Article

Magnetic Isotropy/Anisotropy in Layered Metal Phosphorous Trichalcogenide MPS$_3$ (M = Mn, Fe) Single Crystals

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Abstract: Despite the fact that two-dimensional layered magnetic materials hold immense potential applications in the field of spintronic devices, tunable magnetism is still a challenge due to the lack of controllable synthesis. Herein, high-quality single crystals MPS$_3$ (M = Mn, Fe) of millimeter size were synthesized through the chemical vapor transport method. After systemic structural characterizations, magnetic properties were studied on the bulk MPS$_3$ layers through experiments, along with first principle theoretical calculations. The susceptibilities as well as the EPR results evidently revealed unique isotropic and anisotropic behavior in MnPS$_3$ and FePS$_3$ crystals, respectively. It is worth noting that both of these materials show antiferromagnetic states at measured temperatures. The estimated antiferromagnetic transition temperature is 78 K for bulk MnPS$_3$ and 123 K for FePS$_3$ crystals. The spin polarized density functional theory calculations confirmed that the band gap of the antiferromagnetic states could be generated owing to asymmetric response all over the energy range. The ferromagnetic state in MnPS$_3$ and FePS$_3$ is less stable as compared to the antiferromagnetic state, resulting in antiferromagnetic behavior. Additionally, frequency-dependent dielectric functions for parallel and perpendicular electric field component vectors, along with the absorption properties of MPS$_3$, are thoroughly investigated.

Keywords: layered material; bulk single crystal; isotropy; anisotropy; chemical vapor transport (CVT); density-functional theory (DFT)

1. Introduction

Magnetism has been proven to be widely helpful in the understanding of the quantum nature of materials. Although 2D transition metal dichalcogenides (TMDs) have been the center of attention in the recent era, transition metal chalcogenophosphates (TMCs) with general formula of MPX$_3$ (M = Mn, Fe, Ni, Co and X = S, Se) have also proven to be unique materials with their low-dimensional magnetic properties. These MPX$_3$ have secured renewed interest owing to their importance, not only for fundamental research, but also as potential candidates for numerous technological applications [1–10]. They belong to one of the few layered systems having 2D lattice for both magnetic and crystallographic systems. These materials possess two spin channels, one conducting and the other insulating. This family of materials is considered to be the best suited for applications in spintronic [11,12]. Over the last few years, MPX$_3$ have gained attention because of their enormous potential as a material.
For next generation electronics. In this regard, MnPS$_3$ has been the focus because of electron valley freedom coupled with antiferromagnetic order [13]. A minute amount of magnetic field leak makes these antiferromagnetic materials a well-suited choice for use in robust data storage applications [14,15]. In recent years, layered antiferromagnetic materials have been used to induce deterministic switching without an external magnetic field [16]. Additionally, the higher magnetic resonance frequency of antiferromagnetic materials, in comparison with ferromagnetic materials, has attracted their use in providing high-speed data processing [17].

MnPS$_3$ and FePS$_3$ belong to the same MPX3 class of materials with isotropic and anisotropic magnetic susceptibilities, respectively [18]. Both MnPS$_3$ and FePS$_3$ are layered magnetic materials with weak Van der Waal forces separating the layers. The presence of the Van der Waal gap rules out the possibility of superexchange pathways as well as minimizes the possibility of direct exchange owing to metal-metal interlayer distance of ~6.5 Å and 6.4 Å in MnPS$_3$ and FePS$_3$, respectively. These materials can be exfoliated into a single layer [19] and possess a magnetic ground state, dependent on transition metal element [18].

MPX3 materials have been mostly investigated for their intercalation properties [9]. These are wide bandgap, highly resistive semiconductors having bandgap of the order of 3 eV. Bandgaps for MnPS$_3$ and FePS$_3$ are approximately 2.4 and 1.5 eV, respectively. The adequate amount of bandgap makes these materials a suitable semiconductor for optoelectronic [20], optoelectronic material processing [6], while MnPS$_3$ has also been realized as a promising photocatalyst for water splitting [21]. MnPS$_3$ is optically transparent with a greenish color [22], while FePS$_3$ has a brownish appearance. More importantly, the magnetic character of MnPS$_3$ arises from Mn$^{2+}$ having spin 5/2 that forms a honeycomb lattice in a, b plane. The weak Van der Waal interlayer coupling is attributed to S atoms, but the antiferromagnetic phase transition at 78 K points towards an interplane exchange that can be associated with some degree of metal-ligand covalency [23,24]. FePS$_3$ is a striking compound because of the fact that it exhibits stronger magnetic interactions between Fe$^{2+}$ ions in comparison with Mn$^{2+}$ as well as due to the reason that electronic structure of the Fe$^{2+}$ ions demonstrate strong anisotropy [18,25]. The isotropic/anisotropic nature affects the frequency-dependent dielectric and absorption properties of MPS$_3$ as well. All these facts make these MPS$_3$ ideal candidates for 2D magnetic as well as optoelectronic systems.

