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# Synthesis and Structure of a Nonstoichiometric Zr<sub>3.55</sub>Pt<sub>4</sub>Sb<sub>4</sub> Compound

Sheng Li,<sup>†</sup> Xiaoyuan Liu,<sup>†</sup> Maurice Sorolla, II,<sup>‡</sup> Gregory T. McCandless,<sup>§</sup> Hanlin Wu,<sup>†</sup><sup>®</sup> Huifei Zhai,<sup>†</sup> Julia Y. Chan,<sup>§</sup><sup>®</sup> and Bing Lv<sup>\*,†</sup><sup>®</sup>

<sup>†</sup>Department of Physics, The University of Texas at Dallas, Richardson, Texas 75080, United States

<sup>‡</sup>Department of Chemistry, University of Houston, Houston, Texas 77204, United States

<sup>§</sup>Department of Chemistry and Biochemistry, The University of Texas at Dallas, Richardson, Texas 75080, United States

Supporting Information

**ABSTRACT:** A nonstoichiometric ternary antimonide, Zr<sub>355</sub>Pt<sub>4</sub>Sb<sub>4</sub>, with a new structure type (hP24), has been synthesized via arc-melting. Its crystal structure was determined by single-crystal X-ray diffraction with hexagonal space group P63/mmc and lattice parameters a = 4.391(3) Å, c = 30.53(2) Å, and V = 509.7(8) Å<sup>3</sup>. It features the unique  $Pt_4Sb_4$  slab with Pt-Pt bonds and is reminiscent to hexagonal diamond substructures. Three different Zr atoms, occupying three different sites, aid in the closepacking of the Pt and Sb atoms. Electronic structure calculations show the half occupancy of one Zr site creates a pseudogap at the Fermi level and optimizes the Pt-Sb bonding interactions. This enhances the electronic stability and accounts for the very narrow phase width observed for this nonstoichiometric compound. Furthermore, strong Zr-Pt and Zr-Sb interactions play a crucial role in the chemical bonding of the title compound. Electrical transport measurements show metallic behavior of this compound down to 2 K, consistent with the band structure calculations.



#### 1. INTRODUCTION

Since the discovery of the unconventional superconductivity in the iron pnictide compounds<sup>1-5</sup> topological  $Bi_{1,-x}Sb_x^{-6}$  and Weyl semimetal in the TaAs,<sup>7-12</sup> the study of transition metal pnictides has made a tremendous impact over the last 10 years.<sup>13–17</sup> Considering the ternary Pt-based pnictide phases, which coupled with remarkable structure diversity and bonding features, a wide variety of interesting electronic, magnetic, thermoelectric, and superconducting properties<sup>18-26</sup> have also been realized. Given the rich structural features of Pt-based compounds, i.e, honeycomb lattices in BaPtSb and SrPtAs,<sup>27</sup> tetrahedra in the Li<sub>2</sub>PtSb<sup>28</sup> and REPtSb<sup>29,30</sup> square nets in the K<sub>2</sub>PtAs<sub>2</sub><sup>31</sup> and Rb<sub>2</sub>PtAs<sub>2</sub><sup>32</sup> square pyramids in DyPt<sub>8</sub>P<sub>2</sub><sup>33</sup> trigonal prism in SrPt<sub>6</sub>P<sub>2</sub><sup>24</sup> and anti-perovskite in SrPt<sub>3</sub>P<sup>22,23</sup> and  $\operatorname{SrPt}_{10}P_4$ ,<sup>25</sup> it is reasonable to believe that a different structure type other than a filled Mn<sub>5</sub>Si<sub>3</sub>-type structure may form in the electron-rich group IV ternary pnictide system. In fact, only a few compounds in the (Ti, Zr, Hf)-Pt-Pnictide systems are known thus far, which are mainly stabilized as an interstitial-stabilized hexagonal Mn<sub>5</sub>Si<sub>3</sub>-type structure.<sup>34,35</sup> The only systematical phase investigation for these series thus far is in the Zr-Pt-Sb ternary system back in 2007,<sup>34</sup> where several new compounds are reported, but no further studies are carried out. Structurally, both the size and valence of the cation affect the crystal structures of the Pt-based compounds significantly. For example, the isoelectronic Li<sub>2</sub>PtSb<sup>28</sup> and BaPtSb (SrPtSb)<sup>27</sup> have distinguishable coordination environments: tetrahedra for Heusler Li<sub>2</sub>PtSb and honeycomb lattice in

BaPtSb (SrPtSb). The REPtSb (RE = rare earth) compounds,<sup>29,30</sup> with one more additional electron, on the other hand, adopt completely different structures depending on their cation sizes. The early lanthanides crystallize the modified CaIn<sub>2</sub>-type structure, and the smaller ones adopt a half-Heusler MgAgAs-type structure. With our interest to study the influence of size and electron count on the stability of group IV based intermetallics such as Zr and Hf Pt-pnictides, we report the synthesis, structural investigation, chemical bonding, and electrical transport measurements of a new nonstoichiometric ternary Pt-based antimonide Zr<sub>3.55(2)</sub>Pt<sub>4</sub>Sb<sub>4</sub> crystallizing in a unique structure type (hP24).

