### CHEMISTRY

**Defect-mediated ferromagnetism in correlated two-dimensional transition metal phosphorus trisulfides**

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Controlling the magnetic spin states of two-dimensional (2D) van der Waals (vdW) materials with strong electronic or magnetic correlation is important for spintronic applications but challenging. Crystal defects that are often present in 2D materials such as transition metal phosphorus trisulfides (MPS$_3$) could influence their physical properties. Here, we report the effect of sulfur vacancies on the magnetic exchange interactions and spin ordering of few-layered vdw magnetic Ni$_{1-x}$Co$_x$PS$_3$ nanosheets. Magnetic and structural characterization in corroborations with theoretical calculations reveal that sulfur vacancies effectively suppress the strong intralayer antiferromagnetic correlation, giving rise to a weak ferromagnetic ground state in Ni$_{1-x}$Co$_x$PS$_3$ nanosheets. Notably, the magnetic field required to tune this ferromagnetic state (<300 Oe) is much lower than the value needed to tune a typical vdw antiferromagnet (> several thousand oersted). These findings provide a previously unexplored route for controlling competing correlated states and magnetic ordering by defect engineering in vdw materials.

#### INTRODUCTION

Two-dimensional (2D) van der Waals (vdW) materials offer a versatile platform to study novel physical properties and explore their potential applications in electronic, optical, and spintronic devices (1–3). The realization of magnetism in easily exfoliated 2D vdw crystals provides accessibility to control and manipulate magnetic properties at a single atomic layer level (2, 4–12). Among various families of magnetic vdw materials, transition metal phosphorus trichalcogenides (MPX$_3$, X = S or Se; M cations are generally 3d elements: Mn, Fe, Co, Ni, etc.) (10, 13) gained recent attention due to their pressure-induced superconductivity (14), optoelectronic (15–17), and catalytic (18–20) properties. Bulk crystals of MPX$_3$ have a monoclinic crystal structure (space group of C2/m), in which the transition metal cations (M) are surrounded by an octahedral cage of [P$_2$X$_6$]$^{4-}$ bipyramids, and the neighboring metals have a 2D graphene-like honeycomb lattice arrangement (21, 22). Resulting from long-range anion-mediated magnetic exchange interactions, MPX$_3$ compounds exhibit various types of antiferromagnetic (AFM) ordering such as zigzag, Néel, and stripy pattern below their respective Néel temperatures ($T_N$) (22–25).

Among magnetic MPX$_3$, NiPS$_3$ particularly exhibits intriguing quantum properties owing to the presence of strong charge-spin correlation effects (15, 22, 26, 27). It shows zigzag antiferromagnetism with weak in-plane anisotropy below $T_N$ ~155 K, in which ferromagnetically arranged spin chains are antiferromagnetically coupled out of the crystal lattice down to bilayer stacking. The solution to the XXZ Heisenberg spin model of NiPS$_3$ reveals strong AFM exchange coupling between the third nearest neighboring M, while the nearest and second nearest neighboring M exhibit weak ferromagnetic (FM) exchange interaction and hence supports the existence of zigzag AFM ground state (15, 26–29). This long-range AFM interaction is mediated through S atoms located in the same chalcogen sublayer and is governed by a super-supercurrent mechanism. In addition, NiPS$_3$ behaves as a negative charge transfer (NCT) insulator and adopts a lower energy self-hole doped ground state where the S (3p orbital) ligand ends up donating an electron to the attached Ni (3d orbital) atom (15, 22). Low-temperature optical conductivity measurements revealed that these intersite transitions are allowed only between AFM Ni neighbors and demonstrated strong correlation between electronic and magnetic structures in NiPS$_3$ (22). Notably, NiPS$_3$ is the only known magnetic vdw material that exhibits NCT ground state with a close resemblance to the hole-doped high-temperature cuprate superconductors (27).

The control and manipulation of correlated interactions can lead to new and tunable physical properties in vdw materials. Recently, stacking-dependent pressure-induced tunability and electrical control over long-range magnetic exchange interactions have enabled the investigation of novel quantum phenomena and magnetooptoelectronics in magnetic vdw materials (4–9, 30, 31), including NiPS$_3$ (27). On the other hand, the incorporation of atomic defects and chemical substitutions in 2D materials could affect and potentially control the electronic and magnetic interactions by altering the local atomic coordination and make nonmagnetic 2D materials, such as graphene and molybdenum disulfide, magnetic (32–35). It is hoped that the vacancy defects in vdw antiferromagnets could be used to potentially control intrinsic AFM ordering to manipulate the spin states of the materials at a much lower applied magnetic field compared to the high-field spin-flop transitions (40 to 53 kOe for MnPS$_3$ layers and 8 to 9 kOe for CrI$_3$), and such modulation of magnetic properties could be appealing for spintronic applications (9, 13).