Herein, we report the chemical vapor transport (CVT) synthesis of highly crystalline, millimeter-size MPS$_3$ (M = Mn, Fe) single crystals. Furthermore, the magnetic isotropic/anisotropic properties of bulk MPS$_3$ single crystals were tested using electron paramagnetic resonance (EPR) and vibrating sample magnetometer (VSM). Experimental results revealed the antiferromagnetic nature of these materials with MnPS$_3$ exhibiting isotropic whereas, FePS$_3$ showed highly anisotropic properties measured by magnetic susceptibilities. The magnetic and dielectric properties of these materials were confirmed using first principle spin polarized density-functional theory (DFT) calculations.

2. Experiments

The millimeter-sized MnPS$_3$ and FePS$_3$ single crystals were prepared using CVT method. The charge for MnPS$_3$ and FePS$_3$ was prepared by using a stoichiometric amount of Mn, P, S and Fe, P, S for MnPS$_3$ and FePS$_3$, respectively. Iodine was used as transport agent for this growth. The charge was kept in a 17-cm long silica tube, and was sealed under vacuum ($\approx 10^{-1}$ atm). The sealed ampoule was placed inside a two-zone furnace with a hot zone temperature of 650 °C and cold zone temperature of 600 °C for 7 days. The reaction yielded pale green colored single crystals and brownish single crystals at the low temperature end of ampoule for MnPS$_3$ and FePS$_3$, respectively.

The structural study of as-prepared samples was carried out by using X-ray diffraction (XRD) and high-resolution transmission electron by microscope (TEM); phonon spectrum was studied by using Raman Spectroscopy, chemical composition by using X-ray photoelectron spectroscopy (XPS), the morphology of the samples was investigated by using scanning electron microscope (SEM). The magnetic properties of these bulk crystal samples were studied by using electron paramagnetic
resonance (EPR), and physical properties measurement system (PPMS) through vibrating sample magnetometer (VSM).

3. Results and Discussions

Typical SEM images of as-obtained MnPS$_3$ and FePS$_3$ samples are shown in Figure 1a,b. It can be seen that both MnPS$_3$ and FePS$_3$ exhibit smooth surfaces with roughly hexagonal morphology. The SEM images also show a layered structure of MPS$_3$. Inset Figure 1a,b depict millimeter size as grown single crystals of MnPS$_3$ and FePS$_3$, respectively. Figure 1c,d represent the Raman spectra of MnPS$_3$ and FePS$_3$ recorded at room temperature using 532 nm laser excitation. For MnPS$_3$, the Raman peaks at 114.3, 152.2, 245 and 568 cm$^{-1}$ are identified as $E_g$ vibrating mode, and 273.3, 283.1 and 580 cm$^{-1}$ are recognized as $A_{1g}$ mode [21]. In the case of FePS$_3$, the Raman peaks at 97.3, 155.9, 224.1, 246.8 cm$^{-1}$ are identified as $E_g$ vibrating mode whereas, peaks at 279 and 379.2 cm$^{-1}$ are referred to as $A_{1g}$ mode [23].

![SEM images and Raman spectra](image_url)

Figure 1. (a,b) Scanning electron microscope (SEM) images, inset shows millimeter sized as grown single crystals and (c,d) Raman spectra of as-obtained MnPS$_3$ and FePS$_3$ single crystals, respectively.