#### 2. EXPERIMENTAL SECTION

2.1. Material Synthesis. The starting materials used were Zr pieces (99.9%), Pt pieces (99.95%), and Sb shots (99.999%). The sample has been prepared through arc-melting on a water-cooled copper hearth inside an arc furnace under an argon-filled atmosphere with a Zr-gas-getter. Different Zr:Pt molar ratios ranging from 3:4 to 4:4 have been used, and the 3.5:4.0 ratio yielded the best quality of samples. Typically, 5% excess Sb was added to the starting materials to compensate for its evaporative losses during arc-melting. During the arc-melting process, the melted ball-shaped sample was flipped and re-arc-melted several times to ensure homogeneity. The shinning and metallic product formed is stable in air, and crystals up to 2 mm in size were obtained after crushing the sample and were used for the subsequent single-crystal diffraction and resistivity measurements.

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The attempts to synthesize the isotypic Ti- and Hf-based analogues are unsuccessful, implying the atom size might also play an important role for stabilizing the structure.

**2.2.** X-ray Crystallography. Phase identification and crystal structure were determined by single-crystal X-ray diffraction. Single crystals were cut to appropriate sizes from larger crystals and mounted to glass fibers with two-part epoxy. The fibers were mounted on a Bruker D8 Quest Kappa single-crystal X-ray diffractometer equipped with a Mo K $\alpha$  I $\mu$ S microfocus source ( $\lambda = 0.71073$  Å) operating at 50 kV and 1 mA with a HELIOS optic monochromator and a CMOS detector. The collected data set was integrated with Bruker SAINT and scaled with Bruker SADABS (multiscan absorption correction).<sup>36</sup> A starting model was obtained using the intrinsic phasing method in SHELXT,<sup>37</sup> and atomic sites were refined anisotropically using SHELXL2014.<sup>38</sup> Crystallographic parameters and refinement details for Zr<sub>3.55(2)</sub>Pt<sub>4</sub>Sb<sub>4</sub> are provided in Table 1. Atomic coordinates,

Table 1. Crystallographic Data for Zr<sub>3.55(2)</sub>Pt<sub>4</sub>Sb<sub>4</sub>

·····	7. Dt Cl
empirical formula	$Zr_{3.55(2)}Pt_4SD_4$
temperature	298 K
wavelength	0.71073 Å
space group	<i>P6</i> <sub>3</sub> / <i>mmc</i> (No. 194)
unit cell dimensions	a = 4.391(3) Å, $c = 30.53(2)$ Å
volume	509.7(8) Å <sup>3</sup>
Ζ	2
absorption coefficient	68.44 mm <sup>-1</sup>
F(000)	1316
crystal size	$0.04 \times 0.04 \times 0.14 \text{ mm}^3$
heta range for data collection	2.7-30.6°
reflections collected	6230
independent reflections	369 [R(int) = 0.050]
max. and min. transmission	0.746 and 0.287
refinement method	full-matrix least-squares on $F^2$
data/restraints/parameters	369/0/22
goodness-of-fit on F <sup>2</sup>	1.338
final R indices $[I > 2\sigma(I)]$	R1 = 0.0247, wR2 = 0.0723
R indices (all data)	R1 = 0.0282, wR2 = 0.0738
extinction coefficient	0.0038(3)
largest diff. peak and hole	2.538 and $-2.034 \text{ e}\cdot\text{\AA}^{-3}$

anisotropic displacement parameters, and occupancies are included in Table 2. Selected interatomic distances are provided in Table 3, and selected interatomic angles are provided in the Supporting Information Table S1. Integrated precession images along different planes are also shown in Figure S1, where the green circles indicate the indexed Bragg reflections. No indication of a superstructure is observed in the title compound. Powder X-ray diffraction measurements were collected from  $5^{\circ} < 2\theta < 90^{\circ}$  on the Rigaku Smartlab Diffractometer.

