Optical study of two-dimensional ternary and quaternary metal phosphorus chalcogenide crystals

Wang, Xingzhi

2018

Wang, X. (2018). Optical study of two-dimensional ternary and quaternary metal phosphorus chalcogenide crystals. Doctoral thesis, Nanyang Technological University, Singapore.

<http://hdl.handle.net/10356/73289>

<https://doi.org/10.32657/10356/73289>

**OPTICAL STUDY OF TWO-DIMENSIONAL TERNARY AND
QUATERNARY METAL PHOSPHORUS CHALCOGENIDE
CRYSTALS**

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A thesis submitted to the Nanyang Technological University
in partial fulfillment of the requirement for the degree of
Doctor of Philosophy

2017

Acknowledgments

I would like to take this chance to acknowledge the people who have helped me during my PhD study. This thesis would have been impossible to complete without their help.

First of all, I would like to specially acknowledge my supervisor Professor Xiong Qihua for his abundant guidance and support during my Ph.D. training. I benefited a lot from his passion and patience on research, and his understanding and experience have greatly helped me to broaden my knowledge and enhance my abilities on research. Especially, his positive attitude towards research and live encourages me every time when I face difficulties.

I would like to express my deep gratitude to Professor Zhang Jun for his fruitful helps, discussions and guidance in experiment. He inspires me a lot about the experiment design and theoretical discussions. I am really benefited from his expertise in spectroscopy. Thank Dr. Du Kezhao for his help in the experiments and discussions in the data analysis. His willingness to assist in any moment is greatly appreciated. I also want to express my appreciation to Professor Li Dehui for his training on the equipment at the beginning of my PhD study.

Furthermore, I also would like to express my great appreciation to my group members and former group members for their suggestions, discussions and encouragement. They are Professor Zhang Qing, Dr. Huang Lijian, Dr. Xing Jun, Dr. Xu Weigao, Dr. Zhang Chaohua, Dr. Zhao Weijie, Dr. Deep Talukdar, Dr. Zhao Yanyuan, Dr. Wen Xinling, Dr. Yuan Yanwen, Lu Xin, Zhu Yue, M. Iqbal Bakti Utama, Liu Yu Yang Fredrik and Li Zhenpeng.

Finally, I would like express my love and gratitude to my beloved family. They always gave me unconditional support at any moment. This thesis is dedicated to them.

Abstract

The exploration of functional two-dimensional (2D) materials beyond graphene has gone into eruption in recent years aimed at new materials and functionalities. The interest of individual layers of 2D materials mostly focuses on the unique electronic and optical properties to the bulk counterpart. In this thesis, a systematic study has been conducted on a new family of 2D semiconducting crystals – metal phosphorus chalcogenides (MPCs), mainly focusing on a variety of physical property of ultrathin MPCs.

The investigation has started from the synthesis of high-quality single crystal by chemical vapor transport method, followed by the preparation of atomically thin sample on SiO₂/Si substrate by mechanical exfoliation. Several compounds in this group are well crystallized with structural characterized techniques. A first principle calculation on cleavage energies of MPCs is calculated to confirm the feasibility and stability of monolayer structure. The transmission spectra of this series of crystal show a wide-range band gaps from 1.3 to 3.5 eV with element substitution, suggesting their potential on optoelectronic applications. Therefore, the MPC monolayers can be used to build the heterostructures by van der Waals stacking, which is significant in the fundamental research in optoelectronics, as well as unusual ferroelectric and magnetic properties.

A comprehensive study on the lattice dynamics has been performed on MPC crystals by Raman spectroscopy. The similar Raman spectra in high-frequency region ($> 200\text{ cm}^{-1}$) of MPCs suggest that those modes are originated from the internal vibration of $[\text{P}_2\text{S}_6]^{4-}$ anion, while the large differences in low-frequency region ($< 200\text{ cm}^{-1}$) among MPCs are directly related to the metal ion vibrations. Similar Raman spectra in atomically thin FePS₃ show that

the Raman modes are mainly from intra-layer vibrations. The phonon dispersion relationship of FePS_3 has been calculated by the first principle density function theory. A qualitative explanation of the dynamical behaviors of those materials was obtained to motivate further fundamental physical study, as well as the potential optical and optoelectronic 2D device based on this family of materials.

We further demonstrate a systematic study on high-quality atomically thin iron phosphorus trisulfide (FePS_3) crystal prepared by mechanical exfoliation. Raman spectroscopy is used to probe the spin-phonon coupling, spin interactions and magnetic phase transition on microscale mono- and few-layer FePS_3 samples. The magnetic persistence shown in the thin sample suggests a promising future of ultrathin magnetic device, while the spin-phonon coupling in 2D materials promotes a better understanding on many critical problems in various research fields, such as magnetic Raman scattering and possibly on iron based superconductivity. A calculation on total energy of magnetic phases is performed to support our experimental results. Our studies advocate the intriguing magnetic properties in 2D crystals and suggest FePS_3 is a promising candidate material for future magnetic applications.

The first observation of second harmonic generation (SHG) in 2D atomically thin silver indium phosphorous sulfide (AgInP_2S_6) crystals has been reported. The nonlinear signal facilitates the use of thickness-dependent SHG intensity to investigate the lattice symmetry and the stacking type of this material. Moreover, the crystal-orientation dependent SHG of monolayer sample can be applied to probe the rotational symmetry and grain boundary of the AgInP_2S_6 lattice in plane. Besides, the ferroelectric property in CuInP_2S_6 flakes has been investigated by SHG based on the noncentrosymmetric lattice structure. The first observation of ferroelectricity in 2D materials with the thickness below 50 nm has been demonstrated. Our

temperature dependent Raman spectroscopy measurement of 20-nm CuInP_2S_6 flakes also supports the demonstration. An anisotropy in CuInP_2S_6 along layer has been detected by SHG signal. Our studies expand the 2D crystals family in nonlinear effect field, which opens considerable promise to in the functionalities and potential applications of 2D materials.

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Citations to Published Work

Majority of Chapter 3 appears as:

"Weak Van der Waals Stacking, Wide-Range Band Gap, and Raman Study on Ultrathin Layers of Metal Phosphorus Trichalcogenides", K. Z. Du, **X. Z. Wang**, Y. Liu, P. Hu, M. I. B. Utama, C. K. Gan, Q. H. Xiong*, and C. Kloc*, *ACS Nano* 2016 10(2), 1738-1743

Majority of Chapter 4 and 5 appears as:

"Raman Spectroscopy of Atomically Thin Two-Dimensional Magnetic Iron Phosphorus Trisulfide (FePS₃) Crystals", **X. Z. Wang**, K. Z. Du, Y. Liu, P. Hu, J. Zhang, Q. Zhang, M. H. S. Owen, X. Lu, C. K. Gan, P. Sengupta, C. Kloc, Q. H. Xiong, *2D Mater.* 2016 3(3), 031009

Majority of Chapter 6 appears as:

"Second-Harmonic Generation in Quaternary Atomically Thin Layered AgInP₂S₆ Crystals", **X. Z. Wang**, K. Z. Du, W. W. Liu, P. Hu, X. Lu, W. G. Xu, C. Kloc, Q. H. Xiong, *Appl. Phys. Lett.* 109 (12), 123103

Chapter 1 Introduction

1.1 Low-Dimensional Nanomaterials

“Dimension” is a common concept which is extensively used in a variety of subjects from natural science, like mathematics and physics, to philosophy. In mathematics and physics, the dimension of a space or object can be defined as the minimum number of coordinates needed to specify a point in it. According to definition, the world we live in, as well as the most of physical objects we touch is three-dimensional. However, when facing various complex problems, mathematicians and physicists are not satisfied to be limited by the three dimensions. For example, the superstring theory requires 10 space-time dimensions, while a more fundamental theory called M-theory describes 11 dimensions. Nonetheless, no experimental evidence or observation can prove the existence of extra dimensions, which may be hidden by some physical mechanism. In contrast to higher-dimensional spaces, the world of lower dimensions is friendlier and provides us the possibility to explore it through certain media, such as low-dimensional nanomaterials.

Nanomaterials generally refer to materials with the size from 1 to 100 nm in at least one dimension. In 1959, the nanoscience and nanotechnology were firstly proposed by Feynman in his talk *“There is a plenty of room at the bottom”*, where he described the possibility of direct manipulation of the individual atom for chemistry synthesis. The field of nanoscience and nanotechnology advanced the developments based on the synthesis of a variety of nanomaterials. Structures with three-, two- and one-dimensional nanoscale are named zero-dimensional (0D), one-dimensional (1D), and two-dimensional (2D)

nanostructures, respectively. The common examples of 0D, 1D and 2D nanostructures are fullerenes,¹ carbon nanotubes,² and graphene³ in the carbon material system, and quantum dots,⁴ quantum wires,⁵ and quantum wells⁶ in the semiconductor systems. With the development of nanostructure synthesis and advance in characterization tools, the study on nanoscience and nanotechnology has become one of the most extensive topics in the last three decades, which will continuously attract more attention to this field in the future.

In physics, the macrocosm is governed by the classical Newton's law, while the world in atomic and sub-atomic scale obeys the quantum mechanics. Nanostructures bridge the gap between the two worlds. New phenomena emerge in nanoscale, where neither the classical Newton's law nor quantum mechanics can completely rule. Therefore, nanomaterials with high crystalline quality provide an ideal platform to explore this specific regime through conducting the fundamental research, such as the electric transport properties, magnetic transport properties, optical properties, thermal transport properties, chemical reaction mechanism, *etc.*

Different from that in the bulk case, unique properties can be observed in nanostructures. Quantum effect is one of the unique properties of nanostructures. As structures shrink down to nanoscale, the quantum confinement effect starts to dominate in the system due to the limited number of atoms along the confinement direction. One good example is the GaAs quantum well, of which the energy band is split to many sub-bands when the width of the quantum well is reduced to around the Bohr radius of the bulk exciton in GaAs (~10 nm).⁷ Moreover, when the size of the nanostructures is shorter than the Bohr radius in at least one dimension, the exciton binding energy and band gap energy will become larger due to the increasing separation between electron and hole, owing to the squeezed orbits of excitons.⁸

Further, the exact quantization of quantum Hall effect is demonstrated in the 2D electron systems - gallium arsenide heterostructures and graphene.⁹⁻¹⁰

Nanostructures play an important role not only in fundamental research but also for potential applications in many areas. Benefited from their large surface-to-volume ratio, nanostructures show various potential applications, including the supercapacitors,¹¹ lithium ion battery¹²⁻¹³ and medicine.¹⁴ Moreover, a large number of semiconductor nanostructures have been proved as good candidates for gas sensors and biosensors.¹⁵⁻¹⁶ Furthermore, the catalysts with nanostructures can largely improve the performance because of their large surface.¹⁷⁻¹⁸

In general, the synthesis methods of nanostructures can be divided into two mainstream types: bottom up and top-down.¹⁹⁻²⁰ In bottom up methods, the nanostructures are assembling from atoms or molecules. The raw material sources can be in the form of gas, liquid or solid. This approach offers the possibility to precisely control the chemical composite, dimensionalities, shape and size of nanostructure following the unique requirement and purpose. The typical bottom up approach has been widely used to synthesize nanostructures, including solution growth, chemical vapor deposition, *etc.*¹⁹ In contrast, top-down method is a very powerful approach in traditional nanostructure manufacturing techniques, in which the nanostructures are created in bulk materials by a combination of lithography and etching techniques. The most mature products of nanotechnology, such as modern CPUs and integrated circuits, are based on top-down processes. The traditional example of a top-down technique for fabrication is lithography where the instruments are used to shrink the size of structure to nanoscale.

In summary, the field of low-dimensional nanostructures has become more attractive in the research of condensed matter physics. The prominent quantum confinement effect in low-

dimensional nanostructures provides a platform in fundamental researches and in potential applications. More and more novel physics and accompanying challenges are approaching to this field in the future.

1.2 Dimensionality and Size Dependence of Properties in Semiconductor

Compared to their bulk counterparts, low-dimensional semiconductors show significant differences in both electronic and optical properties, which are strongly dependent on their electronic band structure and density of states. This is because both electronic band structure and density of states are strongly affected by quantum confinement effect and surface effect. In the low-dimensional systems, the movement of electrons can be spatially confined into certain directions, leading to the large modulation of both the electronic structure and density of states. Besides that, due to the larger surface area in low-dimensional system, the surface states will induce compositional variation and local dielectric environment, which will further influence the electronic and optical properties of low-dimensional materials.

Generally, the energy dispersion relationship of the system hinges on $E \propto k^2$, where k is wave vector. Considered a simple particle-in-box model in which free electrons are put into a three-dimensional box with volume of $\Omega = L_x \times L_y \times L_z$, with the periodic boundary conditions, the energy dispersion relationship of this system can be represented by²¹

$$E(k_x, k_y, k_z) = \frac{\hbar^2}{2m_e} (n_x^2 k_x^2 + n_y^2 k_y^2 + n_z^2 k_z^2) \quad (1-1)$$

where n_x, n_y, n_z are integers; m_e is the effective mass of electrons; k_x, k_y, k_z are wave vectors related to the box of dimensions L_x, L_y, L_z via $(k_x, k_y, k_z) = \left(\frac{2\pi}{L_x}, \frac{2\pi}{L_y}, \frac{2\pi}{L_z}\right)$ (Figure 1-1a). In 3D

materials, the wave vectors k_x , k_y , k_z are very small, due to the large L_x , L_y , L_z , leading to the continuous states in three dimensions and the density of state can be described as a function of energy by $n_{3D}(E) = \frac{m}{\pi^2 \hbar^3} \sqrt{2mE}$, as shown in Figure 1-1e. If the size along one dimension decreases down to the Bohr radius of bulk exciton (Figure 1-1b), the wave vectors become quantized along the corresponding direction and maintain continuous in the other two directions. Consequently, the density of state will become irrelevant to the energy and form a step-like shape in 2D (Figure 1-1f). When one more direction is decreased, a 1D structure is formed (Figure 1-1c). In this case, the eigenstates will be continuous only along one direction in momentum space. Therefore, the $\frac{1}{\sqrt{E}}$ dependent density of state would display spike-like structure for each quantized state, which is known as von Hove singularity (Figure 1-1g). Finally, in the limit of 0D, the energy states become discrete points along all axes in the momentum space and the density of state becomes to discrete lines (Figure 1-1h). Figure 1-1 represents the general situations in quasi-low-dimension, thus the density of states shows the multiple steps, spikes and lines, which will reduce to only single one in the absolute low-dimensional cases. However, some systems would have unique energy dispersion relation and density of state, which are different from the situation shown in Figure 1-1. For example, Figure 1.1f is not valid for graphene system, where the energy dispersion relation exhibits a circular cone shape.

Figure 1-1 The schematic images of structures with different dimensionalities: (a) bulk semiconductors – 3D; (b) nanobelts, nanoribbons or quantum wells – 2D; (c) nanowires or nanotubes – 1D; (d) quantum dots – 0D. (e-h) Density of states for 3D, 2D, 1D and 0D structures²²

Dimensionality-dependence of the electron density of states opens a pathway to the fundamental study of quantum confinement effect, which takes place in low dimensional structures with the size comparable to the Bohr radius of bulk exciton in at least one dimension. The optical properties of semiconductors can be detected by many optical spectroscopic approaches, such as optical absorption and photoluminescence spectroscopy. Therefore, the transition between discrete energy bands in low dimension can be observed by those optical spectroscopic methods. For example, the confined discrete states in 0D have been identified through optical absorption in CdSe quantum dots, as well as electronic transport measurements

in GaAs quantum dots.²³⁻²⁴ The emission peaks in photoluminescence spectra or the band edge in absorption spectra will show a blue shift as the size further decreases. For instance, the PbS quantum dot photodetectors have been proved to be largely tuned from mid-infrared to visible range through the size and shape control.²⁵⁻²⁶ Besides the absorption and photoluminescence spectroscopy, quantum confinement is also responsible for the size dependent electronic structures,²⁷ photoconductivity,²⁸ and phonon properties²⁹ in low dimensional structures. Apart from the quantum confinement, the surfaces of semiconductor nanostructures are critical to the electronic and optical properties. The large amount of surface states in nanostructures results in the strong surface depletion and surface electric field, which will induce the confinement effect beyond the quantum confinement regime.³⁰

Furthermore, the theory of magnetism in low dimension has to date back to the quantum mechanics, because the analytical or numerical solutions of a spin chain are easier to obtain. The corresponding experimental investigations have also attracted extensive attention for several decades. It is well-known that a magnetic system can show a crossover from a long range ordered state to quasi 1D magnetic behavior or even high-Tc superconductivity.³¹ This drastic change in the spin correlations might be evoked by an external parameter that influences the spin system. In general, a spin chain is characterized by one dimensionally coupled spins.³² However, chains are locally separated from each other preventing magnetic exchange between them. The degrees of freedom of the spins can vary between Ising, XY and three dimensional Heisenberg behaviors. The investigation on magnetic properties of nanostructures offers a platform to understand the low dimensional spin system, which is the intriguing challenge at present.

In summary, the physical properties semiconductor can be modified in low dimensional situation, owing to both the quantum confinement and surface effects. Quantum confinement effects can modify the electronic band structures in the quantum confinement regime while surface effects of the materials are induced by surface states due to the large surface area in nanostructure. Motivated by the interesting phenomena and related possible applications, the investigations on low-dimensional physical properties, including electronic, optical and magnetic properties, have attracted lots of attention and researchers to devote to this field.

1.3 Layered 2D Crystals

1.3.1 General Layered 2D Crystals

2D crystals are crystalline materials with the size of atomic scale in one dimension. 2D material offers a golden playground for investigating the physics in low dimensions. Layered combinations of different 2D materials are generally called van der Waals heterostructures. Since the first discovery of 2D material - graphene in 2004, a large number of 2D materials have been found with their unusual characteristics in the intense researches, which have grown more rapidly than that on graphene.³³⁻³⁴ 2D materials can generally be categorized as allotropes of elements and compounds.

Graphene

Before the discovery of graphene, 2D materials were speculated to be thermodynamically unstable due to the strong thermal fluctuation, because the 2D lattice is comparable to the lattice constant at finite temperature.³⁵ This speculation was overturned in 2004 by the isolation of atomic thin graphene layers from graphite.³⁶

Figure 1-2 (a) Schematic representation of graphene. (b) Electronic band structure of graphene.³³ (c) Typical dependences of few layer graphene's resistivity on gate voltage for different temperatures ($T = 5, 70$, and 300 K for top to bottom curves, respectively). (d) Example of changes in the film's conductivity at 70 K curve. (e) Hall coefficient *versus* gating voltage at 5 K. (f) Temperature dependence of carrier concentration in the mixed state for the film in (c) (open circles), a thicker few layer graphene film (squares), and multilayer graphene (~ 5 nm; solid circles). The insets in (e) are the models of a 2D semimetal.³⁶

Graphene is a crystalline allotrope of carbon in the form of a nearly transparent (to visible light) one atom thick sheet. The carbon atoms are arranged as honeycomb structure in a plane (Figure 1-2a). The electronic band structure of graphene, of which a specific energy

band stays over the Fermi level in the Brillouin zone, indicates the system is semimetallic (Figure 1-2b). It has the high thermal and electrical conductivity, displaying current densities much higher than that of copper. Figure 1-2c to f shows the field effect in few-layer graphene device. The resistivity exhibits a sharp peak with the value at the kilo-ohm level when the Fermi level is tuned to the Dirac points, while its conductivity increases linearly with gate voltage on both two directions.

Graphene has a theoretical specific surface area of $2630 \text{ m}^2/\text{g}$, which will result in a plenty of properties in electronic, optical and magnetic field in low-dimensional systems.³⁷ The progress on graphene-based potential application still keeps going till nowadays.

Transition Metal Dichalcogenide

The great success on graphene research also focuses people's attention on other graphene-like 2D crystals. Similar with graphene, other 2D atomic crystals generally can be isolated from their corresponding bulk layered materials in theoretical. A variety of layered materials have been investigated in the following days with various properties. For example, categorized by the electronic property, 2D materials cover the areas of insulators (h-BN), semiconductor (MoS_2), semimetals (TiSe_2), metals (VSe_2) and superconductors (NbSe_2). Among them, the most extensively studied 2D crystals are Mo and W chalcogenide 2D crystals, which belong to transition metal dichalcogenides (TMD) for their novel optical and electronic properties.³⁸⁻³⁹

As shown in Figure 1-3, MX_2 ($\text{M} = \text{Mo}, \text{W}$; $\text{X} = \text{S}, \text{Se}$) has the same crystalline structure. Each layer is around 0.7 nm and composed of three atomic layers, where one M layer

sandwiched between two X layers. For MX_2 , 2H is the most stable and common type in nature, where two adjacent atomic layers stack alternately.

Figure 1-3 (a) Stick-and-ball crystal structure of MX_2 ($\text{M}=\text{Mo}, \text{W}$; $\text{X}=\text{S}, \text{Se}$) monolayer (top view). (b) Side views of 2H MoS_2 . Blue and red spheres correspond to metal and chalcogen atoms, respectively.⁴⁰

With the same crystalline structure, MX_2 exhibits similar electronic and optical characteristics. The fanciest property of MX_2 is the thickness dependent electronic structure, where the band gap transits from indirect to direct when the crystal shrinks from bulk to monolayer. This electronic behavior can be depicted by the first principles calculated band structure (as shown in Figure 1-4a) and proved by the photoluminescence spectra (as shown in Figure 1-4b). Moreover, a symmetry breaking from D_{3d} to D_{3h} will occur when MX_2 is isolated from bulk to monolayer, showing the viability of optical valley control.⁴¹⁻⁴² Because of inversion symmetry breaking and strong spin-orbit coupling, coupled spin and valley polarization can be naturally achieved in monolayer MX_2 .⁴³ The two split valence band tops at

a given valley which correspond to A and B excitons are spin-polarized at the band edges around the K points. The reversed spin-polarization leads to a valley- and spin-dependent optical selection rule.⁴³

Figure 1-4 (a) First principles calculated band structures of bulk, four-layer, bilayer, and monolayer MoS₂, indicating an indirect-to-direct band gap transition from bilayer to monolayer. (b) Normalized PL spectra by the intensity of peak A of thin layers of MoS₂ from six- to monolayer.⁴¹⁻⁴² (c) Schematic drawing of the band structure at the band edges located at the K points.⁴³

The intriguing transition on electronic and optical properties from 3D to the 2D system reveals the importance of dimensionality in the study of fundamental physics. TMDs provide an excellent platform for 2D system, where the understanding will open a pathway to unexpected fundamental phenomena and potentially ultrathin applications.

1.3.2 Metal Phosphorus Chalcogenides 2D Crystals

Although the number of 2D materials is huge to date, only few of them could be isolated into stable monolayer.⁴⁴ The available 2D nanomaterials still cannot cover most of the research field. For example, the study on short wavelength optoelectronic applications, intrinsic magnetism and ferroelectricity, is still missing in the current 2D atomic crystals.⁴⁵⁻⁴⁶ Exploring mono- or few-layer magnetic crystals is not only important for understanding the mechanism of low-dimensional magnetism but also significant for magnetic devices, such as ferromagnetic–antiferromagnetic heterostructures.⁴⁷⁻⁴⁹ So far, identification and assessment of new 2D semiconductors with stable mono- or few-layer are still main scientific directions and technological objectives, such as transition metals carbides.⁵⁰⁻⁵²

Crystalline Structure

Metal phosphorus Chalcogenides (MPCs), which have a long history beginning at nineteenth century, have not been fully explored on the atomically thin level.⁵³⁻⁵⁴ The general formulas of MPCs could be represented as $M^{\text{II}}\text{PX}_3$ and $M^{\text{I}}_{1/2}M^{\text{III}}_{1/2}\text{PX}_3$ (mainly $M^{\text{II}} = \text{V, Mn, Fe, Co, Ni, Zn, Cd, Mg}$; $M^{\text{I}}_{1/2} = \text{Cu, Ag}$; $M^{\text{III}} = \text{Cr, V, Al, Ga, In, Bi, Sc, Er, Tm}$; $\text{X} = \text{S and Se}$), irrespective of various doped compounds.⁵⁴⁻⁵⁶ MPCs family spreads on a wider area of the periodic table (mainly from vanadium to zinc) than TMDs, in which the M is confined to IVB, VB and VIB.⁵⁴ The higher chemical diversity and structural complexity would induce the more comprehensive properties.⁵¹ For example, MnPS_3 and FePS_3 are 2D magnetic systems with anisotropic Heisenberg model and Ising mode, respectively.⁵⁷⁻⁶⁰ And CuInP_2S_6 is a 2D ferroelectric material with optical second harmonic generation.⁶¹⁻⁶²

Figure 1-5 The arrangement of metal, phosphorus and sulfur or selenium atoms of MPCs. (a) The Monoclinic structure of MPS_3 (M = Fe, Mn, Ni, Zn and Cd). (b) The rhombohedral structure of MPSe_3 (M = Fe and Mn).⁶³

A detailed single crystal structure calculation has been performed on the MPCs family.⁶⁴⁻⁶⁵ MPS_3 compounds (M=Mn, Fe, Ni, Zn, Cd) are layered crystals corresponding to the $C_{2/m}$ space group, while MPSe_3 compounds (M=Mn, Fe) belong to $R\bar{3}$ space group (Figure 1-5).^{64, 66} The same crystal structure in sulfides or selenides offers a good platform to achieve substitution of metal cations in these systems, at least when the atomic radii of metal cations are close to each other, such as $\text{Zn}_{1-x}\text{Fe}_x\text{PS}_3$ and $\text{Zn}_{1-x}\text{Ni}_x\text{PS}_3$ ($0 < x < 1$).⁵⁴ Large radius differences between cations may induce structure distortion, which prevents homogeneous substitution, while the heterocharge substitution still deserves attention. The structure of MPCs suggests the possibility of replacing M^{II} by a couple of $(\frac{1}{2}\text{M}^{\text{I}} + \frac{1}{2}\text{M}^{\text{III}})$. The full structure determinations of four compounds ($\text{Cu}_{0.5}\text{Cr}_{0.5}\text{PS}_3$, $\text{Ag}_{0.5}\text{Cr}_{0.5}\text{PS}_3$, $\text{Ag}_{0.5}\text{V}_{0.5}\text{PS}_3$ and

$\text{Ag}_{0.5}\text{In}_{0.5}\text{PS}_3$) show layered arrangements closely related to the MPS_3 structural type.⁶⁷⁻⁶⁸ Another subclass of heterocharge cation substitution is created by the families $\text{M}^{\text{II}}_{0.87}\text{Cu}_{0.26}\text{PS}_3$ ($\text{M} = \text{Mn}, \text{Cd}$) and $\text{M}^{\text{II}}_{1/2}\text{AgPS}_3$ ($\text{M} = \text{Mn}, \text{Cd}$), where interesting features on both thermal and electrical conductivity are shown.⁶⁹⁻⁷⁰

Magnetic Structure

Magnetism is one of the fundamental properties of matter. At its root, magnetism arises from two sources: electronic magnetic moments of electron and nuclear magnetic moments of atomic nuclei. Nuclear magnetic moments are usually negligible in the determination of magnetization of materials, since they are thousands of times smaller than the magnetic moments of electrons.

Figure 1-6 Antiferromagnetic ordering (The blue and red arrows stand for the up- and down-spin direction, respectively.)

Generally, a large number of electrons in material are arranged such that their magnetic moments cancel out. When unpaired electrons exist, the materials will show different magnetic behaviors in different magnetic phase. When an unpaired electron is free to align its magnetic moment in any direction, the material will show its paramagnetic behaviors. In ferromagnetic phase, there is a tendency for these magnetic moments to align parallel to each other to maintain

a lowered-energy state. In contrast, in antiferromagnetic phase, the tendency is to make the magnetic moments of neighboring electrons to point in opposite directions.

The dimensionality of system is a critical parameter in determining its physical properties. Most of the magnetism are studied in 3D system. The MPCs are rather attractive compounds because they present a plenty of original physical and chemical properties, which are not generally encountered in other 2D materials. The most valuable one is the magnetic characteristics. The manganese, iron, cobalt and nickel compounds in this family belong to low-dimensional magnetic systems, where Curie-Weiss law is obtained only at quite high temperatures, while the spins order of metal cations are antiferromagnetic at low temperature (Figure 1-6).^{66, 71}

The observed moments in MnPS_3 and FePS_3 agree well with the spin moment of M^{2+} high spin ions, while strong short-distance magnetic interaction in NiPS_3 can be observed above the Néel temperature, even at 300 K.⁶⁶ For CoPS_3 , Co^{2+} presents a high spin orbit coupling, due to the $3d^7$ configurations and the fundamental state $4T_1$ in octahedral field.

The distribution of the magnetic moments is not the same in magnetic MPCs. In 1982, Le Flem *et al.* firstly proposed two types of magnetic structure: type A and type B shown in Figure 1-7a and 1-7b.⁷² Both two types can be described in a 2D layer, due to the ferromagnetic coupling between neighboring layers. The magnetic structure of type B is expected for MnPS_3 and MnPS_3 . This magnetic structure consists of a magnetic ion coupled antiferromagnetically to its three nearest neighbors in the layer, with the magnetic moments pointing perpendicularly to the layer planes. Type A is suitable to describe the other compounds, including FePS_3 , FePS_3 , NiPS_3 , and CoPS_3 . In this model, each metal cation is ferromagnetically coupled in a layer with two of the three nearest neighbors, while antiferromagnetically with the third one.

The parallel ferromagnetic chains are formed and antiferromagnetically coupled to each other in layer. The magnetic moments are oriented perpendicular to the layers in iron compounds, while they list along the c and a axis in NiPS_3 and CoPS_3 , respectively.⁷²

Figure 1-7 Magnetic structures presented by the MPCs: (a) type A, (b) type B and (c) type C.⁵⁴

(d) and (e) show two different in-plane magnetic structures. Black and white circles are up and down atomic spins.

It is worth mentioning that the magnetic structure of MPCs is still controversial even though it has been investigated for over three decades. For instance, Kurosawa *et al.* conduct a neutron diffraction experiment on FePS_3 and report another magnetic structure type C (as shown in Figure 1-7c), where the spins of Fe^{2+} ions are distributed the same as type A within layer but coupled antiferromagnetically between layers.⁷³ Moreover, Rule *et al.* claims that their neutron diffraction experiments prove that the intra-layer magnetic structure of FePS_3 is different from above types (as indicated in Figure 1-7d), where the ferromagnetic chains of Fe atom are rotated by 60° compared with type A or C (Figure 1-7e).⁵⁷

When the distortion is not involved, magnetic interactions between neighboring ions in the lattice can be described by the Heisenberg Hamiltonian,

$$\hat{H} = -2 \sum \left\{ J_{\parallel} (\hat{S}_{ix} \hat{S}_{jx} + \hat{S}_{iy} \hat{S}_{jy}) + J_{\perp} (\hat{S}_{ix} \hat{S}_{jz} + \hat{S}_{iz} \hat{S}_{jx}) \right\} \quad (1-2)$$

where the summation is over all pairs of magnetic ions in the lattice. Several subtypes of model can be defined in special situation, such as the Ising model, the XY model and the isotropic Heisenberg Hamiltonian when $J_{\perp} = 0$, $J_{\parallel} = 0$ and $J_{\parallel} = J_{\perp}$, respectively. The above form of the Hamiltonian is only valid on the condition that the ground state is orbitally nondegenerate with Fe^{3+} or Mn^{2+} , or when the orbital angular momentum L is quenched by the crystal field like Cr^{3+} or Ni^{2+} in an octahedral field.

