**GeP and $(\text{Ge}_{1-x}\text{Sn}_x)(\text{P}_{1-y}\text{Ge}_y)$ ($x \approx 0.12$, $y \approx 0.05$): Synthesis,
structure, and properties of two-dimensional layered tetrel
phosphides**

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Abstract

GeP and Sn-doped GeP were synthesized from elements in bismuth and tin flux, respectively. The layered crystal structures of these compounds were characterized by single crystal X-ray diffraction. Both phosphides crystallize in a GaTe structure type in the monoclinic space group $C2/m$ (No. 12) with GeP: $a = 15.1948(7) \text{ \AA}$, $b = 3.6337(2) \text{ \AA}$, $c = 9.1941(4) \text{ \AA}$, $\beta = 101.239(2)^\circ$; $\text{Ge}_{0.93(3)}\text{P}_{0.95(1)}\text{Sn}_{0.12(3)}$: $a = 15.284(9) \text{ \AA}$, $b = 3.622(2) \text{ \AA}$, $c = 9.207(5) \text{ \AA}$, $\beta = 101.79(1)^\circ$. The crystal structure of GeP consists of 2-dimensional GeP layers held together by weak electron lone pair interactions between the phosphorus atoms that confine the layer. Each layer is built of Ge-Ge dumbbells surrounded by a distorted antiprism of phosphorus atoms. Sn-doped GeP has a similar structural motif with a significant degree of disorder emphasized by the splitting of all atomic positions. Resistivity measurements together with quantum-chemical calculations reveal semiconducting behavior for the investigated phosphides.

1. Introduction

The recent discovery of graphene has given rise to significant interest in two-dimensional (2D) materials and their three-dimensional prototypes, where the 2D layers are stacked with weak van der Waals interactions.^{1,2,3} Graphene has been extensively studied and while investigations into other layered materials, such as transition metal dichalcogenides, are underway, there is also interest in 2D materials based on heavier tetrel elements, Si and Ge.^{4,5} Carbon readily forms π -bonds and may crystallize in the 3D diamond structure with 4 σ -bonds to four other carbon atoms as well as in the 2D graphite structure with $3\sigma+1\pi$ bonds to the three neighboring carbon atoms. Graphite is the most stable modification among all carbon allotropes. Silicon and germanium are not capable of forming π -bonds and both crystallize in diamond-like structures. This explains why more sophisticated methods are required to produce 2D Si- or Ge-based materials.

The number of σ -bonds formed by the main group elements in periods 3-6 is determined by their valence electron concentration, VEC. Silicon and germanium form diamond-like structures since they have four valence electrons, $VEC = 4$ (Fig. 1 left). This is the number of electrons required to form four covalent homoatomic σ -bonds. Increasing the VEC results in an “excess” of electrons. These “excess” electrons will be localized on atoms in the form of electron lone pairs. Repulsion of the electron lone pairs will reduce the total dimensionality of the structure resulting in layered structures

with strong covalent bonding within the layers and weak van der Waals interactions between the layers, similar to graphite. For example, in the structure of black phosphorus (VEC = 5) each phosphorus atom has a 3+1 coordination, *i.e.* three phosphorus atoms and one electron lone pair (Fig. 1 right). Other interesting examples of layered materials are monpnictides of silicon and germanium with the general formula TX (T = Si, Ge; X = P, As) and VEC = 4.5 (Fig. 1 middle).⁶⁻¹² Among all of the TX materials, GeP is the least studied compound. In the current work, we report the flux-assisted syntheses together with detailed structural, bonding, and properties characterization of GeP and Sn-doped GeP.

Figure 1. Crystal structures of bulk Ge, GeP and black P with corresponding atomic local coordination and VEC. Ge: black, P: yellow.