It is worthwhile to mention that the possibility of the Wyckoff 2a site is partially occupied by a Pt atom rather than a Zr3 atom has also been investigated. Arbitrarily assigning Pt atoms in the Zr3 position will result in the further reducing of the occupancy to ~25%, but a

Table 3. Selected Interatomic Distances for Zr<sub>3.55(2)</sub>Pt<sub>4</sub>Sb<sub>4</sub>

distance	(Å)	distance (Å)		
Zr1—Pt1 (×6)	2.886 (2)	Zr3—Pt2 (×2)	2.703 (2)	
Zr1—Sb1 (×6)	3.338 (2)	Zr3—Sb2 (×6)	2.967 (2)	
Zr2—Pt2 (×3)	2.671 (2)	Pt1—Sb1 (×3)	2.656 (2)	
Zr2—Pt1 (×1)	2.709 (3)	Pt1—Pt1 (×1)	2.757 (2)	
Zr2—Sb1 (×3)	3.178 (2)	Pt2—Sb1 (×1)	2.758 (2)	
Zr2—Sb2 (×3)	3.231 (2)	Pt2—Sb2 (×3)	2.789 (2)	

significant increasing of  $U_{\rm eq}$  from 0.0157(18) Å<sup>2</sup> to 0.0204(19) Å<sup>2</sup>. Together with the band structure calculations discussed later, we believe our model best represents the actual structure of the compound.

2.3. Electronic Band Structure Calculations. Electronic structure calculations were performed using two different methods: (1) Stuttgart TB-LMTO-ASA program employing the tight-binding (TB) version of the linear muffin-tin orbital (LMTO) method<sup>39</sup> in the atomic sphere approximation (ASA); (2) full-potential linearized augmented plane wave (FP-LAPW) method as implemented in the WIEN2k code.<sup>40</sup> For the LMTO method, the Barth-Hedin local exchange correlation potential was implemented.<sup>41</sup> Radii of the atomic spheres and interstitial empty spheres were obtained as implemented in the TB-LMTO-ASA program. The tetrahedron method was selected for the k-space integration.<sup>42</sup> The calculations utilized as basis sets for: Zr 5s/(5p)/4d/(4f); Pt 6s/6p/5d/(5f); and Sb 5s/5p/(5d) (downfolded orbitals in parentheses).<sup>43</sup> Reciprocal space integrations were performed using 305 irreducible k-points. The chemical bonding analysis was investigated using the crystal orbital Hamilton population (COHP)<sup>44</sup> technique as implemented in the TB-LMTO-ASA 4.7 program package. For the WIEN2k method, the exchange and correlation energies were treated within the density functional theory (DFT) using the Perdew-Burke-Ernzerhof generalized gradient approximation (GGA).45 The muffin-tin radius (R<sub>MT</sub>) values 2.34, 2.50, and 2.38 au were used for Zr, Pt, and Sb, respectively. The self-consistencies were carried out using 1000 kpoints  $(10 \times 10 \times 10 \text{ mesh})$  in the irreducible Brillouin zone. The computational results from both methods are compared and consistent with each other.

#### 3. RESULTS AND DISCUSSION

**3.1. Structure and Description.** The title compound  $Zr_{3.55(2)}Pt_4Sb_4$  crystallizes in a new structure type (*hP24*) in the centrosymmetric hexagonal space  $P6_3/mmc$  with lattice parameters a = 4.391(3) Å and c = 30.53(2) Å. It features two  $Pt_4Sb_4$  slabs within the unit cell that are related by inversion symmetry (Figure 1) and stacked along the crystallographic *c*-axis. As provided in Table 2, there are two crystallographic sites each for the Pt [Pt1 (4*f*), Pt2 (4*e*)] and Sb [Sb1 (4*e*), Sb2 (4*f*)] atoms. The Pt1 atoms, located in the middle of the slab, are tetrahedrally coordinated to one Pt1 and three Sb1 atoms, while the Pt2 atoms are linked to one Sb1 and three Sb2 atoms, yielding the tetrahedral (Pt2)(Sb1)-

Fable 2. Atomic Coordinates ar	d Equivalent	Isotropic Disp	lacement Parameters	$(U_{eq})$	) of Zr <sub>3.55(2)</sub> Pt <sub>4</sub> Sb <sub>4</sub>
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atom	Wyckoff site	point symm.	x	у	z	occ.	$U_{\rm eq}^{\ a}$ (Å <sup>2</sup> )
Zr1	2 <i>c</i>	$\overline{6}m2$	1/3	2/3	1/4	1	0.0047(5)
Zr2	4 <i>f</i>	3 <i>m</i>	2/3	1/3	0.11610(6)	1	0.0048(4)
Zr3	2 <i>a</i>	$\overline{3}m$	0	0	0	0.547(16)	0.0157(18)
Pt1	4 <i>f</i>	3 <i>m</i>	2/3	1/3	0.20484(2)	1	0.0049(2)
Pt2	4 <i>e</i>	3 <i>m</i>	0	0	0.08853(2)	1	0.0054(2)
Sb1	4e	3 <i>m</i>	0	0	0.17888(4)	1	0.0047(3)
Sb2	4 <i>f</i>	3 <i>m</i>	1/3	2/3	0.05047(4)	1	0.0085(3)

 ${}^{a}U_{eq}$  is defined as one-third of the trace of the orthogonalized  $U_{ii}$  tensor.



