

The crystal structures of PdNi₂P and Pd₈Ni₃₁P₁₆

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Abstract

Two new ternary intermediate phases in the Pd–Ni–P system have been synthesized and the crystal structures have been determined by single-crystal X-ray diffraction. PdNi₂P crystallizes in the MgCuAl₂-type structure with the unit cell parameters $a = 3.4708(3) \text{ \AA}$, $b = 8.4437(8) \text{ \AA}$, $c = 6.6083(5) \text{ \AA}$, $Z = 4$, space group *Cmcm*. Pd₈Ni₃₁P₁₆ is tetragonal with the unit cell parameters $a = 14.9375(4) \text{ \AA}$ and $c = 5.8071(3) \text{ \AA}$, $Z = 2$, space group *P4₂/nmc*. The unit cell contains 110 atoms distributed on 12 crystallographic non-equivalent positions. This does not correspond to any previously reported structure.

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1. Introduction

The ternary palladium–nickel–phosphorus system is the simplest prototype of a bulk metallic glass [1]. Even though the binary Pd–P and Ni–P systems contain several complex intermediate phases [2–9], only a few studies of the crystalline phases in the ternary Pd–Ni–P systems have been reported. The following phases; Pd₄₅Ni₃₄P₂₁ orthorhombic, Ni₅₉Pd₄₀P₁ cubic F-centered, Ni₁₄Pd₆₈P₁₈ orthorhombic were reported by Donovan et al. [10] based on TEM investigations. The crystal structure of Ni₁₄Pd₆₈P₁₈ was recently described as a solid solution of nickel in Pd₃P with a composition of Pd_{2.7}Ni_{0.3}P_{0.94} [11], where the nickel atoms preferentially substitute one of the two palladium sites. A cubic high-pressure phase with composition Pd₂Ni₂P has been observed at 4 GPa pressure [12]. Two new ternary intermediate phases are reported in the present study.

2. Experimental

2.1. Sample preparation

A master alloy of Ni₂P was synthesized in a high-frequency furnace in an argon atmosphere, by dropping lumps of red phosphorus into a melt of nickel (nickel

rods 99.995% Johnson and Matthey) [13]. The sample was powdered and heat-treated in evacuated silica tubes at 800° C for 2 weeks. Pd_x(Ni₂P)_{1-x} ($x = 0.14, 0.27, 0.30, 0.38, 0.50, 0.53, 0.54, 0.66$) were synthesized by mixing appropriate amounts of palladium (Cerac, 99.95%) and Ni₂P powder. The mixtures were pressed to pellets and then heat-treated in evacuated silica tubes at 750° C for 5 days. The samples were crushed and the heat treatment was repeated at 700° C. The silica tubes were cooled in air. To improve the sharpness of the diffraction lines, the powders were stress relieved at temperatures between 600° C and 700° C, for 20–40 min. The phase stabilities at 600° C were also investigated after heat treatments for 2 weeks.

2.2. X-ray powder diffraction

Phase analysis was performed and unit cell dimensions were determined using X-ray powder diffraction techniques. Powder patterns were recorded using a Guinier–Hägg-type focusing camera with CuK α ₁ radiation and silicon as internal calibration standard ($a = 5.431065 \text{ \AA}$ at 25° C). The crystal systems were obtained using the program TREOR [14].

2.3. Structure determination

Crystals of PdNi₂P and Pd₈Ni₃₁P₁₆ were glued to glass fibers and mounted on a Bruker APEX

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diffractometer equipped with a 2K CCD detector and using MoK α radiation. Data were collected using 0.2° ω scans and 40 s exposure time for the PdNi₂P crystal; 0.3° ω scans and 60 s exposure time for the Pd₈Ni₃₁P₁₆ crystal. The detector was set at $2\theta = 28^\circ$ (covering $2\theta = 0^\circ - 56^\circ$) for both data collections. Data reductions, cell refinements, space-group determinations and numerical absorption corrections were all done using the SAINT+ program package [15]. Direct methods for initial starting structures and crystal structure refinements were done using the SHELXTL program package [15]. Due to the severe absorption in the crystals, which could not be sufficiently corrected, two new data sets were collected on a Stoe diffractometer, which enabled better absorption corrections of the intensities. New crystals of PdNi₂P and Pd₈Ni₃₁P₁₆ were mounted on a Stoe & Cie four-circle diffractometer using MoK α

