarization, both phases compete very closely in enthalpy, with differences LP and HP-I now on the meV/f.u. scale.

6.1.1 Coexistence of the LP and HP-I

The transition from LP to HP-I occurs via the relative sliding of the neighbouring layers and the change of interlayer magnetic coupling from AFM to FM. We display the enthalpy evolution in response to the interlayer sliding in LP and HP-I as a function of the β angle

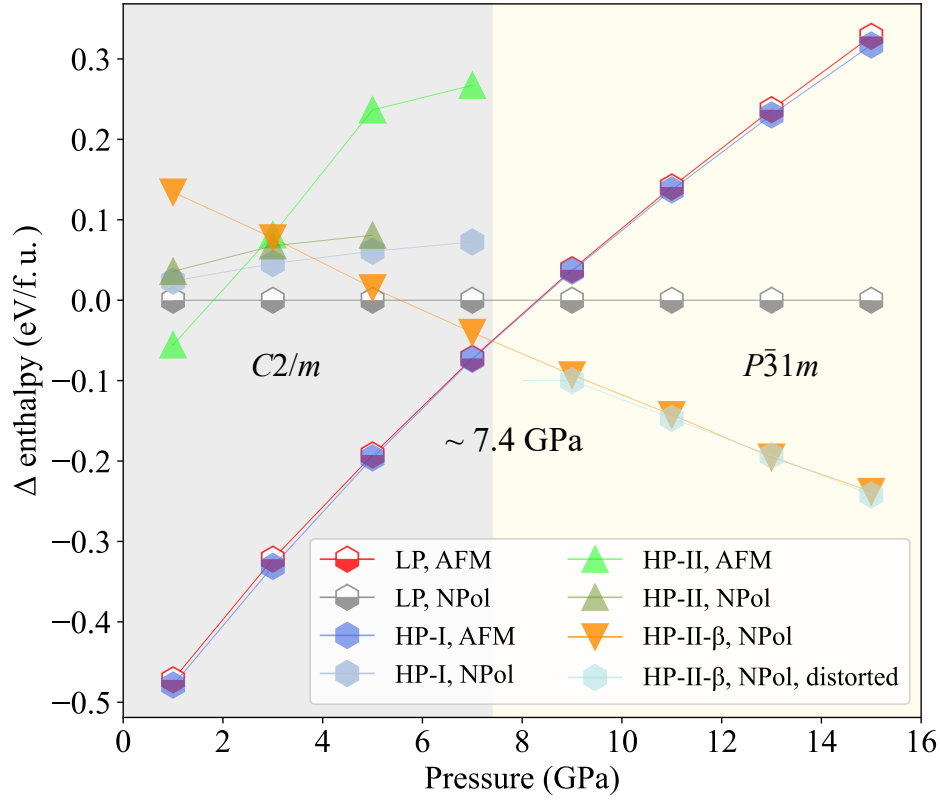


Fig. 6.2 Pressure dependence of the enthalpy difference $\Delta H = H - H_{\text{ref}}$ of various phases with respect to the reference non-spin-polarized low-pressure phase (LP, NPol, half-grey hexagons). ΔH is shown for: the low-pressure phase with antiferromagnetically coupled spin chains (LP, AFM, half-red hexagons), high-pressure phase I, both AFM (blue hexagons) and non-polarised (HP-I, NPol, full light blue hexagons) and, high-pressure phase II, HP-II, both in the Néel AFM state (light green triangles) and NPol (dark green triangles) and the non-polarised HP-II- β phase (orange triangles). The figure shows that below a transition pressure of ~ 7.4 GPa the antiferromagnetic LP and HP-I phases are very close in enthalpy, LP being very slightly favoured at low pressures, but very close to unshearing to the HP-I phase (see Fig. 6.3). Above the transition pressure, the HP-II phase becomes the stable one in its β form, that is, with interlayer P-P bonds. The structure was relaxed allowing for a distortion breaking the triangular symmetry. The relaxation recovered the symmetry up to a residual distortion of $0.006 \text{ \AA}$ in the difference of inequivalent Fe-Fe nearest neighbour distances.

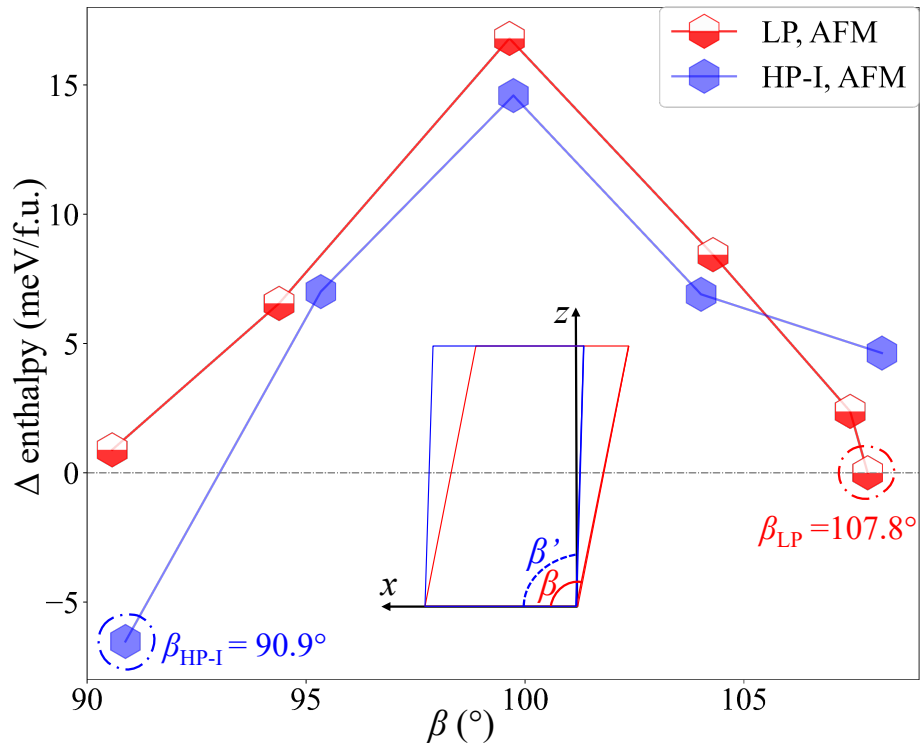


Fig. 6.3 Enthalpy difference as a function of the β angle for the LP and HP-I AFM phases of FePS₃ at 1.0 GPa. The enthalpy of LP relaxed at a fixed $\beta_{LP} = 107.8^\circ$ is set as reference. The difference between both curves at the same pressure and shear is the different interlayer spin arrangement of the LP and HP-I phases.

in Fig. 6.3 at 1 GPa of pressure. The inset in the figure illustrates the shear in terms of the lattice viewed from the b axis. For each phase, we manually slide the neighbouring layers and then relax the geometry with a fixed β angle. The enthalpy of the fully optimised LP phase at $\beta = 107.8^\circ$ is set as the reference. The first conclusion extracted from this plot is that already at this pressure the almost unsheared phase would be the stable one. However, a significant energy barrier (~ 15 meV per f.u.) becomes very apparent in the figure for both phases, which could explain the experimentally observed coexistence of LP and HP-I shown in Fig. 6.1 (b) between 2 and 6 GPa, due to kinetic effects in the relaxation of the loading. In addition, experimentally the pressure cannot be ideally hydrostatic and phase coexistence might persist over a pressure range, depending on experimental conditions as it seems to have happened in experiments on powder samples [59].

6.1.2 The Dimensionality Change in HP-II and HP-II- β

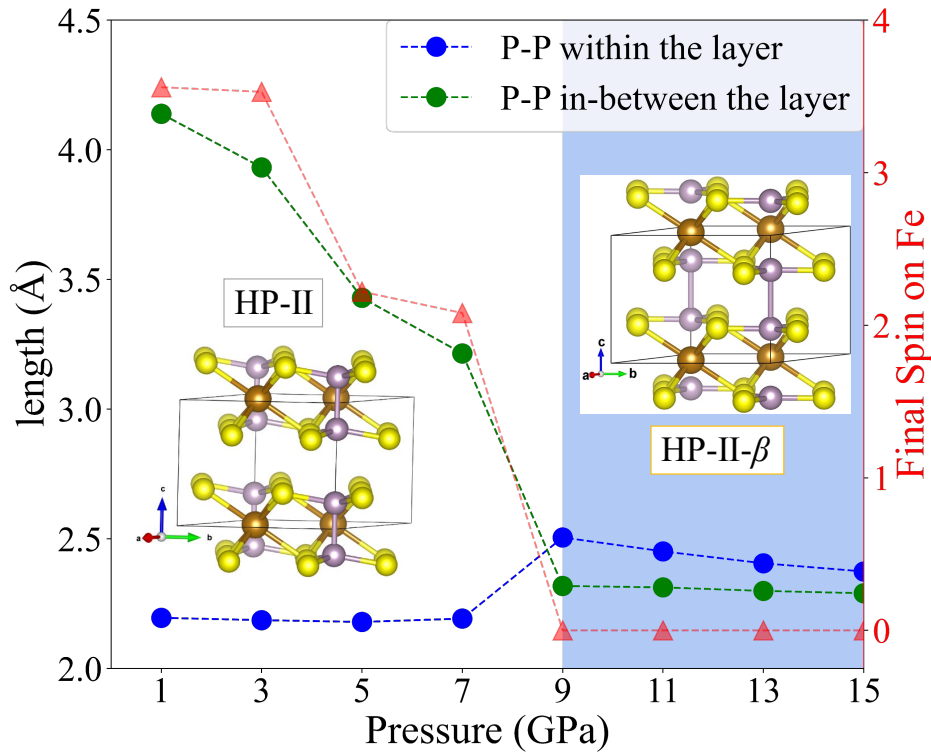


Fig. 6.4 Evolution with the pressure of P-P interatomic distances for P nearest neighbors along the direction perpendicular to the layers, in the $P\bar{3}1m$ FePS_3 phase. Intralayer (interlayer) distance is shown as blue (green) circles. Red triangles show the localised spin on a Fe atom.

Back in Fig. 6.2, there is a symmetry transition at $P \sim 7.4$ GPa from $C2/m$ (LP, HP-I) to $P\bar{3}1m$, which is qualitatively similar to the previous experimental findings. Such symmetry

change also occurs when the bulk is reduced to monolayer thickness [156]. The trigonal symmetry for every single layer at that pressure is recovered by releasing the constraint of the monoclinic β angle. When starting from a distorted geometry (HP-I), the structure relaxes towards the trigonal phase. The average in-equivalent Fe-Fe nearest neighbour distance is about 3.350 Å and the difference is 0.006 Å for the residual distortion. The enthalpy for the HP-II- β phase with residual distortion is also shown in Fig. 6.2.

For the two trigonal phases, HP-II and HP-II- β distinguish from one another in the P-P intra- and interlayer bonding behaviours. In order to investigate whether they are degenerate in energy or relax into the same local minimum after geometry optimisation, we explore the evolution of crystal structure including lattice parameters at the applied pressure, especially following the interatomic distance of P-P within and in-between the layers.

Fig. 6.4 shows the evolution of P-P distances within the layer (blue circles) and between the layers (green) for the relaxed HP-II phase from 1 to 15 GPa in steps of 2 GPa. The prediction is that HP-II transforms into the HP-II- β phase around 9 GPa. The novel HP-II- β phase is more 3D-like, compared to the HP-II phase. As far as we understand, it is difficult to experimentally determine the detailed P positions. In addition, further experimental evidence may be impeded by the substantial kinetic energy barrier expected for the change in connectivity, which implies P-P chemical bond restructuring.

Fig. 6.4 was obtained with the PBE functional, corrected by the vdW Trachenko-Scheffler approach, and a value of the Hubbard $U = 2.5$ eV on the Fe d orbitals including spin polarization for the Fe atoms. We extensively explore the sensitivity of such a transition to the simulation parameters and approximations mentioned in the subsequent section. The key prediction is that the dimensionality changes from 2D to 3D under pressure. Yet, increased values of Hubbard U postpone the transition to higher pressure, bringing it into closer agreement with experiments, and thereby suggesting that the correlation strength in the FePS₃ system is quite substantial and makes a difference.

Sensitivity of dimensional crossover at high pressure for various approximations

We also investigated the sensitivity of pressure-induced P-P from adjacent layers forming stronger bonds with respect to the choice of simulation parameters in detail. Considering the fact that FePS₃ is a layered vdW compound with Fe being able to host finite magnetic moments, we postulate a few starting scenarios in HP-II phase and then fully relax the structure with CASTEP. The P-P interatomic distances within each double sulfur layer and

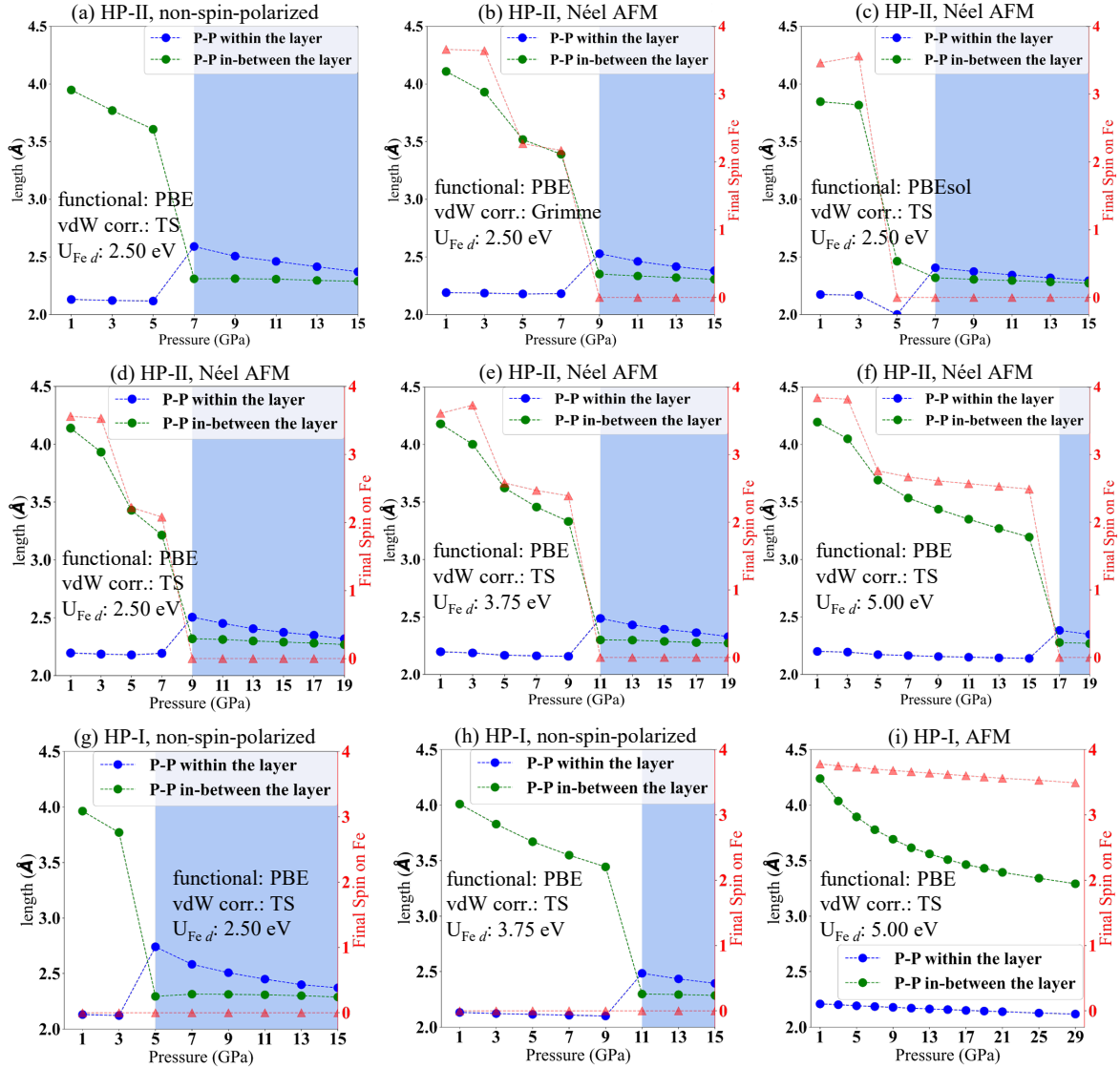


Fig. 6.5 Evolution of P-P interatomic distances within (blue) and in-between (green) the layers in response to simulated hydrostatic pressure for the HP-II (a-f) and HP-I (g-i) phase under different simulation scenarios.

in between the neighbouring layers are evaluated from the post-optimized phases. Fig. 6.5 summarizes the two P-P interatomic distances as a function of pressure, with the former in blue and the latter in green.

In Fig. 6.5 (a), the non-spin-polarized HP-II phase has been relaxed from 1 to 15 GPa with a step size of 2 GPa. The functional is chosen as PBE [115], and the vdW correction methodology follows the Tkatchenko-Scheffler (TS)'s approach [140]. There are the parameters that we have discussed and utilized for most of the calculations in the main text. We also compared the S. Grimme's semiempirical approach (2006) [141] (equivalent to the DFT-D2 in the Vienna *ab initio* simulation package (VASP) [157]) to tackle the vdW interactions. It can be seen from Fig. 6.5 (b) that the P-P interlayer dimerization with pressure will not be affected by the choice of vdW correction methodology qualitatively. Similarly, the PBESol [158] as functional has been explored in Fig. 6.5 (c), without qualitative effect on the transition.

In Fig. 6.5 (d-f), we explored the effect of Hubbard U on Fe d orbitals at 2.5, 3.75 and 5.0 eV. The strength of Hubbard U has the most prominent influence. The transition point having been postponed to as high as around 17 GPa when U is 5.0 eV. In addition, we also explored the effect of symmetry in Fig. 6.5 (g-i). We create the supercell with 4 f.u. inside one simulation cell from HP-II phase to allow for zigzag FM chains along a axis being antiferromagnetically coupled to each other within each layer. The relaxed structures by symmetry analysis shall be classified as HP-I phases instead. The formation of interlayer P-P dimer is more sensitive to the correlation effect when the C_3 rotation symmetry has been broken. The neighbouring layers remain to be gapped via vdW interaction.

To conclude, P atoms tend to form shorter and stronger bonds across neighbouring layers at higher pressure. The high-pressure phase stabilizes in HP-II- β energetically within the DFT+ U methodology. The choice of different vdW corrections to the final energy and density functionals barely affects the system to stabilize in the HP-II- β at high-pressure region. Meanwhile, the Hubbard U on Fe d orbitals influences the formation of interlayer P-P bonds substantially, which is consistent with the picture of correlated electrons in FePS₃.

6.1.3 The Dynamical Stability of HP-II and HP-II- β

We have also explored the dynamical stability for HP-II and HP-II- β phases under the same pressure before the transition occurs, here 7.0 GPa. The phonon spectrum has been calculated using the finite displacement method [159] in conjunction with nondiagonal supercells [160].