**Figure 1.** (a) Ball-and stick representation of the unit cell of  $Zr_{3.55(2)}Pt_4Sb_4$ . The interactions between Zr and other atoms are intentionally omitted for clarity. (b) Stacking sequence of the "PtSb layers" in the  $Pt_4Sb_4$  slab, in comparison with that of (c) the PtSb layers in the modified CaIn<sub>2</sub>-type NdPtSb. The "interlayer" Pt–Pt and Pt–Sb bonds in (b) are emphasized. The dotted lines in (c) denote nonbonding interactions.

 $(Sb2)_3$  building units. Within the slab are Sb1 atoms which are tetrahedrally connected to one Pt2 and three Pt1 atoms, forming the Sb1(Pt2)(Pt1)<sub>3</sub> building units. In contrast, the terminating Sb2 atoms are joined to three Pt2 atoms. Three Sb1(Pt2)(Pt1)<sub>3</sub> units corner-share a Pt1 atom, giving the inner Sb1(Pt2)(Pt1)<sub>3/3</sub> backbone. In a similar manner, the outer Pt2(Sb1)(Sb2)<sub>3/3</sub> backbone is constructed thru corner-sharing of Sb2 atoms in the (Pt2)(Sb1)(Sb2)<sub>3</sub> units. The Sb1(Pt2)-(Pt1) and Pt2(Sb1)(Sb2) backbones condense to form the Pt1(Pt2)(Sb1)(Sb2) mini-slab. The top and bottom mini-slabs are joined together by Pt1-Pt1 bonding, thus generating the (Pt1-Pt1)(Pt2)<sub>2</sub>(Sb1)<sub>2</sub>(Sb2)<sub>2</sub> slab.

The Pt<sub>4</sub>Sb<sub>4</sub> slab, to a certain extent, is reminiscent of the PtSb layers in the modified CaIn2-type NdPtSb.<sup>29</sup> However, there are several differences between these two Pt-Sb structures. As can be seen in Figure 1b,c, the stacking pattern of the PtSb layers in the Nd-phase is ...ACAC..., whereas that of the four "PtSb layers" in the Pt<sub>4</sub>Sb<sub>4</sub> slab is *ABB'A'*. Note the (') symbol denotes mirror-plane symmetry relationships. Since the interlayer Pt...Sb contact [3.550(4) Å] is quite long, there are no bonds within the adjacent PtSb layers in NdPtSb. In contrast, bonding interactions are present between the four neighboring "PtSb layers" in Zr<sub>3.55(2)</sub>Pt<sub>4</sub>Sb<sub>4</sub>, thus forming the  $Pt_4Sb_4$  slab. The A layer [(Pt2)(Sb2)] is bridged to the B layer [(Pt1)(Sb1)] by Pt2–Sb1 bonds. Unlike the A and C layers in NdPtSb, the stacking of the neighboring layers in the Zr<sub>3.55(2)</sub>Pt<sub>4</sub>Sb<sub>4</sub> structure is related by mirror symmetry. The adjacent A and B layers, A' and B' layers are stacked in a staggered fashion akin to a zinc-blend structure which is derived from the cubic diamond, while the B and B' layers are stacked together in an eclipse manner, similar to the structure of hexagonal diamond (modified wurtzite-type structure). Consequently, this unique packing creates six-membered rings that are in a boat configuration and a Pt1-Pt1 bonding between two adjacent (Pt1)(Sb1) layers. The Pt1-Pt1 separation [2.757(2) Å] is a typical single Pt-Pt covalent bond.<sup>46</sup> All the Pt–Sb bonds in  $Zr_{3.55(2)}Pt_4Sb_4$  [2.656(2) Å for Pt1-Sb1, 2.758(2) Å for Pt2-Sb1, and 2.789(2) Å for Pt2-Sb2] are comparable with those in NdPtSb [2.6457(8) Å],<sup>29</sup> and the half-Heusler compounds Li<sub>2</sub>PtSb [2.706(2) Å]<sup>28</sup> and YPtSb [2.8016(9) Å].<sup>27</sup> However, these are longer than those

in the isotypic compounds SrPtSb [2.600(2) Å] and BaPtSb [2.618(2) Å] with the honeycomb  $AlB_2$ -structure type.<sup>27</sup> The shortest interslab distance is between the terminal Sb2 atoms [3.990(3) Å], and the Pt–Sb–Pt and Sb–Pt–Sb angles moderately deviate from the ideal 109.5° angle expected for a regular tetrahedron (Table S1 in the Supporting Information).