radiation. The PdNi₂P data set was collected using $\omega/2\theta$ scan; step 0.01° and step time 0.3–3 s. Data was collected up to $2\theta = 90^\circ$. The Pd₈Ni₃₁P₁₆ data was collected using $\omega/2\theta$ scan; step 0.02° and step time 0.3–6 s. Data was collected up to $2\theta = 65$. Four standard reflections were monitored every 4 h for both crystals. The data were corrected for background [16] intensities and corresponding standard deviations were corrected for time variations according to McCandlish et al. [17]. The complex crystal morphology was optimized using the program X-SHAPE [18]. The DUPALS program package was used for data reduction, numerical absorption correction and crystal structure refinements [19]. The function minimized was $\sum w(F_o^2 - F_c^2)$ with $w = 1/\sigma^2(F^2)$. A type I isotropic extinction parameter with Lorentzian distribution of the mosaic blocks was used [20]. The most extinction corrected reflections were

Table 1
Experimental and refinement details for Stoe data

	PdNi ₂ P	Pd ₈ Ni ₃₁ P ₁₆
Empirical formula	PdNi ₂ P	Pd ₈ Ni ₃₁ P ₁₆
Crystal system	Orthorhombic	Tetragonal
Space group	<i>Cmcm</i>	<i>P4₂/nmc</i>
<i>Unit cell parameters determined from X-ray powder diffraction data</i>		
<i>a</i> (Å)	3.4708(3)	14.9375(4)
<i>b</i> (Å)	8.4437(8)	—
<i>c</i> (Å)	6.6083(5)	5.8071(3)
Volume (Å ³)	193.66(3)	1295.73(8)
<i>Z</i>	4	2
<i>D_x</i> (mg/m ³)	8.90	8.15
Temperature	293 K	293 K
Crystal color	Metallic gray	Metallic gray
Crystal size (mm)	0.04 × 0.025 × 0.02	0.09 × 0.03 × 0.02
<i>Data collection</i>		
Diffractometer	Stoe four-circle	Stoe four-circle
Data collection method	$\omega/2\theta$ scan	$\omega/2\theta$ scan
Absorption correction	Integration	Integration
<i>T_{min}</i> (Å ³)	0.42	0.14
<i>T_{max}</i> (Å ³)	0.60	0.51
Linear absorption coefficient (mm ⁻¹)	28.67	28.25
<i>Refinement limits</i>		
θ (deg)	45	32.5
<i>h, k, l</i>	−6 → <i>h</i> → 6 −13 → <i>k</i> → 12 −15 → <i>l</i> → 15	−20 → <i>h</i> → 22 −9 → <i>k</i> → 22 −6 → <i>l</i> → 8
Reflections collected	2730	5648
Independent reflections	464	1422
Reflections in refinements (<i>I</i> > 4 σ)	378	1101
Variable parameters	17	77
<i>R_{int}</i>	0.052	0.118
Refinement on	<i>F</i> ²	<i>F</i> ²
<i>R</i>	0.034	0.068
<i>R_w</i>	0.042	0.050
Extinction coefficient	6674(233)	2983(111)
Extinction correction method	Becker and Coppens (1974), Isotropic type I, Lorentzian	Becker and Coppens (1974), Isotropic type I, Lorentzian
Goodness-of-fit	2.04	2.83
Largest diff. peak and hole (e ⁻ /Å ³)	2.61/−1.37	5.48/−5.02

(200) $y = 0.63$ in PdNi_2P and (800) $y = 0.77$ in $\text{Pd}_8\text{Ni}_{31}\text{P}_{16}$. Results and experimental details are presented in Table 1.

The low intensity of the high-angle reflections, due to the high absorption of the crystals made it difficult to determine the unit cell parameters with high accuracy. However, the unit cell parameters obtained from the single crystals are within experimental errors in agreement with the X-ray powder diffraction results. All unit cell dimensions reported are based on X-ray powder diffraction data.

3. Results and discussion

The crystal structures of two new ternary intermediate phases PdNi_2P and $\text{Pd}_8\text{Ni}_{31}\text{P}_{16}$ have been determined. PdNi_2P was found in samples $\text{Pd}_x(\text{Ni}_2\text{P})_{1-x}$ ($x = 0.38\text{--}0.66$). As judged from X-ray powder diffraction patterns, small variations in unit cell volumes, less than 1.5 \AA^3 , indicate a small range of homogeneity. Samples, $\text{Pd}_x(\text{Ni}_2\text{P})_{1-x}$ ($x = 0.14\text{--}0.30$), prepared at 700°C , showed diffraction lines from a common phase. The unit cell parameters from different samples were all the same within experimental errors. This phase is stable at 700°C but disproportionates at 650°C to Ni_2P , Ni_{12}P_5 and an unidentified phase. The X-ray powder diffraction patterns of several samples contained diffuse extra lines, which did not improve in quality despite several attempts to stress relieve the powders. The phase relations of the ternary system were not determined due to the presence of additional phases.

