Weak ferromagnetism and magnetoelectric coupling in van der Waals antiferromagnet MnPSe$_3$

Cite as: Appl. Phys. Lett. 124, 172903 (2024); doi: 10.1063/5.0206361
Submitted: 1 March 2024 · Accepted: 16 April 2024 ·
Published Online: 25 April 2024


AFFILIATIONS
1 Laboratory of Solid State Microstructures, Nanjing University, Nanjing 210093, China
2 Department of Applied Physics, College of Science, Nanjing Forestry University, Nanjing 210037, China
3 Institute for Advanced Materials, Hubei Normal University, Huangshi 435002, China
4 School of Science, Nanjing University of Posts and Telecommunications, Nanjing 210023, China

ABSTRACT

With the discovery of two-dimensional (2D) ferroelectricity and ferromagnetism in van der Waals (vdW) materials, there has been significant interest in 2D multiferroics. Herein, we report the occurrence of weak ferromagnetism and magnetoelectricity in vdW antiferromagnet MnPSe$_3$ single crystals. Our results demonstrate that MnPSe$_3$ undergoes an antiferromagnetic transition at the Néel temperature $T_N = 70$ K with weak ferromagnetism along the [1–10] direction. Detailed magnetoelectric (ME) data show that MnPSe$_3$ exhibits a linear ME tensor $x_{ij}$ with nine nonzero components. Additionally, a magnetically induced electric polarization as large as 98.5 $\mu$C/m$^2$ is observed along the [110] direction, with a ME coefficient of 13.5 ps/m at 10 K for a magnetic field of 9 T applied along the [110] direction. Importantly, we discuss our experiments based on symmetry and microscopic analysis, thereby suggesting that the spin-dependent $p$-$d$ hybridization mechanism plays an important role in the emergence of magnetic-field-induced ferroelectricity. Hence, our findings provide insights for exploring the ME coupling in vdW materials.

Multiferroics, in which more than one ferroic order coexist, have attracted considerable attention owing to their intriguing physics and promising applications in multifunctional devices. In the past two decades, substantial efforts have been devoted to designing and searching for single-phase multiferroics with effective cross coupling between the magnetic and ferroelectric orders, such as TbMnO$_3$, Fe$_3$Nb$_2$O$_7$, and Ni$_2$TeO$_4$. However, owing to the constraining factors like size limitation, interface effects, and dangling bonds, traditional three-dimensional (3D) multiferroic materials have been found difficult to meet the development demands for the miniaturization of electronic devices. Compared with 3D multiferroics, van der Waals (vdW) materials exhibit different physical properties, such as stable layered structure and no surface dangling bonds, making them promising to avoid these issues. Indeed, significant advancements have been made in the field of 2D multiferroics in recent years, such as ferroelectricity in CuInP$_2$S$_6$ (Ref. 16) and In$_2$Se$_3$ and ferromagnetism in Cr$_2$Ge$_2$Te$_6$ (Ref. 18) and Fe$_2$GeTe$_2$. While there are numerous 2D magnets available, the 2D vdW multiferroics with intrinsic coupling between magnetic and ferroelectric orders are yet rare. This has led to the research of 2D vdW multiferroics as a highly prominent research area in recent years.

Recently, manganese phosphorous trichalcogenides, namely, MnPX$_3$ ($X = S, Se$), have attracted extensive studies due to their rich physical properties. Among them, MnPS$_3$ crystallizes in monoclinic space group $C2/m$ and undergoes an antiferromagnetic (AFM) transition at temperature $T \sim 78$ K, forming an Ising-type magnetic structure with an angle of 8° between the Mn$^{2+}$ spins and the normal to the $ab$ plane. Such a magnetic structure exhibits $2/m$ symmetry, allowing a linear non-diagonal ME effect. Using optical second harmonic generation (SHG) rotational anisotropy and polarized neutrons, the linear ME effect of MnPS$_3$ has been investigated, but direct evidence for ME coupling is still limited. In this sense, the success in observing the non-diagonal ME phase in MnPS$_3$ stimulates us to further explore the ME effect in MnPSe$_3$.