In situations where the ground state is orbitally degenerate such as in Fe^{2+} , a slightly different procedure has to be adopted. Only the lower triplet is to be considered for analysis due to the much larger crystal field in cubic crystal. The total Hamiltonian for the triplet state can be expressed as⁷⁴

$$H = \Delta \frac{3}{2} + \alpha \lambda l \cdot \frac{3}{2} + \mu_B (\alpha l + 2 \frac{3}{2} \cdot \frac{3}{2}) \quad (1-3)$$

where $S = 2$ in high spin d^6 system. The first term corresponds to the trigonal splitting of the triplet ${}^5T_{2g}$ to the doublet 5E_g with $L_z = 1$ and the singlet ${}^5A_{1g}$ with $L_z = 0$. The second term originates from the spin-orbit coupling. For a free ion Fe^{2+} (d^6), the spin-orbit coupling coefficient $\lambda = -100 \text{ cm}^{-1}$ is negative, because the shell is more than half filled.⁷⁵ The last term is the Zeeman term. The triplet level may be labeled by a fictitious angular momentum $l = 1$ and $\alpha = -1$ is an coefficient for Fe^{2+} in a cubic crystal field.⁷⁶

Figure 1-8 Magnetic susceptibility of (a) MnPS_3 , (b) FePS_3 and (c) NiPS_3 single crystals, parallel ($\chi_{||}$) and perpendicular ($\chi_{\perp}$) to the trigonal axis, as a function of temperature.⁵⁹

The magnetic order in this family of layered magnetic materials has been shown to change with composition in a very fundamental way. Figure 1-8 shows the susceptibility *versus* temperature in MnPS_3 , FePS_3 and NiPS_3 to find out the Néel temperature. Although all three compounds are isostructural, with the magnetic lattice being the 2D honeycomb, the spin dimensionalities of these three materials have a big difference, and they can be described by different spin models. MnPS_3 is best described by the isotropic Heisenberg Hamiltonian. FePS_3 is most effectively treated by the Ising Hamiltonian, while NiPS_3 is best described by the anisotropic Heisenberg Hamiltonian.⁵⁹

Electronic Band Structure

The electronic band structure of several compounds in MPCs family was calculated since 1980s'.⁷⁷⁻⁸⁰ Most of the calculation work was performed on the bulk MPCs until recent papers, which presented the electronic band structure on monolayer counterpart, were published.⁸¹⁻⁸² The band structures of MPS_3 ($\text{M} = \text{Fe}, \text{Mn}, \text{Ni}, \text{Cd}, \text{Zn}$) and MPSe_3 ($\text{M} = \text{Fe}, \text{Mn}$) monolayers calculated with Heyd-Scuseria-Ernzerhof (HSE06) functional are shown in Figure 1-9. MnPS_3 and MnPSe_3 monolayers are direct-band-gap semiconductors, while the other monolayers are all indirect-band-gap semiconductors.^{81, 83} The conduction band minimum (CBM) and valence band maximum (VBM) of monolayer MPCs mainly originate from the p states of chalcogen atoms and the d states of metal atoms, respectively. Furthermore, the band edges in most of MPCs (except FePSe_3) straddle the redox potentials of water at $\text{pH} = 0$ and 7, indicating the potential for water-splitting photocatalysts without an external bias voltage in these.⁸¹

Figure 1-9 Electronic band structures near Fermi level for a) FePS₃, b) MnPS₃, c) NiPS₃, d) CdPS₃, e) ZnPS₃, f) FePSe₃, and (g) MnPSe₃ monolayers.⁸¹

To the best of our knowledge, no experimental study of monolayer MPCs has been done up to now. Only some calculations on magnetic and electronic properties have been reported.^{45, 83-84} A better knowledge of fundamental study on ultrathin MPCs will be useful for the design of atomic 2D device applications in the future.

1.4 Motivation and Objectives of This Thesis

TMD and other 2D semiconductors have attracted considerable interests for their novel physics and potential applications in ultrathin devices. Contrary to extensive progresses on the studies of optical and electronic properties, 2D materials with non-trivial polar properties, such as magnetism and ferroelectricity, are rarely explored. Besides, a deep understanding of the optical process in 2D crystals is not only important to the fundamental investigation of the materials itself, but also ingenious and indispensable for studying their various physical properties through certain coupling. Especially, the magnetic and ferroelectric properties of 2D materials as a dependence of dimensionality remain elusive. It is timely to explore novel 2D magnetic and ferroelectric materials, particularly to understand how the spin properties and ion polarity are affected in atomic thickness. The objective of this thesis is to comprehensively investigate the nonlinear optics and expand research area beyond optics and electronics based on a new family of 2D semiconductor –MPCs. The lattice dynamics, magnetic structure and ferroelectric polarity of ultrathin MPCs have been investigated by the combination of Raman spectroscopy, second-harmonic-generation, first principle calculation and relatively fundamental analysis. Four major issues are going to be addressed in this thesis, which including: (1) what the intrinsic phonon property and the corresponding assignment are in this relatively new 2D crystal in atomically thin region; (2) how the spin-phonon coupling activate the zone-boundary phonon modes by Brillouin-zone-folding and how it is affected with thickness in magnetic 2D materials; (3) how the SHG is originated from the symmetry breaking with the layer-number decreasing in AgInP_2S_6 ; (4) how the ferroelectricity and the relative polar structure varies with the thickness decreasing in ferroelectric 2D materials.

1.5 Organization of the Thesis

Based on the discussion in Section 1.4, besides the general introduction in this chapter, the rest of this thesis is organized as follows:

In Chapter 2, the introduction of the principle of chemical vapor transport (CVT) is presented which has been used in the synthesis of the high-quality MPC single crystal. The instruments for the characterization of structural property of material is also introduced with their underline principle of physics. Furthermore, the Raman spectroscopy and second-harmonic-generation (SHG) measurement is discussed in detail in both their basic conception and instrumentation. An introduction of the UV/visible/Near-IR Microspectrophotometer, which is used to measure the transmission spectrum of materials, is presented in the final part.

A systematic synthesis of a new family of 2D semiconductors – MPC single crystal by CVT method is presented in Chapter 3. Nine compounds in this group, including five ternary sulfides (MPS_3 ; $\text{M} = \text{Fe, Mn, Ni, Cd and Zn}$), two ternary selenides (MPSe_3 ; $\text{M} = \text{Fe and Mn}$), and two quaternary sulfides (MInP_2S_6 ; $\text{M} = \text{Cu and Ag}$) have been synthesized, crystallized and exfoliated into monolayer. The wide-range band gaps, which can be adjusted by element substitution in the range of 1.3~3.5 eV, suggest the optoelectronic applications in broad wavelength range. The calculated cleavage energies of MPCs are ideal to form the mono- and few-layer flakes, which are useful for building heterostructures by Van der Waals stacking and manipulating artificial 2D materials with unusual magnetic and ferroelectric properties.

In Chapter 4, we present a comprehensive investigation on the lattice dynamics on MPCs from bulk crystal down to atomically thin region. The Raman spectra of monolayer FePS_3 and 3-layer FePSe_3 show strong intra-layer vibrations and structure stability of the

atomically thin layers in ambient condition. Beyond that, a systematic Raman spectroscopy study was performed in atomically thin FePS₃ based on the consideration on the whole primitive cell. The phonon dispersion relations of FePS₃ calculated by using the density-functional perturbation theory (DFPT) reached a satisfactory agreement with the measured Raman spectra at room temperature.

Furthermore, the spin-phonon coupling in FePS₃ can be explored by spin-dependent Raman spectra in Chapter 5. The layer-number and temperature dependent Raman spectroscopy suggests a magnetic persistence in FePS₃ even down to monolayer regime through the spin-phonon coupling. The intriguing magnetic properties in 2D crystals suggest FePS₃ is a promising material for future magnetic applications.

In Chapter 6, we investigate the second-harmonic generation (SHG) in quaternary MPCs. On one hand, the observation of optical SHG in 2D atomically thin silver indium phosphorous sulfide (AgInP₂S₆) crystals due to the symmetry breaking is presented for the first time. On the other hand, the SHG signal, which is related to the noncentrosymmetric lattice structure and ferroelectricity, is detected in the CuInP₂S₆ flakes with the thickness from 12.5 to 50 nm. The nonlinear signal facilitates the use of thickness-dependent SHG intensity to investigate the stacking type, crystal orientation and the ferroelectric polarization in this family of 2D materials.

Finally, the conclusion of the whole thesis and a brief outlook on the future research of various physical properties on MPCs is given in the Chapter 7.

Chapter 2 Fabrication and Characterization of Metal

Phosphorus Chalcogenide Crystals

2.1 Chemical Vapor Transport Reactions

Plenty of methods in crystal growth have been achieved via various processes. Among them, chemical vapor transport (CVT) is one of the general methods to obtain solid product, usually in the form of crystals with high purity and good crystalline quality. CVT describes a process for purification and crystallization of non-volatile solids.⁸⁵ The condensed phase of reactants is volatilized in the presence of a gaseous reactant (transport agent) and deposits elsewhere, usually in the form of crystals.⁸⁶ Actually, CVT reaction occurs in nature without the influence of human being. Bunsen firstly observed and described that the presence of volcanic gases, which contains gaseous hydrogen chloride, was essential to the formation of crystalline Fe_2O_3 at high temperature.⁸⁷ A systematic research on chemical transport reactions was summarized by Schäfer in the 1960s.⁸⁸

Figure 2-1 The schematic of CVT reactions for crystallization of solids.

Generally, the deposition or crystallization appears in the place with different external conditions for the chemical equilibrium. Temperature gradient is the most common external condition as driving force in volatilization and crystallization.

Figure 2-2 (a) Composition of the gas phase for the thermal decomposition of ZnO. (b) Composition of the gas phase for the CVT of ZnO with chlorine.⁸⁶

The whole process of CVT are generally distinguished by three steps: forward reaction, gas flow and back reaction.⁸⁵ During the reaction, the transport agent is usually added for the dissolution of a solid in the gas phase. This characteristic can be illustrated by the example of vapor transport of zinc oxide with existence of chlorine as transport agent. As shown in Figure 2-2a, the equilibrium pressure of ZnO is below 10^{-10} bar even at 1000 K, which is an extremely high requirement compared with the standard lab condition. In contrast, with the existence of chlorine, the transport effective gases (ZnCl₂ and O₂) are formed in heterogeneous equilibrium,⁸⁶

Thereby transport effective vapor pressures (10^{-4} bar) of the gas species can be observed below 600 K as shown in Figure 2-2b.

On the basis of the example of ZnO, a general principle of CVT can be described. The source material is reversibly transformed into gaseous products in the assistance of transport agent as shown in following expression,

In laboratory, a closed system, typically a sealed ampoule, is usually chosen for the practical realization. The transport agent remains in the system and constantly re-enters the reaction. A transport ampoule typically has a length of 10 to 20 cm and a diameter of 10 to 20 mm. In order to achieve an effective CVT reaction, several qualitative and key conditions should be considered. For example, the suitable transport agent and the temperatures of different zones should be carefully decided based on both the phase diagram of materials and physical condition of lab, while the rate of mass transport needs to be predicted to control the time of synthesis.

Figure 2-3 (a) The solid-state quartz-tube sealing system. (b) Two-zone furnace. (c) Three-zone furnace.

Various solid crystals with high purity and good crystalline structure, including elements,⁸⁹⁻⁹⁰ metal halides,⁹¹⁻⁹² pnictides,^{86, 93-94} chalcogenides,^{86, 93, 95} *etc.*, have been successfully synthesized by CVT method. The system we used for CVT reactions contains two parts – the solid-state-tube sealer and two/three-zone furnace.

2.2 Characterization of Materials

2.2.1 X-Ray Diffraction

X-ray diffraction (XRD) is a non-destructive technique to identifying the atomic and molecular structure of a crystal, where the incident X-rays diffract into many specific directions due to the crystalline atoms. X-ray is an electromagnetic radiation with very short wavelength, which is comparable to the atomic interplanar spacing in crystals. The X-ray wave is scattered by atoms, primarily the atoms' electrons, and undergo a Bragg's diffraction. The angles and intensities of these diffracted beams contain the information of the density of electrons, which reflects the mean positions of the atoms within the crystal. Bragg's law plays a significant role in determining the crystalline structures and it can be expressed as,

$$n\lambda = 2d \sin \frac{\theta}{2} \quad (2-3)$$

where n is an integer, λ is the wavelength of the incident X-ray, d is the atomic interplanar spacing and θ is the angle between the specific crystal plane and the incident X-ray.

In this thesis, powder XRD patterns were collected by a Bruker D8 Advance diffractometer using $Cu K\alpha$ ($\lambda = 1.54178 \text{ \AA}$) radiation at room temperature.

2.2.2 Scanning Electron Microscopy

Scanning electron microscopy (SEM) is a type of technique which can scan specimen with a focused beam of electrons. The electrons can interact with atoms of the sample to produce various signals about the sample's surface morphology. Theoretically, the maximum resolution d of optical microscope is limited by the wavelength of the photons used to probe the sample due to optical diffraction as shown in the expression,

$$d = \frac{\lambda}{2n \sin \alpha} \approx \frac{\lambda}{2NA} \quad (2-4)$$

where λ is the wavelength of the photons and NA is the numerical aperture of the system. Therefore, the resolution of optical microscopy are limited down to the half wavelength of the light in general case. Based on Louis De Broglie's description, electron simultaneously possesses both wave-like and particle-like character. The wavelength of an electron can be defined by $\lambda = h / p$, where h is Planck constant and p is the momentum of electron. In SEM, the wavelength of the moving electron can be very small when the electron moves with high kinetic energy. The wavelength of the electron beam after considering correction from relativistic effect can be expressed as⁹⁶

$$\lambda = \frac{h}{\sqrt{2m_0 eV \left(1 + \frac{eV}{2m_0 c^2}\right)}} \quad (2-5)$$

where m_0 is rest mass of the electron, V is the electric potential used to accelerate the electron beam, e is the element electron charge and c is the speed of light in vacuum. As described in expression (2-5), a larger accelerating electric potential leads to a shorter wavelength of the electron beam, which would give a higher resolution in the system. The accelerating electric

potential for common SEM systems ranges from 0.1 to 50 kV, leading to a shorter wavelength compared with light. For instance, with a standard accelerating electric potential of 30 kV, the wavelength of the electron beam can reach at pm level. However, the resolution in a real system is around 1 nm due to the limitation of magnetic lenses, which would greatly reduce the resolution capability.

To understand the principle of the SEM, it is essential to know how the electron interacts with matter. When the high-energy electron-beam impacts on a specimen, a variety of signals are produced, which include secondary electrons, back-scattered electrons, photons of characteristic X-rays and cathodoluminescence, absorbed current and transmitted electrons. There are various specialized characterization techniques aiming at collecting certain specific signals. Secondary electron detectors are the standard detector equipped in typical SEMs. The secondary electrons are the outer electrons dropping from the atoms of surface layer when impacted by the incident energetic electrons. The secondary electrons are very sensitive to the surface morphology which usually exhibit the energy less than 50 eV, normally around several eV, so that the morphology image can be captured⁹⁷

Figure 2-4 SEM images of as-grown CdSe nanoribbons on Si wafer from JEOL 7001F system.

The SEM images in this thesis were taken on JEOL 7001F field emission SEM. This system has the capacity to take the image from the top view, tilt view and cross section of the specimen. The accelerated voltage was usually set below 5 kV to avoid the damage to the sample and the charging effect. For a nonconductive sample, the incident electrons will accumulate at the surface and form a local electric field, which will repel the subsequent incoming electrons causing serious astigmatism. This will cause a series of problem on imaging, including the constantly drift, the reducing resolution and the inaccurate boundary position of the image. Using lower accelerated voltage and shorter scanning time is helpful to minimize the charging effect.

2.2.3 Atomic Force Microscopy

Figure 2-5 Description of the principle operation of an AFM. The tip follows contour B to maintain constant force between tip and sample.⁹⁸

Atomic-force microscopy (AFM) is a type of scanning probe microscopy (SPM) with resolution on the order of nanometer in z-scanning direction.⁹⁸ AFM is a powerful and multifunctional technique for force measurement, imaging and manipulating the matter in nanoscale. The principle of AFM is based on the Van der Waals force, which can be either attractive or repulsive depending on the distance between any two objects. AFM images are

obtained with the measurement of the force sensed by a cantilever with a very sharp tip approaching to the surface of the sample. The radius of curvature of the prevailing commercial tips is usually below 10 nm. The tip can move following the surface contours when the force is kept at a constant level with a feedback mechanism (as shown in Figure 2-5). During the process of imaging, a position-sensitive detector (PSD) is used to detect the small displacement of the cantilever with the help of a laser beam, which magnifies the bending or twisting signal of cantilever. According to the type of forces between the cantilever and sample surface, two imaging modes are available for AFM: contact mode (repulsive force) and non-contact mode (attractive force).

Figure 2-6 (a) The topography image of an exfoliated 2D materials (FePS₃). (b) The section profile along the red line in (a). The thickness of the measured flake is around 5 nm.

In this thesis, all AFM images were performed on Asylum Research Cypher™ AFM (Oxford Instrument). The non-contacted mode was used to protect both sample surface and tip of AFM. An example of the topography image of an exfoliated 2D materials flake was shown in Figure 2-6a. In order to obtain the thickness information, a red line was drawn across the flake and the section profile along the red line was shown in Figure 2-6b.

2.2.4 Transmission Electron Microscopy and Selected Area Electron Diffraction

Transmission electron microscopy (TEM) is an indispensable microscopy technique to investigate the crystalline structure, composites and other properties of ultra-thin specimen. As a beam of electrons passes through the specimen, an image is formed from the interaction between the electrons and specimen. Due to its high resolved capabilities, TEMs have been widely used in the field of material science, chemistry and electronics.

TEMs can image the specimen at a much higher resolution than optical microscopy, owing to the small de Broglie wavelength of the energized electron beam used. The resolution of TEMs can reach the level of atomic interplanar spacing of crystals, which is three-order smaller than that of light. For example, the de Broglie wavelength of electron can reach around 2.5 pm with the energy of 200 keV, which is typical to be used in TEMs. Similar to SEM, the principle of a TEM is based on interaction between the electrons and matter as well. The TEM collects the transmitted electrons, while SEM collects the secondary electrons. Therefore, the specimens used for TEM should be thin enough to make the electrons pass through the specimens, whose thickness is generally thinner than 100 nm for high resolution TEM.

When passing through a thin specimen, the electrons will be scattered differently according to the thickness and composites. Therefore, the different contrasts of each parts of specimen will be caused and used to form the images. Similar with the interaction between X-ray and the crystalline specimens, Bragg's diffraction will occur when the energetic electrons pass through the crystalline specimen. A crystalline sample can disperse electrons into discrete locations in the back focal plane and exhibit diffraction contrast, which obeys the Bragg's law stated in equation (2-5) as well. By the placement of a group of objective lens and aperture, the Bragg reflections can be selected and magnified. Only parts of the sample cause the electrons

scattering, which end up projected onto an imaging device, such as photodiode or charge coupled device (CCD) to record the information.

The selected area electron diffraction (SAED) pattern of a crystalline specimen can be acquired by adjusting the intermediate lens of TEM. When an electron beam pass through a crystal sample, the electron diffraction governed by the Bragg's law will occur. Because the direction of the diffracted electrons depends on the orientation of the crystals, the SAED pattern obtains the information about the reciprocal space, which is significant in the study of lattice structures of a crystal. In this thesis, TEM images and SAED were obtained from Energy Filtered Carl Zeiss TEM, LIBRA® 120.

2.3 Raman Scattering Spectroscopy

2.3.1 Basic Conception of Raman Scattering

Raman scattering, which is the inelastic scattering of a photon, was discovered by C. V. Raman and K. S. Krishnan in 1926.⁹⁹ Raman spectroscopy has become a capable and effective tool with non-destructivity and high sensitivity in the study of elemental excitations, including phonons, excitons, polarons, polaritons and plasmons in condensed matter physics.

When the light incidences on material, the photon will interact with the atoms or molecules and the electrons in materials will be perturbed and oscillate as photons are electromagnetic waves as well. The majority of the scattered photons have the same energy and momentum as the incident ones, which are elastically scattered (Rayleigh scattering). Besides that, a small fraction of the scattered photons have an energy gain or loss during the interaction. Raman scattering usually occur with a change in energy of photons due to a transition to another energy level. The first-order inelastic Raman scattering process involves

the absorption of an incident photon and subsequent emission of a photon via intermediate states.

Figure 2-7 Schematic of Raman scattering, Rayleigh scattering, and IR absorption processes.

Raman scattering can be divided into two types, Stokes Raman scattering and anti-Stokes Raman scatterings, corresponding to the situations of energy loss and gain, respectively. During the Stokes Raman scattering, the emitted photons have a lower energy with an energy difference $\Delta\nu$ corresponding to the created phonon energy. In contrast, the phonons are annihilated in the process of anti-Stokes Raman scattering. The energy gain of the emitted photon equaling to the annihilated phonon energy $\Delta\nu$ can also be detected in the IR absorption process. The intensity of the anti-Stokes Raman scattering reflects the population of the excited vibrational states, which is dependent on the temperature.

In the processes of Raman scattering, the energy and momentum of photons can be expressed as:

$$h\nu_i = h\nu_f \pm h\nu_q \quad (2-6)$$

$$\mathbf{k}_i = \mathbf{k}_f \pm \mathbf{q} \quad (2-7)$$

where ν_i , ν_f and ν_q are the frequency of the incident photons, scattered photons and phonons, respectively; while $\mathbf{k}_i$, $\mathbf{k}_f$ and $\mathbf{q}$ are the wave vector of incident photons, scattered photons and phonons. In the Equation (2-6) and (2-7), '+' represents to the creation of phonons in Stokes process, and '-' corresponds the annihilation of phonons in anti-Stokes process.

In nanostructures, surface phonons become significant due to the large surface-to-volume ratio. The electron-phonon coupling is greatly enhanced in nanoscale as well. As a consequence, Raman scattering spectroscopy will exhibit a variety of interesting phenomena with significant fundamental physics when the system goes into nanoscale form. For instance, the phonon energy shows redshift when the size of the materials is down to quantum confinement regime. In some special and critical cases of nanostructure, new modes, such as breathing modes, can be observed in addition to the quantum confined phonon states.

2.3.2 Raman Scattering in Magnetic Materials

In magnetic materials, the Raman scattering can be excited by magnetism. The magnetic susceptibility tensor space is modulated periodically by the magnons. The modulation of magnetic susceptibility tensor $\chi^{(ij)}(r)$ can be expressed by spin operation Taylor series as,¹⁰⁰

$$\begin{aligned} \chi^\beta(r) = & \chi^\beta(r) + \sum_{\mu} K_{\mu}^{\alpha\beta}(r) S_r^{\mu} + \sum_{\mu,\nu} G_{\mu\nu}^{\alpha\beta}(r) S_r^{\mu} S_r^{\nu} + \sum_{\delta} \sum_{\mu,\nu} H_{\mu\nu}^{\alpha\beta}(r, \delta) S_r^{\mu} S_{r+\delta}^{\nu} \\ & + \dots \end{aligned} \quad (2-8)$$

where K , G , and H represent the strength of coupling between magnetic materials and light; the constant term $\chi^\beta(r)$ contributes to the elastic scattering; the linear term S_r^{μ} can be described as the group of operators of generation S_r^{+} and annihilation S_r^{-} of single magnon. The quadratic spin operator $S_r^{\mu} S_r^{\nu}$ also contributes to the one-magnon scattering of ions at r , because it can be written as linear transverse spin operator.

Figure 2-8 Schematic of energy level transition of (a) one- and (b) two-magnon Raman scattering.

Figure 2-8 shows a simplified energy level transition between angular momentum $L = 0$ and $L = 1$. With the virtual intermediate state $L = 1$, the electric dipole jumps from ground state $S^z = S$ to excited state $S^z = S-1$. The coupling coefficient K (in Eq. 2-8) can be calculated by the spin-orbit coupling constant λ .

Figure 2-9 (a) Schematic of energy level transition of two-magnon Raman scattering; (b) The two-spin pair and adjacent spins (in plane) in the process of exchange scattering.

Two-magnon Raman scattering originates from two-spin-flip caused by the conservation of coulomb interaction of total spin component along z axis. Two-magnon Raman scattering is a more advanced scattering process, but it has a larger scattering area compared to one-magnon scattering. As shown in Figure 2-9a, the spins of ion μ and ν change through the second order term of electric dipole interaction, while the first order of exchange interaction between two electrons is achieved by coulomb interaction. Therefore, the effective Hamiltonian of two-magnon can be expressed as,

$$H_{2-magnon} \propto \sum_{i,j} E_S^i E_I^j S_\mu^- S_\nu^+. \quad (2-9)$$

The two-magnon Hamiltonian is effective to the adjacent spins in the antiferromagnetic system, where the exchange constant and the magnon-magnon interaction could be determined by detecting short-range exchange coupling (as indicated in Figure 2-9b).

In many magnetic systems, the total energy, which is not constant, generally vibrates around its average value. This causes the quasi-elastic scattering, which make the tails on both

Stokes and anti-Stokes sides increase with the increasing of temperature. The scattering intensity can be written by the pair correlation function of spin energy as,

$$I(\frac{\omega}{\omega_0}) \propto \int_{-\infty}^{+\infty} \ll E(k, t) E^*(-k, t) \gg e^{-i\omega t} dt \quad (2-10)$$

where $E(k, t)$ is the energy density, which decided by the Fourier transform of the i th spin energy $E(r) = -\langle \sum_{i>j} J_{ij} S_i \cdot S_j \delta(r - r_i) \rangle$ at position of r_i . The Eq. 2-10 can be simplify in the condition of high temperature in hydrodynamics as,

$$I(\frac{\omega}{\omega_0}) \propto C_m T^2 \frac{D_T k^2}{\frac{\omega}{\omega_0} + (D_T q^2)^2}. \quad (2-11)$$

The integral intensity and half-width at half maximum of quasi-elastic scattering can be decided by the magnetic specific heat C_m and the thermal diffusion constant D_T . It implies the possibility to measure the thermodynamic quantity in magnetic system by optical spectroscopy.

2.3.3 Instrumentation

In this thesis, the Raman scattering measurement was carried in the backscattering configuration on two different spectrometer systems – Horiba Jobin Yvon T64000 and Horiba Jobin Yvon LabRAM HR Evolution.

Lasers

The excitations with a broad range of wavelength from ultraviolet to near-IR are available in our lab. A variety of lasers which we can choose in experiment are listed below:

Several solid state lasers (473 nm, 532 nm, 543 nm, 671 nm, 785 nm, 1064 nm); A He-Ne ion laser (632 nm); A He-Cd laser (325 nm, 442 nm); A tunable Ar ion laser with eight

discrete wavelengths (457 nm, 465 nm, 472 nm, 477 nm, 488 nm, 496 nm, 502 nm, 514 nm); A tunable Ti-sapphire laser (Matisse) with continuously wavelength (700-990 nm); A tunable dye laser (Matisse; Rhodamine 6G) with continuously wavelength (650-780 nm).

Horiba Jobin Yvon T64000 Spectrometer

Figure 2-10 Optical image of our Horiba Jobin Yvon T64000 micro-Raman spectrometer system.

The Horiba-JY T64000 spectrometer equips a confocal microscope (Olympus U-5RE-2) to view the testing sample and a liquid nitrogen cooled charge-coupled detector (CCD) to collect the spectra. Figure 2-10 is the photo of our Raman spectroscopy system, with the main

components including the spectrometer, external optics and cryostat (for low temperature measurements).

Figure 2-11 Schematic of the spectrometer optics.

The simplified schematic of the spectrometer optics is demonstrated in Figure 2-11. The spectrometer equips a 640 mm focal length spectrograph followed by a set of 640 mm focal length double subtractive pre-monochromator. With three 1800 g/mm^{-1} gratings, the spectral resolution can reach $\sim 0.5 \text{ cm}^{-1}$. More than ten individual lasers, including single-wavelength lasers, tunable wavelength laser and femtosecond pulse laser are available to be chosen in our lab. The excited light beam is aligned onto a beam splitter, which reflects the excitation beam on the testing sample through the objective and allows the objective to collect the scattered photons at the same time. By tuning the size of pinhole in the confocal microscope,

the volume of collected light can be adjusted according to the sample condition and experimental requirements.

Equipping three gratings, the spectrometer has two available modes: single mode and triple mode. The single mode is normally used for the photoluminescence measurement and high frequency Raman mode measurement. A notch or bandpass filter is applied to cut Rayleigh scattering light of sample so that the Stokes or anti-Stokes scattering can be dispersed by grating and effectively collected by the CCD. With single mode, the spectrometer is normally hard to detect the signals below 50 cm^{-1} due to the large background from Rayleigh scattering light. The triple mode is configured as subtractive mode, which is widely applied to detect low frequency phonon mode ($\sim 5\text{ cm}^{-1}$) and anti-Stokes photoluminescence by using the three gratings and effective filter. The subtractive double-grating acts like a spectral bandpass filter, which can sharply filter the Rayleigh scattering light coordinated with the internal slit in the subtractive mode. With a liquid helium continuous flow microscopy cryostat, the spectrometer is able to measure the optical spectra from 4.2 K to 350 K.

Horiba Jobin Yvon LabRAM HR Evolution

The Labram HR Evolution spectrometer equips a confocal microscope (Olympus U-5RE-2) to view the testing sample. Figure 2-12a shows the optical photo of the Raman spectroscopy system, with the main components such as the spectrometer and cryostat (for low temperature measurements).

Figure 2-12 (a) Optical image of our LabRAM HR Evolution spectrometer system. (b) Schematic of the optics in the spectrometer.

As shown in Figure 2-12b, the schematic of LabRAM HR Evolution spectroscopy system is similar to one of Horiba Jobin Yvon T64000 Spectrometer in single mode. The two systems share the same low temperature measurement setup and external optics, including

grating, mirror and lasers. Besides, a He-Ne laser (632 nm) was set as internal laser inside the LabRAM HR Evolution spectrometer.

LabRAM HR Evolution spectroscopy system is mainly designed for the high collective efficient photoluminescence and Raman measurement in high frequency region, which generally larger than 150 cm^{-1} depending on the chosen notch or edge filter. Its modular design also provides easier access in terms of beam alignment. Two liquid nitrogen cooled charge-coupled detectors coupled with three sets of collected optical elements are used to collect the spectra of ultra violet to infra-red regions (220-2200 nm).

