Matthew Cheng,<sup> $\perp$ </sup> Yea-Shine Lee,<sup> $\perp$ </sup> Abishek K. Iyer, Daniel G. Chica, Eric K. Qian, Muhammad Arslan Shehzad, Roberto dos Reis, Mercouri G. Kanatzidis, and Vinayak P. Dravid\*

**Read Online** Cite This: Inorg. Chem. 2021, 60, 17268-17275 ACCESS Article Recommendations Metrics & More s Supporting Information Co<sub>(pure)</sub>, Co<sub>1</sub>Fe<sub>1</sub> Fe Ρ .Fe<sub>(pure)</sub> **ABSTRACT:** Metal chalcophosphates,  $M_2P_2Q_6$  (M = transition metals; Q = Co S Fe<sub>0.25</sub>Co<sub>1.75</sub> & Fe<sub>1.75</sub>Co<sub>0.25</sub> chalcogen), are notable among the van der Waals materials family for their

potential magnetic ordering that can be tuned with an appropriate choice of the metal or chalcogen. However, there has not been a systematic investigation of the basic structural evolution in these systems with alloying of the crystal subunits due to the challenge in the diffusion process of mixing different metal cations in the octahedral sites of  $M_2P_2Q_6$  materials. In this work, the  $P_2S_5$  flux method was used to enable the synthesis of a multilayered mixed metal thiophosphate  $Fe_{2-x}Co_xP_2S_6$  (x = 0, 0.25, 1, 1.75, and 2) system. Here, we studied the structural, vibrational, and electronic fingerprints of this mixed  $M_2P_2Q_6$  system. Structural and elemental analyses indicate a

endations Supporting information Co Fe P S Co<sub>(pure)</sub>, Fe<sub>(pure)</sub>, Fe<sub>(25</sub>Co<sub>1.75</sub> & Fe<sub>1.75</sub>Co<sub>2.55</sub>  $e_{vac}$   $e_{vac}$ 

homogeneous stoichiometry averaged through the sample over multiple layers of  $Fe_{2-x}Co_xP_2S_6$  compounds. It was observed that there is a correlation between the intensity of specific phonon modes and the alloying concentration. The increasing Co alloying concentration shows direct relations to the in-plane  $[P_2S_6]^{4-}$  and out-of-plane P–P dimer vibrations. Interestingly, an unusual nonlinear electronic structure dependence on the metal alloying ratio is found and confirmed by two distinct work functions within the  $Fe_{2-x}Co_xP_2S_6$  system. We believe this work provides a fundamental structural framework for mixed metal thiophosphate systems, which may assist in future studies on electronic and magnetic applications of this emerging class of binary cation materials.

# 1. INTRODUCTION

Metal chalcophosphates  $(M_2P_2Q_6)$  (M = transition metals; Q = chalcogen), which were overlooked for some time, have recently gained attention as an emerging set of twodimensional (2D) van der Waals (vdW) layered binary cation systems due to their tunable structure and properties, especially magnetism. These  $M_2P_2Q_6$  are hexagonal 2D layered systems composed of "ethane-like"  $[P_2Q_6]^{4-}$  units, where each P is tetrahedrally bonded to three S and one P atom with a honeycomb extended structure. Each metal cation fills 2/3 of the octahedral sites, while the remaining 1/3 is filled by the P– P dimers. The P–P dimer bond distance is dependent on the metal cations, which can lead to the stretching or shrinking of the entire crystal structure.<sup>1-7</sup> The structure and properties of each  $M_2P_2Q_6$  system can be tailored by customizing metal cations and chalcogen anions.<sup>8-16</sup>  $M_2P_2Q_6$  have been studied for their application as battery electrodes, catalysts for HER or OER, and ferroic materials.<sup>1,17–2</sup>

In particular, Fe<sub>2</sub>P<sub>2</sub>S<sub>6</sub> and Co<sub>2</sub>P<sub>2</sub>S<sub>6</sub> show unique magnetic properties. Magnetic ordering in Fe<sub>2</sub>P<sub>2</sub>S<sub>6</sub> has been reported in several studies, and transformations at the Néel temperature  $(T_N)$  have been reported.<sup>1,22,23</sup> As the temperature drops below  $T_N = 120$  K, the antiferromagnetic (AFM) phase arises with magnetic moments, forming a 2D Ising-type AFM.<sup>22</sup> The moment of each Fe<sup>2+</sup> ion forms ferromagnetic chains along the *a*-axis, AFM relative to adjacent chains.<sup>1,22</sup> Co<sub>2</sub>P<sub>2</sub>S<sub>6</sub>, however, has been reported to have a different type of AFM ordering. In Co<sub>2</sub>P<sub>2</sub>S<sub>6</sub>, although each ferromagnetic chain in-plane is coupled antiferromagnetically to adjacent chains in-plane, each magnetic moment of the Co<sup>2+</sup> ions points in-plane.<sup>1</sup> In both cases (Fe<sub>2</sub>P<sub>2</sub>S<sub>6</sub> and Co<sub>2</sub>P<sub>2</sub>S<sub>6</sub>), the magnetic susceptibility along the magnetization axis drops sharply below  $T_N$  but is stable along the other axes.<sup>23</sup> It has also been shown that the transition from the paramagnetic to AFM phase is accompanied by a structural distortion.<sup>22</sup>