The formation of the  $Pt_4Sb_4$  slab through stacking and condensation of the  $PtSb_4$  and  $SbPt_4$  tetrahedra and the Pt-Ptbonding create three unique vacancy sites in the structure which allow the occupancy of Zr atoms. The first site (2*c*) lies in the hexagonal packing of the Pt and Sb atoms, where the Zr1 atoms sit in the center coincidently formed by  $Pt_6$  and  $Sb_6$ trigonal prisms, as shown in the Figure 2a. The Zr1-Pt1



**Figure 2.** Coordination environment around the three different Zr atoms with surrounding Pt and Sb atoms. Thermal ellipsoids are represented at 90% probability.



**Figure 3.** Three models representing different Zr3 occupancies in the crystal structure: (a) Zr3 = 0% ( $Zr_3Pt_4Sb_4$ ,  $72e^-$  per formula unit), (b) Zr3 = 100% ( $Zr_4Pt_4Sb_4$ ,  $76e^-/f.u.$ ), and (c) Zr3 = 50% ( $Zr_3_5Pt_4Sb_4$ ,  $74e^-/f.u.$ ). For (c), a  $2 \times 2 \times 1$  supercell has been employed. The other atoms have been omitted for clarity. Density of states (DOS) plots for (d)  $Zr_3Pt_4Sb_4$ , (e)  $Zr_4Pt_4Sb_4$ , and (f)  $Zr_{3.5}Pt_4Sb_4$  models calculated using TB-LMTO-ASA. The Fermi level ( $E_F$ ) is set at 0 eV. Dotted lines denote various total electron counts.

distance is 2.886(2) Å, while the Zr1–Sb1 distance is 3.338(2) Å. Both Zr1(Pt1)<sub>6</sub> and Zr1(Sb1)<sub>6</sub> trigonal prisms are edgeshared along the *ab* plane. The ZrSb<sub>6</sub> trigonal prisms have Sb– Zr–Sb bond angles less than 1° deviation from the ideal angles (Table S1 in the Supporting Information). In contrast, due to the formation of Pt–Pt bonds, ZrPt<sub>6</sub> trigonal prisms are more compressed along the *c*-axis direction and have significant deviations from the ideal angles.

The second interstitial site (4*f*), occupied by Zr2 atoms, is formed as a combination of the distorted octahedral site by six surrounding antiprismatic Sb<sub>6</sub> atoms, and the tetrahedra site by four surrounding Pt<sub>4</sub> atoms (Figure 2b). The Zr2(Pt1)(Pt2)<sub>3</sub> tetrahedra are corner-shared with each other through Pt2 atoms along the *ab* plane. The Zr2(Sb1)<sub>3</sub>(Sb2)<sub>3</sub> octahedra are slightly distorted (Table S1 in the Supporting Information) and have a tilt angle from the *c*-axis of ~52°. Comparing to the octahedral coordination of the Zr1 atom, the Zr2–Pt1 [2.709(3) Å] and Zr2–Pt2 [2.672(2) Å] distances are slightly shorter under tetrahedral conditions as expected.

The third interstitial site (2a), occupied by Zr3 atoms, is also a distorted octahedra site created by six  $Sb_6$  atoms (Figure 2c). These  $ZrSb_6$  octahedra are tilted from the *c*-axis by ~58.7° and also distorted from ideal orthogonal Sb-Zr-Sb by approximately 5.5° (Table S1 in the Supporting Information). Meanwhile, Zr3 atoms are linearly connected to two Pt2 atoms along the c-axis. The Zr3-Sb2 distance is 2.967(2) Å, while the distance between Zr3 and the adjacent Pt atoms is 2.703(2) Å. Interestingly, if all of the three interstitial sites are fully occupied by Zr atoms, an equiatomic Zr<sub>4</sub>Pt<sub>4</sub>Sb<sub>4</sub> compound will be formed. Although Zr1 and Zr2 sites are fully occupied, the occupancy at the Zr3 site is only 0.55(2), resulting in a nonstoichiometric Zr<sub>3,55(2)</sub>Pt<sub>4</sub>Sb<sub>4</sub> with a new structure type. The Zr-Pt distances in this new Zr<sub>3.55(2)</sub>Pt<sub>4</sub>Sb<sub>4</sub> compound are also comparable with the Zr-Pt distances in the  $Zr_6PtSb_2$  [2.697(3) Å] and  $Zr_5Pt_{0.7}Sb_3$  [2.7204(7) Å].<sup>34</sup>