Here, we target the strongly correlated vdw magnets Ni$_{1-x}$Co$_x$PS$_3$ (0 ≤ x ≤ 0.50) (Fig. 1A) and demonstrate the tuning of magnetism with sulfur vacancy defects ($S_v$) in Ni$_{1-x}$Co$_x$PS$_3$ nanosheets (NS) synthesized through the chemical vapor conversion method. Magnetic characterization, combined with x-ray absorption spectroscopy and electron spin resonance (ESR) spectroscopy measurements, reveals that the incorporation of $S_v$ in Ni$_{1-x}$Co$_x$PS$_3$ NS results in the
emergence of a weak FM ground state at low temperatures (<100 K) due to the suppression of AFM correlations at a low applied magnetic field range (<300 Oe), while no such phenomenon is observed in the Ni$_{1-x}$Co$_x$PS$_3$ single-crystal counterparts. Theoretical calculations suggest that the presence of S$_v$ disrupts anion-mediated AFM interactions, highlighting the magnetic instability of NiPS$_3$. The experimental findings and theoretical calculations demonstrate the concept of tuning defect-mediated magnetic exchange interactions to manipulate magnetism in magnetic vdW materials.

RESULTS

Synthesis and structural characterization of Ni$_{1-x}$Co$_x$PS$_3$ NS and single crystals

We synthesized Ni$_{1-x}$Co$_x$PS$_3$ (0 ≤ x ≤ 0.50) NS with the lateral dimension of a few micrometers, which are distributed uniformly on the surface of carbon cloth via a two-step process (see Materials and Methods and fig. S1). (i) The metal hydroxide precursor NS with various Ni:Co ratios were first synthesized on carbon cloth, and (ii) then these metal hydroxide precursor NS were converted to the corresponding Ni$_{1-x}$Co$_x$PS$_3$ (0 ≤ x ≤ 0.50) NS through chemical vapor conversion process. During the second vapor conversion step, the ratio of P:S precursors (mixed elemental powders) was adjusted to a value slightly higher than the stoichiometric ratio (1:3). Figure 1B shows the powder x-ray diffraction (PXRD) patterns obtained from different compositions of as-synthesized Ni$_{1-x}$Co$_x$PS$_3$ NS on carbon cloth and compared with the standard patterns of NiPS$_3$ and CoPS$_3$ (fig. S2). There are no other crystalline impurity phases detected in our samples. The slight shift of the most intense (001) diffraction peak highlighted at 2θ ~14° for Ni$_{1-x}$Co$_x$PS$_3$ (0 < x < 0.5) suggests alloying of Co into the NiPS$_3$ crystal lattice. Energy-dispersive spectroscopy (EDS) results represented in the form of histogram (fig. S3) yield the average cobalt substitution (x) in these Ni$_{1-x}$Co$_x$PS$_3$ NS samples. Furthermore, the elemental mapping results (Fig. 1, C and D, and fig. S4) show a homogeneous distribution of Ni, Co, P, and S throughout the Ni$_{1-x}$Co$_x$PS$_3$ NS. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) imaging (fig. S5A) and Ni$_{0.68}$Co$_{0.32}$PS$_3$ NS (Fig. 1E) reveals the arrangement of atoms on the (001) basal plane with lattice parameters close to the theoretical values (a = 0.584 nm and b = 1.014 nm) for NiPS$_3$ (fig. S5B). The corresponding selected-area electron diffraction (SAED) pattern is indexed to the monoclinic crystal structure along the (001) zone axis (Fig. 1F). Atomic force microscopy determines the thickness of few-layered Ni$_{1-x}$Co$_x$PS$_3$ NS in the range of ~4 to 11 nm (Fig. 1G and fig. S6). Raman spectra of various Ni$_{1-x}$Co$_x$PS$_3$ (0 ≤ x ≤ 0.5) NS.
show five in-plane $E_g$ and three out-of-plane $A_{1g}$ phonon modes (36). The $A_{1g}$ modes at higher frequencies are attributed to the intramolecular vibrations from (P$_2$S$_6$)$^{4-}$ bipyramid structures (26). No other phonon modes were observed in the Raman spectra of Ni$_{1-x}$Co$_x$PS$_3$ NS, suggesting the absence of Ni- or Co-based chemical impurities, which are Raman active except for the Ni or Co metal impurities.

