

# KNiPS<sub>4</sub>: A New Thiophosphate with One- and Two-Dimensional Structural Arrangements

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Single crystals of a new ternary thiophosphate, KNiPS<sub>4</sub>, have been synthesized by reaction of the elements in an evacuated silica tube at 873 K for two weeks. The structure was solved in the tetragonal space group  $P4_2/mnm$  with  $a = 8.2538(4)$  Å,  $c = 10.7553(6)$  Å, and  $Z = 4$ . The refinements led to  $R = 0.0250$  ( $R_w = 0.0190$ ) for 425 independent reflections and 26 variables. The structure of KNiPS<sub>4</sub> consists of nickel in square planar sulfur coordination linked by edge-sharing PS<sub>4</sub> tetrahedral groups to produce one-dimensional chains. The chains are aligned in a parallel manner to form layers perpendicular to the  $c$ -axis and they are separated by layers of potassium. Tight-binding band structure calculations suggest that the nickel atoms should be in a low-spin Ni<sup>II</sup> state resulting in an overall charge balance of  $K^+Ni^{II}P^V(S^{II})_4$ . UV-visible spectroscopic measurements indicate KNiPS<sub>4</sub> to be semiconducting. © 1995 Academic Press, Inc.

## INTRODUCTION

The structures and physical properties of transition metal thiophosphates have been known and studied for many years. One structural feature common to many of these compounds is the presence of isolated and/or interconnected PS<sub>4</sub> tetrahedra within the structure (1). In other thiophosphates, in particular MPS<sub>3</sub> ( $M =$  transition metal) compounds and related phases, phosphorus is found in ethane-like (P<sub>2</sub>S<sub>6</sub>)<sup>4-</sup> anionic groups (2, 3, 4). The addition of electropositive metals to transition metal thiophosphates has opened the way to discovery of ternary thiophosphates with new structural arrangements and transition metal oxidation states not accessible in the binary thiophosphates. In addition, the introduction of a spherical, highly ionic species such as an alkali or coinage metal

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may lead to anharmonic behavior of the cation, adding interest to the study. For instance, the type of cation disorder encountered in these structures (static or dynamic) can be determined through variable temperature structural studies.

We were interested in synthesizing new, low-dimensional ternary thiophosphates with covalent transition metal/sulfur/transition metal bonding within the low-dimensional region. As part of this search, we have discovered a new low-dimensional ternary thiophosphate, KNiPS<sub>4</sub>. Here, we report the synthesis and structural physical properties of this new compound.

## EXPERIMENTAL

### Synthesis

Single crystals of KNiPS<sub>4</sub> were prepared by reacting a stoichiometric mixture of the elements in an evacuated silica tube at 873 K for two weeks. After this time the tube was radiatively cooled to room temperature. The reaction product contained dark reddish-brown, three-dimensional single crystals along with small amounts of secondary phases. We were unsuccessful in obtaining single-phase material under these reaction conditions, but the secondary phases could be completely removed by washing the reaction product with a 1% (v/v) HCl solution. There was no observed degradation of the single crystals as a result of this washing, which was verified by X-ray powder diffraction. Qualitative scanning electron microscopy (SEM) analyses on these single crystals yielded a stoichiometry of  $K_{1.2}Ni_{1.0}P_{1.0}S_{4.1}$ . The SEM analysis also showed KNiPS<sub>4</sub> to have a striated appearance on the single crystal edges, indicating it to be a layered phase. This was later supported when we were able to

TABLE 1  
Crystal Data and Intensity Collection and Refinement  
for KNiPS<sub>4</sub>