**3.2. Discussion.** Several questions are considered naturally upon our understanding of the crystal structure of  $Zr_{4-x}Pt_4Sb_4$ : (1) What is the phase stability and range of *x*? Could we make compounds with different *x* ranging from  $Zr_3Pt_4Sb_4$  (where Zr3 site is not occupied), to  $Zr_4Pt_4Sb_4$  (where Zr3 site is fully

occupied)? (2) Could these three vacancy sites be selectively occupied? Would it be possible to synthesize the compounds with only one Zr position (Zr1, Zr2, or Zr3) or a combination of two sites occupied? In other words, how important and what are the roles of different Zr atoms to stabilize the structure? (3) Could Zr atoms be replaced by other transition metal ions such as Cu and Zn and form isostructural compounds as Zr<sub>4-x</sub>Pt<sub>4</sub>Sb<sub>4</sub>? A series of experiments thus are carried out, and the results are the following: (1) To determine the phase stability and the solubility of transition metals, we varied the concentration of Zr substitution. Samples from  $0 \le x \le 1$  show identical powder X-ray diffraction (PXRD) patterns. Due to the c-axis orientation of PXRD data, we cannot conclusively examine the lattice parameter changes with the nominal Zr composition. However, refinement of Zr occupancies from single-crystal X-ray diffraction for several single crystals selected with different nominal x values does not show variability in the Zr concentration within standard deviation.

Since the characteristic of the X-ray energy spectrum of Zr L $\alpha$  (2.044 keV) and Pt M $\alpha$  (2.048 keV) is nondistinguishable, no precise chemical analysis could be performed on the selected crystal using SEM analysis. We therefore conclude, on the basis of X-ray refinement results, that  $Zr_{3.55(2)}Pt_4Sb_4$  is a nearly line compound or a compound with very narrow phase width if there is any. (2) Samples with  $1 \le x \le 3$  are evaluated, and no indication of the  $Zr_{4-x}Pt_4Sb_4$  phase being formed based on PXRD results. This suggests that selectively occupancy at only one Zr site (either Zr1, Zr2, or Zr3 site) is unlikely. (3) Transition metal M (M = Cu and Zn) analogues with nominal M:Pt = 0.9:1 and 1:1 ratios were also explored and did not lead to phase formation of the  $M_{4-x}Pt_4Sb_4$  phase based on PXRD results.

**3.3. Band Structure Analysis.** To gain insights on the role of the partial occupancy of the Zr3 atoms in the stability of the title compound, electronic structure calculations have been performed. As illustrated in Figure 3a-c, three models have been considered to represent the various Zr3 contents in the crystal structure: (a) Zr3 = 0% (Zr<sub>3</sub>Pt<sub>4</sub>Sb<sub>4</sub>, 72e<sup>-</sup> per formula unit), (b) Zr3 = 100% (Zr<sub>4</sub>Pt<sub>4</sub>Sb<sub>4</sub>, 76e<sup>-</sup>/f.u.), and (c) Zr3 = 50% (Zr<sub>3.5</sub>Pt<sub>4</sub>Sb<sub>4</sub>, 74e<sup>-</sup>/f.u.). The corresponding density of

states (DOS) plots, calculated using TB-LMTO-ASA, are shown in Figure 3d–f. Computations using WIEN2k produce similar results and are depicted in the Supporting Information Figures S2–S4. The Fermi level of the  $Zr_3Pt_4Sb_4$  model resides in the shoulder of a peak. Furthermore, there is a pseudogap in the DOS corresponding to a total electron count of 74 $e^-$ . Assuming a rigid band model, this suggests supplying an additional  $2e^-/f.u.$  in  $Zr_3Pt_4Sb_4$  provides a great electronic stability. In the hypothetical  $Zr_4Pt_4Sb_4$  model, the Fermi level lies near a pseudogap. At 74 $e^-$  count, a pseudogap in the DOS is also present. Considering high-DOS peaks are in between 74 $e^-$  and 76 $e^-$  levels, the rigid band model is somewhat invalid in this region.

The partial occupancy in the Zr3 atoms has been modeled by employing a  $2 \times 2 \times 1$  supercell and removing half of the Zr3 sites (Figure 3c). To simplify calculations, a 50% overall occupancy of the Zr3 sites has been used in lieu of the 55(2)% partial occupancy of the Zr3 atoms obtained using singlecrystal X-ray diffraction. This leads to the Zr35Pt4Sb4 model which best represents the title compound among the three models. With the Fermi level lying in a pseudogap, Zr<sub>3.5</sub>Pt<sub>4</sub>Sb<sub>4</sub> is predicted to be a poor metal. In contrast, both the  $72e^{-}$  and  $76e^{-}$  levels are situated in high-DOS peaks which do not favor electronic stability. At 76e<sup>-</sup> count, there is no gap or pseudogap unlike in the previous  $Zr_4Pt_4Sb_4$  model. This confirms a rigid band model is not valid going from 74 to 76e<sup>-</sup> counts. Summarizing, the formation of  $Zr_{35}Pt_4Sb_4$  (Zr3 = 50%,  $74e^{-}$ ) is electronically favorable and supplying or removing valence electrons (e.g., variation in the occupancy of the Zr3 atom) does not enhance its electronic stability. This is consistent with the experimental results of the extremely narrow phase width observed in the title compound.