The X-ray diffraction data (XRD) of the samples were analyzed to study the crystal planes and crystallinity of MnPS$_3$ and FePS$_3$ single crystals. It is evident from Figure 2a,b that these results are well in accordance with the standard JPCDS cards belonging to (PDF#33-0903, PDF#30-0663) MnPS$_3$ and FePS$_3$, respectively. The crystal lattice and phase identification revealed that both MnPS$_3$ and FePS$_3$ exhibit high-quality single crystals with major (001) and (002) peaks. The absence of any impurity peak suggests that these samples have pure phases. Inset in Figure 2a,b shows the crystallographic model of MnPS$_3$ and FePS$_3$ along (001) plane, respectively. Figure 2c,d displays the TEM images of MnPS$_3$ and FePS$_3$, suggesting that both samples are highly crystalline with growth as single crystal. The d-spacing calculated from Figure 2c,d is estimated as 0.25 nm and 0.30 nm corresponding to (202) and (201).
planes in MnPS$_3$, while 0.25 nm and 0.29 nm correspond to (131) and (201) planes in monoclinic unit cell of FePS$_3$.

The chemical composition and bonding state of the samples were studied by using XPS analysis, as shown in Figure 3. The Mn 2p peaks of MnPS$_3$ detected at 652.8 and 641 eV can be assigned to 2p$_{3/2}$ and 2p$_{1/2}$, respectively. The S 2p, peaks identified at 162.75 and 163.9 eV can be assigned to 2p$_{3/2}$ and 2p$_{1/2}$. For P 2p, two peaks at 132.5 eV and 133.6 eV are assigned to 2p$_{3/2}$ and 2p$_{1/2}$. In case of FePS$_3$, the Fe 2p peaks at 709 and 722 eV are assigned to 2p$_{3/2}$ and 2p$_{1/2}$. Both S 2p and P 2p peaks of FePS$_3$ show quite similar position and shape as those peaks for MnPS$_3$. All these values are consistent with the previous reports [26,27].

Magnetic susceptibility indicates the magnetic properties of a material. It depicts the degree of magnetization of a material with respect to temperature at constant applied magnetic field. The magnetic susceptibility ($\chi$) as a function of temperature for both MnPS$_3$ and FePS$_3$ crystals is represented in Figure 4a,b. The susceptibility plots of MnPS$_3$ and FePS$_3$ were examined through field cooling (FC) and zero field cooling (ZFC) curves. From the susceptibility plots, we can observe the isotropic behavior of MnPS$_3$, while for FePS$_3$ a considerable anisotropic trend has been noticed. The susceptibilities of MnPS$_3$ and FePS$_3$ increase with decreasing temperature till at 120 K and 128 K, respectively. Beyond this point it shows rapid decrease, exhibiting a Curie like tail at lowest temperatures. Furthermore, the susceptibility is seen to follow the Curie-Weiss law at higher temperatures (inset Figure 4a,b), which is an identification feature of the antiferromagnetic nature of these materials [7]. It can be inferred from Figure 4a,b that Neel temperature for MnPS$_3$ and FePS$_3$ are 78 K and 123 K, while the corresponding Curie temperatures are found to be at 365 K and 324 K,

Figure 2. (a,b) X-ray diffraction patterns and (c,d) high resolution transmission electron by microscope (TEM) images for MnPS$_3$ and FePS$_3$ single crystals prepared by ball-milling and sonication process.
respectively. These values of Neel temperature and Curie temperature are well matched with the previous reports [28,29]. The broad maxima above Neel temperature is a result of short-range spin-spin correlation in typical magnetic systems. We can observe that magnetic susceptibility for FC is higher than ZFC throughout the observed range for both MnPS$_3$ and FePS$_3$. The increased Curie temperature beyond room temperature shows that these materials are favorable for spintronic applications.

Figure 3. X-ray photoelectron microscopy of (a–c) MnPS$_3$ and (d–f) FePS$_3$ single crystals.

Figure 4. Magnetic susceptibility of (a) MnPS$_3$ and (b) FePS$_3$ single crystals with millimeter size. Electron paramagnetic resonance spectra of (c) bulk MnPS$_3$ and (d) FePS$_3$ single crystals.
The electron paramagnetic resonance (EPR) method was employed to study the quantum mechanical mixed spin states of both samples. The EPR signal typically originates from the surface of electrons, which increases by the exposures of some metals. The EPR spectra of the samples were measured at 120 K, 200 K and 300 K at constant frequency of 9 GHz. Figure 4c,d depicts the EPR spectra of MnPS$_3$ and FePS$_3$ with unpaired electrons. For MnPS$_3$, the EPR spectra is isotropic, with the magnetic signals containing a single narrow resonance peak (Figure 4c). On the other hand, EPR spectra for FePS$_3$ is highly anisotropic with multiple magnetic resonance peaks (Figure 4d). The magnetic resonance peaks for MnPS$_3$ occurs at 404.1, 410 and 410.33 mT, while multiple resonance peaks were observed for FePS$_3$ at all measured temperatures as described in Table 1. The strong signals at 300K for FePS$_3$ can be attributed to the shortening of relaxation time with temperature in anisotropic materials [30,31].