In contrast to MnPS$_3$, which has out-of-plane magnetic moments, MnPSe$_3$ features in-plane spins with large XY anisotropy, offering richer magnetic domain structures and ME properties.
MnPSe$_3$ crystallizes in centrosymmetric crystal structure with R-3 space group, which can be visualized as the ABCABC stacking of the Mn$_2$P$_2$Se$_6$ layer along the c-axis, as plotted by the VESTA software$^{27}$ shown in Fig. 1(a). Within each Mn$_2$P$_2$Se$_6$ layer, the magnetic Mn ions are arranged in a honeycomb lattice with the ethane-like [P$_2$Se$_6$]$^{4-}$ polyanion cluster located in the voids of the honeycomb. Neutron powder diffraction measurements indicate that MnPSe$_3$ undergoes an AFM transition at the temperature $T \sim 72$ K with the magnetic point group of $-1^c$, which allows the ME effect with nine nonzero ME components.$^{27}$ As shown in Fig. 1(b), the nearest neighboring magnetic moments of Mn$^{2+}$ ions in each layer are antiferromagnetically arranged, while the moments between the adjacent layers are ferromagnetically coupled. The recent SHG study on MnPSe$_3$ as a function of layer thickness demonstrates that such long-range magnetic order can persist down to the monolayer limit.$^{28}$ Unfortunately, no research has been reported on the ME response in MnPSe$_3$ to date. In this sense, experimental explorations of the ME effect in bulk MnPSe$_3$ through direct measurements are urgently needed for exploring ME devices based on vdW materials.

Motivated by the aforementioned discussion, in this work, we systematically investigate the magnetism and ME coupling in MnPSe$_3$ single crystals by performing a series of magnetic, specific heat, and ME measurements. Our results reveal that MnPSe$_3$ is a linear ME material that exhibits weak ferromagnetism along the [1–10] direction and strong ME effect along the [110] direction. Detailed ME measurements do show that MnPSe$_3$ exhibits a linear ME tensor with nine nonzero ME components, further confirming the magnetic point group of $-1^c$ for MnPSe$_3$. Based on the magnetic symmetry of the antiferromagnetic ordering in a honeycomb network and microscopic analysis, the ME coupling mechanism in MnPSe$_3$ is discussed.

Figure 1(c) displays the room-temperature XRD pattern of MnPSe$_3$ single crystal. Using Bragg’s law, the layer distance $d$ calculated from the (00l) diffraction peaks is 6.64 Å, in excellent agreement with the value of 6.65 Å in a previous report.$^{29}$ The insets in Fig. 1(c) are the optical photograph of an as-grown MnPSe$_3$ single crystal and the Laue diffraction spots obtained along the [001] orientation. Furthermore, the measured EDX spectroscopy reveals the atomic ratio of Mn:P:Se as 0.965:1.062:2.975, consistent with the stoichiometry of MnPSe$_3$. I nFig. 1(d), we show the Rietveld refined XRD pattern of the crushed crystals, in which all the diffraction peaks can be well fitted by R-3 space group with lattice parameters $a = b = 6.4891$ Å and $c = 20.0479$ Å, consistent with a previous report.$^{28}$

Figure 2(a) presents the $T$-dependent magnetic susceptibility $\chi(T)$ curves under zero-field-cooling (ZFC) mode with the measuring field $H = 0.1$ T applied along the [110], [1–10], and [001] directions, namely $\chi_{[110]}$ and $\chi_{[1–10]}$ and $\chi_{[001]}$, respectively. Upon cooling from...
300 K, the in-plane susceptibilities $\chi_{[110]}$ and $\chi_{[1\bar{1}0]}$ gradually increase to their maximum at $T = T_{\text{max}} = 85$ K and then decrease, followed by a kink observed at $T \approx 70$ K. Given the quasi-two-dimensional nature of MnPSe$_3$, the broad peak suggests the emergence of AFM ordering. With further decrease in temperature, susceptibilities $\chi_{[110]}$ and $\chi_{[1\bar{1}0]}$ display a gradual drop, with $\chi_{[1\bar{1}0]}$ exhibiting a sharper decrease. On the other hand, the $\chi_{[001]}$ curve demonstrates a weak $T$-dependence, implying that the magnetic moments are mainly lying in the ab-plane with the easy-axis along the [110] direction. Furthermore, the significant disparity between the in-plane and out-of-plane $\chi(T)$ curves indicates the pronounced XY anisotropy of MnPSe$_3$.