2.4 Second Harmonic Generation Measurement

2.4.1 Basic Conception of Second Harmonic Generation

In the early 20th century, the studies of optics basically focus on the propagation of weak light in the dielectric material, where the polarization is linearly proportional to the applied electric field. However, since the coherent light source with high intensity was invented around 1960, people found that the linearity is only an approximation while the higher order nonlinear effect must be considered. The polarization P_i can be expanded in terms of applied electric field as¹⁰¹

$$P_i = \varepsilon_0 \left(\chi_{ij}^{(1)} E_j + \chi_{ijk}^{(2)} E_j E_k + \chi_{ijkl}^{(3)} E_j E_k E_l + \dots \right), \quad (2-12)$$

where ε_0 is the permittivity of vacuum; E_j, E_k, E_l are the applied electric field; $\chi^{(n)}$ is the n^{th} order susceptibility tensor. When the induced light intensity (or the magnitude of applied electric field) is large, the nonlinear terms, such as the second or third order terms, become important.

Second harmonic generation (SHG) is an even-order nonlinear optical process. A nonlinear material interacts with photons with the same frequency and generates new photons, which is twice the energy/frequency and half the wavelength of the initial photons. SHG is only allowed in media without inversion symmetry. SHG was first demonstrated by Peter Franken *et al.* in 1961, mainly contributed to the invention of the laser, which offers the high intensity coherent light.¹⁰¹ The signal of collected light was found at 347 nm when a ruby laser (694 nm) was focused on a quartz sample. The formulation of SHG was initially described by N. Bloembergen *et al.* in 1962.¹⁰² Several rules for the interaction between light and non-linear mediums were elucidated in their extensive evaluation of Maxwell's equations at the planar interface between a linear and nonlinear medium.

Figure 2-13 Energy level scheme of SHG process.

The media with inversion symmetry are forbidden from the generation of second harmonic light. Therefore, surfaces and interfaces become interesting subjects for the study of SHG, which discriminates against signals from the bulk and is labeled as surface specific

techniques.¹⁰³ SHG light in characteristic spectra and its electronic transitions are measured as reflection from the surface and display a quadratic power dependence on the excitation power.

In SHG spectroscopy, the measured signal with twice the incident frequency (2ω) is given by an incoming electric field $E(\omega)$ to reveal information about surface. The induced second-harmonic dipole per unit volume $P^{(2)}(2\omega)$ can be expressed as¹⁰⁴

$$E(2\omega) \sim P^{(2)}(2\omega) = \chi^{(2)} E(\omega) E(\omega) \quad (2-13)$$

where $\chi^{(2)}$ is the nonlinear susceptibility tensor, which is a characteristic of the materials at the interface study. The generated electric field $E(2\omega)$ and corresponding $\chi^{(2)}$ reveal the information of materials, such as the interfacial analytical chemistry of surfaces, the orientation of molecules at a surface/interface, and chemical reactions at interfaces.

A general method to estimate the second order susceptibility tensor $\chi^{(2)}$ of atomically thin 2D materials is comparing the measured SHG intensity of detected material and materials with known second order susceptibility. Alpha quartz bulk crystal ($\chi^{(2)} = 0.8 \pm 0.04 \text{ pm/V}$)¹⁰⁵ was usually set as a reference in the estimation of second order susceptibility tensor $\chi^{(2)}$ of atomically thin 2D materials by the following expression,¹⁰⁶

$$\frac{\chi_{sheet}^{(2)}}{\chi_{bulk}^{(2)}} \approx \frac{\chi^{(2)} N^2 f \sqrt{I_{sheet}(2\omega)} / I_{sheet}(\omega)}{4nk_0 \sqrt{I_{bulk}(2\omega)} / I_{sheet}(\omega)} \quad (2-14)$$

where n is the refractive index of quartz; N is the objective numerical aperture; f is numerical integration constant, $k_0 = 2\pi/\lambda$ is the magnitude of the vacuum fundamental wave vector.

Another more convenient method to estimate the $\chi^{(2)}$ of atomically thin 2D materials is comparing the measured SHG intensity of detected material with other atomically thin

materials. SHG of MoS₂ monolayer is widely investigated since 2013. The $\chi^{(2)}$ of MoS₂ monolayer was reported to be 10⁻⁷ m/V level.¹⁰⁶⁻¹⁰⁷ The second-order nonlinear susceptibility $\chi^{(2)}$ could be estimated by¹⁰⁶⁻¹⁰⁷

$$I_{2\omega} \sim [\chi^{(2)}]^2 I_{\omega}^2 \cdot \frac{d^2}{n_{2\omega} n_{\omega}^2}, \quad (2-15)$$

where n_{ω} and $n_{2\omega}$ are the refractive index at frequency of ω and 2ω , respectively; d is the monolayer thickness. Therefore, if the SHG spectra of monolayer MoS₂ and other detected 2D materials are measured under the same conditions, including the substrate, excitation wavelength and other measuring parameters, the second-order nonlinear susceptibility $\chi^{(2)}$ of

detected 2D monolayer can be estimated by $\chi_{dec}^{(2)} = \sqrt{\frac{I_{2\omega}^{dec}}{I_{2\omega}^{MoS_2}}} \chi_{MoS_2}^{(2)}$, regardless of the difference of monolayer thickness and refractive index.

2.4.2 Instrumentation

Since the intensity of SHG is quadratically dependent on the power of pump laser, a pulsed laser is usually chosen as the excitation in the SHG measurement. In this thesis, we used Mai Tai mode-locked Ti:sapphire laser as excitation in all the SHG measurement.

Mai Tai Mode-Locked Ti:Sapphire Laser

A Mai Tai laser system comprises four main elements: the Mai Tai mode-locked laser head, the Model J80 power supply, the rack-mountable chiller and the control computer. Two lasers, a continuous-wavelength (CW) diode-pumped laser and a mode-locked Ti:sapphire pulsed laser, are squeezed into a single small enclosure. The laser head includes two chambers. The CW pump chamber contains a diode-pumped, intra-cavity, frequency-doubled, solid-state

532-nm laser, while the pulsed output chamber contains a mode-locked Ti:sapphire cavity. The 532-nm laser is an ideal pump source for the Ti:sapphire laser due to the broad absorption band in the blue and green regions of Ti:sapphire. A chiller is used to water-cool and control the temperature of the CW pump laser Nd:YVO₄ crystal, the pulsed chamber Ti:sapphire rod and the base of the laser head for a better stability of performance. The Mai Tai delivers continuously tunable output over a range of near infra-red (IR) wavelengths (from 710 to 920 nm) at an 80 MHz repetition rate with the pulses of 100 fs duration.

Both Horiba Jobin Yvon T64000 and LabRAM HR Evolution can be applied to collect the SHG spectrum when they coupled with certain optical elements. A femtosecond laser (800-nm) from oscillator is coupled in to the spectrometer. The polarizer and neutral density filter is set to respectively adjust the polarization and intensity of excited laser. The laser is reflected by a beam splitter and focused on sample by an objective. The reflected light passes the objective, beam splitter, polarization analyzer, short-pass filter and finally dispersed by grating. The short-pass filter is used to block the Rayleigh scattering light (800-nm) and protect the CCD.

2.5 Transmission and Reflection Microspectroscopy

The matter will absorb, reflect or emit the electromagnetic radiation with specific wavelength when the incident radiation is resonant with the matters. In the case we need to measure the transmission spectrum in a very broad range of wavelength, usually the light source is a lamp and it is not trivial to focus and collect the signal in that small area. In this thesis, the transmission spectroscopy measurement is conducted on a UV-visible-near infrared microspectrophotometer (CRAIC 20/20 PVTM).

Figure 2-14 Overview of CRAIC 20 diagram.

Craic 20 is an integrated instrument by constructing a spectrophotometer together with an optical microscope. The microscope and its optics components in this system are specially designed to be capable to operate the measurement from UV to near infrared range. Since the dispersion will be induced when the wide-range-wavelength light is focused by a convex lens, the objective is specially designed based on reflective optics to collect the signal from the sample and focus it onto the aperture of the spectrophotometer.

This instrument is capable of measuring the transmission, absorbance and reflection. In the mode of the transmission/absorbance measurement, the light comes from the bottom lamp and is focused on the sample by a condenser. The transmitted light can be collected by the objective. While in the reflection measuring mode, the light comes from the top lamp and strikes on the sample through the objective. As a consequence, the reflective light can be collected by the same objective. The principle of the three measurement modes is indicated in Figure 2-15.

Figure 2-15 Schematic of the measurement principle in Craic 20 system. (a) Light path in transmission or absorbance measurement. (b) Light path in reflection measurement.

As indicated in the schematic, in all measuring modes, the collected signal light will be dispersed by a grating to separate the light with different wavelength to different angles. Therefore, spectrum of signal light can be collected by the CCD detector. The CCD in Craic 20 contains two detectors: one covers the UV-visible range (300-900 nm) and the other one covers the near infrared range (900-2100 nm).

For the transmission measurement in this system, the spectrum we obtained is the relative percentage referring to the scanning on the area without the sample as shown in following expression,

$$C = \frac{S - D}{R - D} \quad (2-16)$$

where C is the transmission; D is the dark scan; S and R are the sample scan and reference scan respectively. The noise from environment can be efficiently excluded when R and S is much

larger than D . So, it is critical to align the light path well to get higher incident intensity during the measurement.

The absorbance A of the sample can be obtain with the formula

$$A = -\log\left(\frac{I}{I_0}\right) \quad (2-17)$$

where I_0 is the intensity of light irradiated on the sample, I is the intensity of light emerging from the sample. In this system, I and I_0 in the absorbance measuring mode are the intensity S and R we obtain respectively in the transmission measuring mode as indicated in expression 2-17.

This Craic 20 microspectrophotometer is a nondestructive and efficient instrument. Furthermore, a polarizer can be integrated into this system to polarize the incident light for the polarization dependence measurement if necessary.

Chapter 3 Crystal Synthesis, Preparation of Ultrathin Layers and Characterization in Metal Phosphorus Chalcogenides

3.1 Introduction

Graphene and other 2D materials, such as TMD and black phosphorus, have attracted considerable interest.^{36, 44, 53, 108-114} Mono- and few-layer 2D materials have unique electronic and optical properties compared with their bulk counterparts, which are not only important for opto-electronic devices with technological applications but also of fundamental physical interests. For instance, in finite thickness regime, new phonon modes become Raman active due to symmetry breaking, which have been observed in a variety of 2D layered crystals, such as TMD, topological insulators and black phosphorus.¹¹⁵⁻¹¹⁹ The intense research on decreasing thickness of 2D materials requires more understanding of the layer-dependent properties.

The exploration of new stable monolayers is one of the main directions in the study of 2D materials. New material can provide candidates with various properties for the research of both material science and physics. For example, short-wavelength optoelectronic and intrinsic magnetic applications are still absent in the current 2D atomic crystals.⁴⁵⁻⁴⁶ Exploring atomically thin crystals is not only important for understanding the mechanism of low-dimensional physics but also significant for various potential devices.

Although the number of materials in 2D family is huge, only a few with small cleavage energy that could be exfoliated into monolayer.⁴⁴ Moreover, with a large surface-to-volume ratio, ultrathin layer is not stable due to the strong reactivity with oxygen and water moisture in atmosphere. For example, the phosphorene protected in vacuum chamber only lasts for

several hours during the experiments.¹¹⁵ As a result, most of published works on the monolayer materials are performed by theoretical calculations.^{34, 120} The experimental identification and assessment of new 2D semiconducting thin layers is still one of the main scientific directions and technological objectives.⁵⁰⁻⁵²

As a multinary semiconductor, MPCs have a long history traced back to the nineteenth century, while they have not been comprehensively explored on the atomically thin level.⁵³⁻⁵⁴ The general formulas of MPCs could be represented as $M^{\text{II}}\text{PX}_3$ and $M^{\text{I}}_{1/2}M^{\text{III}}_{1/2}\text{PX}_3$ ($M^{\text{I}} = \text{Cu, Ag}$; $M^{\text{II}} = \text{V, Mn, Fe, Co, Ni, Zn, Cd, Mg}$; $M^{\text{III}} = \text{Cr, V, Al, Ga, In, Bi, Sc, Er, Tm}$; $X = \text{S and Se}$).⁵⁴⁻⁵⁶ Compared with TMDs, where the metal atoms are confined to IVB, VB and VIB, MPCs spread on a wider area of the periodic table due to the rich choices of element composition.⁵⁴ This high chemical diversity and structural complexity induce a variety of interesting and comprehensive properties.⁵¹ For instance, MnPS_3 and FePS_3 are 2D magnetic materials with anisotropic Heisenberg model and Ising model, respectively.⁵⁷⁻⁶⁰ Besides that, CuInP_2S_6 was reported as a 2D ferroelectric material.⁶¹⁻⁶² To the best of our knowledge, in the study on monolayer MPCs, only few calculations have been reported, while the corresponding experimental study is still absent until now.^{45, 83-84}

In this chapter, we report a systematic work on synthesis, crystallization and exfoliation of the bulk crystals of MPCs, including ternary sulfides (MPS_3 , $M = \text{Fe, Mn, Ni, Cd and Zn}$), ternary selenides (MPSe_3 , $M = \text{Fe and Mn}$) and quaternary sulfides (MInP_2S_6 , $M = \text{Cu, Ag}$). Powder X-ray diffraction (PXRD), transmission electron microscopy (TEM), selected area electron diffraction (SAED), atomic force microscopy (AFM), and optical absorption (OA) have been conducted on those as-grown MPCs. Additionally, the cleavage energies (E_{cl}) of MPCs have been calculated and compared with that of graphite.

3.2 Ternary Metal Phosphorus Chalcogenides

The general formulas of ternary MPCs could be represented as $M^{II}PX_3$ ($M^{II} = V, Mn, Fe, Co, Ni, Zn, Cd, Mg$; $X = S$ and Se). In this section, seven ternary MPC compounds, including five sulfides (MPS_3 , $M = Fe, Mn, Ni, Cd$ and Zn) and two selenides ($MPSe_3$, $M = Fe$ and Mn) were synthesized and characterized.

3.2.1 Sample Preparation

Synthesis of Metal Phosphorus Chalcogenides 2D Crystals

Figure 3-1 The optical photos of bulk 2D crystals. They were put on the coordinate paper, where the smallest square is $1\text{ mm} \times 1\text{ mm}$.

The bulk ternary MPCs crystals were synthesized by chemical vapor transport (CVT) in a two-zone furnace.¹²¹ 1 gram stoichiometric amount of high-purity elements following the molar ratio $M: P: X = 1:1:3$, were sealed into a quartz ampoule together with transport agent iodine (about 10 mg). The quartz ampoule is around 160 mm in length and 13 mm in external

diameter. The ampoule with an inside pressure down to 1×10^{-4} Torr was kept in two-zone furnace with the temperature of 650 °C and 600 °C. The temperature ramp-up rate was set as 3.5 °C /min. After heated for one week, the ampoule was gradually cooled down to room temperature (with ramp-down rate ~ 1 °C /min) and flexible plate crystals were found inside the ampoule (Figure 3-1).

Mechanical Exfoliation for Ultrathin Flakes

Figure 3-2 The optical microscopy photographs and the corresponding AFM images of FePS₃ from monolayer to 6 layers.

Though MnPS₃ and CdPS₃ nanosheets have been achieved by liquid exfoliation in previous report,¹²² the direct proofs on thickness of samples have not been provided (except the X-ray diffraction) and the components of sheets in the solution were proved to become Mn_{0.8}PS₃ and Cd_{0.8}PS₃. Moreover, the stability of MPCs monolayer has not been verified in the ambient conditions.

Herein, the feasibility of mechanical exfoliation using Scotch tape has been confirmed to achieve the mono- or few-layer on the Si substrates with 285-nm SiO_2 layer. As an example, FePS_3 from monolayer to 6 layers were obtained and the optical microscopy photographs and corresponding AFM images were shown in Figure 3-2, which indicated the thickness of monolayer was 0.75 ~ 0.80 nm. The samples with different layer-number are distinct on the surface of 285-nm SiO_2 . In the same way, FePSe_3 could be exfoliated into at least tri-layer flakes (Figure 3-3). The thinner samples should be achieved with more effort on exfoliation of FePSe_3 , as well as the other MPCs. This top-down method could provide high quality atomically thin flakes of MPCs for structural, optical and electronic research.

Figure 3-3 The optical microscopy photograph and the corresponding AFM topography of exfoliated FePSe_3 sample.

3.2.2 Characterization of Metal Phosphorus Chalcogenide Crystals

Powder X-Ray Diffraction

Figure 3-4 The PXRDs of the MPC single bulk crystals. The red traces are XRD patterns from MPC single crystals grown in lab, while the blue traces are the standard patterns from database.

The PXRDs of MPCs were directly performed on the as-grown bulk crystals to confirm the phase purity. They were collected by a Bruker D8 Advance diffractometer using $\text{Cu } K\alpha$ radiation ($1.54 \text{ \AA}$) at room temperature. The diffraction patterns distinctly showed the good crystalline quality of the as-grown MPC single crystals with layered structures (Figure 3-4). The diffraction peaks of sulfides could be indexed to the monoclinic structure, while the diffraction peaks of selenides were indexed to the trigonal phase. For the plate-like samples, (001) peaks were preferred orientation in the PXRDs, while the peaks of other orientation were only shown in simulated patterns. The positions of (001) peaks of all measured crystals were in a good agreement with the references (PDF). No peaks of impurities were detected, indicating the high purity of the synthesized single crystal.

Transmission Electronic Microscope

Figure 3-5 Transmission electron microscopy (TEM) images of (a) FePS₃ (zone axis = [002]) and (b) FePSe₃ (zone axis = [211]) flakes. The insets are the selective area electron diffraction patterns (SAED) of corresponding materials.

The exfoliated MPC samples could be transferred from the SiO₂ surface to copper grids by NaOH solution (10% concentration) for TEM measurement. As the representatives of

sulfides and selenides, FePS_3 and FePSe_3 were selected to conduct the TEM and SAED measurement to study their structural symmetry (Figure 3-5a and 3-5b). The TEM images showed clear layered structure with flat surface for both FePS_3 and FePSe_3 . The diffraction patterns exhibited their good crystallinity in accordance with their structural symmetry.

Crystal Structure

Figure 3-6 (a) The arrangement of metal, phosphorus and sulfur or selenium atoms in the plane of MPS_3 (M = Fe, Mn, Ni, Zn and Cd) and MPSe_3 (M = Fe and Mn); (b) the packing structure of MPS_3 ; (c) the packing structure of MPSe_3 ;

On the basis of the matching results of PXRDs, SAED patterns and corresponding crystal structures, the MPCs exhibit two types of packing modes with the similar plane structure (Figure 3-6). As shown in Figure 3-6a, the metal atoms are coordinated with six S atoms, while P atoms are tetrahedral coordinated with three S atoms and one P atom to form a

[P₂S₆]⁴⁺ unit. The [P₂S₆]⁴⁺ units are connected with six Fe atoms, which are arranged in a honeycomb plane structure. The packing structures are different between sulfides and selenides. The layers of the sulfides stack in *C2/m* space group (Figure 3-6b), while those of the selenides stack in *R* $\bar{3}$ (Figure 3-6c). The inter-layer spacing (between two centers of layer) is about 6.42 Å.

Transmission Spectra

Compounds	FePS ₃	MnPS ₃	NiPS ₃	ZnPS ₃	CdPS ₃	FePSe ₃	MnPSe ₃
Bandgap (eV)	1.5	3.0	1.6	3.4	3.5	1.3	2.5

Table 3-1 Reported band gaps of some compounds in MPC family.⁷¹

The band gaps of MPC compounds measured by absorption edge has been reported in the previous papers (Table 3-1).⁷¹ In order to confirm the band gaps of our synthesized MPS₃ (M = Fe, Mn, Ni, Cd and Zn) and MPSe₃ (M = Fe and Mn) single crystals, the optical transmission spectra of this series of compounds were conducted on CRAIC 20 Microspectrophotometer (as shown in Figure 3-7). The abrupt edge on transmission spectra of each material are in accordance with the reported band gaps listed in Table 3-1, as well as the color of corresponding bulk crystals shown in Figure 3-1. The band gaps of those MPCs range from 1.3 to 3.5 eV, which suggest a series of potential candidates for the opto-electronic application with the response in a wide-wavelength range.

Figure 3-7 Transmission spectra of MPS₃ (M = Fe, Mn, Ni, Zn and Cd) and MPSe₃ (M = Fe and Mn).

3.2.3 Theoretical Calculation on MPCs

Figure 3-8 The interlayer distances of MPS₃ (M = Fe, Mn, Ni, Zn and Cd) and MPSe₃ (M = Fe and Mn). The atomic radii of elements are from reference.¹²³⁻¹²⁴

The crystalline structures of MPCs indicate a large van der Waals gap existing between layers in these bulk crystals. The interlayer distances – *d* is defined as the distance between the

centers of two adjacent layers, which is varied from 6.3 Å to 6.7 Å in these compounds (Figure 3-8). The trend of interlayer distances of MPCs is consistent with that of the atomic radius (r) of the containing elements. For example, $d_{\text{MnPS}_3} > d_{\text{FePS}_3} > d_{\text{NiPS}_3}$ agrees with $r_{\text{Mn}} > r_{\text{Fe}} > r_{\text{Ni}}$, and $d_{\text{FePSe}_3} > d_{\text{FePS}_3}$ agrees with $r_{\text{Se}} > r_{\text{S}}$. The interlayer distance, which equals to one-layer thickness plus an interspace of large van der Waals gap, is approximate to the calculated thickness of monolayer on a substrate, which is the sum of one-layer thickness and a van der Waals gap against to the substrate).

Figure 3-9 The original interlayer distance (d_o) and fractured (d). The difference value between them is defined as separation.

The cleavage energies of the compounds in MPC family were calculated using density function theory (DFT) implemented in the Vienna *ab initio* simulation package (VASP).¹²⁵⁻¹²⁶ The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerh of parametrization of the exchange-correlation function was used.¹²⁷⁻¹²⁹ A plane-wave cutoff energy of 500 eV was applied. Van der Waals interaction correction by DFT-D2 method of Grimme was added to the DFT calculations.¹³⁰ The criterion for the total energy convergence

was set as 1×10^{-6} eV. During the simulation, the positions of all atoms were relaxed until the force was less than 0.01 eV/Å.

The separation in the calculation was defined as the difference between the original interlayer distance (d_o) and fractured one (d) as shown in Figure 3-9. The total energy was calculated when the interlayer distance changed. As a result, the cleavage energy as a function of the separation was plotted in Figure 3-10a. In a general trend, the cleavage energy increased with the increasing separation and finally converged at an ideal cleavage cohesion energy. The cleavage energy of graphite was estimated around 0.36 J/m².⁸³ The feasibility of exfoliation on MPC crystals in experiments was evaluated by the comparison of cleavage energy with graphite. The values of cleavage energy in seven MPC compounds, together with graphite were shown in Figure 3-10b. Only FePSe₃ has a slightly larger cleavage energy than that of graphite, while the other compounds have smaller cleavage energies.

Figure 3-10 (a) The cleavage energy (E_{cl}) versus the separation (defined as the difference of interlayer distance before and after fractured); (b) The comparison on the saturated E_{cl} between graphite and the compounds of MPS₃ (pink squares) and MPSe₃ (blue stars). The E_{cl} of graphite and MnPSe₃ are from reference.⁸³

One thing should be noted that the theoretically calculated cleavage energy cannot totally reflect the complexity in actual difficulty of micromechanical exfoliation. For instance, the surface adhesive force, which determined the possibility of combination between substrate and layered sample, was not considered in this theoretical calculation.

3.3 Quaternary Metal Phosphorus Chalcogenides

The general formulas of quaternary MPCs could be represented as $M^{I}_{1/2}M^{III}_{1/2}PX_3$ or $M^IM^{III}P_2X_6$ ($M^{I}_{1/2} = \text{Cu, Ag}$; $M^{III} = \text{Cr, V, Al, Ga, In, Bi, Sc, Er, Tm}$; $X = \text{S and Se}$). In this section, two quaternary MPC compounds, AgInP_2S_6 and CuInP_2S_6 , were selected as the representative to conduct the synthesis and characterization.

3.3.1 Sample Preparation

Synthesis of AgInP_2S_6 and CuInP_2S_6 Crystals

Figure 3-11 The optical images of AgInP_2S_6 and CuInP_2S_6 crystals.

The AgInP_2S_6 and CuInP_2S_6 crystals have been synthesized by chemical vapor transport (CVT) in two-zone furnace.¹²¹ Stoichiometric amount of high-purity elements (mole ratio $\text{Ag/Cu: In: P: S} = 1: 1: 2: 6$, around 1g in total) were sealed into a quartz ampoule with

the pressure of 1×10^{-4} Torr inside the ampoule. The length of the quartz ampoule was about 15~18 cm with the 13 mm external diameter. The ampoule was kept in two-zone furnace with the temperature of 680 and 600 °C for one week. After the furnace was cooled down to room temperature, the flexible plate crystals could be found inside the ampoule (Figure 3-11).

Mechanical Exfoliation

Figure 3-12 (a) The optical microscopy photograph of exfoliated AgInP₂S₆ flakes on 100-nm SiO₂/Si substrates. The optical contrast between AgInP₂S₆ flakes shows the different thickness. (b) Atomic force microscopy (AFM) image of exfoliated AgInP₂S₆ flakes, corresponding to the area of red frame in (a). (c) Height profiles of exfoliated AgInP₂S₆ flakes from bi- to four-layer corresponding to the lines indicated in (b). (d) The AFM image of monolayer AgInP₂S₆

flakes. The insets are the optical microscopy photograph and height profile of the monolayer sample.

Mechanical exfoliation is a popular method to prepare monolayer sample, which is usually carried out on graphite and TMDs. The mono- and few-layer AgInP_2S_6 flakes on Si substrates with 100-nm SiO_2 layer were mechanically exfoliated from the bulk crystal by Scotch tape. The optical microscope photograph and corresponding atomic force microscope (AFM) images of AgInP_2S_6 from mono- to four-layer were shown in Figure 3-12. The thickness of monolayer is ~ 0.80 nm, which is closed to the value of other metal phosphorous sulfides in previous reports.¹³¹

Figure 3-13 (a) The optical microscopy photograph of exfoliated CuInP_2S_6 flakes on 100-nm SiO_2/Si substrates. The optical contrast shows the different thickness of CuInP_2S_6 flakes. (b) AFM image of exfoliated CuInP_2S_6 flakes, corresponding to the area of red frame in (a). (c) Height profiles of exfoliated CuInP_2S_6 flakes corresponding to the lines indicated in (b).

Similar to AgInP_2S_6 , the few-layer CuInP_2S_6 flakes were obtained on same substrates by mechanical exfoliation from the bulk crystal. The optical microscopy photograph, corresponding atomic force microscopy (AFM) images and plots of height for CuInP_2S_6 flakes

were shown in Figure 3-13. The optical contrast between thin samples with different thickness is distinct on the surface of 100-nm SiO₂.

3.3.2 Characterization of AgInP₂S₆ and CuInP₂S₆ Crystals

Figure 3-14 PXRDs of (a) AgInP₂S₆ and (b) CuInP₂S₆ crystals. TEM images of (c) AgInP₂S₆ and (d) CuInP₂S₆ flakes. The insets are the SAED patterns of corresponding materials.

From the comparison of (00l) peak positions, the experimental powder X-ray diffraction (PXRD) of AgInP₂S₆ agreed with the simulated one from crystal structure of ICSD 202185 well with $P\bar{3}1c$ space group (Figure 3-14a), while pattern of CuInP₂S₆ was in good agreement with the simulated data from crystal structure of ICSD 79219 with Cc space group. As described in Section 3.2.2, the diffraction peaks of other orientation were only shown in

simulated patterns, due to the orientated preference of the measured sample. No peaks of impurities were detected, indicating the high purity of the synthesized single crystal. The flakes of these two compounds were transferred to Cu grid in the same method mentioned above to carry out the TEM and SAED measurements. Both TEM images of AgInP_2S_6 and CuInP_2S_6 showed clear layered structure with flat surface (Figure 3-14c and d). SAED patterns shown in the inset also confirmed the corresponding crystal symmetry.

As shown in Figure 3-15, Ag and In atoms are six coordinated with S atoms. P atoms are tetrahedral coordinated to form a binuclear $[\text{P}_2\text{S}_6]^{4-}$ cluster ($[\text{P}_2]$), which are located in the center of hexagon composed by alternative three Ag atoms and three In atoms. In monolayer AgInP_2S_6 , the metal (Ag and In) layers are sandwiched by two layers of S atoms, while the $[\text{P}_2]$ pairs act as stanchions inside the layer. The $[\text{P}_2]$ pairs and Ag atoms stack alternately in the nearby two layers. In multilayer AgInP_2S_6 , the neighboring layers are coupled by van der Waals interactions.

Figure 3-15 Schematic in-plane and packing structure of layered AgInP_2S_6 crystal.

In the plane structure of CuInP_2S_6 , the In, P and S atoms distribute in the similar positions as they are in AgInP_2S_6 . The layers of CuInP_2S_6 also stack in AB sequence along c

axis. The largest difference of lattice structure of CuInP_2S_6 comes from the Cu hopping motion, which induces the noncentrosymmetry to this material. The Cu^{I} ion will hop between upper and lower site with a certain probability, which can be varied with temperature changing. The disorder of Cu atoms in these two positions would induce interesting physic properties of CuInP_2S_6 ranged from bulk crystal to flake with atomic thickness.

Figure 3-16 Schematic in-plane and packing crystal structure of layered CuInP_2S_6 crystal.

Similar to the result on ternary MPCs, the cleavage energy of AgInP_2S_6 and CuInP_2S_6 as a function of the separation was plotted in Figure 3-17 according to the theoretical calculation of total energy. The cleavage energy increased and gradually converged at the cleavage cohesion energy when the separation increased. The values of cleavage energy of AgInP_2S_6 and CuInP_2S_6 are both around 0.20 J/m^2 , which is lower than that of graphite (0.36 J/m^2).⁸³ This result indicates that both AgInP_2S_6 and CuInP_2S_6 are the excellent candidates in various studies on ultrathin layers of quaternary MPC family.

Figure 3-17 The cleavage energy (E_{cl}) vs. the separation of AgInP_2S_6 and CuInP_2S_6 .

3.4 Summary

In summary, we have explored a new family of 2D semiconductors – MPCs. Particularly, the bulk crystals of ternary sulfides (MPS_3 ; $\text{M} = \text{Fe}, \text{Mn}, \text{Ni}, \text{Cd}$ and Zn), ternary selenides (MPSe_3 ; $\text{M} = \text{Fe}$ and Mn) and quaternary sulfides (MInP_2S_6 ; $\text{M} = \text{Cu}$ and Ag) were successfully synthesized by CVT methods. The mono- or few- layer of several typical representatives have been obtained by mechanical exfoliation and characterized on a variety of structural properties. The band gaps of those MPCs have been verified by transmission spectroscopy, while their cleavage energies have been calculated to prove their promising capability to form monolayer. In contrast to TMDs, the wide-range band gaps of MPCs from 1.3 to 3.5 eV suggest their optoelectronic applications in broad wavelength range. Therefore, the monolayers are the perfect candidates for exploration of the novel artificial compounds by Van der Waals stacking. In addition, the presence of magnetic metal atoms (Fe , Mn and Ni) allows us to study the magnetic properties in atomically thin 2D materials, and the hopping

motion of Cu atoms offer us an interesting platform to investigate how the ferroelectricity varies when the system decreases from bulk to 2D region.