For comparison purposes, we also grew single crystals of Ni$_{1-x}$Co$_x$PS$_3$ ($x \approx 0.17, 0.32$, and $0.50$) with millimeter lateral dimensions (fig. S7, A to C) using a chemical vapor transport (CVT) method (see Materials and Methods for details). Their phase purity was checked using PXRD (fig. S7B), which show high intensity peak only for the (00$l$) crystallographic planes—the expected preferential orientation of the Ni$_{1-x}$Co$_x$PS$_3$ single crystals. The uniform alloying of constituent elements in Ni$_{1-x}$Co$_x$PS$_3$ single crystals is also confirmed through the EDS elemental mapping (fig. S7, D to E).

**Determination of sulfur vacancy defects in Ni$_{1-x}$Co$_x$PS$_3$ samples**

To learn more about the local bonding environments, we acquired and analyzed hard x-ray absorption spectra (XAS) for both Ni$_{1-x}$Co$_x$PS$_3$ NS and single crystals. Figure 2A and fig. S8A show the Ni K-edge x-ray absorption near-edge structure (XANES) spectra for NiPS$_3$, Ni$_{1-x}$Co$_x$PS$_3$ NS, and single crystals along with their corresponding reference samples. The XANES profiles of these Ni$_{1-x}$Co$_x$PS$_3$ NS and single crystals reveal a nearly identical Ni valence state of +2, strongly suggesting the same coordination environment around Ni atoms in the crystal and the absence of any Ni-based impurities (such as Ni metal clusters). The relatively small prepeaks at $\sim 8331.0$ eV further suggest octahedral coordination (37) of Ni with S ligands along with the $1s \rightarrow e_g^*$ (the lowest unoccupied molecular orbital) transition. Similarly, the Co K-edge XANES spectra (Fig. 2B and fig. S8B) show a weak pre-edge peak $\sim 7709.0$ eV, revealing the same Co oxidation state of +2 and octahedral coordination around Co atoms in Ni$_{0.68}$Co$_{0.32}$PS$_3$ NS and single crystals. The Co K-edge XANES profiles are substantially different from the reference Co-based compounds such as CoS$_2$, Co$_3$O$_4$, and Co foil, which further confirms the chemical purity of as-synthesized Ni$_{0.68}$Co$_{0.32}$PS$_3$ NS and single crystals.

Next, the phase-uncorrected extended x-ray absorption fine structure (EXAFS) spectra (38) were collected to understand the chemical coordination environments. The Ni K-edge $k^3$-weighted Fourier transform curves for NiPS$_3$, Ni$_{0.68}$Co$_{0.32}$PS$_3$ NS, and bulk single crystal samples are well fitted with the standard monoclinic NiPS$_3$ and Ni$_5$Co$_3$P$_8$S$_{24}$ structures (optimized by theoretical calculations; see Materials and Methods for details) and show identical characteristic features (fig. S9, A to B). The main peak at approximately 2.01 Å in the $k^3$-weighted Fourier transform curves at $R$ space is attributed to the scattering interaction between the Ni atoms and the first ligand shell (Ni-S), where each Ni atom is coordinated with six

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**Fig. 2. Structural characterization by XAS and ESR spectroscopy of various Ni$_{1-x}$Co$_x$PS$_3$ samples.** (A and B) Ni K-edge and Co K-edge XANES spectra of Ni$_{0.68}$Co$_{0.32}$PS$_3$ NS and single crystals together with NiO, Ni foil, and Co foil, pyrite-type CoS$_2$, and Co$_3$O$_4$, where pre-edge peak represents $1s \rightarrow 3d$ ($e_g^*$) transition. (C) First shell fitting (Ni-S) of Fourier transform of EXAFS spectra for NiPS$_3$, Ni$_{0.68}$Co$_{0.32}$PS$_3$ NS, and single crystals along with their corresponding reference samples. The XANES profiles of these Ni$_{1-x}$Co$_x$PS$_3$ NS and single crystals reveal a nearly identical Ni valence state of +2, strongly suggesting the same coordination environment around Ni atoms in the crystal and the absence of any Ni-based impurities (such as Ni metal clusters). The relatively small prepeaks at $\sim 8331.0$ eV further suggest octahedral coordination (37) of Ni with S ligands along with the $1s \rightarrow e_g^*$ (the lowest unoccupied molecular orbital) transition. Similarly, the Co K-edge XANES spectra (Fig. 2B and fig. S8B) show a weak pre-edge peak $\sim 7709.0$ eV, revealing the same Co oxidation state of +2 and octahedral coordination around Co atoms in Ni$_{0.68}$Co$_{0.32}$PS$_3$ NS and single crystals. The Co K-edge XANES profiles are substantially different from the reference Co-based compounds such as CoS$_2$, Co$_3$O$_4$, and Co foil, which further confirms the chemical purity of as-synthesized Ni$_{0.68}$Co$_{0.32}$PS$_3$ NS and single crystals.