By fitting the linear part of the $\chi^{-1}(T)$ data between $T = 150$ and 300 K using the Curie–Weiss law, the effective magnetic moments along three directions labeled in the subscript can be obtained, and they are $\mu_{[110]} \approx 6.2$, $\mu_{[1\bar{1}0]} \approx 6.1$, and $\mu_{[001]} \approx 6.1$ $\mu_B$/Mn, respectively, very close to the spin-only magnetic moment of 5.97 $\mu_B$ for Mn$^{2+}$ in the high-spin configuration, where $\mu_B$ represents the Bohr magnetic moment. In addition, the corresponding Curie–Weiss temperatures are $\theta_{[110]} = -163$, $\theta_{[1\bar{1}0]} = -157$, and $\theta_{[001]} = -318$ K, respectively, indicating that the dominant magnetic interactions are antiferromagnetic. The large difference in the Curie–Weiss temperature between the in-plane and out-of-plane direction may be due to the large ligand spin-orbit contribution of the heavier selenium.30

To further characterize the magnetic transition of MnPSe$_3$, the special heat $C_v(T)$ under zero field was measured, shown in Fig. 2(b), where the $\gamma(T)$ curves with measuring field $H$ applied along the [110] and [1–10] directions are also plotted for reference. The typical $\gamma$-shaped peak is observed at $T \approx 70$ K, which denotes the Néel temperature $T_N$ indicating the onset of long-range AFM ordering. Apart from this ordering, no $C_v(T)$ anomaly over the whole temperature range is identified.

To obtain more details of the magnetic properties of MnPSe$_3$, the $H$-dependent magnetization along the [110], [1–10], and [001] directions are measured at various temperatures. The magnetization $M$ at 5 K shown in Fig. 2(c) exhibits linear behavior below the critical magnetic field $H_c \approx 0.5$ T for $H//[110]$ and $[1\bar{1}0]$. Beyond this point, a significant deviation from the linear behavior can be observed. Above $H \approx 1$ T, all the $M(H)$ curves show linear behavior. Such a nonlinear deviation of $M(H)$ is also observed in other ME materials such as Co$_3$Nb$_2$O$_9$ (Ref. 31) and Fe$_2$Nb$_2$O$_9$11 which can be attributed to the realignment of three types of magnetic domains and the reorientation of spins within it. Owing to the triple symmetry of MnPSe$_3$ along the c-axis, the [001] direction is equivalent to [100] and [110] directions. Consequently, three types of magnetic domains may also exist, and the nonlinear deviation of $M(H)$ curves can also be attributed to the realignment of magnetic domains with spin reorientation. In contrast to the linear behavior observed in the $M_{[110]}(H)$ curve for $H < H_c$, the $M_{[1\bar{1}0]}(H)$ curve shows a significant nonlinear behavior below 0.1 T with a magnitude larger than that of $M_{[110]}(H)$ and $M_{[001]}(H)$. Figure 2(d) presents the $M_{[1\bar{1}0]}(H)$ curves in low field region $H < 0.2$ T at various temperatures. The observable noteworthy hysteresis suggests weak ferromagnetism along the [1–10] direction with a coercive field of $H_c = 167$ Oe. Keeping in mind that the spins are antiferromagnetically aligned along the [110] direction, it can be inferred that the weak ferromagnetism along the [1–10] direction most likely originates from the canting antiferromagnetic order caused by the Dzyaloshinskii–Moriya interaction.

We now turn our attention to the ME effect in the MnPSe$_3$ single crystals. Given the complexity of magnetic domains, the [110] magnetic domain is selected to investigate the ME effect in MnPSe$_3$, in which the magnetic moments are antiferromagnetically aligned along the [110] direction. To analyze the ME tensor, the $x$, $y$, and $z$ axes are designed along the [110], [1–10], and [001] directions, respectively. Figures 3(a)–3(c) present the $T$-dependent pyroelectric current density $J_{[001]}(T)$ along the [001] direction under selected $H$ applied along different orientations. Consistent with long-range antiferromagnetic ordering appearing at $T \approx 70$ K, the sharp peaks in $J_{[001]}(T)$ are observed at 71.5 K, indicating the emergence of magnetic-induced ferroelectric polarization. Moreover, by reversing $E$, a change in the sign of the $J_{[001]}(T)$ curves is observed, shown in the inset of Fig. 3(a), indicating the nature of ferroelectricity of the magnetic-field-induced polarization.

