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van der Waals material

$$\langle M \rangle = \langle P \rangle \langle S \rangle^3$$

for Ni and Mn

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Highly sensitive spin-flop transition in antiferromagnetic van-der Waals material MPS_3 ($M = Ni$ and Mn)

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Abstract

Recent developments in two-dimensional (2D) magnetism have motivated the search for novel van-der Waals (vdWs) magnetic materials to explore new magnetic phenomenon in the 2D limit. Metal thiophosphates, MPX_3 , is a class of magnetic vdWs materials with antiferromagnetic (AFM) ordering persisting down to the atomically thin limit. The magnetism in this material family has been found to be highly dependent on the choice of transition metal M . In this work, we have synthesized the intermediate compounds $Ni_{1-x}Mn_xPS_3$ ($0 \leq x \leq 1$) and investigated their magnetic properties. Our study reveals that the variation of Ni and Mn content in $Ni_{1-x}Mn_xPS_3$ can efficiently tune the spin-flop transition, likely due to the modulation of the magnetic anisotropy. Such effective tuning offers a promising candidate to engineer 2D magnetism for future device applications.

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Recent breakthroughs in two-dimensional (2D) magnetic materials open a new route in exploring intrinsic magnetism in the 2D limit. The discoveries of novel 2D magnets [1–6] provide opportunities not only to understand the mechanism of low dimensional magnetism but also to design next-generation devices. For example, advances in devices and heterostructures involving 2D magnets enable the effective tuning of their electronic and magnetic properties, providing a fascinating platform to study fundamental physics [7–18]. These breakthroughs have greatly enriched our understanding of magnetism in the 2D limit.

Among 2D magnetic materials, one model system is metal thiophosphates MPX_3 (M = transition metal ions, X = chalcogen ions). MPX_3 materials crystallize in a monoclinic layered structure with $C_{2/m}$ space group, in which the transition metal ions form a honeycomb layer and carry localized magnetic moments [19–22]. The van der Waals (vdW)-type crystal structure allows for the inter-layer intercalation [23–27] and mechanical exfoliations down to atomically thin layers [5,28–36]. The magnetic and electronic properties of the MPX_3 family are strongly dependent on the choice of the transition metal M . $MnPS_3$, $NiPS_3$, and $FePS_3$ have been found to exhibit Heisenberg-type, XY or XXZ -type, and Ising-type antiferromagnetism, respectively [37–42]. The Neel temperature (T_N) also varies with transition metal M , increasing from 78 K for $MnPS_3$, to 118, 122, and 155 K for $FePS_3$, $CoPS_3$, and $NiPS_3$, respectively [38,40,42–45]. Besides magnetism, the electronic properties of MPX_3 are also tunable with M , exhibiting a wide range of band gaps from 1.3 eV for $FePSe_3$ to 3.5 eV for $ZnPS_3$ [22]. Recent studies on $NiPS_3$ and $MnPS_3$ have established these materials as platforms to study correlated electrons in 2D magnetic materials [32,46,47]. Furthermore, theoretical and experimental high-pressure studies revealed

insulator-to-metal transitions in MnPS_3 [47,48], MnPSe_3 [48], FePS_3 [49–52], NiPS_3 [47,53] and $\text{V}_{0.9}\text{PS}_3$ [51,54], and even the emergence of superconductivity in FePSe_3 [55].

The structural similarity of the MPX_3 materials allows for the synthesis of polymetallic “mixed” compounds with substitution of transition metal M [56–66]. Varying lattice constant and magnetic moments through elemental substitution is an effective way to tune magnetism and probe the underlying physics of magnetic materials. Coupling of magnetism with lattice constants and symmetries in MPX_3 has been theoretically predicted [67]. Tuning of magnetism has also been observed in mixed compounds such as $\text{Mn}_x\text{Fe}_{1-x}\text{PS}_3$, $\text{Mn}_{1-x}\text{Fe}_x\text{PSe}_3$, $\text{Fe}_{0.5}\text{Ni}_{0.5}\text{PS}_3$ and $\text{Mn}_{1-x}\text{Zn}_x\text{PS}_3$ [56–66]. For example, magnetic order and spin orientations in MnPS_3 can be systematically tuned by Zn substitution for Mn [56–58]. Spin glass is also found to arise from the competing $3d$ magnetism in Mn substituted FePS_3 [59–61].