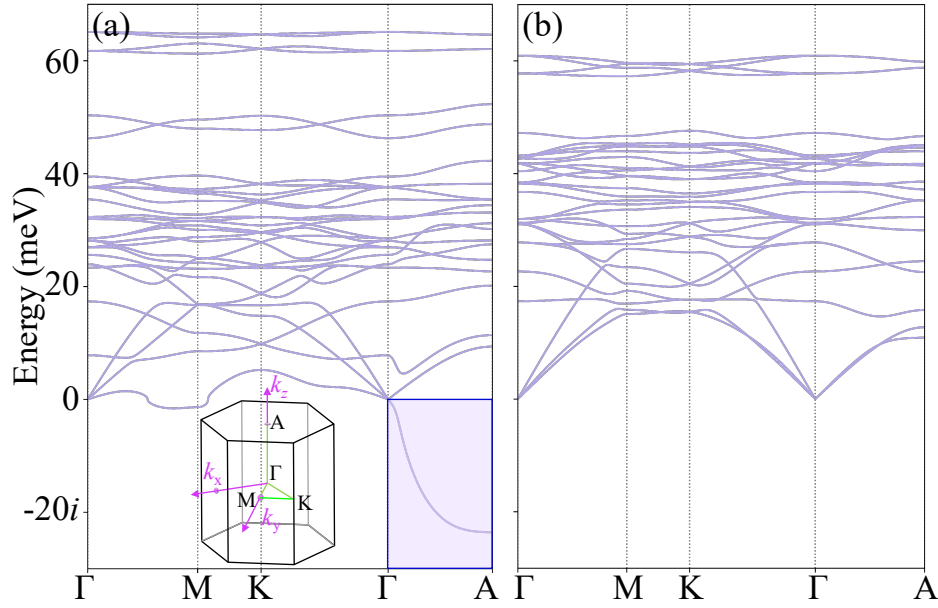


Fig. 6.6 The phonon spectrum calculated within DFT+ U (Fe d : $U = 2.5$ eV) for fully relaxed (a) HP-II and (b) HP-II- β phases at 7.0 GPa. The selected high symmetry path has been illustrated as an inset in (a).

Multiple commensurate supercells have been first constructed where atoms are perturbed from equilibrium positions. And then SCF calculations have been performed to evaluate the force-constant matrix. The finite displacement method allows the use of any electronic structure theory to obtain the lattice dynamics of FePS₃, taking the vdW interaction and Fe d -orbital correlation into account. A $3 \times 3 \times 3$ q-point grid has been adopted to sample the dynamical matrix of HP-II and HP-II- β phases.

The phonon dispersions for the two phases are shown in Fig. 6.6 along a selected high-symmetry path within the Brillouin zone. Though there is no imaginary phonon at the zone centre (Γ point) for HP-II, the imaginary part along Γ to A, highlighted in the shaded region, suggests certain instability for the HP-II structure along the vertical direction, which means that the HP-II phase tends to distort itself along the direction to lower its energy. The symmetry constraint of the $P\bar{3}1m$ space group might give the reason why HP-II can still be found via the structure search and geometry relaxation before the transition occurs. By contrast, there is no imaginary phonon frequency across the whole Brillouin zone for the HP-II- β phase, suggesting that this predicted new phase featuring P-P interlayer bonding geometry is indeed dynamically stable. This is consistent with the fact that a more compact structure along the vertical direction will be favoured at high pressure.

In addition, it is also worth noting that the volume of HP-II is about 8.8 % larger than that of HP-II- β , mainly arising from the c lattice parameter being 5.407 Å for the former while being 4.915 Å for the latter, more 3D-connected phase. The P-P bonding length within the layer versus that in-between the layer is 2.192/3.215 for HP-II, and 2.605/2.310 for HP-II- β . The significant volume shrinkage along the vertical direction and the rearrangement of P-P bonding lead to the fact that the high-frequency optical modes in HP-II are softened in HP-II- β . We have observed that the optical modes around 63 meV refer to strong vibrations of P and S atoms with all Fe atoms remaining static. Those around 47 meV refer to the vibrations of predominantly S atoms. From the 2D layered structure (HP-II) to the 3D bonded structure (HP-II- β), the vibration modes in FePS₃ within the ab plane have similar energy while those related to the perpendicular direction are heavily affected.

6.2 Electronic Properties of FePS₃

6.2.1 LP and HP-I

We have also investigated the evolution of electronic properties along with the structural transition in response to external pressure. The projected density of states (PDOS) are calculated with DFT+ U (Fe d : $U = 2.5$ eV) methodology, using CASTEP code and then post-processed with the OptaDOS package [161, 162]. In the LP and HP-I phases, the spin-up and spin-down magnetic arrangements for all Fe atoms are equivalent as they both stabilize with long-range AFM order. Fig. 6.7 displays the PDOS involving the projection of Kohn-Sham states onto the spin-up and spin-down Fe 3*d* orbitals, together with the ones for P 3*p* and S 3*p*, for LP at 0.0 GPa and 4.0 GPa (b), and for HP-I at 4.0 GPa (c) and 10.0 GPa (d). The apparent perfect spin-up-down compensation is characteristic of net zero moments in AFM arrangements. It should be noted, however, that, if projected on separate Fe atoms, they show mostly up (or down) according to their net polarization obtained and displayed in Fig. 6.1.

The obtained electronic structure is consistent with the attributed Mott insulating state, with a clear split between occupied and unoccupied Fe 3*d* orbitals, the weight of the S anions staying clear of the bands around the Fermi level, thereby ruling out a charge-transfer character for the insulating state. This fact is especially clear for LP, but less clean cut for the HP-I phase, and in both cases, P states significantly mix with the Fe 3*d* states, complicating the modelling. This latter fact is probably what is behind the less idealised parameterizations needed in

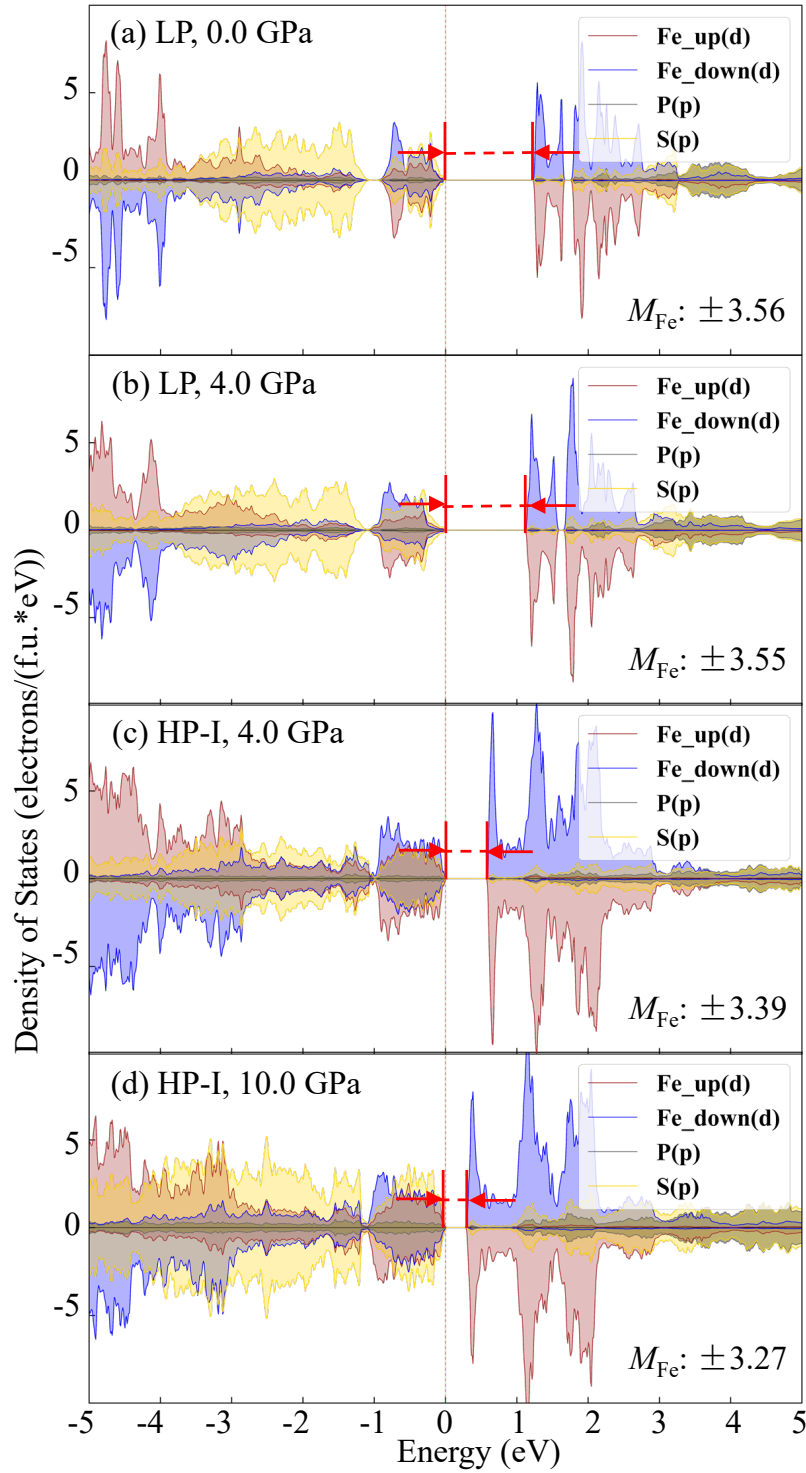


Fig. 6.7 Projected density of states (PDOS) as calculated within DFT+ U (Fe d : $U = 2.5$ eV), post-processed with the OptaDOS package [161, 162], showing the projection of Kohn-Sham states onto the Fe 3d states for spin-up (positive sign, red) and down (negative sign, blue). Grey PDOS indicate P 3p and yellow is for S 3p. Panels (a) and (b) for LP at 0.0 GPa and 4.0 GPa (b), respectively, (c) and (d) show HP-I at 4.0 GPa and 10.0 GPa. M_{Fe} refers to the final spin moments on Fe.

spin models [84], which gives rise to the frustration effects that result in the observed spin arrangements, instead of the pure Néel state expected from the bipartite honeycomb Fe substructure. The obtained electronic structure for this phase is also consistent with the fact that the energy scales for the definition of spin moments, the high spin state for Fe²⁺ ($S = 2$) and the effective spin-spin interactions dominate over any crystal field splitting parameter, Δ , that would tend to reduce the net spin on individual Fe atoms.

The obtained band gap, as determined by the bottom of the conduction and the top of the valence Kohn-Sham bands, for the LP phase at 0.0 GPa is about 1.2 eV. This is qualitatively consistent with previous optical measurements of the band gap [91]. It is well known that band gaps are not quantitatively predicted from this level of theory. Although the DFT+ U correction (including sensible, phenomenological values of U) somewhat improves their reliability, we will follow them here qualitatively as support for consistency and an indicator of trends.

With increasing pressure, the band gap for LP gradually shrinks down to ~ 1.1 eV at 4.0 GPa. However, when LP transforms into HP-I, the band gap becomes significantly smaller, ~ 0.56 eV for the HP-I at 4.0 GPa. The HP-I phase remains insulating at the applied pressure $P = 10.0$ GPa with a reduced band gap of ~ 0.27 eV. Though the increased pressure would increase the crystal field splitting energy Δ and thus affect the competition between Δ and the exchange energy J , the high-spin state of Fe²⁺ ($S = 2$) is still maintained in both the LP and HP-I phases within the pressure range being discussed.

6.2.2 HP-II and HP-II- β

Figure 6.8 shows the same PDOS decomposition as Fig. 6.7 now for $P = 11.0$ GPa and the HP-II phases. Panel (a) shows the HP-II- β phase, which appears clearly beyond the insulator-to-metal transition, using the same level of theory as employed so far. No spin decomposition is obtained. The dimensionality difference, introduced by the distinctive interlayer P bonding behaviour, affects the electronic structure across the Fermi level. With continuous contributions from P and S states, the metallicity also significantly affects the distribution of the 3d orbitals of Fe.

There is uncertainty in the most suitable choice for the value of the Hubbard U . The experimental IMT observed at higher pressures (see Fig. 6.1) seems to indicate stronger correlation effects than for other Fe compounds. In Fig. 6.8 we explore the effect of on-site Coulomb repulsion by tuning the Hubbard U on Fe d orbitals from 2.5 to 3.75 and 5.0 eV. The

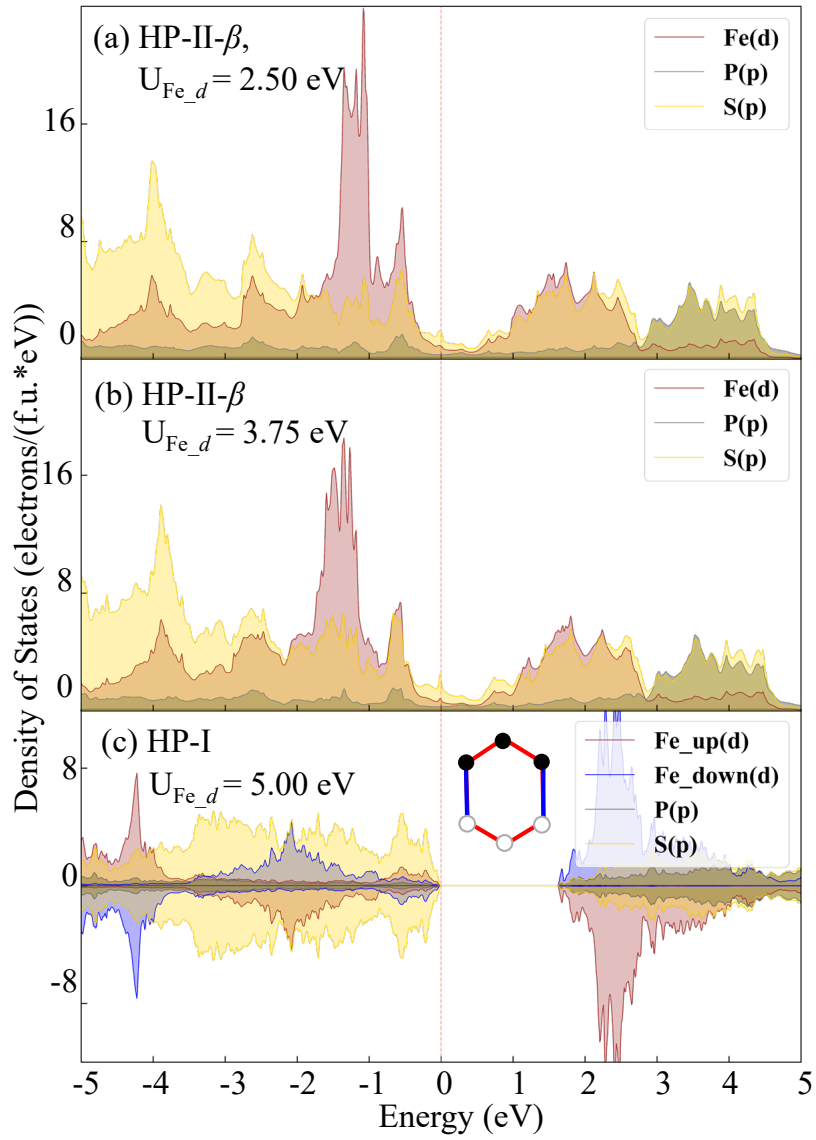


Fig. 6.8 PDOS for HP-II- β [panels (a) and (b)] and HP-I (c), respectively at $P = 11.0$ GPa (same conventions as for Fig. 6.7). Hubbard $U = 2.50$ eV (a), 3.75 eV (b), and 5.00 eV (c) on the Fe $3d$ orbitals.

geometries are relaxed at 11.0 GPa with different U , and the corresponding PDOS are then calculated as shown. The increased U values push the insulator to metal transition to higher pressures, in closer agreement with experiments, the insulating phase always remaining HP-I (panel c) with the same spin arrangements (inset). The increased electron-electron repulsion seems to inhibit the formation of strong chemical inter-layer P-P bonds, while retaining the long-range order (LRO) zigzag structures within planes. Interestingly, whenever the gap closes, we obtain the β phase.

The fact that the calculations lose spin polarization upon metalization has to be properly interpreted. The DFT+ U calculations rely on the mean-field treatments of the electronic problem (even at the Hubbard level) and cannot describe short-range spin correlations. Coak *et al.*[62] observe from their experiments that short-range order (SRO) magnetism persists in the high-pressure region, resembling that of the HP-I magnetic configuration. It is an interesting finding, compatible with the physics close to the Mott transition. There could be ways to query the calculations in that direction, by introducing constrained spins by hand at selected locations, and seeing the spin texture decaying from those sites in large-simulation-box settings. In an AFM situation the procedure is however quite arbitrary, since the individual magnetic moments develop for the electrons associated with a given atom, which is always an ill-posed proposition. Higher levels of theory, such as dynamical-mean-field theory (DMFT) [122] would also help in this regard, but they represent a substantially increased computational and theoretical effort, well beyond the scope of this work.

In addition to the displayed PDOS for various phases, Figs. 6.9 and 6.10 show the corresponding band-structure dispersion relations along paths crossing selected high-symmetry points. Fig. 6.9 shows these for LP and HP-I, from 0.0 GPa to 10.0 GPa. The Γ -A and M-L Brillouin-zone segments are along the k_z direction, (nearly) perpendicular to the layer planes in real space. The bands along these directions are quite flat, as expected for weakly interacting 2D layers.

Fig. 6.10 shows the band dispersion for the metallic high-pressure phases, very close to the insulator-to-metal transition ($P = 7.4$ GPa, as obtained for $U + 2.5$ eV), in both its originally proposed layered form HP-II and its 3D HP-II- β version. The metallization is much clearer in the latter, the former representing a weak semimetal. In Fig. 6.10 (a), electron and hole pockets emerge near the Fermi level along the high symmetry path H-A. It suggests that the HP-II phase would transit through a semimetal phase before becoming fully metallic at slightly higher pressures. From our results, however, it is difficult to ascertain whether there could be such an intermediate region of stability.