To investigate the ME effect in MnPSe$_3$, we performed comprehensive $T$-dependent polarization measurements along $P/[110]$, [1–10], and [001] directions under different $H$ orientations, shown in Figs. 3(d)–3(h). Here, several interesting features deserve highlighting. First, our measurements show that the ME tensor of MnPSe$_3$ exhibits nine nonzero components, consistent with the magnetic point group $-1$ determined by the powder neutron diffraction measurements. Second, under the magnetic field $H = 9$ T applied along the [110] and [1–10] directions, the measured $P_{[110]}$ and $P_{[1\bar{1}0]}$ at 10 K reach up to 98, 75, and 63.5 $\mu_C$/cm$^2$, respectively, which are larger than the value of 13 and 12 $\mu_C$/cm$^2$ for $H//[001]$, indicating the...
majority of polarization is along the [110] direction. Taking the $P_{[110]}$ data at 10 K for $H//\{110\}$ and $H//\{110\}$ and plotting them as a function of $H$, one can obtain the ME response $P(H)$ curves, shown in the inset of Figs. 3(d) and 3(e). By fitting the $P(H)$ curves with $P = aH$, the ME coefficients of $x_{xx}$ and $x_{yy}$ are determined to be 13.8 and 10.6 ps/m, respectively, which are comparable to the reported linear ME materials, such as MnTiO$_3$ ($x_{xx}$, $x_{yy}$),$^{17}$ Cr$_2$O$_3$ ($x_{xx}$, $x_{yy}$),$^{33}$ and Sm$_2$BaCuO$_5$ ($x_{xx}$, $x_{yy}$).$^{34}$ Third, no matter which direction the ferroelectric polarization is along, the polarizations under $H//\{001\}$ are always smaller than the ones measured under $H//\{110\}$ and $\{10\}$ directions. This may be attributed to the large XY anisotropy of the magnetic structure that can be more easily changed under the $H$ applied along the ab plane.

Finally, we would like to give some qualitative discussion on the ME coupling in MnPSe$_3$. As shown in Fig. 1(a), the crystal structure of MnPSe$_3$ can be seen as the ABCABC stacking of the Mn$_3$P$_2$Se$_6$ layer along the c-axis. Within each Mn$_3$P$_2$Se$_6$ layer, the Mn$^{2+}$ spins are anti-ferromagnetically aligned along the [110] direction, exhibiting the 2/m and hidden $-1'\prime$ symmetry, shown in Fig. 4(a). Here, 2' is the twofold symmetry along the [110] plus a time-reversal symmetry, m is the mirror symmetry perpendicular to [110] direction. Owing to the presence of $-1'$ symmetry, no macroscopic polarization can be expected in the ground state, i.e., $H = 0$. However, when the applied magnetic fields along the [110] and $\{10\}$ directions exceed the critical field $H_c$, three types of magnetic domains realign into single one with the spins reoriented perpendicularly to $H$. Consequently, the $-1'$ symmetry breaks and macroscopic ferroelectric polarization emerges. For example, when $H//\{110\}$ and $H > H_c$ the twofold axis 2'/[110] can be unchanged, while the symmetry $m'//\{110\}$ breaks, giving rise to electric polarization along the [110] direction, shown in Fig. 4(b). Similarly, as shown in Figs. 4(c) and 4(d), the application of $H//\{110\}$ and [001] retains 2'/[110] but breaks m//\{110\}, leading to the electric polarization appearing along the [110] direction. To summarize, based on our magnetic symmetric analysis, an application of a magnetic field along three axes always induces the electric polarization along the [110] direction, implying the largest electric polarization can be expected along the [110] direction. Experimentally, the major electric polarization of MnPSe$_3$ is indeed along the [110] direction for $H//\{110\}$, $\{10\}$, and [001], although a smaller $\{10\}$ component is observed.

Subsequently, we will discuss the possible microscopic origin of ME coupling in MnPSe$_3$. Up to now, the magnetic-induced electric polarization can be explained by three well-known mechanisms: (1) the spin current mechanism,$^{35}$ (2) the exchangestriction mechanism,$^{36}$ and (3) the spin-dependent p-d hybridization mechanism.$^{37}$ However, in the honeycomb network consisting of six Mn$^{2+}$ ions, the first two mechanisms are not in work since the summary of the vector spin chirality $S_1 \times S_2$ in each honeycomb is zero, and the $S_1S_2$ for all the Mn–Mn bonds are uniform, where $S_1$ and $S_2$ are the magnetic moments at neighboring sites. In the spin-dependent p-d hybridization mechanism, a local electric polarization $\Delta \propto (S \cdot \nabla) \tau|$ between the transition metal and the ligand can be induced through the spin–orbit coupling, where $S$ is the magnetic moment of the transition metal ion, and $\tau$ is the vector connecting the transition metal and the ligand. As the Mn$^{2+}$ ions are located in a noncentrosymmetric environment with threefold symmetry along the c-axis, a local electric dipole moment is generated in each MnPSe$_3$ octahedron.