2. Experimental

2.1 Synthesis. Samples of GeP and Sn-doped GeP were prepared via solid-state reactions from elements in either a Bi or Sn metal flux. The starting materials (all from Alfa Aesar), Ge pieces (Alfa Aesar, 99.999%), amorphous red P powder (Spectrum Chemicals, 99.99%), Sn shot (Alfa Aesar, 99.7%), and Bi chunks (Alfa Aesar, 99.999%), were used as received. GeP was synthesized by combining Ge:P:Bi in a 1:2:2 molar ratio with a total mass of 0.5 g. The elements were sealed inside an evacuated silica ampoule and heated to 1223 K, annealed for 96 h, then slowly cooled to 773 K over 120 hours. The sample was quickly cooled to 573 K and annealed at 573 K for 24 hours to convert any remaining white phosphorus to red phosphorus. The Bi flux was removed via centrifugation of the synthesized samples at 873 K. At this stage, the excess red phosphorus was removed via sublimation. The traces of Bi were removed by washing in a dilute HCl/H₂O₂ solution. Sn-doped GeP samples were prepared in a similar fashion by combining finely ground Ge, red P, and Sn in a 1:2:3 molar ratio. The reaction mixture was sealed in an evacuated silica ampoule and annealed using the same temperature profile as GeP. Excess Sn and any tin-phosphides that formed during annealing were removed by centrifugation at 873 K followed by washing in a dilute HCl solution. Both GeP and Sn-doped GeP crystallized as black plate-like crystals resistant to air and acid treatments.

2.2 X-ray diffraction. The samples were characterized by powder X-ray diffraction (XRD) using a Bruker D8 Advance diffractometer with Cu-K α radiation. GeP and Sn-doped GeP were also analyzed by single crystal X-ray diffraction with a Bruker AXS SMART diffractometer with an APEX-II CCD detector using Mo-K α radiation. Single crystal data were collected at 90 K under a N $_2$ stream. The single-crystal data sets were recorded as ω -scans with a 0.3° step width and integrated with the Bruker SAINT software package. Structure determination and refinement of the crystal structure was carried out using the SHELX suite of programs.¹³ Additional information pertaining to the structure solutions is discussed below. Details of the X-ray diffraction experiments for GeP and Sn-doped GeP are presented in Table 1 and atomic coordinates and selected interatomic distances are listed in Tables 2 and 3.

Table 1. Data collection and structural refinement parameters for GeP and Sn-doped GeP.^{a)}

	GeP	Ge _{0.93(3)} P _{0.95(1)} Sn _{0.12(3)}
CSD number	427243	427244
Space group	<i>C2/m</i> (No. 12)	
Temp. [K]	90(2)	
<i>a</i> [Å]	15.1948(7)	15.284(9)
<i>b</i> [Å]	3.6337(2)	3.622(2)
<i>c</i> [Å]	9.1941(4)	9.207(5)
β [degrees]	101.239(2)	101.79(1)
<i>V</i> [Å ³]	497.90(4)	498.9(5)
<i>Z</i>	12	
λ [Å]	0.71073	
ρ [g/cm ³]	4.145	4.446
μ [mm ⁻¹]	18.775	19.274
θ [degrees]	2.26 < θ < 32.50	2.72 < θ < 26.32
Data/parameters	1018 / 37	598 / 49

R_1	0.017	0.051
wR_2	0.040	0.118
Goodness-of-fit	1.077	1.087
Diff. peak/hole [e/Å ³]	0.75 / -0.65	2.04 / -2.59

^{a)} Further details of the crystal structure determination may be obtained from Fachinformations-zentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany, by quoting the corresponding depository CSD numbers.

Table 2. Atomic coordinates and atomic displacement parameters for GeP and Sn-doped GeP.^a