3.1. PdNi_2P

PdNi_2P has a small range of homogeneity, with palladium substitutions on the nickel position. The unit cell parameters for $\text{Pd}(\text{Ni}_{1-x}\text{Pd}_x)_2\text{P}$ ($x = 0.06$) were determined from X-ray powder diffraction patterns to $a = 3.4708(3) \text{ \AA}$, $b = 8.4437(8) \text{ \AA}$, $c = 6.6083(5) \text{ \AA}$ with a unit cell volume of $193.66(3) \text{ \AA}^3$ and $Z = 4$, space group $Cmcm$, Table 1. PdNi_2P crystallizes in the MgCuAl_2 -type structure [21]. This structure type has three crystallographic sites, with aluminum at the $8f$ -position, magnesium at $4c$ and copper at $4c$. In PdNi_2P , the nickel atoms occupy the 8-fold aluminum site and the palladium and phosphorus atoms occupy the $4c$ magnesium and copper positions, respectively. The refinements indicated a small substitution of palladium on the nickel site and full palladium occupancy on the other metal position. The structural parameters calculated in the last single-crystal refinement cycle are shown in Table 2. The crystal structure is shown in projection on the bc plane in Fig. 1. The MgCuAl_2 -type structure is a ternary ordered derivative of the Re_3B -type structure. The atomic arrangement is

Table 2

Fractional atomic coordinates and equivalent isotropic displacement parameters for the PdNi_2P structure

Atom	Position	x	y	z	Occ (%)	$U_{\text{eq}} (\text{Å}^2)$
Ni/Pd1	$8f$	0	0.14510(5)	0	94.8(5)/5.2(5)	0.0075(1)
Pd2	$4c$	0	0.44552(4)	1/4	100	0.00801(8)
P1	$4c$	0	0.7321(2)	1/4	100	0.0071(2)

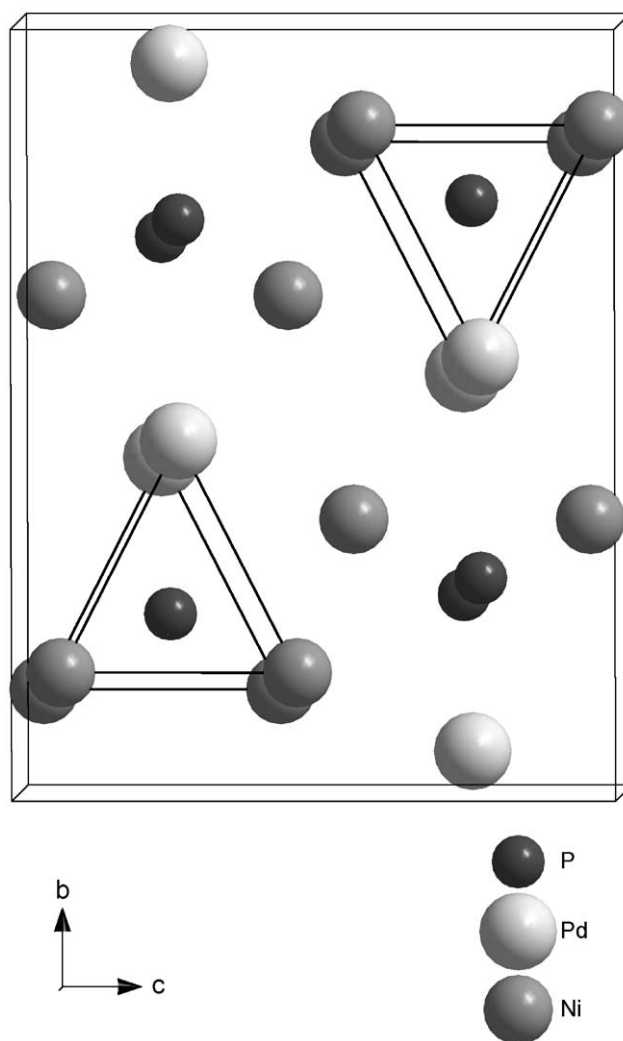


Fig. 1. The crystal structure of PdNi_2P .

easily described in terms of columns of filled trigonal prisms along the a -axis, with one phosphorus atom in the middle of each prism. Each phosphorus atom coordinates nine metal atoms. Four nickel and two palladium atoms are situated at the vertices of the prism, two nickel and one palladium atoms are found outside the rectangular faces.