In this work, we report the systematic study on previously unexplored $\text{Ni}_{1-x}\text{Mn}_x\text{PS}_3$ ($0 \leq x \leq 1$). We synthesized single crystals and characterized the evolution of magnetic properties with substitutions. In addition to the known field-induced spin-flop (SF) transition in MnPS_3 , we have also discovered the previously unreported SF transitions in NiPS_3 . Furthermore, we found these SF transitions are extremely sensitive to magnetic substitutions, likely due to the re-orientation of the magnetic moments of $3d$ elements controlled by trigonal distortion of MS_6 octahedral. Such tunable magnetism offers a promising platform for studying new phenomenon arising from 2D magnetism and future device applications.

Single crystals of $\text{Ni}_{1-x}\text{Mn}_x\text{PS}_3$ ($0 \leq x \leq 1$) used in this work were synthesized by the chemical vapor transport method using I_2 as the transport agent. Elemental powders with stoichiometric ratio were sealed in a quartz tube and placed in a two-zone furnace with a temperature gradient from 750 to 550 °C for 1 week. Millimeter to centimeter size single crystals

with various colors have been obtained, as shown in the insets of Fig. 1a. These crystals are thin plate-like and easily exfoliable with hexagonal facets which is consistent with the vdW structure of MPX_3 shown in Fig. 1b. The elemental compositions examined by energy-dispersive x-ray spectroscopy (EDS) reveal successful Ni-Mn substitution. We have carefully characterized the compositions of all the $Ni_{1-x}Mn_xPS_3$ single crystals used in this paper. The Mn contents x throughout this paper are measured values. In addition to composition analysis, the x-ray diffraction (XRD) on single crystals also indicates successful substitution. As shown in Fig. 1 (a), the $(00L)$ diffraction peaks exhibit a systematic low-angle shift with increasing x in $Ni_{1-x}Mn_xPS_3$, which is consistent with the greater ionic radius of Mn^{2+} as compared with Ni^{2+} , respectively.

In Fig. 2 we present the magnetic property characterizations for pristine $MnPS_3$ and $NiPS_3$. For $MnPS_3$, below the Néel temperature $T_N \sim 78$ K, a spin-flop (SF) transition can be observed in the isothermal magnetization measured under out-of-plane magnetic field ($H \perp ab$) [Fig. 2(a)] but is absent under in-plane field ($H // ab$) [Fig. 2(b)], which is consistent with the previous reports [5,34,65,68,69]. Although the SF transition is largely explored in both bulk and atomically thin $MnPS_3$, it has not been *directly* discovered in other members of this family except $FePS_3$, in which a metamagnetic transition occurs at very high field ($\mu_0 H > 35$ T) [70]. Here we report the first discovery of SF transition in $NiPS_3$. Unlike in $MnPS_3$ in which the SF transition occurs when $H \perp ab$, the metamagnetic transition in $NiPS_3$ takes place with in-plane field, which is characterized by a clear upturn in magnetization above a critical spin-flop field $\mu_0 H_{SF} \approx 6$ T below the Néel temperature $T_N \approx 155$ K, as shown in Figs. 2(d) and 2(e). The need for relatively high magnetic field could be the reason that prevented the discovery of SF transition in earlier studies [38,71]. On the other hand, the recent magneto-photoluminescence experiment implies a spin re-orientation in bulk $NiPS_3$ under a much higher in-plane magnetic field of 15 T [32]. Such a high critical field,

which is 2.5 times higher than that in our magnetization measurements, might be attributed to the nature of photoluminescence as an indirect probe.

In MnPS_3 and NiPS_3 , the SF transition occurring under different field directions is in line with their magnetic structures: The Mn moments in MnPS_3 are aligned along out-of-plane direction [58,69], while the Ni moments in NiPS_3 mostly lie within the plane [31,38,71], as shown in the insets of Figs. 2b and 2c, respectively. In collinear AFM systems, a magnetic field along the easy axis exceeding a critical spin-flop field H_{SF} forces the magnetic moments to rotate [72,73]. In such a SF state, the moments re-orient themselves to a canted configuration perpendicular to the field direction, resulting in a net moment along the easy axis [72,73]. Therefore, the SF transition behaves differently in MnPS_3 and NiPS_3 , as illustrated in Figs. 2g and 2h. Furthermore, because the in-plane projection of Ni moments in NiPS_3 forms a collinear AFM structure along the a -axis (Fig. 2c, lower inset), the SF transition is expected to show in-plane anisotropy. To examine this, we measured magnetization with the magnetic field applied along or perpendicular to the hexagonal edges of a NiPS_3 single crystal, as shown in Fig. 2(e). Indeed, magnetization and SF transition are found to be dependent on in-plane field-orientations.