GeP					
Atom	x/a	y/b	z/c	s.o.f.	U_{eq}^b or U_{iso}
Ge(1)	0.06997(2)	0	0.09338(3)	1	0.00403(6)
Ge(2)	0.62714(2)	0	0.42764(3)	1	0.00416(6)
Ge(3)	0.74777(2)	0	0.28610(3)	1	0.00414(6)
P(4)	0.65278(4)	0	0.68738(7)	1	0.0048(1)
P(5)	0.65959(4)	0	0.04701(7)	1	0.0046(1)
P(6)	0.03478(4)	0	0.33487(7)	1	0.0048(1)
Ge _{0.93(3)} P _{0.95(1)} Sn _{0.12(3)} ^c					
Ge(1)	0.0681(4)	0	0.0955(5)	0.86(1)	0.0075(6)
Sn(11)	0.0857(15)	0	0.076(2)	0.11(2)	0.0075(6)
Sn(12)	0.035(4)	0	0.138(7)	0.023(4)	0.0075(6)
Ge(2)	0.6294(5)	0	0.4252(5)	0.88(2)	0.0082(6)
Sn(21)	0.665(4)	0	0.385(6)	0.025(4)	0.0082(6)
Sn(22)	0.6102(19)	0	0.444(2)	0.10(2)	0.0082(6)
Ge(3)	0.7466(7)	0	0.2876(8)	0.89(1)	0.0081(6)
Sn(31)	0.767(3)	0	0.261(4)	0.07(2)	0.0081(6)
Sn(32)	0.718(5)	0	0.317(5)	0.04(1)	0.0081(6)
P(4)	0.6520(5)	0	0.6898(7)	0.95(1)	0.012(1)
Ge(4)	0.671(4)	0	0.663(6)	0.05(1)	0.012(1)
P(5)	0.6575(5)	0	0.0481(6)	0.96(1)	0.011(1)
Ge(5)	0.681(4)	0	0.024(6)	0.04(1)	0.011(1)
P(6)	0.0377(5)	0	0.3312(8)	0.93(1)	0.013(1)
Ge(6)	0.021(2)	0	0.352(4)	0.07(1)	0.013(1)

^aAll atomic positions are $4i$ Wyckoff site.

^b U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

^cPrecise determination of atomic occupancies is hampered by the correlation of occupancies with the scale factor. Thus, the actual composition may vary from the occupancies obtained from refinement.

Table 3. Selected interatomic distances in GeP and Sn-doped GeP.^a

Atoms	GeP	Sn-doped GeP
Ge1–Ge1	2.4590(5)	2.435(6)
Ge2–Ge3	2.4460(4)	2.396(13)
Ge1–P5	2.3587(4) x2	2.363(7) x2
Ge1–P6	2.3829(7)	2.309(11)
Ge2–P4	2.3435(7)	2.389(9)
Ge2–P6	2.3519(4) x2	2.344(5) x2
Ge3–P4	2.3453(4) x2	2.365(9)
Ge3–P5	2.3453(4)	2.343(6)
P4–P5	3.2878(9)	3.28(1)
P4–P6	3.3522(8) x2	3.391(9) x2
P5–P5	3.539(1) x2	3.62(1) x2
P6–P6	3.404(1)	3.53(1)

^aFor the Sn-containing compound only distances comparable with those in GeP are shown.

2.3 Differential scanning calorimetry (DSC). GeP and Sn-doped GeP were analyzed with a Netzsch Differential Scanning Calorimeter. DSC measurements were performed on 30 mg of samples sealed inside evacuated and sealed silica ampoules. The samples were heated to 1273 K, cooled to 373 K, heated to 1273 K, and finally cooled to 323 K with a heating/cooling rate of 10 K/min.

2.4 Scanning electron microscopy (SEM). Elemental analysis of selected single crystals of GeP and Sn-doped GeP were carried out on a Hitachi S4100T SEM with energy-dispersive X-ray analysis (EDX) (Oxford INCA energy).

2.5 Quantum chemical calculations. Electronic structure calculations for GeP, including band structure, density of states (DOS), and Electron Localization Function (ELF), were carried out using the tight binding–linear muffin tin orbital–atomic sphere approximation (TB–LMTO–ASA) program.^{14–18} The Barth–Hedin exchange potential was employed for the local density approximation (LDA) calculations.¹⁵ The radial scalar-relativistic Dirac equation was solved to obtain the partial waves. A basis set containing Ge(4s,4p) and P(3s,3p) orbitals was employed for the self-consistent calculation, with downfolded Ge(4d) and P(3d) functions. The density of states and band structure were calculated after convergence of the total energy on a dense k -mesh of $24 \times 24 \times 16$ points with 2414 irreducible k -points. The Electron Localization Function (ELF), η ,^{16–18} was evaluated with the modules implemented within the TB–LMTO–ASA program and visualized with the ParaView program.^{19,20} Bonding analysis was performed for selected atomic pairs using crystal orbital Hamilton population (COHP) analysis implemented in the TB-LMTO-ASA program.²¹ The integrated COHP values were calculated as a measure of relative overlap populations.