<i>Physical, crystallographic, and analytical data</i>	
Mol. Wt., g	257.03
Space group	<i>P4<sub>2</sub>/mnm</i> (136)
<i>a</i> , Å	8.2506(14)
<i>c</i> , Å	10.7534(13)
<i>V</i> , Å <sup>3</sup>	732.7
<i>Z</i>	4
Linear abs. coeff., cm <sup>-1</sup>	42.6
Crystal vol., mm <sup>3</sup>	9.6 × 10 <sup>-4</sup>
Color	Reddish-brown
<i>Data Collection</i>	
Diffractometer	Siemens P4
<i>T</i> of data collection, K	300
Radiation	MoK-L <sub>(2,3)</sub>
Scan mode	ω
Recording range	-1 to 21, -1 to 21, -1 to 19
Standard reflections	800,080,444 (every 100 reflections)
<i>Refinement conditions</i>	
Number of recorded reflections	2932
Independent reflections with <i>I</i> > 3.0 σ( <i>I</i> )	425
Number of variables	26
<i>R</i> <sub>int</sub>	0.0172
<i>Refinement results</i>	
<i>R</i> ( <i>F</i> <sub>0</sub> )	0.0250
<i>R</i> <sub>w</sub> ( <i>F</i> <sub>0</sub> ) <sup>a</sup>	0.0190
Minimum and maximum peak in difference Fourier map, e/Å <sup>3</sup>	-0.57 at $\frac{1}{2}, \frac{1}{2}, 0.052$ 0.58 at 0.24, 0.24, 0

$$^a R_w(F_0) = [\sum_w (|F_0| - |F_c|)^2 / \sum_w |F_0|^2]^{1/2} \text{ with } w = 1/\sigma^2(F_0).$$

mechanically cleave the crystals into thin, reddish-brown transparent sheets.

### Crystallographic Studies

A single crystal with approximate dimensions of 0.2 × 0.1 × 0.05 mm<sup>3</sup> was selected. Preliminary Weissenberg photography established the unit cell as tetragonal, which was later confirmed by diffractometry. All single crystal diffraction data were recorded on a Siemens P4 diffracto-

TABLE 2  
Final Positional and Equivalent Isotropic Displacement  
Parameters for KNiPS<sub>4</sub>

Atom type	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub> × 10 <sup>2</sup> Å <sup>2a</sup>
Ni(1)	0	0	0	2.21(3)
Ni(2)	0	0	$\frac{1}{2}$	2.32(3)
S(1)	0.3635(1)	0.3635(1)	0.1442(1)	3.10(3)
S(2)	0.0043(2)	0.2679(1)	0	2.92(4)
P	0.2506(2)	0.2506(2)	0	2.57(4)
K	0	$\frac{1}{2}$	$\frac{1}{2}$	4.13(4)

$$^a U_{eq} \text{ defined as } \frac{1}{3} \text{ trace } U.$$

TABLE 3  
Anisotropic Displacement Parameters (ADP) for KNiPS<sub>4</sub>:  
*U*(*ij*) (×10<sup>2</sup> Å<sup>2</sup>)<sup>a</sup>

Atom name	<i>U</i> (1,1)	<i>U</i> (2,2)	<i>U</i> (3,3)	<i>U</i> (1,2)	<i>U</i> (1,3)	<i>U</i> (2,3)
Ni(1)	2.02(6)	2.02(6)	2.60(7)	-0.84(7)	0	0
Ni(2)	2.18(4)	2.18(4)	2.60(7)	0.98(7)	0	0
S(1)	3.45(4)	3.45(4)	2.40(6)	-1.71(6)	-0.07(6)	-0.07(6)
S(2)	2.44(7)	2.15(7)	4.17(7)	-0.69(7)	0	0
P	2.47(6)	2.47(6)	2.77(10)	-1.14(9)	0	0
K	4.59(6)	4.59(6)	3.20(8)	0	0	0

<sup>a</sup> The form of the Anisotropic Displacement Parameter is exp  $[-2\pi^2\{h^2a^{*2}U(1,1) + k^2b^{*2}U(2,2) + l^2c^{*2}U(3,3) + 2hka^*b^*U(1,2) + 2hla^*c^*U(1,3) + 2klb^*c^*U(2,3)\}]$ .