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S atoms shown in the inset of Fig. 2C. The peak at ~3.1 Å is attributed to the scattering path of Ni-Ni or Ni-Co. After Co substitution, a slightly enlarged radial distance is observed for both Ni_{0.68}Co_{0.32}PS_{3} NS and single crystal, indicating the slight change in intralayer radial distance of Ni_{0.68}Co_{0.32}PS_{3}. The detailed fitting results of first shell (Ni-S) EXAFS data collected on these samples are summarized in table S1. The coordination numbers (CNs) of the S atom in the first coordination sphere of Ni are estimated to be 5.8 and 5.9 in NiPS_{3} NS and Ni_{0.68}Co_{0.32}PS_{3} single crystals, respectively. In contrast, a much lower CN of 5.2 is found for Ni_{0.68}Co_{0.32}PS_{3} NS. This substantial difference from the expected CN of 6 in Ni_{0.68}Co_{0.32}PS_{3} NS suggests the presence of sulfur vacancy defects (**S_v**). Furthermore, the calculated formation energy (**E_f**) of single-crystal counterparts (Fig. 2D) confirm the presence of S_v in the NS. The peak at ~3.1 Å is attributed to the scattering path of Ni-Ni or Ni-Co. After Co substitution, a slightly enlarged radial distance is observed for both Ni_{0.68}Co_{0.32}PS_{3} NS and single crystal, indicating the slight change in intralayer radial distance of Ni_{0.68}Co_{0.32}PS_{3}. The detailed fitting results of first shell (Ni-S) EXAFS data collected on these samples are summarized in table S1. The coordination numbers (CNs) of the S atom in the first coordination sphere of Ni are estimated to be 5.8 and 5.9 in NiPS_{3} NS and Ni_{0.68}Co_{0.32}PS_{3} single crystals, respectively. In contrast, a much lower CN of 5.2 is found for Ni_{0.68}Co_{0.32}PS_{3} NS. This substantial difference from the expected CN of 6 in Ni_{0.68}Co_{0.32}PS_{3} NS suggests the presence of sulfur vacancy defects (**S_v**). Furthermore, the very different ESR spectra of S^2 in x-ray photoelectron spectra (fig. S11, A to B), which also shows that, after Co substitution, it is more energetically favorable to incorporate **S_v** because **E_f** is much lower in the case of Ni_{5}Co_{5}P_{5}S_{5} (1.38 eV) than NiPS_{3} (2.19 eV).

**Defect-mediated FM state in Ni_{1−x}Co_{x}PS_{3} NS**

To study the magnetic properties of as-synthesized Ni_{1−x}Co_{x}PS_{3} NS and single crystals, we performed temperature-dependent zero field cooling (ZFC) and field cooling (FC) magnetization measurements using a superconducting quantum interference device (SQUID) magnetometer. The results after subtracting the small diamagnetic background signal from the carbon cloth for these samples are shown in Fig. 3A (selected samples for the sake of clarity) and fig. S12 (full datasets). The ZFC curves reveal a typical AFM behavior for these Ni_{1−x}Co_{x}PS_{3} samples with a broad peak ~155 K, which corresponds to the **T_N** (22, 26). As the x value increases in Ni_{1−x}Co_{x}PS_{3}, the peak shifts to a lower temperature value of **T_N** for both Ni_{1−x}Co_{x}PS_{3} NS and single crystals (inset of Fig. 3A and fig. S13). This is more or less expected with the uniform alloying of Co, because the isostructural and AFM CoPS_{3} has a lower **T_N** ~ 120 K (25). However, a marked increase in the magnetic moment at the low temperatures (<110 K) is observed in ZFC and FC curves of the Ni_{1−x}Co_{x}PS_{3} NS (Fig. 3A for Ni_{0.68}Co_{0.32}PS_{3} and Ni_{0.60}Co_{0.40}PS_{3} NS, see all NS samples in figs. S12, B to C, and S13). A slight increase in magnetization of NiPS_{3} NS at low temperatures (<25 K) is also shown in Fig. 3A. In contrast, no such features could be observed in Ni_{1−x}Co_{x}PS_{3} single-crystal samples even when compared at a similar composition (x ~ 0.32). In principle, the chemical alloying of two isostructural compounds (NiPS_{3} and CoPS_{3}) with the same ground-state AFM ordering and minimal difference in lattice parameters should not alter the magnetic arrangements. Here, in these Ni_{1−x}Co_{x}PS_{3} NS, the AFM ordering is suppressed at the low temperatures, resulting in the emergence of uncompensated magnetic moments below the transition temperature (**T_N**) ~ 25, 61, 87, and 110 K in NiPS_{3}, Ni_{0.68}Co_{0.32}PS_{3}, Ni_{0.60}Co_{0.40}PS_{3}, and Ni_{0.60}Co_{0.40}PS_{3} NS, respectively. After considering the structural differences between the NS and single crystals of Ni_{0.68}Co_{0.32}PS_{3}, we hypothesize that the