Alloying different metal cations within the metal thiophosphates leads to altered magnetic properties.<sup>1</sup> The magnetic ordering temperature,  $T_N$ , of the alloyed system depends on the degree of substitution, as reported in  $Mn_xZn_{2-x}P_2S_6$ .<sup>24</sup> The alloying process also gives rise to disordered glassy states due to the magnetic frustration between the magnetic moments of different nearest neighbor cations as in FeMnP<sub>2</sub>S<sub>6</sub> and FeNiP<sub>2</sub>S<sub>6</sub>.<sup>11,25</sup> A glassy state consists of clusters of randomly

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**Figure 1.** (a) Crystal structure of  $Fe_2P_2S_6$  (or  $Co_2P_2S_6$ ) along the *a*-axis (in-plane direction) and the *c*\*-axis, which is nearly parallel to the [103]zone axis. (b) Elemental composition of Fe–Co thiophosphates based on SEM and STEM–EDS techniques. (c) Zoom-in display of the (002) Bragg reflection showing a shift toward higher  $2\theta$  values with increasing cobalt concentration. (d) Zoom-in display of the (060) Bragg reflection showing a shift toward higher  $2\theta$  values with increasing cobalt concentration. (e) fwhm values of (002) and (060) Bragg reflections.

oriented magnetic moments that are frozen over experimental time scales. Thus, an alloyed system between  $Fe_2P_2S_6$  and  $Co_2P_2S_6$  has potential to exhibit novel magnetic properties.

There are numerous challenges in the synthesis of these mixed metal chalcophosphates. One primary challenge has been the long reaction times (up to 3 months) in obtaining a pure and stable phase product.<sup>15,26,27</sup> The flux method is critical for stabilizing Co-containing chalcophosphates such as FeCoP<sub>2</sub>S<sub>6</sub>, and we have recently reported the synthesis of these thiophosphates by using a P<sub>2</sub>S<sub>5</sub> flux, where Ni<sub>2</sub>P<sub>2</sub>S<sub>6</sub> and two new bimetallic thiophosphates, MnCoP<sub>2</sub>S<sub>6</sub>, and FeCoP<sub>2</sub>S<sub>6</sub>, could be synthesized in much shorter timeframes.<sup>28</sup> However, the mixed metal cation series, Fe<sub>2-x</sub>Co<sub>x</sub>P<sub>2</sub>S<sub>6</sub>, have not yet been investigated. Therefore, it is vital to gain an insight into the structural, vibrational, and electronic properties of these Fe<sub>2-x</sub>Co<sub>x</sub>P<sub>2</sub>S<sub>6</sub> systems in order to probe and potentially tailor the structure–property relationship of such mixed cation thiophosphates in a meaningful manner.

Here, we report on the systematic synthesis of a series of  $Fe_{2-x}Co_xP_2S_6$  using the rapid reactive flux technique.<sup>28</sup> We conduct a thorough investigation of the structural and

electronic changes and establish "fingerprints" for specific metal cation stoichiometries. We find that in-plane and out-ofplane vibrations of the  $[P_2S_6]^{4-}$  and P–P units are specific, having direct correlations in the Co alloy concentration with in-plane  $[P_2S_6]^{4-}$  and out-of-plane P–P vibrations, and vice versa. Moreover, an unexpected nonlinear behavior of Fe and Co 2p states is explained by two distinct work functions within the Fe<sub>2-x</sub>Co<sub>x</sub>P<sub>2</sub>S<sub>6</sub> series, dependent on the alloying ratio.

### 2. EXPERIMENTAL METHODS

**2.1. Synthesis.** 2.1.1. Chemical Reagents. The following reagents were used as they were received: iron powder (99.9%, CERAC), cobalt powder (99.8%, CERAC), phosphorus pentasulfide powder (99%, Sigma-Aldrich), phosphorus chunks (99.999%, Puratronic), and sulfur pieces (99.98%, Aldrich). The solvents used were house-deionized (DI) water, anhydrous ethanol (Fisher Chemical), and acetone (Fisher Chemical, 99.5%).