As illustrated in Figs. 4(a)–4(d), the magnetic structure of each honeycomb network in MnPSe$_3$ can be represented by two different sites $S_1$ and $S_2$ depending on the environment of the Mn$^{2+}$ ions and their magnetic moment direction. Each site consists of three Mn$^{2+}$ ions and forms an equilateral triangular. Thus, the local electric polarization $P_{S_1}(P_{S_2})$ for $S_1(S_2)$ sites can be obtained by the superposition of three local dipoles at $S_1(S_2)$ sites, while the total electric polarization $P$ of each honeycomb network is the superposition of $P_{S_1}$ and $P_{S_2}$.

According to Ref. 11, the local electric polarization for $S_1$ and $S_2$ sites can be expressed as

$$P_{S_1} = \begin{cases} A \sin^2 \beta_1 \cos 2\beta_1 + C \sin 2\beta_1 \cos \beta_1, \\ C_1 \sin^2 \beta_1 + C_2 \cos^2 \beta_1 \end{cases}$$

$$P_{S_2} = \begin{cases} A \sin^2 \beta_2 \cos 2\beta_2 + C \sin 2\beta_2 \cos \beta_2, \\ C_1 \sin^2 \beta_2 + C_2 \cos^2 \beta_2 \end{cases}$$

where $A$, $C$, $C_1$, and $C_2$ are the coupling constants correlated with the structure parameter of MnSe$_6$ octahedral, $\beta_1(\beta_2)$ is the angle of the spins at $S_1(S_2)$ site with respect to the z-axis, $\beta_1(\beta_2)$ is the angle of the projection of S on the xy plane with respect to the x-axis.

As shown in Fig. 4(a), in the ground state, the Mn$^{2+}$ ions related by the inversion symmetry have oppositely directed magnetic moments. As a result, the local electric dipoles arising from the spin-dependent p-d hybridization mechanism are antiferroelectrically aligned, thereby leading to an absence of macroscopic polarization. For $H//\{110\}$ and $H > H_c$, the spin directions $\beta_1, \beta_2, \beta_1, \beta_2$ can be expressed as $\beta_1 = \beta_2 = 90^\circ$, $\beta_1 = -\beta_2 = \beta$, shown in Fig. 4(b). Putting these relations into Eq. (1), the total polarization can be expressed as
It is important to note from Eqs. (2) and (3) that the electric polarization along the [110] direction is proportional to \( \sin 2\beta \). For a weak external magnetic field \( H \), the canting angle \( \beta \) (or \( \beta' \)) is small, and \( \sin 2\beta \) (or \( \sin 2\beta' \)) \( \propto H \) is expected; hence, the linear ME effect appears. However, for \( H \parallel [001] \), the spins will tilt to \( H \), i.e., the \( c \)-axis, resulting in the angle relations \( \alpha_1 = -\alpha_2 = \pi \), \( \beta_1 = -\beta_2 = \beta' \), as shown in Fig. 4(d). Substituting these relations into Eq. (1), one can obtain the total polarization \( P = 0 \), implying no electric polarization along the \([110]\) direction can be obtained through the spin-dependent \( p-d \) hybridization mechanism for \( H \parallel [001] \). Our microscopic analysis shows that the major electric polarization along the \([110]\) direction can be generated by the spin-dependent \( p-d \) hybridization mechanism for \( H \parallel [110] \) and \([1-10]\).

In conclusion, we have presented our systematic investigation of the magnetism and ME effect in MnPSe₃ single crystals. Our study demonstrates that MnPSe₃ is a linear ME material with weak ferromagnetism along the \([1-10]\) direction and strong ME coupling along the \([110]\) direction. The observation of nine nonzero components of the ME tensor aligns with the magnetic point group \(-I\) as determined by powder neutron diffraction measurements. Importantly, our symmetry and microscopic origin analyses suggest that the spin-dependent \( p-d \) hybridization mechanism plays an important role in the emergence of magnetically induced ferroelectricity. This work sheds light on the exploration of 2D multiferroic materials as well as the development of next-generation functional nanodevices based on 2D van der Waals materials.

See the supplementary material for the experimental details, the refined parameters obtained from Rietveld refinement, energy-dispersive x-ray spectroscopy mapping images, and the spectrum of MnPSe₃ single crystals. This work was financially supported by the National Key Projects for Basic Researches of China (Grant Nos. 92163210, 12274231, 12304119, 12304124, 12074111, and 52272108).

AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

J. H. Zhang: Conceptualization (lead); Data curation (lead); Formal analysis (lead); Writing – original draft (equal). L. Lin: Conceptualization (equal); Writing – original draft (equal); Writing – review & editing (equal). S. H. Zheng: Data curation (equal); Funding acquisition (equal).


DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding authors upon reasonable request.

REFERENCES