2.5 Transport properties. Transport properties were characterized using the commercial Physical Properties Measurement System (PPMS, Quantum Design).

Temperature dependencies of electrical resistivity were measured on single crystals of GeP and Sn-doped GeP by a standard 4-point *ac* technique to exclude resistance of the leads.

3. Results and Discussion

3.1 Synthesis. *Wadsten* first reported the synthesis of GeP using stoichiometric amounts of elements heated in a temperature gradient with the hot end at 1173 K.⁶ Based on X-ray powder diffraction data GeP was assumed to be isostructural to other Si and Ge monpnictides, although no information pertaining to the crystal structure and purity of the product was provided. Additionally, it was mentioned that GeP could be formed from the direct reaction of elements at 1023 K.^{7,8} All of our attempts to reproduce these syntheses failed. Additional attempts to synthesize GeP from elements at a lower temperature of 793 K, below the decomposition temperature of GeP, also failed. Based on our experience with other tetrel monpnictides, we attempted additional temperature gradient reactions using a temperature gradient of 1273 K to 873 K with iodine as a transport agent. Nevertheless these reactions also resulted in unreacted Ge and P as the products.

GeP was obtained as the minor product of the reaction of elemental Ge and P at 1173 K with slow cooling to 773 K. The main products of this reaction were Ge and P, so flux syntheses were attempted. High yields of GeP were observed using Sn as the flux and through slow cooling from high temperatures. Powder XRD shows a small amount of

Ge remained unreacted in the sample, but the primary product was GeP. The use of metal flux, extended annealing at high temperatures, and slow cooling to low temperatures increased the yield and decreased the amount of unreacted Ge left in the reaction product. Single crystal X-ray diffraction in conjunction with elemental analysis by EDX uncovered that Sn partially incorporates into the crystal structure of GeP by substitution of ~10% of Ge atoms. To synthesize pure GeP, Bi flux was used instead of Sn, as no known binary pnictides of Bi are known. Similar success was recently achieved with Bi flux in the syntheses of La-Co arsenides.²²

Both GeP and Sn-doped GeP were resistant against dilute acid treatment. A dilute HCl:H₂O (1:1) solution was sufficient to remove any excess Sn flux. However, Bi was stable against dilute HCl, so a small amount of H₂O₂ was added to remove trace amounts of Bi left after centrifugation.

3.2 Stability of GeP and Sn-doped GeP. According to the Ge-P phase diagram GeP decomposes incongruently at 998 K forming Ge and liquid.²³ This diagram was studied at a pressure of 4.6 MPa to avoid evaporation of phosphorus. The pressure inside evacuated sealed silica ampoules under the reaction condition is definitely lower than 4.6 MPa since those ampoules are only capable of holding pressure up to ~1 MPa. We performed DSC investigations of the stability of GeP (Figure 2a) under our synthetic conditions. GeP was heated inside evacuated sealed silica ampoule for DSC analysis.

Upon heating the broad melting or decomposition peak with an onset at 1025(10) K and maximum at 1080(5) K were observed. This process was probably accompanied with partial evaporation of phosphorus. Upon cooling a sharp crystallization peak was observed at 1017(2) K. According to the phase diagram, the cooling of the melt with composition GeP should result in the crystallization of Ge at 1038 K. We observed GeP and no elemental Ge in the sample after DSC investigation. Thus the evaporation of phosphorus plays an important role in the phase equilibrium in this system.

Difficulties in the synthesis of GeP at temperatures below the reported decomposition temperature ($T < 1000$ K) are due to kinetic factors since at these temperatures Ge is essentially unreactive. Reactions at sustained high temperatures allow Ge to become reactive, but GeP is unstable. Slow cooling from high temperatures, in combination with a metal flux to avoid enrichment of liquid phase with Ge by means of phosphorus evaporation were necessary to synthesize GeP.