Assuming the Zr atoms merely act as electron donors,  $Zr_{3.5}Pt_4Sb_4$  can be formulated as  $(3.5Zr^{4+})[Pt_4Sb_4]^{14-}$  by simple electron counting. All the Sb atoms (Sb1 and Sb2) can be assigned as Sb<sup>3-</sup> since the 5s and 5p states are completely filled and there are no Sb–Sb bonds present. While a net formal charge of -12 is allotted to the four Sb atoms, the remaining -2 charge is distributed among the four Pt atoms. Considering the presence of single Pt–Pt bonds, two Pt1 atoms can be formulated as  $[Pt-Pt]^{2-}$ . The formal charge of the Pt2 atoms, which are tetrahedrally coordinated to Sb atoms only, is 0. This Pt<sup>0</sup> assignment is consistent with the complete filling of the *d* electrons and the absence of Pt–Pt bonds in Pt2 atoms. As such,  $[Pt_4Sb_4]^{14-}$  can further be formulated as  $[(Pt-Pt)^{2-}](Pt^0)_2(Sb^{3-})_4$ .

To shed light on role of the Zr atoms in the chemical bonding in Zr<sub>3.5</sub>Pt<sub>4</sub>Sb<sub>4</sub>, crystal orbital Hamilton populations (-COHP) have been calculated, with results shown in Figure 4 and Supporting Information Figures S5-S7. As can be seen in Figure 4, all the Pt-Sb bonds are optimal: the antibonding states are unfilled, while only the bonding and nonbonding states are below the Fermi level. Hence, increasing the occupancy of the Zr3 atoms from 0.5 to 1.0 would result in the filling-up of the Pt-Sb antibonding states and thus destabilizing the Pt<sub>4</sub>Sb<sub>4</sub> slab. Replacing the half-occupied Zr3 atoms with fully occupied Pt atoms also results in the filling up of the antibonding Pt-Sb states (Figure S8 in the Supporting Information). In addition, the Zr-Pt and Zr-Sb interactions are also optimized (see Figures S5 and S6 in the Supporting Information). The integrated -COHP (-ICOHP) up to the Fermi level for the respective nearest-neighbor interactions in Zr<sub>3.5</sub>Pt<sub>4</sub>Sb<sub>4</sub> has been computed (Table 4). The Pt-Sb (1.66-



**Figure 4.** Crystal orbital Hamilton population (–COHP) of the (a) Pt1–Sb1 (2.656 Å), (b) Pt2–Sb1 (2.758 Å), and (c) Pt2–Sb2 (2.789 Å) bonds in  $Zr_{3.5}Pt_4Sb_4$  calculated using TB-LMTO-ASA. The Fermi level ( $E_F$ ) is set at 0 eV. The bonding, nonbonding, and antibonding states are represented by green, gray, and dark red areas, respectively.

Table 4. Integrated Crystal Orbital Hamilton Population (-ICOHP) up to the Fermi Level in Zr<sub>3.5</sub>Pt<sub>4</sub>Sb<sub>4</sub>

interaction	d (Å)	–ICOHP (eV/bond)	N per unit cell	% contribution
Pt1-Sb1	2.656	2.19	6	13.3
Pt2-Sb1	2.758	1.83	2	3.7
Pt2-Sb2	2.789	1.66	6	10.0
Zr1-Pt1	2.886	1.80	12	21.8
Zr2-Pt1	2.709	2.05	2	4.1
Zr2-Pt2	2.671	2.16	6	13.1
Zr3-Pt2	2.703	1.90	4	3.8
Zr1-Sb1	3.338	0.80	12	9.7
Zr2-Sb1	3.178	0.71	6	4.3
Zr2-Sb2	3.231	0.74	6	4.5
Zr3-Sb2	2.967	1.43	12	8.7
Pt1-Pt1	2.757	1.52	2	3.1

2.19 eV/bond) and Zr-Pt (1.80-2.16 eV/bond) interactions account for the largest contribution per bond. The highest contribution per unit cell, due to frequency, are those from the Zr-Pt interactions which account for 42.8% of the ICOHP values itemized in Table 4. Although the Zr-Sb interatomic distances are longer (2.967-3.338 Å), the Zr-Sb interactions (27.2%) have similar influence as those of the Pt-Sb bonds (27.0%). Although Pt-Pt bonds (1.52 eV/bond) are present, they are the smallest contributors to the overall chemical bonding (3.1%). Therefore, the title compound can be viewed as stacking of "Pt<sub>4</sub>Sb<sub>4</sub> slabs" that are held together by strong Zr-Pt and Zr-Sb interactions. As such, the Zr atoms are not merely electron donors, but play a crucial role in the chemical bonding in the title compound. This is also apparent in the DOS (Figure 3f) where the Zr atoms mix effectively with the Pt and Sb atoms in the valence orbital region. We could now explain our experimental observation that the other transition metal analogue  $M_{4-x}$ Pt<sub>4</sub>Sb<sub>4</sub> (M = Cu and Zn) does not form,