![Fig. 3. Characterization of magnetic properties of selected NS and single crystals of Ni_{1−x}Co_{x}PS_{3}.](image)

(A) Temperature dependence of the ZFC magnetization measured at **H** = 200 Oe on various Ni_{1−x}Co_{x}PS_{3} NS (x = 0, 0.32, and 0.40) and the Ni_{0.60}Co_{0.40}PS_{3} single crystal. (B) **M-H** curves measured at 5 K of various Ni_{1−x}Co_{x}PS_{3} NS (x = 0, 0.12, 0.32, and 0.40) in comparison with that of the Ni_{0.68}Co_{0.32}PS_{3} single crystal. (C) **M-H** curves of the Ni_{0.60}Co_{0.40}PS_{3} NS at different temperatures. Magnetic hysteresis is clearly observed at low temperatures below 100 K.
presence of \( S_x \) in the \( \text{Ni}_{0.68}\text{Co}_{0.32}\text{PS}_3 \) NS may be responsible for the suppression of long-range AFM correlations, while other competing FM exchange interactions dominate at low temperatures, creating a magnetically frustrated system. The exchange interactions between the \( S_x \) and metal ions and the local atomic distortion in the vicinity of defects could also induce robust ferromagnetism, as shown in nonmagnetic 2D materials like graphene and molybdenum disulfide (32, 33, 35).

Moreover, the field-dependent magnetization (\( M-H \)) curves of various \( \text{Ni}_{1-x}\text{Co}_x\text{PS}_3 \) NS (\( x = 0.12, 0.32, \) and 0.40) at 5 K reveal a hysteretic feature over a low applied magnetic field range (\( |H| < 300 \text{ Oe} \)), and the feature is enhanced as \( x \) increases (Fig. 3B). However, there is no hysteretic feature for the \( \text{Ni}_{0.68}\text{Co}_{0.32}\text{PS}_3 \) single crystal in contrast to the NS with the same composition (\( x = 0.32 \)). The \( M-H \) curves of various \( \text{Ni}_{1-x}\text{Co}_x\text{PS}_3 \) NS collected at different temperatures (Fig. 3C, specifically for the \( \text{Ni}_{0.68}\text{Co}_{0.40}\text{PS}_3 \) NS, and all samples are shown in Fig. S14) clearly show the well-defined hysteretic feature below their respective \( T^{	ext{N}} \), further confirming the existence of a weak FM ground state arising from uncompensated magnetic moments in an AFM system. Unlike the case for other magnetic 2D materials (5, 42), the reduced dimensionality is unlikely to govern the ferromagnetism shown in \( \text{Ni}_{1-x}\text{Co}_x\text{PS}_3 \) NS. The average thickness of as-synthesized \( \text{Ni}_{1-x}\text{Co}_x\text{PS}_3 \) NS is 8 nm (around 10 layers), and the persistence of the AFM ordering is experimentally reported in both \( \text{CoPS}_3 \) (43) and \( \text{NiPS}_3 \) (26) down to pristine monolayer and bilayer samples, respectively. Furthermore, this soft magnetic behavior (Fig. S15) is not related to the presence of magnetic imperfections such as the formation of Ni/Co clusters during synthesis, as the measured saturation magnetization of the \( \text{Ni}_{0.60}\text{Co}_{0.40}\text{PS}_3 \) NS \( N[0.0364 \text{ Bohr magneton (} \mu_B \text{) per formula unit}] \) is around three orders of magnitude smaller than expected for Ni/Co metals in a metal cluster (-1 to 2 \( \mu_B \) per formula unit). The Co alloying in \( \text{NiPS}_3 \) not only induces the slight shifts in \( T_N \) but also promotes the incorporation of \( S_x \) during the synthetic process for \( \text{Ni}_{1-x}\text{Co}_x\text{PS}_3 \) NS. The contrasting magnetic behaviors observed in \( \text{Ni}_{1-x}\text{Co}_x\text{PS}_3 \) NS synthesized via chemical conversion and single crystals grown by CVT, even if they have the same chemical compositions (for example, the \( \text{Ni}_{0.60}\text{Co}_{0.32}\text{PS}_3 \) highlighted in Fig. 3, A and B), show that the structural difference caused by \( S_x \) between these two types of samples is crucial for the weak ferromagnetism observed in the \( \text{Ni}_{1-x}\text{Co}_x\text{PS}_3 \) NS. The weak FM ground state in \( \text{Ni}_{1-x}\text{Co}_x\text{PS}_3 \) NS emerges at much lower applied magnetic field \( (< 300 \text{ Oe}) \) in comparison to the high-field spin-flop transitions \( (> \text{several thousand oersted}) \) in typical 2D vdW antiferromagnets (9, 13). This suggests that the defect-mediated magnetic ordering in 2D vdW antiferromagnets, such as \( \text{Ni}_{1-x}\text{Co}_x\text{PS}_3 \), could reduce the applied field requirement for causing the magnetic state transitions in the AFM materials used in spintronic applications.