Doping of Sn into the GeP structure significantly reduces the stability. Sn-doped GeP melts or decomposes at much lower temperature, 797(2) K (Figure 2b). Additional effects were observed at 880-930 K temperature range. Upon cooling Sn-doped GeP crystallizes at 774(2) K. An additional exothermic peak was observed at 833 K, which corresponds to the crystallization of binary tin phosphide. XRD analysis of the sample after DSC experiment confirmed presence of Sn-doped GeP and tin phosphide.

Figure 2. Thermal behavior of GeP (top) and Sn-doped GeP (bottom) in vacuum.

3.3 Crystal structure of GeP. GeP crystallizes in the GaTe structure type²⁴ in the $C2/m$ (No. 12) space group in a layered crystal structure (Fig. 3). It is isostructural to the known binary tetrel pnictides SiP, SiAs, and GeAs.⁶⁻¹² Within each layer, Ge-Ge pairs are surrounded by six P atoms forming a distorted trigonal antiprism shown as blue and red polyhedra in Figs. 3B and 3D. Each layer consists of edge-sharing Ge_2P_6 antiprisms. The Ge(2)-Ge(3) bonds are perpendicular to the GeP layer while the Ge(1)-Ge(1) bonds are parallel to the GeP layer (Fig. 3C). Thus, the two types of corresponding

antiprisms (blue and red) are orthogonal to each other (Fig. B). The layers stack through lone-pair interactions between the P atoms that confine the layer. Each phosphorus atom is pointed towards the triangle of phosphorus atoms from the adjacent layer (Fig. 3C). The shortest P-P distances are 3.29-3.35 Å and the interlayer spacing is 2.3 Å.

Figure 3. Crystal structure of GeP represented with a ball-and-stick model and with polyhedra. (A) Stacking of GeP layers with the unit cell shown in red; (B) side view of a single layer with a ball-and-stick model and with polyhedra; (C) fragment showing the Ge pairs and selected interlayer distances; (D) top view of a single layer in a ball-and-stick model and with polyhedra. Ge: black, P: yellow, Ge(1)-Ge(1) pairs: red polyhedra, Ge(2)-Ge(3) pairs: blue polyhedra.

Each Ge atom is coordinated by 3 P atoms and 1 Ge atom while each P atom is coordinated by 3 Ge atoms. The Ge-P bond distances found in GeP, 2.34-2.38 Å, are within the range of Ge-P distances in other Ge- and P-containing compounds. This distance is similar to the Ge-P distances found in the transition metal germanium phosphide, $\text{Ag}_3\text{Ge}_3\text{Sn}_2\text{P}_6$ (2.34 Å).²⁵ The Ge-P distances in GeP are slightly larger than those found in alkali metal germanium phosphides, such as Cs_5GeP_3 (2.27-2.28 Å)²⁶ and Rb_5GeP_3 (2.24-2.28 Å)²⁷, and are slightly smaller than those found in the clathrates $\text{Ge}_{38}\text{P}_8\text{Br}_8$ and $\text{Ge}_{38}\text{P}_8\text{I}_8$ (2.40 Å and 2.43 Å, respectively).²⁸ The Ge-P framework is quite flexible and may exhibit a wide range of distances as was recently demonstrated by the Ge-P-Te semi-clathrates where Ge-P distances vary in the range of 2.28-2.43 Å within the same framework.²⁹

Two high-pressure modifications of GeP were reported.^{30,31} In both modifications no Ge-Ge bonds are present and Ge atoms are surrounded only by P atoms. The Ge-P bonds in the high-pressure (hp) modifications are longer than those found in the ambient modification of GeP. Cubic hp-GeP crystallizes in the sphalerite structure type with a Ge-P distance of 2.42 Å.³¹ In the crystal structure of the tetragonal hp-GeP modification, each Ge atom is coordinated by a square-pyramid of five P atoms with four equatorial distances of 2.54 Å and one axial distance of 2.38 Å.³⁰

SEM imaging shows the GeP crystal morphology as stacks of sheets (Fig. 4). Elemental analysis with EDX of GeP crystals synthesized from bismuth flux resulted in

the composition $\text{Ge}_{1.01(1)}\text{P}_{0.99}$, which is in good agreement with the crystal structure solution (Tables 1 and 2). No traces of Bi were detected in the crystals of GeP. For the crystals produced from tin flux, a significantly different composition was observed, $\text{Ge}_{48(2)}\text{P}_{49.3(6)}\text{Sn}_{3(1)}$, indicating that a portion of Ge atoms was replaced with Sn. This assumption was further confirmed with single crystal X-ray diffraction analysis.