Chapter 4 Lattice Dynamics Property in Two-Dimensional Ternary Metal Phosphorus Chalcogenide Crystals

4.1 Introduction

MPCs are good examples of 2D semiconductor with a variety of unique properties, such as magnetism and ferroelectricity. The magnetic,^{72-73, 132} optical,¹³³⁻¹³⁴ and structural properties^{71, 135} of both pure and intercalated MPCs have been investigated in the past three decades.

Light scattering in MPCs systems has become an attractive field of research since 1980's. Lattice dynamics of the materials in this family has been investigated to explore the structural information by infrared and Raman spectroscopy.^{63, 136-137} For example, spin-dependent Raman scattering in FePS₃ crystal has been reported with intense discussion on a correlation between the Raman tensor and the antiferromagnetic order.¹³⁸ The Raman spectra of a variety of compounds were measured with good spectral resolution on single crystals. The polarization dependent Raman spectra were performed for the help to distinguish the assignment of vibrational modes.

Despite the complex unit cell of MPCs, most of analysis on phonon modes is interpreted in a simplified way.^{136, 138} The unit cell is considered as a pseudo-cell constituted by metal cations and a [P₂X₆]⁴⁻ anion. Therefore, the phonon modes of MPCs are considered from two parts – intramolecular modes and metal atom related modes.³⁷ This interpretation requires much stronger internal bond interactions of [P₂X₆] (P-X, P-P and X-X) than metal-related bonds interactions (M-P and M-X). This assumption is simply on the basis of a

molecular picture of these compounds. However, several theoretical calculations on band-structure of MPCs show that the covalent contribution to the M-S bond in MPS_3 is not negligible.^{77, 139} For example, it has been pointed out that the M-S interaction plays an important role in determining the electronic structure around the Fermi level.⁷⁷ As a consequence, the Raman modes of MPCs could not be properly assigned by the pseudo-cell model, especially in the low-frequency region ($< 200 \text{ cm}^{-1}$), where the internal normal modes of the $[\text{P}_2\text{X}_6]$ group cannot be separated from the dynamics of metal ions.

For these reasons, it is significant to analyze and assign the Raman modes on the premise of considering the whole MPCs primitive cell to acquire structural and optical information more accurately. A lattice-dynamics calculation based on a whole MPCs primitive cell has been performed using an axially symmetric force-constant model, which corrects the misleading attributions from the molecular model and provides an interpretative scheme for the vibrational spectra.⁶³ The calculated phonon dispersion curves for a set of significant materials are presented and discussed together with Raman spectroscopy. A large number of experimental and calculated studies have been done on the MPCs single crystal. As a 2D layered material, MPC offers an excellent platform to reduce the dimension of system. The investigation of various properties on ultrathin MPCs material is rarely explored, while it is worth filling in the gaps here.

Since the identification and assessment of new 2D semiconductors with stable monolayers or a few-layers is still a main scientific direction and technological objective, here we conducted Raman spectroscopy measurement on MPCs single crystal from bulk to atomically thin samples, which were obtained by micromechanical exfoliation, to investigate the structural property and lattice dynamics in 2D system. A qualitative explanation of the

dynamical behaviors of those materials was obtained to motivate further fundamental physical study, as well as the potential optical and optoelectronic 2D device based on this family of materials.

4.2 Raman Spectra of Metal Phosphorus Chalcogenides

4.2.1 Raman Spectra of Metal Phosphorus Chalcogenides in Bulk Crystal

To study the lattice dynamics of MPCs, Raman spectroscopy measurements were conducted with the excitation of 532-nm laser at both room temperature (296 K) and liquid nitrogen temperature (77 K). Seven ternary MPC single crystals, including five kinds of sulfides (FePS_3 , MnPS_3 , NiPS_3 , ZnPS_3 and CdPS_3) and two kinds of selenides (FePSe_3 and MnPS_3), was placed on the Si wafer with 285-nm SiO_2 . The laser beam was collimated and focused thorough a 50 $\times$ objective (low temperature $\sim 77\text{K}$) onto the sample surface. All of the spectra were collected using a confocal triple-grating spectrometer (Horiba-JY T64000). The Raman spectra were shown in Figure 4-1 and 4-2.

Figure 4-1 The Raman spectra of metal phosphorus trisulfides bulk crystals ((a) FePS₃, (b) MnPS₃, (c) NiPS₃, (d) ZnPS₃, and (e) CdPS₃) with 532 nm laser excitation at room temperature (296 K, black line) and low temperature (77 K, red line).

Figure 4-2 The Raman spectra of metal phosphorus triselenides bulk crystals ((a) FePSe_3 and (b) MnPSe_3) with 532 nm laser excitation at room temperature (296 K, black line) and low temperature (77 K, red line).

As shown in Figure 4-1, the Raman spectra of the sulfides of MPCs exhibited a similar structure in high-frequency region ($> 150 \text{ cm}^{-1}$), while large differences on Raman modes were observed in low-frequency region ($< 150 \text{ cm}^{-1}$) with the metal cation substitution. This effect support the early simplified picture, where the Raman modes of MPCs could be considered as originating from two parts of the structure.^{136, 138} In this picture, the Raman modes related to metal cations are mainly observed in low-frequency region, while the normal modes from $[\text{P}_2\text{S}_6]^{4-}$ anion, which belongs to the D_{3d} symmetry group, are observed in high-frequency region. More specifically, four modes located around 230 cm^{-1} , 250 cm^{-1} , 280 cm^{-1} and 380 cm^{-1} , which were observed in the Raman spectra of all the sulfides, were adequately attributed to the vibrational modes of $[\text{P}_2\text{S}_6]^{4-}$ anion. Besides, two weak features were observed from 550 cm^{-1} to 600 cm^{-1} in MnPS_3 , NiPS_3 and ZnPS_3 , while they degenerated to one structure in FePS_3 and CdPS_3 . The corresponding assignment of those Raman modes will be discussed in the following section in this chapter. Moreover, two or three Raman peaks were detected below

150 cm^{-1} in MPCs, while those modes blue shifted as the mass of metal cation increased, implying that they were strongly related to the vibration of M-P or M-S bonds.

Compared to sulfides, the Raman modes shown in the spectra of selenides (Figure 4-2) systematically shift to lower frequency. FePSe_3 and MnPSe_3 exhibit a quite similar Raman spectrum with five peaks located at relatively same positions (75 cm^{-1} , 120 cm^{-1} , 149 cm^{-1} , 170.8 cm^{-1} and 217 cm^{-1}), while a mode located at 160 cm^{-1} was observed only in MnPSe_3 . Similar to the sulfides, the Raman modes in high-frequency region are attributed to the internal vibrations from $[\text{P}_2\text{Se}_6]^{4-}$ anion. The three strong modes located at 149 cm^{-1} , 170.8 cm^{-1} and 217 cm^{-1} in selenides are assigned as the same geometry of the modes at 230 cm^{-1} , 280 cm^{-1} and 380 cm^{-1} in sulfides with the assistance of polarized Raman spectroscopy.¹³⁸

From the comparison between the Raman spectra at room temperature (296 K) and low temperature (77 K) of each compounds, several differences, such as enhancement or quenching on intensity of Raman peaks, are observed. Those differences are mainly caused by lattice dynamics affected by the thermal effect, while some of the differences are induced by more interesting physical mechanism. For example, two peaks located at 30 cm^{-1} and 190 cm^{-1} are found in the spectrum of CdPS_3 only at low temperature rather than room temperature, which is possibly attributed to the structural phase transition occurring at 295 K. A dramatic change was also detected in the low-frequency region of Raman spectra of antiferromagnetic material FePS_3 , which would undergo a magnetic phase transition between paramagnetic phase and antiferromagnetic phase. However, no noticeable change was observed on the Raman spectra between antiferromagnetic and paramagnetic phase in other magnetic compounds, such as FePSe_3 , MnPS_3 , MnPSe_3 and NiPS_3 , because this effect was strongly dependent on the

magnetic order of FePS₃. The details of Raman spectroscopy related to the spin-order and magnetism will be discussed in next chapter.

4.2.2 Raman Spectra of FePS₃ and FePSe₃ Few-Layer Samples

Despite that Raman spectroscopy has been intensively studied in MPCs bulk crystal, the corresponding research area of the atomically thin samples is not explored yet, where new physics may be uncovered in low dimensional system. Regarding the similar behaviors in Raman spectra, two compounds, FePS₃ and FePSe₃, were selected to represent MPS₃ and MPSe₃ for further investigation in atomically thin 2D system.

The fresh FePS₃ and FePSe₃ flakes were mechanically exfoliated on Si wafer with 285-nm SiO₂ layer. The Raman spectroscopy was conducted at 77 K excited by 532-nm laser. According to the simple molecular picture of MPCs, the Raman modes of FePS₃ and FePSe₃ come from two parts of the structure.^{136, 138} The Raman modes with relatively low frequency (<150 cm⁻¹), such as 88 cm⁻¹ and 95 cm⁻¹ peaks in FePS₃ and 73 cm⁻¹ and 117 cm⁻¹ peaks in FePSe₃, mainly involve with the metal atom vibrations. In contrary, other modes with frequency higher than 150 cm⁻¹ originate from the vibrations of [P₂X₆]⁴⁻ anion, which belongs to D_{3d} symmetry group. Six Raman active modes, three polarized modes (*A_{1g}*) and three depolarized modes (*E_g*), are expected in D_{3d} symmetry group (as shown in Figure 4-3).

Figure 4-3 Six Raman modes of $[P_2X_6]^{4-}$ anion (D_{3d})

From the low-temperature Raman spectra of $FePS_3$, the modes at 160 cm^{-1} (Raman counterpart of E_u), 229 cm^{-1} (E_g), 281 cm^{-1} (E_g), and 381 cm^{-1} (A_{1g}) were resolved in both the bulk and monolayer sample (as shown in Figure 4-4a). The corresponding modes, which located at 149 cm^{-1} (E_g), 170.8 cm^{-1} (A_{1g}), and 217 cm^{-1} (A_{1g}), could be found in both the bulk and tri-layer $FePSe_3$ samples (as shown in Figure 4-4b). As the thickness decreased, no

noticeable shift of Raman modes is observed in the Raman spectra (Figure 4-4). This phenomenon is different from that in the layer-number-dependent Raman spectroscopy of TMDs, where several interlayer shear modes and breathing modes dramatically change in the few-layer region.^{116, 119}

Figure 4-4 The Raman spectra of FePS₃(a) and FePSe₃ (b) with 532 nm laser excitation at liquid nitrogen temperature (77 K). The green lines in the Raman spectra are the curves fitted by a Lorentzian function, while the red lines are the sum of fitting curves.

4.2.3 Stability of Metal Phosphorus Chalcogenides by Raman Spectra

In Figure 4-4, the exfoliated monolayer FePS₃ and trilayer FePSe₃ were kept in ambient conditions over 24 h before the Raman measurement. The Raman spectra showed completely the same features, suggesting that the ultrathin FePS₃ and FePSe₃ can maintain stable structure in ambient condition.

Figure 4-5 The Raman spectra of (a) FePS_3 , (b) MnPS_3 , (c) NiPS_3 , (d) ZnPS_3 , (e) CdPS_3 , (f) FePSe_3 and (g) MnPSe_3 with 532 nm laser excitation at liquid nitrogen temperature (77 K). The blue curves are the Raman spectra of bulk sample, while the red curves are the spectra of flakes. The peak at $\sim 520 \text{ cm}^{-1}$ is due to the TO phonon scattering from silicon substrate.

In order to further confirm the stability of MPC sample, we conducted a series of contrast experiment on all the synthesized ternary MPCs. Firstly, the Raman spectroscopy measurement was conducted on MPC bulk crystals at 77 K (Figure 4-5); Secondly, after the measurement, all the MPC crystals had been stored in dry box, which could be treated as in ambient conditions, for half year; Thirdly, the MPC crystals was exfoliated to the thin flakes with the thickness ranging from 10 to 20 nm, and they were stored in dry box for 3 days; Finally, the Raman spectra of the MPC flakes were collected (Figure 4-5). From the comparison for each compound, Raman spectra of flakes showed the approximately same features with the spectra of crystals. This result demonstrated that the bulk and exfoliated ternary MPCs can maintain stable structure in ambient condition for a relative long time, which is enough for conducting various research on both bulk and exfoliated samples. Since the stability is a critical

point in the research of 2D materials,⁴⁴ the stable structure can provide us the solid sample to study the fundamental physics, including a variety of studies on optics, electronics, and magnetism.

4.3 Raman Spectra of Iron Phosphorus Trisulfides

As mentioned in the introduction part, the theoretical calculations on band-structure of MPCs show that the covalent contribution to the M-S bond in MPS_3 is not negligible.^{77, 139} Therefore, it is necessary to accurately analyze and explain the experimental data in Raman study considering the MPCs primitive cell as a whole. In this section, more specific and systematical study of Raman spectroscopy on FePS_3 , as a typical example of MPCs, has been conducted in both bulk and atomically thin samples. The phonon dispersion curves have been calculated by first-principle density-functional theory (DFT).

4.3.1 Raman Spectra of FePS_3 with Different Excitation Wavelength

The Raman spectra of FePS_3 samples were measured with different excitation lasers. From the absorption spectrum of FePS_3 bulk sample, the absorption edge was around 800 nm. Based on this result, four excitation lasers with different wavelength shorter than 800 nm (473 nm, 532 nm, 633 nm, and 785 nm) ranging from visible to near infrared (NIR) region were selected. The excitation power was kept below 1 mW to avoid the possible heating effect from laser.

The interference in thin film case can be given by $nd = (2k - 1)\lambda/4$ for enhancement case, while $nd = k\lambda/2$ for quenching case, where the n is the refraction index of material; d is the thickness of film; λ is the light wavelength and k is a positive integer. Therefore, when we only consider the interference between the top and bottom interface of SiO_2 layer, the

calculated enhanced wavelengths are 554.8 nm and 332.9 nm, while the quenched ones are 416.1 nm and 832.2 nm.

Figure 4-6 (a) Absorption spectrum of FePS₃ bulk crystal at room temperature (296 K). (b) The Raman spectra of FePS₃ thick flake (70 nm) in different excitation (473-nm at 0.39 mW, 532-nm at 0.54 mW, 633-nm at 0.51 mW and 785-nm at 1.02 mW).

From the excitation-wavelength dependent Raman spectra of FePS₃ thick flake (as shown in Figure 4-6), the 532-nm excitation gives us the best intensity and resolution in Raman spectroscopy measurement with the competition of absorption of FePS₃ film and interference from SiO₂ layer. The spectrum excited by 633-nm laser was slightly weaker, attributed to both the weaker absorption and less enhancement from interference. Fewer Raman modes of FePS₃ were observed when excited by 473-nm laser, probably due to the absence of enhancement induced by interference. Only Raman modes of Si wafer substrate were detected with the excitation of 785-nm laser, which is close to the absorption edge of the sample.

4.3.2 Thickness-Dependent Raman Spectra of FePS₃

Figure 4-7 Thickness-dependent Raman spectra of FePS₃ obtained with different excitation wavelength powered ~0.5 mW at 296 K.

Thickness-dependent Raman spectra of FePS₃ flakes was conducted with different excitation wavelengths with a power of ~0.5 mW at 296 K (as shown in Figure 4-7). The Raman spectra excited by 473-nm laser showed a clear structure at 380 cm⁻¹ even in the sample

with thickness around 1 nm, while the other modes were relatively weak and hard to be detected in the sample thinner than 10 nm. When the excitation was changed to 633-nm laser, the Raman modes in low-frequency part were more effectively excited compared with that excited by 473-nm laser. The strongest signal came from the modes located at the 380 cm^{-1} with these two excitation. In contrast, the Raman spectra excited by 532-nm laser exhibited a much better result on efficiency, especially for the modes in low-frequency region. The relative intensity of the mode at 380 cm^{-1} became weaker. Six Raman peaks, whose values were shown in Table 4-1, could be resolved in the spectrum of thick sample ($> 10\text{ nm}$). With decreasing thickness of sample, only few strong modes (at 100 cm^{-1} , 280 cm^{-1} and 380 cm^{-1}) could be observed in 3-nm sample, while they were not detected in 1-nm sample. The strong peak located at 521 cm^{-1} in all spectra and the weak feature located at 302 cm^{-1} in the spectra of thin samples were from silicon substrate.

Figure 4-8 Raman spectra of FePS₃ 3-layer (a) and bulk (b) sample obtained with an excitation wavelength of 532 nm and power $\sim 0.5\text{ mW}$ at 293 K.

In order to clearly investigate the Raman spectroscopy of FePS₃, we increased the integral time to obtain more distinct Raman peaks in both few-layer and bulk samples. Raman spectra for few-layer and bulk FePS₃ samples at room temperature (293 K) were shown in Figure 4-8. Five and seven Raman peaks, whose values were shown in Table 4-1, could be resolved in the tri-layer and bulk samples, respectively.

As we mentioned in last section, the simplification of pseudo-cell did not fit well for the case of FePS₃ due to the strong Fe-S bond.⁶³ As a consequence, several experimental results, such as the missing $A_{1g}(\nu_3)$ mode of $[\text{P}_2\text{S}_6]^{4-}$ anion and the assignment of 150 cm⁻¹ peak, could not be explained sufficiently with this assumption. It is thus significant to assign the Raman modes in FePS₃, by considering the FePS₃ unit cell as a whole.

4.3.3 Polarization Dependent Raman Spectra of FePS₃ Flakes

The bulk FePS₃ crystal belongs to $C_{2/m}$ symmetry group, which is expected to have 30 irreducible zone-center phonon modes denoted by $\Gamma = 8A_g + 6A_u + 7B_g + 9B_u$, among which A_g and B_g are Raman active modes. The corresponding Raman tensors are,¹⁴⁰

$$A_g: \begin{pmatrix} a & 0 & d \\ 0 & b & 0 \\ d & 0 & c \end{pmatrix} \quad (4-1)$$

$$B_g: \begin{pmatrix} 0 & e & 0 \\ e & 0 & f \\ 0 & f & 0 \end{pmatrix} \quad (4-2)$$

The experimental scattering geometries in Raman spectroscopy can be described by the Porto notations.¹⁴¹ In our back-scattering geometry, $\bar{z}(xx)\bar{z}$ and $\bar{z}(xy)\bar{z}$ correspond to parallel and perpendicular polarization configurations, respectively. Therefore, the polarization

dependence of the Raman active modes can be predicted. The A_g modes can only be observed under parallel $\bar{z}(xx)z$ configuration, while the B_g modes can only be observed under cross $\bar{z}(xy)z$ configurations.

Figure 4-9 Polarization-dependent Raman spectra of 10 nm thick FePS₃ sample obtained with an excitation wavelength of 532 nm and power of ~ 0.5 mW at 293 K.

Since the A_g and B_g modes exhibit different behavior on polarization, polarization-dependent Raman study was carried out to distinguish the modes of FePS₃. In Figure 4-9, the peaks at 248 and 381 cm⁻¹ were clear in $\bar{z}(xx)z$ configuration, while they were suppressed significantly in $\bar{z}(xy)z$ configuration. Therefore, they are assigned to the A_g modes.¹³⁶ However, the Raman peaks at 100, 150, 230, 280 and 564 cm⁻¹ could be observed in both parallel $\bar{z}(xx)z$ and cross $\bar{z}(xy)z$ polarization configurations. The insensitiveness to polarization means one cannot attribute those peaks to either pure A_g or B_g modes.

Experimental Data				Calculation Data	
Bulk		Trilayer		Value [cm ⁻¹]	Assignment
293 K [cm ⁻¹]	77 K [cm ⁻¹]	293 K [cm ⁻¹]	77K [cm ⁻¹]		
564	565			585, 564	<i>A_g, B_g</i>
378	381	381	382	372	<i>A_g</i>
277	283	279	283	299, 294	<i>A_g, B_g</i>
246	249			258	<i>A_g</i>
224	231	227	231	214, 234	<i>A_g, B_g</i>
156	160	157	160	172, 173	<i>A_g, B_g</i>
100		100		102 ^{b)}	
	95		95	95 ^{a)}	
	88		88	86 ^{a)}	

^{a)} Branch on M point; ^{b)} Branch on K point.

Table 4-1 Raman shifts at room and liquid nitrogen temperature of bulk and trilayer FePS₃ sample. The assignment in terms of normal modes and the values were calculated by first-principles calculations.

4.3.4 First Principles Calculations of Phonon Modes

Figure 4-10 Calculated phonon dispersion relations of FePS₃.

To further explore the origin of all the Raman modes shown in the spectra, a first-principle study on the phonon dispersion was performed. As shown in Figure 4-10, several dispersionless phonon branches were found above 380 cm^{-1} . They were contributed by the vibrations in the P_2S_6 group, involving P-S and P-P bond stretching. However, the branches at lower frequencies were largely dispersed along the directions between high symmetric points. Thirty branches were observed at the Γ point, in accordance with the number of modes in the C_{2h} point group. After the normal modes were analyzed, the assignment of modes and frequencies were shown in Table 4-2. The Raman modes observed at the high frequencies ($> 130\text{ cm}^{-1}$) in our experiment agree with the calculated branches at the Γ point within experimental accuracy. The two polarized peaks at 248 and 381 cm^{-1} correspond to the A_g branches at 258 and 372 cm^{-1} , which are attributed to the symmetric stretching vibration of the P-S bonds. The other peaks shown in the Raman spectra, located at 150 , 230 , 280 and 564 cm^{-1} , could be observed in both $\bar{z}(xx)z$ and $\bar{z}(xy)z$ configurations. This symmetry property is similar to E modes' and it could be explained by the origin of the pairs of quasi-degenerate A_g mode and B_g mode. This explanation could be supported by our calculations. In bulk crystal, a weak structure was observed at 564 cm^{-1} , which could be attributed to the intra-molecular vibrations of the P_2S_6 group, while the other three modes are related to the Fe-S bonds. The Fe-S bond stretching dominates the peaks centered at 230 and 280 cm^{-1} , whereas the Fe-S tangential force influences the modes at 150 cm^{-1} . Raman spectra of other metal phosphorus trisulfides at high frequencies ($> 130\text{ cm}^{-1}$) had similar structures.¹³⁶ On the other hand, the lower frequency Raman peaks exhibited a larger difference when the metal cation is different,¹³⁶ indicating a greater influence from the metal atom vibration. As shown in Fig. 3a, the high frequency Raman modes exhibited a slight blue shift within 3 cm^{-1} at room temperature as the sample

thickness was decreased to three layers, while almost no difference in frequency was observed at low temperature (77 K) (Table 1). Negligible change on the shift of frequency with temperature and layer number supports our conclusion that the modes are attributed to the intra-layer vibration.

Wave Number [cm ⁻¹]	Assignment	Wave Number [cm ⁻¹]	Assignment	Wave Number [cm ⁻¹]	Assignment
0	<i>B_g</i>	216	<i>A_u</i>	304	<i>B_u</i>
0	<i>B_u</i>	232	<i>B_u</i>	328	<i>B_u</i>
0	<i>B_u</i>	234	<i>B_g</i>	328	<i>B_g</i>
143	<i>A_g</i>	258	<i>A_g</i>	372	<i>A_g</i>
172	<i>A_g</i>	261	<i>B_g</i>	416	<i>B_u</i>
173	<i>B_g</i>	292	<i>A_u</i>	539	<i>A_g</i>
180	<i>B_u</i>	294	<i>A_u</i>	542	<i>A_u</i>
211	<i>A_u</i>	294	<i>B_g</i>	558	<i>B_u</i>
212	<i>B_u</i>	298	<i>A_u</i>	564	<i>B_g</i>
214	<i>A_g</i>	299	<i>A_g</i>	585	<i>A_g</i>

Table 4-2 Calculated phonon modes and their assignments at the Γ point of the bulk FePS₃ sample

4.3.5 Excitation-Power Dependent Raman Spectra of FePS₃

Since it is the first Raman study carried on FePS₃ thin flakes, the thermal effect from laser would be considered in the further measurement. The laser power was kept around 0.5 mW in the measurements of this chapter to minimize the heating effect, except in the specially intended cases, such as the following excitation-power dependent measurement.

Here we roughly investigated the thermal effect from excitation laser using the optical method. Since Raman spectroscopy studies the lattice vibration of material, intensity, peak position, and full width at half maximum (FWHM) of the Raman modes can be used to detect

the variation of sample's temperature. To minimize the influence of fitting error, we chose the two strong Raman modes, which located at 280 cm^{-1} and 380 cm^{-1} , as the temperature probes.

Figure 4-11 (a) Temperature-dependent Raman spectra of few-layer FePS_3 sample obtained with an excitation wavelength of 532 nm and power of $\sim 0.5\text{ mW}$. The plot of (b) peak position and (c) integral intensity of two Raman modes (located at 280 cm^{-1} and 380 cm^{-1}) versus temperature.

The temperature dependent Raman spectra were conducted above 130 K for calibration (as shown in Figure 4-11a). Two peaks blue shifted as temperature decreased due to lattice

contraction (Figure 4-11b). The integral intensity of Raman peaks did not greatly change with temperature changing (Figure 4-11c). When temperature increased, the integral intensity increased under 200 K, while decreased above 200 K.

Figure 4-12 (a) Excitation-power dependent Raman spectra of few-layer FePS₃ sample obtained with an excitation wavelength of 532 nm at room temperature. The plot of (b) peak position and (c) integral intensity of two Raman modes (located at 280 and 380 cm⁻¹) versus excitation laser power.

The excitation-power dependent Raman spectra (Figure 4-12a) prove that 0.5 mW is a “safe” power. From the comparison of Figure 4-11b and Figure 4-12b, the peak position of Raman modes does not show appreciable shift when the excitation power was below 3 mW, indicating that no serious heating effect in this power region. As shown in Figure 4-12c, Raman intensity was linearly dependent on the excitation power below 2.5 mW. When the excitation power was over 2.5 mW, the Raman intensity lost the linear dependence on the excitation power, partially due to the heating effect participating in this region. As a consequence, the higher temperature results in a lower intensity of Raman peak. Therefore, 0.5 mW was considered as a safe power, which could minimize the heating effect during the experiment.

4.4 Summary

The Raman spectroscopy of seven bulk compounds of MPC was investigated with the interesting lattice dynamical properties and analyzed considered as a pseudo-cell constituted by metal cations and a $[P_2X_6]^{4-}$ anion. Moreover, as the representative of sulfides and selenides, ultrathin $FePS_3$ and $FePSe_3$ layers were chosen to for further Raman spectroscopy measurement, which suggests strong intralayer vibrations and structure stability of the atomically thin MPCs. It is the first time that the Raman study of mono- and few-layer MPC sample is reported.

Beyond that, a systematic study was performed in atomically thin $FePS_3$ with an analysis based on the consideration of whole primitive cell. The phonon dispersion relations of $FePS_3$ calculated using the density-functional perturbation theory (DFPT) reached a satisfactory agreement with the measured Raman spectra at room temperature. The polarization dependent Raman spectra in a backscattering geometry was conducted to help on the

assignments of modes. We believe that the study on lattice dynamics on FePS_3 should also be applicable to other compounds of the MPCs family due of the similar crystal structure and optical properties.

Furthermore, a variety of properties in MPCs can be investigated based on the Raman spectroscopy. For example, the spin-phonon coupling in FePS_3 can be explored by spin-dependent Raman spectra. We hope that this work on Raman spectroscopy will motivate further studies on both fundamental physics and future applications based on atomically pure or intercalated MPCs.

Chapter 5 Spin-Phonon Coupling in Atomically Thin Two-Dimensional Magnetic Crystals

5.1 Introduction

5.1.1 Magnetism in 2D Materials

The dimensionality of a physical system is a critical parameter in determining properties. Most of the studies on magnetism were focused in 3D materials, while the magnetism of natural 2D materials is mostly investigated by theoretical calculation and simulation. The magnetic 2D materials offer the researchers a good platform to explore the interplay between the dimensionality of the lattice and the spins involved properties, such as Ising, spin dimensionality, and magnetic phase transition.

Weak Ferromagnetism in MoS₂

Most of the common 2D materials, such as graphene and TMDs, are not magnetic. It is hard to produce a magnetic behavior in these materials, because no unpaired electron or non-filled subshells exist in the electron configuration of the atoms. However, the magnetic properties can be generated in several special cases. For example, the magnetism can be induced in MoS₂ nanosheets due to the presence of magnetic edge states,¹⁴² while in MoS₂ single crystals it is attributed to zigzag edges at grain boundaries.¹⁴³

Figure 5-1 (a) Magnetic MoS₂ nanosheets induced by the presence of magnetic edge states.¹⁴² (b) Strain-induced magnetism in single-layer MoS₂.⁴⁶ (c) Magnetization *versus* field curve at 300 K (upper) and at 10 K (lower) for a pristine and irradiated MoS₂ after subtracting the substrate Si contribution.¹⁴⁴

Besides that, when exposed to a proton beam, MoS₂ is also found to show magnetic ordering at room temperature, which is attributed to a combination of point defects and edge states.¹⁴⁴ Theoretical calculations also provide evidence for magnetic ordering at edges of nanoribbons and nanoflakes, as well as defect and dopant-induced magnetism.¹⁴⁵

Metal Phosphorous Chalcogenides (MPCs)

To study the magnetic properties in 2D system, the materials with unpaired electrons would be the excellent candidates. According to the exchange interaction rule, a general feature of magnetic materials is that they contain some magnetic elements, such as iron (Fe), nickel

(Ni), cobalt (Co), chromium (Cr) or Manganese (Mn). As a relatively new family of 2D materials, MPCs with weak van der Waals force shows their potential in the field of magnetic property and ultrathin spintronic devices.

In MPCs, several compounds, such as FePS₃, MnPS₃ and NiPS₃, are good examples of 2D antiferromagnetic materials with the magnetic ions arranged in a honeycomb lattice. A magnetic phase transition from the paramagnetic phase to antiferromagnetic phase occurs in a certain temperature – Néel temperature. As we have performed in Chapter 3 and Chapter 4, atomically thin MPCs sample can be obtained by mechanical exfoliation on SiO₂ substrate. This result offers the researcher an excellent opportunity to investigate the magnetic properties in 2D materials, where new physics would occur due to the lower dimension. Moreover, the low dimensionality in 2D magnetic materials provides us the opportunity to distinguish between the intra-layer and the inter-layer magnetic interactions. However, most of the measuring techniques, such as magnetic susceptibility,²⁰ neutron diffraction³² and x-ray diffraction,¹³² could only access macroscopic magnetic properties, thus they are not suitable for the few-layer samples, partially due to the weak signal of magnetic properties. Raman spectroscopy provides a powerful technique to probe the phonon and electronic properties down to monolayer regime. Beyond that, a great number of studies have been carried out on the electronic or magnon Raman scattering in magnetic compounds.¹⁴⁶ For example, several studies on spin properties in various systems using Raman spectroscopy were reported based on spin-phonon coupling and quasi-elastic scattering.¹⁴⁷⁻¹⁴⁸

Moreover, the investigation on the interaction between spin properties and electron-phonon coupling is significant for various research areas, such as the iron-based superconductors.¹⁴⁹⁻¹⁵⁰ The study on the coupling among spin, phonon, and electron in iron-

based materials may provide key insight to understand and develop the mechanism of non-BCS-theory superconductivity.