The scenario of SF transition in NiPS_3 is also supported by the temperature dependence of magnetic susceptibility. As shown in Fig. 2(f), susceptibility measured with in-plane field (χ_{\parallel}) displays a low temperature upturn, which becomes more significant at higher fields ($\mu_0 H > 5$ T). A similar low temperature upturn has been observed in MnPS_3 [65]. In addition, the zero-field cooling (ZFC, solid lines) and field cooling (FC, dashed lines) data display weak but clear irreversibility above 5 T, which also becomes more visible at higher fields. The development of low temperature upturn and irreversibility can be understood in terms of the ferromagnetic component from the uncompensated canted moments along the easy axis in the SF state, as

illustrated in Fig. 2h. This irreversibility disappears at 140 K when applying 9 T field, coinciding well with the temperature above which the SF transition vanishes as seen in the isothermal magnetization [Fig. 2(d), inset]. Such 140 K “disappearing temperature” is lower than the magnetic ordering temperature $T_N \approx 155$ K, which can be attributed to the fact that a greater field is needed for SF transition at higher temperatures, particularly when approaching T_N . H_{SF} enhancement upon increasing temperature is widely seen in other SF systems [5,74–78], which can be interpreted using the molecular field theory [73,78]: In a weakly anisotropic antiferromagnet, spin-flop field H_{SF} can be estimated by $(H_{SF})^2 = 2K/(\chi_{\perp} - \chi_{\parallel})$, where K is the anisotropy constant, χ_{\perp} and χ_{\parallel} are the perpendicular and parallel susceptibilities, respectively [58,73,78,79]. Generally, in AFM systems the difference between χ_{\perp} and χ_{\parallel} reduces more quickly than the magnetic anisotropy constant K upon increasing temperature, leading to enhanced H_{SF} [78].

The distinct SF transitions in NiPS₃ and MnPS₃ due to their different magnetic structures (Figs. 2g and 2h) motivate us to further study the “mixed” compounds Ni_{1-x}Mn_xPS₃. As shown in Fig. 3, the magnetism is highly tunable with Ni-Mn substitution. Under both in-plane ($H \parallel ab$, Fig. 3a) and out-of-plane ($H \perp ab$, Fig. 3b) magnetic fields, the magnetization exhibits a systematic enhancement with increasing Mn content x , which is consistent with the much larger magnetization of the pristine MnPS₃ than that of NiPS₃ [Figs. 2(a-d)] and can be ascribed to greater magnetic moment of Mn²⁺ than Ni²⁺. Interestingly, we found that the SF transitions are extremely sensitive to Ni-Mn substitution. The SF transition in NiPS₃ under in-plane field disappears with 5% Mn substitution (*i.e.*, $x = 0.05$ in Ni_{1-x}Mn_xPS₃). Similarly, under out-of-plane field, H_{SF} in MnPS₃ is reduced by half with 5% Ni substitution (*i.e.*, $x = 0.95$) and disappears upon 10% substitution ($x = 0.9$).

Further insights can be gained from the careful comparison between the isothermal magnetizations. In Fig. 3d we show isothermal magnetization $M(H)$ of NiPS₃ (*i.e.*, $x = 0$) and 5% Mn-substituted (*i.e.*, $x = 0.05$) samples, reproduced from Figs. 3a and 3b. With Mn substitution, in addition to the enhancement of magnetization and the absence of SF transition as mentioned above, another interesting behavior is the sublinear field dependence at low fields. Such nonlinear $M(H)$ is more pronounced under in-plane field [Inset, Fig. 3(d)], *i.e.*, the magnetic field direction that SF transition occurs for NiPS₃. Similarly, at the MnPS₃ side, 5% Ni-substitution ($x = 0.95$) also introduces remarkable low field nonlinearity in $M(H)$ under out-of-plane field, as shown in the inset of Fig. 3e. Such nonlinearity has been verified with multiple samples and careful removal of background signal from the sample holder. The observed low field sublinear $M(H)$ in lightly substituted compounds is in sharp contrast with the linear $M(H)$ in pristine NiPS₃ and MnPS₃, implying the development of ferromagnetic component with substitution. Such behavior has also been observed in Zn-substituted MnPS₃. The previous study [58] on Zn substitution for Mn in MnPS₃ suggests the breakdown of long-range magnetic order due to non-magnetic impurities in local substituted regions, which leads to “weakly bound” Mn moments. The polarization of these Mn moments causes the low-field nonlinear $M(H)$. Another study [57] also propose that for MnPS₃ in which the dipolar anisotropy dominates, the local dipole field is along the out-of-plane direction. As the consequence, when Mn-magnetism is diluted by Zn substitution, the absence of the magnetic moment of one Mn site would affect the closest Mn in the neighboring layers and cause their magnetic moments to be canted, leading to an average staggered magnetic moment in a larger scale [57]. Similarly, the nonlinear $M(H)$ at low fields in our Ni_{1-x}Mn_xPS₃ samples can likely be attributed to the polarization of canted moment originating from substitution. This scenario is further supported by the temperature dependence of susceptibility measurements. As shown in Fig.