2.1.2. Synthesis of  $Fe_2P_2S_{6r}$  Co<sub>2</sub> $P_2S_{6r}$  and  $Fe_{2-x}Co_xP_2S_6$  (x = 0.25, 1, and 1.75). The compounds were synthesized using the reactive  $P_2S_5$  flux method, which is described in the paper reported by Chica et al.<sup>28</sup> The M (M/M') to  $P_2S_5$  ratio was 2:3 and 1:1:3 for the monometallic and bimetallic thiophosphates, respectively. In a nitrogen-filled glovebox, metal and  $P_2S_5$  powders were loaded into



**Figure 2.** (a-e) TEM images for each  $Fe_{2-x}Co_xP_2S_6$  system. Scale bar is 1  $\mu$ m. (f-j) Associated SAED pattern. Scale bar is 5 nm<sup>-1</sup>. (k) Schematic of a 120° twin boundary. (l) Simulated diffraction pattern along the [103]-zone axis with corresponding twin boundaries of 120° in blue and 240° in red. (m) Simulated diffraction patterns for  $Fe_2P_2S_6$  in black and  $Co_2P_2S_6$  in violet.

12.7 mm OD and 10.5 mm ID fused silica tubes with a total charge mass of 2 g. The amounts used are tabulated in Table S1. The tubes were sealed with an oxy/natural gas torch under a pressure of  $\sim$ 3 ×  $10^{-3}$  mbar. After sealing, the tubes were mechanically agitated for 10 min to ensure mixing of the reagents. The tubes were heated using a computer-controlled tube furnace with the heating profiles shown in Table S2. The synthesis of  $Co_2P_2S_6$  was performed at 580 °C to avoid the Co(PS) impurity at higher temperatures. Details of this can be found in the paper reported by Chica et al. The Le Bail fit was performed for quantitative PXRD analysis to confirm the phase purity (Figure S9). Warning: The removal of the flux must be performed in a fume hood as this reaction releases H<sub>2</sub>S gas. In a fume hood, the silica ampule was opened, and the ingot was placed in a 20 mL scintillation vial with 10 mL of a 50/50 vol/vol mixture of DI water and ethanol (50/50  $\rm H_2O/EtOH)$  and heated to  ${\sim}70~^{\circ}\rm C$  for 1 h. If any flux remained, the solution was decanted and 10 mL of  $50/50 \text{ H}_2\text{O}/$ EtOH was added and heated for 1 h. After the removal of the flux, the product was washed twice with DI water and twice with acetone. The residual thiols were left to off-gas overnight.

**2.2. Raman Spectroscopy.** Samples were crushed in a mortar and pestle and then bath-sonicated in ethanol for 3 min. Next, the samples were dropcast on silicon wafers with 300 nm of SiO<sub>2</sub> thermal oxide. The Raman spectra were obtained with a Horiba LabRam confocal Raman spectrometer equipped with a HJY detector and a laser of wavelength of 532 nm at room temperature. The grating used was 600 g/mm with a 1% ND filter.

**2.3.** X-ray Photoelectron Spectroscopy and Ultraviolet Photoelectron Spectroscopy. The samples were crushed in a mortar and pestle and then bath-sonicated in ethanol for 3 min. Then, the samples were dropcast on silicon wafers with 300 nm of SiO<sub>2</sub> thermal oxide. The Thermo Scientific ESCALAB 250Xi X-ray photoelectron spectrometer was used to obtain the X-ray photoelectron spectra at room temperature using a 500  $\mu$ m spot size and a monochromatic Al K $\alpha$  source, and the spectra were calibrated relative to the carbon peak at 284.8 eV. The background subtraction was done using the Shirley method. The same Thermo Scientific ESCALAB 250Xi spectrometer was used for ultraviolet photoelectron spectroscopy (UPS) studies. A leak valve enabled control of the pressure in the chamber with He gas up to 10<sup>-7</sup> Torr pressure from a base pressure of 10<sup>-8</sup> Torr.

**2.4.** Scanning/Transmission Electron Microscopy. Transmission electron microscopy (TEM) samples were prepared by liquid exfoliation of thiophosphates in ethanol and dropcast onto lacey carbon-coated molybdenum grids. High-resolution TEM (HRTEM) and selected area electron diffraction (SAED) patterns were obtained using a JEOL ARM300 microscope at 300 kV along the out-of-plane direction, *c\**, which is parallel to the [103]-zone axis. SAED patterns were simulated using *SingleCrystal*.<sup>29</sup> Scanning TEM (STEM)—energy dispersive X-ray spectroscopy (EDS) was conducted with an Oxford silicon drift detector to analyze the stoichiometry and homogeneity of each thiophosphate sample. The convergence angle of the probe was 24 mrad, which at an acceleration voltage of 300 keV corresponded to a probe size of 1.1 Å full width at half-maximum (fwhm). The collection angle of the Oxford detector was 0.98 sr.