Figure 4. SEM micrographs and corresponding EDX spectra of GeP (left) and Sn-doped GeP (right).

3.4 Crystal structure of Sn-doped GeP. Several crystals were selected from the GeP samples grown from tin flux. Refinement of those crystals with the structural model determined for GeP converged to high R-values (~8%), very large anisotropic displacement parameters for all atoms with $U_{11}/U_{33} > 4$, and high difference electron

density peaks on the level of 5-7 e/Å³. Isotropic refinement reveals large difference electron density peaks in the vicinity (closer than 1 Å) of all Ge positions. Those peaks were refined as Sn atoms taking into account the results of EDX analysis. The atomic coordinates of Ge and Sn were unconstrained, while the isotropic displacement parameters were kept equal for the Ge and Sn split positions. The total occupancy of each set of split positions was fixed to be 100%. At the next stage of refinement, large difference electron density peaks in the vicinity (closer than 1 Å) of all P positions were found on the difference electron density map. Since the Sn-P distances are larger than Ge-P distances, it is reasonable that the displacement of Sn atoms would introduce displacements in the surrounding P atoms. The shortest Sn-P distance reported is 2.44 Å in Ba₃Sn₂P₄,³² while on average these distance are in the range of 2.55-2.65 Å in binary and ternary tin phosphides.³³⁻⁴⁴ Independent refinement of all split positions for P atoms with the only constraint of equal isotropic displacement parameters resulted in occupancy greater than 100% for each P position. This indicates that Ge may be present in the phosphorus positions. Examples of joint occupancy of the same or two split atomic positions by Ge and P are known in the crystal structures of Cu-, Ni-, Mn- and Fe-containing ternary germanium phosphides.⁴⁵⁻⁴⁸ Such structural features are essential for the magnetocaloric and thermoelectric properties of ternary phosphides. Thus, in the final stage of refinement each phosphorus position was treated as a split position of P+Ge with a total occupancy of 100%. The constraints were required to avoid significant

correlations with the scale factor since every atomic position is split and occupied by atoms of different nature. Anisotropic refinement of this model was unstable due to the numerous positions in close proximity to each other. The final isotropic refinement for all atoms converged to an R -value of 5.1% and composition of $\text{Ge}_{0.93(3)}\text{P}_{0.95(1)}\text{Sn}_{0.12(3)}$, which is close to the composition $\text{Ge}_{0.91(3)}\text{P}_{0.95(1)}\text{Sn}_{0.06(3)}$ determined by EDX analysis if normalized to 0.95 P atoms. We consider this structural model an approximation of the crystal structure of Sn-doped GeP anticipating that the real structural arrangement may be more complex.

Figure 5. Crystal structure of Sn-doped GeP. Main Ge atoms: black; P: yellow; Sn: red; Ge atoms substituting P atoms: blue. The shortest interlayer Ge-Ge distances are shown as blue dashed lines. Note that the occupancies of red and blue atoms do not exceed 14%.

In the crystal structure of $(\text{Ge}_{0.88}\text{Sn}_{0.12})(\text{P}_{0.95}\text{Ge}_{0.05})$ regular Ge atoms (Ge(1), Ge(2), and Ge(3) (shown in black in Fig. 5) together with phosphorus atoms (shown in yellow in Fig. 5) form Ge-P layers similar to those present in the prototype GeP. Bond distances