4a, consistent with the nonlinear $M(H)$ seen under $H\parallel ab$ in the $x = 0.05$ sample (Fig. 3d, inset), the in-plane susceptibility (χ_{\parallel}) displays a clear upturn at low temperatures that suggests the development of a ferromagnetic component due to moment canting. Likewise, close to the MnPS_3 side, for $x = 0.95$ sample in which the nonlinear $M(H)$ is significant (Fig. 3e, inset), a susceptibility upturn is also seen, as shown in Fig. 4c. The upturn become more obvious with increasing the Ni content to 10% ($x = 0.9$), as shown in Fig. 4b.

The tunable SF transition and the presence of a ferromagnetic component by Ni-Mn substitution is expected because of the distinct magnetic structures in NiPS_3 and MnPS_3 . However, the observed high sensitivity to light substitution is surprising. For example, only 5% Ni substitution can substantially reduce H_{SF} by half in MnPS_3 , which is much less than the amount of Zn needed ($\sim 20\%$) to reduce H_{SF} by the same amount [58,65]. The H_{SF} suppression by non-magnetic Zn substitution has been ascribed to the reduction of magnetic anisotropy with magnetic dilution [58]. The Ni-Mn substitution in our $\text{Ni}_{1-x}\text{Mn}_x\text{PS}_3$, however, induces magnetic impurities. Hence, it is necessary to consider the magnetic interaction to understand the observed sensitive doping dependence in $\text{Ni}_{1-x}\text{Mn}_x\text{PS}_3$. In MPX_3 compounds, magnetism has been found to be related to a structural distortion [23,80–83]. As illustrated in Fig. 3c, every metal atom M in MPX_3 is located at the center of an octahedron formed by six X atoms. Such MX_6 octahedra, however, possess a trigonal distortion that is characterized by the angle θ between the trigonal axis (perpendicular to the ab -plane) and the M -S bond. Therefore, magnetism in MPX_3 can be described by an isotropic Heisenberg Hamiltonian with additional single-ion anisotropy due to the combined effect of crystal field and spin-orbit splitting: $H = -2\sum J S_i S_j + D S_{iz}^2$, where J and D are the exchange and crystal field parameters, respectively [37]. The relative strength of J and D leads to various magnetic structures in MPX_3 , so the trigonal distortion plays critical role in determining

the nature of magnetic interactions in MPX_3 [37,80]. In $NiPS_3$ and $MnPS_3$, θ has been found to be 51.05° and 51.67° , respectively [80]. Compared with $\theta \approx 54.75^\circ$ for the undistorted octahedra, the greater trigonal distortion in $NiPS_3$ leads to much stronger single-ion anisotropy (0.3 meV) than that of $MnPS_3$ (0.0086 meV), as revealed by inelastic scattering measurements [42,80,81]. This causes the Ni moments to be aligned within the basal plane perpendicular to the trigonal axis, with a small out-of-plane component likely due to weak dipolar anisotropy, as shown in the insets of Figs. 2c [37,43,82]. In contrast, the effect of crystal field and spin-orbit splitting is found to be negligible for the high spin ground state of Mn^{2+} in $MnPS_3$ [37], so the magnetism of the less distorted $MnPS_3$ is governed by the dipolar anisotropy that leads to out-of-plane moment direction with small tilt towards a -axis [42,69,82], as shown in the inset of Fig. 2b. Therefore, the tuning of trigonal distortion by Ni-Mn substitution would significantly affect the magnetic isotropy and further efficiently modify the SF transitions. A similar mechanism has also been proposed for the suppression of H_{SF} in $MnPS_3$ under pressure [82].

In addition to magnetic anisotropy, magnetic exchange interaction may also play an important role. The magnetism in MPX_3 is mainly mediated through superexchange interaction, thereby affected by the M - X - M bonding angle [37,81]. Additionally, the d -electron occupancy of M is important in determining the sign and the nature of the superexchange [37,80,81]. The $3d$ orbitals of M^{2+} ion consist of high energy e_g and low energy t_{2g} groups, and their occupancies determine the strength of the exchange interactions [80,83]. This has recently been demonstrated by the inelastic neutron scattering measurements which reveals reduced exchange interactions in $CoPS_3$ as compared to $NiPS_3$ due to distinct occupancy of t_{2g} orbital [80]. A similar scenario should also occur in $Ni_{1-x}Mn_xPS_3$, in which the Ni-Mn substitution modifies the magnetic exchange. Indeed, the magnitudes of all the exchanges, except the weakest second nearest-neighbor

interaction (J_2), are found to systematically increase with decreasing spin on M^{2+} ion and increasing M -S- M bond angles from MnPS_3 to NiPS_3 [80,81,83].