# 3. RESULTS AND DISCUSSION

Compared to typical transition-metal dichalcogenides, the interlayer spacing between the sulfur layers in metal thiophosphates is larger, close to 3.22-3.24 Å.<sup>1</sup> Both iron and cobalt thiophosphates crystallize in the monoclinic space group C2/m, which has an AAA stacking sequence. The perfect monoclinic crystal unit cell has a  $\beta$  angle of 107.16°, which is satisfied by Co<sub>2</sub>P<sub>2</sub>S<sub>6</sub> and Fe<sub>2</sub>P<sub>2</sub>S<sub>6</sub>, suggesting that these compounds are perfect monoclinic cells. Figure 1a shows a schematic of iron thiophosphate or cobalt thiophosphate.<sup>30</sup> The structure is made up of  $[P_2Q_6]^{4-}$  units with Fe<sup>2+</sup> and Co<sup>2+</sup> cations occupying 2/3 of the octahedral sites. Though the crystal structures of both Fe<sub>2</sub>P<sub>2</sub>S<sub>6</sub> and Co<sub>2</sub>P<sub>2</sub>S<sub>6</sub> are similar, as previously reported, the lattice parameters are different when the cations are incorporated in the material system.<sup>31,32</sup> The experimentally measured lattice parameters, in Å, for  $Fe_2P_2S_6$  $(Co_2P_2S_6)$  are a = 5.95 (5.90), b = 10.30 (10.22), c = 6.72(6.67), and  $\beta = 107.21^{\circ}$  (107.22°).

In order to study the changes in these new bimetallic cation thiophosphate systems, we varied the stoichiometry of the Fe and Co in the  $Fe_{2-x}Co_xP_2S_6$  system (x = 0, 0.25, 1, 1.75, and 2; refer to the Experimental Methods Section). In order to



**Figure 3.** (a) Normalized Raman spectra of Fe–Co thiophosphates. Peaks of interest analyzed in (b) are marked with symbols accordingly. Distinction between modes due to the metal cation and P–P;  $[P_2S_6]^{4-}$  units are marked with a red dashed line. The blue arrow indicates a phonon mode attributed to cation vibrations. (b) Ratio of  $A_{1g}$  (~245 cm<sup>-1</sup>) and  $E_g$  (~275 cm<sup>-1</sup>) intensities of each compound fitting a linear trend with a  $R^2$  value of 0.99, and the ratio of  $A_{1g}$  (~380 cm<sup>-1</sup>) and  $E_g$  (~150 cm<sup>-1</sup>) intensities of each compound fitting a linear trend with a  $R^2$  value of 0.93.

confirm the chemical composition of the thiophosphates, EDS was used at two different length scales. Figure 1b confirms an expected inverse relationship of at % for Fe and Co, respectively, with both SEM and STEM. The associated elemental maps of Fe, Co, P, and S in Figure S2 show no variation in intensity that is not accounted for due to the thickness effects, which indicates a homogeneous distribution in multilayers of these compounds.

Structural analysis was carried out using PXRD, as shown in Figure S4. Spectra for  $Fe_2P_2S_6$  and  $Co_2P_2S_6$  closely match those reported previously.<sup>8,33</sup> The peaks were normalized with respect to (001), which is the most prominent peak, consistent with previous reports.<sup>10,20,21</sup> This peak has the largest intensity as expected due to the vdW layered structure that stacks in the out-of-plane z-direction. Similarly, the other  $\{00l\}$  are prominent throughout the spectra for the five varied compounds. As indicated in the simulated spectra shown in Figure S3, there is a shift of  $0.3^{\circ}(2\theta)$  for the (002) Bragg reflection and 0.6° for the (060) Bragg reflection between  $Fe_2P_2S_6$  and  $Co_2P_2S_6$ , which confirm that  $Co_2P_2S_6$  is a more relaxed structure as compared to Fe<sub>2</sub>P<sub>2</sub>S<sub>6</sub>. As expected, upon increasing the Co concentration, the spectra of  $Fe_2P_2S_6$  show a distinct shift in all of the peaks to a higher  $2\theta$ . The (002) and (060) Bragg reflections confirm a total shift of  $0.3^{\circ}(2\theta_{(002)})$ and  $0.6^{\circ}(2\theta_{(060)})$ , respectively. The black dashed lines in Figure 1c,d show that the Fe-Co thiophosphates evolve linearly, obeying Vegard's Law.<sup>34</sup>

Because of the vdW forces in this 2D system, an anisotropic strain is expected between the in-plane ( $\{h00\}$  and  $\{0k0\}$ ) and out-of-plane ( $\{00l\}$ ) axis directions. The (002) Bragg reflection, whose broadening represents variations in the periodicity in the out-of-plane direction, and the (060) Bragg reflection, whose broadening represents variations in the periodicity in the in-plane direction, are selected for analysis. The fwhm's of the (002) and (060) Bragg reflections were derived based on peak fitting, as shown in Figure S8. Figure 1e confirms that there is a larger change in the fwhm of (060) Bragg reflection throughout the series, which accounts for a larger in-plane periodicity variance than out-of-plane. This suggests that alloying two metals induces a much greater change in the periodicity in the in-plane direction compared to the out-of-plane direction.