between those atoms are also similar to bond distances in pristine GeP (Table 3). Occupancies for these atomic positions are in the range of 86-95%. Partial substitution of Ge for Sn results in the elongation of metal-metal bonds and displacement of the surrounding P and Ge atoms. Detailed analysis of the local coordination of Sn atoms is hampered by the presence of multiple partially occupied positions. Similar severe disorder with multiple partially occupied positions is present in the crystal structure of the Zn_4Sb_3 thermoelectric material.⁴⁹ Disorder due to partial occupancies or several competing structural arrangements is also common for tin pnictides. Two out of the four known binary tin phosphides, Sn_3P_4 and SnP , are highly disordered.^{33,35} Some degree of disorder is also present in ternary tin-phosphorus compounds.^{39-44,50} $(\text{Ge}_{0.88}\text{Sn}_{0.12})(\text{P}_{0.95}\text{Ge}_{0.05})$ was produced from samples containing an excess of tin and probably represents the Sn-rich composition within the homogeneity range of Sn-substituted GeP.

One important feature of the crystal structure of $(\text{Ge}_{0.88}\text{Sn}_{0.12})(\text{P}_{0.95}\text{Ge}_{0.05})$ is that the Ge atoms located in the vicinity of P positions that confine the layers are pushed further into the interlayer space (blue atoms in Fig. 5). These atoms form relatively short bonds (2.88-2.92 Å) with similar Ge atoms from the adjacent layer, which are shown as blue dashed lines in Fig. 5. These distances are significantly longer than the covalent Ge-Ge bond, but are also significantly shorter than the non-bonding P-P interlayer distances of 3.3 Å. Thus, weak bonds are formed between the layers of Sn-doped GeP. More detailed

analysis of the local structure with spectroscopic methods such as ^{119}Sn and ^{31}P solid-state NMR spectroscopy, ^{119}Sn Mössbauer spectroscopy, and transmission electron microscopy is required to fully understand the structure of Sn-doped GeP.

Figure 6. Band structure and density of states (DOS) for GeP.

3.5 Electronic structure. GeP is expected to exhibit semiconducting properties. Ge atoms attain a closed shell electron configuration by forming four covalent bonds, while P atoms form three covalent bonds and an electron lone pair. Band structure calculations confirmed that GeP is a semiconductor with an indirect band gap of 0.52 eV

(Fig. 6). Ge and P have similar contributions to the states across the studied energy range.

ELF analysis confirmed the expected bonding model: each phosphorus atom forms three covalent bonds (attractors ①) and has an electron lone pair (attractors ②) (Fig. 7A). The lone pair of each P atom is directed towards the triangle of the electron lone pairs of P atoms from an adjacent layer. The ELF slice across two phosphorus atoms from adjacent layers (Fig. 7B) clearly shows a minimum of the localized electron density distribution between the P atoms indicating that there are no covalent bonds between the layers.

There are ELF maxima between the Ge-Ge pairs indicating the presence of covalent bonds between Ge atoms (Figs. 7C and 7D). The ELF maximum ③ between the Ge(1)-Ge(1) pair is centered across the bond (Fig. 7C), however the ELF maximum ④ between the Ge(2)-Ge(3) pair is slightly shifted from the bond center (Fig. 7D). The shift from the center of the Ge(2)-Ge(3) bond may be caused by distortions from the ideal tetrahedral angle. While the $\angle\text{P-Ge(1)-Ge(1)}$ angles (109.6° and 109.0°) are close to the ideal tetrahedral angle, the local coordination of the other two types of Ge atoms are more distorted with $\angle\text{P-Ge(2)-Ge(3)}$ and $\angle\text{P-Ge(3)-Ge(2)}$ angles of 105.3° , 123.3° , and 118.6° . Similar shifts of the ELF maxima from the line connecting two strained phosphorus atoms was recently observed in P_7^{3-} clusters.⁵¹

Figure 7. (A) 3D isosurfaces of the Electron Localization Function ($\eta = 0.82$) for the two layer fragment of the GeP crystal structure. ELF slices across the (B) GeP layers; (C) Ge(1)-Ge(1) pair; (D) Ge(2)-Ge(3) pair.