**Governing mechanism for the defect-mediated magnetism in \( \text{Ni}_{1-x}\text{Co}_x\text{PS}_3 \) NS**

To understand the underlying mechanism responsible for \( S_x \) defect-mediated ferromagnetism in \( \text{Ni}_{1-x}\text{Co}_x\text{PS}_3 \) (\( 0 \leq x < 0.5 \)), it is important to explore the competing electronic and magnetic correlations that could be affected by the presence of \( S_x \). In correlated \( \text{NiPS}_3 \), the half-filled Ni \( e_g \) orbitals couple with half-filled S 3p orbitals, which mediates the effective electron hopping between neighboring Ni sites (15, 22, 27). This mechanism is known as the superexchange interaction, which is governed by the Goodenough-Kanamori-Anderson rules (44), where the atomic arrangement is the key to effective Ni-S orbital overlapping, which dictates the strength of the exchange interaction. The first nearest Ni neighbors in \( \text{NiPS}_3 \) octahedra with corner sharing S atoms attain \( \sim 90^\circ \) Ni-S \( \text{[Ni(1)\(-\text{S(1)}\(-\text{S(3)}\(-\text{Ni(3)})\] orbital overlapping results in a weak FM coupling \( (J_1) \), while the second nearest Ni neighbors result in weaker FM exchange interaction \( (J_2) \) mediated by two S atoms \( \text{[Ni(1)\(-\text{S(1)}\(-\text{S(3)}\(-\text{Ni(3)})\] located on different atomic planes and separated by a long distance of \( \sim 0.4 \text{ nm} \) (Fig. 4, A and B) (27). The magnetic ordering in \( \text{NiPS}_3 \) constitutes of FM chains coupled strongly with AFM interaction, forming a zigzag pattern with alternating chains of anti-aligned Ni atoms (Fig. 4C) as a consequence of strong third-nearest neighbors (TNN) exchange interaction \( (J_3 > J_1, J_2) \) mediated by two S atom located on the same chalcogen sublayer \( \text{[Ni(1)\(-\text{S(1)}\(-\text{S(2)}\(-\text{Ni(4)})\] \) (Fig. 4B). This suggests that the presence of \( S_x \) could change the lattice configurations locally and disrupt the long-range effective hopping between two antiferromagnetically aligned TNN, inducing spin fluctuations in the system.