As shown in Figure 2a–e, all samples of  $Fe_{2-x}Co_xP_2S_6$  examined with TEM exhibit characteristic terraces expected

for exfoliated layered systems. The accompanying SAED patterns (Figure 2f–j) indicate that each thiophosphate system is single crystalline in nature. Moreover, the observed six-fold rotation in Figure 2f–j is due to the presence of 120° twin boundaries, as shown in Figure 2k. In Figure 2l, a diffraction pattern with projection along the [103]-zone axis simulated by *SingleCrystal*<sup>29</sup> illustrates the diffraction pattern along the [103]-zone axis in black. Rotations of 120° in blue and 240° in red are the representations of the diffraction patterns from the 120° twin boundaries. Previously, Murayama et al. have also reported similar six-fold rotations observed in the SAED pattern of Fe<sub>2</sub>P<sub>2</sub>S<sub>6</sub>, which is attributed to the presence of 120° rotational twins.<sup>22</sup>

The distance between the brightest spots and the central (000) spot, which corresponds to  $\{331\}$  and  $\{060\}$ -planes as shown in Figure 2f-j as represented by the yellow arrows, is within 10% of error. Due to the  $120^{\circ}$  rotational twins along the  $c^*$ -axis, the  $\{331\}$  and  $\{060\}$  diffraction spots will overlap one another. In Figure 2m, the simulated diffraction patterns along the [103]-zone axis for Co and Fe thiophosphate are nearly identical, demonstrating that the variations in the distances between the  $\{331\}$  and  $\{060\}$  are less than 10% in length. Representative HRTEM images for each thiophosphate system are included in Figure S5 along the  $c^*$ -axis. As is expected from the SAED patterns in Figure 2f-j, a distinctive six-fold symmetry is apparent.

The structural changes in the  $Fe_{2-x}Co_xP_2S_6$  series can yield different phonon contributions of the atoms present on/within the lattice. Raman spectroscopy is crucial to determine these atomic vibrations. Figure 3a shows Raman spectra between 20 and 700 cm<sup>-1</sup> for  $Fe_{2-x}Co_xP_2S_6$  systems under ambient conditions. Phonon modes at wavenumbers less than 150 cm<sup>-1</sup> are dominated by metal cation vibrations, while those at higher wavenumbers are dominated by P-P and  $[P_2S_6]^{4-}$  unit vibrations.<sup>9,35</sup> Wavenumbers beyond the cation region are reported to have eight Raman modes: three  $A_{1g}$  and five  $E_{g}$ modes.<sup>9,35</sup> A definitive description for mixed metallic systems is currently absent; however, phonon modes on Co<sub>2</sub>P<sub>2</sub>S<sub>6</sub> and Fe<sub>2</sub>P<sub>2</sub>S<sub>6</sub> have been previously reported.<sup>9,13,36,37</sup> Co<sub>2</sub>P<sub>2</sub>S<sub>6</sub> and  $Fe_2P_2S_6$  have a  $D_{3d}$  symmetry at room temperature and show the representative phonon modes for this space group.<sup>9</sup> These are used as guidelines to understand the analogous phonon modes observed in the  $Fe_{2-x}Co_xP_2S_6$  systems.



**Figure 4.** XPS and UPS spectra of the  $Fe_{2-x}Co_xP_2S_6$  system. (a) XPS spectra showing the  $2p_{3/2}$  and  $2p_{1/2}$  contributions of  $Fe_2P_2S_6$  and  $Co_2P_2S_6$  marked in dashed lines. (b) Integrated  $2p_{1/2}$  and  $2p_{3/2}$  intensities for Co, with  $Fe_{1.75}Co_{0.25}P_2S_6$  and  $Fe_{0.25}Co_{1.75}P_2S_6$  at low intensities shaded in blue. (c) UPS spectra showing the inelastic high-binding-energy cutoffs with linear fits. (d) Extracted work function difference within the  $Fe_{2-x}Co_xP_2S_6$  system.