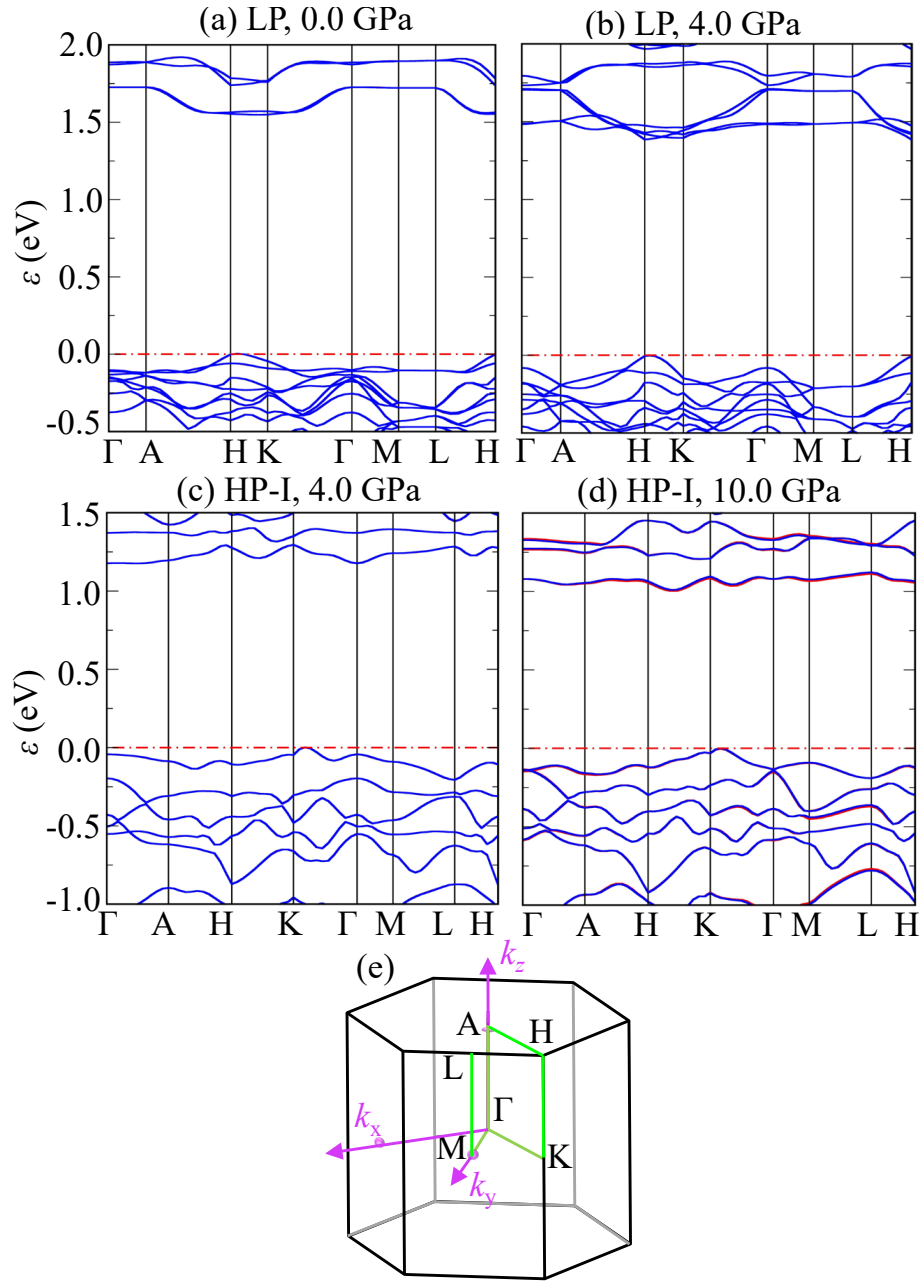


Fig. 6.9 Band structures for (a) LP at 0 GPa and (b) 4.0 GPa, and for (c) HP-I at 4.0 GPa and (d) 10.0 GPa, and (e) a Brillouin zone diagram indicating the symmetry points defining the band dispersion plots.

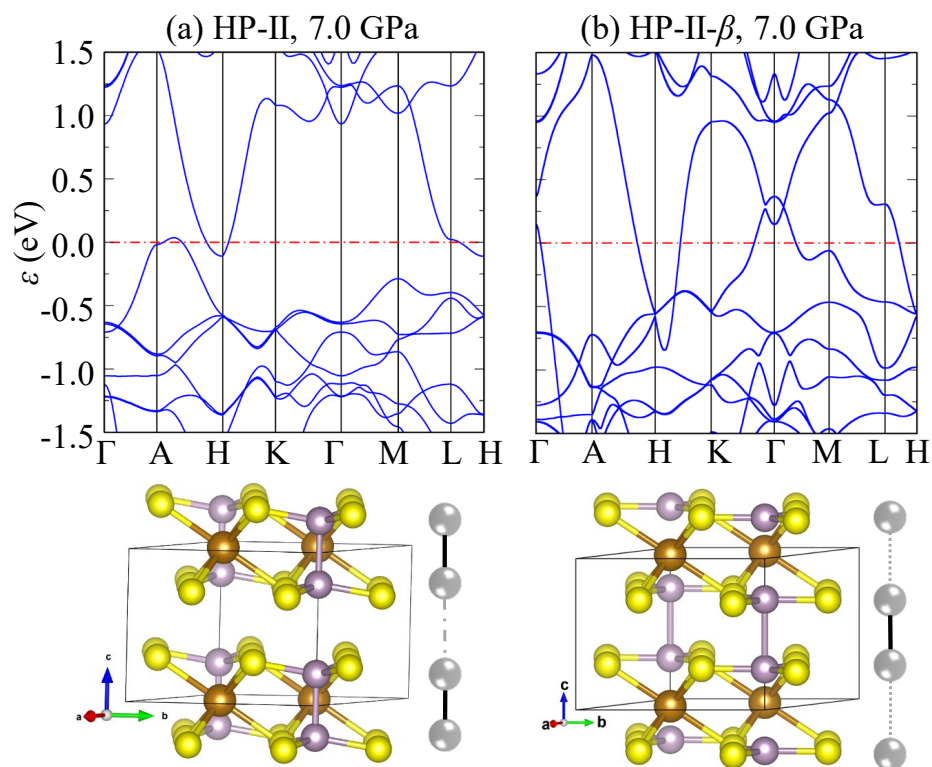


Fig. 6.10 Band structures for (a) HP-II and (b) HP-II- β phases at 7.0 GPa (both $P\bar{3}1m$), close to the transition point, with structural sketches under each corresponding panel.

Several bands cross the Fermi level in HP-II- β , as can be seen in Fig. 6.10 (b). Our results suggest that the metallicity would emerge at the high-pressure region regardless of the dimensionality collapse in the c axis. Our calculations offer another scenario in this case. It should be noted that for the high-pressure phase reported in [100, 107] the band structure is actually very similar to the one we obtain for HP-II- β , in spite of their not reporting on the dimensionality change implied by the β phase. The c -axis collapse and P-P interlayer bonds appearing in the HP-II- β phase should affect electronic transport significantly. Further investigation is needed to understand the effect of dimensionality crossover on electronic transport. It would require the deployment of more sophisticated techniques (like DMFT [122], whenever accessible to these system sizes) to describe the effect of the strong electron correlations induced by the strength of on-site Coulomb repulsion for $3d$ orbitals.

6.3 Conclusions

With AIRSS random structure search, we have reproduced the previously proposed LP, HP-I and HP-II phases, and a novel HP-II- β phase. LP and HP-I crystallise in the monoclinic space group $C2/m$ while HP-II and HP-II- β stabilize in the trigonal one $P\bar{3}1m$. The HP-II- β is intrinsically different from HP-II in that the P atoms form stronger chemical bonds in-between the neighbouring layers. The full simulation of the enthalpy-pressure phase diagram, taking into consideration spin polarisation, is found to be consistent with the previous experimental observations.

We rationalize the coexistence region of the LP and HP-I phases by quantifying the energy barriers for neighbouring planes to slide against each other, regardless of the interplanar coupling being antiferromagnetic (LP) or ferromagnetic (HP-I). Despite the gradual decrease of the band gap size, both phases remain insulating in this pressure region.

At higher pressure, the symmetry crossover from $C2/m$ to $P\bar{3}1m$ takes place concurrent with the emergence of metallicity. The intra- or inter-layer P-P bonding affects the energy bands near the Fermi level and might be responsible for a possibly different explanation for the origin of metallicity. The predicted dynamically stable HP-II- β phase defines a scenario for FePS₃ turning metallic while becoming 3D-connected under high pressure.

The magnetic moments on the transition metal sites are suppressed when the system turns from quasi-2D to the 3D limit. The strength of the on-site Coulomb repulsion also influences the dimensionality change. The actual correlation strength deserves further investigation as

it could facilitate quantitative theory in the low-dimensional $TMPX_3$ and other AFM Mott systems.

Considering the complexity of correlation effects in the system and the competition among exchange and anisotropy, more effort is needed to further our understanding of the nature of the insulator-to-metal transition and how dimensionality is involved in the process. This work has been carried out with the DFT+U technique, which is insensitive to environmental factors like the nature of the pressure medium. The theoretical modelling can be expected to guide future experimental explorations in the $TMPX_3$ compound family and could possibly be extended to other 2D magnets, where pressure or other tuning parameters could tune the phases to be novel metal or unconventional superconductors.

Chapter 7

Intermediate 2.5D Phase from Soft Mode in FePS_3 at High-pressures

In the previous chapter, the HP-II and HP-II- β phases have been explored under the same pressure level before the transition occurs, 7.0 GPa. The focus was on exploring their dynamical stability and electronic properties. In this chapter, I will extend our examination to delve deeper into the instability mode within HP-II. Furthermore, I will engage in a discussion regarding a potential intermediate phase, which has been suggested by DFT+ U simulations.

7.1 Phonons and the Physical Interpretations

To start with, I would like to recap the concept of *phonons* in crystals. More detailed and elementary discussions can be found in various textbooks [163]. Here I intend to discuss it briefly to establish the context for this chapter.

7.1.1 Nature of Phonons

If we visualise an atom in an ideal crystal in terms of its ion core and valence electrons, the core of an atom vibrates about its equilibrium position while the electrons move around the core. The concept of *phonons* is introduced to represent the collective vibrations of atoms at different lattice sites. Taking advantage of lattice translation periodicity, the motion of all the

ion cores and electrons can be simplified into the problem of the dynamics of the atoms in the primitive unit cell. There are two assumptions for this simplification,

- **Adiabatic approximation:** the motion of the ion core and the valence electrons can be treated separately as the cores are much heavier than the electrons.
- **Harmonic approximation:** Consider the total potential energy of a crystal in terms of interatomic potentials $U(\mathbf{R})$, where $\mathbf{R}$ is the distance between a pair of atoms. At the equilibrium position, this distance is $\mathbf{R}_0$. Hence the displacement is $x = \mathbf{R} - \mathbf{R}_0$. Despite the complicated shape of the potential, it can be expressed in a Taylor expansion series when x is extremely small:

$$U(\mathbf{R}) = U(\mathbf{R}_0) + \left(\frac{\partial U}{\partial \mathbf{R}} \right)_0 \cdot x + \frac{1}{2} \left(\frac{\partial^2 U}{\partial \mathbf{R}^2} \right)_0 x^2 + \dots \quad (7.1)$$

The first term is a constant and the second term will vanish in the equilibrium configuration. Hence the first important term in Eq. 7.1 is the quadratic term of displacement x . The harmonic approximation applies when only the quadratic term is being considered. The crystal, in this case, can be described as a 3D simple harmonic oscillator.

Under such approximations, the atoms in a crystal can be seen as being joined by harmonic springs. The crystal dynamics can be analysed in terms of a linear combination of normal modes of vibration.

A normal mode of vibration can be expressed as a propagating wave of

$$A \exp[i(\mathbf{q} \cdot \mathbf{r} - \omega t)] \quad (7.2)$$

where $\mathbf{q}$ represents the direction of wave propagation, ω is the frequency of the wave and A is the amplitude of the vibration mode. This relative motion of the atoms can be described with the concept of a phonon with the energy $\hbar\omega(\mathbf{q})$.

7.1.2 Phonon Dispersion and the *ab initio* Treatment

The relationship between energy $\hbar\omega(\mathbf{q})$ and wave vector $\mathbf{q}$ is phonon dispersion. It can serve as a critical tool for gaining insights into the vibration modes of the crystal.

Experimental methods such as inelastic neutron scattering or Raman spectroscopy offer avenues for its measurement, while theoretical calculations employing approaches like Density

Functional Theory (DFT), as employed in this thesis, or molecular dynamics simulations provide complementary insights.

To calculate the phonon spectrum, we need to solve the dynamical matrix equation for vibration modes. The efforts yield a set of phonon frequencies. These frequencies may assume real values, signifying stable modes. Or they may take imaginary values, indicating the presence of unstable or soft mode.

7.2 Structural Instability of HP-II Phase

7.2.1 k -dependence of the Soft Modes

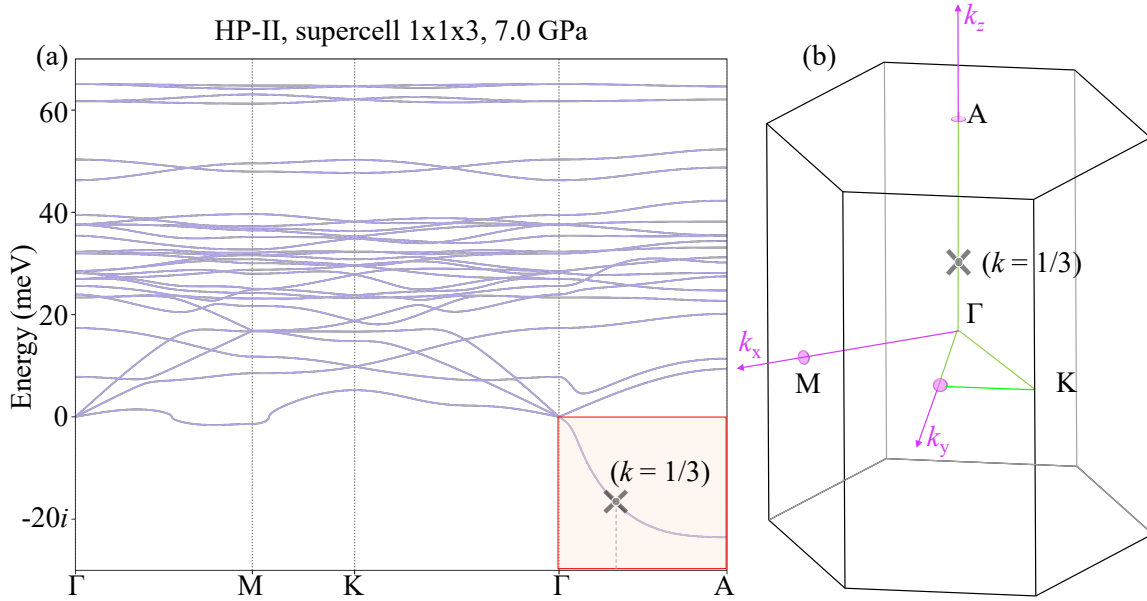


Fig. 7.1 (a) The phonon spectrum calculated with DFT+ U (Fe d : $U = 2.5$ eV) for fully relaxed HP-II phase using supercell 1x1x3. (b) The selected high-symmetry path in the first Brillouin zone. The position of $k = 1/3$ is marked with grey bold crosses for eye guidance.

In the case of the HP-II phase of FePS₃ before the transition pressure, we calculated the phonon spectrum using the finite displacement method [159] in conjunction with non-diagonal supercells [160]. This approach involves the creation of multiple commensurate supercells, where atoms are perturbed from their equilibrium positions.

The dimensions of these supercells are expressed as multiples of the original unit cell, for instance, 1x1x3 means the simulation cell is enlarged by 3 times along the c lattice compared to the original primitive one. We created a series of supercells 1x1x N (where N ranges from 2 to 5), and calculated the corresponding phonon spectra. These computations revealed the presence of imaginary phonon branches, providing valuable insights into atomic instability and displacements.

It is worthwhile to emphasise that the imaginary mode computed with different sizes of supercells represents distinctive vibration modes. These results correspond to different k values along the Γ -A path. Fig.7.1 (a) displays the phonon spectrum calculated using the 1x1x3 supercell, with the imaginary mode being highlighted in the shaded light red region. This vibration mode corresponds to $k = 1/3$ along the k -path from Γ (0, 0, 0) to A (0, 0, 0.5) in the first Brillouin zone of the primitive cell, as is marked in Fig.7.1 (b).

7.2.2 Vibration Mode and Atomic Displacement

The vibration mode corresponding to the imaginary part is related to the movement of P atoms along the c axis in real lattice space. However, the exact movement varies at different k values. Using the example of the 1x1x3 supercell, the vibration mode can be described as follows: P atoms in the central plane remain stationary, while P atoms from the top and bottom planes move towards the central plane in the form of P₂ dimers. This scenario is illustrated in Figure 7.2 (a). Since the other atoms are not involved in this vibration mode, we simplify the movement using P₂ dimers to represent each plane. This representation is shown in Figure 7.2 (b).

In the case of a 1x1x2 supercell, or for $k = 1/2$, the P₂ dimers move toward each other in a unit cell with two layers of planes. When considering a 1x1x4 supercell, at $k = 1/4$, each unit cell contains four planes. If we describe the four layers from bottom to top, the P₂ dimers within the bottom or upper two layers move in the same direction, but they move in opposite directions in the middle two layers.

Atomic displacements are quantified as a percentage of the interatomic spacing changes for these movement modes at different k values away from the initial equilibrium configuration. A sequence of 'new' structures is then generated by applying these displacements along the direction defined by the soft mode. Static DFT calculations are performed to obtain the total energy of these 'new' structures with different amplitudes of the atomic displacement. Fig. 7.3 presents the total energy as a function of displacement away from the symmetric

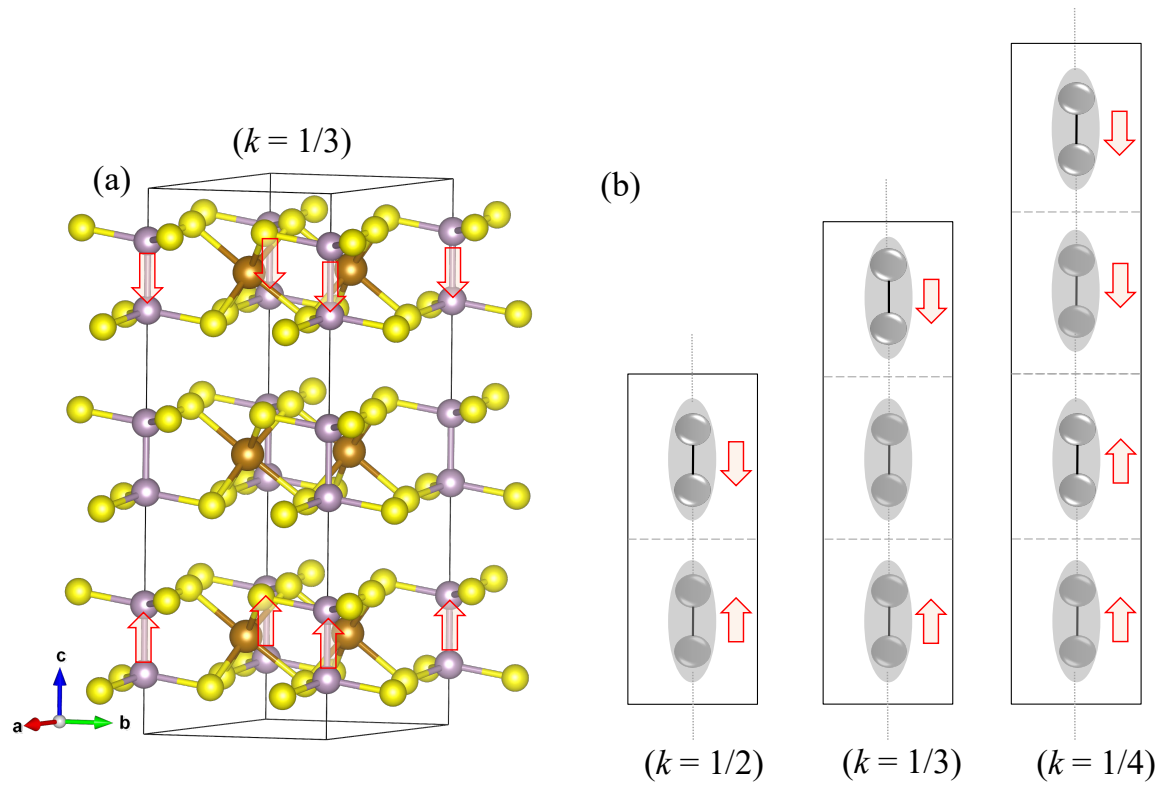


Fig. 7.2 (a) The P atomic movement in a $1 \times 1 \times 3$ supercell of FePS₃ HP-II phase. The movement is marked with light red arrows. This corresponds to the vibration mode at $k = 1/3$. (b) The cartoon of P₂ dimers within each plane moving along the (001) direction for $k = 1/2$, $1/3$ and $1/4$.