Among the magnetic anisotropy and magnetic exchange interactions, the former may govern the SF transitions in $\text{Ni}_{1-x}\text{Mn}_x\text{PS}_3$. The magnetic ordering temperature be related to the strength of the magnetic interaction. We have extracted T_N for $\text{Ni}_{1-x}\text{Mn}_x\text{PS}_3$ from magnetic susceptibility and heat capacity measurements, as summarized in Fig. 4 (e). For both NiPS_3 and MnPS_3 , T_N decreases with substitution until reaching to a minimum value of ~ 12 K in $x = 0.5$ sample. A similar trend has also been observed in other mixed MPX_3 systems such as $\text{Mn}_{1-x}\text{Zn}_x\text{PS}_3$ [65], $\text{Mn}_{1-x}\text{Fe}_x\text{PS}_3$ [61], and $\text{Mn}_{1-x}\text{Fe}_x\text{PSe}_3$ [66]. Several mechanisms [65] [61] [66] have been proposed for the suppression of T_N , such as the attenuation of the magnetic interaction due to disordered arrangements of the mixed metals ions with dissimilar ionic radius and outer shell electrons, and magnetic frustration among the 3d metal ions in the magnetic sites owing to competition between two different AFM structures. The strong variation of T_N in heavily substituted $\text{Ni}_{1-x}\text{Mn}_x\text{PS}_3$ samples may also share similar scenarios. However, for lightly substituted samples with x close to 0 or 1, T_N only changes slightly as compared to the parent compounds NiPS_3 and MnPS_3 . It is quite interesting to find that the light Ni-Mn substitution only weakly alters the magnetic ordering temperature but drastically suppresses the SF transitions. This suggests that the efficient suppression of the SF transition with light magnetic substitution in $\text{Ni}_{1-x}\text{Mn}_x\text{PS}_3$ can be attributed to the tuning of single ion isotropy rather than exchange interaction.

In conclusion, we have demonstrated very efficient tuning of the SF transition by light Ni-Mn substitution, which is likely attributed to single ion isotropy tuned by trigonal distortion. Such strong sensitivity suggests that magnetic substitutions can be an effective technique to control magnetism in MPX_3 vdWs magnetic materials, leading to a deeper understanding of low

dimensional magnetism and providing insight into strategies for future magnetic device development.