The vibrational modes of metal thiophosphates can be attributed to three distinct structural units: phosphorus—phosphorus (P–P) dimers, a shell of phosphorus—sulfur ([ $P_2S_6$ ]<sup>4–</sup>) units, and metal cations.<sup>9</sup> For monometallic thiophosphates, the peak at ~245 cm<sup>-1</sup> is attributed to the stretching of the P–P bond, while the peak at ~275 cm<sup>-1</sup> is attributed to the in-plane vibration of P–P bonds in the [ $P_2S_6$ ]<sup>4–</sup> units (schematic shown in Figure S6a).<sup>9</sup> Therefore, any structural changes can be signaled by these phonon modes. These peaks are marked with red dots in Figure 3a. The peak at ~380 cm<sup>-1</sup> is attributed to the out-of-plane vibration of two [ $P_2S_6$ ]<sup>4–</sup> units, <sup>13,36</sup> while the peak at ~580 cm<sup>-1</sup> is assigned to the out-of-plane stretching of the P–P bond.<sup>13</sup> Finally, the peak at ~100 to 110 cm<sup>-1</sup> is assigned to the in-plane Fe or Co presence, which is marked with a blue arrow in Figure 3a. <sup>13,36</sup>

The ratios of select two peaks can also offer information regarding the thickness of the sample flakes. The ratio between the two  $A_{1g}$  peaks at ~245 and ~380 cm<sup>-1</sup> for Fe<sub>2</sub>P<sub>2</sub>S<sub>6</sub> has been reported to give thickness information, where smaller ratios correspond to thicker flakes.<sup>36</sup> For Fe<sub>2-x</sub>Co<sub>x</sub>P<sub>2</sub>S<sub>6</sub> with increasing Co alloy concentration, the ratio is 0.15, 0.2, 0.2, 0.3, and 0.3, respectively, which indicate that the flakes are bulk. This is further corroborated by the fact that the substrate peak is absent throughout all spectra. Moreover, the distinct E<sub>g</sub> peak at ~275 cm<sup>-1</sup> in Figure 3a is reported to be characteristic of bulk samples.<sup>36</sup>

Furthermore, there is a clear evolution in the intensity ratio between the  $A_{1g}$  peak at ~245 cm<sup>-1</sup> and the  $E_g$  peak at ~275 cm<sup>-1</sup>, which are marked with red squares representing P–P vibrations in Figure 3a. The ratio  $A_{1g}$  (~245 cm<sup>-1</sup>)/ $E_g$  (~275 cm<sup>-1</sup>) increases in the Fe<sub>2-x</sub>Co<sub>x</sub>P<sub>2</sub>S<sub>6</sub> system with increasing Co alloy concentration. This linear trend with additional Co can be explained by an increase in out-of-plane P–P vibrations. A linear fit can be extrapolated as shown in Figure 3b. Contrary to this, the intensity ratio between the  $A_{1g}$  peak at ~380 cm<sup>-1</sup> and the  $E_g$  peak at ~150 cm<sup>-1</sup>, marked with black circles representing  $[P_2S_6]^{4-}$  phonon modes in Figure 3a, shows an inverse relationship. The  $A_{1g}$  (~380 cm<sup>-1</sup>)/ $E_g$  (~150 cm<sup>-1</sup>) ratio decreases in the  $Fe_{2-x}Co_xP_2S_6$  system with increasing Co or Fe concentration as shown in Figure 3b.

This can be succinctly expressed as

$$\frac{X_{\Delta Co}}{X_{\Delta Fe}} \propto \frac{E_g^{[P_2 S_6]^{4^-}}}{E_g^{[P-P]}}, \frac{A_{1g}^{[P-P]}}{A_{1g}^{[P_2 S_6]^{4^-}}}$$

where  $X_{\Delta Co}$  and  $X_{\Delta Fe}$  represent the atomic concentration of Co and Fe, respectively.  $E_g^{[P_2S_6]^{4-}}$  and  $A_{1g}^{[P_2S_6]^{4-}}$  represent the integrated intensity of  $[P_2S_6]^{4-}$  in-plane and out-of-plane modes.  $E_g^{[P-P]}$  and  $A_{1g}^{[P-P]}$  represent the integrated intensity of P–P in-plane and out-of-plane modes. These characteristic ratios between the  $A_{1g}$  and  $E_g$  peak intensities can be used to identify the stoichiometry of thiophosphate systems.