| Temperature | Peak 1 | Peak 2 | Peak 3 | Peak 4 | Peak 5 | Peak 6 |
|-------------|-------|-------|-------|-------|-------|-------|
| 300 K       | 1.080 (593.62) | 1.057 (608.36) | 1.032 (623.11) | 1.007 (638.5) | 0.983 (653.9) | 0.9589 (670.6) |
| 200 K       | 1.088 (590.9) | 1.062 (605.0) | 1.036 (621.0) | 1.007 (638.5) | 0.986 (651.85) | 0.9592 (670.6) |
| 120 K       | 1.082 (594.27) | 1.066 (602.95) | 1.043 (616.39) | 1.018 (631.13) | 0.990 (649.14) | 0.9646 (666.59) |

The magnetic coupling factor or g-factor “$g_{\text{eff}}$” was computed from EPR spectra using the following relationship [32]:

$$g_{\text{eff}} \simeq \frac{\hbar \gamma}{\mu_B H_{\text{center}}}$$

where “$\gamma$” is the frequency, “$\hbar$” is Planck constant, “$\mu_B$” indicating Bohr magnetron and $H_{\text{center}}$ is the resonance magnetic field. The calculated values of $g_{\text{eff}}$ are found to be 1.5921, 1.5684, and 1.5679 at 120, 200 and 300 K for MnPS$_3$.

Anisotropy of magnetization originates from the anisotropy of the particles themselves in the form of shape or crystalline anisotropy and degree of alignment. The crystalline anisotropy relies on lattice forces and subsequent magnetization along an easy axis. EPR spectrum intensity is affected by number, position and nature of magnetic ions as well as the spin environment e.g., electron spin exchange with identical and non-identical atoms or molecules or with the spin of unpaired electrons of neighboring molecules. Additionally, in case of single crystals having equal orientations, it is expected that one defect will exist in all orientations with equal probability. For a low symmetry g-tensor and at an arbitrary direction of magnetic field, different effective values of g-factors are possible for the different orientations of the defect that can give rise to different magnetic field positions of EPR lines [33]. In fact, isotropy and anisotropy also affect the dielectric and absorption properties of materials. Isotropic materials display uniform dielectric functions along different directions, whereas anisotropic materials possess direction-dependent dielectric properties. In order to further understand the effect of isotropic and anisotropic behavior, spin-polarized first-principle density functional theory (DFT) calculations were performed to describe the magnetic response of MPS$_3$ (M = Fe, Mn). The computations were carried out by using DFT through Vienna ab initio simulation package (VASP) [34]. A projector augmented wave (PAW) method [35,36] was used to characterize the ion-electron interface and the generalized gradient approximation (GGA) was stated by the PBE functional [37,38]. The plane wave cutoff energy was set to 500 eV with energy precision of $10^{-5}$ eV. The force criteria on each atom was less than $10^{-2}$ eV/Å. The Brillouin zone Γ-centered was sampled with a $12 \times 12 \times 1$ Monkhorst−Pack of k-points grid for geometry optimization, while the static electronic calculation $8 \times 8 \times 1$ and self-consistent calculations of the MPS$_3$ (M = Mn, Fe) system were made. Unit cells were considered for these calculations. To obtain electronic and magnetic results, we employed a partition by hybrid HSE06 functional [38,39] with an accurate Fock exchange and typically achieved much better results than...
the DFT and DFT+U methods [40]. A single unit cell with lattice parameters of MnPS$_3$ ($a = 6.076$ Å, $b = 10.524$ Å and $c = 6.796$ Å) and FePS$_3$ ($a = 5.949$ Å, $b = 10.288$ Å and $c = 6.72$ Å) from the experimental data has been used for calculations.

According to our magnetic energy calculations that are listed in Table 2, the ferromagnetic state in both cases is less stable as compared to the antiferromagnetic state, with an energy difference of about 0.601 eV for MnPS$_3$, while for FePS$_3$ the difference in energies is around 1.02 eV. Total energy calculations clearly defined that the room temperature antiferromagnetic (RTAFM) state is in the ground state of MPS$_3$ ($M = Fe, Mn$).