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Figures

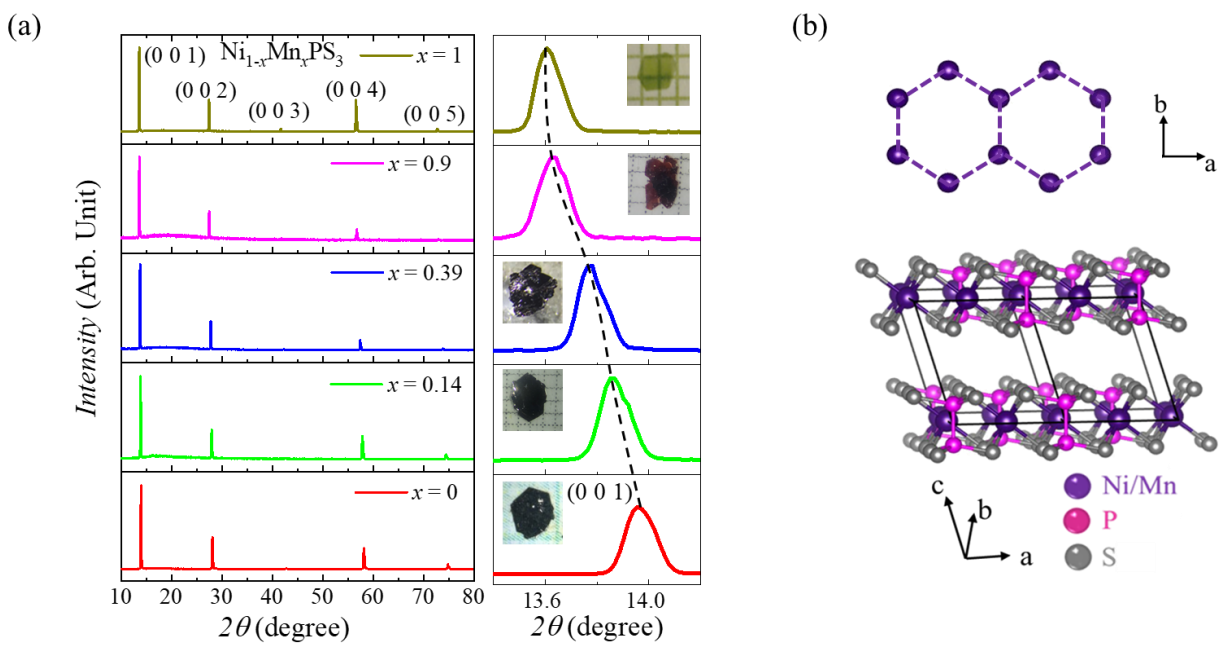


FIG. 1. (a) Single-crystal x-ray-diffraction pattern for $\text{Ni}_{1-x}\text{Mn}_x\text{PS}_3$ showing the $(00L)$ reflections. Right panels show (001) diffraction peak. Inset: Optical microscope images of the single crystals. (b) Crystal structure of MPS_3 ($M = \text{Ni/Mn}$).