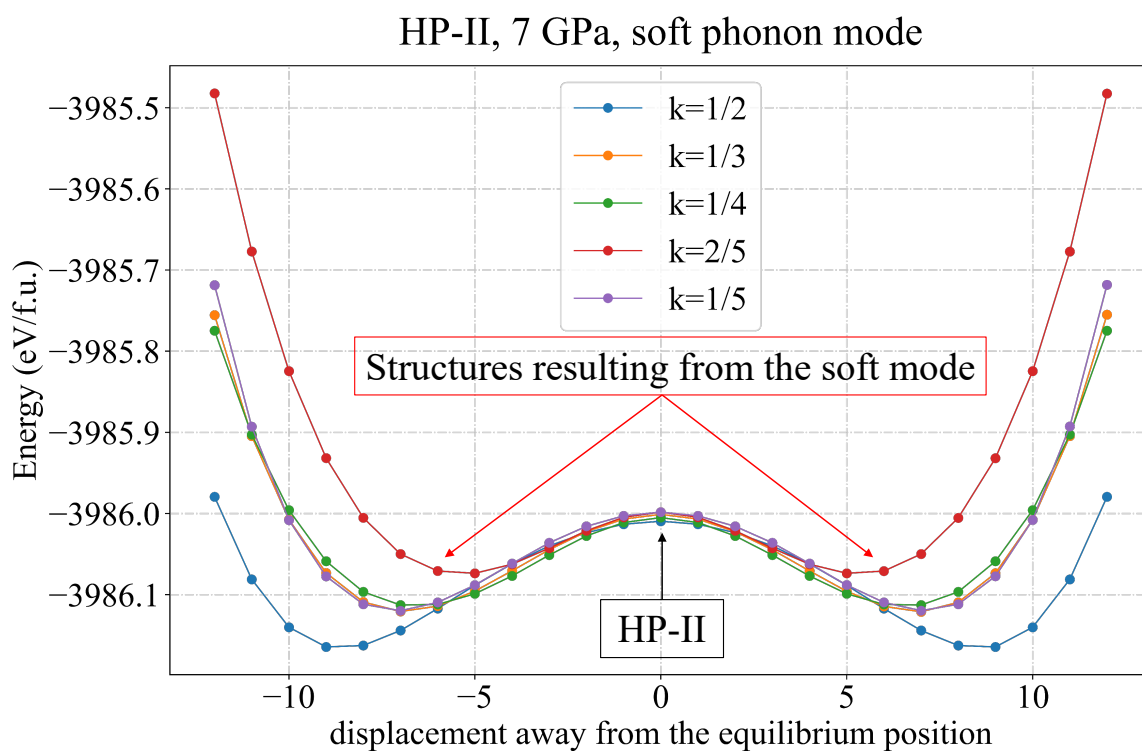


Fig. 7.3 The static energy of the HP-II phase from original position to displacement. The different colours represent the choice of the simulation cell size.

equilibrium position. It can be seen that the vibration modes lead to local minimum structures, away from the translationally invariant structure of the HP-II phase.

The notion of a "soft mode" is closely linked to local energy extrema within the crystal's potential energy landscape. While soft modes have been extensively investigated in the context of ferroelectric transitions, they hold great significance in our study of phase transitions as well.

7.3 Phases resulting from Soft Mode

7.3.1 Crystal Structures between 2D and 3D

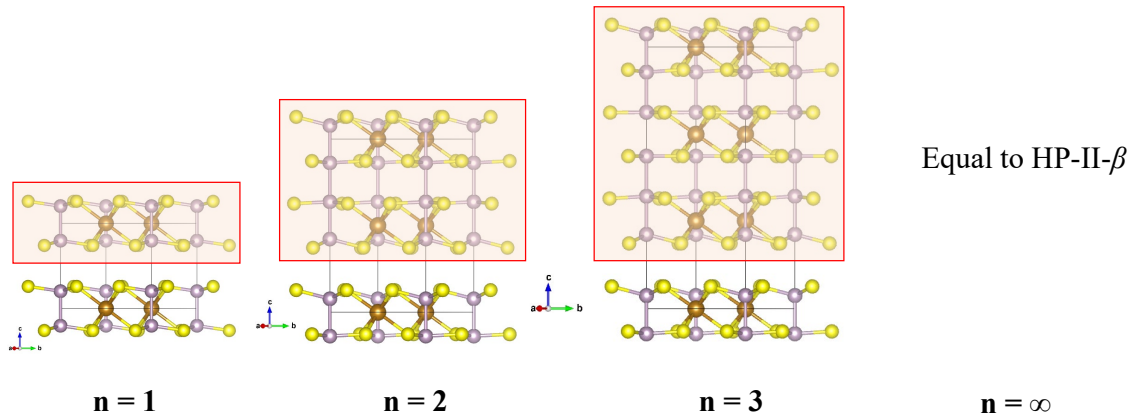


Fig. 7.4 The structures obtained from relaxing the soft mode geometry in different supercells.

Novel phases are constructed based on the instability mode of HP-II supercells following relaxation. Different sizes of supercells give rise to distinct hidden structures, as illustrated in Fig. 7.4, which provides a summary of these relaxed structures. In these novel phases, the stacking unit comprises multiple layers of the double-sulfur planes, while the van der Waals gap remains intact. Such configuration shows quasi-three-dimensional characteristics, between 2D and 3D. In the limit as N approaches infinity, this phase turns HP-II- β phase.

In the vicinity of the phase transition into the high-pressure region, the competing phases are HP-I, HP-II, HP-II- β and the novel phases obtained from the phonon soft mode. The enthalpy of formation for these phases within the pressure range of 7.0 to 10.0 GPa has been computed carefully. It is worth noting that these phases, particularly those related to HP-II, all represent local minima within the energy potential surface. The structure obtained after optimisation

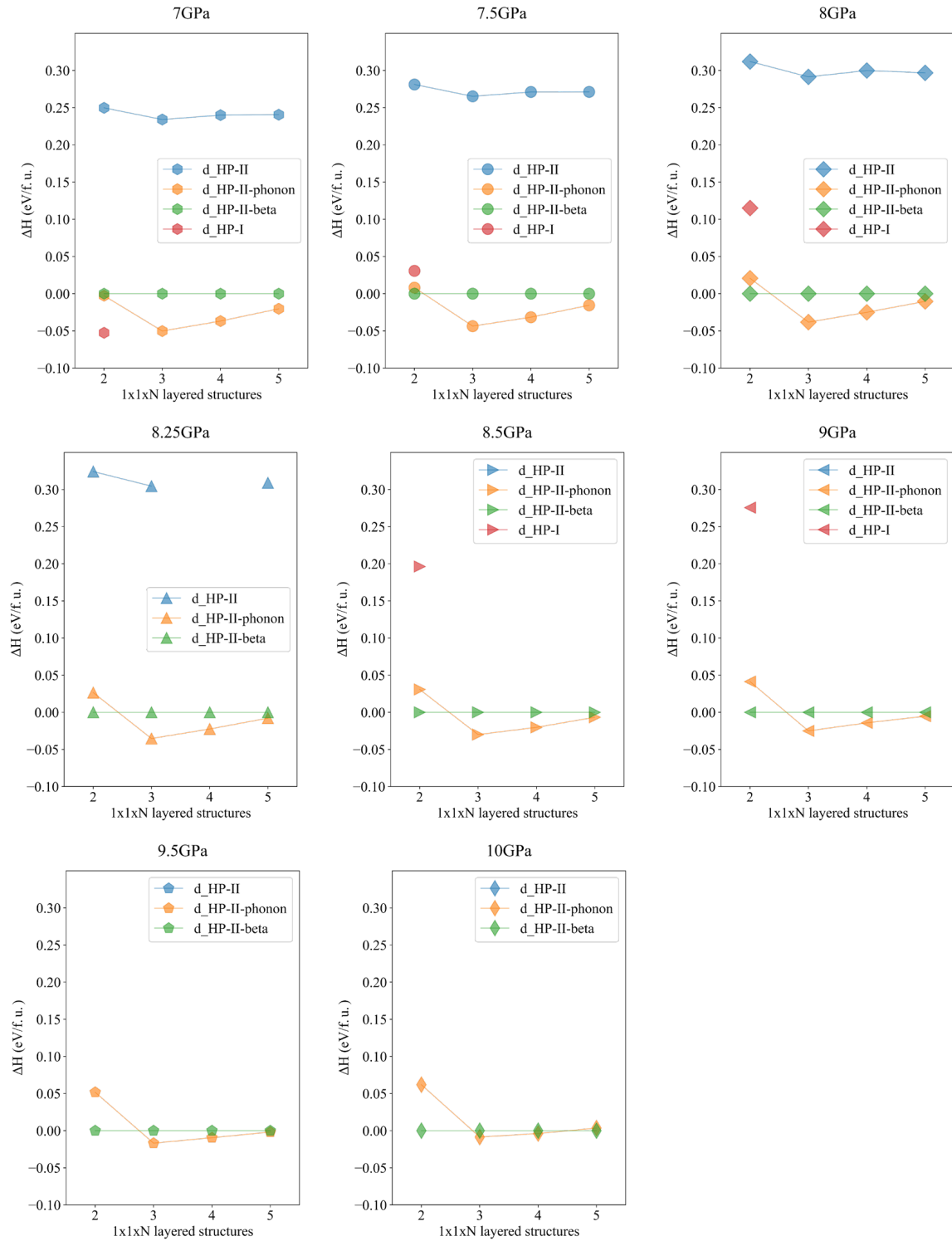


Fig. 7.5 The enthalpy difference $\Delta H = H - H_{\text{ref}}$ of competing phases HP-I, HP-II, HP-II- β and soft mode structure resulting from 1x1xN supercells within the range of 7 to 10 GPa. The non-polarised HP-II- β phase is selected as the reference phase. The notion $d_{\text{-}}$ represents taking the difference of the enthalpy value between the targeted phase and the reference phase.

at a lower pressure point was used as the starting geometry for the corresponding pressure point. For instance, the out structure file put at 7.5 GPa is utilised as the input for structure relaxation at 8.0 GPa. At 7.0 GPa, the HP-I phase is most favourable, while the relative enthalpy of the HP-II phase increases with increasing pressure.

It is particularly intriguing that the soft mode structure with the triple-layer as stacking units is the most stable phase from the perspective of energy after the symmetry crossover transition. Hereafter I will refer to this phase as HP-II- γ . Adding this novel HP-II- γ phase to the phase diagram, there emerges an intermediate pressure range from approximately 7.0 to 10.8 GPa where the HP-II- γ , shaded in green. These preliminary results form an example of a 2.5D phase when layered materials change from 2D to 3D.

7.3.2 Electronic Properties

Fig. 7.7 exhibits the band dispersion for the HP-II- γ and HP-II- β at 7.0 GPa. The side view of the crystal structures is also shown below. It can be seen that the band spectrum is essentially different between the 2.5D HP-II- γ phase and the 3D HP-II- β phase, both exhibiting metallic features with multiple bands crossing the Fermi energy level. Further investigation would be required to gain a more comprehensive understanding of the emergence of this 2.5D phase.

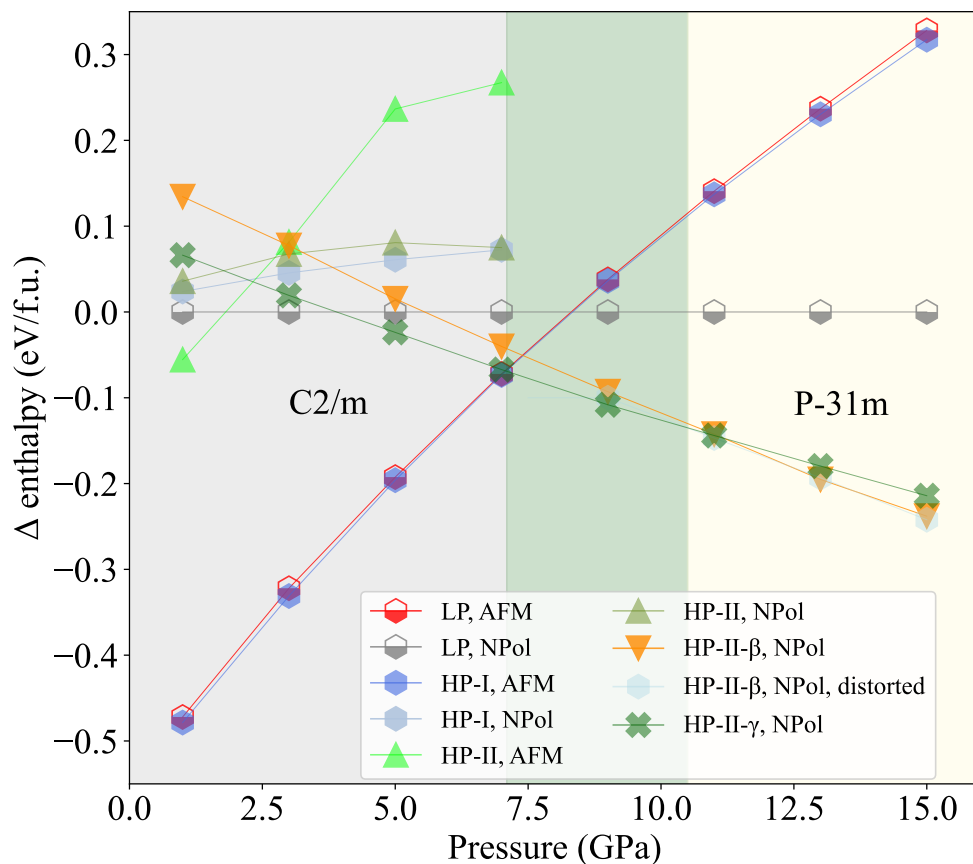


Fig. 7.6 The updated pressure dependence of the enthalpy difference $\Delta H = H - H_{\text{ref}}$ of various phases with respect to the reference non-spin-polarised low-pressure phase (LP, NPol, half-grey hexagons). ΔH is shown for: the low-pressure phase with antiferromagnetically coupled spin chains (LP, AFM, half-red hexagons) and non-polarised (LP, NPol, half-grey hexagons), high-pressure phase I, both AFM (blue hexagons) and non-polarised (HP-I, NPol, full light blue hexagons) and, high-pressure phase II, HP-II, both in the Néel AFM state (light green triangles) and NPol (dark green triangles), the non-polarised HP-II- β phase (orange triangles) and with slight distortion (light blue hexagons), and the non-polarised soft mode structure HP-II- γ (dark green crosses). An extra intermediate pressure region from approximately 7.0 GPa to 10.5 GPa has been identified where the soft mode phase is the most stable one.

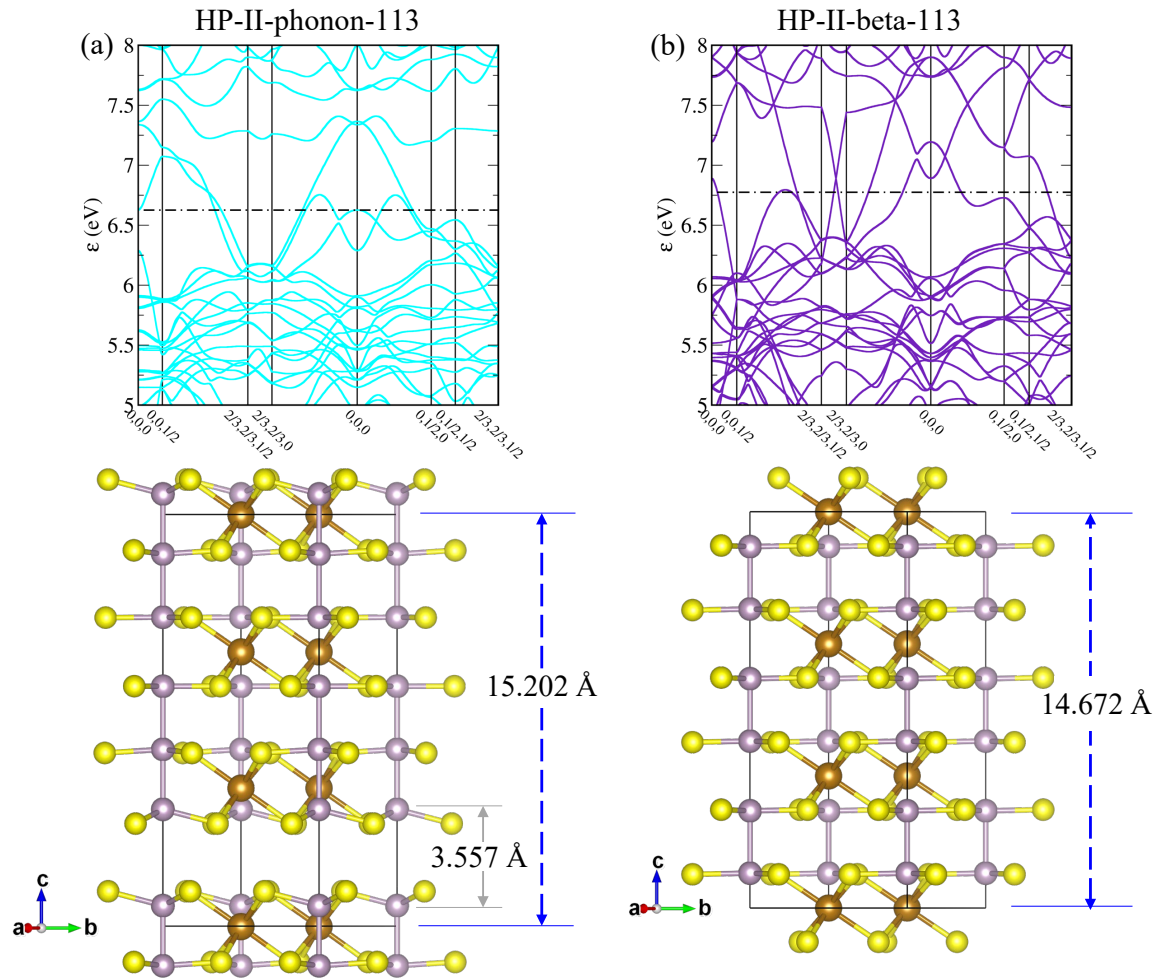


Fig. 7.7 The band structures for (a) the soft mode structure from the instability mode in HP-II 1 $\times$ 1 $\times$ 3 supercell and (b) the HP-II- β 1 $\times$ 1 $\times$ 3 supercell. The crystal structures are displayed underneath, respectively.