Crystal orbital Hamilton population (COHP) calculations were performed for GeP for additional bonding analysis.²¹ The COHP curves for the different types of interactions in GeP are shown in Figure 8. COHP analysis shows that the Ge-Ge and Ge-P interactions display the expected bonding characteristics below the Fermi energy and antibonding

characteristics above the Fermi energy. The Ge(1)-Ge(1) pair has a larger integrated COHP value in comparison to the Ge(2)-Ge(3) pair, 2.83 eV/cell·mol and 1.90 eV/cell·mol, respectively. This is in agreement with ELF results which also indicate the difference in Ge(1)-Ge(1) and Ge(2)-Ge(3) bonds. All Ge-P pairs showed similar characteristics so one representative pair is shown in Fig. 8.

Figure 8. Top: -COHP curves for interactions within the layers across Ge-Ge and Ge-P bonds. Bottom: -COHP curves for interactions across the layers in GeP for the shortest P-P distances.

COHP analysis for P-P interlayer interaction is also in agreement with the ELF results. COHP showed strong antibonding characteristics of P-P interactions below the Fermi energy together with small negative integrated COHP values (Fig. 8, bottom). Bonding analysis by means of ELF and COHP confirmed that GeP indeed has a layered 2D structure with weak interactions between the layers.

Bonding analysis for Sn-doped GeP cannot be performed due to the significant degree of disorder in this compound. The substitution of Sn for Ge is isoelectronic and should not affect the charge carrier concentration. In turn, the substitution of Ge for P is not isoelectronic and expected to depopulate the conduction band since Ge has a smaller number of valence electrons compared to P. This should result in metallic properties and a decrease in the electrical resistivity. Contrary to this argument the severe disorder present in Sn-doped GeP may scatter charge carriers and result in an increase in resistivity compared to GeP due to Anderson localization.⁵²⁻⁵⁵ For example, disordered tin phosphide, Sn_3P_4 , exhibits significantly larger resistivity compared to Sn_4P_3 .^{33,56} To verify the effect of tin substitution we characterized the resistivity of GeP and Sn-doped GeP single crystals.

3.6 Transport properties. Electrical resistivity measurements for GeP confirm the semiconducting nature predicted by electronic structure calculations (Fig. 9). EDX was performed on the crystals prior to the electrical resistivity measurements to confirm that no Bi was present. Several single crystals were measured and all of them exhibit

overlapping normalized $\rho(T)/\rho(300\text{ K})$ dependences. The room temperature values of resistivity for GeP vary in the range of 20-60 m Ω ·cm. Small variations in the values of resistivity are probably due to uncertainties in the geometric characteristics (thickness) of the measured crystals.

Semiconducting behavior was also found for the Sn-doped GeP (Fig. 9). Similar to pristine GeP, several single crystals were measured and all of them exhibit overlapping normalized $\rho(T)/\rho(300\text{ K})$ dependences. The Sn-doped compound exhibits resistivity values (500-1500 m Ω ·cm at room temperature) that are orders of magnitude larger than the resistivity of pristine GeP. Moreover, the steep increase of the resistivity below 250 K was observed, unlike for pristine GeP. The semiconducting properties of the Sn-doped compound can be rationalized by formation of weak Ge-Ge bonds across the layers (see Fig. 5). Another mechanism for the increased resistivity can be explained by Anderson localization where large amounts of structural disorder cause localization of the charge carriers.⁵²⁻⁵⁵

Figure 9. Electrical resistivity for crystals of GeP (red) and Sn-doped GeP (black).

4. Conclusion.

The synthesis, crystal structure, chemical bonding and physical properties of layered germanium and germanium-tin phosphides were explored. The GeP layer is made of Ge dumbbells surrounded by a distorted antiprism of phosphorus atoms. GeP layers are held together by weak lone pair – lone pair interactions and can be easily cleaved. Sn is able to substitute ~10% of Ge atoms forming a ternary germanium-tin phosphide preserving the general structural motif of GeP. However, the incorporation of tin is accompanied by strong disorder emphasized by the splitting of all atomic positions and the formation of relatively short Ge-Ge interatomic distances between the layers. This

results in a significant decrease in the thermal stability of Sn-doped GeP. GeP and Sn-doped GeP exhibit semiconducting behavior. Investigation of the thermoelectric properties and exfoliation of GeP into a 2D material are currently underway.

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