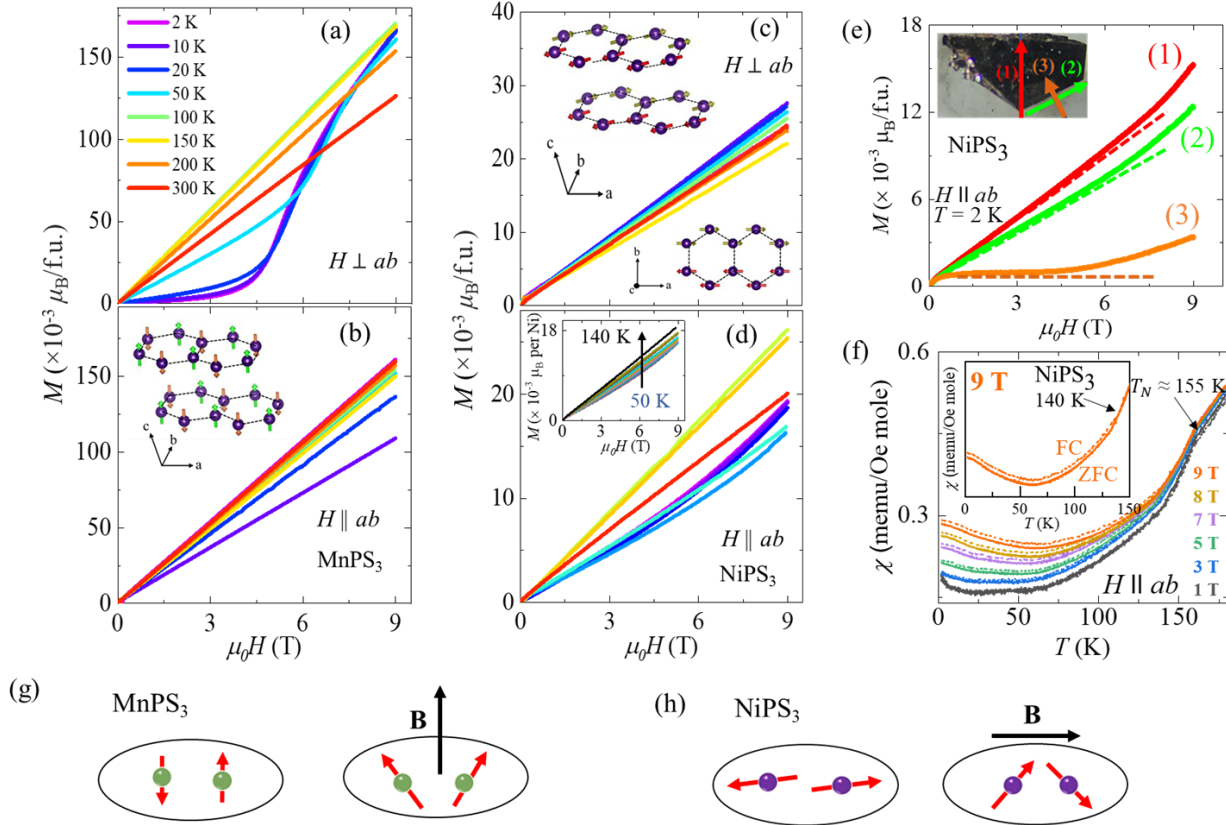


FIG. 2. Field induced spin flop transitions in pristine MnPS₃ and NiPS₃. (a-b) Isothermal magnetization of MnPS₃ at different temperatures under (a) $H \perp ab$ and (b) $H \parallel ab$. Inset in (b): magnetic structure of MnPS₃. (c-d) Isothermal magnetization of NiPS₃ at different temperatures under (a) $H \perp ab$ and (d) $H \parallel ab$. Upper inset in (c): 3D view of magnetic structure of NiPS₃. Lower inset in (c): Top view of magnetic structure of NiPS₃. Inset in (d): Isothermal magnetization at 50 – 140 K measured with $H \parallel ab$. The same color code is used indicate temperatures for (a-d). (e) Isothermal magnetization at 2 K under $H \parallel ab$ with different in-plane field orientations. Inset: Optical microscope image of NiPS₃ single crystal with arrows pointing the applied field direction. (f) Temperature dependence of susceptibility of NiPS₃ measure with 1, 3, 5, 7, 8, and 9 T fields, measured with $H \parallel ab$. Inset: Temperature dependence of susceptibility at 9 T under $H \parallel ab$. The solid and dotted lines represent zero-field cooled (ZFC) and field-cooled (FC) data, respectively.

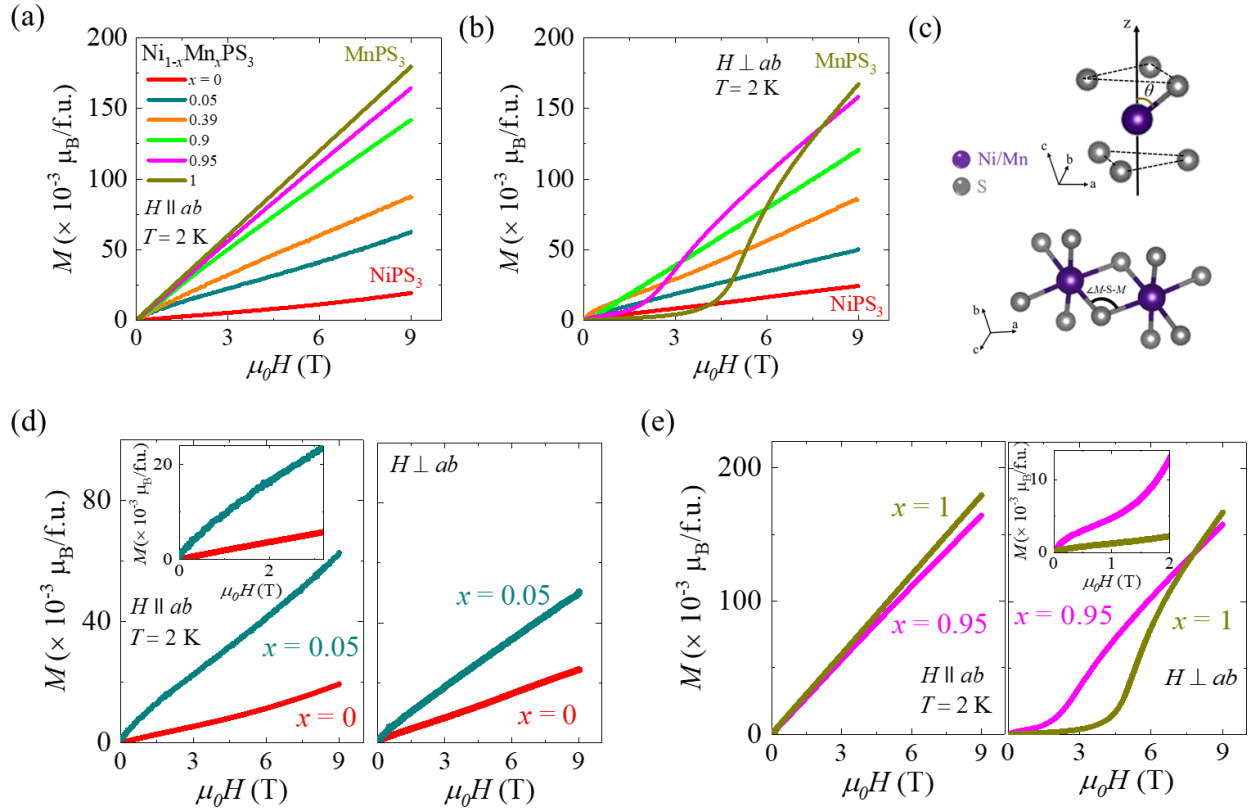


FIG. 3. (a-b) Isothermal magnetization of $\text{Ni}_{1-x}\text{Mn}_x\text{PS}_3$ samples ($0 \leq x \leq 1$) at $T = 2$ K under (a) $H \parallel ab$ and (b) $H \perp ab$. The same color code is used to indicate temperatures for (a) and (b). (c) Trigonal distortion in MPS_3 compounds. z -axis is the trigonal axis. (d) Isothermal magnetization of $\text{Ni}_{1-x}\text{Mn}_x\text{PS}_3$ ($x = 0$ and 0.05) at $T = 2$ K under $H \parallel ab$ (Left panel) and $H \perp ab$ (Right panel). Inset: zoom in of the low-field magnetization. (e) Isothermal magnetization of $\text{Ni}_{1-x}\text{Mn}_x\text{PS}_3$ ($x = 0.95$ and 1) at $T = 2$ K under $H \parallel ab$ (Left panel) and $H \perp ab$ (Right panel). Inset: zoom in of the low-field magnetization.