As discussed above, peaks  $< 150 \text{ cm}^{-1}$  can be attributed to the metal ions in the thiophosphate system. There is an ambiguity, however, in assigning the 155 cm<sup>-1</sup> phonon mode to a specific ionic unit. While it is often reported as in-plane vibrations of two  $[P_2S_6]^{4-}$  units in adjacent layers,<sup>9,36</sup> others have assigned this phonon mode to the in-plane metal cation vibrations.<sup>13</sup> According to Figure 3a, the intensities of the peaks at ~155 and ~110 cm<sup>-1</sup> are inversely related throughout the  $Fe_{2-x}Co_xP_2S_6$  series. It has been previously reported that both peaks show similar trends below the Néel temperature, where the material undergoes a phase transition from a paramagnetic to AFM state. In the case of  $Fe_2P_2S_6$ , new peaks arise at 88 and 95 cm<sup>-1</sup> below its Néel temperature of 118 K.<sup>3</sup> These new sharp peaks increase in intensity with decreasing temperature and replace the broad peak observed at  $\sim 100$  $cm^{-1.37}$  Similarly, the peak at ~155  $cm^{-1}$  has also been observed to split into two components: the A<sub>g</sub> mode at 149  $cm^{-1}$  and the  $B_g$  mode at 157  $cm^{-1}$  at 25 K.<sup>13</sup> Such similarities in the splitting of ~100 and ~155  $\text{cm}^{-1}$  peaks give further

evidence that the two phonon modes may be closely related to the cation, which is critical to the material's magnetic property.

Changes in the alloying ratio of the  $Fe_{2-x}Co_xP_2S_6$  system may also alter the electronic structure of each thiophosphate. X-ray photoelectron spectroscopy (XPS) is critical to observe these changes at the atomic scale. XPS is conducted under ultrahigh vacuum (refer to Experimental Methods) conditions with a Cu K $\alpha$  source. The expected oxidation state for the cations is 2+ for the monometallic thiophosphates,  $Fe_2P_2S_6$  and  $Co_2P_2S_6$ , which neutralizes the charge of the compound with the  $[P_2S_6]^{4-}$  units. The XPS spectra, which indicate oxidation states for the mixed cation compounds, are shown in Figure 4a. The  $2p_{3/2}$  and  $2p_{1/2}$  at 711 and 724 eV correspond to the Fe 2p states, while 781 and 797 eV correspond to the Co 2p states, respectively.<sup>38</sup> The states at 711 and 781 eV correspond to the Fe<sup>2+</sup> and Co<sup>2+</sup> in the octahedral sites, respectively.<sup>39</sup>

Upon introduction of Co to  $Fe_2P_2S_6$ , unexpected changes in the contribution of the Fe 2p states are observed. A similar trend is observed in Co 2p states with the introduction of Fe into  $Co_2P_2S_6$ . This behavior is contrary to the linear dependence in stoichiometry as discussed above. Figure 4b shows the contribution of each 2p state for Fe and Co throughout the series. Interestingly, this trend shows a dependence on the alloying ratios of Fe and Co. The monometallic (0 at %) and 1:1 ratio compounds (50 at %) show a strong contribution from the 2p states in Figure 4b. In contrast, as highlighted with a blue background in Figure 4b, the Fe- or Co-rich mixed cation system shows a distinct suppression of all 2p states, which can be attributed to the change in electronic excitations.

To evaluate this unusual behavior, UPS was used to investigate the electronic structural changes occurring in Fe<sub>2-x</sub>Co<sub>x</sub>P<sub>2</sub>S<sub>6</sub>. Figure S7 shows the complete UPS spectra for each system. The extracted high binding energy region corresponding to the inelastic high binding energy cutoff ( $E_{cutoff}$ ) is shown in Figure 4c. For all spectra, linear fits were used to determine  $E_{cutoff}$ .<sup>40</sup> The work function for each compound was extracted using  $\Phi = h\nu - (E_{cutoff} - E_F)$ , where  $h\nu$  is the incident photon energy of 21.2 eV, and  $E_F$  is the Fermi energy level of 0 eV.<sup>40</sup>

Two distinct  $E_{\text{cutoff}}$  were identified analogous to what was observed in XPS. Based on this, the work functions for  $Fe_2P_2S_{6\prime}^{\ \ 41}$   $Co_2P_2S_{6\prime}$  and  $FeCoP_2S_6$  were calculated to be  ${\sim}6$ eV, while those for  $Fe_{0.25}Co_{1.75}P_2S_6$  and  $Fe_{1.75}Co_{0.25}P_2S_6$  were ~6.8 eV, as illustrated in Figure 4d. Therefore, UPS provides direct evidence for evolution of the electronic structure in the  $Fe_{2-x}Co_{x}P_{2}S_{6}$  series and explains the unexpected suppression of the Co and Fe 2p states. Because all samples were prepared under the same conditions, surface adsorbates should nominally be the same and minimal. Thus, two distinct work functions are due to variations in the distribution of the Fe and Co occupation in the lattice.<sup>42,43</sup> In the case of Fe- and Co-rich systems, the distribution of Co and Fe in the vdW layers will be much more dispersed as compared with FeCoP2S6 and likely accounts for this shift. Therefore, the uneven distribution of cations leads to a nonlinear behavior of the electronic system.