5.1.2 Spin-Order-Induced Phonon Raman Scattering

The spin-dependent Raman scattering has been discussed theoretically in previous literatures.¹⁵¹⁻¹⁵⁴ The Raman scattering $I(\omega)$ related to the electronic susceptibility is expressed as,

$$I(\omega) = \frac{\hbar^4}{2\omega^3} \sum_{a,b,a',b'} E_a^s E_b^s E_b^i E_a^i \frac{1}{2\hbar} \int_{-\infty}^{+\infty} e^{-i\omega t} \langle \hat{S}_{b,a}(t) \hat{S}_{a,b}(0) \rangle dt, \quad (5-1)$$

$$\hat{S}_{b,a}(t) = e^{\frac{itH}{\hbar}} \hat{S}_{b,a} e^{-\frac{itH}{\hbar}}, \quad (5-2)$$

$$\hat{S} = \hat{S}_\uparrow - \hat{S}_\downarrow. \quad (5-3)$$

Where E_a^i and E_a^s are the polarization vector component of the incident and scattered photon; ω_i and ω_s are the frequencies of the light; c is the light velocity; H is the Hamiltonian; the $\langle \rangle$ represents the canonical ensemble average.

The spin-order-induced Raman scattering can be explained by one-spin-one-phonon mechanism. The interaction between the displacements of the ion spin originates from the electron-phonon interaction and the spin-orbit interaction, which couples the electron angular momentum to the localized spin. So considering the spin-order related term, the spin-dependent Raman spectrum may be rewritten as,

$$\begin{aligned}
 I(\mathbf{q}) &= \frac{\hbar^3}{2\omega_{\mathbf{q}}^3} \sum_{a,b,a',b'} E_a^s E_b^s E_b^i E_a^i \sum_{\mathbf{q}} \chi_{ab}^{\prime a}(j, s; \mathbf{q}; m; \mathbf{q}) \chi_{ab}^{\prime b}(j', s'; \mathbf{q}; m'; \mathbf{q}) \\
 &\quad \times \frac{N\hbar}{2} \left(\frac{1}{M_s M_{s'} \omega_n(\mathbf{q}) \omega_{n'}(\mathbf{q})} \right)^{\frac{1}{2}} \varepsilon_{nj}(s, \mathbf{q}) \varepsilon_{n'j'}^*(s', \mathbf{q}) \\
 &\quad \times \frac{1}{2\omega_{\mathbf{q}}} \int_{-\infty}^{+\infty} e^{-i\omega t} \langle A_n(\mathbf{q}; t) A_{n'}^{\dagger}(\mathbf{q}; 0) \rangle \langle S_{m\sigma}(-\mathbf{q}; t) S_{m'\sigma'}^*(-\mathbf{q}; 0) \rangle dt, \quad (5-4)
 \end{aligned}$$

$$A_n(\mathbf{q}) = \alpha_n(\mathbf{q}) + \alpha_n^{\dagger}(\mathbf{q}). \quad (5-5)$$

where $\alpha_n(\mathbf{q})$ and $\alpha_n^{\dagger}(\mathbf{q})$ is the annihilation and creation operator of the normal mode of branch n with frequency $\omega_n(\mathbf{q})$, wave vector $\mathbf{q}$, and the j -th component of the polarization vector $\varepsilon_{nj}(s, \mathbf{q})$. Besides, $\chi_{ab}^{\prime a}(j, s; \mathbf{q}; m; \mathbf{q})$ is a Fourier component of $\chi_{ab}^{\prime a}(j; \kappa, s; \mathbf{q}; m)$, which is the spin-related component the electronic susceptibility $\chi_{ab}^{\prime a}$

In the temperature region where the magnon picture does not hold, spin correlation is approximately independent of ω or the time t and represented as: ¹⁵⁵

$$\begin{aligned}
 \sum \langle S_{m\sigma}(-\mathbf{q}; t) S_{m'\sigma'}^*(-\mathbf{q}; 0) \rangle &\sim \langle S_{mz}(-\mathbf{q}) \rangle \langle S_{m'z}(\mathbf{q}) \rangle \delta(\mathbf{q} - \mathbf{q}^*/2) \\
 &+ \sum \langle \tilde{S}_{m\sigma}(-\mathbf{q}) \tilde{S}_{m'\sigma'}(\mathbf{q}) \rangle \delta_{\sigma\sigma'}, \quad (5-6)
 \end{aligned}$$

where the first term presents the gives the Raman scattering for the normal mode of branch n at $\mathbf{q} = \mathbf{q}^*/2$, which is induced by the spin ordering below T_N :

$$\begin{aligned}
 I(\hbar\omega) &= C_n^2(\frac{\hbar\omega}{2}) \frac{\Gamma_n(\frac{\hbar\omega}{2})}{\hbar\omega(1 - e^{-\beta\hbar\omega})(\frac{\hbar\omega}{2})} \left(\frac{1}{[\hbar\omega - \hbar\omega_n(\frac{\hbar\omega}{2})]^2 + \Gamma_n^2(\frac{\hbar\omega}{2})} \right. \\
 &\quad \left. - \frac{1}{[\hbar\omega + \hbar\omega_n(\frac{\hbar\omega}{2})]^2 + \Gamma_n^2(\frac{\hbar\omega}{2})} \right) \\
 &\quad \times \sum_{m,m'} \langle S_{mz}(-\frac{\hbar\omega}{2}) \rangle \langle S_{mz}(\frac{\hbar\omega}{2}) \rangle, \tag{5-7}
 \end{aligned}$$

where $C_n(q)$ is proportional to the Raman tensor as,

$$\begin{aligned}
 C_n^2(\mathbf{q}) &= \frac{\hbar^4}{2\hbar^3} \sum_{a,b,a',b'} E_a^s E_{b'}^s E_b^i E_a^i \sum \hbar_{b',a}^{\parallel}(j,s; \hbar\omega, m; \mathbf{q}) \hbar_{a,b}^{\parallel}(j',s'; \hbar\omega, m'; \mathbf{q}) \\
 &\quad \times \frac{N\hbar}{2} \left(\frac{1}{M_s M_{s'}} \right)^{\frac{1}{2}} \varepsilon_{nj}(s, \mathbf{q}) \varepsilon_{n',j'}^*(s', \mathbf{q}) \tag{5-8}
 \end{aligned}$$

As a result, the momentum conservation is assured by the elastic scattering in the spin system. This modulation activates the Raman modes at other symmetric point, leading to the appearance of additional Raman peaks of some antiferromagnetic materials below Néel temperature.

5.1.3 Zone-Boundary-Phonon Raman Scattering in Magnetic Materials

Figure 5-2 (a) Temperature-dependent Raman spectra of VI_2 . The inset shows the temperature dependence of the integrated intensity of the 66-cm^{-1} peak.¹⁵¹ (b) Spin structure (thick arrows) of VI_2 within the layer and for one eighth the volume of the magnetic cell.¹⁵¹ (c) Temperature-dependent Raman spectra of FePS_3 crystal excited by 488-nm laser.¹³⁸

The onset of magnetic ordering lowers the crystal symmetry, resulting in variation of Raman intensity and possibly activation of new Raman modes.¹⁵⁶ The first observation of zone-

boundary-phonon Raman Scattering was reported in VI_2 due to modulation of exchange interaction in 1979 (as shown in Figure 5-2a).¹⁵¹

The magnetic structure (both in x - y plane and 3D perspective) of VI_2 in antiferromagnetic phase was shown in Figure 5-2b, in which the spins reside in the y - z plane under 60° with respect to the y axis. The magnetic super-cell is expanded compared to the crystalline primitive cell. This induces an exchange interaction in the spin-ordering phase and provides an additional spin-phonon coupling mechanism in Raman scattering, resulting in variation on Raman spectrum and activation of new mode.¹⁵¹ Similarly dramatic variation in the Raman spectrum, such as the anomalous intensity enhancements and the appearance of new phonon peaks, can be observed in other magnetic crystals at the magnetic ordering phase.¹⁵⁷⁻¹⁵⁹ Generally, the spin-independent and the spin-dependent Raman scattering have different selection rules and resonant behaviors. Therefore, the investigation on Raman spectroscopy of magnetic materials in magnetic phase can explore the new physics on the lattice dynamics.

As a family of 2D magnetic materials, MPCs offers an excellent medium to study the spin-dependent Raman modes in 2D system. Among those magnetic materials in MPCs, FePS_3 was reported to exhibit the most dramatic change in Raman spectroscopy, especially new Raman peak emerged in the antiferromagnetic phase.^{138, 160} This fact motivates us on the investigation of the spin-dependent Raman scattering in ultrathin MPCs samples to understand the spin-phonon coupling and modulation of interaction exchange in 2D system.

5.2 Spin-Phonon Coupling in FePS₃

5.2.1 Magnetic Structure and Magnetic Susceptibility of FePS₃

Iron phosphorus trisulfide, whose crystalline structure is shown in Figure 5-3, has been of interest for its realization of antiferromagnetic 2D Ising model on a honeycomb lattice.^{57, 59} As temperature decreases across ~ 118 K, FePS₃ would undergo a magnetic phase transition from the paramagnetic to the antiferromagnetic phase.⁷²⁻⁷³ Although the magnetic structure of FePS₃ has been investigated for over three decades, it is still controversial, particularly for intra-layer magnetic ordering (in ab plane).

Figure 5-3 (a) Crystal structures of FePS₃ bulk crystal on top views. (b) The unit cell (black line) and the primitive cell (red line) of FePS₃.

Two most accepted models of magnetic structure were proposed by Le Flem and Kurosawa, respectively.⁷²⁻⁷³ For instance, Le Flem *et al.* proposed that the intra-layer spin moments are arranged ferromagnetically in chains, but are coupled antiferromagnetically with their neighboring chains (Figure 5-4a). The planes were also coupled ferromagnetically along the c direction (Figure 5-4b).⁷² However, Kurosawa *et al.* reported that the ferromagnetic chains of Fe atom are rotated by 60° compared with Le Flem's model (Figure 5-4c), while the

planes were coupled antiferromagnetically along the c direction (Figure 5-4d).⁷³ The primary spin interaction was explained differently in the two modes, which would be the key point to predict the magnetic stability in the ultrathin sample. Therefore, a better knowledge of this interaction will be useful for the design of future atomically 2D device applications.

Figure 5-4 Magnetic structure of FePS₃ within the layer (a) and between layers (b) proposed by Le Flem. For simplicity, only Fe atoms are plotted. The blue and red balls represent the Fe atoms with up- and down-spin, respectively. Magnetic structure of FePS₃ within the layer (c) and between layers (d) proposed by Kurosawa.

Measurement of magnetic susceptibility on FePS₃ bulk sample was carried out in the physical property measurement system (PPMS) apparatus (as shown in Figure 5-5a). The first derivative of susceptibility curve indicates a transition temperature of ~ 118 K - in agreement with previous studies (as shown in Figure 5-5b).⁷²⁻⁷³

Besides that, the magnetic susceptibility *versus* magnetic field in bulk FePS₃ crystal was measured at 10 K. No hysteresis was observed as shown in the Figure 5-5c (excluding the error from measuring system). As an antiferromagnetic material, FePS₃ in the antiferromagnetic phase has a net zero magnetic moment, meaning no field can be directly detected macroscopically, which makes the magnetic property difficult to be detected in

antiferromagnetic material compared to the ferromagnetic one. For the same reason, the hysteresis loop, which is related to the existence of magnetic domains in the material, cannot be observed in FePS_3 crystal.

Figure 5-5 (a) Plot of magnetic susceptibility of FePS_3 bulk crystal *versus* temperature measured in (black) cooling and (red) heating process. (b) The first derivation of susceptibility with inflection points around 118 K. (c) Magnetic susceptibility of bulk FePS_3 crystal vs. magnetic field. No hysteresis loop was observed.

5.2.2 Spin-Dependent Raman Scattering in FePS₃ Crystal

In order to find out the actual magnetic structure of FePS₃, the microscopic magnetic interactions along different axis require more detailed investigations. Raman active phonons are sensitive to crystal symmetry and can be used to detect the magnetic phase transition. The onset of magnetic ordering lowers the crystal symmetry, resulting in the variation of Raman intensity and possibly activation of new Raman modes.¹⁵⁶ The spin-dependent Raman scattering of bulk FePS₃ has been extensively investigated in both experiments and theory. The results showed that additional phonon peaks (88 and 95 cm⁻¹) were observed below the Néel temperature, due to the spin-dependent electron-phonon coupling.^{60, 138, 160-164}

Before the investigation of spin-dependent Raman spectroscopy in ultrathin FePS₃ flakes, the corresponding measurement were first performed in bulk crystal. When the temperature was decreased to 77 K, the modes below 130 cm⁻¹ changed dramatically with temperature (Figure 5-6): At 77 K, two strong and symmetric peaks located at 88 and 95 cm⁻¹ were resolved in the antiferromagnetic phase whereas when the temperature was increased to 296 K, the two peaks disappeared accompanied by the appearance of a broad asymmetric peak at around 100 cm⁻¹ in the paramagnetic phase. As these Raman signals were related to the iron atom and varied around the magnetic phases transition temperature, we concluded that these phonon modes were strongly dependent on the magnetic properties of this material and the interaction between iron moments played a crucial role in determining the low frequency part (< 130 cm⁻¹) of the Raman spectrum. To explore the origin of these spin-dependent Raman peaks, the corresponding phonon modes are expected to be found in phonon dispersion curves. However, no Raman modes are obtained from first-principle calculations in the frequency range of 0 to 130 cm⁻¹ at the Γ point (Figure 4-9).

Figure 5-6 Raman spectra of bulk FePS_3 crystal obtained with an excitation wavelength of 532 nm and power ~ 0.5 mW at 77 K and 296 K.

This result suggests that the spin-dependent modes, including two spin-order-induced modes at 88, 95 cm^{-1} and a spin-disorder-induced mode at 100 cm^{-1} , do not arise from lattice vibrations alone, but are instead, spin-related. Besides, the spin-order-induced Raman peaks broaden at around the Néel temperature without any shift in their frequencies. These observations exclude the hypothesis of one-magnon Raman scattering, because the magnon bands generally broaden and soften around the magnetic ordering temperature.¹⁶⁵⁻¹⁶⁶ The fact that spin-order-induced peaks totally disappear above Néel temperature is contrary to the behavior of two-magnon Raman scattering, which could persist at the temperature far above

Néel temperature due to the presence of large regions with short-range antiferromagnetic-order.¹⁶⁷ According to previous studies, zone boundary phonons can be activated by magnetic superstructure under certain conditions.^{151, 157}

5.2.3 Zone-Boundary-Phonon Raman Mode Activation in 2D Magnetic Materials

Figure 5-7 Temperature-dependent Raman spectra of bulk FePS₃ sample obtained with an excitation wavelength of 532 nm and power ~0.5 mW around Néel temperature. The line shapes of fitting curves are Fano asymmetric and two-Lorentzian peaks above and below Néel temperature, respectively.

To explore the origin of the spin-dependent Raman signals, a detailed temperature dependent study was performed around Néel Temperature. As shown in Figure 5-7, the intensity of the spin-order-induced Raman peaks located at 88 and 95 cm⁻¹ decreased rapidly

near the Néel temperature. Above the Néel temperature of 118 K, these peaks disappeared completely and were replaced with a spin-disorder-induced Raman peak, centered at about 100 cm^{-1} .

The spectral analysis in this thesis were conducted in the OriginPro 9. In the general case, the Raman phonon line shape follows Lorentz function. The Lorentzian line shape could be expressed as,

$$I(\omega) = y_0 + \frac{2A}{\omega} \frac{W}{4(\omega - \omega_0)^2 + W^2}, \quad (5-9)$$

where ω_0 is the phonon frequency; A is the amplitude; W is the full width at half maximum (FWHM); y_0 is the baseline.

The low-frequency Raman spectrum of FePS_3 in the antiferromagnetic phase was fitted by two-Lorentzian peaks. In contrast, the spin-disorder-induced phonon peak with strong asymmetry in the paramagnetic phase is hard to be fitted by Lorentzian line shape plus linear baseline. Therefore, a Fano asymmetric line shape,¹⁶⁸

$$I(\omega) = A \frac{[q + E(\omega)]^2}{1 + E(\omega)^2}, \quad (5-10)$$

was induced, which shows a good agreement ($R_{max}^2 = 0.97$) in fitting, where

$$E(\omega) = \frac{2(\omega - \omega_0)}{W}. \quad (5-11)$$

Here, ω_0 is the phonon frequency in the absence of interaction, A is the amplitude, W is FWHM, and q is the asymmetry parameter. The asymmetry parameter ($q = -6.41$) is negative in bulk case. Fano asymmetric line shape is a kind of more comprehensive fitting choice, in

which the Lorentzian line shape is a special case when the asymmetry parameter q equals to infinite. The asymmetric features in Raman spectrum are usually induced by Fano resonance between discrete phonon energy and other continuous state.¹⁶⁹⁻¹⁷¹ Based on the fitting results, the transition temperature of Raman spectra of bulk FePS₃ sample agrees with the Néel temperature we measured in PPMS, as well as previous report.⁷²⁻⁷³

Figure 5-8 Schematic of Brillouin-zone halves with respect to the previous one along c axis.

According to expression in Eq. 5-6, zone boundary phonons can be activated by magnetic superstructure under certain conditions.^{151, 157} In the case of antiferromagnetic material, the spin of unpaired electron in each metal atom lists randomly in paramagnetic phase, leading to each metal atom in parity. However, some atoms of the same element become different due to the opposite electronic spin after the material transforms to the antiferromagnetic phase. In some special case, for instance when the atoms at the same position of neighboring crystalline cell lose their equivalence, the symmetry of the lattice would become lower. As shown in Figure 5-8, when the magnetic primitive cell doubles compared to the crystalline one, Brillouin-zone halves with respect to the previous case in reciprocal space. The lattice vibrational modes in the material mediate the exchange interaction and provide an additional term to the phonon Raman tensor, leading to the observation of the zone-boundary

phonon modes in the Raman spectrum. In the case of FePS_3 , the spin order of Fe atoms induces the magnetism, accompanying Raman modes variation in magnetic phase due to this effect. The magnetic fluctuations would increase when the dimension of the system reduces, and affect the stability of spin, which is a main obstacle to fabricate the atomically thin magnetic device with high density data storage and retention time. Besides that, the exchange interaction will also be modified with the decreased dimension, probably due to the breaking of inversion symmetry or modification of the electronic/lattice structure in 2D materials.⁴⁵ Therefore, it is significant to study the magnetism and spin properties in 2D system. Even so, as a 2D magnetic crystal, FePS_3 have not been studied on the related properties in ultrathin samples before.

Figure 5-9 Thickness-dependent Raman spectra of few-layer and bulk FePS_3 obtained with an excitation wavelength of 532 nm and power ~ 0.5 mW at (a) 296 K and (b) 77 K.

The detail on how dimensionality affects the spin-dependent Raman spectra and the magnetic phase transition in FePS_3 was investigated on exfoliated FePS_3 samples (Figure 5-9). No noticeable shift was observed for all the Raman modes when the thickness of samples

decreased from bulk to atomically thin at both 296 K and 77 K. The most striking result is that the two pronounced peaks centered at 88 and 95 cm^{-1} are even observed in monolayer sample at 77 K (Figure 5-10). The spin-dependent Raman modes showed the similar behavior both in the paramagnetic phase and the antiferromagnetic phase as the material transformed from 3D system to 2D systems. The results imply that the magnetic exchange interaction which modulates the phonon modes are mainly along a - b plane.

Figure 5-10 Raman spectra of monolayer FePS₃ obtained with an excitation wavelength of 532 nm and power ~ 0.5 mW.

According to the explanation of a previous report, the changes in the spin-dependent Raman signal around the Néel temperature were due to Brillouin-zone folding, which is caused by the magnetic cell doubling along the c axis.¹³⁸ This effect neglects the intra-layer interactions that determine the spin texture in the a - b plane and is attributed to primarily the inter-layer interactions between the Fe spins, which can largely affect the magnetic property when the sample is decreased to few-layer regime. However, it was also claimed that the

Brillouin-zone folding could occur in a - b plane.¹⁶⁰ Our Raman spectroscopy measurement on exfoliated few- to mono-layer FePS₃ samples provided an opportunity to distinguish the intra-layer interaction from inter-layer one. The observation of Brillouin-zone-boundary phonon monolayer sample directly confirms the conjecture that the Brillouin-zone folds in a - b plane. This is because monolayer FePS₃ only has a layer of iron atoms, which is impossible to have double-sized magnetic cell along the c axis.

Figure 5-11 Magnetic structure of FePS₃ within the layer proposed by Le Flem. The red and black frames indicate the crystalline primitive cell and magnetic super cell of FePS₃, respectively.

As shown in Figure 5-11, when the spins of Fe atoms are considered, the crystalline primitive cell of FePS₃ is different from the neighboring ones in a - b plane. Therefore, the physical properties of FePS₃ in the antiferromagnetic phase should be determined by magnetic supercell, which is larger than crystalline primitive cell along a - b plane. This results in the Brillouin-zone folding in ab plane and activates the certain Brillouin-zone-boundary Raman modes.

The spin-phonon coupling activates Raman scattering from selected phonon modes on other symmetric points induced by a modulation of the exchange interaction.¹⁵²⁻¹⁵⁴ The additional peak appearing in the antiferromagnetic phase is attributed to the inelastic scattering from the zone-boundary phonons induced by the elastic magnetic scattering from the magnetic superstructure. However, only the modes providing a modulation of the spin-orbit coupling or the exchange interaction could activate spin-dependent phonon on Raman scattering.¹⁵¹ From the calculated phonon dispersion curve shown in Figure 4-9, two branches located at 86 and 95 cm^{-1} were found at the M point. In general, since the FePS_3 magnetic cell is doubled within a - b plane with respect to the crystallographic one, the Brillouin zone is halved in the reciprocal space. The inversion center of the magnetic cell in the antiferromagnetic phase is at the middle of two crystallographic cells, leading to the u mode on M point becoming g mode. As a consequence, the zone-boundary phonons at 88 and 95 cm^{-1} on M point are activated, leading to an observation of additional peaks in the Raman spectrum in the antiferromagnetic phase.

5.2.4 Thickness Dependence of Magnetic Phase Transition

As we have mentioned above, the spin-order-induced Raman signal at 88 cm^{-1} , which reflects the ordered spin of iron atoms, can be treated as an ingenious “probe” of the magnetic phase for micro-size mono- and few-layer FePS_3 samples. Therefore, the investigation of magnetic phase transition of FePS_3 down to nanometer region was performed by measuring the temperature-dependent Raman spectra of few-layered (from bilayer to 6-layer) and bulk FePS_3 , which was shown in Figure 5-12.

Figure 5-12 Temperature-dependent Raman spectra of few-layered (from bilayer to 6-layer) and bulk FePS₃ obtained with an excitation wavelength of 532 nm and power ~0.5 mW.

Figure 5-13 Temperature-dependent Raman spectra of FePS₃ from mono- to six-layer obtained with an excitation wavelength of 532 nm and power ~ 0.5 mW.

The temperature of magnetic phase transition in ultrathin FePS₃ flakes was explored based on the variation on spin-dependent Raman spectra in low-frequency region from mono- to six-layer (Figure 5-13). Herein, the annihilation of the 88 cm⁻¹ peak was applied as a signal for magnetic phase transition from the antiferromagnetic to paramagnetic phase. Temperature dependent Raman intensity of different sample was plotted in Figure 5-14. The Raman peak in the bulk sample completely disappeared around 117 K, in good agreement with the value of the Néel temperature obtained in the susceptibility measurement. Therefore, a correlation

between the magnetic phase transition and the disappearance of the Raman peak is identified. Following this correlation, the relation between the phase transition temperature and the layer number was plotted in Figure 5-15a.

Figure 5-14 Plots of intensity of Raman peak at 88 cm^{-1} *versus* temperature of samples in different thickness.

As a general trend, the magnetic ordering temperature decreases as the layer number reduces. Moreover, the peak located at 88 cm^{-1} exhibited broadening, which indicates a coexistence of the paramagnetic and the antiferromagnetic phases around the Néel temperature.

This result was proven in a previous report on the Mössbauer measurements.¹³² The FWHMs of 88 cm^{-1} peak in few-layer started to broaden at lower temperature, which also showed a slightly less magnetic stability, compared to the bulk sample (Figure 5-15b).

Figure 5-15 (a) Plot of Néel temperature (T_N) measured by optical method *versus* thickness of samples, compared with the result of bulk sample measured by PPMS. (b) Plots of FWHM of Raman peak at 88 cm^{-1} *versus* temperature of trilayer and bulk samples.

To further understand the mechanism, we calculated electronic structures and magnetic stability of FePS_3 based on the van der Waals density functional theory (DFT).^{130, 172} The generalized gradient approximation (GGA)¹⁷² was used to describe the exchange-correlation potential. The cell structural and ionic position were optimized *via* the Vienna *ab-initio* Simulations Package (VASP) code^{125, 173} with the full-potential projector augmented wave (PAW) method.¹²⁷ A pairwise interatomic term to describe van de Waals interactions, DFT-D2 method of Grimme,¹³⁰ was added to the DFT calculations along with the GGA+U method to determine the correlation effects on the localized d-orbital of Fe atoms. The plane wave cutoff energy was set to 500 eV, and $8 \times 4 \times 8$ k-point grids were set in the Brillouin zone. The

energy convergence criterion was set to 10^{-6} eV. The theoretical equilibrium structure was obtained when the forces and stresses acting on all the atoms were less than 0.01 eV/Å. The Hubbard U with $U = 6.8$ eV and $J = 0.89$ eV were used for Fe 3d in FePS₃.

Figure 5-16 Magnetic structure of FePS₃ crystal proposed by Le Flem.

The structural stability was estimated by calculating the energy difference of the different magnetic configurations. The self-consistent electronic structures of the paramagnetic and the antiferromagnetic phases were calculated for both bilayer and bulk FePS₃. The antiferromagnetic state is controlled by a chain of Fe atoms followed by another chain with opposite spin direction proposed by Le Flem *et al.* shown in Figure 5-16. Antiferromagnetic phase is the most stable state with the lowest energy in both cases. With corrections from the GGA+U and DFT-D2 calculation, the energy required to undergo from the antiferromagnetic to the paramagnetic phase for bilayer sample was 848.2 meV/f.u., while that for bulk sample was 874.1 meV/f.u. (Table 5-1).

Magnetic Phase	Total Energy (eV/f.u.)	
	Bilayer	Bulk
AFM phase	-414.317	-415.810
PM phase	-415.165	-416.684
Energy difference	0.848	0.874

Table 5-1 Total energy of the magnetic phases of FePS₃ as proposed by Le Flem with same number of atoms.

Therefore, the few-layer structure needs less energy for the magnetic transition, which results in the descending of Néel temperature from the bulk to the monolayer sample. In the thin layer case, the higher magnetic energy, which would lead to a lower Néel temperature, is attributed to the absence of long-range exchange interaction between the Fe atoms from adjacent layers. As a typical 2D Ising model, the magnetic order in FePS₃ is mainly dominated by three in-plane magnetic exchanges (J_1 , J_2 and J_3). The exchange interaction along c-axis is much weaker compared with in-plane ones, but it indeed exists and contributes to a lower magnetic energy and higher Néel temperature in bulk case.^{45, 174} However, the phenomenon that the magnetic phase transition temperature increases slightly by ~ 2.0 K in monolayer sample. The hardening of magnetism in monolayer is possibly caused by the various reasons, such as the modification of the electronic or lattice structure,⁴⁵ which may need further investigations on both magnetic experiments and theoretical calculations.

Figure 5-17 (a) Temperature-dependent Raman spectra of bulk FePS₃ sample obtained with an excitation wavelength of 532 nm and power of ~ 0.5 mW. (b) Zoom-in for the low-frequency region shown in (a). The spin-dependent Raman modes and fitting results in low-frequency region at (c) 77 K, (d) 90 K, (e) 100 K and (f) 110 K.

Besides that the magnetic phase transition temperature was identified by layer-number dependent Raman spectra, another interesting behavior was also found in the variation of intensity of the spin-order-induced Raman mode at 88 cm^{-1} . As shown in the Figure 5-14, a more dramatic change in the intensity was observed in thin layers than that in bulk. To further study the variation of intensity, the temperature dependent Raman spectra of bulk FePS_3 sample are carried with the intensively selected temperature point below T_N (from 100 K to 118 K) to observe the formation of spin-dependent Raman mode located at 88 cm^{-1} (shown in Figure 5-17a). The bulk sample shows an increasing intensity of spin-related Raman modes ($88, 95, 160\text{ cm}^{-1}$) with temperature decreasing in antiferromagnetic, while the intensity of other modes ($> 200\text{ cm}^{-1}$) does not dramatically change. In Figure 5-17b, it is clear that the intensity of three spin-related Raman peaks all increase with temperature decreasing in antiferromagnetic phase below T_N . Four spectra were picked out and fitted by two-Lorentzian curve (Figure 5-17c to f). The corresponding fitting parameters were listed in Table 5-2.

Temperature (K)	Peak Position (cm^{-1})	Error	FWHM (cm^{-1})	Error	Integral Intensity	Error
77 K	88.28	0.02	3.03	0.06	3247	52
90 K	88.43	0.03	3.65	0.10	2554	60
100 K	88.59	0.05	4.15	0.17	1500	54
110 K	89.32	0.16	6.19	0.52	1083	102

Table 5-2 The fitting parameters of the spin-dependent Raman peak located at 88 cm^{-1} as shown in Figure 3b-e.

The less dramatic change of spin-dependent Raman intensity in bulk than that in layers is exactly from the experimental data. This effect occurs below magnetic phase transition temperature may be contributed by the long-range exchange interaction (mainly along c axis), which may need lower temperature to become fully stable. In contrast, the absence of exchange interaction along c axis makes the magnetic ordering much more relying on the short-range magnetic exchange in ab plane, resulting in a more dramatic variation on spin-order-induced Raman intensity.

5.3 Summary

In conclusion, the layer-number dependent Raman spectroscopy of high quality atomically thin 2D magnetic materials FePS_3 has been investigated for the first time to study the spin-phonon coupling and the magnetic property. With thickness decreasing from bulk to monolayer, FePS_3 exhibits the same magnetic transition from the antiferromagnetic to the ferromagnetic phase, which can be traced by the characteristic Raman-active modes at $\sim 88 \text{ cm}^{-1}$. This result suggests that intra-layer spin interaction dominates the magnetic structure of FePS_3 , leading to a magnetic persistence even in mono- and few-layer samples. Furthermore, the Neel temperature shows pronounced dependence on the layer number, suggesting that magnetic ordering even occurs in-plane at monolayer regime. Our work motivates further systematic studies on the 2D magnetic systems, which are significant for not only the potentially diverse applications in future ultrathin magnetic device, but also the fundamental understanding in physics of areas, such as nonlinear optics, magneto-optics and high-temperature superconductivity.