meter. SHELXTL PLUS (5) was used to calculate an empirical absorption correction (the absorption coefficient was relatively small, see Table 1) and to determine the space group as *P4<sub>2</sub>/mnm*. The structure was solved by direct methods and refined using XTAL3.2(6). Final refinements were on *F*<sub>0</sub> and involved Anisotropic Displacement Parameters (ADP). Table 1 summarizes all analytical and crystallographic data from the diffraction study. Secondary extinction was not included in the final refinement because it did not improve the results. Table 2 lists the atomic positional parameters and equivalent isotropic displacement parameters and Table 3 lists the anisotropic displacement parameters for KNiPS<sub>4</sub>.<sup>2</sup>

X-ray powder diffraction data for KNiPS<sub>4</sub> were collected on an INEL XRG 3000 diffractometer to confirm and improve the lattice constants determined from the single crystal study. A statistically random powder could not be used for the powder diffraction study due to the almost complete loss of crystallinity upon mechanical grinding of the single crystals, which is often observed for layered phases. To circumvent this problem, the outside of a 200-μm silica glass capillary was coated with a thin layer of vacuum grease and then with a layer of single crystals that had been sieved through a 100-μm screen and "powder" diffraction data were collected. We assumed an approximately random orientation of the crystals on the capillary since the uncleaved single crystals are essentially three-dimensional. The refined lattice constants of *a* = 8.2538(4) Å and *c* = 10.7553(6) Å compared quite well with the refined lattice constants determined from the single crystal study (Table 1). Table 4 lists observed and calculated *d*-spacings (7) and intensities (8) obtained from the powder diffraction study.

### Electronic Structure Calculations

Tight-binding band structure calculations (9) were carried out using an extended Hückel type Hamiltonian (10).

TABLE 4

Calculated and Observed  $d$  Spacings and Intensities for KNiPS<sub>4</sub> from X-Ray Powder Diffraction ( $a = 8.2538(4)$  Å and  $c = 10.7553(6)$  Å)

$h k l$	$d_{\text{obs}}$ (Å)	$d_{\text{calc}}$ (Å)	$I_{\text{obs}}$ (%)	$I_{\text{calc}}$ (%)
1 1 0	5.8363	5.8360	22	26
0 0 2	5.3776	5.3775	87	82
1 1 1	5.1297	5.1296	100	100
2 0 0	4.1269	4.1267	27	25
1 1 2	3.9548	3.9546	89	97
2 1 0	3.6912	3.6910	25	25
2 1 1	3.4913	3.4911	21	25
1 0 3	3.2883	3.2882	40	43
2 1 2	3.0433	3.0431	3	2
2 2 0	2.9182	2.9180	12	12
2 2 1	2.8163	2.8162	7	8
0 0 4	2.6888	2.6888	36	21
3 0 1	2.6655	2.6653	29	28
2 1 3	2.5717	2.5716	19	14
3 1 1	2.5365	2.5363	1.0	1.2
1 1 4	2.4421	2.4420	1.0	0.7
3 1 2	2.3481	2.3480	74	72
3 2 0	2.2892	2.2891	4	4
2 2 3	2.2632	2.2631	13	9
2 0 4	2.2528	2.2528	13	14
3 2 1	2.2390	2.2389	4	3
2 1 4	2.1733	2.1733	11	9
3 1 3	2.1101	2.1100	11	11
1 0 5	2.0815	2.0815	3	2
4 0 0	2.0635	2.0633	20	14
1 1 5	2.0183	2.0183	1	1
2 2 4	1.9774	1.9773	8	6
4 1 1	1.9681	1.9679	9	8
3 3 0	1.9454	1.9453	5	6
4 0 2	1.9265	1.9264	22	23
3 1 4	1.8728	1.8727	12	9
2 1 5	1.8585	1.8584	4	3