Chapter 8

Pressure-induced Structural Evolution and Polar Metallicity in FePSe₃

We explored the structure and dimensionality change of FePSe₃ in response to the applied pressure, by comparison, considering different sample conditions and experimental environments. The single crystal and powder samples loaded with a helium pressure-transmitting medium in diamond anvil cells (DAC), providing the most hydrostatic condition, consistently exhibit structural transitions from ambient to high pressures. Additionally, another DAC loaded purely with FePSe₃ powder samples has been investigated. In this chapter, I will delve into the measured scattering patterns of FePSe₃ under pressure and the corresponding high-pressure structure model.

Production of high-quality powder samples is a non-trivial challenge. The nature of van der Waals (vdW) interplanar interactions often causes stacking planes to slide across one another when subjected to a shear force. As a result, powder samples often show significant preferred orientations.

8.1 Crystalline Structures

Previous comparisons of the ambient-pressure phases have established that the LP phase of FePSe₃ primarily differs from the LP phase of FePS₃ in the stacking of the double chalcogen layers. However, it remains ambiguous whether this difference in ambient-pressure phase stacking influences the pressure-induced evolution of structural, electronic, and magnetic

properties. In the following sections, I will discuss the high-pressure phases observed in FePSe₃ through the synchrotron X-ray diffraction experiments recently conducted at Diamond Light Source.

8.1.1 Single-crystal X-ray Diffraction Data

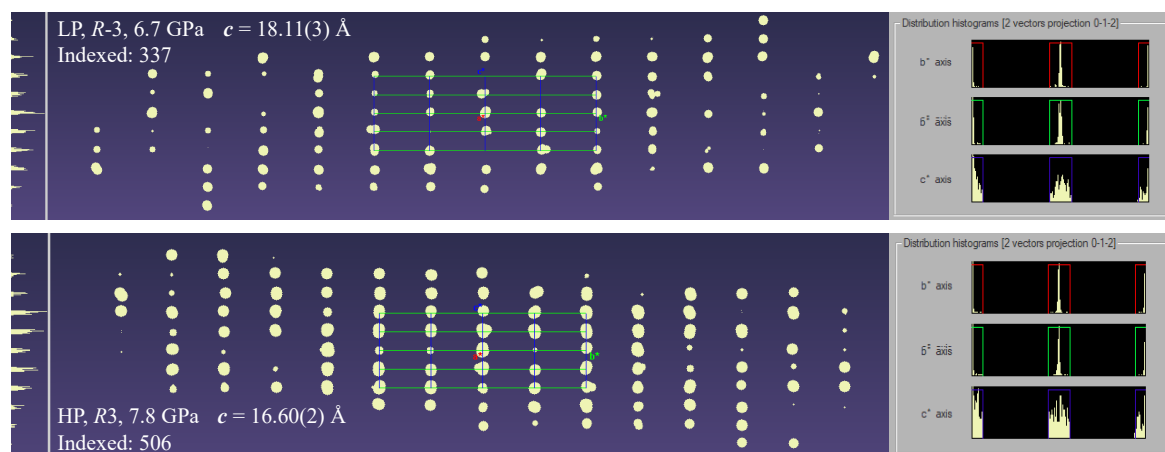


Fig. 8.1 The reciprocal lattice viewer for LP and HP phase before and after the c lattice collapse. The main window on the left displays the peaks found during the peak hunting process. The quality of indexation for a , b and c is shown on the right. The plots are generated by Ewald^{Pro} as implemented in CrysAlis^{Pro} software package.

Table 8.1 The lattice parameters of FePSe₃ at ambient pressure, before and after the transition pressure, obtained from the single-crystal X-ray diffraction experiment. Here we use the primitive hexagon cell description for describing the lattice parameters.

	0 GPa	6.7 GPa	7.8 GPa
phase	LP	LP	HP
space group	$R\bar{3}$	$R\bar{3}$	$R3$
lattice parameters	$a = b = 6.262 \text{ \AA}$	$a = 6.0477(11) \text{ \AA}$	$a = 6.0220(10) \text{ \AA}$
	$c = 19.805 \text{ \AA}$	$b = 6.0481(6) \text{ \AA}$	$b = 6.0233(6) \text{ \AA}$
	$\gamma = 120.0^\circ$	$c = 18.00(2) \text{ \AA}$ $\gamma = 120.0^\circ$	$c = 16.40(2) \text{ \AA}$ $\gamma = 120.0^\circ$

The single-crystal measurements give complete structural information about FePSe₃ at the atomic level as a function of quasi-hydrostatic pressure at room temperature. Due to the experimental geometry, the 001 peak was exclusively observed in single-crystal

Table 8.2 The crystallographic data for FePSe₃ at 4.4 GPa and 10.0 GPa from the single-crystal X-ray diffraction experiment. Here we use the primitive hexagon cell description for the lattice parameters.

	4.4 GPa	10.0 GPa
phase	LP	HP
space group	$R\bar{3}$	$R3$
a (Å)	6.0971(6)	6.0155(7)
c (Å)	18.279(19)	15.34(6)
Volume (Å ³)	588.5 (6)	480.8 (18)
Refinement		
$R[F^2 > 2\sigma(F^2)]$	0.0038	0.090
$wR(F^2)$	0.095	0.221
S	0.88	2.1
reflections	36	125

Table 8.3 Wyckoff positions of FePSe₃ at 4.4 GPa with the $R\bar{3}$ space group.

	x	y	z
Fe1(6c)	0.667	0.333	0.667
P1(6c)	0.333	0.667	0.593
Se1(18f)	0.659	0.663	0.580

Table 8.4 Wyckoff positions of FePSe₃ at 10.0 GPa with the $R3$ space group.

	x	y	z
Fe1(3a)	0.333	0.667	0.516(5)
Fe2(3a)	0.667	0.333	0.537(7)
P1(3a)	0.0	0.0	0.474(13)
P2(3a)	0.0	0.0	0.621(15)
Se1(9b)	0.6239(12)	0.0053(10)	0.599(3)
Se2(9b)	0.0016(16)	0.3536(18)	0.4291(15)

measurements. However, we were able to access peaks at $0kl$, which provided objective measures of the lattice parameters.

In this context, it's essential to note that the directions $\mathbf{b}^*$ and $\mathbf{c}^*$ directions lie within and normal to the ab plane, respectively. The separation between reflection index points in l , expressed in $\text{\AA}^{-1}$, corresponds to the interlayer spacing. Meanwhile, the positions in k , also in $\text{\AA}^{-1}$, represent the intraplanar distance. These values are independent of the choice of the space group, ensuring model-independent lattice spacings.

Throughout our experiments at varying pressures, the collected data reveal a noticeable loss of resolution of diffraction peaks along the c^* direction, in contrast to the a^* and b^* directions. This can be attributed to the presence of stacking faults in the compound, which lack consistent long-range order along the stacking direction, resulting in smeared intensity from sharp peaks in reciprocal space. This, in turn, affects the accuracy of the lattice parameter along the plane stacking direction. Supplementary information from the primary (003) peak in PXRD data can help mitigate these challenges.

The reduced resolution of diffraction peaks has also been observed in single crystal XRD data for FePS₃ [104, 67]. In the current study on FePSe₃, the relative resolution of c^* is lower than that of a^* and b^* , nevertheless, it remains within acceptable tolerances for lattice identification of c .

In FePSe₃, from ambient to the highest measured pressure of 28.0 GPa, we observe a single structural transition from the single-crystal diffraction data. The well-indexed reflection can unambiguously conclude the dimensionality collapse in the interlayer distance between the measured points of 6.7 GPa and 7.8 GPa in FePSe₃, as illustrated in Fig. 8.2. Hereafter I shall refer to the high-pressure phase of FePSe₃ as HP, in comparison to the low-pressure phase (LP). The lattice parameters and relative crystallographic information at ambient pressure (0 GPa), before (6.7 GPa) and after the transition (7.8 GP) are summarised in Table 8.1.

The refinement of LP at 4.4 GPa and HP at 10.0 GPa gave convincing solutions to the lattice parameters and atomic positions have been listed in Table 8.2. The atomic positions for these two phases are listed in Table 8.3 and Table 8.4. The full information sheets of the crystal phases and refinements can be found in the appendices.

The high-pressure phase in FePSe₃ exhibits a distinct feature compared to the low-pressure phase. It involves local distortions within the Fe-Se octahedra, effectively breaking the inversion symmetry of the crystal system. This structural transformation is illustrated in the schematic diagram presented in Fig. 8.2, which provides a visual representation of how

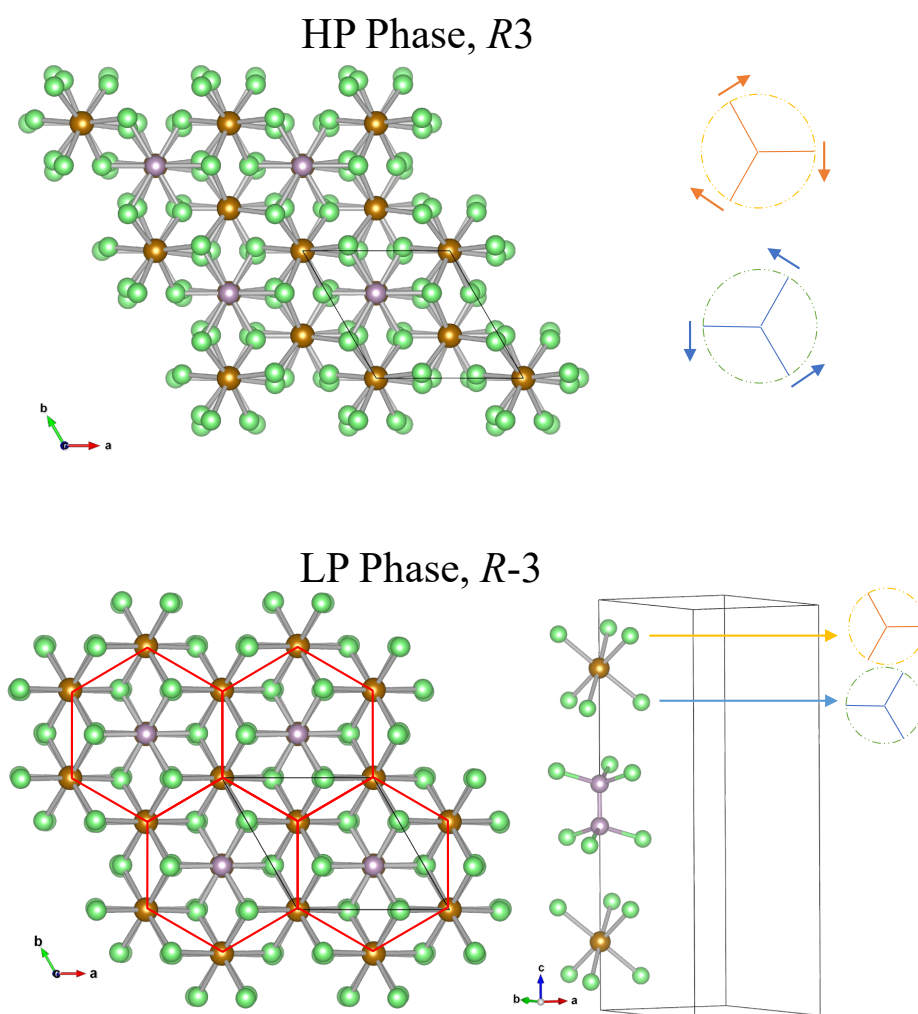


Fig. 8.2 The crystalline structures of the ambient pressure (LP) and high-pressure (HP) phase of FePSe_3 .

the Se atoms adjust their positions, as observed from the perpendicular direction to the Fe-hexagon plane.

The consequential loss of the inversion centre, in conjunction with the pressure-induced development of metallic properties observed in prior transport experiments [60] strongly suggest that FePSe₃ may qualify as a candidate polar metal emerging above the transition pressure threshold, approximately at 7.8 GPa.

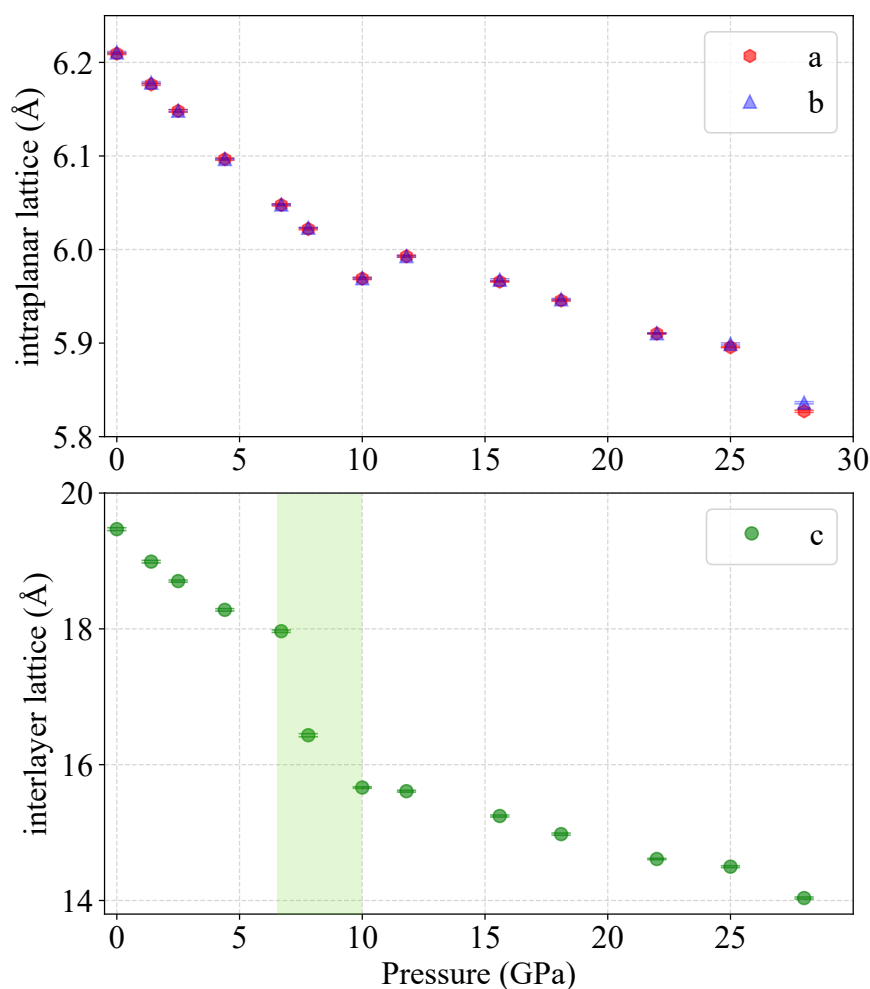


Fig. 8.3 The evolution of the lattice parameters of FePSe₃ with elevated pressure (GPa), determined from single crystal diffraction data of FePSe₃ in DAC loaded with helium as the pressure-transmitting medium. The upper panel shows the intraplanar lattice parameters a and b , while the bottom panel shows the lattice c , which corresponds to the interlayer spacing. The error bar is smaller than the dot size. The colour block indicates the region where the c collapse occurs.

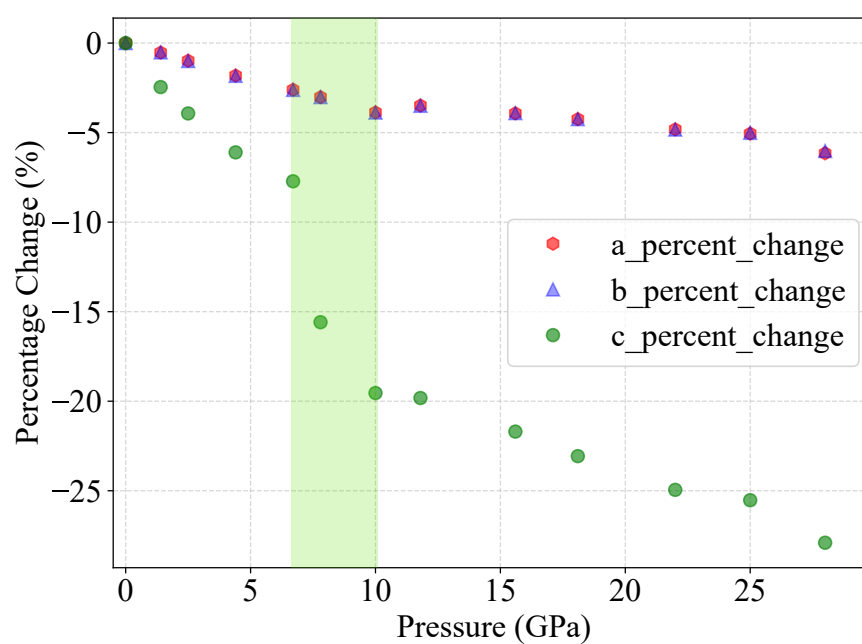


Fig. 8.4 The relative evolution of the lattice parameters of FePSe_3 with elevated pressure (GPa), determined from single crystal diffraction data of FePSe_3 in DAC loaded with helium as the pressure-transmitting medium. The lattice parameters at the first measured pressure point are taken as the reference point. The colour block indicates the region where the c collapse occurs.

The lattice parameters are refined employing the LP structure model up to 6.7 GPa, and subsequently, switched to the HP model for pressures exceeding 7.8 GPa. Fig. 8.3 presents the evolution of the lattice parameters a (red hexagon), b (blue triangle) and c (green circle) with elevated pressure. It is evident that a and b maintain their equivalence across all pressure points, in accordance with the symmetry constraint imposed by the $R\bar{3}$ and $R3$ space groups. These two intraplanar lattice parameters exhibit a continuous change from 6.209 (6.210) Å at ambient pressure to 5.827 (5.836) Å at 28.0 GPa. In contrast, the interlayer lattice parameter c undergoes a significant transformation between 6.7 and 7.8 GPa, which we identify as the phase transition.

Fig. 8.4 provides a visual representation of these refinements, highlighting a noteworthy reduction of 8.89% in the interplanar distance. Remarkably, the intraplanar lattice parameters exhibit a smooth evolution throughout this transition. Different from the behaviour observed in FePS₃ [59], there is no sign of interplanar sliding in FePSe₃ across all pressure ranges examined. The rhombohedral symmetry remains intact even as pressure increases.

8.1.2 Powder X-ray Diffraction Data

Powder diffraction patterns were acquired from samples placed in a helium pressure medium, as well as from samples where FePSe₃ alone filled the gasket without the presence of a pressure medium. Good agreement is observed between the PXRD data and the previous single crystal diffraction results. Furthermore, the PXRD analysis offers additional insights, notably providing more affirmative information regarding the interplanar distance by tracking the evolution of the position of the primary peak (003).

Producing high-quality powder samples presents a non-trivial challenge. FePSe₃ crystals, similar to their counterparts in the same family of compounds, resist grinding into an isotropic powder state. This resistance stems from the nature of van der Waals interactions between the ab planes. During the grinding process, crystals tend to shear parallel to the ab plane, resulting in the formation of small platelets with preferred orientation. To ensure the averaging of good quality, we employed the powder samples from growth and filled the diamond anvil cell with as many of these powder samples as possible. The diffraction patterns shown in Fig. 8.5 serve as good evidence that our sample loading procedures were effectively minimising the impact of strongly preferred orientation.