Chapter 6 Nonlinear Optical Properties of Quaternary Metal Phosphorus Chalcogenides 2D Crystals

6.1 Introduction

6.1.1 Second Harmonic Generation (SHG) in 2D materials

The exploration of functional 2D materials beyond graphene has gone into eruption in recent years aimed at new materials and functionalities.^{37, 44, 108, 112-116, 119} The interest of individual layers of 2D materials mostly focuses on the unique electronic and optical properties in contrary to the bulk counterpart, such as indirect–direct band gap transition and inversion symmetry breaking.¹⁷⁵⁻¹⁷⁹ Nonlinear effects in the atomically thin region have attracted a variety of interest in fundamental physical study and expanded the functionalities and potential applications of 2D materials.^{176-178, 180-182} The broken inversion symmetry in monolayer 2D materials has shown many special properties, including second-harmonic-generation (SHG), chiral electroluminescence and the viability of optical valley control, which may disappear in the centrosymmetric bulk counterpart.⁴¹⁻⁴² The external modulation opens a new path to explore the physical properties and technological applications furthermore.

SHG is a nonlinear optical process, in which photons with the same frequency interacting with a nonlinear material.¹⁰¹ It is an even-order nonlinear optical effect, and it is only allowed in media without inversion symmetry.¹⁰¹⁻¹⁰² SHG in atomically thin 2D materials has been explored in many different compounds, such as TMDs, h-BN, GaSe, *etc.*^{176-178, 183}

Figure 6-1 (a) Orientational dependent SHG intensity from single-layer h-BN and MoS₂. (b) Illustration of the model of the SHG intensity as a function of layer thickness in few-layer h-BN.¹⁷⁸ (c) The polarization angle θ dependent SHG intensity in monolayer GaSe. (d) Optical image and (e) SHG mapping for GaSe bilayer with twist angle of $\phi = 60^\circ$.¹⁸³

Strong SHG signal can be generated from atomically thin samples of h-BN and MoS₂ with odd-layer thickness, while it is not observed in materials with even layers. This effect is originated from the transformation between noncentrosymmetric and centrosymmetric structure for odd layers and even layers, respectively.¹⁷⁸ Moreover, the optical SHG is measured in monolayer GaSe, which is reported as the strongest SHG in 2D atomic crystals with nonresonant excitation and emission.¹⁸³ The nonlinear signal of ultrathin sample can be used to detect various information of lattices symmetry, such as the crystal orientation and the stacking orders.

Figure 6-2 (a) SHG image of MoS₂ flakes pumped at 1300 nm. The brim of crystal shows a strong nonlinear optical (SHG) edge state.¹⁷⁶ (b) Reversible SHG induced by back gate from the pristine bilayer WSe₂ sample. (c) The plot of I_{sd} versus V_G for the bilayer WSe₂ device. SHG intensities as a function of gate voltage are superimposed on I_{sd} versus V_G curve.¹⁷⁹

Besides the translational symmetry breaking of a crystal, SHG will also be induced by a variety of mechanism in 2D system. For example, the electronic structure variation at the edges of the monolayer MoS₂ crystal results in strong resonant optical second-harmonic susceptibilities (Figure 6-2a).¹⁷⁶ In addition, the electric field applying on the 2D materials will also induce the observation of SHG due to the symmetry breaking of electronic structure of materials.^{179, 184-185} For example, the charge accumulation in a 2D WSe₂ bilayer crystal caused by a back gate field results in a charge-induced SHG, while SHG is supposed to be absent in a bilayer sample. This new mechanism has been analyzed on the basis of a bond-charge model, where the accumulated sub-monolayer screening charge in the tungsten plane cause the non-uniform field distribution within a single monolayer. This leads to symmetry breaking and thus generate the SHG. These works on nonlinear optics provide a route toward understanding of fundamental physics and potentially valuable applications of the emerging 2D materials and devices.

6.1.2 SHG in MPCs

Compared with common 2D crystals, such as TMDs, h-BN and GaSe, MPCs are newcomers to this field. In general, it is not trivial to form a stable lattice structure when the materials are doped by elements with the valence state different from the original one. Therefore, MPCs, which can contain metal elements with valence of +1, +3 in quaternary compound and +2 in ternary compound, offer a more artistic platform to manipulate artificial layered materials by providing more available positions for doping. Especially, the alloy and doping work in MPCs are more frequently conducted in the quaternary compound due to the rich choice of elements. ($M^{I}_{1/2}M^{III}_{1/2}PX_3$ or $M^I M^{III}P_2X_6$, $M^I = \text{Cu, Ag}$; $M^{III} = \text{Cr, V, Al, Ga, In, Bi, Sc, Er, Tm}$; $X = \text{S, Se}$).¹³¹ For example, besides the traditional X elements in $M^I M^{III}P_2X_6$, we can make the doping in the M^I position as compound $\text{Ag}_{0.1}\text{Cu}_{0.9}\text{InP}_2\text{S}_6$, or M^{III} position as compound $\text{Ag}_{1/2}\text{Cr}_{(1/2-x)}\text{In}_x\text{PS}_3$.¹⁸⁶⁻¹⁸⁷ This would greatly improve function of 2D materials with additional properties, including tunable band gap, magnetism and ferroelectricity in the MPCs.^{182, 188}

The nonlinear effect of MPCs bulk crystal has been reported in the past three decades.^{61, 138, 189-190} Among those, the investigation of SHG has been intensively conducted in quaternary MPCs, especially in ferroelectric material CuInP_2S_6 . It is widely accepted that a first-order paraelectric-ferroelectric phase transition occurs at $T_C = 315 \text{ K}$ in CuInP_2S_6 caused by the copper hopping motion (Figure 6-3a and b).¹⁹¹ As a 2D nature, thin flakes of CuInP_2S_6 can be obtained by mechanical exfoliation and the ferroelectricity has been confirmed down to 50 nm region by piezoresponse force microscopy (PFM) (Figure 6-3c and d).¹⁸⁸ However, the response in PFM measurement is too weak to be detected, probably due to the limitation of this technique. Moreover, an accompanying lattice structural transition from

noncentrosymmetric space group Cc to centrosymmetric $C2/c$ around T_c can be detected by the variation of optical SHG signal (Figure 6-3e).⁶¹ The sensitivity of SHG offers us an opportunity to investigate the ferroelectric polarization in CuInP_2S_6 flakes thinner than 50 nm.

Figure 6-3 (a) Thermal evolution of the different copper site occupancies and the corresponding probability density contours in CuInP_2S_6 . (b) The corresponding Cu sites in a sulfur octahedral cage.¹⁹¹ (c) Contact AFM image of an exfoliated piece of CuInP_2S_6 , the inset indicates the thin flakes is around 50 nm thick. (d) Band excitation PFM image of the area in c.¹⁸⁸ (e) Temperature dependence of the SHG intensity for single crystal CuInP_2S_6 .⁶¹

However, SHG will be induced by a plenty of mechanism, such as the symmetry breaking, in atomically thin 2D material.^{176-178, 183} To better distinguish the mechanism of SHG in thin CuInP_2S_6 flakes, the systematic SHG study on AgInP_2S_6 with the similar crystal

structure is conducted. The bulk AgInP_2S_6 crystal belongs to the centrosymmetric space group $P\bar{3}1c$, where no atom hopping motion occurs.

In this work, for the first time, we observed the inversion symmetry breaking of atomically thin quaternary AgInP_2S_6 with odd-layer thickness by SHG measurement. The absence of SHG in even layer and bulk AgInP_2S_6 can be attributed to the AB staking of neighboring layers. With this method, the symmetry variations were probed in few-layer AgInP_2S_6 by the layer-number dependent SHG intensity. Crystal orientated dependence of SHG intensity indicated the three-fold lattice symmetry of flakes with odd-number layer. In contrast, the SHG measured in thin CuInP_2S_6 flakes suggests the ferroelectric polarization remains below 50 nm. The crystal orientated dependence of SHG and Raman measurement in thin CuInP_2S_6 flakes imply an electronic anisotropy.

6.2 Optical Characterization of Bulk AgInP_2S_6 and CuInP_2S_6

Raman spectra of bulk AgInP_2S_6 and CuInP_2S_6 samples at room temperature (293 K) were investigated (Figure 6-4). Raman measurements were carried out on a triple-grating micro-Raman spectrometer (Horiba-JY T64000). A solid state laser ($\lambda = 532$ nm) was used to excite the sample. The backscattered signal was collected through a 100 $\times$ objective, dispersed with a 1800 g/mm grating. To avoid sample heating by the laser beam only few hundreds of microwatts are used in the experiments.

Figure 6-4 Raman spectra of (a) AgInP_2S_6 and (b) CuInP_2S_6 bulk crystal at room temperature excited by 532-nm continuous-wave (CW) laser.

Ten and fourteen prominent Raman peaks could be resolved in AgInP_2S_6 and CuInP_2S_6 , respectively, with the Raman shift values labeled in Figure 6-4. AgInP_2S_6 and CuInP_2S_6 show a similar spectrum, as well as with some ternary metal phosphorous sulfides, especially in the range from 200 to 500 cm^{-1} .^{131, 136, 138, 189} Some fingerprint modes of metal phosphorous sulfides are observed in high frequency region and they are mainly attributed to the inner vibrations of $[\text{P}_2\text{S}_6]$ units.¹³⁶ The Raman spectra in these two quaternary MPCs exhibit a larger difference in the low frequency part ($< 200 \text{ cm}^{-1}$), where the Raman modes are largely affected by the vibration of metal atoms. For example, no Raman peak shows below 50 cm^{-1} in AgInP_2S_6 ; while a peak around 25 cm^{-1} was observed in the spectrum of CuInP_2S_6 . This phenomenon implied a possibility that the distribution of metal atoms and related bonds in these two materials might be largely different. In order to explore the details of lattice structure of AgInP_2S_6 , more experiments have been performed.

The SHG measurements were performed in a reflection geometry using normal incidence excitation. A mode-locked Ti/Sapphire oscillator was used as the pumping source at an 80 MHz repetition rate. The pulses were of 100 fs duration and centered at a wavelength of 800 nm. Through a 100× objective, we focused the pump light to a spot size of $\sim 3 \mu\text{m}$ in diameter on the sample. The laser power was limited to around 1 mW to avoid sample heating and burning (except in the power dependent experiment).

Figure 6-5 SHG spectrum from AgInP_2S_6 bulk crystal in room temperature excited by 800-nm fs laser. SHG spectrum from noncentrosymmetric CuInP_2S_6 bulk crystal was set as reference.

The SHG spectrum of AgInP_2S_6 bulk crystal was measured by an 800-nm femtosecond laser (Figure 6-5). In comparison, we also measured the SHG signal from bulk CuInP_2S_6 crystal, which is proved noncentrosymmetric at room temperature.⁶¹ The absence of SHG signal from bulk AgInP_2S_6 crystal suggests the lattice structure is centrosymmetric, thus leading to the disappearance of second-order optical nonlinearity. The contrast on SHG spectra of AgInP_2S_6 and CuInP_2S_6 distinctly points out the variation of crystal symmetry when the metal atoms are substituted in the bulk case. Therefore, it is significant to acquire more detailed information about the lattice structure in this family of materials.

6.3 Thickness Dependent SHG and Lattice Symmetry Breaking in ultrathin AgInP_2S_6 Flakes

In this section, our investigation is focused on AgInP_2S_6 , which is rarely explored in previous reports. As a layered material, AgInP_2S_6 offers us an opportunity to distinguish the *ab* plane and *c* axis in the study of crystal structure by fabricating atomically thin samples. The physical properties can also be investigated when the system transits from three- to two-dimension.

Figure 6-6 (a) The SHG spectra of AgInP_2S_6 monolayer sample under excitation of an 800-nm fs laser. SHG spectrum from AgInP_2S_6 bulk crystal was set as reference. (b) The incident power dependence of SHG intensity from AgInP_2S_6 monolayer sample.

The preparation of monolayer AgInP_2S_6 by mechanical exfoliation has been introduced in Chapter 3. Typical nonlinear spectra of monolayer AgInP_2S_6 flakes under excitation of 800-nm laser with certain azimuthal angle θ were shown in Figure 6-6a. A conspicuous peak, which is centered at 400 nm, can be exactly assigned as SHG signal. The dependence of SHG intensity

on the excited femtosecond laser power was conducted. The electric dipole theory predicts that SHG intensity I_{SHG} is determined by the following formula under the first-order perturbation.¹⁹²

$$I_{SHG} = |E(2\omega)|^2 \propto |P(\omega)|^2, \quad (6-1)$$

where $E(2\omega)$ and $P(\omega)$ are the SHG electric field vector and excited laser power, respectively. As a consequence, the SHG intensity should be quadratically dependent on the excitation power. In our experiment, the SHG intensity of monolayer sample was plot as the function of excitation power in log scale (Figure 6-6b). The fitting line shows that the exponent is around 2.1, in consistent with the theoretical value. The consistency indicates that the measured signal at 400 nm is indeed originated from the second-order nonlinear process in monolayer AgInP_2S_6 , which can be well described by the electric dipole theory.

Figure 6-7 (a) The SHG spectra of AgInP_2S_6 monolayer sample under excitation of an 800-nm fs laser with different azimuthal angle. (b) The azimuthal angle θ dependent SHG intensity.

The SHG intensity from monolayer AgInP_2S_6 exhibited a strong dependence on the azimuthal angle θ , which is defined as the angle between the polarization of the excitation

beam and one of the armchair edges (as indicated in Figure 6-7). The monolayer polarization $\vec{P}$ can be explained by a bond charge model.¹⁹³ The potential difference between two different ions in each bond $\vec{r}_{ij}$ will cause a position shift of center of the bond charge. The shifting of bond charge center gives rise to a second-order bond hyperpolarizability $\beta_n^{(2)}$ related to the second-order nonlinear susceptibility $\chi^{(2)}$ of the whole structure. When light incidents along the sample surface normal, the second-order dipole moment $\mathbf{p}_{2\omega,n} = \beta_n^{(2)}(\vec{E}_\omega \cdot \vec{r}_{ij})^2$ is generated in each bond. Based on this, the non-inversional symmetric distribution of bond charges leads to the arising of monolayer polarization. Figure 6-8a indicates the lattice symmetry and orientation of monolayer AgInP₂S₆. In detail, the non-inversional symmetry of lattice structure in *a-b* plane is mainly attributed to the triangle distribution of In atoms, as well as that of Ag atoms and [P₂] pairs (Figure 6-8b). The relative in-plane positions of any two kinds of atoms are comparable with the atom distribution of B and N in monolayer h-BN.¹⁷⁷⁻¹⁷⁸ Besides that, the distribution of S atoms, which is not exactly hexagonal, also introduces a non-inversional symmetric bond charge in the monolayer lattice structure. For example, the neighboring in-plane angles of P-S bonds from a [P₂] pair are 54.2° and 65.8°, due to the bond twisting between upper and lower P atoms (Figure 6-8c). Therefore, monolayer AgInP₂S₆ has 3-fold symmetry in plane, where the SHG intensity is expected to exhibit a 6-fold rotational symmetric response when rotating the sample about its surface normal. The angle resolved SHG intensity exhibits a symmetric pattern with 6 petals, which can be described as $I = I_0 \cos^2(3\theta)$, where I and I_0 are the SHG intensity and the maximum SHG intensity, respectively. According to the in-plane lattice structure, the direction parallel to a mirror plane of the crystal line has the maximum of dipole moment, leading to the maximum SHG intensity.

Figure 6-8 (a) The in-plane configuration of monolayer AgInP₂S₆ along c axis. (b) The relative position of Ag and In atoms. (c) In-plane schematic of six P-S bonds from a [P₂] pair. The neighboring angle θ_1 and θ_2 are different.

In monolayer crystal, the second-order nonlinear susceptibility $\chi^{(2)}$ could be estimated by,¹⁰⁷

$$I_{2\omega} = [\chi^{(2)}]^2 I_{\omega}^2 \cdot \frac{d^2}{n_{2\omega} n_{\omega}^2}, \quad (6-2)$$

where I_{ω} is the intensity of excitation laser; $I_{2\omega}$ is the SHG intensity; n_{ω} and $n_{2\omega}$ are the refractive index of material at frequency ω and 2ω , respectively; d is the thickness of monolayer. In order to estimate the second-order nonlinear susceptibility of AgInP₂S₆ monolayer, the SHG measurement was conducted on monolayer MoS₂, which is exfoliated on the same substrate and excited with the same excitation power. The $\chi^{(2)}$ of MoS₂ monolayer was reported to be 10^{-7} m/V level.¹⁰⁶⁻¹⁰⁷ The SHG intensity of MoS₂ monolayer is around 100 times larger than that of AgInP₂S₆ monolayer. According to our results, regardless the related minor difference from the refractive index and the sample thickness, the difference is mainly

originated from the second-order nonlinear susceptibility $\chi^{(2)}$, which is estimated at the 10^{-8} m/V level.¹⁷⁸

Further investigation has been conducted on the dependence of SHG spectra on the layer-number. The SHG spectra of AgInP₂S₆ from mono- to four-layer under excitation of 800-nm laser were shown in Figure 6-9a. In the SHG spectra of monolayer and tri-layer AgInP₂S₆, SHG peak could be distinctly observed at 400 nm. However, no SHG signal was observed in the spectra of bilayer and four-layer AgInP₂S₆ (Figure 6-9b). Since the SHG response of the materials can be treated as an optical method to probe the symmetry lattice structure, the contrast of the SHG signal reflects the different lattice symmetry of AgInP₂S₆ between odd and even layer number samples.

Figure 6-9 (a) SHG spectra of exfoliated AgInP₂S₆ flakes from mono- to four-layer. (b) The layer-number dependence of SHG intensity from mono- to four-layer sample.

Monolayer AgInP₂S₆ belongs to a noncentrosymmetric structure, which is supposed to have nonzero SHG signal. However, in the bulk and multilayer samples, the [P₂] pairs and Ag atoms stack alternately in the neighboring layers, leading to the AB stacking order of the adjacent layers. In even-layer number samples, the bonds in one layer have the opposite symmetry with respect to the bonds in the adjacent layer in ab plane, leading to the dipole

$p_{2\omega,n}$ in each bond cancel each other. Therefore, the even layer number and bulk AgInP_2S_6 indeed exhibit inversion symmetry, where no SHG signal should be observed. Nonetheless, a weak SHG signal, which can be observed in the bulk AgInP_2S_6 crystal at a large excitation power and long integral time, is attributed to the lattice reconstruction on the surface of bulk crystal.¹⁹⁴ This similarity to TMDs on lattice symmetry implies the various potential functions in AgInP_2S_6 , such as valleytronic properties in monolayer.

Figure 6-10 The packing configuration of lattice structure of AgInP_2S_6 from mono- to tri-layer. The stacking sequence of AgInP_2S_6 crystal shows different lattice symmetry between odd- and even-layer samples.

The SHG technique has several advantages in the study of atomically thin AgInP_2S_6 materials. First, the prominent difference of SHG intensity between odd-layer and even-layer number sample shows a potential to easily determine the layer number of AgInP_2S_6 sample assisted with their optical contrast analyses. Optical method is widely used to determine the thickness of the different exfoliated 2D materials. For example, the layer number of MoS_2 can be determined by the central wavelength and intensity of the photoluminescence,^{175, 195} and

the wavenumber of interlayer Raman modes. However, for few-layer AgInP_2S_6 flakes (< 20 nm), the Raman signal is too weak to be detected, while no photoluminescence can be observed probably due to its indirect band gap nature. Therefore, the SHG technique becomes an excellent optical tool to clearly probe the layer number of AgInP_2S_6 . Second, the SHG intensity varies with the crystal orientation rotating in odd layer number AgInP_2S_6 . This phenomenon provides a pure optical method to precisely probe the crystallographic axes of local sample without chemical damage. Third, the SHG measurement in AgInP_2S_6 reveals the potential to precisely detect the local crystal symmetry, including the orientation symmetry in ab plane and stacking order, of doping MPCs in the further investigation.

6.4 SHG and Phase Transition in CuInP_2S_6

6.4.1 Variation of Raman Modes of CuInP_2S_6 in Phase Transition

The lattice dynamics of CuInP_2S_6 has been studied during transition from the ferroelectric to the paraelectric phase.¹⁸⁹ Relaxational behavior of Raman modes was observed with the order-disorder character in transition. The variation of Raman spectra caused by the phase transition suggests copper hopping motions, which results in the polarity in ferroelectric phase, is induced by a coupling between internal $[\text{P}_2\text{S}_6]^{4-}$ modes and Cu^{I} related vibrations.

Figure 6-11 Raman spectra of exfoliated CuInP_2S_6 flake with the thickness of 20 nm at room temperature excited by (a) 532-nm and (b) 633-nm continuous-wave (CW) laser.

The Raman measurements of exfoliated 20-nm thick CuInP_2S_6 flake were carried out on a micro-Raman spectrometer (Horiba-JY T64000), collected through a $100\times$ objective and dispersed with a 1800 g/mm grating (as shown in Figure 6-11). The Raman spectrum excited by 532-nm laser (Figure 6-11a) was acquired in triple-grating mode, which is capable for measurement of low-frequency modes. In contrast, the spectrum excited by 633-nm laser (Figure 6-11b) was conducted in single-grating mode with a long-pass filter.

The Raman peaks in bulk CuInP_2S_6 were summarized in Table 2. At room temperature, CuInP_2S_6 crystal belongs to Cc symmetric group, which is expected to have 60 irreducible zone-center phonon modes denoted by $\Gamma = 30 A' + 30 A''$, where both A' and A'' are Raman and infrared active. The corresponding Raman tensors are,¹⁴⁰

$$A'(x, z): \begin{pmatrix} a & 0 & d \\ 0 & b & 0 \\ d & 0 & c \end{pmatrix} \quad (6-3)$$

$$A''(y): \begin{pmatrix} 0 & e & 0 \\ e & 0 & f \\ 0 & f & 0 \end{pmatrix} \quad (6-4)$$

Compared with the ternary MPCs, such as FePS₃, CuInP₂S₆ is expected to have much more fine structural information in Raman spectrum, while the number of observed modes of CuInP₂S₆ is approximate to that of ternary MPCs. This may be probably because some of modes only can be observed in certain excitation wavelength and incident geometry.¹⁹⁶

Figure 6-12 (a) Temperature-dependent Raman spectra of a 20-nm CuInP₂S₆ flake crystal around phase transition temperature excited by 532-nm continuous-wave (CW) laser, and (b) is the zoom in for low-frequency part (<100 cm⁻¹).

In comparison between the Raman spectra with different excitation wavelengths, a few different features could be resolved. For example, both two Raman modes located at 215 and 239 cm⁻¹ could be observed when excited by 633-nm laser, while only the former peak was resolved when excited by 532-nm laser. In contrast, two clear vibrations were observed around

550 cm^{-1} with 532-nm excitation, while only one could be observed with 633-nm excitation (Figure 6-11).

The phase transition temperature of bulk CuInP_2S_6 crystal is around 315 K, where the material will transit from the ferroelectric phase to the paraelectric phase with the temperature increasing. As a consequence, the space group of lattice structure will change from Cc to $C2/c$ symmetry group, which both belong to monoclinic crystal system. When the temperature increased upon 315 K, CuInP_2S_6 crystal with $C2/c$ symmetry is also expected to have 60 irreducible zone-center phonon modes while denoted by $\Gamma = 14A_g + 14A_u + 16B_g + 16B_u$, among which A_g and B_g are Raman active modes. The corresponding Raman tensors can be given by,¹⁴⁰

$$A_g: \begin{pmatrix} a & 0 & d \\ 0 & b & 0 \\ d & 0 & c \end{pmatrix} \quad (6-5)$$

$$B_g: \begin{pmatrix} 0 & e & 0 \\ e & 0 & f \\ 0 & f & 0 \end{pmatrix} \quad (6-6)$$

Temperature-dependent Raman spectra of CuInP_2S_6 flake in 20 nm around phase transition temperature (315 K) were conducted with 532-nm excitation as shown in Figure 6-12. The variation on Raman spectra dependent on the phase was investigated. Similar to the result of bulk CuInP_2S_6 crystal reported in previous paper, no peak addition or vanishing was observed in 10 nm thick sample.¹⁸⁹ However, some variation on intensity of Raman peaks could be found when the temperature went through the phase transition temperature in bulk crystal. For instance, the intensity of Peak 4 at 136 cm^{-1} increased when temperature increased across 315 K, while the Peak 9 at 317 cm^{-1} became weak and asymmetric. The ratio of integral

intensity between different selected Raman peaks was plotted as a function of temperature (Figure 6-13). The distinct variation indicates a structural phase transition occurs in 10-nm CuInP_2S_6 flake around 315 K, which is in accordance with the ferroelectric phase transition temperature of bulk CuInP_2S_6 crystal.

Figure 6-13 The intensity ratio of selected Raman modes *versus* temperature in a 20-nm CuInP_2S_6 flake.

6.4.2 SHG Study of CuInP_2S_6

Compared with Raman spectroscopy, optical SHG signal would be a much more sensitive probe for the phase transition between the ferroelectric phase and the paraelectric phase in CuInP_2S_6 . This idea is on the basis of the accompanying lattice structural transition from noncentrosymmetric space group Cc to centrosymmetric $C2/c$ around T_c can be detected by the variation of optical SHG signal, which has been applied in the CuInP_2S_6 bulk crystal.⁶¹

Figure 6-14 (a) Thickness-dependent SHG spectra of CuInP_2S_6 flakes at room temperature excited by 800-nm femtosecond pulse laser. (b) Plot of normalized intensity of SHG vs. thickness of CuInP_2S_6 flakes.

The sensitivity of SHG offers us an opportunity to investigate the ferroelectric polarization in CuInP_2S_6 flakes thinner than 50 nm. The SHG measurements were conducted on CuInP_2S_6 flake in different thickness down to 5.4 nm (Figure 6-14a). The result indicated that a distinct second-harmonic signal was generated in 12.5 nm thick CuInP_2S_6 flake at room temperature, while no SHG could be observed in thinner CuInP_2S_6 flake (such as 9.6 and 5.4 nm). The integral intensity of SHG peak was plotted as a function of sample thickness in Figure 6-14b. The SHG intensity exhibited a dropping edge when the sample thickness decreased from 100 nm to 10 nm. This result is in consistence with the PFM measurement of CuInP_2S_6 flake, which suggests that the domain structure starts to degenerate when the sample thickness below 100 nm.¹⁸⁸ However, the PFM measurement of CuInP_2S_6 flake indicates that the polarization of CuInP_2S_6 flake disappears below 50 nm, while our SHG measurements suggests a noncentrosymmetric structure in the samples with the thickness of 12.5 and 26 nm.

Figure 6-15 (a) Temperature-dependent SHG spectra of CuInP_2S_6 flakes around phase transition temperature excited by 400-nm femtosecond pulse laser. (b) Plot of normalized intensity of SHG vs. temperature for CuInP_2S_6 flakes with different thickness.

To verify the absence of centrosymmetry, which induces the SHG signal in the CuInP_2S_6 flakes below 50 nm, is related to the ferroelectric polarization in materials, the temperature-dependent SHG spectra of CuInP_2S_6 thin flake were conducted as shown in Figure 6-15a, where the 96-nm thick sample was measured as a reference. The integral intensity of SHG was normalized and plotted as a function of temperature in three samples with different thickness (Figure 6-15b).

As shown in Figure 6-15, the 12.5 nm thick CuInP_2S_6 flake generated a distinct second-harmonic signal at room temperature, while the SHG signal vanished at higher temperature. Based on this result, a structural phase transition, which was associated to the ferroelectric-paraelectric phase transition, was identified in CuInP_2S_6 flakes.

The interdependence between the structural variation and ion hopping motion was previously interpreted by the Raman spectroscopy measurement and neutron diffraction.^{189, 197}

The Cu^{I} in the upper off-center minimum causes a twisting of $[\text{P}_2\text{S}_6]^{4-}$ group, while the reversals of this force would result in the up and down flipping of the Cu^{I} dipole. As a consequence, although the SHG measurement could only be consider as an indirect evidence of ferroelectricity, this is the first statement of ferroelectricity in 2D materials with the thickness below 50 nm. Besides that, from Figure 6-16b, the decreasing edge of the plot of 12.5 nm sample is on the left side of the other two plots. This phenomenon implies a lower phase transition temperature in the 12.5 nm sample, which might be caused by the higher surface energy in nanometer region.

Figure 6-16 (a) The azimuthal angle θ dependent SHG intensity of CuInP_2S_6 . (b) Plane lattice structure of CuInP_2S_6 viewing from the direction normal to ab plane.

The azimuthal angle dependent SHG measurement of 12.5 nm multilayer CuInP_2S_6 flake was conducted by rotating the sample to investigate the crystal orientation. The SHG intensity exhibited a strongly dependence on the azimuthal angle θ . As indicated in Figure 6-16a, the angle resolved SHG intensity exhibited an asymmetric pattern with 6 petals when rotating the sample about its surface normal. This behavior is different from the angle resolved

SHG intensity of monolayer AgInP_2S_6 , where the 6-petal-pattern is symmetric. The plane structure of CuInP_2S_6 is the same as that of AgInP_2S_6 regardless the copper hopping motion (Figure 6-16b). The 6-petal pattern in the angle resolved SHG intensity of CuInP_2S_6 thin flake in is in consistence with the 3-fold symmetry in plane.

Figure 6-17 The azimuthal angle θ dependent Raman intensity of CuInP_2S_6 .

For comparison, the crystal-orientation-dependent Raman spectroscopy measurement on CuInP_2S_6 thin flake has been conducted. All the spectra were measured in $\bar{z}(xx)z$ configuration by rotating sample. The intensity of three strong Raman peaks plotted as a function of rotating angle vibrated around a certain value in error range. The results suggested that no anisotropy of Raman signal and lattice structure was observed. The results suggesting the isotropy of lattice structure in ab plane is in consistence with the plane structure of CuInP_2S_6 . The different behaviors of the angle resolved intensity between Raman and SHG implicate that the anisotropy of SHG intensity is attributed to the copper hopping motion.

When the bond charge model is applied to CuInP_2S_6 ,¹⁹³ the potential difference between two different ions in each bond $\vec{\mathcal{E}}_{ij}$ will be affected by the copper hopping motion, and become different along each direction. Therefore, the position shift of center of the each bond charge will vary, inducing an anisotropy to the second-order bond hyperpolarizability $\beta_n^{(2)}$ and the second-order nonlinear susceptibility $\chi^{(2)}$ of the whole structure. When light incidents along the sample surface normal, the anisotropy can be passed to the second-order dipole moment through $\mathbf{p}_{2\omega,n} = \beta_n^{(2)} (\vec{\mathcal{E}}_\omega \cdot \vec{\mathcal{E}}_n)^2$ in each bond. Moreover, in the angle resolved SHG measurement, three set of (opposite) petals exhibited different intensity, which implied that the polarization of anisotropy was not along the direction of any bonds in CuInP_2S_6 . This result suggests that the mechanism induced by copper hopping motion is rather complex. The exploration of detailed mechanism of the anisotropy may need the assistance of more crystalline structure information in further investigation.