A modified Wolfsberg-Helmholz formula was used to calculate the nondiagonal  $H_{\mu\nu}$  values (11). The ionization potentials (eV) and exponents used were  $-19.0$  and  $1.75$  for  $P 3s$ ,  $-12.0$  and  $1.75$  for  $P 3p$ ,  $-20.0$  and  $1.817$  for  $S 3s$ ,  $-13.3$  and  $1.817$  for  $S 3p$ ,  $-9.70$  and  $2.10$  for  $Ni 4s$ , and  $-5.15$  and  $2.10$  for  $Ni 4p$ . Double- $\zeta$  type orbitals were used for  $Ni 3d$ . The ionization potential exponents and contraction coefficients were  $-13.49$ ,  $5.75$ ,  $2.30$ ,  $0.57979$ , and  $0.57819$ , respectively.

## RESULTS AND DISCUSSION

The structure of KNiPS<sub>4</sub> consists of nickel in square planar coordination by sulfur; these NiS<sub>4</sub> square planes are linked in one dimension by edge-sharing PS<sub>4</sub> tetrahedra. Thus, alternating NiS<sub>4</sub> square planes are rotated approximately 90° to each other in an individual NiPS<sub>4</sub> chain. The chains are in turn aligned in a parallel fashion

to form layers. Figure 1 illustrates one layer of NiPS<sub>4</sub> chains running in the (110) direction. The potassium ions shown in Fig. 1 reside above and below the NiPS<sub>4</sub> chains, not between the chains in a given layer. The chains in the layer directly above and below this layer run in a perpendicular direction. Figure 2 shows how the layers of chains are stacked. Potassium is in bi capped trigonal prismatic coordination by sulfur (Fig. 3). With this perspective the structure is best described as being made up from one-dimensional NiPS<sub>4</sub> chains arranged in two-dimensional sheets and these sheets are separated by layers of K<sup>+</sup>. To the best of our knowledge this represents a new structure type.

Selected bond distances and angles for KNiPS<sub>4</sub> are given in Table 5. The average Ni-S distance of 2.218 Å in KNiPS<sub>4</sub> compares well with previously studied compounds containing square planar Ni-S groups. For example, the average Ni-S distance is 2.218 Å for the square planar groups in Ta<sub>2</sub>Ni<sub>3</sub>S<sub>8</sub> (12), 2.237 Å in BiCuNiS<sub>3</sub> (13), 2.220 Å in Cs<sub>2</sub>Ni<sub>3</sub>S<sub>4</sub> (14), and 2.325 Å in Pt<sub>5</sub>Pd<sub>2</sub>NiS<sub>8</sub> (15). It is worthwhile to point out that a Ni-S distance of 2.22 Å requires that the Ni<sup>II</sup> radius be 0.38 Å (assuming a S<sup>2-</sup> radius of 1.84 Å), which is 22% shorter than the expected radius for Ni<sup>2+</sup> in a square planar coordination of 0.49 Å