The Ni–P distances are shorter than the Pd–P distances. Interatomic distances shorter than 3.0 \AA are listed in Table 3. Iso-structural compounds have been

reported in ternary aluminum, gallium, tin and indium compounds [22–25]. The crystal structure of Pd₆P [3] is a superstructure also related to the Re₃B-type structure. Every second trigonal prism within the columns accommodates one phosphorus atom and the columns are stacked in a certain order to each other.

3.2. Pd₈Ni₃₁P₁₆

Pd₈Ni₃₁P₁₆ has a tetragonal unit cell with the unit cell parameters $a = 14.9375(4)$ Å and $c = 5.8071(3)$ Å, determined from X-ray powder diffraction pattern, space group $P4_2/nmc$, Table 1. The unit cell of tetragonal Pd₈Ni₃₁P₁₆ contains 110 atoms distributed on 12 crystallographic non-equivalent positions. The crystal structural parameters, from the last crystal structure refinement cycle, are listed in Table 4. Table 5 shows interatomic distances shorter than 3.0 Å. The metal atoms form capped trigonal prisms, which accommodate the phosphorus atoms P2 and P3, respectively. The P2 and P3 thus have nine close metal neighbors, six at

the vertices of the prism and three situated outside each of the quadrilateral faces. The prisms are linked together to form columns of prisms pairs along the c -axis (see Fig. 2 and 3). The 10 metal neighbors surrounding the third phosphorus atom, P1, cannot be described in terms of a regular polyhedron. The P1 coordination polyhedra share one edge and buckled rings are formed around the columns of the capped P2 and P3 trigonal prisms. The pure nickel sites in Pd₈Ni₃₁P₁₆ have four phosphorus neighbors except for Ni7 that coordinates three phosphorus atoms.

Two metal sites have mixed occupancies of palladium and nickel, Ni/Pd5 and Pd/Ni1. The Ni/Pd5 site, which is substituted by palladium to almost 50%, has four phosphorus close neighbors. Pd/Ni1, which is occupied to 80% by palladium, has five phosphorus neighbors. The shortest metal–phosphorus distance is 2.17 Å between Ni7 and P1. Such a short Ni–P distance has previously been reported for the rhombohedral α -Ni₈P₃ [9]. The shortest Pd–P distances are 2.302, 2.327 and 2.341 Å for Ni/Pd5, Pd/Ni1 and Pd2, respectively. There are several metal-rich palladium phosphides but Pd₇P₃ and Pd₃P_{0.8} have the metal-to-phosphorus ratio closest to Pd₈Ni₃₁P₁₆. The shortest interatomic distances between phosphorus and palladium in these structures are 2.18 and 2.22 Å. Palladium has a larger metal radius than nickel so the shortest Me–P distance increases with increased occupancy of palladium at a particular position.

3.3. Structural properties in the Pd–Ni–P system

Pd₃P, crystallizing in the cementite structure, Fe₃C-type, has previously been reported to form a solid solution with nickel. The cementite structure has two crystallographic metal positions: one surrounded by three and one by two phosphorus atoms. Nickel substitutes on the palladium position coordinating three phosphorus atoms with the longest metal–phosphorus distances.

Table 3
Interatomic distances in PdNi₂P (Å)

Ni/Pd1	P1	2.2606(8)
	2 P1	2.2868(5)
	Ni/Pd1	2.5906(7)
	2Pd2	2.7440(4)
	2Pd2	2.7627(4)
	Pd2	2.8482(5)
Pd2	P1	2.419(1)
	2P1	2.501(1)
	2Ni/Pd1	2.7440(4)
	4Ni/Pd1	2.7627(4)
	Ni/Pd1	2.8482(5)
P1	2Ni/Pd1	2.2606(8)
	4Ni/Pd1	2.2868(5)
	Pd2	2.419(1)
	2Pd2	2.501(1)

Table 4
Fractional atomic coordinates and equivalent isotropic displacement parameters for the Pd₈Ni₃₁P₁₆ structure