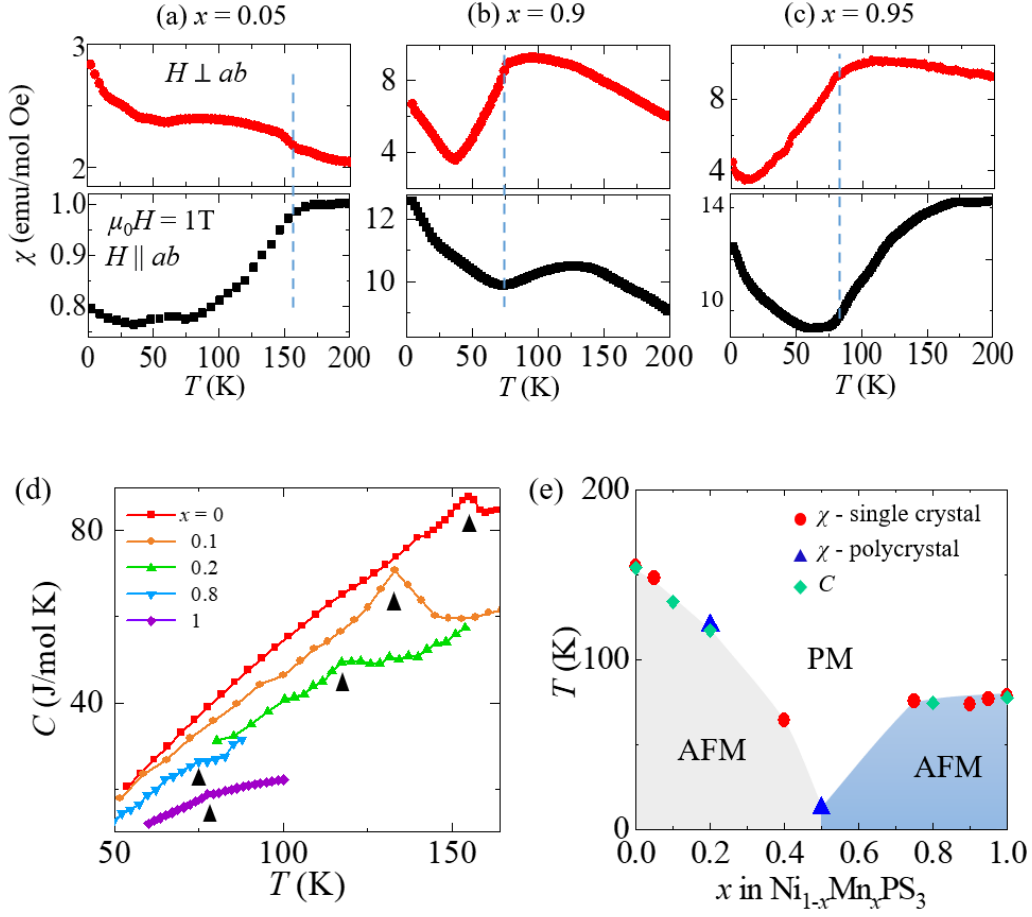


FIG. 4. (a-c) Temperature dependence of out-of-plane ($H \perp ab$, red, upper panels) and in-plane ($H \parallel ab$, black, lower panels) susceptibilities of (a) $\text{Ni}_{0.95}\text{Mn}_{0.05}\text{PS}_3$, (b) $\text{Ni}_{0.1}\text{Mn}_{0.9}\text{PS}_3$, and (c) $\text{Ni}_{0.05}\text{Mn}_{0.95}\text{PS}_3$ samples. The dashed lines denote T_N . (d) Temperature dependence of heat capacity of $\text{Ni}_{1-x}\text{Mn}_x\text{PS}_3$ samples with $x = 0, 0.1, 0.2, 0.8$ and 1 . The black triangles denote T_N . Data are shifted for clarity. (e) Magnetic phase diagram of $\text{Ni}_{1-x}\text{Mn}_x\text{PS}_3$ ($0 \leq x \leq 1$). The transition temperatures are determined by susceptibility measurements on single- (χ -single crystal) and poly-crystals (χ -polycrystal), and heat capacity (C).