After identifying the influence of \( S_x \) on the magnetic ordering in \( \text{NiPS}_3 \), we investigate the possible effect on the spin-charge density and magnetic structures in the vicinity of \( S_x \) using density functional theoretical (DFT) calculations (see Materials and Methods for details) on the \( \text{NiPS}_3 \) model system just to simplify the calculation process. In a charge transfer insulator such as \( \text{NiPS}_3 \), the magnetic and electronic properties of the system are dependent on the ease of electron transfer between the anion and cation (22). In this regard, \( \text{NiPS}_3 \) acquires a "ligand hole-doped" correlated state where the S ligand transfers one electron to the half-filled \( e_g \) Ni 3d orbital and forms a \( d^L \) ground state \( (L \text{ represents ligand hole}) \) owing to the low charge transfer energy (15, 22). The calculated electronic structure of monolayer \( \text{NiPS}_3 \) also supports this representation of insulating NCT ground state where the projected density of states (PDOS) of occupied \( p \) orbital bands is located closer to the Fermi energy \( (E_F) \) than the Ni 3d orbital bands (Fig. 4D). The corresponding spin-charge density spectrum of zigzag AFM \( \text{NiPS}_3 \) with easy in-plane anisotropy shows a reduced magnetic moment \( (1.462 \mu_B) \) of individual Ni\(^{2+}\) cation (expected value \(-2.83 \mu_B\)) due to possible mixed valance state configurations \( (d^8, d^10L^2) \) of the NCT state (Fig. 4E). This NCT state in \( \text{NiPS}_3 \) is expected to dominate between antiferromagnetically aligned neighboring Ni atoms, which is also demonstrated in previous studies via optical conductivity measurements (22). A single \( S_x \) created in the \( \text{NiPS}_3 \) supercell within the chalcogen sublayer disrupts the superexchange interaction between Ni neighbors, and the energetically relaxed structure shows marked changes in the characteristically electronic and magnetic properties. The presence of a single \( S_x \) shifts the occupied S bands away from the \( E_F \), reducing the NCT character (Fig. 4F). Furthermore, we observe the emergence of unoccupied in-gap-like states in the electronic structure, which might arise from a local five-coordinated environment around Ni atoms. These in-gap states could serve as a carrier trap sites (45–47) and hinder the charge transfer process, which could further affect the magnetic properties of \( \text{NiPS}_3 \). The charge density distribution of Ni orbitals is more affected in the vicinity of the \( S_x \) site, and the equilibrium spin configuration transforms to uncompensated magnetic state with a net magnetic moment of \(-0.17 \mu_B\) per formula unit (Fig. 4G), highlighting the magnetic instability of the AFM arrangement in \( \text{NiPS}_3 \) (48). We anticipate that the incorporation of \( S_x \) also increases the concentration of n-type carriers in the self-hole doped \( \text{NiPS}_3 \), which was predicted to suppress the long-range AFM correlation and might enable other competing magnetic phases and correlated states to
emerge including topological superconductivity (27, 49). It may be possible that, in the strongly correlated environment of NiPS₃, the charge carriers introduced by Sᵥ or Co alloying can be delocalized rather than remain in a magnetic bound state (32, 50, 51) and result in the formation of mobile magnetic polarons, which could disturb the AFM spin lattice and lead to unexpected emergent properties (52, 53). This further opens the prospect for electrostatic doping control of magnetism in few layers or even a monolayer of NiPS₃ and encourages future studies into the rich magneto-optical physics of NiPS₃ in the presence of point defects, as these properties couple strongly with intrinsic magnetic ordering of the crystal (9, 15, 17, 54).

DISCUSSION

We demonstrate the effective tuning of magnetic exchange interactions and magnetic ordering in chemically converted NS of vdW magnets Ni₁₋ₓCoₓPS₃ (0 ≤ x < 0.5) due to sulfur vacancy defects. X-ray spectroscopy and ESR spectroscopy confirm the presence of sulfur vacancy defects in Ni₁₋ₓCoₓPS₃ NS in contrast to single crystals of the same Ni₁₋ₓCoₓPS₃ compositions. Magnetic characterization of S-deficient Ni₁₋ₓCoₓPS₃ NS clearly shows a weak FM ground state at low temperatures (<100 K). Theoretical calculations show that the presence of Sᵥ disrupts the anion-mediated superexchange interaction, i.e., two antiferromagnetically aligned TNNs, resulting in effective suppression of the long-range AFM correlation in the NiPS₃ system. Defect-mediated ferromagnetism emerges at an applied magnetic field (<300 Oe) that is much smaller than the high-field spin-flop transition in MPX₃. This result suggests that defect engineering could reduce the high applied field requirement to tune the magnetic order and make 2D vdW antiferromagnets more attractive for spintronic applications. It is evident from the structural characterization that herein both Co alloying and the growth kinetics of the vapor conversion synthesis process are necessary to promote the formation of Sᵥ in NiPS₃ NS. However, it is difficult to tune the concentration of Sᵥ while fixing the Co alloying through the vapor conversion method used here. This work encourages future studies to develop a method that allows independent tuning of defect concentration in NiPS₃ and other correlated 2D magnets. Defect-tunable magnetism has not been studied in the broad class of 2D magnetic vdW materials and warrants further studies in the future. These findings shed new insights into the magnetic instability in correlated vdW magnetic systems, which could provide new and effective routes to control and manipulate the magnetic spin states of 2D vdW magnets by defect engineering.