6.5 Summary

In summary, the nonlinear optical properties have been studied in quaternary MPCs, AgInP_2S_6 and CuInP_2S_6 thin layers, which is prepared by mechanical exfoliation from bulk crystal.

The first observation of SHG on monolayer AgInP_2S_6 has been reported. The layer-number dependent SHG measurement has been conducted to probe the crystal symmetry. The distinct contrast of SHG intensity between odd- and even-number layers indicates that the even-layer number samples have inversion symmetry, which is broken for odd-layer number counterpart. The orientation dependent SHG intensity of monolayer AgInP_2S_6 reveals the 3-

fold rotational symmetry of the lattice. The SHG spectrum offers a potential method to probe the grain boundary of monolayer AgInP_2S_6 in ab plane.

The SHG measurement was also conducted on CuInP_2S_6 thin flakes. In the sample with the thickness below 50 nm, the variation of SHG signal with temperature changing around the ferroelectric-paraelectric phase transition temperature of bulk CuInP_2S_6 crystal. On the basis of this result, the first observation of ferroelectricity in 2D material with the thickness below 50 nm is demonstrated in CuInP_2S_6 flakes. The azimuthal angle dependent SHG intensity of CuInP_2S_6 suggests that an anisotropy on electronic field is induced by the copper hopping motion.

Our study of nonlinear optics on quaternary MPCs provides a platform to explore the crystal structure and related physical property in thin flakes of metal phosphorous sulfides. We believe that our works opens a new path to manipulate artificial and stable 2D material with various properties by doping metal atoms.

Chapter 7 Conclusions and Future work

7.1 Conclusions

In this dissertation, the optical properties of MPCs 2D crystals are systematically investigated through Raman spectroscopy and SHG. The special behaviors in MPCs, such as magnetic and ferroelectric properties, show that this new family of 2D semiconductor is not only significant for the fundamental understanding in physics of areas in 2D system, but also promising candidate material for potentially diverse applications in future ultrathin magnetic or ferroelectric device. Therefore, this dissertation focuses on the optical properties on MPCs. Beyond that, the several unique properties, such as magnetism and ferroelectricity, which are seldom reported in 2D crystal, are ingeniously and systematically investigated through optical spectroscopy methods.

High-quality MPC single crystals with the size from several to tens of millimeters have been synthesized through the chemical vapor transport (CVT) in sealed quartz tubes. Nine materials in this group, including ternary and quaternary compounds, have been mechanically exfoliated to few-layer, even down to monolayer on SiO₂/Si substrates from as-grown bulk crystals. The lattice structure of MPCs crystallized by a variety of characterization techniques and the calculated cleavage energies indicates the feasibility of conducting research on the ultrathin MPC flakes. The band gaps from 1.3 to 3.5 eV by element substitution suggest that they can be excellent candidates for potential optoelectronic applications in wide wavelength range.

The precise Raman spectroscopy measurement on several MPCs crystal suggests the high-frequency modes ($> 200 \text{ cm}^{-1}$) are originated from the internal deformation of $[\text{P}_2\text{S}_6]^{4-}$

anion, while the low-frequency modes ($< 200 \text{ cm}^{-1}$) are more largely affected by metal vibration. The monolayer FePS_3 and 3-layer FePSe_3 respectively exhibit quite similar Raman spectra with their bulk counterparts, implying that the phonon modes rely on the intra-layer vibrations more rather than the inter-layer interactions.

Due to the existence of iron ions in crystal, FePS_3 is interesting for its antiferromagnetic properties in bulk case. A systematic Raman spectroscopy measurement conducted in atomically thin FePS_3 layers offers a pathway to explore the crystalline and magnetic structure. The precise assignment of Raman modes in FePS_3 is completed by the polarization dependent Raman spectroscopy in assistant with phonon dispersion relations calculated by first principle calculation density-functional theory. The spin-dependent Raman modes is activated by the Brillouin-zone folding through spin-phonon coupling in antiferromagnetic phase. The layer-number dependent Raman spectroscopy suggests a magnetic persistence in FePS_3 monolayer, which indicates a promising future of ultrathin magnetic device. The magnetic phase transition temperature decreases with the thickness decreasing, which is attributed to the reducing superexchange along c axis in thin sample. This Raman spectroscopy measurement in 2D magnetic materials would promote a better understanding on many critical problems in various research fields.

Finally, a systematic investigation of the second-harmonic generation (SHG) in quaternary MPCs has been presented. The observation of optical SHG in 2D atomically thin silver indium phosphorous sulfide (AgInP_2S_6) crystals can be attributed to the symmetry breaking from bulk to monolayer. Based on that, the nonlinear signal can be used to detect the layer number, stacking order and crystal orientation of ultrathin flakes. The SHG signal can be observed in thin copper indium phosphorous sulfide (CuInP_2S_6) crystals with the thickness

ranging from 12.5 to 50 nm. The mechanism of SHG in this sample is related to the polar structure and ferroelectric polarization. As a result, the ferroelectricity is first demonstrated in natural 2D crystal below 50 nm.

Overall, our results in this dissertation display a systematic optical study on a new family of 2D semiconducting crystals – MPCs. The experiments are mainly performed on Raman spectroscopy and SHG measurement, while investigations spread on a variety of research areas, including the structural characterization, phonon properties, magnetic structure and ferroelectric polarization in thin MPC layers. Our studies expand the 2D crystals family in nonlinear effect field, which not only promote a better understanding on many critical problems in various research fields, but also open the door to functionalities and potential applications of 2D materials.

7.2 Future Work

Piezoresponse Force Microscopy (PFM) Measurement of CuInP₂S₆ Flakes

Figure 7-1 (a) Band excitation amplitude image and (b) band excitation phase image of bulk CuInP₂S₆ surface after writing a $\pm 5\text{ V}_{\text{dc}}$ square sequence.¹⁸⁸

Piezoresponse force microscopy (PFM) study can be used to verify the ferroelectricity of materials. The PFM amplitude reflects the absolute magnitude of the local piezoelectric response, while the phase indicates the polarization direction in each individual domain. Figure 7-1 showed the band excitation amplitude image and phase image of the surface of bulk CuInP_2S_6 after writing a $\pm 5 \text{ V}_{\text{dc}}$ square sequence. This result confirms three-dimensional ordering of polarization in this material.¹⁸⁸ Based on this technique, the ferroelectricity has been verified in CuInP_2S_6 thin flakes down to 50 nm, as shown in Figure 6-3d.

As we demonstrate in Section 6.4, the ferroelectricity of our as-grown CuInP_2S_6 has been detected by SHG down to $\sim 10 \text{ nm}$ region based on the structural phase transition during the ferroelectric-paraelectric transition. It will be more convincing to do a PFM measurement on the exfoliated CuInP_2S_6 sample to detect the ordering of polarization as the direct evidence of ferroelectricity. Therefore, the PFM measurement can largely support the SHG measurement on the statement of ferroelectricity in CuInP_2S_6 below 50 nm thick.

Electronic Properties of FePS_3 Nanoflakes

As mentioned in Chapter 3, the wide-range band gaps from 1.3 to 3.5 eV in MPCs suggest their potential on atomically thin optoelectronic applications. However, the electronic and optoelectronic properties have not been explored in the field emission transistor (FET) of MPC nanostructures.

The FET device of micro-size few-layer FePS_3 has been successfully fabricated by electron-beam lithography technique (as shown in Figure 7-2). The metal contact, (10-nm Ni plus 40-nm Au) was deposited on the top of sample by thermal evaporator. Several kinds of metals, such as Ti, Cr and Fe, had been tested as the contacted electrode for FePS_3 flakes, while

Ni gave a best contact with semiconducting sample. The source-drain current of FePS_3 was measured in both ambient and vacuum condition. The symmetric I-V curve in vacuum, which was linear in low voltage (< 1 V), showed an ideal contact between FePS_3 and metal contact (Figure 7-2b). The disorder and unstable I-V curve with a large hysteresis in ambient condition was attributed to the influence from oxygen/moisture in the environment to the surface state of sample. The resistance of the devices ranged from hundreds of $\text{M}\Omega$ to several $\text{G}\Omega$, which increased with the sample thickness decreasing (Figure 7-2c).

Figure 7-2 (a) Optical microscopy image of FET device of ultrathin FePS_3 flake on the SiO_2/Si substrate. The metal contact is 10-nm Ni plus 40-nm Au. (b) Source-drain current *versus* bias voltage of FePS_3 device in ambient and vacuum condition. (c) Source-drain current *versus* bias voltage of FePS_3 devices in sample different thickness.

The temperature dependent I_{sd} - V_{sd} curves were measured in FePS_3 device (as shown in Figure 7-3a) and the I_{sd} was plotted as a function of temperature (as indicated in Figure 7-3b). The conductivity of the device decreased with the decreasing temperature and the FePS_3 sample became insulated below 200 K. The trend of variation of conductivity is in consistence with the traditional semiconductors, because the carriers are easier to be trapped at lower temperature.

Figure 7-3 (a) Temperature dependent I_{sd} - V_{sd} curves of FePS₃ device in vacuum condition. (b) Plots of I_{sd} versus temperature of FePS₃ device.

Beyond these measured electronic data, the mobility of FePS₃ ultrathin device can be estimated by conducting a back-gate tuning measurement. Moreover, the photoconductivity measurement of this series of MPC ultrathin devices can be achieved based on the nano-device coupled with the monochromator.

Raman Spectroscopy Measurement of CdPS₃ based on the Structural Phase Transition

A structural phase transition in CdPS₃ bulk crystal has been demonstrated by X-ray diffraction¹⁹⁸ and Raman spectroscopy measurement.¹⁹⁹ The structural phase transition in CdPS₃ is unique among all the ternary MPCs. This result suggests the special structural properties are originated from the existence of Cd²⁺ ions. The pure CdPS₃ crystal will transit from the trigonal symmetry D_{3d} to the triclinic symmetry C_i with decreasing temperature crossing phase transition temperature around 295 K.¹⁹⁹ In our Raman spectroscopy measurement of CdPS₃ bulk crystal (Figure 7-4), two new peaks are observed only at low temperature (77 K), which is also reported in previous literatures.

Figure 7-4 (a) Raman spectra of CdPS₃ bulk crystal at room temperature (296 K) and liquid nitrogen temperature (77 K). (b) and (c) are the close-up views for two additional peaks at 31 cm⁻¹ and 188 cm⁻¹, respectively.

Since the ultrathin CdPS₃ flakes can be obtained by mechanical exfoliation, they offer us an excellent opportunity to explore the variation of the structure, as well as the phase transition when the dimension of system decreases from 3D to 2D. Compared with other structural techniques, such as powder X-ray diffraction, Raman spectroscopy has its advantages to assign the symmetry of crystal structure and lattice vibration of micro-size ultrathin samples. Therefore, it is significant to conduct a systematic Raman spectroscopy measurement on CdPS₃ from bulk down to monolayer region. The better understanding on the structural variation and lattice dynamics of this compound in 2D system is much helpful for the manipulation of artificial and stable 2D MPC crystals with various properties by doping metal atoms.

References

1. Dresselhaus, M. S.; Dresslhaus, G., Fullerenes and fullerene derived solids as electronic materials. *Annu. Rev. Mater. Sci.* **1995**, *25* (1), 487-523.
2. Mauricio, T., Science and technology of the twenty-first century: synthesis, properties, and applications of carbon nanotubes. *Annu. Rev. Mater. Res.* **2003**, *33* (1), 419-501.
3. Castro Neto, A. H.; Guinea, F.; Peres, N. M. R.; Novoselov, K. S.; Geim, A. K., The electronic properties of graphene. *Rev. Mod. Phys.* **2009**, *81* (1), 109-162.
4. Reimann, S. M.; Manninen, M., Electronic structure of quantum dots. *Rev. Mod. Phys.* **2002**, *74* (4), 1283-1342.
5. Law, M.; Goldberger, J.; Yang, P., Semiconductor Nanowires and Nanotubes. *Annu. Rev. Mater. Res.* **2004**, *34*, 83-122.
6. Keith, B.; Dimitri, V., *Low-dimensional semiconductor structures: fundamentals and device applications*. Cambridge University Press: Cambridgeshire, 2001.
7. Eshlaghi, S.; Worthoff, W.; Wieck, A. D.; Suter, D., Luminescence upconversion in GaAs quantum wells. *Phys. Rev. B* **2008**, *77* (24), 245317.
8. Prasanta, K., Basu, *Theory of Optical Processes in Semiconductors: Bulk and Microstructures: Bulk and Microstructures*. Oxford University Press: Oxford, 1998.
9. Klitzing, K. v.; Dorda, G.; Pepper, M., New Method for High-Accuracy Determination of the Fine-Structure Constant Based on Quantized Hall Resistance. *Phys. Rev. Lett.* **1980**, *45* (6), 494-497.
10. Zhang, Y.; Tan, Y.-W.; Stormer, H. L.; Kim, P., Experimental observation of the quantum Hall effect and Berry's phase in graphene. *Nature* **2005**, *438* (7065), 201-204.
11. Yu, G.; Hu, L.; Vosgueritchian, M.; Wang, H.; Xie, X.; McDonough, J. R.; Cui, X.; Cui, Y.; Bao, Z., Solution-Processed Graphene/MnO₂ Nanostructured Textiles for High-Performance Electrochemical Capacitors. *Nano Lett.* **2011**, *11* (7), 2905-2911.
12. Wessells, C. D.; Huggins, R. A.; Cui, Y., Copper hexacyanoferrate battery electrodes with long cycle life and high power. *Nature Commun.* **2011**, *2*, 550.
13. Wu, H.; Chan, G.; Choi, J. W.; Ryu, I.; Yao, Y.; McDowell, M. T.; Lee, S. W.; Jackson, A.; Yang, Y.; Hu, L., *et al.*, Stable cycling of double-walled silicon nanotube battery anodes through solid-electrolyte interphase control. *Nature Nano.* **2012**, *7* (5), 310-315.
14. Hu, M.; Chen, J.; Li, Z.-Y.; Au, L.; Hartland, G. V.; Li, X.; Marquez, M.; Xia, Y., Gold nanostructures: engineering their plasmonic properties for biomedical applications. *Chem. Soc. Rev.* **2006**, *35* (11), 1084-1094.

15. Wan, Q.; Li, Q. H.; Chen, Y. J.; Wang, T. H.; He, X. L.; Li, J. P.; Lin, C. L., Fabrication and ethanol sensing characteristics of ZnO nanowire gas sensors. *Appl. Phys. Lett.* **2004**, *84* (18), 3654-3656.
16. Tian, B.; Cohen-Karni, T.; Qing, Q.; Duan, X.; Xie, P.; Lieber, C. M., Three-Dimensional, Flexible Nanoscale Field-Effect Transistors as Localized Bioprobes. *Science* **2010**, *329* (5993), 830-834.
17. Harmer, M. A.; Farneth, W. E.; Sun, Q., High Surface Area Nafion Resin/Silica Nanocomposites: A New Class of Solid Acid Catalyst. *J. Am. Chem. Soc.* **1996**, *118* (33), 7708-7715.
18. Zhong, C. J.; Maye, M. M., Core-Shell Assembled Nanoparticles as Catalysts. *Adv. Mater.* **2001**, *13* (19), 1507-1511.
19. Lieber, C. M.; Wang, Z. L., Functional Nanowires. *MRS Bull.* **2007**, *32* (02), 99-108.
20. Yang, P.; Yan, R.; Fardy, M., Semiconductor Nanowire: What's Next? *Nano Lett.* **2010**, *10* (5), 1529-1536.
21. John, H. D., *The physics of low-dimensional semiconductors: an introduction*. Cambridge university press: 1997.
22. Yoffe, A. D., Low-dimensional systems: Quantum size effects and electronic properties of semiconductor microcrystallites (zero-dimensional systems) and some quasi-two-dimensional systems. *Adv. Phys.* **2002**, *51* (2), 799-890.
23. and, C. B. M.; Kagan, C. R.; Bawendi, M. G., Synthesis and Characterization of Monodisperse Nanocrystals and Close-Packed Nanocrystal Assemblies. *Annu. Rev. Mater. Sci.* **2000**, *30* (1), 545-610.
24. Reed, M. A.; Randall, J. N.; Aggarwal, R. J.; Matyi, R. J.; Moore, T. M.; Wetsel, A. E., Observation of discrete electronic states in a zero-dimensional semiconductor nanostructure. *Phys. Rev. Lett.* **1988**, *60* (6), 535-537.
25. Konstantatos, G.; Clifford, J.; Levina, L.; Sargent, E. H., Sensitive solution-processed visible-wavelength photodetectors. *Nature Photon.* **2007**, *1* (9), 531-534.
26. McDonald, S. A.; Konstantatos, G.; Zhang, S.; Cyr, P. W.; Klem, E. J. D.; Levina, L.; Sargent, E. H., Solution-processed PbS quantum dot infrared photodetectors and photovoltaics. *Nature Mater.* **2005**, *4* (2), 138-142.
27. Zhao, X.; Wei, C. M.; Yang, L.; Chou, M. Y., Quantum Confinement and Electronic Properties of Silicon Nanowires. *Phys. Rev. Lett.* **2004**, *92* (23), 236805.
28. Calarco, R.; Marso, M.; Richter, T.; Aykanat, A. I.; Meijers, R.; v.d. Hart, A.; Stoica, T.; Lüth, H., Size-dependent Photoconductivity in MBE-Grown GaN-Nanowires. *Nano Lett.* **2005**, *5* (5), 981-984.
29. Li, B.; Yu, D.; Zhang, S.-L., Raman spectral study of silicon nanowires. *Phys. Rev. B* **1999**, *59* (3), 1645-1648.

30. Li, D. H.; Zhang, J.; Xiong, Q. H., Surface depletion induced quantum confinement in CdS nanobelts. *ACS Nano* **2012**, 6, 5283-5290.
31. José, B.; Jean-Louis, H.; Mogens, S. L.; Jean-Rene, R.; Claire, S., *Neutron and synchrotron radiation for condensed matter studies*. Springer Verlag: Berlin, 1993.
32. Stephen, B., *Magnetism in condensed matter*. Oxford University Press Inc.: New York, 2001.
33. Garcia, J. C.; de Lima, D. B.; Assali, L. V. C.; Justo, J. F., Group IV Graphene- and Graphane-Like Nanosheets. *J. Chem. Phys. C* **2011**, 115 (27), 13242-13246.
34. Elizabeth, G., The super materials that could trump graphene. *Nature* **2015**, 522 (7556), 274-276.
35. Mermin, N. D., Crystalline Order in Two Dimensions. *Phys. Rev.* **1968**, 176 (1), 250-254.
36. Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; Grigorieva, I. V.; Firsov, A. A., Electric Field Effect in Atomically Thin Carbon Films. *Science* **2004**, 306 (5696), 666-669.
37. Bonaccorso, F.; Colombo, L.; Yu, G.; Stoller, M.; Tozzini, V.; Ferrari, A. C.; Ruoff, R. S.; Pellegrini, V., Graphene, related two-dimensional crystals, and hybrid systems for energy conversion and storage. *Science* **2015**, 347 (6217), 1246501.
38. Chhowalla, M.; Shin, H. S.; Eda, G.; Li, L.-J.; Loh, K. P.; Zhang, H., The chemistry of two-dimensional layered transition metal dichalcogenide nanosheets. *Nature Chem.* **2013**, 5 (4), 263-275.
39. Wilson, J. A.; Yoffe, A. D., The transition metal dichalcogenides discussion and interpretation of the observed optical, electrical and structural properties. *Adv. Phys.* **1969**, 18 (73), 193-335.
40. Suzuki, R.; Sakano, M.; Zhang, Y. J.; Akashi, R.; Morikawa, D.; Harasawa, A.; Yaji, K.; Kuroda, K.; Miyamoto, K.; Okuda, T., *et al.*, Valley-dependent spin polarization in bulk MoS₂ with broken inversion symmetry. *Nature Nano.* **2014**, 9 (8), 611-617.
41. Zeng, H.; Dai, J.; Yao, W.; Xiao, D.; Cui, X., Valley polarization in MoS₂ monolayers by optical pumping. *Nature Nano.* **2012**, 7 (8), 490-493.
42. Mak, K. F.; He, K.; Shan, J.; Heinz, T. F., Control of valley polarization in monolayer MoS₂ by optical helicity. *Nature Nano.* **2012**, 7 (8), 494-498.
43. Xiao, D.; Liu, G.-B.; Feng, W.; Xu, X.; Yao, W., Coupled Spin and Valley Physics in Monolayers of MoS₂ and Other Group-VI Dichalcogenides. *Phys. Rev. Lett.* **2012**, 108 (19), 196802.
44. Geim, A. K.; Grigorieva, I. V., Van der Waals heterostructures. *Nature* **2013**, 499 (7459), 419-425.

45. Sivadas, N.; Daniels, M. W.; Swendsen, R. H.; Okamoto, S.; Xiao, D., Magnetic ground state of semiconducting transition-metal trichalcogenide monolayers. *Phys. Rev. B* **2015**, *91* (23), 235425.
46. Yun, W. S.; Lee, J. D., Strain-Induced Magnetism in Single-Layer MoS₂: Origin and Manipulation. *J. Chem. Phys. C* **2015**, *119* (5), 2822-2827.
47. Fang, H.; Battaglia, C.; Carraro, C.; Nemsak, S.; Ozdol, B.; Kang, J. S.; Bechtel, H. A.; Desai, S. B.; Kronast, F.; Unal, A. A., *et al.*, Strong interlayer coupling in van der Waals heterostructures built from single-layer chalcogenides. *Proceedings of the National Academy of Sciences* **2014**, *111* (17), 6198-6202.
48. Jariwala, D.; Sangwan, V. K.; Lauhon, L. J.; Marks, T. J.; Hersam, M. C., Emerging Device Applications for Semiconducting Two-Dimensional Transition Metal Dichalcogenides. *ACS Nano* **2014**, *8* (2), 1102-1120.
49. Kuch, W.; Schäfer, R.; Fischer, P.; Hillebrecht, U., *Magnetic Microscopy of Layered Structures*. Springer: 2014.
50. Ferrari, A. C.; Bonaccorso, F.; Fal'ko, V.; Novoselov, K. S.; Roche, S.; Boggild, P.; Borini, S.; Koppens, F. H. L.; Palermo, V.; Pugno, N., *et al.*, Science and technology roadmap for graphene, related two-dimensional crystals, and hybrid systems. *Nanoscale* **2015**, *7* (11), 4598-4810.
51. Anasori, B.; Xie, Y.; Beidaghi, M.; Lu, J.; Hosler, B. C.; Hultman, L.; Kent, P. R. C.; Gogotsi, Y.; Barsoum, M. W., Two-Dimensional, Ordered, Double Transition Metals Carbides (MXenes). *ACS Nano* **2015**, *9* (10), 9507-9516.
52. Xu, C.; Wang, L.; Liu, Z.; Chen, L.; Guo, J.; Kang, N.; Ma, X.-L.; Cheng, H.-M.; Ren, W., Large-area high-quality 2D ultrathin Mo₂C superconducting crystals. *Nature Mater.* **2015**, *14* (11), 1135-1141.
53. Nicolosi, V.; Chhowalla, M.; Kanatzidis, M. G.; Strano, M. S.; Coleman, J. N., Liquid Exfoliation of Layered Materials. *Science* **2013**, *340* (6139), 1226419.
54. Brec, R., Review on structural and chemical properties of transition metal phosphorous trisulfides MPS₃. *Solid State Ionics* **1986**, *22* (1), 3-30.
55. Pfitzner, A.; Seidlmayer, S., Synthesis and Structure Determination of AgScP₂Se₆, AgErP₂Se₆ and AgTmP₂Se₆. *Z. Anorg. Allg. Chem.* **2009**, *635* (4-5), 704-707.
56. Pfeiff, R.; Kniep, R., Quaternary selenodiphosphates(IV): M^IM^{III}[P₂Se₆], (M^I = Cu, Ag; M^{III} = Cr, Al, Ga, In). *J. Alloy. Compd.* **1992**, *186* (1), 111-133.
57. Rule, K. C.; McIntyre, G. J.; Kennedy, S. J.; Hicks, T. J., Single-crystal and powder neutron diffraction experiments on FePS₃: Search for the magnetic structure. *Phys. Rev. B* **2007**, *76* (13), 134402.

58. Wildes, A. R.; Ronnow, H. M.; Roessli, B.; Harris, M. J.; Godfrey, K. W., Static and dynamic critical properties of the quasi-two-dimensional antiferromagnet MnPS_3 . *Phys. Rev. B* **2006**, 74 (9), 094422.
59. Joy, P. A.; Vasudevan, S., Magnetism in the Layered Transition-Metal Thiophosphates MPS_3 ($\text{M} = \text{Mn, Fe, and Ni}$). *Phys. Rev. B* **1992**, 46 (9), 5425-5433.
60. Balkanski, M., Spin-Dependent Light Scattering in Two-Dimensional Magnetically Ordered Systems. In *New Horizons in Low-Dimensional Electron Systems*, Aoki, H.; Tsukada, M.; Schlüter, M.; Lévy, F., Eds. Springer Netherlands: 1992; Vol. 13, pp 71-84.
61. Misuryaev, T. V.; Murzina, T. V.; Aktsipetrov, O. A.; Sherstyuk, N. E.; Cajipe, V. B.; Bourdon, X., Second harmonic generation in the lamellar ferrielectric CuInP_2S_6 . *Solid State Commun.* **2000**, 115 (11), 605-608.
62. Simon, A.; Ravez, J.; Maisonneuve, V.; Payen, C.; Cajipe, V. B., Paraelectric-Ferroelectric Transition in the Lamellar Thiophosphate CuInP_2S_6 . *Chem. Mater.* **1994**, 6 (9), 1575-1580.
63. Bernasconi, M.; Marra, G. L.; Benedek, G.; Miglio, L.; Jouanne, M.; Julien, C.; Scagliotti, M.; Balkanski, M., Lattice Dynamics of Layered MPX_3 ($\text{M} = \text{Mn, Fe, Ni, Zn}$; $\text{X} = \text{S, Se}$) Compounds. *Phys. Rev. B* **1988**, 38 (17), 12089-12099.
64. Ouvrard, G.; Brec, R.; Rouxel, J., Structural determination of some MPS_3 layered phases ($\text{M} = \text{Mn, Fe, Co, Ni and Cd}$). *Mater. Res. Bull.* **1985**, 20 (10), 1181-1189.
65. Prouzet, E.; Ouvrard, G.; Brec, R., Structure determination of ZnPS_3 . *Mater. Res. Bull.* **1986**, 21 (2), 195-200.
66. Taylor, B. E.; Steger, J.; Wold, A., Preparation and properties of some transition metal phosphorus trisulfide compounds. *J. Solid. State. Chem.* **1973**, 7 (4), 461-467.
67. Colombet, P.; Leblanc, A.; Danot, M.; Rouxel, J., Coordination inhabituelle de l'argent dans un sulfure lamellaire a sous-réseau magnétique 1 D: le composé $\text{Ag}_{1/2}\text{Cr}_{1/2}\text{PS}_3$. *Nouv. J. Chim.* **1983**, 7, 333-338.
68. Colombet, P.; Leblanc, A.; Danot, M.; Rouxel, J., Structural aspects and magnetic properties of the lamellar compound $\text{Cu}_{0.50}\text{Cr}_{0.50}\text{PS}_3$. *J. Solid. State. Chem.* **1982**, 41 (2), 174-184.
69. Mathey, Y.; Michalowicz, A.; Toffoli, P.; Vlaic, G., Resolution of a structural disorder through apparently inconsistent x-ray diffraction and EXAFS data: structure of the new layered system manganese copper phosphorus sulfide ($\text{Mn}_{1-x}\text{Cu}_x\text{PS}_3$ ($x = 0.13$)). *Inorg. Chem.* **1984**, 23 (7), 897-902.
70. Poizat, O.; Sourisseau, C., A comparative vibrational study of $\text{Cr}^{\text{III}}_{0.5}\text{M}^{\text{II}}_{0.5}\text{PS}_3$ and $\text{Mn}^{\text{III}-x}\text{M}^{\text{II}x}\text{PS}_3$ layer-type compounds with $\text{M}^{\text{I}} = \text{Cu}$ ($x = 0.13$) and Ag ($x = 0.5$). *J. Solid. State. Chem.* **1985**, 59 (3), 371-378.

71. Brec, R.; Schleich, D. M.; Ouvrard, G.; Louisy, A.; Rouxel, J., Physical-Properties of Lithium Intercalation Compounds of the Layered Transition Chalcogenophosphates. *Inorg. Chem.* **1979**, *18* (7), 1814-1818.
72. Le Flem, G.; Brec, R.; Ouvrard, G.; Louisy, A.; Segransan, P., Magnetic interactions in the layer compounds MPX_3 (M = Mn, Fe, Ni; X = S, Se). *J. Phys. Chem. Solids* **1982**, *43* (5), 455-461.
73. Kurosawa, K.; Saito, S.; Yamaguchi, Y., Neutron Diffraction Study on $MnPS_3$ and $FePS_3$. *J. Phys. Soc. Jpn.* **1983**, *52* (11), 3919-3926.
74. Nozaki, H.; Umehara, M.; Ishizawa, Y.; Saeki, M.; Mizoguchi, T.; Nakahira, M., Magnetic properties of V_5S_8 single crystals. *J. Phys. Chem. Solids* **1978**, *39* (8), 851-858.
75. John, S., Griffith, *The theory of transition-metal ions*. Cambridge University Press: Cambridge, 1961.
76. Anatole, A.; Brebis, B., *Electron paramagnetic resonance of transition ions*. Oxford: Clarendon, 2012.
77. Whangbo, M. H.; Brec, R.; Ouvrard, G.; Rouxel, J., Reduction sites of transition-metal phosphorus trichalcogenides MPX_3 . *Inorg. Chem.* **1985**, *24* (15), 2459-2461.
78. Mercier, H.; Mathey, Y.; Canadell, E., On the electronic structure of MPS_3 phases. *Inorg. Chem.* **1987**, *26* (6), 963-965.
79. Kurita, N.; Nakao, K., Band Structure of Magnetic Layered Semiconductor $NiPS_3$. *J. Phys. Soc. Jpn.* **1989**, *58* (1), 232-243.
80. Kurita, N.; Nakao, K., Band Structures and Physical Properties of Magnetic Layered Semiconductors MPS_3 . *J. Phys. Soc. Jpn.* **1989**, *58* (2), 610-621.
81. Zhang, X.; Zhao, X.; Wu, D.; Jing, Y.; Zhou, Z., $MnPSe_3$ Monolayer: A Promising 2D Visible-Light Photohydrolytic Catalyst with High Carrier Mobility. *Adv. Sci.* **2016**, *3* (10), 1600062.
82. Bheema, L.; Chittari; Youngju, P.; Dongkyu, L.; Moonup, H.; Allan, H. M.; Euyheon, H.; Jeil, J., Electronic and magnetic properties of single-layer MPX_3 metal phosphorous trichalcogenides. *arXiv preprint arXiv:1604.06445* **2016**.
83. Li, X.; Wu, X.; Yang, J., Half-Metallicity in $MnPSe_3$ Exfoliated Nanosheet with Carrier Doping. *J. Am. Chem. Soc.* **2014**, *136* (31), 11065-11069.
84. Liu, J.; Li, X. B.; Wang, D.; Lau, W. M.; Peng, P.; Liu, L. M., Diverse and tunable electronic structures of single-layer metal phosphorus trichalcogenides for photocatalytic water splitting. *J Chem Phys* **2014**, *140* (5), 054707.
85. Binnewies, M.; Glaum, R.; Schmidt, M.; Schmidt, P., Chemical Vapor Transport Reactions – A Historical Review. *Z. Anorg. Allg. Chem.* **2013**, *639* (2), 219-229.