However, the compounds studied in this work are in the multilayer form, and we may potentially observe different trends for thin, few-layer systems when the contribution from individual layers becomes dominant. This ability to vary the work function of this class of layered materials is of great importance as it opens new opportunities to integrate these novel vdW materials into heterostructure devices as is the case with the ferroelectric field-effect transistors,  $CuInP_2S_6$  and  $MoS_2$ .<sup>44</sup> Of particular interest are  $Fe_{1.75}Co_{0.25}P_2S_6$  and  $Fe_{0.25}Co_{1.75}P_2S_6$ , whose sudden increased work function may be due to the site occupancy of Co and Fe, respectively, in a majority Fe and Co lattice arrangement. Further studies on few-layer systems are required to confirm this anomalous behavior.<sup>45</sup>

## 4. SUMMARY AND CONCLUSIONS

The elemental and structural analyses of Fe<sub>2-x</sub>Co<sub>x</sub>P<sub>2</sub>S<sub>6</sub> confirm that the atomic distribution is homogeneous when averaged over the length scale of several hundred nanometers in their multilayer form. Alloying, whether with Co or Fe, induces a larger change in lattice periodicity in the in-plane direction (060) than the out-of-plane (002) Bragg reflection. Phonon mode fingerprints of the mixed metal cation thiophosphate series are presented in terms of in-plane and out-of-plane vibrations of  $[P_2S_6]^{4-}$  and P-P units. We found a direct relation in the Co alloy concentration in Fe<sub>2</sub>P<sub>2</sub>S<sub>6</sub> with in-plane  $[P_2S_6]^{4-}$  and out-of-plane P-P vibrations. An inverse trend is observed with  $Co_2P_2S_6$  with respect to the Fe alloy. Interestingly, an unexpected nonlinear behavior of Fe and Co 2p states provides direct evidence for evolution of the electronic structure within the Fe2-xCoxP2S6 system. Moreover, it is realized that these electronic changes are dependent on alloying ratios, which is further confirmed by two distinct work functions within the system. Further investigation on fewlayer forms that show a structural deviation from the multilayer forms may reveal the origin of this unexpected electronic structure change. Regardless, this work has provided structural, vibrational, and electronic fingerprints of a mixed metal cation thiophosphate series and will open new avenues toward tailoring thiophosphates for desired applications.

# ASSOCIATED CONTENT

## **③** Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.1c02635.

Details of characterization methods including PXRD, SEM-EDS, and STEM-EDS; observed stoichiometry based on TEM and SEM; EDS maps, TEM images, Raman modes, and UPS spectra; mass of reagents used for the flux reaction; and heating profiles for the synthesis of mono- and bimetallic thiophosphate compounds (PDF)

## AUTHOR INFORMATION

#### **Corresponding Author**

Vinayak P. Dravid – Department of Material Science and Engineering, Northwestern University, Evanston, Illinois 60208, United States; Northwestern University Atomic and Nanoscale Characterization Experimental (NUANCE) Center and International Institute for Nanotechnology (IIN), Northwestern University, Evanston, Illinois 60208, United States; orcid.org/0000-0002-6007-3063; Email: vdravid@northwestern.edu

## Authors

Matthew Cheng – Department of Material Science and Engineering, Northwestern University, Evanston, Illinois 60208, United States; • orcid.org/0000-0002-1062-5974 Yea-Shine Lee – Department of Material Science and Engineering, Northwestern University, Evanston, Illinois 60208, United States

Abishek K. Iyer – Department of Chemistry, Northwestern University, Evanston, Illinois 60208, United States; orcid.org/0000-0002-8582-3895

Daniel G. Chica – Department of Chemistry, Northwestern University, Evanston, Illinois 60208, United States; orcid.org/0000-0001-8616-9365

Eric K. Qian – Department of Chemistry, Northwestern University, Evanston, Illinois 60208, United States

Muhammad Arslan Shehzad – Department of Material Science and Engineering, Northwestern University, Evanston, Illinois 60208, United States; Northwestern University Atomic and Nanoscale Characterization Experimental (NUANCE) Center, Northwestern University, Evanston, Illinois 60208, United States; Orcid.org/0000-0002-6260-5764

**Roberto dos Reis** – Department of Material Science and Engineering, Northwestern University, Evanston, Illinois 60208, United States; Northwestern University Atomic and Nanoscale Characterization Experimental (NUANCE) Center, Northwestern University, Evanston, Illinois 60208, United States

Mercouri G. Kanatzidis – Department of Chemistry, Northwestern University, Evanston, Illinois 60208, United States; orcid.org/0000-0003-2037-4168

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.inorgchem.1c02635

## **Author Contributions**

<sup>⊥</sup>M.C. and Y.-S.L. contributed equally.

#### Notes

The authors declare no competing financial interest.

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