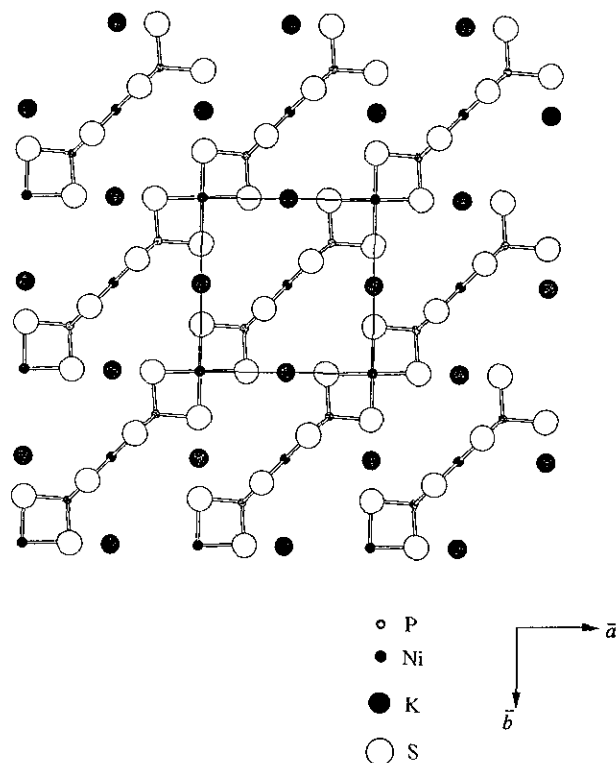


FIG. 1. A view (in the (001) direction) of a portion of the KNiPS<sub>4</sub> structure emphasizing the arrangement of the NiPS<sub>4</sub> filaments. Note that the potassium resides in layers above and below the layer of NiPS<sub>4</sub> filaments.

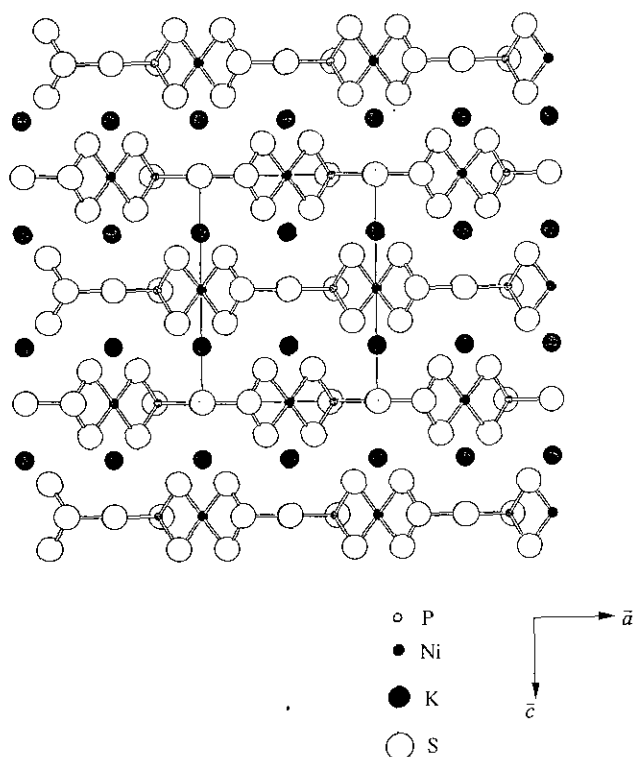


FIG. 2. A view (in the (010) direction) of a portion of the  $\text{KNiPS}_4$  structure emphasizing layers of  $\text{NiPS}_4^-$  filaments separated by  $\text{K}^+$ . Note that the  $\text{NiPS}_4^-$  filaments run in the (110) and  $(-110)$  directions in alternating layers.

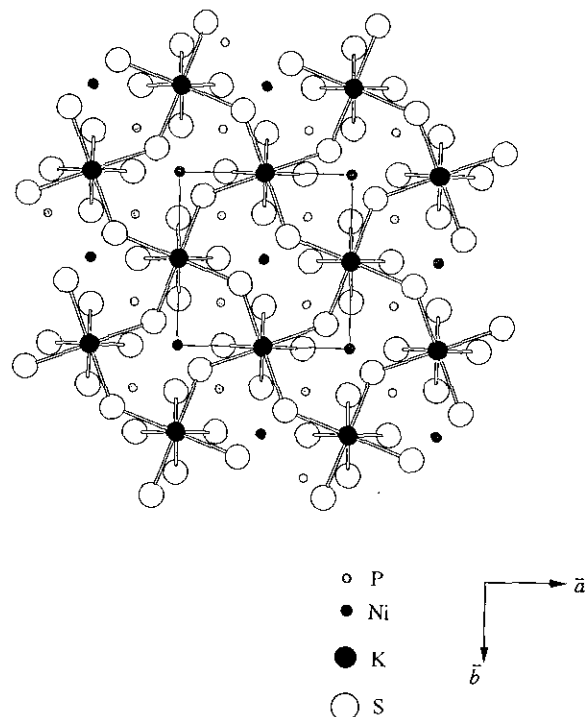


FIG. 3. A view (in the (001) direction) of the  $\text{KNiPS}_4$  structure emphasizing the bicapped trigonal prismatic coordination of sulfur around potassium (linked atoms).