Atom	Position	x	y	z	Occ (%)	U_{eq} (Å ²)
Ni1	2a	3/4	1/4	3/4	100	0.0077(7)
Ni2	8g	0.5135(1)	1/4	0.7476(2)	100	0.0083(5)
Ni3	8f	0.51179(9)	0.48821(9)	3/4	100	0.0212(4)
Ni4	8f	0.62956(7)	0.37044(7)	3/4	100	0.0067(3)
Ni/Pd5	16	0.38122(6)	0.35661(6)	0.8001(2)	62/38(1)	0.0131(3)
Ni6	16h	0.5349(1)	0.14006(9)	0.3901(2)	100	0.0119(4)
Ni7	8g	0.4471(1)	1/4	0.1370(3)	100	0.0097(5)
Pd/Ni1	8g	0.63656(8)	1/4	0.1124(1)	80/20(1)	0.0087(4)
Pd2	4d	1/4	1/4	0.5756(1)	100	0.0143(4)
P1	16h	0.5100(2)	0.1223(2)	0.0109(4)	100	0.0097(7)
P2	8g	0.4035(2)	1/4	0.4942(6)	100	0.013(1)
P3	8g	0.8688(2)	1/4	0.5130(5)	100	0.0072(9)

Table 5
Interatomic distances in Pd₈Ni₃₁P₁₆ (Å)

Ni1	4P3	2.246(3)
	4Ni4	2.544(1)
	4Pd/Ni1	2.7019(9)
Ni2	P2	2.206(3)
	P3	2.224(3)
	2P1	2.445(2)
	Ni7	2.469(2)
	2Ni4	2.498(2)
	2Ni/Pd5	2.556(2)
	2Ni6	2.666(2)
	Pd/Ni1	2.804(2)
Ni3	2P1	2.241(2)
	2P1	2.459(3)
	Ni4	2.487(2)
	2Ni6	2.508(2)
	2Ni/Pd5	2.784(2)
	2Ni6	2.856(2)
	2Ni3	2.9460(3)
Ni4	2P3	2.265(2)
	2P1	2.345(2)
	Ni3	2.487(2)
	2Ni2	2.498(2)
	2Ni6	2.528(1)
	Ni1	2.544(1)
	2Pd/Ni1	2.7706(8)
Ni/Pd5	P1	2.302(3)
	P2	2.367(2)
	P2	2.409(2)
	Ni2	2.556(2)
	Ni7	2.562(1)
	Ni7	2.707(2)
	Ni6	2.732(2)
	Ni3	2.784(2)
	P1	2.841(2)
	Pd2	2.842(1)
	2Ni/Pd5	2.949(2)
	Pd2	2.989(1)
	Ni6	P1
P3		2.297(2)
P1		2.410(3)
Ni3		2.508(2)
Ni4		2.528(1)
Ni7		2.564(2)
P2		2.630(2)
Ni2		2.666(2)
Ni/Pd5		2.732(2)
Ni6		2.753(2)
Pd/Ni1		2.757(2)
Ni3	2.856(2)	
Ni7	P2	2.174(3)
	2P1	2.249(3)
	Ni2	2.469(2)
	2Ni/Pd5	2.562(1)
	2Ni6	2.564(2)
	2Ni/Pd5	2.707(2)
	Pd/Ni1	2.833(2)
	Pd2	2.965(2)
Pd/Ni1	P3	2.328(3)
	2P3	2.559(2)

Table 5 (continued)

	Ni1	2.7019(9)
	2P1	2.750(3)
	2Ni6	2.757(2)
	2Ni4	2.7706(8)
	Ni2	2.804(2)
	Ni7	2.833(2)
	2Pd/Ni1	2.880(1)
Pd2	2P2	2.341(3)
	4Ni/Pd5	2.842(1)
	2Pd2	2.9035(8)
	2Ni7	2.965(2)
	4Ni/Pd5	2.989(1)
P1	Ni3	2.241(2)
	Ni6	2.249(2)
	Ni7	2.249(3)
	Ni,Pd5	2.302(3)
	Ni4	2.345(2)
	Ni6	2.410(3)
	Ni2	2.445(2)
	Ni3	2.459(3)
	Pd/Ni1	2.750(3)
	Ni/Pd5	2.841(2)
	P2	Ni7
Ni2		2.206(3)
Pd2		2.341(3)
2Ni/Pd5		2.367(2)
2Ni/Pd5		2.409(2)
P3	2Ni6	2.630(2)
	Ni2	2.224(3)
	Ni1	2.246(3)
	2Ni4	2.265(2)
	2Ni6	2.297(2)
	Pd/Ni1	2.328(3)
	2Pd/Ni1	2.559(2)

In both structures, at least one site can be occupied alternately by nickel or palladium.