MATERIALS AND METHODS

Synthesis of Ni₁₋ₓCoₓPS₃ (0 ≤ x < 0.5) NS

The Ni₁₋ₓCoₓPS₃ NS were synthesized in two steps. (i) The metal hydroxide precursor NS containing different Ni:Co ratios were first synthesized on carbon cloth through a wet chemical method (section S1 in the Supplementary Materials) and then (ii) converted in a vapor phase process to make Ni₁₋ₓCoₓPS₃ (0 ≤ x < 0.5) NS. A mixed powder (1 g) of phosphorus (red phosphorus, 98.5%; Alfa Aesar) and sulfur (99.5%; Alfa Aesar) with a molar ratio of 2:5 was placed into the bottom of a custom-designed fused silica socket tube, and the corresponding metal hydroxide precursors were positioned on
the other side of the fused silica tube (19). Then, the fused silica tube was placed inside a two-zone tube furnace with P and S powder in the upstream (front zone) and the hydroxide precursor in the downstream (back zone) and evacuated. The two zones were simultaneously heated to 270°C (upstream, 9°C/min) and 480°C to 490°C (downstream, 16°C/min) over 30 min under a flow of 100 sccm (standard cubic centimeters per minute) argon gas (99.999%). The ultrathin Ni$_{1-x}$Co$_x$PS$_3$ NS evenly covering the surface of the carbon cloth were synthesized over a reaction time of 90 min at 480°C to 490°C. The mass loading of the NS was ~1 to 3 mg/cm$^2$.

**Magnetic measurements**

Temperature-dependent DC magnetometry measurements of the various Ni$_{1-x}$Co$_x$PS$_3$ (0 ≤ x < 0.5) NS on carbon cloth and single crystals were carried out on a SQUID magnetometer (Quantum Design MPMS3) with the ZFC and FC modes with a slow cooling rate of 2 K/min. The carbon cloth with NS was cut into pieces and sealed in a gel capsule, which was fixed in a plastic straw for measurement. As a comparison, pure carbon cloth with the same mass was also measured under the same condition. Field-dependent magnetization measurements of these samples were performed with an applied magnetic field range of −700 to 700 Oe at the field sweep rate of 14 Oe/s. The hysteresis features shown in M-H curves for Ni$_{1-x}$Co$_x$PS$_3$ NS are apparent even without subtracting the paramagnetic component of the corresponding magnetization. The magnetization data were collected and compared at different temperatures (5 to 300 K). Magnetization measurements of individual Ni$_{1-x}$Co$_x$PS$_3$ (0 < x < 0.5) single crystals with a size of ~0.1 to 0.2 cm were conducted with the applied magnetic field parallel to the easy plane (ab plane) of magnetization for the crystal.

**Theoretical calculations**

Collinear spin-polarized electronic structure calculations were performed using the periodic density function code Vienna Ab Initio Simulation Package (65–59) and interfaced with the Python Environment Atomic Simulation Environment (60). Projector augmented wave pseudopotentials with a cutoff of 500 eV (61) were used to treat core electrons. Geometry optimizations were carried out using the Perdew-Burke-Ernzerhof (PBE) functional (62, 63) to treat correlation and exchange. Single-point calculations were then evaluated using the range-separated HSE06 functional and the PBE geometries (64, 65). The use of HSE06 allows for the accurate description of insulator bandgaps compared to PBE, which systematically underestimates bandgaps. Dispersion was treated using the Tkatchenko-Scheffler method (DFT-TS/HI) with iterative Hirschfeld partitioning (66). A (2 × 2) rhombic cell was adopted for Ni$_x$P$_8$S$_{24}$ and Ni$_x$Co$_x$P$_8$S$_{24}$ slab with the vacuum spacing set at least 15 Å. The Brillouin zone was sampled with an 8 × 8 × 1 Monkhorst pack gamma-centered mesh (67). For geometry optimization, atoms were allowed to relax until forces on them were less than 0.005 eV/Å. The Co-substituted cases in the supercell were further screened and confirmed. In general, there are eight Ni sites that can be replaced by three Co atoms, which provides C$_8^3$ = 56 substitution cases. Under the constraint of periodic boundary conditions, we screened out three different substitution cases shown in fig. S16. We named them chain substitution case (CS), triangle substitution case (TS), and right angle substitution case. After comparing the total energy of the different substitution cases (table S2), the CS is the stable doping case of Ni$_{1-x}$Co$_x$PS$_3$ (0 ≤ x < 0.5) in ground state. Thus, the lowest energy chain (CS) Ni$_{15}$Co$_9$P$_8$S$_{24}$ was used for all doped calculations. For sulfur vacancies, calculations were performed on all possible sulfur vacancies (along with all three initial spin states), and the lowest energy sulfur vacancy systems (geometry and final spin state) are the ones reported. We calculate the vacancy formation energy ($E_v$) according to Eq. 1

$$E_v = E_A + n\mu_s - E_p$$

where $E_p$ and $E_A$ are the energy of the supercell with and without vacancies, respectively. $\mu_s$ and $n$ represent the chemical potential.
and number of sulfur atoms removed from the surface. The chemical potential of sulfur is calculated from its elemental phase $S_8$ (68).

**SUPPLEMENTARY MATERIALS**

Supplementary material for this article is available at https://science.org/doi/10.1126/sciadv.abj4086

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