(16). This trend of short Ni-S bonds and reduced ionic radii may be attributable to extensive covalent interaction within the Ni/S square planes.

This short Ni-S contact necessitates the presence of short S-S contacts in the square plane. The shortest intrachain S-S contact is 3.08 Å, which occurs within a Ni(1)-S(2) square plane, while the S-S contact in the Ni(2)-S(1) square plane is 3.10 Å. Using a hard sphere model an expected  $\text{S}^{2-}$ - $\text{S}^{2-}$  contact distance would be 3.68 Å. However, it has been previously shown in  $\text{PV}_2\text{S}_{10}$ , which has a S-S contact distance of 2.984 Å, that there is no S-S bonding interaction (17). The shortest interchain (between two chains in the same plane) S-S contact is 3.83 Å ( $\text{S}_2$ - $\text{S}_2$ ). The average P-S distance of 2.037 Å is in good agreement with those found in  $\text{RbVP}_2\text{S}_7$  (18),  $\text{Ag}_4\text{P}_2\text{S}_7$  (19), and  $\text{Hg}_2\text{P}_2\text{S}_7$  (20). The average K-S distance of 3.351 Å is the value obtained by summing the effective ionic radii for  $\text{K}^+$  and  $\text{S}^{2-}$  (16).

Another structural aspect is the presence of unusually large  $U_{\text{eq}}$ 's for all the atoms. This may be due to high mobility of potassium within the potassium layer. The movement of potassium would influence its sulfur neighbors, and this in turn would affect the nickel and phosphorus, causing unusually large  $U_{\text{eq}}$ 's for all atoms. This is

TABLE 5  
Selected Bond Distances (Å) and  
Angles (°) for  $\text{KNiPS}_4$

Ni(1)-S(2) × 4	2.212(1)
Ni(2)-S(1) × 4	2.223(1)
P-S(1) × 2	2.035(1)
P-S(2) × 2	2.038(2)
K-S(1) × 4	3.401(1)
K-S(2) × 4	3.301(1)
S(2)-Ni1-S(2) × 2	180.0(3)
S(2)-Ni1-S(2) × 2	91.82(6)
S(2)-Ni1-S(2) × 2	88.18(6)
S(1)-Ni2-S(1) × 2	91.56(4)
S(1)-Ni2-S(1) × 2	180.0(2)
S(1)-Ni2-S(1) × 2	88.44(4)
S(1)-P-S(2) × 4	115.13(6)
S(1)-P-S(1)	99.29(7)
S(3)-P-S(3)	98.05(8)
S(1)-K-S(2) × 4	61.69(3)
S(1)-K-S(1) × 4	96.43(2)
S(1)-K-S(1) × 2	140.89(3)
S(1)-K-S(2) × 4	85.93(3)
S(1)-K-S(2) × 4	76.34(4)
S(1)-K-S(2) × 4	141.34(3)
S(2)-K-S(2)	70.93(3)
S(2)-K-S(2) × 4	131.55(3)

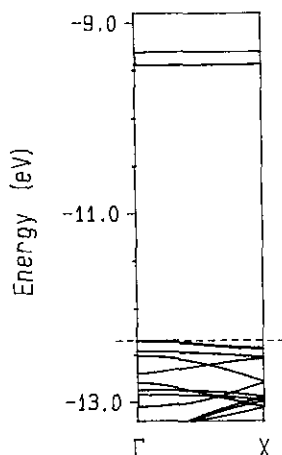


FIG. 4. Band structure for the  $[\text{NiPS}_4]_2^-$  chains in  $\text{KNiPS}_4$ .  $\Gamma = 0$  and  $X = \pi/d$ , where  $\mathbf{d} = \mathbf{a} + \mathbf{a}$ , i.e., the repeat vector of the chain. The dotted line refers to the energy of the highest occupied level of the chain.