In the orthorhombic structure, nickel substitutes on one palladium site and in the tetragonal structure two metal positions have a mixed occupancy of palladium and nickel, Ni/Pd5 and Pd/Ni1. The nickel atoms prefer the metal positions with high coordination of phosphorus. The Pd1/Ni1 position has five phosphorus neighbors in the tetragonal structure and in the cementite structure nickel prefers the site with three phosphorus neighbors. The metal-to-phosphorus distances increase at higher palladium content in accordance with the larger radius of palladium.

4. Conclusion

The crystal structures of two new ternary intermediate phases have been determined in the Pd–Ni–P system. PdNi₂P crystallizing in the MgCuAl₂-type structure has

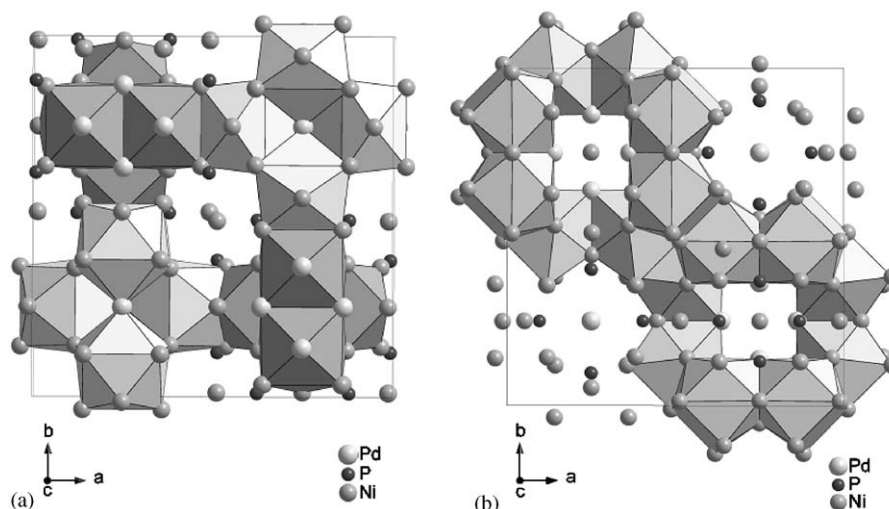


Fig. 2. Capped trigonal prisms occupied by (a) P2 light grey and P3 dark gray, and (b) P1 in the crystal structure of $\text{Pd}_8\text{Ni}_{31}\text{P}_{16}$.

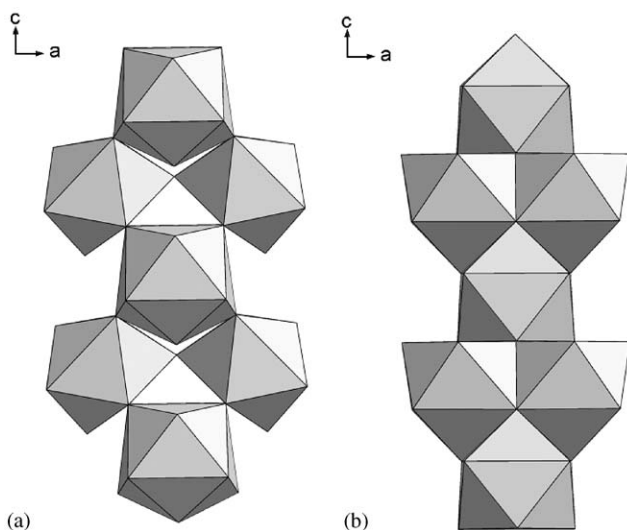


Fig. 3. Columns of capped trigonal prisms occupied by (a) P2, and (b) P3.

a small range of homogeneity with some substitution of palladium on the nickel site. A high-temperature phase with the approximate composition $\text{Pd}_8\text{Ni}_{31}\text{P}_8$ is stable above 700°C . The range of homogeneity is very narrow, since no variations of the unit cell were detected.

All sites mainly occupied by nickel are closer to the phosphorus atoms than the palladium positions. Nickel occupies the metal sites with the highest coordination of phosphorus. Higher palladium occupancies on a metal position increase the metal–phosphorus distance due to its larger radius compared to nickel.

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