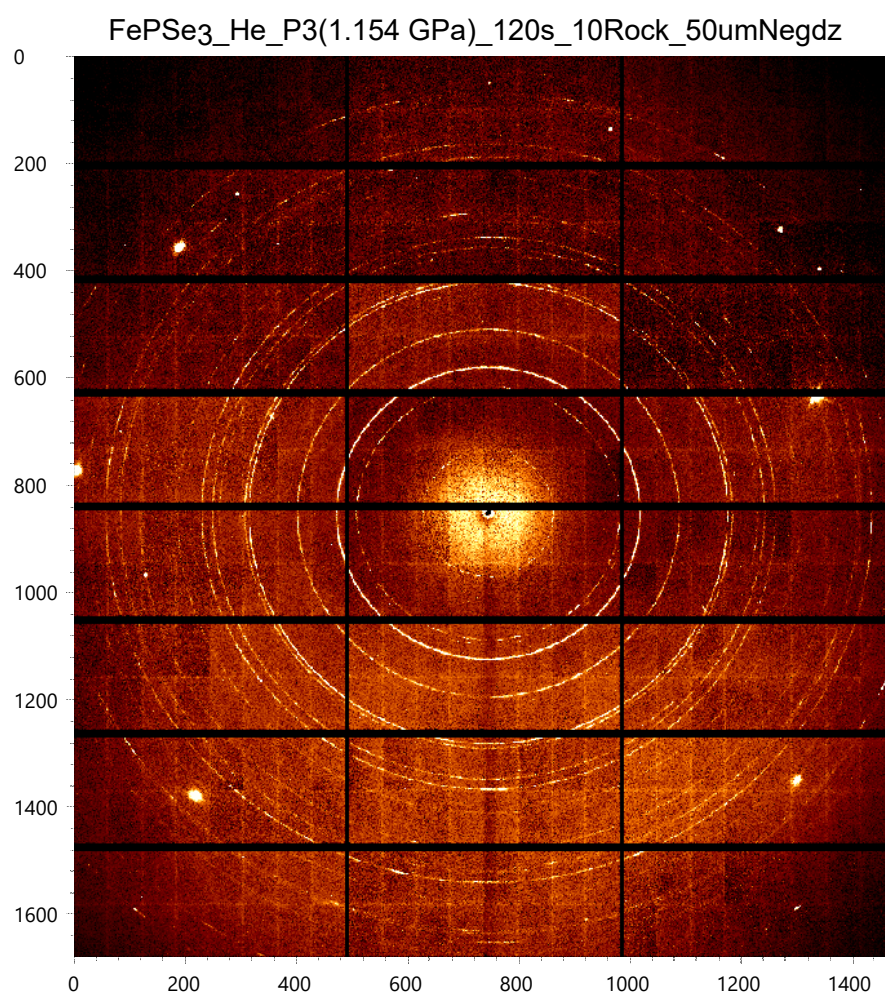


Fig. 8.5 The original diffraction patterns of FePSe₃ powder sample in DAC with helium pressure medium at 1.15 GPa. The shiny dots are identified as reflections from the diamond lattice. The rings are from the averaged powder samples.

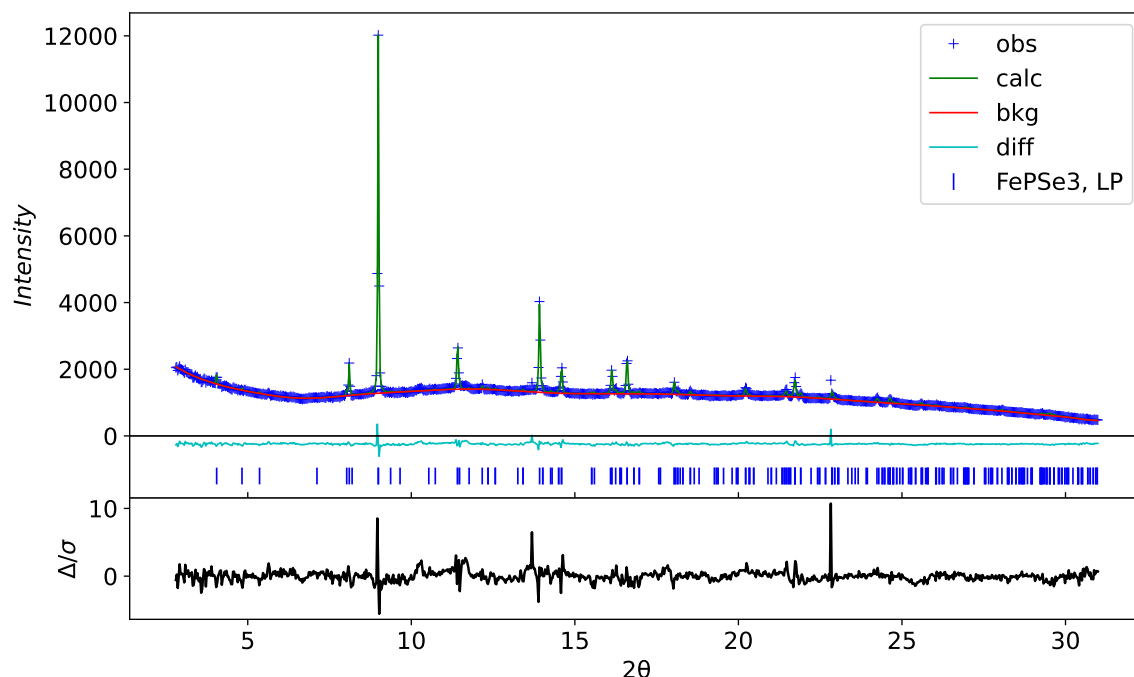


Fig. 8.6 The refinement of powder diffraction data of FePSe₃ at 7.5 GPa using the ambient pressure structure model. At this pressure, FePSe₃ is still in the LP phase.

Sample loaded with Helium Medium

In measurements of FePSe₃ using helium as the pressure-transmitting medium, the starting point was 0.7 GPa and the maximum value reached for PXRD measurements was 34.1 GPa. Given that the single-crystal XRD measurements indicated a transition pressure range between 6.7 GPa and 7.8 GPa, we meticulously collected PXRD data with fine increments, especially in the vicinity of the anticipated transition pressure point.

The raw 2D detector intensity data were processed using the *Data Analysis Workbench* (DAWN – II) software [146], which transformed the data into a *xy* format diffraction pattern file. A systematic, step-by-step analysis procedure was established for the data collected at the initial pressure point, and this process was subsequently applied to process the remaining raw data sets.

The geometry of the PXRD experiment was calibrated using LaB₆ as the reference material. This calibration file was consistently applied to all pressure points throughout the processing stages. Additionally, we applied a threshold mask to eliminate any overexposed pixels present in the raw data. Further refinement involved the masking of spurious intensity spots, potentially arising from the diamond anvil or the rhenium gasket, thus enhancing the accuracy

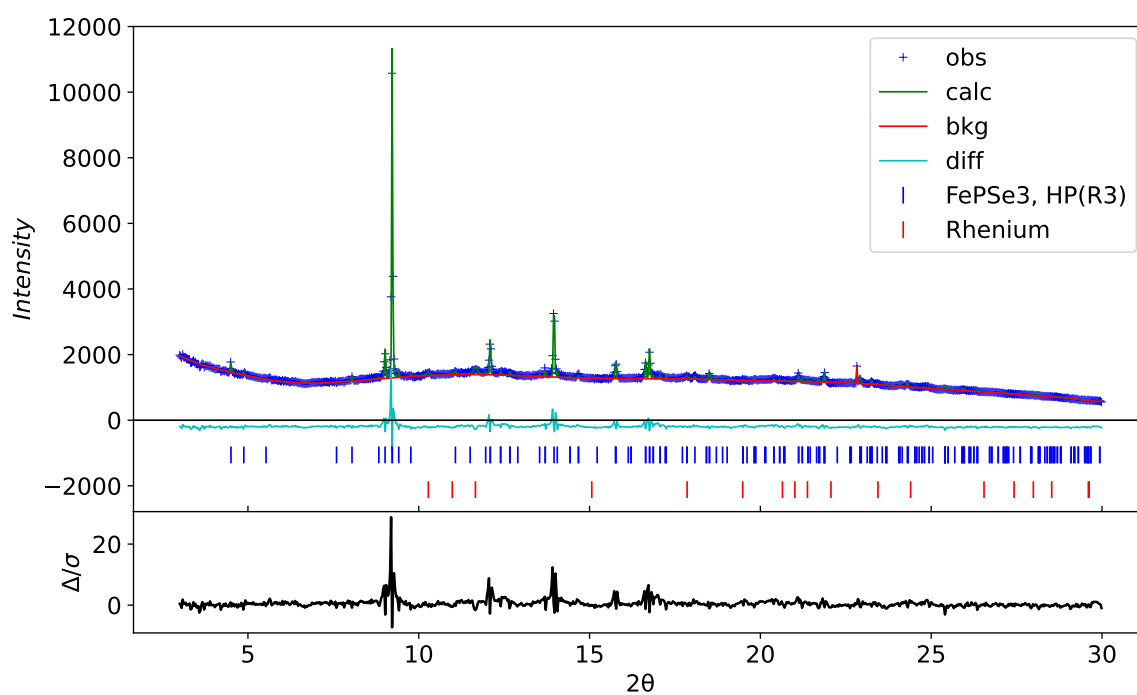


Fig. 8.7 The refinement of powder diffraction data of FePSe₃ at 8.1 GPa using the high-pressure structure model constructed from the single crystal diffraction measurements. At this pressure, FePSe₃ changes to HP phase as clearly indicated by the abrupt movement of the (003) peak position in the 2θ space.

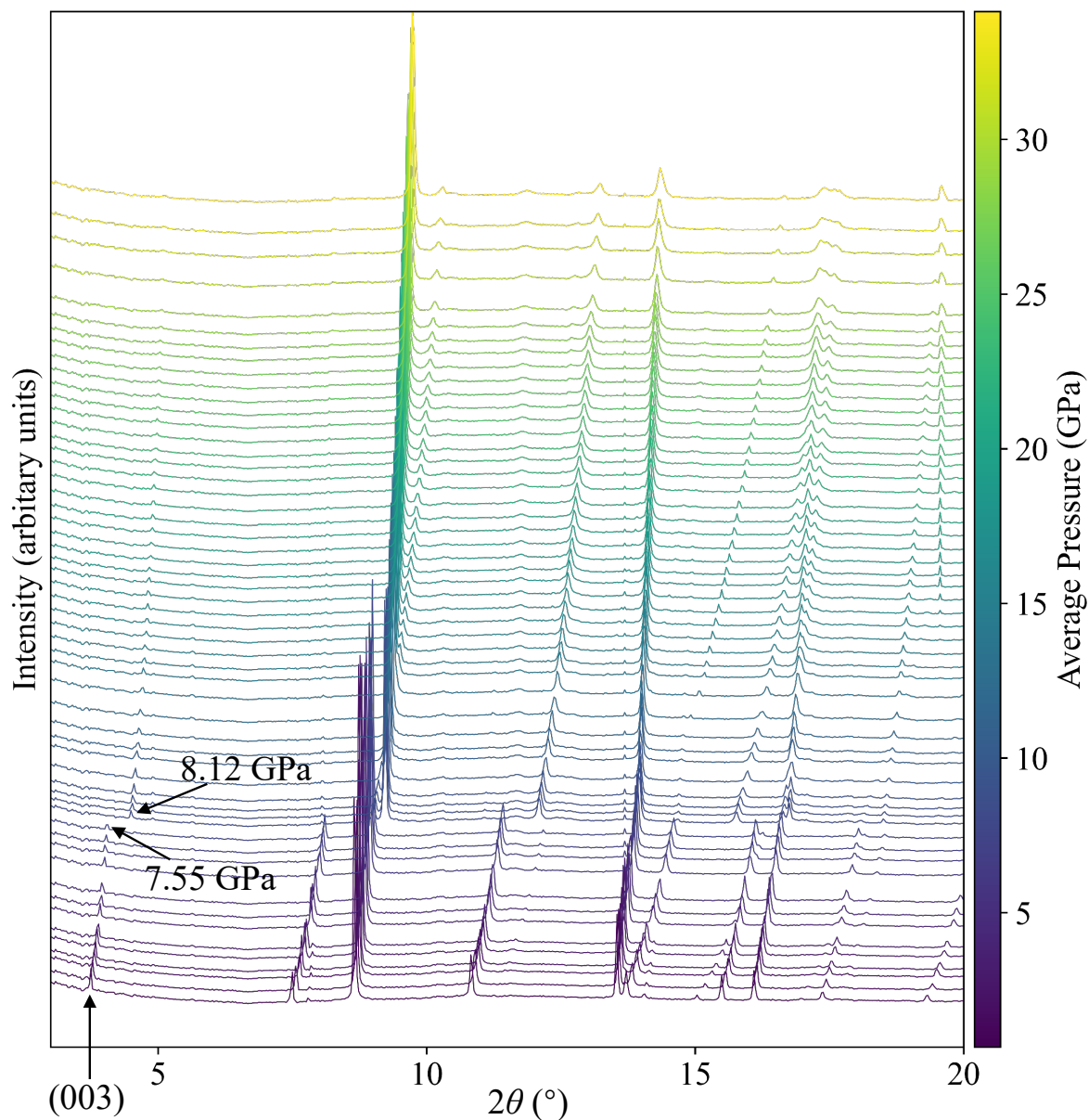


Fig. 8.8 The integrated diffraction patterns of FePSe₃ powder sample in DAC with helium pressure medium at different measured pressure values. The intensity data have been normalized to arbitrary intensity and the offset is linearly scaled following the increased pressure value for clarity. The colour map of the pressure values is plotted on the right. The pressure value is taken as the average before and after the transition.

of the data. Eventually, the 2D intensity data was integrated into the 2θ space, generating a corresponding 1D xy file.

Fig. 8.8 presents a comprehensive summary of the post-processed diffraction patterns obtained from FePSe_3 powder samples loaded with helium as measured across a range of pressures, determined via Ruby optical spectroscopy. Notably, a distinct phase transition between 7.5 and 8.1 GPa becomes evident as the (003) peak undergoes a sudden shift in its 2θ position.

During the phase transition, new diffraction peaks appear while the peaks from the previous structure model disappear. There is no peak broadening with pressure, indicating that sliding of planes does not occur in FePSe_3 , which is different from the counterpart compound FePS_3 . The clear transition suggests the possibility of employing a single-phase model to fit the two regions respectively.

Given our knowledge of the ambient pressure structure (LP), we use it as the structure model before the transition occurs, denoted as LP. It is reasonable to assume that the crystalline structure experiences no substantial reconstruction at this point. Consequently, we utilize the lowest-angle peak (corresponding to the highest d spacing) within the 2θ range of $3^\circ \sim 4^\circ$ in Fig. 8.6 to monitor the interlayer distance's change from ambient to the last pressure point before the transition takes place.

As for the high-pressure regime, it is critical to establish an appropriate model that could be used to fit the diffraction patterns. The single crystal diffraction data gave the high-pressure phase model a definitive solution. Our analysis indicated that both $R\bar{3}$ and $R3$ space groups could accommodate the data. The most suitable match with the powder data was achieved using the $R3$ model, as is shown in Fig. 8.7.

The same analysis was applied to each dataset using the respective LP and HP structure models. The lattice parameters were subtracted, and the relative changes are visualized in Fig. 8.9 to facilitate a more distinct comparison between the intraplanar and interlayer responses to the applied pressure.

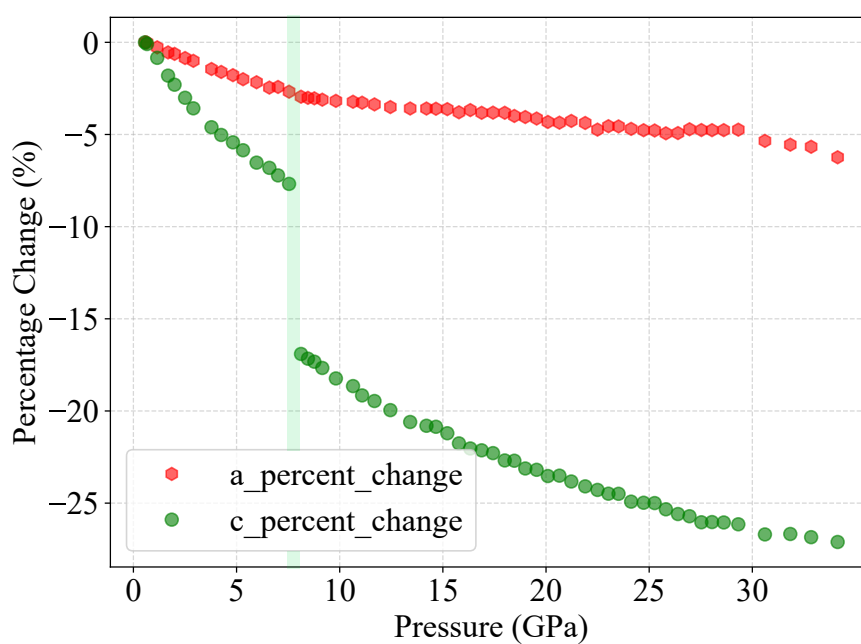


Fig. 8.9 The relative evolution of the lattice parameters a and c of FePSe₃ with elevated pressure (GPa), obtained from FePSe₃ powder samples loaded with helium pressure-transmitting medium in DAC. The lattice parameters at the first measured pressure point are taken as the reference point. The colour block indicates the region where the c collapse occurs.

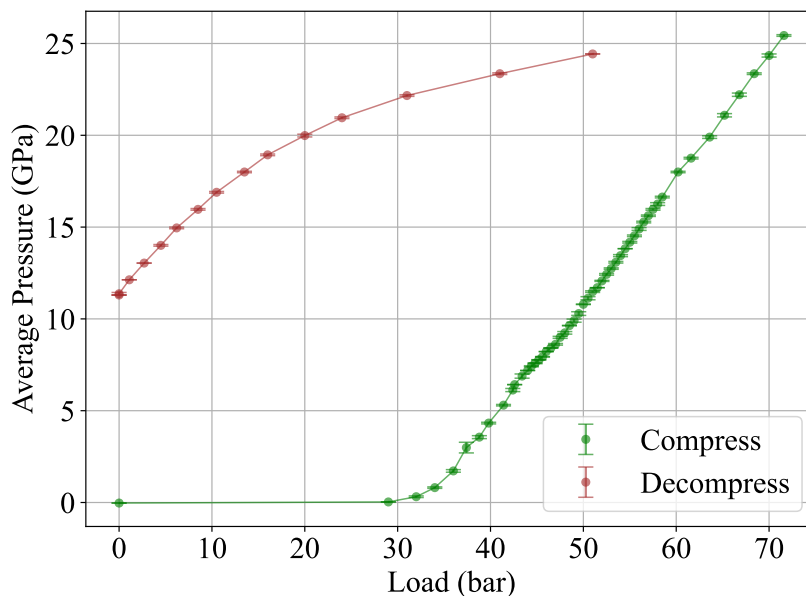
Sample loaded without Helium Medium

Fig. 8.10 The measured pressure as a function of the applied load within the DAC, loaded with just FePSe₃ powder samples.

Experimental observations have revealed that the dimensionality of FePSe₃ is quite sensitive to the pressure environment, so as its counterpart FePS₃ and other compounds in the family [104, 67]. To process the raw 2D intensity data collected exclusively from the DAC filled with FePSe₃ powder samples, we employed similar techniques as those applied to the helium-loaded samples. The highest pressure reached during these measurements was 25.4 GPa. After that, a decompression dataset was acquired while the load on the membrane of the DAC was gradually released. Fig. 8.10 tracks all the measured pressure points, determined from Ruby spectroscopy, as a function of the applied load on the membrane of the DAC.