Figure 5. (a) Temperature dependent resistivity data for  $Zr_{3.55}Pt_4Sb_4$  compound. The red line shows the low temperature fitting data between 20 and 100 K. (b) Hall effect measurement data at three different temperature points.

and therefore, formulating  $Zr_{3.5}Pt_4Sb_4$  as  $(3.5Zr^{4+})[Pt_4Sb_4]^{14-}$  is an oversimplification.

3.4. Physical Characterization. Resistivity as a function of temperature  $\rho(T)$  was measured with a PPMS-9T (Quantum Design) down to 2 K using a standard four-probe technique. The temperature dependent resistivity data at zero field on the selected crystal of  $Zr_{3.55}Pt_4Sb_4$  are shown in the Figure 5. The material shows an overall metallic behavior over the measured temperature range between 2 and 300 K, which is consistent with the band structure calculation results. The room temperature resistivity value is 10 m $\Omega$  cm and is comparable with the values of other Pt-based pnictides, such as BaPtSb, NdPtSb, and YPtSb. The resistivity shows a linear temperature dependent behavior between 100 and 250 K. The low temperature resistivity data between 20 and 100 K, presumably contributed by electrons, can be fitted by  $\rho = \rho_0 + \rho_0$  $AT^{n}$ , where  $\rho_{0} = 7.38 \text{ m}\Omega \text{ cm}$ ,  $A = 8.95 \times 10^{-5}$ , and n = 1.93. The power law index of n is close to 2, indicating the material is close to Fermi liquid behavior at low temperature. An upturn of resistivity below 20 K is observed which might due to the localization effect caused by the vacancies of Zr atoms at the Zr3 site.

Field dependent Hall resistivity measurement at 10, 120, and 300 K is shown in Figure 5b. The Hall resistivity shows a linear dependence as a function of the magnetic field. Positive longitudinal resistivity indicates hole carriers dominate in the  $Zr_{3.55}Pt_4Sb_4$  system, consistent with the band structure calculation. There is no sign reversal as we change the temperature from 300 to 10 K. This suggests the multiband effect is not dominate as the magnitude of the Hall resistivity did not change significantly from 10 to 300 K. From the equation of  $\rho_{xy} = 1/ne \times B$ , the calculated room temperature carrier concentration is ~1.22 × 10<sup>20</sup> cm<sup>-3</sup>, consistent with the metallic behavior.

#### 4. CONCLUSIONS

In summary, we reported a new nonstoichiometric ternary antimonide  $Zr_{3.55(2)}Pt_4Sb_4$  through an arc-melting process with a new structure type (*hP24*). It features the unique  $Pt_4Sb_4$  slab with simultaneous cubic and hexagonal diamond substructures. The formation of this slab with Pt–Pt bonding affords three interstitial sites. These vacancy sites are occupied by Zr atoms, and this creates strong Zr–Pt and Zr–Sb interactions. Chemical bonding analysis shows the partial occupancy at one particular Zr site (Zr3 site) creates a pseudogap and optimizes the Pt–Sb bonding in the title compound. This enhances the electronic stability and accounts for the very narrow phase width observed for this nonstoichiometric compound. In addition, electrical transport measurements show metallic behavior of this compound down to 2 K with mainly hole carriers over the whole temperature range, consistent with the electronic structure calculations. The formation of  $Zr_{3.55(2)}Pt_4Sb_4$  opens the possibility in synthesizing other zirconium-based platinum pnictides with new structure types, which are currently under investigation.

#### ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.9b01170.

The density of state (DOS) plot from WIEN2k calculation in comparison with the results from the linear muffin-tin orbital (LMTO) method for  $Zr_3Pt_4Sb_4(Zr3 = 0\%)$ ,  $Zr_4Pt_4Sb_4(Zr3 = 100\%)$ , and  $Zr_{3.5}Pt_4Sb_4(Zr3 = 50\%)$ , and COHP plots for Zr-Pt, Zr-Sb, Pt-Pt interactions for the  $Zr_{3.5}Pt_4Sb_4$  model (PDF)

### **Accession Codes**

CCDC 1911328 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

#### AUTHOR INFORMATION

#### **Corresponding Author**

\*E-mail: blv@utdallas.edu.

#### **ORCID**

Hanlin Wu: 0000-0002-7920-3868 Julia Y. Chan: 0000-0003-4434-2160 Bing Lv: 0000-0002-9491-5177

#### Notes

The authors declare no competing financial interest.

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