86. Schmidt, P.; Binnewies, M.; Glaum, R.; Schmidt, M., *Chemical Vapor Transport Reactions - Methods, Materials, Modeling*. InTech: Rijeka, Croatia, 2013; Vol. 9.
87. Bunsen, R., Vulkanische exhalation. *J. prakt. Chem* **1852**, 56, 53.
88. Schäfer, H., *Chemische Transportreaktionen*, Verlag Chemie. Wiley-VCH: Weinheim, 1962.
89. Schäfer, H.; Morcher, B., Chemical transport reactions. III. The transport of silicon in a temperature gradient through the agency of the silicon (II) halides and the pressure dependence of the transport direction. *Z. Anorg. Allg. Chem.* **1957**, 290 (5-6), 279-291.
90. Schäfer, H., Chemical Transport of Silver with Iodine and Inversion of Transport Direction in Temperature-Gradient. *Z. Anorg. Allg. Chem.* **1973**, 401 (3), 227-232.
91. Lely, D.; Hamburger, L., Preparation of the Elements-Thorium, Uranium, Zirconium and Titanium. *Z. Anorg. Chem.* **1914**, 87 (1), 209-228.
92. Schäfer, H., Gaseous Chloride Complexes with Halogen Bridges—Homo-Complexes and Hetero-Complexes. *Angew. Chem., Int. Edit. Engl.* **1976**, 15 (12), 713-727.
93. Binnewies, M.; Glaum, R.; Schmidt, M.; Schmidt, P., *Chemical vapor transport reactions*. Walter de Gruyter: Berlin, 2012.
94. Glaum, R.; Gruehn, R., Chemical Transport of Vanadium Phosphate with Iodine. *Z. Anorg. Allg. Chem.* **1989**, 568 (1), 73-84.
95. Schöneich, M.; Schmidt, Marcus P.; Schmidt, P., Chemical Vapour Transport of Bismuth and Antimony Chalcogenides M_2Q_3 ($M = Sb, Bi$, $Q = Se, Te$) *Z. Anorg. Allg. Chem.* **2010**, 636 (9-10), 1810-1816.
96. David, B.; Barry, C. C., *Transmission electron microscopy: A textbook for materials science*. Springer: 2009.
97. Unakar, N. J.; Tsui, J. Y.; Harding, C. V., Scanning Electron Microscopy. *Ophthalmic Res.* **1981**, 13 (1), 20-35.
98. Binnig, G.; Quate, C. F.; Gerber, C., Atomic Force Microscope. *Phys. Rev. Lett.* **1986**, 56 (9), 930-933.
99. Raman, C. V.; Krishnan, K. S., A new type of secondary radiation. *Nature* **1928**, 121, 501-502.
100. Bassani, G. F.; Liedl, G. L.; Wyder, P., *Encyclopedia of Condensed Matter Physics*. Academic: 2005.
101. Franken, P. A.; Hill, A. E.; Peters, C. W.; Weinreich, G., Generation of Optical Harmonics. *Phys. Rev. Lett.* **1961**, 7 (4), 118-119.
102. Bloembergen, N.; Pershan, P. S., Light Waves at the Boundary of Nonlinear Media. *Phys. Rev.* **1962**, 128 (2), 606-622.

103. Heinz, T. F.; Chen, C. K.; Ricard, D.; Shen, Y. R., Spectroscopy of Molecular Monolayers by Resonant Second-Harmonic Generation. *Phys. Rev. Lett.* **1982**, *48* (7), 478-481.
104. Shen, Y. R., Surface properties probed by second-harmonic and sum-frequency generation. *Nature* **1989**, *337* (6207), 519-525.
105. Yuen, R., Shen. *Principles of nonlinear optics*. Wiley-Interscience: New York, 2003.
106. Malard, L. M.; Alencar, T. V.; Barboza, A. P. M.; Mak, K. F.; de Paula, A. M., Observation of intense second harmonic generation from MoS₂ atomic crystals. *Phys. Rev. B* **2013**, *87* (20), 201401.
107. Kumar, N.; Najmaei, S.; Cui, Q.; Ceballos, F.; Ajayan, P. M.; Lou, J.; Zhao, H., Second harmonic microscopy of monolayer MoS₂. *Phys. Rev. B* **2013**, *87* (16), 161403.
108. Sun, Z.; Chang, H., Graphene and Graphene-like Two-Dimensional Materials in Photodetection: Mechanisms and Methodology. *ACS Nano* **2014**, *8* (5), 4133-4156.
109. Bonaccorso, F.; Colombo, L.; Yu, G.; Stoller, M.; Tozzini, V.; Ferrari, A. C.; Ruoff, R. S.; Pellegrini, V., 2D materials. Graphene, related two-dimensional crystals, and hybrid systems for energy conversion and storage. *Science* **2015**, *347* (6217), 1246501.
110. Xu, M. S.; Liang, T.; Shi, M. M.; Chen, H. Z., Graphene-Like Two-Dimensional Materials. *Chemical Reviews* **2013**, *113* (5), 3766-3798.
111. Sun, Y.; Gao, S.; Xie, Y., Atomically-thick two-dimensional crystals: electronic structure regulation and energy device construction. *Chem. Soc. Rev.* **2014**, *43* (2), 530-546.
112. Xia, F.; Wang, H.; Xiao, D.; Dubey, M.; Ramasubramaniam, A., Two-dimensional material nanophotonics. *Nature Photon.* **2014**, *8* (12), 899-907.
113. Yazyev, O. V.; Chen, Y. P., Polycrystalline graphene and other two-dimensional materials. *Nature Nano.* **2014**, *9* (10), 755-767.
114. Youngblood, N.; Chen, C.; Koester, S. J.; Li, M., Waveguide-integrated black phosphorus photodetector with high responsivity and low dark current. *Nature Photon.* **2015**, *Advance Online Publication*.
115. Luo, X.; Lu, X.; Koon, G. K.; Castro Neto, A. H.; Ozyilmaz, B.; Xiong, Q.; Quek, S. Y., Large Frequency Change with Thickness in Interlayer Breathing Mode--Significant Interlayer Interactions in Few Layer Black Phosphorus. *Nano Lett.* **2015**, *15* (6), 3931-3938.
116. Lu, X.; Utama, M. I. B.; Lin, J.; Luo, X.; Zhao, Y.; Zhang, J.; Pantelides, S. T.; Zhou, W.; Quek, S. Y.; Xiong, Q., Rapid and Nondestructive Identification of Polytypism and Stacking Sequences in Few-Layer Molybdenum Diselenide by Raman Spectroscopy. *Adv. Mater.* **2015**, *27* (30), 4502-4508.
117. Luo, X.; Zhao, Y.; Zhang, J.; Toh, M.; Kloc, C.; Xiong, Q.; Quek, S. Y., Effects of lower symmetry and dimensionality on Raman spectra in two-dimensional WSe₂. *Phys. Rev. B* **2013**, *88* (19), 195313.

118. Zhang, J.; Peng, Z.; Soni, A.; Zhao, Y.; Xiong, Y.; Peng, B.; Wang, J.; Dresselhaus, M. S.; Xiong, Q., Raman spectroscopy of few-quintuple layer topological insulator Bi₂Se₃ nanoplatelets. *Nano Lett.* **2011**, *11* (6), 2407-2414.
119. Zhao, Y.; Luo, X.; Li, H.; Zhang, J.; Araujo, P. T.; Gan, C. K.; Wu, J.; Zhang, H.; Quek, S. Y.; Dresselhaus, M. S., *et al.*, Inter layer Breathing and Shear Modes in Few-Trilayer MoS₂ and WSe₂. *Nano Lett.* **2013**, *13* (3), 1007-1015.
120. Reich, E. S., Phosphorene excites materials scientists. *Nature* **2014**, *506* (7486), 19.
121. Nitsche, R.; Wild, P., Crystal Growth of Metal-Phosphorous-Sulfur Compounds by Vapor Transport. *Mater. Res. Bull.* **1970**, *5* (6), 419-424.
122. Frindt, R. F.; Yang, D.; Westreich, P., Exfoliated single molecular layers of Mn_{0.8}PS₃ and Cd_{0.8}PS₃. *J. Mater. Res.* **2005**, *20* (5), 1107-1112.
123. Clementi, E.; Raimondi, D. L., Atomic Screening Constants from SCF Functions. *J. Chem. Phys.* **1963**, *38* (11), 2686-2689.
124. Clementi, E.; Raimondi, D. L.; Reinhardt, W. P., Atomic Screening Constants from SCF Functions. II. Atoms with 37 to 86 Electrons. *J. Chem. Phys.* **1967**, *47* (4), 1300-1307.
125. Kresse, G.; Furthmüller, J., Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Comput. Mater. Sci.* **1996**, *6* (1), 15-50.
126. Kresse, G.; Hafner, J., Ab Initio Molecular-Dynamics Simulation of the Liquid-Metal-Amorphous-Semiconductor Transition in Germanium. *Physical Review B* **1994**, *49* (20), 14251-14269.
127. Kresse, G.; Joubert, D., From Ultrasoft Pseudopotentials to the Projector Augmented-Wave Method. *Phys. Rev. B* **1999**, *59* (3), 1758-1775.
128. Perdew, J. P.; Burke, K.; Ernzerhof, M., Generalized Gradient Approximation Made Simple. *Physical Review Letters* **1996**, *77* (18), 3865-3868.
129. Blöchl, P. E., Projector Augmented-Wave Method. *Phys. Rev. B* **1994**, *50* (24), 17953-17979.
130. Grimme, S., Semiempirical GGA-type density functional constructed with a long-range dispersion correction. *J. Comput. Chem.* **2006**, *27* (15), 1787-1799.
131. Du, K.; Wang, X.; Liu, Y.; Hu, P.; Utama, M. I. B.; Gan, C. K.; Xiong, Q.; Kloc, C., Weak Van der Waals Stacking, Wide-Range Band Gap, and Raman Study on Ultrathin Layers of Metal Phosphorus Trichalcogenides. *ACS Nano* **2016**, *10* (2), 1738-1743.
132. Jernberg, P.; Bjarman, S.; Wappling, R., FePS₃ - a 1st-Order Phase-Transition in a 2D Ising Antiferromagnet. *J. Magn. Magn. Mater.* **1984**, *46* (1-2), 178-190.
133. Khumalo, F. S.; Hughes, H. P., Reflectance Spectra of Some FePS₃-Type Layer Compounds in the Vacuum Ultraviolet. *Phys. Rev. B* **1981**, *23* (10), 5375-5383.

134. Grasso, V.; Santangelo, S.; Piacentini, M., Optical-Absorption Spectra of Some Transition-Metal Thiophosphates. *Solid State Ionics* **1986**, *20* (1), 9-15.
135. Clement, R.; Girerd, J. J.; Morgensternbadarau, I., Dramatic Modification of the Magnetic Properties of Lamellar MnPS_3 upon Intercalation. *Inorg. Chem.* **1980**, *19* (9), 2852-2854.
136. Sourisseau, C.; Forgerit, J. P.; Mathey, Y., Vibrational Study of the $[\text{P}_2\text{S}_6]^{4-}$ Anion, of Some MPS_3 Layered Compounds ($\text{M}=\text{Fe, Co, Ni, In}_2\text{S}_3$), and of Their Intercalates with $[\text{Co}(\eta^5\text{-C}_5\text{H}_5)_2]^+$ Cations. *J. Solid. State. Chem.* **1983**, *49* (2), 134-149.
137. Makimura, C.; Sekine, T.; Tanokura, Y.; Kurosawa, K., Raman scattering in the two-dimensional antiferromagnet MnPS_3 . *J. Phys. Condens. Mat.* **1993**, *5* (5), 623-632.
138. Scagliotti, M.; Jouanne, M.; Balkanski, M.; Ouvrard, G.; Benedek, G., Raman-Scattering in Antiferromagnetic FePS_3 and FePSe_3 Crystals. *Phys. Rev. B* **1987**, *35* (13), 7097-7104.
139. Kurita, N.; Nakao, K., Self-Consistent Band Structure of Layered Semiconductor ZnPS_3 . *J. Phys. Soc. Jpn.* **1987**, *56* (12), 4455-4465.
140. Loudon, R., The Raman effect in crystals. *Advances in Physics* **1964**, *13* (52), 423-482.
141. Damen, T. C.; Porto, S. P. S.; Tell, B., Raman Effect in Zinc Oxide. *Phys. Rev.* **1966**, *142* (2), 570-574.
142. Zhang, J.; Soon, J. M.; Loh, K. P.; Yin, J.; Ding, J.; Sullivan, M. B.; Wu, P., Magnetic Molybdenum Disulfide Nanosheet Films. *Nano Lett.* **2007**, *7* (8), 2370-2376.
143. Tongay, S.; Varnoosfaderani, S. S.; Appleton, B. R.; Wu, J.; Hebard, A. F., Magnetic properties of MoS_2 : Existence of ferromagnetism. *Appl. Phys. Lett.* **2012**, *101* (12), 123105.
144. Mathew, S.; Gopinadhan, K.; Chan, T. K.; Yu, X. J.; Zhan, D.; Cao, L.; Rusydi, A.; Breese, M. B. H.; Dhar, S.; Shen, Z. X., *et al.*, Magnetism in MoS_2 induced by proton irradiation. *Appl. Phys. Lett.* **2012**, *101* (10), 102103.
145. Vojvodic, A.; Hinnemann, B.; Nørskov, J. K., Magnetic edge states in MoS_2 characterized using density-functional theory. *Phys. Rev. B* **2009**, *80* (12), 125416.
146. Cardona, M.; Güntherodt, G., *Light Scattering in Solids III*. Springer Berlin Heidelberg: 1982; Vol. 51.
147. Sandilands, L. J.; Shen, J. X.; Chugunov, G. M.; Zhao, S. Y. F.; Ono, S.; Ando, Y.; Burch, K. S., Stability of exfoliated $\text{Bi}_2\text{Sr}_2\text{Dy}_x\text{Ca}_{1-x}\text{Cu}_2\text{O}_{8-x}$ studied by Raman microscopy. *Phys. Rev. B* **2010**, *82* (6), 064503.
148. Ko, W.-H.; Liu, Z.-X.; Ng, T.-K.; Lee, P. A., Raman signature of the $\text{U}(1)$ Dirac spin-liquid state in the spin -1/2 kagome system. *Phys. Rev. B* **2010**, *81* (2), 024414.

149. Kamihara, Y.; Watanabe, T.; Hirano, M.; Hosono, H., Iron-Based Layered Superconductor $\text{La}[\text{O}_{1-x}\text{F}_x]\text{FeAs}$ ($x = 0.05\text{--}0.12$) with $T_c = 26$ K. *J. Am. Chem. Soc.* **2008**, *130* (11), 3296-3297.
150. Kamihara, Y.; Hiramatsu, H.; Hirano, M.; Kawamura, R.; Yanagi, H.; Kamiya, T.; Hosono, H., Iron-Based Layered Superconductor: LaOFeP . *J. Am. Chem. Soc.* **2006**, *128* (31), 10012-10013.
151. Guntherodt, G.; Bauhofer, W.; Benedek, G., Zone-Boundary-Phonon Raman-Scattering in VI_2 due to Modulation of Exchange Interaction. *Phys. Rev. Lett.* **1979**, *43* (19), 1427-1430.
152. Sakai, O.; Tachiki, M., Theory of Raman scattering in Europium-chalcogenides. *J. Phys. Chem. Solids* **1978**, *39* (3), 269-283.
153. Suzuki, N., Theory of Spin-Dependent Phonon Raman Scattering in Magnetic Crystals. II Application to Europium Sulphide. *J. Phys. Soc. Jpn.* **1976**, *40* (5), 1223-1231.
154. Suzuki, N.; Kamimura, H., Theory of Spin-Dependent Phonon Raman Scattering in Magnetic Crystals. *J. Phys. Soc. Jpn.* **1973**, *35* (4), 985-995.
155. Güntherodt, G., Light scattering in magnetic semiconductors. *J. Magn. Magn. Mater.* **1979**, *11* (1), 394-402.
156. Anastassakis, E.; Burstein, E., Morphotropic effects. V. Time reversal symmetry and the mode properties of long wavelength optical phonons. *J. Phys. C: Solid State Phys.* **1972**, *5* (17), 2468.
157. Bauhofer, W.; Guntherodt, G.; Anastassakis, E.; Frey, A.; Benedek, G., Raman-Scattering and Far-Infrared Studies of the Vanadium Dihalides with Layered Structure. *Phys. Rev. B* **1980**, *22* (12), 5873-5886.
158. Suzuki, N.; Kamimura, H., Theory of phonon Raman scattering in transition metal compounds. *Solid State Commun.* **1972**, *11* (12), 1603-1606.
159. Güntherodt, G.; Abstreiter, G.; Bauhofer, W.; Benedek, G.; Anastassakis, E., Magnetic "Bragg" scattering in antiferromagnets observed through Raman scattering from phonons. *J. Magn. Magn. Mater.* **1980**, *15*, 777-778.
160. Sekine, T.; Jouanne, M.; Julien, C.; Balkanski, M., Light-scattering study of dynamical behavior of antiferromagnetic spins in the layered magnetic semiconductor FePS_3 . *Phys. Rev. B* **1990**, *42* (13), 8382-8393.
161. Scagliotti, M.; Jouanne, M.; Balkanski, M.; Ouvrard, G., Spin Dependent Phonon Raman - Scattering in Antiferromagnetic FePS_3 Layer-Type Compound. *Solid State Commun.* **1985**, *54* (3), 291-294.
162. Balkanski, M.; Jouanne, M.; Ouvrard, G.; Scagliotti, M., Effects Due to Spin Ordering in Layered MPX_3 Compounds Revealed by Inelastic Light-Scattering. *J. Phys. C: Solid State Phys.* **1987**, *20* (27), 4397-4413.

163. Balkanski, M.; Jouanne, M.; Scagliotti, M., Magnetic-ordering induced Raman-scattering in FePS₃ and NiPS₃ layered compounds. *Pure Appl. Chem.* **1987**, *59* (10), 1247-1252.
164. Ferloni, P.; Scagliotti, M., Magnetic Phase-Transitions in Iron and Nickel Phosphorus Trichalcogenides. *Thermochim Acta* **1989**, *139*, 197-203.
165. Cardona, M.; Güntherodt, G., *Light Scattering in Solids II: Basic Concepts and Instrumentation*. Springer-Verlag: Berlin Heidelberg New York, 1982; p p. 32-37.
166. Fleury, P. A.; Loudon, R., Scattering of Light by One- and Two-Magnon Excitations. *Phys. Rev.* **1968**, *166* (2), 514-530.
167. Fleury, P. A., Paramagnetic Spin Waves and Correlation Functions in NiF₂. *Phys. Rev.* **1969**, *180* (2), 591-593.
168. Fano, U., Effects of Configuration Interaction on Intensities and Phase Shifts. *Phys. Rev.* **1961**, *124* (6), 1866-1878.
169. Mishra, D. K.; Sathe, V. G., Corrigendum: Evidence of the Fano resonance in a temperature dependent Raman study of CaCu₃Ti₄O₁₂ and SrCu₃Ti₄O₁₂. *J. Phys. Condens. Mat.* **2012**, *24* (36), 369501.
170. Marrocchelli, D.; Postorino, P.; Di Castro, D.; Arcangeletti, E.; Dore, P.; Guidi, M. C.; Ray, S.; Sarma, D. D., Pressure and temperature dependence of the Fano resonance in the Raman spectrum of A₂FeMoO₆ systems (A = Sr,Ca). *Phys. Rev. B* **2007**, *76* (17), 172405.
171. Banerjee, S.; Kim, D.-I.; Robinson, R. D.; Herman, I. P.; Mao, Y.; Wong, S. S., Observation of Fano asymmetry in Raman spectra of SrTiO₃ and Ca_xSr_{1-x}TiO₃ perovskite nanocubes. *Appl. Phys. Lett.* **2006**, *89* (22), 223130.
172. Kohn, W.; Sham, L. J., Self-Consistent Equations Including Exchange and Correlation Effects. *Phys. Rev.* **1965**, *140* (4A), A1133-A1138.
173. Kresse, G.; Hafner, J., Ab initio molecular dynamics for open-shell transition metals. *Phys. Rev. B* **1993**, *48* (17), 13115-13118.
174. Joy, P. A.; Vasudevan, S., Magnetism and Spin Dynamics in MnPS₃ and Pyridine Intercalated MnPS₃ - an Electron-Paramagnetic-Resonance Study. *J. Chem. Phys.* **1993**, *99* (6), 4411-4422.
175. Mak, K. F.; Lee, C.; Hone, J.; Shan, J.; Heinz, T. F., Atomically Thin MoS₂: A New Direct-Gap Semiconductor. *Phys. Rev. Lett.* **2010**, *105* (13), 136805.
176. Yin, X.; Ye, Z.; Chenet, D. A.; Ye, Y.; O'Brien, K.; Hone, J. C.; Zhang, X., Edge Nonlinear Optics on a MoS₂ Atomic Monolayer. *Science* **2014**, *344* (6183), 488-490.
177. Grüning, M.; Attacalite, C., Second harmonic generation in h-BN and MoS₂ monolayers: Role of electron-hole interaction. *Phys. Rev. B* **2014**, *89* (8), 081102.

178. Li, Y.; Rao, Y.; Mak, K. F.; You, Y.; Wang, S.; Dean, C. R.; Heinz, T. F., Probing Symmetry Properties of Few-Layer MoS₂ and h-BN by Optical Second-Harmonic Generation. *Nano Lett.* **2013**, *13* (7), 3329-3333.
179. Yu, H.; Talukdar, D.; Xu, W.; Khurgin, J. B.; Xiong, Q., Charge-Induced Second-Harmonic Generation in Bilayer WSe₂. *Nano Lett.* **2015**, *15* (8), 5653-5657.
180. Zhang, Y. J.; Oka, T.; Suzuki, R.; Ye, J. T.; Iwasa, Y., Electrically Switchable Chiral Light-Emitting Transistor. *Science* **2014**, *344* (6185), 725-728.
181. Peeters, E.; Christiaans, M. P. T.; Janssen, R. A. J.; Schoo, H. F. M.; Dekkers, H. P. J. M.; Meijer, E. W., Circularly Polarized Electroluminescence from a Polymer Light-Emitting Diode. *J. Am. Chem. Soc.* **1997**, *119* (41), 9909-9910.
182. Kleemann, W.; Shvartsman, V. V.; Borisov, P.; Banys, J.; Vysochanskii, Y. M., Magnetic and polar phases and dynamical clustering in multiferroic layered solid solutions CuCr_{1-x}In_xP₂S₆. *Phys. Rev. B* **2011**, *84* (9), 094411.
183. Zhou, X.; Cheng, J.; Zhou, Y.; Cao, T.; Hong, H.; Liao, Z.; Wu, S.; Peng, H.; Liu, K.; Yu, D., Strong Second-Harmonic Generation in Atomic Layered GaSe. *J. Am. Chem. Soc.* **2015**, *137* (25), 7994-7997.
184. Hsieh, D.; McIver, J. W.; Torchinsky, D. H.; Gardner, D. R.; Lee, Y. S.; Gedik, N., Nonlinear Optical Probe of Tunable Surface Electrons on a Topological Insulator. *Phys. Rev. Lett.* **2011**, *106* (5), 057401.
185. Cai, W.; Vasudev, A. P.; Brongersma, M. L., Electrically Controlled Nonlinear Generation of Light with Plasmonics. *Science* **2011**, *333* (6050), 1720-1723.
186. A., D.; J., B.; V., S.; Y., V., Dielectric and ultrasonic studies of new Ag_{0.1}Cu_{0.9}InP₂S₆ layered ferroelectric compound. *Ultragarsas* **2008**, *63* (3), 7-10.
187. Leblanc, A.; Ouili, Z.; Colombet, P., Ordered and disordered distribution of metallic cations in the new system Ag_{1-2x}Cr_(1/2-x)In_xPS₃; spin-glass behavior. *Mater. Res. Bull.* **1985**, *20* (8), 947-954.
188. Belianinov, A.; He, Q.; Dziaugys, A.; Maksymovych, P.; Eliseev, E.; Borisevich, A.; Morozovska, A.; Banys, J.; Vysochanskii, Y.; Kalinin, S. V., CuInP₂S₆ Room Temperature Layered Ferroelectric. *Nano Lett.* **2015**, *15* (6), 3808-3814.
189. Vysochanskii, Y. M.; Stephanovich, V. A.; Molnar, A. A.; Cajipe, V. B.; Bourdon, X., Raman spectroscopy study of the ferrielectric-paraelectric transition in layered CuInP₂S₆. *Phys. Rev. B* **1998**, *58* (14), 9119-9124.
190. Maisonneuve, V.; Evain, M.; Payen, C.; Cajipe, V. B.; Molinié, P., Room-temperature crystal structure of the layered phase Cu^IIn^{III}P₂S₆. *J. Alloy. Compd.* **1995**, *218* (2), 157-164.
191. Maisonneuve, V.; Cajipe, V. B.; Simon, A.; Von Der Muhll, R.; Ravez, J., Ferrielectric ordering in lamellar CuInP₂S₆. *Phys. Rev. B* **1997**, *56* (17), 10860-10868.

192. Shen, Y. R., *The principles of nonlinear optics*. John Wiley & Sons, Inc.: Hoboken, NJ, 2003.
193. Levine, B. F., Bond-Charge Calculation of Nonlinear Optical Susceptibilities for Various Crystal Structures. *Phys. Rev. B* **1973**, 7 (6), 2600-2626.
194. Wagoner, G. A.; Persans, P. D.; Van Wagenen, E. A.; Korenowski, G. M., Second-harmonic generation in molybdenum disulfide. *J. Opt. Soc. Am. B* **1998**, 15 (3), 1017-1021.
195. Splendiani, A.; Sun, L.; Zhang, Y.; Li, T.; Kim, J.; Chim, C.-Y.; Galli, G.; Wang, F., Emerging Photoluminescence in Monolayer MoS₂. *Nano Lett.* **2010**, 10 (4), 1271-1275.
196. Yu, M. V.; V. Yu, S.; Voroshilov, Y. V.; Gurzan, M. I.; Chepur, D. V., Polarization spectra of Raman scattering for Sn₂P₂S₆ ferrosemiconductor. *Sov. Phys. Solid. State* **1979**, 21, 123-127.
197. Maisonneuve, V.; Reau, J. M.; Dong, M.; Cajipe, V. B.; Payen, C.; Ravez, J., Ionic conductivity in ferroic CuInP₂S₆ and CuCrP₂S₆. *Ferroelectrics* **1997**, 196 (1), 257-260.
198. Lifshitz, E.; Francis, A. H.; Clarke, R., An ESR and X-ray diffraction study of a first-order phase transition in CdPS₃. *Solid State Commun.* **1983**, 45 (3), 273-276.
199. Sekine, T.; Ohmamiuda, A.; Tanokura, Y.; Makimura, C.; Kurosawa, K., Raman-Scattering Study of Structural Phase Transition in Layered Compound CdPS₃. *J. Phys. Soc. Jpn.* **1993**, 62 (2), 800-807.

Publications

1. **X. Wang**[#], K. Du[#], Y. Y. F. Liu, P. Hu, J. Zhang, Q. Zhang, M. H. S. Owen, X. Lu, C. K. Gan, P. Sengupta, C. Kloc, Q. Xiong*, "Raman Spectroscopy of Atomically Thin Two-Dimensional Magnetic Iron Phosphorus Trisulfide (FePS₃) Crystals", *2D Mater.* 3 (3), 031009 (2016)
2. **X. Wang**, K. Du, W. Liu, P. Hu, X. Lu, W. Xu, C. Kloc, and Q. Xiong*, "Second-harmonic generation in quaternary atomically thin layered AgInP₂S₆ crystals", *Appl. Phys. Lett.* 109 (12), 123103 (2016)
3. K. Du[#], **X. Wang**[#], Y. Liu[#], P. Hu, M. I. B. Utama, C. K. Gan, Q. Xiong*, and C. Kloc*, "Weak Van der Waals Stacking, Wide-Range Band Gap, and Raman Study on Ultrathin Layers of Metal Phosphorus Trichalcogenides", *ACS Nano* 10 (2), 1738-1743 (2016)
4. K. Du[#], **X. Wang**[#], J. Zhang, X. Liu, C. Kloc*, and Q. Xiong*, "CdS Bulk Crystal Growth by Optical Floating Zone Method: Strong Photoluminescence Upconversion and Minimum Trapped State Emission", *Opt. Eng.* 56 (1), 011109 (2017)
5. J. Zhang*, Q. Zhang, **X. Wang**, L. C. Kwek, and Q. Xiong*, "Resolved Sideband Raman Cooling of an Optical Phonon in Semiconductor Materials", *Nat. Photon.* 10, 600–605 (2016)
6. T. Ye, X. Jiang, D. Wan, **X. Wang**, J. Xing, T. Venkatesan, Q. Xiong and S. Ramakrishna*, "Behavior in a CH₃NH₃PbI₃/Carbon nanocomposite and its application in a metal-electrode-free solar cell", *ChemPhysChem*, 17, 4102-4109 (2016)
7. K. Du, X. Qi, M. Feng, J. Li, **X. Wang**, C. Du, G. Zou, M. Wang, and X. Huang* "Synthesis, Structure, Band Gap, and Near-Infrared Photosensitivity of a New Chalcogenide Crystal, (NH₄)₄Ag₁₂Sn₇Se₂₂." *Inorg. Chem.* 55 (11), 5110–5112 (2016)
8. G. Li, X. Liu, **X. Wang**, Y. Yuan, T. C. Sum, and Q. H. Xiong*, "Purified plasmonic lasing with strong polarization selectivity by reflection", *Opt. Express* 23, 15657-15669 (2015)

9. K. Du, A. Chaturvedi, **X. Wang**, Y. Zhao, K.K. Zhang, M.I.B. Utama, P. Hu, H. Jiang, Q.H. Xiong and C. Kloc*, "Plasma-enhanced microwave solid-state synthesis of cadmium sulfide: reaction mechanism and optical properties", *Dalton Trans.* 44, 13444-13449 (2015)
10. Z. Yang, M.Q. Wang, S. Shuka, Y. Zhu, J.P. Deng, H. Ge, **X. Wang**, and Q.H. Xiong*, "Developing Seedless Growth of ZnO Micro/Nanowire Arrays towards ZnO/FeS₂/CuI P-I-N Photodiode Application", *Sci. Rep.* 5, 11377 (2015)

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