Fig. 8.11 presents an overview of all post-processed diffraction patterns of FePSe₃ powder samples as a function of measured pressures, ranging from ambient to the highest pressure point, obtained via Ruby optical spectroscopy. Remarkably, the PXRD patterns measured with and without helium pressure medium exhibit excellent agreement in both low and high-pressure regions. Initial attempts of fitting the PXRD patterns with LP and HP structure models for low and high pressures yield consistent results, aligning with the single crystal and powder data with helium medium.

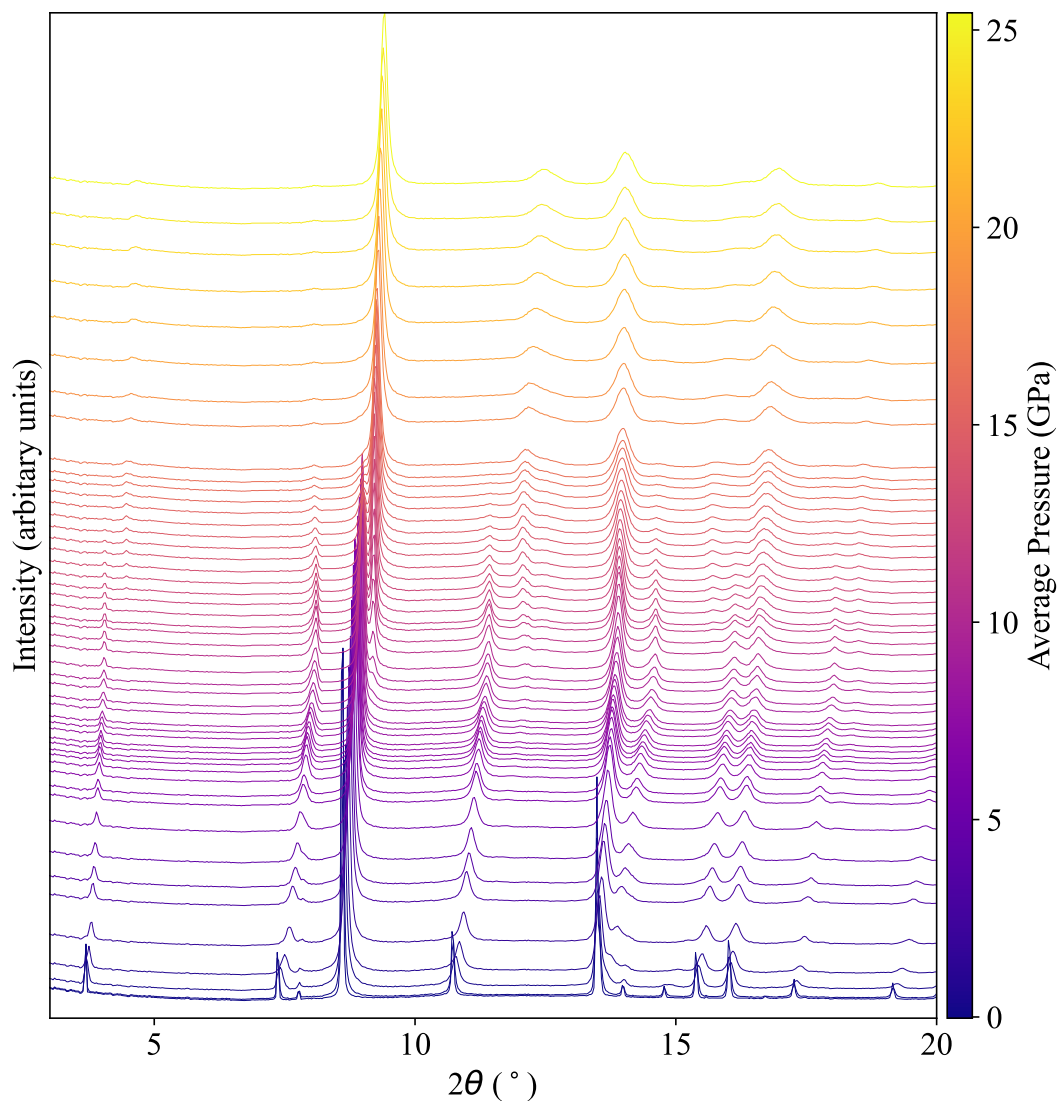


Fig. 8.11 The integrated diffraction patterns of FePSe₃ powder sample in DAC without helium pressure medium at different pressure values. The intensity has been scaled to arbitrary units. The main peak splitting indicates a coexistence region of LP and HP-I from 9.6 GPa to 16.3 GPa.

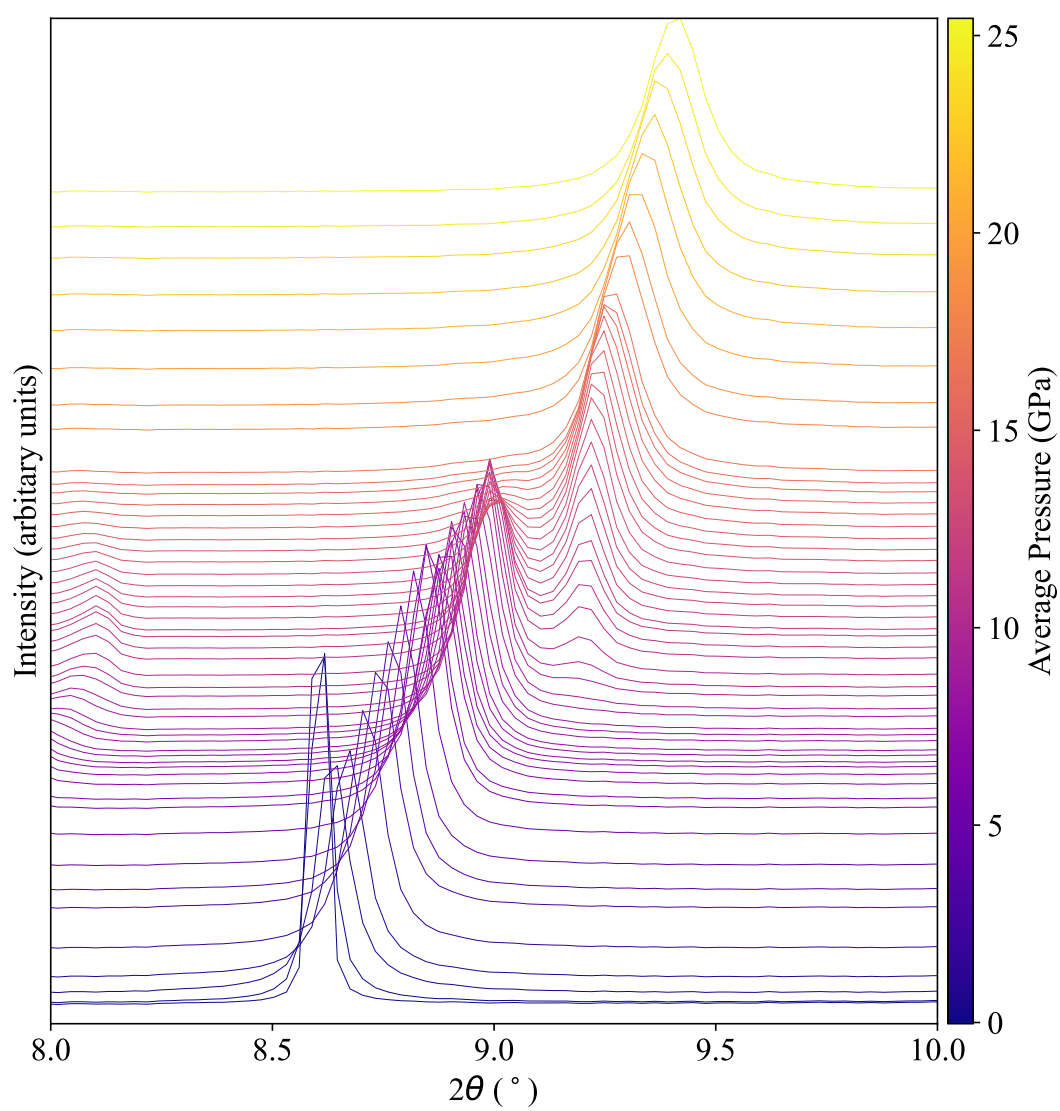


Fig. 8.12 The integrated diffraction patterns around the (113) peak position from 8° to 10° in the 2θ space.

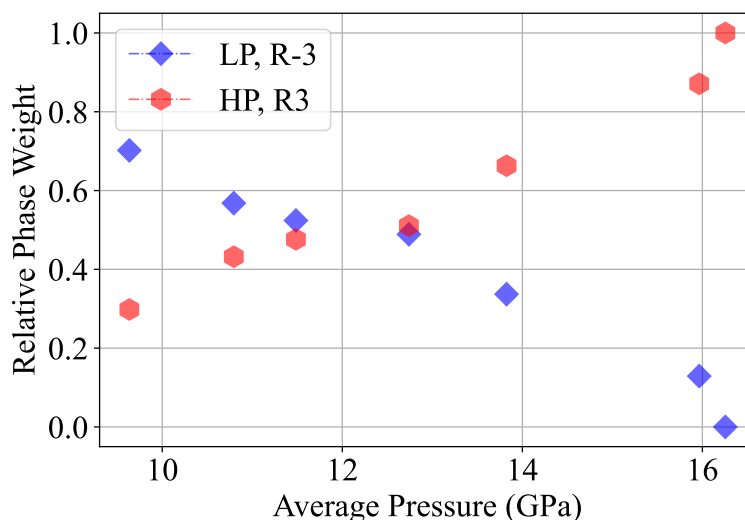


Fig. 8.13 The relative weight factor of the LP and HP phases across the coexistence region.

Around the transition point, however, the PXRD patterns collected from the DAC filled merely with FePSe₃ and no helium show deviations from a clear transition. It can be seen from the main peak (003) and the highest intensity peak (113) that there is a region where the old and new peaks coexist and the relative intensity of the peaks evolves with pressure. Fig. 8.12 is a zoomed plot showing the coexistence of the (113) peaks from LP and HP phases. Further attempts to fit the data with two phases provide insight into how the relative weight of the LP and HP phases change with pressure, as shown in Fig. 8.13.

Despite this coexistence, we consider the first pressure value where the new peaks from the HP phase begin to appear as the transition pressure point. The lattice parameters from LP and HP phases before and after the transition point are summarised in Fig. 8.14, in the format of relative percentage changes.

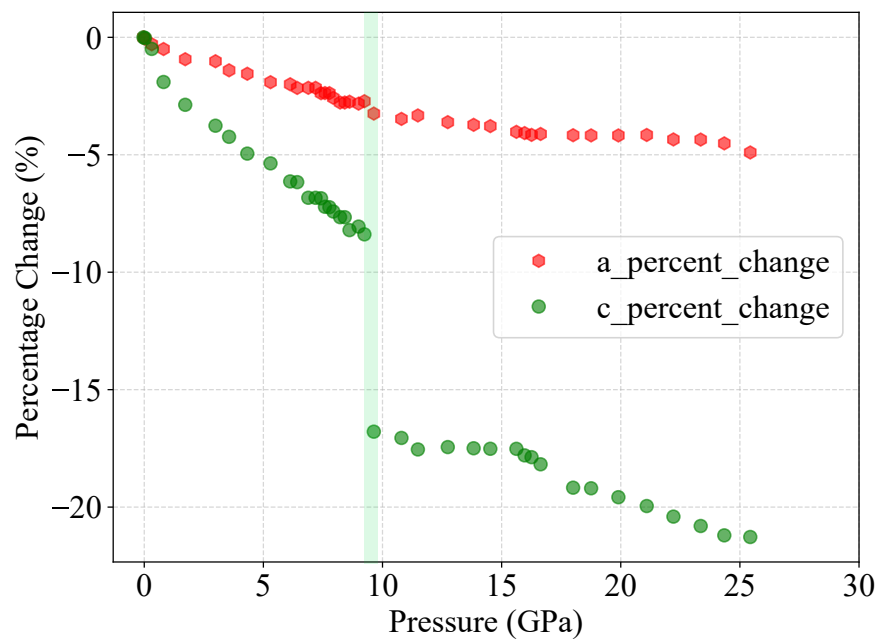


Fig. 8.14 The relative evolution of the lattice parameters a and c of FePSe_3 with elevated pressure (GPa), obtained from purely FePSe_3 powder samples in the DAC. The lattice parameters at the first measured pressure point are taken as the reference point. The colour block indicates the region where the c collapse occurs.

8.1.3 Summary

Figure 8.15 summarises how the intra- and inter-planar lattice parameters a and c evolve in response to the increased pressure at different experimental conditions. It can be concluded that different pressure conditions can effectively affect structural evolution, with differences in the value of the transition pressure and the occurrence of phase-coexistence depending on the choice of the pressure medium.

The powder data analysis was based on the correct indexation of diffraction peaks. The previous data collection by Wang *et al.* [60] was sensible but misidentifying peaks in the high-pressure region.

The reliable hydrostatic pressure environment is essential to the correct data interpretation of the observed diffraction patterns. In the main paper, we use helium as the pressure medium for single crystal and powder samples, as helium is documented as the best available pressure-transmitting medium, even in its solid state after ~ 12.1 GPa [164]. Meanwhile, Wang *et al.* [60] used pre-compressed FePSe₃ pellets and silicone oil as the pressure-transmitting medium. Upon compression, the van der Waals nature of the FePSe₃ might lead to a preferred orientation in the powder sample.

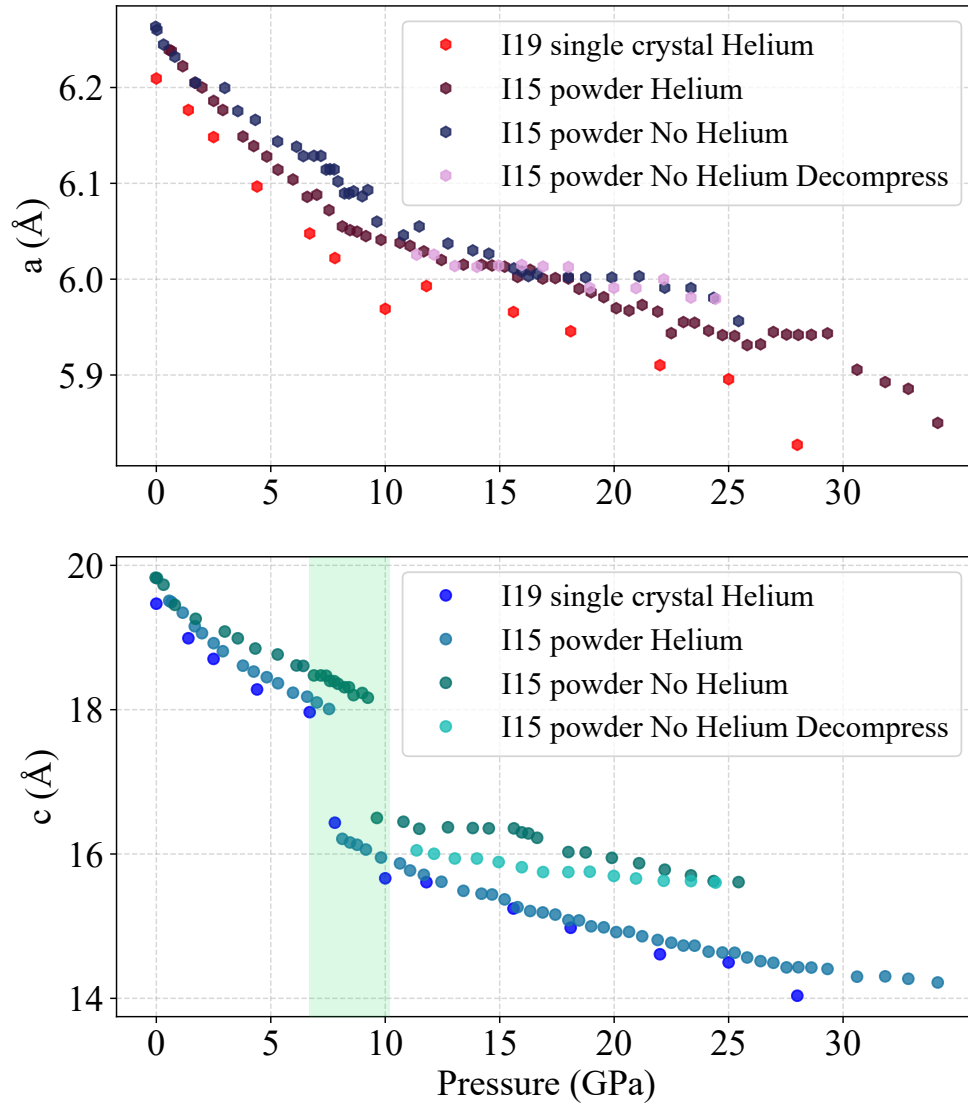


Fig. 8.15 The comparative evolution of the lattice parameters a and c of FePSe_3 in single-crystal with He, powder with He and powder without He states at different pressure values. The colour block indicates the region where the c collapse occurs, showing good consistency across these experiments.

8.2 Magnetic Properties

Alongside the comparative exploration of the crystalline structures, the exploration of the magnetic phases in FePSe₃ has also been conducted on beamline D20, ILL (Grenoble, France) with the proposal 5-31-2847 [165]. A double-toroidal sintered-diamond anvil cell filled solely with FePSe₃ powder samples has been employed. The pressure apparatus was provided and tested by Prof. Stefan Klotz and Dr. Thomas Hansen.

A monochromatic neutron beam of wavelength 2.42 Å was used to allow for the highest flux and sufficient Q range to access both magnetic and nuclear structural peaks from the sample. The pressure within the cell was gradually elevated through the application of increased load to the pressure membrane. The precise pressure values were calibrated using the accurate lattice parameters, acquired through our synchrotron X-ray diffraction data.

It is noteworthy that the measurements, focusing on the magnetic peaks, were conducted at lower temperatures, while the pressurisation process was carried out at room temperature. This approach allowed us to perform measurements in both the high-temperature paramagnetic phase and the low-temperature magnetic phase, as is shown in the upper panel of Fig. 8.16 for each pressure point in red and blue, respectively. Through a process of data subtraction, we successfully isolated the intensity of the magnetic peaks, effectively eliminating the contribution of nuclear peaks.

The Néel temperature, characterising the magnetic transition in FePSe₃ at ambient pressure, is situated at approximately 125 K. For the first two pressure points (1.2 and 4.1 GPa), the temperature was brought down to ~ 80 K, a temperature regime where magnetic peaks were conspicuously identifiable. As for the highest pressure condition during the measurements (8.3 GPa), the temperature was further reduced to ~ 1.6 K.