Similarly, the density of states (DOS) calculations in Figure 5 show the asymmetry between the spin-up and spin-down state of MPS$_3$ ($M = Fe, Mn$). Figure 5a,b shows the evidence of magnetism for both MnPS$_3$ and FePS$_3$ layers with asymmetric density states in different energy levels. It can be seen that the electronic density of MnPS$_3$ mainly stems from M’d, P’p and S’p states. Particularly, strong hybridization of Mn’d, P’p and S’p states is found between −7 eV and −1 eV, while strong P’p and weak Mn’d, and S’p was witnessed between 4 eV and 5 eV. However, near the Fermi level, strong S’p and weak Mn’d states exist, as shown in Figure 5a. Similarly for FePS$_3$, Fe’d, P’p and S’p states exist between −7 eV and −2 eV, and strong P’p and weak Mn’d, and S’p appear between 4 eV and 6 eV. Likewise, strong S’p and a weak Fe’d states exist near the Fermi level, as shown in Figure 5b. All these states (spin-up and spin-down) are asymmetric and contribute to the magnetic isotropic/anisotropic trend throughout the energy range. The d-orbitals of Mn and Fe have the most obvious contribution of spinpolarization, which mainly contributes towards the magnetism of MPS$_3$.

![Figure 5.](image-url) (a,b) Projected density of states of MnPS$_3$ and FePS$_3$ (c,d) structure of MnPS$_3$ and FePS$_3$ under incident electromagnetic wave (e,f) calculated dielectric function for MnPS$_3$ and FePS$_3$, respectively.
The frequency-dependent dielectric functions have been calculated using parallel and perpendicular electric field component vectors along the c-axis, as shown in Figure 5c,d. The frequency-dependent dielectric functions in Figure 5e,f show a strong isotropic and anisotropic behavior in lower and higher energy ranges for MnPS$_3$ and FePS$_3$, respectively. It was found that MnPS$_3$ shows strong isotropic behavior for perpendicular and parallel polarization at lower and higher energy ranges. On the contrary, FePS$_3$ exhibits a strong anisotropic trend for both perpendicular and parallel polarization with an increased number of peaks for dielectric constants at the given energy range. Moreover, the calculated frequency-dependent dielectric functions show a similar trend between 5 eV to 40 eV and 60 eV to 100 eV with increased number peaks of FePS$_3$ for both perpendicular and parallel polarization as compared to MnPS$_3$, which clearly demonstrates the effect of isotropic and anisotropic trend on MnPS$_3$ and FePS$_3$, respectively.

| Materials | $E_0$ (FM Calculation) | $E_0$ (AFM Calculation) | $dE_0$ (FM-AFM) |
|-----------|------------------------|------------------------|-----------------|
| MnPS$_3$  | 114.92800 eV           | 114.32689 eV           | 0.601 eV        |
| FePS$_3$  | 164.99485 eV           | 163.97464 eV           | 1.02 eV         |

### 4. Conclusions

High-quality single crystals of MnPS$_3$ and FePS$_3$ were synthesized by using CVT. The EPR and VSM were used to corroborate the existence of antiferromagnetic behavior and to study isotropy/anisotropy in these materials. The probe for the magnetic character of MnPS$_3$ and FePS$_3$ was carried out at 120 K, 200 K and 300 K. The susceptibility showed a typical antiferromagnetic behavior in MnPS$_3$ with an isotropic trend, while an anisotropic behavior was witnessed for FePS$_3$. Moreover, our calculations further confirmed that the antiferromagnetic state was additionally stable than the ferromagnetic state for both MnPS$_3$ and FePS$_3$. The projected density of states (PDOS) manifested a vital irregularity between spin-up and spin-down channels of Mn and Fe 3d states, which is responsible for the primary contribution to the antiferromagnetic states near the Fermi level. The frequency-dependent dielectric function calculations have shown that MnPS$_3$ possessed strong isotropic behavior for both perpendicular polarization and parallel polarization at lower and higher energy ranges. On the contrary, FePS$_3$ exhibited strong anisotropic trend for both perpendicular as well as for parallel polarizations at the given energy range.

**Author Contributions:** L.S. conceived and designed the experiments; Z.u.R. performed the experiments and analyzed the data; Z.M. performed the computational study, O.A.M, C.W. and Q.H helped in analysis of the data; W.Z. contributed in providing analysis tools; M.H. provided help in writing the paper.

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