possible because of the high degree of displacement freedom of the parallel arranged chains and because of weaker ionic bonds between  $\text{K}^+$  and  $\text{NiPS}_4^-$  chains as opposed to more constraining simple close stacking. Higher  $U_{\text{eq}}$ 's have been reported for other chain containing phases, for example  $\text{Ta}_4\text{P}_4\text{S}_{29}$ , which has a sulfur chain enclosed in a tunnel framework. The chain-sulfurs exhibit  $U_{\text{eq}}$ 's over two times larger than the sulfurs within the tunnel framework (21). Likewise, the compounds  $\text{KFeS}_2$  (22),  $\text{Bi}_2\text{Al}_4\text{Se}_8$  (23), and  $\text{NbS}_3$  (24) possess chain-like structures and have  $U_{\text{eq}}$ 's at least two times greater than anticipated. Further studies need to be performed, in particular variable temperature X-ray and spectroscopic studies, to confirm the origin of the atomic displacement.

Short chalcogen · · · chalcogen contacts have recently been shown (25–28) to have strong control of the electronic structure and oxidation states of transition metal atoms in binary and ternary transition metal chalcogenides. In view of the short  $\text{S} \cdot \cdot \cdot \text{S}$  contacts in  $\text{KNiPS}_4$ , we carried out tight-binding band structure calculations for the  $\text{NiPS}_4^-$  chains present in this phase. The calculated band structure is shown in Fig. 4, where the dashed line indicates the highest occupied energy level. The highest occupied bands are built from sulfur lone pairs and the four low energy levels of Ni in the square planar coordination. The two lowest empty bands are built from the highest  $d$  energy level of Ni in the square planar coordination (note that there are two square planar units in the unit cell of the chain and thus two bands). There is a large band gap of 2.9 eV, which suggests that nickel atoms should be in a low-spin  $\text{Ni}^{2+}$  configuration. In addition, the calculated overlap populations for the four different short  $\text{S} \cdot \cdot \cdot \text{S}$  contacts (3.08, 3.10, 3.18, and 3.19 Å) are all slightly negative (−0.049, −0.047, −0.016, and −0.016)

indicating that there is no S–S bonding interaction despite the short distances. Thus we conclude that the usual oxidation states of  $\text{Ni}^{\text{II}}$  and  $\text{S}^{-\text{II}}$  are appropriate for  $\text{KNiPS}_4$  and that the nickel atoms should be in a low-spin configuration thus giving the charge balance of  $\text{K}^+\text{Ni}^{\text{II}}\text{P}^{\text{V}}(\text{S}^{-\text{II}})_4$ . The overlap populations for the two different Ni–S bonds (2.21 and 2.22 Å) are also normal (0.410 and 0.403) for a low-spin, square planar  $\text{Ni}^{\text{II}}$ . Preliminary UV–visible spectroscopic measurements indicate a band gap of about 1.9 eV and semiconducting behavior in agreement with the electronic structure calculations and the reddish-brown, transparent appearance of the single crystals (29).

## CONCLUSION

Our attempt to synthesize low-dimensional, covalent ternary thiophosphates was successfully realized through the discovery of  $\text{KNiPS}_4$ . The one-dimensional/two-dimensional nature of the structure is unique and it gives rise to a new structure type. The presence of potassium layers may make  $\text{KNiPS}_4$  amenable for substitution of different electropositive metals within these layers to obtain different oxidation states for nickel, for intercalation/deintercalation studies, or to alter the layering arrangement altogether. These points will be the focus of our future ternary thiophosphate work.

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