The lower panel of Fig. 8.16 presents an illustrative summary of the intensity of powder neutron diffraction data obtained in the 2θ space. The measurements were conducted at three distinct pressure conditions: 1.2 GPa (blue), 4.1 GPa (wine) and 8.3 GPa (red). This plot effectively conveys the results of subtracting the intensity observed in the high-temperature paramagnetic phase (300 K) from the intensity recorded in the low-temperature magnetic phases. This subtraction process successfully eliminated the contribution of nuclear peaks. The intensity of the magnetic peak diminished as pressure increased and ultimately disappeared at the highest pressure point during the measurements (8.3 GPa). This preliminary interpretation contrasts with the previous findings in FePS₃, where short-range magnetic ordering persisted in the HP-II phase up to 18.3 GPa [62]. Further investigations are essential

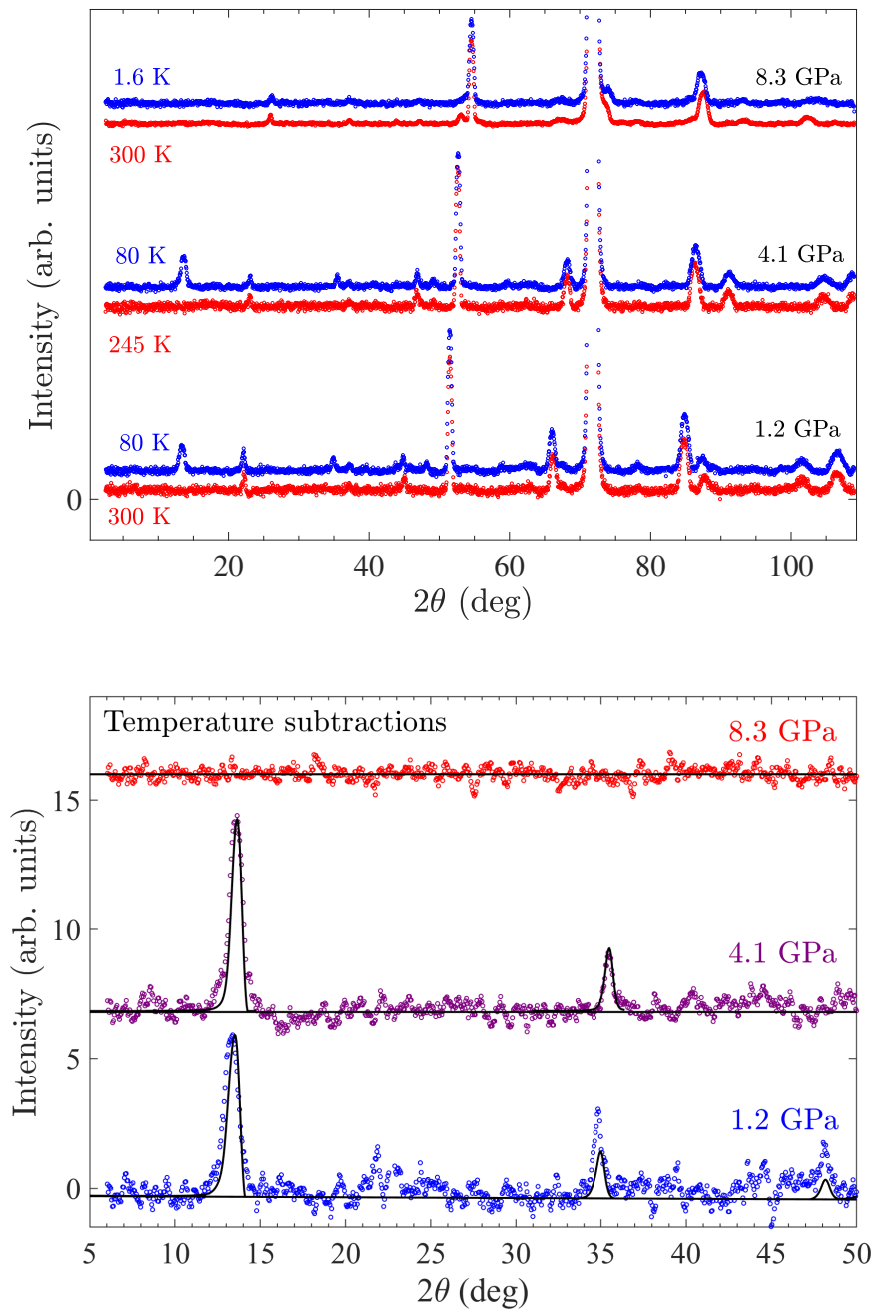


Fig. 8.16 Neutron powder diffraction patterns under pressure. (a) The magnetic diffraction data of FePSe₃ at pressures of 1.2 GPa, 4.1 GPa and 8.3 GPa, taken at high (red) and low temperatures (blue), respectively. (b) The result of performing temperature subtractions for 1.2 GPa (blue), 4.1 GPa (wine) and 8.3 GPa (red) in the zoomed low-angle region for a better demonstration of the evolution of magnetic peaks. For each pressure point in panel (a), the high-temperature data are subtracted from the low-temperature data. Solid black lines are taken from refinements of the data. At 8.3 GPa it can be seen that all magnetic peaks are now absent and the temperature subtraction is hence flat.

to attain a more comprehensive understanding of the high-pressure magnetic behaviours of FePSe₃.

8.3 Conclusions

In conclusion, our recent synchrotron X-ray high-pressure structural investigations of both single crystal and powder samples of FePSe₃, conducted using helium as the ideal pressure transmitting medium, have provided conclusive evidence for the high-pressure structure model. FePSe₃ undergoes a transition from the LP phase with $R\bar{3}$ symmetry to the HP phase with $R3$ space group around 7.3 GPa. Our comparative explorations have effectively ruled out previously proposed models. This phase transition is accompanied by a dramatic collapse in dimensionality, a trend commonly observed in van der Waals compounds.

Notably, our observations reveal no evidence of the sliding of neighbouring planes during the measurements, in contrast to the behaviour of FePS₃ under varying pressure conditions. The distinctive stacking patterns of the LP phases of FePS₃ ($C2/m$) and FePSe₃ ($R\bar{3}$) may be the origin of the differing pressure-induced structure transition models. As previously discussed, both compounds feature layers superimposed in an $ABC\ ABC$ sequence at ambient pressure. However, the translation direction and distance of the stacking layers make these two compounds behave differently, and the underlying S or Se atoms are closely packed distinctively. The initial stacking geometry may impose constraints on how the crystal structures evolve with increasing pressure.

In addition to changes in the crystalline structure, the application of pressure has induced several alterations in physical properties. The direct probing of the magnetic orderings in FePSe₃, following the delicate setup of the recorded first use of an extreme pressure double-toroidal anvil at ILL measuring the neighbouring compound FePS₃, indicates that there is no short-range magnetic ordering up to the highest pressure being measured. The intriguing question arises: why does short-range magnetic ordering persist in FePS₃ but not in FePSe₃? With the structural model now confidently resolved, it provides a foundation for further exploration of structural-related physical properties. Further efforts are required to understand the difference in the high-pressure magnetic properties and the emergence of superconductivity merely in FePSe₃ while it remains absent in FePS₃ as well.

Chapter 9

Conclusions and Prospects

This concluding chapter summarises the findings of the investigation into van der Waals layered compounds, specifically FePS_3 , FePSe_3 , and related compounds within this family. It is intriguing to recognise the existence of long-range magnetic ordering at ambient pressure and the emergence of strongly correlated electrons from the $3d$ orbitals of the transition metal (TM) atoms when these materials are constrained to a two-dimensional limit.

With increased pressure, the transport properties exhibit nontrivial behaviours including an upturn in the high-pressure and low-temperature region of FePS_3 . This is beyond any available phenomenological model. Additionally, there is the presence of short-range magnetic ordering in the high-pressure metallic phase of FePS_3 , which persists even at high temperatures. When S is substituted by Se in this compound family, superconductivity has been observed in FePSe_3 with $T_c \sim 2.5$ K at 9.0 GPa, and in NiPSe_3 starting with $T_c \sim 4.8$ K at 8.0 GPa.

These $TMPX_3$ compounds, unlike cuprates, are tunable under the clean and controllable parameter of pressure while having a much simpler chemical composition. These characteristics make them an ideal and fertile ground for exploring the underlying physics and potential technological applications.

The primary objective of this research was to utilise pressure as a tuning parameter so as to provide insights into how external pressure influences the crystalline structure, magnetic configuration, and relevant physical properties of these compounds. The work presented in this thesis involved a significant component of Density Functional Theory modelling and incorporated data obtained from synchrotron and neutron diffraction studies. We also consid-

ered data from laboratory-based magnetic and electrical measurements to comprehensively understand the compound system.

In the following sections, I will summarise the results and express the outlook in terms of crystalline structural, magnetic and electronic properties. Extended research endeavours relative to this compound family will also be discussed eventually.

9.1 Crystalline Structure

A profound knowledge of the crystallographic structure is essential for a full understanding of tuning the materials' properties with pressure. On the one hand, it is challenging for theoretical explorations to capture the intricate physics of strongly correlated electrons while maintaining computational efficiency. The predictive construction of high-pressure structure models, using random structure search methodology and substitution construction, provides a valuable avenue for exploring high-pressure phases. The previously proposed LP, HP-I and HP-II phases have been successfully reproduced in FePS₃. Moreover, a novel HP-II- β phase has been predicted and investigated in detail. In addition, a 2.5-D HP-II- γ phase, characterised by three-layer-thick stacking units, has been predicted as the result of the soft mode instability in the HP-II phase near the transition pressure. This methodology holds promise for extension to other compounds within this family, as well as other layered materials, providing careful consideration of the correlation effects and magnetic interactions.

On the other hand, experimental tools and techniques have been designed and employed to probe the interactions at the atomic level. Synchrotron X-ray scattering experiments, in conjunction with diamond anvil cells, have been carefully performed with both powder and single-crystal samples. Furthermore, the impact of employing helium, a well-established pressure-transmitting medium, has been thoroughly investigated.

The pressure-induced crystal structure transition model in FePSe₃, resolved from our recent comprehensive synchrotron X-ray experiments on both single-crystal and powder samples, diverges from that observed in FePS₃-type structures. FePS₃ and other isostructural phases crystallise in monoclinic space group $C2/m$ at ambient pressure. With elevated pressure, a two-step transition model applies, albeit with the transition pressure values varying in regard to different transition-metal ions. In this two-step model, a sliding of neighbouring planes occurs initially from LP to HP-I. The interlayer stacking angle evolves from monoclinic angle ($\sim 107^\circ$) to nearly 90° without changing the monoclinic space group symmetry. Then,

the HP-I phase turns into HP-II with an essential inter-planar collapse and a gain of C_3 rotation symmetry. The Fe-hexagon is not distorted and the HP-II phase crystallises in the $P\bar{3}1m$ space group.

As for FePSe_3 , it crystallise in the rhombohedral space group $R\bar{3}$ at ambient pressure. There is no evidence of the sliding of neighbouring planes before the interlayer collapse occurs. The HP phase data fits better with the $R3$ space group. It is worth noting that the HP phase of FePSe_3 does not have an inversion centre, thus allowing polarisation in the compound. This characteristic has also been reported in NiPS_3 previously.

In a recent check using the $R3$ structure model obtained from FePSe_3 to fit the powder X-ray data of NiPS_3 suggests a more favourable solution compared to using the HP-II model for data fitting. Nevertheless, further investigations are required to obtain robust solutions and precise atomic positions.

9.2 Magnetic Properties

Another significant area of interest lies in the exploration of how magnetic phases and interactions evolve in these van der Waals antiferromagnetic compounds. The magnetic interactions within TMPX_3 compounds are intricate, providing fertile ground to explore the underlying physics [166–168]. Correlation effects consistently present a challenge for computational simulations. Experimentally observed spin-spin short-range correlations can be particularly challenging to address through first-principles calculations. However, it remains worthwhile to meticulously examine these effects, especially in the vicinity of the transition from 2D to more 3D bonded configurations.

As a result, it is critical to design and execute experiments capable of probing the magnetic structures and any dynamics inherent to these compounds. There has been an extensive history of exploring the magnetic properties of this compound family, involving the utilisation of techniques such as magnetic susceptibility measurements, neutron scattering and Raman spectroscopy to investigate the magnetic dynamics and magnetic configurations. The van der Waals nature of these compounds poses essential challenges, particularly concerning the mosaicity of single crystal samples and the preferred orientation of powder samples.

Explorations at high pressures are even more demanding, as the application of pressure introduces an additional layer of complexity to the experimental setups. Our successful

endeavours are conducted in line with the recent developments in high-pressure techniques and collaborative efforts with experts from various sectors.

It is natural to set up laboratory measurements of magnetic susceptibility in pressure cells and to measure the magnetic response on a Physical Property Measurement System (PPMS). That could facilitate the exploration of the dynamics of the magnetic phase transition as a function of temperature at various pressure values. In that sense, a full temperature-pressure phase diagram can be generated. Work on such attempts is currently underway in the group of S. S. Saxena.

The exact magnetic structures can be probed with neutron scattering at large facilities. The recent development of neutron scattering with specially designed high-pressure cells opens up the possibility for fundamental studies utilising pressure as the tuning parameter in layered magnetic compounds. It is an intriguing and contrasting finding that short-range magnetic ordering persists in FePS_3 at elevated pressures, whereas such ordering is not observed in FePSe_3 even at the lowest temperature recorded at the highest pressure point during the measurements.

Conventionally, the magnetic structures are measured with a two-axis instrument. Using a triple-axis spectrometer for elastic scattering can significantly improve the signal-to-noise ratio compared to the conventional two-axis instrument. It could play an invaluable role in studies of the magnetic phase transitions of $T\text{MPX}_3$ compounds. In particular, the major advantage lies in the versatility of changing the energy of both incident and scattered neutron beams. Double-scattering processes, which frequently bring in erroneous results, could be examined by checking whether the intensity of a Bragg peak fluctuates substantially when the energy of the neutron beams varies. If the intensity remains constant with changing energy, the scattering process can be eliminated from the double scattering interference.

Double scattering can also plague the exploration of magnetic transitions as the size of the magnetic unit cell is usually doubled compared to the nuclear one. Consequently, magnetic superlattice peaks appear with half-integer values of the Miller indices, which could lead to a half-integer peak at some forbidden position in combination with a pure nuclear peak.

High-resolution neutron powder diffraction studies have developed essentially in recent years. It could facilitate the exploration of peaks at large Q where overlapping occurs frequently.

9.3 Electronic Properties

Another intriguing aspect is to explore the electronic properties, particularly considering the rich physics associated with strongly correlated electrons. The ability to fine-tune transport properties in layered compounds, particularly as we move towards the two-dimensional or three-dimensional limit, has the potential to inspire innovative ideas for the design of high-performance electronics.

FePS₃ exhibits short-range magnetic ordering in the metallic phase, while FePSe₃ turns superconducting without any indication of short-range magnetic ordering. This difference is intriguing and is worthy of further exploration.

Moreover, the recently reported metallicity observed in the polar phase of FePSe₃ and NiPS₃ represents a novel discovery, opening up a new research direction in this compound family. Polar metals remain rarely observed in experiments, though Anderson and Blount predicted the possibility of a ferroelectric metal as early as 1965 [169]. There are only a few documented examples, including the realisation in LiOsO₃ [170], bulk crystalline van der Waals WTe₂ [171], the pressure-induced ferroelectric-like transition in Hg₃Te₂X₂ [172], and its existence in doped SrTiO₃ [173].

Notably, there is recent evidence supporting the possible existence of a polarised state within the metallic phase of the chalcogenide NiPS₃ at pressures above ~ 23 GPa [174]. Our findings suggest that FePSe₃ represents another viable candidate for the presence of a polarised state at room temperature and within a considerably lower pressure range, ~ 7 GPa instead.

9.4 Extended Outlooks

9.4.1 Quantum Critical Phenomenon and Tuning with Pressure

Quantum criticality in strongly correlated systems continues to bring about novel phenomena at low temperatures which can also extend to a higher temperature regime. The veiled underlying physics, and promising applications of high- T_c superconductors for energy harvesting and saving, motivate further studies. However, there exist fundamental difficulties in properly detecting quantum criticality in realistic systems, so it is with theoretical modelling [175].

From an experimental perspective, to determine different states close in energy the only way is to compare their behaviours with a sufficiently low energy scale. In other words, the

system has to be cooled down substantially which already poses as one technical challenge. In addition, quantum criticality would naturally enhance the fluctuations and even tiny imperfections in the sample would affect the observations. Samples of high quality are thus required, and compounds with clean and simple formula while exhibiting emergent phenomena would be ideal for a future research effort.

From the theoretical perspective, one would expect theories could give microscopic explanations of the observed macroscopic properties based on well-developed quantum mechanics. However, the predictive power has to be carefully examined and justified in the field of strongly correlated electrons, and in the vicinity of quantum critical phases. Several recent discoveries have reported unconventional phenomena and novel states beyond the current theoretical modelling capacity.

The $TMPX_3$ compounds present themselves as an ideal model system to explore quantum criticality near antiferromagnetic ordering. The unconventional upturn in the low-temperature resistivity of $FePS_3$ at high-pressure metallic phase, for instance, might relate to hidden orders or complex coupling between quantum fluctuations and other ordering in the system. The dimensionality control using hydrostatic pressure or chemical pressure (Se substituting S) provides a clean and controllable tuning approach, particularly in the context of emergent superconductivity.

9.4.2 Coupled Properties: Magnetoelectric Effect

In the previous sections, I discuss the magnetic and electronic properties independently. An extended and fascinating avenue to investigate is the magnetoelectric (ME) effect. The simplest form can refer to the case where an external magnetic field induces an electric polarisation, or vice versa. Such effect has significant potential in the design of multifunctional materials for energy efficiency or spintronics.

Materials that lack both spatial inversion and time-reversal symmetries can allow for the ME effect. As most of the van der Waals crystals are structurally centrosymmetric, a convenient strategy is to utilise the magnetic ordering to break inversion symmetry. This suggests that one should focus on antiferromagnetic (AF) rather than ferromagnetic (FM) materials because the latter generally do not break the inversion symmetry of the underlying lattice.

In 2018, Huang *et al.* first realised the linear ME effect in the exfoliated CrI_3 down to bilayer thickness, where its magnetic order transforms from being FM to AF and thus breaks

inversion symmetry [176, 177]. However, there are no further reports of an ultrathin single crystalline compound that hosts a direct linear ME response.

$TMPX_3$ compounds display themselves as a promising family worthwhile further investigation. Though $MnPS_3$, $FePS_3$, and $NiPS_3$ all exhibit long-range antiferromagnetic ordering, only that in $MnPS_3$ breaks the inversion symmetry and thus allows for a linear ME effect as documented [81]. Further efforts extend such discussion into ultrathin limit via optical second harmonic generation (SHG) - rotational anisotropy (RA) methodology [178].

9.4.3 Control of Dimensionalities

The dimensionality of van der Waals magnets can be adjusted to reach either 2D or 3D limits, employing well-established techniques such as using adhesive tapes to thin the bulk structure to just a few layers or using pressure to tune the 2D structure towards the 3D limit.

In this thesis, the primary focus is on tuning the layered materials from 2D towards 3D with the application of pressure. It is worth highlighting the potential to reduce the bulk structure to a monolayer or just a few layers thick, as observed in cases like monolayer $FePS_3$, which maintains Ising antiferromagnetic ordering. Such capabilities open doors to designing high-performance transistors using monolayers, as has been achieved in the case of MoS_2 for instance.

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